UNIVERSITÉ DE MONTRÉAL

LE PLOMB PARTICULAIRE DANS L’EAU DU ROBINET: SOURCE, OCCURRENCE, ENLÈVEMENT ET BIOACCESSIBILITÉ

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Cette thèse intitulée:

LE PLOMB PARTICULAIRE DANS L'EAU DU ROBINET: SOURCE, OCCURRENCE, ENLÈVEMENT ET BIOACCESSIBILITÉ

Présentée par : DESHOMMES Elise

en vue de l'obtention du diplôme de : Philosophiae Doctor

a été dûment acceptée par le jury d'examen constitué de :

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RÉSUMÉ

Le plomb dans l’eau du robinet a été démontré comme un contributeur significatif des concentrations de plomb dans le sang des jeunes enfants. Récemment, des effets neurotoxiques irréversibles ont été mesurés chez les enfants de 6 ans et moins pour des concentrations de plomb dans le sang inférieures au seuil de plombémie de 10 µg Pb/dL ayant servi à l’élaboration des normes. Aucun seuil d’absence d’effet significatif ne peut par conséquent être défini, et les règlementations sont en mutation. Le plomb total mesuré dans l’eau du robinet est présent sous deux formes, le plomb dissous et le plomb particulaire. Le plomb particulaire comprend des colloïdes et des particules, mais est généralement défini comme la fraction retenue par un filtre d’une porosité de 0.45 µm. Il apparait cependant que les protocoles d’échantillonnages et les méthodes d’analyses élaborés pour la détection du plomb total dans l’eau du robinet sous-estiment la fraction particulaire du plomb, et par conséquent l’exposition du consommateur au plomb particulaire. Or les concentrations élevées en plomb recensées dans l’eau des grands bâtiments (écoles) et à Washington D.C., et parfois reliées aux concentrations de plomb dans le sang mesurées chez de jeunes enfants, suggèrent une contribution importante du plomb particulaire. Ainsi, plusieurs pistes semblaient indiquer une contribution significative du plomb particulaire à l’exposition, et donc l’importance de mieux le considérer dans les protocoles d’échantillonnage et d’analyse, et dans l’analyse de l’exposition.

L’objectif principal de ce projet de recherche était de déterminer si le plomb particulaire pouvait contribuer de façon significative à l’exposition au plomb de l’enfant. Pour cela, il était essentiel de caractériser le plomb particulaire dans l’eau du robinet auquel le consommateur est exposé (concentrations, sources, occurrence, facteurs influents), d’estimer la fraction bioaccessible du plomb particulaire, et d’intégrer ces données dans un modèle biocinétique de plombémie. Aussi, il était urgent de valider une méthode efficace pour l’enlèvement du plomb particulaire, et rapide à mettre en place, pour la proposer aux populations vulnérables exposées.

La première phase de ce projet a consisté en des échantillonnages effectués dans des zones cibles de l’exposition du jeune enfant, soit des résidences avec ESP à Montréal, et un grand bâtiment représentatif des écoles à Laval. L’objectif était de caractériser les concentrations et les formes de plomb particulaire, ainsi que les paramètres influençant son occurrence. Le plomb particulaire mesuré dans l’eau du robinet des résidences avec ESP à Montréal a été associé (i) à la corrosion

des éléments en laiton et des soudures dans la tuyauterie interne, (ii) au détachement de dépôts de fer présents dans les conduites, ayant absorbé du plomb dissous avec le temps, et (iii) au détachement des dépôts de carbonates de plomb des ESP. La forme de type (i) était détectée au 1^{er} litre en échantillonnage aléatoire, et montrait sporadiquement des concentrations élevées. La forme de type (ii) était constamment présente à concentrations faibles, et plus facilement détectée dans les échantillons collectés après le 1^{er} litre en échantillonnage aléatoire. La forme de type (iii) n'était visible que dans les échantillons collectés après 5 minutes d'écoulement sous l'effet de perturbations hydrauliques, dans les échantillons de plomb dissous de part sa forme colloïdale. Les concentrations en plomb total très élevées mesurées dans le grand bâtiment ont démontré une contribution majeure du plomb particulaire, et étaient principalement associées à la corrosion des éléments en laiton/bronze dans la tuyauterie interne. La comparaison des divers protocoles d'échantillonnage appliqués dans les résidences avec ESP a démontré qu'un échantillonnage après 30 minutes de stagnation était inadapté pour la détection du plomb particulaire. Au contraire, un échantillonnage aléatoire ou après une longue stagnation, était adéquat. La création de perturbations hydrauliques a augmenté drastiquement les concentrations de plomb particulaire mesurées dans l'eau du robinet après 5 minutes d'écoulement, démontrant l'importance d'échantillonner à débit élevé pour représenter adéquatement les habitudes de consommation et ne pas sous-estimer l'ampleur des concentrations d'exposition.

Considérant les concentrations élevées de plomb particulaire pouvant être mesurées dans les résidences, mais surtout dans les grands bâtiments, la deuxième phase du projet a consisté à valider une méthode fiable de réduction du plomb particulaire de l'eau du robinet, pouvant être appliquée immédiatement à moindre coût dans l'attente de la mise en place de solutions à long terme. Deux études ont été menées sur les dispositifs de filtration au point d'utilisation (POU): une étude pilote et une étude terrain. L'étude pilote évaluait au laboratoire trois types de dispositifs POU (pichet, sur robinet, et sous évier) pour l'enlèvement du plomb dissous et du plomb particulaire, en accéléré sur 120% de leur capacité, avec l'eau de Montréal. Les dispositifs étaient certifiés NSF-53 pour l'enlèvement du plomb avant la modification du protocole en 2007. Les dispositifs sous évier et sur robinet, composés d'un bloc de charbon actif de faible porosité, ont démontré une très grande efficacité à réduire les concentrations de plomb particulaire dans l'eau, et une efficacité plus modérée mais acceptable selon les critères de NSF-53 pour l'enlèvement du plomb dissous. Ces dispositifs ont donc été sélectionnés pour validation supplémentaire de leur performance pour l'enlèvement du plomb dans des conditions réelles d'utilisation. Les pichets ont démontré au contraire une grande performance pour enlever la fraction dissoute du plomb de part leur résine échangeuse d'ions, tandis que la fraction particulaire était peu réduite. Ceci était expliqué par le milieu granulaire et poreux du matériau filtrant. De plus, la présence de particules emprisonnées dans le filtre pouvait générer des concentrations élevées de plomb dans plusieurs volumes filtrés successifs, augmentant ainsi la fréquence d'exposition du consommateur. Ainsi, de tels dispositifs, en dépit de leur certification NSF-53 avant 2007, ne sont pas recommandés.

L'étude terrain a été menée avec un des dispositifs sous évier testé dans l'étude pilote, installé à cinq robinets de consommation d'un grand bâtiment. Les POUs ont été suivis durant un an pour leur efficacité d'enlèvement du plomb dissous et du plomb particulaire, et leur impact sur la qualité microbiologique de l'eau. L'étude a démontré une réduction très efficace du plomb dissous et du plomb particulaire par les dispositifs. Les concentrations à l'effluent des dispositifs étaient significativement en deçà de celles mesurées lors de l'étude pilote, démontrant une bonne efficacité des POUs dans des conditions d'utilisation réelles, et sur du long terme. Les matériaux en aval des POUs (fontaine ou robinet) ont contribué dans des mesures acceptables à augmenter le plomb total mesuré au robinet. Une colonisation plus importante a été mesurée aux robinets avec POU en amont (+ 1 Log), comparativement aux robinets du bâtiment non équipés de POU. Néanmoins cette hausse n'était pas notable par les comptes de bactéries hétérotrophes aérobies (BHA). Aussi, elle n'était pas expliquée par le passage à l'effluent de bactéries ayant colonisé le charbon actif dans les POUs, mais par la colonisation des conduites et robinet en aval des POUs, favorisée par l'enlèvement du résiduel de chlore par ces derniers. Ainsi, les POUs représentent une solution efficace pour l'enlèvement du plomb dans l'eau des grands bâtiments, économiquement viable, et ne créant pas de dégradation significative de la qualité microbiologique de l'eau.

La dernière phase de cette thèse a été initiée par une recherche et une analyse rigoureuse de la littérature sur la bioaccessibilité et la biodisponibilité des particules de plomb des sols et poussières. Les tests adéquatement calibrés pour l'analyse de l'exposition de l'enfant ont été identifiés, et le test présentant le niveau de validation le plus élevé a été sélectionné pour adaptation, puis application aux particules de plomb de l'eau potable. Les adaptations apportées à la procédure RBALP de Drexler & Brattin (2007) ont été soigneusement appliquées, en maintenant fixes les facteurs influençant les résultats de bioaccessibilité identifiés dans la revue de littérature. Le test RBALP adapté a été validé par les pourcentages de récupération du plomb avec des solutions de plomb et des particules de plomb tétravalent. Le test a ensuite été appliqué à 5 types de particules générées au laboratoire et représentatives des particules de plomb typiquement présentes dans l'eau potable, puis à 65 échantillons de particules terrain collectées derrière les aérateurs de robinets de résidences avec ou sans ESP, et d'un grand bâtiment. Les résultats ont démontré une grande variabilité de la bioaccessibilité, répartie de façon très homogène entre 0 et 100%. La majorité des particules testées était hautement bioaccessible (> 30%), tandis que les particules de soudures largement représentées dans les échantillons étaient très faiblement bioaccessibles (1-5 %). Aucune différence de bioaccessibilité, ou de teneur en plomb des particules n'a été observée entre les résidences avec ou sans ESP, cependant les particules terrain collectées étaient globalement représentatives de la tuyauterie interne des résidences et non de l'ESP. La teneur élevée en plomb dans les particules collectées, couplée avec le nombre élevé d'aérateurs échantillonnés positifs pour la présence de particules, a démontré une autre forme d'exposition aux particules de plomb, commune à tous les types de logements.

Les résultats de concentrations de plomb particulaire et de plomb dissous dans l'eau du robinet des résidences avec ESP et du grand bâtiment échantillonnés ont été intégrés dans le modèle IEUBK d'estimation des concentrations de plomb dans le sang des enfants de 7 ans et moins. Les concentrations de plomb particulaire ont été ajustées en tenant compte de leur bioaccessibilité évaluée préalablement au laboratoire. Les concentrations de plomb dans le sol, la poussière, et les aliments, et les taux d'ingestion relatifs à chacune de ces sources entrés dans le modèle IEUBK étaient fixes et représentatifs de récentes études canadiennes. Des simulations ont été successivement effectuées, en augmentant progressivement la concentration de plomb particulaire dans l'eau selon sa distribution, afin de déterminer un seuil à partir duquel le plomb particulaire contribuait significativement à l'exposition. Les résultats ont démontré clairement que l'exposition au plomb particulaire dans les grands bâtiments susceptibles d'en contenir est du même ordre que celle associée à la présence d'entrées de service en plomb dans les résidences. Il apparait donc urgent de quantifier la présence de plomb particulaire dans les grands bâtiments en utilisant des protocoles analytiques et d'échantillonnage adéquats, particulièrement dans les établissements ayant des populations vulnérables, tels que les hôpitaux pédiatriques, les écoles primaires et les garderies.

ABSTRACT

Lead in drinking water has been shown to contribute significantly to the BLL of children less than 6 years old. Irreversible negative neurobehavioral impacts, including a loss of IQ of children under 6 years old, have been documented at BLLs far below the current health action level of 10 µg Pb/dL. A threshold corresponding to a non significant effect cannot be defined for lead, and modifications of the current regulations for lead in drinking water are under consideration. Two forms of lead are present in tap water and confounded in total lead concentrations, dissolved lead and particulate lead. Particulate lead includes colloids and particles, but is generally defined as the fraction retained by a 0.45 µm porosity filter. However, sampling protocols and analytical methods currently prescribed for total lead in tap water underestimate its particulate lead fraction, and therefore the consumer's exposure. Extreme lead concentrations measured in some schools and in Washington D.C. houses, in some cases related to children BLLs, have suggested a significant contribution of particulate lead. Because of these findings, it appears important to adequately consider particulate lead in sampling protocols, analytical methods, and exposure analysis.

The main objective of this project was to determine if particulate lead could significantly contribute to young children's exposure. To this purpose, it was essential to characterize particulate lead in tap water to which the consumer is exposed (concentrations, sources, occurrence, and influencing factors), to estimate the bioaccessibility of particulate lead, and to integrate these data in a biokinetic model such as IEUBK. As well, it was urgent to validate a remediation method for particulate lead in tap water that could be applied immediately, in order to protect vulnerable populations before the implementation of long-term solutions.

The first part of this project consisted of sampling campaigns carried out in locations representative of the environment in which children are exposed to lead, such as residences with a lead service line (LSL) in Montreal and a large building representative of schools in Laval. The main objective was to generate distributions of particulate lead concentrations, and to identify the parameters that influence the occurrence of particulate lead at the tap. Particulate lead at the tap of residences with an LSL in Montreal was associated with (i) the corrosion of brass components and solders in the premise piping, (ii) the detachment of iron scales from the piping, which adsorbed dissolved lead concentrations over time, and (iii) the detachment of lead carbonates

scales from the LSL. Particles of form (i) were detected in the 1st liter collected using the random daytime protocol and were associated with sporadic spikes of lead. Particles of form (ii) were constantly present in tap water, but easier to detect in the samples collected after the 1st liter. Form (iii) particles were only detected in samples collected under hydraulic disturbances after 5 minutes of flushing, in the dissolved lead samples fraction since it was composed of colloids. Extreme total lead concentrations measured in the large building were associated with a major contribution of particulate lead, which was mainly caused by the corrosion of brass fixtures and faucets in the building. The comparison of the results obtained with the different sampling protocols carried out in the residences showed that a sampling performed after 30 minutes of stagnation is not adapted for the detection of particulate lead. On the contrary, random daytime sampling, or sampling after an overnight stagnation, was more adequate. Creating hydraulic disturbances increased dramatically the particulate lead concentrations measured at the tap after 5 minutes of flushing. Therefore, it appears important to collect samples at a high flow rate that is more representative of consumer usage patterns, to avoid underestimating the concentrations of exposure.

Considering the very high particulate lead concentrations measured in the residences resulting from hydraulic disturbances, and especially those measured in the large building, the second part of the project consisted of validating a method to remove particulate lead at the tap. The focus was on validating at the tap treatment that could be applied immediately at a reasonable cost to protect the consumer before the implementation of long term solutions. Two studies were carried out on point-of-use devices (POUs): a pilot study and a field study. Three types of POUs (pour-through, tap-mounted, under-the-sink) were tested at pilot scale using Montreal tap water, and were tested in an accelerated mode up to 120% of the manufacturer's prescribed capacity. The POUs tested were NSF-53 certified for lead before the modification of the protocol in 2007. Under-the-sink and tap-mounted POUs, composed of a carbon block of low porosity, showed excellent efficiency to remove particulate lead levels, and an acceptable efficiency to reduce dissolved lead concentrations according to the NSF-53 criteria. Therefore, these devices were selected to further validate their performance for lead removal under field conditions. Conversely, the ion-exchange resin in the pour-through POUs removed dissolved lead from influent water, whereas the particulate lead fraction was not efficiently reduced due to the high porosity of the filter granular media. Moreover, if particles were retained in pour-through type filters, high lead levels could be released in several successive volumes of filtered water, increasing therefore the consumer exposure. As a consequence, such devices, even if NSF certified for lead before 2007, are no longer recommended.

The field study was carried out in the large building sampled for lead levels in tap water. Five identical under-the-sink POUs previously tested at pilot scale were installed at five taps in the large building. The POUs were monitored over one year for the removal of dissolved and particulate lead in tap water of the building. Their impact on the microbiological quality of tap water was also evaluated. Results showed excellent efficiency of the POUs to remove particulate lead and dissolved lead concentrations. Total lead levels in POU effluent water were significantly lower than those measured during the pilot study, demonstrating a good efficiency of the POUs under typical consumption patterns in a large building over a period of one year. Materials downstream from the POUs (fountain or faucet) contributed to increase total lead levels at the tap, however this increase was in general moderate. Higher total bacteria counts were measured at the taps equipped with a POU (+ 1 Log) as compared to other taps in the building. However, this difference was not detectable with heterotrophic plate counts (HPC). Moreover, this increase did not result from the release of bacteria colonizing the carbon block in the POU, but from the colonization of the POU downstream piping enhanced by the absence of chlorine residual. Therefore, the installation of carbon block under-the-sink POUs represent an efficient and economical solution to reduce lead concentrations at the tap in large buildings, and they do not cause any significant microbial deterioration of water quality.

The last part of this project was initiated by a thorough research and critical review of the existing literature on bioaccessibility and bioavailability of lead in soil and dust particles. The procedures adequately calibrated for children exposure assessment were identified, and the test presenting the highest level of validation was selected for adaptation and application to lead particles from tap water. The modifications of the RBALP procedure developed by Drexler & Brattin (2007) were carefully selected. From this literature review, parameters affecting bioaccessibility estimates were identified and kept constant. The adapted test was validated with acceptable recoveries using lead solutions and tetravalent lead particles. The test was then applied to 5 types of lab-generated particles representative of the lead particles present in tap water, and then to 65 samples of field particles collected behind the tap aerator of residences with(out) an LSL, and from a large building. Results showed a wide range of bioaccessibility, which was quite homogeneously distributed between 0 and 100%. The majority of the set of particles tested were highly bioaccessible (> 30%), whereas solder particles widely represented in the samples were low bioaccessible (1-5%). No significant differences were found between the bioaccessibility of particles collected from residences with or without an LSL, which was consistent with the fact that the field-collected particles were globally representative of the composition of premise piping rather than of an LSL. The high lead content in the particles collected and the high number of tap aerators positive for the presence of particles, confirmed another pathway of exposure to lead common to all housing types.

The results of particulate and dissolved lead concentrations at the tap of residences with an LSL, and from the large building were then used as input to the IEUBK model to estimate the BLL of children less than 7 years old. The concentrations of particulate lead were adjusted taking into account their bioaccessibility previously evaluated at the laboratory. Lead levels in soil, dust, and diet, as well as ingestion rates relative to each of these sources entered in the IEUBK model were constant and representative of the latest values from studies conducted in Canada. Simulations were run successively, by increasing progressively the particulate lead concentration in tap water according to its distribution, in order to determine a threshold at which particulate lead would contribute significantly to exposure. Results clearly showed that exposure to particulate lead in large buildings with particulate lead issues, is comparable to the exposure to lead associated with the presence of LSLs. It appears therefore urgent to quantify particulate lead levels in large buildings with adequate sampling protocols and analytical procedures, particularly in buildings serving vulnerable populations, such as pediatric hospitals, primary schools and daycare.

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ABA	Absolute bioavailability
AL	Action level
ANSI	American national standard institute
AUC	Area under the curve
BARGE	Bioaccessibility research group Europe
BDL	Below detection limits
BLL	Blood lead level
BMD	Benchmarck dose
BHA	Bactéries hétérotrophes aérobies
bw	Body weight
CDC	United States centers for disease control and prevention
CONTAM Panel	Panel on contaminants in the food chain
COT	Carbone organique total
CX	Cation exchange
dL	Decilitre
DIN	German method E DIN 19738
DPASV	Differential pulse anodic stripping voltammetry
EDS	Energy Dispersive Spectrometry
EFSA	European food safety agency
ESP	Entrée de service en plomb
5M (5MIN FLUSH)	Sampling after 5 minutes of flushing
G	Gastric
GAC	granular activated carbon
GI	Gastro-intestinal
H (hr)	Hour
HCl	Hydrochloric acid
HNO_3	Nitric acid
HPC	Heterotrophic plate count
I	Intestinal
ICP-MS	Inductively coupled mass spectrometry
IDM	Internal dose metrics
IEUBK	Integrated exposure uptake biokinetic model for lead in children
IQ	Intellectual quotient
ISE	Ion selective electrode
iv	Intravenous
IVBA	*In vitro* bioaccessibility
IVG	*In vitro* gastro-intestinal test
IX	Ion exchange
JECFA	Joint FAO/WHO expert committee on food additives

kg	Kilogram
kg bw/d	Kilogram body weight/day
kg p.c.	Kilogramme de poids corporel
L	Litre
LCR	Lead and copper rule
Lpm	Litre par minute — Litre per minute
LSL	Lead service line
MAC	Maximum acceptable concentation
MCL	Maximum contaminant level
MDDEP	Ministère de l'environnement du développement durable et des parcs
µg	Microgram
µm	Micrometer
MIN	Minutes
$Na(HCO_3)$	Sodium bicarbonate
NaOH	Sodium hydroxide
NIST	National institute of standards and technology
NSF	National sanitation foundation
PAH	Polycyclic aromatic hydrocarbon
Pb	Lead
Pb_3O_4	Lead tetraoxide
PbAc	Lead acetate
$PbCO_3$	Cerussite
$(PbCO_3)_2Pb(OH)_2$	Hyrocerussite
PBET	Physiologically based extraction test
PbO	Massicot — Litharge
PbO_2	Lead dioxide — Tetravalent lead
PCB	Polychlorinated biphenyl
POE	Point-of-entry
POU	Point-of-use
PP	Premise plumbing — Premise piping
PSS	Particulate stimulation sampling
QA/QC	Quality assurance/Quality control
RBA	Relative bioavailability
RBALP	Relative bioaccessibility leaching procedure
RDT	Random daytime
RIVM	National institute for public health and the environment (Holland)
RO	Reverse osmosis
S/L	Solid to liquid ratio — Solid to fluid ratio — Soil to liquid ratio
SBAC	Solid block of activated carbon
SBET	Simple bioaccessibility extraction test
SBRC	Solubility bioavailability research consortium test

SCC	Service correctionnel Canada
SD	Standard deviation
SDWA	Safe drinking water act
SEM	Scanning Electron Microscopy
SHIME	Simulator of human intestinal microbial ecosystem of infants
SRM	Standard reference material
30MS (30MIN)	30 minutes of stagnation sampling
TIM	TNO gasto-intestinal model
TM	Test material
TOC	Total organic carbon
TOF-SIMS	Time of flight-secondary ion mass spectrometry
12H	12 hours of stagnation sampling
UBM	Unified BARGE method
UF	Ultra filtration
USEPA	United States environmental protection agency
WHO	World health organization
XANES	X-ray absorption near edge structure
XRD	X-ray diffraction

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INTRODUCTION

Mise en contexte

Le plomb est un élément actuellement «sous la loupe» des réglementations européennes et nord-américaines. En effet, il est présent dans diverses sources environnementales auxquelles sont exposées les populations, et plus particulièrement les nourrissons et jeunes enfants en raison de leur taux d’absorption élevé comparé aux adultes (Mushak 1998). Diverses actions ont été menées historiquement pour réduire les niveaux de plomb dans la nourriture, l’air, la peinture, les sols et poussières, les jouets, et l’eau du robinet. Cependant, plusieurs de ces sources persistent, et de récentes études démontrent l’impossibilité de définir un seuil d’absence d’effet critique suite à l’exposition au plomb. Ainsi, l’Autorité Européenne de sécurité des aliments a retiré en 2010 ses recommandations de dose hebdomadaire acceptable provisoire de 25 µg Pb/kg p.c. (EFSA 2010). Cette décision a été fondée principalement sur les effets neurotoxiques du plomb chez les enfants de 1 à 7 ans, notamment les baisses significatives de quotient intellectuel enregistrées pour des niveaux de plomb dans le sang en deçà de 10 µg/dL, seuil considéré jusqu’alors comme critique et ayant servi de référence à l’élaboration de la norme de plomb dans l’eau de 0.01 mg/L au Canada et en Europe (INSERM 1999, Canfield *et al.* 2003, Jusko *et al.* 2008).

L’exposition des enfants au plomb est souvent associée aux peintures au plomb, ou encore à des sols et poussières contaminés et présents dans l’environnement de l’enfant. En effet, les enfants de 1 à 3 ans sont particulièrement exposés à ces sources de par leur tendance à porter les objets à la bouche. Ils peuvent ainsi ingérer de fortes doses de plomb, les cas d’intoxications aiguës résultant d’ingestions importantes étant reportés comme des cas « pica » (Mushak 1998). De faibles concentrations de plomb ingérées de façon fréquente, notamment via les poussières, peuvent aussi contribuer significativement à l’exposition résidentielle de l’enfant (Lanphear *et al.* 2002, Oulhote, 2012). De nombreux cas d’intoxication liés à la peinture ont été relevés aux États-Unis de par l’application massive de peinture au plomb jusqu’en 1978 (Needleman 2004). Cette exposition est facilitée lors de la dégradation des peintures ou lors de la mise en suspension des particules de peinture et de poussières (e.g. travaux de rénovation). Aussi, de nombreux sites aux sols contaminés persistent, et les populations environnantes y sont exposées (USEPA 2006a, USEPA 2006b). Ces cas d’exposition, bien que largement répandus et pouvant générer des cas d'intoxication au plomb très graves, représentent des cas relativement « isolés » et principalement associés aux enfants de 1 à 3 ans. Ainsi, l'exposition générale au plomb des populations, nourrissons et enfants de 6 ans et moins inclus, est principalement liée à la nourriture et à l'eau du robinet (EFSA 2010).

Triantafyllidou & Edwards (2011a) rapportent 14 études établissant une association entre les concentrations de plomb dans l'eau du robinet et les concentrations de plomb dans le sang entre 1977 et 2009. Ces études constituent des cas de concentrations de plomb dans l'eau relativement élevées. Cependant, Lanphear *et al.* (2002) a aussi évalué que des concentrations de plomb dans l'eau supérieures à 5 µg/L, soit la moitié de la recommandation actuelle au Canada, contribuaient à environ 20% (1.2 µg/dL) des concentrations de plomb dans le sang des enfants de 6 à 24 mois. Ainsi, la contribution de l'eau du robinet à l'exposition au plomb, et ce même pour des niveaux de plomb dans l'eau considérés jusqu'à présent comme « faibles », est démontrée.

Le plomb dans l'eau du robinet peut provenir de multiples sources, et celles-ci sont principalement localisées dans l'entrée de service des résidences, et dans la tuyauterie interne des résidences et grands bâtiments. Les entrées de service en plomb (ESP) sont encore fortement répandues dans les résidences datant d'avant 1975 au Canada, leur remplacement est couteux et ne peut être envisagé que sur le long terme (Health Canada 2009). À titre d'exemple, la ville de Montréal a estimé le nombre total d'ESP à plus de 75,000 et s'est engagée, avec l'accord du MDDEP en 2008, dans un programme de remplacement progressif dont le coût s'élèvera à environ 300$M. Cependant, le remplacement des ESP n'engendre pas nécessairement une exposition zéro liée à l'entrée de service. En effet, le plomb libéré des ESP durant plusieurs années peut générer, avec d'autres contaminants, des dépôts dans la tuyauterie interne des résidences. Ces dépôts peuvent être progressivement dissous et/ou détachés dans l'eau du robinet, et constituent ainsi des « réservoirs » de contaminants qui persistent après le remplacement d'une ESP (Schock *et al.* 2008). Aussi, puisque l'entrée de service appartient en partie à la municipalité (rue-vanne de raccordement) et en partie au propriétaire (vanne de raccordement-résidence), la majorité des remplacements d'ESP ne sont en fait que partiels. Ainsi, une nouvelle conduite de cuivre est mise en contact avec une ancienne conduite de plomb, hors de récentes études montrent que de tels raccordements peuvent aggraver considérablement les concentrations de plomb dans l'eau par un phénomène de corrosion galvanique (Triantafyllidou & Edwards 2011b). Les autres sources de plomb sont principalement localisées dans la tuyauterie interne et la robinetterie des résidences avec ou sans ESP, et des grands bâtiments. Sont inclus les soudures à base de plomb, les éléments de plomberie en laiton ou bronze, tels que les vannes, les compteurs d'eau, les robinets, et les fontaines. Les soudures au plomb, pouvant contenir jusqu'à 60% de Pb, sont interdites depuis 1990 au Canada (Health Canada 2009). Cependant les anciennes soudures persistent pour de nombreuses années et des soudures au plomb sont parfois encore appliquées illégalement. Les éléments en laiton et/ou bronze installés sur les conduites d'eau potable pouvaient contenir légalement 8% de plomb massique jusqu'à récemment (Health Canada 2009, Lytle & Schock 1996). Un amendement du Safe Drinking Water Act (SDWA) aux États-Unis prévoit baisser cette teneur à 0.25% d'ici 2014. En effet, certains laitons/bronzes pouvaient contenir 8% de plomb massique total mais présenter, de part les procédures de fabrication et de refroidissement de l'alliage, des teneurs en plomb nettement supérieures sur la surface interne de l'alliage directement en contact avec l'eau (Elfland *et al.* 2010).

Les concentrations de plomb dans l'eau du robinet sont déterminées d'abord par la présence d'une ou de plusieurs des sources énumérées ci-dessus, mais aussi par des facteurs spécifiques variant d'un type d'eau à un autre, et d'un logement à un autre. Les caractéristiques physico-chimiques de l'eau sont déterminantes des concentrations de plomb générales dans l'eau: la dissolution du plomb sera accrue pour une eau de pH et/ou d'alcalinité faible, la combinaison des deux étant un facteur aggravant (Dodrill & Edwards 1995). D'autres facteurs spécifiques de l'eau distribuée, tels que le carbone inorganique dissous, le ratio chlorure sur sulfate, et la matière organique naturelle, influenceront la dissolution du plomb dans l'eau (Edwards & Triantafyllidou 2007, Korshin *et al.* 1999, Korshin *et al.* 2005, Schock 1980, Schock 1990, Valentine & Lin 2009). Aussi, la dissolution du plomb augmente avec la température, ce qui implique d'échantillonner les résidences avec ESP spécifiquement durant la période d'été. Enfin, l'historique de traitement de l'eau des municipalités influence aussi la concentration de plomb dans l'eau. Un exemple flagrant est celui de Washington D.C., qui a appliqué durant les années 90 des doses importantes de chlore dans le réseau de distribution, puis a effectué un changement pour les chloramines dans les années 2000. Les fortes doses de chlore avaient permis de former des dépôts de plomb tétravalent très peu solubles en surface interne des ESP, avec pour conséquence de très faibles concentrations de plomb dans l'eau. La mise en place des chloramines a créé un changement de potentiel d'oxydoréduction, avec pour conséquence la déstabilisation et la solubilisation des dépôts de plomb tétravalent, et donc une hausse drastique des concentrations de plomb dans l'eau des résidences desservies par des conduites de plomb (USEPA 2007a).

La concentration de plomb varie selon la stagnation dans les conduites, et selon le volume et la configuration de l'entrée de service et de la tuyauterie interne. En effet, la concentration en plomb dissous augmente avec le temps de stagnation dans les conduites atteignant un maximum après 6 à 10 heures de stagnation et se poursuivant ensuite à moindre degré (Lytle & Schock 2000). La teneur en plomb dissous diminue significativement après un rinçage de 5 à 15 minutes permettant d'acheminer de l'eau fraîche et non stagnée depuis la conduite principale alimentant la résidence. Ce rinçage peut par contre être beaucoup plus long pour le cas des grands bâtiments dépendamment de la longueur de conduite entre l'eau de l'aqueduc et le point d'échantillonnage (Abdo *et al.* 1999). La concentration de plomb variera donc en fonction de sa provenance dans la tuyauterie interne/entrée de service, et de la localisation des sources de plomb. Ainsi, dépendamment de l'échantillon considéré (1er litre, 2^{e} litre, litre après 5 minutes de rinçage), la concentration de plomb sera variable et donc l'exposition du consommateur déduite sera variable. Par conséquent, la sélection du protocole d'échantillonnage sera déterminante des concentrations de plomb dans l'eau.

Il est compréhensible que, durant les dernières années, les actions pour diminuer le plomb dans l'eau du robinet aient été focalisées sur le remplacement des ESP, ou sur l'application de traitements anticorrosion pour limiter la dissolution des ESP. Cependant, les sources de plomb de la tuyauterie interne, bien qu'apparaissant négligeables comparativement à une ESP de 6 à 30 m de longueur, peuvent générer des concentrations de plomb dans l'eau extrêmement élevées. Ceci est un cas plus spécifique aux grands bâtiments. En effet, ces derniers combinent deux facteurs aggravant les concentrations de plomb dans l'eau: un très grand volume de tuyauterie interne et de très longs temps de stagnation (e.g. vacances scolaires). Ces cas spécifiques sont à considérer puisque les grands bâtiments tels que les écoles, garderies, et hôpitaux abritent les populations les plus vulnérables au plomb, et ce pour une fréquence d'exposition plus que significative. Des concentrations en plomb anormalement élevées ont ainsi été mesurées dans diverses écoles aux États-Unis (Boyd *et al.* 2008a, Bryant 2004, Maas *et al.* 1994, Triantafyllidou & Edwards 2009, Triantafyllidou & Edwards 2011a). Ceci a résulté en 1994 à l'implantation du Lead Contamination Control Act (LCCA) aux États-Unis, document spécifiant aux écoles et garderies des méthodes d'échantillonnages pour détecter les sources de plomb, et des moyens d'y remédier

(USEPA 1994a, USEPA 2006c). De même, en Ontario le règlement 243/07 impose des échantillonnages réguliers, ainsi que le rinçage quotidien des conduites dans toutes les écoles et garderies (Government of Ontario 2009). Enfin, Santé Canada a récemment émis un guide de contrôle de la corrosion, indiquant les échantillonnages et moyens d'actions pour réduire le plomb spécifiquement dans les grands bâtiments (Health Canada 2009).

Le remplacement des ESP des résidences ou de l'ensemble de la tuyauterie interne d'un grand bâtiment ne peut être envisagé que sur du long terme. En effet, les coûts engendrés sont énormes, et demandent encore réflexion pour ce qui est des bénéfices réels des remplacements partiels d'entrées de services (Triantafyllidou & Edwards 2011b). De même, la mise en place de traitements chimiques anticorrosion efficaces demande des essais préalables, et n'est pas toujours bien acceptée par les municipalités (ajout de phosphates dans les eaux usées) et par la population. Un moyen de protection du consommateur consiste en l'installation de dispositifs de filtration au point d'utilisation (POU). En effet, de tels dispositifs sont relativement peu couteux, et peuvent être installés immédiatement au robinet. Ils constituent une barrière au plomb après toutes les sources de plomb dans l'entrée de service et la tuyauterie interne. De tels dispositifs ont été recommandés, et parfois même distribués, par diverses autorités de Santé Publique pour les résidences avec ESP (e.g. Montréal, Hamilton, Washington D.C.). Aussi, les dispositifs POU sont proposés comme solution pour réduire les concentrations de plomb dans l'eau du robinet des grands bâtiments, par le LCCA aux États-Unis, et par le document conseil émis par Santé Canada récemment (Health Canada 2009, USEPA 1994a, USEPA 2006c). Des efforts ont aussi été effectués en Europe afin de développer des systèmes POU efficaces pour l'enlèvement du plomb dans l'eau du robinet (Sublet *et al.* 2002, 2003). On répertorie divers types de dispositifs POU: des pichets filtrants, des dispositifs montés sur robinet, et des dispositifs montés sous évier fournis avec un robinet indépendant. Certains de ces dispositifs sont certifiés pour l'enlèvement du plomb dans l'eau, soit par NSF International (Standard NSF-53), soit par un laboratoire indépendant.

La vaste quantité d'informations citée dans les paragraphes précédents pourrait amener le lecteur à se demander ce qu'il reste à apporter à la recherche sur le plomb dans l'eau potable, puisqu'il s'agit d'un sujet largement couvert depuis la fin des années 70. Cependant, il apparait que dans chacun des aspects de la problématique du plomb dans l'eau du robinet énumérés ci dessus, un facteur inconnu est redondant, évident, mais non pris en compte: le plomb particulaire. En effet, le plomb est présent dans l'eau sous deux formes physiques: une forme « dissoute » généralement définie comme la fraction < 0.1 µm du plomb, et une forme « colloïdale et particulaire » définie comme la fraction ≥ 0.1 µm du plomb. Hors les facteurs influençant la présence et l'ampleur du plomb particulaire dans l'eau du robinet divergent de ceux influençant la présence et l'ampleur de la fraction dissoute du plomb. En effet, le détachement de plomb particulaire depuis des dépôts, des soudures, ou autre est peu prévisible. Au gré de l'écoulement, le plomb particulaire peut être transporté dans la tuyauterie interne des bâtiments, rester bloqué quelque temps dans un coude, puis finalement être remis en suspension par un débit élevé, pour enfin arriver un jour ou l'autre dans le verre puis dans l'estomac du consommateur. Comme le plomb dissous, la formation de plomb particulaire est facilitée par la corrosion des éléments portant du plomb, et donc aussi par les caractéristiques de l'eau. Il peut résulter du détachement des dépôts de plomb formés dans les ESP ou en surface des éléments corrodés, mais aussi de dépôts de fer, carbonates de calcium, ou autre sur lesquels le plomb serait absorbé et accumulé au cours du temps (Schock 1990). Hulsmann (1990) reporte deux formes de particules de plomb : (i) le plomb particulaire/colloïdal résultant de l'adsorption du plomb sur les particules de fer, et (ii) les « flocons » de plomb de taille > 12 µm et résultant du détachement des dépôts dans les ESP sous l'influence des perturbations hydrauliques. On isole usuellement le plomb particulaire dans un échantillon de plomb total par une filtration à 0.22 µm voire 0.45 µm, ce qui rend la définition « pratique » du plomb particulaire comme la fraction > 0.22 µm voire > 0.45 µm. Cependant, étant donné l'absorption du plomb dissous observée sur certains filtres par Schock & Gardels (1983), et considérant le fait que le consommateur ingère à la fois le plomb particulaire et le plomb dissous, on a depuis lors confondu plomb dissous et plomb particulaire dans le plomb total, en attribuant toujours la variabilité inexpliquée du plomb total au plomb particulaire (Schock 1990).

Excepté les trois études mentionnées ci dessus, aucune information précise sur le plomb particulaire n'était disponible jusqu'à présent. Ainsi, malgré la connaissance du plomb particulaire et de son comportement « libéré » depuis presque 30 ans, il est totalement ignoré dans les protocoles d'échantillonnages, dans les méthodes d'analyse au laboratoire, et dans l'analyse de l'exposition. En effet, les protocoles d'échantillonnage développés en premier lieu pour les résidences avec ESP sont principalement basés sur la cinétique de dissolution du plomb dans l'eau. Par exemple, le protocole d'échantillonnage après 30 minutes de stagnation largement utilisé au Canada, et le protocole d'échantillonnage après 6 heures de stagnation imposé par le

Lead and Copper Rule (LCR) aux États-Unis, se basent sur les courbes de dissolution du plomb dans les ESP. Aussi, le rinçage de 5 minutes effectué bien souvent avant la stagnation, et le fait de recommander un échantillonnage à très faible débit peu représentatif des habitudes de consommation (< 5 Lpm), limitent fortement les chances de collecter du plomb particulaire dans l'échantillon et donc en sous estiment potentiellement l'importance. Par ailleurs, les derniers documents du LCCA préconisent d'échantillonner l'eau des grands bâtiments à très faible débit, et l'exemple donné est celui d'un mince filet d'eau (USEPA 2006c). Ceci suggère que les données de plomb dans les grands bâtiments, bien que déjà très élevées, sont sous-estimées. En effet, les valeurs de l'ordre du mg/L reportées par Maas *et al.* (1994), Bryant (2004), Boyd *et al.* (2008a), Lambrinidou & Edwards (2008), et Triantafyllidou & Edwards (2011a) suggèrent un problème accru de plomb particulaire spécifiquement dans les grands bâtiments, puisque de telles concentrations ne peuvent être seulement dues au plomb dissous (concentration de saturation maximale). Ainsi, le plomb particulaire ne serait pas un phénomène sporadique pour ce type de bâtiments, et pourrait contribuer de façon majeure à l'exposition des enfants dans les écoles et garderies.

Un autre aspect de la sous estimation du plomb particulaire relève de la méthode de conservation et d'analyse des échantillons. En effet, les échantillons de plomb total sont généralement traités selon la méthode 200.8 de l'USEPA, soit une acidification à pH < 2 avec 0.15% d'acide nitrique, une conservation minimale de 16 heures à 4 °C, puis une analyse à l'ICP-MS. Cette acidification est principalement pensée pour éviter que le plomb n'adhère aux parois des bouteilles d'échantillonnage, et pour le conserver en solution. Cependant, il s'avère que cette méthode de digestion soit insuffisante pour dissoudre certaines formes de plomb particulaire, en particulier le plomb tétravalent, et qu'il faille pour ces formes procéder à une digestion à chaud à pourcentage d'acide nitrique plus élevé (Triantafyllidou *et al.* 2007). Ainsi, le plomb particulaire est encore une fois négligé, oublié, et sous estimé. Un exemple frappant de cette négligence, et de la nouvelle prise de conscience du plomb particulaire, est la modification du protocole de certification NSF-53 pour la réduction du plomb dans l'eau du robinet. En effet, l'ancien protocole consistait certes à mettre les dispositifs à l'épreuve d'une forte concentration de plomb, mais seule la forme dissoute du plomb était testée. Le protocole modifié de 2007 a ajouté la forme particulaire du plomb à l'eau du test. Cet ajustement a entrainé le retrait de la certification NSF-53 pour le plomb pour les pichets filtrants, témoignant de l'inefficacité de ces derniers pour l'enlèvement des particules de plomb, et de l'importance de considérer les deux formes de plomb séparément.

Toutes ces considérations ont mené à une série de questions sur la contribution réelle du plomb particulaire à l'exposition. Le fait que le plomb particulaire soit « masqué » dans le plomb total, et souvent sous estimé dans la fraction du plomb total, empêche d'estimer l'exposition réelle du consommateur au plomb particulaire dans l'eau potable. Cependant, des pistes indiquent que le plomb particulaire serait potentiellement un fort contributeur à l'exposition. Tout d'abord, le plomb particulaire est associé à des concentrations de plomb total dans l'eau potentiellement extrêmes, notamment dans les écoles. Ensuite, la fraction de plomb particulaire serait augmentée sous l'effet de perturbations hydrauliques (e.g. débit élevé) très courantes des habitudes de consommation, et représentant donc des cas fréquents d'exposition. Par ailleurs, les concentrations extrêmes de plomb dans l'eau recensées à Washington D.C., suggérant une présence significative de plomb particulaire, ont été reliées aux concentrations de plomb dans le sang des enfants du district (Brown *et al.* 2011, Edwards *et al.* 2009, Miranda *et al.* 2007). Enfin, cinq cas documentés d'intoxication au plomb ont été associés à une concentration élevée de plomb total dans l'eau, mais aussi à la présence de particules contenant 3 à 100% de Pb dans l'eau du robinet (Triantafyllidou & Edwards 2011a). Bien que n'établissant aucun lien direct entre l'intoxication au plomb et la présence de particules de plomb, ces observations suggèrent que le plomb particulaire pourrait au même titre que le plomb dissous, contribuer au plomb dans le sang et il serait par conséquent justifié de mieux le considérer dans les protocoles d'échantillonnage et d'analyse.

Afin de vérifier cette hypothèse, il convient de :

(1) Qualifier plus précisément le plomb particulaire du point de vue de ses sources et de son occurrence.

(2) Générer des distributions de plomb particulaire représentatives de l'exposition des consommateurs les plus vulnérables (enfants et nourrissons) dans les résidences avec ESP et dans les grands bâtiments.

(3) Caractériser la bioaccessibilité des particules de plomb typiques de l'eau potable, c'est-à-dire la fraction du plomb contenu dans les particules qui se dissous lors du processus gastro-intestinal et devient donc accessible au passage dans le sang.

Plan de la dissertation

Cette thèse présente tout d'abord une revue de littérature sur la biodisponibilité et la bioaccessibilité des particules de plomb dans l'environnement (chapitre 1). Cette étape était capitale dans le développement de cette thèse, puisqu'il s'agissait de « défricher » le domaine très vaste de la biodisponibilité/bioaccessibilité, très spécifique aux sols et poussières, et comprenant une large variété de protocoles et d'opinions scientifiques, pour en faire ressortir le test le plus adapté pour application aux particules de l'eau potable et à l'exposition des jeunes enfants. Ensuite, le chapitre 2 énumère les hypothèses de travail, les objectifs, et la démarche expérimentale adoptée. Le chapitre 3 présente une étude sur les concentrations de plomb particulaire dans l'eau du robinet de résidences avec ESP, ainsi qu'une analyse des sources et de l'occurrence des particules de plomb dans l'eau du robinet. Le chapitre 4 présente une étude regroupant divers tests effectués sur trois types de dispositifs au point d'utilisation, avec une eau contenant les formes dissoutes et particulaires du plomb, pour en valider ou non l'efficacité et justifier ou non leur recommandation pour les populations à risque. Le chapitre 5 présente un combiné des thèmes traités aux chapitres 3 et 4, mais appliqués spécifiquement à un grand bâtiment présentant des concentrations très élevées de plomb dissous et de plomb particulaire: une analyse des concentrations de plomb dissous et de plomb particulaire y est menée (source, occurrence, concentrations), puis des dispositifs POU sont testés sous les conditions de consommation réelles et spécifiques des grands bâtiments. Le chapitre 6 présente l'adaptation d'un test de bioaccessibilité aux particules de plomb de l'eau potable, l'application de ce test à des particules représentatives du plomb particulaire, et enfin l'estimation de la contribution du plomb particulaire à l'exposition. La synthèse des travaux de ce doctorat est effectuée au chapitre 7. Enfin, les conclusions et recommandations émanant de ces travaux sont détaillées en dernière partie.

CHAPITRE 1 PUBLICATION #1 – REVUE DE LITTÉRATURE: EXPERIMENTAL DETERMINATION OF THE ORAL BIOAVAILABILITY AND BIOACCESSIBILITY OF LEAD PARTICLES

Ce chapitre présente une revue de littérature, soumise au journal *Critical Reviews in Environmental Science and Technology*. La réflexion critique menée dans cette revue a permis d'abord de justifier les travaux menés dans la présente thèse, à savoir l'absence et le besoin d'informations sur l'exposition des jeunes enfants au plomb particulaire présent dans l'eau potable, comparativement aux autres sources de plomb dans l'environnement (air, sol, poussières) et au plomb dissous dans l'eau du robinet. Aussi, la recherche bibliographique et l'analyse réalisées ont permis d'identifier le test de bioaccessibilité apparaissant comme le plus adapté pour (1) l'application aux particules de plomb de l'eau potable, et (2) une analyse de l'exposition.

EXPERIMENTAL DETERMINATION OF THE ORAL BIOAVAILABILITY AND BIOACCESSIBILITY OF LEAD PARTICLES

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ABSTRACT

In vivo estimations of Pb particle bioavailability are costly and variable, because of the nature of animal assays. The most feasible alternative to multiply investigations on Pb particle bioavailability is in vitro testing. The Relative Bioaccessibility Leaching Procedure, which is calibrated with in vivo data on soils, presents the highest degree of validation and simplicity. This method could be applied to Pb particles, including those in paint and dust, and those in drinking water systems, which although relevant, have been poorly investigated up to now for childhood exposure assessment. Further investigations are needed, however, considering results using other validated procedures.

Keywords: oral bioavailability, bioaccessibility, lead [Pb] particles, *in vivo* tests, *in vitro* tests.

1.1 Introduction

Lead [Pb] is hazardous to humans, and is of particular concern for fetuses, infants, children, and women of child-bearing age (Counter *et al.* 2009a, Counter *et al.* 2009b, Lamadrid-Figueroa *et al.* 2006). Knowledge of Pb toxicity has progressed significantly since the 1970s. Initially considered toxic only at blood lead levels [BLLs] over 60 µg/dL, it is now considered to have no definable threshold below which "no harmful effect" can be determined (Bellinger *et al.* 1992, Needleman 2004). Early studies demonstrate the immediate and long-term effects of low Pb level exposure during childhood, such as neurobehavioral and neurodevelopmental deficiencies, and effects on growth, hearing, and blood pressure (Needleman & Landrigan 1981, Needleman & Bellinger 1991). Pb uptake may reduce the intelligence quotient [IQ] of infants and children, and affect some brain responses, even at BLLs well below the current public health action threshold of 10 µg/dL. Recently, the effect on IQ has been shown to be even stronger at low BLLs, since decrements in IQ were steeper between BLLs categories < 5 µg/L and 5-9.9 µg/L than between 5-9.9 µg/L and ≥10 µg/L (Canfield *et al.* 2003, Gump *et al.* 2008, Jusko *et al.* 2008, Lanphear *et* *al.* 2000, Lanphear *et al.* 2005, Surkan *et al.* 2007). Considering the neurocognitive and neurophysiological effects observed at low BLLs, health advisory levels are likely to drop to less than the current 10 µg/dL. The European Food and Safety Agency (EFSA) has set the 95th percentile lower confidence limit of the benchmark dose [BMD] of an incremental 1% risk (BMDL01) at 1.2 µg Pb/dL as a reference point when assessing the risk of intellectual deficits in children measured by the Full Scale IQ score (EFSA 2010). Also, the EU Risk Assessment Report states that Pb exposure effects cannot be measured reliably at BLLs <5 µg/dL, due to the limited precision of methods of behavioral testing and Pb quantization in blood (European Commission 2009).

Early studies on the health impacts on children led to public policies to remove Pb sources from food and leaded gasoline, resulting in the steady decline of BLLs in recent years (Iqbal *et al.* 2008, Jones *et al.* 2009, Needleman 2004, Pirkle *et al.* 1998, USEPA 2006a, USEPA 2006b). Remedial actions have also been taken to decrease Pb levels in the soil and dust of Pb-contaminated sites, although decreasing these levels may not always result in lower BLLs in children (USEPA 2006a, USEPA 2006b, von Lindern *et al.* 2003a, von Lindern *et al.* 2003b). Lead paint is a common cause of clinical Pb poisoning, and remains a strong contributor to childhood exposure, as it is still present in houses built before 1978 in the United States; its abatement cost is estimated in the billions of dollars (Needleman 2004, USEPA 2006a, USEPA 2006b). Now, as BLL guidelines become more stringent, the relative contribution of tap water to total Pb exposure may become highly significant (Gulson 2008, Lanphear *et al.* 1996, Lanphear *et al.* 1998a, Lanphear *et al.* 1998b, Lorenzana *et al.* 2003, Ranft *et al.* 2008, Vargas *et al.* 2001). Lanphear *et al.* (2002) report that Pb occurrence in water > 5 µg/L after 1 min of flushing increases the BLLs of children aged 6-24 months by 1.02 µg/dL, contributing to about 20.4% of the total BLL. Recently, abnormal BLLs in young children have been associated with elevated Pb concentrations in drinking water, particulate Pb representing a significant fraction of this (Edwards *et al.* 2009, Miranda *et al.* 2007, Triantafyllidou *et al.* 2007). However, because of its sporadic occurrence, exposure to particulate Pb in drinking water is especially difficult to characterize (Deshommes *et al.* 2010a, Triantafyllidou & Edwards 2011a). Most regulatory and research efforts have assumed that soluble Pb is the predominant form of exposure. Interest in particulate Pb is now growing, because of its potential contribution to chronic and acute exposure (Deshommes *et al.* 2010a, Triantafyllidou *et al.* 2007, Triantafyllidou & Edwards 2011a).

The most direct approach to assessing the contribution of various Pb sources to human exposure is to conduct epidemiological studies or *in vivo* studies. Numerous epidemiological studies of particulate Pb exposure from various media (i.e. air, soil, paint, and dust) have been reviewed by Mushak (1991), Needleman & Bellinger (1991), and the USEPA (2006a, 2006b). Some of these revealed a significant relationship between environmental Pb levels and BLLs, and a decrease in BLLs after remediating Pb sources, providing direct measurements of exposure and its impacts on body burden. However, they are challenging to carry out because of cost, the variability of exposure among the population studied, and BLL evolution since exposure (Guérin *et al.* 2003, Wright & Welbourn 2002).

In vivo experiments are much simpler to plan and perform than epidemiological studies. Key parameters can be controlled, such as exposure levels and conditions, and the relationships between exposure levels and levels of Pb absorbed by the *in vivo* specimen tested can be quantified. However, the measurements are indirect, based on animal models, and require extrapolation to human exposure conditions. A primary outcome of *in vivo* studies of oral Pb exposure is the oral bioavailability of Pb occurring in both dissolved and particulate form. Several *in vivo* experiments have been performed, first with readily soluble Pb forms such as Pb acetate [PbAc], and then mostly with Pb-contaminated soils. But comprehensive bioavailability experiments are long, expensive, demanding, and the use of animal models can raise ethical issues. Moreover, bioavailability results show significant variability, which is inherent to the use of animal models.

In vitro experiments are simpler, faster, cheaper, and highly reproducible, and do not raise ethical concerns, and therefore are best suited to test replication. However, they can only assess the bioaccessibility of Pb, defined as the fraction of ingested Pb dissolved during the digestion process and available for absorption into the systemic circulation (bloodstream). Bioavailability is the fraction actually available and taken up by an organism, while bioaccessibility is an experimentally determined estimate of what is potentially bioavailable (NAS/NRC 2002). If well calibrated, an *in vitro* test can adequately predict *in vivo* results. A significant number of bioaccessibility studies have been conducted on Pb contaminated soils. However, the bioaccessibility of other sources of Pb particles to which infants/children can be exposed (paint, dust, drinking water particles, toys, and food) has not been thoroughly investigated. *In vivo* testing of these particulate forms can be limited by experimental constraints, which can be addressed using *in vitro* tests.

This review summarizes the information available on the bioavailability and bioaccessibility testing that have been proposed for estimating the oral bioavailability of Pb particles in children. Our objectives are to identify the strengths and weaknesses of these procedures, to highlight differences between them to support the interpretation of study conclusions, and, finally, to draw attention to gaps in the data on Pb particles that are relevant for childhood exposure assessment.

1.2 Approaches to estimating Pb bioavailability

Many definitions of bioavailability have been proposed for soil and sediments (NAS/NRC 2002). In this review, the term “oral bioavailability” refers to the amount of ingested Pb that reaches the systemic circulation and that is likely to accumulate in the body, including organs and bones.

Historically, bioavailability has been determined in the laboratory using *in vivo* testing. *In vivo* testing to estimate Pb bioavailability must be carried out over an extended period to ensure that the metal is absorbed, retained, and excreted. The half-life of Pb is estimated to be about 25 days in blood, 40 days in soft tissues, and 25 years in bones (Heath *et al.* 2003). Early human experiments were conducted using Pb in the diet, Pb tracers, or Pb salts labeled with radioactive Pb^{203} (James *et al.* 1985, Rabinowitz *et al.* 1980, Ziegler *et al.* 1978). A detailed review and critical evaluation of these studies is available in Mushak (1991). Such studies helped identify soluble Pb absorption mechanisms and interactions with food. However, these results cannot be directly extrapolated to Pb particles in soil, dust, paint, or drinking water, because of potential matrix effects. A more recent study by Maddaloni *et al.* (1998) measured the bioavailability of soilborne Pb in human adults, and is the only study performed on humans with Pb-contaminated soil. The target population was adults, whose digestive absorption processes differ markedly from those of infants and children (Mushak 1991).

Most *in vivo* experiments have been conducted with young animals using various experimental designs. In general, several groups of animals are involved: a control group receiving a purified diet without any Pb; a group receiving a Pb salt-based solution, such as PbAc, either orally or intravenously (or both, if there are two groups), at different dosages representing the Pb dose range of the test materials; and, finally, a group administered with different doses of the test materials. Defined as 100% bioavailable, Pb salts such as PbAc are used as references to compare test materials and calculate bioavailability. Administering Pb salts intravenously allows the absolute bioavailability [ABA] – the fraction of Pb that enters the bloodstream – to be calculated. If PbAc is delivered orally, the relative bioavailability [RBA] – the bioavailability of the test material relative to that of PbAc – is calculated. The intravenous dosage for determining ABA is also used to set minimum and maximum BLLs for a range of doses and to better characterize Pb distribution in a steady state (Freeman *et al.* 1994, Schoof *et al.* 1995, Weis *et al.* 1994). RBA is also called "oral bioavailability", but relative to an appropriate reference material (PbAc) (Casteel *et al.* 2006, Weis *et al.* 1994). RBA is more informative, because it takes the exposure matrix into account (USEPA 2007b). The ABA can be calculated, as opposed to measured by intravenous injections, by multiplying the RBA by a set factor, corresponding to the Pb absorption fraction of PbAc administered orally. The following equations detail the general calculation of oral ABA and RBA:

- ***Oral ABA calculation:***

$$ABA_{TM} = \frac{IDM_{oral\ TM}}{IDM_{iv\ PbAc}} \times \frac{Dose_{iv\ PbAc}}{Dose_{oral\ TM}} \quad (Equation\ 1)$$

$$ABA_{PbAc} = \frac{IDM_{oral\ PbAc}}{IDM_{iv\ PbAc}} \times \frac{Dose_{iv\ PbAc}}{Dose_{oral\ PbAc}} \quad (Equation\ 2)$$

Notes: IDM – Internal Dose Metrics (BLL, Pb in tissues, etc.); iv – intravenous; TM – Test Material

- ***Oral RBA calculation:***

$$RBA_{TM} = \frac{ABA_{TM}}{ABA_{oral\ PbAc}}$$

$$RBA_{TM} = \frac{IDM_{oral\ TM}}{IDM_{oral\ PbAc}} \times \frac{Dose_{oral\ PbAc}}{Dose_{oral\ TM}} \quad (Equation\ 3)$$

- ***Link between ABA and RBA:***

$$ABA_{TM} = Pb\ set\ factor \times RBA_{TM}\ (Equation\ 4)$$

The internal dose metrics [IDM] measured during *in vivo* experiments can also vary. Several kinetic pools for Pb in the human body with varying rates of turnover, partly depending on the time elapsed since the administration of the Pb dose, affect bioavailability estimation. To address this, sequential blood samples can be collected during the experiment, as well as blood and tissue samples on the last day of the test. The tissue samples most frequently collected are from the liver, kidneys, and femurs. The amount of Pb stored in other parts of the body is considered to be small, in the order of 4% of total Pb measured in blood, bones, liver, and kidneys for short-term experiments (Freeman *et al.* 1996). So, RBA calculation can be based on Pb levels either in blood or in tissues: blood-based RBA is calculated by measuring the ratio between BLL following test material ingestion and BLL following oral ingestion of PbAc for a similar dosage (Equation 3). This ratio is measured under presumed steady state conditions after repeated exposure, resulting in a stable BLL, or at various times during the experiment to monitor BLL evolution (Freeman *et al.* 1996). Similar ratios can be established for bones, kidneys, and liver on the last day of the experiment (Freeman *et al.* 1992, Smith Jr. *et al.* 2008a, Smith Jr. *et al.* 2008b).

The most commonly used approach for evaluating bioavailability, and a comprehensive one, is based on monitoring BLLs over the course of the experiment for different dosages, as well as the Pb content in bones, kidneys, and liver at the end of the exposure period for different dosages. The "area-under-the-blood concentration versus time curve" [AUC] of BLL is then calculated for each Pb dose and test material (Figure 1-1). The AUC approach for BLL has the advantage of including the whole dose-response relationship of the BLL over the time of the experiment. However, the information it provides on the evolution of absorption over that time is poor (Weis & LaVelle 1991). AUC BLL (e.g. µg×day/dL), bone Pb levels, or other kinds of IDM for Pb salt and test material are then fitted versus Pb dose. Identical absorbed doses of Pb delivered to target Pb pools are assumed to produce an equivalent IDM (Schoof *et al.* 1995). Bioavailability is determined by calculating the ratio of Pb test material dose and the PbAc dose that yields an identical IDM (Casteel *et al.* 1997, Schoof *et al.* 1995) (Figure 1-2). This calculation is equivalent to Equation 3, since the IDM for both the test material and the PbAc administered orally cancel each other out:

- ***Oral RBA based on equivalent IDM:***

$$RBA_{TM} = \frac{Dose_{PbAc\ oral\ producing\ equivalent\ IDM\ to\ TM}}{Dose_{TM\ oral\ producing\ equivalent\ IDM\ to\ PbAc}}\ (Equation\ 5)$$

This approach requires finding the most suitable mathematical model for both the PbAc dose and the Pb test material dose IDMs. Indeed, an IDM per unit of absorbed Pb dose does not depend on the Pb source. The best fit for bone, liver, and kidney Pb levels is usually linear, whereas for BLL/AUC, which increases gradually and then reaches a plateau (steady state), the best fit is non linear and varies (Casteel *et al.* 1997, Casteel *et al.* 2006). Doses of Pb test material and Pb salt producing the same IDM can be calculated from the best fitting equations, and the bioavailability ratio calculated for each endpoint studied (AUC, BLL, Pb in bones, etc.). The BLL/AUC used for this ratio is usually the point before the rate of uptake of Pb from the test material starts to decrease owing to increasing dosage (Schoof *et al.* 1995). The ratio can also be calculated for a range of doses that reflects currently estimated exposure. Finally, a point estimate can also be calculated, combining the bioavailability relative to each of the endpoints studied simultaneously, weighted according to its uncertainty (Casteel *et al.* 1997, Casteel *et al.* 2006).

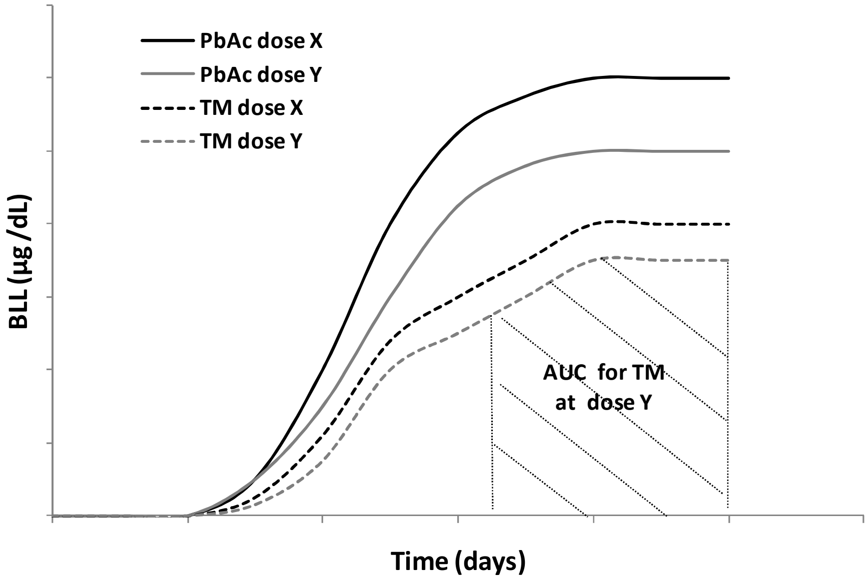
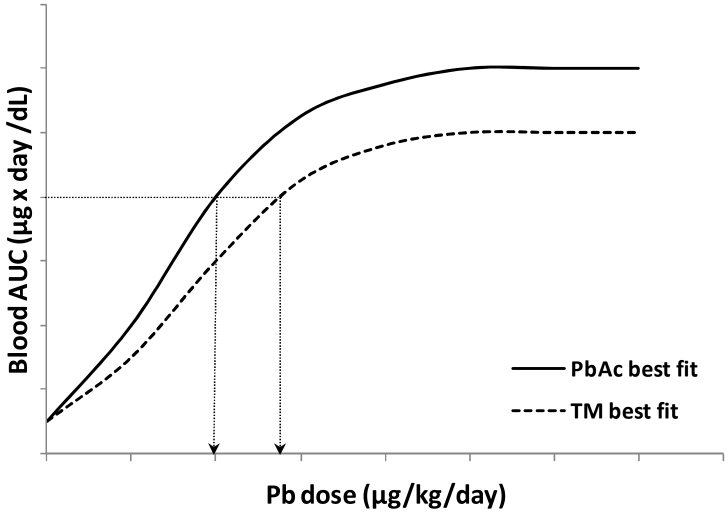


Figure 1-1. Calculation of blood Area Under the Curve (AUC). *TM – Test Material.*

(a)



(b)

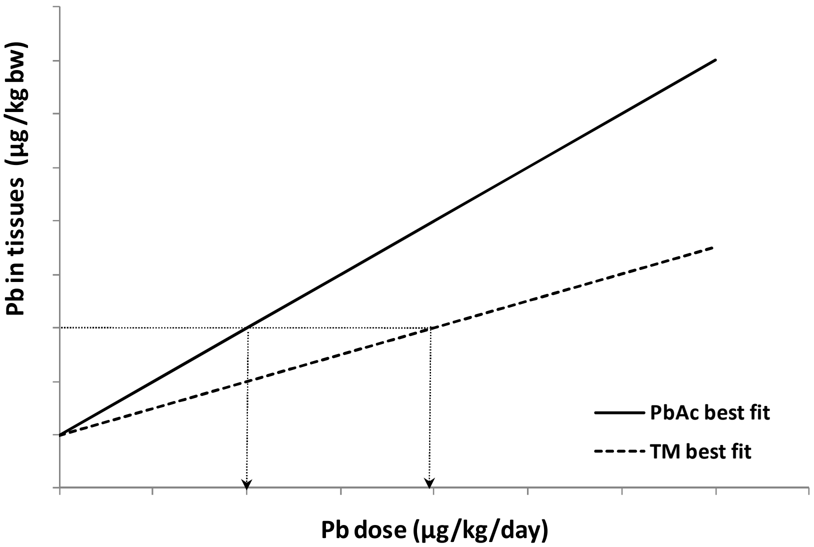


Figure 1-2. Calculation of RBA based on equivalent Internal Dose Metrics (IDM) for (a) blood; and (b) tissues (bones, liver, kidney, etc.). *TM – Test Material.*

Another way to evaluate bioavailability is to complete a total mass balance. This method requires sequential BLL sampling, as well as total collection of urine and feces to recover all the excreted Pb. Pb content in feces and urine is subtracted from total Pb intake, and provides an estimate of the body's net retention (Ziegler *et al.* 1978). Urine samples represent the absorbed dose of Pb that is primarily excreted, whereas fecal samples provide the fraction of Pb that is unabsorbed

(Schoof 2003). When BLLs reach a steady-state with multiple dosing, bioavailability can be determined by calculating the ratio of *total Pb in the urine plus total Pb retained in the body* to *total Pb recovered*. Such results have limited value if the total net excretions are underestimated. However, this method is nearly non invasive for the test subject, and can provide information on Pb accumulation in the body after repeated exposure. This makes it useful for studies on Pb uptake and Pb distribution in the whole body (Weis & LaVelle 1991).

The method for calculating the bioavailability and IDM on which it is based directly influences the bioavailability estimates. Understanding these differences is important when comparing results based on different methodologies. An RBA based on BLL is unlikely to provide the same results as global bioavailability based on the whole body's Pb uptake derived from a complete mass balance. If bioavailability is based on the blood AUC, the results will be influenced by the duration of the experiment and the timing of sampling. Furthermore, as shown by Polak *et al.* (1996), the interactions between Pb in soft tissues, bones, and blood determine the fractional absorption, and thus the bioavailability. The timing of the sampling should be chosen carefully, considering the evolution of BLL over time, whether or not steady state is reached (Mushak 1998).

1.3 Experimental factors influencing Pb bioavailability

The *in vivo* experimental design parameters affecting the estimation of Pb bioavailability include: the animal model (species), its age, the addition of food, the duration of the experiment, and the dosage. The selection of these parameters and corresponding bioavailability results for published studies are summarized in Table 1-1.

Table 1-1. *In vivo* experiments on Pb particles and bioavailability results.

REFERENCE	SPECIMEN	SUBSTRATE	STATE, DURATION, DOSE	RBA/ABA
Freeman *et al.* 1992	Rats (7-8 wk)	Mine wastes	• Fed • 30 d • 0.12- 24 mg Pb/kg bw/d	• 12.1±3.6-26.8±4.8 (blood RBA %) • 4.8±1.9-13.3±2.2 (bone RBA %) • 0.6±3.1-13.6±3.1 (liver RBA %)
Dieter *et al.* 1993	Rats (6-7 wk)	Pb oxide, Pb sulfide, Pb ore concentrate	• Fed • 30 d • 0-100 ppm Pb	• 69-93 (blood RBA %, Pb oxide) • ND-36 (blood RBA %, Pb sulfide) • ND-10 (blood RBA %, Pb ore)
Freeman *et al.* 1993	Rats (7-8 wk)	Mine wastes	• Fed • 30 d • 5 to 20 ppm Pb	• 0.36±1.04-7.32±1.57 (blood ABA %) • 0.51±0.15-2.25±0.23 (bone ABA %)
Ruby *et al.* 1993	Rabbits (12 wk)	Mine wastes	• Fast • 0.5-36 h • 7.8 mg Pb/kg bw	• 9±4 % Pb soluble in stomach
Freeman *et al.* 1994	Rats (7-8 wk)	Mine wastes	• Fed • 30 d • 0.12 to 24 mg Pb/kg bw/d	• 2.7±1.5 (% blood RBA) • 0.40±0.16 (% bone RBA) • 0.55±0.68 (% liver RBA)
Schoof *et al.* 1995	Rats (4 wk)	Smelter soil	• Fed • 31 d • 0.11-3.4 mg Pb/kg bw/d	• 41 (% blood RBA) • 20 (% blood ABA)
Freeman *et al.* 1996	Rats (~ 4 wk)	Soil, Pb sulfide	• Fed • 44 d • 17.6-127 ppm	• 0.8-8.7 (soil, % RBA) • 1.2-5 (Pb sulfide,% RBA)
Lorenzana *et al.* 1996	Swine (40-50 d)	Tacoma smelter soil & slag	• Fast (small dough) • 0-7 d • 34-567 µg Pb/kg bw (single dose)	• Mean ABA§ (%,PbAc$_{iv}$): 10 (soil), 4 (slag)
Casteel *et al.* 1997	Swine (8-9 kg)	Berm and residential soils	• Fast (small dough) • 15 d • 71-732 µg Pb/kg bw/d	• 74-75 (point estimate RBA %‡)
Casteel *et al.* 1997-1998$^{\#}$	Swine	Joplin smelter soil treated or not with 1% phosphate		• Point estimate RBA (%): 59-67 (not treated) to 38-45 (treated 1% phosphate)
Maddaloni *et al.* 1998	Humans (21-40 yr)	Bunker Hill residential soil	• Fast & Fed • 30 h • 250 µg Pb/70 kg bw	• Fasting state: 26.2±8.1 (% ABA) • With breakfast meal: 2.52±1.7 (% ABA)
Ellickson *et al.* 2001	Rats (0.18-0.2 kg)	SRM 2710 Montana soil	• Fast • 3 d • 7-8 mg Pb (single dose)	• 0.4-0.9 (% RBA)
Brown *et al.* 2003	Rats (3-4 wk)	Urban soil treated with biosolids (n=9)	• Fed • 35 d • 71-125 mg Pb/kg diet	• RBA not calculated in %

Table 1-1. *In vivo* experiments on Pb particles and bioavailability results (continued).

REFERENCE	SPECIMEN	SUBSTRATE	STATE, DURATION, DOSE	RBA/ABA
Hettiarachchi *et al.* 2003	Rats (12 wk)	Joplin soil treated or not with Mn, phosphate, or CRYP (n=15)	• Fed • 21 d • 1-6 mg Pb/kg bw/d	• Blood RBA%: 34 (not treated); 19-33 (treated) • Kidney RBA%: 48 (not treated); 19-39 (treated) • Liver RBA%: 27 (not treated); 19-21 (treated) • Bone RBA%: 34 (not treated); 20-24 (treated)
USEPA 2004, 2009	Juvenile swine	2 Omaha smelter soils	• Fast (small dough) • 15 d • 75-675 µg Pb/kg bw/d	• 83 & 96 (point estimate RBA %)
Casteel *et al.* 2006	Swine (5-6 wk)	19 soil or soil-like materials[†]	• Fast (small dough) • 15 d • 75-675 µg Pb/kg bw/d	• 1-105 (point estimate RBA %[*])
Marschner *et al.* 2006	Swine (70 d)	5 soils	• Semi-fed (milk powder after 5 h fast) • 28 d • 0.1-3.2 mg Pb/kg bw/d	• 17-63 (RBA %)
MSE Technology Application 2006	Swine (5-6 wk)	Smelter soil HER-2930	• Fast (small dough) • 15 d • 77-686 µg Pb/kg bw/d	• 82 (point estimate RBA %)
Smith Jr. *et al.* 2008b	Rats (~ 21 d) Micropigs (~ 30 d)	2 smelter soils	• Fed • 30 d • 50 µg Pb/g diet	• Rats RBA %: 88 (blood), 62 (bone) • Micropigs RBA %: 81 (blood), 68 (bone)
Smith Jr. *et al.* 2008a	Rats (~ 21 d)	5 soils	• Fed • 35 d • 6.8-150 µg Pb/g diet.	• 85±48 (blood RBA %) • 91±12 (bone RBA %)
Bannon *et al.* 2009	Juvenile swine	8 small arms range soils	• Fast (small dough) • 15 d • 75-675 µg Pb/kg bw/d	• 108±18 (point estimate RBA %)
Caboche 2009	Swine (28 d)	15 mining and smelting soils	• Fast (small dough) • 14 d • <1 to 8 mg Pb/kg bw/d	• 6-100 (kidney RBA %) • 8-100 (urine RBA %) • 9-100 (bone RBA %) • 10-85 (liver RBA %)
Juhasz *et al.* 2009	Swine (6-8 wk)	5 incinerator and urban soils	• Fast • 5 d • 0.1-1.2 mg Pb/kg bw (single dose)	• 10.1±8.7-19.1±14.9 (blood RBA %)
Smith *et al.* 2011a	Adult mice	12 Pb impacted soils from various sources	• Fast • 48 h • 0.1-1.7 mg Pb (single dose)	• 10±2.8-89±15.3 (blood RBA %)

RBA — relative bioavailability; ABA — absolute bioavailability; ND — not determined; [§]estimates include 0 & 100% in the confidence interval; [‡]USEPA (2007b) and Casteel et al. (2006) point estimate; [#]Data from the Ruby et al. (1999) review; [†]including soils tested by Schroder et al. (2004); [*]Also available in USEPA (2007b).

1.3.1 Animal model

A major factor affecting bioavailability estimation is the animal species used, and includes its age and its developmental stage. Intra-species differences in anatomy, feeding behavior, absorption rate, and digestion processes influence the results. As shown in Table 1-1, rats, piglets, and rabbits have been used to estimate Pb particle bioavailability. Pioneer studies by Freeman *et al.* (1992, 1993, 1994, 1996), Battelle (1993), PTI Environmental Services (1994a, 1994b), and Ruby *et al.* (1993, 1996) used rodents and rabbits to determine bioavailability and the risk to infants/children.

Although rodents and lagomorphs are widely used and well-known animal *in vivo* models, differences in their digestive systems compared to the human prevent direct extrapolation to the Pb exposure of human children. First, rodent stomachs have a smaller glandular region than human stomachs, and consequently less surface area for parietal cells secreting acid (Weis & LaVelle 1991). This results in a higher stomach pH of 3.9 and 3.2 in the fasting and fed states respectively (McConnell *et al.* 2008). In contrast, rabbits present a relatively low pH of 1.6 in the fed state, which is significantly lower than that of humans (Merchant *et al.* 2011). Also, the surface area of the small intestine of a rat is about one-fifth the size a human one, which implies decreased Pb bioavailability, since some absorption mechanisms in the small intestine are surface area-dependent (Klaassen 2008, Weis & LaVelle 1991). Another significant difference is that the rat's small intestine is mature at weaning, unlike that of the human newborn, and its Ca absorption capacity decreases rapidly within 30 days (Weis & LaVelle 1991). This results in a drastic decrease in the rat's Pb absorption rate, from about 80% between 0 and 30 days to about 50% between 1-2 weeks and 6-8 weeks (Mushak 1991, Polak *et al.* 1996). Several *in vivo* studies listed in Table 1-1 have used rats aged 4 weeks and 6-7 weeks (Ellickson *et al.* 2001, Freeman *et al.* 1992, Freeman *et al.* 1993, Freeman *et al.* 1994, Freeman *et al.* 1996, Schoof *et al.* 1995), which may have been too old to be representative of the high Pb absorption rates found in children 0-6 years old (Mushak 1998). Differences in the soils tested aside, the animal's age may actually explain the significantly higher blood RBA (85-88%) observed in weaning rats aged 21 days by Smith Jr. *et al.* (2008a, 2008b), compared to that of rats aged 4 weeks and older (0.8-41%) (Freeman *et al.* 1992, Freeman *et al.* 1993, Freeman *et al.* 1994, Schoof *et al.* 1995). Also, the 12 week old rabbits used by Ruby *et al.* (1993) may be more representative of adult digestive conditions, as a 5 week old rabbit absorbs twice as much Pb as an older rabbit (Mushak 1998). The declining absorption rates within a relatively short period constitute a challenge in itself, since bioavailability tests must extend over several weeks owing to the half-life of Pb in blood. During a subchronic testing period of 15-30 days, the weanling rat's Pb absorption can vary significantly, depending on its age at the start of the testing period.

Specific behavior and defense mechanisms of rats and rabbits also influence absorption. For example, in response to exposure to Pb, rats lower their body temperature, which decreases its RBA. Furthermore, the constant feeding pattern of rats and rabbits and their cellulose-type diet are not favorable to Pb dissolution in the stomach, as this organ rarely empties completely, resulting in a pH buffer effect and the constant availability of ligands for Pb ions (Weis & LaVelle 1991). Finally, coprophagic behavior in both species can lead to an inaccurate estimation of Pb bioavailability, because of Pb recirculation. Coprophagy is essential to the assimilation of all the nutrients necessary for the growth and development of rodents and rabbits, which, if impeded, can cause deficiencies in some minerals/vitamins that interfere with Pb absorption. Biliary excretion is also greater in rodents than in humans, and can generate errors in the estimation of Pb excreted and absorbed (Schoof *et al.* 1995, Smith Jr. *et al.* 2008a, Smith Jr. *et al.* 2008b, Weis & LaVelle 1991). Despite these differences, rats and rabbits are species commonly used for *in vivo* experiments, and so are very well characterized. Interpretation of the results, adjustments to them, and extrapolation to humans may therefore be more accurate than for other animal models that are less often used in laboratories. Moreover, even with the marked differences between their digestive systems and those of children, these species remain highly useful for studying many aspects of Pb exposure, such as estimating the potential health risks of Pb (e.g., Huang & Schneider 2004).

Smith Jr. *et al.* (2008b) compared Pb bioavailability in weanling micropigs and rats for various test materials, concluding that the micropig model is superior, because of a greater Pb concentration in their tissues and the ability to detect bioavailability trends in their bones, blood, liver, and kidneys. Juvenile swine appear to be a better surrogate for predicting digestive and absorption processes in infants, because of the similarities between them with respect to: gastric hydrochloric acid (HCl) and protease secretion; small intestine configuration; limited digestive capacity, which impedes solid food digestion; and gut maturity (Heath *et al.* 2003, Moughan *et al.* 1992). At birth, the digestive organs of both species are comparable in size, and the anatomy of the stomach and small intestine is similar. Also, although the immature swine grows faster than the newborn/child, it remains at prepubertal state throughout the experiment (Weis *et al.* 1994). Similar patterns for secretions of HCl, pepsin, and other enzymes are present in the stomach, although gland distribution differs. Stomach capacities for babies at birth, 2 weeks, and 4 weeks approach piglet stomach volumes at 0, 10, and 20 days. Finally, the length of the small intestine and the microscopic gut structure of infants and juvenile swine are similar (Moughan *et al.* 1992). Marked differences also exist in the capacity of the digestive tract relative to the body weight of the piglet, which is three times greater than the newborn's. The piglet's stomach volume is 260 cm^3, compared to 130 cm^3 for infants of the same weight (5.75 kg). In the piglet, the length of the small intestine increases dramatically within the first ten days of life compared to that of the newborn. This implies that adjustments need to be made, notably in terms of increases in feed levels/dosage. However, the piglet's gastro-intestinal [GI] tract is well characterized, and the relationships between body weight and stomach/small intestine weight/length are known, so that adequate adjustments can be made. To account for the fact that the juvenile swine grows seven times faster than the human baby, intake is expressed relative to gut capacity at similar developmental stages. This rapid growth can be an advantage, since it provides an accelerated model for postnatal human growth and development. Finally, the piglet's size allows serial blood sampling without stressing the animal (Moughan *et al.* 1992). However, the cost of conducting piglet experiments can limit the use of this model to investigating multiple substrates.

USEPA Region VIII scientists conducted *in vivo* experiments on piglets to estimate the bioavailability of soil Pb particles, and from there the potential burden for infants/children (LaVelle *et al.* 1991, Ruby *et al.* 1999, Weis *et al.* 1993, Weis *et al.* 1994). The juvenile swine model experimental procedure for assessing oral bioavailability from soils, detailed in Weis *et al.* (1994) and further developed by Casteel *et al.* (1997), was then applied to a wide variety of soils (Bannon *et al.* 2009, MSE Technology Application 2006, Ruby *et al.* 1999, Schroder *et al.* 2004, USEPA 2004), in some cases with modifications to the original EPA procedure (Marschner *et al.* 2006, Smith Jr. *et al.* 2008b). The protocol detailed in Casteel *et al.* (1997) was adopted as a USEPA standard for assessing oral bioavailability from soils. It was also used by USEPA Region VIII and others for similar experiments on soils contaminated with arsenic (Juhasz *et al.* 2007, Rodriguez *et al.* 1999, Ruby *et al.* 1999).

1.3.2 Conditions of dose and application

The dosage and its frequency are key factors affecting bioavailability estimation (Weis *et al.* 1994). Generally, a fixed quantity of soil/dust is administered based on the estimated average daily soil/dust intake for children, which corresponds to a variable Pb dosage depending on the Pb content of the soil. However, for some animal models, such as the rat, it is often necessary to increase dosages in order to increase BLLs to detectable levels that permit reliable differentiation between the PbAc and the test material (Freeman *et al.* 1992). However, bioavailability results obtained under such conditions may be underestimated, as the rate of elimination of Pb at these high dosages could be much higher, especially if they exceed the saturation concentration for active transport mechanisms in the gut (LaVelle *et al.* 1991).

Childhood soil/dust ingestion rates from hand-to-mouth activity refer to small quantities ingested repeatedly during the day, resulting in a cumulated dose of around 100 mg/day (Mushak 1998). The bioavailability estimation based on *in vivo* experiments is only valuable if the ingestion of the test material/PbAc and subsequent absorption by the test animal are representative of those of children ingesting Pb from diet, soil, dust, paint, or water (Mushak 1998, Weis & LaVelle 1991). Mushak's (1998) review stresses that the dosages for *in vivo* testing should be representative of children's exposure in terms of amount and number of ingestions. For example, the single high dose of 4.2 g of test material in the Ruby *et al.* (1993) study is not representative, but more so to soil geophagia, a form of pica ingestion (Mushak 1998). Realistic exposures can be achieved by administering lower doses twice daily, as performed in swine studies by Casteel *et al.* (1997, 2006), USEPA (2004, 2009), Schroder *et al.* (2004), MSE Technology Application (2006), Bannon *et al.* (2009), and Caboche (2009) (Table 1-1). These studies suggest that realistic dosages administered through multiple daily ingestions are preferable, and represent a better simulation of the exposure of the infant/child.

The choice of a fasting or a fed state when administering Pb doses is a major factor in calculating bioavailability, since it affects the stomach's retention time and pH. *In vivo* studies presented in Table 1-1 were performed either in fasting or fed state. The uptake of PbAc is reduced by about half when Pb is administered in food, rather than in a fasting state as in rat-based experimental studies (USEPA 2007b). Maddaloni *et al.* (1998) also observed a decrease in RBA of about 24% from fasting to feeding conditions in adult humans after ingesting contaminated soil (Table 1-1).

The lower bioavailability of Pb in a fed state is partly attributed to the adsorption of dissolved Pb from the stomach on non digested particles at the entry of the intestine as a consequence of the pH increase (Ruby *et al.* 1993). The type of food also significantly influences bioavailability, as shown by the wide retention range associated with food type (3.5-56.8%), as compared to 61.3% for fasting adults dosed with PbAc (James *et al.* 1985). That study concluded that Pb ingestion during meals, as well as the presence of calcium, phosphate, and phytate in the meals, notably decreases Pb bioavailability three hours before and after ingestion. Indeed, calcium, iron, and phosphate were shown to compete with Pb for absorption through the intestine because of similar uptake mechanisms (Heath *et al.* 2003, Mushak 1991). Higher estimates of Pb bioavailability were reported by James *et al.* (1985) for liquids poor in nutritional elements (33-72%), and the lowest for milk (11-17%), traditional breakfast (0-8%), and calcium phytate (1-9%). Given the significant impact of food, the fasting state appears to be the conservative choice simulating the worst, but still plausible scenario, since soil, dust, and paint can be ingested by children during playtime between meals. However, Pb particles ingested via drinking water or formula, or incorporated into food during cooking can be ingested in both the fasting and the feeding state.

1.3.3 *In vivo* testing of Pb particles

Table 1-1 summarizes results from *in vivo* experiments completed with Pb-contaminated soils and Pb paint chips. Significant differences between the animal models, their age, the dosages, the duration, and the calculation method for generating RBA/ABA values must be taken into account when comparing these estimates. The extent of fasting is highly variable in these studies, and only a few studies were conducted in a complete fasting state (Ellickson *et al.* 2001, Juhasz *et al.* 2009, Maddaloni *et al.* 1998, Ruby *et al.* 1993, Smith *et al.* 2011a). However, subject to interpretation because of methodological differences, these estimates provide useful relative measurements for different sources and conditions of Pb exposure, and helped in assessing cleanup goals and in refining exposure assessments for contaminated sites (NAS/NRC 2002). Such estimates can also provide information on the effectiveness of remediation actions, since swine tested with Joplin soils showed a decrease in RBA following remediation with phosphates. However, a greater reduction in RBA was observed in adult human test subjects, suggesting that the estimates of Pb remediation in swine may be conservative (Ryan *et al.* 2004).

In conclusion, several experimental factors should be considered, so that the results of *in vivo* Pb oral bioavailability estimates using animal models can be extrapolated appropriately to infants and children. In terms of the animal model, juvenile swine carefully controlled for age appear to be the best surrogate for human children. Nonetheless, as *in vivo* experiments carried out with rodents are generally cheaper than with other species, the use of these animal models should not be excluded. To improve the significance of these outcomes, more results using weanling rodents calibrated to the responses obtained using piglets would be useful. Of all the reported experiments and procedures, the conditions proposed by Casteel *et al.* (1997, 2006), who used juvenile swine over a subchronic period of 15 days with 0.5-5 g soil (75-675 µg Pb/kg bw/day) delivered twice per day, appear the best suited for simulating the conditions of ingestion of soil/dust/paint particles by infants/children. Bioavailability calculation can be based on multiple IDM, such as the widely used AUC for BLL, and the analysis of Pb accumulated in target tissues, such as bone, liver, and kidneys. Such an approach provides information on the distribution of body Pb and the interaction between accumulated lead in blood, soft tissues, and bones. Bioavailability based solely on BLL may ignore a significant fraction of Pb that has already been transferred to target organs through the systemic circulation.

1.4 *In vitro* bioaccessibility testing procedures

Bioaccessibility can be estimated at laboratory scale using chemical extractions of Pb contaminated test material in solution and under experimental conditions that mimic the mixing and processing of GI fluids. The total recoverable Pb is generally determined by subjecting a subsample of the test material [TM] to strong acid digestion, as, for example, in Method 3050 developed by the USEPA for soils and sediments. *In vitro* bioaccessibility [IVBA] is calculated as follows:

$$Pb\ IVBA = \frac{mg\ Pb\ leached\ in\ extraction\ fluid\ per\ g\ of\ TM}{mg\ total\ recoverable\ Pb\ \ per\ g\ of\ TM}\ (Equation\ 6)$$

Several experimental factors affect the estimates of bioaccessibility yielded by *in vitro* tests, and their impact varies according to the type and form of the Pb sources investigated. Choosing an adequate combination of these factors is important for generating bioaccessibility results that can be correlated to bioavailability results. Key factors include the physico-chemical conditions maintained during the *in vitro* test, especially gastric and intestinal pH, but also the co-presence of food, mixing conditions, the solid to liquid [S/L] ratio, and the retention time. Their relative importance is summarized in Table 1-2.

Table 1-2. *In vitro* tests design: main factors affecting bioaccessibility results.

Parameters	**Degree of Importance**	**General impact on IVBA%**	**Notes**	**References (non exhaustive)**
Gastric pH	+++	IVBA ↑ when pH ↓	- Check the pH increase at the end of the G phase.	*Ruby et al. 1992, 1999* *Oomen et al. 2002* *Yang et al. 2003* *Drexler & Brattin 2007*
Intestinal pH	+++	↓ IVBA as compared to gastric IVBA Major ↓ IVBA from pH 4 to 6 Slight ↑ IVBA at pH 7.5 compared to pH 6.0-7.0	- Adjust intestinal IVBA to Pb salt solubility during the intestinal phase - Increase in solubility of bile/pancreatin-Pb complexes at pH 7.5	*Oomen et al. 2003a, 2006* *Caboche 2009* *Juhasz et al. 2009*
Temperature	-	No impact between 20°C and 37°C	- May be important when enzymes are added	*Drexler & Brattin 2007*
Phases simulated	+++	Gastric IVBA > Intestinal IVBA	- Adjust intestinal IVBA to Pb salt solubility during the intestinal phase	*Juhasz et al. 2009*
Extraction	+	IVBA ↓ in the range: centrifugation > microfiltration > UF	- No difference between 0.2 and 0.45 µm filtration	*Drexler & Brattin 2007,* *Van De Wiele et al. 2007*
Fluid composition	+	Contradictory results (↑ or ↓ IVBA) Physiologically based fluids do not seem important for the G phase	- Physiologically based fluids may be important when food is added - Bile/pancreatin would create soluble complexes with Pb	*Ruby et al. 1993* *Medlin 1997* *Oliver et al. 1999* *Oomen et al. 2003a, 2004* *Juhasz et al. 2009*
Retention time	++	IVBA ↑ when gastric phase time ↑ No information on intestinal extraction time effect	- Lower impact on more soluble Pb forms: IVBA plateau reached after 20-30 min	*Ruby et al. 1996, 1999* *Gasser et al. 1996* *Medlin 1997*
Mixing	++	Aggressive mixing (Ar gas) ↑ IVBA	- End-over-end agitation adapted to maximize solid/fluid contact, but not too aggressive	*Ruby et al. 1996, 1999* *Drexler & Brattin 2007*
S/L ratio (g/mL)	+++	IVBA ↓ with high S/L > 1/100 No effect between low ratio 1/100 and 1/5000	- High S/L ↑ the effect of TM on pH ↑ - Low ratios (< 1/125) give poorer reproducibility	*Hamel et al. 1998* *Yang et al. 2003* *Drexler & Brattin 2007*
Food addition	+++	IVBA ↓ with food, except powdered milk	- Effect variable depending on food type - Fed tests linked to lower recovery rates	*Medlin 1997* *Scheckel & Ryan 2003* *Marschner et al. 2006* *Van De Wiele et al. 2007*

+++ *high importance,* ++ *moderate importance,* + *light importance,* - *no importance, based on the studies published to date.*

1.4.1 pH

Pb dissolution is very sensitive to pH. The correlation of *in vitro* to *in vivo* results for weanling rats, for example, has been shown to be critically dependent on the pH in gastric simulations (Ruby *et al.* 1996). The solubility of mineral species under the conditions that prevail in the stomach and upper intestinal tract determines their bioavailability, the factors affecting solubility being the mineral form, association, inclusion, and size distribution. Overall, chemical species formed under acidic conditions (e.g. Pb sulfate) will tend to be more stable in simulated acidic conditions and yield lower bioaccessibility values than those formed under alkaline conditions, such as Pb oxide and Pb carbonate (Ruby *et al.* 1999). Notwithstanding the specific dissolution rates of these forms of Pb, gastric pH stands out as a dominant factor influencing bioaccessibility results for a similar particle size distribution. For mine waste impacted soil and anglesite soil, Ruby *et al.* (1992) found that the rate of Pb dissolution was linearly dependent on HCl content during the first two hours of gastric retention. Yang *et al.* (2003) measured Pb bioaccessibility values ranging from 50 to 80% for soil with a gastric pH of 2, those figures dropping to 10 to 20% at pH 3 or 4. Drexler & Brattin (2007) showed that pH was the most sensitive parameter in the RBALP: a variation in pH between 1.5 and 3.5 resulted in a variation in bioaccessibility by a factor from 2 to 7 that was only statistically significant above pH 2.5. Bruce *et al.* (2007) found significantly higher rates of gastric bioaccessibility for mine wastes tested at pH 1.3 (47%), as compared to pH 2.5 and 4 (17-18%). Oomen *et al.* (2002) concluded that gastric simulation pH was the major source of variability between the results of a round robin test of five *in vitro* models. The stability of pH during the gastric phase also appears to be critical. In fact, Oliver *et al.* (1999) found a higher bioaccessibility (26-46%) when the pH of the test was maintained at 1.3 than when the test was performed without any pH control (20-30%). Therefore, pH should be controlled at the end of the gastric phase, in order to provide the same acidic conditions for the various substrates tested. Results from the RBALP, RIVM, and UBM tests are only considered valid if the pH at the end of the experiment does not exceed a set reference value (Caboche 2009, Drexler & Brattin 2007, Oomen *et al.* 2006).

Juhasz *et al.* (2009) showed that the solubility of PbAc salt decreases greatly under simulated intestinal conditions (pH 4-7.5), reflecting the gradual increase in pH at the entrance to the intestine: from nearly 100% at pH 1.5, the IVBA decreases markedly between pH 4 and 6 to about 14.3±7.2% at pH 6-7 (Figure 1-3). Overall, initial concentrations in the range of 1 to 10 µg Pb/L did not influence solubility in the pH 1.5-7.5 range; slight differences were noted for high dosages of 5 and 10 µg/L with lower solubility at pH 5.5, and small but significant increases in solubility at pH 7.5. The steep decrease in PbAc solubility between pH 4.0 and 6.0 corresponds to the gradual increase in pH in the duodenum and jejunum, where most of the absorption and transport of Pb cations and complexes takes place (Mushak 1991, Mushak 1998). Therefore, an intestinal phase carried out at pH 5.0 may not give the same results as an intestinal phase performed at pH 7.0. An adapted representation of the intestinal phase, but posing huge challenges, would include a gradual pH increase and a series of sample collections during this increase.

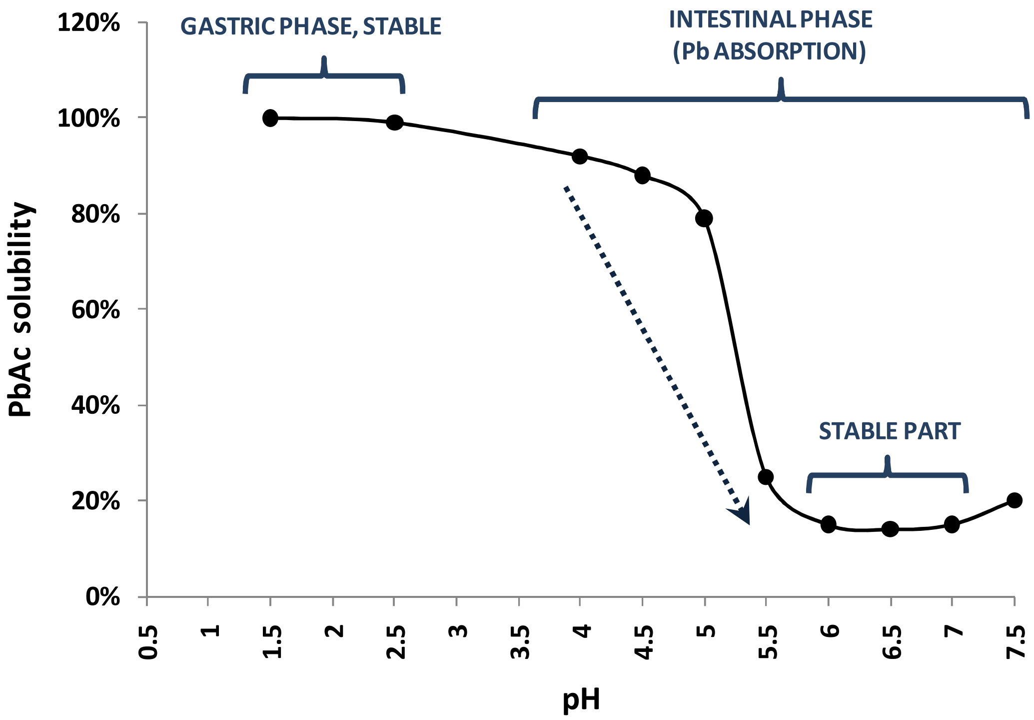


Figure 1-3. Changes in Pb acetate (PbAc) solubility with pH, during the gastric and intestinal phases. Adapted from Juhasz *et al.* (2009).

1.4.2 Temperature

The kinetics of Pb dissolution is known to be affected by temperature. However, for the conditions typical of *in vitro* experiments, temperature is not as strong a determinant of Pb dissolution as it is of the optimal activity of enzymes in the digestive juices. Drexler & Brattin (2007) found no significant difference between the RBALP results obtained at ambient temperature and those at human body temperature for seventeen test materials. Most of the procedures apply a 37°C temperature by default, since temperature is a fixed parameter in the digestive process and closely mimics biological conditions.

1.4.3 Separation of the liquid from the solid

The separation method is an essential step in determining the bioaccessible Pb fraction (Van De Wiele *et al.* 2007), and the definition of the separation limit between particulate and dissolved Pb varies significantly in the literature and between models. Extraction can be achieved by centrifugation (e.g. Denys *et al.* 2007, Oomen *et al.* 2002, Ruby *et al.* 1993), centrifugation followed by filtration of the supernatant (e.g. Bruce *et al.* 2007, Yang *et al.* 2003), or direct filtration (e.g. Drexler & Brattin 2007, Oliver *et al.* 1999). Others have used epithelial Caco-2 cells, in order to better represent the intestinal wall morphology (Oomen *et al.* 2003b). Also, an aliquot of the digestion product can be analyzed directly, based on the hypothesis that the analytical instrument will only detect dissolved Pb (Triantafyllidou *et al.* 2007, Turner & Simmonds 2006).

In the absence of an extraction step, the digestion product should be analyzed immediately. Centrifugation can be applied at various combinations of rotational speed and time, which can influence separation and impact estimates of bioaccessible Pb. In filtration, the filter cut-off varies. Medlin (1997), Oliver *et al.* (1999), and Drexler & Brattin (2007) used 0.45 µm filters. Others, like Bruce *et al.* (2007) and Juhasz *et al.* (2009), used 0.2 µm filters, while the TIM model recommends ultra filtration [UF] (Oomen *et al.* 2002, Van De Wiele *et al.* 2007). However, filtration at the end of the intestinal phase may bias results, since some filter materials are known to absorb dissolved Pb at neutral pH, the absorbed quantity varying with Pb concentration (Weltje *et al.* 2003).

The impact of the various extraction methods identified above can be classified by magnitude of bioaccessibility, as follows: no extraction > centrifugation > microfiltration > UF > Caco-2 cells. Van De Wiele *et al.* (2007) applied various extraction methods to the fed-RIVM, and bioaccessibility decreased from 31.5% (centrifugation) to 22% (microfiltration) to 3.5% (UF). Bioaccessibility results with UF were closest to *in vivo* data on the same single soil tested (Maddaloni *et al.* 1998); however, they stressed that UF decreased the consistency of the results considerably. Finally, Drexler & Brattin (2007) found no significant difference between bioaccessibility estimated with a filtration at 0.45 µm and one at 0.2 µm, suggesting that non bioaccessible Pb would be mainly particles > 0.45 µm for the test materials in question.

1.4.4 Fluid composition

The primary function of digestive enzymes is the decomposition of proteins (pepsin and trypsin) and carbohydrates (pancreatic and small intestine enzymes), while bile emulsifies lipids. Ruby *et al.* (1993) found an increased bioaccessibility of about 20% with the addition of organic acids and/or enzymes. This was explained by the chelating characteristics of organic acids and by the binding of Pb to organic acids and enzymes that kept Pb in the intestinal fluid and prevented precipitation. In contrast, Oliver *et al.* (1999) showed that adding pepsin to the gastric fluids decreased the amount of dissolved Pb by about 28%, and that bioaccessibility was unchanged in the presence or absence of pancreatin and bile salts during the intestinal step. However, gastric pH was not kept constant, and increased from 1.3 to 3 after the addition of the dust substrate. This could have impacted the pepsin and its interaction with soluble Pb, since pepsin is more active in a highly acidic environment. Medlin (1997) compared bioaccessibility results using a physiologically based gastric fluid and diluted HCl, and found little difference for cerussite, anglesite, and SRM 2710 at pH 1.5. At pH 2.8, the use of pepsin-based fluid increased bioaccessibility significantly, compared to diluted HCl fluid (difference of up to 42%). Finally, Oomen *et al.* (2004) found bioaccessibility results about 10 to 40% higher for chicken bile than for ox and pig bile, which means that bile will affect bioaccessibility differently, depending on its animal origin.

These contradictory results and the absence of conclusive evidence prevent any meaningful conclusions being drawn on the impact of adding enzymes. The simulation of physiological secretions may however be more important for intestinal extraction. In fact, Juhasz *et al.* (2009)

explained the increase in Pb solubility at pH 7.5 (compared to pH 6.0-7.0) by the formation of organo (pancreatin/bile)-Pb complexes. Oomen et al. (2003a) also suggested that the formation of Pb-bile complexes could increase Pb^{2+} concentrations. Finally, in the case of an *in vitro* procedure simulating a fed state, the introduction of food may require the addition of enzymes and bile from both the gastric and intestinal phases, since they play a role in food degradation prior to absorption and in Pb complex formation (Van De Wiele *et al.* 2007).

1.4.5 Retention time

Retention times vary considerably between test methodologies and can impact the estimates of Pb bioaccessibility. Intuitively, for particles with limited solubility, longer stomach retention time should enhance bioaccessibility, since the extent of Pb dissolution increases with more contact time at a given rate. Ruby *et al.* (1996) evaluated Pb bioaccessibility in the stomach and intestine, and observed an average increase of 4.8% between 30 min and 1 h during the gastric phase, while an unsystematic decrease was noted during the intestinal phase. Gasser *et al.* (1996) studied Pb dissolution in a stomach environment using a stirred flow reactor, and observed a rapid increase in Pb dissolution rate initially, which tended to decrease over time (0-60 min) and pH (1-3). Both the time and pH increment of this dissolution rate was substrate dependent. Moreover, Ruby *et al.* (1999) stated that, if the dissolution of the Pb bearing mineral is controlled by a surface reaction rate, then the transit time will control that dissolution, suggesting that the impact of retention time in an *in vitro* test will depend on the form of the substrate studied. For low solubility minerals, the dissolution kinetics would be controlled by surface reactions, and so the major parameter governing Pb release during digestion for these minerals would be stomach retention time. This is illustrated by Medlin's (1997) results: less soluble Pb bearing minerals (anglesite, pyromorphite, galena) exhibited the highest dissolution rate, which continued to rise after the 1 h stomach simulation, whereas more soluble Pb ones (e.g. cerussite) generally reached a plateau after the first 20 min of the gastric simulation. In another study, however, Drexler & Brattin (2007) applied 1, 2, and 4 h retention time to 11 substrates from comparable sources (mining sites) and found no significant differences.

1.4.6 Mixing

Determination of the mixing type and intensity depends on the test material studied. Ruby *et al.* (1999) stated that mixing controls the dissolution of Pb bearing materials through transport mechanisms. For more soluble minerals, the kinetics of dissolution is controlled by transport mechanisms in which dissolved ions are quickly detached from the particle surface, accumulate, and form a saturation solution at the boundary layer. As a result, the most influential factor during digestion in this case could be mixing, as it determines the thickness of the boundary layer and therefore the diffusion gradient. In addition, mixing conditions should be set to keep the Pb particles in suspension. Ruby *et al.* (1996) mixed by means of argon [Ar] injection, which efficiently kept the particles in suspension, but this type of aggressive mixing may overestimate bioaccessibility. According to Drexler & Brattin (2007), end-over-end mixing is the most appropriate for such experiments, because it maximizes the contact between sample and fluid (substrate surface area), and consequently Pb dissolution rate, and minimizes contamination caused by interacting devices (paddle, etc.). Moreover, it prevents the test material from sticking to the bottom of the tube/beaker, as observed for procedures using shaking water-bath (the authors' observations in the laboratory).

1.4.7 Solid to liquid ratio [S/L]

The S/L ratio is another major factor impacting Pb dissolution and the resulting bioaccessibility estimation. According to Dean & Ma (2007), the most common S/L ratios used for *in vitro* extractions vary between 1/2 and 1/250 $g.mL^{-1}$. Lower ratios, such as 1/1800 (Brandon *et al.* 2006), 1/2160 (Hamel *et al.* 1999), 1/5000 (Hamel *et al.* 1998), and 1/16,667 (Triantafyllidou *et al.* 2007), are also reported. Drexler & Brattin (2007) explain that the gastric ratio should be limited to reduce the effect of metal dissolution (observed for 1/5 and 1/25 ratios) and to prevent Pb chloride crystal precipitation upon cooling (for media containing over 50,000 mg Pb/kg). However, gastric ratios as high as 1/2.5 (Oomen *et al.* 2002), 1/10 (e.g. Oliver *et al.* 1999, Ruby *et al.* 1993), and 1/30 to 1/40 have been applied (e.g. Ljung *et al.* 2007, Saikat *et al.* 2007). Such ratios may also increase the positive impact of the test material on the pH, if the latter is not controlled, and consequently underestimate bioaccessibility (Oomen *et al.* 2006). For the same BMW soil and similar PBET conditions at a 1/100 ratio, Ruby *et al.* (1996) found higher bioaccessibility (9.5-35%) than at a 1/10 ratio (≤ 6%). The 1/10 ratio used in Oliver *et al.* 1999 may have influenced the low bioaccessibility range found for dusts (20-30%), compared to other studies on dust for which Pb bioaccessibility generally exceeded 50% in the gastric phase. Yang *et al.* (2003) demonstrated that Pb bioaccessibility in soil increased by about 10% between gastric ratios of 1/40 and 1/100. Hamel *et al.* (1998) had concluded that Pb bioaccessibility was only slightly affected with ratios between 1/100 and 1/5000. Medlin (1997) found evidence of the significant influence of S/L ratio on the arsenic bioaccessibility estimate of SRM 2710 soil between 1/100 and 1/500, but she also found that Pb bioaccessibility increased to a lesser degree (11%) between those ratios. Drexler & Brattin (2007) standardized the procedure and recommended applying a ratio of 1 g of substrate per 100 mL fluid for media containing Pb in amounts less than 5% by weight (0.5/100 for substrates > 5 wt % Pb). Ratios below 1/125 are not recommended because of poorer reproducibility (substrate heterogeneity, weighing errors), as well as issues with the detection of low Pb concentrations during subsequent analysis. The effect of the S/L ratio during the intestinal phase has not been studied systematically, but could influence the precipitation reactions and also the stability of the solution, which has been shown to be difficult to maintain.

1.4.8 Food/substrate

The presence of food/substrate during digestion and its type will influence bioaccessibility, and a systematic decrease in bioaccessibility following the addition of food has been reported in most *in vitro* experiments, especially for gastric phase results. Indeed, dissolved Pb is adsorbed on non digested elements, and forms complexes with some elements. Scheckel & Ryan (2003) found a Pb bioaccessibility close to zero for highly soluble hydrocerussite-based paint after the addition of a cola soft drink to the gastric fluid. These results were explained by the reaction of soluble Pb with phosphates in the drink to form pyromorphite solid. Also, *in vivo* experiments on rats showed a decrease in RBA following addition of solid hydroxyapatite to the dissolved Pb solution of ingestion (Arnich *et al.* 2003). Results obtained by Schroder *et al.* (2004) showed that the median bioaccessibility without dough added was 36.3% and 0.62% for the gastric and the intestinal phase respectively, while the test performed with dough resulted in bioaccessibility medians of 27.1% and 0.58%. The swallow model performed by Brandon *et al.* (2006) in fasting conditions estimated the Pb bioaccessibility of 'real-life' paint at about 10%, while it was about 4.5% for the test performed with 4.5 g of infant food. This decrease may be partly attributed to the difference in the stomach pH used to simulate a fasting state (1.6) or a fed state (2.5), but the presence of food may also have an influence. Additionally, the RIVM and TIM models run with and without solid food for the same soil resulted in higher bioaccessibility values for the fasting state (32-47%) than for the fed state (RIVM: 24-39%; TIM: 7%) (Van De Wiele *et al.* 2007). Retention times and pH were quite close between the tests performed with and without food, suggesting that food would be partly responsible for this decrease. Recovery efficiencies influence these estimates, and the fed tests were linked to lower recoveries (70-93%) than were observed in fasting tests (≥ 83%) (Van De Wiele *et al.* 2007).

Remarkably, some studies performed with whole milk powder show the opposite trend, with an increase in bioaccessibility in a fed state. Marschner *et al.*'s (2006) two-phase enzymolyzis showed higher bioaccessibility for the fed state (11-56%) than for the fasting state (2-21%). With controlled retention time, pH, and fluid formulas, Van De Wiele *et al.* (2007) observed a higher bioaccessibility with the addition of whole milk powder to the fluid for the PBET and DIN tests (fed: 22-29%; fasting: 13-14%). Medlin (1997) investigated different types of food (banana, milk, oatmeal, and rice) and substrates (Pb phosphates, slag, galena, and Pb oxide). Trends varied depending on the food, the Pb form, and the amount tested, showing the huge challenges involved in the design of a representative fed state (Drexler & Brattin 2007).

1.5 *In vitro* testing bioaccessibility procedures and validation

Various methods have been published to investigate the bioaccessibility of Pb particles in environmental media, using simple to more complex methodologies aimed at reproducing to a various extent the conditions in the digestive tract to which the particles are exposed. These methods can be classified in two categories:

- Non physiologically based tests simulating the conditions of acidic pH and retention time in the stomach, without enzymes or other physiological fluids representative of real digestive conditions (or only additions that were shown to impact IVBA), namely: HCl extractions, the Relative Bioaccessibility Leaching Procedure [RBALP] or Simple Bioaccessibility Extraction Test [SBET], the Solubility Bioavailability Research Consortium procedure [SBRC], and variants of these tests.

Physiologically based extraction tests which attempt to simulate the physiological fluids and conditions of the digestive tract, namely: the Physiologically Based Extraction Test [PBET], the *In Vitro* Gastrointestinal method [IVG], the RIVM model, the Unified Barge Method [UBM], the DIN model, the TIM model, the SHIME model, and variants of these tests, either dynamic or static.Table 1-3 summarizes the results obtained for the same test materials using various *in vitro* procedures. Depending on the procedure applied, the estimated IVBA varies widely, especially the intestinal IVBA. Results obtained with different *in vitro* test designs should be compared with caution, in light of the differences in testing conditions discussed previously. A more important aspect to consider is whether or not these tests provide estimates of bioaccessibility that are useful for refining bioavailability and Pb exposure assessments. In fact, the main objective of a bioaccessibility test is to offer a rapid and low cost alternative to bioavailability testing. Therefore, the optimal bioaccessibility test should produce data that can be adequately correlated to *in vivo* data. Correlations between *in vitro* and *in vivo* methods can be used to calibrate *in vitro* testing conditions, which is highly desirable as it would ensure that an *in vitro* method is an acceptable alternative to animal investigations. These correlations are usually presented as linear regression models, and their strength will depend on the number of substrates tested and the range of IVBA/RBA available. According to Drexler & Brattin (2007), a strong correlation is determined by an $R^2 > 0.6$ and a significant relationship with a slope as close as possible to 1. However, it is suggested that the correlation coefficient may be more important than the slope, since a slope ≠ 1 does not impede to relate bioaccessibility to bioavailability (BARC, 2011).

Another important aspect to consider in the selection of the *in vitro* testing procedure is the validation of the *in vitro* test. *In vitro* procedures should ideally be subjected to round robin testing to verify the ability of the results to be accurately reproduced or replicated. Inter-laboratory testing is needed to standardize the procedure, so that it can be applied in any laboratory on multiple test materials (Caboche 2009, Drexler & Brattin 2007). Then, multiple low cost experiments can be completed and extrapolated using existing data on animals and/or humans, and can be expected to be semi-quantitatively accurate. *In vitro* procedures that have not been calibrated or validated can nevertheless be useful, but should be considered as approximations and interpreted with caution.

Table 1-3. Comparison of bioaccessibility results obtained with the same test materials. Tests simulating a fasting state.

MATERIAL	TEST TYPE	GASTRIC IVBA %	INTESTINAL IVBA%	REFERENCES
Montana SRM 2710 soil ***RBA 76%†***	PBET	67.3		Medlin 1997
	PBET	29±5 to 46±29		Hamel *et al.* 1998
	PBET		54-62±1*	Hamel *et al.* 1999
	PBET	76.1±11	10.7±2.3	Ellickson *et al.* 2001
	PBET		30-35	Oomen *et al.* 2004
	RIVM	79±4	25±1	Denys *et al.* 2007
	RBALP	75±5		Drexler & Brattin 2007
	UBM	75	27	Caboche 2009
Montana SRM 2711 soil	DIN		46±2	Oomen *et al.* 2002, 2004
	SHIME		3±0.3	
	TIM		17±3	
	RIVM		11±2	
	SBET	90±2		
	PBET		10-20 (60 for chicken bile)	
	PBET	85±5	13±1	Denys *et al.* 2007
	RBALP	84±6		Drexler & Brattin 2007
	UBM	80	33	Caboche 2009
Bunker Hill soil ***RBA adults 62±25%‡***	PBET	75		Medlin 1997
	PBET		70±11*	Hamel *et al.* 1999
	RIVM	87.6 ± 8.4	45.4 ± 4.0	Oomen *et al.* 2006
	PBET		13±0.8	Van De Wiele *et al.* 2007
	DIN		13.6±0.6	
	SHIME		2.0±0.1	
	RIVM		31.8±2.5-47.4±3.2	
	TIM		32.5±4.5	
Flanders soil	DIN		31±3	Oomen *et al.* 2002
	SHIME		4±1	
	TIM		13±3	
	RIVM		66±9	
	SBET	91±4		
Oker 11 soil ***RBA 55%§***	DIN		16±2	Oomen *et al.* 2002
	SHIME		1±0.1	
	TIM		4±1	
	RIVM		29±2	
	SBET	56±4		
	IVG		20	Marschner *et al.* 2006
	SBRC	66.8±2.3	62.9±11	Juhasz *et al.* 2009

*IVBA – in vitro bioaccessibility; *Bioaccessible Pb (mg) included Pb leached in G&I phases; †RBA on juvenile swine (Caboche 2009); ‡RBA on human adults (Maddaloni et al. 1998, Oomen et al. 2006); §RBA on juvenile swine (Marschner et al. 2006).*

1.5.1 *In vitro* test results compared to *in vivo* data

Table 1-4 lists *in vitro* tests that have been correlated to *in vivo* data, including variants of the PBET and IVG procedures: RIVM, UBM, RBALP, and SBRC.

1.5.1.1 PBET and IVG procedures

The PBET introduced by Ruby *et al.* (1993, 1996) was, in fact, the first test that used simulated biological fluids in both the gastric and intestinal phases, and correlated the results to *in vivo* data. As shown in Table 1-4, a synthetic gastric fluid composed of HCl, pepsin, and organic acids is added to the soil sample in a 1/100 g.mL^{-1} ratio. Initial incubation is performed at 37°C with varying initial pH (1.3, 2.5, 3.0, and 4.0), reflecting different digestion conditions under mixing with argon. After an hour, pH is progressively adjusted to 7.0 using sodium bicarbonate [$NaHCO_3$], simulated intestinal fluids (pancreatin and bile) are added, and mixing is continued for another four hours. The mixture is then centrifuged and settled, and the supernatant analyzed. Medlin (1997) developed a similar PBET test, using a comparable gastric S/L ratio and the similar synthetic gastric fluid formula. The impact on the results of modifying the pH, time, particle size, and food addition, as well as the addition of a two-hour intestinal phase, was investigated. The final test applied only a gastric phase at pH 1.5 for 1 h, with continuous pH measurement, a mixing step combining Ar gas on the surface of the reaction vessel with the stirring rod moving at 60 rpm, and an extraction via 0.45 µm filtration. Brown *et al.* (2003) and Hettiarachchi *et al.* (2003) applied a similar version of PBET, as recommended by Ruby *et al.* (1996), although the intestinal phase was either not simulated or faster (1 h) (Table 1-4).

Results from the gastric phase using the Ruby *et al.* (1996) procedure were calibrated for Pb in mine wastes with previous *in vivo* studies on Sprague Dawley rats. Only *in vitro* results of the gastric phase at pH 1.3 and 2.5 were linearly correlated to *in vivo* results ($R^2 = 0.93$), with a slope closer to 1 at pH 2.5 (Battelle 1993, Freeman *et al.* 1992, PTI Environmental Services 1994a, PTI Environmental Services 1994b, Ruby *et al.* 1996). The Medlin (1997) procedure also showed that gastric bioaccessibility predicted *in vivo* juvenile swine data better than intestinal bioaccessibility (Table 1-4). Bioaccessibility estimates from the intestinal phase (tested for SRM 2710 and Pb oxide) underestimated the bioavailability data from *in vivo* calibration studies. Brown *et al.* (2003) observed a significant relationship between gastric RBA reduction and IVBA reduction following different Pb remediation methods performed on the tested soil. Finally, Hettiarachchi *et al.* (2003) observed a stronger correlation of the RBA point estimates in rats with gastric IVBA, than with intestinal IVBA (Table 1-4). This lack of strong and significant correlations demonstrates the extent of the challenges in relating intestinal phase results from PBET to *in vivo* data, possibly due to precipitation reactions and the complexity of the mechanisms involved in intestine wall absorption.

Although the demonstration of a strong correlation with an animal model is highly valuable, the significance of the calibration is maximized if it is obtained using an adapted animal model that can be used to estimate exposure and risk assessment in human populations. The correlation observed using rats in Ruby *et al.* (1996) and Hettiarachchi *et al.* (2003), although significant, may not be as valuable for studying childhood exposure, however, because of the *in vivo* test design (animal model and/or dose administered), as underlined by Mushak (1998). In contrast, the PBET later developed by Medlin (1997) was correlated to *in vivo* data in juvenile swine, which are considered to be a better model for simulating digestion and absorption processes in children. In addition, this test was performed on a significant number of soils (n=15) using an extensive QA/QC protocol. Therefore, it appears to be more reliable than the Ruby *et al.* (1996) initial PBET. Nonetheless, this test has not been subjected to the inter-laboratory validation and statistical analysis that would demonstrate good laboratory reproducibility of the results.

The IVG model, initially developed by Hack & Selenka (1996) for PAH and PCB, was subsequently applied to Pb. It reproduces the PBET gastric and intestinal phases using physiological fluids, but the formulation of the fluids, retention time, and pH are different (Table 1-4). Schroder *et al.* (2004) and Marschner *et al.* (2006) compared the IVG results to *in vivo* results on swine using the same soils. The absence of *in vitro* to *in vivo* correlation in the Marschner *et al.* (2006) study was attributed to the technical difficulties during the intestinal phase simulation. However, Schroder *et al.* (2004) did find significant relationships between *in vivo* and *in vitro* results performed with and without dough: blood-based bioavailability was correlated to gastric *in vitro* results ($R=0.93$; $p < 0.001$) and to intestinal *in vitro* results ($R=0.80$; $p < 0.001$) with dough. *In vitro* tests performed without dough showed significant correlation to *in vivo* blood-based bioavailability in the gastric phase, but not in the intestinal phase (Table 1-4). However, the *in vivo* data used for this correlation were later corrected by Casteel *et al.* (2006) and the USEPA (2007b), and so the relationship would need to be re-evaluated with the corrected data prior to any use for other test materials. Finally, this test cannot be considered as a fully validated standardized *in vitro* procedure, because of the limited use of a QA/QC protocol and incomplete statistical analysis (Drexler & Brattin 2007). Nonetheless, it can be noted that, here again, the highest correlation was observed with *in vitro* gastric results.

1.5.1.2 RBALP and SBRC procedures

Considering the apparently good correlation of bioavailability and gastric bioaccessibility and the limited benefit of including an intestinal phase, as observed by Medlin (1997), a protocol reproducing only the gastric phase was developed in Dr. John Drexler's laboratory. The RBALP was proposed after some investigation into the impact of temperature, contact time, pH, and S/L ratio to maximize correlation to *in vivo* data (Drexler & Brattin 2007, Medlin 1997). The RBALP includes an extraction (1 h, pH of 1.5, 1/100 g.mL^{-1}) with a synthetic fluid composed of glycine and HCl at 37°C. End-over-end mixing is performed (28±2 rpm), and extraction is achieved via filtration at 0.45 μm. The test also includes criteria allowing for rigorous, reliable, and reproducible results that are only considered valid if: (1) the pH at the end of the extraction is within 0.5 units of the initial pH, which ensures that glycine buffering capacity is not exceeded; (2) the maximum holding time before analysis is one week; and (3) a rigorous QA/QC protocol is applied, including analysis of a bottle blank, a blank spike, a matrix spike, a duplicate sample, and a control soil at a 5-10% frequency. The test was applied to two SRM materials and nineteen test materials through round robin testing by four laboratories, and the results were compared via a statistical analysis. Intra-laboratory results showed good precision and agreement, with a CV of 2-6%, and the laboratory results respecting SRM standards were highly reproducible (CV of 7%). These observations confirm good reproducibility, precision, and standardization of the method.

As shown in Table 1-4, the RBALP was highly correlated to *in vivo* juvenile swine results using the nineteen test materials, including one NIST paint, galena, and soils impacted by mining and smelting activities (Casteel *et al.* 2006, Drexler & Brattin 2007). Moreover, it is easier to perform than the PBET, because of the formulation of the synthetic fluids and the rapidity of the test. The British Geological Survey adapted the RBALP and renamed it the Simple Bioacessibility Extraction Test (SBET). The SBET protocol has been applied with some modifications by Yang *et al.* (2003), and Bosso & Enzweiler (2008). Others applied the original RBALP, like Schaider *et al.* (2007), Bannon *et al.* (2009), and Morman *et al.* (2009). The test applied by Bannon *et al.*

(2009) to eight soils of small shooting ranges also revealed results comparable to an *in vivo* swine study (Table 1-4). Considering the number of substrates tested with the RBALP, calibrated with *in vivo* data on a recognized representative animal model, and further confirmed through a validation method, a rigorous QA/QC protocol, and round robin testing, this test stands out as a reference for application to other test materials. However, as underlined by the USEPA (2007b) and Juhasz *et al.* (2009), the substrates used for the calibration of this procedure were from similar sources (mining sites), for which Pb dissolution is limited during the gastric phase. Therefore, the RBALP *in vivo-in vitro* relationship may not hold for any other test material. Specifically, the RBALP applied to substrates containing more soluble forms of Pb than those found on mine sites, which partially precipitate/react during the intestinal phase, may overestimate Pb bioavailability (Juhasz *et al.* 2009). Finally, results performed on soils following remediation with phosphates showed a better *in vivo-in vitro* correlation with IVBA results performed at pH 2.5, suggesting that the RBALP would give more valuable results at pH 2.5 for evaluating soil remediation effectiveness (Ryan *et al.* 2004, Zia *et al.* 2011).

To respond to these concerns, Juhasz *et al.* (2009) added an intestinal phase to the RBALP and compared the results obtained for the gastric and intestinal phases to *in vivo* bioavailability results on juvenile swine. The SBRC intestinal test simulates a gastric phase identical to that of the RBALP, except that the agitation is performed at 40 rpm and the filtration on 0.2 µm filters, and then a 4-h intestinal phase is simulated at pH 6.5 with the addition of NaOH, bile, and pancreatin. In order to take into account precipitation reactions occurring during the intestinal phase and better relate intestinal IVBA to *in vivo* results, a relative intestinal IVBA was calculated. This was adjusted with the solubility of PbAc at pH 6.5 in the synthetic fluid, which was estimated at about 10-20%, as compared to 100% during the gastric phase at pH 1.5 (Equation 7). The application of an intestinal pH of 6.5 was justified by the fact that PbAc solubility was quite stable between 6.0 and 7.0, making the results more robust.

$$Relative\ Pb\ IVBA = \frac{\dfrac{in\ vitro\ Pb_{TM}}{total\ extractable\ Pb_{TM}}}{\dfrac{in\ vitro\ Pb_{PbAc}}{total\ Pb_{PbAc}}}\ (Equation\ 7)$$

Gastric IVBA and absolute intestinal IVBA were poorly correlated to *in vivo* data for the five soils tested, while relative intestinal IVBA was satisfactorily correlated ($R^2 = 0.53$). Although based on a weak fit ($R^2 = 0.12$), the authors state that the slightly negative Pearson correlation coefficient observed for the gastric phase may be indicative of an overestimation of the gastric phase estimates for some Pb forms. Applied to the same soils tested in the Marschner *et al.* (2006) study, relative intestinal IVBA estimates were well correlated to blood RBA on piglets, unlike the IVG results obtained by Marschner *et al.* (2006). This suggests that the calculation of relative bioaccessibility is a better RBA predictor. Interestingly, Smith *et al.* (2011a) tested soils with a wide range of bioavailability (10-83%) and report excellent correlations between *in vivo* mouse data and both the RBALP test and the SBRC-intestinal test (Table 1-4). The slightly lower correlation is explained by the overprediction of the RBA using the RBALP for some soil types. Indeed, the presence of iron reduced the intestinal estimates, but not the gastric estimates, and, as a consequence, the iron soil results correlated better using the SBRC-intestinal test (Smith *et al.* 2011a). The *in vivo-in vitro* relationship was then applied to the SBRC relative bioaccessibility results for thirty-one peri-urban soils, and compared to bioavailability predictions using the USEPA (2007b) regression equation on the SBRC results for the gastric phase. The bioavailability predictions were in agreement for shooting range soils, however different predictions were found for soils with high iron content, incinerator soils, historical fill soils, gasworks soils, and gossan soils. Overall, the RBALP relationships applied to the SBRC gastric results yielded more conservative bioavailability predictions than when the SBRC relationships were applied to the relative intestinal results (Smith *et al.* 2011b). This suggests that the addition of an intestinal phase to the RBALP, and the use of relative bioaccessibility instead of absolute bioaccessibility, may yield bioaccessibility estimates that are closer to actual bioavailability results for some soil matrices. Nonetheless, as emphasized previously, additional inter-laboratory testing and statistical analysis would be desirable to standardize the addition of the intestinal phase.

1.5.1.3 RIVM and UBM procedures

The RIVM digestion model includes five minutes of simulated contact with saliva, followed by gastric and intestinal phases (two hours each) with end-over-end rotation at about 55 rpm in the presence of complex fluids. Simulation of the salivary phase is not generally added to *in vitro* models, because of the relatively short duration and neutral pH of this step. However, this step may be relevant when food is added, which is considered in the RIVM. For the test performed in the presence of food (macaroni, infant formula), adjustments are made in pH and fluid compositions to represent 'stimulated' conditions. Chyme pH is adjusted to 5.5-6.5 using $NaHCO_3$ (Table 1-4). As for the RBALP, the test procedure is rigorously controlled for pH: 2.0 for the gastric phase, and 6.5 for the intestinal phase. Extraction is performed by centrifugation at 3,000 g and the pellet is kept for analysis and mass balance (Oomen *et al.* 2002, Oomen *et al.* 2006, Van De Wiele *et al.* 2007). Bioaccessibility results for the fasting case were adjusted to PbAc solubility during the intestinal phase (relative IVBA) and compared to the USEPA data on juvenile swine on eleven soil-like materials. The relationship found was significant for the two S/L ratios tested (1/37.5 and 1/375 $g.mL^{-1}$), for either the gastric or the intestinal phase (Oomen *et al.* 2006). The test was further applied in other studies (Denys *et al.* 2007, Ljung *et al.* 2007). Nonetheless, calibration of the RIVM was performed with bioavailability data from soils used for the RBALP calibration. It would be desirable to test the relationship with soils from more widely varied sources to verify this calibration, although the addition of the intestinal phase and the calculation of relative bioaccessibility suggest that this test may be valid for a broader range of soils than the RBALP.

The Unified BARGE Method (UBM) was developed by the Bioaccessibility Research Group Europe (BARGE) with the aim of selecting and standardizing a common procedure for bioaccessibility testing. In the UBM, which is similar overall to the RIVM, the retention time of the gastric phase is reduced to 1 h, and it is increased to 4 h for the intestinal phase (Oomen *et al.* 2006). IVBA results obtained with this approach were compared to *in vivo* kidney-based RBA on juvenile swine for fourteen mining and smelting soils. Gastric and intestinal bioaccessibility showed strong correlation with the RBA, and the relative intestinal bioaccessibility was even closer to RBA estimates considering the slope of the relationship (Caboche 2009; Table 1-4). The strength of the fit suggests again that the addition of the intestinal phase, which is desirable since it is where Pb absorption takes place in the digestive system, can be successfully linked to RBA results using the relative IVBA. The validated UBM was then applied to twenty-seven urban topsoils (Roussel *et al.* 2010).

The simulation of both the gastric and the intestinal phase greatly impacts the estimates of Pb bioaccessibility. Bruce *et al.* (2007) measured a bioaccessibility of 47% for the mine wastes at the end of the gastric phase, and these values dropped to 7% at the end of the intestinal phase. Yu *et al.* (2006), Bosso *et al.* (2008), Juhasz *et al.* (2009), Sialelli *et al.* (2010), and the authors of other studies observed the same range of decrease in bioaccessibility. Results using Pb-ISE and DPASV in chyme following GI *in vitro* digestion showed that the free Pb^{2+} is indeed negligible, and that most of the Pb was present as Pb-phosphate and Pb-bile complexes in dynamic equilibrium with solubilized Pb (Oomen *et al.* 2003a). This solubilized Pb is largely removed from the solution by precipitation or adsorption on non digested and compatible particles (Juhasz *et al.* 2009, Ruby *et al.* 1996). These observations show that Pb bioaccessibility could be overestimated if limited to the gastric phase. However, significant experimental challenges arise from the precipitation reactions, the gradual pH increase and parallel absorption, the eventual adsorption of soluble Pb on non digested particles, and the increase of labile complexes that are difficult to maintain in equilibrium in the intestinal chyme (Oomen *et al.* 2003a, Ruby *et al.* 1996). Precipitation conditions may not be as well simulated in a closed system as in the gut, which is a thermodynamically open system (Mushak 1998), but spiking and correction for recovery could account for these losses. Comparison of Pb speciation by XANES after the gastric and intestinal phases has clearly shown the dominance of solubilized Pb after the gastric phase and the importance of the presence of co-precipitation with amorphous iron in soils containing iron oxyhydroxides (Smith *et al.* 2011a). To address some of these concerns, intestinal bioaccessibility can be adjusted relative to estimates of a soluble Pb form (e.g. PbAc), at a ‘stable’ intestinal pH (6.0-7.0) (Juhasz *et al.* 2009). With this adjustment, relative bioaccessibility estimates from the intestinal phase are slightly lower than gastric bioaccessibility estimates, and seem to better relate to *in vivo* data (Caboche 2009, Juhasz *et al.* 2009).

In conclusion, the RBALP test appears to be best suited to date for estimating the potential for childhood exposure to multiple Pb sources, even though it is not fully physiologically based. This test is best adapted for cost effective testing of multiple sources of Pb particles. The RBALP is likely to overestimate bioavailability for some test materials, and will produce a conservative estimate. However, it is a simple and rapid test which has been validated with *in vivo* data on the best suited animal surrogate for childhood digestion conditions, and it is the only procedure that has been validated through a complete statistical analysis and round robin testing. Consequently, it is well standardized and can be applied in many laboratories on multiple test materials.

Adding an intestinal phase and adjusting for the decreased bioaccessibility estimate with PbAc solubility will provide *in vitro* results that are closer to the *in vivo* results for juvenile swine. This may be an advantage for estimating the relative Pb bioavailability for more soluble Pb sources, leading to refined exposure assessments. Several tests have been validated with such an adjustment (SBRC-intestinal, RIVM, UBM), and results from the intestinal phase in PBET tests may need to be reevaluated for full validation. So, in order to refine the exposure model, it would seem desirable to standardize such procedures. The SBRC-intestinal test may be easier to standardize, as this test is simpler and quicker than the RIVM/UBM procedures. However, the RIVM and UBM procedures better reflect human *in vivo* physiological conditions. In addition, these two models have been validated for cadmium and arsenic (Caboche 2009, Oomen *et al.* 2006), and so bioaccessibility estimates can be performed for several trace elements in the same procedure. Finally, to reinforce their validity, complete statistical analysis and inter-laboratory testing would be needed.

Table 1-4. *In vitro* procedures applied to Pb particles and compared with *in vivo* data for subsequent calibration.

References	Substrate	Oral phase	Gastric phase	Intestinal phase	Comparison with *in vivo* data
Ruby et al. 1993 *PBET-GI*	Mine wastes		1/10 g.mL^{-1} 2 h @ pH 1.3 Pepsin; organic acids; HCl	2 h @ pH 7.0 NaHCO$_3$; pancreatin; bile	• *In vivo* results on rabbits (1 sample): 10.7% (blood based RBA at t = 1 h), and $9^{\pm 4}$ % (gastric solubility, t = 1.5 h)
Ruby et al. 1996 *PBET-GI*	Mine wastes Residential soils Tailings		1/100 g.mL^{-1} 1 h @ pH 2.5 Pepsin; organic acids; HCl	4 h @ pH 7.0 NaHCO$_3$; pancreatin; bile	• *In vivo* relative Pb bioavailability in rats (based on BLLs, Y axis) correlation to IVBA results from the G phase (X axis): R^2 = 0.93, n=7, intercept 3.2, slope 1.4 • Correlation with I phase: R^2 = 0.76
Medlin 1997 *PBET-G*	15 soils or soil-like materials (EPA Region VIII)		1/111 g.mL^{-1} 1 h @ pH 1.5 Pepsin; organic acids; acetic acids; HCl		• *In vivo* point estimates in piglets (Y-axis) correlated to *in vitro* results (X-axis): R^2=0.63, n=15, intercept -8.21, slope 0.90, $p < 0.001^*$ • Extensive QA/QC protocol
Brown *et al.* 2003 *PBET-G*	Urban soil treated with various biosolids (n=9)		1/100 g.mL^{-1} 1 h @ pH 2.3 Pepsin; organic acids; HCl		• *In vivo* bone bioavailability reduction % in rats correlated to *in vitro* bioaccessibility reduction with the treatment of soils (R=0.9)
Hettiarachchi *et al.* 2003 *PBET-GI*	Joplin soil treated or not with Mn, P, or CRYP (n=15)		1/100 g.mL^{-1} 1 h @ pH 2.0 Pepsin; organic acids; HCl	1 h @ pH 6.5 NaHCO$_3$; pancreatin; bile	• *In vivo* point estimate RBA in rats (Y-axis) correlated to *in vitro* results (X-axis) G phase: R^2=0.95, intercept 11, slope 0.82 I phase: R^2=0.77, intercept 12, slope 1.87
Schroder *et al.* 2004 *IVG*	18 soils (EPA Region VIII)		1/150 g.mL^{-1} 1 h @ pH 1.8 Pepsin; NaCl; HCl	1 h @ pH 5.5 Pancreatin; bile; NaHCO$_3$; decanol	• *In vivo* blood RBA (X-axis) in piglets correlated ($p < 0.001$) to *in vitro* data (Y-axis)†: - G (R=0.93) & I (R=0.80) results, with dough - G results no dough (R=0.89) • Best correlation for G phase with dough: R^2=0.86, n=18, intercept 2.97, slope 0.39
Marschner *et al.* 2006 *IVG*	5 soils, with or without milk powder		1/40 g.mL^{-1} 2 h @ pH 2.0 Pepsin; NaCl; HCl	6 h @ pH 7.5 NaHCO$_3$; trypsin; bile; pancreatin; urea; inorganics	• Absence of correlation between *in vivo* bioavailability in piglets and *in vitro* results

Table 1-4. *In vitro* procedures applied to Pb particles and compared with *in vivo* data for subsequent calibration (continued).

References	Substrate	Oral phase	Gastric phase	Intestinal phase	Comparison with *in vivo* data
Oomen *et al.* 2006 *RIVM*	11 soils or soil-like material (EPA Region VIII)	5 min @ pH 6.5 (in)organics, mucin, uric acid, alpha-amylase	1/37.5 or 1/375 g.mL^{-1} 2 h @ pH 1.0-2.0 (in)organics, pepsin, mucin, BSA	2 h @ pH 5.5-6.5 (in)organics, pancreatin, bile, BSA, lipase, $CaCl_2$	• *In vivo* point estimates in piglets (X-axis) correlated to relative *in vitro* fasted model results (Y-axis): G phase: R^2=0.68-0.79, intercept 0, slope 0.79-1.08 I phase: R^2=0.66-0.81, intercept 0, slope 0.69-1.16
Drexler & Brattin 2007, USEPA 2007b *RBALP*	19 soil-like materials from EPA region VIII,		1/100 g.mL^{-1} 1 h @ pH 1.5 Glycine; HCl		• *In vivo* RBA point estimates in piglets (Y-axis) correlated to *in vitro* results (X-axis) : weighted R^2=0.924, n=19, intercept -0.028, slope 0.878, $p < 0.001$ • Extensive QA/QC protocol and statistical analyses • Precision 7% within samples, and 4-6% within laboratories (round robin testing)
Bannon *et al.* 2009 *RBALP*	8 small arms range soils		1/100 g.mL^{-1} 1 h @ pH 1.5 Glycine; HCl		• *In vivo* point estimates on piglets: $108^{\pm 18}$% • *In vitro* results: $83^{\pm 1}$-$100^{\pm 3}$%
Caboche 2009 *UBM*	14 mining and smelting soils	5 min @ pH 6.5 (in)organics, mucin, uric acid, alpha-amylase	1/37.5 g.mL^{-1} 1 h @ pH 1.2-1.7 (in)organics, pepsin, mucin, BSA	4 h @ pH 5.8-6.8 (in)organics, pancreatin, bile, BSA, lipase, $CaCl_2$	• *In vivo* kidney RBA in piglets (X-axis) correlated to *in vitro* results adjusted by PbAc solubility in the G and I phases (Y-axis): G phase: R^2=0.93, intercept 1.10, slope 1.86, $p < 0.01$ I phase: R^2=0.89, intercept 1.09, slope 1.09, $p < 0.01$
Juhasz *et al.* 2009 *SBRC*	5 incinerator & urban soils; 5 soils from Marschner *et al.* 2006		1/100 g.mL^{-1} 1 h @ pH 1.5 Glycine, HCl	4 h @ pH 6.5 NaOH, pancreatin, bile	• *In vivo* blood RBA in piglets (Y-axis) correlated to relative *in vitro* data for the I phase (X-axis): R^2=0.53, intercept 1.98, slope 0.58 (urban & incinerator soils) R^2=0.47, intercept 29.5, slope 0.42 (soils from Marschner et al., 2006 study)
Smith *et al.* 2011a *RBALP*	12 soils impacted from a variety of Pb sources		1/100 g.mL^{-1} 1 h @ pH 1.5 Glycine, HCl		• *In vivo* blood RBA in mice (X-axis) correlated to relative *in vitro* data (Y-axis): R^2=0.78, intercept 30.207, slope 0.69
Smith *et al.* 2011a *SBRC*	12 soils impacted from a variety of Pb sources		1/100 g.mL^{-1} 1 h @ pH 1.5 Glycine, HCl	4 h @ pH 6.5 NaOH, pancreatin, bile	• *In vivo* blood RBA in mice (X-axis) correlated to relative *in vitro* data (Y-axis): R^2=0.88, intercept -7.02, slope 1.06 (SBRC, I phase results)

IVBA – in vitro bioaccessibility; RBA – relative bioavailability; G – gastric; I – intestinal. [*]*Relationship with corrected EPA in vivo data indicated in Drexler & Brattin (2007).*[†] *In vitro-in vivo relationship not performed with EPA corrected data (in vivo bioavailability or bulk Pb concentrations).*

1.5.2 Tests not compared with *in vivo* data

Several *in vitro* tests that have not been compared with *in vivo* data have been proposed. These tests are important, since they may be validated in the future or be useful for studying factors influencing Pb bioaccessibility and bioavailability. Table 1-5 and Table 1-6 summarize the various parameters applied in some of these tests either not physiologically based (Table 1-5) or physiologically based (Table 1-6). Procedures that are not physiologically based (Table 1-5) include a large number of batch acid extractions using dilute HCl performed at various S/L ratios, durations, and pH. Since 1994, HCl extraction has been a standard method for assessing the toxicity of toys used to establish the European Standard on the Safety of Toys. The toy material is reduced to a particle size < 500 μm and added to a HCl solution using a 1/50 $g.mL^{-1}$ ratio (pH 1.5; 37°C; 2 h) (Ruby 2004, Schoof 2003, Wragg & Cave 2002). As pointed out by Le Bot *et al.* (2011), such tests may be helpful in preventing Pb poisoning. In fact, Pb leached during HCl extractions simulating stomach conditions may provide more a relevant indication of potentially bioavailable Pb than standard total Pb extractable measurements on wastes and solids. Some sources could have high values of total extractable Pb even though it is poorly soluble in the stomach, or, inversely, they could impair the interpretation of BLLs and environmental Pb levels.

Among the physiologically based models presented in Table 1-6, many are modifications of the PBET, IVG, or RIVM procedure. The German method, E DIN 19738 [DIN] mimics gastrointestinal digestion for infants/children, in a fasting case or a fed state, through the addition of whole milk powder. Gastric fluids are composed of a mixture of pepsin, mucin, and HCl. Intestinal fluids contain bile, trypsin, pancreatin, and phosphate buffer. The gastric phase takes place at pH 2 over 2 hours, and a pH of 7.5 is applied to the intestinal phase over 6 hours. Extraction is achieved by a two phase centrifugation at 7,000 g, decantation, and analysis of the supernatant (Oomen *et al.* 2002, Van De Wiele *et al.* 2007) (Table 1-6). Although somewhat laborious, DIN appears to be a relevant method, as there is a need for a test with whole milk powder for infants exposed to Pb particles in drinking water via baby feeding bottles.

The TIM, SHIME, and flow-through methods using online extractions are dynamic, physiologically based tests (Chu & Beauchemin 2004, Jimoh *et al.* 2005, Van De Wiele *et al.* 2007). The TIM model (or TNO GI model) mimics the contact with saliva and further GI digestion by the progressive addition of fluids, the progressive adjustment of pH, and the simulation of peristaltic contractions. Gastric pH and retention times are adjusted differently if the simulation is aimed at representing a fed state (pH decreases gradually from 5 to 2 over 90 min) or a fasting state (pH decreases gradually from 4.5 to 1.8 over 40 min). Then, intestinal fluids are added at 1 mL/min to increase the pH from 6.5 to 7.2, at which point ultra filtration is performed. This model has been validated with *in vivo* dissolution profiles of drugs with or without food; however, it was not calibrated for Pb particles (Oomen *et al.* 2002, Oomen *et al.* 2006, Van De Wiele *et al.* 2007). The SHIME (Simulator of Human Intestinal Microbial Ecosystem of Infants) model, developed in Belgium, simulates 3 h gastric and 5 h intestinal digestion in the same reactor (150 rpm). Gradients of pH can be applied if a series of reactors is used (dynamic model), and a phase including a mixed microbial community can be added to the model (Laird *et al.* 2007, Oomen *et al.* 2002). Constant stomach retention times are applied for fasting conditions (pH ~ 2.0) and fed conditions (pH ~ 4.0) (Van De Wiele *et al.* 2007). Centrifugation at 7,000 g is conducted and the supernatant is analyzed. The pellet is then digested to mass balance (Oomen *et al.* 2002). These procedures cannot be used routinely to measure Pb bioaccessibility on Pb particles, however, since they take too long to perform and are highly complex. Nevertheless, it appears that they could be highly useful for studying specific factors affecting Pb bioavailability that have been poorly studied up to now, such as the effect of bacteria.

Table 1-5. Examples of variants of non-physiologically-based *in vitro* procedures applied to Pb particles.

GENERAL				GASTRIC			INTESTINAL	
Reference	**Mixing**	**T °C**	**Extraction**	**S/L (g.mL^{-1})**	**Time, pH**	**Fluid**	**Time, pH**	**Fluid**
Sheppard *et al.* 1995			Filtration 0.5 µm	1/167	24 h, pH 2.0	HCl		
Gasser *et al.* 1996	Stirred-flow reactor	24 °C	Filtration 0.22 µm	1/100	1 h, pH 1.0 to 3.0	HCl, ammonium acetate		
Gasser *et al.* 1996	Horizontal shaker	24 °C	Centrifugation (400 RCF; 10 min)	1/200	1 h, pH 1.0	HCl		
Rieuwerts *et al.* 2000	Inversion by hand 5 times at t = 1h	Ambient	Centrifugation (2,000 rpm; 2 min)	1/100	2 h, pH 1.2	HCl		
Yang *et al.* 2001	Rotation 30 rpm	37 °C	Filtration 0.2 µm	1/100	1 h, pH 2-2.5	HCl		
Mercier *et al.* 2002	End-over-end 30 rpm, at 20 min intervals, for 20 min	35-39 °C	Decantation, filtration	1/22	160 ±10 min, pH 6.0 to 2.0	HCl, acetic acid		
Yang *et al.* 2002	Rotation 30 rpm	37 °C	Filtration 0.2 µm	1/100	1 h, pH 2.0	HCl		
Scheckel & Ryan 2003	Continuous stirring	37 °C	Filtration 0.45 µm	1/160	1 h, pH 2.0	HCl	5 h, pH 7.0	
Yang *et al.* 2003	End-over-end, 30 rpm	37 °C	Decantation, filtration 0.45 µm	1/40 and 1/100	1 h, pH 1.5 to 4.0	HCl, glycine	3 h, pH 7.0	$NaHCO_3$
Beak *et al.* 2006	Variable speed mixer (150 rpm); 2 mL/min Ar	37 °C	Filtration 0.45 µm	1/167	2 h, pH 1.8	HCl	4 h, pH 7.0	NaOH
Turner & Simmonds 2006		Ambient		1/100	Overnight	HCl, pepsin		
Bosso & Enzweiler 2008	Orbital, 100 rpm	37 °C	Centrifugation (5,000 rpm; 20 min)	1/100	1 h, pH 1.5	HCl, glycine OR HCl, pepsin, NaCl	2 h, pH 7.0	$NaHCO_3$
Le Bot *et al.* 2010, 2011	Ultrasonication	37 °C	Filtration 0.45 µm		1 h, pH 1.5	HCl , 0.75-1.4% diluted		
Rasmussen *et al.* 2011		37.5 °C	Centrifugation (5,000 g, ≤ 10 min)	1/2000	2 h, pH 1.5	HCl		

Table 1-6. Examples of variants of physiologically based *in vitro* procedures applied to Pb particles.

GENERAL			ORAL		GASTRIC			INTESTINAL	
References	**Mixing**	**Extraction**	**Time, pH**	**Fluid**	**S/L ($g.mL^{-1}$)**	**Time, pH**	**Fluid**	**Time, pH**	**Fluid**
Sheppard *et al.* 1995		Centrifugation, filtration 0.2 µm				4 h, pH 2.0	NaCl; pepsin; HCl	18 h, pH 7.5	$NaHCO_3$; NaCl; bile; pancreatin; α-amylase
Berti & Cunningham 1997	Stir bar				1/100	1 h, pH 2.5	Pepsin; organic acids; HCl	2 h, pH 7.0	$NaHCO_3$; pancreatin; bile
Davis *et al.* 1997	Wrist action shaker	Centrifugation (2,100 g; 25 min)			1/10	2 h, pH 1.3	Pepsin; organic acids; HCl	2 h, pH 7.0	$NaHCO_3$; pancreatin; bile
Hamel *et al.* 1998	Shaking water bath	Centrifugation (1,380 g; 10 min)			1/100 to 1/5000	2 h	NaCl; pepsin; HCl		
Hamel *et al.* 1999	Water bath, 90 cyc/min	Centrifugation (906 g; 10 min), filtration 0.45 µm	5 s, pH 5.5	Mucin; urea; KCl; NaCl; Na_2HPO_4; $CaCl_2.4H_2O$	1/2160	2 h	NaCl; pepsin; HCl	2 h	$NaHCO_3$
Oliver *et al.* 1999	Wrist action shaker	Filtration 0.45 µm			1/10	2 h, pH 1.3 to 3.0	Organic acids; HCl; with(out) pepsin	16 h, pH 7.0	$NaHCO_3$ with(out) bile & pancreatin
Ellickson *et al.* 2001	Bath set, 90 cyc/min	Centrifugation (200 g; 20 min) & (906 g; 15 min); HNO_3, 48 h; filtration 0.45 µm		Mucin; urea; $CaCl_2.H_2O$; NaCl; KCl; Na_2HPO_4	1/2160	2 h, pH 1.4	Pepsin; NaCl; HCl	4 h, pH 6.5	$NaHCO_3$
Oomen *et al.* 2002, Van De Wiele *et al.* 2007; *DIN test*	Agitator, 200 rpm	Centrifugation (7,000 g; 10 min)			1/50	2 h, pH 2.0	HCl; [pepsin; mucin]*	6 h, pH 7.5	Phosphate buffer; [bile; trypsin; pancreatin]*
Oomen *et al.* 2002, Van De Wiele *et al.* 2007; *SHIME test*	Stirring, 150 rpm	Centrifugation (7,000 g; 10 min)			1/2.5 to 1/40	3 h, pH 2.0 (fast) or 4.0 (fed)	Nutrilon plus; pectin; mucin; cellobiose; proteose peptone; starch; glucose	5 h, pH 6.5	$NaHCO_3$; pancreatin; bile
Oomen *et al.* 2002, Van De Wiele *et al.* 2007; *TIM test*	Peristaltic	Ultrafiltration	5 min, pH 5.0			●Fast: 40 min, pH 4.5 to 1.8 ●Fed: 1.5 h, pH 5.0 to 2.0	HCl; lipase; pepsin* 0.5 mL/min	●Fast: 5.3 h, pH 6.5 to 7.2 ●Fed: 4.5 h, pH 6.5 to 7.2	$NaHCO_3$; pancreatin; bile* 1 mL/min

Table 1-6. Examples of variants of physiologically based *in vitro* procedures applied to Pb particles (continued).

GENERAL			ORAL		GASTRIC			INTESTINAL	
References	**Mixing**	**Extraction**	**Time, pH**	**Fluid**	**S/L ($g.mL^{-1}$)**	**Time, pH**	**Fluid**	**Time, pH**	**Fluid**
Yu *et al.* 2006	Water bath, 90 rpm	Filtration 0.45 µm		Mucin; urea; KH_2PO_4; $CaCl_2.H_2O$; NaCl, KCl	1/400	2 h, pH 1.4	NaCl; pepsin; HCl	2 h, pH 6.5	$NaHCO_3$
Bruce *et al.* 2007	Ar	Centrifugation (10,000 g; 15 min), filtration 0.22 µm			1/100	1 h pH 1.3 (fast) to 4 (fed)	Pepsin; HCl; organic acids	3 h pH 7.0	$NaHCO_3$; bile; pancreatin
Saikat *et al.* 2007		Centrifugation (2,100 g; 25 min)			1/38-1/100	1 h pH 1.1 or 2.5	Pepsin; organic acids; HCl	4 h, pH 5.5 or 7.0	$NaHCO_3$; pancreatin; bile
Triantafyllidou *et al.* 2007	Gentle mixing	No separation			1/16,667	3 h, pH 1.2	NaCl; pepsin; HCl		
Turner & Ip 2007	End-over-end	Centrifugation (2,100 g;10 min)			1/200	2 h, pH 2.5	Pepsin; HCl; Na malate & citrate; lactic & acetic acids	4 h, pH 7.0	$NaHCO_3$; bile; pancreatin
Van De Wiele *et al.* 2007	Water rotator set	Filtration 0.45 µm			1/100	1 h pH 2.5	Pepsin; HCl; Na citrate & malate; lactate, acetate	4 h, pH 7.0	$NaHCO_3$; bile; pancreatin
Bosso & Enzweiler 2008, Bosso *et al.* 2008	Slow orbital + Ar flux	Centrifugation (5,000 rpm; 20 min)			1/100	1 h, pH 1.7	Pepsin; HCl; citric, malic, acetic, & lactic acids	2 h, pH 7.0	$NaHCO_3$; bile; pancreatin
Turner *et al.* 2009	Constant, lateral	Centrifugation (2,000 g; 10 min)			1/100-1/143	1 h, pH 2.5	Pepsin; HCl; Na malate, citrate; lactic & acetic acids	4 h, pH 7.0	$NaHCO_3$; bile; pancreatin
Sialelli *et al.* 2010	Orbital, 150 rpm				1/100	1 h, pH 1.5	Pepsin; HCl; Na citrate; malic & lactic acids	3.5 h, pH 7.0	Pancreatin, $NaHCO_3$

1.6 Bioavailability/bioaccessibility of Pb particles in relation to Pb speciation, particle size, and surrounding matrix

Physical and chemical aspects of Pb particles are major factors influencing the dissolution of particles containing Pb. Table 1-7 summarizes the IVBA results for validated procedures, bioavailability and bioaccessibility results varying widely with the test material: from 1.7-6% for galena to 100% for shooting range soil, which is in agreement with the *in vivo* swine data (Bannon *et al.* 2009, Casteel *et al.* 2006, Drexler & Brattin 2007, Oomen *et al.* 2006, Smith *et al.* 2011a). Pb was also found to be highly bioaccessible in NIST Paint (75-86%), which is in agreement with previous epidemiological studies referenced in Mushak (1991). In addition, Pb is generally highly bioaccessible in smelter soils, with about 68-69% for some Omaha community soils, and about 70-85% for the Herculaneum smelter (MSE Technology Application 2006, USEPA 2009), and 34-90% for ten smelting soils from northern France (Caboche 2009). However, variability in the bioavailability and bioaccessibility data can be noted for certain substrates, which reflects the highly heterogeneous nature of these substrates in terms of Pb form, particle size, etc. The bioaccessibility of three slag materials was evaluated at 17, 20, and 73% by Drexler & Brattin (2007). Also, among mining site soils and urban topsoils, the IVBA was shown to vary from low (9-14%) to high (63-75%) (Caboche 2009).

1.6.1 Pb speciation

Speciation in the particles can be a strong indicator of the potential bioaccessibility/bioavailability of Pb. Indeed, as highlighted by Casteel *et al.* (2006), RBA estimates can vary widely (6-105%) for Pb particles across the same site or region (e.g. California Gulch, CO), reflecting variability in their mineral composition and the potential of Pb to be liberated. According to Schoof *et al.* (1995), the solubility of Pb minerals present in the test material explains the observed differences in bioavailability results. In addition, Rasmussen *et al.* (2011) successfully predicted their bioaccessibility results on dust from 924 Canadian homes by identifying the Pb phases present with XANES, and further cumulating the bioaccessibility specific to each phase. Identifying the major species present in a soil would therefore help in predicting the extent of bioavailability. Schoof *et al.* (1995) classified the range of solubility of Pb minerals as very high for Pb oxide [PbO]; average for Pb-manganese [Pb-Mn] oxides, Pb-iron

[Pb-Fe] oxides, and Pb carbonates; moderate for Pb sulfates and Pb arsenate; and minimal for Pb phosphates [Pb-P]. The reference USEPA (2007b) classification for bioavailability (and therefore bioaccessibility) after several *in vivo* and *in vitro* studies varies from high for cerussite [$PbCO_3$] and Pb-Mn oxide (> 75%), to medium for Pb-P and PbO (25-75%), to low for anglesite, galena, Fe-Pb species and remaining Pb-based oxides (< 25%). Drexler & Brattin (2007) observed the lowest bioaccessibility for substrates containing anglesite or galena as dominant Pb species (6-21%). On the contrary, substrates with either $PbCO_3$ or MnOOH as the dominant Pb mineral systematically presented a high bioaccessibility (65-90%), in agreement with the data on juvenile swine. Pb carbonate species are easily soluble, and this is reflected in other *in vitro* results: Pb carbonates were estimated to be 97% bioaccessible in the Schaider *et al.* (2007) study; hydrocerussite paint 69% bioaccessible prior to cola addition in the Scheckel & Ryan (2003) study; and Pb was 56% (gastric) and 25% (intestinal) bioaccessible in the high carbonate garden soil G1 in the Denys *et al.* (2007) study.

Soil remediation with phosphates has been shown to decrease Pb bioaccessibility, in agreement with the expected low solubility of Pb-phosphate particles (Bosso *et al.* 2008, Yang *et al.* 2001, 2002, Zhang *et al.* 1998). Nonetheless, a low bioavailability/bioaccessibility fraction should not be interpreted as representing a low hazard potential. Indeed, in the Schroder *et al.* 2004 study, the bioavailability of Pb in the Pb-rich soil 9 (10,600 mg Pb/kg soil) is medium to low (RBA 20%, ABA ~ 10%), but a dose of 100 mg of soil ingested daily will release the same quantity in the body, about 0.1 mg of Pb, like the highly Pb-bioavailable but less Pb-rich soil 15 (RBA 74%, ABA ~ 37%, 3230 mg Pb/kg soil) (authors' calculation). Another facet of speciation concerns the major impact of the rate of pH change on the solution and mineralogical composition found at a given pH. Zhang *et al.* (1998) showed that there are marked differences in solubility between tests conducted in dynamic versus static pH adjustment conditions for a soil dominated by cerussite and modified with hydroxyapatite. The differences reached up to three orders of magnitude in the presence of phosphates, and were attributed to the mechanisms that govern the amount of soluble Pb, with adsorption/desorption phenomena decreasing the amount of soluble Pb in dynamic systems.

1.6.2 Particle size

It is generally accepted that a small particles size provide a high surface to volume ratio and an elevated potential for dissolution (Ruby *et al.* 1999). Indeed, Casteel *et al.* (1997) found a high RBA (57-58%) for soils of ≤ 250 µm containing a majority of particles ≤ 10 µm. The significant BLLs observed in piglets dosed with "predicted low bioavailable" tailings were partly explained by the small size of the galena crystals (mostly < 10 µm) that were completely dissolved within 50-100 min at a low gastric pH (LaVelle *et al.* 1991). Rieuwerts *et al.* (2000) reported a bioaccessibility of about 61-116% for particles < 64 µm, while particles > 64 µm were 21 to 72% bioaccessible. Mercier *et al.* (2002) showed that Pb bioaccessibility generally decreased with increasing granulometry (< 63 µm to 125-250 µm), but remained stable or varied without any trend between 125-250 µm and < 2 mm depending on the substrate. Yu *et al.* (2006) did not find any significant differences in the bioaccessibility estimates between the dust size fractions < 75 µm, 75-150 µm, and 150-250 µm, and, finally, Morman *et al.* (2009) found similar ranges for soil particles < 2 mm (8.5-77%) as compared to particles < 250 µm (3.7-45%), suggesting that small particles are not always more bioaccessible. Such differences may be partly explained by the Pb phase of the particles tested: less soluble Pb phases (anglesite, pyromorphite, and galena) were more influenced by particle size than the more soluble Pb phases in the Medlin (1997) study, bioaccessibility increasing about 4- to 13-fold between the fractions < 38 µm and < 250-125 µm. Moreover, Ruby *et al.* (1992) showed that Pb dissolution rates are not affected by particle size, except for diameters less than 2.4 µm. Finally, Oliver *et al.* (1999) noted that greater bioaccessibility for small particles is more evident for equivalent diameters below 100 µm, so the impact of particle size on bioaccessibility results would only be significant for very small and colloidal particles.

For a given test material, an increase in bioaccessibility/bioavailability that is in inverse proportion to particle size may reflect a relative enrichment in smaller size fractions. Indeed, Juhasz *et al.* (2011) report up to five times more Pb in the < 50 µm particle size fraction of sixteen peri-urban soils. Also noted were significant increases in gastric-SBRC IVBA for six of those soils, but no differences in intestinal-SBRC IVBA between the size fractions. Madrid *et al.* (2008a, 2008b) observed a higher Pb content in the clay fraction (< 2 µm) of urban soils from Sevilla, as well as an increase in the bioaccessible Pb in this size fraction. Finally, a 110% average Pb enrichment was measured in the particle size fraction adhering to hands for different types of soils in Canada, as compared to the bulk Pb content (Siciliano *et al.* 2009). As the fraction adhering to hands is usually smaller than the < 250 µm particle size fraction traditionally used for soils, these authors recommend conducting bioaccessibility experiments on small particles, for example < 45 µm.

1.6.3 Matrix characteristics

The characteristics of the matrix surrounding Pb can also influence Pb release for a given type of particle. Pb bioaccessibility has been related to total Pb content in soils, but also to other metal levels in the soils tested, such as zinc, iron, and cadmium (Pelfrêne *et al.* 2010, Roussel *et al.* 2010). Strongly positive linear relationships were found between Pb bioaccessibility and Pb content in the soils (Roussel *et al.* 2010). It can be expected that a higher Pb content will result in greater bioaccessibility. However, Morman *et al.* (2009) found no correlation between total element content (Pb, Cd, Ni, Cr, and As) and the bioaccessible fraction for the twenty soils from various sources. Comparable RBA results (56-58%) were obtained with Aspen Berm and residential soils of comparable particle size, matrix, and mineral type, although the Berm soil contained four times as much Pb (Casteel *et al.* 1997). Oomen *et al.* (2002) found also higher bioaccessibility for Flanders sandy loam (91%) than for Oker 11 sandy loam (56%), although the latter contained ten times more Pb. This indicates that bioavailability is more influenced by the particle type distribution than by its Pb content.

Poggio *et al.* (2009) and Roussel *et al.* (2010) related bioaccessible Pb to other characteristics of the soil matrix than total metal content, such as carbonates, clay, and organic matter, in soils from similar sources. However, Denys *et al.* (2007) did not find a significant relationship between Pb bioaccessibility and the total amount of carbonates in a variety of high Pb-carbonate soils. Caboche *et al.* (2010) found significant correlation to the cation exchange capacity; organic matter; and clay, manganese, phosphorus, and iron content for soils from the same source. However, no correlations were found when soils from all the sources tested were pooled. In addition, the bioaccessibility of twenty soils from various sources in Morman *et al.* (2009) study was not correlated to the organic carbon, pH, and clay percentage in the soils. These findings suggest that significant relationships with soil characteristics can be found for soils from the same source type, but that they cannot be generalized to other matrices.

Overall, soil characteristics will impact Pb bioaccessibility differently, depending on the Pb species present, and cannot be used as a general predictor of bioaccessibility, while Pb speciation may be more predictive of bioaccessibility.

Table 1-7. Main bioaccessibility results for materials tested using an *in vitro* procedure calibrated with *in vivo* data.

SUBSTRATE	**IVBA%**	**REFERENCES**
Flanders soil	91±4	*Oomen et al. 2002* *USEPA 2004, 2009* *MSE Technology Application 2006* *Drexler & Brattin 2007* *USEPA 2007b* *Bannon et al. 2009* *Morman et al. 2009* *RBALP*
Oker 11 soil	56±4	
47 Omaha community smelter soils, US	68-69 (average)	
HER-2930 smelter soil, US	69±1.5 (using Dr Drexler's Pb levels) 85±1.1 (using EPA's average bulk Pb levels)	
17 residential soils, tailings, and slags from mining waste sites, US	14±1.7 to 90±3.1	
1 NIST paint	75±3.8	
1 Galena	6±2.3	
8 shooting range soils, US	83±1 to 100±3	
20 soils from the N-S transect, US (agricultural, grazing land, open range, forested land, residential, desert)	3.7 to 39	
9 soils from mining sites*	3.1±0.1 to 99.3±14.3	*Oomen et al. 2006* *RIVM*
1 NIST paint* + soil	86.2 ± 2.3	
1 Galena*	1.7 ± 0.2	
15 mining soils, France	9-75	*Caboche 2009,* *Caboche et al. 2010* *Roussel et al. 2010* *UBM*
10 smelting soils, France	34-90	
27 urban topsoils, France	11-63	
2 urban residential soils, Australia	20.0±4.0 to 26.1±6.5	*Juhasz et al. 2009* *Smith et al. 2011a,* *Smith et al. 2011b* *SBRC*
3 domestic incinerator soils, Australia	11.7±2.8 to 22.5±5.0 3.2±2.6 to 8.5±0.6†	
Brushal, Carl-1, Hamburg, and Oker-11 soils§	30.7±6.1 to 62.9±11.0	
9 shooting range soils, Australia	21.3-102.6 59±3.7 to 92±9.0 (3 soils)†	
5 historical fill soils, Australia	5.5-26.1 (4 soils) 10.7±0.7 to 16.6±1.1 (2 soils)†	
13 mining/smelting soils, Australia	11.6-82.5 31±18.4 to 74±17.3 (3 soils)†	
1 gasworks, Australia	27.2 27±1.6†	
1 geogenic, Australia	12.5	

*IVBA % for SBRC, RIVM, and UBM tests calculated based on relative bioaccessibility data from intestinal extraction.*same test materials as in RBALP studies, 0.06 g. § Soils tested by Marschner et al. (2006).† Smith et al. 2011a.*

1.7 Gaps in bioaccessibility data

This review documented an abundance of peer-reviewed studies on *in vitro* testing, on topics ranging from simple leaching procedures to validated procedures calibrated to *in vivo* animal studies, and their application to a range of Pb bearing substrates. Among all the methods developed to estimate Pb bioaccessibility, only a few have been successfully compared with *in vivo* data (Table 1-4), and only the RBALP by Drexler & Brattin (2007) has been calibrated, validated, and fully standardized. Other procedures, such as UBM, RIVM, and SBRC, have been highly correlated to *in vivo* data, so their results can also be considered as valid for improving exposure assessment and public health protection. However, additional validation with statistical analysis and round robin testing will be needed to standardize these procedures.

A significant number of substrates were tested using these validated procedures (Table 1-7). However, no data are available on bioaccessibility on dust, although dust Pb content was evaluated at some of the sites studied. Also, only one paint substrate was tested and the NIST material used may not necessarily be representative of paint chips to which children are exposed. However, paint containing Pb is not unusual in toys and old buildings (CDC 2010a), and recent results on paint chips using HCl extraction show high variability of leachable Pb, ranging from 4 to 100% (Le Bot *et al.* 2011). As well, some HCl extractions performed on dust particles have shown that the amount of leachable Pb is generally high (Davis *et al.* 1997), and this is partly attributed to the small size of these particles. Pb dust and Pb paint have been shown to be major contributors to the BLLs of children (Lanphear *et al.* 2003). Further research is needed to quantify the variability in bioaccessibility for these particles, to support the estimation of the contribution of paint and dust particles to exposure, and to help analyze the reported pica-caused BLL cases associated with ingestion of these particles. There is also a significant data gap regarding Pb particles from drinking water systems, as only one peer-reviewed study is available on this topic (Triantafyllidou *et al.* 2007). Early results using the RBALP adapted for Pb particles from tap water show that the bioaccessibility of particles generated from plumbing metals and collected from distribution systems varies widely (Deshommes *et al.* 2010b). Such data are needed, considering that: (i) particulate Pb can be sporadically high and is currently not fully considered in drinking water sampling and analysis methods; (ii) baby bottles may be prepared with tap water; and (iii) tap water Pb particles and colloids are small and may be highly soluble, depending on the forms present (Deshommes *et al.* 2010a, McNeill & Edwards 2004, Triantafyllidou *et al.* 2007).

Finally, most of the bioaccessibility results were measured in a fasting state, which is considered to be the worst case ingestion scenario. This ingestion state may be realistic for soil, paint, and dust particles, but not for tap water Pb particles, which can be ingested in either the fasting or the fed state. The oral bioavailability of Pb in food cooked or prepared with high Pb particulate water might also be a relevant route of exposure to study (Triantafyllidou *et al.* 2007). However, the development and validation of a standardized *in vitro* test for a fed state would certainly be a challenge, considering the variability of food that can be ingested by children (other than milk) and the divergent results observed by Medlin (1997) for several types of food. The most disturbing finding is that higher bioaccessibility values are found for *in vitro* tests performed with whole milk powder than for those simulating a fasting state (Marschner *et al.* 2006, Van De Wiele *et al.* 2007). In fact, early studies show that milk consumption increases the absorption of PbAc in rats (Bell & Spickett 1981). This has also been observed for hydrophobic organic compounds, and can be explained by the formation of soluble metal complexes with milk constituents (Hack & Selenka 1996, Oomen *et al.* 2000). Such information may not have been considered in the past because the major sources of Pb exposure were air and soil, and Pb exposure from these sources is not likely to occur at the same time as milk ingestion. However, considering that water is now established as a significant residual source of Pb exposure and that baby bottles are often prepared with tap water, the ingestion of formula made in this way probably constitutes the worst case exposure, as it involves both the dissolved and the particulate Pb in tap water. Therefore, it is not clear that *in vitro* procedures in a fasting state will provide worst case assessments of exposure for bottle-fed infants/children. One *in vivo* study was performed with the simultaneous dosage of soil and milk powder on juvenile swine (Marschner *et al.* 2006). However, the dosage of soil was not tested on its own, precluding any comparison between Pb absorption from soil particles alone and Pb absorption from particles in the presence of milk. The apparent increase in Pb bioavailability when Pb is ingested with milk certainly needs to be confirmed with an *in vivo* test on piglets, to compare both soluble and particulate Pb ingestion, with and without milk.

1.8 Conclusion

In vivo experiments on Pb particles have been carried out using animal models on a wide range of particulate Pb forms, mostly from contaminated soils. It is established that there are substantial anatomical and physiological differences between animal species and humans, especially children. The scarcity of data providing a direct estimate of the human absorption of Pb particles is a significant limitation on our ability to estimate bioavailability, a shortcoming that is partially addressed by the use of the most representative animal model. Of all the animal models evaluated, juvenile swine are considered the most appropriate animal model for human exposure studies. However, results from animal models should always be considered with caution when extrapolated to humans or used to validate results from *in vitro* testing. Critical factors to consider in order to ensure relevance to public health decision making include: (1) the limitations and specific features of the animal model; (2) targeting the human population in the design of animal studies, specifically the appropriate developmental stage; and (3) the use of plausible environmental doses and Pb speciation.

Results reporting Pb bioaccessibility reflect the experimental conditions considered, and, in the absence of a standard procedure, cannot be compared. At the same time, this variability is inextricably linked to the natural variability of human exposure to Pb particulates. The RBALP procedure seems well suited to Pb particles, since its results for gastric extraction can be successfully correlated to *in vivo* data on piglets. This test was completely validated and submitted to a rigorous QA/QC protocol. The addition of an intestinal bioaccessibility phase to better mimic Pb solubility at the neutral pH of absorption appears desirable, and is slightly better correlated to bioavailability. Therefore, a complete validation of RIVM, UBM, and SBRC tests simulating an intestinal phase will be needed to reinforce the level of standardization of these tests. Such tests are more costly and tedious than the RBALP, but may provide better results for Pb exposure assessment.

Finally, the validated tests were applied on a significant number of substrates, but mostly soils. The selection does not cover the whole variety of possible matrices surrounding Pb in environmental sources and other significant sources of exposure, such as those of paint, as well as dust and tap water. Testing these types of particles *in vitro* raises experimental challenges, because of their heterogeneity and the small amounts of some of them, but is needed to complete the input in exposure models and risk assessment studies. As a first step, the RBALP could be adapted for estimating bioaccessibility from these sources, since this test is quite simple to perform compared to other procedures, and presents the highest degree of standardization.

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CHAPITRE 2 OBJECTIFS DE RECHERCHE ET MÉTHODOLOGIE

2.1 Évaluation critique des besoins de recherche

Comme expliqué en introduction, la recherche sur le plomb dans l'eau potable s'est surtout intéressée au plomb dissous, et très peu au plomb particulaire. De ce fait, la fraction de plomb particulaire contribuant au plomb total dans l'eau du robinet apparait sous estimée par les protocoles d'échantillonnage et les méthodes d'analyse laboratoire utilisés actuellement (Triantafyllidou *et al.* 2007). Ainsi, les données de plomb total dont la recherche dispose pour évaluer l'exposition du consommateur ne reflètent pas l'exposition réelle du consommateur.

Les concentrations anormalement élevées de plomb total sont souvent attribuées à la présence de plomb particulaire. Toutefois la concentration et la fréquence d'occurrence de ce dernier ne sont jamais précisément évaluées. Hors il apparait que ces phénomènes de concentrations élevées en plomb soient fréquents dans le cas des grands bâtiments, incluant les écoles et garderies. Par ailleurs, plusieurs cas d'intoxications au plomb reliés à l'eau potable suggèrent une contribution du plomb particulaire (Brown *et al.* 2011, Edwards *et al.* 2009, Miranda *et al.* 2007, Triantafyllidou & Edwards 2011a). Ainsi, le plomb particulaire ne serait pas un phénomène à négliger dans l'exposition du consommateur, notamment dans l'exposition de l'enfant.

Par conséquent, des recherches sont nécessaires pour :

1) Évaluer les différentes formes de plomb particulaire de l'eau potable.
2) Estimer l'occurrence du plomb particulaire dans l'eau potable, les facteurs influençant son détachement et/ou sa collecte dans les échantillons.
3) Générer des distributions des concentrations de plomb particulaire dans l'eau potable réalistes de l'exposition du consommateur.

Ces trois informations permettront de mieux caractériser les formes de plomb particulaire auxquelles la population est exposée, la fréquence d'exposition, et les concentrations d'exposition.

En omettant de considérer le plomb particulaire, les modèles biocinétiques tel que IEUBK appliquent par défaut une biodisponibilité du plomb ingéré via l'eau potable fixée à 50%, toutes catégories d'âge confondues (< 7 ans). Le modèle multiplie ensuite cette biodisponibilité par la dose moyenne de plomb ingérée, dose préalablement corrigée par IEUBK selon la catégorie d'âge de l'enfant pour tenir compte des différences d'absorption variant avec le poids de l'enfant (variation de la fraction absorbée par transport actif). Cependant, la biodisponibilité appliquée n'est valable encore une fois que pour la forme dissoute du plomb dans l'eau. En effet, l'absorption du plomb particulaire dans le système sanguin dépendra de la solubilisation préalable des particules dans le tractus gastro-intestinal, c'est-à-dire de leur bioaccessibilité. Ainsi, l'ingestion de particules de plomb (sols, poussières, ou peintures) est traitée différemment du plomb dissous dans les modèles d'exposition. Le taux d'absorption considéré se base sur l'estimation de la bioaccessibilité d'une variété d'échantillons. Au même titre, il est nécessaire d'évaluer la bioaccessibilité des diverses particules de plomb de l'eau potable. Cela permettra de raffiner les modèles biocinétiques d'exposition au plomb, en ajustant la fraction particulaire du plomb total ingéré avec sa bioaccessibilité. Enfin, la confrontation des résultats donnés par le modèle en considérant ou non les données de plomb particulaire permettra d'estimer la contribution du plomb particulaire à l'exposition du consommateur.

Enfin, considérant le fait que les mesures pour remédier au plomb ne sont souvent faisables que sur du long terme, il apparait important de proposer une solution permettant de protéger rapidement et à moindre coût les consommateurs du plomb présent dans l'eau potable. Les dispositifs POU représentent une alternative très intéressante et recommandée par les organismes de Santé Publique. Cependant, le retrait de la certification NSF-53 pour l'enlèvement du plomb pour certains de ces dispositifs, après considération du plomb particulaire dans le protocole NSF, amène à réflexion. En effet, peu d'information est disponible sur l'enlèvement du plomb par les POU excepté les études de Boyd *et al.* (2005, 2008a, 2008b) effectuées en laboratoire et dans plusieurs écoles de Seattle. Aucune information n'est disponible sur l'enlèvement du plomb particulaire par ces dispositifs, et il apparait donc justifié d'établir quelles technologies des POUs proposés sur le marché permettent d'enlever efficacement à la fois le plomb dissous et le plomb particulaire. Aussi, l'évaluation de l'efficacité des dispositifs POU sur le long terme n'a jamais été effectuée dans un grand bâtiment. Hors les longues stagnations spécifiques aux grands bâtiments pourraient entrainer une percée du filtre, mais aussi la corrosion des éléments localisés après le filtre, limitant ainsi la pertinence d'installer des dispositifs POU. Enfin, les POU ont été conçus en premier lieu pour usage domestique, et non pour usage collectif. Ainsi, leur temps de vie dans un grand bâtiment sera beaucoup plus long que dans une résidence typique, compte tenu de la plus faible consommation d'eau en bâtiment non-résidentiel. Hors il est connu que les filtres au charbon actif sont sujets à la colonisation bactérienne, et que cette dernière est favorisée avec le temps et les stagnations. Il apparait donc important de vérifier, en plus de l'efficacité d'enlèvement du plomb dans l'eau, l'effet de l'installation de tels dispositifs sur la qualité de l'eau, sur le long terme.

2.2 Objectifs et hypothèses de travail

Considérant les besoins de la recherche énoncés précédemment, les objectifs de ce projet étaient:

1. **Caractériser la source, l'occurrence, et les concentrations de plomb particulaire dans l'eau du robinet des résidences avec ESP à Montréal**. *Cet objectif permet d'estimer les formes de particules de plomb auxquelles le consommateur est exposé dans sa résidence, et à quelle ampleur (fréquence et concentration).*
2. **Caractériser la source de plomb particulaire dans l'eau du robinet d'un grand bâtiment, et les concentrations maximales de plomb particulaire auxquelles le consommateur peut être exposé**. *Cette étape permet d'estimer les formes de particules de plomb auxquelles le consommateur est exposé dans un grand bâtiment, et à quelle ampleur maximale.*
3. **Comparer divers protocoles d'échantillonnage du plomb en termes d'information sur le plomb particulaire.** *Cet objectif permet de suggérer une forme d'échantillonnage adaptée pour l'estimation du plomb dissous et du plomb particulaire.*
4. **Estimer l'efficacité d'enlèvement du plomb dissous et particulaire par des dispositifs de filtration domestiques POU de divers types pour une eau de distribution typique, avec des particules de plomb représentatives de celles présentes dans l'eau potable**. *Cette étape permet d'évaluer si les dispositifs POU sont efficaces pour l'enlèvement du plomb particulaire en plus du plomb dissous, et donc adaptés pour la protection des populations.*

5. **Conclure si les dispositifs POU sous évier constituent un choix économiquement viable pour remédier au plomb dans les grands bâtiments présentant des problèmes de corrosion.** *Cet objectif complète l'étape précédente pour valider l'efficacité des dispositifs et permet aussi de juger de l'applicabilité ou non des POUs pour les grands bâtiments dont la problématique est totalement différente de celle de résidences privées. Les résultats contribueront à aider les grands bâtiments dans le choix de leur méthode pour remédier au plomb.*
6. **Estimer la fraction bioaccessible des particules de plomb à l'être humain**. *Cet objectif permet de générer des résultats utiles à l'élaboration de modèles biocinétiques d'exposition au plomb par l'ajout d'informations sur l'élément manquant de ces modèles, soit la prise en compte du plomb particulaire.*
7. **Estimer la contribution du plomb particulaire à l'exposition au plomb du consommateur**. *Cette étape finale permet de montrer si le plomb particulaire contribue de façon significative ou non à l'exposition du consommateur, et donc s'il est important ou non de prendre en compte le plomb particulaire dans les protocoles d'échantillonnages et d'analyse, dans l'analyse de l'exposition et du risque, et dans la réglementation en général.*

Ce projet de recherche a été orienté selon les hypothèses suivantes:

1. Le plomb particulaire survient de façon sporadique dans les résidences et son importance varie d'un site à un autre.
2. Au 1^{er} jet, le plomb particulaire survient de façon constante dans les grands bâtiments, et à concentration très élevée.
3. Le plomb particulaire dans l'eau du robinet des résidences avec ESP à Montréal est principalement le résultat (i) de la corrosion de la tuyauterie interne et (ii) de l'adsorption du plomb dissous sur des particules/dépôts de fer dans la tuyauterie interne et l'entrée de service. Le phénomène (i) génère des concentrations de plomb particulaire généralement faibles avec aléatoirement des pics importants. Le cas (ii) génère constamment des concentrations faibles de plomb particulaire.
4. Le plomb particulaire dans les grands bâtiments est principalement issu de la corrosion des éléments en laiton et des soudures de la tuyauterie interne contenant du plomb.
5. Les perturbations hydrauliques influencent l'occurrence du plomb particulaire.

6. Le protocole d’échantillonnage et la stagnation influencent directement la probabilité de passage de plomb particulaire. Un échantillonnage de type « aléatoire » augmenterait la probabilité de passage des particules de plomb et faciliterait donc la réalisation d’un profil d’occurrence du plomb particulaire. Un échantillonnage avec stagnation de 30 minutes précédée d’un rinçage serait inadapté à l’étude du plomb particulaire car il éliminerait la majorité des particules de plomb lors du rinçage préalable à la stagnation, et la stagnation de 30 minutes serait insuffisante pour générer d’autres particules. La prise du 1er jet sans rinçage ou après un long temps de stagnation (e.g. 6 h) serait adaptée pour l’échantillonnage du plomb particulaire.

7. Les concentrations de plomb dissous à l’effluent des dispositifs de filtration POU certifiés NSF/ANSI 53 pour le plomb après 2007 pourraient dépasser les prévisions de NSF pour certaines conditions d’eau du robinet.

8. L’efficacité des dispositifs de filtration POU à enlever le plomb particulaire dépend du type de filtre, et notamment de la présence d’une barrière physique. Les pichets à filtration gravitaire seraient inefficaces pour enlever le plomb particulaire de part leur concept à base de résine échangeuse d’ions. Pour les autres dispositifs ayant des filtres sous forme de bloc de charbon actif (porosité 0.5-1 µm), l’efficacité d’enlèvement du plomb total serait influencée par la présence et l’accumulation de particules. Pour ces dispositifs, les concentrations de plomb à l’effluent pourraient excéder 10 µg/L avant pleine capacité du filtre dans le cas (i) d’une qualité d’eau différente, (ii) de temps de stagnation élevés causant un largage des particules captées, (iii) de particules de plomb colloïdal en excès.

9. La présence de particules de plomb et de fer détermine la durée de vie du filtre. Une grande teneur en métaux particulaires causerait un colmatage précoce du filtre de POU. Les teneurs en plomb à l’effluent n’en seraient pas augmentées, cependant la durée de vie des filtres pourrait être fortement diminuée rendant ainsi la solution des POU pour remédier au plomb peu viable d’un point de vue économique.

10. À long terme, l’installation de dispositifs POU sous évier (bloc de charbon actif) dans un grand bâtiment entraine la colonisation des filtres POU, et une percée des filtres.

11. La bioaccessibilité telle qu’estimée par un test *in vitro* dépend de la composition et de la taille des particules.

12. Le plomb particulaire, lorsqu'il survient, peut contribuer de façon plus importante que le plomb dissous dans l'exposition du consommateur selon sa composition. Cette contribution ne serait pas stable, car l'occurrence du plomb particulaire ne l'est pas en général.

2.3 Méthodologie

La méthodologie adoptée pour remplir chacun des objectifs énoncés précédemment est la suivante:

2.3.1 Objectif 1

« Caractériser la source, l'occurrence, et les concentrations de plomb particulaire dans l'eau du robinet des résidences avec ESP à Montréal » (hypothèses 1, 3, 5-6)

Des échantillonnages d'eau ont été effectués avec la ville de Montréal en 2007 dans 45 résidences avec ESP. La fraction dissoute et la fraction particulaire du plomb, cuivre, fer, zinc, étain, antimoine, et cadmium étaient évaluées dans les échantillons. Le protocole d'échantillonnage adopté était dit « aléatoire »: le 1er litre et le 2^{e} litre étaient prélevés au robinet de cuisine sans stagnation fixe ni rinçage préalables, puis un rinçage de 5 minutes était effectué et un dernier échantillon de 1 litre était collecté. Les caractéristiques de l'eau et la longueur de l'entrée de service étaient mesurées, la tuyauterie interne était inspectée, et les particules retenues derrière l'aérateur du robinet étaient collectées. Les données obtenues ont été compilées puis analysées à l'aide du logiciel *Statistica Soft*. Aussi, les dépôts internes de plusieurs ESP excavées à Montréal ont été étudiés par microscopie Raman et ion TOF-SIMS. Enfin, un échantillon représentatif des particules recueillies dans les aérateurs a été analysé par ion TOF-SIMS. Les corrélations obtenues entre les concentrations des différents métaux et les données mesurées, par type d'échantillon prélevé, ont permis de déduire les sources de plomb particulaire et leur occurrence. L'analyse a été appuyée par les résultats de composition (i) des dépôts en surface interne des ESP, et (ii) des particules collectées derrière les grilles des robinets. Les concentrations de plomb particulaire obtenues dans le 1er litre aléatoire, 2^{e} litre aléatoire, et litre après 5 minutes de rinçage ont permis de générer une distribution des concentrations de plomb particulaire auxquelles les populations sont exposées.

2.3.2 Objectif 2

« Caractériser la source de plomb particulaire dans l'eau du robinet d'un grand bâtiment, et les concentrations maximales de plomb particulaire auxquelles le consommateur peut être exposé» (hypothèses 2, 4)

Quarante-cinq robinets ont été échantillonnés dans un grand bâtiment, au 1^{er} jet le matin (250 mL), pour les formes dissoutes et particulaires du plomb et d'autres métaux représentatifs de la tuyauterie interne (cuivre, fer, zinc, étain, antimoine, cadmium). L'analyse des fractions dissoutes et particulaires des métaux dans les échantillons collectés, en fonction des robinets échantillonnés (sous-sol, étage), et une inspection de la tuyauterie interne du bâtiment, ont permis d'établir les diverses sources de plomb particulaire dans le bâtiment, et de dégager les sources les plus importantes. Aussi, les résultats obtenus ont permis de générer une distribution des concentrations élevées de plomb particulaire auxquelles les populations peuvent être exposées dans les grands bâtiments.

2.3.3 Objectif 3

« Comparer divers protocoles d'échantillonnage du plomb en termes d'information sur le plomb particulaire » (hypothèses 5-6)

Des résultats de plomb particulaire ont été obtenus durant les campagnes d'échantillonnage de la ville de Montréal en 2006 (109 résidences) et 2007 (45 résidences). L'échantillonnage utilisé en 2007 était différent de celui appliqué en 2006, afin de comparer les deux protocoles en termes d'information sur le plomb particulaire. En 2006, l'échantillonnage pratiqué consistait en un rinçage initial de 5 minutes et en la collecte d'un litre après ce rinçage. Ensuite, l'eau était laissée à stagner durant 30 minutes, puis deux litres consécutifs étaient échantillonnés. En 2007, l'échantillonnage du 1^{er} et 2^e litre n'était pas précédé d'un rinçage fixe et d'une stagnation fixe, ces échantillons étaient prélevés dès l'arrivée dans les résidences (aléatoire), puis un échantillon était collecté après 5 minutes de rinçage. Aussi, en 2007, 9 résidences ont été sélectionnées pour y effectuer, après l'échantillonnage « aléatoire », un échantillonnage visant à stimuler le détachement de plomb particulaire par la création de perturbations hydrauliques. Cet échantillonnage consistait à ouvrir et fermer le robinet à plusieurs reprises, avec alternativement un débit élevé ou un débit « normal ». La comparaison des résultats obtenus pour les trois protocoles d'échantillonnage a permis de (i) dégager les facteurs influençant le détachement du plomb particulaire sous ses diverses formes, (ii) déduire un protocole adapté à la fois pour la détection du plomb dissous et du plomb particulaire dans les résidences avec ESP.

2.3.4 Objectif 4

« Estimer l'efficacité d'enlèvement du plomb dissous et particulaire par des dispositifs de filtration domestiques POU de divers types pour une eau de distribution typique, avec des particules de plomb représentatives de celles présentes dans l'eau potable » (hypothèses 7-8)

Un pilote a été monté au laboratoire, muni d'un grand réservoir et de plusieurs robinets permettant de tester (i) deux dispositifs POU de type « sous-évier », (ii) trois dispositifs POU de type « monté sur robinet », et (iii) deux dispositifs POU de type « pichet ». L'eau testée était l'eau du réseau de distribution de Montréal, additionnée d'une solution mère de plomb dissous et de particules de plomb tétravalent. Les dispositifs ont été testés en quasi continu durant 6 jours consécutifs, jusqu'à atteinte de 120% de leur capacité de volumes d'eau filtrés. Afin de vérifier l'effet des stagnations sur l'efficacité d'enlèvement du plomb par les dispositifs, deux stagnations étaient effectuées chaque jour: une courte de 30 minutes le midi, et une stagnation d'une nuit. Après chacune de ces stagnations, un échantillon de l'affluent, et un échantillon de l'effluent de chacun des dispositifs étaient prélevés et analysés pour le plomb total et le plomb dissous. Aussi, après chacun de ces échantillonnages, des mesures de la qualité de l'eau étaient effectuées (pH, Cl_2, turbidité, température) à l'affluent et à l'effluent des dispositifs, afin d'observer un éventuel impact des dispositifs sur les caractéristiques de l'eau. Les résultats obtenus ont permis de conclure sur l'efficacité des POUs à réduire le plomb dissous, et le plomb particulaire, dans des conditions différentes du protocole NSF.

2.3.5 Objectif 5

« Conclure si les dispositifs POU sous évier constituent un choix économiquement viable pour remédier au plomb dans les grands bâtiments présentant des problèmes de corrosion » (hypothèses 7-10)

Quarante-cinq robinets d'un grand bâtiment ont été échantillonnés au 1er jet le matin (250 mL) pour l'évaluation globale des concentrations de métaux dissous et particulaires (Pb, Cu, Fe, Zn, Sn, Cd, Sb). Ensuite, trois éviers de cuisine(tte) et deux fontaines ont été sélectionnés pour l'installation d'un dispositif POU de type sous-évier préalablement testé lors d'une étude pilote (objectif 4). Le choix de ces cinq points a été effectué selon (i) les résultats de l'échantillonnage global, et (ii) leur relativement fréquente utilisation le jour et (iii) leur non utilisation la nuit. Avant l'installation des dispositifs POU, les cinq points sélectionnés ont été suivis pour leurs concentrations en plomb et fer dissous et particulaires (1er jet le matin). Lors de l'installation des dispositifs POU, deux vannes d'échantillonnage ont été placées directement en amont et en aval de chaque dispositif afin d'étudier spécifiquement leur efficacité. Aussi, un compteur d'eau était mis en place en amont de l'installation afin de suivre la consommation d'eau au robinet étudié. Le robinet séparé vendu avec chaque dispositif POU a été installé seulement pour les éviers de cuisine(tte) étudiés. Des échantillonnages de plomb total et dissous effectués aux vannes amont et aval de chaque POU, après une stagnation d'une nuit et une stagnation de 30 minutes, permettaient d'étudier l'efficacité d'enlèvement du plomb dissous et particulaire par les dispositifs POU ainsi que l'effet de la stagnation sur cette efficacité. Pour la moitié des échantillons, le fer était aussi mesuré (indicateur de colmatage potentiel). Par ailleurs, le robinet de consommation était échantillonné afin de vérifier si les matériaux post-dispositifs contribuaient à augmenter les concentrations de plomb au robinet.

Aussi, des échantillonnages ont été effectués pour vérifier si la qualité microbiologique de l'eau distribuée dans le grand bâtiment était affectée par la présence de dispositifs POU. Les échantillonnages étaient effectués au 1er jet le matin, et après 5 minutes d'écoulement. Les mesures effectuées étaient les suivantes : bactéries hétérotrophes aérobies (BHA), bactéries viables et totales (épifluorescence Baclight^{TM}), carbone organique total (COT), nitrites, nitrates, chlore résiduel, pH, et température. Des échantillons ont été collectés aux vannes amont et aval de chaque dispositif POU pour étudier spécifiquement chaque filtre POU. Des échantillons ont aussi été prélevés aux robinets de consommation avec filtre POU en amont, et à des robinets de consommation sans filtre POU en amont. La comparaison des mesures obtenues dans les échantillons aux vannes avant et après filtre POU, et dans les échantillons aux robinets avec et sans POU en amont a permis de conclure sur l'effet du POU sur la qualité microbiologique de l'eau. Aussi, après 1 an d'installation, un filtre POU a été démonté et analysé pour estimer la colonisation du matériau (BHA, épifluorescence Baclight^{TM}, microscopie électronique à balayage—MEB), et la structure/conception du matériau (MEB, rayons-X).

Le suivi durant 1 an de l'enlèvement du plomb, du nombre de litres filtrés (compteur d'eau), des niveaux de fer dans l'eau (indice de colmatage), du débit (indice de colmatage), et de la qualité microbiologique de l'eau, sous les conditions « réelles » des habitudes de consommation des grands bâtiments, a permis de conclure sur la viabilité économique des dispositifs POU installés dans un grand bâtiment pour remédier aux concentrations de plomb dans l'eau.

2.3.6 Objectif 6

« Estimer la fraction bioaccessible des particules de plomb à l'être humain » (hypothèse 11)

Une revue critique de la littérature a d'abord été effectuée sur les essais de biodisponibilité et de bioaccessibilité effectués sur les particules de plomb (sols, poussières, peintures) afin de (i) mettre en lumière le test de bioaccessibilité le plus simple calibré et validé pour l'exposition du jeune enfant, et (ii) dégager les paramètres des tests *in vitro* ayant un impact sur l'estimé de la bioaccessibilité. Une fois le test sélectionné (RBALP de Drexler & Brattin 2007), ce dernier a été adapté pour les particules de l'eau potable. Essentiellement, le test a été miniaturisé et adapté de façon à estimer la fraction bioaccessible et la fraction totale du plomb dans les particules à partir d'un échantillon inconnu, indivisible, et de petite taille. Les paramètres identifiés dans la revue de littérature comme affectant les résultats de bioaccessibilité ont cependant été maintenus par rapport au test initial, afin de conserver la relation *in vivo-in vitro* du protocole original valide. Des validations du test *in vitro* adapté ont été effectuées par le recouvrement du plomb total de solutions de plomb dissous, et de particules de plomb (IV). Le test *in vitro* a ensuite été appliqué à: (i) des particules générées au laboratoire, représentatives des particules de l'eau potable (dépôts d'ESP de Montréal, plomb (IV), laiton, bronze, soudures); et (ii) 65 échantillons de particules collectées derrières les aérateurs de robinet d'un grand bâtiment (bâtiment échantillonné pour les objectifs 2 & 5), de résidences avec ESP (échantillonnage 2007 des objectifs 1 & 3, échantillonnage d'une étude parallèle au projet de Ph.D.), et de résidences sans ESP (échantillonnage d'une étude parallèle au projet de Ph.D.). Les échantillons ont été analysés pour l'ensemble des métaux (balayage ICP-MS). Des analyses statistiques ont été effectuées à l'aide du logiciel *Statistica Soft* dans l'objectif d'étudier l'impact de la taille des particules, du type de particules (phases dominantes), et du type de logement (avec/sans ESP, grand bâtiment, résidence) sur l'estimation de la bioaccessibilité. Ces résultats ont permis d'obtenir (i) des valeurs de bioaccessibilité pour des particules typiques de l'eau potable (particules laboratoire), (ii) une distribution des teneurs en métaux de particules collectées derrière l'aérateur de logements variés, (ii) une distribution de la bioaccessibilité de particules collectées derrière l'aérateur de logements variés (particules « réelles »).

2.3.7 Objectif 7

« Estimer la contribution du plomb particulaire à l'exposition au plomb du consommateur » (hypothèse 12)

La concentration médiane de plomb dissous et la concentration médiane de plomb particulaire obtenues lors des échantillonnages effectués (i) dans les résidences avec ESP (objectifs 1 & 3) et (ii) dans un grand bâtiment (objectif 2) ont été utilisées afin d'établir des scénarios d'exposition plausibles d'un enfant buvant l'eau du robinet, évoluant dans une résidence avec ESP, et allant à l'école ou la garderie. Les concentrations de plomb dissous ont d'abord été entrées seules dans la source « eau du robinet » du modèle IEUBK d'estimation des concentrations de plomb dans le sang des enfants de 7 ans et moins. Les données d'exposition aux sols, poussières, et aliments entrées dans le modèle étaient fixes, et correspondaient aux résultats des plus récentes études canadiennes disponibles (sinon, valeurs par défaut IEUBK). Ensuite, pour chaque scénario établi, les concentrations de plomb particulaire ont été ajoutées aux concentrations de plomb dissous, selon leur distribution réelle obtenue par les échantillonnages (0, 10e percentile, 25e percentile, médiane, 75e percentile, 95e percentile). Des simulations ont aussi été effectuées pour vérifier l'impact de la fréquence de consommation d'eau dans un grand bâtiment sur la concentration de plomb dans le sang de l'enfant, en tenant compte ou non du plomb particulaire. Les concentrations de plomb particulaire étaient préalablement ajustées en considérant leur biodisponibilité, déduite de la valeur médiane de bioaccessibilité obtenue dans l'objectif 6, et de la relation *in vitro-in vivo* de Drexler & Brattin (2007). Les résultats de plomb dans le sang obtenus pour chaque scénario, et pour chaque fréquence d'occurrence de plomb particulaire, ont permis de déterminer un seuil d'occurrence à partir duquel le plomb particulaire contribue de façon significative à l'exposition.

La méthodologie spécifique pour confirmer ou infirmer chacune des hypothèses posées précédemment est décrite dans la Table 2-1 ci dessous.

Table 2-1. Approche expérimentale adoptée pour valider (ou invalider) chacune des hypothèses.

Hypothèses	Échelle expérimentale	Approche expérimentale	Produit de réponse
1. Le Pb particulaire survient de façon sporadique dans les résidences et son importance varie d'un site à un autre	Réelle/Réseau	- Mesure du Pb particulaire dans l'eau du robinet, et du Pb dans et dans les particules retenues par l'aérateur	- Distribution des concentrations de Pb particulaire en fonction de l'écoulement - Pourcentage d'aérateurs avec des particules de Pb
2. Au 1^{er} jet, le Pb particulaire survient de façon constante dans les grands bâtiments, et à concentration très élevée	Réelle/Réseau	- Mesure du Pb particulaire dans l'eau du robinet, au 1^{er} jet, à 45 points de consommation	- Distribution des concentrations de Pb particulaire dans l'eau du robinet des grands bâtiments, au 1^{er} jet
3. Le Pb particulaire dans l'eau du robinet des résidences avec ESP à Montréal est principalement le résultat (i) de la corrosion de la tuyauterie interne et (ii) de l'adsorption du Pb dissous sur des particules et/ou dépôts de fer dans la tuyauterie interne et l'ESP	Réelle/Réseau, Numérique, & Laboratoire	- Analyse multi-métaux (i) des concentrations de Pb particulaire dans l'eau, (ii) de la composition des particules de Pb retenues par l'aérateur, et (iii) des oxydes de Pb en surface interne des ESP	- Correspondance du Pb particulaire avec les autres métaux - Correspondance et cohérence entre les analyses statistiques, l'analyse des particules, et l'analyse des oxydes de Pb
4. Le Pb particulaire dans les grands bâtiments est principalement issu de la corrosion des éléments en laiton et des soudures de la tuyauterie interne contenant du Pb	Réelle/Réseau & Numérique	- Analyse multi-métaux des concentrations de Pb particulaire dans l'eau, en fonction des robinets échantillonnés, et inspection visuelle de la plomberie du bâtiment	- Correspondance du Pb particulaire avec les autres métaux
5. Les perturbations hydrauliques influencent l'occurrence du Pb particulaire	Réelle/Réseau	- Mesure du Pb particulaire dans l'eau avec un échantillonnage reproduisant des perturbations hydrauliques	- Variation de l'occurrence du Pb particulaire entre l'échantillonnage « aléatoire», et l'échantillonnage avec perturbations hydrauliques
6. Le protocole d'échantillonnage et la stagnation influencent directement la probabilité de passage de Pb particulaire	Réelle/Réseau	- Mesure du Pb particulaire dans l'eau selon un échantillonnage « aléatoire », un échantillonnage après 30 min de stagnation, un échantillonnage après 8h de stagnation. - Mesure du Pb particulaire selon l'écoulement (1L, 2L, 5min)	- Distribution du Pb particulaire selon les protocoles et selon l'écoulement

Table 2-1. Approche expérimentale adoptée pour valider (ou invalider) chacune des hypothèses (suite).

Hypothèses	Échelle expérimentale	Approche expérimentale	Produit de réponse
7. Les concentrations de Pb dissous à l'effluent des dispositifs de filtration POU certifiés NSF/ANSI 53 pour le Pb après 2007 pourraient dépasser les prévisions de NSF pour certaines conditions d'eau du robinet	Pilote & Réelle/Réseau	• Mesure de l'efficacité d'enlèvement du Pb dissous de différents types de POU avec une eau naturelle • Étude de l'impact des fréquences d'utilisation sur l'enlèvement du Pb dissous	• Validation des performances des POUs pour l'enlèvement du Pb dissous dans le cas d'une eau naturelle
8. L'efficacité des dispositifs de filtration POU à enlever le Pb particulaire dépend du type de filtre, et notamment de la présence d'une barrière physique	Pilote & Réel	• Mesure de l'abattement du Pb particulaire à échelle pilote, et échelle réelle • Vérification de l'influence de la stagnation (8 h, 30 min) sur les concentrations de Pb à l'effluent des filtres et sur et la qualité d'eau (pH, Cl_2, turbidité, COT, BHA, épifluorescence Baclight^{TM}, nitrites et nitrates)	• Validation des performances des POUs pour l'enlèvement du Pb particulaire et du Pb total • Vérification de l'effet de la stagnation sur la qualité d'eau • Recommandations d'utilisation
9. La présence de particules de Pb et de fer détermine la durée de vie du filtre	Pilote & Réel	• Mesure du débit des dispositifs POU en fonction du temps et de la charge de particules de Pb et de Fe	• Estimation de la durée de vie des dispositifs POU en fonction de la charge en particules de Pb et Fe
10. À long terme, l'installation de dispositifs POU sous évier (bloc de charbon actif) dans un grand bâtiment entraine la colonisation des filtres du POU, et une percée des filtres	Réel	• Mesure de BHA, épifluorescence Baclight^{TM}, COT, nitrites et nitrates, Cl_2, température, pH en affluent et effluent des filtres POU, et aux robinets avec/sans POU en amont • Mesure de la colonisation du filtre POU après 1 an d'exploitation	• Recommandations d'utilisation et de la fréquence de changement de filtre
11. La bioaccessibilité telle qu'estimée par un test *in vitro* dépend de la composition et de la taille des particules	Laboratoire	• Simulation de digestions *in vitro* sur (i) des particules de Pb générées au laboratoire et typiques des sources principales en eau potable, et (ii) des particules de Pb collectées *in situ*	• Valeurs de bioaccessibilité de 5 types de particules représentatives de l'eau potable • Distribution de la bioaccessibilité de diverses particules *in situ* (N=65) • Valeurs de bioaccessibilité en fonction des phases dominantes dans les particules *in situ*
12. Le Pb particulaire, lorsqu'il survient, peut contribuer de façon plus importante que le Pb dissous dans l'exposition du consommateur selon sa composition	Numérique	• Simulation de scénarios dans le modèles IEUBK avec pour l'eau potable (i) le Pb dissous seul, et (ii) le Pb dissous et le Pb particulaire à différentes concentrations selon sa distribution réelle mesurée, en ajustant le Pb particulaire avec sa biodisponibilité médiane	• Distribution des concentrations de Pb dans le sang, et du pourcentage d'enfants ayant une concentration de Pb dans le sang > 5 ou 10 µg/dL selon (i) la distribution du Pb particulaire dans l'eau du robinet, et (ii) la fréquence de consommation d'eau dans un grand bâtiment

CHAPITRE 3 PUBLICATION #2: SOURCE AND OCCURRENCE OF PARTICULATE LEAD IN TAP WATER

Ce chapitre présente la première partie de la démarche expérimentale de la présente thèse, menée dans l'objectif ultime d'estimer la contribution du plomb particulaire dans l'eau potable à l'exposition. Ces travaux ont permis d'identifier, pour 45 résidences avec ESP à Montréal, les diverses sources de plomb particulaire et les échantillonnages adéquats pour sa détection. Aussi, cette étude a permis d'obtenir une première distribution des concentrations de plomb particulaire dans l'eau potable pour divers types d'échantillons. Ceci était novateur puisque les échantillonnages traditionnels évaluent le plomb total sans en différencier la fraction dissoute et la fraction particulaire, empêchant ainsi de souligner ou non l'importance de la contribution du plomb particulaire dans la concentration totale de plomb. Cette étude a été publiée dans le journal *Water Research*.

SOURCE AND OCCURRENCE OF PARTICULATE LEAD IN TAP WATER

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ABSTRACT

Lead samples were collected at the tap from homes with lead service lines (LSLs) in a full-scale utility using both random daytime (RDT) and particulate stimulation sampling (PSS) protocols. Analysis of the results revealed two sources and occurrences of particulate lead. A first source is due to corrosion of lead-bearing elements in the premise plumbing (PP) and occurs mostly at low to moderate concentrations < 3 µg/L, with some sporadic higher concentrations (4-12 µg/L). These spikes were consistently observed and considerably increased using PSS, showing that current sampling protocols may miss a significant portion of particulate lead. The second source results from the adsorption of dissolved lead onto iron deposits in LSL/PP, and is continuously present at low to moderate concentrations. Statistical analyses were validated by physical analyses of: (i) lead scales from LSLs; and (ii) lead particles from tap aerators.

Keywords: particulate lead, tap water, source, occurrence, sampling protocol.

3.1 Introduction

Lead in drinking water is a major public health concern. It can create irreversible intellectual impairment in infants and young children, even at blood lead levels (BLLs) below 10 µg/dL (Gump *et al.* 2008, Jusko *et al.* 2008, Lanphear *et al.* 2000). Assessing the impact of lead from tap water on BLLs can be difficult due to multiple exposure pathways, temporal variability of waterborne lead, and inter-individual and day-to-day variability in exposure studies (Lanphear *et al.* 2002, Schock 1990). Nonetheless, the rise in lead levels in tap water significantly increased the number of children with elevated BLLs in some studies (Edwards *et al.* 2009, Lanphear *et al.* 1998a). Lanphear *et al.* (2002) also reported that water lead levels above 5 µg/L after 1min of flushing significantly increase the BLLs of children aged 6-24 months. Finally, recent cases of lead intoxication in children have been related to solder particle ingestion (Triantafyllidou *et al.* 2007).

Numerous utilities still serve homes with lead service lines (LSLs), which can contribute to 50-75% of the total lead mass measured at the tap during profile sampling and for which a replacement time frame is a commitment issue (Sandvig *et al.* 2008). Lead in tap water is also increased by leaching from lead-bearing materials in premise plumbing (PP), such as lead-tin solders containing up to 50% lead (Subramanian *et al.* 1995), and brass materials containing up to 8% lead (Dudi *et al.* 2005).

Current standards and guidelines on lead in drinking water are mostly in the 0.010-0.015 mg/L range; however, sampling protocols differ widely among countries, in terms of variations in stagnation time, sampling volume, and number of samples collected, which influence the recovery of lead (Schock 1990). The US action level is set at 0.015 mg/L in at least 90% of the samples collected from high-risk locations. The sampling protocol consists of taking a 1L sample of cold tap water after at least 6 hours of stagnation, and aims to assess the contribution of both LSL and PP. However this approach can underestimate peak concentrations occurring in subsequent liters, depending on PP volume (Giani *et al.* 2005). In Europe, random daytime (RDT) sampling (1st liter taken during office hours, without fixed stagnation) and sampling after 30 minutes of stagnation (30MS) (1st and 2nd liter) were identified as the best approaches for estimating exposure and detecting homes with elevated lead concentrations in tap water. RDT is cost-effective and convenient for consumers, when compared to 30MS sampling; however, it is difficult to reproduce (van den Hoven & Slaats 2006). Health Canada recently issued a corrosion control guidance document (Health Canada 2009) proposing both the American and the European approaches: 1st option performed following the LCR protocol, and 2nd option with 30MS sampling. Compliance in Ontario (Canada) is based on meeting a 0.010 mg/L action level in the highest of the 2 subsequent liters taken after 30MS in at least 90% of homes sampled (Government of Ontario 2002).

Particulate lead is usually defined as the fraction of lead retained by a 0.45 μm filter. Current sampling protocols and methods of analysis may underestimate total lead because of particulate lead. The prescribed EPA 200.8 method recommends digesting samples directly in the bottle with nitric acid at pH<2 for at least 16h at 4°C, and then, if turbidity exceeds 1NTU, performing a rigorous heated-digestion on an aliquot of the sample. However, this method may not entirely dissolve lead solders and lead (IV) oxide particles, which may underestimate particulate lead (Triantafyllidou *et al.* 2007). Also, if samples are not acidified immediately, low soluble tetravalent lead particles can adhere to the sampling bottles, resulting in a turbidity reading below 1NTU, and consequently to total lead underestimation (Edwards & Dudi 2004). Furthermore, particulate lead losses can occur when the aliquot is extracted for the heated-digestion, and when the hot-digested aliquot is centrifuged prior to analysis. Finally, suspended colloidal lead in the centrifuged vial may not be quantified by the usual analytical methods (Triantafyllidou *et al.* 2007).

Sampling approaches prescribed by regulation do not include the filtration of samples, therefore, could estimate total lead. However, the prescribed conditions are designed to prevent the adsorption of dissolved lead onto the bottle and its precipitation, not the optimal solubilization of particulate lead. Dissolved lead increases with stagnation time up to an equilibrium level (reached within 8 to 24 hours) and its source can be estimated by measuring concentration profiles, PP and LSL length. In contrast, particulate lead occurs sporadically and is mainly caused by physical factors, making its contribution difficult to predict with any certainty (Schock 1990, Triantafyllidou & Edwards 2009). The transport of particles that detach from LSL/PP to the tap depends on flow rate, hydraulic regimen, and particle characteristics (Slaats *et al.* 2003). Particulate lead occurrence increases with increasing flow rate; though, protocols specify sampling at a low flow rate, lower than typical faucet usage (~7-12 L/min) (Triantafyllidou & Edwards 2009).

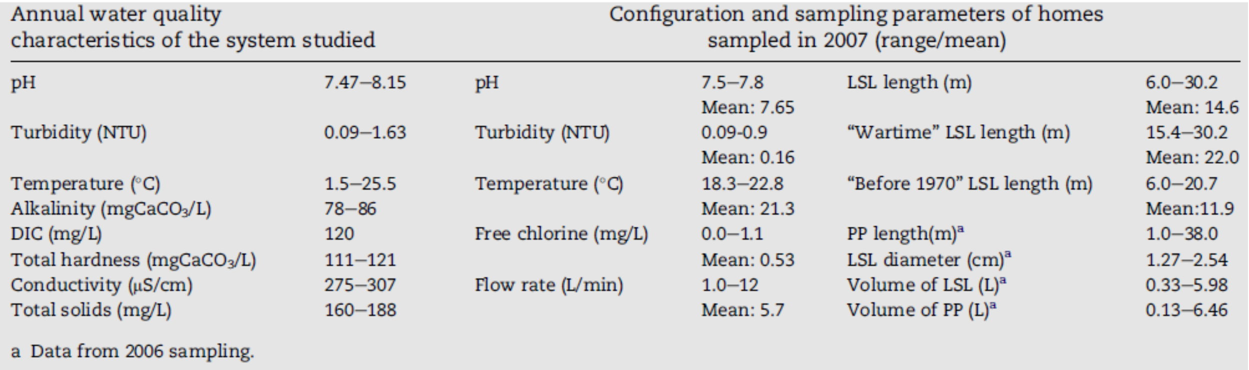
Thus, existing sampling protocols and analytical methods were not developed to detect particulate lead, and so may underestimate total lead exposure. The main objectives of this study were: (i) to characterize the source and occurrence of particulate lead in homes supplied with water by LSLs; and (ii) to evaluate a protocol method to detect particulate lead specifically.

3.2 Materials and methods

3.2.1 Distribution system: general characteristics and water quality

The 45 homes sampled were selected on the basis that they represent all the communities served by the distribution system and the presence of lead in at least a part of the service line (6 partial LSLs). Two types of homes were sampled: “wartime”, built during WWII, with 2 to 3 times longer LSLs than those built “before 1970”, as observed during sampling. Inside piping in all homes was mainly made of copper, except in 3 cases (either galvanized-iron (n=1) or a mix of lead and copper pipes with the majority being copper (n=2)). Table 3-1 summarizes the water quality parameters of the system studied, and information on the configuration and sampling parameters of the homes studied.

Table 3-1. Water quality characteristics of the system studied and information on the configuration and sampling parameters of the homes sampled.



Annual water quality characteristics of the system studied		Configuration and sampling parameters of homes sampled in 2007 (range/mean)			
pH	7.47–8.15	pH	7.5–7.8	LSL length (m)	6.0–30.2
			Mean: 7.65		Mean: 14.6
Turbidity (NTU)	0.09–1.63	Turbidity (NTU)	0.09-0.9	"Wartime" LSL length (m)	15.4–30.2
			Mean: 0.16		Mean: 22.0
Temperature (°C)	1.5–25.5	Temperature (°C)	18.3–22.8	"Before 1970" LSL length (m)	6.0–20.7
Alkalinity (mg$CaCO_3$/L)	78–86		Mean: 21.3		Mean:11.9
DIC (mg/L)	120	Free chlorine (mg/L)	0.0–1.1	PP length(m)[a]	1.0–38.0
Total hardness (mg$CaCO_3$/L)	111–121		Mean: 0.53	LSL diameter (cm)[a]	1.27–2.54
Conductivity (μS/cm)	275–307	Flow rate (L/min)	1.0–12	Volume of LSL (L)[a]	0.33–5.98
Total solids (mg/L)	160–188		Mean: 5.7	Volume of PP (L)[a]	0.13–6.46

a Data from 2006 sampling.

3.2.2 General protocol

30MS sampling is defined as sampling after 30 minutes of stagnation preceded by 5min of flushing, and the collection of the 1st liter, 2nd liter, one liter after 1min of flushing, and one liter after 5min of flushing. RDT sampling is defined as the immediate sampling after entering the home without fixed stagnation or any flushing (1st liter: 1L; 2nd liter: 2L; liter after 5min: 5min). Samples were collected in cold water (kitchen tap) at "normal" flow rate (typically ≤ 8L/min).

Between May and July 2006, 109 "wartime" and "before 1970" homes were sampled using a 30MS protocol, this protocol was not the goal of the study (RDT-2007), but will serve as a basis for comparison in the discussion. Between July and September 2007, 45 homes were sampled using RDT. Among these homes, 23 were sampled in 2006 and others were in the same range of age and configuration (Table 3-1). Between the 2nd liter and the liter after 5min, physicochemical parameters potentially affecting lead leaching were measured: flow rate, temperature (mercury thermometer, SM 2550-B), pH (Oakton PhTestr 10, SM4500-H^+ B), free, total and combined chlorine (Hach Pocket Colorimeter II, 4500-CL G). Dissolved metals were obtained by on-site filtration immediately after the 1L sample collection using the following procedure: each bottle was mixed, then a 50mL aliquot was taken using a 60mL disposable syringe (BD Luer Lok^{TM}), and filtered in a 50mL vial using a 0.45 μm porosity PVDF membrane cartridge (Millipore Millex HV, Durapore, 33mm). In addition, experiments with standard multi-metal solutions at two different concentrations (5 and 10 μg/L) showed that these filters do not absorb significant levels of the metal tested (difference <-0.05 μg Pb/L, <-0.06 μg/L for other metals) but could release dissolved zinc (up to 13 μg/L). Samples were transported to the laboratory and acidified preferentially the day of the sampling or within 24h (precisions 3.2.4.). LSLs were sampled (scraping), and LSL lengths were measured on-site. After water sampling, particles retained by the tap aerator were collected and excess water was removed to avoid particle oxidation.

3.2.3 Particulate stimulation sampling (PSS)

In 2007, additional PSS was added after RDT sampling in 9 homes, in order to stimulate particulate lead detachment. Following the collection of the last RDT sample (5min), a 1L bottle (S1) was placed under the closed tap, and then the tap was opened and closed 5 times at maximal flow rate. The bottle was then completely filled at normal flow rate. The 2nd liter, S2, was collected immediately after, S1, at normal flow rate. The 3rd liter, S3, was collected using the same procedure as described for S1.

3.2.4 Laboratory analysis

Lead, copper, iron, zinc, cadmium, and antimony were measured for dissolved and particulate forms using an ICP-MS (Agilent 7500a). In 2007, tin was also analyzed (ICP-MS Agilent 7500cs). The particulate metal fraction was determined by deducting total metal from dissolved metal. ICP-MS detection limits (µg/L) were: Cd = 0.03; Cu = 0.09; Fe = 5; Pb = 0.02; Sb = 0.03; Sn = 0.1; Zn = 0.4. For low concentrations of total zinc, the release of soluble zinc from the filter led to some negative values of particulate zinc. Because of the very high positive values of particulate zinc when present (up to 632 µg/L), negative values were kept and assigned a zero value. Polypropylene sampling bottles and vials were washed using the following procedure (System Plus Ltd, method C): phosphate-free detergent wash, nitric acid rinse, ultra-pure water rinse, and drying in a lead-free environment. Samples were acidified at pH < 2 by adding 0.5% HNO_3 (optima grade, Fisher Scientific), and stored for at least 16h at 4°C before analysis. If turbidity in the 1st liter exceeded 1NTU, samples underwent a heated-acid digestion: 0.5% HCl + 0.5% HNO_3, 2h, 95°C (ICP-MS manufacturer's recommendations). Preliminary testing investigating the impact of heated-acid digestion was performed on 76 samples in 2006 (19 samples of each type: 1L, 2L, 1min, 5min). Every sample underwent digestion, using the EPA 200.8 protocol (16h, 4°C, pH < 2), and was analyzed for lead, followed by further digestion at 85°C for 48h (pH < 2) and was analyzed for lead again. Lead concentrations measured by the two digestion methods did not vary significantly and t-tests comparing the two values were not significant ($p > 1$). Thus, the EPA 200.8 digestion standard was used for all samples.

On-site and laboratory measurements were analyzed using Statistica statistics software (version 8.0, StatSoft). Significant factors were stated for $p < 0.05$.

3.2.5 LSL deposits and particles analysis

Six LSLs were collected between July and October 2007 from three districts well spaced out on the distribution system (two per district). Pipes were handled horizontally after plugging each opening to keep the humidity in the pipes. Interior scale was studied on multiple spots using micro-RAMAN inVia spectroscopy and ION TOF-SIMS IV. The RAMAN analysis conditions were: wavelength 785 nm, power 5-10%, magnifying power 20X or 50X, acquisition time ~50 s, and spectrum width 200-2000 cm^{-1}. These conditions were adjusted using preliminary testing because the power of the laser beam and the time of exposure could denature the sample. Selected standards (Alfa-Aesar) included: Pb (99% (metal basis)), PbO (99%), PbO_2 (Lead IV oxide, 97%), $PbCO_3$ ($PbCO_3$ ACS grade), $(PbCO_3)_2Pb(OH)_2$ (basic, 99% (metal basis)), and Pb_3O_4 (Lead (II, IV) oxide). TOF-SIMS analysis conditions were: $^{69}Ga^+$ ion source, 25KeV energy, static mode, 3.7 pA current, acquisition surface 20*20 µm, and mass resolution on $^{29}Si \geq 8000$. Charge neutralization was achieved with an electron flood gun.

Ten typical particles taken from tap aerators (2007) were analyzed by TOF-SIMS. Analysis conditions were the same as for LSL analysis, except for current (2.7 pA), mass resolution on ^{29}Si (≥ 9000), and acquisition zone (40*40 µm and 9*9 µm).

3.3 Results

3.3.1 Sampling

Figure 3-1 (a, b) presents dissolved and particulate lead concentrations versus sample type for 2007 RDT sampling. All sample types were considered on a 90th percentile basis, dissolved lead and particulate lead representing 94-96% and 4-6% of total lead respectively. Dissolved lead levels were comparable for the 1st and 2nd liters (90th percentile: 43 and 44 µg/L respectively), and drop twofold and significantly after 5min of flushing ($p < 0.05$, Kruskal-Wallis test). The particulate lead profile differed because concentrations decreased after the 1st liter (2L-RDT) but not significantly so with the liter collected after 5min flushing ($p < 0.01$, Kruskal-Wallis test).

Figure 3-2 illustrates the cumulative distribution of particulate lead for each type of RDT sample. The 90th percentile in the 1st liter was half the WHO guideline value of 0.010 mg/L, and maximum values were higher than this value. For the 2nd liter and the liter after 5min, the 90th percentile and median decreased rapidly. However, some higher values (2L: 4.5-7.4 µg/L; 5min: 2.5-3.5 µg/L) remaining after flushing the 1st liter showed that partial rinsing was insufficient to avoid the sporadic occurrence of particulate lead.

Table 3-2 presents metal levels measured in tap water for RDT and PSS samplings (2007). Cadmium and antimony were not considered further in the analysis, either because their levels were constant (Sb) or below detection limits (Cd).

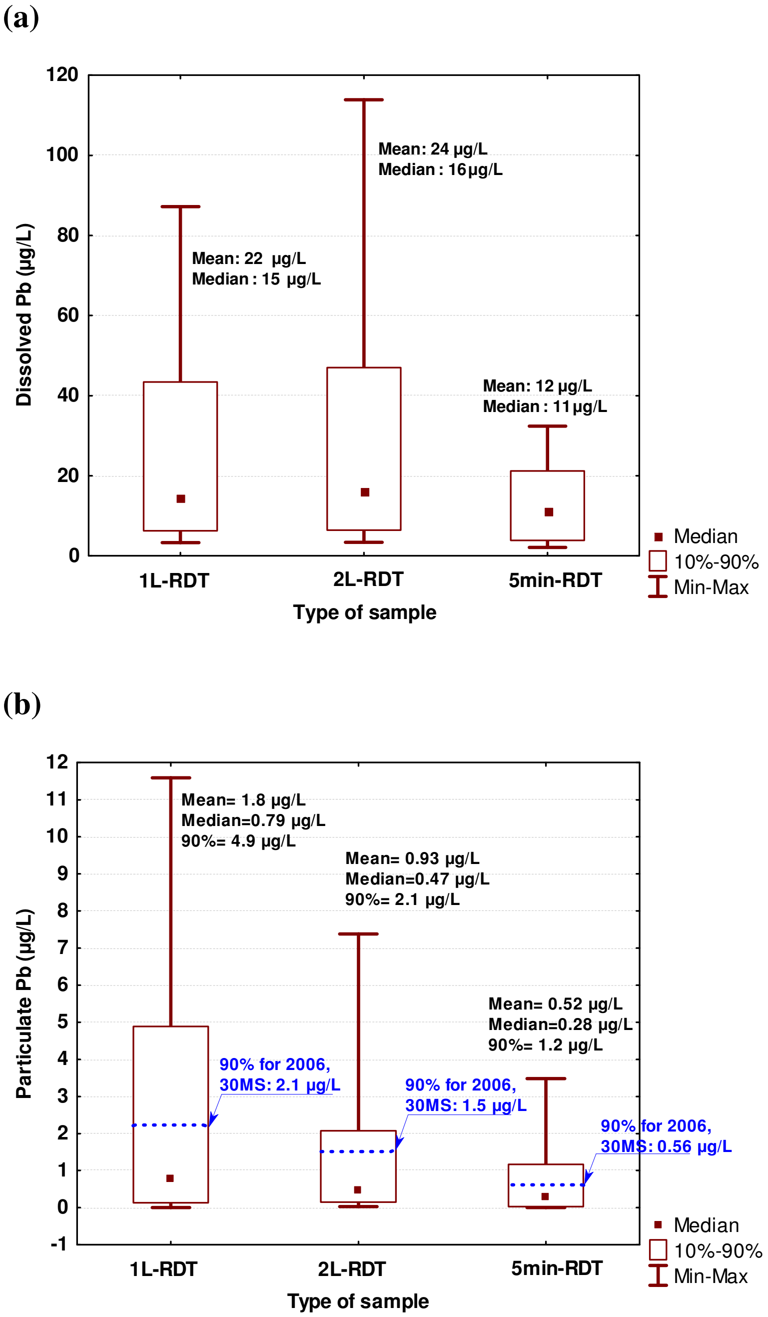


Figure 3-1. Dissolved Pb (a) and particulate Pb (b) concentrations versus type of sample in 2007 RDT sampling. N=45 homes for each box.

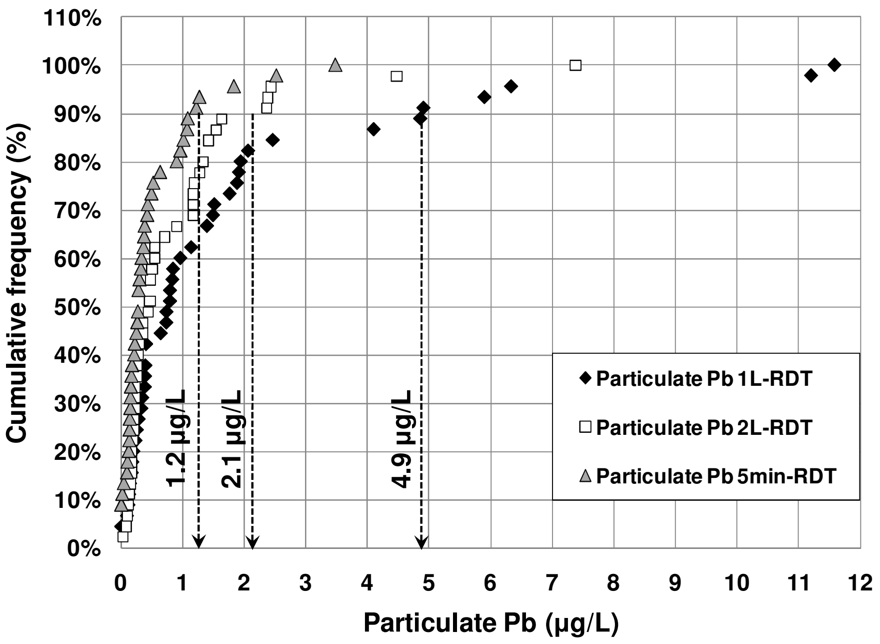


Figure 3-2. Cumulative frequency (%) vs. particulate Pb concentration (µg/L) for each type of sample, RDT sampling 2007.

Table 3-2. Concentrations of metals analyzed at the tap (µg/L), 2007.

Metals	RDT sampling 2007: 1 L, 2 L, 5 min						PSS sampling 2007: S1, S2, S3					
	N	Average	Median	Min	Max	90th	N	Average	Median	Min	Max	90th
Pb_{diss}	135	19	14	2.1	114	43	27	23	16	3.8	69	56
Pb_{part}	135	1.1	0.39	BDL	12	2.4	27	8.2	2.9	0.36	50	27
Cu_{diss}	135	176	96	9.4	780	440	27	143	141	33	332	227
Cu_{part}	135	3.4	1.2	BDL	47	9.0	27	16	9.5	BDL	175	25
Fe_{diss}	135	22	16	BDL	130	58	27	23	17	BDL	71	69
Fe_{part}	135	10	3.2	BDL	247	17	27	9.1	4.8	BDL	48	36
Zn_{diss}	135	22	11	3.5	220	37	27	14	13	6.3	41	22
Zn_{part}	135	1.1	–	BDL	119	–	27	58	6.0	BDL	632	327
Sn_{diss}	135	–	–	BDL	0.23	–	27	0.01	–	BDL	0.18	–
Sn_{part}	135	0.03	BDL	BDL	1.3	0.02	27	2.5	0.44	BDL	33	4.5
Cd_{diss}	135	–	–	BDL	0.03	–	27	–	–	BDL	–	–
Cd_{part}	135	–	–	BDL	BDL	–	27	–	–	BDL	0.04	–
Sb_{diss}	135	0.16	0.16	0.13	0.23	0.18	27	0.15	0.15	0.13	0.17	0.17
Sb_{part}	135	–	–	BDL	0.06	0.02	27	–	–	BDL	0.02	0.02

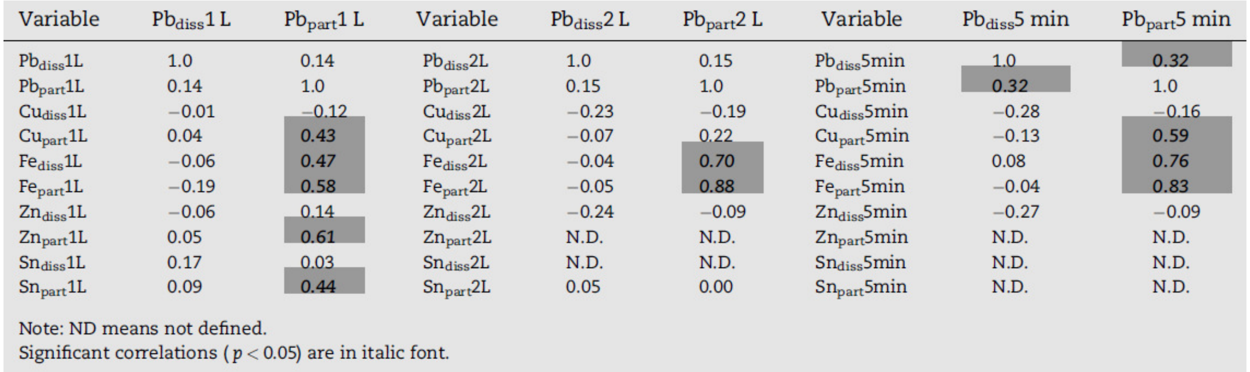
Note: BDL means below detection limit.

3.3.2 Statistical analyses

Table 3-3 introduces correlations between dissolved lead, particulate lead, and other metals. For RDT samples, dissolved lead in the 1st and 2nd liters was not correlated with any of the other metals. On the contrary, particulate lead in the 1st liter was clearly correlated with metals from PP and iron ($p < 0.01$): particulate zinc ($R = 0.61$), dissolved iron ($R = 0.47$), particulate iron (R=

0.58), particulate tin (R = 0.44), and particulate copper (R = 0.43). Most of the time, high particulate zinc values and particulate lead spikes occurred simultaneously. In the 2nd liter and the liter after 5min, particulate lead correlation with particulate iron (R = 0.83-0.88, $p<0.01$) and dissolved iron increased (R = 0.70-0.76, $p<0.01$), while correlations with PP metals nearly disappeared (particulate Cu only). Also, after 5min of flushing, dissolved lead and particulate lead were significantly correlated (R = 0.32, $p<0.04$), suggesting a common source.

Table 3-3. Correlations (R) between metals analyzed at the tap, 2007 RDT sampling. Significant correlations ($p<0.05$) are in bold and italic font.



Variable	Pb_{diss}1 L	Pb_{part}1 L	Variable	Pb_{diss}2 L	Pb_{part}2 L	Variable	Pb_{diss}5 min	Pb_{part}5 min
Pb_{diss}1L	1.0	0.14	Pb_{diss}2L	1.0	0.15	Pb_{diss}5min	1.0	0.32
Pb_{part}1L	0.14	1.0	Pb_{part}2L	0.15	1.0	Pb_{part}5min	0.32	1.0
Cu_{diss}1L	−0.01	−0.12	Cu_{diss}2L	−0.23	−0.19	Cu_{diss}5min	−0.28	−0.16
Cu_{part}1L	0.04	0.43	Cu_{part}2L	−0.07	0.22	Cu_{part}5min	−0.13	0.59
Fe_{diss}1L	−0.06	0.47	Fe_{diss}2L	−0.04	0.70	Fe_{diss}5min	0.08	0.76
Fe_{part}1L	−0.19	0.58	Fe_{part}2L	−0.05	0.88	Fe_{part}5min	−0.04	0.83
Zn_{diss}1L	−0.06	0.14	Zn_{diss}2L	−0.24	−0.09	Zn_{diss}5min	−0.27	−0.09
Zn_{part}1L	0.05	0.61	Zn_{part}2L	N.D.	N.D.	Zn_{part}5min	N.D.	N.D.
Sn_{diss}1L	0.17	0.03	Sn_{diss}2L	N.D.	N.D.	Sn_{diss}5min	N.D.	N.D.
Sn_{part}1L	0.09	0.44	Sn_{part}2L	0.05	0.00	Sn_{part}5min	N.D.	N.D.

Note: ND means not defined.
Significant correlations ($p < 0.05$) are in italic font.

Multiple regression analyses were performed on particulate lead versus metals in water, and sampling parameters potentially affecting particulate lead release (flow rate, pH, chlorine, turbidity, temperature, LSL length). Data were separated by sample type for a two-step analysis (1L, 2L, 5min): (i) particulate lead versus other metals, (ii) particulate lead versus sampling parameters. Temperature, pH and chlorine did not significantly affect lead release. The length of LSL, even if well distributed (6.0-30 m) and correlated with dissolved lead (Cartier *et al.* 2008), was not correlated with particulate lead. Moreover, t-tests showed that particulate lead was not significantly different in homes "before 1970" and "wartime" ($p > 0.2$ for 1L-RDT, 2L-RDT, 5min-RDT) even if the latter had significantly longer LSLs. Factors significantly associated with particulate lead in the 1st liter include turbidity ($R^2_{adjusted} = 0.48$, $p < 0.01$), particulate iron, particulate zinc, and dissolved lead ($R^2_{adjusted} = 0.64$, $p < 0.01$). Particulate tin was almost significant ($p = 0.07$), and all metals increased with particulate lead (Figure 3-3 (a)). The data also revealed that particulate lead spikes and particulate spikes of zinc, tin, iron, or copper, or a combination of these metals, occurred simultaneously.

Flow rate was significantly correlated with particulate lead in the 2nd liter ($R^2_{adjusted}$=0.12, $p < 0.02$), as did particulate and dissolved iron, total zinc, and dissolved lead ($R^2_{adjusted} = 0.86$, $p < 0.01$) (Figure 3-3 (b)). After 5min of flushing (Figure 3-3 (c)), the same factors were significant for particulate lead in the 2nd liter, except for total zinc.

Linear regressions showed a stronger relationship between particulate lead and particulate iron than with dissolved iron (Table 3-4). The lower level of association for dissolved iron is readily understandable considering the low solubility that would exhibit iron oxyhydroxides at pH 7.5-7.8. For the 2L-RDT and the 5min-RDT analysis on particulate lead versus particulate iron, few values (n = 2 for 2L-RDT, n = 3 for 5min-RDT) were outside the prediction interval (0.95). Interestingly, four of these outliers corresponded to the highest flow rates measured (8.7 and 12 L/min).

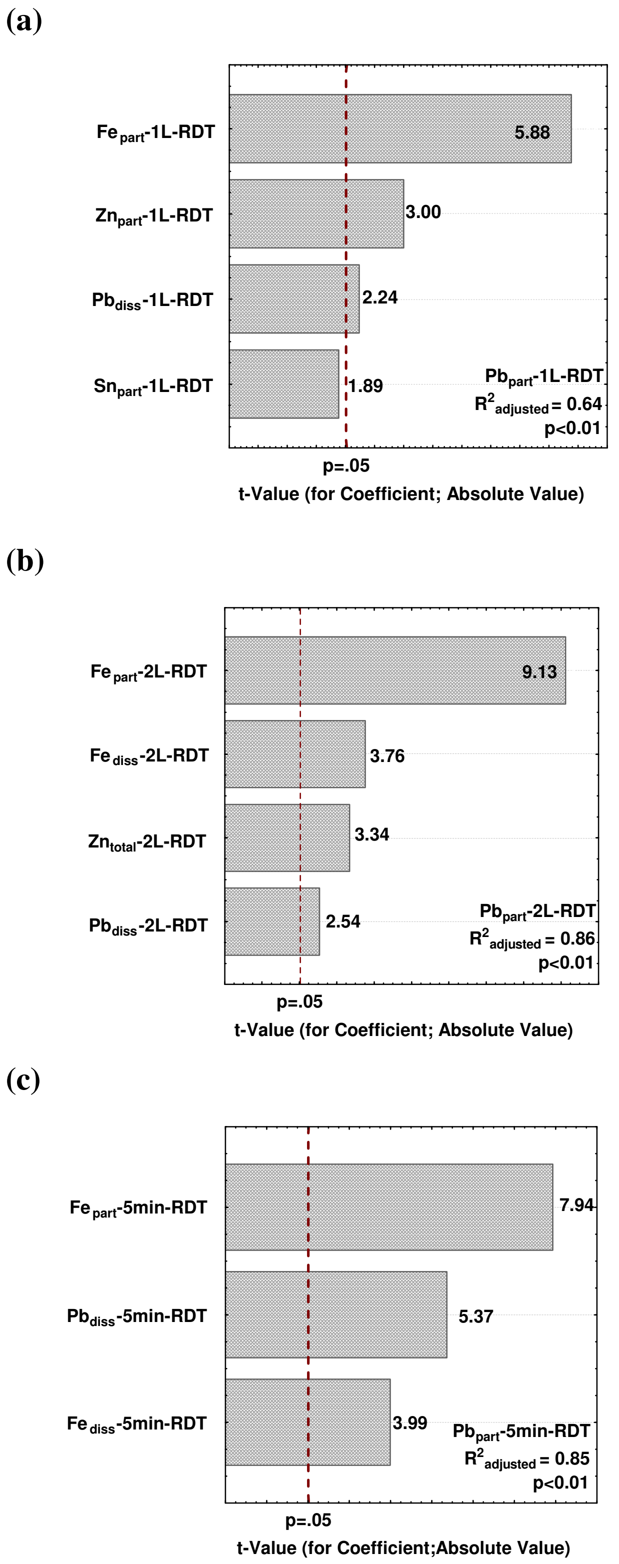
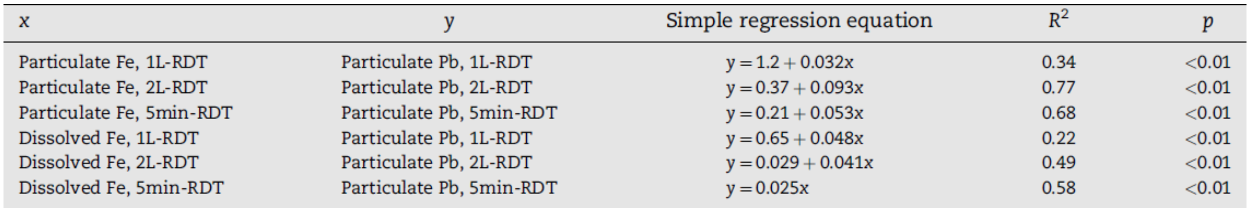


Figure 3-3. Multiple regressions on particulate Pb 2007 results, 45 homes, inputs = metals measured at the tap. (a) Particulate Pb 1L-RDT, (b) Particulate Pb 2L-RDT, (c) Particulate Pb 5min-RDT.

Table 3-4. Linear regression analysis of particulate lead versus dissolved iron, and versus particulate iron, for each sample type.



x	y	Simple regression equation	R^2	p
Particulate Fe, 1L-RDT	Particulate Pb, 1L-RDT	$y = 1.2 + 0.032x$	0.34	<0.01
Particulate Fe, 2L-RDT	Particulate Pb, 2L-RDT	$y = 0.37 + 0.093x$	0.77	<0.01
Particulate Fe, 5min-RDT	Particulate Pb, 5min-RDT	$y = 0.21 + 0.053x$	0.68	<0.01
Dissolved Fe, 1L-RDT	Particulate Pb, 1L-RDT	$y = 0.65 + 0.048x$	0.22	<0.01
Dissolved Fe, 2L-RDT	Particulate Pb, 2L-RDT	$y = 0.029 + 0.041x$	0.49	<0.01
Dissolved Fe, 5min-RDT	Particulate Pb, 5min-RDT	$y = 0.025x$	0.58	<0.01

3.3.3 Particulate stimulation sampling (PSS)

Figure 3-4 presents RDT and PSS results on particulate lead for the 9 homes. RDT results show that flushing decreased particulate lead when sampling flow rates were used (2.1-8.7 L/min). Tap stimulation (S1) dramatically increased the levels of particulate lead, far more than the levels found in 1L-RDT (90th percentile +16 µg/L). Levels decreased somewhat in sample S2 without any added faucet operation. Finally, the 2nd tap stimulation (S3) created another remarkable increase in particulate lead, with the 90th percentile value more than double that observed for S2 (29 µg/L versus 12 µg/L).The 90th percentile value for S3 was also higher than that measured for S1, however, the maximum values were lower (33 µg/L versus 50 µg/L). Considering the limited number of homes investigated with PSS, the establishment of significant correlations with other metals was not possible. Particulate metals from PP also increased with PSS (Table 3-2, Figure 3-5 (b)): the 90th percentile values measured for S1, S2, and S3 taken together are: 4.5 µg Sn_{part} /L, 25 µg Cu_{part} /L, and 327 µg Zn_{part}/L. Particulate iron also increased, but not as much. Also, although no stagnation was provided prior PSS, notable increases in the concentrations of dissolved lead (mean +8.2 µg/L), zinc (mean +6.7 µg/L), and copper (mean +88 µg/L) are measured for PSS when compared to the values after 5min RDT flushing (Figure 3-5 (a)). Iron concentrations remained stable (the mean increased by only 1 µg/L).

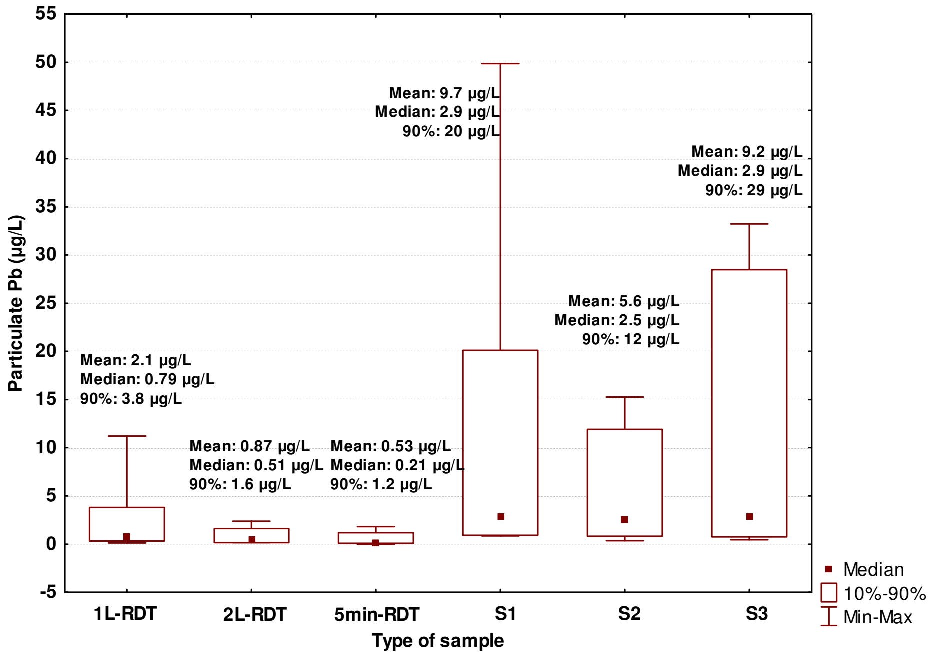
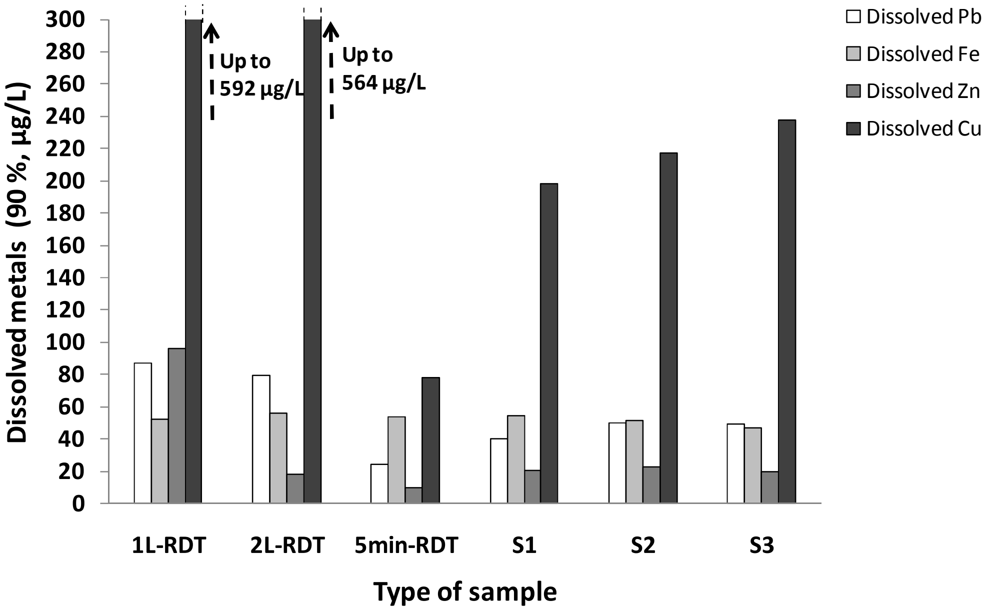


Figure 3-4. Particulate Pb concentrations at the tap for 9 homes sampled with RDT+PSS sampling. N=9 homes for each box.

(a)



(b)

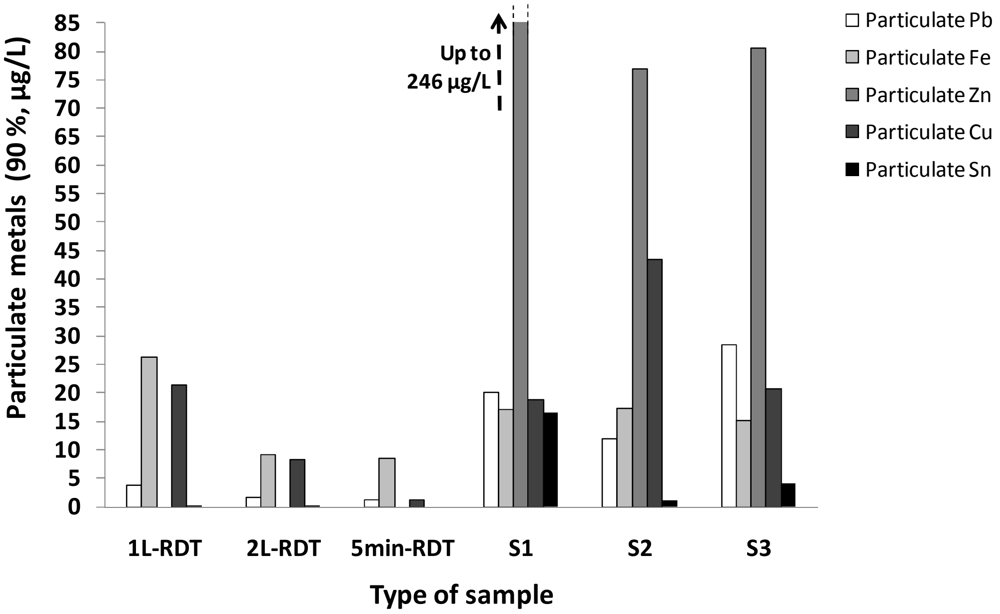


Figure 3-5. 90th percentile of: (a) dissolved and (b) particulate metal concentrations measured at the tap for 9 homes sampled with RDT+PSS sampling. N=9 for each bar.

3.3.4 Scale deposits and particles

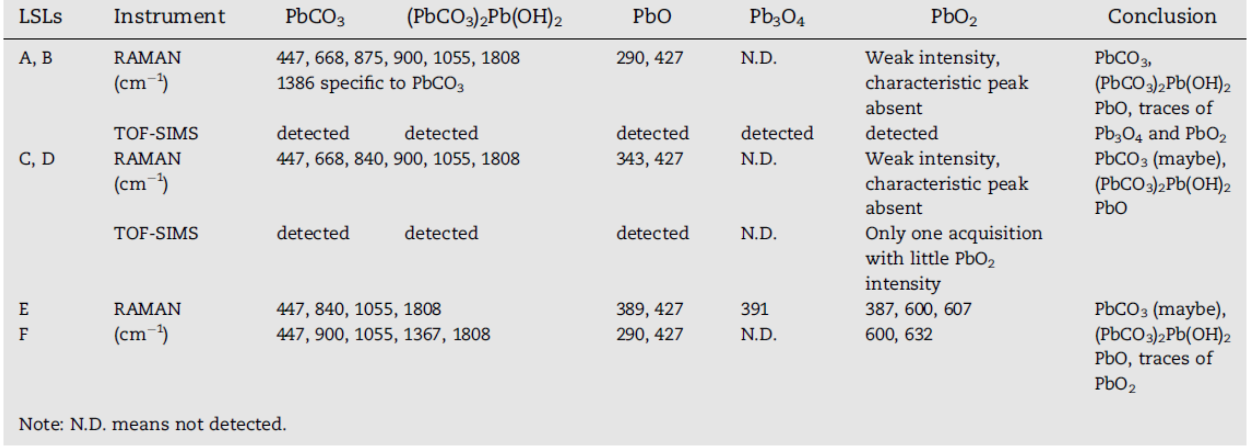
Micro-RAMAN spectroscopy carried out on 2 LSLs from the 1st district (A, B) showed 6 characteristic peaks of both cerussite ($PbCO_3$) and hydrocerussite ($(PbCO_3)_2Pb(OH)_2$), including the main peak at 1055 cm^{-1}. A peak at 1386 cm^{-1} specific to cerussite was noted, as well as, two peaks characteristic of massicot/litharge (PbO), including the main peak (290 cm^{-1}). Thus, these two species were both present. Some peaks specific to tetravalent lead (PbO_2) were possibly present, but, because of their weak intensity, along with noise interference, and the absence of a main peak (510 cm^{-1}), this could not be confirmed. Also, due to the limitations in intensity and exposure time explained previously, there was little possibility of spectrum improvement. Regarding the 2nd district (C, D), PbO peaks (343 cm^{-1}, 427 cm^{-1}) were noted on most spectra acquired, but the main peak at 290 cm^{-1} was not measured. Cerussite and hydrocerussite peaks detected were superposed, impeding differentiation of both species. Some peaks of weak intensity could be attributed to PbO_2, with strong reservation, because of noise interference and absence of the main characteristic peak. In the last municipality, the two LSLs (E, F) came from adjacent homes, but, surprisingly, one presented whitish scale (E) and the other reddish scale (F) (Figure 3-6 (a)). However, even if being careful with the transport of the pipes, a part of the scale could have dislodged from one of the pipe during the extraction, explaining the difference of color. Whitish scale analysis revealed the presence of cerussite and/or hydrocerussite (peaks superposed) and PbO. Three peaks for PbO_2 were recurrent and marked: 387, 600, and 607 cm^{-1}. Thus, even in the absence of the main PbO_2 characteristic peak, the presence of PbO_2 was suggested. Finally, one peak for Pb_3O_4 (391 cm^{-1}) was visible and recurrent, but the absence of any other peaks made confirmation impossible. The analysis of the reddish deposits (F) revealed the presence of cerussite and/or hydrocerussite (peaks superposed), PbO, and PbO_2 (600 and 632 cm^{-1}).

As some doubts persisted with respect to the RAMAN results, complementary analyses using TOF-SIMS were carried out. A signal was difficult to obtain because of the high isolating power of lead oxides. The spectrum width analyzed could not include the hydrocerussite high atomic mass, and so hydrocerussite was reconstructed using oxide fragments. Species detected on A, B were: Pb, PbOH, PbO, $PbCO_3$, $(PbO)_2(H)_2$, Pb_3O_4, and PbO_2. Thus, the presence of hydrocerussite ($PbCO_3$+PbOH), PbO, Pb_3O_4, and PbO_2 was inferred. Cerussite was potentially present, but not validated. Low RAMAN detection of Pb_3O_4 and PbO_2 suggested that these species were present in trace amounts. On C and D, Pb, PbO, $PbCO_3$, and PbOH were detected. Only one spectrum presented PbO_2 at weak intensity. Thus, the presence of hydrocerussite, PbO and traces of PbO_2 were inferred.

To conclude, LSL deposits analysis revealed lead (II) oxides (carbonates, massicot/litharge) as predominant and traces of PbO_2 (Table 3-5).

Ten typical particles collected in the faucet aerator were analyzed with TOF-SIMS. Analysis did not reveal the presence of lead-based oxides (as found in LSL scale) on the particles, but many metals representative of PP (Sn, Cu, Zn) and iron were detected (Figure 3-6 (b, c, d)).

Table 3-5. Summary of oxides detected on LSLs with micro-RAMAN spectroscopy and TOF-SIMS.



LSLs	Instrument	$PbCO_3$	$(PbCO_3)_2Pb(OH)_2$	PbO	Pb_3O_4	PbO_2	Conclusion
A, B	RAMAN (cm^{-1})	447, 668, 875, 900, 1055, 1808 1386 specific to $PbCO_3$		290, 427	N.D.	Weak intensity, characteristic peak absent	$PbCO_3$, $(PbCO_3)_2Pb(OH)_2$ PbO, traces of Pb_3O_4 and PbO_2
	TOF-SIMS	detected	detected	detected	detected	detected	
C, D	RAMAN (cm^{-1})	447, 668, 840, 900, 1055, 1808		343, 427	N.D.	Weak intensity, characteristic peak absent	$PbCO_3$ (maybe), $(PbCO_3)_2Pb(OH)_2$ PbO
	TOF-SIMS	detected	detected	detected	N.D.	Only one acquisition with little PbO_2 intensity	
E	RAMAN (cm^{-1})	447, 840, 1055, 1808		389, 427	391	387, 600, 607	$PbCO_3$ (maybe), $(PbCO_3)_2Pb(OH)_2$ PbO, traces of PbO_2
F		447, 900, 1055, 1367, 1808		290, 427	N.D.	600, 632	

Note: N.D. means not detected.

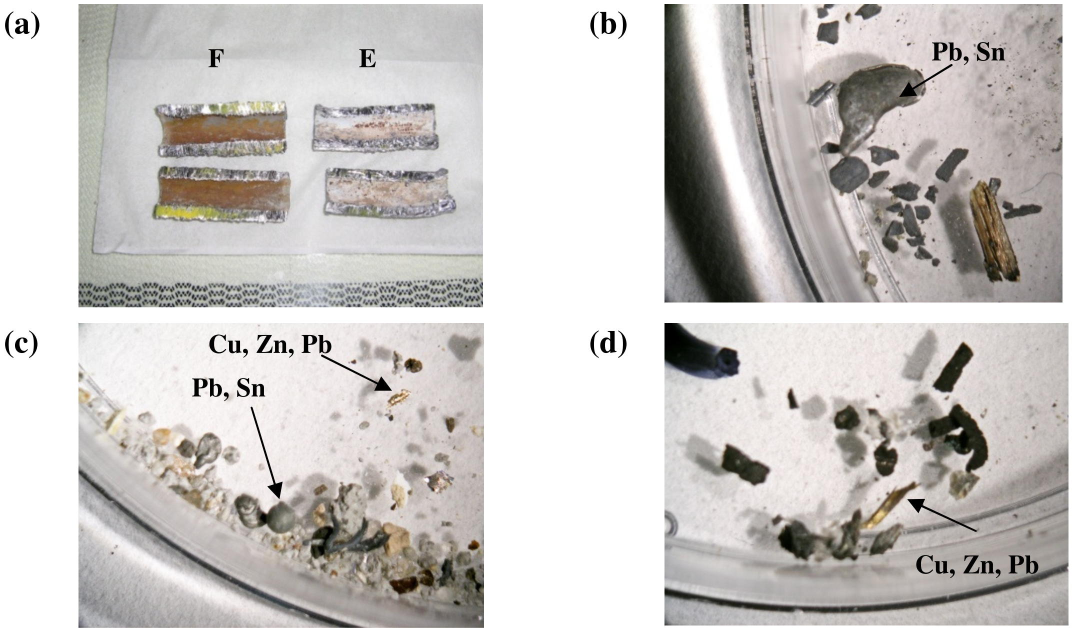


Figure 3-6. (a) Portions of lead service line E (right) and F (left); (b), (c), (d) examples of particles collected in the aerator tap after 2007 sampling.

3.4 Discussion

3.4.1 Relationship with metals from PP

Particulate lead, as opposed to dissolved lead, decreased significantly after flushing the 1st liter, and was not correlated with LSL length. Particulate lead in the 1st liter was correlated with particulate metals from PP and peaks concentrations occurred simultaneously with particulate tin and/or particulate copper/zinc spikes. Establishing the source of the leaded particles is a challenge given that multiple sources of particulate lead can contribute sporadically and will produce different multi-metal signatures. Particulate lead at the tap has been weakly correlated with copper and zinc in samples collected using a wide range of sampling procedures and various PP materials (HDR Engineering Inc. 2009). Schock *et al.* (2008) investigated the composition of lead-based deposits in lead pipes and found moderate levels of copper, tin and zinc. Based on the simultaneous occurrence of particulate lead and other metals in the present study, a significant portion of the particulate lead measured in the 1st liter originates from the corrosion of lead-bearing materials in PP, namely by brass, solders and erosion of lead containing deposits. According to Sandvig *et al.* (2008), PP including faucets can contribute (21-38%) to the total lead mass measured at the tap from sequential samples collected at homes with LSLs. The simultaneous occurrence of zinc and lead is an indication of significant contribution of brass. In some homes, the sporadic spikes of particulate lead occurring at the same time as Zn/Cu spikes could be due to brass dezincification, or to the presence of high leaded-brass (Grosvenor *et al.* 2005). Indeed, brass material from PP may contain lead up to the regulated level of 8% (LCR), or possibly more in older components (Lytle & Schock 1996). Stagnation of water in faucets creates conditions favorable to corrosion that can lead to the detachment of particles of lead, zinc, or copper, or a combination of these elements (Dudi *et al.* 2005). In other homes, milder brass corrosion or the presence of low leaded-brass could explain the lower levels of particulate lead, zinc, and copper. However, identifying the leading mechanism causing particulate lead release from brass is difficult in light of its sporadic release and the fact that different types of particles can be present at the same time. The simultaneous occurrence of lead and tin particles is a clear marker of solders. Tin occurred mainly in the particulate form, with concentrations measured either BDL (0.1µg/L) or at relatively high levels (max RDT: 1.3 µg/L, max PSS: 33 µg/L) simultaneous to the highest concentrations of particulate lead. Pb-Sn solders joining copper piping have been shown to corrode and release particulate lead (Subramanian *et al.* 1995, Triantafyllidou *et al.* 2007). Particulate lead from solders was not as frequent as particulate lead from brass, and then only in the 1st liter.

Particulate lead decreased rapidly after the 1st liter sampled, and only weak correlations with PP metals remained. Consequently, for the system studied, flushing the 1st liter can eliminate most of the particulate lead originating from PP corrosion.

3.4.2 Relationship with particulate iron

Particulate lead in RDT samples was correlated with particulate iron. This correlation was even stronger in the 2L-RDT and 5min-RDT samples, and was accompanied by a correlation between particulate lead and dissolved lead. Strong correlations between lead particles/colloids at the tap and iron were also found in other studies (HDR Engineering Inc. 2009, Hulsmann 1990). The observed correlation is most likely the result of the sorption of dissolved lead from the LSL onto iron particles/deposits in LSL and PP, generating lead-loaded iron colloids and particles. Indeed, Schock *et al.* (2008) found major quantities of iron among other contaminants in lead-based internal deposits on lead pipes. Also, Jar-Tests conducted by HDR Engineering Inc. (2009)

demonstrated that a lead-rich iron corrosion scale with variable lead levels (up to 7-8% Pb) could form via sorption mechanisms. Other studies show that iron scales in the distribution system can absorb and accumulate continuously low concentrations of many contaminants, such as arsenic. These scales can then release metals at hazardous levels in tap water following, for example, a change at the treatment plant (Lytle *et al.* 2004, Reiber & Dostal 2000, Schock 2005). Because of its affinity to iron scales, lead could accumulate in scales after years of exposure to low-lead levels in water, as observed for other metals such as arsenic in lead pipe scales (Schock *et al.* 2008). The presence and impact of leaded iron scales should be considered if any treatment modifications leading up to water quality changes are scheduled because such changes could destabilize the scale or mobilize lead into solution, as observed for arsenic (Copeland *et al.* 2007, Schock 2005). Except when the PP is galvanized-iron, iron originates from the corrosion of grey iron and unlined cast iron mains pipes in the distribution network, and subsequent deposits of that iron in the LSL and PP (AWWARF & DVGW-TZW 1996). In the present study, PP was investigated and galvanized-iron pipes were present in only one home. It is however possible that some inaccessible sections of the PP contained old galvanized-iron pipes potentially harboring lead-rich deposits. Also, iron scales could be present in copper piping due to the deposit of iron particles from the distribution main. These scales could generate sporadic release of lead-iron particles in RDT samples. The greater correlation with iron observed in the 2L-RDT and 5min-RDT samples is explained by the flushing of lead particles originating from the PP into the 1st liter. Actually, the correlation between particulate lead and dissolved lead increases with the presence of particulate iron as the PP and LSL are flushed. Iron-lead particles are considered to be the main contributor of particulate lead in the 2L-RDT and the 5min-RDT samples.

3.4.3 Relationship with LSL

Analysis of the interior scale of 6 LSLs revealed the presence of a thin scale (~ 40 µm) of lead (II) oxides, with only traces of tetravalent lead. The water quality in the distribution system studied is probably in the lead (II) formation zone of the Eh-pH diagram, but not far from the lead (IV) formation zone. Free chlorine residuals varied from 0.1 to 1.1 mg Cl_2/L, the higher range at some locations/periods possibly leading to the formation of patches of PbO_2 on lead (II) scale. Lead (IV) oxide has been mostly observed when high chlorine residuals were applied (Lytle & Schock 2005, Schock *et al.* 2001, Schock *et al.* 2005). Our observations are consistent with the low to moderate chlorine residuals applied historically by this utility. Tetravalent lead is very stable, and detached particles exhibit low solubility (Edwards & Dudi 2004). In contrast, lead carbonates are more soluble, but can still generate colloidal and particulate lead (McNeill & Edwards 2004).

In this study, particulate lead was: (i) not correlated with LSL length, (ii) not significantly lower in “before 1970” homes, as compared to “wartime” homes with LSLs 2 to 3 times longer. This lack of correlation suggests that the detachment of lead oxides from LSLs is not a major source of particulate lead in this system. It is possible however that colloidal lead (0.1-0.45 μm) was present in our samples due to lead (II) scale detachment from LSLas observed by McNeill & Edwards (2004). Smaller colloids are included in the measurement of dissolved lead because of the 0.45 μm cutoff used.

The TOF-SIMS analysis of the particles collected in the aerators revealed the presence of elemental lead, but no traces of either lead (II) or lead (IV) oxides. However, several metals typically found in PP (Cu, Sn, Zn) and iron were detected simultaneously with lead. These findings support the conclusions of the statistical analyses, i.e. that particulate lead is the result of iron-lead scale detachment from PP/LSL and the local corrosion of lead-bearing materials in PP.

3.4.4 Relationship with dissolved iron¸

The statistical analyses suggest that particulate lead increases with dissolved iron, particularly in the 2L-RDT and 5min-RDT samples. Iron release is related to the corrosion rate and constitutes a general indicator of the corrosivity of water (AWWARF & DVGW-TZW 1996). Broo *et al.* (2001) proposed a model relating the corrosion rate in distribution systems to dissolved iron concentrations. If higher dissolved iron concentrations are indicative of greater water corrosivity, then greater corrosion of lead-bearing materials in PP and more frequent particulate lead detachment are expected. The impact of dissolved iron on particulate lead is more evident in the 2L-RDT and 5min-RDT samples, because most of the particulate metals originating from PP are flushed in the 1st liter.

3.4.5 Influence of sampling parameters

Turbidity was found to be a significant factor determining particulate lead concentrations in the 1L-RDT samples. As particulate lead in these samples was correlated with concentrations of particulate metals from PP and iron, all these metals may contribute directly to turbidity.

The incidence of particulate lead at the tap can originate from the removal of existing deposits by scouring or sloughing during water flow (Schock 1990). In this study, the passage of particulate lead (including lead-iron particles) was influenced in 2L-RDT, and 5min-RDT samples by flow rate. Indeed, particulate lead spikes of 2.5, 2.4 µg/L (2L-RDT) and 4.5, 1.8 µg/L (5min-RDT) were recorded at the two highest flow rates (12 and 8.7 L/min, i.e. ~1.1-1.6 m/s for a ½ in diameter pipe). However, a higher particulate lead release event was recorded at a lower flow rate of 7.5 L/min, i.e. ~1 m/s for a ½ in diameter pipe (2L-RDT: 7.4 µg/L, 5min-RDT: 3.5 µg/L). This is consistent with results for small iron oxide particles (45-250 µm) suspended at a velocity > 0.13 m/s, and fully suspended at a velocity > 0.22 m/s. Large particles grouped into "islands" required a 0.4 m/s velocity (Slaats *et al.* 2003). The impact of flow rate on the presence of a particle at the tap depends on particle characteristics, piping configuration defining the flow regime, and the distance of detached particles to the tap. It is therefore expected that the relationship between flow rate and particulate lead at the tap would be site-specific and more difficult to establish in many homes with particles of varying size and density. Moreover, recent pipe loop testing has shown that lead particles released from galvanized-iron pipes were sensitive to modifications in flow regime, but that the level of sensitivity was really variable between the pipes tested (HDR Engineering Inc. 2009).

In the present study, flow rates ranged from 3.0-7.5 L/min (76% of homes sampled), very low and very high flow rates being less common (1-2.5 L/min: 11%; > 7.5 L/min: 13%). Systematic tap sampling at increasing flow rates may provide a clearer picture. In a high-risk home in Washington D.C., increasing the flow rate from 1 to 22 L/min resulted in a dramatic increase in particulate lead (Triantafyllidou & Edwards 2009). However, similar tests conducted in our system at flow rates between 4.6 and 15 L/min showed no increase in dissolved and particulate lead at the tap (Nour *et al.* 2007). Finally, flow rate did not influence particulate lead in the 1st liter, because particulate lead in these samples reflects an accumulation of particulate metals during stagnation.

3.4.6 Influence of the sampling protocol

The importance of the sampling protocol can be evaluated by comparing particulate lead in the 1st liter collected with the 2007-RDT and 2006-30MS sampling protocols. Overall, a greater proportion (30%) of samples collected with RDT sampling (45 homes) contained more than 1 µg/L of particulate lead when compared to 11% for the 30MS sampling (109 homes). Moreover, the 90th percentile value for the 1L-RDT samples exceeded the value for the 1L-30MS samples by 57% (Figure 3-1 (b)). When using the 30MS sampling, the 5min flushing prior to stagnation is often performed at maximum flow rate, which is likely to eliminate most particles. The subsequent stagnation of 30min may not be long enough to regenerate particles. The RDT sampling appears to be a better approach of estimating particulate lead at the tap, because: (i) particles are not systematically flushed out of the system shortly before sampling; (ii) prior usage patterns vary and may have been favorable to particle flow transport to the tap. Moreover, RDT sampling is considered to provide a better range of typical consumer exposure, provided that sufficient samples are taken (Cardew 2009, van den Hoven & Slaats 2006). However, it is possible that RDT sampling would reveal less particulate lead than the reference LCR sampling (≥ 6h stagnation). A possible approach to obtaining pertinent information on both particulate and dissolved lead would be to sample the 1st liter upon arrival for particulate lead analysis (RDT), and then to flush and analyze the 30MS samples for dissolved lead.

After 5min of flushing, hydraulic disturbances caused by PSS increased the passage of particulate metals, including particulate lead, into the tap water to levels higher than those found in the 1L-RDT samples. Indeed, the particulate lead to total lead ratio increased from 2% in the RDT samples to 33% (90th percentile) in the PSS samples. Increases were higher for particulate metals from PP corrosion (Cu, Zn, Sn). These observations support the conclusions that particulate lead originates partly from brass element/solder corrosion and increases with flow rate. The repeated activation (5 times) of the faucet at high flow rate created hydraulic disturbances and friction that have been shown to impact particulate lead release (van den Hoven & Slaats 2006). Also, hydraulic disturbances such as water hammer were shown to increase particulate lead detachment from lead-iron scales in galvanized-iron piping (HDR Engineering Inc. 2009). Water quality determines corrosivity, and combined with hydraulic and physical conditions, determines the formation and release of particulate lead. However, the detection of particles is a function of particle transport to the tap and passage through the aerator (if present). The conditions of particle accumulation and transport vary depending on the flow rate and prior flushing. In this system, the selection of the sampling protocol would directly influence compliance, as particulate lead may contribute to more than action levels when using PSS.

Additionally, PSS increased dissolved metals, especially lead, copper, and zinc. PSS samples were collected immediately after the 5min-RDT sample without any stagnation providing time for the dissolution of lead. It is consequently inferred that the higher dissolved lead content with the PSS (versus RDT) is due to colloidal lead detachment, either from LSL or PP. This raises issues regarding the definition of dissolved lead as the fraction < 0.45 µm. Dissolved lead measured in this way may include a significant colloidal fraction that behaves as particulate lead and is sensitive to flow rate and hydraulic disturbances.

3.5 Conclusion

This study provides an analysis of the source, occurrence, and parameters affecting the release of particulate lead. Particulate lead, for the system investigated, was attributed to PP corrosion and leaded-iron scale detachment. Results show that current sampling protocols are not adapted for the detection of particulate lead and may underestimate a part of the consumer exposure at the tap. Consumers' usage patterns and high flow rates can stimulate the detachment of lead particles and should be considered in sampling protocols. The strong relationship observed between iron and particulate lead raises concerns about the potential accumulation and subsequent release from scales in PP, especially in the presence of galvanized-iron. Also, the traditional definition of particulate lead might be revised to account for the colloidal detachment observed during PSS. Finally, efforts to measure particulate lead are justified by the sporadic but sometimes extreme concentrations that can occur and their potential impact on health.

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CHAPITRE 4 PUBLICATION #3: LEAD REMOVAL FROM TAP WATER USING POU DEVICES

Ce chapitre présente la seconde étape de la démarche expérimentale, à savoir l'étude d'une méthode d'enlèvement du plomb particulaire de l'eau potable, les dispositifs de filtration au point d'utilisation (POU). En effet, la mise en place de tels dispositifs peut se faire immédiatement à un coût relativement faible. De tels dispositifs ont par ailleurs été recommandés par plusieurs organismes de Santé Publique pour les résidences avec ESP et les grands bâtiments (écoles, garderies). Plusieurs types de dispositifs de filtration domestique ont été évalués pour l'enlèvement du plomb dissous et du plomb particulaire respectivement, mais aussi pour leur effet sur la qualité de l'eau. Cette étude a été publiée dans le journal *Journal of American Water Works Association*.

LEAD REMOVAL FROM TAP WATER USING POU DEVICES

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ABSTRACT

Common point-of-use (POU) devices that met NSF/ANSI-53 certification standards for lead removal before July 16, 2007, were evaluated for the reduction of lead and other trace metals in drinking water. Systematic testing and evaluation of various POUs focused on particulate and dissolved lead removal efficacy, under conditions different from those addressed in the NSF-53 testing protocol (particle type, water tested, lead levels). Tap-mounted and under-the-sink POUs showed, globally, adequate removal performance, although the NSF threshold value for lead of 10 µg/L was occasionally slightly exceeded. Pour-through POUs failed to remove particulate lead, decreased pH, did not reduce turbidity, and were the least efficient for chlorine removal. Copper removal was effective for any concentration tested, and silver was detected in effluent water. Nitrification did not increase the dissolution of lead particles trapped in the filters.

4.1 Introduction

Point-of-use (POU) devices can contribute to the improvement of water quality and safety (USEPA 2006d). A recent nationwide survey on the household domestic water use patterns in the United States conducted by the US Environmental Protection Agency (USEPA) showed an increase in the use of water treatment devices between 1995 and 2002 (37% of the household respondents in 2002; USEPA 2003). POU devices are commercially available in various forms, including under-the-sink, tap-mounted, and pour-through devices. The most widely used POU devices are the pour-through (pitcher-style filter) and tap-mounted treatment systems. Under-the-sink devices are more expensive and not easy to install (USEPA 2006e). POU devices are widely used to remove taste and odor compounds from drinking water. They can also be used as a temporary remediation strategy to reduce lead (Pb) exposure during the establishment of adequate corrosion control treatment, or during lead service line replacement. In Canada, some provincial public health authorities have issued advisory notices recommending that pregnant women and children under six years old use bottled water or NSF/ANSI-certified filtration devices if a lead service line is in use or when total or partial replacement does not result in lead levels below the Canadian drinking water threshold of 10 µg/L total lead (MPHD 2006, WDGPH 2007). Tens of thousands of filters were also distributed to residents of Washington, D.C., to mitigate hazards from high lead levels in drinking water (Edwards *et al.* 2009).

Of the NSF/ANSI certifications, standards NSF-53 and NSF-42 specifically concern POU and point-of-entry (POE) devices. NSF-53 covers POU/POE devices that reduce health-related contaminants, including lead in drinking water, whereas NSF-42 covers POU/POE devices that remove aesthetic and nonhealth-related contaminants (chlorine, particulate matter, turbidity). In 2007, in response to reports of particulate lead occurrence in tap water (McNeill & Edwards 2004, NSF International 2006, Triantafyllidou *et al.* 2007), changes were made to the lead-testing protocol for the NSF-53 certification of water treatment units. The protocol before 2007 focused on soluble lead and did not test for the removal of lead particles. In the NSF-53 protocol, two types of water are used to verify manufacturers' claims. The first is low-alkalinity aggressive water (pH 6.5, alkalinity 10–30 mg/L calcium carbonate) and the second is more mineralized water (pH 8.5, alkalinity 100 mg/L calcium carbonate). It is expected that the demonstration of claims using these two waters will be sufficient to predict performance in a wide range of natural waters, as indicated by the capacity not to exceed 10 µg/L lead in the filtered water (up to 120% of the service lifetime of the POU filter). The revised protocol (2007) includes both particulate lead of different sizes and soluble lead in water at pH 8.5, specifically: 0.15 mg/L of total lead, consisting of at least 20%, 0.1–1.2-µm particulate lead, and 30±10% total particulate lead. The lead colloids/particles used are generated from an insoluble lead stock solution made from soluble lead nitrate [$Pb(NO_3)_2$; NSF International Standard & American National Standard 2007]. Most of the pour-through POU devices failed to meet the standards set out in the revised protocol and subsequently lost their certification for total lead removal (Renner 2007).

POU devices are based on various treatment technologies, including ion exchange resin (IX), granular activated carbon (GAC), solid block activated carbon (SBAC), reverse osmosis (RO), and distillation (Molloy *et al.* 2008, USEPA 2006d). Some of these technologies applied to POU filters have been identified by the USEPA as small system compliance technologies for lead: cationic exchange (CX) resins, and RO (USEPA 2006d, USEPA 2006e). CX resins are the IX resins commonly used for water softening, but they can be formulated to preferentially exchange metallic cations, including lead. They are, however, subject to fouling and channeling (Chen *et al.* 2006). GAC is often found in POU filters mixed with IX resin. GAC has high and nonuniform porosity and can present a high surface area. It is particularly well adapted for the removal of organic compounds, chlorine, and taste and odor compounds. However, as with IX, water can easily channel through the relatively large filter media. SBAC is composed of tiny particles of activated carbon that are fused together, resulting in a block of uniform pore size. They present smaller pore sizes (0.5–1.0 µm) than GAC and can intercept pathogenic protozoa (*Giardia* cysts and *Cryptosporidium* oocysts) as well as inorganic particles. They are effective in removing some organic compounds and chlorine. Carbon can also be formulated to remove lead (USEPA 2006e). Carbon-based filters are prone to bacterial regrowth because of accumulated organic matter; however, this does not appear to pose a human health concern (USEPA 2006d). To help reduce microbial regrowth, silver (Ag) is often added as a bactericide in the filter material (Molloy *et al.* 2008). Nitrification can also occur in these filters, especially in chloraminated systems, which decreases pH and alkalinity. This can result in increasing lead release from lead-containing plumbing materials downstream of the devices if such devices are installed upstream of a faucet or drinking water fountain (Zhang *et al.* 2008).

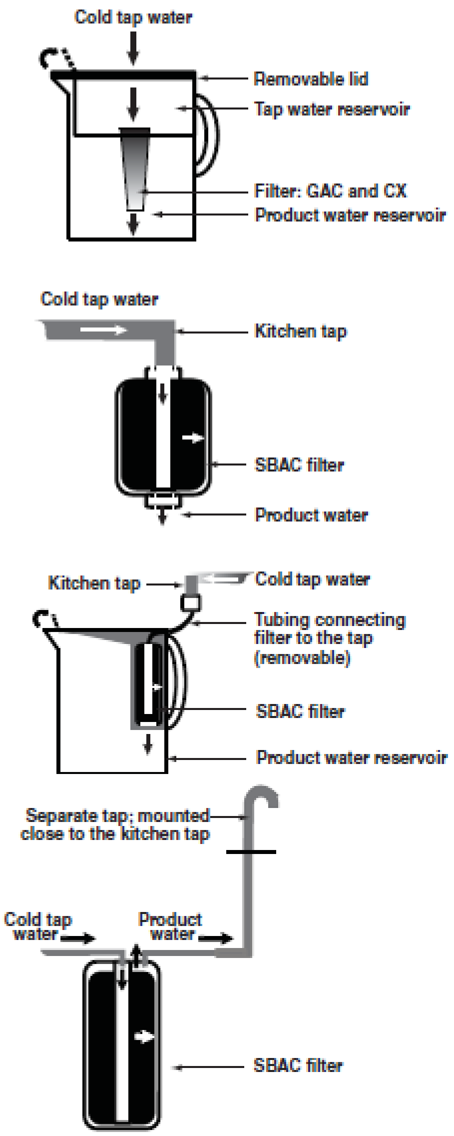
POU filtration devices have been extensively used for the removal of arsenic, copper (Cu), fluoride, and nitrate and have been shown to be generally effective, although breakthrough in a POU filter can often occur earlier than predicted (Abdo *et al.* 1999, Environmental Quality Program 2008). In Missouri schools, more than 90% of the POU devices installed in drinking water fountains met the lead action level (AL; USEPA 2006d). In schools in Seattle, Wash., under-the-sink filters installed in drinking water fountains were highly effective at removing lead (effluent < 1 µg/L), cadmium, iron, and turbidity, under normal use, intermittent flow, or without filter preconditioning (Boyd *et al.* 2005). Influent lead concentrations were, in general, relatively low (< 10 µg/L), but higher concentrations were also tested at lab scale (up to 136 µg/L). The same kind of POU devices showed good results in a school remediation program; however, materials downstream of the POU device could release lead (Boyd *et al.* 2008a). In Australia, Gulson and colleagues (1997) studied lead removal by pour-through POU filters for various water qualities. Removal varied widely (25–95%) because of differences in initial lead content in the feedwater and the ions and lead species present. Low efficiency was attributed to low initial lead levels (< 4 µg/L). In lab-scale testing, lead removals decreased from 80 to 60% during the filter lifetime.

This study provides insight into the performance and reliability of POU devices when applied to typical tap water from a distribution system. POU units tested included under-the-sink and tap-mounted devices, which currently meet the revised NSF-53 protocol for lead reduction. Water quality and influent lead levels could affect the operation of POU devices and influence their efficiency. There is also concern that the colloids formed from an insoluble lead solution made from soluble $Pb(NO_3)_2$ may not be representative of particulate lead in tap water, and the particles trapped in the POU filter may release lead after a period of stagnation. Validation of certified POU devices appears justified because of problems reported in the earlier literature and because of legal concerns associated with advisories regarding recommended use of POU devices by health authorities to protect vulnerable populations such as pregnant women, infants, and young children. Also, pour-through POU filters that were NSF-53-certified for lead removal before 2007 were tested to better understand their malfunction and whether or not they could still be used in some cases. Indeed, these devices are widely used and had been recommended by some health authorities to limit exposure to lead at the tap before July 2007. The objectives of this study were to: (1) compare common POU devices that were NSF-53-certified before 2007 for dissolved and particulate lead removal in water from a distribution system, (2) evaluate the behavior of some POU devices for the removal and release of other metals, (3) measure the effect of POU devices on water quality, and (4) evaluate whether nitrification in the filter could increase lead release from particles trapped in the filter.

4.2 Materials and methods

Four experiments were carried out (1, 2, 3, and 4). Figure 4-1 shows the POU devices tested and their characteristics. They are widely used brands typically available in local stores (four brands, seven stores).

Table 4-1 and Table 4-2 summarize the various experimental conditions for these POU devices. All labware was thoroughly washed with a nonphosphate detergent, soaked in 10% nitric acid (HNO_3) for at least 24 h, rinsed six times in distilled water and distilled–deionized water, dried in clean air, and stored in sealed plastic bags until use. Samples were taken in polypropylene bottles and vials. Analyses were conducted in different laboratories, except for tests 1 and 3. The four tests are described in the following sections.



Pour-through device:
- Devices X (tests 1 and 3), Y (test 2), G, and H (test 4)
- NSF-53-certified for Pb before 2007
- Device H: NSF-42-certified for particulate class 5 (30–<50 μm)
- Treatment technology: GAC and CX resin (~200 cm^3)
- Capacity: 150 L
- Recommended lifetime: approximately two months
- Recommended water temperature: 2–30°C
- Pb removal (claimed): > 95%
- Filtration method: gravity

Tap-mounted device, type 1:
- Devices C and D (test 4)
- NSF-53-certified for Pb before and after 2007
- NSF-42-certified for particulate class 1 (0.5–<1 μm)
- Treatment technology: SBAC (~125 cm^3)
- Capacities: 378 L (D) and 757 L (C)
- Recommended lifetime: approximately three to four months
- Recommended water temperature: 1–38°C
- Pb removal (claimed): > 98%
- Filtration method: filtration under pressure
- Service flow: 2.2 L/min

Tap-mounted device, type 2:
- Device F (test 4)
- NSF-53-certified for Pb before and after 2007
- NSF-42-certified for particulate class 1 (0.5–<1 μm)
- Treatment technology: SBAC (~100 cm^3)
- Capacity: 150 L
- Recommended lifetime: approximately two months
- Recommended water temperature: < 34°C
- Pb removal (claimed): > 99%
- Filtration method: filtration under pressure
- Service flow: 3.8 L/min

Under-the-sink device:
- Devices A and B (test 4)
- NSF-53 certified for Pb before and after 2007
- NSF-42 certified for particulate class 1 (0.5–<1 μm)
- Treatment technology: SBAC (A: ~180 cm^3, B: ~650 cm^3)
- Capacities: 2,840 L (A) and 1,515 L (B)
- Recommended lifetime: approximately six to 12 months
- Recommended water temperature: 4–38°C
- Pb removal (claimed): > 99%
- Filtration method: filtration under pressure
- Service flow: ~2 L/min
- Separate tap in chromate brass (A) or plastic (B)

CX—cationic exchange, GAC—granular activated carbon, Pb—lead, POU—point of use, SBAC—solid block activated carbon

Figure 4-1. Schema and characteristics of each POU tested.

Table 4-1. Summary of testing conditions.

Test	Device; Number Tested, Study Type	NSF-53 Certification for Pb: Before 2007	NSF-53 Certification for Pb: After 2007	Duration	Spiking in Feedwater	Water Quality Parameters Measured: pH	Metals	NH_3-N	Cl_2	Temp °C	Turbidity
1	Pour-through (X), 4, lab scale*	Yes		Three days, up to 100% of capacity (150 L total, 50 L/d)	Part A: dissolved Pb, Cr, Cu Part B: no addition		Pb, Cr, Cu, Co, Ni, Ag				
2	Pour-through (Y), 3, laboratory nitrification†	Yes		12 batches of 1.6 L filtered over 23 days (19.2 L)	Particulate Pb (Pb–Sn solder and PbO_2), NH_3-N	Yes	Pb	Yes		4 and 20	
3	Pour-through (X), 3, domestic use pattern*	Yes		Nine weeks (≤ 150 L)			Pb, Cu, Cr, Co, Ni, Ag				
4	Pour-through (G, H), 2; tap-mounted (C, D, F); under-the-sink (A, B), 2, all lab scale*	Yes	Yes (except for G and H)	Six days, up to 120% of POU device capacities	Dissolved Pb and particulate Pb (PbO_2)	Yes	Pb		Yes	10	Yes

Ag—silver, Cl_2—free chlorine, Co—cobalt, Cr—chromium, Cu—copper, NH_3-N—ammonia nitrogen, Ni—nickel, Pb—lead, PbO_2—lead dioxide, POU—point of use, Sn—tin, Temp—temperature

*Distribution system 1 water
†Distribution system 2 water

Table 4-2. Distribution system water quality characteristics*.

Test	Utility	pH	Turbidity *ntu*	Alkalinity *mg/L as $CaCO_3$*	Ca^{2+} *mg/L*	Mg^{2+} *mg/L*	Hardness *mg/L as $CaCO_3$*	P *mg/L*
1, 3, 4	1	7.5–8.2 (7.7)†	0.09–1.63 (0.24)	78–86 (82)	29–33 (32)	7.5–8.5 (8.0)	111–121 (116)	0.005–0.012 (0.008)
2	2	7.9‡	0.03–0.08	32‡	12‡	5‡	51‡	0.5‡
NSF-water 1		6.5±0.25	< 1	10–30			10–30	< 0.5
NSF-water 2		8.5±0.25		100±10%			100±10%	

$CaCO_3$—calcium carbonate, Ca^{2+}—calcium cation, Mg^{2+}—magnesium cation, P—phosphates

*Data from annual reports on drinking water quality
†Numbers in parentheses indicate mean value
‡Data from measurements during test 2

4.2.1 Test 1: Pour-through POU devices, lab-scale study on the reduction of Pb and other metals

Four identical pour-through POU devices (devices X) were tested for total Pb, chromium (Cr), Cu, cobalt (Co), nickel (Ni), and Ag before and after filtration at time 0 and after 40, 80, 120, and 150 L (POU recommended lifetime) in duplicate and over three days in the laboratory. The delay between each batch of water put through the filter was as recommended by NSF-53 (15–60 s). Time 0—referring to time 0 of the POU device lifetime—does not correspond exactly to 0 L. In fact, the manufacturer recommended not drinking the first two batches of filtered water because of possible initial carbon release from the filter (not included in the POU device recommended lifetime). Municipal tap water 1 (Table 4-2) taken directly from two different laboratory faucets was tested as-is and spiked with Pb, Cr, and Cu (faucet 1: spiked/not spiked, faucet 2: spiked/not spiked). The tap water used was the first morning flush after overnight stagnation to maximize metal concentrations. Influent and effluent waters were sampled as in Gulson *et al.* (1997), using the following procedure: (1) the first morning flush was sampled in a 500-mL bottle, (2) the sample was mixed, (3) two aliquots of 100-mL were taken in two 100 mL bottles (tap water: influent), (4) the remaining water was poured into the POU device reservoir, and (5) two aliquots of 100 mL of product water (filtered tap water, effluent) were taken in two 100-mL bottles (at least one unit volume is recommended by NSF, i.e., ≥ 200 mL for the pour-through POU devices tested). Spiked tap water was prepared with two concentrated solutions of 500 mL, the first with Cr only and the second with Pb and Cu. The 500-mL concentrated solutions were prepared using 0.389 g of chromium(III) chloride ($CrCl_3$) × $6H_2O$, 0.020 g of lead(II) chloride ($PbCl_2$), and 4.008 g of copper(II) chloride ($CuCl_2$) × $2H_2O$. Five millilitres of each concentrated solution were diluted in 15 L of tap water. Final spiked concentrations poured into the POU device reservoir did not exceed maximum acceptable concentrations (MAC) for each metal: 10 µg/L Pb, 1,000 µg/L Cu, 50 µg/L Cr (Canadian levels). Spiked waters were filtered and sampled as for tap water. Samples were acidified to $pH < 2$ with ultrapure HNO_3, and stored at 4°C for a minimum of 16 h before analysis according to method 200.8 (USEPA 1994b). Samples were analyzed for Pb, Ni, Cu, Cr, Co, and Ag by an inductively coupled plasma mass spectrophotometer (ICP/MS, Ultra Mass 700, Varian Inc.), and the quantitation limits were: 0.3 µg/L Pb, 0.6 µg/L Ni, 0.6 µg/L Cu, 1 µg/L Cr, 0.1 µg/L Co, and 0.3 µg/L Ag (three standards and blanks for 20 samples, five duplicates for 100 samples). Metals other than lead were chosen for the following reasons: Cu is regulated in the United States with an AL of 1.3 mg/L under the Lead and Copper Rule (LCR), and for aesthetic objectives at 1 mg/L in Canada and is released from copper pipes and brass materials that are frequently found in premise plumbing. Cr is regulated (US MCL of 0.1 mg/L, Canadian MAC of 0.05 mg/L) and can be leached from faucets and brass devices. Ni is a concern in Europe (it is a suspected carcinogen) and may be regulated in the near future because it is released from taps and fittings (World Health Organization [WHO] provisional guideline value of

0.02 mg/L). Ag was analyzed because of its potential release from filter material. Finally, Co was analyzed for comparison with the removal of other metals (selectivity of the IX resin).

4.2.2 Test 2: pour-through POU devices, lab-scale study on particulate Pb reduction and effect of nitrification

Three identical pour-through POU devices (devices Y) were challenged with tap water 2 (Table 4-2) containing added lead particles. Treated water was monitored for total lead, pH, and ammonia nitrogen at 4 and 20°C (duplicates). Before filtering, the water was dechlorinated, 1 mg/L of ammonia was added, and the pH was adjusted to 7.9. The filters were inoculated with water from a GAC filter in which nitrification had been established for more than a year. Particulate lead (lead dioxide [PbO_2] and Pb–tin [Sn] solder, ~57 mg Pb) was added to the first batch of water (day 0), and then 12 batches of 1.6 L of water with undetectable lead (< 1 µg/L Pb) were filtered over 23 days. All particles were passed through a medium-sized aerator screen, as described in Triantafyllidou *et al.* (2007). Filtration was conducted on days 2, 6, 7, 9, 13–16, and 20–23 (one batch per day). All the treated water was collected and subjected to heated and strongly acidic digestions that were proven (Triantafyllidou *et al.* 2007) to recover all the lead during later analysis with ICP/MS (blank and standard every five samples, quantitation limit: 0.03 µg/L, detailed in Zhang *et al.* 2008). The lead concentrations used, although high, are representative of the "worstcase" samples collected by a water utility in Washington, D.C., (48,000 µg/L) in 2003 (Edwards & Dudi 2004). The oxidation–reduction potential was not maintained, so PbO_2 oxides were inherently unstable, as in the case of Washington, D.C., after a switch from chlorine to chloramines (Lytle & Schock 2005). Nitrification was tracked with mass balances on nitrate, nitrite, and ammonia, as detailed elsewhere (Zhang *et al.* 2008).

4.2.3 Test 3: pour-through POU devices, domestic-use-pattern study on the reduction of Pb and other metals

Three identical pour-through POU devices (devices X as in test 1) were tested for Pb, Cr, Cu, Ni, and Ag in three homes, during real-time household use. Water from the kitchen tap (Table 4-2, distribution system 1) was tested before and after filtration at time 0 POU device lifetime, and after three, six, and nine weeks of normal domestic use in duplicate (POU device recommended lifetime). Residents were instructed to filter about 2 L/d if possible and to note each batch in order to comply with the POU device capacity (150 L) after nine weeks of use. The first morning flush water was filtered in order to maximize metal levels. Sampling procedure, methods, and analysis were the same as in test 1.

4.2.4 Test 4: three types of POU devices, lab-scale study on dissolved and particulate Pb reduction (Pb_{diss}, Pb_{part})

Three types of POU devices were tested: two under-the-sink devices (A and B), three tap-mounted devices (C, D, and F), and two pour-through devices (G and H). POU devices were fed with Pb-spiked municipal tap water 1 (Table 4-2), tested for lead (particles and soluble) over six days and up to 120% of their capacity, and left to stagnate overnight (> 8 h). The Pb-spiked feedwater was prepared daily by adding either 46 or 231 mg of PbO_2 (Alfa-Aesar) sieved with a standard screen to a fraction > 0.45 µm directly into a mixing tank (~2,000 L) plus a lead-concentrated solution containing 156 mg of $Pb(NO_3)_2$ (Sigma). Target concentrations were ~20 µg/L or ~100 µg/L of $Pb_{particulate}$ and ~50 µg/L of $Pb_{dissolved}$. Water in the mixing tank was pumped to a pilot-testing POU device (Figure 4-2) with a configuration approximately similar to the test apparatus prescribed by the NSF-53 protocol. In the presence of lead particles in test water with such an apparatus, calculated particulate removal ($Pb_{particulate}$ effluent/$Pb_{particulate}$ influent) is not as precise as calculated dissolved lead removal because of nonhomogeneous mixing in the water supply tank. However, calculated particle removals give an idea of POU device efficiency. Influent water was sampled for $Pb_{dissolved}$ and $Pb_{particulate}$ twice daily (the first 1 L in the morning and 1 L at noon), and effluent water from the POU devices was sampled at the same time. Effluent water was analyzed from day 1 to day 4 for total lead only, and the last two days for $Pb_{dissolved}$ and $Pb_{particulate}$. When analysis for both $Pb_{dissolved}$ and $Pb_{particulate}$ was required, 50 mL of the mixed 1-L sample were collected and filtered on a 0.45-µm filter (Durapore HV, Millipore) using a 60-mL disposable syringe (BD^{TM}, Cole Parmer). Samples were acidified to pH < 2 with ultrapure HNO_3 and stored at 4°C for at least 16 h before analysis, according to protocol 200.8 (USEPA 1994b). Lead was analyzed using an ICP/MS (7500a, Agilent) with a quantitation limit of 0.06 µg/L (blank and standard every 29 samples, duplicates every 24 samples). The pH (Accumet AB15 pH-meter, Fisher), turbidity (2100 AN turbidimeter, Hach), temperature, and chlorine content (Cary 100 Scan spectrometer, Varian) were measured for each sample.

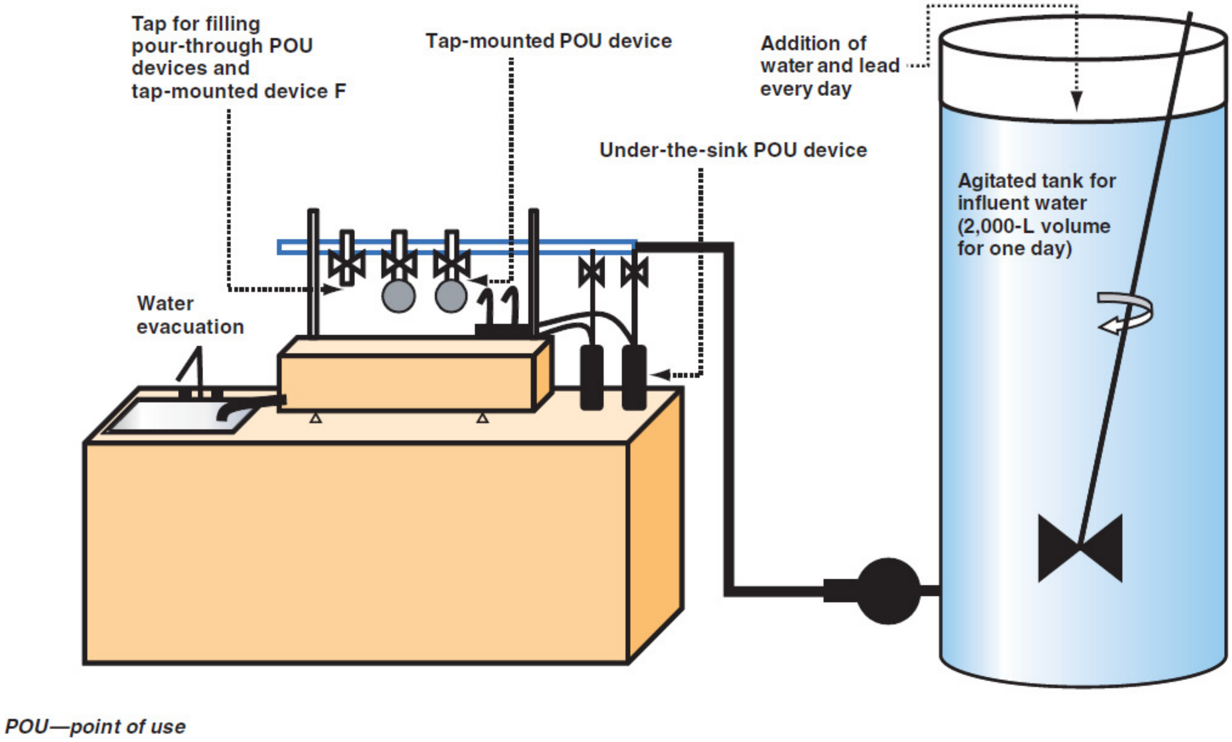


Figure 4-2. Configuration of the pilot test designed for test 4.

4.3 Results

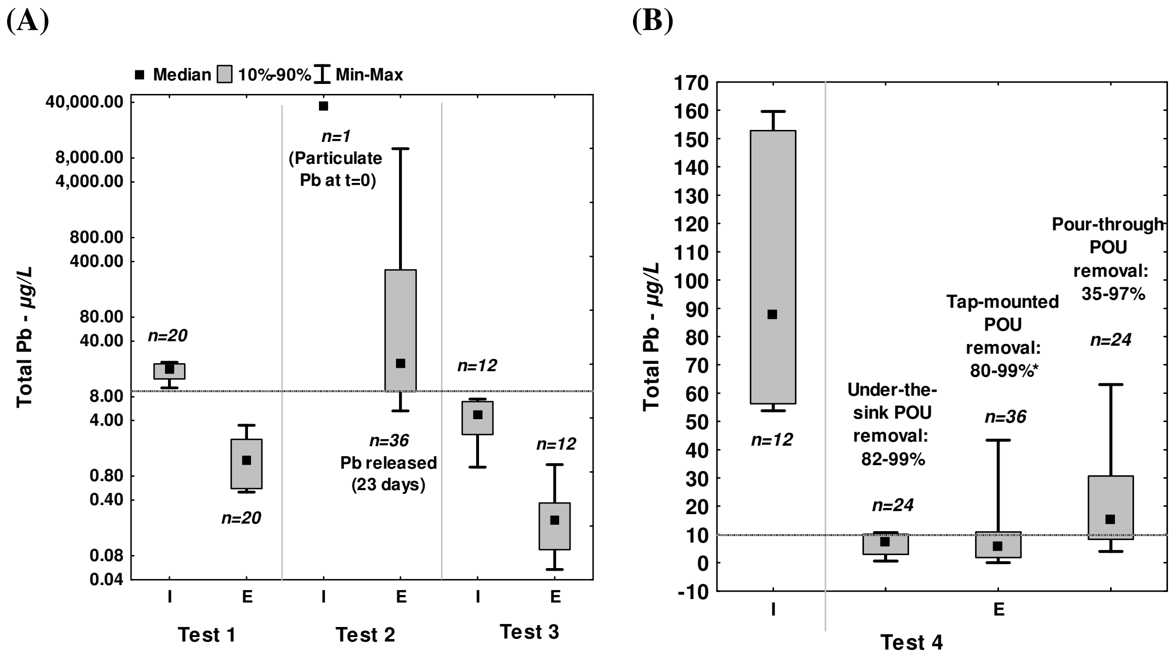
4.3.1 Total lead removal

Figure 4-3, part A, summarizes the results for total lead removal for pour-through POU filters in test 1 (pour-through X, lab-scale), test 2 (pour-through Y, lab-scale, and initial addition of high $Pb_{particulate}$), and test 3 (pour-through X, household). Overall, significant removals of lead by pour-through POU devices were observed, ranging from 68 to 99%. For the same device (X) and water (from distribution system 1; tests 1 and 3, Figure 4-3, part A), total lead levels in filtered water decreased and remained well below 10 µg/L, the reference level for POU NSF-53 certification for lead, regardless of the usage pattern. Effluent lead levels were greater for test 1 (maximum = 3.5 µg/L) than for test 3 (maximum = 1.1 µg/L); however, lead concentrations were higher in influent 1 (10–22 µg/L versus 1.0–7.4 µg/L for influent 3, Figure 4-3, part A). When challenged with an initial batch of water containing a high mass of lead particles (57 mg, i.e., 36,000 µg/L Pb), pour-through Y retained a portion of the lead particles. However, the lead levels in the filtered water were extremely high and persisted in the filtered water of the 12 batches of water without spiked lead (up to 10,470 µg/L; Figure 4-3, part A, test 2). The cumulative lead release was estimated using the following equation:

$\text{Pb}_{\text{released, mg}} = \Sigma_{i\,=\,1\ldots12}$ (volume of filtered $\text{water}_{i,\ \text{L}} \times$ Pb concentration in filtered $\text{wate}_{\text{r}i,\ \text{mg/L}}$) (1)

About 19 mg of lead was released at 4°C (34% of $\text{Pb}_{t\,=\,0}$), and 2–7 mg was released at 20°C (3–12% of $\text{Pb}_{t=0}$). The mass of lead trapped in the POU filter was calculated (Pb at $t = 0$: cumulative Pb released or “influent Pb”), and, despite high lead levels in effluent water of the 12 batches cited previously, the calculated removal percentage was high; removal < 95% was observed in only two samples.

A comparison of total lead removal by various types of POU devices challenged with water containing dissolved and particulate lead is shown in Figure 4-3, part B (test 4, 54–160 µg/L of Pb_{total}; $\text{Pb}_{\text{total}} = \text{Pb}_{\text{particulate}} + \text{Pb}_{\text{dissolved}}$). Two under-the-sink POU devices (A, B), three tap-mounted POU devices (C, D, F), and two pour-through POU devices (G, H) were tested. Total lead concentrations in effluent water below or above 10 µg/L and their ranges are shown in Table 4-3. Variable and sometimes very low removals (35–97%) were observed for the pour-through POU devices tested, whereas the others showed global adequate removal efficiency (80–99%). Total lead concentrations from the under the-sink POU devices showed limited variability (mean = 6.5 µg/L, median = 7.7 µg/L, standard deviation [SD] = 3.26), and levels rarely exceeded 10 µg/L (three values of 10–11 µg/L, number [n] = 24). For tap-mounted POU devices, similar and stable lead concentrations in the filtered water were observed (mean = 7.5 µg/L, median = 6.1 µg/L, SD = 7.0), and levels barely exceeded 10 µg/L, except for one outlier at 43 µg/L (nine values of 10–12 µg/L, n = 36). Lead concentrations in the filtered water from the two pour-through POU filters were much higher and variable, with 16 of 24 values > 10 µg/L up to 63 µg/L Pb (mean = 19 µg/L, median = 15 µg/L, SD = 13). The minimum observed for these devices was nearly half the target level of 10 µg/L (4 µg/L Pb). Overnight stagnation was not found to increase lead levels or any filter breakthrough.



E—effluent, I—influent, n—number of samples, Pb—-lead, POU—point of use, t—time

****Not including the outlier at 43 µg/L***

Test parameters: test 1—lab scale, water spiked and not, pour-through device, 83–97% removal; test 2—lab scale, particulate

Pb at t = 0, pour-through device, 71–99% removal; test 3—household, pour-through device, 68–99% removal; test 4—lab scale,

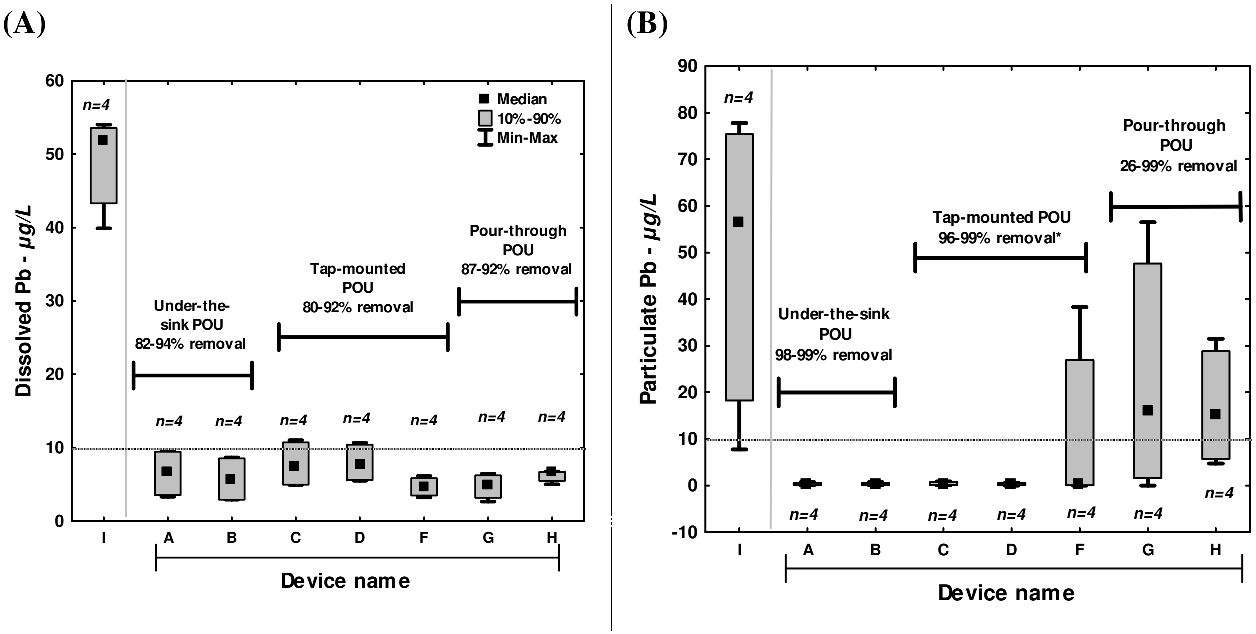
seven POUs comprising three types, dissolved and particulate Pb

Dotted line indicates the NSF International limit for total Pb.

Figure 4-3. Total lead before and after filtration by pour-through POU devices X and Y (A) and POU devices A–D and F–H (B).

4.3.2 Dissolved and particulate lead removal

The removal of dissolved and particulate lead by the devices in test 4 (seven POUs, three types) are shown in Figure 4-4 and Table 4-3. Test 4 was conducted by adding dissolved and particulate lead to the feedwater. Figure 4-4 shows measurements taken on the last two days of the experiment because the POU effluents were only analyzed for dissolved and particulate lead on those days (total lead, days 1–4). Dissolved lead removals were consistently high for all the devices tested. However, dissolved lead concentrations in three out of 12 effluent samples for the tap-mounted POU devices were somewhat above 10 µg/L (10–11 µg/L, influent range = 40–54 µg/L; Figure 4-4, part A, Table 4-3). In terms of dissolved lead removals, pour-through POU units performed slightly better (effluent ≤ 6.8 µg/L Pb) than the under-the-sink POU devices (effluent ≤ 9.6 µg/L). In terms of particulate lead, the removal pattern was considerably different (Figure 4-4, part B, Table 4-3). With an influent range of 7.8–78 µg/L $Pb_{particulate}$, particulate lead removal for all under-the-sink and tap-mounted devices tested was high and remarkably stable, with low concentrations of particulate lead in the filtered water (≤ 0.9 µg/L) except for one outlier, at 38 µg/L. This outlier corresponded to the total lead outlier cited previously (43 µg/L). Inconsistent and sometimes low removals (26–99%) were observed for the pour-through POUs. The two pour-through devices (G, H) were ineffective at removing particulate lead, and elevated particulate lead remained in the filtered water (up to 57 µg/L).



I—influent, n—number of samples, Pb—lead, POU—point of use

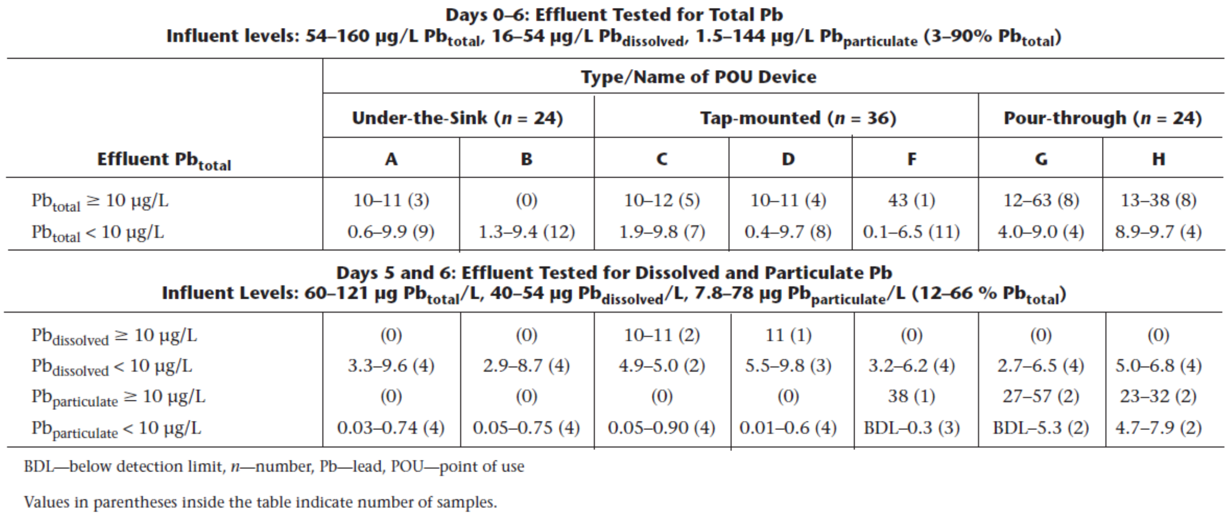
**Not including the outlier at 38 µg/L*

Test parameters: lab scale, seven POUs comprising three types

Dotted lines indicate NSF International limit for total Pb.

Figure 4-4. Dissolved lead (A) and particulate lead (B) before and after filtration by POU devices in test 4.

Table 4-3. Number and ranges of values below or above 10 µg/L Pb in effluentwater of POU devices in test 4.



Days 0–6: Effluent Tested for Total Pb
Influent levels: 54–160 µg/L Pb_{total}, 16–54 µg/L $Pb_{dissolved}$, 1.5–144 µg/L $Pb_{particulate}$ (3–90% Pb_{total})

	Type/Name of POU Device						
	Under-the-Sink (*n* = 24)		**Tap-mounted (*n* = 36)**			**Pour-through (*n* = 24)**	
Effluent Pb_{total}	**A**	**B**	**C**	**D**	**F**	**G**	**H**
$Pb_{total} \geq 10$ µg/L	10–11 (3)	(0)	10–12 (5)	10–11 (4)	43 (1)	12–63 (8)	13–38 (8)
$Pb_{total} < 10$ µg/L	0.6–9.9 (9)	1.3–9.4 (12)	1.9–9.8 (7)	0.4–9.7 (8)	0.1–6.5 (11)	4.0–9.0 (4)	8.9–9.7 (4)
Days 5 and 6: Effluent Tested for Dissolved and Particulate Pb **Influent Levels: 60–121 µg Pb_{total}/L, 40–54 µg $Pb_{dissolved}$/L, 7.8–78 µg $Pb_{particulate}$/L (12–66 % Pb_{total})**							
$Pb_{dissolved} \geq 10$ µg/L	(0)	(0)	10–11 (2)	11 (1)	(0)	(0)	(0)
$Pb_{dissolved} < 10$ µg/L	3.3–9.6 (4)	2.9–8.7 (4)	4.9–5.0 (2)	5.5–9.8 (3)	3.2–6.2 (4)	2.7–6.5 (4)	5.0–6.8 (4)
$Pb_{particulate} \geq 10$ µg/L	(0)	(0)	(0)	(0)	38 (1)	27–57 (2)	23–32 (2)
$Pb_{particulate} < 10$ µg/L	0.03–0.74 (4)	0.05–0.75 (4)	0.05–0.90 (4)	0.01–0.6 (4)	BDL–0.3 (3)	BDL–5.3 (2)	4.7–7.9 (2)

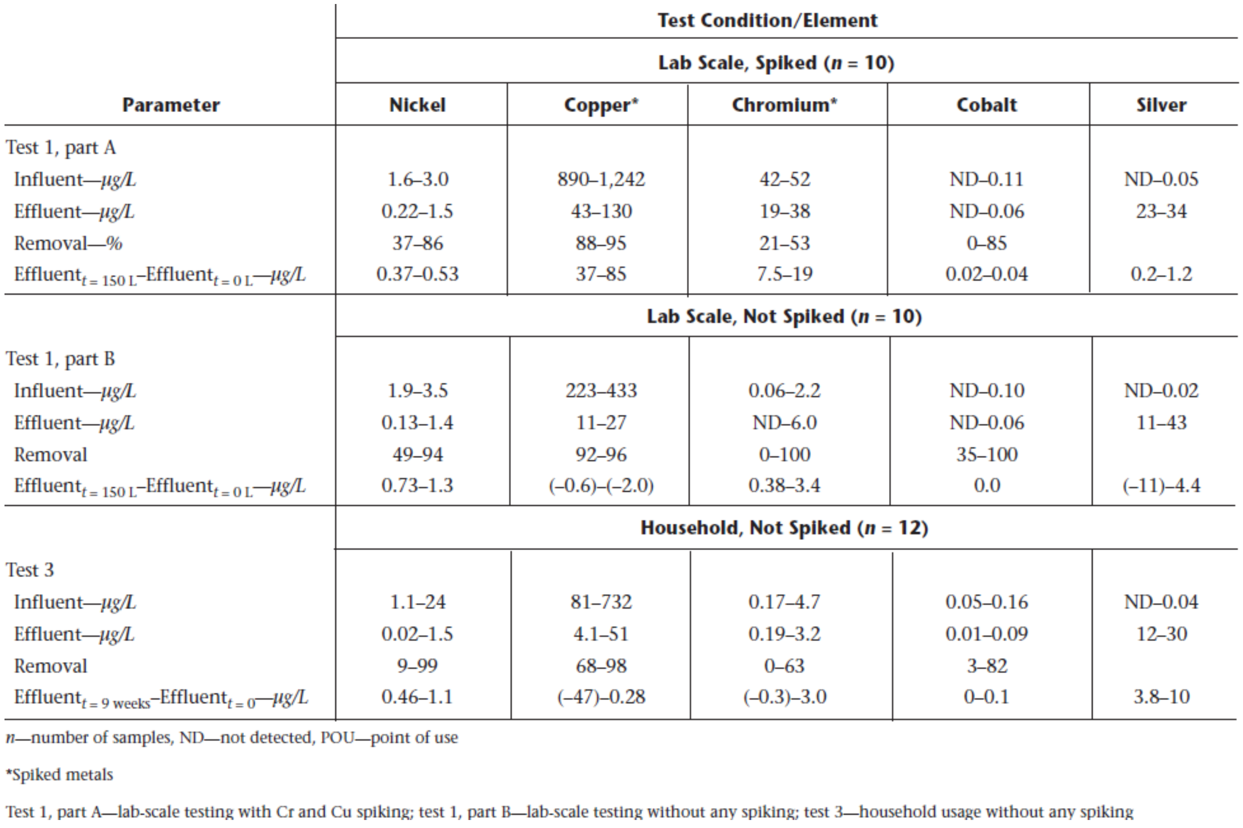
BDL—below detection limit, *n*—number, Pb—lead, POU—point of use

Values in parentheses inside the table indicate number of samples.

4.3.3 POU behavior for other metals (Cu, Cr, Co, Ni, and Ag)

Table 4-4 shows the results for other metals (tests 1 and 3). For different testing conditions and initial metal levels, good and stable copper removal was observed: all removals exceeded 88%, except for a single event at 68% (*t* = 0 week, house number 1). Copper concentrations in effluent water were higher for Cu-spiked influent water (43–130 µg/L) than for water that was not Cu spiked (4.1–51 µg/L). Other elements showed variable results: removal ranges were 9–99% for Ni and 0–100% for Cr and Co. Metal levels in effluent water versus litres of filtered water (because test 3 examined household use, metals effluent levels were studied versus time [0–9 weeks] rather than the number of filtered litres) were studied for each of the seven identical POUs (X) sampled in tests 1 and 3 (1-not spiked-lab, 2-not spiked-lab, 1-spiked-lab, 2-spikedlab, and 1-house, 2-house, 3-house). Metal levels in effluent water between *t* = 0 and *t* = 150 L (or nine weeks) increased for all the POU devices for Ni (maximum +1.3 µg/L) and Cr (maximum +19 µg/L, nil for two POU devices). Such increases were not systematic for Co (+0 µg/L), Cu (–47 to +85 µg/L), and Ag (–11 to +10 µg/L). No clear tendency was noted for Cr, Co, Ag, or Cu effluent concentrations versus filtered litres (or time). Ni levels increased linearly with filtered volumes within the POU filter lifetime for all the POU devices, except for two house-tested POU devices (1-house, 2-house, nonlinear). The best relationship was obtained for the 1-not spiked-lab POU device (Figure 4-5). Silver release was detected in the effluent of these devices. Maximum metal levels measured at the effluent were 130 μg/L Cu, 38 μg/L Cr, 1.5 μg/L Ni, 0.09 μg/L Co, and 43 μg/L Ag (Table 4-4).

Table 4-4. Concentration and removal ranges of other metals measured in water before and after filtration with pour-through POU devices.



	Test Condition/Element				
	Lab Scale, Spiked (n = 10)				
Parameter	**Nickel**	**Copper***	**Chromium***	**Cobalt**	**Silver**
Test 1, part A					
Influent—μg/L	1.6–3.0	890–1,242	42–52	ND–0.11	ND–0.05
Effluent—μg/L	0.22–1.5	43–130	19–38	ND–0.06	23–34
Removal—%	37–86	88–95	21–53	0–85	
Effluent$_{t = 150\text{ L}}$–Effluent$_{t = 0\text{ L}}$—μg/L	0.37–0.53	37–85	7.5–19	0.02–0.04	0.2–1.2
	Lab Scale, Not Spiked (n = 10)				
Test 1, part B					
Influent—μg/L	1.9–3.5	223–433	0.06–2.2	ND–0.10	ND–0.02
Effluent—μg/L	0.13–1.4	11–27	ND–6.0	ND–0.06	11–43
Removal	49–94	92–96	0–100	35–100	
Effluent$_{t = 150\text{ L}}$–Effluent$_{t = 0\text{ L}}$—μg/L	0.73–1.3	(–0.6)–(–2.0)	0.38–3.4	0.0	(–11)–4.4
	Household, Not Spiked (n = 12)				
Test 3					
Influent—μg/L	1.1–24	81–732	0.17–4.7	0.05–0.16	ND–0.04
Effluent—μg/L	0.02–1.5	4.1–51	0.19–3.2	0.01–0.09	12–30
Removal	9–99	68–98	0–63	3–82	
Effluent$_{t = 9\text{ weeks}}$–Effluent$_{t = 0}$—μg/L	0.46–1.1	(–47)–0.28	(–0.3)–3.0	0–0.1	3.8–10

n—number of samples, ND—not detected, POU—point of use

*Spiked metals

Test 1, part A—lab-scale testing with Cr and Cu spiking; test 1, part B—lab-scale testing without any spiking; test 3—household usage without any spiking

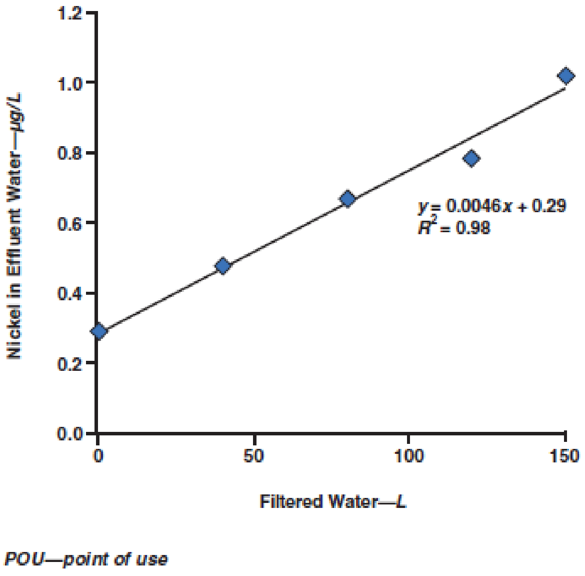
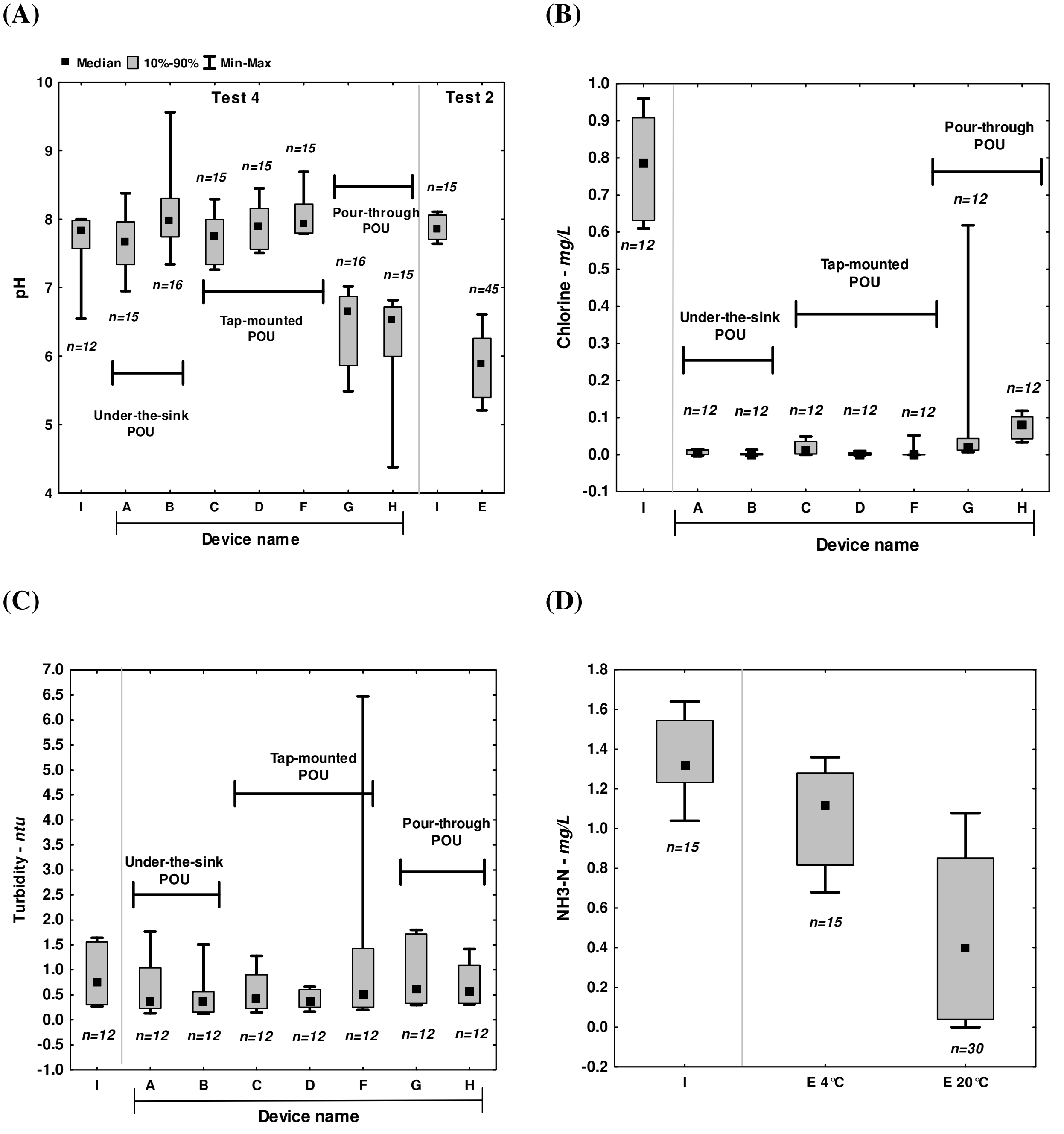


Figure 4-5. Best relationship between nickel concentrations in the effluent of pour-through POU devices and the number of filtered litres.

4.3.4 Effect of POU filters on water quality

Figure 4-6 shows the effect of POU devices on water quality parameters (tests 2 and 4). The pH was relatively stable for most of the devices, except for the pour-through POU filters; a decrease of 1.2–2.0 pH units (based on the median values, Figure 4-6, part A) was observed for pour-through devices G, H, and Y. The decrease was greatest for Y. Also, pH values as low as 4.4 (test 4) and 5.2 (test 2) were observed in the effluent of pour-through POU filters (Figure 4-6, part A). As expected with carbon filters, chlorine was almost totally reduced by all the devices (Figure 4-6, part B). Some trace chlorine remained for devices G and H (up to 0.62 mg/L free chlorine [Cl_2]), whereas the effluent levels for the other POU filters remained < 0.05 mg/L Cl_2. SBAC POUs did not efficiently decrease turbidity, with median values decreasing from 0.8 to 0.4–0.5 ntu (Figure 4-6, part C). An extreme value of 6.5 ntu corresponded to a single breakthrough of particulate lead: 38 µg/L (device F). For pour-through POU devices, median values decreased slightly (0.8–0.6 ntu), but the maximum values and the 90th percentile were close to the influent water values, especially for device G. Ammonia measured in the effluent suggests that nitrification can take place during 24 h of stagnation (test 2; Figure 4-6, part D). The pH dropped in all instances after filtration during test 2, and, as expected, water temperature influenced the activity of the nitrifying bacteria (because reductions of ammonia were lower at 4°C than at

20°C). However, no impact of nitrification on lead release was observed because Pb release (19 mg) was higher at 4°C, i.e., when nitrification was less active.



E—effluent, I—influent, n*—number of samples, NH3-N—ammonia-nitrogen, POU—point of use*

Figure 4-6. Water quality parameters before and after POU filtration for pH in tests 2 and 4 (A), chlorine in test 4 (B), turbidity in test 4 (C), and nitrification in test 2 (D).

4.4 Discussion

4.4.1 Total Pb removal by pour-through POU devices: effect of influent Pb concentrations (Figure 4-3, A)

Removals for tests 1, 2, and 3 (68–99%) were lower than those indicated by the manufacturers (> 95%, Figure 4-1). In fact, removals are affected by influent concentrations (Gulson *et al.* 1997), which, in this study, were variable (1.0-36,000 µg Pb/L) and different from those of NSF-challenged water (150 µg Pb/L). The low removal efficiency of test 3 could be associated with low influent lead levels (< 10 µg/L); however, the lead concentrations in the filtered water remained low and were not considered to be hazardous (≤ 1.1 µg/L). Furthermore, effluent lead concentrations increased with influent lead concentrations. Therefore, a high removal rate may not be a reliable indicator of a low lead level in effluent water if the influent lead concentration is not considered. As shown in test 2, despite substantial lead removal (71– 99%), lead levels in the effluent water were extremely high (maximum 10,470 µg/L).

4.4.2 Total Pb removal by pour-through POU devices: effect of dissolved Pb in influent water (Figure 4-3, Figure 4-4, part A; Table 4-3)

The composition of the total lead influenced the efficiency of pour-through POU devices. When challenged with total lead containing significant levels of particulate lead in test 4, pour-through POU devices G and H were ineffective because total lead in effluent water exceeded the 10-µg/L NSF threshold in most of the samples collected. In contrast, lead levels in the effluent of pour-through device X tested in tests 1 and 3 were always ≤ 3.5 µg/L. This is surprising, because POU X had the same brand name and the same media filter as POU G, which had shown inconsistent removal. The efficiency gap can be partly explained by the predominance of soluble lead in challenge water in tests 1 and 3. Indeed, the tap water used in these two tests was taken from a distribution system (system 1) showing moderate levels of particulate lead (random daytime sampling in 45 homes with lead service lines: median = 0.39 µg/L, average = 1.1 µg/L; Deshommes *et al.* 2010a). Also, the spiked water in test 1 was prepared with soluble lead. Thus, the majority of total lead in test waters 1 and 3 was soluble, and the pour-through POU filters appeared effective in this case. Furthermore, for the devices evaluated in test 4, the dissolved lead concentrations measured in the effluent water over two days never exceeded 6.8 µg/L (dissolved

Pb in influent: 40–54 μg/L). Thus, pour-through POU devices seem effective for dissolved lead removal from tap water. Moreover, pour-through filters were composed of GAC and CX resin, the latter being recognized as a small system compliance technology for lead removal (USEPA 2006d). The limited efficiency observed in the author's tests may be attributable to the nature of CX resins, which are designed to remove ions and not particles (Chen *et al.* 2006). These results support cancellation of the NSF-53 certification for pour-through POU filters for lead removal in 2007, following the addition of lead particles to the test water (Renner 2007).

4.4.3 Particulate Pb removal by pour-through POU devices (Figure 4-3, Figure 4-4, part B; Table 4-3)

The pour-through POU filters tested were not capable of reliably removing particulate lead. In test 2, a high concentration of particulate lead added to the first batch of influent water for pour-through device Y resulted in high lead levels continuously released into the filtered water. No lead particles were added after *t* = 0, indicating that the particulate lead added initially was eventually released sporadically. Extremely high particulate lead concentration, as used in the water for test 2 (*t* = 0: 36,000 μg/L) considerably exceeded the lead levels in NSF test challenge water (150 μg/L). Pour-through device Y had been certified for the removal of about 150 μg/L of soluble lead but not for such extreme concentrations of particulate lead. However, high lead levels can occur, as demonstrated in Washington, D.C. (Edwards & Dudi 2004), when lead–tin particles from solder are released into the water (Triantafyllidou *et al.* 2007), or following partial lead pipe replacement (Boyd *et al.* 2004, Sandvig *et al.* 2008). Numerous samples containing more than 10,000 μg Pb/L were collected after partial lead service line replacements in Washington, D.C. (Edwards *et al.* 2009), and, to counter this risk, consumers were advised about potential elevated lead levels in tap water under these circumstances (USEPA 2000). More recently, the Centers for Disease Control and Prevention has determined that children living in homes with partial lead service line replacements have a 400% higher likelihood of elevated blood lead (CDC 2010b), and, in response, the use of filters to mitigate lead spikes is under consideration. In view of the results of test 2, pour-through POU devices—even if certified for lead before 2007—might no longer be considered in the effort to reduce lead exposure at the tap because particulate lead can potentially be released into the filtered water. The breakthrough of particulate lead and the resulting high total lead in filtered water also occurred with lower influent levels of particulate lead in test 4. Particulate lead influent levels in test 4 were closer to those of the NSF-revised protocol but still different: particulate lead ($PbO_2 \geq 0.45$ µm) varied between 1.5 and 144 µg/L and represented 3–90% of total lead (median = 37 µg/L, 42%), whereas concentrations used in the revised NSF protocol are 150 µg/L Pb_{total}, including at least 20% of fine lead particles (0.1–1.2 µm) and 20–40% of total $Pb_{particulate}$. As stated previously, these results support cancellation of the NSF-53 standard for lead in 2007. Pour-through POU devices that were NSF- 53-certified for lead before 2007 should not be used for water containing particulate lead.

The inconsistent removal of particulate lead by pour-through POU devices can be partly explained by the composition of their type of filter. For example, pour-through POU filters made of GAC and CX resin have a tendency to develop channels (USEPA 2006e) that provide a pathway for particles to pass through and contaminate the water, as was observed in the tests conducted in this study. Moreover, PbO_2 particles, as used in tests 2 and 4, are fragile and could break into smaller particles. Particles smaller than 30 µm are likely to pass directly into the filtered water, which is why NSF-42 certified pour-through POU devices are not rated for the removal of particulate lead. The highest level of NSF-42 certification observed for particle removal was class 5, i.e., removal of particles > 30–50 µm (Figure 4-1). The significant release of lead measured in test 2 could also be the result of the low pH in the device during stagnation; the pH decreased in that test from 7.9 to 5.9 (median values), as shown in Figure 4-6, part A. Fresh solder particles (Pb–Sn) without any protective coating are pH-sensitive and could partially dissolve. Long stagnation times for the particles in the filter might also contribute to the dissolution of lead particles (Reiber 1991).

Until now, few pour-through POU devices have passed the revised NSF-53 certification for lead reduction (NSF International 2008). These can be found on the NSF consumer website (www.NSF.org/consumer) under “search for certified products” category. After some POU devices lost their certification in 2007, labels using a variety of indirect references to certification were found, which might mislead consumers to falsely conclude that a device is NSF-certified for lead removal with the revised testing protocol. For example, notes such as “Laboratory tests follow the NSF protocol,” and “Effluent lead levels were under the NSF protocol prescribed limit,” were used on the package labels. No indication of NSF certification of these devices was found on the NSF website at the time of their purchase.

4.4.4 Comparison of various types of POU devices for Pb removal (Figure 4-4, Table 4-3)

Pour-through POU filters (G and H) removed slightly more dissolved lead than the other types of POU filters and with notably more consistency in test 4. Thus, the CX resin removes dissolved lead more effectively than the SBAC filters, which are used in the other POU filters, and results in lower concentrations of dissolved lead in the filtered water (≤ 6.8 µg/L for G and H, ≤ 11 µg/L for the other devices tested). The concentration of dissolved lead in the filtered water from the tested tap-mounted devices somewhat exceeded the 10-µg/L Pb NSF threshold on three occasions, indicating a possible lack of consistency. In addition, some dissolved lead values in the effluent of tap-mounted and under-the-sink POU filters were close to 10 µg/L (e.g., 8.7, 9.6, and 9.8 µg/L), and thus could slightly exceed this limit when combined with low particulate lead levels in the effluent (0.01–0.9 µg/L). As mentioned previously, values in excess of the 10-µg/L NSF threshold limit were not high, but present (10–12 µg/L Pb_{total}, an outlier at 43 µg/L Pb_{total} because of 38 µg/L $Pb_{particulate}$), although the water quality tested was typical tap water.

All non pour-through devices were very effective at removing particulate lead. The tap-mounted and under-the-sink POU devices contained SBAC filters, and their performances were higher for particulate lead (96–99%, effluent $Pb_{particulate}$ ≤ 0.9 µg/L) than for dissolved lead removal (80–94%, effluent $Pb_{dissolved}$ ≤ 11 µg/L). Only one particulate lead value in the filtered water significantly exceeded the 10-µg/L NSF threshold (device F, 38 µg/L). This outlier seemed to be linked to particulate lead leaching from particles trapped in the filter, as particulate lead concentration was higher in the effluent than in the influent (the reason why the removal percentage could not be calculated). The combined capabilities of tap-mounted and under-the-sink POU filters to adsorb dissolved lead and capture particulate lead explain their recent certification by the revised NSF-53 protocol.

When comparing the under-the-sink devices tested, it appears that total lead in effluent water for POU device A slightly exceeded 10 µg/L on three occasions (10–11 µg/L), whereas POU device B maintained levels ≤ 9.4 µg/L. As stated previously, dissolved lead contributed to these levels. A plausible explanation is that the brass faucet (not NSF-61 certified for Pb) included in POU device A could have contributed some lead, whereas the plastic faucet supplied with POU device

B did not. Indeed, Boyd *et al.* (2008a, 2008b) showed those elements downstream of POU units could contribute to lead levels in tap water.

Regarding total lead removals for POU devices that passed the revised NSF-53 protocol (under-the-sink and tap-mounted), tap-mounted POUs failed to produce filtered water with lead levels consistently < 10 µg/L (exceeded 10 times). Although they exceeded 10 µg/L only marginally, this performance was surprising, given that the lead levels tested (dissolved plus particulate) were lower (≤ 160 µg/L, mean = 97 µg/L) compared with the NSF challenge water (150 ± 30 µg/L for single point, mean = 150 ± 15 µg/L). However, many parameters differed from those of the NSF testing protocol: the percentage of particulate lead (3–90% for test 4, 20–40% for NSF) and its size (≥ 0.45µm for test 4, at least 20% between 0.1–1.2 µm for NSF), the type of particles [PbO_2 for test 4, Pb particles from insoluble solution of $Pb(NO_3)_2$ for NSF], and the type of water used (tap water for test 4, two synthetic waters for NSF). Values of the under-the-sink POU devices in test 4 that were slightly in excess of the 10-µg/L NSF threshold limit were attributed to lead leaching from the tap sold with the device. Thus, under-the-sink POU filters seem more efficient than tap-mounted ones. Results obtained for under-the-sink devices agree with those presented by Boyd *et al.* (2005), showing satisfactory global total lead removal efficiency for under-the-sink devices containing SBAC filters.

Finally, for all of the POU devices examined in test 4, stagnation was not found to create any POU filter breakthrough. However, the authors believe that the accumulation of lead particles in POU filters and the effect of stagnation warrant further investigation. Few studies are available on the efficiency of these devices for particulate lead removal. The use of prefilters might be considered in the case of high-particulate-lead concentrations (Boyd *et al.* 2008a, Boyd *et al.* 2008b). POU devices may represent cost-effective short and long-term solutions for large buildings facing lead issues resulting from long stagnations and large volumes of internal plumbing.

4.4.5 Removal/addition of other metals by pour-through POU filters (Figure 4-5, Table 4-4)

Overall, metal concentrations remained below most drinking water guidelines and standards: the USEPA action level of 1,300 µg/L for Cu (maximum observed: 130 µg/L) and the WHO provisional guideline of 20 µg/L for Ni (maximum observed: 1.5 µg/L). Residual Cr reached 38 µg/L, which is below the USEPA MCL of 100 µg/L but close to the Canadian MAC of 50 µg/L. However, this high value corresponded to Cr-spiked influent water. Cu was removed effectively for all the influent concentrations tested and did not show any decrease in efficiency during the entire POU lifetime, in accordance with Gulson *et al.*'s observations (1997) for similar devices. The trend of Ni levels versus filtered water was not observed for other metals, suggesting that either Ni is more sensitive to saturation of the filter material or it is desorbed from the filter material. The affinity of CX resin for a given cation depends on its valence, hydrated radius, complex formation, functional group reactivity, and the ionic strength of the solution. The resulting expected order of selectivity for the cations measured is $Pb^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+}$ (no data for Cr), making Pb the preferred cation and Co the less-readily retained (Chen *et al.* 2006). Ni cations should have higher affinity than Cu cations; however, the opposite trend was observed. These differences probably reflect the presence of complexes that change the order of selectivity, especially for Cu, Ni, and Co the resin. This could also be caused by Cu levels in the influent water, which were higher than those of Ni. Ag release detected in filtered water (11–43 µg/L) is in agreement with a previous study on similar POU devices. Gulson *et al.* (1997) found variable Ag levels in the same range (first filtration ≤ 80 µg/L, subsequent filtrations ≤ 40 µg/L), although the current study did not find higher Ag release at the beginning of the POU lifetime. However, filtered water was analyzed in tests 1 and 3 after two batches of water had passed through the filter, in accordance with the manufacturer's recommendations; Gulson and co-workers analyzed the first batch of filtered water. Ag is not considered hazardous to health; however, a secondary MCL of 0.10 mg/L has been set by the USEPA. Ag levels measured in the effluent water were 2–10 times lower than this MCL and so did not cause any concern.

4.4.6 Effect of POU on water quality (Figure 4-6)

Passage of water through the pour-through POU devices and stagnation resulted in significantly lower pH levels. This study suggests that the pH decrease is mostly the result of CX resin action, simply the exchange of ions that control pH. In fact, CX is acidic and can exchange its hydrogen ions with cations from the water (Chen *et al.* 2006). Carbon dioxide incorporation is unlikely to create such a high decrease, given the short filtration time, the absence of cartridge opening, and the absence of any stagnation of the sampled water during test 4. The additional pH depletion in test 2 could result from nitrification. Residual chlorine was removed by all POU devices, increasingly so with greater carbon content in those using SBAC, as expected. Turbidity removal was not as high as expected for SBAC devices with NSF-42 certification for class 1 particles (0.5–1.0 µm). However, turbidity can be created by particles smaller than 0.5–1.0 µm. The unchanged turbidity for pour-through POU filters is explained by the absence of a physical barrier for particles < 30 µm in size (NSF-42, class 5). Moreover, the highest turbidity values were observed in effluent water of device G, which is not NSF-42-certified for particle removal (Figure 4-1). Finally, nitrification created in the filters was not found to affect lead release. Further research is needed because GAC combined with chloraminated distribution systems can cause nitrification and a consequent decrease in pH and alkalinity, which could result in lead release into the filtered water (Zhang *et al.* 2008).

4.5 Conclusion

Pour-through POU devices were the most efficient for removing dissolved lead because of the presence of CX resin. However, if lead particles are retained by the filter media, they can be released or the filter media can leach them into the filtered water. Other POU devices tested consisting of an SBAC filter, overall, reduced dissolved lead effectively and removed particulate lead extremely well. Some of these devices slightly exceeded the NSF threshold of 10 µg/L; however, the testing conditions differed from those of the NSF. The accumulation of the tested particles (PbO_2) in POU filters using SBAC was not associated with lead release from the devices. Copper was removed effectively by pour-through POU devices for any concentration tested. Silver levels detected in effluent water were below the secondary MCL of 0.1 mg/L. Pour-through POU devices decreased the pH, maintained turbidity, and removed chlorine less efficiently than the other devices.

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CHAPITRE 5 PUBLICATION #4: POUS IN LARGE BUILDINGS: LEAD REMOVAL AND WATER QUALITY

Ce chapitre présente une étude sur le plomb dans l'eau du robinet des grands bâtiments. En effet, les grands bâtiments tels que les écoles et garderies peuvent présenter des concentrations de plomb majeures car ils combinent deux facteurs aggravants pour le plomb dans l'eau du robinet: un grand volume de tuyauterie interne, et de très longs temps de stagnations. Ils constituent donc des cas potentiels d'exposition élevée au plomb, très spécifiques, et différents des résidences. Ils sont à considérer puisque les enfants de 6 ans et moins constituent les populations les plus vulnérables au plomb et peuvent occuper de tels bâtiments de façon quasi permanente (écoles, garderies, services pédiatriques d'un hôpital). La présente étude fait d'abord l'état des concentrations de plomb dissous et particulaire dans un grand bâtiment (distribution, source, occurrence). Ensuite, l'efficacité des dispositifs au point d'utilisation comme solution de réduction du plomb dans l'eau du robinet de ces bâtiments est évaluée selon les habitudes de consommation spécifiques à ces bâtiments. Enfin, l'effet de tels dispositifs sur la qualité de l'eau des grands bâtiments a été évalué. Cette étude a été soumise pour publication dans le journal *Journal of American Water Works Association*, et récemment acceptée avec révisions mineures.

POUs IN LARGE BUILDINGS: PB REMOVAL AND WATER QUALITY

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ABSTRACT

High Pb levels have been reported in the tap water of large buildings. This is a growing concern for schools and daycare facilities, because children are particularly vulnerable to Pb exposure. Point-of-use devices (POUs) are a useful remediation solution that can be applied immediately. To investigate the performance of POUs in the usage patterns typical of large buildings, they were installed in a federal government building in which high levels of dissolved and particulate Pb had been measured. Pb was efficiently removed over the one year period of the study, although materials downstream of the POUs slightly increased total Pb levels at the tap. Moreover, while measurements of HPCs, and total and live bacteria on the POU material itself showed no significant colonization, small but significant increases in viable bacteria at the tap suggest that colonization occurred in the piping and tap downstream of the POUs.

5.1 Introduction

High lead (Pb) concentrations were measured at the tap in schools in North America, and can be explained by two specific characteristics of large buildings: long stagnation times and a large volume of premise piping containing Pb-bearing materials, such as brass fixtures and faucets, fountains, and solders (Boyd *et al.* 2008a, Elfland *et al.* 2010, Triantafyllidou & Edwards 2009). Concerns over high Pb levels in schools are growing, since Pb can cause irreversible neurodevelopmental effects on children, even at blood lead levels far below current action levels (Jusko *et al.* 2008). Recently, the European Food Safety Authority has challenged the provisional tolerable intake of 25 µg Pb/kg bw/wk, mainly based on the cognitive effects of Pb in children. In the United States, the Lead Contamination Control Act (LCCA) was implemented by the US Environmental Protection Agency (USEPA) to reduce Pb at the tap in schools and daycares. The LCCA suggests a two-step sampling program to detect Pb issues, find the sources of Pb, and propose remedial measures. The first step is to take a 1st flush sample (250 mL) after at least 8 hours of stagnation. If the Pb content exceeds 20 µg/L in the sample, the second step is to take a follow-up sample after letting the water run for 30 seconds. The comparison between the initial and the follow-up samples provides an indication of the Pb source. Finally, remediation methods are proposed, such as the replacement of Pb-bearing materials or the installation of point-of-use devices (POUs) (USEPA 1994a). In Ontario (Canada), Regulation 243/07 specifies mandatory monitoring, as well as daily flushing, in every school and daycare facility. First flush samples and 30-35 min stagnation samples are collected during the summer, in older parts of the building, every year or every 3 years, depending on the Pb levels recorded in the building. Flushing is performed at the tap at the end of each branch of pipe (5 min), and at every tap used by children (≥ 10 s) (Government of Ontario 2009). Finally, in Canada, a new guidance document recommends a two-step protocol for non residential buildings which is similar to the LCCA, with a 20 µg/L threshold level to proceed to corrective action. POUs are also suggested as a remediation method (Health Canada 2009).

Several types of POU are currently available, including pour-through, tap-mounted, and under-the-sink versions, some of them certified NSF-53 for total Pb removal. In 2007, following modification to the NSF-53 Pb testing protocol, several pour-through devices lost this certification. This is because pour-through POU media, a mix of granular activated carbon and ion-exchange resin, remove dissolved Pb efficiently, but their ability to remove particulate Pb is limited. By contrast, POUs using a solid block of activated carbon (SBAC, or carbon block) of fine porosity are better suited to removing both forms of Pb (Deshommes *et al.* 2010c). Typically, two approaches are taken to test the efficiency of POUs in removing Pb at the tap: an accelerated test alternating preset conditions of flow and stagnation (e.g. NSF-53 certification protocol), or a field demonstration under realistic water usage patterns. Boyd *et al.* (2005, 2008a, 2008b) investigated the efficiency of some under-the-sink POUs in reducing high Pb levels in drinking water fountains at Seattle schools. Several brands of POUs were tested, containing a 5 µm prefilter and activated carbon media, some NSF certified for Pb removal and some not. Overall, Pb levels were reduced to ≤ 11 µg/L in all but one source where the POUs were tested (≤ 29 µg/L), but brass elbows (3-8% Pb) downstream of the POUs contributed to raising Pb levels at the tap. Another accelerated pilot study revealed that under-the-sink POUs continue to remove total Pb levels to over 120% of the manufacturer's prescribed capacity, and that particulate Pb was removed more efficiently than dissolved Pb (Deshommes *et al.* 2010c). One concern about POUs is the bacterial colonization of the material they contain. Indeed, it has been documented that culturable bacteria could proliferate on activated carbon filters, and therefore potentially aggravate the quality of POU effluent water (Tobin *et al.* 1981). In addition, Su *et al.* (2009) showed in-device and post-device colonization by heterotrophic plate counts (HPCs) during an accelerated laboratory study on carbon block POUs, with accumulation of biofilm in dead end spaces. This colonization resulted in an increase in HPCs in the effluent by a factor of 2 to 5.

Although POUs are recommended as a remediation option for schools, limited information is available on their application in large buildings. Further investigation appears necessary to characterize long-term POU removal efficiency for dissolved and particulate Pb under realistic usage patterns, as well as the contribution of materials installed downstream of POUs. Moreover, the long-term impact of installing POUs on the microbiological quality of tap water in such buildings has yet to be evaluated. With these limitations in mind, the objectives of this study were: (1) to estimate the efficiency over a period of one year of an under-the-sink carbon block POU for the removal of dissolved and particulate Pb in a large building; (2) to evaluate whether or not long stagnation times can lead to water quality issues and to Pb breakthrough; (3) to estimate the potential of materials downstream of POUs to contribute to raising Pb levels in tap water; and (4) to assess whether or not installing POUs decreases the microbiological quality of the tap water compared to other taps in the building.

5.2 Materials and methods

The large building studied was a federal penitentiary complex composed of several buildings (inauguration year > 1932), including cell blocks and administration buildings, as well as buildings dedicated to training and recreational activities. The distributed drinking water in these buildings had a mean pH of 7.5 and a mean alkalinity of 26 mg $CaCO_3$/L. Comprehensive sampling was initially carried out at 45 taps around the complex to include incoming water from the utility, bathroom, kitchen, and cell taps, as well as from drinking water fountains and a coffee maker. A 1st flush of 250 mL was collected after at least overnight stagnation. Then, a 50 mL aliquot of the sample was filtered on a 0.45 µm PVDF filter (Durapore HV, Millipore) using a 60 mL disposable syringe (BD, Cole Parmer). The 250 mL samples were analyzed for total metals, and the 50 mL aliquots for dissolved metals, namely: Pb, copper (Cu), zinc (Zn), iron (Fe), tin (Sn), cadmium (Cd), and antimony (Sb).

Five drinking water taps, used during the daytime only, were then selected for the installation of POUs considering results from the comprehensive sampling campaign. Two fountains (F2 &

F20) were selected in buildings 2 and 20 (sport activities, administration), and three kitchen sinks (S3, S7, & S14) were selected in buildings 3 (medical staff), 7 (prison guards), and 14 (administration). Before any POU was installed (Phase 1), the five selected taps were sampled weekly over four weeks, after overnight stagnation (~ 12 h) and after exactly 30 minutes of stagnation (250 mL sample, 50 mL filtered sample). Water was flushed for 5 minutes at the sampling taps prior to the stagnation periods. The 250 mL samples were analyzed for total Pb and total Fe (indicator of clogging), and the 50 mL filtered samples were analyzed for dissolved Pb and dissolved Fe. The devices installed at the five taps were identical under-the-sink SBAC POUs, supplied with a separate chrome-plated brass faucet dedicated to water consumption (Figure 5-1), which had previously been tested in Deshommes *et al.* (2010c) pilot study (POU A). All the POUs were installed using polypropylene (PP) tubing and valves that are NSF-61 certified Pb-free (June 2009). The PP valves were placed just upstream and downstream of each POU, so that the POU itself could be monitored. The separate faucet was installed only at the kitchen sinks, since fountains are dedicated to providing drinking water. In addition, a water meter was installed on the piping line upstream of the POUs to measure the number of liters filtered by each of them (Figure 5-2).

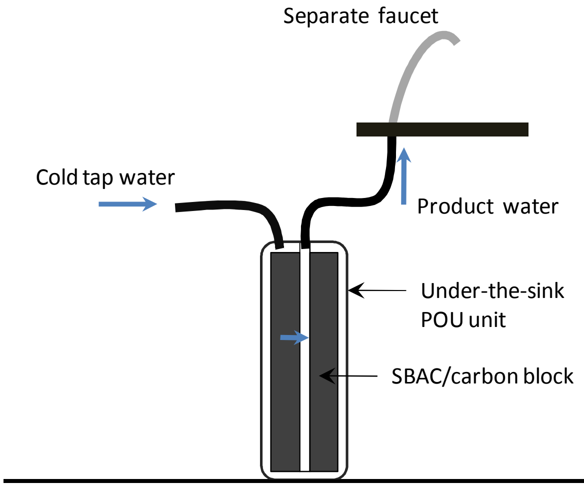
The efficiency of POUs for Pb removal was monitored over a one year period (Phase 2) by collecting 1st flush samples after 12 hours (12H) and after 30 minutes (30M) of stagnation, as in Phase 1 before the installation of the POUs. Sampling was conducted monthly between June and December 2009, and two additional samplings were performed in March and May 2010. For each sampling event, the first sample was collected at the valve upstream of the POU ("influent"), the second was collected at the downstream valve ("effluent"), and the third was collected at the tap ("tap") (Figure 5-2). Influent and effluent samples were analyzed for total and dissolved Pb and Fe (except for the March and May 2010 samplings, where only total Pb was measured), and tap samples were analyzed for total Pb only (Phase 2). After each sampling, the flow rate was measured as an indication of clogging, and the number of filtered liters was noted.

All the samples analyzed for metals were acidified at pH < 2 using nitric acid on the day of sampling, and held at 4°C for at least 24 hours before analysis, which is greater than the holding time specified by EPA 200.8 method (≥ 16 h). After digestion, a more stringent digestion (85°C, 2 h) was performed on a subset of 60 samples, in order to determine whether or not the initial digestion was sufficient to dissolve the total Pb in the samples. Total Pb levels measured using both digestions were well correlated (R^2=0.99) and not significantly different (p = 0.18). Therefore, the first digestion was applied to all the samples, except when turbidity exceeded 1 NTU (85°C, 2 h), or when particles/deposits were visible. Samples were analyzed using an ICP-MS (Elan 6100, Perkin Elmer) with detection limits for total metals of 0.1 µg Pb/L, 5 µg Fe/L, 0.1 µg Cu/L, 2 µg Zn/L, 1 µg Sn/L, 0.04 µg Cd/L, and 0.04 µg Sb/L.

Microbiological monitoring was mostly performed between October 2009 and September 2010. The upstream and downstream valves were first cleaned with 8% chlorine (Cl_2) solution to prevent any exterior contamination, rinsed, and allowed to dry for several minutes. Then, samples of 125 mL were collected, first at the upstream valve and then at the downstream valve, at 1st flush (1st FLUSH) and after 5 minutes of flushing (5MIN FLUSH). The temperature and pH of the water (portable pH meter sensION1, Hach), as well as residual Cl_2 (portable spectrophotometer DR/2400, Hach), were measured on a volume of water collected just after each collected sample. The POUs were sampled alternately, either for Total Organic Carbon (TOC), nitrates and nitrites (NO_3, NO_2), or for HPCs and *Bac*Light^{TM} LIVE/DEAD epifluorescence. All the samples were held at 4°C and analyzed within 12 hours following collection. TOC samples were collected in carbon-free bottles, preheated in a muffle oven at 500°C for 4 hours, and analyzed using the standard method 5310C and a Sievers 5310C Laboratory TOC analyzer. NO_3 and NO_2 were analyzed with an aliquot of the TOC samples, using ionic chromatography coupled with a UV detector (ICS-3000, Dionex, MA. 303 – Ions 3.1). Epifluorescence and HPC samples were collected in autoclaved PP bottles containing 0.125 mL of sodium thiosulfate to quench residual Cl_2. Viable and total counts of epifluorescence were performed according to the method described in Boulos *et al.* (1999). HPCs were measured using an R2A agar medium and an incubation period of 7 days at 20°C (standard method, 9215D).

Also, water from taps with an upstream POU was compared to water from taps without an upstream POU in the buildings, in terms of TOC, HPCs, and total and viable bacteria (March-May, 2010). 1st FLUSH and 5MIN FLUSH samplings were performed, but only at the consumption taps. Prior to these sample collections, the volume of water between the POU and the tap was evaluated, so that the water collected in the samples (125 mL) included at least some of the water from the POU's interior core.

At the end of the study, a POU was removed and split into two parts (September 2010). A small mass of 0.1 g was scraped off the surface at the entry, in the middle, and at the exit of the carbon block. It was then diluted and blended in 100 mL of trisbuffer (0.01M), peptone (0.01%), and Zwittergent solution, according to the homogenization procedure described in Camper *et al.* (1986). Samples were analyzed for HPCs and using *Bac*Light$^{\text{TM}}$ epifluorescence. Finally, sections of the POU were cut, dried, and analyzed using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS) (JEOL JSM-7600TFE for photographs, and JEOL JSM-840A equipped with an EDS detector for chemical analysis).



- NSF-53 certified for Pb
- NSF-42 certified for particulate class I (0.5 to < 1 μm)
- SBAC (carbon block) ~180 cm^3
- POU interior core ~14 mL
- Capacity: 2,840 L
- Prescribed lifetime: 6-12 months
- Prescribed water temperature: 4-38°C
- Pb removal (claimed): > 99%
- Filtration under pressure
- Service flow: ~2 L/min
- Separate faucet in chrome-plated brass

Figure 5-1. Characteristics of the POU tested. Adapted from Deshommes *et al.* 2010c.

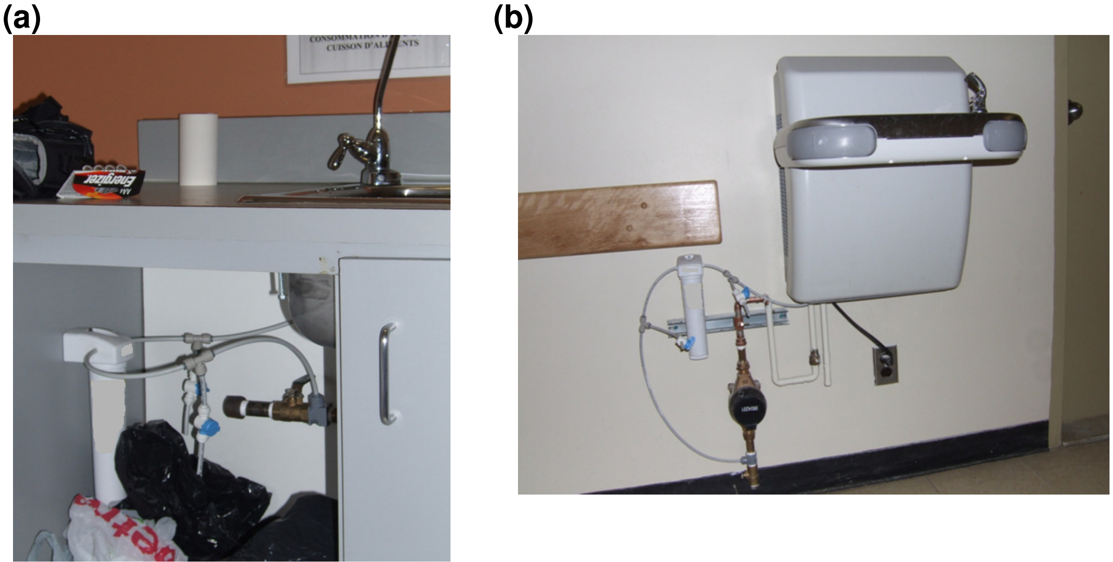


Figure 5-2. Installation of POUs for the field study at the penitentiary facility. (a) POU installed under a kitchen sink, with the separate tap; and (b) POU installed at a drinking water fountain.

5.3 Results and discussion

5.3.1 System-wide assessment of metal levels and forms

Figure 5-3 (a) summarizes the metal concentrations for the 45 taps. Concentrations of total Pb, Zn, and Cu were elevated and highly variable, with median values ranging from 100 µg/L for Pb to 1,200 µg/L for Cu. Although generally modest (median: 43 µg/L), total Fe varied widely, from 2.5 to 1,948 µg/L for the 10th and 90th percentile respectively. Total Sn levels remained mostly low (median: 1 µg/L), with some spikes as shown by the 90th percentile at 50 µg/L and the maximum at 5,000 µg/L. Finally, Cd and Sb were low, compared to other metals, but Cd concentrations exceeded the 0.005 mg/L EPA standard in five samples. The 45 points selected included nine basement taps connected to the main cast iron pipes leading to copper risers. These taps actually simulated the dead ends of the main feeder pipe that were infrequently used. The highest concentrations were recorded at these taps, with maximum total levels reaching 192,000 µg Fe/L, 23,000 µg Pb/L, 23,000 µg Cu/L, 5000 µg Sn/L, 1,120 µg Zn/L, 11 µg Cd/L, and 8 µg Sb/L. Generally lower, but still high concentrations of 32,300 µg Zn/L, 3,900 µg Cu/L, 1,870 µg Fe/L, 1,000 µg Pb/L, 160 µg Sn/L, 21 µg Cd/L, and 5 µg Sb/L were measured at the remaining taps. This can be explained by the low frequency of usage of these taps and the fact that flushing was not conducted prior to this comprehensive sampling campaign. The cumulated stagnation times before sampling may have been significantly higher than an overnight stagnation, increasing the metal release potential. In addition, these taps were not chrome-plated, so the brass was directly exposed to water. Although not designed for drinking water consumption, such taps can reflect the potential of metal release at taps or dead end sections rarely, or intermittently used in a large building.

Figure 5-3 (a) also shows the median levels of particulate metals, and it can be observed that Fe and Sn were present mainly in particulate form. A significant fraction of particulate Pb was measured: medians ranged from 20 to 24 µg/L, including (N=36) or excluding (N=45) basement taps, and particulate Pb was strongly and significantly correlated to total Pb ($R > 0.99$, $p < 0.05$), unlike dissolved Pb ($p > 0.05$). High particulate Cu levels were also observed in some cases (median: 251 µg/L). Median particulate concentrations suggest that Zn was mainly dissolved, but some spikes were measured, and not at the basement taps in particular, the 90th percentile and the maximum for particulate Zn being 361 and 1,300 µg/L respectively when these nine taps were excluded. Finally, the amounts of particulate Cd and Sb were, in general, negligible (≤ 1 µg/L), except in the basement (≤ 11 µg/L).

The Pearson correlation matrix for total metals, excluding basement taps, showed that total Pb was significantly ($p < 0.05$) positively correlated with total Zn ($R = 0.68$), Fe ($R = 0.63$), Sn ($R = 0.53$), Cd ($R = 0.43$), and Sb ($R = 0.38$), but not with Cu. Similar correlations were observed when inlet taps were included, except for Zn (no significant, $p = 0.85$) and Cu (significant, $R = 0.80$, $p < 0.05$). The extremely high levels of metals recorded, the correlation between these concentrations, and the absence of any Pb pipe suggest that there are multiple sources of Pb in this building, with brass being the dominant one. Indeed, brass can contain 2-8% Pb, and possibly more, at some inner surfaces of the alloy (Elfland *et al.* 2010). In addition, there were a large number of brass fixtures in these buildings, especially in the piping connections immediately upflow of the cells. Total Pb levels could not be correlated to total Cu when the basement taps were excluded, although they were correlated with total Zn and Sn. This may indicate brass dezincification (Zhang & Edwards 2011). However, Cu concentrations were correlated to total Pb when the basement taps were included. Copper piping is used for the building risers, both for splitting the flows between the various levels and for connections. This abundance of Cu could mask a significant association with Pb when only the taps downstream of copper piping are considered. The correlation of Pb concentrations to concentrations of Sn (mostly particulate), Cd, and Sb may be partly attributed to Pb release from brass, but also from the leaded solders that were still present in some parts of the buildings and that can contain such elements. Actually, the galvanic corrosion of Pb/Sn solders linking copper pipes has been shown to be a significant cause of Pb and Sn release in tap water (Subramanian *et al.* 1995). Moreover, some studies reported significant amounts of solder particles trapped behind the aerator taps in homes, which indicates that solder release in particulate form is likely (Deshommes *et al.* 2010a, Triantafyllidou *et al.* 2007). Finally, the Pb-Fe correlation may indicate the presence and sporadic detachment of iron deposits/particles into the piping, and the adsorption of dissolved Pb onto those deposits/particles over time (Deshommes *et al.* 2010a). Since most of the galvanized steel piping had been replaced by copper in the buildings in our study, such scales might have formed following Fe release from the cast iron mains.

Figure 5-3 (b) shows the total, particulate, and soluble Pb levels measured in the 1st flush at the drinking water taps in the building, namely the kitchen, bathroom, cell, and fountain taps, and the feed pipe to the cafeteria coffee maker. The total Pb levels were noticeably high, especially for the kitchen and cell taps, with a minimum of 40-48 µg/L, twice the threshold level prescribed by Health Canada for applying remedies. Pb concentrations at bathroom taps ranged from 7 to 510 µg/L, and from 1 to 120 µg/L at fountain taps. Finally, 16 µg Pb/L was measured at the coffee maker, mainly in particulate form. Notwithstanding the differences in sampling protocol, the soluble Pb levels in this study are comparable to those measured in homes with up to 30 meters of lead service line in another distribution system, but significantly higher in terms of particulate Pb (Cartier *et al.* 2011, Deshommes *et al.* 2010a). Triantafyllidou & Edwards (2009) also report dramatically high Pb levels at some taps in schools in the United States, which was explained by a combination of three factors: the corrosiveness of the water, the presence of Pb-bearing materials, and the long stagnation times (Elfland *et al.* 2010).

The mean particulate Pb fraction was about twice the soluble fraction at the kitchen and cell taps, contributing to the extremely high total Pb levels measured at those taps, as compared to the bathroom and fountain taps. The cell taps were not equipped with aerators, a configuration favorable to the passage of particulate Pb (high flow and absence of a mesh strainer). In contrast, lower average particulate Pb (24 µg/L) was measured at the fountain taps, which did not have an aerator either. However, flow rates were significantly lower (≤ 2 Lpm) at the fountains than at other taps (≤ 4 Lpm), and particulate Pb has been shown to increase with this parameter (Triantafyllidou & Edwards 2009). In light of these data, it is clear that particulate Pb can significantly increase the total Pb levels and may substantially increase exposure at the tap. However, the health risk associated with the ingestion of Pb particles from drinking water still needs to be fully determined, taking into account two aspects: the frequency of particulate Pb release, and the bioaccessibility of these particles. Previous investigations on laboratory generated Pb particles have shown that bioaccessibility can vary widely, depending on the particle type (Deshommes *et al.* 2010b, Triantafyllidou *et al.* 2007). Finally, considering the levels of particulate Pb levels reported, a heated, strongly acid digestion should be mandatory, in order to correctly assess the concentration of total Pb in the samples collected. The reason for this is that traditional EPA 200.8 digestion can underestimate total Pb levels, owing to the incomplete digestion of some particulate Pb forms (Triantafyllidou *et al.* 2007), although this was not observed in this present study, perhaps due to the long holding times applied (2-5 days in average) and/or the forms of Pb particles present. A thorough characterization of total Pb levels in large buildings appears to be extremely urgent in the case of schools and daycare facilities, because of their vulnerable populations.

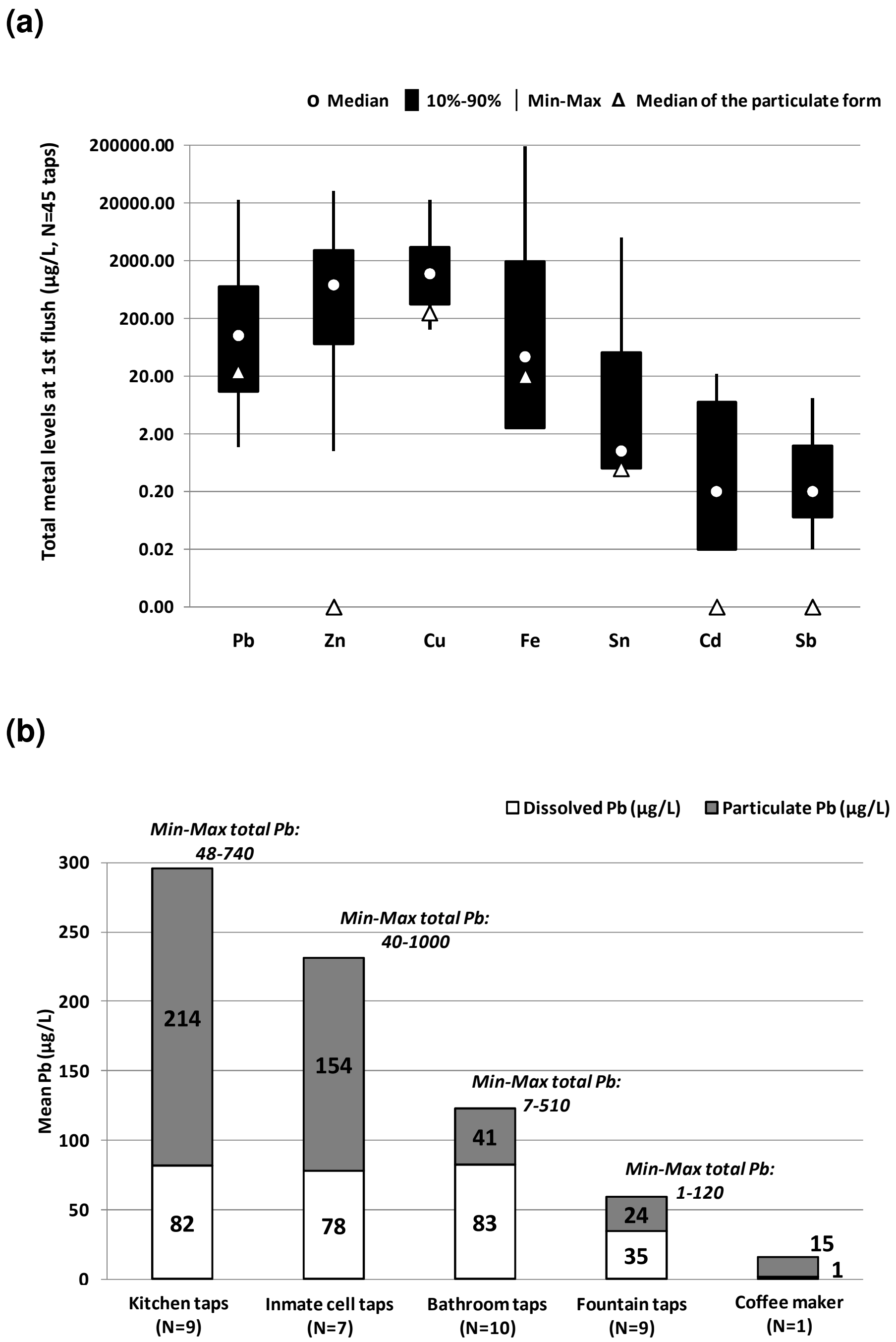


Figure 5-3. 1st flush results for samples collected after at least overnight stagnation at 45 taps in the large building: (a) total metal levels at the 45 taps; (b) mean concentrations of particulate and soluble Pb measured at the taps dedicated to drinking water consumption (N=36).

5.3.2 Total, particulate, and dissolved Pb removal using POUs

The three sinks and two fountains were sampled over one year after POU installation. Figure 5-4 (a) presents the range of Pb concentrations at the POU influent and effluent valves and at the tap after overnight stagnation (12H), while Figure 5-4 (b) presents the results after a shorter stagnation time of 30 minutes (30M). As we found with the screening sampling, total, dissolved, and particulate Pb concentrations increased significantly after overnight stagnation (Figure 5-4 (a)). A median of 111 µg/L and a maximum of up to 270 µg/L were recorded for total Pb at the upstream valves of the five POUs (influent). Total Pb was mostly composed of soluble Pb, since the 10th and 90th percentile ranges were 66-190 µg/L for soluble Pb and 84-237 µg/L for total Pb. However modest in comparison, the 13 µg/L median for particulate Pb represents 65% of the 20 µg/L level of concern for large buildings, and values up to 96 µg/L were measured. After filtration by the POUs, the Pb levels decreased dramatically, with total Pb $\leq$ 2.2 µg/L, dissolved Pb $\leq$ 1.9 µg/L, and particulate Pb $\leq$ 0.9 µg/L (effluent) (Figure 5-4 (a)). Clearly, POUs installed at the five taps studied were capable of efficiently reducing both forms of Pb to below acceptable levels over the one year monitoring period.

Although total influent Pb concentrations were slightly higher, the total Pb levels in the effluent water were significantly lower than those measured for the same device (A) using an accelerated pilot study setup fed by a different tap water over 120% of the POU lifetime ($\leq$ 11 µg/L) (Deshommes *et al.* 2010c). However, as indicated by cumulative flow meters, the POU capacities were far from exhausted by May 2010, as only 25-43% and 15-17% of the filters' prescribed lifetimes were spent for the sinks and fountains respectively. The cumulated filtered POU volume is unlikely to be the factor explaining the improved removals observed at the penitentiary. In fact, the lower removals observed previously with the same POU did not decrease over the time of usage. This raises the possibility of other causes, such as water quality, in particular lower alkalinity, hardness, and pH, and higher levels of natural organic matter in this study, which may influence adsorption by the SBAC. More importantly, usage patterns may be an important factor, as lower performances were observed using accelerated, nearly non-stop flow testing conditions (Deshommes *et al.* 2010c). Another factor to consider is the types of particulate Pb forms present. PbO_2 particles were spiked in the pilot study. In the field study, a mixture of particle types was released from brass, solders, and Fe deposits, according to the screening sampling results.

Influent levels for the 30M sampling were lower than those measured in the 1st flush, but still high (Figure 5-4 (b)). Even after this shorter stagnation time, the concentrations of total Pb (mainly in dissolved form) in most of the samples exceeded the 20 µg/L level of concern (median: 26 µg/L), and reached up to 76 µg/L. Five minutes of flushing may not always be sufficient to lower the Pb concentrations at the tap at all points in a large building. This time depends mostly on the piping configuration and the length from the main to the tap, as well as the water usage pattern in the building. Therefore, water sampled after 30 minutes of stagnation may represent water from another section of the building piping, with varying prior stagnation time. Nevertheless, POUs efficiently reduced Pb levels to below 2.3 µg/L in 30M samples (Figure 5-4 (b)), which are comparable to those in 12H samples. Therefore, results from this study do not indicate a breakthrough of POUs following long stagnation times.

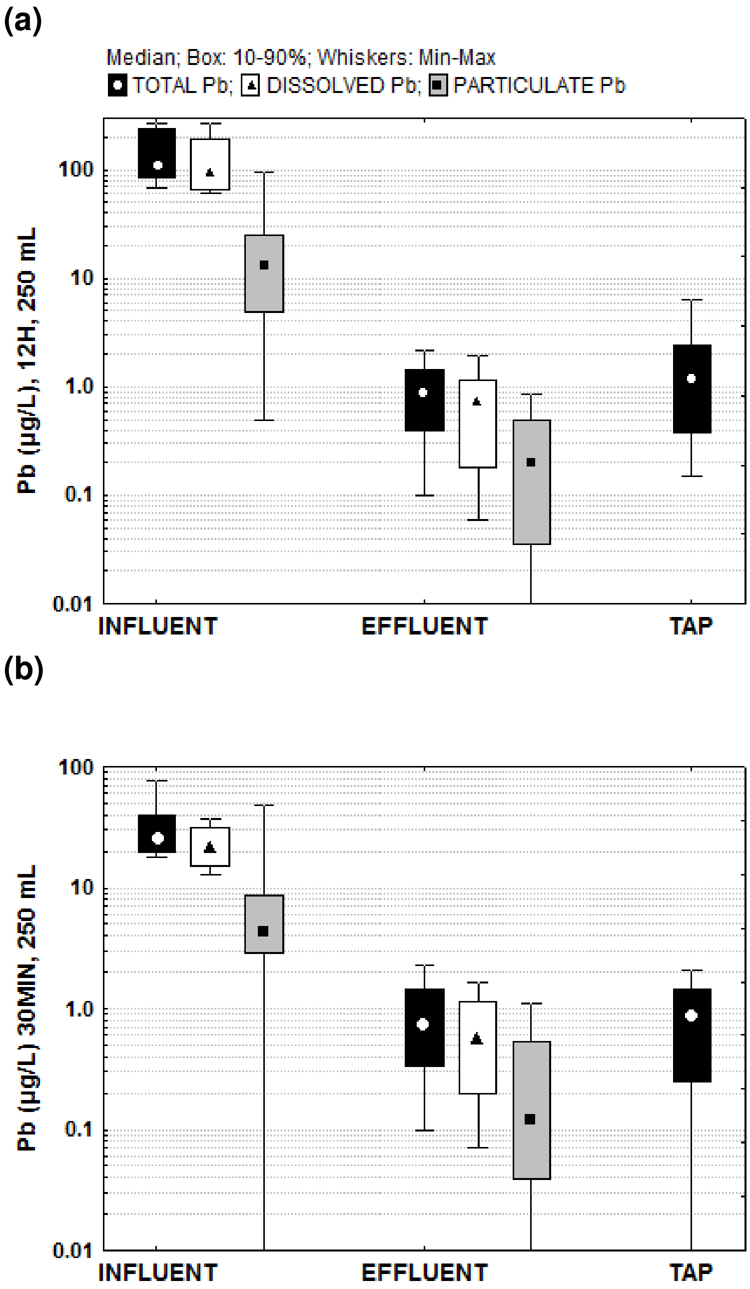


Figure 5-4. Total, dissolved, and particulate Pb measured (a) at first flush and (b) after 30 min of stagnation, at the influent and effluent valves of the POU, and at the downstream tap. Measurements over 1 year: N=50 for total Pb in (a), N=40 for total Pb in (b), and N=40 for dissolved and particulate Pb in (a) and (b).

5.3.3 Contribution of the downstream POU materials

Total Pb levels increased between the effluent valve (0.1-2.2 µg/L) and the consumption tap (0.2-6.3 µg/L) in the 12H samples (Figure 5-4 (a)). As the pipe connecting the POU to the fountain or the separate kitchen faucet was made of certified Pb-free PP, this increase can be attributed mostly to Pb released from the fountain and the separate faucet included in the POU package (sinks). Such an increase was not noted for the 30M samples (Figure 5-4 (b)). Therefore, the contribution of the downstream POU materials only becomes significant after long stagnation periods. The contribution of the fountain or the separate faucet presented in Figure 5-5 was evaluated by subtracting, for the same 12H sampling, the total Pb measured at the tap from the total Pb measured at the effluent valve. In general, fountains did not contribute to elevating the total Pb at the tap; however, sporadic Pb spikes were observed. Up to 5.7 µg Pb/L was recorded for F2, which is quite high, considering that the fountains tested were quite new (≤ 2 years old), and therefore not representative of the worst case, which is older fountains. Moreover, as the fountains were monitored monthly during the first six months of the study, spikes may have occurred between sampling events. Therefore, the contribution of the fountains may be underestimated in this study. The apparent sporadic contribution suggests that the Pb released from the fountain was mostly particulate Pb. Boyd *et al.* (2008b) had attributed sporadic high Pb levels from end-use brass plumbing components to the release of particulates triggered either by the movement of the valves in the components, or by the dezincification of these components. However, as only total Pb was measured in the tap samples, it was not possible to conduct further verification. Finally, it is possible that some spikes were not observed at either of the two fountains, owing to the configuration of their faucets. As the water flows up in fountain faucets, a fraction of the 1st flush tap water may not have been collected in the small opening of the 250 mL bottles used. Large-mouthed bottles are always preferable for Pb sampling; however, bottles of this type are not widely used in analytical laboratories (Triantafyllidou *et al.* 2007). Lead released from the kitchen taps was mostly attributable to the separate faucets provided by the manufacturer. Release was modest (medians 0.1-0.4 µg/L) with maxima reaching 0.7-1.3 µg/L (Figure 5-5). These results are in agreement with those of the previous pilot study using the same POU: under-the-sink POU A, supplied with a chrome plated brass faucet, showed slightly higher effluent Pb levels than under-the-sink POU B, which was supplied with a plastic faucet (Deshommes *et al.* 2010c). It was expected that this release would decrease over time; however, the contribution observed for the three new, identical separate faucets was variable and did not follow any trend. This was also observed by Sandvig *et al.* (2008), since Pb release, most probably from dezincification, varied within and between the faucets studied. This contribution can be considered to be low, but it is nevertheless quite ironic that this faucet is sold as an integral part of a POU claiming to reduce Pb levels.

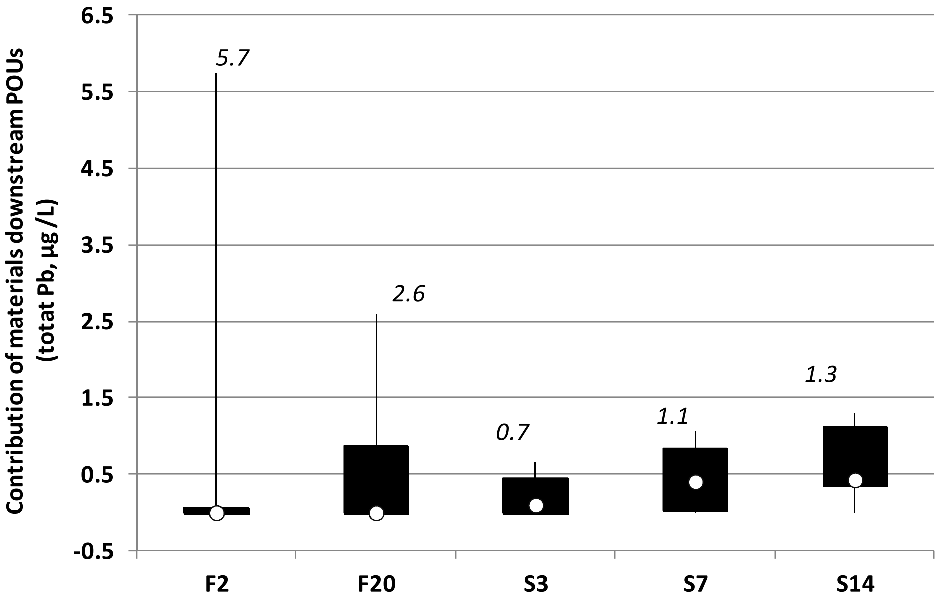


Figure 5-5. Contribution of the materials downstream of POUs to the elevation of total Pb levels measured at the tap for each fountain (F2, F20) and each kitchen sink (S3, S7, S14) studied. N= 18 for each box.

5.3.4 Behavior of POUs over time

Lead levels in POU effluent and at the tap remained stable over time. As mentioned before, usage at the monitored taps was insufficient to even approach the manufacturer's prescribed capacity within the one year period of the study. However, in a previous study, effluent Pb concentrations did not increase over 120% of the prescribed lifetime capacity of this same POU (Deshommes *et al.* 2010c). Therefore, the efficiency of the POU tested is not expected to decrease with longer usage within the prescribed recommendations. The flow rates measured at the five taps did not decrease over time, demonstrating no evidence of POU fouling. This is in agreement with the Fe levels measured in the POU influent, with total Fe ≤ 49 µg/L and particulate Fe ≤ 22 µg/L. Such concentrations are quite low, compared to those reported by Boyd *et al.* (2005), which caused premature clogging of the POUs (≤ 28 mg Fe/L). Therefore, for the large building studied, clogging was not an issue. However, as underlined by Boyd *et al.* (2005), care should be taken before installing POUs in buildings with a large amount of galvanized piping.

5.3.5 Contribution of the water meter

In order to estimate the volume of drinking water consumption in the building, a meter was installed on the piping ahead of every upstream POU valve. Meter readings showed that water was not frequently consumed in the buildings, in spite of the fact that there are people living in them. In fact, only 15 to 43% of the total capacity of the POU was exhausted after one year (426-1,221 L/year). This low consumption reflects the large number of taps installed for drinking water in the penitentiary, the reason for which is that taps must be available in any enclosed area (such as a cell). This is more than would be expected in a school building, but similar to how many there would be in a health care facility. Pb levels measured at the influent POU valve after POU installation (Phase 2) significantly exceeded the Pb levels measured at the taps (F2, F20, S3, S7, S14) prior to POU installation (Phase 1). Median total Pb levels increased by 81-92 µg/L for 12H samples, and by 15-23 µg/L for 30M samples (Figure 5-6). The steeper increase observed for the two fountains is attributed to the automatic flushing system activated every 4 hours by penitentiary staff during Phase 1. Automatic flushing was switched off when the POUs were installed (Phase 2). This significant increase in Pb, mostly in dissolved form (≥ 85% total Pb in 80% of the samples), is attributed to release from the meter and its fixture installed at the end of Phase 1. The contribution of these brass materials was estimated by subtracting median Pb levels at the 1st flush prior to POU installation, to Pb levels at the 1st flush (12H) at the influent valve after POU installation. Only Pb levels from the three kitchen sinks were considered for this calculation, since the fountains were flushed automatically during Phase 1. Figure 5-7 shows the evolution of the contribution of the water meter after installation. The initial estimated contribution of this single element reached up to 219 µg/L and 206 µg/L of total Pb and dissolved Pb respectively, and decreased significantly after 6 months, total influent Pb levels dropping to 54-67 µg/L by December 2009. A spike in total Pb contribution was measured in late March 2010, and was attributed to the low frequency of sampling during this period (no sampling in the previous 3 months), allowing particles to accumulate behind the upstream valves. This could not be confirmed, however, since only total Pb was measured in the March and May 2010 samplings. The exterior materials of the water meter and its fixtures were sampled, digested, and analyzed with ICP-MS for total metals. Meters were made of low-zinc brass, with 6.3% Pb, 6.3% Zn, and 72% Cu by weight of surface, and brass fixtures contained 1.8% Pb, 35% Zn, and 52% Cu (total metal recovery: 88-93%). These levels of Pb content fall within the boundaries of existing regulations, but will fail to meet the recent amendment to the Safe Drinking Water Act (SDWA) that reduced the Pb content allowed in plumbing fixtures to 0.25% by 2014. This is consistent with findings from Sandvig *et al.* (2008), showing Pb release over the Lead and Copper Rule action level from new low-zinc meters containing 6.7% Pb. However, the total Pb release observed by these authors (up to ~ 23 µg Pb/L after 6 hours of stagnation, 250 mL) was considerably lower than the findings from this study, and stabilization was achieved at between 5 months and 4 years (Sandvig *et al.* 2008). Even for equivalent Pb levels, marked differences in release could be caused by the tendency of Pb to leach for different types of brass, especially for low-zinc brass, and variability between meters (Sandvig *et al.* 2008, Zhang & Edwards 2011). Higher Pb release could also be the result of high Pb content on the meter's interior surface, since Elfland *et al.* (2010) measured > 18% Pb on the internal surface of ball valves, whereas the exterior surface contained 6.6% Pb. Levels of up to 100 µg Pb/L in flushed water samples were attributed to these low-zinc brass valves. It must be noted that some conditions of this study were favorable to the identification of the Pb contribution of the meter and its fixtures. Typically, a water meter is installed on the service line at the point of entry of a building, not directly upstream of a consumption faucet. In addition, most regulatory compliance protocols prescribe a 1 L sample volume. The 250 mL samples in this study contained a significant volume of water from the internal meter (155-278 mL, Sandvig *et al.* 2008), and so there was limited dilution. Therefore, concentrations observed in field conditions of operation and sampling are likely to be lower, and the detection of significant contributions of meters may be more difficult. The extent of Pb release observed in this study and reported by others (Elfland *et al.* 2010, Zhang & Edwards 2011) strongly supports the implementation of stringent regulations for new water meters and for the composition of brass materials. It also raises the issue of managing the legacy of these installed meters.

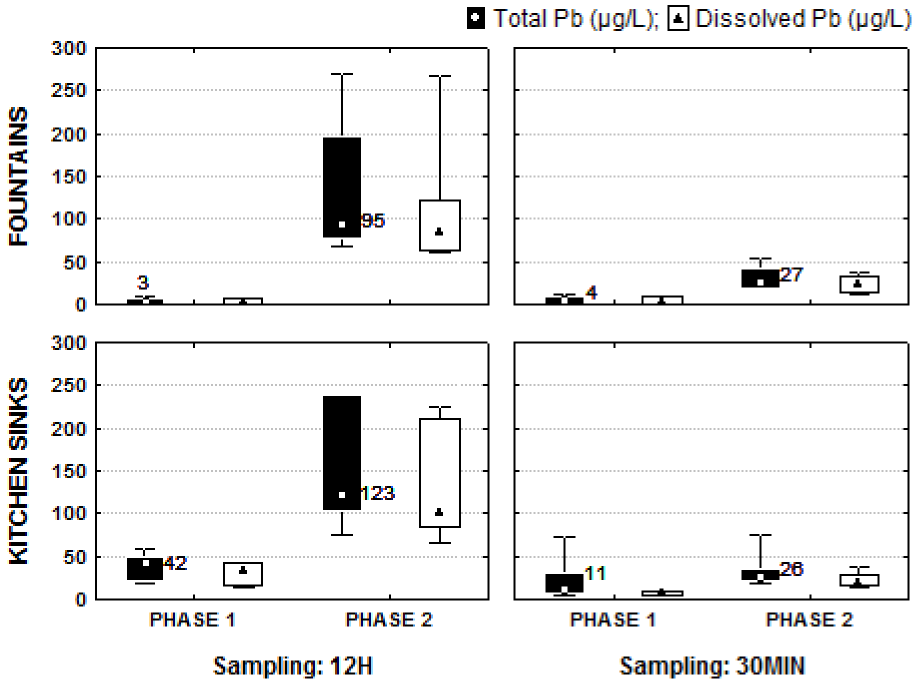


Figure 5-6. Total and dissolved Pb concentrations before water meter installation (tap water, Phase 1, N=40) and after water meter installation (influent POU water, Phase 2, N=90) for the 12H and 30MIN samplings, for fountains (automatic flushing in Phase 1) and sinks. Median; Box 10%-90%; Whiskers: min-max.

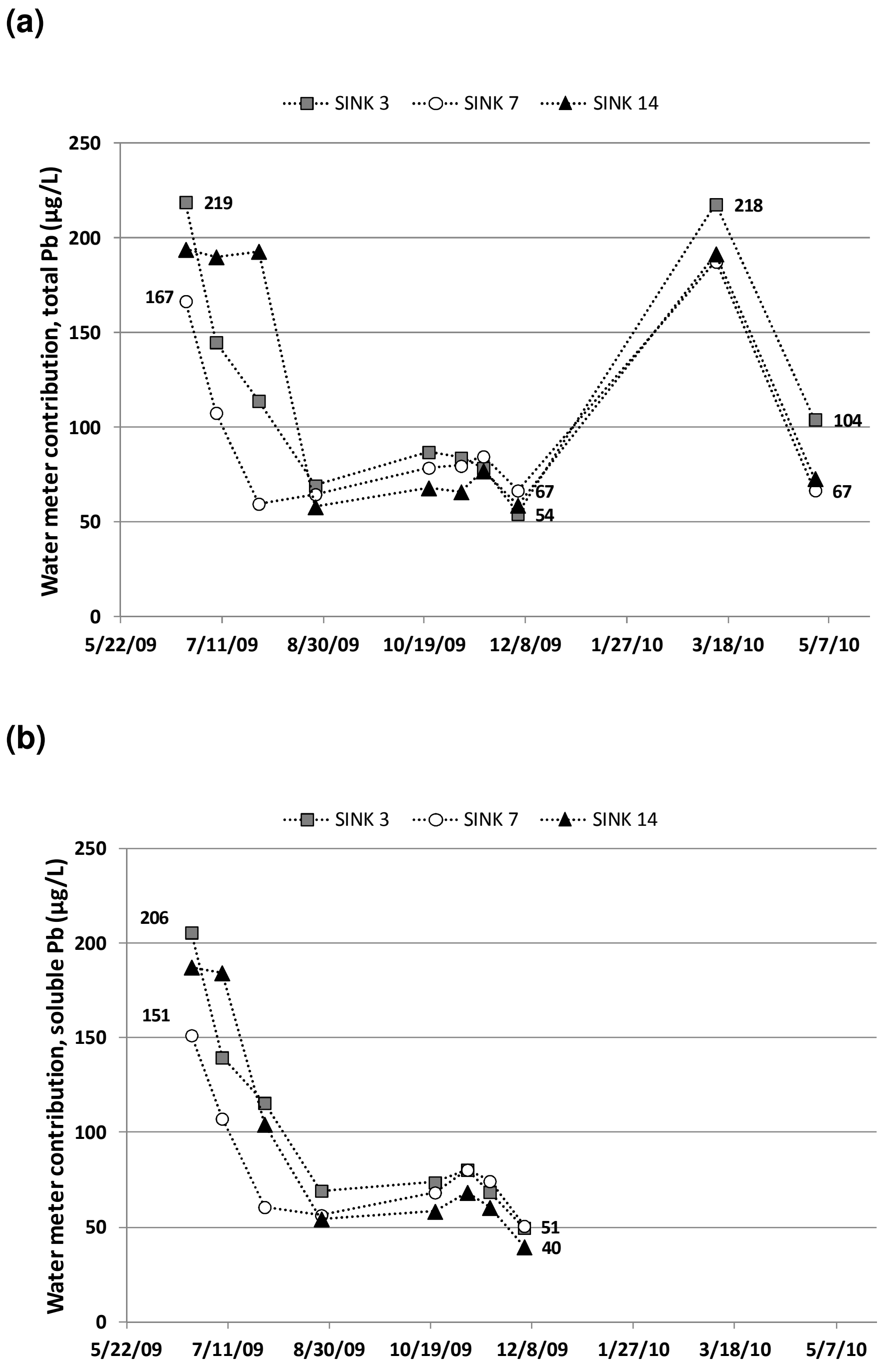


Figure 5-7. Estimated contribution of the water meter to the elevation of: (a) total Pb; and (b) soluble Pb concentrations, in the influent POU water of the three kitchen sinks.

5.3.6 Impact on tap water quality

Figure 5-8 and Figure 5-9 summarize the results of total and viable bacterial counts, HPCs, TOC, NO_2 and NO_3, in the influent and effluent, at 1st flush and after 5 minutes of flushing. As observed in Figure 5-8 (a), total and live bacteria increased after passage through the SBAC. Results are quite stable over time and show significant increases (~ 1 Log) after the POU at 1st flush and after 5 min of flushing ($p < 0.05$). This amplification could be the result of the progressive colonization of the POU (casing and SBAC) and its downflow piping, facilitated by the removal of residual Cl_2 in water by the POU (Cl_2 undetectable in the effluent). Such systematic amplification was not recorded for HPCs ($p \geq 0.1$) (Figure 5-8 (b)). HPC differences across the POU did not show any temporal trends, and variable increases were observed (-0.7 to +2.6 Log). However, they were highly variable over time in the 1st flush (up to 4.5 Log) and less so after flushing (up to 2.0 Log). In contrast, Su *et al.* (2009) measured a progressive increase in HPCs up to 1 Log/mL after a faucet-mounted SBAC POU, and the rise in HPCs occurred after a third of the POU lifetime. However, several differences between the testing conditions and possibly in the device configuration must be noted. These authors tested low flow rates, high temperatures, and long stagnation times, showing that temperatures of 30-40°C are linked to the most marked increases. Surprisingly, the SBAC did not remove Cl_2 residuals, and particulate removal specifications were not indicated. Similar variations were reported by Snyder *et al.* (1995): HPCs in general increased in the POU effluent fed with spring water by a factor of 0.20 to 0.86 times, depending on the season. The present study was conducted during three seasons (summer, fall, and winter), which may also explain such differences. Also, in the distribution system feeding the penitentiary, total direct bacterial counts have been reported to rise from 4.32±0.15 Log/mL in cold water (< 3°C) to 5.17±0.15 Log/mL in warm water (> 13°C); however, maximum HPCs do not vary seasonally, reaching about 4 Log/mL at long residence times, regardless of temperature, but rather directly, reflecting residual Cl_2 concentrations (Prévost *et al.* 1998). Moreover, Prévost *et al.* (1997) have shown that any delayed total direct count amplification in the main distribution system will occur during stagnation in the service lines if biodegradable carbon is available, with 1st flush total counts exceeding those from the feed pipe by 47-107%. In summary, for this distribution system, previous studies have shown that temperature directly influences the maximum level reached for total counts, while Cl_2 residuals determine the fraction of viable bacteria measured by plate counts and bacterial production. In the building studied, Cl_2 residual varied from not detectable to 0.9 mg/L. Therefore, the large variability in the HPCs measured in both the influent and the effluent reflects the variability in Cl_2 residuals (Figure 5-8 (b)). In contrast, while counts of total and viable bacteria in POU influents are in accordance with previously reported direct counts for this distribution system, POU effluent values are slightly higher, even after flushing, most probably resulting from the higher temperatures and longer stagnation times in the large building studied.

TOC decreased significantly between the influent and effluent of the POUs ($p < 0.05$) (Figure 5-9 (a)), but this reduction decreased from 66% in October 2009 to 22% in September 2010 (mean values). The adsorption capacity of activated carbon is expected to decrease progressively over time, although some partial bacterial regeneration may occur during prolonged stagnation. The observed TOC reduction could also be attributed to the consumption of its biodegradable fraction (BDOC) by bacteria colonizing the SBAC, casing, and downstream POU piping. The water treatment plant feeding this system uses post-ozonation and produces water with elevated BDOC (0.34-0.84 mg/L-C), the maximum consumption of which has been shown to vary in the 0.28-0.41 mg/L-C range in a service line (Prévost *et al.* 1997, Prévost *et al.* 1998). However, as shown by Prévost *et al.* (1997), this consumption of BDOC occurred within 6 hours in a relatively short service line, and is therefore most likely to take place in the internal piping upflow of the POU. Considering the low consumption at the POU points investigated, it is highly likely that the activated carbon was still removing TOC mainly through adsorption, rather than by biological degradation. This was further validated by analyses on the inlet and outlet surfaces of the SBAC. One POU was removed and examined at the end of the study (S7). The SBAC was highly compact and no visible biofilm could be observed, suggesting limited colonization. Unexpectedly, the results of HPCs and LIVE/DEAD bacteria assays performed on extracted and resuspended activated carbon from the SBAC were below detection limits. In addition, the SEM examination of a slice of the SBAC did not reveal any evidence of significant bacterial colonization of its outlet and inlet surfaces (Figure 5-10). The reason these results were unexpected is that early work had demonstrated that carbon-based devices are colonized by biofilm (Tobin *et al.* 1981). Also, based on the large increases (up to 4 Log) in HPCs in effluent, Daschner *et al.* (1996) concluded that significant biofilm is rapidly established (< 3 days), both in laboratory- and field-installed POUs, and warned of their potential health effects. It must be noted that the POU technology tested was granular carbon impregnated with silver ions.

Interestingly, they report that a 24 hour exposure to the silver ions released by the POU decreased the HPCs in the filtered water to background levels. Unlike a low porosity dry SBAC (0.5-1 µm), granular media provide multiple biofilm attachment sites throughout the filter volume, which are supplied with a flow of nutrients available for bacterial growth.

The findings of this study also differ from earlier reports by Su *et al.* (2009), showing significant colonization at the inlet surface of an SBAC. The limited level of colonization observed on and in the SBAC in this study may be caused by the bacteriostatic activity of metal accumulations and discrete inclusions in the carbon material. In fact, EDS spectrum revealed that these clusters contained Cu, Zn, Pb, Fe, Sn, and Mn (Figure 5-10 (a)). Such localized accumulations of metals on the POU material can be explained by the presence of spherical inclusions of Si/Ti oxides, which are visible in Figure 5-10 (b), and known to be Pb scavengers in the POU industry. The clusters and Si/Ti oxide inclusions were not observed in the middle section or outlet surface of the carbon block. Although copper was recognized earlier as an efficient bactericide, it is now established that copper stress merely induces a loss of culturability, but not a complete loss of viability (Dwidjosiswojo *et al.* 2011). However, elevated concentrations of metals accumulated on the SBAC tested have all been shown to inhibit growth ($Zn^{2+} < Cu^{2+} < Pb^{2+}$) and to be toxic ($Zn^{2+} < Pb^{2+} < Cu^{2+}$) to planktonic and attached bacteria (Teitzel & Parsek 2003). They most probably also contributed to limiting the colonization of the SBAC. No silver was detected, although it is commonly used as a bacteriostatic additive. In conclusion, our observations suggest that the increased colonization observed between the influent and the effluent of the POUs was not caused by the microbiological colonization of the POU cartridge and further breakthrough, but rather by the colonization of the downstream POU piping enhanced by the temperature of the room, stagnation, and the elimination of the Cl_2 residual. Finally, a small increase in nitrites was recorded at the same time as a decrease in nitrates through POUs (Figure 5-9 (b)). This could suggest the presence of denitrifying bacteria converting nitrates into nitrites, which would thereafter be rapidly converted into ammonia. However, considering that significant levels of metals inhibit denitrifiers, as well as the potential Cu release from the meters, reduction reactions catalyzed by Cu or other metals could have occurred in the POUs, as observed by Filimonov & Shcherbakov (2004).

The relative importance of the water quality changes observed can be best assessed when comparing taps with and without POUs after stagnation. HPCs, total and live bacteria, and TOC measurements were performed in parallel at the taps with an upstream POU and compared to paired measurements at similar taps without an upstream POU. Comparison taps were selected according to the following criteria: same type (kitchen/fountain), building, and floor, and a location as close as possible to the tap with a POU for comparison purposes. The intention was to compare similar conditions of temperature, Cl_2 residual, and upstream piping colonization. Table 5-1 presents the water quality results at taps with and without upstream POUs. This field comparison supports findings from the pre and post POU monitoring in terms of magnitude (Figure 5-8 & Figure 5-9 (a)): HPC counts did not significantly differ, while live and total bacteria increased slightly at taps equipped with a POU, and more TOC was removed in the presence of the carbon blocks. Again, it can be concluded that, if total and viable bacteria are considered, the steady state colonization of the tap and the connection piping closest to it increases with a POU, rather than based on HPC count.

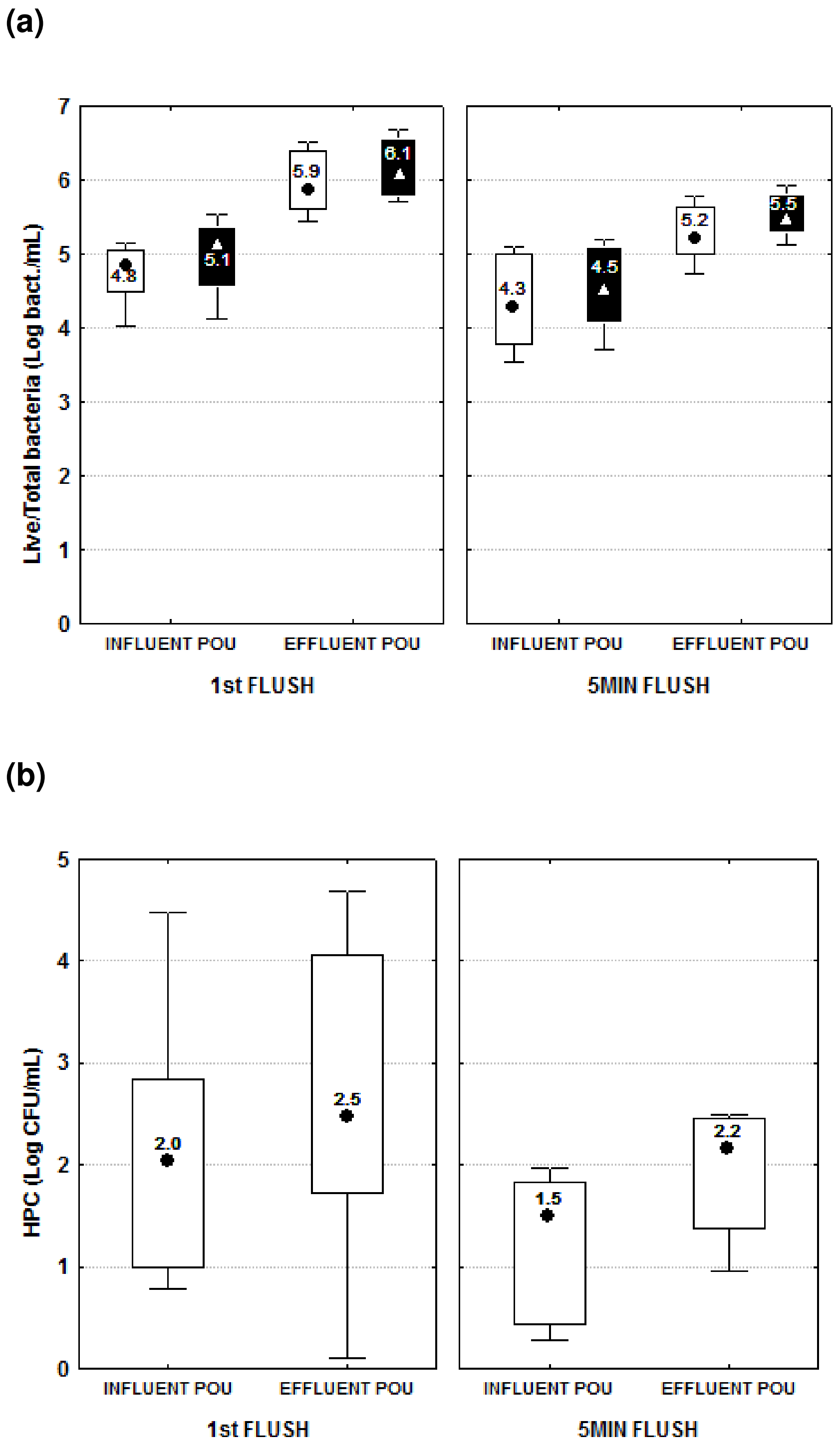


Figure 5-8. Box plots of influent and effluent samples collected between October 2009 and September 2010 at 1st flush (left) and after 5 min of flushing (right) of: (a) live bacteria (white boxes) and total bacteria (black boxes); and (b) HPC. For each box at 1st FLUSH: N=22 (live/total bacteria), N=16 (HPC). For each box at 5MIN FLUSH: N=14 (live/total bacteria), N=9 (HPC). Median; Box: 10-90%; Whiskers: Min-Max.

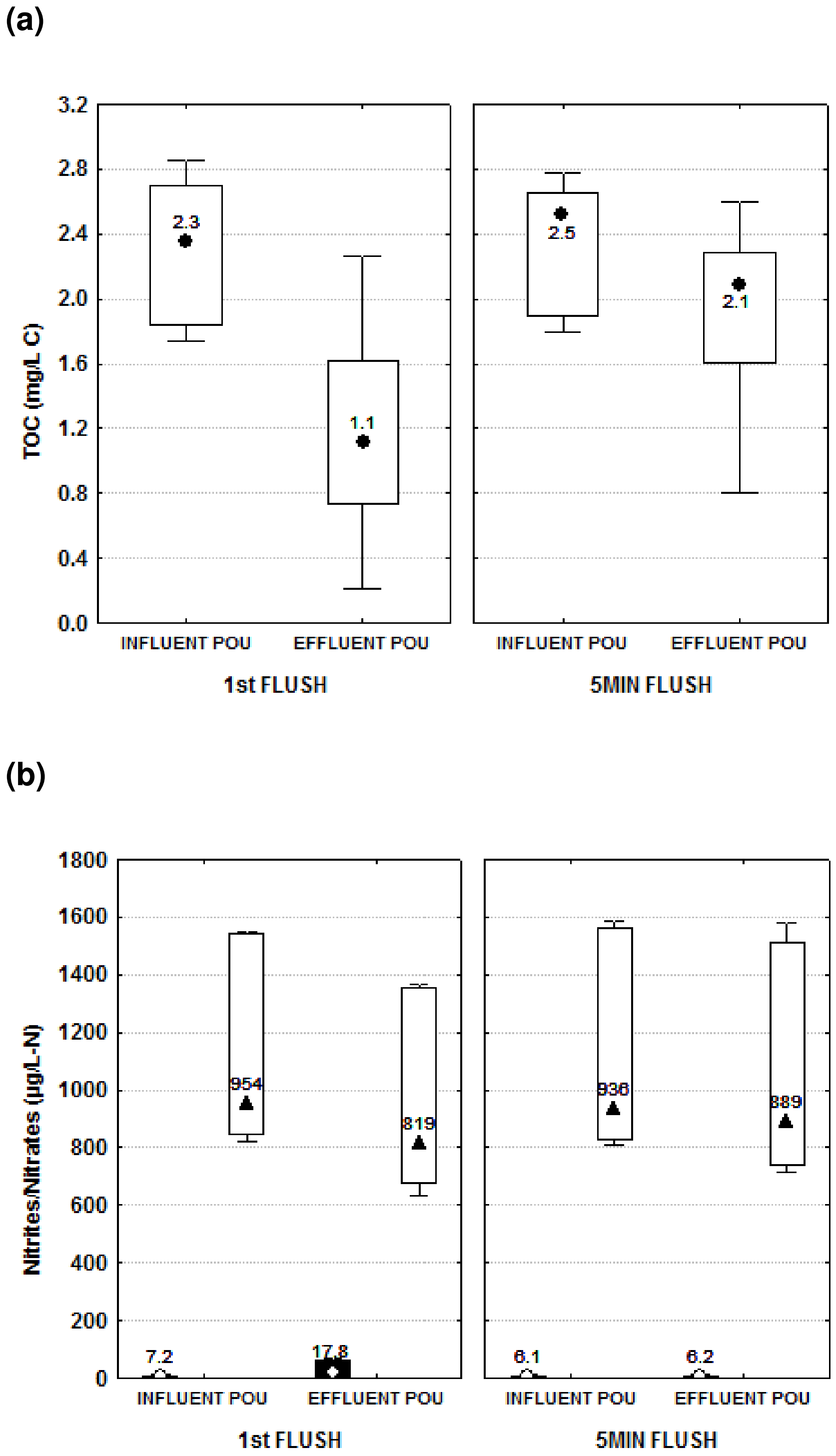


Figure 5-9. Box plots of influent and effluent samples at 1st flush (left) and after 5 min of flushing (right) of: (a) TOC (Oct 2009-Sept 2010); and (b) NO_2 (black boxes) and NO_3 (white boxes) (Jul-Aug 2009). For each box at 1st FLUSH: N=22 (TOC), N=11 (nitrites/nitrates). For each box at 5MIN FLUSH: N=13 (TOC), N=7 (nitrites/nitrates). Median; Box: 10-90%; Whiskers: Min-Max.

Table 5-1. Comparison of the microbiological quality at taps with and without upstream POUs (March-May 2010).

		HPC (Log CFU/mL)	Live bacteria (Log/mL)	Total bacteria (Log/mL)	TOC (mg/L-C)
POU PRESENT	**N**	7	5	5	5
	Median	2.1	5.8	6.0	1.4
	Range	0.6-3.0	5.2-6.1	5.5-6.3	1.1-1.7
POU ABSENT	**N**	6	5	5	5
	Median	2.0	4.9	5.1	1.9
	Range	0.6-2.9	4.5-5.0	4.6-5.2	1.9-2.0
T-test between the two categories		p = 0.42	p < 0.0001	p < 0.0001	p < 0.0001

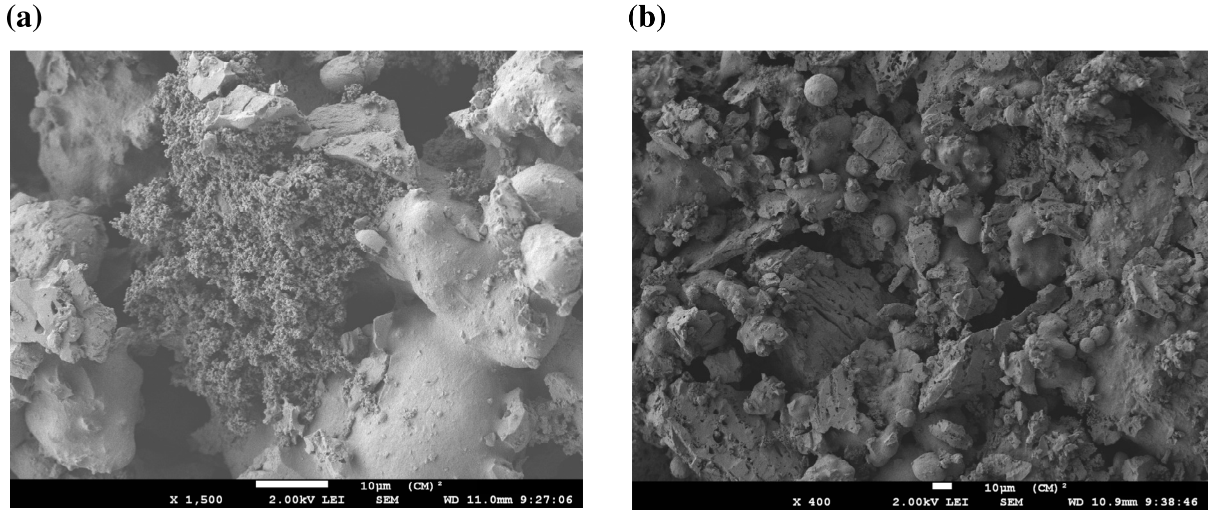


Figure 5-10. SEM photos of the inlet surface of the SBAC showing: (a) clusters concentrating metals (Pb, Cu, Zn, Sn. Fe, Mn; EDS analyses); and (b) Ti/Si oxide inclusions (rounded particles; EDS analyses).

5.4 Conclusion

The installation of under-the-sink POUs for the removal of Pb is feasible and practical in a large building. Excellent and steady Pb reduction to concentrations well below action levels were observed under varying usage patterns, including short and long stagnation times. In the buildings studied, the POU lifetime exceeded the manufacturer's recommended maximum usage period of one year for cartridge replacement. Therefore, cartridges could be replaced every year without risking exceeding the POU capacity. However, care should be taken for frequently used taps, or taps used for the collection of large volumes of water (e.g. cafeteria taps). Considering the price of the POU unit tested (about $115), annual cartridge replacement (about $30), and the relative ease of installation, POUs constitute an easily implemented and efficient solution for reducing Pb at designated taps in large buildings, while awaiting the implementation of permanent solutions. Secondary impacts on water quality include a slight increase in bacterial colonization downflow of the POU, which is only perceptible if total and viable counts are considered, and not observed for HPCs. This amplification was not due to biofilm formation and detachment from the carbon block, and did not increase over time. Colonization of the SBAC was insignificant, and may have been limited by the presence of Si/Ti inclusions that accumulate multiple metals that inhibit bacterial growth. The SBAC removed, on average, 36% of TOC through adsorption, but adsorptive capacity decreased with time. Finally, there are additional issues to take into account when considering the use of POUs to control Pb levels at the tap in large buildings. First, the installation and maintenance of POUs should be planned by the appropriate authorities, since they must be installed at taps adapted for the purpose and carefully monitored to time cartridge replacement. In the United States, the SDWA mandates that the installation and maintenance of POUs in small communities must be performed by the public water utility or by a contractor hired by the utility. However, the installation of POUs in large buildings is not addressed in the guidance documents. Another important issue is the varying performance of the POUs, especially regarding potential bacterial release. As shown by this study, the potential for biofilm support and bacterial release varies widely between models, and adequate certification should be considered. Furthermore, if a POU model is discontinued, then all the POU units must be replaced, which increases the cost of this remediation method. Finally, the population in the large buildings targeted should be advised to take their drinking water from the taps equipped with a POU.

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CHAPITRE 6 PUBLICATION #5: PB PARTICLES FROM TAP WATER: BIOACCESSIBILITY AND CONTRIBUTION TO CHILDREN’S EXPOSURE

Ce chapitre détaille la dernière étude de ce projet de recherche, soit l’estimation de la bioaccessibilité du plomb particulaire. Il présente le développement d’un test de bioaccessibilité spécifique aux particules de plomb de l’eau potable, puis l’application du test à des particules représentatives de l’eau potable. Les valeurs de bioaccessibilité obtenues, couplées aux données d’échantillonnage du plomb particulaire (chapitres 3 et 5), ont été utilisées pour effectuer divers scénarios d’exposition au plomb particulaire. Enfin, le modèle IEUBK d’estimation du plomb sanguin chez les jeunes enfants utilisé avec ces données a permis d’établir la contribution du plomb particulaire à l’exposition. Cette étude a été soumise pour publication à la revue *Environmental Science and Technology.*

PB PARTICLES FROM TAP WATER: BIOACCESSIBILITY AND CONTRIBUTION TO CHILDREN’S EXPOSURE

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ABSTRACT

High particulate lead (Pb) levels can be measured in tap water, but the hazard linked to particulate Pb ingestion is unknown. An in vitro test was developed to determine the bioaccessibility of Pb particles from tap water, based on the Relative Bioaccessibility Leaching Procedure validated for soils, and applied to lab-generated particles and field particles collected behind the aerator tap. Field particles were found in 43% of the 342 taps investigated equipped with an aerator, and contained significant amounts of Pb (0.003-71%, median 4.7%). The bioaccessibility of lab-generated particles ranged from 2 to 96% depending on the particle type (Pb(II) > Brass > Pb(IV) > solder), while that of field particles was homogeneously distributed between 1.5 and 100% (median 41%). The hazard of particulate Pb ingestion depends on the amount and concentration ingested, and the bioaccessibility of the particulate Pb forms involved. Using the Integrated Exposure Uptake Biokinetic model, the exposure of children aged 0.5-7 to particulate Pb was the most significant when considering the exposure from Pb particles found in large buildings for the distribution system studied.

Keywords: bioaccessibility, particulate Pb, drinking water, exposure assessment.

6.1 Introduction

Although blood lead levels (BLLs) have been steadily declining for decades, exposure from residual sources must be reduced, since the current guideline of 10 µg/dL is under review (Codex Alimentarius Commission 2011, European Commission 2011). In fact, no safe threshold can be established, now that irreversible neuro-developmental effects have been measured in children at BLLs < 5 µg/dL (Jusko *et al.* 2008, Lanphear *et al.* 2002). Tap water is a significant remaining contributor to BLLs (Brown *et al.* 2011, Lanphear *et al.* 2005), and there are many sources: numerous lead service lines (LSLs) are still in place in North America, which can result in long-term Pb deposits in premise plumbing (PP) (Schock 2005); there is a legacy of Pb-containing materials in PP; brass fixtures and faucets can contain up to 8% Pb; and solders with 40-50% Pb content can still be found in an estimated 81 million US homes (Sandvig *et al.* 2008, Triantafyllidou & Edwards 2011a). The contribution of particulate Pb to the total Pb exposure from tap water is unknown. It could be considerable, as very high Pb levels in tap water that may indicate a significant fraction of Pb particles, have been linked to high BLLs in children (Edwards *et al.* 2009, Miranda *et al.* 2007). In order to assess the scale of this exposure, more information is needed about the occurrence and bioavailability of particulate Pb.

Drinking water regulations generally require the determination of total Pb, which includes a fraction of 'real' soluble Pb (< 0.1 µm), and an easily dissolved fraction of colloidal and particulate Pb (≥ 0.1 µm). However, particulate Pb can be underestimated. In fact, the historical acidification standard of 0.15% HNO_3 for metal analysis will remove most Pb colloids and particles; however, a strong acidic digestion is needed to make some Pb forms soluble (Lytle *et al.* 1993, Triantafyllidou *et al.* 2007). Also, even though dangerously high concentrations are fairly rare in data obtained with standard protocols, particulate Pb can often occur at significant concentrations at the tap. Moreover, current sampling protocols performed at a low flow rate, or preceded by system flushing, may not reflect the levels to which consumers are exposed (Deshommes *et al.* 2010a). Early reports of Pb release from solders and brass fixtures in a new large building show that small particulates can contribute significantly to Pb levels at the tap (Lytle *et al.* 1993). In Montreal, up to 1,617 µg/L of particulate Pb (> 0.45 µm) has been recorded in houses supplied by a LSL, and the concentrations increased considerably when samples were collected with repeated, rapid, on/off faucet action at high flow rates (Deshommes *et al.* 2010a, Nour *et al.* 2007). In another study, consistently high particulate Pb levels (maximum 912 µg/L) were measured in a large building in Canada (> 0.45 µm) (Deshommes *et al.* 2011a). Large buildings may be prone to particulate Pb release owing to large volumes of PP, which are often associated with long stagnation times. This raises special concern for schools and daycare centers, as their populations are the most vulnerable to Pb effects.

Finally, the impact of particulate Pb ingestion on BLLs can only be evaluated if the bioavailability of the Pb contained in the particles present at the tap is assessed. That impact depends on multiple factors related to their dissolution in the stomach, such as the particle matrix and size (Deshommes *et al.* 2011b, Ruby *et al.* 1999). The *in vitro* bioaccessibility (IVBA) of Pb particles is the fraction of Pb that dissolves under simulated gastro-intestinal digestion conditions, and becomes available for absorption into the systemic circulation through the intestinal wall. IVBA assays have mainly been developed for soil Pb particles to which children aged 2-3 can be exposed due to hand-to-mouth activity. Some of the many *in vitro* protocols developed have been validated with *in vivo* data on animals, piglets being recognized as the animal model best suited to represent the child's digestive system. To date, the only fully calibrated and validated model is the Relative Bioaccessibility Leaching Procedure (RBALP), described by Drexler & Brattin (Deshommes *et al.* 2011b, Drexler & Brattin 2007).

The objectives of this study are: (1) to develop an *in vitro* test to estimate the IVBA of Pb particles from tap water; (2) to establish the IVBA of Pb in lab-generated and field-collected particles; and (3) to evaluate the contribution of particulate Pb to the exposure of children aged 0.5-7 using the Integrated Exposure Uptake Biokinetic model for Pb in children (IEUBK).

6.2 Materials and Methods

6.2.1 In vitro protocol

An IVBA assay for drinking water particles was developed based on the RBALP (Drexler & Brattin 2007). Modifications were performed, but not on parameters recognized to affect IVBA estimates. All the materials used were either metal-free or soaked for at least 24 hours in a 10% HNO_3 bath (trace metal), rinsed with ultra pure water, and dried in a Pb-free environment. A synthetic gastric fluid (0.4 M glycine & ultra pure HCl) was adjusted to pH 1.5±0.05 with HCl at 37°C on the day of the experiment. A volume of gastric fluid was then added to the bulk particle mass previously weighed in a 15 mL tube (0.01-0.08 g), so that the S/L ratio was equivalent to 1 g of particles for 200 mL of fluid for field particles, and from 1/100 to 1/200 $g.mL^{-1}$ for lab-generated particles. The mixture was agitated end-over-end at 28±2 rpm in an incubator at 37°C. After 1 hour, it was filtered on a 0.45 µm cellulose acetate filter using a vacuum device (at least 6 rinsing). The filtrate was collected in a receptor tube and diluted to 50 mL. The filter-retaining particles was collected and subjected to aqua regia digestion (4.5 mL ultra pure HNO_3 + 1.5 mL ultra pure HCl; 15 min; 1000 W, 220°C) using a microwave lab station (Ethos Series, Milestone). All samples were acidified within 12 hours with at least 0.5% HNO_3 and 0.5% HCl (ultra pure). Analyses were carried out with an ICP-MS (Agilent, 7500ce), mostly within 30 days. Metal detection limits were: 0.2 µg Pb/L, 0.6 µg Cu/L, 1 µg Sn/L, 3 µg Zn/L, 10 µg Fe/L, and 50 µg Ca/L. If an insoluble solid remained following microwave digestion, it was isolated, weighed if possible, and analyzed by X-ray diffraction (XRD, Bruker D8-Discover, reflection θ/θ, radiation $CuK\alpha_1$, $\lambda = 1.54056$ Å). Mass balances were performed using results from Pb reference materials (supporting information). The high recoveries for these reference materials (68-106%) are indicative of the value of the proposed adapted protocol. During the *in vitro* digestion, a blank was performed every 10 samples, and the pH of the mixture was checked after 1 hour every 10 samples, so that pH remained < 2. During microwave digestion, a blank and a control (Pb or multi-metal solution) were added to each batch. The IVBA was calculated as follows:

$$IVBA\ (\%) = \frac{Total\ Pb\ (filtrate)}{Total\ Pb\ (filtrate+filter)} \times 100\ (Equation\ 1)$$

$$IVBA\ (mg\ Pb/g\ bulk\ particles) = IVBA\ (mgPb/g) = \frac{mg\ Pb\ (filtrate)}{g\ of\ bulk\ particles}\ \ (Equation\ 2)$$

6.2.2 Lab-generated particles

Five types of particles potentially present in tap water were generated in the laboratory: solder particles (~ 1 mm) from a 50/50 Pb-Sn solder wire (Alfa-Aesar); brass ‘chips’ (~ 50 µm-2 mm) from two ball valves (one of NSF-certified yellow brass (Y-brass), the other of red brass (R-brass) using a small drill bit); and a scale deposit scratched from an LSL collected in Montreal, mostly composed of Pb(II) particles (Deshommes *et al.* 2010a); and Pb(IV) particles < 250 µm (Alfa-Aesar).

6.2.3 Field-collected particles

Particles trapped behind the tap aerator in 351 homes throughout the Montreal area were collected, and in a large building near Montreal (45 taps sampled). The homes were categorized as follows: 216 with an LSL, 127 without an LSL, and 8 ‘probably’ having an LSL (not confirmed). Fifty-eight percent of the taps sampled in the large building and 8% of the kitchen taps in the homes did not have an aerator, and the aerators on some taps could not be removed. A total of 88 samples were collected from the homes with an LSL (41%), 44 samples from homes without an LSL (35%), 4 samples from homes ‘probably’ having an LSL, and 10 samples from the large building, mostly behind the kitchen tap aerators. Photographs were taken of all the samples collected. Forty-two sets of particles from a single tap with sufficient mass (0.01-0.08 g) were used directly, and 23 additional sets were constituted and then tested using the IVBA assay. Sets of particles < 0.01 g were mixed per housing category, and 0.02-0.06 g random subsamples were tested for their IVBA. Sets of particles > 0.08 g were fractioned, and subsamples were tested for their IVBA. Finally, one of the aerator taps sampled presented a significant number of solders and iron corrosion particles. This sample was fractioned by the type and size of identifiable particles of the same total mass, and the remaining particles were tested separately.

6.2.4 IEUBK simulations

Version *IEUBKwin1.1_Build11* was used, and Pb exposure from tap water, soil, dust, and diet was considered, for children aged 0.5-7. Dissolved and particulate Pb concentrations applied for tap water were a combination of those measured in homes with an LSL in Montreal (random daytime—RDT and 5-minute flushing samplings) and in a large building close to Montreal (1st flush) (Cartier *et al.* 2011, Deshommes *et al.* 2010a, Deshommes *et al.* 2011a, Nour *et al.* 2007). To take into account occurrence and absorption differences for dissolved and particulate Pb, the following steps were followed to produce the total Pb input to the model:

Estimate relative particulate Pb bioavailability (RBA) from its estimated IVBA%, using the *in vivo-in vitro* relationship of Drexler & Brattin (2007) (Equation 3).

$$\mathrm{RBA}_{\%} = 0.878 \times IVBA_{\%} - 0.028 \quad \textit{(Equation 3)}$$

Adjust the particulate Pb fraction in the total Pb concentration input by multiplying it by its estimated RBA%, and dividing it by the default RBA of 50% applied by IEUBK for total Pb (Equation 4).

$$Total\ Pb_{\mu g.L^{-1}} = Dissolved\ Pb_{\mu g.L^{-1}} + \left(Particulate\ Pb_{\mu g.L^{-1}} \times \frac{RBA_{\%}}{50_{\%}}\right) \quad \textit{(Equation 4)}$$

In this way, the RBA considered by IEUBK for soluble Pb remained at 50% (default value), and the RBA relative to particulate Pb was taken into account (Equation 5).

$$50\% \times Total\ Pb_{\mu g.L^{-1}} = 50\% \times Dissolved\ Pb_{\mu g.L^{-1}} + \left(Particulate\ Pb_{\mu g.L^{-1}} \times RBA_{\%}\right)$$
$$\textit{(Equation 5)}$$

Pb concentrations in dust, soil, and diet, as well as ingestion rates were selected according to the latest Canadian data (Beausoleil & Brodeur 2007, Health Canada 2011, Ljung *et al.* 2011, Rasmussen *et al.* 2001, Rasmussen *et al.* 2011). In absence of data, the default IEUBK values were applied (Table 6-1).

Table 6-1. Description and justification of the inputs to the IEUBK simulations.

	AGE CATEGORY (yrs)	0-1	1-2	2-3	3-4	4-5	5-6	6-7	JUSTIFICATION
DRINKING WATER	Drinking water intake — L/d	0.742	0.91	0.91	0.91	1	1	1	Values used by Montreal Public Health authorities (Beausoleil & Brodeur 2007)
	RDT concentration* in LSL houses — µg total Pb/L	Range: 4-1683; Median: 20; Mean particulate fraction: 12%							Deshommes *et al.* 2010a, Deshommes *et al.* 2011a Nour *et al.* 2007 Cartier *et al.* 2011
	Frequency for RDT consumption — %	57.5-70							
	5min of flushing concentration§ in LSL houses — µg total Pb/L	Range: 2-35; Median: 11; Mean particulate fraction: 4%							
	Frequency for 5 min of flushing consumption — %	17.5-30							
	1st flush concentration‡ in a large building — µg total Pb/L	Range: 1-1000; Median: 91; Mean particulate fraction: 39%							
	Frequency for 1st flush consumption — %	0-25							
	RBA — %	particulate Pb: 33, dissolved Pb: 50							RBA evaluated with the *in vivo-in vitro* relationship by Drexler & Brattin (2007) using median IVBA from this study
DUST/SOIL	Soil + dust intake — g/d	0.085	0.135	0.135	0.135	0.100	0.090	0.085	Default IEUBK
	Soil/Dust ingestion weighting factor — % soil	40							Higher than default IEUBK (35) considering cold climate
	Soil concentration — µg Pb/g	33.78							Rasmussen *et al.* 2001
	Soil RBA — %	30							Default IEUBK
	Dust concentration — µg Pb bioavailable/g	52.47†							Rasmussen *et al.* (2011) values, adjusted with the *in vivo-in vitro* relationship by Drexler & Brattin (2007)
	Dust RBA — %	100							Dust concentration considers Pb bioavailability
AIR	Indoor Pb concentration — % outdoor	30	30	30	30	30	30	30	Default IEUBK
	Time spent outdoor — hr/d	1	2	3	4	4	4	4	Default IEUBK
	Outdoor air Pb concentration — µg Pb/m^3	0.0015							Health Canada 2011
	Ventilation rate — m^3/d	2	3	5	5	5	7	7	Default IEUBK
	Lung absorption — %	32							Default IEUBK
OTHER	Dietary Pb intake — µg Pb/d	2.26	1.96	2.13	2.04	1.95	2.05	2.22	Default IEUBK values agree with Canadian values (Health Canada 2011, Ljung *et al.* 2011)
	Maternal BLL — µg Pb/dL	1							Default IEUBK values agree with Canadian values (Health Canada 2011)

**2007-2008 Montreal summer sampling campaigns (Cartier et al. 2011, Deshommes et al. 2010a; N=196; 2008 monitoring campaign not published), includes 27 samples performed using particulate stimulation samplings (Deshommes et al. 2010a) and 15 samples collected at high flow rates (Nour et al. 2007); §from 2006-2008 Montreal summer sampling campaigns (Cartier et al. 2011, Deshommes et al. 2010a; N=218; 2008 monitoring campaign not published); ‡from Deshommes et al. (2011a) using only results from taps dedicated to drinking water consumption (N=35); †52% RBA for dust deduced from the in vivo-in vitro relationship by Drexler & Brattin (2007) and the geometric mean IVBA of 62%; then, to obtain the concentration of bioavailable Pb (µg Pb/g dust), the median concentration of bioaccessible Pb (63 µg Pb/g dust) was multiplied by its RBA% (52) and divided by its IVBA% (62).*

6.3 Results and discussion

6.3.1 Lab-generated particles

IVBA% varied with the type of particle tested, in the following decreasing order: Pb(II) > Red brass > Yellow brass > Pb(IV) > solder (Figure 6-1). Such results are quite comparable to the solubility of lab-generated particles reported after about 1 hour at pH 1.2 @ 37°C in a simulated gastric fluid by Triantafyllidou *et al.* (2007). This classification was independent of the Pb content in the particles tested, which was evaluated at, on average, 1.7% for the Y-brass, 6.7% for the R-brass, 46% for the Pb(II) scale, 49% for the solder, and 84% for the Pb(IV), the latter being quite highly bioaccessible (34-45%) under the testing conditions, which included pH acidification after heating, although it is generally poorly soluble in drinking water (Lytle & Schock 2005, Xie *et al.* 2010a, Xie *et al.* 2010b). The LSL deposits mainly composed of Pb carbonates were, not surprisingly, highly bioaccessible (95-96%), considering their high solubility (Deshommes *et al.* 2010a). It must be noted that those two species of high Pb content, presented a significantly higher mean IVBA in mg Pb/g bulk particles (328-439) than other particles tested (7-57) (Figure 6-1). Pb(IV) and Pb(II) scales can develop into the LSL, and therefore may be present at the tap. They can become detached by physical disturbances in the plumbing associated with consumers' water usage patterns (high flow rate, water hammer), and occasionally, but to a large degree, following a disinfectant change (Deshommes *et al.* 2010a, Lytle & Schock 2005, McNeill & Edwards 2004, Xie *et al.* 2010a, Xie *et al.* 2010b). The two types of brass and the solder tested may represent more a "universal" source of exposure to particulate Pb for the consumer, since these Pb-bearing materials are ubiquitous in PP. The relatively low bioaccessibility of the solder and the lower Pb content of brass devices should not be interpreted as constituting a lower risk of significant Pb ingestion compared to that of the Pb scales tested. In fact, the sustained and elevated release of particulate Pb resulting from the corrosion of brass devices and solders has been documented, and may represent a substantial source of chronic exposure for children attending school/daycare every day (Boyd *et al.* 2008a, Boyd *et al.* 2008b, Deshommes *et al.* 2011a).

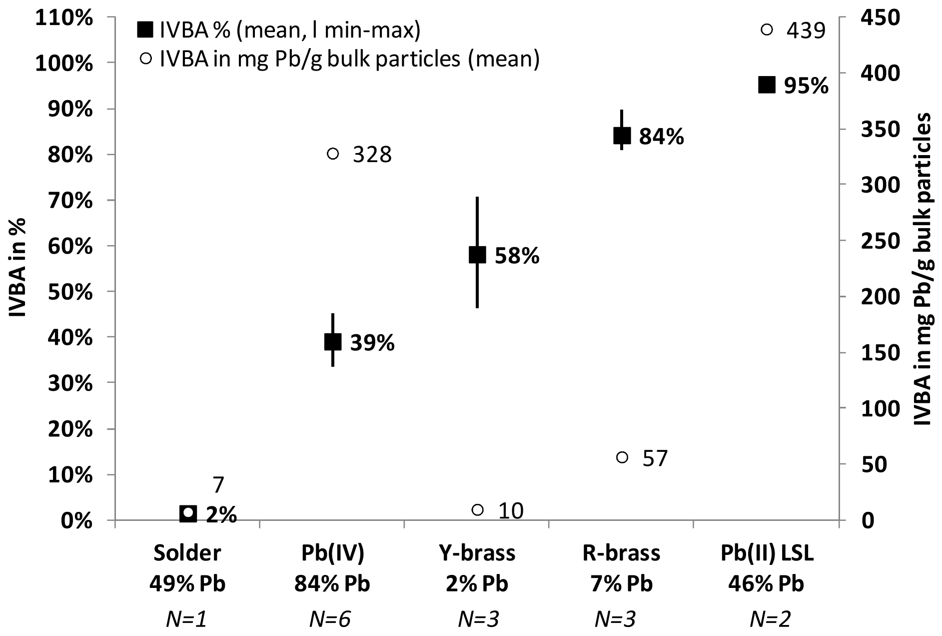


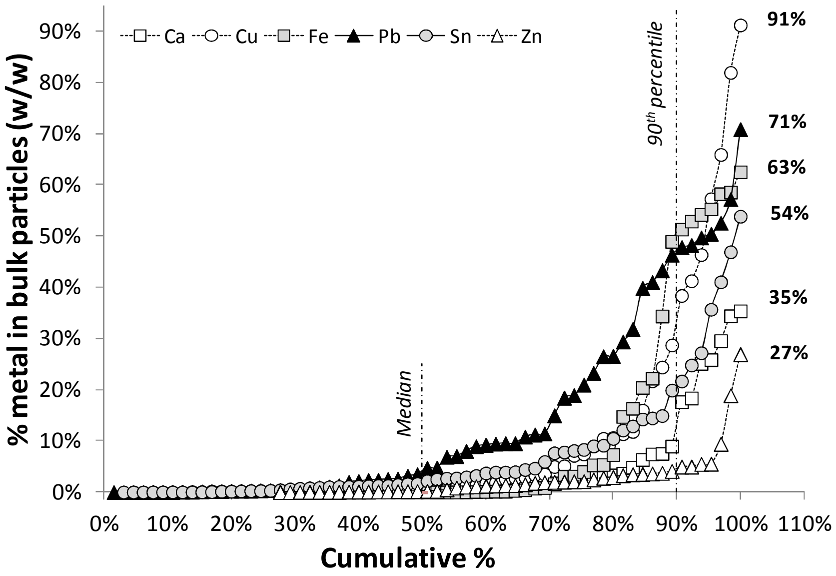
Figure 6-1. *In-vitro* bioaccessibility (IVBA) for lab-generated particles. IVBA % on the left Y-axis (mean, min-max); mean IVBA in mg Pb/g bulk particles on the right Y-axis.

6.3.2 Field-collected particle composition

Figure 6-2 (a) shows the distribution of the main metals composing the 65 sets of field particles tested. In about 90% of the samples, Pb was the main component present. A median of 4.7% and values up to 71% Pb were recorded in the bulk particles tested, and 43% of the sets contained more than the 8% Pb formerly permitted for plumbing devices. Tin was the second largest component of the samples, based on the median (2.2%). The dominant metals measured in the particles were characteristic of PP: brass alloys components (Cu, Zn, Sn, Pb) and solder components (Pb, Sn). Iron and calcium particle content was also significant, and may have come from deposits formed into the piping over time, specifically corroded galvanized iron piping in the case of Fe particles. Overall, no significant difference ($p = 0.42$) was found between the Pb content of particles collected from homes with and without an LSL. However, as illustrated in Figure 6-2 (b), there is clearly a higher Pb content in particles from LSL homes than from homes without an LSL above the 80th percentile. It may be incorrect to conclude from such trends that some LSLs can be a significant source of particulate Pb, since the opposite trend was observed in the 50th to 80th percentile range. In fact, whether or not there was an LSL, 12/13 particles over the 80th percentile and 4/16 particles in the 50th-80th percentile range were high in Sn, suggesting solder, while 9/16 particles in the 50th-80th percentile range were high in Cu-Zn-Sn, suggesting that brass was the most likely source. However, although small, friable, Pb-rich deposits released from an LSL would not be retained by an aerator, they would likely be measured in the total Pb analysis, given an adequate digestion procedure. In general, the multi-metal composition of the particles collected indicates that the PP (solder, brass) rather than the LSL was the source. For the samples with a high Fe content, higher Pb levels were found in homes with an LSL (0.2-0.8%) than in those without an LSL (0.01%), in agreement with prior findings (Deshommes *et al.* 2010a). These results suggest that the absence of an LSL does not greatly influence exposure to Pb particles, since they originate mostly from the PP in the system studied.

An aerator can trap a considerable amount of particles, making this area a significant reservoir of Pb. Considering only the 42 samples taken from a single tap aerator, the bulk particle mass varied within 0.01-0.08 g, corresponding to 0.0009 to 15 mg total Pb (mean: 2.8 mg). Such Pb-bearing particles can dissolve during stagnation, or break down and break through the aerator mesh with sheer from flow over time, contributing to elevated Pb levels at the tap and consequently to consumer exposure (Cartier *et al.* 2011, Triantafyllidou *et al.* 2007). An obvious way to limit potential exposure associated with these particles is to advise cleaning the aerator tap regularly, and to buy faucets in which the aerator can be easily removed.

(a)



(b)

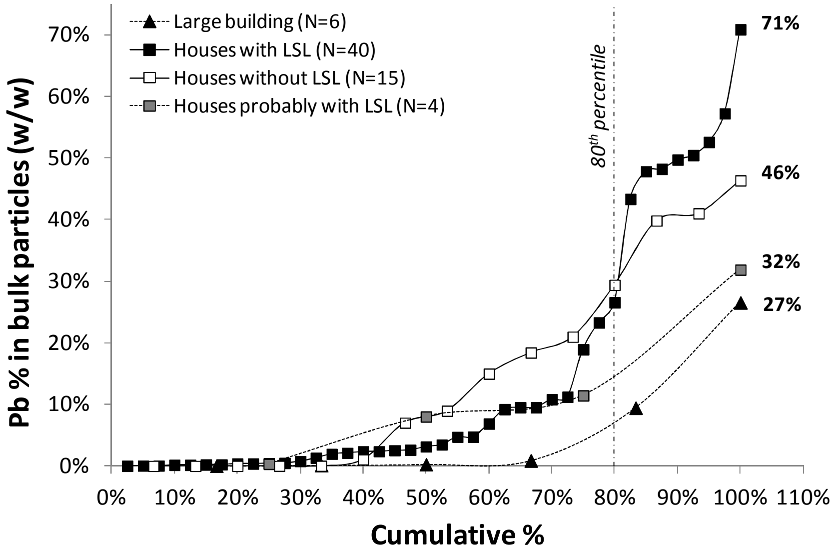


Figure 6-2. Cumulative frequency of % metal content in the 65 sets of field-collected particles tested. (a) Metals for all samples; (b) Pb % per type of building.

6.3.3 Field-collected particle bioaccessibility

Figure 6-3 presents the distribution of IVBA results from field-collected particles. The IVBA% was homogeneously distributed between 0 and 100%, with a median at 41%. From this median

IVBA, a median RBA of 33% could be deduced using the relationship proposed by Drexler & Brattin (2007). IVBA also varies quite homogeneously in terms of mg of Pb bioaccessible per g of bulk particles between 0 and 82, as 64 of the samples are in this range. An extreme at 436 mg Pb/g was also measured, corresponding to the highest Pb content found in the field particle samples (71%). Values for the field particles fall within the range of the IVBA estimates for the lab-generated particles, although they are a bit lower (median: 11 mg Pb/g). However, the lab-generated particles were all Pb-bearing, while the field-collected particles were composed of a mix of particles, only some of which contained Pb, which decreased the overall IVBA estimates. It is worth noting that lab-generated particles exhibiting the highest IVBA (> 400 mg Pb/g) were Pb scales from LSLs, which were not represented in the field particles, as they are too small and friable to be retained by aerators.

The range of IVBA estimates, whether in % or mg Pb/g, is quite broad and represents a correspondingly broad range of potential consumer exposures. As for the Pb content in particles, the IVBA was not significantly different in homes with and without an LSL (t-test, $p > 0.5$, for IVBA in % or mg Pb/g). However, as noted previously, this lack of impact of the LSL is most likely explained by the nature of the particles tested, which originated mostly from the PP. In addition to Pb particles from this source, consumers living in homes with an LSL may be exposed to Pb particles released from LSL scale deposits. However, since particles released from Pb(II) and Pb(IV) scales are likely to be very small or colloidal, their contribution is taken into account in the total and dissolved Pb measurements at the tap (Deshommes *et al.* 2010a, McNeill & Edwards 2004).

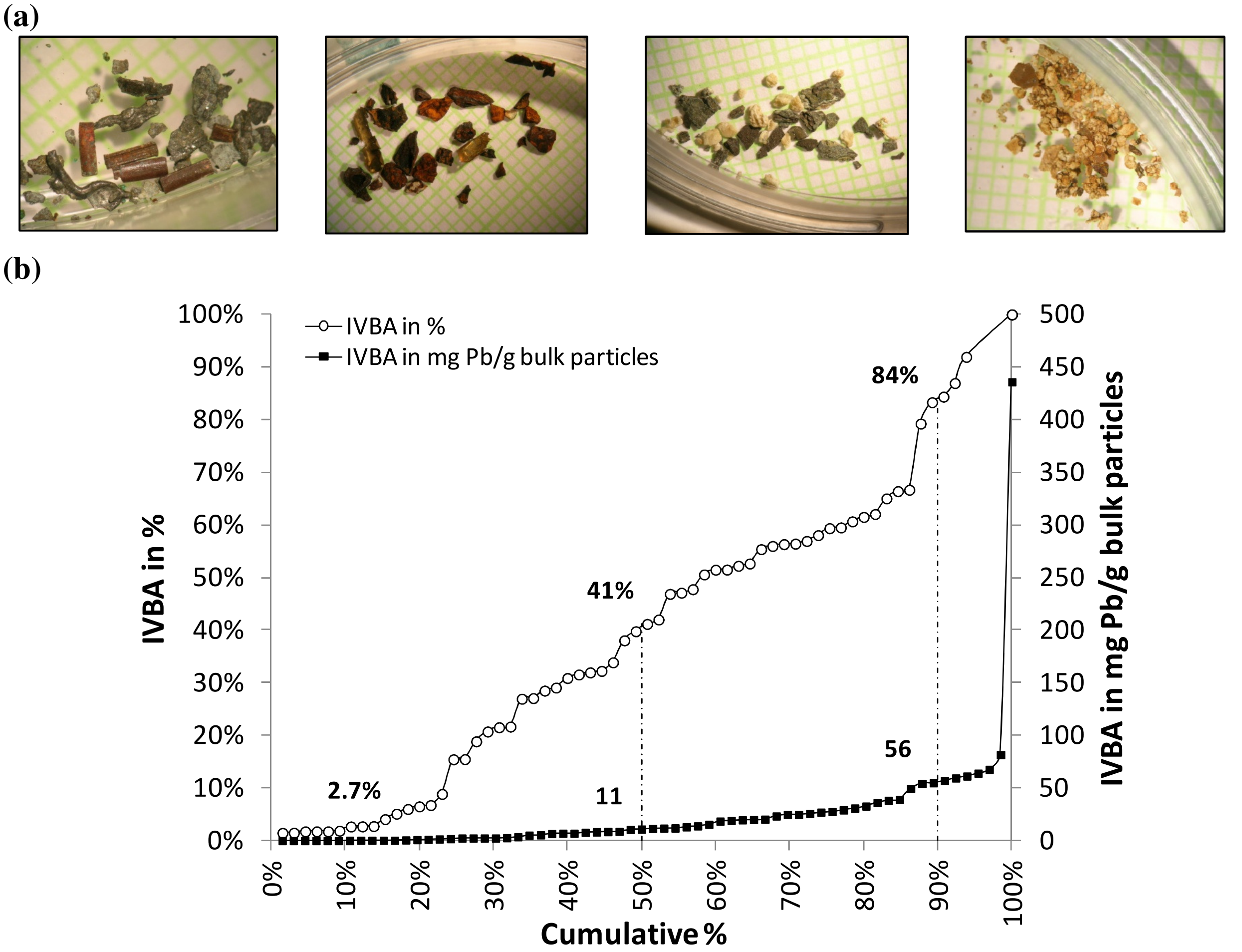


Figure 6-3. (a) Examples of field-collected particles. Note: each side of the squares = 1 mm; (b) Cumulative frequency of IVBA in the 65 sets of field-collected particles tested. Y-left axis: O-IVBA %; Y-right axis: ■-IVBA in mg Pb/g bulk particles.

The samples were classified based on their dominant phase, which was defined as composing at least 15% of the total mass of the sample. Five dominant phase categories were identified, based on the appearance of the particles sampled and on the metal content and proportion in the particles tested: Ca, Fe, Cu-Pb-Sn-Zn, Cu-Pb-Sn, and Pb-Sn. Figure 6-4 illustrates the IVBA% per category. Particles containing on average 27% Ca exhibited the highest IVBA: 32-100%, with a median at 59%. The Fe-based particles and the two categories of copper alloys presented a median IVBA of 47-51%, while the upper values for the Cu-Pb-Sn category were lower. Finally, particles for the most part containing Pb/Sn solders presented the lowest IVBA (median 5%). Besides, the first twelve values of the IVBA distribution curve presented in Figure 6-3 (0-18%) correspond to samples composed exclusively (N=9) or mostly of solders. T-test results comparing the Pb-Sn category and the other dominant phase categories were all significant ($p < 0.0001$), while the other categories were not statistically different ($p = 0.12$-0.86). Therefore, consumer exposure to particulate Pb is determined by particle type, and strongly influenced by the presence of solders. Pb speciation in soil and dust particles has been shown to be a major predictor of their bioaccessibility, since Pb dissolution during digestion varies according to the mineral composition of the Pb particles (Deshommes *et al.* 2011b). By compiling their results from soils, the USEPA was able to generate an IVBA classification based on the dominant phases present in the soils tested: > 75% for cerussite and Pb-Manganese oxide; 25-75% for Pb-Phosphate and PbO forms; and < 25% for anglesite, galena, Fe-Pb species, and the remaining Pb-based oxides (USEPA 2007b). Finally, Rasmussen *et al.* (2011) were able to predict the IVBA by identifying the dominant Pb species in the dust samples tested with X-ray Absorption Spectrocopy. However, for the field-collected particles tested in this study, IVBA differences were most significant between solders and other categories of particles. These results are consistent with trends measured with laboratory particles which reveal a medium to high IVBA% for brasses and typical LSL scales, while solders constitute the only type of Pb particle with a low IVBA%.

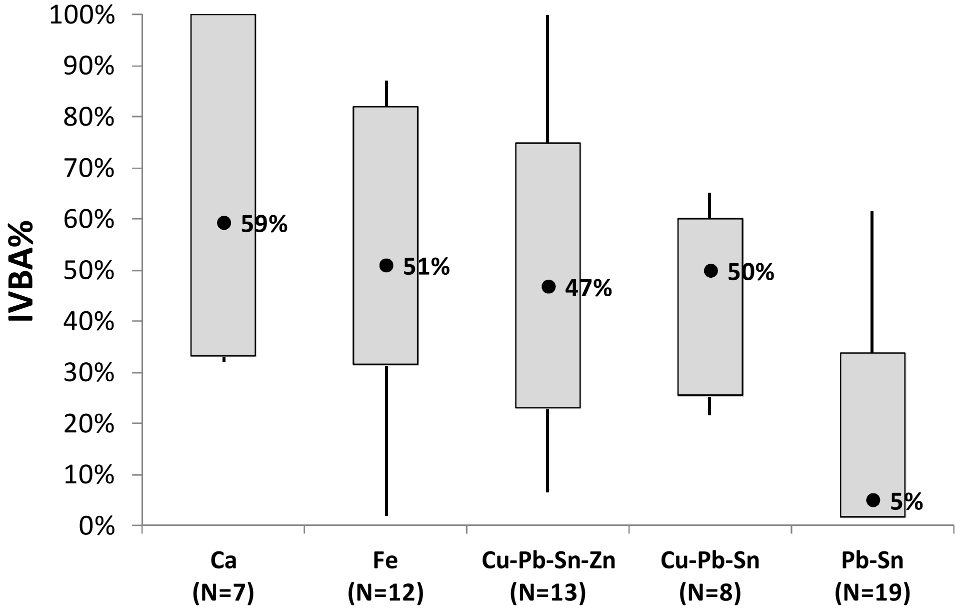


Figure 6-4. IVBA % per category of dominant phase (≥ 15 % of the total mass of particles). Box-plot 10-90%, I Min-Max, • Median.

IVBA results for solder and Fe-based particles collected from the same aerator and separated by particle size are presented in Figure 6-5. Bioaccessibility increased from 1.5% for solder B (approximately 3 mm in diameter) to 2.8% for sample D made up of 35 smooth, rounded solders about 0.5-1 mm in diameter (Figure 6-5 (a)). Surprisingly, the much larger solder sample, A, exhibited the highest bioaccessibility (4.1%) although apparently with a much smaller surface to volume ratio. Differences in IVBA did not correspond to a higher Pb content, as it was quasi-constant in the samples (48-50%). However, the irregular shape and rough surface of sample A may actually provide a larger surface for acid attack than that of other samples that were rounded and smooth. In the case of Fe-based particles containing 0.24-0.45% Pb, IVBA% increased with decreasing particle size (+24%; Figure 6-5 (b)). These trends suggest that the smallest particles collected, most likely the most common form of particulate Pb, are more bioaccessible. These results are in agreement with prior results showing that dust is generally more bioaccessible than coarser soil particles (Ruby *et al.* 1999). The impact of particle size would be greatest for very small or colloidal particles below or far below 250 µm (Mercier *et al.* 2002, Oliver *et al.* 1999, Ruby *et al.* 1992), although the extent of this impact will be greatest for Pb phases with low solubility, like galena, for example (Medlin 1997).

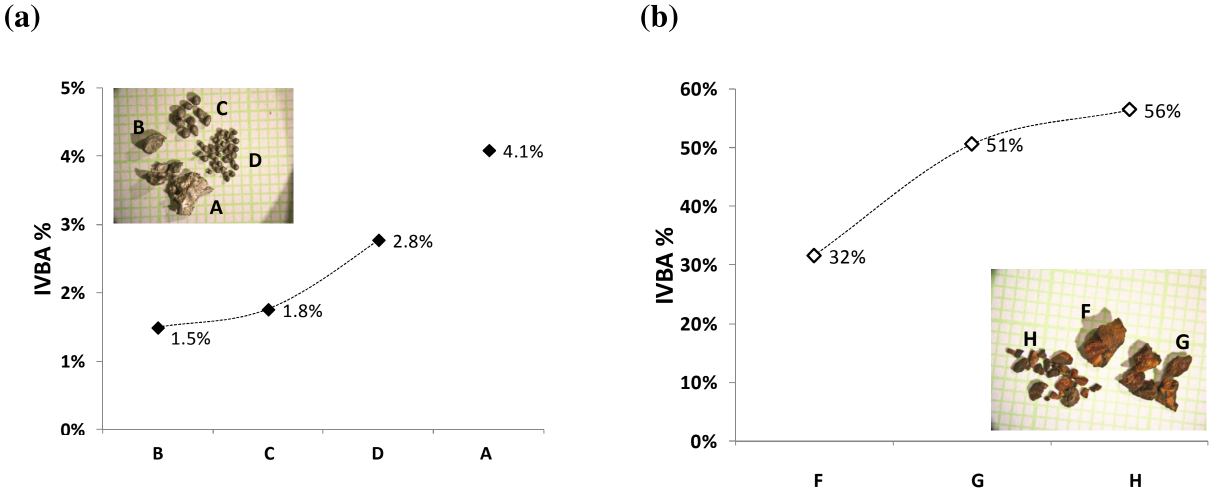


Figure 6-5. IVBA % per size of particles. Particles from the same aerator tap, from a house with an LSL. (a) Solders containing 48% Pb (A, B) and 50% Pb (C, D); (b) Fe corrosion particles containing 0.24-0.25% Pb (F, G) and 0.45% Pb (H). *Note: each side of the squares = 1 mm.*

6.3.4 IEUBK simulations

The IEUBK model was used to estimate the impact of particulate Pb on the exposure of children aged 0.5-7. Soil, dust, air and diet exposures were adjusted to reflect typical Canadian values (Table 6-1), which are significantly lower than the default IEUBK settings, except for dust, which is comparable. The background dissolved Pb median concentration of 19 µg/L in tap water was set from the results of three sampling campaigns conducted in households with LSL, and of a sampling campaign conducted in a large building. Using the median RBA measured from field-collected particles, particulate Pb exposure was added to the background levels and included in the drinking water input. Figure 6-6 (a) represents the impact on BLLs of increasing the particulate Pb content in tap water according to its measured distribution (0-95th percentile). The underlying scenario of drinking water consumption is a weighted mean of 90% from a house with an LSL (median summer RDT concentration of 70% and median summer 5-minute flushing concentration of 20%) and 10% from taps in a large building (median 1st flush). This scenario was selected to represent a conservative estimate of exposure for a child drinking tap water (either directly or through water-based food or beverages), living in a house with an LSL and attending daycare or school. Figure 6-6 (a) shows that the estimated geometric mean (GM) BLL and the fraction of children with BLL exceeding all thresholds are quite stable when concentrations of particulate Pb are lower than the median of the particulate Pb distribution. However, the impact of particulate Pb becomes noticeable from the 75th percentile of the particulate Pb distribution, and considerable at the 90th and 95th percentiles. Specifically, the GM BLL increases from 4.6 µg/dL for no particulate Pb content, to 5.6 and 9.2 µg/dL for the 75th and 95th percentiles of particulate Pb respectively. More strikingly, the estimated number of children with BLL > 10 µg/dL, which is the current health intervention guideline, increases from 5% for no particulate Pb content, to 11% and 43% for the 75th and 95th percentiles. The application of a lower BLL at 5 µg/dL dramatically increases the estimated fraction of children exceeding the action level, to 42-90%. This illustrates the ramifications of the anticipated lowering of the BLL threshold, as the current 10 µg/dL threshold was recently recognized as no longer valid, considering the significant neurodevelopmental effects observed in children BLLs < 5 µg/dL (Codex Alimentarius Commission 2011, European Commission 2011, Jusko *et al.* 2008, Lanphear *et al.* 2002).

Finally, to assess the representativeness of these simulations, the modeled BLLs were compared to BLLs recently reported in Montreal. An adjusted GM of 1.90 µg/dL (95% CI: 1.59-2.27 µg/dL) was measured on 171 children aged 1-6 living in a household with an LSL (INSPQ 2011). The IEUBK estimate of 4.6 µg/dL (without particulate Pb) significantly exceeds the measured BLLs. Several factors explain this difference. The BLL study was completed in fall and winter during which time Pb concentrations at the tap were extremely low (median 4.0 µg/L), due to both the type of homes sampled and the low water temperature (1.4°C in December) (INSPQ 2011, Nour & Prévost 2011). The background water levels used in our simulations, based on measurements performed in households with an LSL during the summer, were much higher with a median of 12.9 µg/L. Although a different pool of houses was sampled, we see that water temperature variations result in significant fluctuations in Pb tap concentrations. These fluctuations, to which the children in the BLL study were exposed, can be taken into account by using a weighted mean of the median concentrations measured at the tap, as in our IEUBK simulations (75% of cold water concentrations from the BLL study: 4.0 µg/L for 30-minute stagnation samples and 2.5 µg/L for 5-minute flushing samples (kitchen tap); and 25% from our warm water dataset from households with an LSL - see Table 6-1). With this weighted mean of median values, the revised modeled GM of BLLs decreases to 2.84 µg/dL, which is still slightly higher than the upper BLL values from the health study (INSPQ 2011). Considering the amplitude of Pb concentrations at the tap and their effect on BLL estimates, a short-term exposure model would be preferable for predicting seasonal BLLs (Donohue *et al.* 2011). The remaining overestimation also reflects the differences between the water consumption scenarios used. The IEUBK simulations consider that children drink a significant volume of tap water daily (742-1000 mL/d), whereas children in the BLL study consumed less tap water (295-385 mL/d, depending on their age) (INSPQ 2011). Selecting higher consumption values is desirable for producing conservative yet realistic estimates of population exposure and to protect susceptible populations (European Commission 2011). Finally, our simulations considered children aged 0.5-7, and our results revealed the highest BLLs among children under 3. The BLL study was mostly conducted on children 3-6 (62%), an age range expected to show lower BLLs.

The significant BLL increases observed in Figure 6-6 (a), resulting from the particulate Pb exposure of children consuming 10% of their water in a large building such as a school, are driven by the distribution of particulate Pb concentrations found in the large buildings studied.

As shown in Table 6-1, the concentrations measured in tap water from the large building complex contained significantly higher particulate Pb than the tap water from residences with an LSL. Figure 6-6 (b) shows the impact of increasing the fraction of tap water consumed in such buildings, reflecting the time spent out of the home during daycare or school. The proportion of tap water consumed in the large building was increased progressively from 0 to 25%. The importance of greater consumption of tap water from these large buildings is clearly shown by the fraction of children with BLLs > 5 µg/dL, which rose from 31% to 54% when the consumption increased to 25%, considering exposure to dissolved Pb only. If median particulate Pb concentrations are added to the background soluble Pb exposure, the fraction of children exceeding the threshold increased from 33 to 62%. If a higher value is used, such as the 90th percentile of particulate Pb, 41 to 94% of children are expected to exceed the 5 µg/dL threshold. These results suggest that particulate Pb can significantly contribute to Pb exposure at the tap, to the same extent as from Pb released from LSLs, especially in light of the anticipated reduction of the BLL threshold. The contribution of particulate Pb at the sites studied was dominated by the fraction of water consumed in these large buildings and the selection of the percentile concentration. Large buildings with elevated particulate Pb should be identified in order to lower Pb exposure from tap water. It would appear to be a matter of urgency, therefore, to conduct sampling campaigns in large buildings using protocols designed to detect both soluble and particulate Pb.

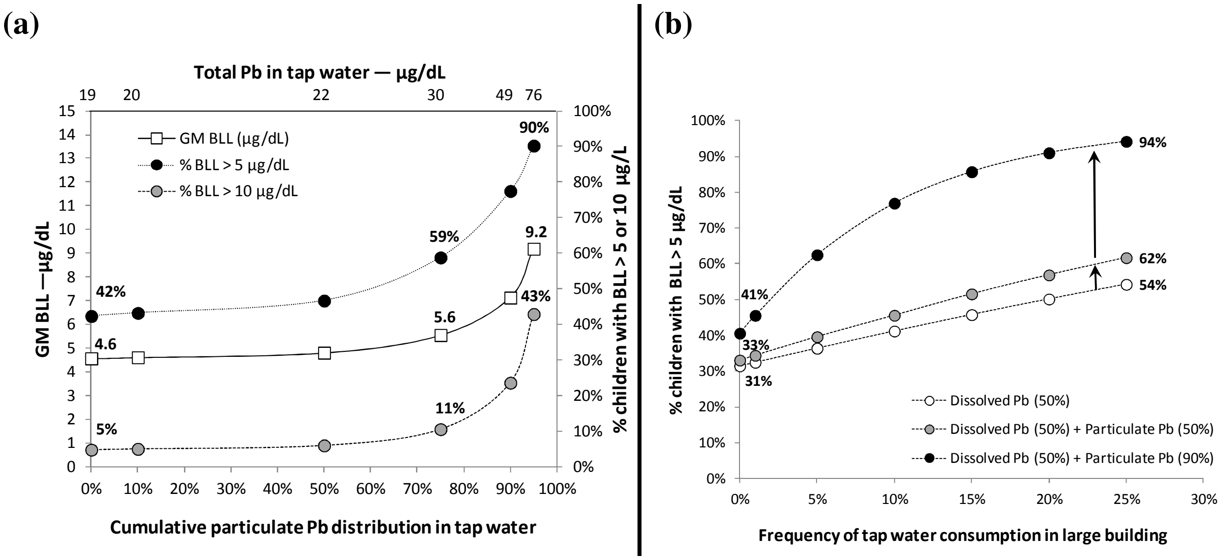


Figure 6-6. IEUBK simulations considering exposure from soil, dust, diet, air, and tap water. (a) Pb concentrations in tap water considered for exposure are a combination of 70% RDT & 20% 5-minutes-flushing concentrations from homes with an LSL, and 10% 1st flush.

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CHAPITRE 7 DISCUSSION GÉNÉRALE

Cette thèse présente un ensemble de travaux variés, ayant tous pour point commun le plomb particulaire et sa relation avec l'exposition du consommateur. La synthèse de ces travaux est présentée en Figure 7-1. L'ensemble des études menées a permis d'explorer divers aspects du plomb particulaire, et d'accumuler des données et des informations sur cette composante peu étudiée du plomb dans l'eau potable. Les données cumulées ont permis tout d'abord d'estimer la contribution du plomb particulaire dans l'exposition du consommateur au plomb par l'eau potable. Par ailleurs, ces données ont aussi permis de valider une méthode d'abattement du plomb particulaire en plus du plomb dissous, pouvant être appliquée immédiatement et à moindre coût dans les résidences, écoles, et garderies, afin de protéger les populations les plus vulnérables au plomb dans l'attente de solutions à long terme. La discussion sera menée selon trois grands axes. Les apports originaux du projet dans chacun de ces axes seront soulignés, ainsi que les manques à combler et nuances à apporter. D'abord on discutera des données de plomb particulaire obtenues dans ce projet, de leur importance en termes d'exposition du consommateur, et de leur utilité dans le cadre d'une analyse de l'exposition. Ensuite, les résultats de bioaccessibilité et de contribution du plomb particulaire à l'exposition du consommateur seront développés. Enfin, les données obtenues sur les dispositifs au point d'utilisation comme moyen de protection du consommateur au plomb particulaire seront discutées.

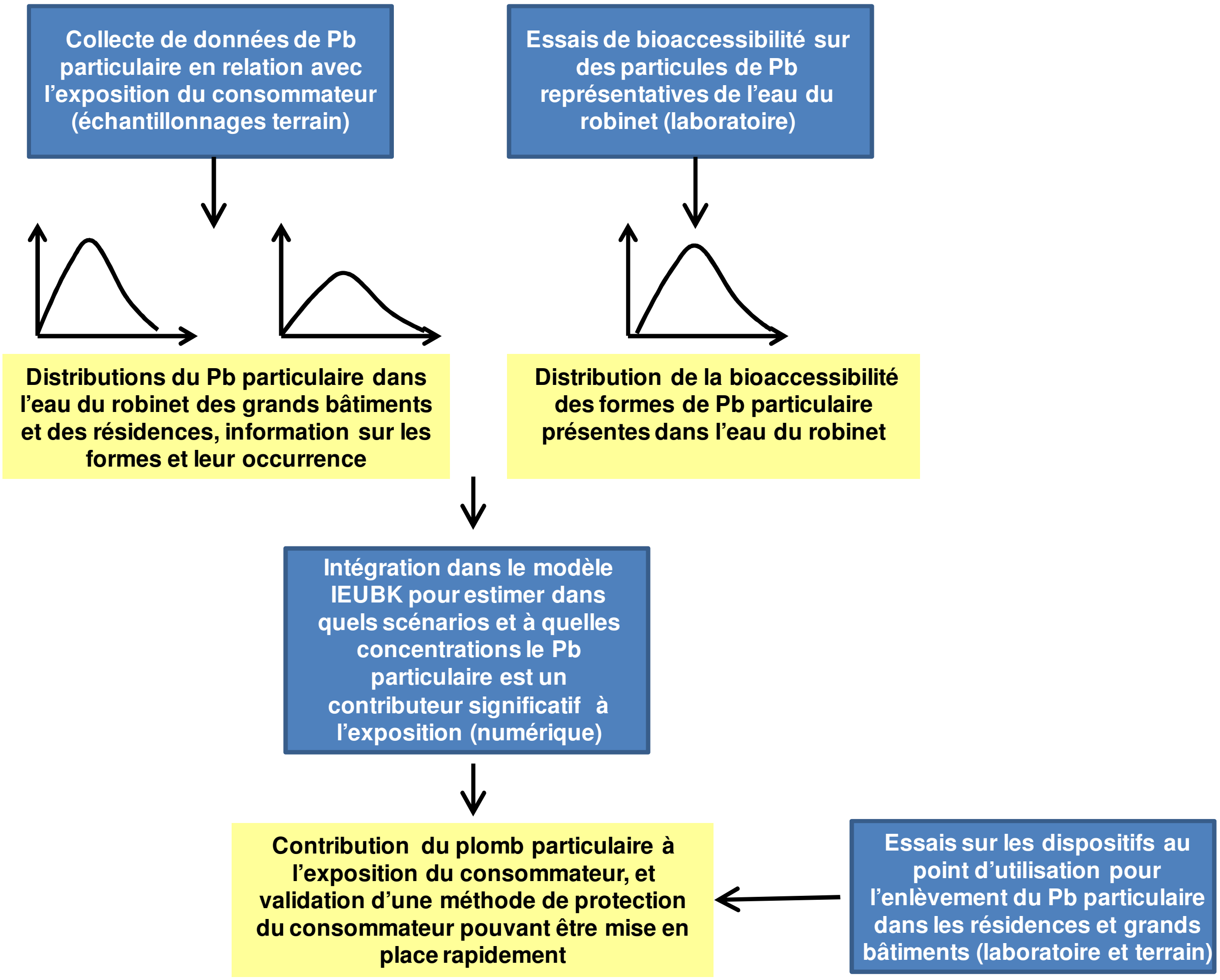

Figure 7-1. Synthèse des travaux de doctorat.

7.1 Distribution des concentrations de plomb particulaire, et importance dans l'exposition du consommateur

La Table 7-1 résume les caractéristiques des données de plomb particulaire dans l'eau collectées pour ce projet. Les analyses de métaux dans l'eau ont été effectuées par des laboratoires accrédités appliquant un protocole de contrôle de la qualité lors de l'analyse ICP-MS (blanc, solution standard, duplicata, tous les 25-30 échantillons; résultats valables aussi pour les résultats d'analyse des essais de bioaccessibilité et des essais POU). La majorité des concentrations de plomb obtenues étaient au-delà de la limite de quantification de l'appareil utilisé, assurant ainsi une bonne fiabilité des résultats (limite de quantification ~ 3 fois la limite de détection). Les quelques valeurs entre la limite de détection et la limite de quantification ont été considérées telles quelles car elles représentaient une faible fraction des échantillons et pouvaient être considérées comme fiables, bien que moins fiables comparativement aux valeurs au-delà de la limite de quantification. Dans le cas de valeurs de plomb en dessous de la limite de détection (résidences avec ESP), les concentrations ont été posées égales à 0 pour l'analyse statistique effectuée. En effet, les résultats de l'analyse étaient comparables pour la valeur 0, la valeur égale à la limite de détection, ou la valeur égale à la moitié de la limite de détection. Les analyses de dépôts d'ESP ont été effectuées en combinant la spectroscopie Raman et le ion TOF-SIMS. Ces méthodes ont été sélectionnées après avoir testé diverses techniques pour lesquelles les résultats étaient moins concluants: la diffraction aux rayons X exigeait un grand volume d'échantillon, et ne permettait pas de distinguer certains oxydes de plomb (superposition des pics); la spectroscopie aux rayons X montrait des interférences entre l'énergie de liaison des oxydes PbO_2 et Pb_3O_4 et était plus coûteuse que la spectroscopie Raman. Ainsi, la spectroscopie Raman était appliquée en première appréciation globale des échantillons, puis les échantillons étaient portés à l'analyse TOF-SIMS lorsqu'un doute subsistait sur certains oxydes, notamment le plomb IV (PbO_2), plus difficile à distinguer avec le Raman (bruit de fond important). Quelques unes des particules collectées derrière les aérateurs de robinet ont été analysées par ion TOF-SIMS en première validation, puis la totalité des particules a été analysée par digestion totale et analyse ICP-MS lors des essais de bioaccessibilité.

Les résultats de métaux dans les échantillons collectés en 2007 ont permis d'effectuer une analyse des sources de plomb particulaire dans les résidences avec ESP à Montréal, ces sources étant majoritairement (i) la corrosion des éléments de tuyauterie interne, et (ii) le détachement de particules/dépôts de fer accumulés dans l'ESP et/ou la tuyauterie interne. Ces conclusions ont été validées par l'analyse des particules collectées derrière l'aérateur des robinets échantillonnés, et par l'analyse de dépôts internes d'ESP excavées à Montréal. La comparaison des données de plomb particulaire obtenues avec les différents protocoles d'échantillonnages appliqués en 2006 et 2007 a permis de démontrer que les échantillonnages après 30 minutes de stagnation n'étaient pas adaptés à la détection de plomb particulaire, et que la création de perturbations hydrauliques (e.g. débit élevé) augmentait considérablement la fraction de plomb particulaire mesurée dans l'eau du robinet. L'analyse multi-métaux des résultats obtenus dans le grand bâtiment échantillonné a aussi permis de déterminer les sources de plomb particulaire présentes dans l'eau du bâtiment, les éléments de plomberie en laiton étant une source majeure. Par ailleurs, ces échantillonnages ont aussi démontré que le plomb particulaire était significativement élevé dans le grand bâtiment étudié, et ce de façon constante. Ainsi, les concentrations anormalement élevées répertoriées pour les grands bâtiments (Boyd *et al.* 2008a, Bryant 2004, Maas *et al.* 1994, Triantafyllidou & Edwards 2009) seraient expliquées par la présence de plomb particulaire. En conclusion, ce projet a permis de clairement identifier les sources de plomb particulaire, et les protocoles adaptés à sa détection. Enfin, les concentrations élevées en plomb particulaire mesurées avec les échantillonnages à perturbations hydrauliques, mais surtout dans le grand bâtiment, ont permis de justifier l'importance du plomb particulaire dans l'eau du robinet, et par conséquent l'importance de sa prise en compte lors de l'élaboration des protocoles d'échantillonnage et d'analyse.

Table 7-1. Synthèse des données de plomb particulaire et de plomb dissous collectées.

Type de logement	**N**	**Protocole**	**Période**	**Eau froide/ chaude**	**Type de robinets échantillonnés**	**Appréciation de la corrosivité de l'eau distribuée**	**Analyses additionnelles**
Résidences-ESP	109	30 min de stagnation (1L, 2L, 5M)	Juil-Sept 2006	Eau froide	Cuisine	Peu corrosive	Dépôts ESP et particules aérateur
Résidences-ESP	45	Aléatoire (1L, 2L, 5M)	Juil-Sept 2007	Eau froide	Cuisine	Peu corrosive	Dépôts ESP et particules aérateur
Résidences-ESP	9	Stimulations hydrauliques (S1, S2, S3; 1L)	Juil-Sept 2007	Eau froide	Cuisine	Peu corrosive	Dépôts ESP et particules aérateur
Grand bâtiment (centre pénitencier)	45	1er jet (250 mL), stagnation ≥ une nuit	Avr-Mai 2009	Eau froide	Cuisine, salle de bain, fontaine, cellule, machine à café, entrée d'eau	Moyennement corrosive	Particules aérateur

Ces données constituent un apport significatif et original au thème du plomb dans l'eau potable. En effet, aucunes données de plomb particulaire mesuré dans l'eau du robinet n'étaient disponibles dans la littérature avant ce projet. Les publications mentionnaient le plomb particulaire pour justifier les concentrations élevées de plomb mesurées dans l'eau du robinet, sans toutefois jamais le mesurer. Récemment, une étude a aussi évalué les concentrations de plomb particulaire dans l'eau du robinet de résidences avec ESP dans un autre système (Kim *et al.* 2011), permettant ainsi d'accroitre la base de données sur le plomb particulaire dans l'eau du robinet. Aussi, dans ce projet les distributions de plomb particulaire ont été obtenues dans des endroits cibles, soit des résidences avec ESP, et un grand bâtiment. Ces zones décrivent adéquatement un environnement à risque dans lequel l'enfant évolue (résidence familiale et école/garderie), et donc les distributions de concentrations sont représentatives de l'exposition potentielle de l'enfant habitant dans une résidence avec ESP. De plus, les protocoles d'échantillonnage effectués étaient d'intérêt pour l'exposition de l'enfant. L'échantillonnage aléatoire permet d'avoir une distribution de concentrations représentative de la consommation d'eau dans une résidence puisque cette dernière est un mélange d'échantillons pris après de longues ou de courtes stagnations. Un échantillonnage après 30 minutes de stagnation est utile pour détecter la présence d'une ESP, ou détecter l'ampleur des concentrations de plomb dissous reliées à la présence de cette dernière. Cependant, il ne représente qu'une fraction de la consommation journalière du résident. L'échantillonnage avec stimulations hydrauliques permet de décrire les concentrations de plomb particulaire dans l'eau représentatives d'habitudes de consommations fréquentes dans les résidences, contrairement aux échantillonnages usuels effectués à faible débit. Dans le cas du grand bâtiment, des échantillons de 250 mL étaient collectés le matin après au moins une nuit de stagnation (1er jet), soit selon les protocoles de l'USEPA et de Santé Canada développés pour détecter les sources de plomb et y remédier. Le volume échantillonné, 250 mL, correspond à un volume de consommation plus usuel que le volume de 1 L appliqué pour les échantillonnages dans les résidences avec ESP. Cependant, le 1er jet ne représente qu'une partie de la consommation d'un enfant évoluant dans une école/garderie, et de part la longue stagnation préalable à la prise de l'échantillon, les concentrations mesurées sont maximisées. Par conséquent, ces concentrations sont représentatives de l'exposition potentielle maximale de l'enfant dans un grand bâtiment, et non de son exposition globale dans le bâtiment. Cependant, il convient de souligner que de longues stagnations telles que celle appliquée pour l'échantillonnage du centre pénitencier sont nettement plus fréquentes dans un grand bâtiment comparativement à une résidence. Ainsi, l'exposition à des concentrations de plomb élevées suite à de longues périodes de stagnation dans un grand bâtiment représente une fraction significative de l'exposition de l'enfant à considérer.

Bien que les réponses apportées par ce projet aient permis de mieux caractériser le plomb particulaire du point de vue de ses concentrations, de ses sources, de sa détection, et des paramètres influençant son détachement, il reste un vaste champ de recherche à étudier pour compléter et améliorer les connaissances obtenues. En effet, l'échantillonnage de type aléatoire permet de reproduire la variété des échantillons d'eau consommés dans une résidence, cependant la fiabilité des résultats obtenus en rapport avec l'exposition du consommateur augmente avec le nombre de résidences échantillonnées (van den Hoven & Slaats 2006). Les 45 maisons échantillonnées en 2007 ne représentent pas un large échantillon, ainsi les concentrations de plomb mesurées ne sont pas parfaitement représentatives de l'exposition du consommateur et il serait judicieux d'échantillonner au minimum le double de résidences. De même, les échantillonnages avec création de perturbations hydrauliques représentent un apport intéressant mais limité, puisque neuf résidences seulement ont été échantillonnées. Considérant les résultats obtenus, soit une augmentation drastique des concentrations de métaux particulaires et colloïdaux, il est très clair que les échantillonnages effectués à faible débit sous estiment les concentrations de plomb particulaire. Or le consommateur utilise rarement l'eau du robinet à un débit ≤ 7 L/min tel qu'utilisé lors des échantillonnages aléatoires et après stagnation appliqués dans les résidences et bâtiments. Il serait par conséquent adapté d'effectuer les échantillonnages (stagnation aléatoire ou non) avec un fort débit pour mieux estimer les concentrations de plomb particulaire auxquelles les consommateurs sont réellement exposés. Dans cette optique, des bouteilles d'échantillonnage à large goulot seraient indispensables.

L'ensemble des résultats obtenus correspondent à la période d'été. En effet, la dissolution du plomb des ESP augmente avec la température, et effectuer les échantillonnages de plomb durant la période d'été permet d'obtenir un estimé des concentrations maximales de plomb dissous auxquelles les populations peuvent être exposées. Il serait cependant intéressant de mesurer les concentrations de plomb particulaire durant la période d'hiver, et durant les transitions de températures au printemps et à l'automne. En effet, les résultats de l'étude santé menée à Montréal récemment ont montré que les concentrations de plomb total mesurées après 30 minutes de stagnation, soit en majorité du plomb dissous, diminuaient drastiquement avec la température, les concentrations les plus basses étant mesurées entre décembre et mars (INSPQ 2011). La température influence la dissolution du plomb et donc les concentrations de plomb dissous mesurées au robinet, cependant, il est probable qu'elle n'ait pas autant d'effet sur le détachement de plomb particulaire. Cela est d'autant plus probable lorsque les principales sources de plomb particulaire se trouvent dans la tuyauterie interne qui ne subit pas de refroidissements hivernaux drastiques. Ainsi, l'exposition au plomb particulaire serait répartie sur toute l'année tandis que l’exposition au plomb dissous aurait lieu majoritairement en été, du moins pour des climats comparables au climat de Montréal. Cette considération est importante car l’exposition annuelle cumulée au plomb particulaire dans les résidences pourrait égaler l’exposition au plomb dissous. De même, les gradients de température durant les changements de saison pourraient causer un stress sur les dépôts d’ESP, et ainsi détacher du plomb particulaire. Il serait par conséquent intéressant de mesurer le plomb particulaire dans l’eau des résidences avec ESP durant ces périodes de transition, en ciblant spécifiquement l’eau provenant des ESP.

Aussi, la majorité des données de plomb dans l’eau ont été mesurées au robinet de cuisine, or il est connu que les enfants ont recours à d’autres robinets plus faciles d’accès pour leur consommation, tels que les robinets de salle de bain. Ces robinets sont en général de moins bonne qualité comparativement aux robinets de cuisine, par conséquent plus sujets à la corrosion, et présentent en général des concentrations en plomb plus élevées (INSPQ 2011). Par ailleurs, bien que non recommandé par les autorités de santé publique, l’eau chaude est souvent utilisée à la cuisine pour la cuisson des aliments. Le plomb dissous et le plomb particulaire contenus dans cette eau pourraient ainsi adhérer aux aliments lors du processus de cuisson, et contribuer à l’exposition du consommateur. Ainsi, pour compléter les données sur l’exposition des enfants au plomb dans l’eau, il serait pertinent de mesurer les concentrations de plomb dissous et de plomb particulaire aux robinets de salle de bain, et dans l’eau chaude.

Dans la même optique, il a été souligné précédemment que les échantillons collectés dans le centre pénitencier représentaient la fraction maximale de l’exposition au plomb dans un grand bâtiment. Il serait plus adapté pour estimer l’exposition globale d’un enfant évoluant dans une école de prélever divers échantillons représentatifs de la consommation de l’enfant dans de tels bâtiments, incluant le premier jet le lundi matin (deux jours de stagnation) et un autre jour de la semaine (une nuit de stagnation), mais aussi des échantillons collectés de façon aléatoire au cours de la journée scolaire. Aussi, la configuration de la tuyauterie interne du centre pénitencier échantillonné ne reflète pas nécessairement celle d’une école ou d’une garderie. En effet, beaucoup de robinets de consommation étaient disponibles dans le bâtiment de part le cloisonnement spécifique au centres carcéraux, et un grand nombre de vannes en laiton étaient présentes notamment au niveau de la tuyauterie en amont des robinets de cellules. Enfin, les habitudes de consommation différaient d’une école, puisque le centre était habité en permanence. Il serait donc pertinent de mesurer les concentrations de plomb dissous et de plomb particulaire dans plusieurs écoles, pour refléter les concentrations de plomb auxquelles les enfants sont réellement exposés.

Enfin, les distributions de plomb particulaire et de plomb dissous dans les résidences avec ESP (Montréal) et dans un grand bâtiment (Laval) correspondent à deux réseaux de distribution distincts. Étant donné la relative faible agressivité de l'eau de Montréal, il serait adapté de procéder à des échantillonnages de plomb dissous et de plomb particulaire pour des réseaux distribuant une eau plus corrosive. En effet, les résultats de Montréal démontrent une faible fraction de plomb particulaire avec des échantillonnages standards, cependant cette fraction augmente drastiquement avec des stimulations hydrauliques. Ainsi, un système relativement peu sujet à des dépassements de plomb de part les caractéristiques de son eau peut aisément dépasser la norme de 10 µg Pb/L avec seule la contribution du plomb particulaire sous l'effet de perturbations hydrauliques. Il serait par conséquent justifié d'évaluer la situation pour une eau de nature plus corrosive, pour compléter la base de données sur le plomb particulaire. Par ailleurs, il serait aussi pertinent de mesurer le plomb particulaire pour des résidences avec ESP présentant du plomb tétravalent très peu soluble. Cette forme de plomb est caractéristique des villes américaines ayant appliqué de fortes doses de chlore dans le réseau durant les années 90 pour limiter la formation de biofilm, cependant sa contribution en terme de plomb particulaire n'a pas été mesurée. Dans le cas de Montréal, les dépôts d'ESP analysés par cette étude ont montré des carbonates de plomb très solubles, se détachant sous une forme colloïdale (mesuré dans le plomb dissous). Enfin, dans le cas des grands bâtiments, il serait pertinent de mesurer la situation pour des eaux moins et plus corrosives que l'eau de Laval. Très peu de données sont disponibles sur les écoles et garderies, or il est important d'estimer l'ampleur du plomb dissous et du plomb particulaire dans ces bâtiments puisque (i) les concentrations en plomb total sont généralement très élevées, et (ii) la consommation dans ces bâtiments représente une fraction significative de la consommation de l'enfant. L'ensemble des distributions de plomb particulaire pour divers types d'eau permettrait d'évaluer l'ampleur des concentrations de plomb particulaire par type d'eau, et ainsi permettre aux municipalités de mieux élaborer leurs stratégies de réduction du plomb dans l'eau.

7.2 Bioaccessibilité du plomb particulaire et contribution à l'exposition

Le développement d'un test de bioaccessibilité spécifiquement pour les particules de plomb de l'eau potable, ainsi que les résultats générés, constituent un apport très original de ce projet. En effet, compte tenu des résultats de biodisponibilité sur les sols, poussière, et peinture observés dans la littérature, il était induit que le plomb particulaire aurait une biodisponibilité en général plus faible que le plomb dissous. Or, étant donné les concentrations de plomb particulaire majeures mesurées dans les grands bâtiments, l'ajustement de ces concentrations ingérées par leur biodisponibilité apparait très important pour ne pas surestimer de façon dramatique l'exposition de l'enfant au plomb particulaire. Dans la littérature, une seule étude relatait des résultats de dissolution de plomb particulaire dans un fluide gastrique synthétique (Triantafyllidou *et al.* 2007). Les particules testées étaient générées au laboratoire, et représentatives de l'eau potable (laiton, PbO_2, soudure), et ont démontré une solubilité variable selon le type de particule testé. Bien que déjà substantielle, cette étude n'avait cependant pas été menée pour obtenir des résultats de bioaccessibilité valides pour une analyse de l'exposition, mais plutôt pour démontrer que les méthodes d'acidification et de digestion du plomb total appliquées par les laboratoires sous-estimaient la fraction particulaire du plomb total. Ainsi, le test *in vitro* appliqué n'était pas calibré par des données *in vivo*, et les facteurs appliqués pour la simulation gastrique (pH 1.2 durant 3 à 24 heures) étaient peu réalistes du processus de digestion, empêchant l'application des résultats dans une analyse de l'exposition. Dans le présent projet, le test *in vitro* sélectionné pour adaptation aux particules de plomb de l'eau potable est la Relative Bioaccessibility Leaching Procedure (RBALP) développée par Drexler & Brattin (2007). En effet, suite à la réflexion menée dans la revue de littérature et présentée au Chapitre 1, la RBALP est apparue comme la procédure *in vitro* présentant le plus haut niveau de calibration et de validation. Les résultats *in vitro* de cette procédure ont été calibrés par des résultats de biodisponibilité *in vivo* sur un animal représentatif du système digestif du petit enfant (cochonnet), la relation obtenue permettant ainsi d'évaluer la biodisponibilité des particules à partir des résultats de bioaccessibilité. Aussi, le test a été appliqué sur un grand nombre de sols (et une peinture), puis validé et standardisé par un protocole qualité/contrôle rigoureux, et une analyse statistique des résultats obtenus par différents laboratoires. Étant donné les différences entre les particules de plomb de l'eau potable (hétérogène, faible masse, indivisible) et les particules de sols ou poussières (masse homogène, divisible), des adaptations ont été apportées à la RBALP originale. Ces adaptations ont été effectuées suite à l'analyse rigoureuse des paramètres influençant la bioaccessibilité menée dans la revue de littérature au Chapitre 1. Ainsi, les facteurs influençant la bioaccessibilité (pH, temps, ratio solide/liquide, agitation) ont été maintenus afin de conserver la relation *in vivo-in vitro* de Drexler & Brattin (2007) valide.

L'application du test sur un grand nombre de particules (70 échantillons), de natures variées (5 types de particules laboratoire, 65 échantillons de particules terrain), et de diverses provenances (résidences avec/sans ESP, grand bâtiment) permet d'avoir une distribution réaliste de la bioaccessibilité du plomb particulaire de l'eau potable. En effet, contrairement aux résultats de bioaccessibilité sur les sols, qui représentent en majorité les sols miniers, les particules testées dans ce projet reflètent la quasi-totalité des particules de plomb recensées dans l'eau potable, soit les particules issues des dépôts d'ESP (carbonates de Pb, PbO_2), des dépôts de calcium, des dépôts de fer, des soudures, et des éléments en laiton. Ainsi, les résultats peuvent être appliqués avec fiabilité dans une analyse de l'exposition. Les résultats de bioaccessibilité, couplés à la relation *in vivo-in vitro* de Drexler & Brattin (2007), ont été appliqués pour ajuster les concentrations de plomb particulaire dans le modèle IEUBK de l'USEPA estimant le plomb dans le sang des enfants de 6 mois à 7 ans exposés au plomb par leur environnement (nourriture, eau, sols, poussières, peinture). Les concentrations de plomb particulaire et de plomb dissous appliquées étaient une combinaison des concentrations mesurées dans les résidences avec ESP et dans le grand bâtiment échantillonnés (section 7.1) pour représenter un enfant évoluant dans une résidence avec ESP et une école/garderie. Les niveaux d'exposition au plomb par le sol, la poussière, la nourriture, et la peinture étaient fixés afin d'observer uniquement l'effet de l'eau, à partir des valeurs médianes/moyennes les plus récentes recensées au Canada lorsque possible (dans le cas contraire, valeurs par défaut de IEUBK). Les résultats obtenus avec IEUBK en augmentant progressivement la concentration d'exposition au plomb particulaire selon sa distribution dans l'eau du robinet, tout en maintenant fixe la concentration de plomb dissous dans l'eau (médiane), ont mis en évidence une contribution significative du plomb particulaire à l'exposition de l'enfant de 7 ans et moins. Cette contribution était notable à partir du 75^e percentile de la distribution du plomb particulaire, et était majoritairement liée à la considération dans le scénario d'exposition des concentrations mesurées dans le grand bâtiment (10% de la fréquence de consommation d'eau totale). Par ailleurs, l'augmentation progressive de la fréquence de consommation d'eau dans le grand bâtiment considérée dans les scénarios d'exposition (0-25%) a résulté en une hausse drastique de l'estimé du pourcentage d'enfants avec une concentration de plomb dans le sang élevée, et ce pour des valeurs conservatrices de plomb dans l'eau (médiane plomb dissous, médiane plomb particulaire) ou non (médiane plomb dissous, 90^{e} percentile plomb particulaire). Ainsi, les résultats de bioaccessibilité couplés aux résultats de concentrations de plomb particulaire dans l'eau du robinet ont permis de démontrer que le plomb particulaire pouvait contribuer de façon significative aux concentrations de plomb dans le sang du petit enfant, et donc de confirmer l'importance de la prise en compte du plomb particulaire dans les protocoles d'échantillonnage et d'analyse. Aussi, il a été possible de démontrer l'importance de cibler les grands bâtiments pour l'échantillonnage du plomb dissous et du plomb particulaire, afin d'identifier les bâtiments ayant une problématique de plomb dans l'eau, et donc de protéger les populations vulnérables au plomb. Ces résultats de bioaccessibilité pourront au même titre être intégrés dans les modèles biocinétiques et les modèles d'analyse de risque sur le plomb, et ainsi raffiner la composante du plomb dans l'eau du robinet par différenciation entre le plomb dissous et le plomb particulaire.

Malgré l'apport significatif fourni par les résultats de bioaccessibilité aux modèles d'exposition, il reste encore des points à éclaircir. En effet, les particules testées englobent la quasi-totalité des formes de plomb particulaire de l'eau potable, cependant les particules de phosphate de plomb n'ont pas été testées pour leur bioaccessibilité. Ce type de particules peut provenir de dépôts en surface interne des ESP et de la tuyauterie interne dans des systèmes appliquant des traitements anticorrosion, or l'application des orthophosphates est largement répandue dans certains pays, notamment aux États-Unis, en Europe continentale et en Angleterre. Ainsi, un estimé de la bioaccessibilité de ces particules serait utile pour confirmer ou non l'effet bénéfique de l'application d'orthophosphates. Il est induit, selon les résultats obtenus par Arnich *et al.* (2003), Casteel *et al.* (2006), Drexler & Brattin (2007), et USEPA (2007b) que les particules de plomb à base de phosphate ont une très faible biodisponibilité. De même, Scheckel & Ryan (2003) ont démontré une diminution drastique de la bioaccessibilité de peinture très soluble à base d'hydrocerussite, suite à l'ajout de boisson gazeuse à base de phosphate dans le fluide gastrique. Ainsi, les particules de plomb générées dans les réseaux avec ajout d'orthophosphates ne contribueraient pas à l'exposition de l'enfant, cependant il conviendrait de vérifier cette hypothèse considérant le nombre de systèmes concernés. Par ailleurs, des tests de bioaccessibilité avec ajout de phosphates dans le fluide gastrique seraient utiles pour éventuellement suggérer la distribution de tablettes de phosphates aux enfants exposés au plomb par l'eau du robinet, pour en limiter l'absorption. Aussi, les particules terrain testées dans ce projet provenaient majoritairement du réseau de distribution de la ville de Montréal. Selon les résultats de composition globale des particules, ces dernières sont représentatives de la tuyauterie interne des logements, qui est relativement similaire d'une ville à l'autre du point de vue des sources de plomb (laiton, soudures, etc.). Ainsi, les résultats seraient représentatifs du plomb particulaire issu de la tuyauterie interne de tout système. Les résultats sur les dépôts d'ESP effectués avec les particules laboratoire (carbonates de plomb, PbO_2) permettent de compléter les données en englobant les systèmes avec des dépôts de Pb(II) ou des dépôts de Pb(IV) en surface interne des ESP. Cependant, des particules à base de fer ou à base de calcium ont aussi été mesurées dans les particules terrain collectées à Montréal. Ces particules peuvent être issues de dépôts de fer/calcium en surface interne de l'ESP et de la tuyauterie interne, ayant adsorbé le plomb dissous contenu dans l'eau au fil des années et jouant ainsi le rôle de « réservoir de plomb » (Schock *et al.* 2008). Il est induit que selon les caractéristiques de l'eau distribuée, le plomb dissous dans l'eau sera variable, et donc de tels dépôts devraient en théorie contenir une plus forte teneur en plomb dans les systèmes distribuant les eaux les plus corrosives. Ainsi, ces types de particules contiendraient une teneur en plomb variable selon les caractéristiques de l'eau. La littérature sur les sols a démontré que la bioaccessibilité des particules est indépendante de leur teneur en plomb, cependant il est possible que cela ne soit pas valable pour des particules de même type mais à teneur en plomb variable, tel qu'observé avec les deux types de laiton testés dans les particules laboratoire (Chapitre 6). Il serait par conséquent d'intérêt de tester la bioaccessibilité de particules provenant de dépôts de fer, calcium ou autre dans différents réseaux, notamment des réseaux distribuant une eau plus agressive comparativement à l'eau de Montréal, pour vérifier si la bioaccessibilité de ces types de particules de plomb est similaire d'un système à un autre. Enfin, très peu de particules issues du grand bâtiment testé ont pu être évaluées pour leur bioaccessibilité. En effet, le grand nombre de robinets sans aérateurs dans le bâtiment a limité le nombre d'échantillons collectés. Or les concentrations de plomb particulaire les plus élevées recensées dans ce projet ont été mesurées dans le grand bâtiment, et non dans les résidences avec ESP. Par conséquent, la collecte de telles particules dans de grands bâtiments, et l'évaluation de leur bioaccessibilité, seraient nécessaires pour compléter les données de bioaccessibilité et raffiner l'estimation de l'exposition du consommateur au plomb particulaire dans l'eau du robinet.

Une des limitations des résultats de bioaccessibilité réside dans la taille des particules testées. En effet, la taille des particules utilisées était de manière générale beaucoup plus grande (0.5-10 mm) que le plomb particulaire de l'eau potable (≥ 0.45 µm) pour des fins de manipulation. Or selon la littérature sur les sols, la bioaccessibilité et donc aussi la biodisponibilité augmenterait avec la diminution de la taille des particules (Ruby *et al.* 1999). Cependant, l'effet de la taille des particules sur la bioaccessibilité n'est pas toujours vérifié. En effet, il semblerait que la fraction la plus fine des sols contienne une plus grande teneur en plomb (Juhasz *et al.* 2011, Madrid *et al.* 2008a, Madrid *et al.* 2008b, Siciliano *et al.* 2009). Ainsi, la bioaccessibilité plus élevée observée pour les fractions les plus fines des sols pourrait être expliquée par leur plus forte teneur en plomb plutôt que par leur taille. Dans le cadre de ce projet, des particules de même type ont pu être classifiées par taille et testées pour leur bioaccessibilité. La bioaccessibilité augmentait avec la diminution de la taille des particules, et les particules de même type démontraient une teneur en plomb comparable. Par conséquent, la bioaccessibilité mesurée dans ce projet pourrait sous-estimer la bioaccessibilité réelle du plomb particulaire. Ainsi, il serait plus adapté de sélectionner le 90^{e} percentile de la distribution des résultats de bioaccessibilité plutôt que la médiane, pour application à la dose de plomb particulaire ingérée dans le modèle IEUBK. Cependant, les résultats du présent projet sont limités à une gamme de taille de particules assez grande relativement au plomb particulaire de l'eau potable. Il est probable que la teneur en plomb dans les particules de l'eau potable soit indépendante de la taille des particules, puisque leur nature est différente de celle des sols, et que le pourcentage en plomb dans les dépôts de conduites, soudures, et laiton, est déterminé avant leur détachement en plus ou moins grandes particules. Par conséquent, des essais complémentaires avec des particules représentatives de l'eau potable, de même type et à teneur en plomb identique, dans une gamme de taille plus fine que celle testée dans ce projet, permettraient de clarifier l'effet de la taille sur la bioaccessibilité, et l'ampleur de cette effet. La réalisation de tels essais représente cependant un défi ardu à compléter considérant l'absence de standards représentatifs des particules de l'eau potable.

Une seconde limitation du test de bioaccessibilité est sa validité pour l'analyse de l'exposition de l'enfant. En effet, dans l'idéal les données de bioaccessibilité obtenues sur des particules de plomb seraient calibrées sur des données de biodisponibilité mesurées chez des enfants exposés à ces mêmes particules de plomb. Ceci est parfaitement inconcevable, donc les données de la RBALP ont été calibrées sur des résultats *in vivo* obtenus sur des cochonnets, soit le modèle reconnu comme le plus représentatif du processus de digestion gastro-intestinal des jeunes enfants. Il s'agit donc d'une première altération de la réalité de l'exposition de l'enfant aux particules de plomb. Aussi, la méthode RBALP a été calibrée avec les résultats *in vivo* et *in vitro* obtenus sur 18 sols et une peinture. Les sols testés étaient majoritairement issus de déchets miniers, or il est probable que la relation *in vivo-in vitro* soit différente pour une plus grande variété de sols et d'autres types de particules de plomb. En effet, il a été démontré que pour certains types de sols, la biodisponibilité était surestimée par la RBALP (Juhasz *et al.* 2009, Juhasz *et al.* 2011, Smith *et al.* 2011b). Ainsi, la calibration du modèle serait à ajuster pour les particules de plomb de l'eau potable. Cependant il est difficilement concevable d'effectuer des essais *in vivo* avec de telles particules pour réaliser cet ajustement. Ainsi, les résultats doivent être interprétés et utilisés avec précaution, puisqu'ils reflètent une altération de l'exposition de l'enfant aux particules de plomb. L'adaptation d'un autre test pour les particules de l'eau potable, tel que le SBRC-intestinal proposé par Juhasz *et al.* (2009), est concevable. Cependant, ce test est plus complexe à adapter que la procédure RBALP. Aussi, l'obtention de résultats conservateurs pour certaines particules avec une procédure telle que la RBALP est relativement utilisé et accepté en analyse de l'exposition (principe de précaution).

Considérant le type de particules « terrain » testées, soit les particules collectées derrière les aérateurs de résidences avec/sans ESP et dans un grand bâtiment, il était notable que leur teneur en plomb était très élevée toutes catégories de logements confondues (médiane 5%). Ainsi, ces particules accumulées derrière l'aérateur du robinet, de taille plus grande en général que le plomb particulaire dans l'eau, ont permis de démontrer une autre forme d'exposition aux particules de plomb du consommateur, et universelle. En effet, Cartier *et al.* (2011) a montré que ces particules contribuaient à augmenter le plomb dissous dans les échantillons collectés au 1er jet. De même, Triantafyllidou & Edwards (2011a) relatent des cas d'intoxication au plomb et la présence simultanée de particules de plomb accumulées derrière l'aérateur du robinet. Aussi, il est concevable que ces particules puissent se fractionner sous l'effet de perturbations hydrauliques causant leur érosion. Ces particules pourraient par conséquent se dissoudre et/ou se fractionner au gré des stagnations et débits ayant lieu dans le robinet. Ainsi, considérant la quantité significative d'aérateurs échantillonnés positifs pour la présence de particules (43% dans les résidences), et la teneur en plomb dans ces particules toutes résidences confondues (5% en médiane), il apparait justifié d'investiguer le comportement de ces particules accumulées derrière l'aérateur (dissolution dans le robinet, érosion sous l'effet du débit). Cependant, il serait d'autant plus utile pour le consommateur que des recommandations soient émises par les autorités de santé publique, tel que nettoyer les aérateurs régulièrement (au minimum tous les 6 mois selon les observations de ce projet), mais aussi installer des robinets pour lesquels l'aérateur peut être facilement enlevé et nettoyé.

Une voie d'exposition par le plomb particulaire a été omise dans l'analyse menée à l'aide du modèle IEUBK et mériterait considération. En effet, un grand volume de l'eau du robinet est utilisé par le consommateur pour la cuisson d'aliments. Or il a été montré par Triantafyllidou *et al.* (2007) que la cuisson de pâtes avec une eau contenant des particules de plomb tétravalent entrainait l'adsorption et/ou l'adhésion des particules de plomb sur les pâtes, et par conséquent l'ingestion des particules de plomb via la nourriture cuisinée avec l'eau du robinet. Considérant les larges volumes d'eau pouvant être utilisés pour la cuisson de pâtes, riz, céréales, ou légumes par exemple, l'exposition au plomb particulaire via les aliments cuisinés pourrait être majeure. Aussi, les particules ne sont plus vraiment visibles lorsque mélangées aux aliments, rendant leur ingestion plus probable. Par conséquent, il serait très valable d'étudier cette voie d'exposition du plomb particulaire. Pour cela, il faudrait tout d'abord estimer la fraction dissoute et la fraction non dissoute des particules suite à la cuisson de divers aliments. Ainsi, il serait possible d'estimer la fraction de plomb dissoute et absorbée sur la nourriture, et la fraction de plomb particulaire adhérée à la nourriture. La fraction du plomb absorbée sur la nourriture pourrait être traitée de la même manière que la dose de plomb ingérée via les aliments dans le modèle IEUBK. Cependant, des essais supplémentaires seraient nécessaires pour estimer la bioaccessibilité des particules ayant adhéré à la nourriture suite au processus de cuisson. Ces essais ne pourraient malheureusement n'être que qualitatifs pour l'instant. En effet, l'ensemble des tests de bioaccessibilité calibrés avec des résultats *in vivo* simulent un état de jeûne (pH gastrique faible, temps de rétention court), or dans des conditions de repas les paramètres de digestion diffèrent (pH gastrique plus élevé, présence de nourriture, temps de rétention plus grand) et par conséquent la bioaccessibilité aussi. Le pH gastrique plus élevé en présence de nourriture aurait tendance à diminuer drastiquement la bioaccessibilité des particules ingérées. Aussi, des phénomènes d'adsorption et de précipitation du plomb solubilisé sur des particules de nourriture non dissoutes sont suggérés lors de la hausse de pH survenant durant la phase intestinale. En effet, les résultats de simulations *in vitro* (non calibrées, non validées) menées en parallèle en conditions de jeûne ou en conditions de repas démontrent de façon générale cette baisse de bioaccessibilité (Medlin 1997, Van De Wiele *et al.* 2007). Malgré cette baisse de bioaccessibilité, il n'est pas évident que l'exposition au plomb particulaire transporté par les aliments soit négligeable, puisque l'exposition est une combinaison de la biodisponibilité des formes de plomb ingérées et des doses de plomb ingérées, or ces doses peuvent être significatives considérant le cumul d'aliments ingérés quotidiennement par l'enfant. Il serait par conséquent pertinent d'évaluer qualitativement la bioaccessibilité du plomb particulaire en présence d'aliments couramment ingérés par l'enfant, cuits à l'eau ou nécessitant l'ajout d'eau, tels que le lait maternisé reconstitué, les céréales (gruau), les pâtes, le riz, les légumes, et les jus reconstitués. Des essais *in vivo* avec ces aliments sont difficilement envisageables, considérant le coût de tels essais et la variété d'aliments à tester. Il serait cependant très pertinent d'effectuer de tels essais sur un animal représentatif du petit enfant (e.g. cochonnet) avec de la poudre de lait maternisé, puisque (i) cela ne constituerait pas un défi majeur des tests *in vivo*, (ii) la poudre de lait est le principal aliment ingéré par les enfants de 0-2 ans nourris au biberon, et (iii) la bioaccessibilité des particules de plomb dans le lait semble augmenter par rapport à l'état de jeûne, contrairement aux autres types d'aliments (Marschner *et al.* 2006, Van De Wiele *et al.* 2007). Les résultats générés permettraient d'attester si la biodisponibilité des particules pourrait effectivement être augmentée en présence de lait, et d'émettre des recommandations ciblées pour les enfants nourris au biberon.

Enfin, l'analyse de l'exposition au plomb particulaire par l'eau du robinet pourrait être considérablement améliorée si menée avec un autre modèle que le modèle IEUBK, ou en adaptant le modèle IEUBK. En effet, le modèle IEUBK simule une exposition chronique, répétée sur un an, à des concentrations de plomb faibles à modérées dans les sols, les poussières, l'eau du robinet, les aliments, et éventuellement la peinture. Les concentrations de plomb dans l'eau sont fixes pour chaque scénario, ainsi le modèle IEUBK ne permet pas de tenir compte de concentrations de plomb particulaire variant d'un jour à l'autre de très élevées à très modérées, de très modérées à très faibles, ou encore de très élevées à très faibles. Or ceci serait plus représentatif de l'exposition au plomb particulaire beaucoup moins prévisible que le plomb dissous en termes d'occurrence. Dans ce projet, la concentration de plomb particulaire a été inclue dans l'exposition selon divers points de sa distribution réelle mesurée (10^{e} percentile, médiane, 95^{e} percentile, etc.), chacun de ces points représentant un scénario d'exposition. Ainsi, il était possible d'estimer à partir de quelles concentrations le plomb particulaire montrait un effet significatif. Cependant, il est peu probable qu'un enfant ingère quotidiennement la même concentration de plomb particulaire. Or la concentration de plomb dans le sang résultant d'une exposition chronique à long terme est différente de celle résultant d'une fréquence d'exposition variable dans le temps. Ainsi, l'estimation de la contribution du plomb particulaire dans l'exposition doit être ajustée. Un modèle permettant de varier l'exposition journalière, hebdomadaire, voire mensuelle au plomb serait une première amélioration. Un tel modèle permettrait par ailleurs de considérer aussi la variation des concentrations de plomb dissous dans l'eau avec les saisons, puisque la température de l'eau démontre un impact majeur sur ces concentrations. Ce type de modèle pourrait être effectué en intégrant une analyse de type Monte Carlo dans le modèle IEUBK. Ceci a été tenté lors de l'élaboration du modèle, cependant le modèle était trop complexe à développer et ainsi, une approche par exposition chronique à une dose de plomb quotidienne fixe a été adoptée. Récemment, Donohue *et al.* (2011) sont parvenus à utiliser IEUBK de manière à simuler des expositions élevées au plomb à court terme. Une telle utilisation du modèle permettrait d'améliorer l'estimation de la contribution du plomb particulaire, mais aussi du plomb dissous.

Enfin, considérant la variabilité de la bioaccessibilité du plomb particulaire, et la variabilité de son occurrence, il serait pertinent d'appliquer une analyse Monte Carlo pour évaluer une distribution des doses de plomb ingérées via l'eau potable. En effet, dans le présent projet, les valeurs médianes des distributions de la bioaccessibilité et des concentrations de plomb particulaire dans l'eau respectivement ont été utilisées pour estimer la dose bioaccessible « médiane » de plomb particulaire ingérée par l'enfant de 7 ans et moins. Bien qu'honorable et représentative d'un scénario d'exposition plausible et relativement conservateur, cette méthode ne permet pas de tenir compte au mieux de la variabilité du plomb particulaire en termes de bioaccessibilité et de concentrations d'occurrence. Ainsi, il serait judicieux de coupler, à l'aide d'une analyse de type Monte Carlo, la distribution des concentrations de plomb particulaire dans l'eau du robinet à la distribution de la bioaccessibilité des particules de plomb, pour générer une distribution des doses ingérées bioaccessibles du plomb particulaire. Plusieurs points significatifs de la distribution, tels que le minimum, le 5^{e} percentile, le 10^{e} percentile, la médiane, le 90^{e}

percentile, le 95^{e} percentile, et le maximum pourraient ensuite être intégrés dans le modèle IEUBK adapté pour une exposition variable dans le temps.

7.3 Protection du consommateur à l'exposition au plomb particulaire dans les résidences, les écoles, et les garderies : dispositifs au point d'utilisation (POU)

L'étude pilote effectuée dans ce projet a permis d'effectuer une seconde évaluation de plusieurs POUs disponibles dans le commerce et certifiés NSF-53 après 2007, pour l'enlèvement du plomb dissous et du plomb particulaire, avec une forme de plomb particulaire et une qualité d'eau différentes de celles appliquées par NSF-53, et typiques des réseaux de distribution. Aussi, pour la première fois l'efficacité d'enlèvement du plomb dissous et l'efficacité d'enlèvement du plomb particulaire ont été mesurées séparément. En effet, les POUs sont généralement suivis pour l'enlèvement du plomb total (e.g., protocole NSF-53, Boyd *et al.* (2005, 2008a, 2008b)), mais leur efficacité pour respectivement réduire le plomb dissous et le plomb particulaire n'avait jamais été évaluée. Cette étude a permis par ailleurs de mieux relier l'efficacité d'enlèvement des POUs à leur technologie de filtration. Le suivi indépendant de l'enlèvement du plomb dissous et du plomb particulaire a démontré que les dispositifs avec bloc de charbon actif étaient plus efficaces pour l'enlèvement du plomb particulaire que pour l'enlèvement du plomb dissous, de par l'excellente barrière physique constituée par le filtre. Les concentrations de plomb total à l'effluent de ces dispositifs étaient en deçà ou excédaient légèrement le seuil NSF de 10 µg Pb/L. Ainsi, les POUs de type « sur robinet » ou « sous évier », comprenant un bloc de charbon actif comme technologie de filtration, ont été une seconde fois validés et sont recommandés pour l'enlèvement du plomb dissous et du plomb particulaire. Au contraire, les dispositifs pichets ne permettaient pas de réduire l'exposition du consommateur en présence de plomb particulaire de par leur milieu granulaire, justifiant ainsi le retrait de la certification NSF-53 pour ces dispositifs en 2007. Ce projet a donc permis de mieux comprendre le retrait de la certification NSF-53 pour les dispositifs de type pichet, et de vérifier le comportement de ces dispositifs en présence de plomb particulaire. Considérant les résultats sur les pichets à base de charbon actif en grains et de résine échangeuse d'ions, il est fortement déconseillé d'utiliser de tels dispositifs pour l'enlèvement du plomb, même si ces derniers étaient certifiés NSF-53 pour le plomb avant 2007.

En effet, ce type de technologie est inefficace pour l'enlèvement du plomb particulaire, et peut éventuellement aggraver les concentrations en plomb de l'affluent par cumul de particules dans le filtre, puis passage d'une forte concentration de plomb issue de ces particules dans l'effluent. Ceci est d'importance majeure puisque ces dispositifs sont largement utilisés par les populations, le plus souvent pour réduire la couleur, et les goûts et odeurs de l'eau du robinet. Or les particules de plomb émanant de la tuyauterie interne ne sont pas rares dans les résidences avec ou sans ESP, comme en témoignent dans la section 7.2 la quantité d'aérateurs échantillonnés positifs pour les particules de plomb, ainsi que la forte teneur en plomb dans ces particules.

Malgré les nombreuses réponses apportées par l'étude pilote sur l'efficacité des POUs, il était important de vérifier cette efficacité dans des conditions réelles d'utilisation, notamment dans les conditions d'usage spécifiques aux grands bâtiments. L'étude menée sur les dispositifs POU au centre pénitencier a permis de démontrer l'efficacité des POUs sous évier, composés d'un bloc de charbon actif, pour l'enlèvement du plomb dissous et du plomb particulaire dans un grand bâtiment, dans les conditions typiques d'utilisation d'eau d'un grand bâtiment, sur une période de un an. Ceci est un apport original aux études de Boyd *et al.* (2005, 2008, 2008) testant ce type de POU pour réduire les concentrations de plomb dans les écoles de Seattle. En effet, ces études n'évaluaient pas l'efficacité des POUs sur du long terme, ni l'effet des stagnations. Aussi, seules les concentrations de plomb total étaient mesurées au robinet en aval des dispositifs étudiés, et l'efficacité des dispositifs POU n'était pas évaluée en différenciant le plomb dissous et le plomb particulaire. Les dispositifs étaient loin d'avoir atteint leur capacité maximale de filtration indiquée après un an, ce qui suggérait, en considérant un remplacement annuel des cartouches de filtration à des robinets indiqués pour la consommation d'eau potable, un coût raisonnable pour l'exploitant dans de telles conditions de consommation. L'installation de POUs a donc été démontrée comme possible d'un point de vue économique. Les résultats de suivi microbiologique de l'eau du robinet suite à l'installation de POUs constituent aussi un apport important et rassurant sur l'applicabilité des dispositifs POU dans les grands bâtiments. En effet, il était suggéré que la combinaison de longues stagnations spécifiques aux sites non résidentiels, de la consommation du résiduel de chlore dans le long volume de tuyauterie interne de ces bâtiments, et de la présence de charbon actif dans les POUs, pourrait engendrer une croissance bactérienne dans les POUs et dégrader la qualité microbiologique de l'eau en aval des POUs. Ainsi, les résultats de suivi de la qualité microbiologique de l'eau après l'installation de POUs apportent une validation supplémentaire quant à la colonisation et l'amplification des bactéries par les dispositifs. L'installation de dispositifs POU dans un grand bâtiment apparait par conséquent très efficace pour réduire les concentrations de plomb dans l'eau du robinet, et donc l'exposition des personnes du bâtiment, sans causer de risque sanitaire lié à la colonisation des dispositifs. La recommandation de tels dispositifs apparait donc adaptée pour les sites non résidentiels dans l'attente du remplacement des sources de plomb, ou de la mise en place de traitements anticorrosion.

Un autre apport du projet pilote et de l'étude menée au centre pénitencier était l'étude de l'effet de la stagnation sur l'efficacité des dispositifs. En effet, il est concevable que de longues stagnations puissent causer une percée des POUs et donc une augmentation des concentrations de plomb à l'effluent des POUs. Or de longues périodes de stagnation sont observées dans les résidences (journée de travail, nuit, etc.) et dans les grands bâtiments (fins de semaines, vacances scolaires, etc.). Il était donc important de tester cette hypothèse dans l'intérêt des populations. Aucune percée des POUs n'a été observée suite aux deux stagnations appliquées (12 h, 30 min), ainsi il a été possible de valider la fiabilité des POUs pour des périodes de stagnations typiques des résidences et des grands bâtiments, et de conserver la recommandation de ces dispositifs pour l'enlèvement du plomb.

Ces deux études, menées respectivement en conditions accélérées dans un laboratoire et en conditions réelles d'utilisation dans un grand bâtiment, ont permis de compléter l'information sur la mise en place de dispositifs POU pour réduire le plomb dans l'eau. En effet, leur efficacité d'enlèvement du plomb dissous et du plomb particulaire, l'effet des stagnations sur cette efficacité, et leur effet sur la qualité microbiologique de l'eau sont maintenant caractérisés. Cependant, certains aspects des deux études nécessitent des recherches supplémentaires. Premièrement, des validations supplémentaires sont nécessaires quand à l'effet des dispositifs sur la qualité microbiologique de l'eau des grands bâtiments. En effet, dans le cas de l'étude menée au Service Correctionnel Canada (SCC) il était suggéré que les métaux accumulés dans les POUs, notamment le cuivre, avaient empêché la colonisation des dispositifs. Les dispositifs POU, malgré leur composition en charbon actif, apparaissent peu propices à la colonisation de part leur très faible porosité hostile à la prolifération de bactéries. Cependant, cette hypothèse n'a pu être vérifiée dans le cas de cette étude, puisque les métaux accumulés dans les POUs, et potentiellement liés (cuivre) à la présence d'un compteur d'eau neuf en amont des dispositifs, semblaient avoir empêché la colonisation du matériau. Les compteurs d'eau étaient installés dans cette étude pour suivre le volume d'eau filtrée par les dispositifs, et ne devraient pas en pratique être installés directement en amont d'un POU. Ainsi, il serait fort utile de vérifier la colonisation de ce type de POU, en conditions réelles des grands bâtiments, mais sans ajout d'une source générant de fortes concentrations de cuivre directement en amont des dispositifs. L'étendue de la colonisation des dispositifs serait ainsi vérifiée dans des conditions de concentrations de cuivre typiques des grands bâtiments. Une autre nuance à souligner est la différence de performance observée entre l'étude pilote et l'étude au SCC, pour l'enlèvement du plomb dissous par les POUs sous évier constitués d'un bloc de charbon actif. En effet, les concentrations de plomb dissous mesurées dans l'affluent des dispositifs POU au SCC étaient en général supérieures à celles de l'étude pilote, or ces concentrations étaient réduites beaucoup plus efficacement par les dispositifs installés au SCC (≤ 2 µg/L) que dans l'étude pilote (≤ 11 µg/L). Deux hypothèses ont été suggérées pour expliquer cette différence : (i) le test de filtration mené de façon quasi continue dans l'étude pilote pourrait avoir diminué l'efficacité d'enlèvement du plomb dissous par les POUs, et/ou (ii) la forme de plomb particulaire testée dans l'étude pilote, le très friable PbO_2, pourrait s'être désagrégée sous la pression d'eau dans le bloc de charbon, et être larguée sous forme de plomb < 0.45 µm (plomb dissous) à l'eau filtrée. Dans le cas de l'hypothèse (i), des validations supplémentaires des POUs aux robinets fortement sollicités pour de larges volumes d'eau dans les grands bâtiments seraient nécessaires, notamment les robinets de cafétéria. Dans le cas de l'hypothèse (ii), des essais sur les POUs, dans des systèmes présentant des dépôts de plomb tétravalent en surface des ESP, seraient utiles. Ainsi, il serait possible de valider ou non les dispositifs POU de type bloc de charbon actif pour un grand nombre de systèmes et de types d'utilisation. Enfin, bien que l'efficacité des POUs pour l'enlèvement du plomb soit démontrée, la gestion de l'installation et de la maintenance de ces dispositifs pour les sites non résidentiels pourrait limiter cette efficacité. Il est nécessaire de désigner une autorité responsable d'effectuer cette maintenance rigoureusement (sélection des points de consommation, remplacement des cartouches de filtration), et de bien informer la population de consommer spécifiquement l'eau des robinets équipés de POUs, pour que cette population soit effectivement protégée.

CONCLUSIONS ET RECOMMANDATIONS

Les travaux réalisés dans ce projet de doctorat ont permis de dégager les conclusions suivantes:

- Le plomb particulaire, dans l'eau du robinet des résidences avec ESP de Montréal provient de (i) la corrosion des éléments en laiton/bronze et soudures de la tuyauterie interne contenant du plomb, (ii) du détachement de dépôts ferriques en surface interne des conduites, et (iii) du détachement des carbonates de plomb en surface des ESP. Les formes de type (i) sont principalement détectées dans le premier jet en échantillonnage aléatoire, et génèrent des concentrations de plomb particulaire sporadiquement élevées. Les formes de type (ii) sont présentes à faibles concentrations dans tous les échantillons, mais sont difficilement identifiables dans les échantillons collectés au 1er jet. Les formes de type (iii) sont majoritairement des colloïdes, détectables dans les échantillons de plomb dissous (< 0.45 µm) collectés après 5 minutes d'écoulement avec création de perturbations hydrauliques.
- Le plomb particulaire, dans l'eau du robinet du grand bâtiment étudié, est élevé de façon constante dans les échantillons collectés au 1er jet après au moins une nuit de stagnation. Dans le grand bâtiment étudié, le plomb particulaire était principalement issu de la corrosion des éléments en laiton et bronze. Les concentrations élevées de plomb total mesurées dans les grands bâtiments peuvent par conséquent être expliquées par une forte concentration de plomb sous forme particulaire.
- Les concentrations de plomb mesurées dans l'eau du robinet de résidences avec ESP avec échantillonnage créant des perturbations hydrauliques, et les concentrations de plomb mesurées dans le grand bâtiment étudié, démontrent une contribution significative du plomb particulaire aux concentrations de plomb total. Il est par conséquent important de considérer le plomb particulaire dans l'élaboration des protocoles d'échantillonnage, des protocoles d'analyse (acidification et digestion des échantillons), et d'intégrer le plomb particulaire dans l'analyse de l'exposition.
- Les échantillonnages consistant en un rinçage de 5 minutes, suivi d'une stagnation de 30 minutes, puis de la collecte des échantillons sont inadaptés pour la détection de plomb

particulaire dans les résidences. La collecte du 1^{er} litre aléatoire, ou du 1^{er} litre après au minimum 6 heures de stagnation apparaissent plus adaptées. Aussi, les échantillonnages avec créations de perturbations hydrauliques augmentent significativement les concentrations de plomb particulaire mesurées au robinet de cuisine. Ainsi, il apparait indispensable d'appliquer un débit élevé lors des échantillonnages, car les débits faibles traditionnellement appliqués lors des échantillonnages sont peu représentatifs des habitudes de consommation de la population et mènent à une sous-estimation du plomb particulaire.

- Les systèmes de filtration domestique POU constitués d'un bloc de charbon actif et certifiés NSF-53 pour le plomb représentent une solution efficace et économiquement viable pour réduire les concentrations de plomb dissous et de plomb particulaire dans l'eau des résidences et des grands bâtiments (excepté en présence d'un important volume de tuyauterie en acier galvanisé pouvant entrainer un colmatage rapide des POUs), et ce sans dégrader de façon majeure la qualité microbiologique de l'eau du robinet. Les pichets à filtration gravitaire anciennement certifiés NSF-53 pour le plomb ne sont pas recommandés car ils sont peu efficaces et peuvent même aggraver la dose cumulée de plomb ingérée par le consommateur en présence de plomb particulaire.
- Le plomb dans les particules de l'eau potable est généralement hautement bioaccessible (30-100%), excepté pour les particules issues de soudures à base de plomb (bioaccessibilité 1-5%). La combinaison de l'ensemble des résultats de bioaccessibilité démontre une grande variabilité. Cette variabilité, couplée à la variabilité des concentrations de plomb particulaire dans l'eau du robinet en termes de concentrations et de fréquence d'occurrence, témoigne aussi d'une exposition variable du consommateur au plomb particulaire dans l'eau du robinet.
- Le pourcentage élevé d'aérateurs échantillonnés positifs pour la présence de particules dans les résidences avec/sans ESP, et le pourcentage élevé de plomb dans ces particules, démontre une autre forme d'exposition du consommateur via les particules de plomb dans l'eau du robinet.
- Les simulations IEUBK démontrent que le plomb particulaire contribue significativement à l'exposition de l'enfant de 7 ans et moins, notamment lorsque les concentrations de

> plomb particulaire dans les grands bâtiments en contenant sont considérées. Il est par conséquent essentiel de cibler les grands bâtiments en priorité pour effectuer des échantillonnages adaptés à la détection du plomb particulaire, avec une acidification adéquate, pour identifier les bâtiments problématiques et ainsi protéger les populations exposées.

L'ensemble de la recherche menée dans cette thèse a permis de caractériser de multiples facettes du plomb particulaire dans l'eau du robinet (concentrations, source et occurrence, facteurs influents, enlèvement, bioaccessibilité), puis d'intégrer les résultats obtenus dans une analyse de l'exposition pour finalement répondre à la question principale de cette thèse, soit: le plomb particulaire dans l'eau du robinet contribue-t-il significativement à l'exposition de l'enfant de 7 ans et moins? Les résultats de cette étude démontrent que le plomb particulaire contribue de façon significative à l'exposition du jeune enfant, et que cette significativité est principalement liée à l'exposition dans les grands bâtiments présentant une problématique de plomb particulaire dans l'eau. La validation de dispositifs POU pour l'enlèvement du plomb dissous et du plomb particulaire effectuée dans ce projet permet par ailleurs de proposer une méthode efficace de protection du consommateur dans ces endroits cibles, dans l'attente de la mise en place de solutions à long terme.

Néanmoins, des recherches supplémentaires sont nécessaires afin d'améliorer la caractérisation du plomb particulaire, et en conséquence raffiner l'analyse de l'exposition au plomb particulaire et le risque lié à son ingestion. En effet, les résidences et le grand bâtiment échantillonnés ne sont pas nécessairement représentatifs de la variété des qualités d'eau desservies par différents réseaux de distribution. Il serait par conséquent pertinent d'effectuer des échantillonnages dans divers réseaux de distribution, ciblés pour la détection du plomb particulaire au robinet de résidences avec ESP et de grands bâtiments (écoles et garderies de préférence). L'échantillonnage devrait être représentatif des habitudes de consommation, soit représenter des périodes de stagnation variées, et être effectué à des débits réalistes de ceux appliqués par le consommateur. Les résultats compilés permettraient d'avoir une base de données plus complète des concentrations de plomb particulaire dans l'eau du robinet de différents systèmes, représentative des variations de concentrations auxquelles sont exposés les enfants de 7 ans et moins.

Aussi, l'analyse de l'exposition au plomb particulaire, et de la concentration de plomb dans le sang résultant de cette exposition, demande à être raffinée. En effet, dans le présent projet, le modèle IEUBK a été appliqué avec un scénario d'exposition fixé, en augmentant successivement pour chaque scénario la concentration de plomb particulaire ingérée, selon sa distribution réelle mesurée. Les concentrations de plomb dans le sang générées pour chaque scénario sont par conséquent représentatives d'une exposition chronique quotidienne fixée sur un an, et la comparaison des résultats de chaque scénario permet de déterminer un seuil de contribution significative du plomb particulaire. Bien que cette analyse permette une première évaluation honorable, elle ne représente pas une exposition réaliste au plomb particulaire, puisque une telle exposition devrait intégrer des concentrations de plomb particulaire variant dans le temps. Ainsi, il est suggéré de générer, à l'aide d'une analyse Monte Carlo appliquée aux distributions de concentration et de biodisponibilité du plomb particulaire, une distribution des doses de plomb particulaire ingéré biodisponible. Cette distribution permettrait de coupler la variabilité des concentrations de plomb dans l'eau à la variabilité de la bioaccessibilité du plomb particulaire, et donc de refléter la variabilité de l'exposition de l'enfant. Ensuite, il serait pertinent d'utiliser le modèle IEUBK récemment adapté pour des doses variant dans le temps par Donohue *et al.* (2011). L'application d'un tel modèle est désirable pour refléter la variabilité temporelle de l'exposition de l'enfant au plomb particulaire, variabilité non prise en compte par le modèle IEUBK classique. Les distributions de plombémies produites avec ces modifications permettraient de mieux estimer le nombre d'enfants à risque de développer des plombémies élevées en raison de l'ingestion de plomb particulaire provenant de l'eau potable.

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ANNEXE

ANNEXE 1 – SUPPORTING INFORMATION, PUBLICATION #5: PB PARTICLES FROM TAP WATER: BIOACCESSIBILITY AND CONTRIBUTION TO CHILDREN'S EXPOSURE

Journal: Environmental Science and Technology

Title: Pb particles from tap water: bioaccessibility and contribution to children's exposure

Authors: Elise Deshommes and Michèle Prévost

Length: 6 pages.

SI.1. Justifications for the modifications made to the RBALP

Issue linked to drinking water particles. In general, soil particle samples are large and fairly homogeneous, and several subsamples can be analyzed, in duplicate testing, to determine the following: (1) Pb dissolved from soil particles during *in vitro* digestion, and (2) total Pb in soil particles. The IVBA is then calculated as a ratio (1) to (2) (Figure S1). Soil can also be quite well characterized using other subsamples in order to analyze soil composition and mineralogy (e.g. SEM analyses). Tap water samples, by contrast, contain relatively small numbers of particles and are highly heterogeneous. Therefore, a sample cannot simply be divided into subsamples for duplicate testing, and the IVBA must be reliably evaluated using this single sample alone.

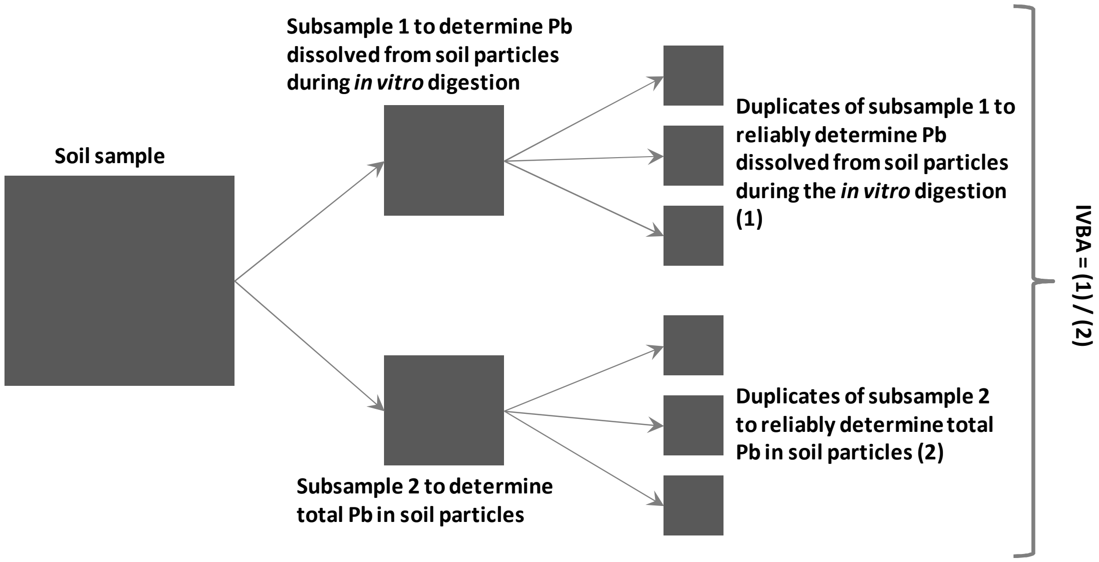

Figure S1. Schematic representing the process generally followed to determine the IVBA of a soil sample.

Table S1 presents the adaptations made to the RBALP, along with the justification for these adaptations.

Table S1. Adaptations made to the RBALP and justifications.

Parameter	RBALP for soil particles	Adapted RBALP for tap water particles	Justification
Fluid	Glycine (0.4M), HCl	Glycine (0.4M), HCl	Comparable
pH at t = 0 h	1.5±0.05	1.5±0.05	Comparable
Bulk particle mass	1g	0.01-0.08g	The small mass range used for the adapted RBALP is not recommended as a means to obtain good recoveries within the duplicates tested, and therefore reliability in the results. However, in the adapted RBALP, the soluble fraction and the particulate fraction of Pb particles at the end of the *in vitro* test can be determined using a single sample. The reliability of the adapted RBALP can therefore be assessed by quality of the recoveries of Pb solutions and Pb particles (Table S2).
Bulk particle size	Usually < 250µm	< 1 to 10mm	It is impossible to collect smaller particles that are representative of particulate Pb in tap water. Also, considering the small number of particles collected, this size was adapted for manipulation and detection purposes. Tests show no dissolution limitations of large Pb(IV) particles as compared to Pb(IV) powder. Also, the literature on soils indicates that significant differences in IVBA are only visible in the smallest range of bulk particle size (e.g. < 50µm), and that usually speciation is more influential than size.
Agitation	End-over-end, 28±2 rpm	End-over-end, 28±2 rpm	Comparable
S/L (g/mL)	1/100; 1/200 for Pb-rich particles	1/200	No impact on IVBA with S/L ratio ≤ 1/100; however, small ratios << 1/200 decrease recoveries. Tests comparing 1/200 to lower ratios that may be more representative of the ingestion of tap water particles (1/3000) show no limitation of Pb(IV) particle dissolution with the 1/200 ratio.
Temperature	37°C, water bath	37°C, incubator	Comparable
Extraction	Filtration at 0.45µm (syringe) of a sample aliquot (cellulose acetate filter)	Vacuum filtration at 0.45µm of the whole sample (cellulose acetate filter)	Comparable
Bioaccessible Pb mass	Pb mass in the filtrate	Pb mass in the filtrate	Comparable
pH at t = 1 h	Verify pH of the remainder mixture is within 1.5±0.5 to validate the sample	One out of 10 samples, final pH verified < 2	All the mixture is used to determine the IVBA in the adapted RBALP, so, in order to limit any mixture loss, the pH is checked on one of 10 samples. Additional verifications performed on several Pb forms found in drinking water show that final pH remains within the 1-2 range.
Total Pb mass	Total digestion on another soil sample (duplicates)	Total digestion of the filter retaining Pb particles Total Pb = Pb mass in (filtrate + filter)	No duplicates were needed for the adapted RBALP, since total Pb is determined with the sample used for the *in vitro* digestion. The reliability of the test was assessed by the recovery of Pb with solutions/particles (section 2).
IVBA calculation	$\frac{Pb\ (filtrate)}{Pb\ (total)}$	$\frac{Pb\ (filtrate)}{Pb\ (filtrate + filter)}$	Comparable

SI.2. Validation of the adapted in vitro assay: recoveries

The reliability of the adapted RBALP was assessed by the recovery of Pb with Pb solutions and Pb particles (Pb(IV), field collected) (Table S2). Pb(IV) particles were tested because they are difficult to dissolve. Microwave digestion was also validated by testing Pb-based solutions and Pb(IV) particles. Good recoveries were obtained for all the metals except tin. The microwave digestion of field collected solders of unknown content also yielded good recoveries, although tin recovery was lower than expected in two of the three samples. A very low recovery was measured for a field collected white deposit of unknown content, which was subsequently identified by XRD analysis as an amorphous phase of this solid (Table S3).

Table S2. Total test recoveries with two types of Pb solutions and Pb(IV) particles.

	N	Method used for filter digestion	Pb recovery % in the filtrate	Pb recovery % on the filter	Pb recovery % for total procedure
5mg Pb/L with(out) glycine	12	Water bath, 105°C, HNO_3	102-106%	0.06-0.11%	102-106%
45µg Pb/L with(out) glycine	10	Water bath, 105°C, HNO_3	98-102%	0.4-1.1%	99-103%
Pb(IV), 0.01g	2	Micro-wave	34-38%	34-38%	68-76%
Pb(IV), 0.05g	2	Micro-wave	41-45%	41-46%	82-91%
Pb(IV), 0.25g	1	Micro-wave	41%	56%	97%

Table S3. Recoveries of Pb-based solutions, Pb(IV) particles, and field-collected particles using microwave digestion.

	N	% Pb	% Cu	% Zn	% Fe	% Sn	% Ca	% Mn, Ni	% Mass
Multi-metal solution, 2-5mL: 1mg Pb/L, 1mg Cu/L, 2mg Zn/L, 10mg Fe/L	5	**101±2***	**102±4***	**105±7***	**99±3***	-	-	-	-
50µg Pb/L, 5mL	2	**101, 105**	-	-	-	-	-	-	-
4mg Pb/L, 1mL	1	**107**	-	-	-	-	-	-	-
Pb-Sn solution, 0.5-1mL: 4mg Pb/L, 5mg Sn/L	3	**100±4***	-	-	-	**99±23***	-	-	-
Pb(IV), 0.05g	1	**100**	-	-	-	-	-	-	**88.5**
Field-collected solder, 0.06g	1	48	< DL	< DL	< DL	40	< DL	< DL	**88**
Field-collected solder, 0.08g	1	48	< DL	< DL	< DL	18	< DL	< DL	**66**
Field-collected solder, 0.07g	1	51	< DL	< DL	< DL	22	< DL	< DL	**73**
Field-collected white deposit, 0.03g	1	0.006	0.063	0.049	< DL	0.002	0.23	0.04	**0.4**

*Note: *Mean and standard deviation; < DL-below detection limit.*

SI.3. Validation of the adapted in vitro assay: pH, S/L ratio, and size

In vitro digestions were performed, using several Pb particle forms and sizes, to check whether (i) the pH after 1 hour digestion was within 1.5±0.5, and (ii) the 1/200 ratio would limit the dissolution of particles. Measurements of pH and potential were performed using two ratio, 1/200 and 1/2000 (or 1/3000), and the following particles: $PbCO_3$ powder; PbO powder; 1-2mm Pb(IV) particles; Pb IV powder; 1-2mm brass particles; < 1 mm brass particles; and Pb(II)-based LSL scale. Results indicated that the pH remained within the acceptable range for the 1/200 ratio selected (1.50-1.84), although the lower ratios showed a narrower pH range (1.50-1.62). The 1/200 ratio was kept for the adapted RBALP, in order to avoid any detection difficulty and for ease of manipulation. The potential measured for most of the particles did not vary between t = 0 and t = 1 hour, showing that homogeneous solubility conditions were maintained during the 1 hour digestion period. In contrast, Pb(IV) particles showed (i) an increase between t = 0 and t = 1 hour for the two ratios tested, and (ii) an increase at t = 0 that was more important for the smallest particles and the highest ratios. Such increases were explained by interference in the redox probe reading, probably caused by PbO_2 particles sticking on the platinum probe.

SI.4. Decrease of tin in the samples over time

Lower recoveries were observed when Sn was present in the samples (Table S3). An insoluble white solid was formed during the microwave digestion of samples containing solders. This deposit was mostly composed of SnO_2, according to the XRD analysis (Figure S2). Four samples, containing mostly Sn, Pb, and Cu and dating back to June 22 or June 24, were analyzed three times (June 29; July 5; July 20). Tin decreased dramatically in three of the four samples re-analyzed, although Pb and Cu remained stable, and the decrease was sample-dependent (Figure S2—33 to 93% decrease from the initial Sn concentration within a month during holdup). These data suggest analyzing samples containing Sn immediately, or within a day at most, to ensure better results (when performing multi-metal analysis that requires HNO_3 addition). In the case of tin analysis only, the addition of HCl as a conservative acid is adapted.

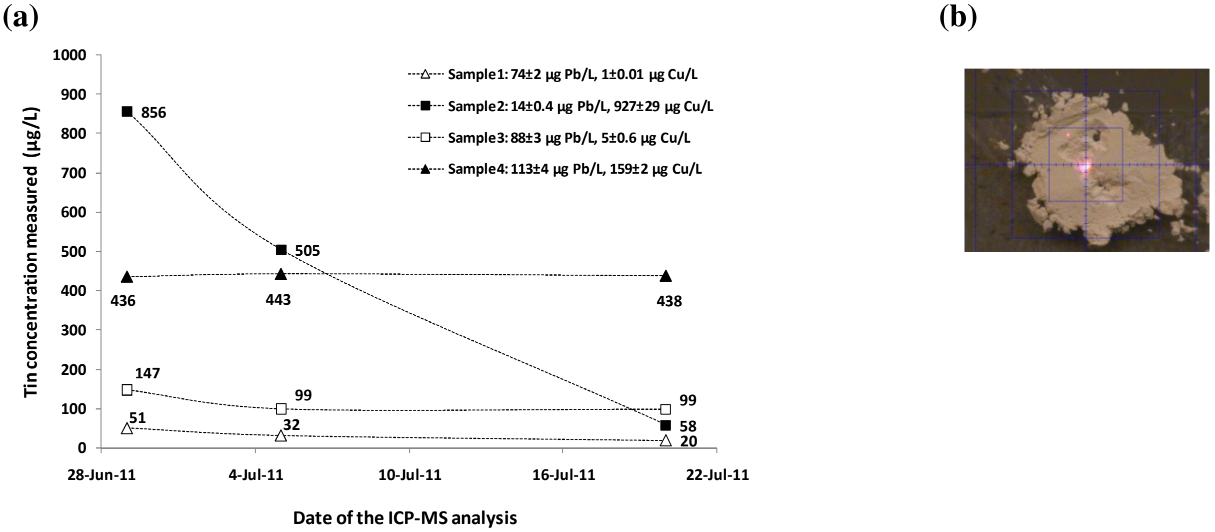

Figure S2. (a) Decrease in the tin concentration analyzed with ICP-MS over time. N=4 samples. (b) Insoluble white solid (SnO_2) remaining after the microwave digestion of some samples containing visible solders.

SI.5. Field collected particles: collection and categorization

Table S4. Number of samples collected per type of tap and category of housing, and categorization of the sets of particles for testing their bioaccessibility

Type of housing		Residence-LSL	Residence-No LSL	Residence-Probably with LSL	Large building	TOTAL
No. of samples collected	Kitchen taps	78	43	4	2	**127**
	Bathroom taps[§]	10	1	0	2	**13**
	Other taps	0	0	0	6	**6**
	TOTAL	**88**[*]	**44**[**]	**4**	**10**	**146**
Categorization for IVBA test	Single taps	23	11	3	5	**42**
	Mixed taps	7	1	1	1	**10**
	Fractioned taps	10	3	0	0	**13**
	TOTAL	**40**	**15**	**4**	**6**	**65**

Note: [§]Only a few were sampled; [*]41% of the residences with an LSL sampled; [**]35% of the residences without an LSL sampled; IVBA=in vitro bioaccessibility.

SI.6. Drinking water input for IEUBK: distribution of Pb concentrations

Table S5. Drinking water input for IEUBK: distribution of Pb concentrations detailed.

	MIN	10%	50%	90%	MAX	N	SAMPLING
Dissolved Pb — µg/L	3	6	17	47	114	196	RDT (N=154), PSS (N=27), and high flow rate samplings (N=15); LSL house,-Montreal; summer; 1L samples
Particulate Pb — µg/L	0	0.1	0.9	7	1617	196	
Dissolved Pb — µg/L	2	4	10	19	35	218	5-minutes-flushing; LSL houses, Montreal; summer; 1L samples
Particulate Pb — µg/L	0.00	0.04	0.2	0.9	5	218	
Dissolved Pb — µg/L	0.7	18	51	137	337	35	1st flush of 250 mL; consumption taps in a large complex of several buildings
Particulate Pb — µg/L	1.2	26	91	442	1000	35	