

Quality Assessment of Three Industry-Derived Organic Amendments for Agricultural Use

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ABSTRACT

The quality of three types of treated sludges (sludge from the paper recycling industry, and sewage sludge treated by composting with pruning waste and thermally dried) was assessed in this work. The amendments were physicochemically characterized and evaluated for their microbiological quality and for contamination with pollutants. All three organic amendments showed an absence of pathogens, so they are microbially suitable for agricultural use. The pollutants studied in the amendments included eight heavy metals and 83 organic compounds. Heavy metals, pesticides, polycyclic aromatic hydrocarbons, octylphenol, bisphenol A, and parabens were found in the organic amendments. The amount and type of contaminants depended on the sample sources and differed between samples from a single origin. The presence of some of the pollutants found has not been previously reported in organic amendments. The germination assay showed that these amendments may be applied to soil in controlled doses. As far as we know, this is the first reported study that has evaluated a great variety of pollutants (heavy metals, pesticides, persistent and emerging organic pollutants) in sludge from the recycled paper industry; moreover, studies in other waste products in which such a broad range of pollutants has been evaluated have been scarce until now due to the complexity of these matrices.

Introduction

Most Mediterranean countries are facing progressive soil degradation in natural and agricultural environments due to anthropogenic activities and climatic conditions. These processes can degrade soil quality (physically, chemically, and biologically) and, in many cases, are due to the loss of soil organic matter from intensive agricultural practices and land use changes in a semiarid environment (García-Orenes et al. 2005). Soil organic matter is a key element in soil quality; decreases in soil organic matter content are detrimental for soil quality and plant cover. To increase the organic matter levels in degraded sites or in agricultural land, a wide array of organic soil amendments of different origins can be used to provide essential nutrients (such as N and P), return soil organic matter to the soil, and re-establish plant cover. Waste management policies encourage the use of different types of residues as soil amendments to improve soil physicochemical properties and to encourage plant growth (Fytily and Zabaniotou 2008; US EPA 2007c; García-Orenes et al. 2005).

Thus, biosolids, manure, compost, anaerobically digested organic wastes, pulp sludge, wood waste, and ethanol production byproducts may be used as organic matter and nutrient sources; additionally, pulp sludge and wood waste have also been used as slope stabilizers or as bulking and structural agents, respectively. Nevertheless, it is essential that the physical, chemical, and microbiological properties of potential soil amendments be carefully characterized (US EPA 2007c).

The paper recycling process creates large amounts of pulp sludge; approximately 220,000 tons per year are produced in Spain (ASPAPPEL 2007). This sludge has been traditionally disposed of in landfills, incinerated, or spread on land (Usherson 1992). Opportunities to make use of this byproduct are being studied and developed by Spanish paper mills. Thus, during the construction boom, a great deal of this waste was managed in the ceramic industry, and various studies have recently sought to formulate blended cements containing thermally activated pulp sludge (Vegas et al. 2009). Nevertheless, an important way to make

use of sludges from the recycled paper industry (RP) is its application as a soil organic amendment, due to its high organic matter content, which enhances physical soil properties and increases soil organic matter content (Lobo et al. 2012). However, the application of RP to soil could cause a temporary immobilization of soil nitrogen as a result of the rather high values of C/N ratios. Moreover, the need to treat urban wastewater (Council Directive 91/271/ECC 1991) leads to the increased production of sewage sludge with high percentages of organic matter and nutrients that could be applied to reclaim agricultural soil.

The potential contamination of soil, water, and plants was one of the major public concerns over the use of RP and other wastes, such as sewage sludge, on agricultural land. While RP sludges and biosolids may provide benefits, they may also contain a wide range of contaminants, such as metals, pathogens, and organic pollutants. It has been described that the contents of heavy metals and different organic contaminants in RP from de-inking plants are generally low, and these materials do not represent a major threat to the environment but can require an environmental follow-up (Baziramakenga, Lalande, and Lalande 2001; Beauchamp et al. 2002a, 2002b).

The application of mixtures of wastes of different origins has been evaluated by several authors (Abdelhamid, Horiuchi, and Oba 2004; Demirbas, Sahin-Dermibas, and Dermibas 2004; Huang et al. 2006; Lobo et al. 2012; Paredes et al. 2002). Nevertheless, the evaluation of the presence of a broad number of potential pollutants in these amendments is scarce. The European Union (EU) regulates the use of sewage sludge in agriculture to protect the environment (Council Directive 86/278/EEC 1986), and has set limits on the concentrations of heavy metals in sludge and soil, but organic contaminants have not yet been considered. The types of pollutants potentially present in the amendments depend on its origin as well as the waste treatment processes (Monteiro et al. 2011; Smith 2009). Thus, composts derived from source-segregated waste streams or green waste are generally reported to contain lower amounts of heavy metals than mechanically sorted products, and the concentration of heavy metals increases during the composting process (Smith 2009). Regarding organic contaminants, the European Commission proposed, in a third draft of the “working document on sludge” (European Commission 2001), limits on some

organic compounds in sludge for land application, although in the “working document on biological treatment of biowaste, 2nd draft” (European Commission 2001) only polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were included. The need to regulate some organic micropollutants is being considered in the revision of the Council Directive 86/278/EEC (1986), despite “emerging contaminants” not being considered, in part due to the lack of data as well as to the major analytical difficulties in determining them (Leschber 2006). Studies carried out in our group showed that different organic pollutants (pesticides, as well as persistent and emerging pollutants) can be found in sewage sludge (García-Valcárcel and Tadeo 2011; Nuñez, Turriel, and Tadeo 2007; Sánchez-Brunete, Miguel, and Tadeo 2007, 2008, 2009; Sánchez-Brunete, Miguel, Albero, and Tadeo 2010; Tadeo et al. 2010). In general, information about the chemical characterization of materials applied as soil amendments is scarce. Over the years, the interest in using RP as a soil amendment and its environmental impact has increased. Beauchamp et al. (2002a, 2002b) analyzed approximately 150 chemicals in RP; however, only a small number of the potential chemicals analyzed were organic compounds. In general, organic contaminants in paper and pulp waste include, among other potential pollutants: surfactants used in flotation processes, fatty and resin acids, PAHs, dioxins, PCBs, phenols, biocides used to stop microbial growth, dyes, fungal treatments for color removal, and other chemicals added to prevent filamentous algae build-up (Beauchamp et al. 2002b, Monteiro et al. 2011). Among the detected compounds in RP, aluminum, copper, and PAHs were selected by Beauchamp et al. (2002a, 2002b) in their evaluation of contaminant content. Vinggaard et al. (2000) identified 18 estrogenic organic compounds in recycled and virgin paper for households, and the results of this study showed that the formerly classic indicator of substances, such as heavy metals, PCBs, pentachlorophenol, and PAHs, do not give a representative picture of the purity of materials containing recycled fibers because the variety of contaminants present seems to be extremely broad. Hawrelak, Bennett, and Metcalfe (1999) described the presence of primary degradation products of alkylphenol ethoxylates (APEOs) in sludge from a paper recycling plant and concluded that more work is required to assess the

toxic potential of APEOs in sludge used as soil amendment. Gehring et al. (2004) detected three xenobiotic endocrine-disrupting compounds (EDCs), bisphenol A (BPA), nonylphenol (NP), and octylphenol (OP), in toilet paper and wastepaper.

In general, some organic pollutants, such as pesticides, PAHs, some EDCs, BPA, and other emerging contaminants, could be contained in sludges or composts of mixed origin. These contaminants could be introduced into the biogeochemical cycle when these products are applied to soil (Kinney et al. 2006). Although the presence of pesticides and other organic contaminants has not been regulated in products for soil amendment, it is important to know their levels and their potential environmental impact. Most reported research on the use of residues as soil amendments has been focused on soil physical properties and crop development, with little attention paid to the potential organic pollutants. This fact may be due to the need of analytical methods suitable for detecting a high variety of contaminants at low concentrations in very complex environmental settings.

In this context, the main objective of this study was to assess the quality and determine the pollutant contents of three different types of treated sludges used as organic amendments: sludge from the recycled paper industry (RP), sewage sludge composted with pruning waste (CP), and thermally dried sewage sludge (TD). Prior to the evaluation of pollutants in the samples, the organic amendments were physicochemically characterized, and their microbiological quality was evaluated. The potential pollutants evaluated in these organic amendments included eight heavy metals and 83 organic compounds. Finally, the phytotoxicity of the organic amendments was studied.

Materials and Methods

Reagents and standards

Dichloromethane, acetonitrile, ethyl acetate, hexane, and acetone, all of residue-analysis grade, and silica Bondesil-C18 (40- μm particle diameter) were purchased from Scharlab (Barcelona, Spain). Anhydrous sodium sulfate, from Merck (Darmstadt, Germany), was heated for 24 h at 180°C before use. A Milli-Q water purification system from Millipore (Bedford, MA, USA) was used to provide deionized water for

this study. Aluminium oxide 90 standardized from Merck (Darmstadt, Germany) was activated at 180°C for 24 h and deactivated with deionized water (3%, w/w) before use. Copper was supplied by Panreac (Barcelona, Spain) and was activated shortly before its use with 30% hydrochloric acid (3N) for 1 min to remove copper oxide from the surface. Subsequently, it was washed with deionized water, cleaned with acetone and hexane, and dried under a stream of nitrogen. A mixture of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) (99:1, v/v) was purchased from Aldrich (Steinheim, Germany) as the silylation reagent.

For mercury determination, reference materials from the Community Bureau of Reference (BCR) were used. For the determination of the other heavy metals, stock standard solutions of 1000 mg L⁻¹ of (NO₃)₂Cd, (NO₃)₂Pb, (NO₃)₂Ni, (NO₃)₂Cu, (NO₃)₂Zn, and (NO₃)₃Cr (in HNO₃ 0.5 mol L⁻¹) and As₂O₅ (in H₂O) from Scharlab (Barcelona, Spain) were used.

Pesticide standards, reported in table 1, were obtained from Reidel-de Haën (Seelze, Germany), and all compounds were 99% pure. Stock solutions (500 $\mu\text{g mL}^{-1}$) of each pesticide were prepared in ethyl acetate. A standard mixture solution in ethyl acetate (0.25 $\mu\text{g mL}^{-1}$), containing all of the pesticides, was prepared for the screening analysis.

The PAHs analyzed were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[b]fluorene, benzo[b]naphtho[2,1-d]thiophene, cyclopenta[cd]pyrene, benzo[ghi]fluoranthene, benzo[a]anthracene, triphenylene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[j]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, perylene, indeno[1,2,3-cd]pyrene, dibenzo[ah]anthracene, dibenzo[ac]anthracene, benzo[ghi]perylene, dibenzo[def,mno]chrysene, anthranthene, and coronene. The standard solution of the twenty-seven PAHs (10 $\mu\text{g mL}^{-1}$ of each in toluene), purity 99%, was supplied by LGC Promochem (Wesel, Germany). The deuterated internal standards anthracene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂ (200 $\mu\text{g mL}^{-1}$ in acetone, purity higher than 98%) were supplied by Supelco (Madrid, Spain). A mixture of 0.2 $\mu\text{g mL}^{-1}$ of PAHs in ethyl acetate was prepared.

BPA, tetrachlorobisphenol A (TCBPA), tetrabromobisphenol A (TBBPA), and their ¹³C₁₂-internal standards (purity >99%, 50 $\mu\text{g mL}^{-1}$ in methanol) were provided by Cambridge Isotope Laboratories

Table 1. Retention times (t_R , min), target (T) and qualifier ions (Q1 and Q2) (m/z) of the pesticides evaluated in the screening assay.

Pesticide	t_R	T	Q1	Q2	Pesticide	t_R	T	Q1	Q2
EPTC	7.87	128	189		Pendimethalin	23.31	252	281	
Molinate	10.71	126	187		Cholfenvinphos	23.76	267	323	295
Propachlor	12.18	120	176		Procymidone	24.08	283	96	
Ethalfuralin	13.20	276	316	264	Methidathion	24.48	145	85	
Trifluralin	13.59	306	264		Endosulfan I	24.71	241	195	339
Simazine	15.02	201	186	200	Profenophos	25.64	208	339	
Atrazine	15.28	200	215	201	Oxadiazon	26.00	175	258	334
Terbutylazine	15.98	214	229		Cyproconazole	26.56	222	139	
Diazinon	16.67	179	137	304	Endosulfan II	26.79	195	237	339
Chlorothalonil	17.16	266	264		Ethion	27.39	231	153	
Triallate	17.26	86	268	269	Ofurace	27.93	132	160	
Metribuzin	18.61	198	199		Benalaxyl	28.06	148	206	
Parathion-methyl	19.01	263	109	125	Endosulfan sulfate	28.15	272	229	387
Tolclofos-methyl	19.21	265	267		Nuarimol	28.72	235	203	314
Prometryn	19.71	241	184		Bromopropylate	29.77	341	183	
Terbutryn	20.38	226	241		Tetradifon	30.47	159	111	356
Fenitrothion	20.50	277	125		Cyhalothrin	31.29	181	197	
Pirimiphos-methyl	20.69	290	276	305	Fenarimol	31.43	139	219	330
Dichlofluanid	20.84	123	224	167	Pyrazophos	31.57	221	373	
Fenthion	21.60	278	279		Coumaphos	32.64	362	226	
Chlorpyrifos	21.69	314	197		Cypermethrin	34.03	181	163	
Triadimefon	21.89	208	181		Fluvalinate tau-I	36.02	250	252	
Butralin	22.61	266	267		Fluvalinate tau-II	36.16	250	252	

(Andover, MA, USA). A mixture of $5 \mu\text{g mL}^{-1}$ of all of these compounds was prepared.

Methylparaben (MeP), ethylparaben (EtP), isopropylparaben (iPrP), propylparaben (PrP), isobutylparaben (iBuP), butylparaben (BuP), benzylparaben (BzP), NP, and OP were obtained from Sigma-Aldrich (St. Louis, MO, USA). Propylparaben- d_4 (PrP- d_4) was purchased from CDN isotopes (Quebec, Canada). Separate $5 \mu\text{g mL}^{-1}$ stock solutions of individual compounds were made up in ethyl acetate, and a working standard mixture of $1 \mu\text{g mL}^{-1}$ with all the compounds was prepared. All of the standard solutions were stored in glass bottles at 4°C prior to use.

Chemical characterization of organic wastes

Electrical conductivity (EC) and pH were measured according to UNE-EN-13038 and UNE-EN-13037 in saturation extract, respectively (AENOR 2001). Organic matter was determined using the Walkley and Black method (1934). Total nitrogen content was evaluated using the Kjeldahl method, and the available nutrients (Ca, Mg, Na, and K) were extracted with 0.1 N ammonium acetate at pH 7 and assessed using atomic absorption spectrometry (Varian, AA 240 FS) according to MAPA (1994). The available phosphorus content was determined according to the Watanabe and Olsen method (1965).

Pathogens analysis

The presence of pathogenic microorganisms in the three organic amendments was determined according to the EPA's methodology for sewage sludge (US EPA 2007a). *Escherichia coli* was determined according to Method 1603, *Salmonella* spp. was determined according to Method 1682, and total and fecal coliforms by Method 1680.

Heavy metal analysis

Prior to the analysis, an acid digestion of the organic amendments was carried out in HCl- NO_3 , using a microwave reactor system (Multiwave 3000, Anton Paar GmbH, Graz, Austria) (US EPA 2007b). Total concentrations of Cd, Cr, Pb, and Ni were determined by inducible conductivity plasma atomic emission spectrometry (Varian Liberty AX, Victoria, Australia), and the Zn and Cu concentrations were measured by atomic absorption spectrometry (Varian AA-600). Arsenic was analyzed with a Zeeman Atomic Absorption Spectrometer (AA240Z, Varian) equipped with a graphite tube atomizer and a programmable sample dispenser. Mercury concentrations were determined using an Advanced Mercury Analyser (AMA-254, LECO Company).

Appropriate quality-assurance procedures and precautions were carried out to ensure reliability of the

results. The quality control consisted of analyzing a reference standard every ten samples. The mean recovery rates ranged between 85 and 115%. The limits of detection were from 1.2 to 5 $\mu\text{g L}^{-1}$ for Zn, Cd, Cu, and Cr. For Hg, As, and Pb, these limits were 0.01, 0.12, and 20 $\mu\text{g L}^{-1}$, respectively.

Organic compounds analysis

Extraction

The analytical procedure employed in the present study is based on previously published papers (Pérez et al. 2012; Sánchez-Brunete, Miguel, and Tadeo 2007, 2009). Briefly, 3 g of deactivated alumina and 2 g of activated copper powder were mixed with the organic amendment (2 g) and placed in a glass mortar. The blended mixture was transferred to a 5 mL glass column with a Teflon frit at the end packed with 2 g of anhydrous sodium sulfate. The columns were extracted in an ultrasonic water bath (2 × 6 mL dichloromethane); the solvent was collected in graduated tubes, and the combined extracts were concentrated to ~0.5 mL and diluted to 2 mL with acetonitrile. These extracts were then purified using C18 (2 g) placed in a glass column. The elution of the organic compounds was carried out with a total volume of 10 mL of acetonitrile, which was concentrated to ~0.1 mL and reconstituted to 1 mL with hexane: ethyl acetate (50:50, v/v) and by adding a small amount of anhydrous sodium sulfate. The extract was stored at 4°C until analyzed by gas chromatography-mass spectrometry (GC-MS).

GC-MS analysis

GC-MS analysis was performed with an Agilent 6890 (Waldbronn, Germany) gas chromatograph equipped with an automatic injector, Model HP 7683, and an inert mass spectrometric detector (MSD), Model HP 5973N. Separations were carried out using a fused silica capillary column ZB-5MS, with 5% phenyl polysiloxane as a nonpolar stationary phase (30 m × 0.25 mm i.d. and 0.25 μm film thickness), from Phenomenex (Torrance, CA, USA).

To carry out the screening of the organic pollutants present in the organic amendments, the operating conditions used in the chromatographic analysis were those previously described as adequate to evaluate each group of compounds (Albero, Sánchez-Brunete, and Tadeo 2004; Pérez et al. 2012; Sánchez-Brunete,

Miguel, and Tadeo 2007, 2009). Retention times and the target and qualifier ions used to identify the pesticides in the screening are listed in table 1.

The compounds detected in the screening were quantified following two chromatographic methods: one for the mixture of pesticides and PAHs and another for a mixture containing emerging organic contaminants (retention times and target and qualifier ions are shown in table 2). The chromatographic conditions used in the first method were: injector port temperature 280°C; column temperature maintained at 80°C for 0.5 min, then programmed at 5°C min^{-1} to 230°C and increased to 300°C at a rate of 5°C min^{-1} , and held for 15 min. The total analysis time was 59.50 min. The chromatographic conditions of the second method were: injector port temperature 270°C; column temperature maintained at 80°C for

Table 2. GC-MS conditions for PAHs, two pesticides and the corresponding trimethylsilyl derivatives of the bisphenols, alkylphenols, and parabens evaluated.

Compounds	t_R	T	Q1	Q2
PAHs and two pesticides				
Naphthalene	8.05	128	129	102
Acenaphthylene	14.79	152	151	153
Acenaphthene-d ₁₀	15.50	162	164	
Acenaphthene	15.63	153	154	152
Fluorene	18.10	166	165	167
Phenanthrene-d ₁₀	22.27	188	187	
Phenanthrene	22.36	178	176	152
Anthracene	22.63	178	176	152
Dichlofluanid	26.00	123	167	224
Triadimefon	26.73	208	181	128
Fluoranthene	27.94	202	203	101
Pyrene	28.90	202	203	101
Benzo[b]fluorene	30.98	215	216	217
Benzo[b]naphtha[2,1-d]thiophene	33.47	234	235	117
Cyclopenta[cd]pyrene	33.63	226	224	227
Benzo[ghi]fluoranthrene	34.51	226	224	227
Benzo[a]anthracene	34.61	228	229	226
Chrysene-d ₁₂	34.66	240	236	
Triphenylene + Chrysene	34.75	228	226	229
Benzo[b+k+j]fluoranthrene	39.42	252	253	126
Benzo[a]pyrene	40.42	252	253	125
Benzo[e]pyrene	40.66	252	253	125
Perylene-d ₁₂	40.86	264	265	
Perylene	40.96	252	253	126
Indeno[1,2,3-cd]pyrene	44.81	276	277	138
Dibenzo[ac+ah]anthracene	44.98	278	276	138
Benzo[ghi]perylene	45.68	276	277	138
Anthranthene	46.37	276	277	138
Coronene	53.10	300	301	150
Parabens and phenols-TMS derivatives				
PrP-d ₄	9.77	197	214	241
OP	9.63	208	209	263
iBuP	10.15	210	195	251
BuP	10.44	210	195	251
NP	11.27	179	292	
BzP	12.46	193	285	300
C ₁₂ -BPA	12.59	369	370	284
BPA	12.59	357	359	372

Note. Retention times (t_R , min), target (T) and qualifier ions (Q1 and Q2) (m/z).

1 min, then programmed at $15^{\circ}\text{C min}^{-1}$ to 200°C and increased to 310°C at a rate of $25^{\circ}\text{C min}^{-1}$, and held for 3 min. The total analysis time was 16.40 min. Helium (purity 99.995%) was used as the carrier gas at a flow rate of 1.0 mL min^{-1} , and a $2 \mu\text{L}$ volume was injected in pulsed splitless mode (pulsed pressure 45 psi = 310 kPa for 1.5 min) with the splitless injector purge valve activated 1.5 min after sample injection, in a double-taper glass liner with a nominal volume of $800 \mu\text{L}$.

A derivatization step is required before the GC analysis of parabens, BPA, OP, and NP to obtain derivatives with a high detector response and better peak shape than the parent compounds. This derivatization was done by transferring an aliquot ($100 \mu\text{L}$) of the standard or extract solution into a 2 mL reaction vial, followed by the addition of $50 \mu\text{L}$ of BSTFA containing TMCS (99:1, v/v). The vials were closed, and the mixture was left to react for 10 min at 60°C . After the derivatization process, an aliquot ($2 \mu\text{L}$) of these solutions was analyzed with the second chromatographic method.

The target and qualifier abundances were determined by the injection of standards under the same chromatographic conditions using full scan with the mass/charge ratio ranging from 100 to 500 m/z. The analytes were confirmed by their retention times, the identification of target and qualifier ions, and the determination of qualifier to target ratios. Retention times must be within ± 0.3 min of the expected time and qualifier-to-target ratios within a 20% range for positive confirmation. The quantification of the two pesticides was based on their relative response to external standards; whereas for the other studied compounds the quantification was based on their relative response to the labeled internal standards.

Phytotoxicity assay

The amendments' phytotoxicity was evaluated according to the standard method proposed by Zucconi et al. (1981). Briefly, a filter paper (Whatman #2) moistened with residue extract (1:10, w/v with deionized water at 60°C) was placed in sterile Petri dishes. Then, 15 seeds of *Lepidium sativum* (watercress) or six seeds of *Hordeum vulgare* (barley) were placed on the filter paper. Deionized water was used as control. Plates were sealed with parafilm to minimize moisture loss and stored for 48 h (*Lepidium*) or 72 h (*Hordeum*) at 26°C in the dark. At the end of the incubation period, the ratio of the number of seeds that germinated (GI) in

the presence of amendment extract to the number of germinated seeds in the control test was calculated and expressed as a percentage (%).

Results and Discussion

Microbiological quality

The current European regulation concerning the application of sewage sludge in agriculture, Council Directive 86/278/EEC (1986), does not include any standard for the presence of pathogens; however, their detection is considered in the 3rd draft of the European Commission, due to the importance of controlling these microorganisms when residues are applied without stabilization treatment. This future regulation includes the control of *Escherichia coli* and *Salmonella* spp. counts. The presence of these organisms, as well as total and fecal coliforms, was evaluated because the determination of these organisms has recently been required by Spanish regulation of the application of sewage sludge to agricultural soils (MAGRAMA 2013).

The three amendments evaluated showed the absence of pathogens, so they are microbially suitable for agricultural use. Composting and heat treatment involving the loss of sample moisture contributes to the elimination of pathogenic organisms (Yeager and Ward 1981). Therefore, it is important that the composting process be complete to ensure the absence of microorganisms before agricultural application.

Organic waste characteristics

The organic wastes characterization (table 3) showed pH values near 7 and organic matter content higher than 22% in the three organic amendments. The nutrient content is significantly higher in biosolids (CP and TD) than in pulp sludge (RP). In general, RP is of poor nutritional quality, with low contents of N, P, and K. Furthermore, the higher C/N ratio makes this material not suitable for direct application to soil because nitrogen may be immobilized. However, it is important to note the high water holding capacity of this material, a parameter of great interest from the point of view of the agricultural application of these amendments to degraded soils.

Among the potential amendments studied, CP showed the highest content of K, whereas TD presented the highest N and P contents. Obviously, TD

Table 3. Organic amendments characteristics.

Organic Waste ^a	Chemical characteristics							Exchangeable cation(mg kg ⁻¹)				Heavy metals found(mg kg ⁻¹)					
	pH	WHC ^b %	EC ^c dS m ⁻¹	O.M.%	C/N	N%	P mg kg ⁻¹	Ca	Mg	Na	K	Ni	Pb	Cd	Cu	Cr	Zn
RP	7.5	41.8	0.9	38.6	79.9	0.3	50	4218	203	576	39	13	14	0.3	145	9	68
CP	7.5	35.2	2.9	22.5	8.1	1.6	288	4705	883	352	2034	33	78	0.4	170	248	1602
TD	6.7	28.5	4.6	25.9	3.3	4.5	400	2770	970	552	974	73	219	1.9	385	280	1118

^aPulp sludge (RP), compost of sewage sludge, and pruning wastes (CP), thermally dried sludge (TD).

^bWHC: water holding capacity; EC^c: Electrical conductivity.

showed a higher value of EC (see table 3), a factor limiting the use of these organic wastes due to the potential salinization risk. Cai and Gao (2007) observed that the composition and total amounts of Na⁺, Cl⁻, Ca²⁺, and Mg²⁺ present in the residues must be monitored carefully before using these materials as an amendment. Moreover, these soluble salts may leach through the soil, posing a potential pollution risk in groundwater (Jordán et al. 2007; Lobo et al. 2011). Therefore, the correct dose of sewage sludge residue must be determined for each soil type (Gascó, Lobo, and Guerrero 2005).

Heavy metal content

Table 3 shows the content of the six heavy metals found in the different materials. The only metals not detected in the organic amendments were Hg and As. All of the values found were below the limits established by EU legislation (Council Directive 86/278/EEC 1986). The lowest values were found in RP. Regarding the biosolids treatment, the highest values were found in TD, except for Zn, which was present at a higher content in CP. It is important to note that Zn is considered an essential micronutrient, so this value is of interest from the point of view of soil fertility.

In terms of their heavy metal content, the three amendments would be suitable for agricultural use, but their dosage should be controlled in order to avoid increasing their content in soil. Several studies have evaluated the mobility of these elements after application of the amendment to agricultural soils. In general, heavy metals are immobilized in soil in the superficial layer (Gascó, Lobo, and Guerrero 2005; Jordán et al. 2007; Sastre, Vicente, and Lobo 2001); however, depending on the soil characteristics, heavy metals can be leached through the soil profile bound to dissolved organic carbon. Thus, the uncontrolled application of these materials is risky (Gascó, Lobo, and Guerrero 2005; McBride et al. 1997).

RP has been used to control heavy metal mobilization due to its favorable physical properties (Pardini et al. 2008). This fact suggests the combined use of RP with biosolids to take advantage of the properties of both materials.

Organic compounds

The three amendments evaluated are highly complex matrices with very variable composition. For this reason, a previous screening of potential organic pollutants of different groups and characteristics was carried out. The organic pollutants included in the screening were: 46 pesticides; 27 PAHs; the organic flame retardants TCBPA and TBBPA; BPA (a metabolite of TBBPA and a major industrial product); OP and NP (persistent degradation products of alkylphenol ethoxylates); and, finally, seven parabens (a group of alkyl esters of *p*-hydroxybenzoic acid that are widely used as preservatives in pharmaceutical and personal care products). Extractions and purifications of the organic compounds from the three organic amendments were carried out by matrix solid-phase dispersion according to the methods previously developed in our group (Pérez et al. 2012; Sánchez-Brunete, Miguel, and Tadeo 2007, 2009). In those studies, recovery assays were performed with four replicates at three fortification levels to validate the method, and the repeatability, linearity, limits of detection, and quantification for each group of compounds were evaluated. The recoveries obtained by these methods were high, from 87 to 109%.

Due to the complexity of the samples, to control for any potential matrix effects, the quantification of the organic compounds in the amendments was based on their relative response factor to labeled internal standards, except for the two pesticides, which were quantified through their relative response to external standards.

The extracts so obtained were directly injected into the chromatograph for the screening of pesticides and

PAHs. An aliquot of the extracts (100 μL) was derivatized before the GC analysis of parabens, BPA, and the two alkylphenols following the procedure described above.

Pesticides were the first group of compounds evaluated. In general, the methods reported in the available scientific literature for the determination of pesticides in sludge have focused mainly on the determination of organochlorine pesticides, although pesticides from other chemical classes, such as triazine herbicides or organophosphorus insecticides, have also been studied in sludge (Tadeo et al. 2010). In the present work, a multiresidue analysis of 46 pesticides of various classes (listed in table 1) was carried out following the chromatographic conditions previously established in our laboratory (Sánchez-Brunete, Albero, and Tadeo 2004). As a result of the pesticide screening, two fungicides were detected in the studied samples. Triadimefon was found in TD, dichlofluanid was detected in RP, and no pesticide was found in CP. Triadimefon is a systemic fungicide of the triazole group, which is usually used to control powdery mildews, rusts, and other fungal pests on cereals, fruits, vegetables, turf, shrubs, and trees. Dichlofluanid is a phenylsulfamide fungicide that has been widely used to control spoilage on various crops through fungal attack but is also used as an additive in antifouling paints (Sakkas, Konstantinou, and Albanis 2001) and as a wood preservative in biocidal products (European Union 2006). Recently, Stamatis, Hela, and Konstantinou (2010) evaluated the occurrence and removal of fungicides in municipal sewage treatment plants and observed that triadimefon was detected at low levels in influent samples. After secondary and tertiary treatment, 37 and 7% of the influent concentration of triadimefon remained, respectively. Nevertheless, neither of the pesticides found in the samples have previously been reported as pollutants of organic amendments.

The second group of organic contaminants to be screened in the organic amendments was the PAHs. These compounds are widely distributed in the environment and have been detected at different concentrations in sludge samples (Khadhar et al. 2010; Sánchez-Brunete, Miguel, and Tadeo 2007). The compounds detected depended on the sample (see figure 1). Thus, although some of them were detected in all of the samples (such as naphthalene, fluorene, phenanthrene, pyrene, or benzo[a]pyrene), others were only detected in some of them, such as

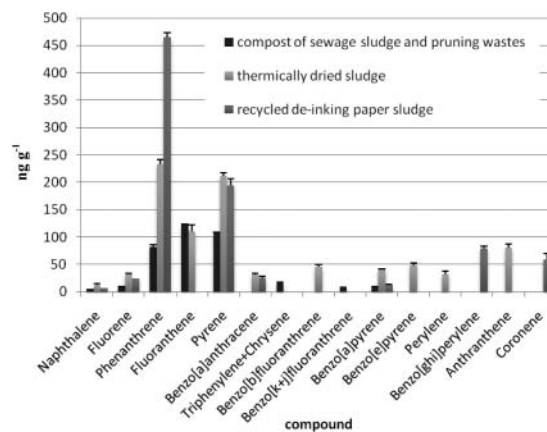


Figure 1. PAHs detected in the three organic amendments.

anthracene in TD or benzo[ghi]perylene and corone in RP.

The third group of compounds evaluated comprised TCBPA, TBBPA, and BPA. The screening of this group was carried out following the chromatographic method described in Sánchez-Brunete, Miguel, and Tadeo (2009). The chromatographic characteristics of the trimethylsilyl derivatives of this group are summarized in table 2. Neither of the halogenated phenolic compounds were detected in the samples, but all of the examined samples contained BPA.

Finally, the presence of a fourth group of organic compounds, composed by NP, OP, and seven parabens was evaluated in the samples. Parabens are emerging contaminants, and the information available about their occurrence in wastes is still scarce, whereas OP and NP are two organic pollutants frequently detected in wastewater and sewage sludge. In this study, NP was not detected in any of the samples, and OP was only detected in TD. Only three of the seven parabens evaluated were found in the samples, iBuP, BuP, and BzP; the first two parabens in CP and the third one in RP and TD.

To quantify the different pollutants present in the samples, two standard mixtures were used. One mixture, containing the two pesticides detected in the screening assay and PAHs, together with the corresponding internal standards, was used for the quantification of these compounds using the chromatographic method described in the experimental section. The results obtained are shown in table 4. The highest pollutant concentrations were obtained for the two pesticides, with 474 ng g^{-1} of dichlofluanid and 1058 ng g^{-1} of triadimefon in RP and TD, respectively.

Table 4. Summary of the mean values (ng g⁻¹) of the organic pollutants detected in the three organic amendments.^a

Compound	Organic waste ^b		
	RP	CP	TD
Σ27 PAHs	866	359	880
Dichlofluanid	474		
Triadimefon			1058
OP			426
iBuP		26	
BuP		65	
BzP	76		14
BPA	56	110	19

^aResults are the mean of three replicates.

^bPulp sludge (RP), compost of sewage sludge and pruning wastes (CP), thermally dried sludge (TD).

The individual PAHs levels found in the samples are given in figure 1, where it can be observed that although PAHs were detected in all of the analyzed samples, the compounds identified and their concentrations depended on the sample origin. The main PAHs found were phenanthrene and pyrene, with concentrations similar to those found in some sewage sludges from Madrid, Spain (Sánchez-Brunete, Miguel, and Tadeo 2007). Other compounds, such as fluoranthene, benzo[ghi]perylene, anthranthene, or coronene were abundant only in select samples. The total concentration of PAHs (sum of the 27 congeners) ranged from 359 to 879 ng g⁻¹. These values are in agreement with those reported by other authors (Sánchez-Brunete, Miguel, and Tadeo 2007). It has been reported that different treatments and sources of wastes could give rise to high variability in the organic pollutants present in the waste or in their concentrations (Khadhar et al. 2010; Monteiro et al. 2011). In this context, the lower PAH values found in CP could be due, among other possible causes, to the dilution of these contaminants by the mixture with pruning wastes. The total PAH content found in the three potential amendments was lower than the limit proposed (6 mg kg⁻¹) in the draft directive of the European Union (2003).

The other standard mixture, containing phenolic compounds and their corresponding internal standards, was used in the quantification of OP, iBuP, BuP, BzP, and BPA, applying the chromatographic method with the derivatization step described in the experimental section. OP was found only in the TD sample (0.43 mg kg⁻¹). This OP value is lower, or in the same concentration range, than the figures reported by Bruno et al. (2002) in sewage sludge before and after

anaerobic digestion treatment (14 and 17 mg kg⁻¹, respectively), by La Guardia et al. (2001) in biosolids (<0.5–12.6 mg kg⁻¹), and by Fernández-Sanjuan et al. (2009) (from 0.33 to 23.5 mg kg⁻¹) in freeze-dried sewage sludge samples.

BPA was found in all three samples at levels ranging from 19 to 110 ng g⁻¹. These results are similar to those reported for this compound in soil, sediments, and sewage sludge (Sánchez-Brunete, Miguel, and Tadeo 2009; Wang et al. 2011; Yu et al. 2011).

Of the seven parabens evaluated, iBuP and BuP were found only in CP (26 and 65 ng g⁻¹, respectively), whereas BzP was detected in TD and RP samples at 19 and 56 ng g⁻¹, respectively. BuP and iBuP are, together with MeP, the parabens most frequently found in soils in Spain (Pérez et al. 2012), although the concentrations detected in soil for these compounds (from 0.5 to 1.0 ng g⁻¹) are lower than those found in CP. The evaluation of parabens in solid environmental samples is relatively recent. The presence of parabens in sewage sludge samples was demonstrated for the first time by Nieto et al. (2009), although in that work, only four parabens were evaluated (MeP, EtP, PrP, BzP), and only three of them were found in real samples (MeP, PrP, and BzP) at levels between 5 and 202 ng g⁻¹. More recently, Yu et al. (2011) evaluated MeP, EtP, PrP, and BuP in sediments and sewage sludge but only found MeP and PrP in the sewage sludge samples at levels between 18 and 44 ng g⁻¹. Similar results were obtained in our group when the occurrence of seven parabens in municipal sewage sludge from wastewater treatment plants in Madrid was evaluated (Albero et al. 2012).

The presence of the organic pollutants evaluated depends on the sample source. This observation underscores the need for studying the presence of organic pollutants in amendments in depth before their soil application. Thus, although in this work a broad number of organic compounds of different groups and characteristics have been evaluated, these are only a part of the potential set of organic pollutants that could be found in treated sludges used as amendments (pesticides, persistent pollutants, and emerging organic pollutants as surfactants, flame retardants, pharmaceuticals, and personal care products). Indeed, currently emerging pollutants that have drawn the attention of the scientific community occur widely in the environment, yet are not commonly monitored, due to the lack of regulation.

Germination assay

The germination assay is commonly used as an indicator of salinity or the presence of toxic compounds, such as polyphenols, in stabilized organic wastes (Zucconi et al. 1981). Other characteristics (such as pH, EC, ammonium nitrogen levels, and heavy metals) can also be responsible for decreases in seed germination rates (Linde and Hepner 2005; Wu, Ma, and Martinez 2000). High values of EC affect plants physiologically, modifying the water relations of the medium and, therefore, influencing the germination of seeds (O'Brien, Herbert, and Barker 2002). Additionally, Linder and Hepner (2005) described that excessive ammonium nitrogen levels in a compost-amended soil delayed seed establishment. Delayed seed establishment was attributed to increased NH_3 volatilization from a compost that resulted from higher total N concentration and a lower C/N ratio in the compost (He et al. 2003).

According to Zucconi et al. (1981), a germination percentage (GI) lower than 50% shows the presence of highly toxic compounds, a GI between 50–80% shows the presence of moderately toxic compounds, and a GI higher than 80% shows a nontoxic sludge. The results of the phytotoxicity test are shown in table 5. In general, germination percentages of 90% were obtained in the case of RP for both seed types. These high percentages indicate that RP is not toxic in this early stage of plant development. CP showed GI values between 80 and 84%, depending on the plant used. This material can also be considered as non-toxic. However, TD shows GI values below 50%, which could be due to the higher values of EC, high nitrogen values, and the concentrations of heavy metals and organic pollutants determined in comparison to the other materials. Careful control of the dose applied to the soil is indicated, with the dosage depending on the original soil properties as well as the tolerance

of the species to the residue's contents. Germination assays using *Raphanus sativus* L. in a soil amended with biosolids (Sastre et al. 2015) found an increased germination percentage at rates of 1 and 2% (w/v) on organic matter basis. Nevertheless, studies carried out in field experiments showed phytotoxicity in olive plants due to sewage sludge application (Gascó and Lobo 2007). Although only CP is commonly used as growing media, the agricultural application of these materials in soils and their incorporation is not always uniform causing the seeds to be in direct contact with the material. In this sense, assessing the tolerance of crops is a useful measure to avoid risks.

Conclusions

The methodologies described in the present study are a simple way to determine the characteristics and the presence of a broad number of pollutants in organic amendments. As far as we know, this is the first study reporting the simultaneous evaluation of a great variety of pollutants (heavy metals, pesticides, persistent and emerging pollutants) in amendments obtained from different treated sludges. The results obtained in this study demonstrate that different pollutants, heavy metals and organic compounds, can be found in commercialized or potentially useful soil amendments. Specifically, heavy metals, pesticides, PAHs, OP, BPA, and parabens were found in the three organic amendments evaluated, and the amount and the type of contaminants depended on the sample source and differed among samples from a single origin. The presence of some of the pollutants found has not been previously reported in organic amendments. According to these results, significant efforts are necessary to characterize residues to be used as soil amendments. Further investigations should be carried out to determine the optimum application dose for each organic waste according to the type of soil, to assess the effect of applying these wastes on the soil characteristics, and to determine the fate and final levels of the pollutants in agricultural soils to avoid the risk of introducing these pollutants into the food chain.

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Table 5. Germination index.

Organic wastes ^a	Percentage of seed germination (%)	
	<i>Lepidium sativum</i>	<i>Hordeum vulgare</i>
RP	90	93
CP	80	85
TD	40	43

^aPulp sludge (RP), compost of sewage sludge and pruning wastes (CP), thermally dried sludge (TD).

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