Tertiary ozonation of industrial wastewater for the removal of estrogenic compounds (NP and BPA): a full-scale case study

G. Bertanza, M. Papa, R. Pedrazzani, C. Repice and M. Dal Grande

ABSTRACT

Wastewater treatment plant (WWTP) effluents are considered to be a major source for the release in the aquatic environment of endocrine-disrupting compounds (EDCs). Ozone has proved to be a suitable solution for polishing secondary domestic effluents. In this work, the performance of a full-scale ozonation plant was investigated in order to assess the removal efficiency of four target EDCs: nonylphenol, nonylphenol monoethoxylate, nonylphenol diethoxylate and bisphenol A. The studied system was the tertiary treatment stage of a municipal WWTP which receives an important industrial (textile) load. Chemical analyses showed that the considered substances occurred with a significant variability, typical of real wastewaters; based on this, ozonation performance was carefully evaluated and it appeared to be negatively affected by flow-rate increase (during rainy days, with consequent contact time reduction). Moreover, EDCs' measured removal efficiency was lower than what could be predicted based on literature data, because of the relatively high residual content of biorefractory compounds still present after biological treatment.

Key words | endocrine-disrupting compounds, industrial wastewater, removal efficiency, tertiary ozonation

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INTRODUCTION

Recent advances in environmental chemistry have brought increasing focus on the presence of anthropogenic substances in the environment; even though the concentrations of these compounds are in the range of μg/L or even ng/L and pg/L (therefore called 'micropollutants'), adverse effects on human health cannot be excluded.

One such group of anthropogenic substances is represented by endocrine-disrupting compounds (EDCs). EDCs are defined as 'exogenous agents that interfere with the synthesis, secretion, transport, binding, action or elimination of natural hormones in the body, which are responsible for the maintenance of homeostasis, reproduction, development and behaviour' (US EPA 1997); in other words, they can alter the normal function of the endocrine system, which is responsible for growth, development and regulation in vertebrates.

Besides the natural steroidal estrogens (mainly estrone (E1), estradiol (E2), and estriol E3)), the synthetic organic compounds that have been shown to interact with estrogens receptors are the alkylphenols (AP), mainly nonylphenol (NP) and octylphenol (OP), which are more estrogenically potent than their short-chain ethoxylated precursors (AP*n*EOs, where *n* is the number of ethoxylic units in the molecule, generally equal to 1–3), and other phenolic compounds, mainly bisphenol A (BPA) (Frassinetti *et al.* 2011). In particular, they may interfere with regulation mechanisms controlled by estrogens by competing for the binding sites of the estrogens receptors (Gerrity & Snyder 2011).

The presence of estrogenic EDCs in the environment is becoming an increasingly serious problem, because they are widely prevalent in aquatic environments and present at higher concentrations than other EDCs. Indeed, AP*n*EOs products are reported to account for approximately 6% of the total surfactant production in the world (Ning *et al.* 2007) and, of all the AP*n*EOs production, 80–85% is sold as nonylphenol ethoxylates (NP*n*EOs), non-ionic surfactants widely used in several industrial applications, such as textile and leather processing, paper industry, formulation of pesticides, paints and washing cleaners (Johnson *et al.*

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2005). NP*n*EOs are easily bio-converted into short-chain NP*n*EOs and NP, but these compounds appear to be recalcitrant to further microbial attack. BPA, in contrast, is widely used as a monomer for epoxy resins and polycarbons synthesis (Snyder *et al.* 2003).

The application of conventional wastewater treatment does not always provide complete removal of all micropollutants, and, subsequently, residues of EDCs enter the aquatic ecosystem through wastewater. Natural waters (both surface and groundwater) represent the most affected environmental media and the most significant exposure pathway (Ning *et al.* 2007), because of the presence of EDCs in wastewater treatment plant (WWTP) effluents. This poses new challenges for wastewater purification: the continuous disposal of WWTP discharges results in a risk for aquatic systems and, consequently, for human health (Isidori *et al.* 2007; Frassinetti *et al.* 2011). In order to prevent this problem, an advanced treatment downstream of the biological process may be implemented.

Several technologies for further micropollutants removal, such as ozonation (Huber *et al.* 2005), advanced oxidation (Huber *et al.* 2003), activated carbon (Westerhoff *et al.* 2005) and filtration (Poseidon 2004), have been investigated. In particular, the application of ozone at laboratory- (Ning *et al.* 2007), pilot- (Bertanza *et al.* 2010; Schaar *et al.* 2010) and full-scale (Leusch *et al.* 2005) experiments proved to be a suitable technology for EDC removal: all these works, indeed, report satisfactory removal efficiencies, higher than 60% without strong oxidation conditions (in terms of O_3 dosage and contact time), operating with almost totally domestic wastewaters. Nevertheless, literature data are neither easily comparable due to different treatment conditions (typically not similar to the real ones of WWTPs) and sampling frequencies (e.g. grab vs composite samples; single sampling vs longer monitoring campaigns) nor always totally reliable (Koester *et al.* 2012). In effect, complete experimentations on full-scale plants are scarce in the literature; this is an important bottleneck for research, because only full-scale tests guarantee truly representative and reliable results, taking into account all possible interferences (related to plant management, quali-quantitative characteristics of wastewater, etc.). On from the other hand, as a drawback of such kind of experimentations, treatment conditions cannot be freely varied for research purposes, due to plant structural limits and the need to ensure compliance with the effluent standards.

This experimental work was conducted at a full-scale WWTP (design daily flow-rate: ≈30,000 m^3/d), treating both domestic and industrial (textile) wastewater (co-treatment) with the aim of emphasizing the influence of wastewater characteristics on the removal of target EDCs (NP, NP1EO, NP2EO and BPA) by means of tertiary ozonation. The presence of a full-scale ozonation plant, together with an appreciably long-lasting monitoring period (40 d), is a particular contribution of this work to technical and scientific knowledge.

MATERIALS AND METHODS

The full-scale WWTP

The Fino Mornasco (Como, Italy) municipal WWTP (design size 140,000 person equivalent) receives domestic and industrial (textile and printing) wastewaters, the latter contributing up to 50% of the total chemical oxygen demand (COD) load. Textile wastewaters are typically characterized by strong colour and presence of recalcitrant compounds, such as dyes, surfactants and sizing agents.

Moreover, wastewaters are conveyed by a combined sewer system; runoff and infiltration waters can in some periods (e.g. in wet weather) heavily affect the influent wastewater volume. This is well shown by Figure 1, which displays the flow-rate data recorded during this study, split up for source.

The process scheme consists of pre-denitrification (volume = 3,600 m^3), oxidation–nitrification (volume = 10,500 m^3) and secondary settling (conventional activated sludge: CAS), followed by coagulation–flocculation–sedimentation (for suspended solids reduction) and ozonation (for the abatement of residual colour and surfactants). The latter is conducted in a 2,000 m^3 chicane reactor, where 300 kgO_3/d are supplied, so as to ensure, for the design flow-rate, a hydraulic retention time of around 90 min and an ozone dosage of 10 mg/L, respectively. Under typical working conditions, the specific ozone dose is 0.5 gO_3/gTOC (total organic carbon). It has to be underlined that no residual O_3 is normally detected in the effluent.

Main (typical) operational data of the WWTP are the following: influent characteristics (after bar racks and grit-chamber): COD 300 mg/L, 5-day biochemical oxygen demand (BOD_5) 150 mg/L, total suspended solids (TSS) 110 mg/L, total nitrogen (N_{TOT}) 35 mg/L, total phosphorus (P_{TOT}) 3.5 mg/L, 10 mg/L surfactants (90% non-ionic); final effluent characteristics (after ozonation): 50 mgCOD/L, 10 mgBOD_5/L, 10 mgTSS/L, 16 mgN_{TOT}/L, 1.2 mgNH_4^+-N/L, 12 mgNO_3^--N/L, <0.1 mgNO_2^--N/L, 0.8 mgP_{TOT}/L, 0.6 mg/L surfactants.

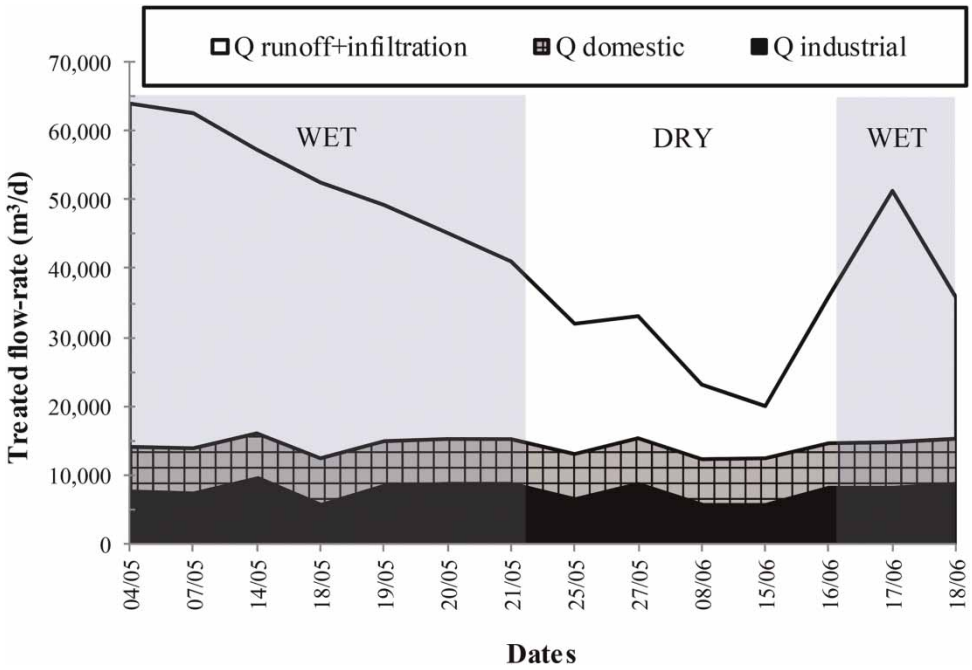

Figure 1 | Trend of flow-rate, as recorded during the monitoring campaign, split up for source.

Monitoring campaign

The monitoring campaign was conducted on the ozonation stage during 6 consecutive spring-time weeks (with dry and wet weather, alternatively): from 4 May to 18 June. The length of the monitoring period was set in order to get significant results, accounting for the inherent variability of wastewater characteristics of real plants.

Fourteen in/out 24-h composite samples (75 mL every 30 min) were collected by automatic refrigerated autosamplers, equipped with Teflon pipes and dark glass containers.

The measured EDCs, as well as references to the environmental quality standards (EQS), are listed in Table 1.

Table 1 | Analysed compounds and EQS, as annual average ([aa]) and maximum allowable concentration ([mac]) for inland surface waters (EU Water Framework Directive 2008/105/EC for NP; other national EQS – Austrian BGBl. II 96 (2006) – for BPA)

Substance (CAS No.)	Abbr.	EQS [μg/L]	List in Directive 2008/105/EC
Bisphenol A (80-05-7)	BPA	1.6[aa]	Substances subject to review for possible identification as priority substances or priority hazardous substances
Nonylphenol (25154-52-3)	NP	0.3[aa] / 2.0[mac]	Priority substances, identified as priority hazardous substance
Nonylphenol monoethoxylate (104-35-8)	NP1EO	–	–
Nonylphenol diethoxylate (20427-84-3)	NP2EO	–	–

Chemical analyses and data processing

The method of Gatidou *et al.* (2007) was successfully adopted for the extraction of analytes from the liquid phase.

The following chemicals were purchased from Sigma Aldrich (Taufkirchen, Germany): (a) standard reagents: BPA, NP1EO, NP2EO and 4-NP technical mixture of isomers, as proposed by ISO 18857–1 (2005); (b) derivatization reagents: MSTFA (N-methy-N-(trimethylsilyl) trifluoroacetamide) and pyridine; (c) internal standard: BPA-d_{16}. Influent samples were filtered on glass fibre filters (Whatman GF/A $\phi = 1.6$ μm). Liquid samples were submitted to enrichment on SPE C18 (Supelco, Bellefonte, USA) and consequent elution. Derivatization was performed with 900 μL MSTFA (5% in isooctane) and pyridine (100 μL). Instrumental analysis was conducted using a gas chromatograph 5975B inert XL EI/CI MSD equipped with a split/splitless injector and

autosampler (Agilent Technologies, Palo Alto, USA). Further details about the analytical procedure will be published in another paper.

Data variability was then analysed by means of the SPSS 15.0 statistics software (SPSS for Windows, Chicago, IL, USA).

RESULTS AND DISCUSSION

EDC concentration

EDC concentrations recorded during the experimentation are shown in Figure 2. Average values turned out to be equal to 0.59 and 0.19 μg/L for BPA, 1.21 and 0.61 μg/L for NP, 0.81 and 0.60 μg/L for NP1EO, 5.18 and 1.32 μg/L for NP2EO, respectively in the inlet and outlet flows of the ozonation reactor.

It has to be underlined that some of the measured values were not taken into account, in case internal standard (BPA-d_{16}) recovery was excessively far from the target (under 50% or above 150%); this may occur as a consequence of the matrix complexity and the presence of interfering compounds (due mainly to the industrial component of the wastewater).

Statistical analysis

Experimental data were elaborated using the SPSS 15.0 statistics software in order to calculate quantile box plots with 95% confidence interval (Figure 3): top, bottom and middle lines of the boxes represent the 75th, 25th and 50th (median) percentile, respectively, whiskers, in contrast, show the highest and lowest values, while dots beyond the whiskers indicate extreme values, falling out of the 1.5 fold interquartile range.

The box plots point out a high degree of variability, for both inlet and outlet samples; this was expected considering the inherent variability of quali-quantitative characteristics of a real wastewater.

Removal efficiency: effect of contact time

Pollutants removal efficiency (Table 2) was estimated on the basis of the calculated daily loads (data not shown);

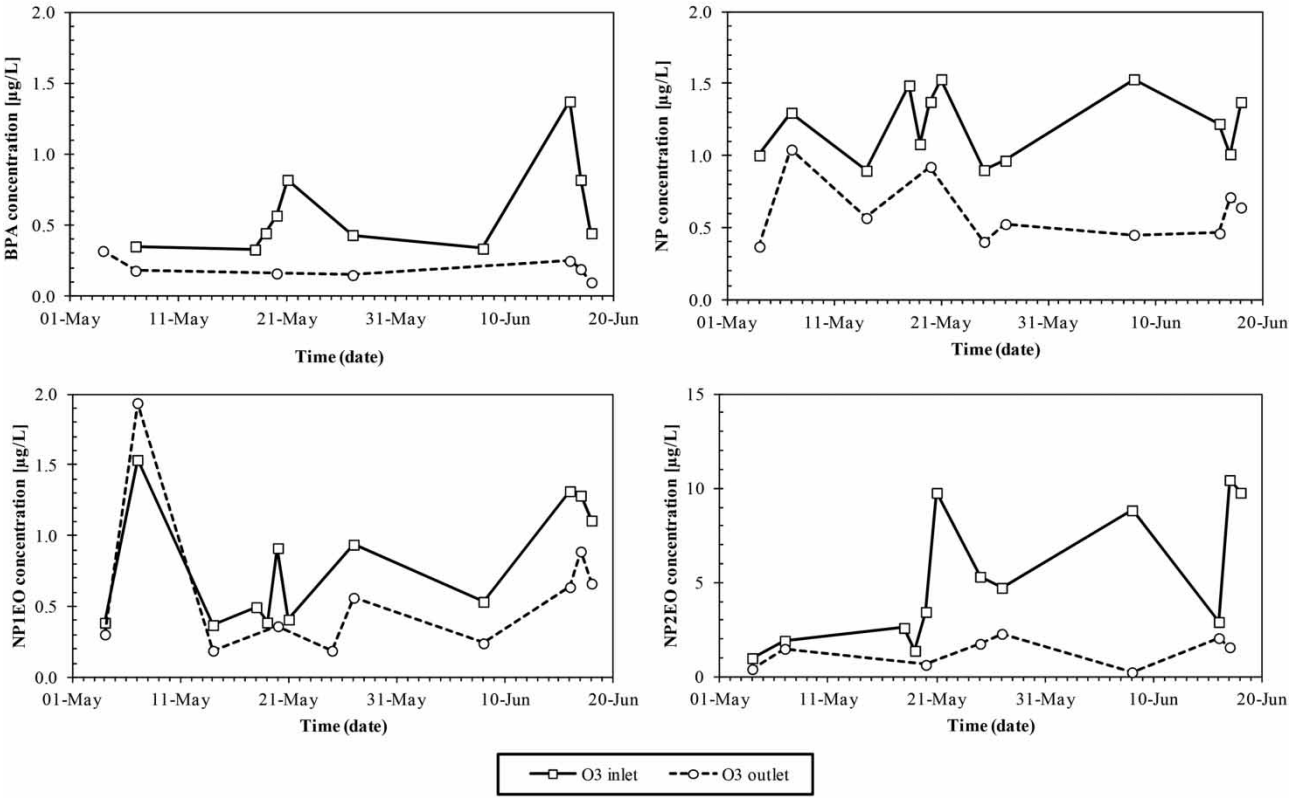

Figure 2 | Daily average concentration (measured on 24-h composite samples) of BPA, NP, NP1EO and NP2EO in ozonation influent (solid line) and effluent (dashed line) wastewater.

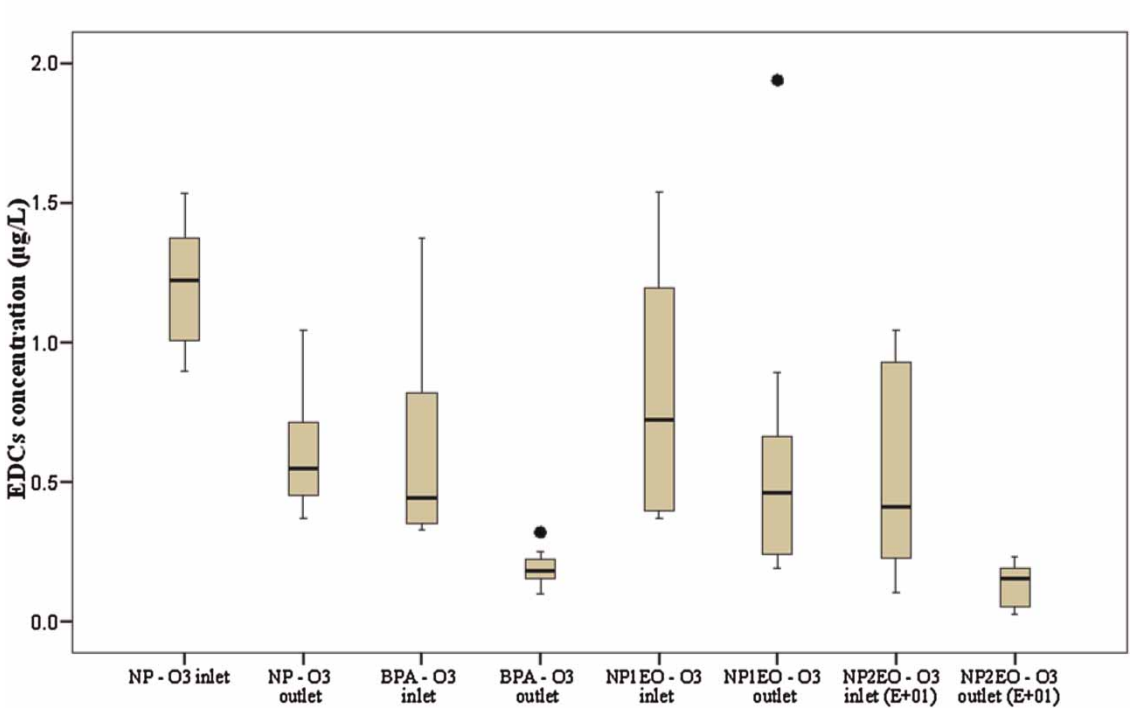

Figure 3 | Statistical analysis: box plots of pollutants concentration in inlet and outlet 24-h composite samples.

Table 2 | Removal efficiency of detected pollutants achieved during wet and dry periods

	Removal efficiency (%)	
EDCs	**Wet periods**	**Dry periods**
BPA	22.4%	70.8%
NP	38.3%	59.0%
NP1EO	≈0%	56.1%
NP2EO	38.1%	66.6%

this is a crucial aspect that must be carefully considered when working on experimental data from real plants, where steady-state conditions cannot be ensured. In effect, based on this, only two values of removal efficiency were calculated for each compound, out of a dozen samples, just considering the distinction between wet and dry periods, in order to take into account the very different flow conditions (and, consequently, operating parameters): during rainy periods (4–21 May and 16–18 June) the average flow-rate was around 50,000 m^3/d, the contact time 60 min and the actual dosage 6 mgO_3/L; under dry weather conditions (21 May–16 June), in contrast, the typical design features were kept: ≈30,000 m^3/d, 90 min contact time, 10 mgO_3/L. For both situations, anyway, the specific ozone dosage (gO_3/gTOC) was approximately the same, due to the influent dilution occurring during wet periods.

Results (Table 2) clearly emphasize that the wet periods were characterized by lower removal efficiencies (around a half of those obtained under dry weather conditions), as expected considering the reduction of contact time.

In any case, the tertiary ozonation stage was not able to achieve satisfactory removal of selected EDCs.

Removal efficiency: effect of wastewater characteristics

In order to understand the reasons for such a low abatement efficiency, the role of the wastewater source was investigated which involved a comparison with literature data.

In previous research (Bertanza *et al.* 2010) the authors found that the effluent of another municipal WWTP (CAS with biological nitrogen removal) was characterized by EDC concentrations lower than those recorded in this study: the variability range of NP and BPA was 0.15–0.45 µg/L, while both NP1EO and NP2EO were below 0.20 µg/L; the higher level of contamination measured in the present experimentation (see 'EDC concentration' section) is clearly a consequence of sewage industrial inputs.

Furthermore, ozonation of the effluent, in the previous experimentation, yielded a greater removal efficiency. Time profiles of NP and BPA normalized concentrations (Figure 4) obtained with 12 mg/L ozone dosage (similar to that of the present experimentation under dry weather conditions) allowed the estimation (assuming first order kinetics and under the hypothesis of plug-flow reactor) of the reaction rate constants, which for both pollutants were around 1.5 h^{-1}; based on this, a removal efficiency around 90% was expected, for 90 min contact time. In contrast, even considering the reasonable differences between the pilot- and the full-scale plants (concerning, for instance, the hydrodynamic scheme and the ozone transfer efficiency), the removal efficiency recorded for the latter was significantly lower (only around 60–70% as displayed in Table 2). This result, as well, has to be ascribed to the different wastewater compositions.

The comparison with the most recent literature also confirmed the poor efficiency recorded in the present study with respect to what could be expected: Schaar *et al.* (2010) achieved satisfactory reductions (50% for NP and 60% for BPA) operating at milder conditions (O_3 dosage ≈6 mg/L, contact time ≈20 min) in a pilot plant (5 m^3), treating a secondary domestic effluent, with concentrations of NP and BPA in the range 0.07–0.20 and 0.04–0.40 μg/L, respectively; Wert *et al.* (2009) recorded 65% BPA reduction with an O_3 dosage ≈2.5 mg/L and contact time ≈25 min, and a complete removal with 6 mgO_3/L, treating (at pilot scale: 60 L/h) the effluent of three municipal WWTPs (CAS systems), where BPA concentration was in the range 0.05–0.10 μg/L; Baig *et al.* (2008) asserted that a removal yield greater than 95% (both for NP and BPA) was achieved with approximately 12 mg/L ozone dose and 45 min contact time, in a pilot test (20 L/h) conducted on the effluent of a municipal WWTP (CAS system), NP and BPA concentrations being in the range 1.0–1.5 and 0.3–0.5 μg/L, respectively.

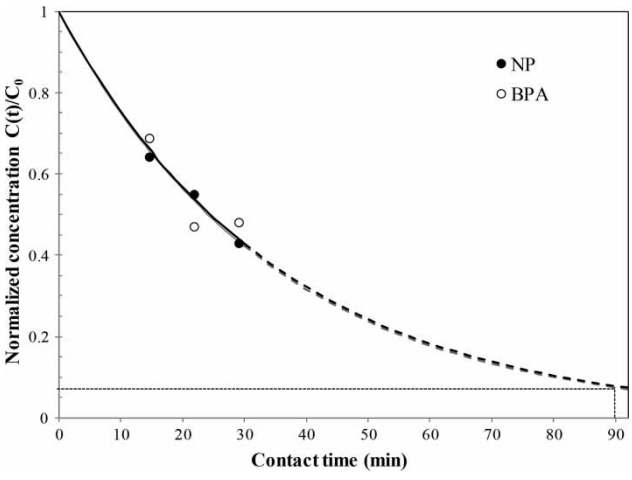

Figure 4 | Ozonation of secondary domestic effluent (12 mgO_3/L dosage): time profiles of NP and BPA normalized concentration recorded in a previous work (Bertanza *et al.* 2010). The expected removal efficiency with 90 min contact time is shown (dashed lines).

In summary, the abatements obtained in the current research were markedly modest with respect to previous works. These incomparable performances highlight the role of the wastewater source: the textile component was likely responsible for the lower abatement efficiencies; in effect, it is characterized by a huge amount of biorecalcitrant compounds (as is well known: see, among others, Tehrani-Bagha *et al.* (2010)) which are competitors of EDCs for O_3 consumption; this is also confirmed by the relatively high residual COD concentration still detected after ozonation (see 'The full-scale WWTP' section).

CONCLUSIONS

In this work, the performance of tertiary chemical ozonation in the removal of target EDCs (NP, NP1EO, NP2EO and BPA) from a wastewater with considerable industrial contribution was evaluated. The research was conducted on a full-scale plant, for a relatively long monitoring period (≈40 d). Chemical analyses showed that the studied substances occurred in the range of μg/L, and statistical data processing revealed their high degree of variability, which is typical of real wastewaters and which has to be taken into account for a proper interpretation of results. In effect, the monitoring period was split into two sub-intervals (characterized by wet and dry conditions, respectively), emphasizing different abatement efficiencies: around 30% for the former, approximately 60% for the latter (as averages of four measured compounds). This difference was due to the decreased contact time (60 vs 90 min), as determined by the higher flow-rate in the wet periods (wastewater is conveyed by a combined sewer system).

In any case, the obtained performance was significantly worse with respect to what could be expected based on results reported in the most recent literature. This was attributed to the presence, in the industrial (textile) wastewater, of a huge amount of biorecalcitrant compounds, competitors of EDCs for O_3 consumption.

In summary, the research showed that, in full-scale applications, many factors, some of which were out of the

control of the operators, affect ozonation performance and can lead to results worse than expected (in this work flow-rate variability and the presence of industrial discharges in the municipal sewer proved to be crucial factors). This has to be taken carefully into account, both when (a) processing and interpreting operation data and (b) designing expensive polishing treatments.

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