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Research Article

Ubiquity of Endocrine Disruptors Nonylphenol and Its Mono- and Di-Ethoxylates in Freshwater, Sediments, and Biosolids Associated with High and Low Density Populations of Buenos Aires, Argentina

In Latin America, use of alkylphenol ethoxylates is unrestricted and widespread. However, their environmental incidence is still little studied. In order to investigate the occurrence, distribution and main sources of the endocrine disruptors nonylphenol (NP), nonylphenol mono- and di-ethoxylate (NP1EO, NP2EO), we analyzed water and sediments from thirteen sites in high and low population densities regions of Argentina. Also ten biosolid samples from a municipal sewage treatment plant were analyzed. Ranges for NP were 21–6359 $\mu g\,kg^{-1}$ in sediments, 0.1–6.2 $\mu g\,L^{-1}$ in water and 64–112 $mg\,kg^{-1}$ in sludge; for NP1EO were 7–3357 $\mu g\,kg^{-1}$ in sediments, 0.1–9.2 $\mu g\,L^{-1}$ in water and 8–140 $mg\,kg^{-1}$ in sludge and for NP2EO were 1–437 $\mu g\,kg^{-1}$ in sediments, 0.1–5.2 $\mu g\,L^{-1}$ in water and 2–23 $mg\,kg^{-1}$ in sludge. The highest levels were associated with proximity to industry and sewage effluents discharge. In biosolids we found predominantly NP, followed by NP1EO and NP2EO, consistently with the metabolic potential of engineered systems. Our findings are in agreement with historical reports for Europe and North America, indicating an important incidence of the xenoestrogens also in this important geographical region. Contrasted to guide values, they show a potential threat to the water and terrestrial environments.

1 Introduction

Nonylphenol polyethoxylates (NPnEO) are among the most widely employed non-ionic surfactants [1–3]. Their biotransformation leads to the formation of recalcitrant metabolites, which are known to have harmful effects on biota such as endocrine disruption in several species [1–5]. NPnEO were early banned in Europe [6] and Canada [4]; however, the low cost and good performance for a broad number of applications, added to the lack of regulations in most countries, make these surfactants and their metabolites ever present in the environment as an "eternal flame" [7]. Little is still known on their fate and distribution in Latin America, where the use of these surfactants is widespread and unrestricted [3]. A reduced number of reports show the presence of the parent compounds and their bio-

refractory metabolites in sewage and freshwater systems of Mexico [8, 9] and Brazil [10–12]. In Argentina, a qualitative study showed their presence among other micro-pollutants [13].

In previous works we reported the development and validation of analytical methods for quantification of nonylphenol (NP), nonylphenol mono- and di-ethoxylate (NP1EO, NP2EO) in natural water [14] and sediments [15], finding environmentally relevant levels.

The above precedents indicate a potential problem in this important geographical region, but there are still too scarce data to attain the knowledge on how to deal with the problem. With the aim of contributing to get a more comprehensive and representative panorama, the objective of the current study was to investigate the occurrence, main sources, and environmental significance of the endocrine disruptors NP, NP1EO, and NP2EO in areas that comprise both high and low population densities.

2 Materials and methods

2.1 Reagents and standards

Technical grade NP (85% 4-NP, Fluka, Switzerland) and a NP1EO/NP2EO technical mixture (Igepal CO-210, Aldrich, USA) were used as analyte standards. For GC–MS analyses individual 4-NP1EO and

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Abbreviations: DCM, dichloromethane; **dw**, dry weight; **NP**, nonylphenol; **NP1EO**, NP mono-ethoxylate; **NP2EO**, NP di-ethoxylate; **NPnEO**, NP polyethoxylates; **SPE**, solid-phase extraction; **STP**, sewage treatment plant; **TEQ**, toxic equivalent

4-NP2EO standards (Promochem, Germany) were employed. All solvents were HPLC grade and other chemicals were p.a. quality. Glass-fiber pre-filters were APFD 04700 from Millipore. For solid-phase extraction (SPE), glass columns and PTFE frits from Merck were employed; C-18 sorbent was CEC-18 (UCT, USA).

2.2 Sample collection and extraction procedures

2.2.1 Water and sediments

Water samples were collected in 1-L amber-glass bottles, added with 1% v/v formaldehyde and stored at 4°C until analysis. Grab sediment samples, mostly clay (except for sample S3, sandy) were collected from the water courses margins with a steel shovel, placed in 500 mL glass flasks with the addition of 2% v/v formaldehyde and stored at −20°C until analysis.

Since details on the extraction conditions are given elsewhere [14, 15] only the outline of the procedures is described here. After filtration through glass-fiber pre-filters and addition of NaCl to the acidified water samples, enrichment of the analytes was carried out by SPE on C-18 and elution with ethyl acetate (EtAc). Following addition of anhydrous Na_2SO_4 and evaporation of the SPE solvent, the extracts were re-dissolved in HPLC mobile phase and analyzed. Sediment samples were dried at 60°C until constant weight and homogenized, obtaining a solid that passed through a 20 mesh sieve. Extraction with EtAc was ultrasound assisted. The extracts were dried under N_2 and re-dissolved in the HPLC elution mixture for measurement. No clean-up operations were performed.

Performance of the extraction procedures with real samples was evaluated through recovery assays at different concentration levels.

2.2.2 Sewage sludge

Biosolids were collected in 250 mL glass flasks, immediately preserved with 2% formaldehyde and stored at −20°C until analysis.

Method development experiments were carried out with a blank material from a laboratory scale reactor operated as semi-continuous activated sludge. The water phase was discarded after settlement and the remaining solid was oven dried at 55−60°C for 2 h. The dried sludge was treated with liquid N_2 to allow mortar disintegration. A stock solution of the three target compounds in hexane/2-propanol (50:50) was spiked into the conditioned sludge and left at room temperature in the dark for 48−72 h, in order to obtain a final concentration of 550 µg NP, 534 µg NP1EO, and 328 µg NP2EO per gram of sludge dry weight (dw). Ultrasonic-assisted extraction was employed. Mixtures of dichloromethane (DCM), methanol (MeOH), and ethyl acetate (EtAC) were assayed as extraction solvents. Three sonication cycles of 5 min each were applied to 0.15 g of spiked blank together with 0.45 mL of the corresponding extraction solvent. The extracts were evaporated to dryness under N_2 and re-dissolved in the HPLC elution mixture for analysis.

A drying period of 50−60 h at 60°C was necessary to achieve constant weight for the decanted solids of real sewage sludge samples (water phase also discarded). Once dried, a homogeneous material (20 mesh) was obtained. Three sonication cycles of 5 min were applied to 0.15 g of dried sample with 0.45 mL of an extraction mixture of MeOH/EtAc 25:75, selected during method development. Performance of the extraction procedures with real samples was evaluated through recovery assays.

2.3 Chromatographic analysis

Quantification of NP, NP1EO, and NP2EO extracted from water, sediments and sludge was carried out by normal-phase HPLC with fluorescence detection (HPLC-FL), following our previous procedures [14, 15]. A SpectraSERIES P200 binary pump (Thermo Separation Products, USA) with a Linear LC-305 fluorescence detector (Linear Instruments, USA) was employed. Separations were performed on an aminopropyl-silica column (5 µm particle, 250 × 4.6 mm, APS-2 Hypersil, Thermo Scientific, USA) at 35°C, using isocratic elution with 4% 2-propanol in hexane. Excitation and emission wavelengths were 230 and 300 nm, respectively. Injection volume was 50 µL, with instrumental detection limits of 0.8 µg L^{-1} for NP1EO and NP2EO, and 1.3 µg L^{-1} for NP. In all cases, the analytes were positively identified by means of standard spiking.

Further confirmation of compounds identities was obtained by GC−MS. For the real samples, every HPLC peak attributed to the analytes was collected as eluted, evaporated to dryness and re-dissolved in cyclohexane for GC−MS analysis. A Shimadzu GC-17A split−splitless gas chromatograph coupled to a MS-QP5050A mass spectrometer was used. A Zebron ZB-1 capillary column (60 m × 0.32 mm id, 0.50 mm film thickness, Phenomenex, USA) was employed. Instrumental conditions for separate measurement of the three analytes are described elsewhere [14].

Laboratory blanks were run among the samples, in order to verify the absence of crossed contamination during the sample preparation and analysis procedures.

2.4 Study area and sampling strategy

Water and sediment samples from 13 sites selected near potential sources of NP*n*EO, as well as ten biosolid samples from a sewage treatment plant (STP), were collected. Also, a number of locations where no sources were anticipated were studied in order to establish background levels, amounting to a total area of approximately 3000 km^2.

In order to track the origin of NP*n*EO derived contamination and detect hot spots, a survey of low, middle and high density population areas was carried out. Sites were sampled along three selected natural water courses (Fig. 1), whose main characteristics are summarized.

2.4.1 Luján River

It emerges from the confluence of Los Leones and El Durazno creeks and runs 128 km through an area of 2690 km^2. Three sections can be distinguished: higher basin (40 km long from the source), with low population density and agricultural and cattle activities; then middle and lower basins, running through regions of increasingly higher population densities and intense industrial activities, receiving wastewater of both industrial and municipal origins. The lower basin, running through the highest population density area, receives the most significant contamination charge, either directly or by means of its tributaries, specially the Reconquista River (www.atlasdebuenosaires.gov.ar) [13]. The higher basin was sampled at El Durazno creek (point N1) and the middle basin was sampled in the nearby of the municipal sewage treatment facility of Luján City (L-STP), namely upstream (N2), directly from the end-pipe (N3), close to the outlet (N4), and downstream the plant (N5).

Taking into account the potential use of biosolids for soil amendment, a survey of the aforementioned pollutants was performed. A new method of analysis was proposed for the study
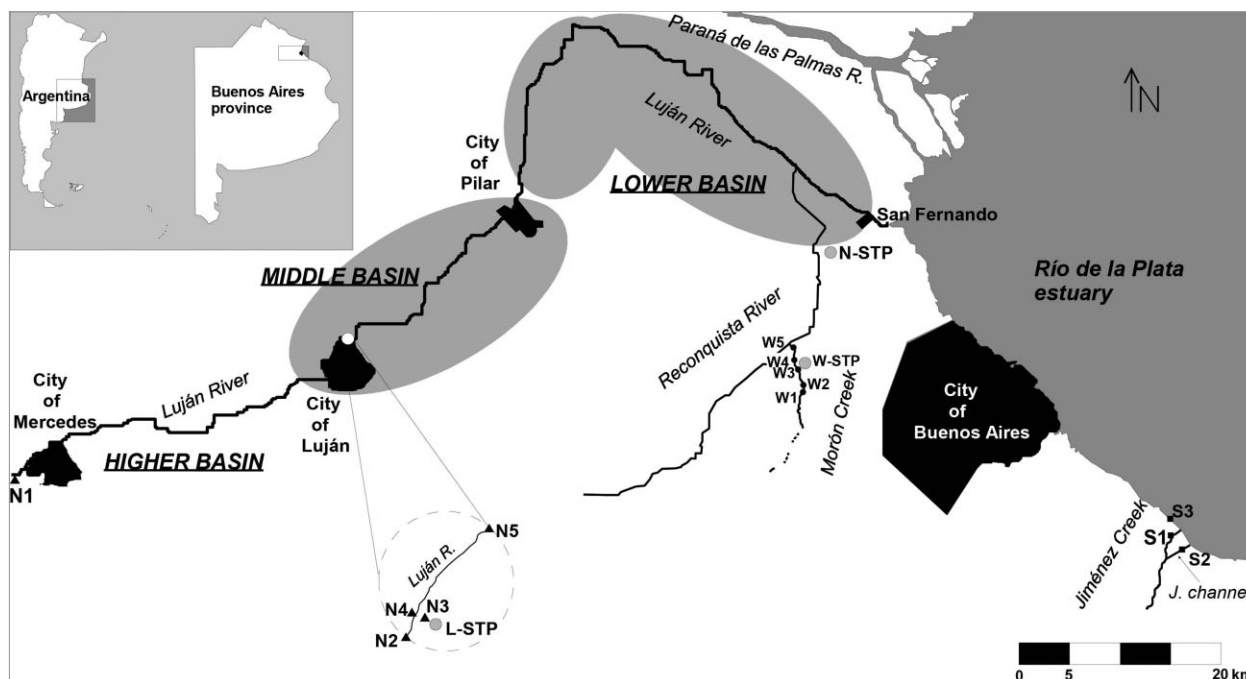
Figure 1. Sampling sites location at the Norwest (N1–N5), West (W1–W5), and South (S1–S3) of the city of Buenos Aires. L-STP, Luján sewage treatment plant; N-STP, North sewage treatment plant; W-STP, West sewage treatment plant. Dashed line represents the piped section of Morón creek. Alleviator of Jiménez creek is pointed by an arrow. Please note that only the water streams and cities or towns relevant for this work are shown in the map.

of biologic sludge. This method was applied in the analysis of the biosolids resulting from a mesophilic anaerobic digestion of secondary sludge (at 35–37°C with a retention time of 21 days) from the main municipal STP of San Fernando district, at the lower basin of Luján River (N-STP). This activated sludge facility serves a population of 270 000 inhabitants, has a capacity of $0.9 \, m^3 \, s^{-1}$ and discharges the liquid effluents into the highly polluted Reconquista River at its confluence with Luján River.

2.4.2 Morón creek

It runs 16 km through one of the most densely urbanized and industrialized zones in the Metropolitan Area of Buenos Aires. The first 4.5 km are piped and the open stream section receives the input of a vast number of human activities. It belongs to the Reconquista River basin and is recognized as one of the most highly polluted ecosystems in the whole country (www.atlasdebuenosaires.gov.ar). Sampling was focused on the nearby of a chemical industry (close to the outlet (W1) and downstream the discharge (W2)) and a municipal STP (W-STP; upstream (W3), close to the end-pipe (W4) and downstream the plant (W5)).

2.4.3 Jiménez creek and its alleviator Jiménez channel

The creek rises as an intermittent water course and is one of the several water courses that are recognized to be highly polluted due the lack of control in effluent discharges. It flows into de la Plata River estuary. Its basin covers an area of $80 \, km^2$ and runs through highly urbanized and industrialized districts. All along its course, it receives discharges from industrial and domestic effluents. The points investigated, located at the city of Quilmes, are indicated as S1 (Jiménez creek), S2 (Jiménez channel), and S3 (irrigation channel).

3 Results and discussion

3.1 Water and sediments

3.1.1 Occurrence and distribution of NPnEO metabolites

The concentrations measured by HPLC-FL are shown in Tab. 1. Recovery rates obtained after standard addition resulted always >80% and therefore no correction factor was applied to the quantitative results. As reported before [1, 16], concentrations of the analytes in the solids were 1–3 orders of magnitude higher than the aqueous levels, reflecting accumulation due to their lipophilic nature. Figure 2a and b shows their molar distribution in water and sediments. Partitioning of organic compounds between these two phases is usually controlled by physical, chemical, and biological processes; fully de-ethoxylated NP and short-chain NP1EO and NP2EO would display different behaviors because of their different physico-chemical properties [17]. The less water soluble the metabolite the higher the enrichment of the sediment that may be expected [16]. As stems from the figure, there is not a clear tendency in terms of a major compound in the water phase: NP, NP1EO, or NP2EO are present at the highest molar fractions in the different sites, talking about varying compositions of the discharges affecting the water compartment. However, accumulation of NP in the sediments becomes apparent; NP is always the major compound, with percent molar fractions mostly >50%, followed by NP1EO and much smaller amounts of NP2EO, except for point N1. In the latter site, a major proportion of longer chain NP2EO is observed, probably due to the presence of less adapted micro-biota in a slightly impacted site (as this rural area is) in contrast with the metabolisms found in engineered systems.

Table 1. Quantitative results for water, sediment, and biosolid samples

Sample	NP		NP1EO		NP2EO	
	Liquid ($\mu g\,L^{-1}$)	Solid[a]	Liquid ($\mu g\,L^{-1}$)	Solid[a]	Liquid ($\mu g\,L^{-1}$)	Solid[a]
(S1) Jiménez creek – motorway	0.9 ± 0.2 (2)	21 ± 2 (2)	0.4 ± 0.06 (2)	7 ± 0.6 (2)	0.7 ± 0.02 (2)	1 ± 0.09 (2)
(S2) Jiménez channel – motorway	1.6 ± 0.1 (5)	249 ± 13 (8)	3.3 ± 0.2 (5)	173 ± 29 (8)	2.5 ± 0.05 (5)	84 ± 10 (8)
(S3) Irrigation channel – mouth	0.7 ± 0.1 (5)	437 ± 17 (3)	0.5 ± 0.07 (5)	120 ± 9 (3)	0.8 ± 0.1 (5)	72 ± 4 (3)
(W1) Morón creek – industry discharge	1.9 ± 0.1 (3)	384 ± 28 (4)	8.2 ± 0.3 (3)	163 ± 22 (4)	4.8 ± 0.3 (3)	33 ± 5 (4)
(W2) Morón creek – railway	2.3 ± 0.2 (3)	2229 ± 47 (2)	9.2 ± 0.1 (3)	1372 ± 34 (2)	5.2 ± 0.02 (3)	217 ± 5 (2)
(W3) Morón creek – cemetery	0.5 ± 0.02 (2)	1436 ± 107 (2)	5.1 ± 0.06 (2)	642 ± 89 (2)	3.8 ± 0.1 (2)	350 ± 72 (2)
(W4) Morón creek – STP discharge	6.2 ± 0.6 (4)	6359 ± 1058 (3)	7.0 ± 0.3 (4)	3357 ± 614 (3)	4.9 ± 0.2 (4)	437 ± 55 (3)
(W5) Morón creek – motorway	4.2 ± 0.9 (3)	–	8.6 ± 0.2 (3)	–	2.8 ± 0.05 (3)	–
(N1) El Durazno creek	0.1 ± 0.005 (2)	21 ± 2 (2)	0.1 ± 0.002 (2)	11 ± 3 (2)	0.2 ± 0.008 (2)	22 ± 3 (2)
(N2) Luján River – upstream STP	0.4 ± 0.03 (4)	544 ± 2 (2)	0.3 ± 0.02 (4)	370 ± 10 (2)	0.1 ± 0.01 (4)	148 ± 6 (2)
(N3) Discharge of Luján STP	7.0 ± 0.3 (4)	–	7.0 ± 0.2 (4)	–	5.4 ± 0.7 (4)	–
(N4) Luján River – Luján STP discharge	3.0 ± 0.06 (2)	985 ± 9 (2)	3.0 ± 0.3 (2)	847 ± 7 (2)	2.4 ± 0.2 (2)	214 ± 27 (2)
(N5) Luján River – downstream Luján STP	0.3 ± 0.03 (5)	606 ± 62 (3)	0.4 ± 0.03 (5)	197 ± 44 (3)	0.3 ± 0.02 (5)	24 ± 2 (3)
(B1) San Fernando STP biosolid	–	112 ± 10 (2)	–	35 ± 0.2 (2)	–	7 ± 0.6 (2)
(B2) San Fernando STP biosolid	–	64 ± 2 (2)	–	8 ± 0.1 (2)	–	2 ± 0.07 (2)
(B3) San Fernando STP biosolid	–	69 ± 7 (2)	–	10 ± 0.6 (2)	–	2 ± 0.07 (2)
(B4) San Fernando STP biosolid	–	79 ± 15 (2)	–	24 ± 4 (2)	–	6 ± 0.8 (2)
(B5) San Fernando STP biosolid	–	71 (1)	–	140 (1)	–	3 (1)
(B6) San Fernando STP biosolid	–	101 ± 9 (4)	–	30 ± 3 (4)	–	6 ± 0.8 (4)
(B7) San Fernando STP biosolid	–	91 ± 3 (2)	–	25 ± 1 (2)	–	4 ± 0.1 (2)
(B8) San Fernando STP biosolid	–	62 (1)	–	38 (1)	–	5 (1)
(B9) San Fernando STP biosolid	–	97 (1)	–	54 (1)	–	13 (1)
(B10) San Fernando STP biosolid	–	101 ± 12 (2)	–	107 ± 7 (2)	–	23 ± 2 (2)

In brackets are given the number of replicate samples analyzed for each site (n). Blank space (−) indicates that no sample was analyzed.
[a] Solid phase concentrations (dry basis) are expressed in $\mu g\,kg^{-1}$ for sediments and $mg\,kg^{-1}$ for biosolids.

3.1.2 Sources and impact of NPnEO metabolites

Since NP, NP1EO, and NP2EO occur together, their combined impact was assessed through calculation of NP-toxic equivalents (NP-TEQs), as described in Canadian guidelines for water [18] and sediments [19]. Relative toxicity values, or NP-toxic equivalency factors (TEFs) are as follows: NP is assigned a TEF value of 1 and the shorter NPnEO oligomers (with n up to 8) have TEFs of 0.5. Then, the total concentration of NP-TEQs was calculated as:

$$NP - TEQs = C_{NP} + 0.5\,C_{NP1EO} + 0.5\,C_{NP2EO}$$

where C_{NP}, C_{NP1EO}, and C_{NP2EO} are the concentrations of the respective analytes in the sample. This was compared against the corresponding guidelines ($1\,\mu g\,L^{-1}$ for freshwater and $1.4\,mg\,kg^{-1}$ dw for freshwater sediment, according to the aforementioned Canadian documents).

The results are graphically depicted in Fig. 2a and b. In Tab. 2 we gathered the sites characteristics and their related NP-TEQs. Not surprisingly, the most impacted area was Morón creek (sites W1–W5), a water body strongly influenced by untreated municipal and industrial wastewater, turning it into an "open sewer". The highest TEQs seem to be associated with proximity to industry and sewage treatment effluents discharges; levels both in the aqueous and solid phases reached maximum values at the point of the creek that receives the STP effluent. All in all, the levels found are coherent with a densely populated area, dominated by the continuous discharge of industrial and domestic (many times untreated or deficiently treated) residual water.

The water samples of Quilmes (sites S1–S3) present higher TEQs than those from the comparatively less urbanized Luján River zone

(sites N2 and N5); however, there is a clear disturbance caused by the discharge of Luján City STP effluent into Luján River (sites N3 and N4). The end-pipe water sample (N3) reached $13.2\,\mu g$ TEQs L^{-1}, affecting the river water with $5.7\,\mu g$ TEQs L^{-1} and also the sediments with $1516\,\mu g$ TEQs kg^{-1} (N4). Those were the maximum values accounted for these two areas. Finally, when comparing the results for Jiménez creek and Jiménez channel, it is interesting to note the significantly higher values found in the alleviator channel ($4.5\,\mu g$ TEQs L^{-1} in water and $378\,\mu g$ TEQs kg^{-1} in sediments), possibly due to surreptitious discharges that could be happening into this water stream.

3.2 Sewage sludge

3.2.1 Extraction method

Published literature shows that the most widely employed extractants for this or similar purposes have been for a long time DCM, MeOH, acetone, and hexane, either alone or in binary mixtures [1, 17, 20–22]. Based on our previous experience with sediment extraction [15], performance of MeOH, DCM, and EtAc, individually and in mixtures, was comparatively evaluated, the latter thought as a potentially suitable solvent in replacement of DCM (an environmentally and toxicologically harmful solvent).

Similar extraction performances were achieved with DCM and EtAc when mixed with MeOH, the latter showing to be an essential component of the binary mixtures in order to obtain high recovery rates. Therefore and in accordance with the idea of replacing DCM with a more environmentally friendly and less toxic solvent, and also reducing laboratory manipulation of toxic MeOH, the extraction media selected was a mixture of MeOH/EtAc 25:75, for which
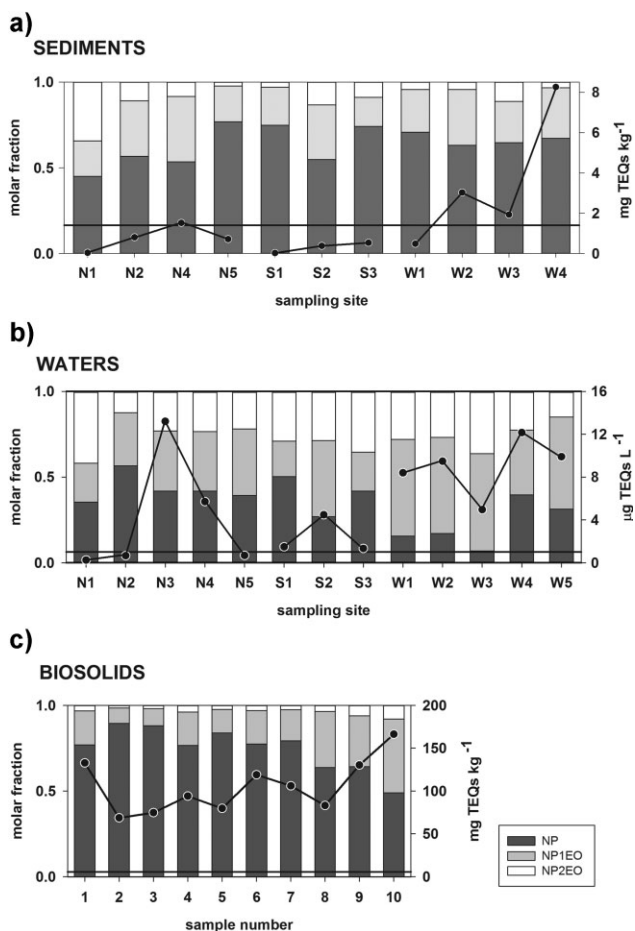
Figure 2. Molar fractions of NP, NP1EO and NP2EO and NP-toxic equivalents (TEQs) in: (a) sediments, (b) water and (c) biosolids. Solid lines indicate the Canadian Water [18], Sediment [19], and Soil [26] Guidelines (NP-TEQs of $1 \mu g L^{-1}$, $1.4 mg kg^{-1}$, and $5.7 mg kg^{-1}$, respectively).

recoveries higher than 80% were obtained for the three analytes. Percentage relative standard deviations for duplicate experiments were always <10%. As no interfering signals were detected during chromatographic analyses of blank extracts, no clean-up procedures were included in the extraction protocol.

Recovery rates in real samples were assessed by spiking two biosolids in the concentration range from 4000 to 55 000 $\mu g kg^{-1}$ (dw), resulting always >85%.

3.2.2 Occurrence and distribution of NPnEO metabolites

Table 1 presents the concentrations found. In terms of molar ratios (Fig. 2c), NP prevailed followed by NP1EO and minute amounts of NP2EO, consistently with the metabolic potential generally found in engineered systems. Output pathways of organic compounds from STPs may be outlined as a sum of biodegradation processes, adsorption on sludge and release via final effluents. Nonylphenolic substances are usually incompletely degraded, leaving relatively high amounts adsorbed onto sludge flocks [17]. As generally observed, the more hydrophobic a molecule the greater the amount that will be retained by the particulate phase. The high proportion of NP, followed by NP1EO and NP2EO found in the sludge samples can be derived therefore from their partitioning to the particulate matter during the earlier stages of wastewater treatment. Further removal of residual oxyethylene groups takes place during anaerobic digestion, making NP to persist in digested sludge [3, 23].

3.3 Environmental significance and literature comparison

As previously pointed out, there are scarce data on micropollutants concentrations in Latin America. Furthermore, there is a lack of regulations related to the environmental hazard of NP and its ethoxylates in the region. However, regarding the environmental significance of the levels measured in this work, we can say that in most cases they are very close or surpass the guidelines for protection

Table 2. Summary of sites characteristics and their related NP-TEQs

Site	Location characteristics/potential sources of high NP-TEQs	NP-TEQs water ($\mu g L^{-1}$)	NP-TEQs sediment ($mg kg^{-1}$)
(N1) El Durazno creek	Low population density; mostly agricultural and cattle activities	0.2	0.04
(N2) Luján River	Middle to high population density; industrial activities	0.7	0.8
(N3) Luján STP	Middle to high population density; industrial activities/Luján City municipal STP discharge (directly from the end-pipe)	13.2	–
(N4) Luján River	Middle to high population density; industrial activities/Luján STP discharge	5.7	1.5
(N5) Luján River	Middle population density; agricultural activities	0.7	0.7
(S1) Jiménez creek	Highly urbanized and industrialized districts	1.5	0.03
(S2) Jiménez channel	Highly urbanized and industrialized districts/surreptitious discharges	4.5	0.4
(S3) Irrigation channel	Highly urbanized and industrialized districts	1.3	0.54
(W1) Morón creek	Among the most densely urbanized and industrialized zones in the Metropolitan Area of Buenos Aires (MABA)/industry discharge	8.4	0.5
(W2) Morón creek	Among the most densely urbanized and industrialized zones in the MABA/downstream industry discharge	9.5	3.0
(W3) Morón creek	Among the most densely urbanized and industrialized zones in the MABA	5.0	1.9
(W4) Morón creek	Among the most densely urbanized and industrialized zones in the MABA/municipal STP discharge	12.2	8.3
(W5) Morón creek	Among the most densely urbanized and industrialized zones in the Metropolitan Area of Buenos Aires/downstream municipal STP	9.9	–

Blank space (−) indicates that no sample was analyzed.

of freshwater ecosystems established in other countries. A graphical comparison of measured NP-TEQs with the Canadian guidelines (Fig. 2a and b), shows that water levels fairly approach or widely surpass safe values in all but one sample; in the case of sediments, this occurs in about 40% of the samples. When we contrast our results for instance with the Dutch Environmental Risk Limits [16], they cause even higher concern. We found that in all cases, with exception of El Durazno creek (N1), NP levels widely exceed maximum permissible concentrations (MPCs) for surface water ($0.33 \, \mu g \, L^{-1}$), by a factor of 10–20 in the worst cases, always related with the vicinity to STP discharges. Also for NP1EO and NP2EO, a combined MPC of $0.12 \, \mu g \, L^{-1}$ is surpassed by all samples, with no exceptions. Talking about the sediments, MPCs of $105 \, \mu g \, kg^{-1}$ (dw) for NP and $150 \, \mu g \, kg^{-1}$ (dw) for NP1EO + NP2EO were mostly widely exceeded, except for the samples taken at Jiménez (S1) and El Durazno (N1) creeks.

Concentrations found in the current study are in accordance with data published for water streams and sediments of highly urbanized and/or industrialized countries (i.e., USA, Canada, Switzerland, Germany, Korea, Spain), which have been extensively reviewed [3]. In those cases the higher values were associated with STP discharges, as well as with urbanized and industrialized areas, a fact that was also observed in our research. This is exalted in the case of Morón creek, where the analytes show high values all throughout its course, consistently with the high anthropogenic impact mentioned above.

Analyte concentrations in the biosolids ranged from 62 to $112 \, mg \, kg^{-1}$ (dw) for NP, from 7.6 to $107 \, mg \, kg^{-1}$ (dw) for NP1EO and from 1.65 to $23 \, mg \, kg^{-1}$ (dw) for NP2EO. Even when these levels did not reach values as high as those eventually found in other countries [3], sometimes one order of magnitude superiors [24], they deserve enough attention because of the increasing, widely spread use of nutrients and organic matter contained in sludge for agricultural purposes [3, 17]. Application of dehydrated stabilized sludge in agriculture is considered a potential input way of alkyphenols into the terrestrial environment. These degradation products have been encountered in soil and also in ground water as a consequence of leaching of sludge fertilized fields [23]. In this regard, the EU proposed a limit value of $50 \, mg \, kg^{-1}$ (dw) for the sum of NP, NP1EO and NP2EO in sludge intended for use in agriculture land [25]. The values measured in the present work certainly surpass this safe limit, raising concern about the possible disposal or final use of the generated biosolids. Finally, when contrasted with the Canadian NP-TEQ of $5.7 \, mg \, kg^{-1}$ (dw) for agricultural use of soil, our results are at least 10 orders of magnitude above safe limits (Fig. 2c) [26].

4 Concluding remarks

In the nearby of Buenos Aires City there exist a vast number of industrial, municipal, and domestic facilities discharging their wastewater into rivers and creeks. These effluents are in some cases treated streams and many other times they correspond to direct discharges of untreated water. Therefore, this area appeared as an important environment to investigate the occurrence of degradation products of NPnEO, given that this is one of the major classes of non-ionic surfactants still employed in all kind of industrial and domestic applications in the country. In addition, the use of NPnEO as a co-adjuvant in several agricultural preparations increases the risk of occurrence of these substances in theoretically slightly impacted areas, such countryside zones. This kind of research had not been carried out before in the country, what acquires even highest relevance taking into account the small number of works of its type

for the whole Latin America, in a context of widespread and unregulated use and disposal of NPnEO. We think that comprehensive information on the occurrence and fate of pollutants should serve for evaluation and management purposes. Concentrations and behavior of NP, NP1EO, and NP2EO found in surface water and sediments, as well as in sewage systems, are in agreement with those reported for several sites of Europe and North America along the last decades, and reflect an important incidence of the target xenoestrogens also in this region. The metabolites of NPnEO were present in all the sites and compartments sampled at concentration levels which contrasted to guide values show a potential threat to the water and terrestrial environments.

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