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ORIGINAL ARTICLE

Alkylphenols and Alkylphenol Polyethoxylates levels in a Mediterranean developing country context: contamination of rivers and coastal sediments

Helmieh Amine[a, b], Fatmé Merhabi[a, b], Jalal Halwani[b], David Rosain[a], Claude Casellas[a], Hélène Fenet[a], Elena Gomez[a]
[a] Hydrosciences Montpellier, Université de Montpellier, France.
[b] Laboratory of Water Sciences and the Environment, University Lebanese
Email: hilmiyaa@yahoo.fr

ABSTRACT

The presence of alkylphenol polyethoxylates (APEO) in the environment is solely a consequence of anthropogenic activities. These polyethoxylated compounds are biodegraded by losing ethoxy groups and subsequently generate more persistent and lipophilic alkylphenols compounds (APs), such as nonylphenols (NPs) and octylphenols (OPs), under aerobic and/or anaerobic conditions. The relatively high log K o/w of APs and APEO (4.00-4.48) suggests that they tend to become associated with suspended solids and ultimately sediments and their surfactant properties confer to those contaminants a mobility that is difficult to predict in the aquatic environment. The present study aims to obtain a first overview of levels of three APs (NPm, 4n-NP and 4-t-OP) and four APEO (NP1-2EO and OP1-2EO) in eastern Mediterranean coastal zone sediments subjected to river inputs (three rivers), untreated wastewater discharges and dumpsite leachates during the hot and humid seasons. The analysis revealed the ubiquity and high point source contamination by APs and APEO with total concentrations ranging between 346.7 and 3 055.1 ng g-1 d.w. Based on site-dependent analysis and discharges types, APs and APEO concentrations showed a significant spatial variation following a decreasing order between transition, upstream and coastal zones of the three studied rivers, for both nonylphenolic and octylphenolic compounds. The results indicate that there is a coastal background contamination by APEO from river input that could be reduced by photo/biodegradation in transition zones leading to high APs concentrations.

Keywords: *alkylphenols, alkylphenol polyethoxylates, Mediterranean coastal zone, sediment, transition zones, wastewater.*

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INTRODUCTION

Alkylphenol polyethoxylates (APEO) represent a wide group of non-ionizing surfactants produced and used on a large scale; in household, agricultural and industrial applications [1, 2]. These environmentally ubiquitous contaminants are classified as high production volume chemicals (HPVC) in Europe. Nonylphenol polyethoxylates (NPEO) are members of the second largest class of nonionic surfactants in use today, namely APEO [3]. They represent about 80-85% of all APEO (U.S. Environmental Protection Agency, 2010) [4]. They have been widely used in domestic detergents, pesticide formulations and industrial products, such as textiles, coatings, paints, lube oils, fuels, metals, plastics, rubber, pulp and paper [5, 6]. According to the most recent statistics provided by the European Committee of Organic Surfactants and their intermediates (CESIO, 2014) [7], the total quantity of surfactants excluding soap produced in Western Europe in 2014 has been estimated to be 2.918 million tons, most of which belong to the group of ethoxylated nonionic surfactants. As a result, some 60% of used APEO are discharged into the aquatic environment primarily via industrial and domestic wastewater with or without treatment, or released directly into receiving water bodies due to their application characteristics [8, 9, 10, 1, 11, 12]. Their presence in the environment, where they are biodegraded to shorter-chain more persistent and lipophilic alkylphenols (APs), such as nonylphenols (NPs) and octylphenols (OPs), under aerobic [13] and/or anaerobic conditions [14, 15, 16], is solely a consequence of anthropogenic activity.

A considerable aquatic toxicity research has occurred on NPEO and particularly on NPs [17]. Over the last few decades, a large number of studies have highlighted endocrine-disrupting potential of APs; and their ethoxylates are of particular concern due to their ubiquity [18, 19, 20, 12]. NPs has been identified as one of the four main endocrine disrupting chemicals found in the environment, namely estrogens, bisphenol A and octylphenols [21]. Due to these concerns, several European countries initiated a voluntary phase-out in mid 1990s to reduce the production and use of NPs, OPs and their derivatives (OSPAR Commission, 2006) [22] and they had been classified within the European Water Framework Directive's list of priority hazardous substances (2013/39/EU). This means that it is requirement of the Directive that discharges, emissions and losses of the substance must cease no later than during 2021. Recently, the U.S. Environmental Protection Agency (U.S. EPA) also initiated both voluntary and regulatory actions on NPs and NPEO in the U.S. (http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/np-npe.html), whereas no stronger initiatives are undertaken in developing countries.

The relatively high log Ko/w of APs and APEO (4.00-4.48) suggests that most of them entering rivers tend to become associated with suspended solids and ultimately sediments. Many studies have demonstrated that sediments in the vicinity of wastewater discharges, especially in proximity of industrialized and agricultural / urban areas, are often heavily impacted by those contaminants, reaching micrograms per gram levels [23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 20, 36]. In addition to their occurrence, their degradation, distribution and dynamics in the sedimentary compartment are important points that determine the fate of these contaminants. The non-oxidative hydrolytic pathway results in short-chain APEO and APs such as NPs and OPs. This itinerary is mainly followed in marine waters and sediments [25, 14, 16]. In estuarine conditions, biodegradation by both the oxidative and the non-oxidative routes have been described [13, 37, 38]. NPs are therefore generally studied as an industrial wastewater/sewage tracer. Dong et al. (2015) [39] investigated NPs and OPs concentrations in the surface sediments of Kaohsiung Harbor, Taiwan. Major sources of sediment APs come from polluted urban rivers. The concentrations were between 18 and 27.882 ng g^{-1} d.w. and 1.1 and 1.150 ng g^{-1} d.w. for 4n-NP and 4-t-OP, respectively. In the pollution hotspots, the direct inflow of pollutants would be the crucial factor that determines the concentration and distribution of organic pollutants in sediments. Choi et al. (2011) [24] detected high NPs and NP1-2EO concentrations (29.3-230 µg g^{-1} d.w.) in marine sediments surrounding the submarine outfall of a wastewater treatment plant (WWTP) in Korea, indicating that it is an important point source also for marine sediment. Arditsoglou and Voutsa (2008) [40] reported APs and APEO presence in coastal sediment of Thessaloniki in northern Greece, where effluents from various urban, industrial and agricultural activities, end up directly or through rivers and streams. However, the presence of APs an APEO in coastal and marine ecosystems is not as well-documented as in freshwater ecosystems, especially in the Mediterranean basin and precisely in the sediment compartment [41, 42, 30, 12].

As mentioned previously, only very limited studies have been carried out in marine sediment from developing countries, especially in the eastern Mediterranean environments where source of contamination can be various (i.e., untreated wastewaters from mainly urban origins, agricultural activities, leachate from dump sites, etc.), and where APEO are still extensively used [28, 43]. For these reasons, coastal environment receiving untreated effluents and rivers carrying untreated wastewaters and agricultural residues were selected in a developing country. In the selected area, APs and APEO contamination has never been described previously. This work aims i) to give a preliminary approach for understanding APs and APEO dynamics and sources in rivers transition zones and coastal marine environment, limited to river run-off and terrestrial inputs, without treatment, that represent the typical situation in the eastern Mediterranean area; ii) to explore the seasonal and spatial trends of these chemicals in surface sediments; iii) to discuss the contamination status in the analyzed sites related to extensive researches made under different climate and anthropogenic conditions.

MATERIALS AND METHODS

2.1 Reagents and standards

Investigated alkylphenols, alkylphenols ethoxylates and deuterated standards abbreviations, and relevant physical data are shown in Table 1.

Nonylphenols mix (NPm) (a mixture of nonylphenol isomers with different branches for the alkyl chains) and 4 n-Nonylphenol (4n-NP) (purity 99.9%) were provided by Sigma-Aldrich (St Quentin Fallavier, France). 4-tert-Octylphenol (4-t-OP) (98.5% purity) was purchased from Cluzeau (Courbevoie, France).

Nonylphenol mono- and di-ethoxylates (NP1EO and NP2EO) (OEKANAL-Fluka®) and Mixed Octylphenol mono- and diethoxylates (OP1EO and OP2EO) (IGEPAL® CA-210) were also provided by Sigma-Aldrich.

N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA, purity> 99%) used for the derivatization (silylation) of APs and APEO was provided by Sigma-Aldrich.

Penta deuterated 4 n-Nonylphenol (4n-NP-D4) (CDN Isotopes, purity 99.3%) was purchased from Cluzeau (Courbevoie, France). 3,6,3-Nonylphenol diethoxylate-D2 (ring-3,5-D2) (4n-NP2EO-D2) was supplied by Sigma-Aldrich (OEKANAL-Fluka®). Deuterated standards have been used to assess sediments microwave assisted extraction (MAE) and derivatization step.

Chrysene-D12 (99.9% purity) was supplied by Sigma-Aldrich (Steinheim, Germany). 2,4,6-Trichlorobiphenyl (PCB 30) (CDN Isotopes, purity 96.5%) was supplied by Dr Ehrenstorfer GmbH (Augsburg, Germany). These surrogate standards have been used to assess chromatography analysis.

All solvents used for extraction and analysis were of pesticide quality, or HPLC ultrapure grade and were supplied by SDS, Carlo Erba. Copper granules (diameter: 0.2 and 0.6 mm) were supplied by Sigma-Aldrich (St Quentin Fallavier, France). Anhydrous sodium sulfate was dried at 110°C for 8 h prior to use. Standard mixtures were prepared in ethanol and used to spike sediments for quality control. All solutions were stored in the dark at -20°C prior to use.

2.2 Sampling campaigns and sampling sites

Three sampling campaigns were conducted at 37 sampling sites in August, October 2010 (dry period) and January 2011 (wet period). 31 sites were located in the upstream (U), transition (T) and coastal (C) zones of three rivers: El-Kebir river (EK), El-Bared river (EB) and Abou Ali river (AA) (Tab. 2). Six sites were positioned in sectors on the El-Mina coastline (M) corresponding to specific activities: one commercial harbor (CH), one fishing harbor (FH) and four sewage outfalls, numbered from 1 to 4 (SO1, SO2, SO3 and SO4) from north to south along M (Fig. 1). The three selected rivers are mainly submitted to urban and agricultural pressure. Sediments analysis were processed at Hydrosciences - Montpellier between 2010 and 2012 and reviewed at the Laboratory of Water and Environment Science - Tripoli in 2015-2016.

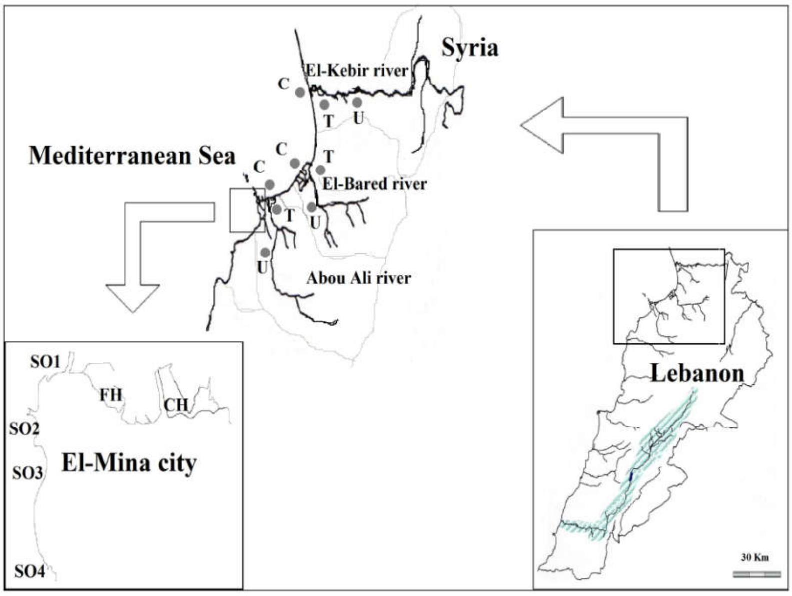

Figure 1. U, T, C refer respectively to the upstream, transition and coastal zones along the three rivers. CH, FH, SO refer respectively to the commercial harbor, the fishing harbor and four sewage outfalls along El Mina city coastline.

2.3 Sediment collection and treatment

Sediment (500 g, 0-20 cm depth) was collected, in accordance with EPA methods (2001) [44], with a stainless steel grab sampler. After collection, sediments were homogenized, air dried in the darkness at the laboratory for 8 to 21 days depending on the sample humidity and under temperature not exceeding 25 ± 2°C, than sieved and the fraction below 2 mm was collected in aluminum boxes, frozen and then freeze-dried to inhibit biological activity, and then stored until analysis in amber glass containers in a clean, cool, dark environment protected from recontamination.

2.4 Extraction, purification and derivatization

5 ± 0.1 g of homogenated samples were extracted via microwave-assisted extraction in a Multiwave 3000 (Anton Paar) with 30 mL of an acetone/heptane mixture (1:1, v:v) after addition of the deuterated standard. The extraction temperature was increased to 115°C within 15 min. After extraction, the liner was rinsed with three portions of 5 mL acetone/heptane mixture. In the extract, 1-2 g of activated copper granules were added for 1-2 h to remove sulfur. Copper granules were activated by the Standard Operating Procedure N° 5-192-05 [45] and the EPA method 3660B [46]. Extracts were then filtered (0.2

µm GF-C) through 10 g of anhydrous sodium sulphate, rotary evaporated to dryness and redissolved in 1.0 mL of heptane for chemical analysis. The presence of investigated compounds in sediment was confirmed by extraction an analysis of duplicates. Prior to the analysis by GC-MS, both standard solutions and sediment extracts were derivatized in a reaction vial by adding N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA). The derivatization process was performed by adding 200 µL of 4-(3,6-Dimethyl-3-heptyl)-phenol-3,5-d2 diethoxylate, used as internal standard, to 200µL of the purified sediment extract. Aliquot of 100 µL of BSTFA was added into the reaction vial that was sealed and kept at 70ºC for 30 min. An aliquot of 1 µL of the derived resultant was injected twice for GC-MS determinations with selected ion monitoring mode (SIM).

2.5 GC-MS analysis

Analysis was carried out on a GC Ultra trace 3000 (Thermo) connected to an ion trap mass spectrometer (MSn) detector Polaris Q (Thermo). An SGE-BPX5 capillary column (30 m, 0.25 mm I/D, 0.25 µm film thickness) was used. 1 µL was injected with an autosampler (AI 3000) in splitless mode at 250°C. Helium was used as carrier gas at a flow rate of 1.7 mL min^{-1}. The GC temperature program was as follows: 80°C, 0.5 min isothermal, 20°C min^{-1} to 160°C, then at 7°C min^{-1} to 270°C, finally at 20°C min^{-1} to 300°C, followed by an isothermal hold of 5 min. The ion trap source and the GC-MS interface temperatures were set at 220°C and 300°C respectively. Data were acquired in the selected ion monitoring (SIM) for internal standards and the investigated APs and APEO. The quantification ion peaks (m/z) and retention times are listed in Table 1. Peak detection and integration were carried out using Xcalibur software (Thermo). Positive identification of each target compound was based on acceptance criteria of its retention time as well as relative intensities of quantification and confirmation ions.

2.6 Quantification and quality control

Spiked samples were analyzed as described above together with a blank sample. A procedural blank was performed with every set of six samples and blank value was subtracted from sample concentration. The linearity (n=7) of the analytical procedure was verified by spiking samples with the investigated APs and APEO over a concentration range of 1 to 50 ng g^{-1} d.w. The concentration of the investigated analytes in the samples was calculated by rationing the analyte integrated peak area with those of the internal standards and was expressed as nanograms per gram on a sediment dry weight basis. Since there are no reference sediments for the analysis of APs and APEO, recovery studies were conducted with sediments spiked with known amounts of the analytes (six replicates of three concentrations: 5, 25 and 50 ng g^{-1} d.w.). The average recoveries, assessed by subtraction concentration observed in non-spiked samples from those spiked, ranged from 92 to 113%. The recoveries of surrogate standards, PCB30 and Chrysene-D12, ranged between 98 and 102% in this study. Surrogate recoveries of 4n-NP-D4 and 4n-NP2EO-D2 ranged between 95% and 107%. The accuracy, calculated as the percent deviation of the mean observed concentrations from the nominal concentration, was under 14%. The precision was evaluated by analyzing spiked samples (three replicates) during three different days. The relative standard deviation (RSD) values obtained were under 13%. The limits of detection (LOD) and the limits of quantification (LOQ) were determined as the concentrations which would give three and ten times, respectively, the standard deviation of the peak area for six replicates of the blank sample. LOD and LOQ were respectively 1.0 and 4.0 ng g^{-1} d.w. for NPm, 4n-NP and 4-t-OP, and 1.5 and 5.0 ng g^{-1} d.w. for NP1EO and NP2EO, and 2.0 and 6.0 ng g^{-1} d.w. for OP1EO and OP2EO.

2.7 Statistical analysis

The software package SPSS (Statistical Package for Social Sciences) version 19.0 was employed for statistical analysis. Assumption tests of normality and equal variance were performed before ANOVA. The Kolmogorov–Smirnov test and Levine's test were applied to test normal distribution and homogeneity of variance, respectively. An adjustment or transformation stage was necessary if the variable distribution was not normal. One-way analysis of variance (ANOVA) followed by Tukey's HSD and Fisher's LSD multiple comparison tests (MCT) were applied, respectively, to assemble sites based on their salinity into homogeneous subsets or zones (C, T and U). A one-way ANOVA test was used to investigate differences between a specific sample variable (APs or APEO concentration) from one sampling period to another (August–October and January) and from one sampling zone to another (C, T and U) for the three rivers (AA, EB and EK) and (M).

RESULTS

Chemical analysis of APs and APEO showed total concentrations ranging between 346.7 and 3055.1 ng g^{-1} d.w. (Fig. 2). Relative standard variation between the three sampling campaigns was under 13% for every measured compound indicating no temporal variation for APs and APEO in our sediments. As expected nonylphenolic (NPm, 4n-NP, NP1EO, NP2EO) compounds shared 68 to 82% of the total alkyphenolic compounds (Fig. 3A, B). The highest concentrations were observed in Abou Ali river (AA) followed by El-Kebir river (EK), and finally El-Bared river (EB) for the three sampling campaigns. Multiple comparison tests applied to the three rivers proved that they were impacted by APs at different extent. Indeed, AA had the highest APs concentrations (145.0-2022.1 ng g^{-1} d.w.), followed by EK (114.0-593.4 ng g^{-1} d.w.), and finally EB (17.5-290.4 ng g^{-1} d.w.). In that concern APEO, the difference between the three rivers involves both concentrations and patterns: AA (<2.0-1033.0 ng g^{-1} d.w.) and EK (312.2-926.3 ng g^{-1} d.w.) had similar concentrations except in coastal sites while EB showed the lowest concentrations (285.0-551.5 ng g^{-1} d.w.).

Three zones were characterized in each river; the upstream (U), transition (T) and coastal (C) zones that had salinities of 0.08, 0.26 and 32 g L^{-1}, respectively. Dissolved oxygen (DO) did not differentiate the zones, but exhibited hypoxia in T zone (1.6 ± 0.2 mg L^{-1}) during the dry season in Abou Ali river (Tab. 2). Average water temperature did not differentiate the three rivers, and varied between 16 ± 5 ºC (January – wet period) and 29.5 ± 2.5 ºC (August – dry period). A common pattern was established in the three watersheds for APs and APEO. Their concentrations showed a significant spatial variation following a decreasing order between T, U and C. This gradient was observed for the three sampling campaigns for both nonylphenolic (NPm, 4n-NP, NP1EO, NP2EO) and octylphenolic compounds (4-t-OP, OP1EO, OP2EO).

The distribution among the investigated nonylphenolic compounds needs a site-dependent analysis. For Abou Ali river, the proportion of ethoxylates (NP1EO and NP2EO) decreases from 70-75% in U zone to 25-35% in T zone, and almost disappear (0-10%) in C zone. For El-Kebir river, the proportion of ethoxylates (NP1EO and NP2EO) was between 53 and 68% and the highest proportion was found in C zone, which contrast with results observed in AA. For El-Bared river, the proportion of ethoxylates (NP1EO and NP2EO) was between 58 and 90% and the highest proportion was found in C zone, which match with results observed in EK and clearly contrast with AA results. In El-Bared and El-Kebir rivers NP2EO were always at higher concentrations than NP1EO, while in Abou Ali river NP1EO were always at higher concentrations than NP2EO (Fig. 4A).

The distribution among the investigated octylphenolic compounds approached by a site-dependent analysis showed similar pattern than nonylphenolic compounds (Fig. 4B). Along the El-Mina coastline, the APs and APEO were detected in all sediments at the same levels for the three sampling campaigns, with no significant temporal trend. The highest concentrations were measured in the commercial harbor (CH) (697.5 ± 58.2 and 599.0 ± 53.2 ng g^{-1} d.w. for APs and APEO, respectively) in comparison to the fishing harbor (FH) (269.0 ± 44.8 and 304.5 ± 44.0 ng g^{-1} d.w. for APs and APEO, respectively) and the sewage outfalls (SO) (101.6 ±16.7 and 246.0 ± 36.0 ng g^{-1} d.w. for APs and APEO, respectively). SO concentrations were in the same range as those observed in C zones. In all the investigated sites along El-Mina coastline diethoxylated forms for NPs and OPs were higher than monoethoxylated forms as was observed in El-Bared and El-Kebir C zones (Fig. 5).

Table 1. Physicochemical properties and analytical parameters used for quantification of APs and APEO in GC-MS SIM mode.

Compound (AP/APEO)	Molecular weight (g mol^{-1})	log Kow[1]	Target ions (m/z)[2]	Retention time (min)
Nonylphenol-Mix (NPm)	220		179+193+207+221 (Σ8 pics)	7.56-11.42
4-n-Nonylphenol (4n-NP)	220	4.48	179	11.87
4-tert-Octylphenol (4-t-OP)	206	4.12	207+208	8.57
Nonylphenol monoethoxylate (NP1EO)	264	4.20	251+265	13.24-14.78
Nonylphenol diethoxylates (NP2EO)	308.5	4.20	295+308+309 (Σ8 pics)	17.07-19.48
Octylphenol monoethoxylate (OP1EO)	250	4.10	251.5+252	12.48
Octylphenol diethoxylates (OP2EO)	294	4.00	295+296	16.03
Deuterated 4n-Nonylphenol (4n-NP-D4)[3]	225		179	7.94
Deuterated Nonylphenol diethoxylates (4n-NP2EO-D2)[c]	310.5		295	17.14

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[1] Ahel and Giger, 1993 [58].

[2] Underlined target ions employed for quantification.

[3] Internal Standards.

Table 2. Type of zone sampled, specific codes, detailed description of each sampled site, with river's length and flow rate, dissolved oxygen concentration and sediments granulometry.

River	Zone / Type	Code	Characteristics	Length (km)	Flow rate ($m^3\ s^{-1}$)[4]	Dissolved Oxygen ($mg\ l^{-1}$) Min-Max[5]	% Granulometric fraction 63-250 µm
El-Kebir	Upstream /river waters	U	Urban, agricultural and industrial/ Lebanese -Syrian boundaries	56	1.0-14.0	4.5-9.2	69-85
	Transition zone / river mouth – estuary	T	River mouth/ wastewater discharges - wild solid waste dumping			2.0-4.4	70-82
	Coastal zone / seawaters	C	Urban, fishing area			8.0-10.5	71-79
El-Bared	Upstream / river waters	U	Urban, agricultural	31.5	1.9-14.0	3.0-7.2	75-80
	Transition zone / river mouth – estuary	T	Urban, agricultural - Palestinian refugees camp			2.0-4.4	71-78
	Coastal zone / seawaters	C	Urban, wastewater discharges			7.6-9.5	72-78
Abou Ali	Upstream / river waters	U	Urban, agricultural and industrial	40	0.9-30.3	3.5-7.3	68-78
	Transition zone / river mouth – estuary	T	River mouth/wild solid waste dump site-leachate run-off - storm wastewater discharges			1.2-5.0	70-85
	Coastal zone / seawaters	C	Urban, wastewater discharges - commercial harbor			4.5-5.5	71-85
El-Mina	Commercial harbor	CH	Commercial			6.3-11.5	79-80
	Fishing harbor	FH	Fishing, touristic			6.0-11.0	78-80
	Sewage outfalls / seawaters	SO	Storm sewage discharges sites			5.6-10.0	75-80

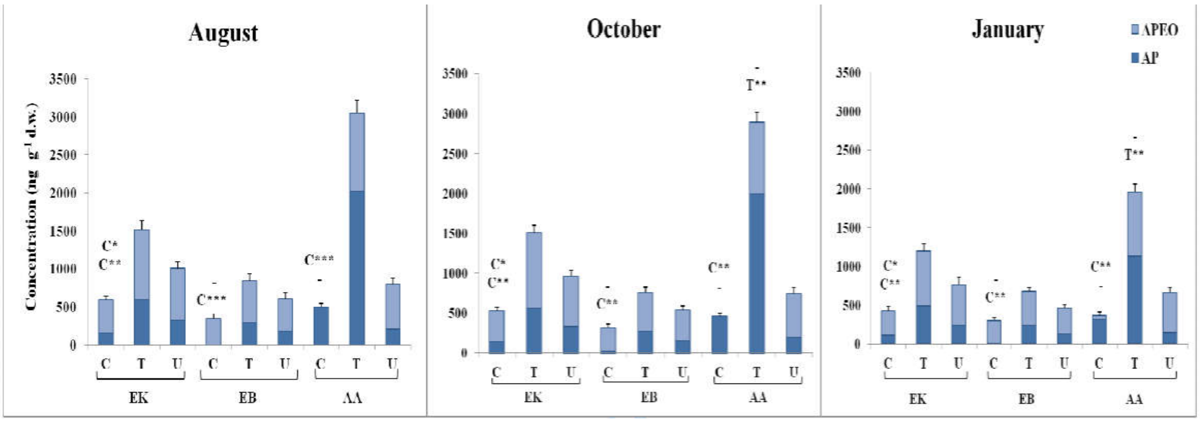

Figure 2. AP and APEO concentrations in surface sediments from EK, EB and AA rivers of north Lebanon for the three sampling campaigns. C, T and U refer to the coastal, transition and upstream zones, respectively. The P-values indicate significant difference (Post Hoc test – Fisher LSD) between mean values of the studied variable from one sampling zone to the two remaining zones at the 95.0% confidence level. P < 0.05 *, P < 0.01 **, P < 0.001***. The letters from above and below correspond to APEO and AP, respectively.

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[4] Flow rate values measured in august and January.

[5] Minimum (Min) and Maximum (Max) values for Dissolved Oxygen (DO) measured between august 2010 and January 2016.

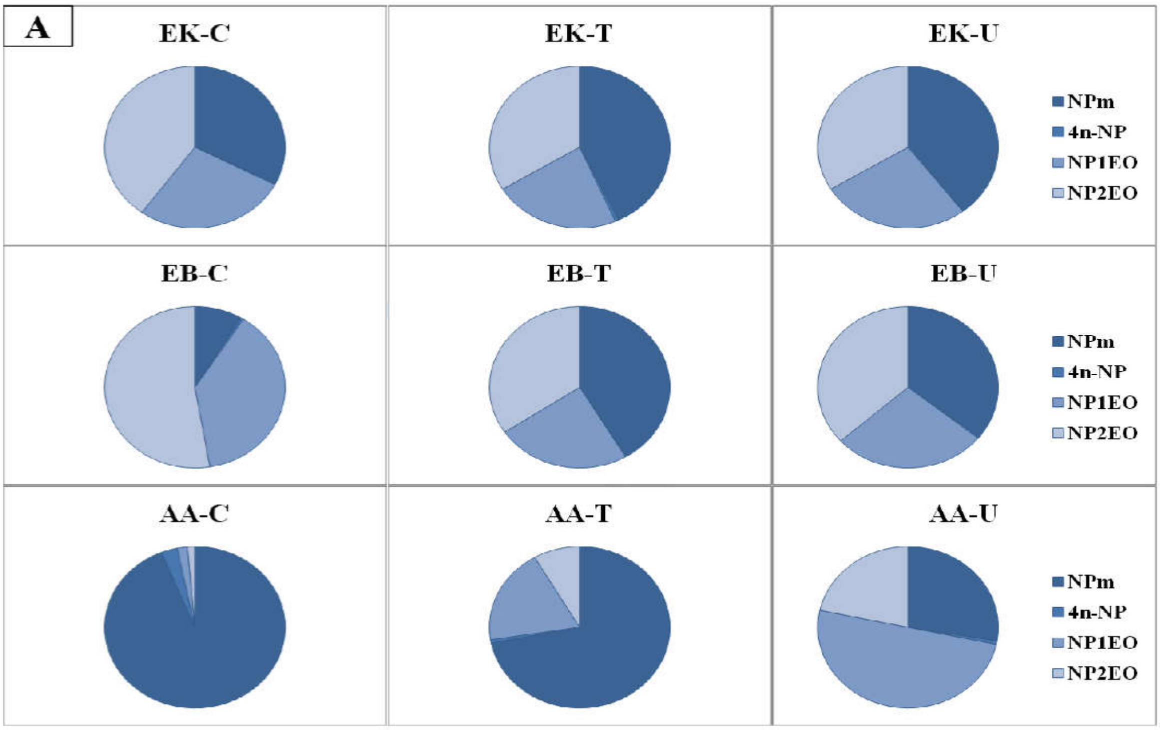

Figure 3. (A).

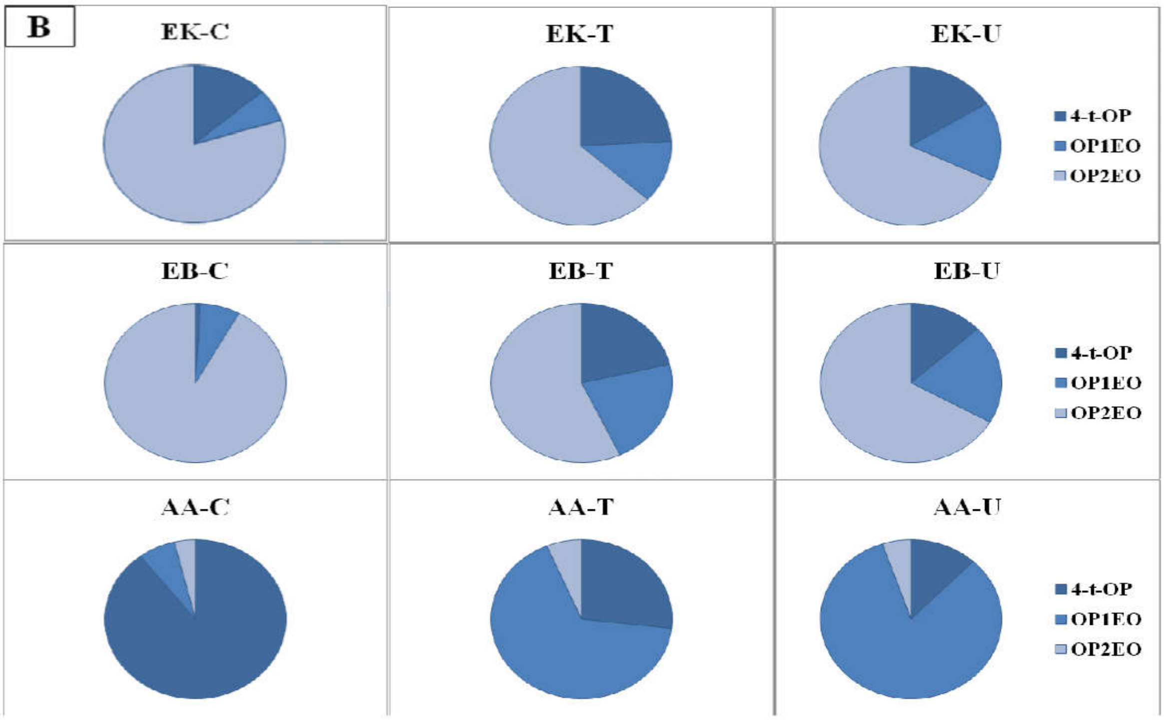

Figure 3. (B).

Figure 3. (A) nonylphenolic compounds (NPm, 4n-NP, NP1EO, NP2EO) and (B) octylphenolic compounds (4-t-OP, OP1EO, OP2EO) average percentages (for the three sampling campaigns) in surface sediments from EK, EB and AA rivers of the north Lebanon for the three sampling campaigns. C, T and U refer to the coastal, transition and upstream zones, respectively.

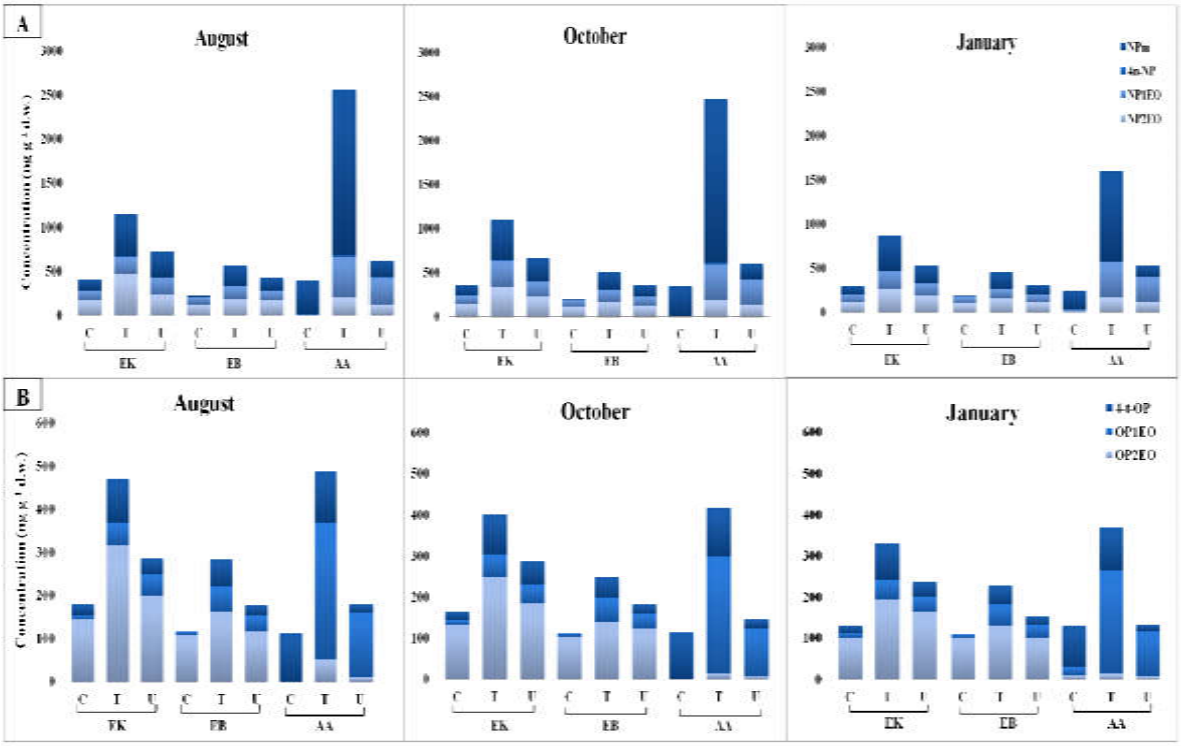

Figure 4. (A) nonylphenolic compounds (NPm, 4n-NP, NP1EO, NP2EO) and (B) octylphenolic compounds (4-t-OP, OP1EO, OP2EO) concentrations in surface sediments from EK, EB and AA rivers of north Lebanon for the three sampling campaigns. C, T and U refer to the coastal, transition and upstream zones, respectively.

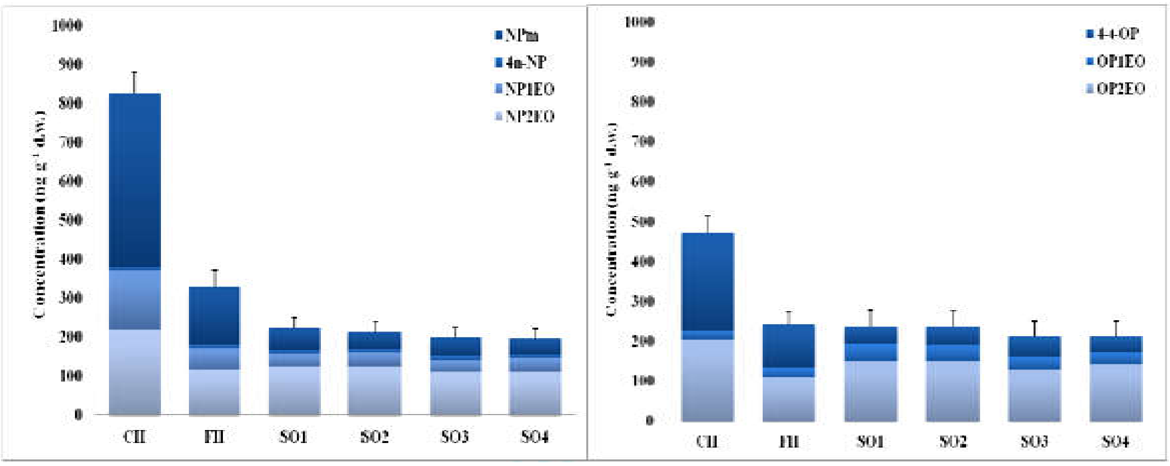

Figure 5. Nonylphenolic compounds (NPm, 4n-NP, NP1EO, NP2EO) and octylphenolic compounds (4-t-OP, OP1EO, OP2EO) average concentrations (for the three sampling campaigns) in surface sediments from the El-Mina coastal city. CH, FH and SO refer to the commercial harbor, the fishing harbor and the sewage outfalls, respectively.

DISCUSSION

In industrial countries, the APEO and APs concentrations observed in recent years in waterways tends to diminish, providing evidence of a past diffuse pollution and of a voluntary policy for use reduction in these countries; in contrast, sediment analyses conducted in developing countries show an increase in APEO content over the last several years [47]. Indeed, Chinese sediment remain being more contaminated by APs and APEO than, for example, sediment from North America and Europe because it resulted from a much longer exposure period due to the past use history of these compounds. Our results showed that a gradient of contamination exist also within the Mediterranean. In the present study, overall, concentrations of the investigated nonylphenolic and octylphenolic compounds at the investigated sites receiving untreated effluents for decades were the highest detected levels around the Mediterranean basin. Indeed, David et al. (2010) [41] reported NPm levels between 4 and 660 ng g^{-1} d.w. in sediment from three French coastal lagoons, while 4-t-OP was below quantification limits (< 4.0 ng g^{-1} d.w.).

Environmental concentrations of APs reported by David *et al*. (2010) [41] were not comparable to ranges measured in the investigated sites where sewage effluent discharges represent the dominant source of entry into rivers estuaries and coastal area of northern Lebanon. Mediterranean rivers have strong seasonal regime and scarce flow [48]. Lebanese studied rivers receiving untreated sewage, urban discharges and agricultural run-off, become a large sink converging continuous inputs of organic pollutants into the sea.

Arditsoglou and Voutsa (2008) [40] reported concentrations in marine sediments from Greece reaching 266 and 137 ng g^{-1} d.w for APs and APEO, respectively, which were also under levels detected in the present study (346.7-3055.1 ng g^{-1} d.w.). Our sediments constitute a trapping compartment where concentrations could reach high levels, especially around untreated wastewater discharge sites; mainly in transition zones. This fact could be related to the most important use of these substances in West Mediterranean combined with rivers torrential flow regime, dissolved oxygen concentration and granulometric sediments composition.

As expected nonylphenolic (NPm, 4n-NP, NP1EO, NP2EO) compounds were the most predominant compounds, accounting for > 80% of the total alkyphenolic compounds. The most predominant compounds were NPm accouting for > 40 % of the total nonylphenolic compounds. Highest levels of NPm, however, were observed in coastal zones revealing the importance of biodegradation and direct sources in rivers transitional areas, especially in Abou Ali. Among the analyzed octylphenolic (4-t-OP, OP1EO, OP2EO) compounds, OP2EO accounted for > 75 % in El-Kebir and El-Bared rivers for the dry and wet periods. While, in Abou Ali river, the most predominant compounds were OP1EO and 4-t-OP.

The highest concentrations were observed in Abou Ali river (AA), with a predominance of APs and monoethoxylated forms along the coastal zone, followed by El-Kebir river (EK), and finally El-Bared river (EB), where diethoxylated forms were the major compounds, for the three sampling campaigns.

Considering the results provided in the present study and those available in the literature points out that any comparison on APs and APEO occurrences in different sites should be made taking into account the climate and seasonal river's regime, the anthropogenic activities and discharges types, and the sediments type. In this study compared to later, a river input was identified as the main source of APs and APEO to coastal seawater, although run-off and direct discharge of untreated urban and agricultural waters cannot be neglected.

We also observed, as expected, that contamination was lower in coastal sediments than in terrestrial sediments, underlining terrestrial impact *via* river input as contamination source in coastal environment. Such evidence has been shown for NPs and OPs [39, 41], where a gradient was noted between river mouth and coastal samples subjected to continental pressure and deep sea samples. The reverse scenario was described by Sanchez-avila et al. (2012) [48]. They revealed that river waters and continuous input of treated and untreated effluents discharging to the North West Mediterranean Sea in the Catalan coast, a highly urbanized region with important industrial and agricultural activities, are the main sources of organic micropollutants including APs as one of the main contributors, to coastal waters. The highest concentrations were measured in port water, followed by coastal and river mouth sea waters. The Catalan coast is characterized by the settlement of intensive industry in special chemical and petrochemical facilities and also receives run-off from agricultural activities and urban treated or untreated discharges contributing to coastal contamination through direct or indirect discharges [48]. Patterns and sources of contamination are clearly different than the three eastern Mediterranean studied rivers.

An APs/APEO sorption/desorption phenomena depending on site physico-chemistry and hydraulic regime changes of rivers may also explain the decrease in marine sediments concentrations. These facts were described respectively by Xu *et al*. [49] for BPA and by Mao *et al.* [50] for APs and APEO. Indeed, sediments became a long-term pollutant-releasing sink for APs and APEO but as APs and APEO are surfactants, their sorption/desorption equilibrium depends on water salinity.

According to Li *et al*. (2004) [51], Mao *et al*. (2012) [50] and Xu *et al*. (2006) [52], APs concentrations were higher in warmer seasons than in colder ones due to an increase in microbial activity at warmer temperatures leading to an enhanced degradation of APEO. In our studied rivers, no temporal variation between dry and wet seasons was observed. Similar concentrations were measured in surface sediments during the dry season (August and October), with a slight decrease in the wet season (January). Thus, it could be suggested that seasonal variations in precipitation, surface runoff and groundwater flow, and biological activity have less influence on the level of APEO and APs in the Mediterranean sediment than the continuous spills related to the various uses of these compounds. Among the studied nonylphenolic and octylphenolic compounds, diethoxylated forms were more concentrated than monoethoxylated ones in El-Kebir and El-Bared rivers, while the reversed scenario was noted for Abou Ali river. This could be attributed to biodegradation or photodegradation of these molecules under anoxic conditions especially in Abou Ali transition zone exhibiting hypoxia during the dry period (Tab. 2). The highest concentration observed for NPm in Abou Ali transition zone, which is known to be recalcitrant, was probably the result of active biodegradation in this zone.

Behavior and fate are strongly influenced by the degradation and sorption of these substances following their release into the environment. APs and APEO often occur in different environmental media simultaneously. Understanding their fate in rivers and coastal environment is an environmental priority not only because of its demonstrated endocrine-disrupting properties but also because of their bioaccumulation potential, widespread occurrence, and apparent persistence in wastewater-impacted rivers [53, 16].

Concern has increased recently about the wide use of APEO because of their relatively stable biodegradation products nonylphenols (NPs) and octylphenols (OPs) [54]. The main source of APs and APEO in sediment appears to be closely related with the discharge of untreated effluents in urban areas and other related anthropogenic activities such as storm water discharges and run-off [23, 55, 56, 57].

The presence of APs and APEO in the rivers is related principally to the direct urban discharges and agricultural run-off in addition to re-suspension of contaminated sediments.

Regarding the three studied rivers, Abou Ali was the main contributor to the coastal pollution due to its much higher flow compared to El-Bared and El-Kebir flows (Tab. 2). Indeed, Tripoli solid waste dumping site at the Abou Ali estuary enhance the leaching of organic micropollutants including surfactants at the river mouth and coastal area.

NPs, OPs and their derivatives had been classified within the European Water Framework Directive's list of priority hazardous substances (2013/39/EU) and Environmental Quality Standards (EQS) were defined in the regulatory context of this Directive. EQS for aquatic organisms are 0.33 µg L^{-1} and 0.0122 µg L^{-1} for NPs and OPs, respectively and 180 ng g^{-1} in sediment for benthic organisms. In our studied sites, several analyzed spots showed higher values compared to these EQS, which leads to the conclusion of an ecological risk.

Data are scarce for river transition and coastal zones in developing countries. In these countries, coastal contamination could be attributed to the pressure of anthropogenic activity (urbanization, agriculture and industrial production) and the lack of wastewater treatment facilities. The eastern Mediterranean coastline is becoming increasingly urbanized, with the concomitant threat of pollution from inland activities discharging their wastes (often untreated) via streams, rivers or directly into the sea. The results obtained in the present study claimed the need of voluntary policy in the eastern Mediterranean for an efficient reduction in use of APEO and APs.

CONCLUSIONS

This study revealed the ubiquity and high point source APs and APEO contamination in eastern Mediterranean transition and coastal zones. A spatial trend was also highlighted in sediment, with higher APs and APEO concentrations in the rivers transition zones.

Environmental transformation in these zones with high pollution levels and intense photo/biodegradation rates, in addition to high temperatures and a salinity gradient, worth to be studied.

As expected nonylphenolic (NPm, 4n-NP, NP1EO, NP2EO) compounds were the most predominant compounds, accounting for > 80% of the total alkyphenolic compounds. Among the analyzed octylphenolic (4-t-OP, OP1EO, OP2EO) compounds, OP2EO are clearly predominant and accounted for > 75 % in El-Kebir and El-Bared rivers for the dry and wet periods. While, in Abou Ali river, the most predominant compounds were OP1EO and 4-t-OP. The highest concentrations were observed in Abou Ali river (AA) followed by El-Kebir river (EK), and finally El-Bared river (EB) for the three sampling campaigns.

The distribution and characteristics of pollution sources along the river affected the spatial variation of APs and APEO. There was a direct relationship between concentrations of these compounds and the presence of mainly urban (mainly untreated wastewater) or industrial (harbors) activities near the sampling point.

High APs and APEO concentrations related to continuous wastewater discharges at the studied rivers and coastal sites made the sediments a long-term pollutant-releasing sink and reservoir. In these sites, the effects of changing conditions on sorption/desorption and biodegradation processes of APs and APEO are essential for acceptable prediction of the fate of these pollutants and the ecological effects of polluted sediments.

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NONSTANDARD ABBREVIATIONS

APEO: Alkylphenol polyethoxylates, APs: Alkylphenols, NPs: Nonylphenols, NPm : Nonylphenol mix-a mixture of nonylphenol isomers with different branches for the alkyl chains (linear n-alkyl chains, or complex branched chains), 4n-NP: 4 n-Nonylphenol, OPs: Octylphenols, 4-t-OP: 4-tert-Octylphenol, NP1-2EO : Nonylphenol mono- and di-ethoxylates, OP1-2EO : Octylphenol mono- and diethoxylates.

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