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Non-target screening of organic contaminants in marine salts by gas chromatography coupled to high-resolution time-of-flight mass spectrometry

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ABSTRACT

Gas chromatography coupled to time-of-flight mass spectrometry (GC–TOF MS) has been applied to characterize the organic pollution pattern of marine salt samples collected in saltworks from the Spanish Mediterranean coast. After dissolving the samples in water, a solid-phase extraction was applied reaching with a 250-preconcentration factor. The screening methodology allowed the detection of sample components without any kind of pre-selection of target pollutants. The identity of components detected was established by accurate mass measurements and comparison of experimental full-acquisition spectra with theoretical MS libraries. Several organic pollutants were identified in the samples, like plasticizers – potentially toxic to humans – and fragrances –included within the group of pharmaceuticals and personal care products-, among others. Our results indicate that these contaminants can be found in the marine salt after the crystallization process. GC–TOF MS is a powerful technique for wide-scope screening of (semi)volatile, low-polar organic contaminants, able to investigate the presence of a large number of compounds. Searching of contaminants is not restricted to a target list of compounds. Therefore, unexpected contaminants can be discovered in an efficient way, with better sensitivity and selectivity than other conventional analytical techniques, and making use of the powerful qualitative information provided by full-spectrum acquisition at accurate mass.

1. Introduction

Marine salt is obtained by evaporation of sea water due to the combined effect of wind blow and sunlight heat in the solar saltworks. Saltpans are located near the sea, becoming peculiar environments inhabited by wildlife species associated with high salinity conditions. Concern has arisen as consequence of the vulnerability of these environments to anthropogenic pollution. Run-off from farms and industries may contain high concentrations of pesticides and industrial sub-products and reach these vulnerable coastal locations, with a deleterious impact on the briny aquatic systems [1]. This fact can also affect to the quality of the marine salt produced. Several authors have reported the presence of contaminants in coastal sea and saline waters, such as pesticides [2], halocarbons, aliphatic and aromatic hydrocarbons and ketones [3]. Badoil and Benanou [4] have detected phenols, phosphates and other volatile and semi-volatile compounds in waste landfill leachates, which reach coastal waters.

Contaminants produced by anthropogenic activities are transported by rivers and water flows from wastewater treatment plants and are frequently deposited on coastal locations like salt marshes or river estuaries and deltas. Several authors have detected a variety of contaminants in these vulnerable areas [5,6]. The marine salts obtained from saltpans can contain the contaminants present in sea water, provided that they remain after the concentration and crystallization processes. As a consequence, monitoring the presence of organic contaminants in marine salts seems necessary to have a realistic knowledge of their quality, since they are widely used for feeding purposes in human and animal nutrition and also for aquaculture activities, such as the arthemia growth. Bath salts could also constitute possible routes of human exposure to the potentially toxic compounds found in the sea salts.

Hyphenation of gas chromatography (GC) with mass spectrometry (MS) is the most widely used and accepted technique for determination of volatile and semivolatile compounds of low-medium polarity in aquatic ecosystems, particularly in surface coastal water and marine environments. Different MS analyzers have been applied for this purpose, from single quadrupole to ion-trap or triple quadrupole, although the two later allow working under tandem MS mode [2,3,7,8]. Recently, Silva et al. [3] reported a methodology based on head space solid phase microextraction and GC–quadrupole mass spectrometry for the analysis of volatile

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compounds in marine salt, able to detect 40 volatile compounds belonging to different chemical groups.

The wide majority of methods reported until now in the environmental field are focused on a limited list of target contaminants. Even in the case that target pollutants investigated belong to priority lists, target methods do not allow the wide-scope screening required to investigate a large number of compounds that might be present in the samples. In most target methods, other non-selected contaminants would not be detected due to the specific-analyte information acquired. Although conventional MS analyzers can also work under scan mode, their capability to detect organic contaminants at low levels in complex-matrix samples is rather limited due to their low sensitivity and selectivity and their nominal mass measurements.

The recent emergence of modern high-resolution time-of-flight (TOF) analyzers opens new perspectives to develop wide-scope screening methodologies. GC–TOF MS offers interesting features for this purpose, as it combines high full-spectrum sensitivity and elevated mass resolution making feasible the accurate mass measurements of the molecular and/or fragments ions of any GC-amenable compound present in the sample. This technique allows searching organic contaminants in a post-target (i.e. searching for selected compounds after MS acquisition) and also in a non-target way (i.e. searching for unknowns, without any kind of compound pre-selection) [9]. GC–TOF MS has been successfully applied for screening, identification and elucidation of organic pollutants in environmental water and biological samples [9,10], and also for confirmation of pollutants in highly complex matrix like wastewater [11].

The limited dynamic range of GC–TOF MS instruments reduces their potential for quantitative analysis. For this reason, in the present study, GC–TOF MS has been used for qualitative purposes because of its high sensitivity in full spectrum acquisition complemented with mass accuracy.

In this work, we have applied GC–TOF MS for the rapid and wide-scope screening of organic pollutants in sea water and in marine salts obtained from solar saltworks and from a pristine sea shore salt marsh sited along the Spanish Western Mediterranean coast. The identity of the sample components detected in a non-target way was established by means of exact mass measurements and by comparison with theoretical spectral libraries. In addition, the organophosphate esters (OPEs) identified were confirmed by injecting reference standards.

2. Materials and methods

2.1. Sampling points

Marine salt samples from four solar saltworks sited in the Spanish Mediterranean shore (see Fig. 1) were collected directly from the crystallized salt stock in saltpans (samples 3 and 5) or purchased from the producers (samples 1 and 4). A seawater sample was also collected from the sea shore in front of a pristine salt marsh located in Torre la Sal, neighbouring a natural protected area (Natural Park of Ribera de Cabanes, Spain), sited close to the city of Castellon (sampling point 2). Sampling point 1 is a solar saltwork sited in the Alfaques bay, south of the Ebro River delta. This river receives domestic and industrial wastewater from numerous minor settlements along its way. Discharges into the Ebro River vary at different locations, showing an increase downstream, probably due to inputs from the tributaries or natural recharge of the stream, and finally it flows into the Mediterranean sea after crossing through the Ebro Delta [12]. Sampling point 3 is a solar saltwork located in the vicinity of an important fishing and middle trade harbour, surrounded by a highly urbanized area. Sampling points 4 and 5 are solar saltworks sited in high valuable natural areas but neighbouring important summer touristic areas. All samples were stored at −20 °C until analysis.

2.2. Reagents

HPLC-grade water was obtained from a MilliQ water purification system (Millipore Ltd., Bedford, MA, USA). Acetone, ethyl acetate, dichlorometane (DCM) and n-hexane (ultra trace quality) used in solid-phase extraction (SPE) experiments were purchased from Scharlab (Barcelona, Spain). Bond Elut cartridges C_{18} (500 mg) (Varian, Harbor City, CA, USA) were used for SPE. Triphenyl phosphate (TPhP) and 2-ethylhexyl diphenyl phosphate (EHDPP) reference standards were purchased from TCI Europe (Zwijndrecht, Belgium). Tri-n-butyl phosphate (TBP) and Tris(1-chloro-2-propyl) phosphate (TCPP) reference standards were purchased from Sigma–Aldrich (Madrid, Spain).

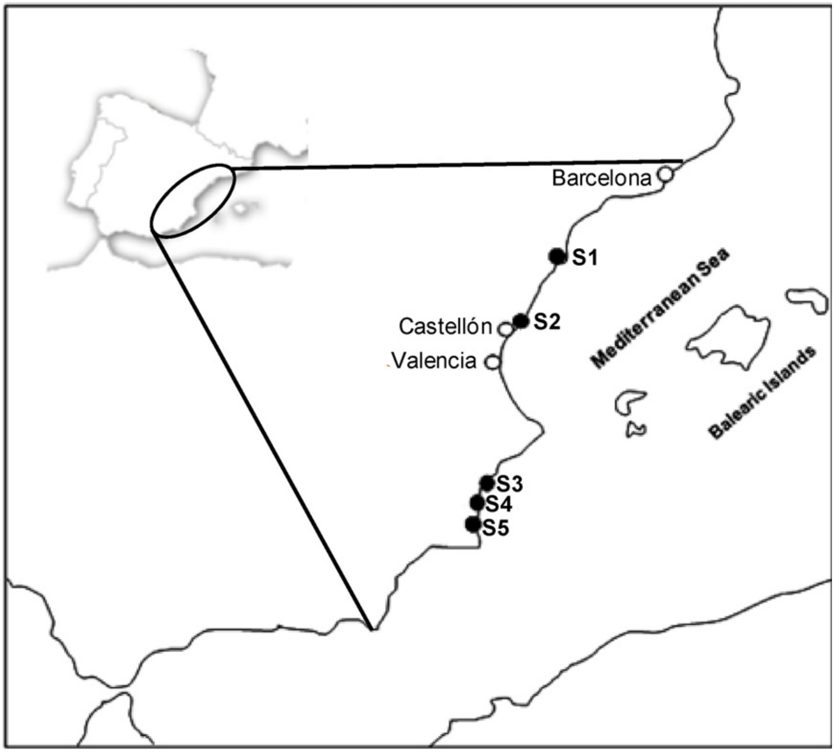
2.3. GC–TOF MS instrumentation

GC system (Agilent 6890N; Agilent, Palo Alto, USA) equipped with an autosampler (Agilent 7683) was coupled to a time-of-flight mass spectrometer (GCT, Waters Corporation, Manchester, UK), operating in electron ionization (EI). GC separation was performed using a fused silica HP-5MS capillary column with a length of 30 m, an internal diameter of 0.25 mm and a film thickness of 0.25 μm (J&W Scientific, Folson, CA, USA). The injector temperature was set to 280 °C. Splitless injections of 1 μL samples were carried out. Helium (99.999%; Carburos Metálicos, Valencia, Spain) was used as carrier gas at a flow rate of 1 mL/min. The interface and source temperature were set to 250 °C and a solvent delay of 4 min was selected.

The oven program in GC–TOF MS analysis was programmed as follows: 90 °C (1 min); 5 °C/min to 300 °C (2 min). The TOF MS operated at 1 spectrum/s, acquisition rate over the mass range m/z 50–650, using a multichannel plate voltage of 2850 V. TOF-MS resolution was approximately 7000 (FWHM). Heptacosa standard, used for the daily mass calibration and as lock mass, was injected via syringe in the reference reservoir at 30 °C for this purpose; the m/z ion monitored was 218.9856. The application manager ChromaLynx and TargetLynx was used to process the qualitative data obtained from standards and from sample analysis. Library search was performed using the NIST 02 Mass Spectral Library (www.nist.gov).

2.4. Recommended analytical procedure

The recommended procedure is based on a generic sampling extraction procedure previously applied for the determination of around 50 compounds, including organochlorine and organophosphorus insecticides, herbicides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, brominated diphenyl ethers, octyl/nonyl phenols and pentachlorobenzene with some modifications [8]. Briefly, 62.5 g of salt was diluted with water to a final volume of 250 mL and filtered. The filtered solution was passed through the C_{18} SPE cartridge, previously conditioned by passing 6 mL methanol, 6 mL ethyl acetate:DCM (50:50), 6 mL methanol and 6 mL water avoiding dryness. After loading the sample (250 mL), the cartridges were washed with 3 mL water and dried by passing air under vacuum for at least 15 min. The elution was performed by passing 5 mL ethyl acetate:DCM (50:50). The extract collected was evaporated under a gentle nitrogen stream at 40 °C and redissolved in 0.25 mL of n-hexane. The overall procedure also involved a method blank to test that no contamination was introduced in the extracts along the analysis.



S1: Delta del Ebro (La Trinitat Saltworks), Tarragona
S2: Sea wáter from Torre la Sal Sea shore, Castellón
S3: Santa Pola Saltworks, Alicante
S4: Torrevieja Saltworks, Alicante
S5: San Pedro del Pinatar Saltworks, Murcia

Fig. 1. Area of study and sampling points.

2.5. GC–TOF MS methodology for non-target screening

GC–TOF MS non-target screening was carried out using the ChromaLynx Application Manager. This software was used to detect the presence of multiple components and to show its deconvoluted MS spectra to be submitted to library search routine (in our case NIST 02 library). Components are reduced to a list of possible candidates using the list factor from the mass library search (library match >700). Then, accurate mass confirmation is automatically performed. The formula from the library list is submitted to an elemental composition calculator and accurate mass measurements of (up to) 5 abundant ions are evaluated for confirmation/rejection of the finding (for more details see [9,10]).

3. Results and discussion

3.1. Method performance

The analytical methodology described was applied to the analysis of one sea water and four marine salt samples collected from different solar saltworks located along the Spanish Mediterranean coast. The sensitive and reliable qualitative analysis was favoured because of the 250-fold pre-concentration in the sample, with low sample handling as corresponds to the SPE procedures, which was combined with the advantages offered by GC–TOF MS. As shown in this paper and confirmed in our previous works [10,13], the non-target methodology applied for screening organic contaminants is able to detect and identify a large number of GC-amenable compounds belonging to different chemical families. However, a genuine non-target analysis is a laborious and time-consuming task, as a consequence of the huge amount of chromatographic peaks from the sample components and to the lack of list of compounds to be searched. Therefore, the use of advanced processing software is required to facilitate this task. This software should be able to detect relevant/abundant sample components and to confirm their identity making use of the accurate full-spectrum data provided by TOF MS. Although a part of the process can be performed (almost) in an automated way, the expertise of the analyst on MS spectra interpretation and the knowledge of the MS fragmentation rules are needed for a successful analysis [9].

3.2. Positive findings in real samples

The samples analyzed contained volatile and semi volatile compounds, including industrial sub-products, pesticides, flame retardants, plasticizers and personal care products (Table 1). This kind of contaminants has been also found in other studies related to water pollution, and they are into the environment as a consequence of anthropogenic activities [4,6,10,14–16].

Table 1 shows the contamination pattern observed in the marine salt and seawater samples studied in this work. The seawater sample collected from the sea shore at Torre la Sal (S2), considered as a protected natural area relatively free of contaminant sources, was almost free of the contaminants found in marine salt, and only two alkyl phenols and one organic acid were identified. On the contrary, the marine salt samples were more contaminated. The type of compounds detected seemed to vary according to the geographical location of the saltwork.

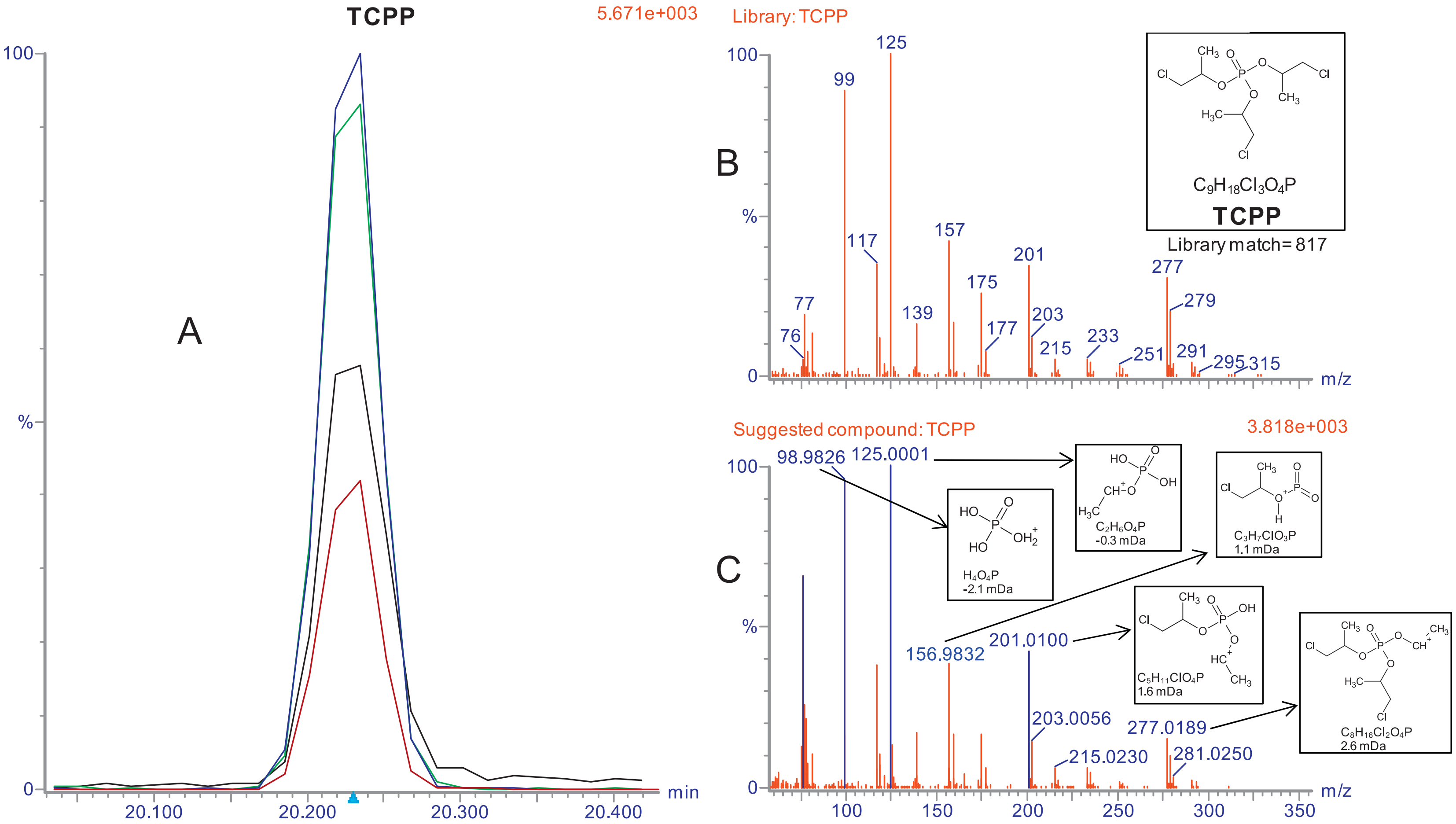


Fig. 2. Detection of TCPP in the salt sample S5 by GC-TOF MS non-target screening. (A) Extracted ion Chromatograms for five fragment ions. (B) Library mass spectrum of TCPP at nominal mass. (C) Experimental EI accurate mass spectrum of the positive finding of TCPP. Chemical structures proposed for the five most abundant EI fragment ions and mass errors.

Table 1
Compounds identified in marine salt and seawater sample.

Compound	CAS number	S1	S2(w)	S3	S4	S5	Observations[a]
1-[4-(1-Methylethenyl)phenyl]-ethanone	5359-04-6	×			×	×	Industrial sub-product
2,4-di-tert-Butylphenol	96-76-4		×	×			Toxic and dangerous for the environment, highly flammable, harmful and irritant.
2-[(Z)-3-Hydroxy-3-methyl-1-butenyl]phenol	17235-14-2		×				Industrial sub-product
2-Phenoxyethanol	122-99-6				×		Anesthesic
2-Oxohexamethylenimine (caprolactam)	105-60-2	×		×	×	×	Toxic by ingestion, inhalation, or absorption through the skin.
3,5-di-tert-Butylphenol	1138-52-9				×		Antioxidants and light-protection agents
3,6-di-tert-Butyl-4-ethylphenol	4130-42-1	×		×		×	Non-toxic
3-Methyl-benzophenone	134-84-9				×	×	UV filter. UV-curing applications
4,5,7-Trichloro-2-methyl-benzofuran	18628-11-0				×	×	Pesticide
4-tert-Amylphenol	80-46-6			×			Intermediate for organic mercury germicides pesticides and chemicals used in rubber and petroleum industries
4-tert-Octylphenol	140-66-9	×		×			Acutely very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment
Benzophenone	119-61-9	×			×		UV filter. UV-curing applications
Benzyl butyl phthalate	85-68-7					×	Plasticizer. Toxic effects such as cellular necrosis
bis(1-Chloro-2-propyl) (3-chloro-1-propyl) phosphate	137909-40-1	×		×			Pesticide, toxic and irritating
BHT	128-37-0			×	×		Synthetic antioxidant
Cyclic octaatomic sulfur	10544-50-0				×		Microbiological activity indicator[a]
di-(2-Ethylhexyl) adipate	103-23-1					×	High toxicity to aquatic organisms
Dihydroactinidiolide	17092-92-1				×		Volatile terpene (large structure hydrocarbon)
EHDPP	1241-94-7	×		×			Pesticide, toxic to aquatic organisms
Galaxolide	1222-05-5	×			×		Musk fragrance
Methyl dihydrojasmonate	24851-98-7	×	×	×			Musk fragrance
Nonanoic acid	112-05-0			×			Irritant
TBP	126-73-8	×		×	×	×	Used as a herbicide and fungicide
TCPP	13674-84-5	×		×	×	×	Pesticide, flame retardant
TPhP	115-86-6	×		×			Pesticide, plasticizer and flame retardant

S1: Delta del Ebro (La Trinitat Saltworks), Tarragona; S2(w): Sea water from Torre la Sal Sea shore, Castellón; S3: Santa Pola Saltworks, Alicante; S4: Torrevieja Saltworks, Alicante; S5: San Pedro del Pinatar Saltworks, Murcia.

[a] International Chemical Safety Cards: www.inchem.org/documents.

As an illustrative example, Table 2 shows the confirmation of identity of the compounds detected in "Santa Pola" salt sample (S3). The elemental composition could be proposed for at least four *m*/*z* fragment ions based on accurate mass measurements. In addition, the experimental accurate mass for the main ions was compared with the theoretical ones. In general, mass errors were below 3 mDa, except for a few low-abundant ions. An example of the non-target detection of TCPP in "San Pedro del Pinatar" salt sample is given in Fig. 2. Five ions were selected from the EI spectrum for the accurate mass confirmation of the identity of TCPP, with mass errors always below 2.6 mDa. In addition, the chemical structure suggested for these ions was in agreement with that of TCPP.

It is worth to notice that several of the compounds detected belong to the OPEs family. These chemicals are produced in large quantities for their use as flame retardants, plasticizers and also as pesticides. Their widespread use and presence in host materials led to a continuous discharge and distribution through wastewaters [15], and coastal areas are the fate of wastewaters from industrial and urban activities containing these and other pollutants. As a consequence of the toxicity and environmental persistence of OPEs, their presence in marine salt intended for human consumption should be under control.

Considering the interest of OPEs, reference standards of TCPP, TBP, TPhP and EHDPP were acquired in a subsequent step to perform additional experiments for confirmation. We could not find the reference standard of bis(1-chloro-2-propyl) (3-chloro-1-propyl)phosphate, which was also detected in the non-target screening. Using reference standards it was feasible to test the retention time and to obtain their TOF MS spectrum to unequivocally confirm the presence of these compounds in the samples. The experiments with reference standards allowed us to confirm all positives previously reported by TOF MS, demonstrating the excellent potential of this technique for identificative purposes, even without reference standards.

As an illustrative example, Fig. 3 shows the eXtracted Ion Chromatograms (XICs) for the positive of EHDPP detected in "La Trinitat Saltwork" salt sample (S1) which could be additionally confirmed using the reference standard. The presence of the chromatographic peaks in the XICs, at the expected retention time, and the attainment of all *Q*/*q* ratios when comparing with the reference standard allowed the confirmation of the finding in the sample. The corresponding EI accurate mass spectra generated by TOF MS are also shown. Mass errors for four representative ions were below 3.2 mDa, which gave more confidence to the confirmation process. Chemical structures for the most abundant fragment ions were suggested based on the elemental compositions proposed accordingly to the accurate mass measurements given by the instrument.

Apart from OPEs, the most abundant compounds detected were alkyl phenols. Fragrances and plasticizers were also identified in some salt samples. The presence of alkylphenols in aquatic environments has been previously reported by several authors [9,17,18]. They are degradation products from alkylphenol polyethoxylates, mainly applied to pesticide formulations and as plastic additives, among other uses [4]. The persistence and accumulation properties of alkylphenols have led to their wide distribution in different environmental compartments [19,20]. The sources of these pollutants are commonly the wastewaters from industrial and municipal treatment plants [21] and their accumulation has been observed in sediments receiving contaminated water flows [22]. The presence of these pollutants might pose a threat to the quality of the salt pro-

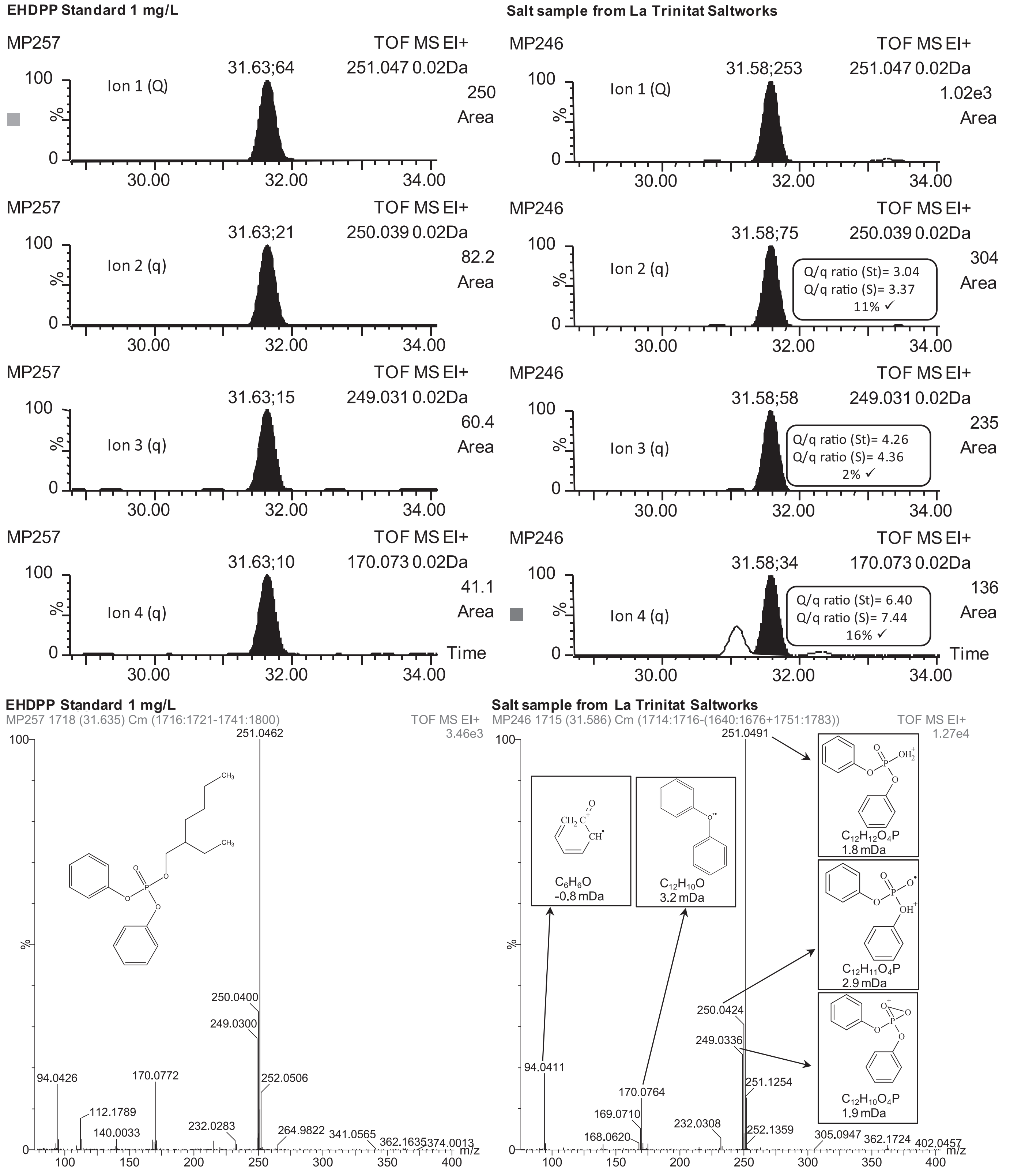


Fig. 3. GC-TOF MS extracted ion chromatograms (top) at different m/z (mass window 0.02 Da) and accurate mass spectrum (bottom) for EHDPP for the reference standard (left) and for one positive salt sample (right). Q, qualitative ion; q, confirmative ion; St, reference standard; S, sample; Q/q ratio within tolerance limits. Chemical structures proposed for the most abundant fragment ions.

duced in saltworks sited in environments like deltaic and estuarine locations receiving water flows from industrial and/or urbanized areas. In fact, most detections of alkylphenols corresponded to sampling points 1 and 3 (which accomplish these characteristics; see description in Section 2). Recently, Navarro et al. [6], making use of GC–MS with single quadrupole, have detected several of these compounds in the Ebro River sediments, in which delta the sampling point 1 is sited, as indicated above.

Table 2

Confirmation of organic compounds in S3 salt sample.

Compound	No. CAS	Molecular peak		Ion 1		Ion 2		Ion 3		Ion 4		Ion 5	
		Molecular formula	Molecular mass	Elemental composition	Experimental m/z (error in mDa)	Elemental composition	Experimental m/z (error in mDa)	Elemental composition	Experimental m/z (error in mDa)	Elemental composition	Experimental m/z (error in mDa)	Elemental composition	Experimental m/z (error in mDa)
2,4-di-tert-Butylphenol	96-76-4	$C_{14}H_{22}O$	206.1671	$C_{14}H_{22}O$	206.1660 (−1.1)	$C_{13}H_{20}O$	192.1483 (−3.1)	$C_{13}H_{19}O$	191.1443 (0.7)	$C_{11}H_{15}O$	163.1120 (−0.3)	$C_9H_{11}O$	135.0802 (−0.8)
3,6-di-tert-Butyl-4-ethylphenol	4130-42-1	$C_{16}H_{26}O$	234.1984	$C_{16}H_{26}O$	234.2013 (2.9)	$C_{15}H_{24}O$	220.1836 (0.9)	$C_{15}H_{23}O$	219.1760 (1.1)	C_6H_6	78.0442 (−2.8)		
4-tert-Octylphenol	140-66-9	$C_{14}H_{22}O$	206.1671	$C_9H_{12}O$	136.0857 (−3.1)	$C_9H_{11}O$	135.0798 (−1.2)	C_8H_7O	119.0475 (−2.2)	C_7H_7O	107.0496 (−0.1)		
4-tert-Amylphenol	80-46-6	$C_{11}H_{16}O$	164.1201	$C_{10}H_{13}O$	149.0969 (0.3)	$C_9H_{11}O$	135.0810 (0)	C_8H_9O	121.0666 (1.3)	C_7H_7O	107.0486 (−1.1)	C_6H_7O	95.0477 (−2.0)
TCPP	13674-84-5	$C_9H_{18}Cl_3O_4P$	326.0008	$C_5H_{11}O_4PCl$	201.0100 (1.6)	$C_3H_7O_3PCl$	156.9818 (−0.3)	$C_2H_6O_4P$	125.0001 (−0.3)	H_4O_4P	98.9826 (−2.1)	C_2H_5OP	76.0058 (−3.0)
TPhP	115-86-6	$C_{18}H_{15}O_4P$	326.0708	$C_{18}H_{15}O_4P$	326.0737 (2.9)	$C_{18}H_{14}O_4P$	325.0656 (2.6)	C_6H_6O	94.0458 (3.9)	C_6H_5	77.0375 (−1.6)		
TBP	126-73-8	$C_{12}H_{27}O_4P$	266.1647	$C_4H_{12}O_4P$	155.0480 (0.7)	$C_2H_6O_4P$	125.0019 (1.5)	H_4O_4P	98.9830 (−1.7)	C_4H_8	56.0567 (−5.9)	$C_8H_{20}O_4P$	211.1109 (1.0)
bis(1-Chloro-2-propyl) (3-chloro-1-propyl) phosphate	137909-40-1	$C_9H_{18}Cl_3O_4P$	326.0008	$C_3H_7ClO_3P$	156.9818 (−0.3)	$C_2H_6O_4P$	125.0003 (−0.1)	$C_2H_3Cl_2O_3P$	116.9509 (0.1)	H_4O_4P	98.9828 (−1.9)	C_2H_5OP	76.0048 (3.0)
EHDPP	1241-94-7	$C_{20}H_{27}O_4P$	362.1647	$C_{12}H_{12}O_4P$	251.0457 (−1.6)	$C_{12}H_{10}O$	170.0750 (1.8)	C_8H_{16}	112.1253 (0.1)	C_6H_6O	94.0412 (−0.7)	C_6H_5	77.0366 (−2.5)
BHT	128-37-0	$C_{15}H_{24}O$	220.1827	$C_{15}H_{24}O$	220.1861 (3.4)	$C_{14}H_{21}O$	205.1611 (1.9)	$C_{11}H_{13}O$	161.0978 (1.2)	$C_{11}H_{13}$	145.0983 (−3.4)		
2-Oxohexamethylenimine (caprolactam)	105-60-2	$C_6H_{11}NO$	113.0841	$C_6H_{11}NO$	113.0822 (−1.9)	C_4H_7NO	85.0555 (2.7)	C_5H_8O	84.0547 (−2.8)	C_2H_2NO	56.0169 (3.3)	C_2HNO	55.0116 (5.8)
Methyl dihydrojasmonate	24851-98-7	$C_{13}H_{22}O_3$	226.1569	$C_{13}H_{22}O_3$	226.1601 (3.2)	$C_8H_{12}O_3$	156.0773 (−1.3)	$C_{10}H_{17}O$	153.1274 (−0.5)	C_5H_7O	83.0504 (0.7)		
Nonanoic acid	112-05-0	$C_9H_{18}O_2$	158.1307	$C_7H_{13}O_2$	129.0920 (0.4)	$C_6H_{11}O_2$	115.0756 (−0.3)	$C_3H_5O_2$	73.0258 (−3.2)	$C_2H_4O_2$	60.0182 (−2.9)		

The presence of di-(2ethylhexyl)adipate in marine salts is also of concern. This compound is used as plasticizer for food packaging, presents high toxicity for aquatic organisms and is considered as endocrine disruptor [23], and it has been reported to be a liver carcinogen in mice [24]. Another plasticizer detected, and also considered as endocrine disruptor, was benzyl butyl phthalate. This compound has been previously reported to be present in marine sediments [25]. Butylated hydroxytoluene (BHT) was detected also in samples 3 and 4. This compound is an antioxidant widely used as food additive and in biological samples for storage before analysis, as well as in cosmetics, pharmaceuticals, jet fuels, among other uses [4], and it has been found in aquatic environments [10,26,27].

2-Oxohexamethylenimine (caprolactam) – the monomer of nylon-6 – has been identified in marine salt samples probably due to the use of ammonium sulfate (a sub product obtained during the manufacture of the polymer) in growing crops as fertilizer. Methyl dihydrojasmonate and galaxolide were other compounds detected. They are used as fragrances, and are included in the group of water contaminants called pharmaceuticals and personal care products (PPCPs), which are suspected to be an environmental problem still not well known [28]. Similarly to other organic contaminants, these compounds could be removed entirely or partly by means of adequate technologies of wastewater treatment [16]. Dihydroactinidiolide, detected in sample 4, is a volatile terpene occurring naturally in a variety of plants and insects, but it has also been prepared synthetically for its use as a fragrance [29].

Other relevant compounds detected in marine salt were benzophenone and 3-methyl-benzophenone, used as photoinitiator in UV-curing applications and as UV filter [4]; cyclic octaatomic sulfur, indicator of microbiological activity [4]; and nonanoic acid, used in the preparation of plasticizers and lacquers, and also as herbicide.

All identifications reported in this work were supported by accurate mass measurements of several EI ions (up to five in most of the cases), by the low mass errors observed in relation to their theoretical exact masses, and by the compatibility of the chemical structures proposed for these ions with the chemical structure of the compound identified.

The contamination pattern observed in the marine salt samples includes up to 25 organic compounds, with around 12 of them being present in every sample. Sources of these contaminants surely are run offs from industries, farms and urbanized areas. Our findings suggest an important presence of these pollutants into the environments around the saltpans, which is in agreements with data reported in similar areas [28,30,31]. The presence of the compounds identified in the marine salt samples indicates that they are concentrated and that they persist along the crystallization process.

4. Conclusion

Without using any previous list of compounds to be investigated, the non-target methodology applied in this work has allowed the detection and reliable identification of several relevant contaminants of anthropogenic origin, belonging to quite different chemical groups. The strong potential of GC–TOF MS for qualitative purposes comes from the full spectrum acquisition at accurate mass, with satisfactory sensitivity, provided by this instrument. Making an appropriate use of all relevant information given by this technique it has been feasible to identify many contaminants in a reliable way, even without reference standards being available, as illustrated in this work. Surely, several of the compounds detected in marine salt would not had been detected using a target approach, as although relevant they might not have been included in a target screening, which is typically focused on a limited list of priority pollutants.

In the light of the results reported, we can conclude that priority pollutants, typically subjected to strict control, constitute only part of the large chemical pollution puzzle. There is a diverse group of unregulated pollutants, including industrial sub-products, PPCPs, and an increasing concern on the risks that they pose on humans and on the environment.

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