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Occurrence of priority pollutants in WWTP's effluents and Mediterranean coastal Waters of Spain (Comunidad Valenciana)

N. Martí[a]*, D. Aguado[b], A. Bouzas[a], L. Segovia[a], A. Seco[b].

[a] Dpto. Ingeniería Química, Universidad de Valencia, Doctor Moliner 50, 46100 Burjassot, Valencia, Spain.
[b] Instituto de Ingeniería del Agua y Medio Ambiente (IIAMA), Universidad Politécnica de Valencia, Camino de Vera s/n 46022 Valencia, Spain.
*Corresponding author. Tel.:+34-963544540; fax:+34-963544898; e-mail address: nuria.marti@uv.es (N.Martí)

Abstract

A comprehensive study aimed at evaluating the occurrence, significance of concentrations and spatial distribution of priority pollutants (PPs) along the Comunidad Valenciana coastal waters (Spain) was carried out in order to fulfil the European Water Framework Directive (WFD). Additionally, PPs concentrations were also analysed in the effluent of 28 WWTPs distributed along the studied area, since these infrastructures are usually considered a significant point source of many of these toxic substances. In coastal waters 36 organic pollutants of the 71 analysed, including 26 PPs (8 of them priority hazardous substances) were detected although many of them with low frequency of occurrence. Only 13 compounds, which belong to four different classes (VOCs, organochlorinated pesticides, phthalates and tributyltin compounds (TBT)) showed a frequency of occurrence above 20% in coastal waters. Toluene was the most ubiquitous pollutant (detected in 100% of the samples) with maximum concentration of 1.6 μg/l. All analysed coastal waters showed the presence of PPs, being di(2-ethylhexyl)phthalate (DEHP) the most frequent one (detected in 57% of the samples) reaching concentrations up to 15 μg/l. In the results obtained until now, there are four compounds that exceed the established Environmental Quality Standards (EQS): octylphenol, pentachlorobenzene, DEHP and TBT exceeded the annual average concentration (EQS-AAC), and only TBT surpassed the maximum allowable concentration (EQS-MAC). Despite its prohibition, endosulfan and hexachlorocyclohexane (HCH) were detected in 9% and 30% of the samples, respectively, and their concentrations were relatively close to their EQS-AAC value (around the 70 %). The most frequent contaminants determined in coastal waters were also present in WWTP's effluents. Generally, effluents from WWTPs exhibited higher frequency of occurrence and concentration than in coastal waters, except for DEPH.

Keywords

Coastal waters; Priority pollutants (PPs); Environmental Quality Standards (EQS); Water Framework Directive (WFD); WWTP's effluents.

1. Introduction

Chemical pollution of surface waters presents a threat to the aquatic environment with effects such as acute and chronic toxicity to aquatic organisms, accumulation in the ecosystem and losses of habitats and biodiversity, as well as a threat to human health (EC, 2008). Among surface waters, sea pollution has been less studied because it shows a self-regulatory system that dilutes the contaminants when they enter the sea. However, this system is not too effective in areas such as coasts or ports where pollutants can be found at high concentrations (Gimeno et al., 2004). Urban or industrial wastewater discharges, agricultural and industrial activities, human settlements, resource use and interventions such as infrastructural development or constructions are common contributions to the pollution of marine environments (Lacorte et al., 2001; Pérez-Carrera et al., 2007; Sánchez-Ávila et al., 2010).

The Water Framework Directive 2000/60/EC (WFD) (EC, 2000) is probably the most significant European legislation introduced in the field of water in many years (Coquery et al., 2005). This policy requires further specific measures for pollution control and sets Environmental Quality Standards (EQS), which are established in the more recent Directive 2008/105/EC (EC, 2008a), for 33 priority substances and certain other pollutants (PPs). These PPs are characterised by high toxicity, high environmental persistence or/and high hydrophobicity. Some of them cause endocrine disruption effects on marine organisms and consequently, they could represent a risk to environment and human health (Belgiorno et al., 2007; Sánchez-Ávila et al., 2009). In order to achieve "good chemical status" the EQS must be achieved for the PPs in all water bodies before 2015. The list of these 33 substances or groups of substances (previously set by Decision No 2455/2001/EC (EC, 2001)) distinguishes certain of them as priority hazardous substances. According to the WFD, Member States should implement measures with the aim of progressively reducing pollution from priority substances, and ceasing or phasing out emissions, discharges and losses of priority hazardous substances. Therefore, implementation of the WFD requires monitoring and controlling PPs concentrations to ensure the protection of coastal ecosystems.

Once PP concentrations in surface waters have been determined, causes of pollution should be identified. Concerning this, WFD requires Member States to gain a

better understanding of PP entering surface waters in order to determine pollution control options. Recent studies have shown that Wastewater Treatment Plants (WWTPs) effluents are a significant point source of many of these priority pollutants (Rule et al., 2006; Belgiorno et al., 2007; Gasperi et al., 2008). Wastewaters arrives to WWTPs from industries or urban areas containing several contaminants such as alkylphenols, phthalates, phenols, polycyclic aromatic hydrocarbons (PAHs), flame retardants, among others (Sánchez-Ávila et al., 2009). Since no regulations exist regarding PP concentrations in WWTP's effluents, WWTPs are designed just to achieve the organic matter and nutrients removal required by the established Regulations (Vogelsang et al., 2006). Therefore, many of these PPs escape to conventional wastewater treatments allowing them to reach surface water streams and distribute in the environment (Tauxe-Wuersch et al., 2005). For this reason, there is an increasing interest in developing different treatment technologies to provide safe treated effluents that minimise their impact in receiving waters.

The purpose of this study is to assess the occurrence, significance of concentration and spatial distribution of PPs in the Comunidad Valenciana coastal waters (Spain) in order to fulfil WFD requirements. Additionally, PPs concentrations were also analysed in the effluents from 28 WWTPs distributed along the coast to determine a possible relation between coastal waters contamination and wastewater effluents discharges.

2. Materials and methods

2.1. Study area and sampling procedure

The study area is focused on the eastern Spanish coast, specifically in the Comunidad Valenciana region, which is an economical and industrial developed area with a population around 5 million people (around 11% of the total Spanish population).

Along the coast of the Comunidad Valenciana (470 km), 24 "water bodies" or areas were defined (Figure 1). 18 of these water bodies were classified as coastal waters whereas 6 of them were classified as heavily modified water bodies (i.e., areas affected by ports). A total of 41 sampling points were established and 4 sampling campaigns were performed from July 2008 to May 2009, with seasonal frequency (July 2008,

November 2008, February 2009 and May 2009). Thus, 160 surface waters samples were analysed.

Samples were taken at 10 cm depth in the water column behind the wave line in order to avoid that the particle resuspension from the sediment could affect its biochemical quality. Samples were placed in precleaned amber glass bottles (250 mL of volume) quickly transported to the laboratory in a portable refrigerator and stored at 4 ºC.

Treated effluents from 28 WWTPs that discharge into the studied coastal waters were sampled during 2008 (3 sampling campaigns: March, June and November). A total of 84 wastewater effluents samples were analysed. The studied WWTPs treated urban, industrial and mixed wastewaters.

2.2. Organic pollutants

Among the different families of organic pollutants the study has focused in those compounds that are regulated by European or Spanish legislation or are common in surface waters or wastewaters (Table 1). A total of 71 organic pollutants were studied, 42 of these regulated by the WFD, including phenols (n=2), volatile organic compounds (VOC, n=11), organochlorinated pesticides (n=11), bromodiphenyl ether (BDE), short chain chlorinated paraffins (SCCP), organophosphorous pesticides (n=2), herbicides (n=5), organotin compounds (tributiltin, TBT), polycyclic aromatic hydrocarbons (PAH, n=7) and di(2-ethylhexyl)phthalate (DEHP). On the other hand, the Spanish Law 42/2007 regulates 5 substances that WFD does not legislate, including 4 VOCs and 1 herbicide. Moreover, 24 metabolites and congeners of the above mentioned compounds were also studied.

2.3. Analytical methods

Several methods were developed to determine priority pollutants concentrations at the detection limits required to ensure the compliance of EQS according to Directive 2008/105/EC (EC, 2008a). For surface water samples, analyses were carried out on the total fraction (dissolved + particulate) as recommended by WFD.

Phenol compounds were analysed by gas chromatography-mass spectrometry (GC-MS). Samples were previously preconcentrated by solid-phase-microextration (SPME) for 30 minutes with a fibre coated with 85 μm thickness polyacrilate (PA), and then thermally desorbed in the chromatographic system.

VOCs were analysed by gas chromatography-flame ionization detector (GC-FID) except some of them such as dichloromethane (DCM) and trichlorobenzene isomers (TCB), that were analysed by gas chromatography-electron capture detection (GC-ECD). Samples were extracted by SPME for 45 minutes with a fibre coated with 100 μm thickness polydimethylsiloxane-divinylbenzene (PDMS-DVB), and then were thermally desorbed in the chromatographic system.

Organochlorinated pesticides and BDE compounds were analysed by GC-ECD, except pentachlorobenzene which was analysed by GC-FID such as VOCs. Samples were extracted by SPME for 45 minutes with a fibre coated with 100 μm thickness polydimethylsiloxane-divinylbenzene (PDMS-DVB), and then were thermally desorbed in the chromatographic system.

SCCP were analysed by GC-ECD. Samples were extracted by SPME for 45 minutes with a fibre coated with 100 μm thickness polydimethylsiloxane (PDMS), and then were thermally desorbed in the gas chromatography system.

Triazine herbicides were analysed following the method described by Cháfer-Pericás et al. (2006). Organophosphorous pesticides were analysed following the method described by Cháfer-Pericás et al. (2007). Phthalates were analysed following the method described by Cháfer-Pericás et al. (2008). All of them and urea herbicides were analysed by in-tube-SPME coupled with capillary liquid chromatography-diode array detection (CLC-DAD).

PAHs were analysed by in tube-SPME-capillary liquid chromatography-diode array detection and coupled with liquid chromatography-fluorimetric detection (CLC-DAD/LC-FD).

TBT were analysed by SPME coupled with GC-MS. Samples were previously derivatized with sodium tetraethyl borate (STEB) and extraction was carried out in headspace (Segovia-Martínez et al., 2009).

2.4. Statistical Analysis

Basic summary statistics, such as frequency of occurrence, minimum, maximum and median, were calculated for each pollutant in all analysed samples. Moreover, for those pollutants exceeding their Environmental Quality Standard, Box-Whisker plot of the pollutant concentration were provided to graphically display the data.

A multivariate approach Principal Component Analysis (PCA) was also used, since it is valuable for the interpretation of complex data matrices, like data-sets from environmental studies where many variables are measured in many samples. PCA explains the data variability of the correlated measured variables obtaining a reduced new set of uncorrelated variables (latent variables or scores) which are linear combinations of the original variables. Thus, PCA compress high-dimensional data into a lower-dimensional space, thus, making data more comprehensible by retaining and highlighting essential information (e.g., relationships among the variables and observations, patterns, trends,…). In mathematical terms, PCA relies upon an eigenvector decomposition of the covariance matrix of the measured variables. PCA decompose the data matrix of the measured variables **X** of size [m,n] into bilinear terms according to $\mathbf{X} = \sum_{a=1}^{A} \mathbf{t}_a \mathbf{p}_a^T + \mathbf{E}$, where $\mathbf{t}_a$ are the latent variables (scores), $\mathbf{p}_a$ the corresponding weighting vectors, **E** is the residual matrix, and *A* is the number of significant components retained. When the numerous collected data are highly correlated, it results that $A \ll n$, and therefore, using PCA, high degree of data compression is achieved. The presentation of the modelling results is graphically-oriented, thus, the essential information in the data can be interpreted from graphical displays of the latent variables (scores) and weights. Further PCA description and the detailed mathematical founding can be found elsewhere (e.g., Jackson, 2003)

SPSS version 17.0 and SIMCA-P 9.0 software (Umetrics, Umea, Sweden) was used for the statistical analysis.

3. Results and discussion

Table 2 shows the summary data for all the analysed compounds in surface waters and effluents from WWTPs, including limit of detection (LOD), frequency of occurrence (% of samples above the LOD), median concentration (only for those pollutants with frequency of occurrence exceeding 50%), minimum and maximum concentrations, and Environmental Quality Standards (EQS) for coastal waters. For calculations, if the concentration of a given pollutant was below the detection limit, it was assigned half the detection limit value for that pollutant.

3.1. Surface waters

3.1.1. General assessment of contamination

As can be observed in Table 2, of the 71 organic pollutants analysed in coastal waters (n=160), a total of 35 were never detected. These undetected compounds were 1 phenol (bisphenol A), 3 VOCs (1,2-dichloroethane, 1,1,1-trichloroethane, 1,3-dichlorobenzene), the 8 triazine herbicides, the 5 urea herbicides, the 7 organophosphorous pesticides, 1 phthalate (dimethyl phthalate), the 9 PAHs and the SCCP compounds.

Some of these non-detected substances such as some pesticides and herbicides (clorphenvinphos, trifluralin…) are restricted or banned by different regulations regarding hazardous substances in waters. Therefore, their presence in coastal water was not expected. Concerning the analysed PAHs, their no detection in waters was not surprising because due to their high hydrophobic character (K_{ow} from 4.5 to 6.8) they tend to become associated with particles (Baumard et al., 1999; Gimeno et al., 2004). For that reason, detection of these compounds in sediments or bivalves is much probable than in the dissolved phase where they normally exist at low concentrations. In fact, previous studies carried out in bivalves collected in coastal waters of Comunidad Valenciana (Martí et al., 2009) showed low levels of these organic pollutants in mussels and clams proving the existence of PAHs in the monitored area.

SCCP were not detected in this study. These compounds are also hardly soluble in water (K_{ow} from 4,4 to 8,7), showing low levels in the dissolved phase. However,

other studies have reported the presence of these compounds in river water, tap water and wastewaters samples (Castells et al., 2004).

According to the results of the monitoring campaigns carried out, the coastal waters of Comunidad Valenciana are affected only by 36 organic pollutants of the 71 analysed, including 26 PPs (8 of them priority hazardous substances) (See Table 2). However, a low frequency of occurrence (% above LOD) can be observed for many of these compounds: only 13 compounds, which belong to 4 different classes (VOCs, organochlorinated pesticides, phthalates and TBT), showed a frequency of occurrence above 20%. These results allow highlighting the most common organic pollutants found in coastal waters of Comunidad Valenciana.

Toluene was detected in all the analysed samples. Its median concentration was evaluated at 0.17 μg/l and the maximum at 1.6 μg/l. Benzene, m,p-xylene and ethylbenzene showed frequencies of occurrence above 50%, and maximum concentrations of 0.3 μg/l, 0.27 μg/l and 0.22 μg/l, respectively. The results obtained by Arambarri et al. (2004) in superficial waters of Guipúzcoa (north of Spain) show higher concentrations for benzene and toluene (9.64 μg/l and 2.44 μg/l, respectively) and slightly lower concentrations for m,p-xylene and ethylbenzene (0.16 μg/l and 0.14 μg/l, respectively). Pérez-Pavón et al. (2007) determined BTEX in Catalonian coasts and found only p-xylene in concentrations up to 2.6 μg/l.

The concentrations for these four frequent VOCs measured in each sampling campaign have been represented in Figure 2 for each water body. As can be observed all the water bodies are affected by benzene, toluene, m,p-xylene and ethylbenzene in any of the sample campaigns. A similar temporal pattern is observed for the four compounds, with higher concentrations measured in the same sampling period, February. This can be due to the low water temperature in winter that decreases VOCs volatilization to the atmosphere.

The mixture of these four VOCs, which is known as BTEX (Benzene, Toluene, Ethylbenzene and Xylene), are present in standard gasoline blends in approximately 18% w/w (Pérez-Pavón et al., 2007). In general, the occurrence of VOCs in surface

waters can be attributed to their use during agricultural practices, as fumigants, herbicides and solvents for pesticides (Nikolau, et al., 2002), and to their wide use in industrial activities including production, handling and use of fuels, solvents, paints, adhesives, deodorants and refrigerants. The extensive use of these compounds makes it difficult to identify their source in order to reduce the release of such toxic substances. It must be highlighted that many VOCs such as benzene, carbon tetrachloride, trichloromethane, 1,2-dichloroethane or 1,1,1-trichloroethane are restricted in several uses, such as industrial chemical for public use, by Regulation (EC) No 689/2008 (EC, 2008b). However, as shown in Table 2, many of them are present in coastal waters of Comunidad Valenciana.

Organochlorinated pesticides were detected in water samples despite being all of them (except pentachlorobenzene) restricted or banned by Regulation (EC) 850/2004 (EC, 2004). As Table 2 shows, most of them displayed a frequency of occurrence below 15%. Only hexachlorocyclohexane (HCH) showed a relatively high frequency of occurrence (30%), being the most frequent organochlorinated pesticide with a maximum concentration of 0.0083 μg/l. This compound has been used in Spain for many years as agricultural pesticide. The presence of HCH in coastal waters and wastewaters effluents reflects that despite its prohibition, this compound is still in use, probably until stocks are exhausted. Others authors have also reported the presence of lindane (γ-HCH) at concentrations up to 0.481 μg/l in Catalonia ports (Sánchez-Avila et al., 2009). Pérez-Ruzafa et al. (2000) also found concentrations of several organochlorinated pesticides (such as HCH, endosulfan and endrin) in organisms, sediments and water in the Mar Menor Lagoon (SE Spain).

The concentrations for HCH measured in each sampling campaign have been represented in Figure 3a for each water body. As can be seen in this figure, high concentrations of HCH were found in most of the studied areas in May. Since during the period April-May most pesticides treatments are applied, these results reflect that this compound is still in use as agricultural pesticide as stated above. The highest levels of HCH were found in areas 001, 006, 008, 0081, 012, 016 and 0161. Some of these coastal areas (001, 006, 008 and 0081) are highly influenced by agricultural activities with significant areas of citrics and horticulture crops, being also important the extension of rice fields in areas 008 and 0081. Areas 012, 016 and 0161 located in the

south of Comunidad Valenciana are not agricultural irrigation zones, so that HCH could be being used for other purposes. In this sense, some uses of HCH that were allowed until the end of 2007 (Regulation (EC) No 850/2004, Anex II), such as intermediate in chemical manufacturing, could be other possible source of HCH pollution.

Among the phthalates studied, DEHP was the most frequent one. The median concentration was 0.25 μg/l and the maximum 15 μg/l. These concentrations are comparable to the values obtained by Gasperi et al. (2009) in the Seine River (Paris), with a median concentration of 1 μg/l and a maximum of 14.63 μg/l. The abundance of DEHP in water samples is mainly related to its extensive use, as this compound is the most widespread being produced by plasticisers manufacturers and has been incorporated into a variety of products (Fromm et al., 2002). The concentrations for DEHP measured in each sampling campaign have been represented in Figure 3b for each water body. As this figure shows, only in one area (014) a significantly high concentration was reached (15 μg/l), but globally no particular pattern can be observed which can be due to its extensive use.

TBT is also relatively frequent in the coastal waters of Comunidad Valenciana, being detected in 28% of the samples analysed. However, most of the samples in which TBT was detected showed concentrations below the quantification level (3.33*LOD). Only one sample from area 0102 (Port of Denia) reached a significant concentration (0.026 μg/l). Other studies have reported significantly higher levels of TBT in ports: 0.161-1.041 μg/l in the port of Genova (Italy) (Rivaro et al., 1999), 0.002-0.2 μg/l at various sites in Corsica (Michel et al., 2001) and up to 1.966 μg/l in the North West coast of Spain (Rodríguez-González et al., 2006). In this study, samples were not taken inside the port, but from its area of influence.

TBT is a toxic chemical compound used for different industrial purposes including antifouling agents, preservation of wood and slime control in paper mills (Antizar-Ladislao, 2008). Its application as antifouling agent in boat paints to prevent algae and other organisms from growing on the hulls is the most widespread of its uses. For this reason, this pesticide is frequently found in aquatic coastal environments especially in ports, where waters are stagnant and maximum TBT concentrations are

reached. As several studies have shown moving away from the ports, TBT concentrations decrease (Rodriguez-González et al., 2006; Thomaidis et al., 2007). Due to its toxicity, persistence and bioaccumulation, and endocrine disruptive characteristics, the application of TBT based paints was banned by Directive 2002/62/EC (EC, 2002). Despite this prohibition, the results obtained show its presence along the coast, particularly affecting areas influenced by ports.

The concentrations for TBT measured in each sampling campaign have been represented in Figure 3c for each water body. Only 3 areas present samples with TBT concentrations higher that the quantification limit. Two of them are areas influenced by ports: 0102 port of Denia (showing the maximum concentration of 0.026 μg/l) and 0161 port of Alicante. Area 017 (Santa Pola-Guardamar del Segura) also shows the presence of this pesticide which can be attributed to the relatively high number of ship moorings and intense ship traffic in this area.

3.1.2. Chemical status of the water bodies: EQS compliance

In order to ensure protection of aquatic environments and human health two types of EQS were defined by the European Parliament: the annual average concentration (EQS-AAC) to provide protection against long-term exposure, and the maximum allowable concentrations (EQS-MAC) to protect against short-term exposure.

With respect to EQS compliance in coastal waters of Comunidad Valenciana, 4 compounds exceeded their EQS-AAC values: octylphenol, pentachlorobenzene, di(2-ethylhexyl)phthalate (DEHP) and tributiltin (TBT). To estimate the magnitude of the EQS-AAC exceedance for these four compounds, the ratio between the annual average concentration (average of the four sampling campaigns) in each water body and the EQS-AAC value has been calculated. For the calculation of the annual average concentration, whenever the concentration of a given pollutant was below the detection limit, it was assigned half the detection limit value for that pollutant. The exceedance ratio of these four compounds for each water body is shown in Figure 4.

As can be observed in Figure 4, octylphenol exceeded the EQS-AAC value only in area 006 (Port of Sagunto). The remaining water bodies present annual average

concentrations far from the EQS-AAC concentration. The OP exceedance in area 006 is due to only one sample taken in the campaign of May, which reached a significant high concentration (0.078 μg/l). The Port of Sagunto is a highly industrialised area with direct WWTP effluents discharges which could explain this high OP concentration. However, without considering this value, the OP concentrations along the coastal waters of Comunidad Valencia ranged from <LD - 0.011 μg/l, which are comparable to the concentrations obtained in Greek coastal waters (0.008-0.029 μg/l) by Arditsoglou and Voutsa (2008). Therefore, future samplings campaigns are needed in order to determine if area 006 complies with the WFD standards.

The main source of alkylphenols, such as octylphenol, in surface waters is the discharge of municipal and industrial wastewater treatment plants (Soares et al., 2008; Navarro et al., 2009). Alkylphenols polyethoxylates are commercially important surfactants with industrial, agricultural, and domestic applications (Isobe et al., 2001). Due to their extensive use, they reach the WWTPs in substantial amounts where they are degraded according to the specific treatment conditions. Sánchez-Avila et al. (2009) reported daily removal efficiency for alkylphenols of 80% in the Mataró's WWTP. Since these compounds are not completely removed at WWTPs they are discharged to the sea where dilution occurs. Thus, possible impacts are restricted near to the area of discharge. Moreover, due to their hydrophobic character, these compounds rapidly tend to become associated with particles and end up in the sediments where they might induce endocrine effects to the marine biota (Antizar-Ladislao, 2008; David et al., 2009).

Pentachlorobenzene (PeCB) exceeded its EQS-AAC value in four water bodies (001, 003, 004 and 008) being the exceedance ratio within 1.21 and 2.05 range. Area 0041 (Port of Castellón) showed an annual average concentration close to the EQS-AAC value but did not exceed it. The main sources of this organic pollutant appear to be combustion of solid wastes and biomass, degradation of an agricultural fungicide (pentachloronitrobenzene) and minor industrial releases (Bayle et al., 2009). As can be observed in Figure 4 most of the areas affected by this compound are located in the north of Comunidad Valenciana (Castellón province). Areas 001, 003, 004 and 008 are influenced by citrics and horticulture (and rice fields only in area 008), which could

explain the high levels of PeCB. However, other sources could also contribute to its presence in coastal waters. Although the use of PeCB is still allowed, it has been proposed for being included in the Stockholm Convention (UNEP, 2009) to its total prohibition.

Di(2-ethylhexyl)phthalate (DEHP) was the compound that exceeded its EQS-AAC value in a major number of water bodies (001, 004, 008, 0081, 010, 014, 016), which are distributed along the Comunidad Valenciana coast. The exceedance ratio in these water bodies ranged from 1.2 (area 010) to 3.9 (area 014). Moreover, there are six areas in which DEHP annual average concentration is close to reach the EQS-AAC value (ratio in the range 0.75-0.91). The high number of areas in which DEHP concentrations are above the established guidelines makes it necessary to increase efforts to control DEHP pollution in coastal waters of Comunidad Valenciana and thus to fulfil WFD requirements. However, as previously mentioned, their extensive use makes it very difficult to determine pollution patterns or emission sources for this pollutant.

As can be observed in Figure 4, tributiltin (TBT) exceeded the EQS-AAC value only in the Port of Denia (area 0102) reaching a noticeable high exceedance ratio (32.6). As mentioned before, the sample taken in May in this area presented a concentration of 0.026 μg/l. Due to this concentration not only the EQS-AAC value was exceeded but also the EQS-MAC value (0.0015 μg/L). Of the 71 analysed compounds, TBT was the only compound that surpassed the EQS-MAC. However, future sampling campaigns are planned to assess the tendency and significance of TBT concentration in this area.

Finally, it should be mentioned that two other compounds reached almost the 70 % of their EQS-AAC values: endosulfan in area 006 and hexachlorocyclohexane (HCH) in areas 001 and 0161. Therefore, although these two compounds did not exceed the established standards, their levels in coastal waters should be monitored in order to ensure the protection of coastal ecosystem.

3.1.3. Multivariate visualization with Principal Component Analysis (PCA)

Principal Component Analysis was used to provide a graphical overview and elucidate similarities and differences between the studied water bodies with respect to the most significant pollutants (i.e., the more frequent contaminants and those that exceeded the EQS). PCA was performed on a data set composed by the annual average concentration of each pollutant in each water body. A PCA-model was fitted to the pre-processed data (mean-centred and scaled to unit variance). Two principal components were retained in the PCA model, explaining 21.9% and 20.4% of the total variance, respectively. The results of the fitted model are graphically displayed in Figure 5. The score plot (Figure 5a) shows how the different areas relate to each other (i.e., similar areas –in terms of the pollutants analyzed– are close in the plot). The loading plot (Figure 5b) shows the relationship among the variables and indicate which variables are responsible for the patterns observed in the corresponding score plot.

In Figure 5a it can be seen that area 0102, which correspond to the area of influence of the Port of Denia, is quite far from the rest. From the loading plot (Figure 5b) it can be concluded that the separation of this area is mainly due to its high TBT concentration as explained before. Figure 5 also reveals that most of the areas geographically close are not affected by the same pollutants. For example, areas 006 and 013 are not geographically close but present a similar contamination pattern as can be observed in the score plot (Figure 5a). The same occurs in areas 011 and 014. However, some interesting relations can be observed: Areas 0041, 0081 and 0161 show similar contamination patterns in agreement to the fact that these areas are classified as heavily modified coastal waters. Moreover, these three areas influenced by ports belong to the main cities of Comunidad Valenciana (Port of Castellón, Port of Valencia and Port of Alicante). It can also be observed that areas 001, 003 and 004, which are located in the north of Comunidad Valenciana, are close in the score plot because all of them are mainly affected by relatively high concentrations of pentachlorobenzene, trichlorethylene and carbon tetrachloride in comparison with the concentrations of these pollutants in the remaining areas, as reflects Figure 5b. Finally, areas 017, 018 and 019, which are located in the south of the Comunidad Valenciana, are grouped as Figure 5a shows, mainly due to their relatively high concentration of o-xylene and low of trichloroethylene.

3.2. WWTP's effluents

As it can be observed in Table 2, of the 69 organic pollutants analysed in WWTP's effluents (n=84), a total of 27 were never detected. These undetected compounds were 1 phenol (bisphenol A), 1 organochlorinated pesticides (DDT), the SCCP compounds, 5 of the triazine herbicides (atrazine, trifluralin, propazine, prometrine, terbutrine), 3 of the urea herbicides (fluometuron, metobromuron, linuron), none of the 7 organophosphorous pesticides, 1 phthalate (dimethyl phthalate) and 7 of the 9 analysed PAHs.

The most frequent pollutants determined in the coastal waters of Comunidad Valenciana (those with frequency of occurrence above 20%) are all present in WWTP's effluents (except TBT which was only measured in coastal waters). Besides these compounds, octylphenol and 7 VOCs (dichloromethane, tetrachloroethylene, 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene, trichloromethane, 1,2-dichlorobenzene, 1,4-dichlorobenzene) were also detected in WWTP's effluents on a frequent basis. The industrial use of these compounds could explain its higher occurrence in WWTP's effluents.

A comparison of coastal waters and WWTPs effluents concentrations of the compounds that exceeded the EQS-AAC (octylphenol, pentachlorobenzene, DEHP, TBT) or reached almost the 70 % of their EQS-AAC value (endosulfan and HCH) is shown in Figure 6.

The higher presence of octylphenol in WWTP effluents than in coastal waters is not surprising due to the wide use of alkylphenols as industrial surfactants. As explained above, different authors found that WWTP effluents and discharges from industries are the main source of alkylphenols in aquatic environments (Ying et al., 2006; Soares et al., 2008). This can be explained by the fact that OP is not completely removed from wastewaters in the WWTPs where the main removal mechanism is the adsorption on sludge particles and subsequent sedimentation (Isobe et al., 2001).

Endosulfan and hexachlorocyclohexane (HCH) are organochlorinated pesticides which are both prohibited in European Union countries. However, as shown in Figure 6,

their occurrence in both wastewaters and coastal waters evidence that they are still in use as pesticides in some areas of the Comunidad Valenciana. Indeed, HCH is one of the most frequent compounds found in WWTPs effluents (frequency of occurrence: 58%) and is relatively frequent in coastal waters (30%). On the contrary, the occurrence of endosulfan is more limited and only is measured significantly in the coastal waters of area 006.

Generally, concentrations of all compounds in WWTP effluents were higher than in coastal waters as it could be expected (See Table 2). The main exception was DEHP, which showed concentrations up to 15 μg/l in coastal waters while only reached concentrations at the LOD level in WWTPs effluents (See Figure 6). Also the frequency of occurrence was significantly higher in coastal waters (57%) than in WWTP effluents (32%). Low DEHP concentrations in WWTP effluents can be explained due to the fact that phthalates are sparingly soluble, rapidly sorbed on particulate matter, and their half lives around 30 h, resulting highly removal efficiency in WWTPs through microbial activity and sorption to sludge (Fausser et al., 2003). Thus, the DEHP burden associated to WWTPs effluents is potentially low.

The results evidence that the same pollutants found in coastal waters are also present in WWTPs effluents in higher frequency of occurrence and concentration. Therefore, WWTPs are clearly a significant point source for PPs in coastal waters. However, geographically speaking, comparing the concentrations of the analysed pollutants in each water body with the concentrations in the WWTP effluents that discharges to that water body, no particular relationship has been observed. This is due to the fact that the pollutant sources are not restricted to the studied WWTPs. Atmospheric deposition, urban and agricultural runoff, direct discharges and combined sewer overflows have also contributed to the pollution observed in coastal waters of Comunidad Valenciana. However, due to the concentrations of some organic micropollutants observed in WWTP effluents and to the important amounts released daily to seawater, their impact in coastal waters should be taken into account.

Conclusions

In this paper, information on the occurrence, significance of concentration and spatial distribution of priority pollutants (PPs) in Comunidad Valenciana coastal waters (Spain) has been provided to assess the chemical quality status according to Water Framework Directive (WFD).

The results obtained show that all analysed coastal waters showed the presence of PPs. A total of 36 of the organic pollutants analysed, including 26 PPs (8 of them priority hazardous substances), were detected although many of them with low frequency of occurrence. Only 13 compounds, which belong to 4 different classes (VOCs, organochlorinated pesticides, phthalates and TBT) showed a frequency of occurrence above 20%. DEHP was the most frequent PP (detected in 57% of the samples) reaching concentrations up to 15 μg/l. As regards the EQS compliance, 4 compounds exceeded their EQS-AAC values: octylphenol, pentachlorobenzene, DEHP and TBT, and only TBT surpassed the EQS-MAC value in one area (port of Denia). Moreover, two prohibited organochlorinated pesticides exhibited concentrations around the 70% of their EQS-AAC: endosulfan and HCH, which presented frequencies of occurrence of 9% and 30%, respectively.

A multivariate approach was used to elucidate similarities and differences between the studied water bodies with respect to the most significant pollutants (i.e. those with higher frequency of occurrence and those that exceeded the EQS). The PCA results showed a relatively similar pattern of contamination for the three main areas affected by ports (Castellón, Valencia and Alicante). It also showed clear differences in the contamination pattern between some northern areas (001, 003 and 004) mainly affected by PeCB, TCEt and TCC, and some southern areas (017, 018 and 019) which presented high concentrations of oXil and low concentrations of TCEt.

The most frequent PPs determined in coastal waters were also present in WWTPs effluents. Benzene was the most frequent PP in WWTP effluents (being detected in 76% of the samples) with maximum concentration of 44 μg/l. Generally, concentrations of all compounds in WWTPs' effluents were higher than in coastal waters as it could be expected, with the exception of DEPH, which only reached

concentrations at the LOD level in WWTPs as this pollutant seems to be efficiently removed in WWTPs. These results evidence that WWTPs are a significant point source for PPs in coastal waters. However, the pollutant sources are not restricted to the studied WWTPs. Atmospheric deposition or urban and agricultural runoff have also a significant contribution. Therefore, further research is needed to investigate these and other diffuse and local sources in order to establish corrective measures able to reduce PP release to aquatic environments as implementation of WFD requires.

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Class	Normative			Method
	WFD[a]	Law 42/2007[b]	others[c]	
Phenols	2		2	SPME/GC-MS
Volatile Organic Compounds (VOC)	6	4	5	SPME/GC-FID
	4			SPME/GC-ECD
Organochlorinated Pesticides	12			SPME/GC-ECD
Bromodiphenyl ether (BDE)	1			SPME/GC-ECD
Short Chain Chlorinated Paraffins (SCCP)	1			SPME/GC-ECD
Triazine Herbicides	3	1	4	*in tube* -SPME-CLC-DAD
Urea Herbicides	2		3	*in tube* -SPME-CLC-DAD
Organophosphorous Pesticides	2		5	*in tube* -SPME-CLC-DAD
Phtalates	1		3	*in tube* -SPME-CLC-DAD
Polycyclic Aromatic Hydrocarbons (PAH)	7		2	*in tube* -SPME-CLC-DAD/LC-FD
Organotin compounds (TBT)	1			SPME-HS/GC-MS

[a] WFD 2000/60/EC

[b] Law 42/2007 Natural Patrimony and Heritage

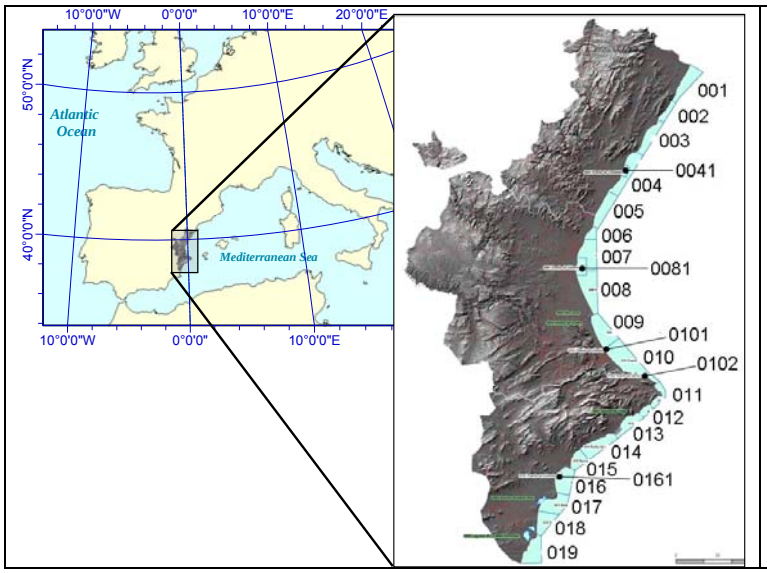
[c] others include metabolites and congeners

Table 1. Pollutants analysed, normative involved and analytical technique employed.

			Surface waters (n=160) in µg/l							WWTP effluents (n=84) in µg/l				
								EQS						
Class	Pollutant	Acronym	LOD	%	Median	Min	Max	EQS-AAC	EQS-MAC	LOD	%	Median	Min	Max
Phenols	4-nonylphenol*	4NP	0,01	10	<	<	LOD	0,3	2	0,01	7	<	<	LOD
	Octylphenol	OP	0,006	13	<	<	0,078	0,01	----	0,01	38	<	<	2,4
	t-nonylphenol	tNP	0,05	16	<	<	0,13	----	----	0,05	15	<	<	0,79
	Bisphenol A	BPA	0,5	0	<	<	<	----	----	0,5	0	<	<	<
VOC	Benzene	B	0,01	51	0,01	<	0,3	8	50	0,01	76	0,03	<	44
	Carbon-tetrachloride	TCC	1	33	<	<	4	12	----	1	50	0,75	<	69
	1,2-Dichloroethane	DCE	1	0	<	<	<	10	----	1	1	<	<	LOD
	Dichloromethane	DCM	0,003	6	<	<	LOD	20	----	0,003	29	<	<	0,23
	Tetrachloroethylene	TeCEt	0,1	3	<	<	5	10	----	0,1	46	<	<	36
	Trichloroethylene	TCEt	0,5	33	<	<	4	10	----	0,5	48	<	<	13
	1,2,3-Trichlorobenzene	TCBI	0,005	10	<	<	0,015	0,4	----	0,01	45	<	<	0,109
	1,3,5-Trichlorobenzene	TCBIII	0,005	5	<	<	LOD	0,4	----	0,01	19	<	<	0,09
	1,2,4-Trichlorobenzene	TCBII	0,005	8	<	<	0,041	0,4	----	0,01	44	<	<	0,109
	Trichloromethane	TCM	1	2	<	<	1	2,5	----	1	39	<	<	44
	Toluene	Tol	0,01	100	0,17	LOD	1,6	----	----	0,01	70	0,1	<	12
	o-Xylene	oXil	0,01	40	<	<	0,05	----	----	0,01	54	0,01	<	1,4
	m,p-Xylene	mpXil	0,01	96	0,05	<	0,27	----	----	0,01	64	0,03	<	2,8
	Etylbenzene	EtB	0,01	78	0,01	<	0,22	----	----	0,01	38	<	<	2,3
	1,1,1-trichloroethane	TCEt	1	0	<	<	<	----	----	----	NA	NA	NA	NA
	Chlorobenzene	CB	0,01	6	<	<	LOD	----	----	0,01	1	<	<	LOD
	1,2-Dichlorobenzene	DCBI	0,01	20	<	<	0,08	----	----	0,01	43	<	<	3
	1,3-Dichlorobenzene	DCBII	0,01	0	<	<	<	----	----	0,01	23	<	<	1,4
	1,4-Dichlorobenzene	DCBIII	0,01	8	<	<	0,05	----	----	0,01	29	<	<	2,5
Organochlorinated Pesticides	Alachlor	Ala	0,005	9	<	<	0,014	0,3	0,7	0,0015	5	<	<	LOD
	Aldrin	Ald	0,003	2	<	<	LOD	Σ 0,005	----	0,0015	1	<	<	LOD
	Dieldrin	Dield	0,0002	6	<	<	0,0026			0,0015	2	<	<	LOD
	Endrin	End	0,0002	3	<	<	LOD			0,0015	11	<	<	0,0141
	Isodrin	Isod	0,003	6	<	<	0,005			0,005	4	<	<	LOD
	Endosulfan*	EndS	0,0001	9	<	<	0,0019	0,0005	0,004	0,002	18	<	<	0,13
	Hexachlorobenzene*	HCB	0,002	14	<	<	LOD	0,01	0,05	0,005	5	<	<	LOD
	Hexachlorobutadiene*	HCBu	0,002	14	<	<	LOD	0,1	0,6	0,01	10	<	<	LOD
	Hexachlorocyclohexane*	HCH	0,0005	30	<	<	0,0083	0,002	0,02	0,003	58	0,003	<	0,124
	DDT	DDT	0,002	4	<	<	LOD	0,025	----	0,5	0	<	<	<
	Pentachlorophenol	PCP	0,003	7	<	<	LOD	0,4	1	0,003	19	<	<	0,148
	Pentachlorobenzene*	PeCB	0,0005	10	<	<	0,007	0,0007	----	0,001	8	<	<	0,069
BDE	Brominated diphenylether*	BDE	0,0001	3	<	<	LOD	0,0002	----	0,005	2	<	<	LOD
SCCP	C10-13 Chloroalkanes*	SCCP	0,4	0	<	<	<	0,4	1,4	0,4	0	<	<	<
Triazine Herbicides	Atrazine	Az	0,2	0	<	<	<	0,6	2	0,2	0	<	<	<
	Simazine	Si	0,1	0	<	<	<	1	4	0,1	2	<	<	4
	Trifluralin	Tf	0,01	0	<	<	<	0,03	----	0,01	0	<	<	<
	Terbutilazine	Tz	0,1	0	<	<	<	----	----	0,1	2	<	<	2,5
	Ametrine	An	0,2	0	<	<	<	----	----	0,2	1	<	<	LOD
	Propazine	Pz	0,2	0	<	<	<	----	----	0,2	0	<	<	<
	Prometrine	Pn	0,1	0	<	<	<	----	----	0,1	0	<	<	<
	Terbutrine	Tn	0,1	0	<	<	<	----	----	0,1	0	<	<	<
Urea Herbicides	Diuron	Din	0,1	0	<	<	<	0,2	1,8	0,5	1	<	<	LOD
	Isoproturon	Isn	0,2	0	<	<	<	0,3	0,1	0,5	1	<	<	20
	Fluometuron	Fln	1	0	<	<	<	----	----	1	0	<	<	<
	Metobromuron	Mbn	0,1	0	<	<	<	----	----	0,1	0	<	<	<
	Linuron	Ln	0,2	0	<	<	<	----	----	0,2	0	<	<	<
Organophosphorous Pesticides	Chlorfenvinphos	Cf	0,05	0	<	<	<	0,1	0,3	0,2	0	<	<	<
	Chlorpyrifos	Cp	0,01	0	<	<	<	0,03	0,1	0,05	0	<	<	<
	Fenamiphos	Ff	0,2	0	<	<	<	----	----	0,2	0	<	<	<
	Fenitrotion	Fntr	0,2	0	<	<	<	----	----	0,2	0	<	<	<
	Fention	Fnt	0,2	0	<	<	<	----	----	0,2	0	<	<	<
	Metylparation	Mpt	0,2	0	<	<	<	----	----	0,2	0	<	<	<
	Fonofos	Fnf	0,1	0	<	<	<	----	----	0,1	0	<	<	<
Phtalates	Di(2-ethylhexyl) phthalate	DEHP	0,25	57	0,25	<	15	1,3	----	0,25	32	<	<	LOD
	Dimethyl phthalate	DMP	0,2	0	<	<	<	----	----	0,2	0	<	<	<
	Diethyl phthalate	DEP	0,2	21	<	<	20	----	----	0,2	17	<	<	29
	Dibutyl phthalate	DBP	0,1	35	<	<	0,3	----	----	0,1	45	<	<	0,9
PAH	Anthracene*	Ant	0,02	0	<	<	<	0,1	0,4	0,02	0	<	<	<
	Fluoranthene	Fluo	0,001	0	<	<	<	0,1	1	0,05	0	<	<	<
	Naphthalene	Natf	0,1	0	<	<	<	1,2	----	0,1	2	<	<	0,4
	Benzo(a)pyrene*	BaP	0,0008	0	<	<	<	0,5	1	0,2	0	<	<	<
	Benzo(b)fluoranthene*	BbF	0,0025	0	<	<	<	0,03	----	0,006	0	<	<	<
	Benzo(k)fluoranthene*	BkF	0,005	0	<	<	<			0,006	0	<	<	<
	Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene*	BgP	0,001	0	<	<	<	0,002	----	0,0025	0	<	<	<
	Benzo(a)antracene	BaA	0,006	0	<	<	<	----	----	0,006	0	<	<	<
	Dibenzo(a h)anthracene	DaA	0,005	0	<	<	<	----	----	0,005	2	<	<	LOD
TBT	Tributyltin compounds*	TBT	0,000025	28	<	<	0,026	0,0002	0,0015	----	NA	NA	NA	NA

LOD	limit of detection	<	below LOD
%	occurence of the pollutants (concentration above LOD)	*	priority hazardous pollutants
n	number of samples	NA	not analysed

Table 2. Occurrence and concentration of organic pollutants in surface waters and WWTP effluents.



COASTAL WATERS	
CODE	**DENOMINATION**
001	Comunidad Valenciana boundary – Irta mountain range
002	Irta mountain range
003	Irta mountain range – Cape Oropesa
004	Cape Oropesa - Burriana
005	Burriana - Canet d'en Berenguer
007	North coast of Valencia
008	Port of Valencia - Cape Cullera
009	Cape Cullera - Port of Gandia
010	Port of Gandia – Cape San Antonio
011	Cape San Antonio – Cape Moraira
012	Cape Moraira – Rock of Ifach
013	Rock of Ifach - Cape Les Caletes
014	Cape Les Caletes - Cliff Aguas de Busot
015	Cliff Aguas de Busot - Cape Huertas
016	Cape Huertas - Santa Pola
017	Santa Pola - Guardamar del Segura
018	Guardamar del Segura- Cape Cervera
019	Cape Cervera – Comunidad Valenciana boundary
HEAVILY MODIFIED COASTAL WATERS	
CODE	**DENOMINATION**
0041	Port of Castellón
006	Port of Sagunto
0081	Port of Valencia
0101	Port of Gandia
0102	Port of Denia
0161	Port of Alicante

Figure 1. Location of the 24 water bodies defined along the Comunidad Valenciana coast.

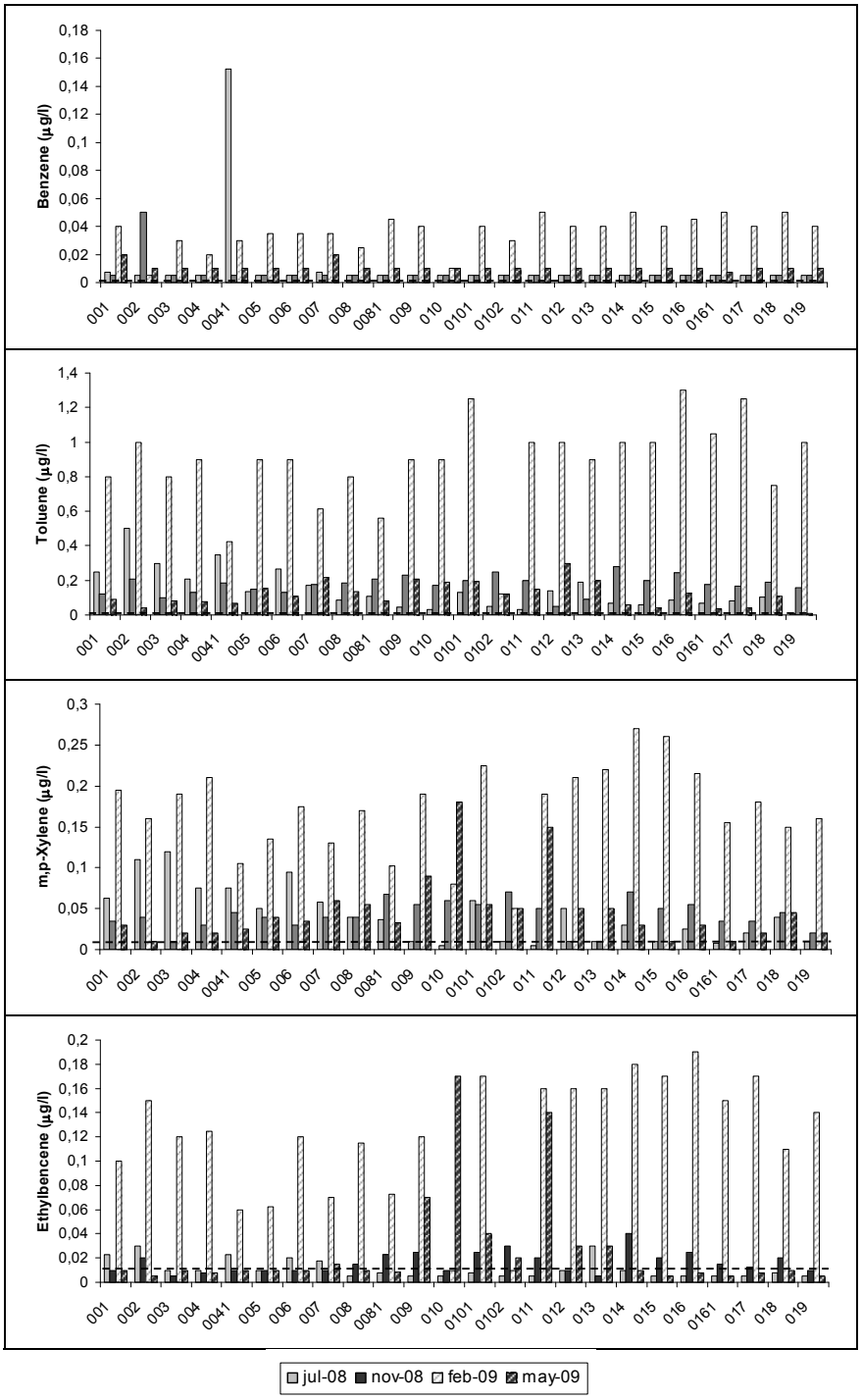


Figure 2. Concentrations of the most frequent VOCs at each water body for the 4 sampling campaigns (- - - LOD)

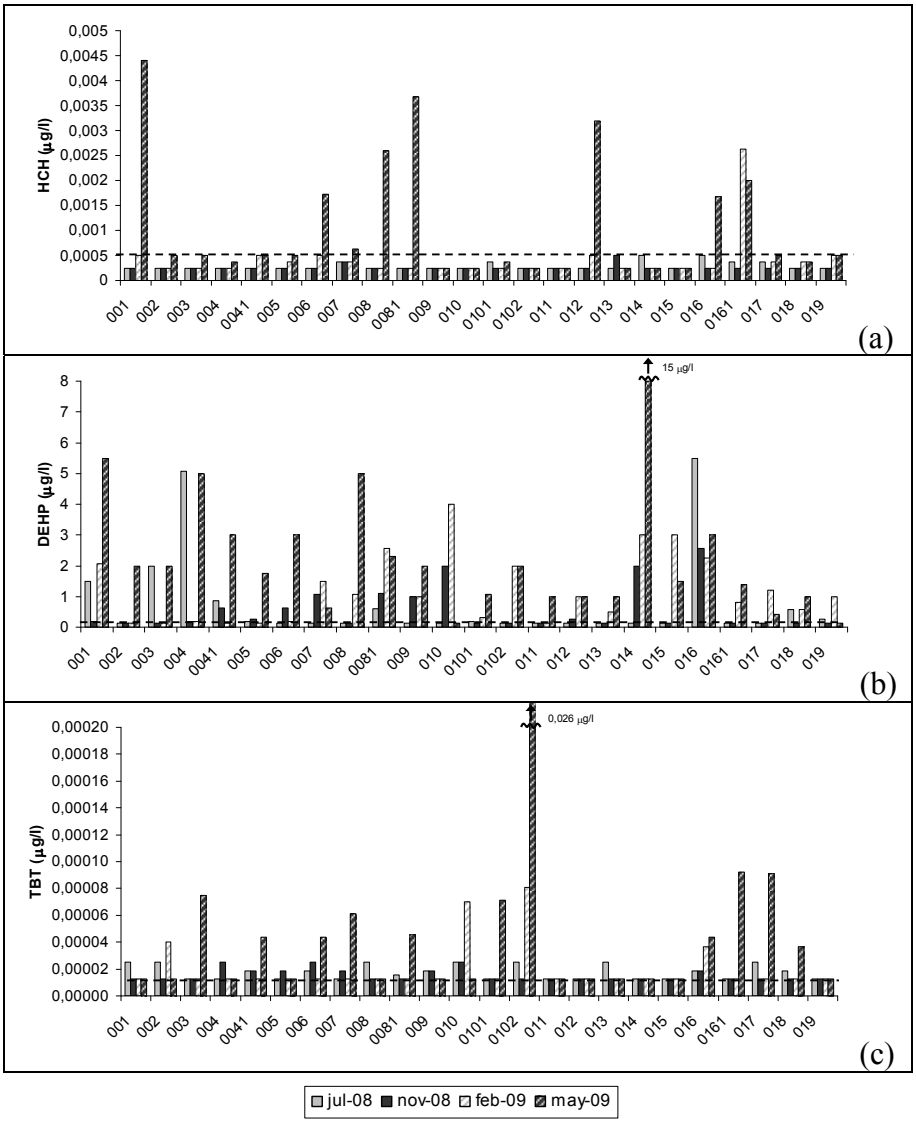


Figure 3. Concentrations of (a) HCH, (b) DEHP and (c) TBT at each water body for the 4 sampling campaigns (- - - LOD)

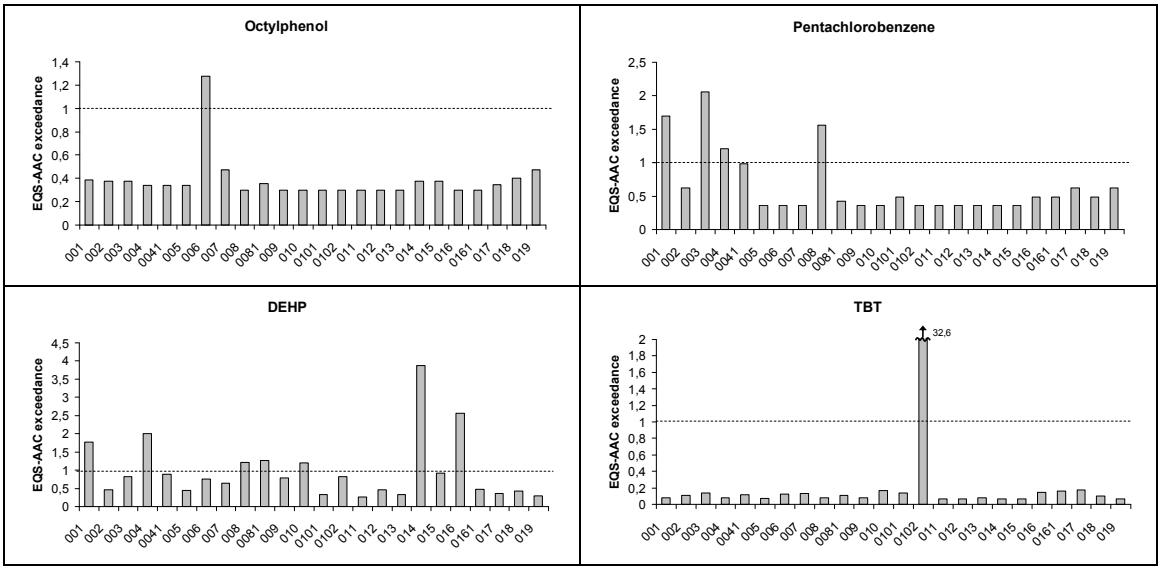


Figure 4. EQS-AAC exceedance ratios for OP, PeCB, DEPH and TBT. Theses ratios are calculated as the annual average concentration in each water body and the EQS-AAC value.

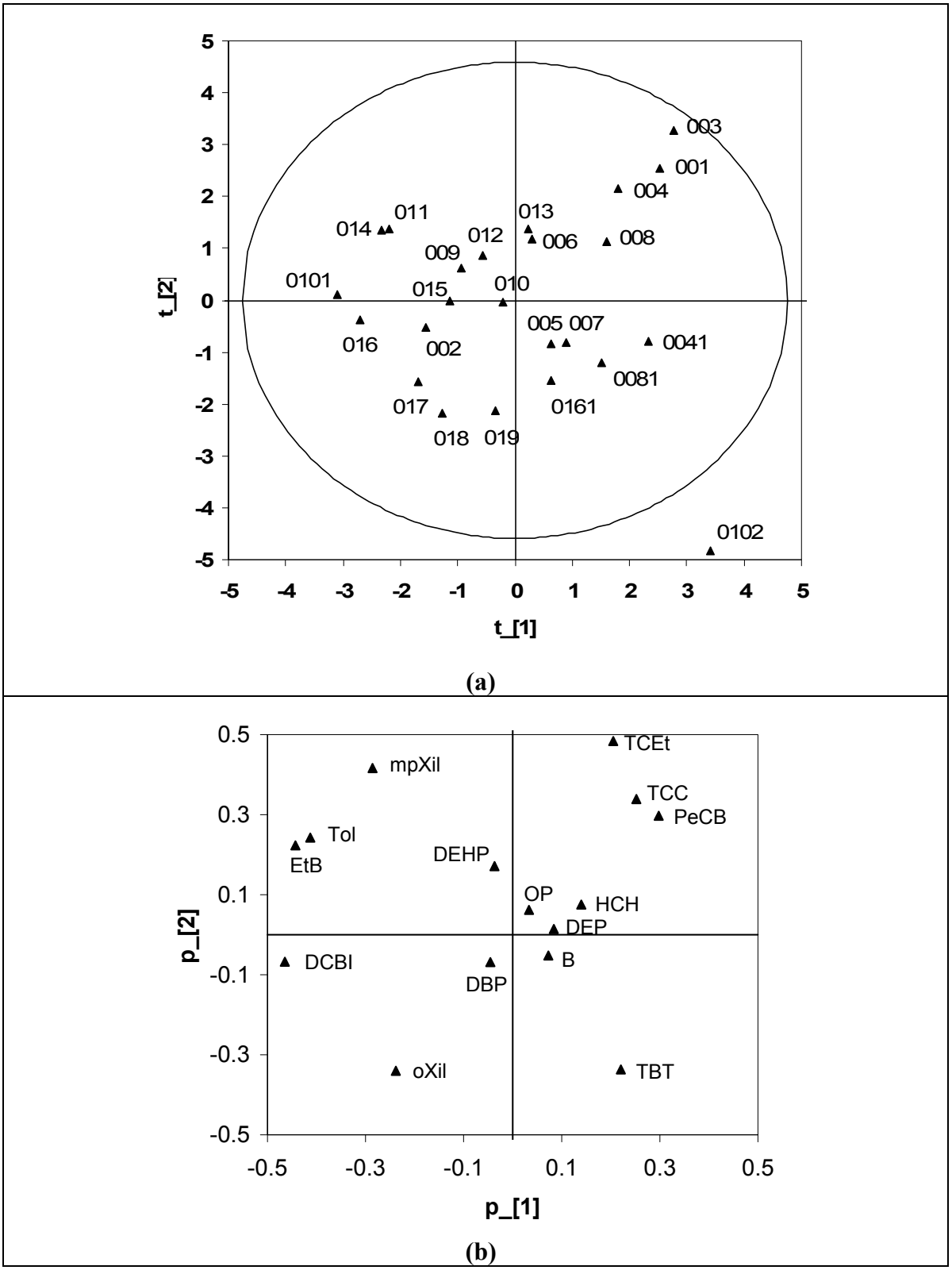
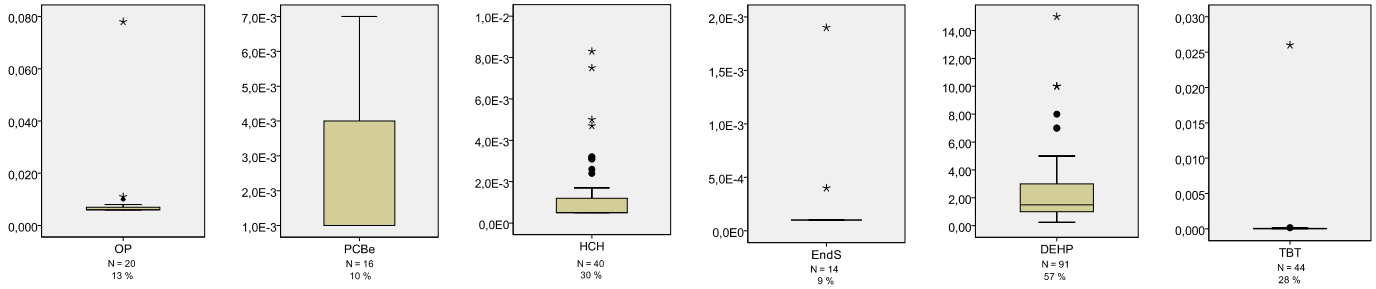
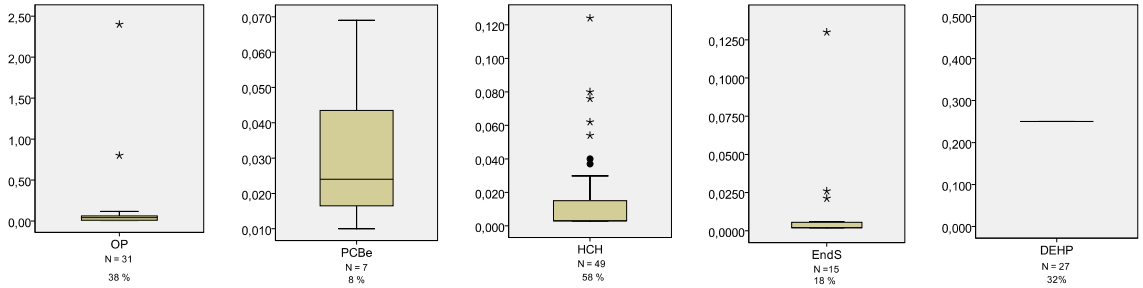


Figure 5. (a) PCA-scores and (b) loadings for the multivariate analysis of 15 pollutants in the coastal waters of Comunidad Valenciana: including the more frequent contaminants and those that exceeded the EQS.



(a) Coastal waters of Comunidad Valenciana (n=164)



(b) WWTPs effluents (n=84)

Figure 6. Box and whisker plot of OP, PeCB, HCH EndS, DEHP and TBT concentrations (µg/l) in (a) coastal waters and (b) WWTPs effluent. The number of positive samples and the corresponding frequency of occurrence is including below its plot.