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Persistent Organic Pollutant in the Venetian Coastal Environment

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Abstract – The Venetian coastal area is characterized by a strong anthropogenic impact and its quality is very important because of local economical activities, such as tourism or fishing. In the context of the Water Framework Directive (WFD, 2000/60/EC), the aim of the project Q-ALiVe (Qualità dell'Ambiente Litoraneo Veneto) is to check the environmental quality of the Venetian coastal area and whether rivers contamination could influence it. We studied an area going from the mouth of the Adige river to the Malamocco inlet of the Venice lagoon (including the mouth of the Brenta river and the Chioggia lagoon inlet), to distance from the coast of up to about a kilometer.

In this work we presented the data relative to Persistent Organic Pollutants (POPs) as PCBs, PBDEs and PAHs, in samples of seawater.

Samples were collected during four different sampling campaigns, in different seasons (June 2011, August 2011, September 2011, November 2011); in each sampling campaign we collected 10 samples of surface water. Analytical samples procedures for POPs include liquid-liquid continuous extraction, followed by an automated purification step, with neutral silica columns. Analysis were made by HRGC-HRMS (PCBs) or HRGC-LRMS (PAHs and PBDEs). Quantification was made by isotope dilution.

Results suggest a negligible influence of rivers contamination to the quality of the sea facing the city of Chioggia and the Venice lagoon.

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Keywords**:** Seawater; Adriatic Sea; POPs; PCBs; PAHs; PBDEs; GC-MS

1. Introduction

Persistent organic pollutants (POPs) are ubiquitous contaminants frequently found in sediments, soil, fish, wildlife, human adipose tissue, serum and milk (Van den Berg et al., 2006; Safe, 2003). The importance of studying POPs is due to their characteristics of persistence and potential for bioaccumulation and long-range transport (Buccini, 2003; Scheringer, 2009).

Polychlorinated biphenyls (Erickson, 1997) are a class of 209 man-made compounds with a biphenyl nucleus produced in complex mixtures (i.e. Aroclor) with a different mean chlorination degree (Schulz et al., 1989) and used in numerous applications such as dielectric fluid in capacitors and transformers, hydraulic and heat transfer fluid and additives in pesticides, paints, copying papers, etc. There is a rising interest in the non-Aroclor congener 3,3′-dichlorobiphenyl (PCB 11), produced unintentionally during the synthesis of diarylide yellow pigments (Herbst and Unger, 1993), and recently detected in air, water, biota, sediment, and suspended sediment (Rodenburg et al., 2010). Monitoring of PCBs in the Mediterranean Sea began in 1970 and was focused mainly on sediments and marine biota (Tolosa et al., 1997; Picer, 2000). However, few data have been reported on the PCB concentrations in the waters, particularly as regards in the Adriatic Sea (Picer, 2000).

Polybrominated diphenyl ethers (PBDEs) are an important group of flame retardants which have been widely used as non-reactive additives in textiles, polyurethane foams, thermoplastics and electronic products (Alaee et al., 2003; Shaw et al., 2010). PBDEs were generally produced as commercial mixture with three different degrees of bromination (Penta-BDE, Octa-BDE and Deca-BDE) and classified according to their average bromine content. PBDEs have become ubiquitous contaminants in environmental media, biota and humans (Domingo, 2012) and shown neurotoxic effects to human and animals (Branchi et al., 2003). Currently, the production of penta- and octa-BDEs has been banned in the European Union (EU) and North America. Deca-BDE has been banned also from some of these countries, but in Asia PBDEs are not restricted yet (Yan-Ping et al., 2010).

Polycyclic aromatic hydrocarbons (PAHs) are an important class of POPs, commonly found in the environment, characterised by two or more fused aromatic rings of carbon and hydrogen atoms. (Malik et al., 2011). PAHs originate from natural as well as anthropogenic sources, including thermal combustion processes, vehicular emissions and biomass burning (Simoneit 1984; McVeety and Hites 1988).

The Adriatic Sea is an elongated basin (139000 km^2) of the northern Mediterranean, extending for 800 km into the heartland of the European continent (Picer, 2000).

The study area is located in the north eastern part of the Adriatic Sea and extends from the mouth of the river Adige to the Malamocco harbour mouth of the Venice Lagoon. Poulain (2001) suggest that the general circulation in this area moves toward south. This particular area is characterized by the influence of the Venice Lagoon and the presence of the rivers Adige and Brenta. The Venice Lagoon is a shallow basin, which covers an area of about 549 km^2 along the north-western coast of the Adriatic Sea and its state of pollution has long been known and very well described (Moret et al., 2000; Moret et al., 2005; Manodori et al., 2006; Guerzoni et al., 2007). The river Adige flows from the west-central Alps to the Adriatic Sea and is the second longest Italian river (409 km) and the third largest in catchment area (12100 km^2) with a mean annual discharge of 6,96 km^3 (Gumiero et al., 2009). The river Brenta originates from Levico and Caldonazzo Lakes (Province of Trento), runs for about 174 km and leads into the northern Adriatic, between the Venice lagoon and the river Adige, near the city of Chioggia. It has an average annual flow of 2,24 km^3 and its catchment area covers an area of 1567 km^2 (Gumiero et al., 2009). These two rivers, with their loads of freshwater and suspended material, greatly influence the study area.

The Northern Adriatic Sea is a region affected by fishing activities and characterized by relevant tourist flows, and evaluation of the quality of water is essential to protect the environment and public health.

2. Materials and methods

2. 1. Sampling

Four sampling campaigns were organized at different times of the year in order to evaluate a possible seasonal variation in the concentrations of pollutants (in particular: June, from 13th to 16th, 2011 - Campaign "A";July, from 25th to 28th, 2011 - Campaign "B"; October, from 4th to 7th, 2011 - Campaign "C"; November, from 22nd to 29th - 2011; Campaign "D").

For each sample the number of the transept, the position along the coastline and the campaign in which the sample was collected is reported.

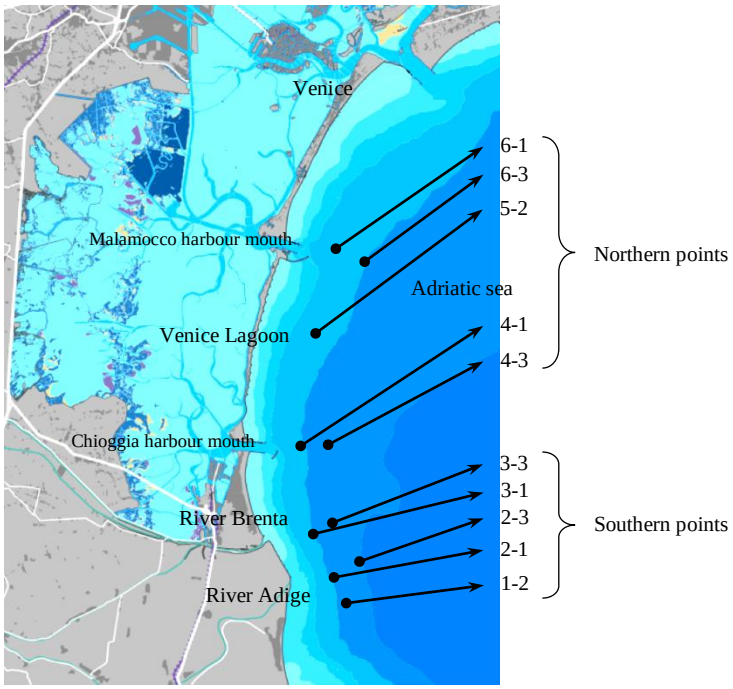

Fig. 1. Study area and samples points (divided into "Northern points" and "Southern Points")

Sampling points (Fig. 1) were reached using a motor boat and the samples were collected by a submersible pump (polyethylene piping). Samples were collected in 20 L stainless steel bins.

2. 2. Extractions and cleanup

The extraction of water samples was carried out according to an internal method (Moret et al., 2005 and further modification). Briefly, 11 litres of sample were extracted for 24 hours by a continuous liquid-liquid extraction system, using a mixture of pentane and dichloromethane (2:1, v/v).

The concentration and cleanup steps were performed as described in Piazza et al. (2013) using, respectively, the Turbovap II® (Caliper Life Science) and PowerPrep ™ (Fluid Management System Inc.) systems.

2. 3. Instrumental analysis

As describe in Piazza et al. (2013) PAH and PBDE analysis were carried out with an Agilent Technologies 7890A gas chromatograph coupled with a quadrupole mass spectrometer (Agilent Technologies 5975C), operating in electron impact mode. PCB analysis was carried out on a Hewlett Packard-Agilent 6890 Series GC System coupled with a MAT 95XP high-resolution double focusing mass spectrometer (ThermoFinnigan) working in electron impact mode. The acquisition was performed using selected ion monitoring (SIM). The gas chromatographic separation was carried out on a 60-m HP-5MS column (0.25 mm I.D., 0.25 μm; Agilent Technologies, Avondale, USA) for PCBs and PAHs, while a similar 15-m column was used for PBDEs. The quantification was performed using isotopic dilution technique and results were corrected with procedural blank values.

3. Results and Discussion

3. 1. PCBs

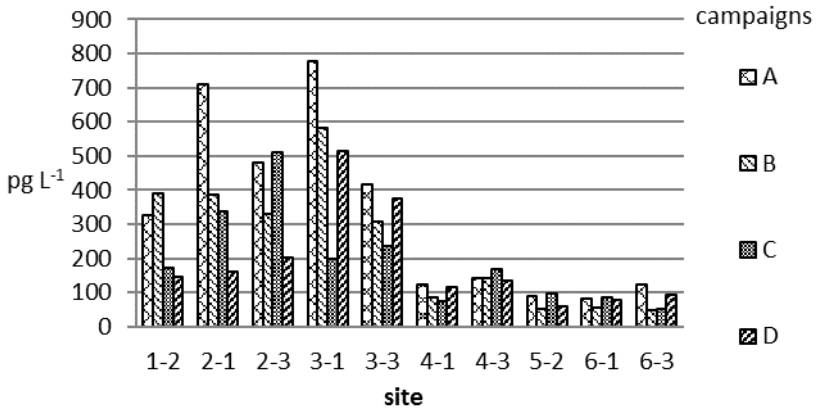

Fig. 2. Total PCB concentrations in each sample for all campaigns (A=June, B=July, C=October, D=November)

The concentrations of PCBs (Fig. 2) in the samples taken at the points 1-2, 2-1, 2-3, 3-1 and 3-3 ("Southern points" in Fig. 1) are, on average, higher than the other samples ("Northern points" in Fig. 1).

Interestingly, as shown in Fig. 3, the global contaminant PCB 11 is present in most samples at noteworthy concentrations. When present, PCB 11 accounts for 0.8–16.4% of total PCBs.

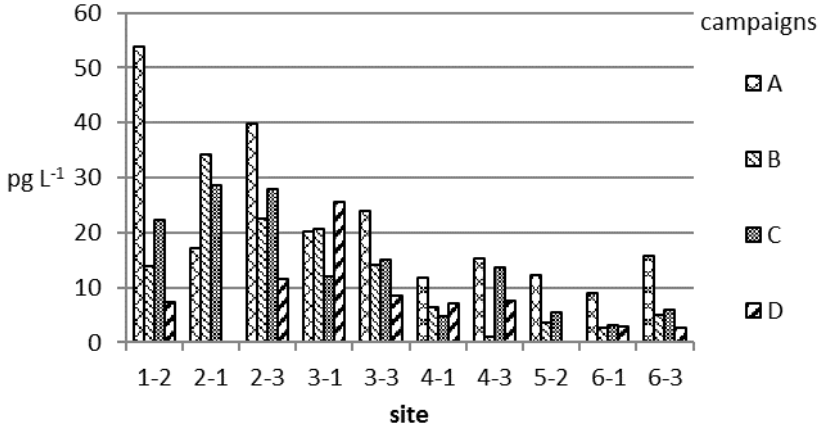

Fig. 3. PCB 11 concentration in each sample for all campaigns (A=June, B=July, C=October, D=November)

3. 2. PBDEs

As seen for PCBs, PBDE concentrations (Fig. 4) in southern samples are higher than the other samples, but this trend is not as evident as for PCBs.

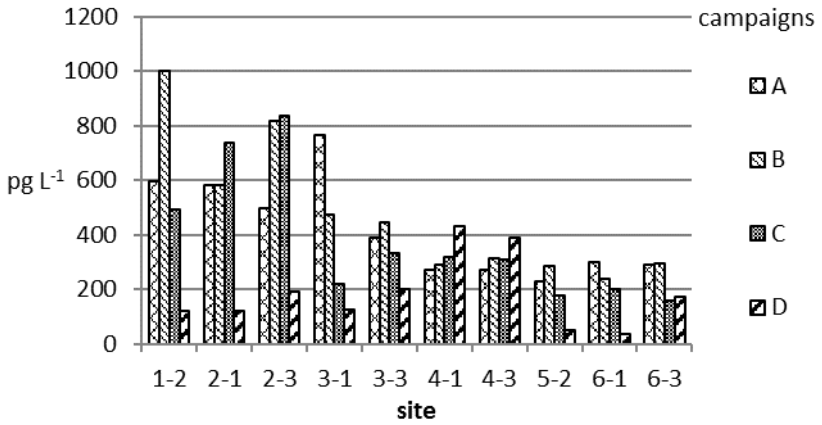

Fig. 4. Total PBDE concentrations in each sample for all campaigns (A=June, B=July, C=October, D=November)

3. 3. PAHs

Regarding PAH concentrations (Fig. 5), the contamination levels found in samples taken during the "D" campaign are much higher than in the other campaigns. Considering the season (Fall) of the "D" campaign, some of this increase may be due to the ignition of the domestic heating systems.

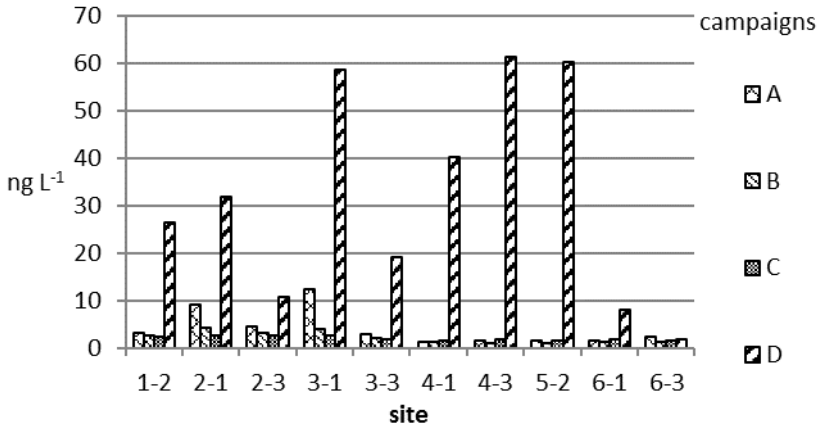

Fig. 5. Total PAH concentrations in each sample for all campaigns (A=June, B=July, C=October, D=November)

3. 4. Legislation

The Italian legislation does not provide concentration limits for PCBs in seawater, so as comparison the values, reported on human health criteria table of national recommended water quality criteria (EPA), were used. In particular, for total PCBs concentration limit should be 64 pg L^{-1}. Most samples analysed exceeded this value.

Italian law concentration limits for PBDEs in sea water should be of 200 pg L^{-1} (environmental quality standard), expressed as annual mean of the sum of congeners PBDE 28, 47, 99, 100, 153 and 154. By the comparison of this value with the results of our analysis (Table 1) most samples largely exceed concentration limits.

Table 1. Average concentrations for the sum of congeners PBDE 28, 47, 99, 100, 153 and 154

Site	Average concentrations (pg L^{-1})
1-2	536
2-1	489
2-3	569
3-1	383
3-3	333
4-1	319
4-3	308
5-2	181
6-1	189
6-3	224

The values reported in Table 1 do not represent a significant annual average concentration because the Italian law requires a higher sampling frequency, but these results could be considered as an alarm signal for the seawater quality.

For what concern PAH concentrations, no violation of maximum concentrations has been detected, both for Italian legislation and EPA guidelines.

4. Conclusions

According to our data the analysed coastal area may be split into two distinct subsystems: the southern one includes the river mouth and the northern one includes the Lagoon harbour mouths. The contamination levels in these two systems were very different. In fact, the northern samples (4-1, 4-3, 5-2, 6-1, 6-3) were much less contaminated than the southern ones (1-2, 2-1, 2-3, 3-1, 3-3), thus the contamination probably moves toward south. The rivers Adige and Brenta strongly affected the seawater quality especially at their mouths but they are less important for the northern part of the study area.

This study shows that these pollutants may represent a risk for the environment, particularly for what concern the PBDE levels; however further studies are needed to better characterize the contamination levels during the whole year in order to fully understand the risk represented by these pollutants in this coastal area.

Moreover, the extension of the study area may be of great help to evaluate the contributions from the north rivers (such as Sile and Tagliamento rivers), and whether the mouths of these rivers may affect the quality of the northern and of the southern coastal areas.

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References

Alaee M., Arias P., Andreas S., Bergman A. (2003). An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. Environment International, 29, 683-689.

Branchi I., Capone F., Alleva E., Costa L.G. (2003). Polybrominated Diphenyl Ethers: Neurobehavioral Effects Following Developmental Exposure. NeuroToxicology, 24, 449-462

Buccini J. (2003). Chapter 2 - The development of a global treaty on persistent organic pollutants (POPs) from: "The handbook of environmental chemistry, vol. 3O. Persistent organic pollutants" Springer-Verlag.

Domingo José L. (2012). Polybrominated diphenyl ethers in food and human dietary exposure: A review of the recent scientific literature. Food and Chemical Toxicology, 50, 238-249.

Erickson M.D. (1997). "Analytical Chemistry of PCBs, 2nd edition" Lewis Publishers.

Guerzoni S., Rossini P., Sarretta A., Raccanelli S., Ferrari G., Molinaroli E. (2007). POPs in the Lagoon of Venice: budgets and pathways. Chemosphere, 67, 1776-1785.

Gumiero B., Maiolini B., Rinaldi M., Surian N., Boz B., Moroni F. (2009). Chapter 12 - The Italian Rivers from: "The Rivers of Europe" Elsevier.

Herbst W., Unger K. (1993). "Industrial Organic Pigments: Production, Properties, Applications" Wiley-VCH.

Malik A., Verma P.,·Singh A.K., Singh K.P. (2011). Distribution of polycyclic aromatic hydrocarbons in water and bed sediments of the Gomti River, India. Environ Monit Assess, 172, 529-545

Manodori L., Gambaro A., Piazza R., Ferrari S., Stortini A.M., Moret I., Capodaglio G. (2006). PCBs and PAHs in sea-surface microlayer and sub-surface water samples of the Venice Lagoon (Italy). Marine Pollution Bulletin, 52, 184-192.

McVeety B.D., Hites R.A. (1988). Atmospheric deposition of Polycyclic Aromatic Hydrocarbons to water surfaces: a mass balance approach. Atmospheric Environment, 22(3), 511-536.

Moret I., Gambaro A., Piazza R., Ferrari S., Manodori L. (2005). Determination of polychlorobiphenyl congeners (PCBs) in the surface water of the Venice lagoon. Marine Pollution Bulletin 50(2), 167-174.

Moret I., Piazza R., Benedetti M., Gambaro A., Paneghetti C., di Domenico A., Miniero R., Cescon P. (2000). Polychlorobiphenyls (PCBs) in surface water of the Venice Lagoon. Organohalogen Compounds 46, 443–446.

Piazza R., Gambaro A., Argiriadis E., Vecchiato M., Zambon S., Cescon P., Barbante C. (2013). Development of a method for simultaneous analysis of PCDDs, PCDFs, PCBs, PBDEs, PCNs and PAHs in Antarctic air. Anal Bioanal Chem, 405, 917-932.

Picer M. (2000). DDTs and PCBs in the Adriatic Sea. Croatica Chemica Acta 73, 123–186.

Poulain P.M. (2001). Adriatic Sea surface circulation as derived from drifter data between 1990 and 1999. Journal of Marine Systems, 29, 3-32.

Rodenburg L.A., Guo J., Du S., Cavallo G.J. (2010). Evidence for Unique and Ubiquitous Environmental Sources of 3,3′-Dichlorobiphenyl (PCB-11). Environ. Sci. Technol., 44, 2816-2821.

Safe S. (2003). Chapter 8 - Toxicology and risk assessment of POPs from: "The handbook of environmental chemistry, vol. 3O. Persistent organic pollutants" Springer-Verlag.

Scheringer M. (2009). Long-range transport of organic chemicals in the environment. Environ Toxicol Chem, 28(4), 677-690.

Schulz D.E., Petrick G., Duinker J.C. (1989). Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. Environmental Science and Technology, 23, 852-859.

Shaw S.D., Blum A., Weber R., Kannan K., Rich D., Lucas D., Koshland C.P., Dobraca D., Hanson S., Birnbaum L.S. (2010). Halogenated flame retardants: do the fire safety benefits justify the risks? Rev. Environ. Health., 25, 261-305.

Simoneit B.R.T.(1984). Organic matter of the troposphere-III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. Atmospheric Environment, 18(1), 51-67.

Tolosa I., Readman J.W., Fowler S.W., Villeneuve J.P., Dachs J., Bayona J.M., Albaiges J. (1997). PCBs in the western Mediterranean. Temporal trends and mass balance assessment. Deep-Sea Research II 44, 907-928.

Van den Berg M., Birnbaum L.S., Denison M., De Vito M., Farland W., Feeley M., Fiedler H., Hakansson H., Hanberg A., Haws L., Rose M., Safe S., Schrenk D., Tohyama C., Tritscher A., Tuomisto J., Tysklind M., Walker N., Peterson R.E. (2006). The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol Sci, 93(2), 223-241.

Yan-Ping D., Xiang-Zhou M., Chao Y., Zhao-Yu P., Ling C., Ran Y., Feng-Ting L. (2010). Polybrominated diphenyl ethers in background surface soils from the Yangtze River Delta (YRD), China: occurrence, sources, and inventory. Environ. Sci. Pollut. Res., 17, 948-956.