Detecting and characterising sources of persistent organic pollutants (PAHs and PCBs) in surface sediments of an industrialized area (harbour of Trieste, northern Adriatic Sea)

Gianpiero Adami, Pierluigi Barbieri, Stefano Piselli, Sergio Predonzani and Edoardo Reisenhofer

aDepartment of Chemical Sciences, University of Trieste, Via Giorgieri 1, 34127 Trieste, Italy
bLaboratory of Marine Biology, Via Piccard 54, 34010 Trieste, Italy

Received 7th February 2000, Accepted 30th March 2000
Published on the Web 3rd May 2000

A sediment sampling based on a two-dimensional mapping was performed in the harbour of Trieste (northern Adriatic Sea), considering 28 sites exposed to pollutant inputs from harbour and industrial activities. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were determined in surface sediments, because these very persistent pollutants seem to be responsible for the depletion of benthic populations observed in this area. The correlation matrix indicates that PAHs and PCBs are non-correlated, and probably have different sources. Both cluster analysis performed on the sampling sites and graphical drawing of the PAH sediment contents make it possible to locate along the shoreline a band of more polluted sediments, clustered around a site facing a steelmaking factory, to be considered as the main source point for PAHs. The evaluation of phenanthrene to anthracene (P/AN) and fluoranthene to pyrene (FL/PY) ratios permits the assessment of the pyrolytic, industrial origin of these PAHs, rejecting a second possible source of hydrocarbons (i.e., an oil-pipeline terminal, situated near the steelmaking factory). Graphical drawing of the total PCB iso-concentrations reveals a different source-point for this other category of very persistent pollutants.

1. Introduction

The present work is part of a study dedicated for several years to the marine ecosystem of the Gulf of Trieste.1–12 This gulf, situated in the northern Adriatic Sea, receives both urban and harbour–industrial contributions from the shore: Muggia Bay, with more than 200 000 inhabitants, is the most densely populated area. The assessment of the quality of its waters and surface sediments has been a concern for evaluating modes and trends of marine pollution. Monitoring chemical–physical parameters in several marine matrices (sea-water, sediments, bioindicator organisms), opportune chosen, supplies the starting material for this evaluation.

The shoreline of Muggia Bay hosts the harbour of Trieste and a large industrial district, in addition to the Trieste–Munich (Bavaria) oil-pipeline terminal. Notwithstanding increased controls, its sea-waters are exposed to many occasional and/or steady inputs of pollutants. The sediments constitute an important repository of persistent chemicals: their pollution has induced in recent years profound alterations and depletion of the benthic populations in the Bay. This situation is favoured by the particular morphology of this area: Muggia Bay is shallow (depth range 8–20 m), and its waters are fairly still, in that they are protected by a three-dam system (see Fig. 1).

The recent worsening of this sea-bottom environment was confirmed by a previous study,4 in which we correlated the heavy metal contents of sediments, sampled in this area along a transect of about 3 km, with biometric parameters of Corbula gibba, a bivalve very resistant to conditions of environmental stress, and therefore it is the unique species present in all sites, also in this compromised sea-bottom.

Persistent organic species have relevance comparable to or higher than that of heavy metals in conditioning the sediment quality; therefore, in parallel work,5 we measured the organic pollutant contents in the same sediments; particular attention was devoted to polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), because these species, as very persistent pollutants, can induce serious alterations to the sea-bottom environment. We found that PAHs and PCBs had concentrations up to two orders of magnitude higher than in sediments sampled also in the Gulf of Trieste but from beyond the dams, in the open sea.

These preliminary studies indicated the shoreline as the main source of pollution. Notwithstanding, the many shipping and industrial activities occurring here suggested the presence of several source-points of wastes. Therefore, we planned a new sediment sampling based not on a linear transect but on a two-dimensional mapping, considering 28 sites facing the industrialised coast of Muggia Bay (see Fig. 1). In this way, we intended to confirm the very high levels of pollution due to PAHs and PCBs formerly observed along the transect, and to check possible different source-points. The PAH analysis was

Fig. 1 Sampling sites in the harbour of Trieste (Muggia Bay); the axes represent Long N and Lat E, measured in degrees.

DOI: 10.1039/b000995o


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performed by GC with flame ionization detection (FID); in previous studies we found that our identification of PAHs by retention times determined with the GC-FID technique was confirmed by the more specific HPLC with fluorimetric detection; GC-FID is suitable for studies of sediments in polluted areas such as the one considered here, where the high sample throughput and reduced analysis costs constitute important features, and low limits of detection are not required.

Moreover, we examined the possibility of extracting from the data matrix the largest amount information about source-points of the monitored pollutants, and of achieving a better understanding of the pattern of pollutant distributions in the different sites. We also attempted to characterise the origin of the PAHs (i.e., pyrolytic or petrogenic–diagenetic). For this purpose, correlation matrix, cluster analysis and graphical output generated by spatial interpolation techniques were used. The analytical results obtained provide information, previously lacking in the literature, about levels and typology of sediment contamination by PAHs and PCBs occurring in this strongly industrialised area of the northern Adriatic.

2. Experimental

2.1. Sampling

Sampling was based on a two-dimensional mapping of about 8 x 3 km, covering 28 sites in the harbour of Trieste (see Fig. 1). Site 11 is missing, because a ship cruising at the same site hindered the sampling operations. Samples were taken in August 1997, using a Van Veen steel grab, which penetrated about 15 cm and collected about 0.1 m³ of surface sediments. All samples were stored at −20 °C in aluminium foil before treatment in the laboratory.

2.2. Reagents

Solvents for elution and/or extraction procedures were purchased from Merck (Darmstadt, Germany). PAH and PCB standards were supplied by Aldrich Chemical (Milwaukee, WI, USA) and Sigma (St. Louis, MO, USA); a standard mixture of PAHs was supplied by Supelco (Bellefonte, PA, USA).

2.3. Sample treatment and extraction

After removing coarse material (> 2 mm), the sediments were freeze-dried at −50 °C and stored in dark bottles. Dry, well-homogenised samples of about 15 g were extracted for 8 h in a cellulose thimble with 15% dichloromethane in hexane-methanol (1+1 v/v). Assays of recovery for the overall procedure were carried out with spiked sediment; for this purpose, hexamethylbenzene (HMB) was added as a quantification standard to sediments before the extraction.

The lipid fraction was eliminated adding 10 g of KOH to the extracted solution and refluxing for 2 h. The hydrolysed solution was then cooled and treated with 100 mL of aqueous NaCl solution (20%). The aqueous phase was extracted three times with hexane and the collected organic phases were dehydrated overnight with anhydrous sodium sulfate. Sulfur present in the sediment was eliminated by passing the sample through an activated copper column. Finally, the sample was fractionated and purified by means of a multilayer column (silica gel, alumina and Florisil) under a mild nitrogen pressure using hexane as eluent. The collected fractions were dried under a slow flow of nitrogen and then dissolved in 0.5 mL of hexane or tetrahydrofuran; octacosane (OCTA) was added as an internal standard before gas chromatographic (GC) analysis.

2.4. GC analysis

The organic pollutants, PAHs and PCBs, were measured by capillary GC using a Perkin-Elmer AutoSystem XL. This two-channel instrument was equipped with FID and electron capture (ECD) detectors, had split–splitless injectors, and programmes for both temperature (PSS) and pneumatic (PPC) controls. A PTE-5 fused silica capillary column (30 m x 0.32 mm id, and 0.25 µm film thickness SE-54 stationary phase) from Supelco was used for both PAH and PCB analyses.

Each PAH was quantified using calibration curves, obtained by dilution of the respective standard, and was identified from its retention time. Chromatograms showing the real sample collected at site 16 and a standard sample containing the 16 PAHs and the two internal standards (HMB and OCTA) are shown in Fig. 2.

Calibration curves were constructed using three standard
solutions; each measurement was performed in triplicate. PAH abbreviations are given in Table 1.

With regard to the PCB analysis, all samples showed chromatograms very similar to that for the Aroclor 1254 standard mixture, with retention times ranging from 11 to 24 min. Therefore, we evaluated their overall concentration [expressed as total PCB (TPCB)] in each sample using a calibration curve obtained by dilution of the above-mentioned standard mixture.31–33

2.5. Evaluation of the analytical procedure

Replicate analyses (n = 7) of various samples of PAHs gave a relative standard deviation (RSD) between 5 and 15% in our working ranges; TPCB had an RSD of 20–30%. The limit of detection was 0.01 μg g⁻¹ for various PAHs and 2 ng g⁻¹ for TPCB. A standard sediment reference material for PAHs (SRM 1941), from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), was used for determining the accuracy of the procedure. All PAHs have an extent of extraction of about 90%, with the exception of the more volatile compounds (i.e., naphthalene and acenaphthylene), for which it can drop to about 60%.

3. Results and discussion

The PAH contents in surface sediments sampled at the 28 sites plotted in Fig. 1 are reported in Table 2, according to their chromatographic retention times: only the 16 PAHs considered for the Aroclor 1254 standard mixture.5,17–19 Table 2 also gives the values of total PAHs (TPAH) and total PCBs (TPCB) as determined in the sediment from each sampled site.

In Table 3 we report the correlation matrix obtained from the 16 individual PAHs, TPAH and TPCB as determined in the sediment from each sampled site.

On the basis of these observations, we decided to treat PAHs and PCBs independently, because their poor correlation indicates that they have different sources. Additionally, we performed a cluster analysis by Ward’s method25 for classifying the 28 sampling sites on the basis of the PAH sediment contents. The similarity dendrogram obtained (see Fig. 3) gives evidence for two clusters and a single, anomalous site, i.e., site 12. One cluster groups the less polluted sites (TPAH < 11.0 μg g⁻¹) and the other hosts the more polluted sites (TPAH > 11.0 μg g⁻¹). It is worth noting that literature data for concentrations of TPAH in sediments of the Mediterranean Sea range between 0.001 and 20.5 μg g⁻¹; the pollution levels can be assigned as high (1.0–5.0 μg g⁻¹) and very high (>5.0 μg g⁻¹).23 Site 12 has the highest TPAH value (64.5 μg g⁻¹); as a consequence, the major source-point of PAH pollution in this area must be found nearby. This site faces a steelmaking factory, but at the same time it lies not far from a second possible source of PAH pollution an oil-pipeline terminal. Therefore, the problem arises of whether the PAHs detected here have industrial or natural (from oil) source.

In deciding about the nature of PAH pollution, we considered the ratios phenanthrene to anthracene (P/AN) and fluoranthene to pyrene (FL/PY), reported in the two last columns of Table 2; these ratios can constitute a very discriminating index for characterising the sediments, making it possible to distinguish between PAHs due to pyrolytic sources and those having petrogenic or diagenetic origin. In our sediments, we found ratios that were generally <10 for P/AN and >1 for FL/PY (see Table 2); these ratio values, as suggested by Baumard et al.,23 strongly support the pyrolytic, i.e., industrial, origin of the PAHs detected here. The activities of the steelmaking factory, involving foundry coke uses, could be the main cause of the diffusion of PAHs in the examined area (uncontrolled pollution events seem to have occurred here, at least in the past: these pollutants are very persistent). On the other hand, the presence of the pipeline terminal should not have implied significant spillage of petroleum here

For detecting the possible source-points of the other category of organic pollutants, PCBs, that we ascertained from the correlation matrix to be non-correlated with PAHs, we have plotted in Fig. 4(a) the iso-concentration curves for TPCB. These curves were obtained by estimating values by linear interpolation,24 weighting the influence of the 28 measured points by considering a decrease that is linear with the distance from the estimated point; computation and plots were produced using the software Surfer 6.04.25 Fig. 4(a) indicates that the sediments more polluted by PCBs are from sites facing the piers in the northern area; in particular, site 26, between piers V and VI, has a TPCB sediment content of 2368 ng g⁻¹; the Italian Directive on sediment disposal (Law 360/91) sets a maximum admissible concentration of 2000 ng g⁻¹ as a limit for TPCB. Also in the Gulf of Trieste, beyond the dam line, TPCB sediment contents not higher than 25 ng g⁻¹ were found.23 Spilling occurrences of these persistent chemicals are evidently non-negligible in this particular area of the harbour of Trieste, which is devoted to shipbuilding, loading and stocking activities. Fig. 4(b) shows

Table 1 PAH abbreviations, molecular weights and boiling points

<table>
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<tr>
<th>No.</th>
<th>Analyte</th>
<th>Abbreviation</th>
<th>MW</th>
<th>Bp/°C</th>
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<tr>
<td>1</td>
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<td>Acenaphthylene</td>
<td>Acl</td>
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<td>340</td>
</tr>
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<td>Anthracene</td>
<td>AN</td>
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<tr>
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<td>Pyrene</td>
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<td>BbP</td>
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the analogous iso-concentration map for TPAH that confirms a different source-point (site 12) for this category of pollutant.

It is worth noting that another area of Muggia Bay potentially suspected of industrial pollution is the south-eastern area (sites 1–9): both a large, recently industrialised area and an oil-refinery district (although no longer active) are situated there. Moreover, these waters are very shallow (5–9 m). Notwithstanding, that we did not find here evidence for critical situations; evidently, the industrial activities here have respected the environment, at least as far as it involves the chemical parameters considered by us.

4. Conclusions

Knowledge of the spatial distribution of persistent chemicals in surface sediments makes it possible to identify source-points of pollution and to characterise them. This information is more precise if the examined seaways are not turbulent, as in our case; indeed, the harbour of Trieste is shallow, closed by three dams, and only a few, small creeks flow into it. The composition of its sediments therefore reflects well the received inputs.

An effective sample treatment and extraction coupled with GC-FID was used for quantifying PAHs in sediments of a polluted area, allowing a high sample throughput with reduced analysis costs.

The correlation matrix indicates that PAHs and PCBs, both being persistent organic pollutants, are non-correlated, and therefore probably have different sources. Both cluster analysis (performed on the sampling sites) and graphical drawing of the PAH sediment contents make it possible to locate along the shoreline a band of highly polluted sediments, clustered around the central site 12, to be considered as the main source-point for PAHs. The evaluation of the PA/N and FL/PY ratios permits the assessment of the pyrolytic, industrial origin of these PAHs, rejecting a second possible source of hydrocarbons (i.e., an oil-pipeline terminal, lying near site 12). Graphical drawing of the TPCB iso-concentration reveals a different source-point, similar results.
located in an area of the harbour devoted to shipbuilding and stocking activities, for this other category of very persistent pollutants.

References