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RELATIVE CONTRIBUTION OF ATMOSPHERIC AND RIVERINE INPUTS OF METALS, NUTRIENTS AND POPs INTO THE LAGOON OF VENICE

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This paper has not been submitted elsewhere in identical or similar form, nor will it be during the first three months after its submission to *Hydrobiologia*.

ABSTRACT

Atmospheric deposition in the lagoon of Venice and river inputs from the watershed were collected and analysed over more than one year (1999-2000) using the same analytical methods. The input from riverine sources largely prevails (>70%) over that from the atmosphere for As, Cr, Fe, Mn, Ni, nitrogen and phosphorus. Equivalent amounts of Hg, Pb, PCB, HCB are discharged into the lagoon from the two sources, whilst atmospheric inputs prevail for Cd, ammonia and dioxins.

A comparison with figures of maximum allowable discharges (MAD) for various compounds, recently set by the Italian Ministry for the Environment, showed that total inputs (riverine + atmospheric) of trace metals were lower than the MAD only for Cr, Cu, Ni and Zn. The total inputs of Cu and Ni, and Cr and Zn were approximately 20% and 40% of the MAD limit, respectively. The total phosphorus input of 284 t was close to the imposed limit, whilst the total inorganic nitrogen load (>4000 t) was much higher than the MAD. For those metals and POPs (As, Cd, Hg, Pb, PCDD/Fs) where the MAD states that the load should tend to “0”(no discharge), the measured inputs of 4.8 (As) and 5.1 t (Pb), 151 (Cd) and 39 kg (Hg), 18 g (PCDD/F) and 440 mg ($TEQ_{PCDD/F}$) are by definition “above” the MAD.

Using principal component analysis (PCA) data have been compared with available input profiles (markers) related to production typologies, both in the watershed and in the industrial zone located on the lagoon border (Porto Marghera). PCA showed that river and atmosphere contributions can be easily separated and recognised due to their different fingerprints. In particular, riverine inputs were more similar to chemical and glass work production markers, whereas atmospheric ones appeared to be mainly influenced by industry (PVC and VCM production), metallurgy and paper-mill.

These results highlight the need to implement improved technologies in order to arrive at a “good ecological status” for all surface and ground water bodies by 2015, as stated by the EU

Water Framework Directive.

INTRODUCTION

The protection of Venice and its lagoon are the subject of an international debate (Gorniz et al., 2000; Bras et al., 2001). Pollution in the lagoon is related to discharge from industrial and urban settlements, as well as agricultural activities in the drainage basin and direct contributions from the inhabited islands. In the last few decades, the role of atmospheric deposition and watershed inputs in environmental deterioration was virtually ignored, and action for safeguarding the lagoon of Venice mainly concerned geomorphological and hydraulic intervention. Managing the input of pollutants is a crucial issue, both for present environmental problems and - even more so - in the case of temporary closure of the lagoon mouths, an event that will limit water circulation and produce negative impacts on the levels of water pollution and on the ecology of the lagoon (Ammerman & McClennen, 2001).

New regulatory action was recently enforced (Ministry for the Environment, 1998; 1999a; 199b), in order to link quality objectives with both maximum allowable loads of pollutants and new quality standards for the treated effluents flowing directly into the lagoon. The regulation refers to a wide range of substances of environmental concern including nutrients, metals, organic and organometallic chemicals. In addition, the implementation of the recent EU Water Framework Directive will put a lot of pressure on Regional and National Authorities to prepare Programmes of Measures by 2006, aimed at ensuring a "good ecological status" for the lagoon by 2015 (WFD, 2000).

With its numerous watercourses, the drainage basin bears the greatest responsibility for polluting the lagoon in terms of many substances. To estimate the overall quantities of pollutants reaching the lagoon, the fluxes of contaminants from the atmosphere must also be taken into account. In this context, two related projects were carried out in the period 1998 – 2000 with the aim of providing a preliminary assessment of the annual load of pollutants which affect the lagoon, and updating information required for environmental risk assessment: (a) the DRAIN project (DeteRmination of pollutAnt INputs from the drainage basin), which focused on the estimate of nutrient and pollutant loads transferred into the lagoon by the rivers and canals draining the catchment area (Zonta et al., in press); (b) the project Orizzonte 2023, designed to estimate the importance of atmospheric transport and deposition of inorganic and organic micropollutants inside the lagoon (Magistrato alle Acque di Venezia, 2000).

The aim of this paper is to provide data about the relative importance of the two contaminant routes into the lagoon, by comparing annual loads during 1999, calculated by a concurrent sampling of 9 river inputs and 4 atmospheric stations (Figure 1). We also tried to shed light on the possible sources by comparing the data with "typology" and "markers" of the prevailing activities in the watershed and in the industrial district, which is located on the lagoon border (Porto Marghera).

FIGURE 1

Past work

Rivers

As far the estimation of pollutant transfer from the drainage basin is concerned, very few investigations in the past dealt with the determination of the discharged load. Two important studies from different periods gave an incomplete estimate of the pollutant load. The first, carried out by Bernardi et al. (1986), produced an estimation of the loads of four total heavy metals (Fe, Cu, Ni, Pb) and of the dissolved species of nitrogen and phosphorus, in the years 1982 – 84.

The second study was part of the Master Plan (i.e. the reference document for remediation actions) drawn up by the Venetian Regional Government (Regione del Veneto, 2000), recently updated. In this study the load of total nitrogen and phosphorus generated in the drainage basin was estimated on the basis of modelling studies.

While knowledge about heavy metals was over 15 years old and the background concerning nutrients was only partial, there was substantially no information about organic micropollutants (especially Persistent Organic Pollutants, POPs) in either the discharged loading and significant sources.

The DRAIN project was the first comprehensive study of the drainage basin-lagoon interaction. It furnished an up-to-date knowledge on the influence of the basin on pollution in the Venice Lagoon, providing an estimate of the annual transfer of fresh water, metals and nutrients, and preliminary information on the load of organic micropollutants.

Among the main outcomes, a spatial differentiation in the average concentration levels was observed for several contaminants, reflecting the distribution of pollution sources in the drainage basin surface and the incidence of the mechanisms of load generation. In particular, the study pointed to the Osellino and Lusore channels (Figure 1) as extreme examples, where the magnitude of the loads are a consequence of the effects of urban and industrial sources respectively.

The role of floods has clearly proven effective in the delivery of contaminants. Due to their higher discharge, the tributaries of the northern basin transfer a significant load to the northern sector of the lagoon during floods. This is particularly true for the species that are mainly associated with the particulate fraction, which undergo a considerable increase of the load (Collavini et al. in press).

Atmosphere

Bertolaccini and Gucci performed an atmospheric pollution survey over a 2-year period, between 1973 and 1977 (Bertolaccini & Gucci, 1985; Bertolaccini & Gucci, 1986). They measured Fe, Mn, Pb, V and Cd contents in the atmospheric aerosol suspended particles collected at three sampling sites in the Venice area: the historical city centre, the industrial area and the urban zone on the mainland. The highest concentrations of Fe, Mn, V and Pb were found on the urban mainland, whereas Cd behaved differently to the other metals, with higher levels in the historical centre.

Since 1993 our group has been conducting studies on total atmospheric deposition using bulk samplers (Guerzoni et al., 1995; Rossini et al., 2001a; Rossini et al., 2003) to investigate the magnitude of atmospheric fall-out of pollutants in the lagoon environment. The acquired data showed inter-annual variability and partitioning of heavy metals; a clear fingerprint of atmospheric deposition of PCDD/Fs related to industrial production was also found (Guerzoni et al., 2004). Atmospheric deposition of trace metals (As, Cd, Cr, Ni, Hg, Pb) was also compared with concentrations in soil samples collected around the industrial district, and the results fit information on “historical” emission trends as recorded in sediments of the lagoon (Scazzola et al., 2004).

MATERIALS AND METHODS

Sampling

Of the approx 30 freshwater inputs for the catchment area, the DRAIN project considered the 12 main tributaries, accounting for about 97% of the total freshwater discharge from the drainage basin. Although the major emphasis was given to metals (Fe, Mn, As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) and nutrients (nitrogen and phosphorus species), organic micropollutants such as dioxins (PCDD/Fs), dioxin-like PCBs and HCB were also included among the analysed species. This made it possible to undertake a baseline investigation on the possible significant contribution of the tributaries freshwater to the overall input of chemicals into the lagoon. The load of PCDD/Fs was estimated for four tributaries (Dese, Osellino, Taglio Nuovissimo, Cuori, Figure 1), accounting for approximately one half (15 m^3/s) of the total annual discharge from the entire drainage basin (35.5 m^3/s). The load for the drainage basin was obtained on the basis of the discharge ratio. Discharge from the monitored tributaries was continuously measured by self-recording current meters (Zuliani et al., in press). For the analytical determinations, the sampling activity was based on the bi-weekly collection of water samples, which was integrated by additional sampling along the vertical profile of the water column and in different flow conditions, including flood events. The pollutant loads were calculated for the year 1999 (Collavini et al., in press), which had average characteristics in terms of total rainfall on the drainage basin and temporal distribution of the events.

In the framework of the project Orizzonte 2023, concurrently with the sampling of river inputs, a subset of 56 atmospheric deposition samples was collected monthly over a one-year period (July 1988 – July 1999) at four sites (A – D, Figure 1). The selected sites were not directly affected by urban or industrial emission sources, according to the classification of the World Meteorological Organization (WMO, 1995), since they are more than 2 km apart. However, some of them could receive inputs from the Industrial Zone of Porto Marghera, due to prevailing winds. In particular, site A was located in the city of Venice, more than 5 km upwind from the discharges of the main industrial district, but still near some possible polluting sources from the glass-making district of Murano. Sites B and C were located in the northern and southernmost ends of the lagoon respectively, 10 km distant from both the

Industrial Zone and the city of Venice, inside two fish farms. The latter are still covered by reed beds and marshes and separated from the rest of the lagoon, both in relatively good environmental condition and without any direct river input. These were considered “remote” sites, receiving principally long-range atmospheric inputs. Site D was located about 5 km downwind (SW) of the Industrial Zone, in an area facing the lagoon. Despite its relative distance from the industrial district, this site can be affected by the atmospheric inputs of Porto Marghera, as it was demonstrated by soil analyses as well (Scazzola et al., 2004).

Atmospheric depositions were collected by 8 bulk samplers similar to those tested by Horstmann and McLachlan (1997) in a rural environment. The samplers were polymer structures, formed by a cylindrical container and a protection ring to avoid damage by birds and animals, clamped to a 60-mm pole. Inorganic micropollutants were collected in a polyethylene bottle with a polyethylene funnel (surface area = 0.066 m^2), placed inside the PVC container (Rossini et al., 2003); a Pyrex bottle with a Pyrex funnel (surface area = 0.043 m^2) treated with dimethyldichlorosilane 5% in toluene was used for organics (Raccanelli et al., 2002).

Analytical work

In riverine samples, heavy metals were analysed for both the total and dissolved concentrations, following the USEPA 6020/94 method. CNR-IRSA (National Research Council of Italy – Water Research Institute) procedures, that correspond to the USEPA methods, were followed for the analysis of the species of nitrogen and phosphorus: ammonia nitrogen, $N\text{-}NH_3$ (Q100/4010/A/94); nitrate nitrogen, $N\text{-}NO_3^-$ (Q100/4020/A2/94); Total Phosphorus, P_{TOT}, and orthophosphate phosphorus, $P\text{-}PO_4^{3-}$ (Q100/4090/94).

Bulk deposition samples were filtered through 0.4-μm diameter Nuclepore© polycarbonate pre-weighed filters. Sampling blanks and laboratory blanks were produced with Milli-Q™

water. Dissolved and particulate metal concentrations were determined by analysing filtered and residual fractions. After dissolution in an acidic mixture, the insoluble fraction was digested in Teflon bottles in a microwave digestion unit. Soluble fractions were also analysed for $N-NO_3^-$, $N-NH_3$ and $P-PO_4^{3-}$. Total phosphorus was determined on total samples following Valderrama (1981). Extraction, clean-up and analytical procedures are extensively described in Rossini et al. (in press).

The following organic compounds were analysed in total atmospheric and riverine samples: PCBs, HCB, PCDD/Fs. Samples were spiked with a series of 15 $^{13}C_{12}$-labelled 2,3,7,8 PCDD/F substituted isomers as internal standards, to deliver 25 pg μL^{-1} in a 10-µL final volume, and then extracted in a separatory-funnel with dichloromethane. The extracts were transferred to hexane before the clean-up treatment. The sample extracts were firstly spiked with $^{37}C_4$-labelled 2,3,7,8 PCDD (EDF6999) and then cleaned up using an automatic system, Dioxin Prep (Fluid Management System Inc.). All solvents (n-hexane, dichloromethane, acetone, toluene, ethylacetate) were Picograde® reagent grade (Pomochem GmbH, Wesel, D). Extraction and clean-up procedures are extensively described in Rossini et al. (2001a).

HRGC/HRMS analyses were conducted using a HP 6890 plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer, operating in EI mode at 35 eV and with a resolution of 10.000 (5% valley). Quantitative determination of PCDD/Fs was performed by an isotope dilution method, using relative response factors previously obtained from 5 standard solution injections (EDF 9999, Cambridge Isotope Laboratories, Woburn, MA), as recommended by the US-EPA (1994). At the beginning of each day of analysis, GC/MS system performance was verified for all PCDD/Fs and labelled compounds with the CS3 calibration verification standard and the isomer specificity test standard. Two $^{13}C_{12}$-labeled PCDD (EDF5999) were added to the extract before injection for recovery calculations. Recovery was always in the range 50-110%. Reproducibility did not exceed 20%.

General characteristics of the drainage basin hydrology

A basic understanding of catchment hydrology is an essential prerequisite in the evaluation of the contaminant delivery. This is particularly true for the drainage basin of the Venice Lagoon, whose morphology has been intensely modified, resulting in a quite complex system that behaves differently from natural catchments. As a part of the extensive monitoring performed within the DRAIN project, an investigation into the hydrology of the system was conducted by Zaggia et al. (2001; 2004). A database of daily rainfall for 39 rain gauge stations distributed across the catchment was developed using data from the bulletins printed by the Italian Hydrological Service (Ufficio Idrografico e Mareografico dei Servizi Tecnici Nazionali, Venice). The database made it possible to compute a time series of daily precipitation on the basin scale, as well as for the single tributary sub-basin, for the period 1921-2000. The statistical analysis of a rainfall time series emphasised the different climatic characteristics of the drainage basin, which result in a non-homogeneous spatial distribution of the rainfall inputs. The area of maximum precipitation, with average values higher than 1000 mm (Figure 2), covers the northern and north-western sectors of the drainage basin. The annual rainfall decreases in the south-eastward direction, determining a zone of minimum precipitation over the southern area, where values lower than 700 mm are found. The analysis also showed that along the coastlines and in the lagoon area as a whole, rainfall propagation is inhibited, focusing on the area of minimum inflow over the lagoon observable in the map of Figure 2. This distribution of the rainfall inputs combines with the peculiar morphology and the variety of aspects connected to the hydraulic management of the catchment, giving rise to a spatially diversified and variable response on the runoff of the different tributaries (Zuliani et al., in press). The comparison of the total annual rainfall depth for 1999 with the long-term averages evaluated for different time intervals within the whole time series for the drainage basin, shows that the total input of 1999 is quite close to the average value for the last 30 years (Figure 2).

FIGURE 2

General anemometry

Table 1 reports wind direction frequencies and mean wind speeds measured during the study period; the prevailing wind directions are highlighted in bold. The main wind direction observed was NE-N, with mean wind speeds of 2-4 m s^{-1}, in agreement with the general anemometry of the area (Carrera et al., 1995). The frequency of winds from the east increases southward, while north directions prevail westward. In particular: i) at site A, located E from the Porto Marghera industrial district (Figure 1), the main wind direction was NE, and the observed frequency of W wind was always <10% for each deposition sample, and ii) at site C, located S of the industrial zone, the percentage of N winds was always <11%, thus confirming that sites A and C were never downwind from the industrial district. On the contrary, site D, located SW of Porto Marghera, received inputs from N-NE for about 40% of wind events (Table 1).

TABLE 1

RESULTS

Load calculations

Rivers

For the calculation of loads from the drainage basin, the sampling strategy adopted within the DRAIN project made it possible for a relatively simple algorithm to be applied for deriving loads (Collavini et al., in press). A large number of samples were, in fact, collected in each tributary and specific sampling were performed during floods. Contemporarily, the significance of the concentration values assumed as characteristic for a certain period was accurately checked.

On this basis, the monitoring period was subdivided into numerous time intervals "i" characterised by a mean concentration C_i and a significantly constant freshwater discharge. The estimate of the load L_i for each interval of Δt_i duration and mean discharge Q_i was obtained by using a simple interpolation:

$$L_i = C_i \; Q_i \; \Delta t_i$$

The annual load was finally calculated by the summation of load values estimated for a number of contiguous intervals covering the year.

Atmosphere

Total annual deposition to the entire lagoon (550 km^2) was calculated by a method in which monthly rain and wind isopleths were combined to normalise monthly deposition values

(Rossini et al., in press). Since it was shown that for many elements bulk deposition is prevailingly affected by wet deposition (Rossini et al., 2001b), atmospheric deposition loads during the study period were calculated using monthly rain isopleths, which were combined to normalise deposition values by means of the equation:

$$\Sigma_i(f_{xi} * a_{xi}) \qquad i = 1 \ldots n$$

where, as above, the index i represents the n contiguous time intervals (months) into which the monitoring period was divided, f_{xi} is the monthly deposition flux estimated at site x for the i^{th} month, and a_{xi} is the area included between isopleths relative to site x during the i^{th} month. The annual riverine and atmospheric loads are shown in Table 2. For PCDD/Fs, the loads are also expressed in terms of the Toxicity Equivalents, TEQs, which are weighted indexes, commonly used to give an estimate of the overall toxicity of a dioxin mixture. Each dioxin congener is assigned a Toxic Equivalency Factor (TEF), indicating its toxicity relative to 2,3,7,8-TCDD, which itself has been assigned a TEF of 1.0. The TEQs for a sample is calculated by multiplying the measured concentration of each PCDD/F congener by the corresponding TEF, and then summing the results.

Table 2

Annual loads of nutrients and major elements ranged from over 3000 t for $N\text{-}NO_3^-$, to ~1000 t for $N\text{-}NH_3$ and Fe, ~300 t for total P and ~80 t for $P\text{-}PO_4^{3-}$. For trace elements, the loads fell to between 39 kg for Hg, 151 kg for Cd, to ~5 t for As, Cr, Ni, Pb, to 35 t for Zn. Organic micropollutants loads were in the range of 18 g for PCDD/F, to ~1 kg for PCBs and ~2 kg for HCB.

The histograms of Figure 3 show the relative contribution of atmosphere and river to the total loads. As revealed by the reported data, the relative importance of riverine and atmospheric loads is characterised by a great variability.

FIGURE 3

Most of metals (Cr, Cu, Fe, Ni and particularly Mn and As) and nutrients ($N\text{-}NO_3^-$, $P\text{-}PO_4^{3-}$ and P_{TOT}) show a prevalent riverine input, with percentages ranging from approximately 70% to 96%. The relative importance of the two inputs was quite similar for Hg, Pb, Zn, and for organic micropollutants (HCB and PCB). A prevailing atmospheric component was instead observed for $N\text{-}NH_3$ and Cd (about 60% of the total), and dioxins (in toxicity equivalents), that show the highest atmospheric origin (>85%).

Multivariate statistics

Principal components analysis (PCA) can be regarded as an ordination technique for reducing data into fewer dimensions. PCA is suitable for finding the directions of maximum variance of the data, using these to ordinate data in one or more dimensions and interpret them as factors influencing the spread of data. The method is well described in Le Maitre (1982) and Swan and Sandilands (1995). PCA is a technique for finding linear compounds of correlated variables, called principal components (PCs), which have two useful properties:

- in general, most of the total variance of the *p* variables in a data set can be accounted for a comparatively small number *k* of the new variables;
- they are uncorrelated, which facilitates examination and analysis of the data.

In this study, PCA was firstly applied to all river and deposition data (monthly loads for the period January – July 1999), except dioxins, which were available only in 4 of the 9 rivers studied.

Two factors were extracted, explaining 81% of variance, and they were sufficient to completely separate riverine from atmospheric inputs, as expected from the previous discussion. Factor 1 (F1) is characterised by Cd, Cr, Cu, Ni, Pb, Zn and PCB, and accounts for 59% of the variance. Factor 2 (F2) is influenced by As, N-NH_3, N-NO_3^- and P-PO_4^{3-}, and represents the variance (22%) due to elements mainly carried by rivers into the lagoon.

In Figure 4, not only we can see a clear separation between riverine and atmospheric samples (upper and lower part of the plot, respectively) along the axis of F2, but a separation between stations along the axis of F1 is also evident, both in atmospheric and riverine samples. Monthly inputs from remote atmospheric stations (B and C) mainly plot on the left side (low values of F1), similar to the rivers located in the southern area of the drainage basin (MO, CU, LO, highlighted in the figure). Those samples indicate lower values for metals and PCBs, in comparison to northern and central river inputs and atmospheric stations in the central lagoon (city of Venice and industrial district).

FIGURE 4

Comparison with maximum allowable discharge (MAD) to the Lagoon of Venice

This section compares atmospheric and riverine annual loads (t y^{-1}) and maximum allowed discharges (MAD) for any source (air, water, solids) for the Venice Lagoon, reported in two documents from the Italian Ministry of the Environment (Ministry of Environment, 1999a,b).

If we compare our input data with the MAD, the total (river + atmosphere) input of trace metals was lower than the MAD only for Cr, Cu, Ni and Zn (Table 3). For Ni and Cu, the fractions derived from atmosphere + rivers is about 20% and 38% of the value reported in the decree, whilst for Cr and Zn it is approximately 45%. Total phosphorus input almost reached the allowed value, whereas dissolved inorganic nitrogen (DIN) load was 1.5 times higher than the MAD. By considering even the nutrient load estimates for the other main sources, especially urban wastewater treatment plants (ASPIV, 2000a,b, Regione del Veneto, 2000), it is clear that the conditions for fulfilling the MAD limits, especially for phosphorus and nitrogen, are far from being achieved.

Finally, for some metals and POPs (As, Cd, Hg, Pb, PCDD/Fs), the MAD indicates that the loads discharged into the lagoon should tend to "0", according to best available technologies. Therefore, the measured inputs of As (4.8 t) and Cd (151 t), Pb (5.1 t) and Hg (39 kg), PCDD/Fs (18 g) and TEQs (0.44 g) represent a major concern, since their loads are by definition "above" the MAD indication. The emission of these compounds into the atmosphere and the watershed should be controlled and drastically reduced as far as possible in the near future.

TABLE 3

Despite the uncertainty associated with the extrapolation of atmospheric deposition to the whole lagoon with only 4 sampling sites, the evaluation performed on the basis of the collected data is the first attempt to compare atmospheric and riverine loads for the lagoon, in order to obtain the necessary information for an integrated management of the river basin and the coastal zone. Clearly, these figures are subject to great variations in relation to inter-annual variability, but controlling the watershed discharge and atmospheric depositions still remains of considerable importance if strict water quality standards for the lagoon of Venice are to be achieved.

Another important point for managing the inputs is the understanding of the potential sources, which is possible through a comparison with "profiles" of discharges relative to the different production activities.

Comparison with markers of production (typology)

Principal components analysis (PCA) has been applied to the monthly data set for all rivers and deposition inputs, expressed in average concentrations instead of loads, to which we have added data derived from a study of the main productions (typologies) of the watershed (Ministry for the Environment, 1999a). These data are the concentrations of trace metals for 13 different production typologies utilised for the calculation of annual loads by the Italian Ministry for the Environment in the year 1998, on the basis of data collected by the Venetian Regional Government. Loads were estimated by multiplying the average concentration of contaminants in the effluents of each typology (Table 4) by the related mean annual discharge obtained from a statistical database. The analyses were referred to less than 20% of the annual discharge, and therefore those figures have to be considered with some caution.

TABLE 4

Two factors were extracted, explaining approximately 65% of the variance. Factor 1 (F1) is characterised by Cd, Pb and Zn, and accounts for 50% of variance. Factor 2 (F2) is influenced by As and Cr, and represents 18% of the variance. In Figure 5, which compares F1 and F2 scores, the different source-related fingerprints are indicated by triangles. From the distribution of the F1 and F2 scores the separation between riverine and atmospheric samples – previously described – is confirmed. Moreover, a close correspondence of two “typologies” (chemical and glass work) with riverine loads is evident, whilst most of the atmospheric samples plot in correspondence of few of the other typologies (paper-mill, textile and metallurgy). The majority of the typologies does not seem to match our samples, and the reason could be the low statistical significance of the monitoring made by the Venetian Regional Government, with data covering less than 20% of the annual river discharge in the catchment area.

FIGURE 5

Dioxin fingerprinting

Atmospheric deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans from the 4 atmospheric sampling sites have already been studied and showed significant differences, with a clear fingerprinting (PCDF>PCDD) in most of the samples collected near the industrial zone (Guerzoni et al., 2004). It is therefore instructive to compare the pattern of PCDD/Fs in river inputs and bulk deposition sampled concurrently at different stations, as this could yield information on the relative transfer of the compounds. Since dioxins were also analysed in 4 of the 9 rivers (OS, DE, TN, CU), a separate PCA was performed by using the homologue profiles, together with profiles of source-related fingerprints. Other authors have applied multivariate analysis to environmental samples collected in the Venice Lagoon. Among them, Fattore et al. (1997) classified sediments samples from the Venice Lagoon and source-related samples from the literature, and Jimenez et al. (1998) compared sediments from the Venice Lagoon to sediments from another Italian lagoon (Orbetello). Both authors found that patterns of samples collected near Porto Marghera and in the central lagoon were very similar to those of sediments affected by the production of ethylene dichloride (EDC) and polyvinyl chloride (PVC), whereas the profiles of most of the other samples were similar to those of sewage sludge, gasoline and diesel engine emissions. Finally, PCA of dioxin and furan patterns in sediments and biota (Wenning et al., 2000) indicated that the composition of PCDD/Fs in sediments was generally different from those in fish and shellfish.

In order to compare deposition profiles of samples collected in this study with those from environmental sources of pollutants, the results obtained by other authors on different kinds of samples were also inserted into the processing, together with data from samples collected in the Venice industrial district (Table 5). In detail, these markers include: (a) “urban" and “rural” aerosol samples (Cole et al., 1999); (b) wastewater derived from PVC production processes (Stringer et al., 1995); (c) solid waste and sludge from production of EDC, VCM and PVC in the USA (Carrol et al., 1996); (d) air samples measured in proximity to 3 municipal solid wastes incinerators (Caserini et al., 2004); (e) lagoon sediments and salt marshes (Marcomini et al., 1997; Bellucci et al., 2000). To these, we added data derived from the direct analysis of wastewater from EDC, sludge from the industrial district of Porto

Marghera (EDC, VCM and PVC production), and wastewater from 2 municipal water treatment plants (Fusina and Campalto, both located on the lagoon border). Unfortunately, no air sample data are available for Porto Marghera.

TABLE 5

Three factors were extracted, accounting for an overall variance of 75%. Factor loadings are listed in Table 6. Factor 1 (30.5%) is characterised by dioxins with low molecular weight, whereas Factor 2 (24.9%) is influenced by octachlorodibenzofuran (OCDF) in the negative sense and by heptachlorodibenzodioxin (HpCDD) and octachlorodibenzodioxin (OCDD) in the positive sense. Factor 3 (19.9%) is influenced by low molecular weight furans.

TABLE 6

Figure 6 compares Factor 2 and Factor 3 scores; the different source-related fingerprints are indicated by triangles. PCA identified 3 main groups of samples, highlighted in the figure, which are related respectively to: (i) urban and rural mixed markers, (ii) incineration and (iii) PVC and VCM production. The left part of the plot shows samples influenced by industrial components, rich in furans; in the right part of the plot, the samples show a gradual decrease of these compounds, approaching profiles related to solid waste incineration and urban air samples.

Riverine and atmospheric inputs are partially combined: most of the river samples are associated with urban and rural markers, and some with incineration. Atmospheric depositions were associated with all of the three typologies, according to the location of sampling sites, as already shown by Guerzoni et al (2004).

FIGURE 6

CONCLUSIONS

The comparison of river inputs and atmospheric deposition allowed us to define their relative importance in the discharge of nutrients, inorganic and organic micropollutants for the Venice Lagoon. Riverine inputs largely prevail (>70%) over the atmospheric ones for As, Cr, Fe, Mn, Ni, nitrogen and phosphorus. Equivalent amounts of Hg, Pb, PCB, HCB are delivered into the lagoon by both sources, whilst atmospheric inputs are dominant for Cd, ammonia and dioxin.

The principal component analysis (PCA) showed a clear separation between riverine and atmospheric loads, and also a separation between stations. Low values for metals and PCBs were detected in remote atmospheric stations and in rivers located in the southern area of the drainage basin.

The comparison of data with maximum allowable discharges (MAD), set by a decree from the Italian Ministry for the Environment, highlighted that most of the examined pollutants are quite close to or higher than the MAD. Among them, As and nutrients will mainly benefit from the control of river water quality, Cd and dioxin mainly from atmospheric emission reduction, whilst Hg and Pb discharges will be reduced by controlling both sources.

PCA was also applied to river and deposition concentrations and compared to production activities (typology, markers) in the watershed and in the industrial zone of Porto Marghera. In spite of the fact that statistics on typologies appeared not strong enough to sustain the unequivocal attribution of respective fingerprints to atmospheric and riverine contributions, most of the rivers appear to show the fingerprint of chemical (industrial and pharmaceutical) and glass work activities, whereas atmospheric depositions are a combination of the others, with a prevalence of paper-mill, metallurgy and plastic production. By considering dioxin fingerprinting as well, river samples were associated with urban and rural markers, and some with incineration, whilst atmospheric depositions were associated with all of the three typologies.

All the results identified a reduction of the nutrients, some trace metals (As, Cd, Hg, Pb) and dioxin delivery as the main target of actions for the improvement of environmental quality in the lagoon. Nevertheless, an effective control of pollution in the lagoon ecosystem deserves a more detailed knowledge of the characteristics of pollutant sources, as well as of the spatial and temporal variability of the delivered load. This should be done by the implementation of the EU WFD, which will push Regional and National Authorities to prepare Programmes of Measures (by 2006) in order to guarantee the quality of the lagoon waters and catchment area.

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CAPTIONS OF FIGURES

Figure 1. Watershed with sampling sites from riverine (Silone, Dese, Osellino, Lusore, Naviglio Brenta, Taglio Nuovissimo, Lova, Montalbano, Cuori) and atmospheric sources (A, B, C, D).

Figure 2. Hysoiet map of the mean annual rainfall depth for the drainage basin (left), for the period 1921-2000. The squares indicate the 39 rain gauge stations. On the right, comparison between mean annual rainfall evaluated over long-term periods and the 1999 value for the drainage basin.

Figure 3. Relative contribution of riverine and atmospheric load to the whole lagoon basin (above = trace metals; below = nutrients and organics)

Figure 4. Plot of all the monthly samples in the space of Factor 1 and Factor 2. Empty squares: atmospheric samples (A-D), full circles: riverine samples (Silone=SI, Dese=DE, Osellino=OS, Lusore=LU, Naviglio Brenta=NB, Taglio Nuovissimo=TN, Lova=LO, Montalbano=MO, Cuori=CU). The ellipse encompasses the majority of samples from the southern area of the drainage basin (MO, CU, LO), which are characterised by low values of Factor 1.

Figure 5. Plot of all the samples (empty squares: atmospheric, empty circles: riverine samples) in the space of factor 1 and 2. Triangles represent the different “typologies” of the productions (see Table 4).

Figure 6. Plot of all the atmospheric samples (empty squares) and four rivers (empty circles) in the space of F2 and F3. The triangles represent the different "markers" (see Table 5).

CAPTIONS OF TABLES

Table1. Wind directions and speeds during study period. Numbers in bold correspond to maximum values. Mws = mean wind speed.

	Site A	**Site B**	**Site C**	**Site D**
N	20.3	18.3	10.1	**22.0**
NE	**21.3**	**18.7**	13.2	17.5
E	5.7	10.7	**18.2**	10.4
SE	11.1	11.9	8.1	15.0
S	9.3	13.1	1.9	8.3
SW	7.7	3.2	5.2	5.0
W	3.6	3.5	4.6	6.0
NW	2.5	8.3	9.9	10.1
<1ms-1	18.5	12.3	28.8	5.7
Mws ms-1	2.1	2.3	2.0	3.9

Table 2. Annual riverine and atmospheric loads measured by the Orizzonte 2023 and DRAIN projects.

	As *(t)*	Cd *(kg)*	Cr *(t)*	Cu *(t)*	Fe *(t)*	Hg *(kg)*	Mn *(t)*	Ni *(t)*	Pb *(t)*	Zn *(t)*
rivers	4.6	63	3.5	6.6	958	24	61	3.9	3.0	18
atmosphere	0.2	88	0.7	2.6	112	15	3	1.2	2.1	18
total	4.8	151	4.2	9.2	1070	39	64	5.1	5.1	36

	N-NH3 *(t)*	N-NO3- *(t)*	DIN *(t)*	P-PO43- *(t)*	P TOT *(t)*		ΣPCBs *(g)*	HCB *(g)*	ΣPCDD/Fs *(g)*	TEQs *(g)*
rivers	480	2634	3114	65	229		449	924	7	0.06

atmosphere	670	702	1372	13	55		522	1125	11	0.38
total	1150	3336	4486	78	284		971	2049	18	0.44

Table 3. Comparison between estimate of total (riverine + atmospheric) discharge and MAD (Maximum allowable discharge, Ministry of Environment, 1999a).

		rivers	atmosphere	total	MAD
As	*(t)*	4.6	0.2	4.8	$0^{\#}$
Cd	*(kg)*	63	88	151	$0^{\#}$
Cr	*(t)*	3.5	0.7	4.2	9.7
Hg	*(kg)*	24	15	39	$0^{\#}$
Ni	*(t)*	3.9	1.2	5.0	25.2
Pb	*(t)*	3.0	2.1	5.1	$0^{\#}$
Cu	*(t)*	6.6	2.6	9.1	23.9
Zn	*(t)*	18	18	36	80
DIN	*(t)*	3114	1372	4486	3000
P TOT	*(t)*	229	55	284	300
ΣPCDD/Fs	*(g)*	6.9	11.0	17.9	$0^{\#}$
TEQs	*(g)*	0.06	0.38	0.44	$0^{\#}$

(#) The Maximum allowable discharge should tend to 0

Table 4. Average concentration of contaminants in the effluents of each typology of production, as reported by the Ministry for the Environment, 1999a.

	As *(µg/l)*	Cd *(µg/l)*	Cr *(µg/l)*	Cu *(µg/l)*	Hg *(µg/l)*	Ni *(µg/l)*	Pb *(µg/l)*	Zn *(µg/l)*
car-washing	1.0	0.98	2.9	7.8	0.98	7.8	11.8	145
galvanic	1.3	0.47	376	11.6	1.02	231	4.5	130
chemical	5.0	0.50	3.0	4.0	1.00	3.0	1.0	8.1
food-stuff	3.6	0.91	7.5	18.2	1.82	5.2	7.0	116
plastic	8.7	0.00	2.9	5.8	1.45	4.3	1.4	39
typography	2.2	0.73	7.3	18.3	0.73	3.7	5.1	217
metallurgy	1.0	0.48	5.7	6.6	0.97	4.9	3.8	91
fish farming	1.0	0.50	1.0	1.0	1.00	1.0	0.5	1.1
textile	1.2	0.40	5.5	9.5	1.01	1.2	2.0	58
abattoirs	5.8	0.41	4.1	3.5	1.03	3.9	0.8	40
paper-mill	3.0	0.50	4.0	1.0	1.00	5.0	0.5	130

concrete	1.9	0.45	2.4	1.0	1.04	2.8	2.7	12
glass	128	0.63	2.2	8.5	0.95	0.9	1.6	5.4

Table 5. Source-related samples used for PCA. EDC, ethylene dichloride; VCM, vinyl chloride monomer; PVC, polyvinyl chloride.

Code	Source-related samples	Type	Reference
URB	Urban air	Air	Cole et al., 1999
RUR	Rural air	Air	Cole et al., 1999
MSWI-lo1	Municipal solid wastes incineration plant	Air	Caserini et al., 2004
MSWI-lo2	Municipal solid wastes incineration plant	Air	Caserini et al., 2004
MSWI-hi	Municipal solid wastes incineration plant	Air	Caserini et al., 2004
PU4043	Heavy ends from distillation of VCM	Liquid waste	Stringer et al., 1995
RS1	EDC, VCM, PVC production	Solid waste	Carroll et al., 1996
RS2	EDC/VCM production	Sludge	Carroll et al., 1996
M1/M2/E1/E14	Urban and industrial pollution	Sediment / salt marsh	Bellucci et al., 2000
GR	Urban and industrial pollution	Sediment	Marcomini et al., 1997
EDC/VCM	Local EDC and VCM production	Wastewater	This study
CL	Local EDC/VCM production	Sludge	This study
FC	Domestic water treatment plants	Wastewater	This study

Table 6. Factor loadings of the PCA performed on dioxin fingerprint.

	Factor 1	Factor 2	Factor 3
TCDD	**0.92**	-0.06	-0.02
PCDD	**0.91**	0.02	0.04
HCDD	**0.88**	0.05	0.19
HpCDD	0.13	**0.81**	0.18
OCDD	-0.18	**0.86**	-0.36
TCDF	-0.02	0.11	**0.71**
PCDF	0.12	0.32	**0.72**
HCDF	0.14	0.01	**0.92**
HpCDF	0.02	-0.38	0.61
OCDF	-0.01	**-0.91**	-0.28

Expl.Var	*30.5*	*24.9*	*19.9*
Cumulat.	*30.5*	*55.4*	*75.3*

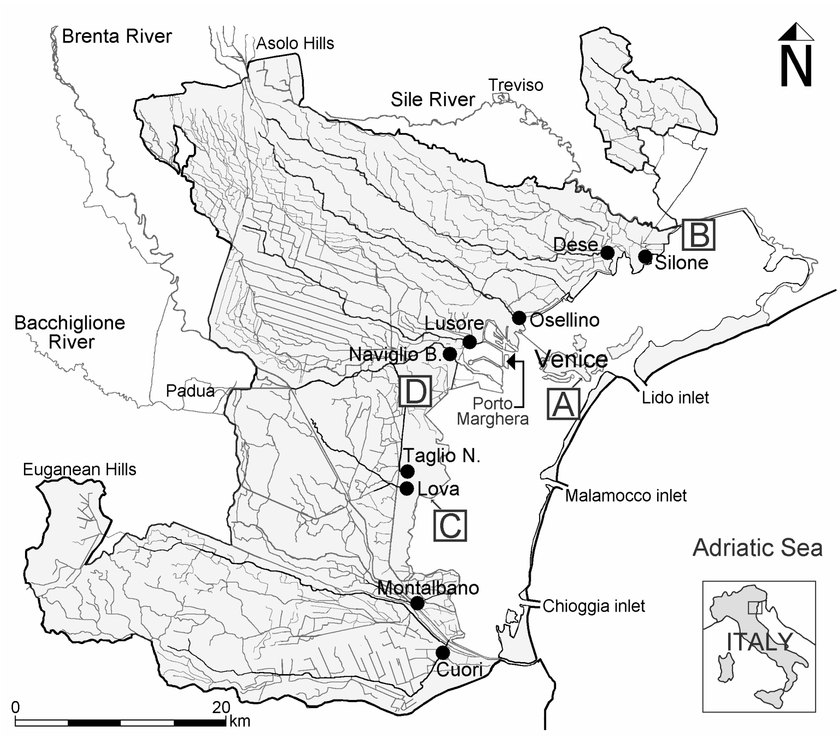

Brenta River
Asolo Hills
Sile River
Treviso
N
B
Dese
Silone
Bacchiglione River
Lusore
Osellino
Naviglio B.
Venice
Padua
D
Porto Marghera
A
Lido inlet
Euganean Hills
Taglio N.
Lova
C
Malamocco inlet
Adriatic Sea
Montalbano
Chioggia inlet
ITALY
Cuori
0
20
km

FIG. 1

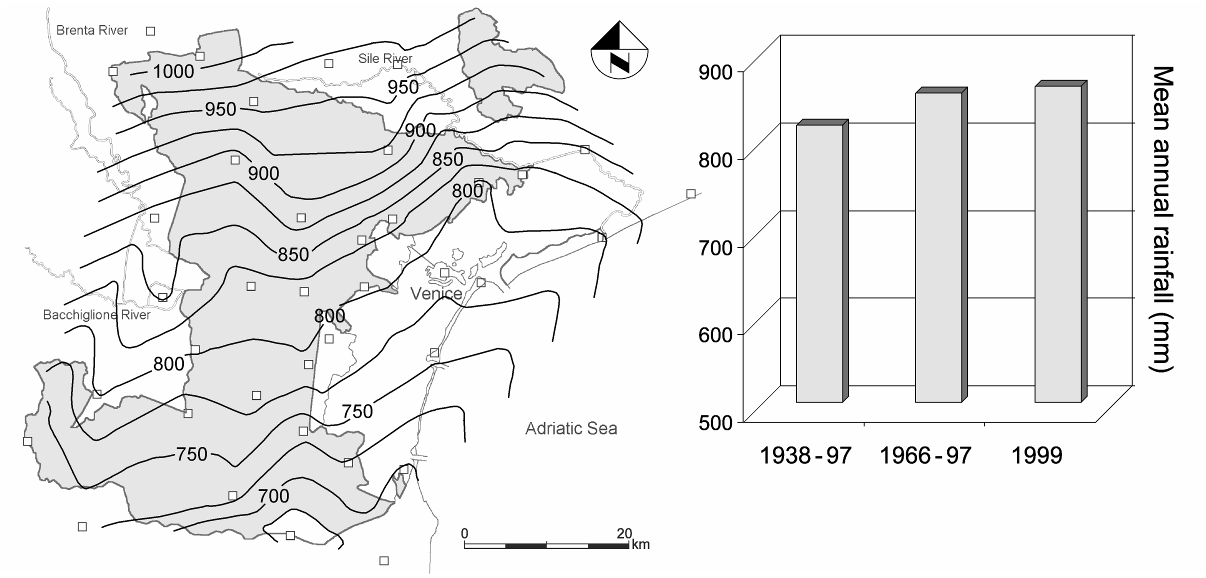
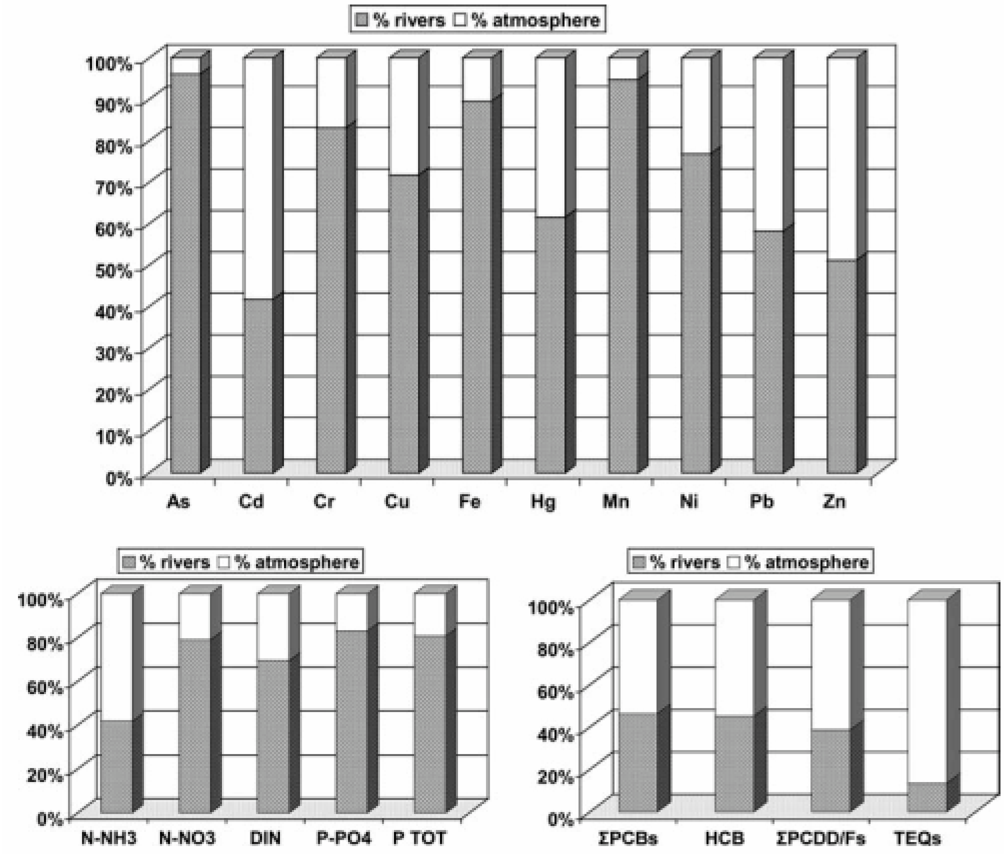
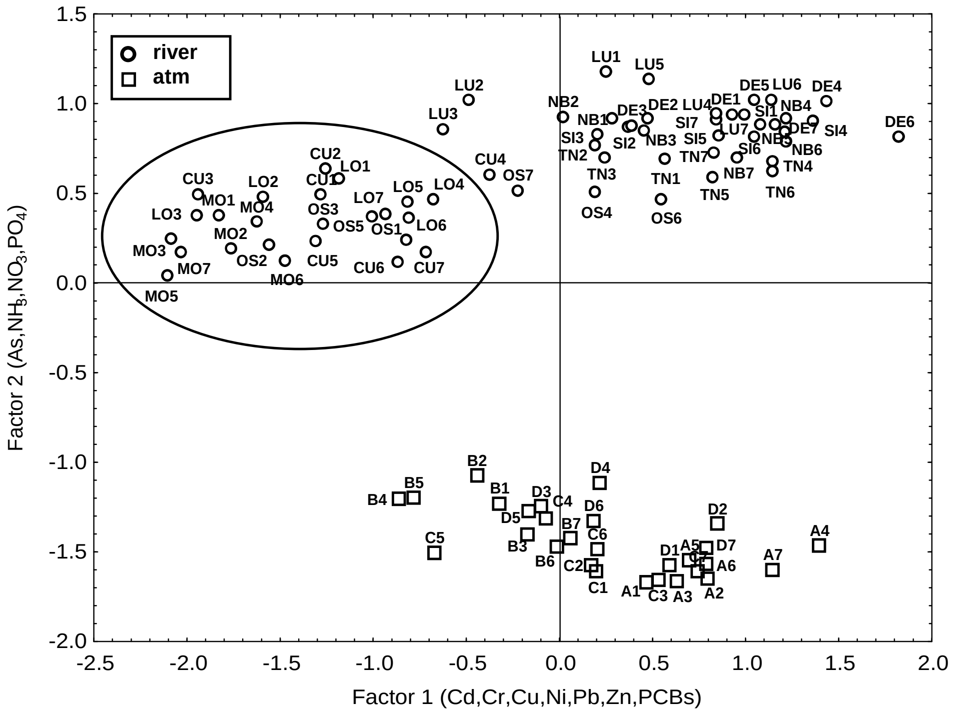

Brenta River
Sile River
1000
950
900
850
800
Venice
Bacchiglione River
750
700
Adriatic Sea
0
20
km
900
800
700
600
500
1938 - 97
1966 - 97
1999
Mean annual rainfall (mm)

FIG. 2



% rivers □ % atmosphere
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Cd
Cr
Cu
Fe
Hg
Mn
Ni
Pb
Zn
% rivers □ % atmosphere
100%
80%
60%
40%
20%
0%
N-NH3
N-NO3
DIN
P-PO4
P TOT
% rivers □ % atmosphere
100%
80%
60%
40%
20%
0%
ΣPCBs
HCB
ΣPCDD/Fs
TEQs

FIG. 3



river
atm
Factor 2 (As,NH3,NO3,PO4)
Factor 1 (Cd,Cr,Cu,Ni,Pb,Zn,PCBs)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

FIG. 4

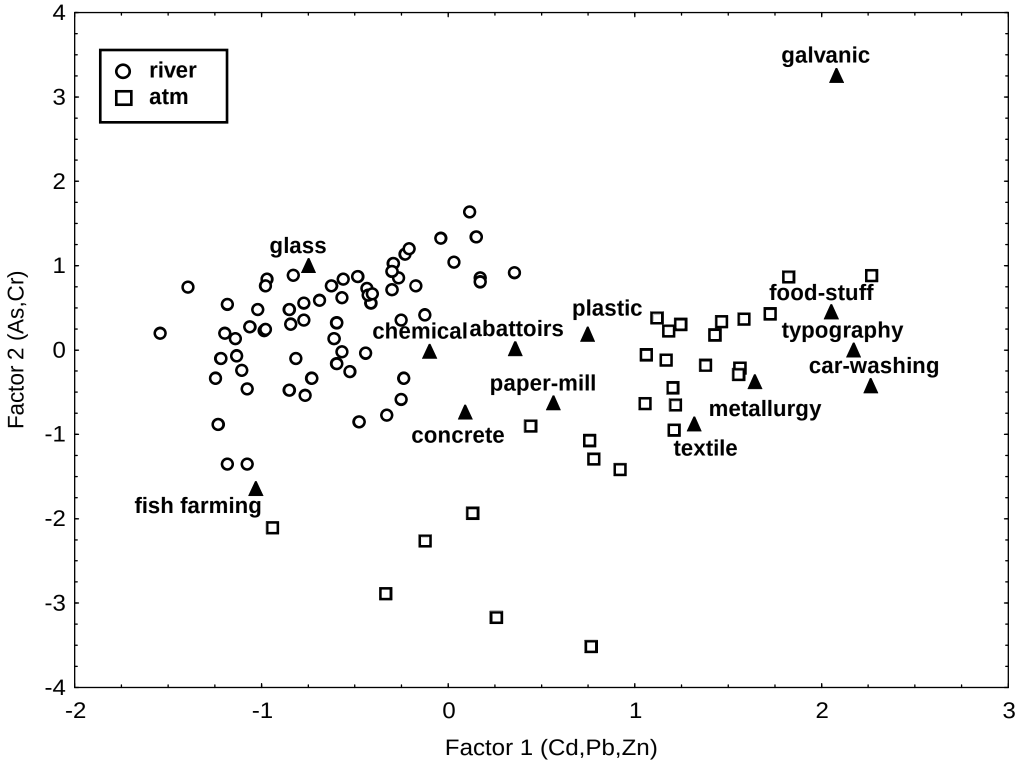

river
atm
galvanic
glass
food-stuff
plastic
chemical
abattoirs
typography
car-washing
paper-mill
metallurgy
concrete
textile
fish farming
Factor 2 (As,Cr)
Factor 1 (Cd,Pb,Zn)
4
3
2
1
0
-1
-2
-3
-4
-2
-1
0
1
2
3

FIG. 5

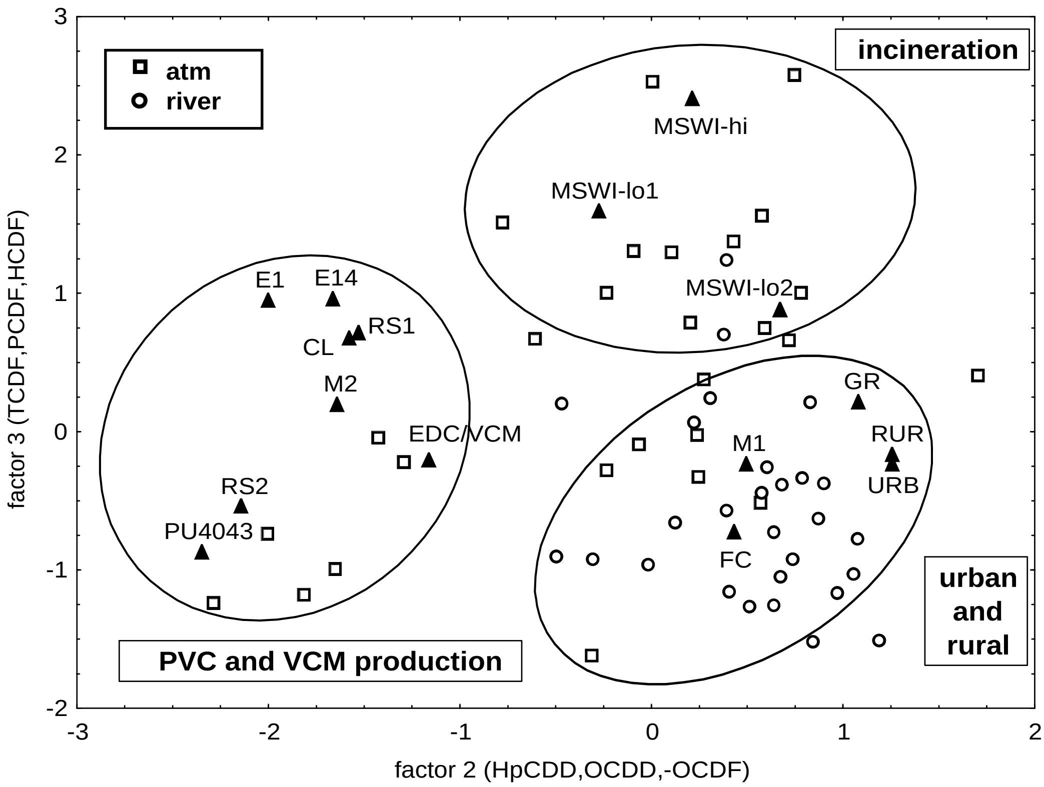

atm
river
incineration
MSWI-hi
MSWI-lo1
MSWI-lo2
E1
E14
RS1
CL
M2
EDC/VCM
RS2
PU4043
GR
RUR
URB
M1
FC
urban
and
rural
PVC and VCM production
factor 3 (TCDF,PCDF,HCDF)
factor 2 (HpCDD,OCDD,-OCDF)
3
2
1
0
-1
-2
-3
-2
-1
0
1
2

FIG. 6