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ATMOSPHERIC BULK DEPOSITION TO THE LAGOON OF VENICE: PART I, FLUXES OF METALS, NUTRIENTS AND ORGANIC CONTAMINANTS.

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Abstract

First available data on atmospheric fall-out were provided by sampling monthly bulk depositions in four sites inside the Lagoon of Venice (550 km²). Sampling was carried out monthly during the period July 1998 – July 1999, in one site near an industrial area (Porto Marghera; site D), another site in the city of Venice (site A), and the remaining two in the southern- and northernmost ends of the Lagoon (Valle Figheri, site C; Valle Dogà site B).

The following determinations were carried out for each samples: pH, conductivity, grain-size, particulate load, and dissolved nutrients (N, P). Samples were then subdivided into soluble

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and insoluble fractions, and Al, Ca, Na, K, Mg, Si, Mn, Fe, Zn, Ni, Cr, Cu, Pb, Cd, As, Hg, Ti, V, S, P, Se and Sb were analysed on both fractions. Total organic micropollutants (PAH, PCB, HCB, DDT, PCDD/F) were measured.

As regards particle size distribution, there was great variability among sampling sites. The percentage of the $\leq 2 \mu\text{m}$ grain-size fraction was higher in the southern and northern ends of the Lagoon.

Small differences were found among sites for major elements, whereas higher variability was observed for inorganic and organic micropollutants, with standard deviations between 20 and 60% of the fluxes measured. Major differences in annual fluxes between the most polluted sites (mostly D and A) and background (site B) were seen for Cd, (0.26 vs. 0.06 $\text{mg m}^{-2}\text{yr}^{-1}$), Hg (41 vs. 15 $\mu\text{g m}^{-2}\text{yr}^{-1}$), PCB (~ 2500 vs. ~ 500 $\text{ng m}^{-2}\text{yr}^{-1}$) and HCB (~ 8000 vs. ~ 1000 $\text{ng m}^{-2}\text{yr}^{-1}$). Comparisons with previous data, collected in the periods 1993-94 and 1995-97, were only available for a few trace metals. A definite decline in the annual Pb flux in the city of Venice was detected, from 18 to 13 mg m^{-2} in 1996/97 and 1995/96 respectively, to ~ 5 mg m^{-2} in the present study.

Total annual deposition was calculated by means of two different methods, which gave very similar results: (i) the mean value of deposition in the four sites was multiplied by lagoon area (550 km^2); (ii) the monthly rain isopleths were combined to normalize deposition values. The figures are: 15-34 kg of Hg and Sb, ~ 200 kg of As, ~ 100 kg of Cd and PAH, 0.7 to 1.3 tons of Cr, Ni and V, more than 2 tons of Cu and Pb, 17 of Zn, 55 of total P, ~ 200 of Al, and 3900 of DIN.

Total fluxes of organics inside the lagoon were: PAH ~ 100 kg; HCB ~ 1 kg; DDT ~ 0.4 kg. PCB and PCDD/F fluxes were ~ 500 g and ~ 10 g, corresponding respectively to 0.1 and 0.4 g I-TE.

The correlations between fluxes of inorganic micropollutants and grain-size were significant. Multivariate statistical analysis was applied to investigate more accurately relationships between the insoluble and dissolved fractions of inorganic micropollutants and grain-size fractions. In particular, significant correlations were highlighted between the dissolved fraction of As and the $\leq 1 \mu\text{m}$ particle size fraction. Relations between levels of ΣPCDDF , ΣPCDD , PCB and PAH congeners and grain-size revealed significant correlation coefficients for the remote sites (B, C), and none in the urban and industrial sites (A, D). In particular, significant correlations were highlighted between ΣPCDDF , ΣPCDD and particle size fraction $\leq 2 \mu\text{m}$, and between benzo(a)pyrene and PCB 167 and particle size fraction 4-8 μm .

Introduction

In the last few decades, it has been demonstrated that the atmosphere is a significant pathway for the transport of many natural and polluting materials from continents to oceans. Therefore, actions aimed at safeguarding the Lagoon of Venice have mainly been addressed to geomorphological and hydraulic interventions, almost completely neglecting the contribution of atmospheric deposition to the decrease in environmental quality.

Some atmospheric pollution surveys were conducted by Bertolaccini and Gucci (1985, 1986), who measured Fe, Mn, Pb, V and Cd contents in atmospheric aerosol suspended particulate collected at three sampling sites in the Venice area over a 2-year period between 1973 and 1977. Other works were undertaken on a regional scale in order to assess the quality of rain (Zilio Grandi and Szpyrkowicz, 1991a, 1991b).

Many studies have also focused on the presence of PCDD/F and other organic chlorinated compounds in bottom sediments and aquatic biota in the Lagoon. Sources of contamination

are often discharges from the industrial zone of Porto Marghera, untreated domestic sewage from the historical city of Venice, and emissions from motorboats and traffic in the nearby mainland town of Mestre (Di Domenico et al., 1997; Fattore et al., 1997; Marcomini et al., 1997; Wenning et al., 2000). Preliminary available data on atmospheric dioxin fall-out came from bulk deposition sampling (Rossini et al., 2001; Guerzoni et al., in press), and a dioxin budget showed that atmospheric deposition accounted for one-quarter of the total load in the Lagoon (Marcomini et al., 1999). Data on soils collected around the industrial zone suggested an airborne PCDD/F fall-out effect up to several km downwind (Della Sala et al., 1999).

This paper presents a compilation of data on atmospheric fall-out, provided by sampling monthly bulk depositions in four sites inside the Lagoon of Venice (550 km²) for one year. The purpose of this study was to estimate the importance of atmospheric transport and deposition of inorganic and organic micropollutants inside the Lagoon, in order to provide a comparison with other sources (e.g., inputs from rivers) and updated information useful for environmental risk assessment.

Materials and methods

Sampling

A total of 96 deposition samples was collected monthly over a 13-month period (July 1998 – July 1999) in one site near an industrial area (Porto Marghera; site D), one in the city of Venice (site A), and two in the more remote southern (site C) and northern (site B) ends of the Lagoon (Fig. 1). Selected sites were not directly affected by urban or industrial emission sources, according to the criteria of the World Meteorological Organization (WMO, 1995). Site A was located inside the city of Venice, upwind from the main industrial zone inputs, but

still near some possible polluting sources from the glass-making district of Murano. Sites B and C were located inside two fishing areas, still covered by reed beds and marshes and separated from the rest of the Lagoon, in relatively good environmental condition, without any direct river input. These were considered “remote” sites, receiving principally atmospheric inputs, far from large industrial and urban sources. Site D was the nearest to the industrial zone of Porto Marghera, some 5 km downwind (SW), facing the Lagoon. Table 1 lists the geographical coordinates of sampling sites.

Table 1. Geographical coordinates of sampling sites. Datum=WGS84.

Fig. 1. Location of atmospheric deposition sampling sites. (A=city of Venice; B=Valle Dogà; C=Valle Figheri; D=Dogaletto). Large circle encloses industrial area of Porto Marghera.

Atmospheric depositions were collected by 8 bulk samplers similar to those tested by Horstmann and McLachlan (1997) in a rural environment (Fig. 2). The samplers were polymer structures, formed of a cylindrical container and a protection ring to avoid damage by birds and other animals, clamped to a 60-mm pole. Inorganic micropollutants were collected in a polyethylene bottle with a polyethylene funnel (surface area = 0.066 m²), placed inside the PVC container; a Pyrex bottle with a Pyrex funnel treated with dimethyldichlorosilane 5% in toluene (surface area = 0.043 m²) was used for organics (Raccanelli et al., 2002).

Bulk sampling was extensively used, since the samplers are easier to operate than wet-and-dry ones, and can also be located at sites with no electrical power supply. Horstmann and McLachlan (1997) recently found that parallel bulk sampling reproducibility is lower than 10% in more than 80% of cases and lower than 20% in 99% of cases, and also that the diffusive fraction is small with respect to total deposition. The limitation of this sampling method is mainly possible under-estimation of fluxes, because of the limited collection of dry

gases which, according to Schröder et al. (1997), are less important for PCDD/F. Advantages are integration of samples over one month and the possibility of large-scale application with low-cost equipment.

Fig. 2. Bulk deposition samplers (modified from Bergerhoff[®]) used in the field. Left: Pyrex[®] unit for organic micropollutants; right: polyethylene unit for inorganics.

Analytical methods

Physical-chemical parameters (pH, conductivity) were measured on samples immediately after collection. Subsamples for mineralogical and grain-size analyses were then taken, and the rest of the solution was filtered through 0.4 µm diameter Nuclepore[®] polycarbonate pre-weighed filters. A Millipore[®] Sterifil unit was used, equipped with a pre-filter on the cover, to avoid contamination with ambient air. In order to obtain total particulate concentrations, the insoluble fraction was dried in a dry-box and re-weighed. Sampling blanks were collected by washing the polyethylene funnel of the sampler with 500 mL of Milli-Q[™] water (DDW); laboratory blanks were also produced with DDW. The resulting solutions were then treated and analysed following the same procedures used for other samples.

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. Filters were weighed and dissolved in Teflon bottles with a microwave digestion unit (Milestone MLS 1200), after addition of 1 mL DDW, 7 mL of 65% HNO₃, 1.5 mL of 30% H₂O₂ and 1 mL of 40% HF. A clean filter was also dissolved for use as a blank. Digested solutions were made up to 50 mL into teflon volumetric flasks. Soluble and insoluble fractions were analysed for major (Si, Al, Ca, Mg, K, Na, Fe)

and trace elements (Zn, Ni, Cr, Cu, Pb, Cd, As, Hg, Ti, V, S, P, Se, Sb) by AAS + ICP mass spectrometry. Soluble fractions were also analysed for Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ and PO_4^{3-} .

All manipulations were conducted in a clean room equipped with a laminar flow bench.

The following organic compounds were analysed on total atmospheric samples: PAH, PCB, HCB, DDT, PCDD/F. Samples were spiked with a series of 15 $^{13}\text{C}_{12}$ -labeled 2,3,7,8 PCDD/F substituted isomers as internal standards, to deliver $25 \text{ pg } \mu\text{L}^{-1}$ in a $10\text{-}\mu\text{L}$ final volume, and then extracted in a separatory funnel with dichloromethane. The extracts were transferred to hexane before clean-up treatment. Sample extracts were first spiked with $^{37}\text{Cl}_4$ -labeled 2,3,7,8 PCDD (EDF6999), and then cleaned 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, Germany). Extraction and clean-up procedures are extensively described in Rossini et al. (2001).

HRGC/HRMS analyses were conducted using an HP 6890 + gas chromatograph coupled with 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/F 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/F and labeled compounds by CS3 calibration verification and isomer specificity test standards. Two $^{13}\text{C}_{12}$ -labeled PCDD (EDF5999) were added to the extracts before injections for recovery calculations. Recovery was always in the range 50-110%. Reproducibility did not exceed 20%.

The size distribution of insoluble particles was analysed by the Galai Cis 1 technique (2×10^4 to 3×10^5 counts). The principle of the device is based on a rotating laser and on the relationship between the transition time of particles moving in a photodefined zone, and their

size. A focused laser beam scans an area of 600 μm diameter with a beam size of 1.2 μm ; when a particle is detected, a photodiode produces a signal proportional to the size of the particle. The Galai system has already been used to analyse aerosol particles, to distinguish desert-dominated from European background samples (Molinaroli et al., 1993, 1995; De Falco and Molinaroli, 1996).

Meteorological data

In order to characterize rain and wind regimes during the study period, data from already existing weather stations were used, kindly made available by the Information Service of the Venice Water Management Authority, Porto Marghera Industrial Zone authority, Servizio Idrografico e Mareografico Nazionale, and by the weather station managed by the Istituto di Scienze Marine of the Italian Research Council.

Results and discussion

Meteorology

During the study period, the main wind direction observed was N NE, with mean wind speeds of 2-4 m s^{-1} , in agreement with the general anemometry of the area (Table 2, Fig. 3). In particular, the main wind direction in site A was NE, and the observed frequency of W winds was always <10% for each deposition sample. Moreover, the percentage of N winds at site C was always <10%, thus confirming that these sites were never downwind from the industrial zone (located NW of site A and N of site C).

Table. 2 Wind directions and speeds during study period. Bold numbers=maximum values. Mws=mean wind speed.

Fig. 3. Mean wind directions and speeds from 1951 to 1990 at Venice (after Carrera et al., 1995).

As shown in Figure 4, the amount of rain recorded during the study period fell in the variability range known for the area (Fig. 4). This means that the sampling period may be considered representative of deposition conditions in the area.

Fig. 4. Amount of rain during study period, compared with local time series data. Bars: minimum and maximum values.

In general, bulk samplers are similar to rain gauges, and Figure 5 compares rain collected by them with data from the rain gauge in the vicinity. Recovery rates were very good.

Fig. 5. Comparison of rain recovered during study period by bulk sampler with measurements of rain gauge at site A.

Based on the amount of rain collected, 8 samples were identified as “dry” samples (rain <10 mm), corresponding to sampling periods with prevailing dry deposition conditions; all the other samples (N=44) are called “wet” samples.

Particle size distributions and TSP

Aerosol samples mainly consist of a clay fraction with unimodal, bimodal and slightly trimodal distributions. Grain-size analysis highlighted the variability among the sampling sites. In site A, bimodal distribution prevailed, with the finer mode centered at 1.0-1.5 μm particles and the second one at 5.5-8.0 μm . Site B contained samples with both bimodal and trimodal distributions, showing the same particle size distribution as in site A. Site C contained samples with bimodal and unimodal distributions. The size distribution at this site

shifted towards the finest particles. Unimodal samples showed a maximum at 5.5 μm . Bimodal distribution prevailed in site D, with some trimodal distribution showing the same characteristic trend as site A.

In particular, differences between sites A and D on one hand and sites B and C on the other were clear for grain-size fractions $\leq 2\mu\text{m}$, 4-8 μm and 8-32 μm (Tab. 3). The percentage of the $\leq 2\mu\text{m}$ grain-size fraction was higher in sites B and C than in the others.

Table 3. Grain-size fractions.

Variations in atmospheric particulate during the sampling period were also detected. The following text highlights the relationship between physico-chemical characteristics and atmospheric particulate.

Table 4. Average amounts of TSP and rain during study period measured in four sites.

Table 4 summarises the mean TSP levels in the four sites. Site D shows the highest mean level and site A the lowest.

The relationship between atmospheric particulate load and total sample volume was also examined. A higher correlation was found between TSP levels and “wet” than between TSP and “dry” samples. It therefore seems that the wet mode accounts for most of the particulate load to the Lagoon. We also observed the same relationship in aerosol samples from Sardinia (Guerzoni et al., 1993, 1995, 1997).

Particle size distribution versus wet and dry samples were also investigated. Wet samples showed the highest (8.0%) average percentage of finest particles (1 μm) compared with dry ones (4.9%) .

Deposition fluxes of inorganic elements

Table 5 shows the daily fluxes of inorganic elements determined during the study period and results are expressed as yearly fluxes in Figure 6. In order to highlight the differences between sites according to their distance from the industrial zone (sites A and D were <10 km from the industrial zone, sites B and C were >10 km), data are represented as aggregate mean fluxes in Figure 6.

A comparison of fluxes among the four sites showed minimum differences for major elements. Standard deviation (SD) between sites was 25-30% of the mean, mainly due to meteorological variability and differences in particle load. For trace metals, SD ranged from 20-40% of measurements, and was sometimes higher than 50% (e.g., Cd: mean $0.15 \pm 0.09 \text{ mg m}^{-2} \text{ y}^{-1}$; SD=59%, and V: mean $2 \pm 1 \text{ mg m}^{-2} \text{ y}^{-1}$; SD=53%). Sites A and D showed maximum flux values for all elements (Table 5, Fig. 6).

Table 5. Daily fluxes of inorganic elements from atmosphere. Units = $\mu\text{g m}^{-2} \text{ d}^{-1}$, * = $\text{ng m}^{-2} \text{ d}^{-1}$; %sol= percentage of soluble fraction.

Fig. 6. Deposition fluxes of metals in four sites. A-D = average of fluxes recorded in sites A and D; B-C = average of fluxes recorded in sites B and C; *= annual flux/10; **= annual flux/100.

Atmospheric depositions have been collected in site A since 1993. Comparisons between data obtained in 1998-99 and former data reveal that fluxes of major elements and some trace metals (Zn, Cd, As, V) are similar to those measured during previous years (variability range, 20-25%), the main differences being observed in the 1993-94 data. Figure 7 shows the annual fluxes of some selected trace metals during three (or four) years of sampling at site A. As may be seen, a remarkable decrease in Pb and Sb fluxes is evident (from 18-13 to $\sim 5 \text{ mg m}^{-2} \text{ y}^{-1}$ and from 0.3-0.4 to $0.1 \text{ mg m}^{-2} \text{ y}^{-1}$, respectively).

Fig. 7. Annual fluxes during three (or four) years of sampling at site A.

Table 6 lists metal fluxes measured at various sites. 1998-99 fluxes of Cd, Cu, Ni, Pb and Zn were comparable to those determined at a coastal site (Cesenatico) in the Adriatic, and fell in the flux range recorded by other authors at various coastal sites in France (see references in table).

Table 6. Comparisons with yearly deposition fluxes in other coastal sites.

Deposition fluxes of nutrients

Table 7 lists daily fluxes of nutrients at the four sampling sites. The amount of marine fraction for sulphates was calculated according to Keene et al. (1986) (considering an SO_4/Na ratio=0.121). As may be seen, nutrient fluxes vary among sites, being about three times higher in site D than in site A, and comparable between sites D and B for total and soluble P, SO_4 and NO_3 .

Table 7. Daily fluxes of nutrients from atmosphere. Units = $\mu\text{g m}^{-2} \text{d}^{-1}$. n.m. =non-marine.

Fig. 8. Comparisons of nutrient fluxes with yearly deposition in other sites. Deposition at Cesenatico from Tartari et al., 1997, Castelporziano from Francaviglia et al., 2001, Tessa from Tait and Thaler, 2000, Pula from Djuricic et al., 2001, and NW Mediterranean from Herut, 2001.

Figure 8 shows comparisons of nutrient fluxes with yearly depositions measured in other sites. Data are represented as aggregate mean fluxes. Cesenatico, Castelporziano and Pula are coastal sites, Tessa is a remote mountain site in the eastern Alps. As Figure 8 shows, SO_4 fluxes in sites A, B, C and D are higher than in other sites except for Cesenatico, and N-NH_4 ,

N-NO₃ and DIN fluxes at sites A, B and C are comparable with the depositions observed at Cesenatico and Pula (Fig. 8A). In particular, all annual fluxes of nutrients in site D are higher than in other lagoonal sites, except for phosphorus, N-NH₄ and DIN being the highest reported among those compared. With regard to phosphorus fractions, the atmospheric input of TP in the Lagoon of Venice appears to be higher than fluxes measured at Cesenatico, P-PO₄ deposition at sites B, C and D being comparable with data from the NW Mediterranean (Fig. 8B). In the lagoonal sites, the lowest phosphorus flux was observed at site A.

Deposition fluxes of organic micropollutants

Table 8 lists the daily fluxes of organic micropollutants determined during the study period, and results are expressed as yearly fluxes in Figure 9. The variability among sites is evident. During the study period, all maxima were observed at sites A and D (“impact” sites) and minima at B and C (“remote” sites). In particular, both DDT and PCB maxima were located at site A, whereas the highest values were detected at site D for all other organics. Atmospheric DDT flux was similar between sites A and D, but deposition of HCB (used as a tracer for organochlorinated compounds) was 3 to 5 times higher in site D than in site A. The SDs of fluxes were always higher than 58% (Table 8).

Table 8. Daily fluxes of organic micropollutants from the atmosphere. TE calculated according to WHO-TEF (van den Berg et al., 1998).

Fig. 9. Yearly deposition fluxes of organic micropollutants in four sites. A-D = average of fluxes recorded in sites A and D; B-C = average of fluxes recorded in sites B and C, calculated from data collected during period November 1998 - July 1999. TEQ was obtained by adding toxicity of PCDD-F, PCB, HCB and PAH (Rossini et al., 2001, Guerzoni et al., in press). ** = annual flux / 100.

Figure 9 shows yearly deposition fluxes of organic micropollutants in the four sites. As data from the first four months of sampling (July to October) were used to check and set up the

sampling and analysis of organics, only sites A and D were active in that period. Thus, as a first estimate, the annual atmospheric deposition reported in Figure 9 for sites B and C was recalculated from data collected during the period November 1998 - July, 1999.

PCDD-F annual loads to the Lagoon of Venice appear quite homogeneous, falling between ~ 10 and $20 \text{ ng m}^{-2} \text{ y}^{-1}$, except for site D, where yearly deposition flux was $\sim 50 \text{ ng m}^{-2} \text{ y}^{-1}$. PCB and DDT depositions at sites A and D were comparable, being at both sites ~ 2700 (PCB) and ~ 10000 (DDT) $\text{ng m}^{-2} \text{ y}^{-1}$ respectively, between 4 and 40 times higher than in sites B and C, and the annual flux of HCB at site D ($\sim 8800 \text{ ng m}^{-2} \text{ y}^{-1}$) was 10 times higher than in the other sites. In addition to the higher deposition observed in the industrial site for all organics, these data also indicate PCB and DDT sources at both “impact” sites.

TSP and volume of rain versus inorganic elements

Some interesting relationships were found among dissolved fractions of heavy metals, atmospheric particulate load, and volume of rain collected for each sample. Figure 10 plots the dissolved fractions of Cd and Pb versus TSP. The solubilities of the two metals were quite different. That of Pb ranged from ~ 1 to 75%, and there was an exponential inverse relationship with the particulate loads (TSP) of the samples; the values for Cd ranged from ~ 10 to 100% of total metal. A decrease in particulate load content led to an increase in solubility, which provides some evidence that dissolution is under solubility control, probably due to the higher content of the fine-grained ($>2 \mu\text{m}$) fraction. Data on Pb and Cd solubilities confirmed the findings of Chester et al. (1993) in Mediterranean aerosols, and also in samples from Sardinia (Guerzoni et al., 1999).

Fig. 10. Percentage dissolution of Cd and Pb in samples collected in four sites as a function of particulate load.

The dissolution percentages of Ni and Zn versus volume of rain for each sample are shown in Figure 11. The solubilities of the two metals were quite similar, between 10 and 100%.

Fig. 11. Percentage dissolution of Ni and Zn in samples collected in four sites as a function of volume of rain.

Influence of particle grain-size on inorganic and organic micropollutants

The relationship between particle grain-size and inorganic micropollutants was studied by applying statistical multivariate analysis. Principal component analysis (PCA) is a technique suitable for ordinate data in one, two or three dimensions (linear compounds of correlated variables) and allows them to be interpreted as factors influencing the data. The method is well described in Le Maitre (1982) and Swan and Sandilands (1995). In this study, PCA was applied to the insoluble (Fig. 12) and dissolved (Fig. 13) fractions of inorganic elements, nutrients and TSP, together with particle size fractions. PCA was used to take the data from the original 27-dimensional space (chemical elements, nutrients, TSP, grain-size) and project them on to a two-dimensional plane which retains most of the information from the original data.

Fig. 12. Biplot based on PCA applied to insoluble fractions of inorganic elements, nutrients, TSP and grain-size. Black dots represent samples.

Each monthly sample, together with all chemical elements and grain-size fractions, could now be plotted in the space of the new variables (axis). PCA fits planes to each variable abundance in the space defined by the ordination axes. The variable points may be connected to the origin (biplot) (Fig. 12). The symbolism in this use of arrows is useful: the arrows point in the direction of maximum variation in variable abundance, and their length is proportional to this maximum rate of change. Consequently, variables on the edge of the

diagram (far from the origin) are the most important in indicating site differences; variables near the center are less important.

The long arrows close to axis 1 indicate nutrients (PO_4 , NH_4 , NO_3).

The long arrows near axis 2 indicate that these variables increase greatly along the second principal component (As, Cd, Hg, TSP, and fine and medium grain-size fractions): the same variables are abundant in samples located close to the arrows and rare in the remaining samples, which lie far from them. Axis 1 separates samples characterized by polluting elements (Cr, Ni, Pb, Cu, V, As, Cd, Hg) from ones characterized by crustal-natural dominated samples.

Figure 13 shows PCA applied to the dissolved fractions of inorganic elements, nutrients, TSP and pH, together with particle size fractions.

Fig. 13. Biplot based on PCA applied to dissolved fractions of inorganic elements, nutrients, TSP, pH, and grain-sizes. Black dots represent samples.

The long arrows near axis 1 indicate that Zn, Ni, Pb, Cd, Cr, As, Cu, Hg, Mn, and fine and medium grain-size fractions increase greatly along the first principal component: the same variables are abundant in samples located close to them (Fig. 13). The arrows close to axis 2 indicate natural sea-salt derived elements and some crustal elements (Si, Ca, Mg) .

Axis 2 separates samples characterized by crustal or natural elements (K, Si, Ca, Mg) together with sea-salt (S, Na, Cl), from micropolluting elements.

From the PCA results, an example was chosen to highlight the relationship between grain-size and inorganic elements. Figure 14 plots the percentage of dissolved arsenic with grain-size fraction $\leq 1 \mu\text{m}$. The solubility of As shows a linear relationship with the finest grain size fraction ($r=0.57$, $p<0.005$).

Fig. 14. Percentage dissolution as a function of grain size fraction $\leq 1 \mu\text{m}$

For improved knowledge of grain-size particulate distributions and their relationships with organic compounds, data from PCDD/F, PCB and PAH were processed together with particle size data. We chose to group together samples from sites A and D and from sites B and C, due to their physical and meteorological characteristics (Rossini et al., 2001).

Several bivariate plots of the fluxes of Σ PCDDF, Σ PCDD, benzo(a)pyrene, and PCB 167 versus particulate grain-size ($\leq 2 \mu\text{m}$; 4-8 μm) in the two groups of sampling sites (B and C; A and D) are shown in Fig. 15.

Fig. 15. Bivariate plots of four organic compounds versus particulate grain size in two groups of sampling sites.

Examination of the relationships among levels of Σ PCDDF, Σ PCDD, PCB and PAH congeners and particulate grain size revealed significant correlation coefficients for sites B and C and none for sites A and D. In particular, significant correlations were found between Σ PCDDF and particle size fraction $\leq 2 \mu\text{m}$ ($r=0.50$), and between Σ PCDD, benzo(a)pyrene and PCB 167 and particle size fraction 4-8 μm ($r=0.50$, $r=0.72$ and $r=0.50$, respectively) (Fig. 15).

The lack of correlations between particle grain-size and organic pollutants in sites A and D may be related to their location (close to the industrial zone).

Atmospheric loads to the Lagoon of Venice

Total annual deposition was calculated by means of two different methods: (i) mean deposition values in the four sites was multiplied by lagoon area; (ii) atmospheric deposition loads during the study period were calculated using monthly rain isopleths, which were combined to normalize deposition values by means of the equation $\Sigma(f_x \cdot a_x)$, where $f_x =$

monthly deposition flux at site x , and a_x = area included between isopleths relative to site x (see Fig. 16 as an example). The second method was preferred, since it has been shown that, for many elements, bulk deposition is prevalingly affected by wet deposition (Rossini et al., 2001b). The total surface area considered for the Lagoon of Venice was 550 km².

Fig.16. Rain isopleths (mm) for Lagoon of Venice during March 1999 sampling.

Method (ii) appears to be the more correct, since it was able to reveal monthly differences, up to +14% (Cd load after normalization) or -15% (NH₄ load after normalization). In practice, working with annual averages gave the same results, as the sampling sites were too few to observe significant spatial differences.

With regard to organic micropollutants, as reported above, the first four months of sampling (July to October) were used to check and set up sampling and analysis at sites A and D. Thus, as a first estimate, the deposition loads to the whole Lagoon were calculated from data collected at four sites during the period November 1998 - July 1999 (Table 9).

Table 9. Supply rates of organic micropollutants from atmosphere to Lagoon of Venice (surface area = 550 km²). TE calculated according to WHO-TEF (van den Berg et al., 1998).

Conclusions

For the first time, atmospheric depositions of metals, nutrients and organics were measured extensively over a period of 13 months, concurrently with other input measurements (e.g. river, sea) and biological studies.

Results show some variability in the grain-size of particulates and in total suspended particulate (TSP) contents among sites. This did not seem to determine differences in fluxes of major (crustal) elements in various parts of the Lagoon.

Instead, grain-size, TSP and rainfall affected the solubility (and thus availability) of several trace metals (Pb, Cd, Zn, Ni, As). Solubility ranged from 70-80% (As, Cd, Zn) and ~ 50% (Cr, Hg, Ni, Mn), down to 10-20% for Cr and Pb, and <5% for crustal lithogenic elements (Al, Fe, Si, Ti).

As expected, fluxes of metals of anthropogenic origin were 3-4 times higher in the two sites nearest the urban and industrial areas, compared with more distant sites (>10 km): for example, Cd, = 0.26 vs. 0.06 mg m⁻²yr⁻¹; Hg = 41 vs. 15 µg m⁻²yr⁻¹.

Organic flux patterns were poorly affected by grain-size, TSP or rainfall, and more related to the distance of the sampling site from industrial sources. In fact, organic flux values in proximal sites were 5-10 times higher than those of the remote sites, e.g., PCB = ~2500 vs. ~500 ng m⁻²yr⁻¹, and HCB = ~8000 vs. ~1000 ng m⁻²yr⁻¹.

Extrapolation of fluxes to the total Lagoon area was tentatively carried out by integrating meteorological (rain and wind) data, although this was somewhat difficult because of the few sites available. Nevertheless, it did represent the first concurrent data-base with watershed sampling activity, which allowed budgetary considerations (see Marcomini et al., this issue).

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Figure and table captions

Fig. 1. Location of atmospheric deposition sampling sites. (A=city of Venice; B=Valle Dogà; C=Valle Figheri; D=Dogaletto). Large circle encloses industrial zone of Porto Marghera.

Fig. 2. Bulk deposition samplers (modified from Bergerhoff[®]) used in the field. Left: Pyrex[®] unit for organic micropollutants, right: polyethylene unit for inorganics.

Fig. 3. Mean wind directions and speeds from 1951 to 1990 at Venice (after Carrera et al., 1995).

Fig. 4. Amount of rain during study period, compared with local time series data. Bars: minimum and maximum values.

Fig. 5. Comparison of rain recovered during study period by bulk sampler with measurements of rain gauge at site A.

Fig. 6. Depositon fluxes of metals in four sites. A-D = average of fluxes recorded in sites A and D; B-C = average of fluxes recorded in sites B and C; *= annual flux/10; **= annual flux/100.

Fig. 7. Annual fluxes during three (or four) years of sampling at site A.

Fig. 8. Comparisons of nutrient fluxes with yearly deposition in other sites. Deposition at Cesenatico from Tartari et al., 1997, Castelporziano from Francaviglia et al., 2001, Tessa from Tait and Thaler, 2000, Pula from Djuricic et al., 2001, and NW Mediterranean from Herut, 2001.

Fig. 9. Yearly depositon fluxes of organic micropollutants in four sites. A-D = average of fluxes recorded in sites A and D; B-C = average of fluxes recorded in sites B and C, calculated from data collected during period November 1998 - July 1999. TEQ was obtained by adding toxicity of PCDD-F, PCB, HCB and PAH (Rossini et al., 2001, Guerzoni et al., 2004). **= annual flux / 100.

Fig. 10. Percentage dissolution of Cd and Pb in samples collected in four sites as a function of particulate load.

Fig. 11. Percentage dissolution of Ni and Zn in samples collected in four sites as a function of volume of rain.

Fig. 12. Biplot based on PCA applied to insoluble fractions of inorganic elements, nutrients, TSP and grain-size. Black dots represent samples.

Fig. 13. Biplot based on PCA applied to dissolved fractions of inorganic elements, nutrients, TSP, pH, and grain-sizes. Black dots represent samples.

Fig. 14. Percentage dissolution as a function of grain-size fraction $\leq 1 \mu\text{m}$

Fig. 15. Bivariate plots of four organic compounds versus particulate grain-size in two groups of sampling sites.

Fig.16. Rain isopleths (mm) for Lagoon of Venice during March 1999 sampling.

Table 1. Geographical coordinates of sampling site. Datum=WGS84.

Table. 2 Wind directions and speeds during study period. Bold numbers=maximum values. Mws=mean wind speed.

Table 3. Grain-size fractions.

Table 4. Average of TSP and rain amount for study period measured in four sites.

Table 5. Daily fluxes of inorganic elements from atmosphere. Units = $\mu\text{g m}^{-2} \text{d}^{-1}$, * = $\text{ng m}^{-2} \text{d}^{-1}$; %sol= percentage of soluble fraction.

Table 6. Comparisons with yearly deposition fluxes in other coastal sites.

Table 7. Daily fluxes of nutrients from atmosphere. Units = $\mu\text{g m}^{-2} \text{d}^{-1}$. n.m. =non-marine.

Table 8. Daily fluxes of organic micropollutants from atmosphere. TE calculated according to WHO-TEF (van den Berg et al., 1998).

Table 9. Supply rates of organic micropollutants from atmosphere to Lagoon of Venice (surface area = 550 km^2). TE calculated according to WHO-TEF (van den Berg et

al., 1998).

Table 1. Geographical coordinates of sampling site. Datum=WGS84.

Site	Location	Lat N	Long E
A	City of Venice	45°25'48"	12°21'12"
B	Northernmost end of Lagoon	45°34'24"	12°32'54"
C	Southernmost end of Lagoon	45°19'06"	12°10'24"
D	Close to industrial zone of Porto Marghera	45°24'24"	12°10'48"

Table 2. Wind directions and speeds during study period. Bold numbers=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
<1 ms⁻¹	18.5	12.3	28.8	5.7
mws ms⁻¹	2.1	2.3	2	3.9

Table 3. Grain-size fractions.

Sites	≤2.0 μm (%)	2-4 μm (%)	4-8 μm (%)	8-32 μm (%)
A	18.8	21.2	24.6	38.2
B	25.0	23.5	27.2	25.1
C	22.2	27.5	34.0	20.8
D	16.7	22.2	24.8	35.6
Average	20.7	23.6	27.6	29.9

Table 4. Average of TSP and rain amount for study period measured in four sites.

Site	TSP mg m ⁻² d ⁻¹			Rainfall mm		
	Mean	Min	Max	Mean	Min	Max
A	21.8	6.3	56.1	42.4	4.3	132.9
B	31.1	7.6	82.3	53.6	3.7	161.3
C	21.6	6.4	45.1	32.2	0.0	160.0
D	35.5	14.0	69.4	54.4	0.0	169.0

Table 5. Daily fluxes of inorganic elements from atmosphere. Units = $\mu\text{g m}^{-2} \text{d}^{-1}$, * = $\text{ng m}^{-2} \text{d}^{-1}$; %sol= percentage of soluble fraction.

	Mn	Cr	Ni	Zn	Pb	Cu	Cd*	Hg*	As*	Ti	V	Sb*	S	Si	Al	Fe	Ca	Mg	Na	K	
A	average	19.3	4.4	6.4	97.6	14.2	14.3	688	113	1333	64.3	5.7	235	3548	2860	991	622	3849	1354	5250	1327
	standard deviation	9.5	1.6	2.4	59.8	4.5	6.4	885	74	400	52.1	2.2	190	1924	1302	726	386	1627	649	3455	2116
	median	18.2	4.60	5.7	76.3	14.5	12.3	398	98	1399	42.3	5.5	233	3290	2473	722	594	3506	1337	3894	804
	min	7.1	2.17	3.0	25.5	8.2	6.6	163	35	438	16.9	2.7	0	1306	1439	342	203	1328	454	1699	193
	max	38.5	7.83	11.5	253.4	23.2	29.3	3512	269	1926	200.1	8.8	614	7650	4985	2868	1452	6267	2746	13764	8160
	sol%	50	7	52	81	15	45	80	51	72	0	60	0	98	1	4	2	88	67	98	76
B	average	11.7	1.67	2.8	54.0	5.8	8.8	151	64	607	38.9	4.1	72	3509	2634	624	361	6046	1759	3925	1024
	standard deviation	3.4	0.8	1.1	32.7	3.8	4.9	127	42	320	22.8	1.6	92	1219	1435	415	198	5274	1761	2768	501
	median	10.6	1.54	2.5	53.7	5.0	6.8	141	45	556	33.2	3.5	14	3431	2695	450	286	4666	1139	3138	959
	min	7.3	0.62	1.4	9.5	2.4	4.4	37	30	200	13.5	2.1	13	1506	870	224	138	1254	389	617	273
	max	17.6	3.54	5.2	118.5	13.5	18.8	536	166	1255	87.7	7.4	290	6155	6257	1480	829	20405	7058	10713	1848
	sol%	38	10	65	71	12	67	64	60	78	0	72	0	97	4	1	1	91	81	97	80
C	average	17.6	2.96	4.5	69.3	11.0	10.1	371	39	609	51.0	6.0	204	2997	2827	792	536	3511	1038	4596	801
	standard deviation	7.7	1.2	1.8	53.6	3.5	4.7	496	24	191	34.4	3.9	180	1343	1626	486	303	1361	481	3433	501
	median	17.7	2.98	4.1	53.8	10.7	8.2	216	36	632	32.9	4.9	199	2615	2240	542	361	3509	1011	2800	800
	min	8.9	0.79	1.9	19.0	6.1	4.9	74	13	204	21.4	2.1	13	889	1381	309	268	1449	363	1356	236
	max	37.8	5.50	8.1	212.4	19.2	18.5	1988	88	862	134.0	15.9	552	6213	6627	1928	1275	5897	1735	11719	2006
	sol%	42	6	54	75	12	56	67	58	73	0	66	0	98	1	2	1	93	79	98	72
D	average	19.8	3.40	6.9	96.7	7.6	12.7	341	55	819	43.0	8.0	125	4343	2727	1054	446	6782	1130	2684	978
	standard deviation	7.1	2.3	2.4	71.0	3.9	11.0	504	31	279	28.6	2.8	152	1854	1710	640	272	4109	574	2108	545
	median	17.8	2.44	6.9	79.4	8.6	8.6	203	46	826	47.1	7.8	14	4387	2091	894	437	6032	1021	1488	927
	min	12.8	0.40	3.2	19.2	1.9	6.1	75	24	358	5.8	3.9	13	1704	713	164	85	2342	537	1040	292
	max	34.7	6.52	11.9	250.5	14.2	47.5	1992	142	1385	85.9	12.5	418	7559	6437	2107	849	18198	2692	7332	1838
	sol%	53	13	64	72	18	64	70	55	78	0	75	0	98	4	6	4	92	76	94	78

Table 6. Comparisons with yearly deposition fluxes in other coastal sites.

	Cd mg m ⁻² y ⁻¹	Cu mg m ⁻² y ⁻¹	Ni mg m ⁻² y ⁻¹	Pb mg m ⁻² y ⁻¹	Zn mg m ⁻² y ⁻¹
Venice 1998-99 ¹	0.15±0.09	4.3±0.8	1.9±0.7	3.6±1.3	29±8
Venice 1993-97	0.22	11.3	3.5	21	30
Adriatic sea ²	0.15	4.5	1.4	3	39
Cap Ferrat ^{3,4}	0.07-0.17	1.8-2.2	1.35	3.1-18.0	--
NW Med ⁵	1.3	2.5	1.3	4.0	65

¹ Present study; ² Cesenatico 1995-96; ³Migon *et al.*, 1997; ⁴ Migon *et al.*, 1991; ⁵Guieu *et al.*, 1997

Table 7. Daily fluxes of nutrients from atmosphere. Units = µg m⁻² d⁻¹. n.m. =non-marine.

	DIN	TP	PO₄	n.m.SO₄	NH₄	NO₃	
A	average	3831	124	27	5992	2329	8947
	standard deviation	2657	71	18	2982	1711	6212
	median	2699	123	24	5424	2019	7055
	min	928	37	7	2842	429	2609
	max	10360	293	74	13551	6090	24901
B	average	7015	432	329	7948	4400	15910
	standard deviation	5994	305	273	3001	1806	25594
	median	6118	387	324	7972	4464	10194
	min	750	57	28	1623	557	1402
	max	25423	1126	1015	12622	7008	99559
C	average	4645	273	268	6748	3332	9093
	standard deviation	2187	369	332	2834	2427	5565
	median	4003	106	93	6891	2799	8827
	min	675	31	26	1973	156	2019
	max	7753	1073	923	12872	8350	19248
D	average	11532	403	220	10443	8983	20127
	standard deviation	16209	273	220	4860	16676	42681
	median	6041	440	115	10063	5206	9172
	min	1312	40	28	3801	154	2593
	max	53505	794	741	17835	63694	161436

Table 8. Daily fluxes of organic micropollutants from atmosphere. TE calculated according to WHO-TEF (van den Berg et al., 1998).

	IPA ng m ⁻² d ⁻¹	HCB ng m ⁻² d ⁻¹	PCB ng m ⁻² d ⁻¹	PCDD/F pg m ⁻² d ⁻¹	DDT ng m ⁻² d ⁻¹	PCB pg TE m ⁻² d ⁻¹	PCDD/F pg TE m ⁻² d ⁻¹	
A	average	842	4.2	6.8	49	30	2.0	2.0
	standard deviation	518	4.5	8.8	36	65	5.1	2.6
	median	673	2.2	3.1	35	3	0.2	0.9
	min	288	0.4	1.4	14	1	0.1	0.2
	max	2035	12.2	31.9	135	198	18.8	9.2
B	average	271	2.1	1.6	29	1	0.2	1.3
	standard deviation	211	3.5	1.2	20	1	0.5	1.2
	median	240	0.9	1.1	25	0	0.0	1.4
	min	18	0.2	0.1	0	0	0.0	0.0
	max	633	11.2	3.1	61	2	1.6	3.2
C	average	286	1.6	1.5	38	1	0.2	1.8
	standard deviation	236	1.7	0.8	32	1	0.5	2.1
	median	232	0.9	1.4	30	1	0.1	1.0
	min	32	0.2	0.3	10	0	0.0	0.0
	max	659	4.8	2.9	109	2	1.5	6.2
D	average	1029	22.6	7.3	124	22	2.7	1.9
	standard deviation	844	33.8	8.5	149	48	5.1	1.5
	median	731	4.1	4.6	59	2	0.9	1.6
	min	77	0.4	0.7	29	0	0.1	0.0
	max	3352	111.6	31.4	470	159	19.1	5.2

Table 9. Supply rates of organic micropollutants from atmosphere to the Lagoon of Venice (surface area = 550 km²). TE calculated according to WHO-TEF (van den Berg et al., 1998).

Parameter	kg y ⁻¹	Parameter	g y ⁻¹	Parameter	ton y ⁻¹
Cr	711	PAH	104501	DIN	1371
Ni	1162	HCB	1125	P_{tot}	55
Zn	17585	DDT	345	PO₄	40
Pb	2122	PCB	522	n.m.SO₄	1664
Cu	2582	PCDD/F	11	NH₄	902
Cd	88	TEQ_{PCB}	0,087	NO₃	2966
Hg	15	TEQ_{PCDD/F}	0,376		
As	189				
V	1323				
Sb	34				
Al	199325				

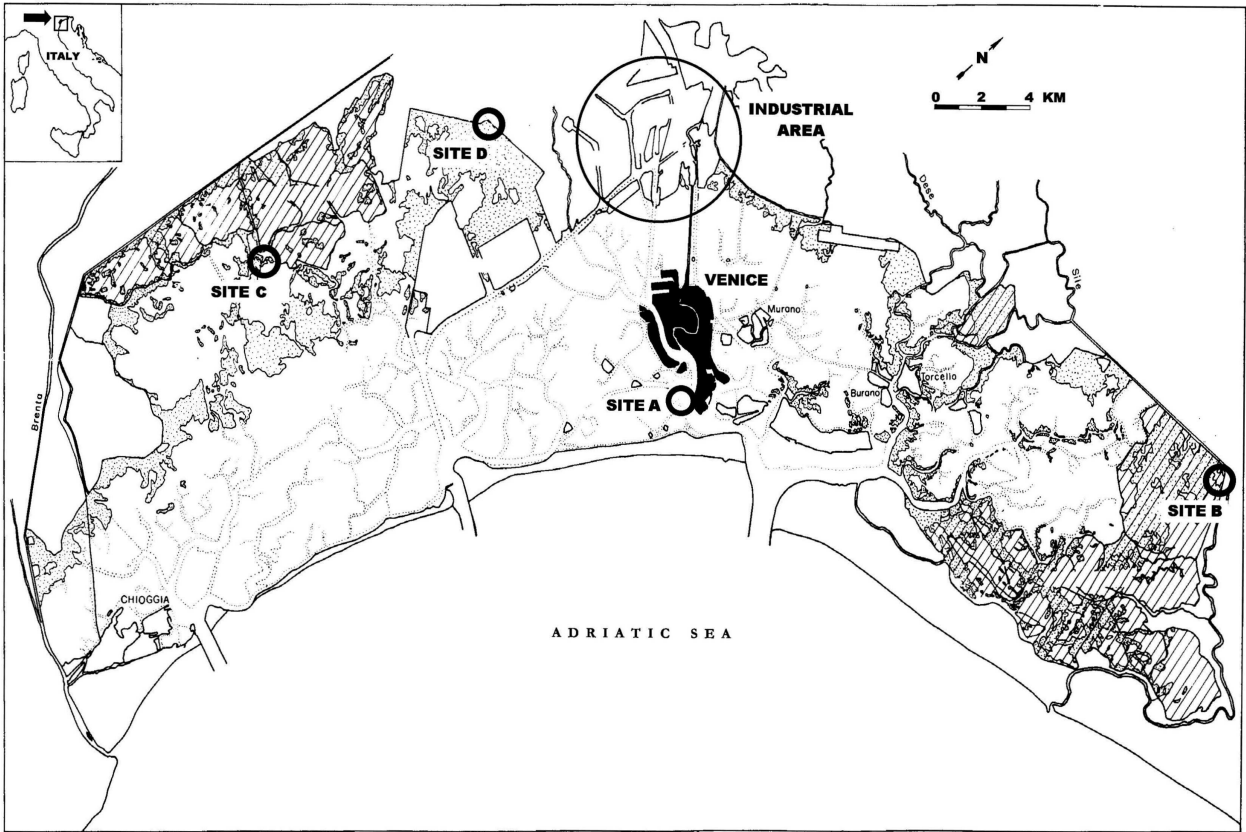


FIG. 1



FIG. 2

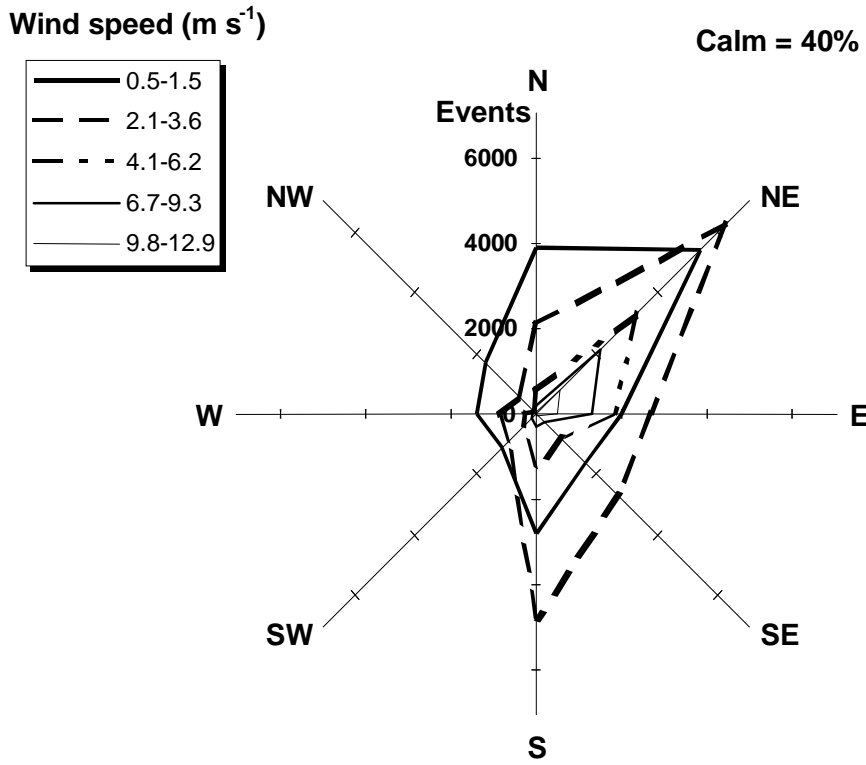


FIG. 3

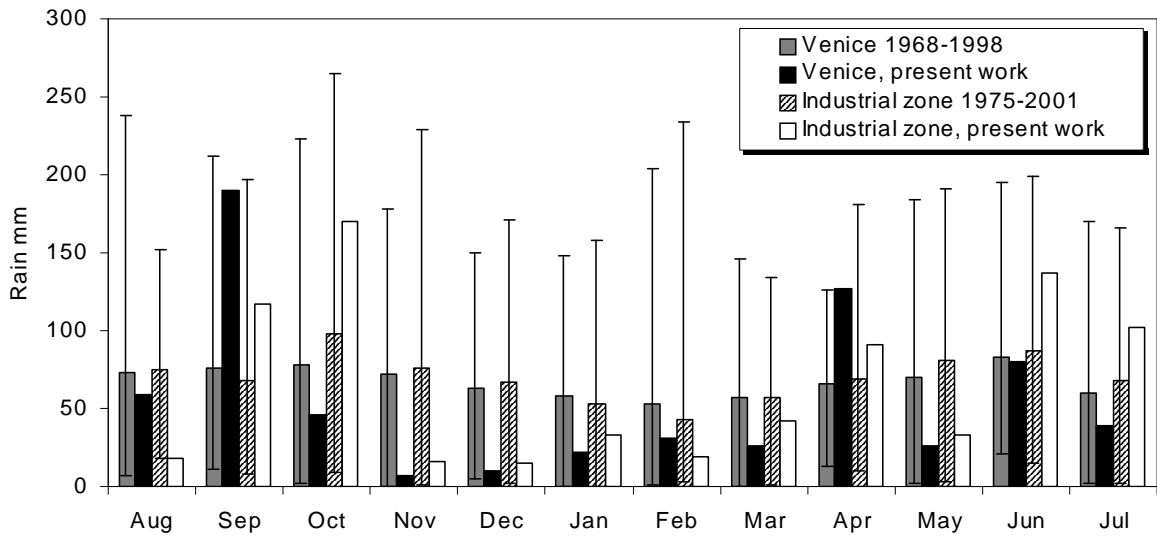


FIG: 4

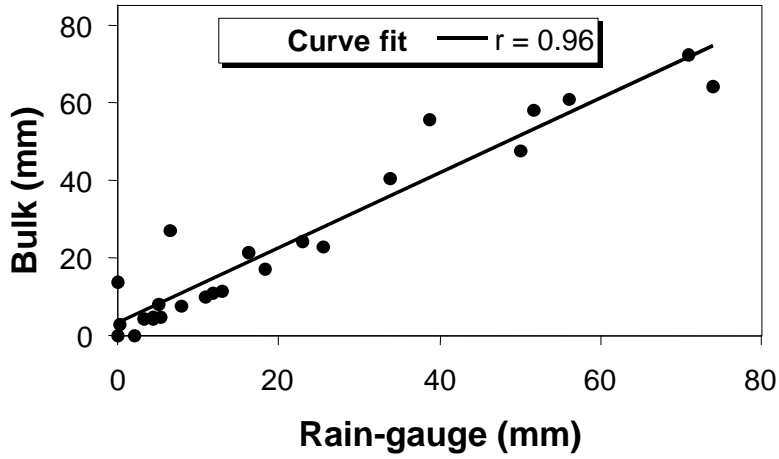


FIG. 5

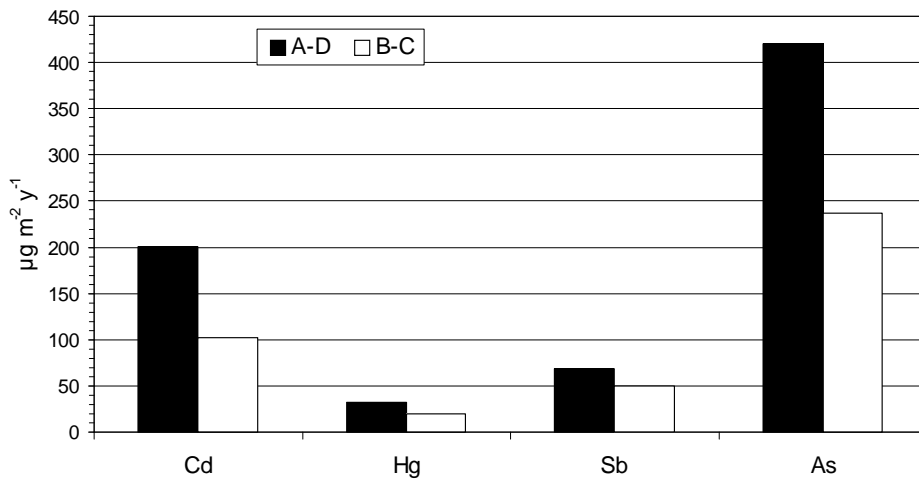
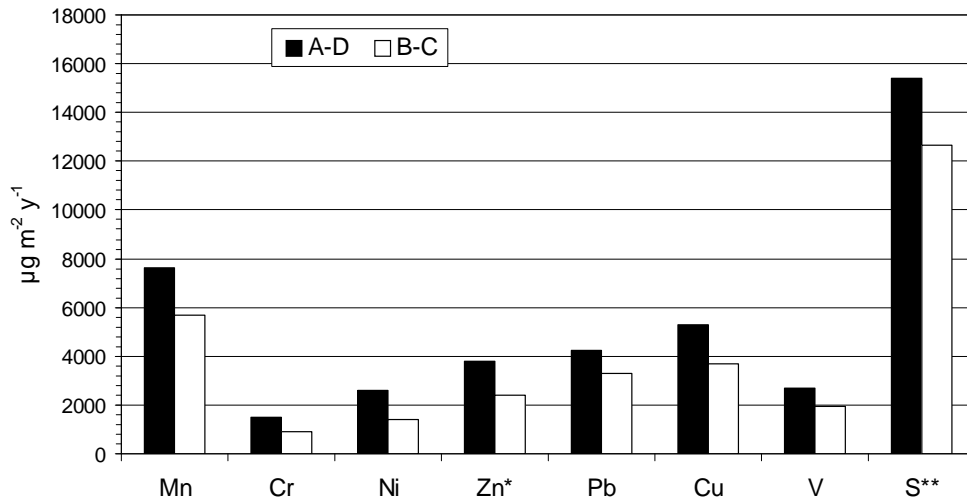


FIG. 6

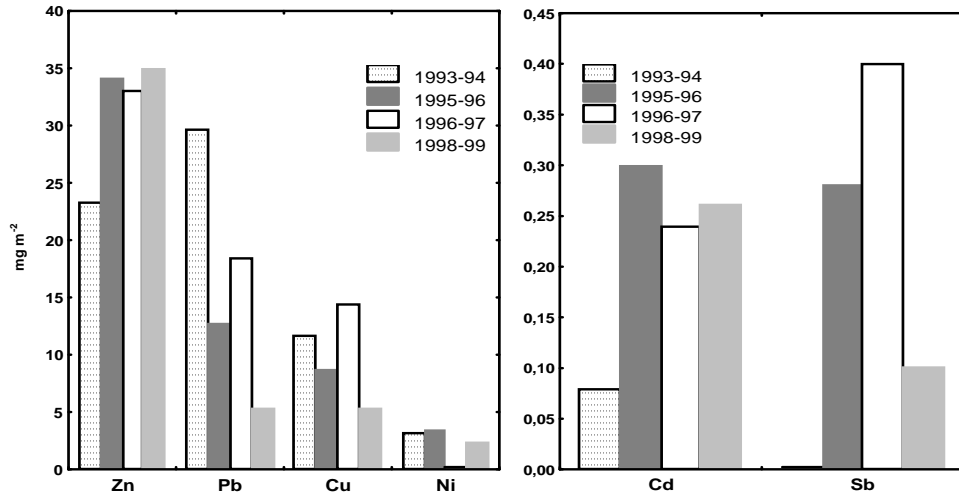


FIG. 7

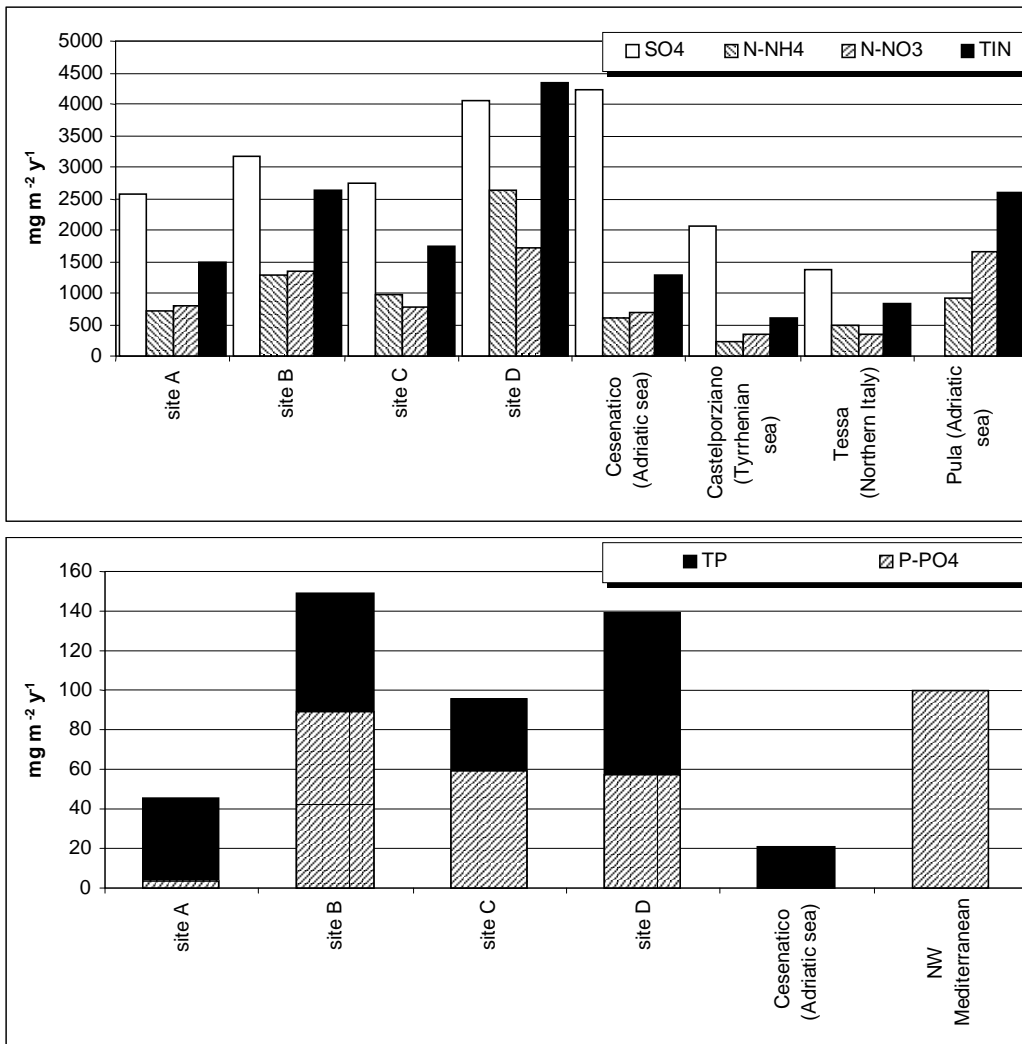


FIG: 8

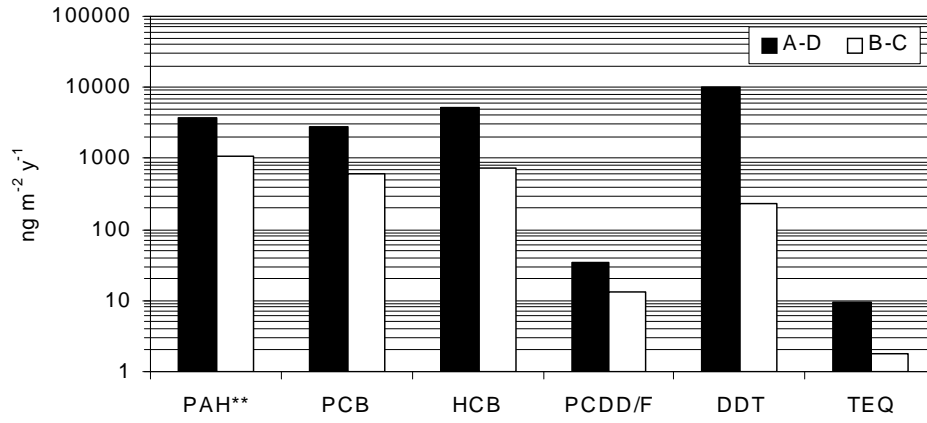


FIG. 9

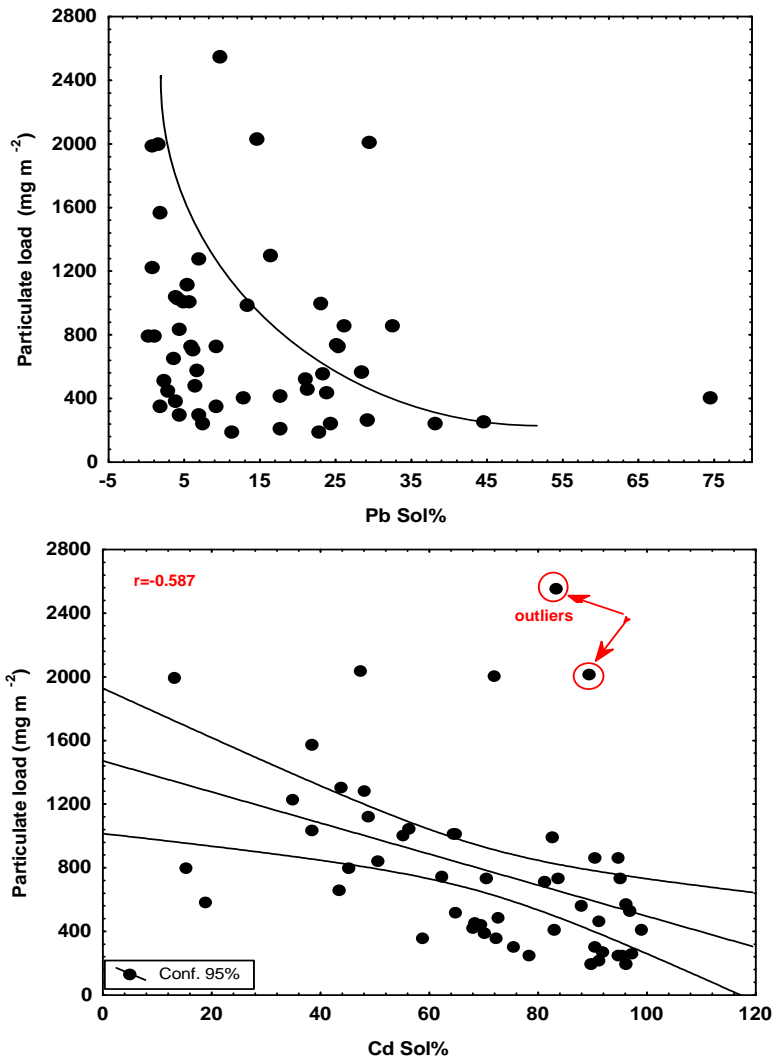


FIG. 10

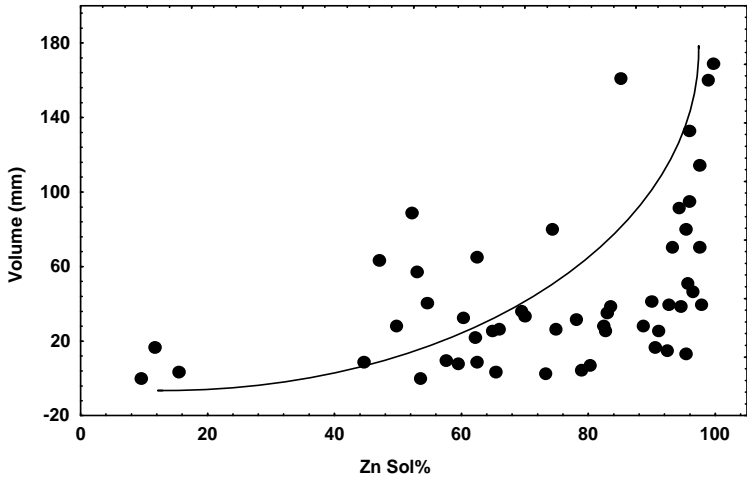
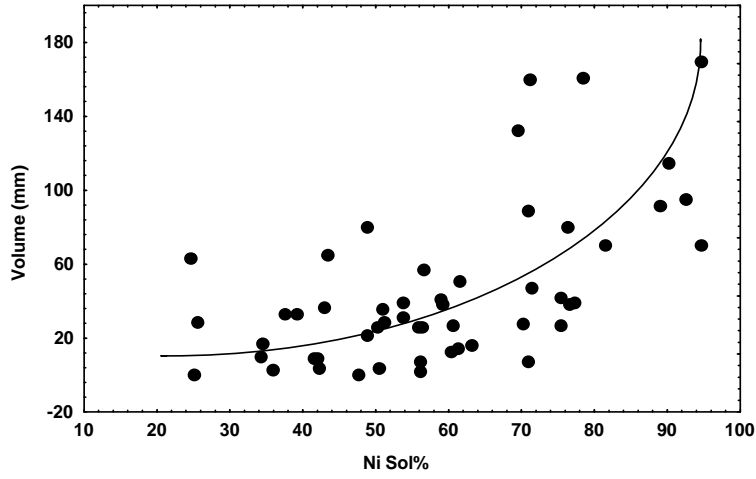


FIG. 11

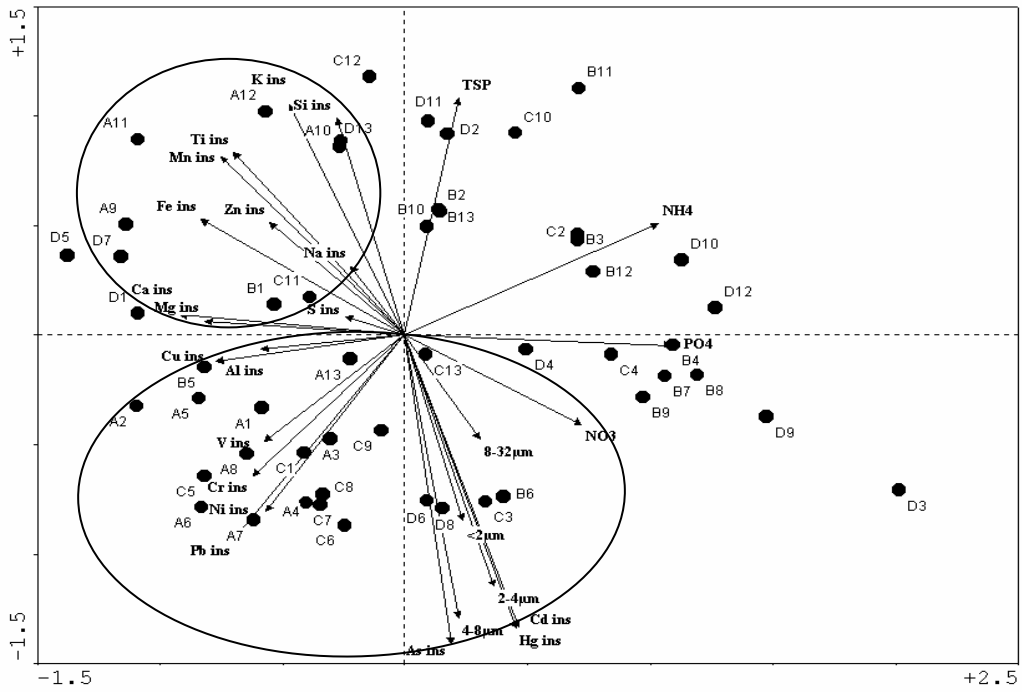


FIG. 12

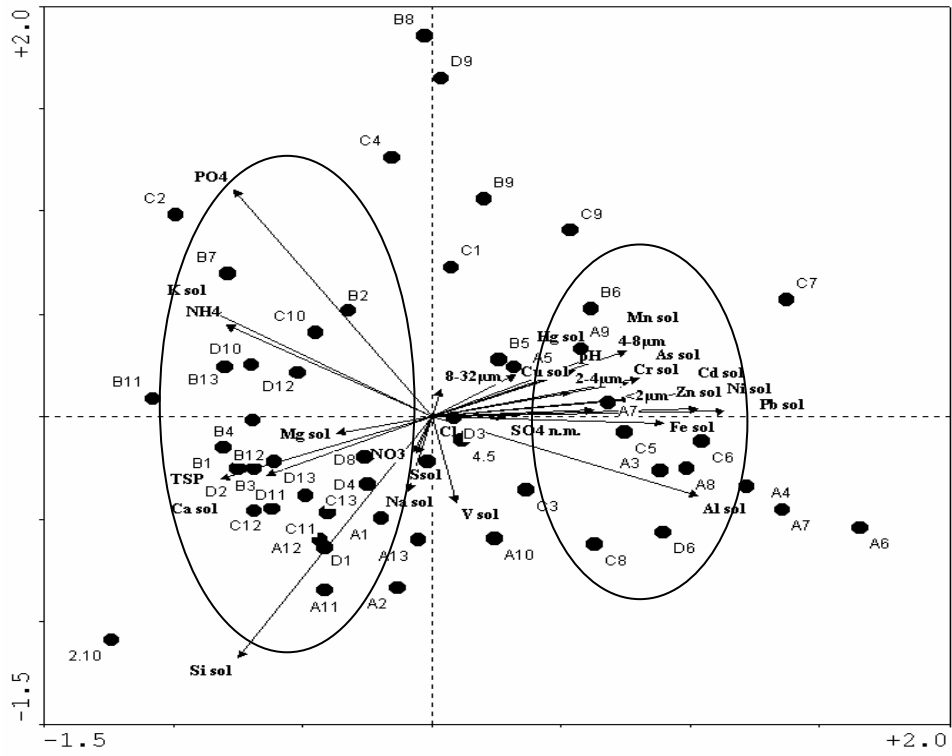
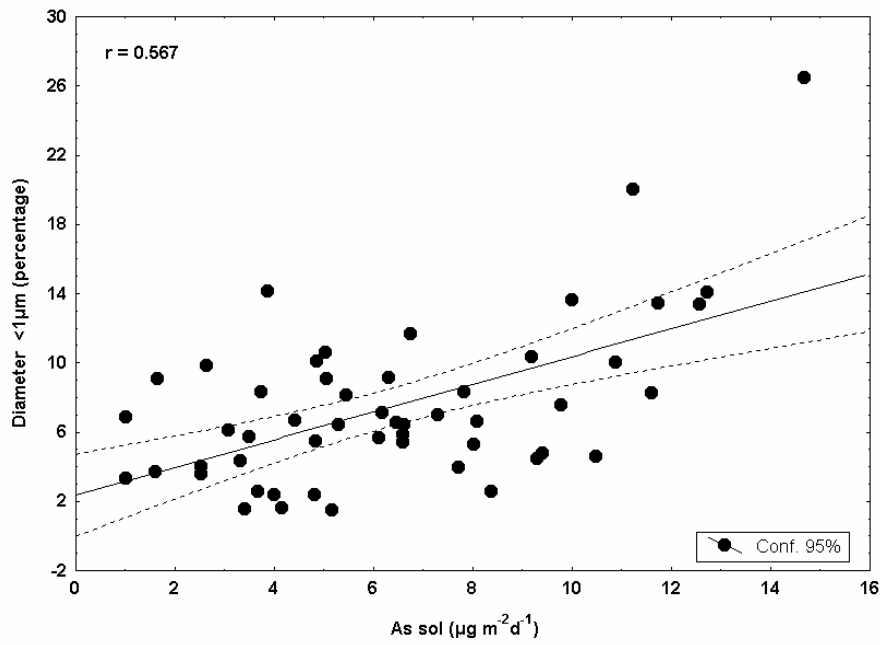


FIG: 13



FIG, 14

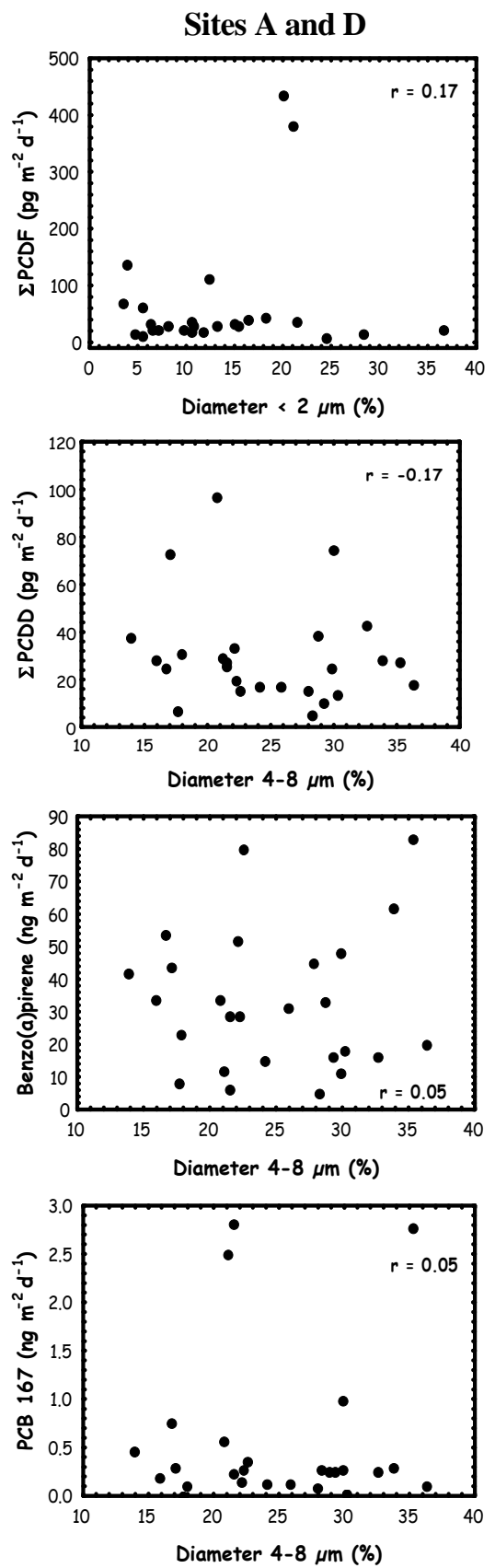
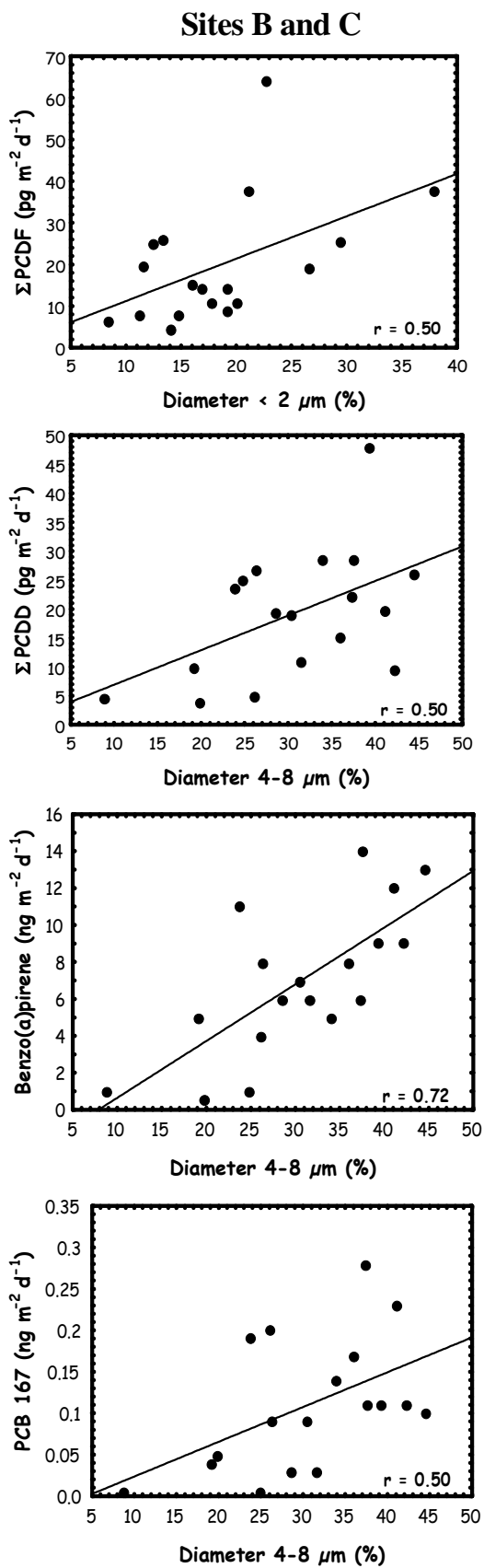


FIG. 15

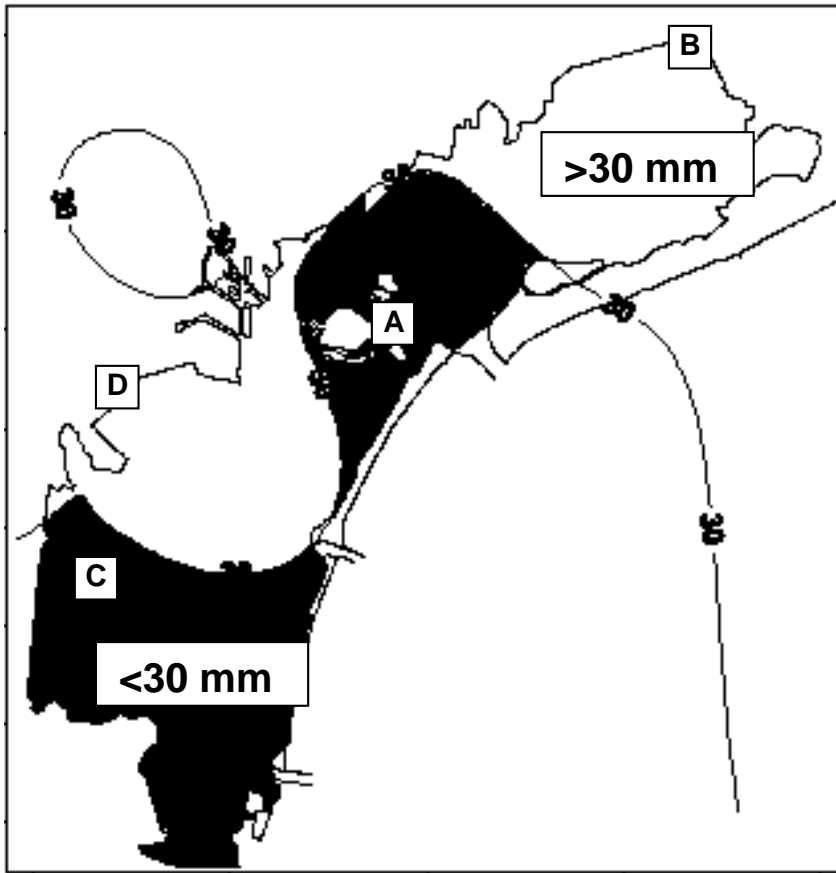


FIG. 16