Measurement of atmospheric deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the Lagoon of Venice, Italy.

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Abstract

Data on atmospheric fall-out of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) were provided by collecting bulk deposition in four stations inside the Lagoon of Venice. A total of 44 monthly samples was collected during the period July 1998 – July 1999 in one site near an industrial area (Porto Marghera), one site in the city of Venice, and two sites in the southern- and northernmost ends of the Lagoon. Fluxes of PCDD/Fs were between 0.1 and 470 pg $m^{-2} d^{-1}$, corresponding to 0-9.2 pg of 2,3,7,8-TCDD equivalents (TEQ) $m^{-2} d^{-1}$, with a gradient increasing from remote to urban/industrial stations. Thus, annual deposition of PCDD/Fs to the Lagoon (total area = 550 km^2), calculated with various methods, turned out to be ~12 g, corresponding to ~ 400 mg TEQ. Significant differences were found among the stations, with a clear fingerprinting signature (PCDF/PCDD>1) of the deposition collected near Porto Marghera, and a reversed pattern (PCDF/PCDD<1) in the rest of the Lagoon, which pattern was similar to the sediments collected in the same locations. Lastly, the amount of bulk ∑TEQ of all stations was compared with the guide values for dioxins in depositions proposed by De Fré *et al.* (2000).

Keywords: Atmospheric fall-out; Dioxins; Furans; Porto Marghera; VCM emission; Guidelines.

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1. Introduction

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Persistent organic pollutants (POPs) are organic chemicals which are stable to photochemical, chemical and biological decomposition. Most of them would not exist in nature without human activity. POPs are present in the atmosphere in gaseous and aerosol phases. They degrade in the atmosphere as a result of various physical-chemical processes and are removed by wet and dry deposition (UNEP/MAP/WMO, 2001).

Among these substances, dioxins and furans (PCDD-Fs) are not especially produced, but are formed as interim species (by-products) in the process of certain human activities, i.e. industrial processes, fossil fuel combustion, or waste destruction. Air is the main distribution pathway for PCDD-Fs, and PCDD/F composition is therefore influenced by different emissions and congener/homologue-selective transport and atmospheric loss processes (Lohmann and Jones, 1998).

Much work has been done in the past 20 years, to study the presence of PCDD/Fs and other organic chlorine in bottom sediments and aquatic biota in the Lagoon of Venice, Italy. Sources of the contamination are often discharges from the industrial district of Porto Marghera, untreated domestic sewage from the historical city of Venice, and traffic from motorboats and the nearby city of Mestre (Fattore *et al.,* 1997; Di Domenico *et al.,* 1997; Marcomini *et al.,* 1997; Wenning *et al.,* 2000).

Preliminary available data on atmospheric dioxin fall-out were provided by bulk deposition sampling (Rossini *et al.,* 2001), and a budget of dioxin showed that atmospheric deposition accounted for one-quarter of the total load in the Lagoon of Venice (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 data of 2,3,7,8,-substituted PCDD/Fs in atmospheric fall-out, provided by sampling monthly bulk depositions in four stations inside the Lagoon of Venice (550 km^2). The purposes of this study were to detect the influence of the industrial district on PCDD/F deposition, to estimate total fluxes inside the lagoon, and to apply statistical multivariate analyses and modelling in order to detect the principal sources of dioxin and furan.

2. Sampling and analytical methods

2.1. Sampling

Atmospheric depositions were collected by 4 bulk samplers similar to those tested by Horstmann and McLachlan (1997) in a rural environment (Figure 1). Bulk samplers were polymer structures formed of a cylindrical container and a protection ring to avoid damage by birds and animals. The structure was clamped to a 60-mm pole. A Pyrex bottle with a funnel properly silanised (treated with dimethyldichlorosilane 5% in toluene) was placed in the support. Bulk sampling has been extensively used, since these samplers are easier to operate than wet & 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 was 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 of minor importance for PCDD/Fs. Advantages are the integration of samples over one month and the possibility of large scale application with low-cost equipment.

Figure 1. Bulk deposition sampler (modified from Bergerhoff[®]) used in the field. Right: Pyrex[®] "funnel-bottle" unit.

Sampling was carried out monthly during the 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 sites in the more remote southern (Site C) and northernmost (Site B) ends of the Lagoon (Figure 2).

Figure 2. Location of atmospheric deposition sampling sites. (A=city of Venice; B=Valle Dogà; C=Valle Figheri; D=Dogaletto). Circle encloses industrial area of Porto Marghera.

2.2. Analytical methods

Total atmospheric 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 $^{37}C_4$-labeled 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.* (2001).

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 five 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%.

3. Results and discussion

3.1. Meteorology

During the study period the main wind direction observed was NE-N, with mean wind speed of 2-4 m s^{-1}, in agreement with the general anemometry of the area (Carrera *et al.,* 1995). In particular, the main wind direction in site A has been from NE, and the observed frequency for winds from W was always <10% for each deposition sample. Moreover, also the percentage of winds from N at site C has been always <10%. This confirms that these sampling stations have never been downwind from the industrial zone (located NW from site A and N from C).

The rain amount recorded during the study period fell in the variability range known for the area. No correlations have been observed between precipitations and PCDD-Fs deposition.

3.2. Deposition of PCDD/Fs

Table 1 presents a comprehensive list of PCDD/F data measured in bulk deposition. In general, fluxes of the sum of tetra- to octa-CDD/F homologues in bulk samples are between 0 and 470 pg m^{-2}d^{-1} (0-9.2 pg TEQ m^{-2}d^{-1}). As expected, there is a gradient, increasing from remote to urban/industrial stations. PCDD/F concentrations for the sum of the tetra through octa-PCDD/F homologues (and the ∑TEQ) are as follows:

~100 pg m^{-2}d^{-1} (ΣTEQ ~ 2pg m^{-2}d^{-1}) near the industrial district of Porto Marghera (station D), ~50 pgm^{-2}d^{-1} in the city of Venice (station A), and ~30 pgm^{-2}d^{-1} in the rest of the Lagoon.

The relations between characteristic grain-size classes of aerosol (<2 µm, 2-8 µm, 8-32 µm, >32 µm) (Guerzoni *et al.,* 1999) and PCDD-Fs deposition have been investigated, and no significant correlation was observed.

The relative contribution of OCDD to the sum of tetra- to octa- CDD/F homologue groups differs widely among stations and monthly samples, from ~2 to ~ 50%. Deposition is in general dominated by the higher chlorinated congeners and, on average, OCDD accounts for ~ 30% of the ΣPCDD/F flux in stations A,B and C, and for only 15% near the industrial station D, thus confirming the data from other industrial districts in Austria (Christmann *et al.* 1989) and elsewhere (Lohmann and Jones, 1988). Possible enhancement of the relative abundances of high-chlorinated dioxins/furans may be due to the dominance of this fraction in the particle phase, whereas the gas phase is dominated by low-chlorinated ones (Oh *et al.,* 2001). Conversely, Jones and Duarte-Davidson (1997) found that the mixture of PCDD/F congeners and homologues was the same in air and in bulk deposition, over given sampling periods and sites. Thus, it was suggested that PCDD/Fs of different levels of chlorination were transferred with similar efficiencies from the air to the collectors, despite different gas/particle partitioning in the air.

The PCDD:PCDF ratio in the deposition also varies, ranging from 0.1 to 4.7. The mean value drops from 0.5 in site D, near Porto Marghera, to 1.7 in the city of Venice (site A), with intermediate values around 1 in the two stations at the northern and southern edge of the Lagoon (sites B and C). This inversion in the PCCD:PCDF ratio is also clearly shown in sediments collected near the industrial district (PCDD:PCDF<0.5), compared with sediments from the channel in the historical centre of Venice, with PCDD:PCDF ratio values >2. The difference in the ratio was taken as a sign of different sources affecting the two locations (Marcomini *et al.,* 1999; Wenning *et al.,* 2000).

3.3. TEQs

ΣTEQ deposition fluxes are in the range 0-10 pg m^{-2} per day (mean ~ 2pg m^{-2}d^{-1}), with 2,3,4,7,8 PeCDD/F contributing, on average, between 20 and 30% of the ΣTEQ (see Figure 3). Mean deposition

fluxes in the whole Lagoon of Venice are at the lower end of the ranges found in remote-rural stations, as reviewed by Lohmann and Jones (1998), who have shown a decline in PCDD/F fluxes in Germany and the UK in recent years. Deposition fluxes in stations A (urban) and D (industrial) in the Lagoon of Venice are approximately one-half to on-quarter of those found in Kyoto Bay by Sakai *et al.* (2001) and are similar to those found in recent years in Hesse, Germany (Fiedler *et al.* 2000).

Table 1. Atmospheric fluxes of 2,3,7,8-substituted dioxins and furans (P4-8CDD/F) in Lagoon of Venice from July 1998 to July 1999, together with information on other variables. Values below detection limit were considered equal to zero. * = 9 months sampling (November 1998 – July 1999). [1]=TE calculation made using WHO-TEF (Van den Berg *et al.*, 1998).

Figure 3. Relative individual contribution to overall TEQs in deposition

3.4. PCDD/F total deposition to Lagoon

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.,* 2001). PCDD/F total fluxes inside the Lagoon were ~12 grams, corresponding to ~ 400 mg TEQ. Higher fluxes were calculated for winter (mean Oct.-Feb.: $\sum$PCDD/F flux ~ 40 mg TEQ/month) than summer (mean March-Sept.: $\sum$PCDD/F flux ~ 15 mg TEQ/month), in line with similar seasonal differences reported by Duarte-Davidson *et al.* (1994) and Halsall *et al.* (1997) (Figure 4).

Figure 4. Pattern of monthly $\sum$PCDD/F deposition (mg TEQ) to the entire Lagoon during study period (July 1998-July 1999).

3.5. Fingerprinting

It is instructive to compare the pattern of PCDD/Fs in bulk deposition sampled concurrently in different stations, because this yields information on the relative horizontal transfer of the compounds. Data from the four sampling sites show significant differences, with a clear fingerprinting signature (PCDF>PCDD) in most of the samples collected near the industrial zone.

Comparisons of the PCDD-F patterns of the homologue groups of each monthly sample show high similarity (with some month-to-month variations) between stations A, B and C (Figure 5). In particular, in

these three stations, 8CDD (and 7CDD) made the prevailing contribution to ∑PCDD/F loading. Instead, station D revealed three different patterns: one (D-γ, 5 samples) was similar to all samples in stations A, B and C; in the other two patterns (D-α, 5 samples, and D-β, 3 samples) OCDF made a different contribution to ∑PCDD/F loading, increasing from ~ 20 (D-γ) to ~ 40% (D-β) and reaching values >70% (D-α), thus reversing the PCDD:PCDF ratio from <1 to ≅ 2. It is interesting to note that, during the last two months of the survey (June and July 1999), all four stations showed a strikingly similar increase in the relative contribution of OCDF to the total PCDD/F loading, possibly related to an accidental release of 900 kg of vinyl chloride monomer (VCM) from the industrial district.

Figure 5. Comparisons of PCDD/F patterns in bulk deposition. Error bars represent one single standard deviation. Above: stations A,B,C =annual average; station D, monthly samples. Below: site D, monthly samples. [Analytical data normalised to total sum of PCDDs+PCDFs = 1000] (see text for details)

3.6. Multivariate statistics

Principal components analysis (PCA) is a technique suitable for ordinate data in one, two or three dimensions (linear compounds of correlated variables) and allows to interpret them 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 homologue profiles of dioxins and furans, together with profiles of source-related fingerprints.

Other authors applied multivariate analysis to environmental samples collected in Venice. Among them, Fattore *et al.* (1997) classified sediments samples of the Venice lagoon and source-related samples from literature, and Jimenez et al (1998) compared sediments from Lagoon of Venice 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 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 furans 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 arising from environmental sources of pollutants, results obtained by other authors on different kinds of samples were also inserted into the processing, together with data from samples from the Venice industrial district (Table 2). In detail, these markers include: (a) "urban" and "rural" aerosol samples (Cole *et al.,* 1999); (b) wastewater and sludge 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). To this, we added data derived from direct analysis of wastewater from EDC, sludge from the industrial district of Porto Marghera (EDC, VCM and PVC production), and wastewater from two municipal water treatment plants (Fusina and Campalto, near Venice).

Table 2. Source-related samples used for principal component analysis. EDC=ethylene dichloride, VCM=vinyl chloride monomer, PVC=polyvinyl chloride.

PCA was used to take the data from the original 10-dimensional space (PCDD/F homologue profiles) and project them onto a two-dimensional plane that retains most of the information from the original data. Three factors were extracted from the analysis, accounting for ~ 75% of total variance (Table 3). Factor 1 (F1) is characterised by tetra- to octa-CDF homologues, mainly of industrial origin, and accounts for 38% of variance. Factor 2 (F2) is influenced by tetra- to hexa-CDD, and represents 23% of variance. Factor 3 (F3) is influenced by heptachlordibenzodioxins (7CDD) and 8CDD in the positive sense and by 8CDF in the negative one, and accounts for 15% of variance.

Table 3. Factor loadings from principal component analysis.

Each monthly deposition sample, together with all markers, can now be plotted in the space of the new variables (factors). As F1 and F3 are factors that better discriminate samples, Figure 6 shows samples ordered in two dimensions (F1, F3), where crosses represent different source-related fingerprints from Table 2.

Figure 6. Plot of samples and markers in dimensional space of factor 1 and factor 3, derived from Principal Components Analysis, applied to homologue profiles of dioxins and furans.

All samples with higher levels of octa-CDF and lower ones of octa-CDD plot in the lower part of the graph plot (solid line). As the figure shows, all industrial markers (i.e., EDC-, VCM-, PVC-related samples) plot in this area (Figure 6, Table 2). Several deposition samples, mainly from site D -i.e. those with α and β fingerprints- fall in this part of the plot, together with two samples collected in July 1999 in the city of Venice (site A) and in the southern part of the Lagoon (site C). The second area (dotted line), in the higher part of the plot, includes samples with low levels of octa-CDF and higher contents of hepta- and octa-CDD, together with the markers of civil water treatment plants, urban and rural aerosols. This area includes most of the A, B, C and D-γ patterns. Briefly, station D, near the industrial zone, is typically influenced by atmospheric emissions of dioxins and furans enriched in OCDF, probably associated with VCM production. The source of emission also occasionally contaminates atmospheric deposition of such substances in the other sites.

3.7. Comparisons with guidelines

Emission into the atmosphere followed by deposition on plants and animal uptake is the main pathway of human exposure to dioxin. The World Health Organisation states that the tolerable daily intake (TDI) of dioxins for humans is 1-4 pg TEQ kg^{-1} day^{-1}. By means of selected transfer models (Prinz *et al.,*1993), daily intake values have been translated into quality objectives for dioxin deposition, and the Flemish Institute for Technological Research (VITO) deduced a target value for dioxin deposition of 3.4-13.6 pg TEQ m^{-2} day^{-1} (De Fré *et al.,* 2000). More recently, the European Union strategy on PCDD-Fs and polychlorobiphenyls (PCBs) has aimed at reducing human intake levels to 14 pg TEQ kg^{-1} $week^{-1}$ (European Commission, 2001, EU strategy on dioxins, furans and polychlorobiphenyls), corresponding to ~ 7 pg TEQ m^{-2} day^{-1}.

On this basis, the frequency of all bulk deposition samples collected in the four stations exceeding the guidelines was calculated (Figure 7). Although the actual atmospheric deposition of dioxins and furans in Venice is not very high, one sample exceeds the deposition value based on the EU target value for human intake. But, as was reported in a previous work (Rossini *et al.,* 2001), in a more realistic exposure scenario, mixtures of dioxin-like and non-dioxin-like compounds should also be considered. For example, Van

Birgelen (1998) reports that hexachlorobenzene (HCB) should be classified as a dioxin-like compound, as its mechanism of action resembles that of mono-ortho-substituted PCBs. According to the limited information available, it is estimated that HCB is about 10,000 times less potent than TCDD, corresponding to a relative potency value of 0.0001 (Van Birgelen, 1999).

Lastly Figure 7 shows the frequency of samples exceeding the guidelines, adding TEQs due to PCBs and HCB to PCDD/F values (recalculated from Rossini *et al.,* 2001). In this way, 9% of samples exceed the limit value, 16% exceed the EU target value, and 27% exceed the guide value (PCDD-F+PCB+HCB curve). Samples exceeding the limit value were collected in July 1998 and October and February 1999, in sites A and D.

Figure 7. Cumulative frequency of samples exceeding guidelines (recalculated from Rossini *et al.*, 2001). [1]De Fré *et al.*, 2000, [2]European Commission, 2001, EU strategy on dioxins, furans and polychlorobiphenyls.

4. Conclusions

- Bulk deposition provided one-year of data on PCDD/F fluxes, which were independent of rainfall and particle grain-size;

- Dioxin and furan fluxes from the atmosphere in the Lagoon of Venice were generally lower than those found in Kyoto Bay and similar to those in Hesse, Germany;

- PCA was used to compare differing PCDD/F patterns among stations, which may indicate different sources;

- The station D nearest the industrial zone showed signs of contamination from EDC and VCM production;

- Between 9% and 27% of the samples exceed the integrated guide-line values, recently proposed by the Flemish Institute for Technological Research.
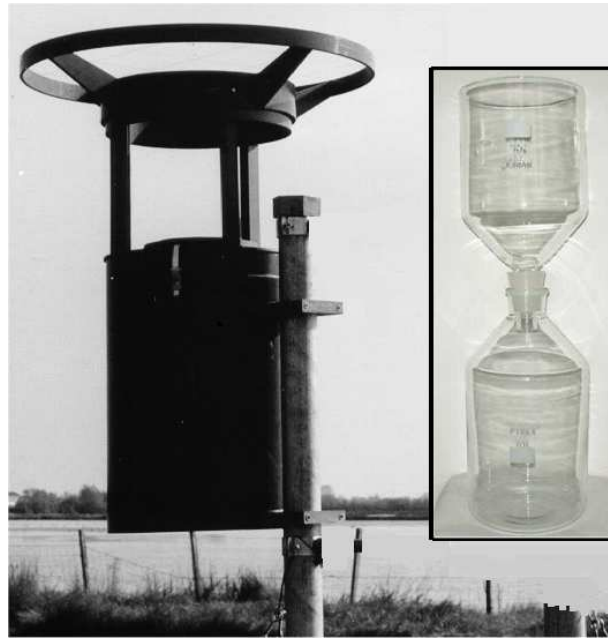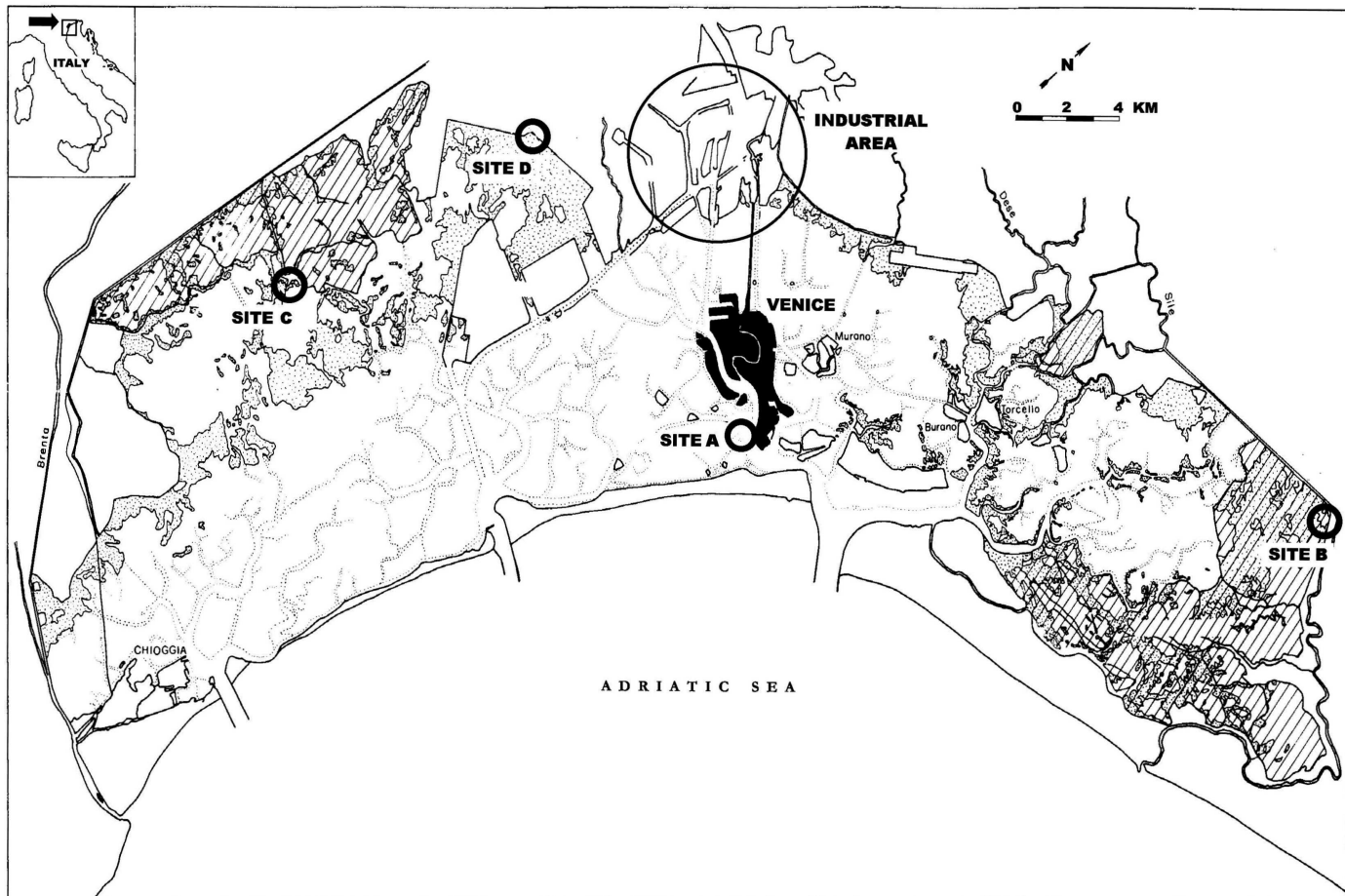
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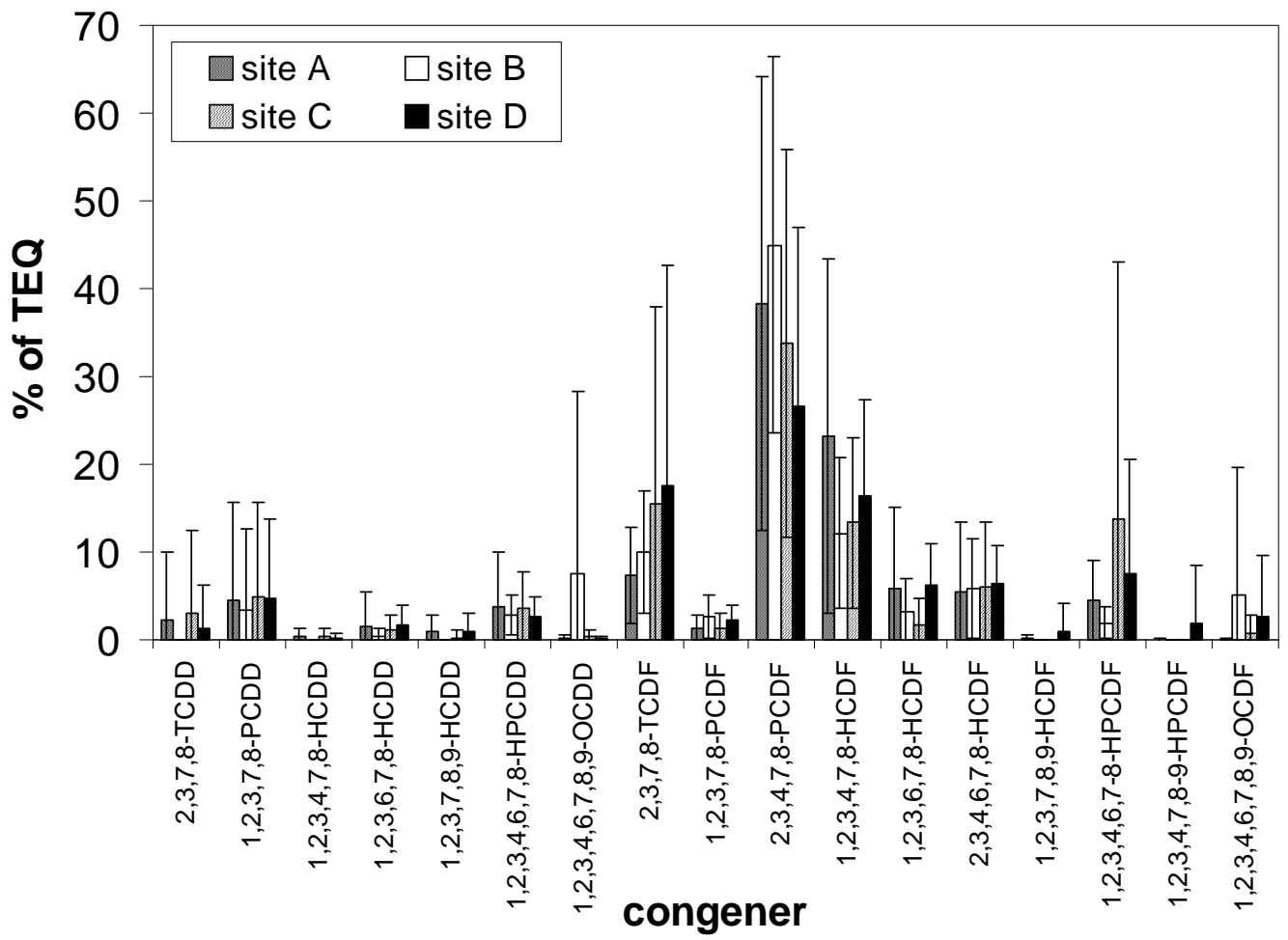
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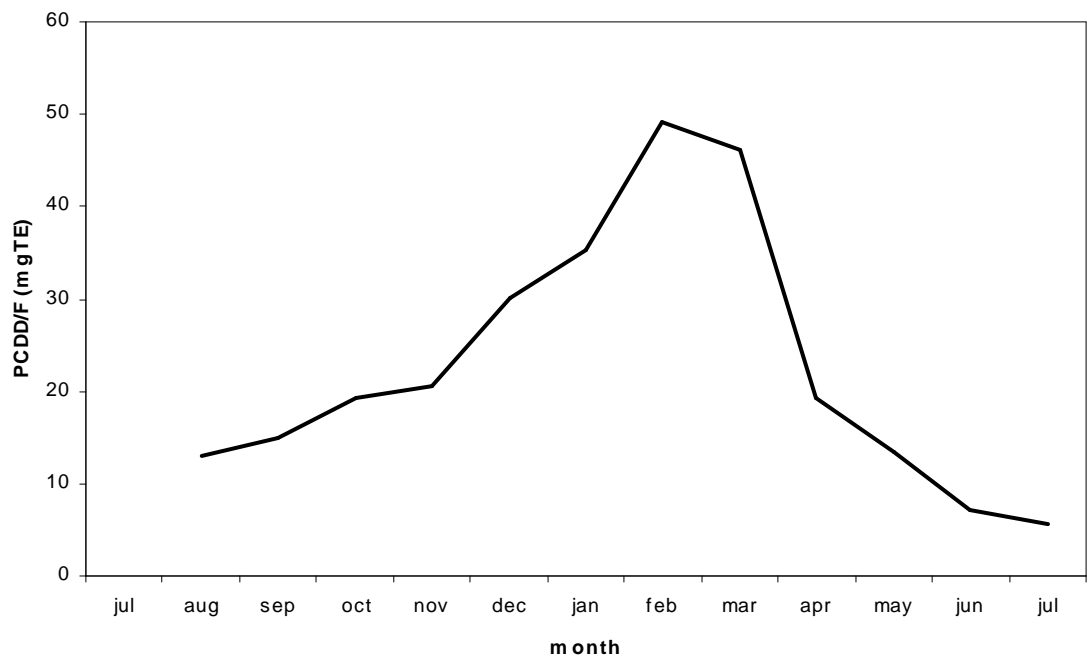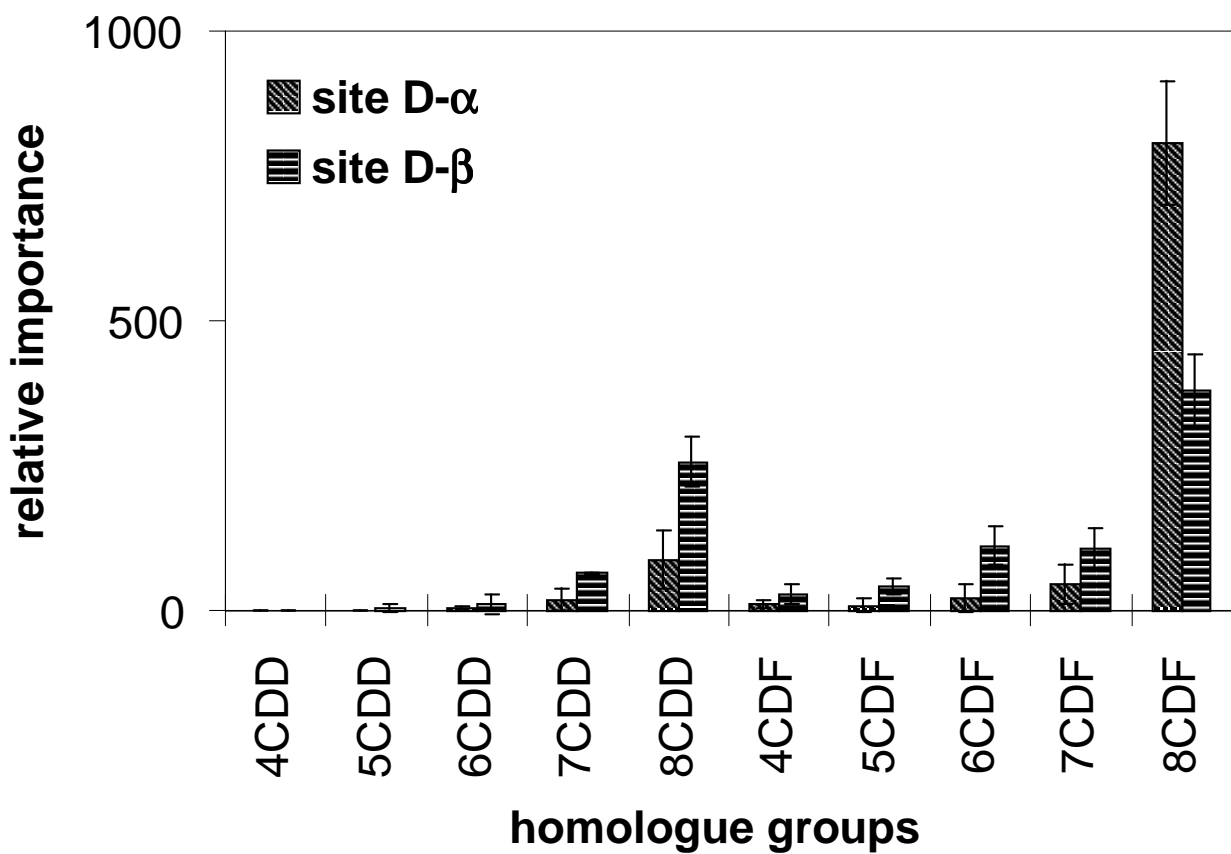
Figure showing two panels of relative importance versus homologue groups. Top panel legend: site B, site C, site A, site D-γ. Bottom panel legend: site D-α, site D-β. X-axis labels: 4CDD, 5CDD, 6CDD, 7CDD, 8CDD, 4CDF, 5CDF, 6CDF, 7CDF, 8CDF. Y-axis: relative importance (0–1000).
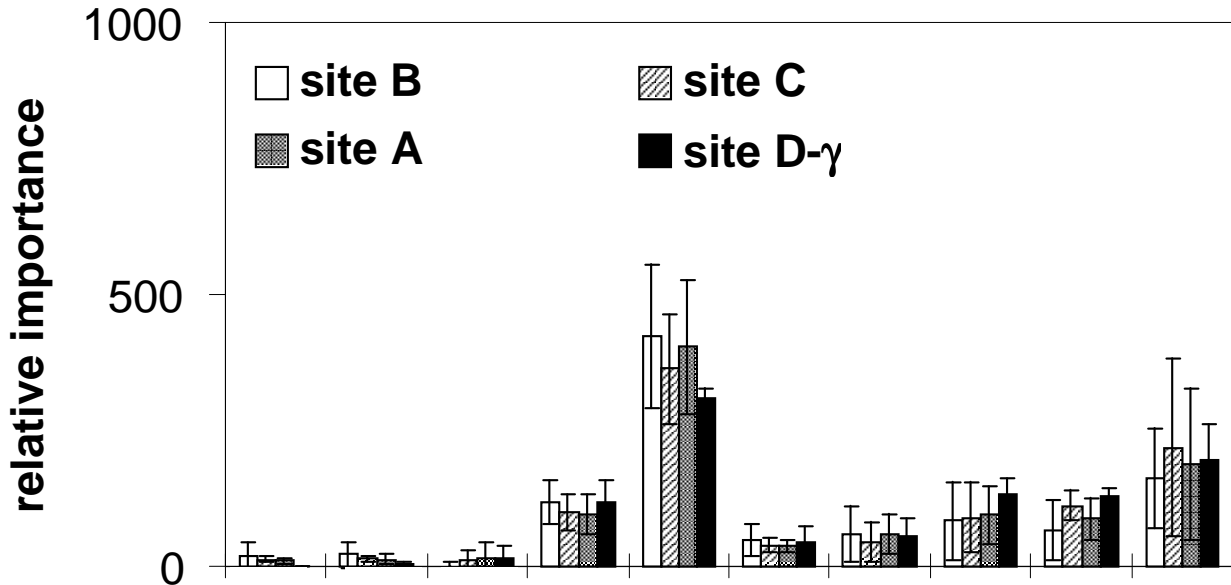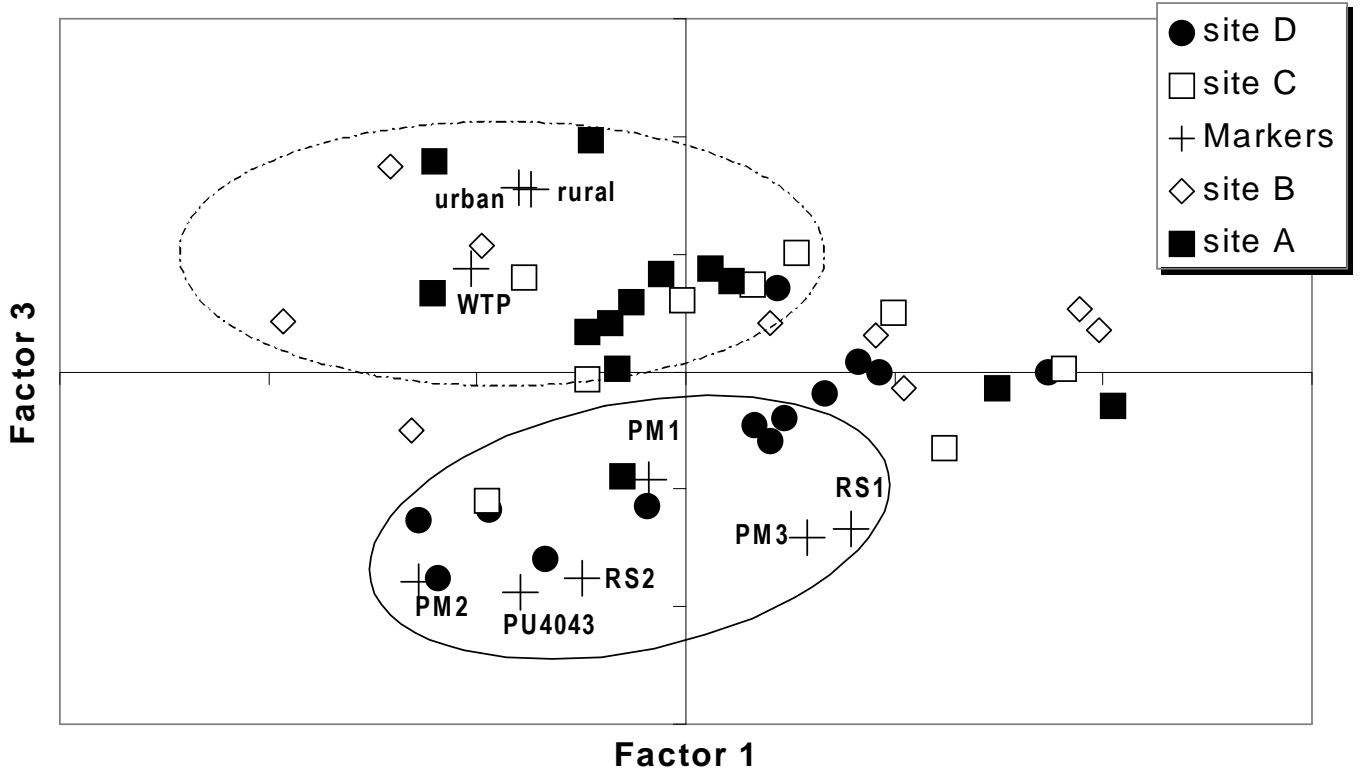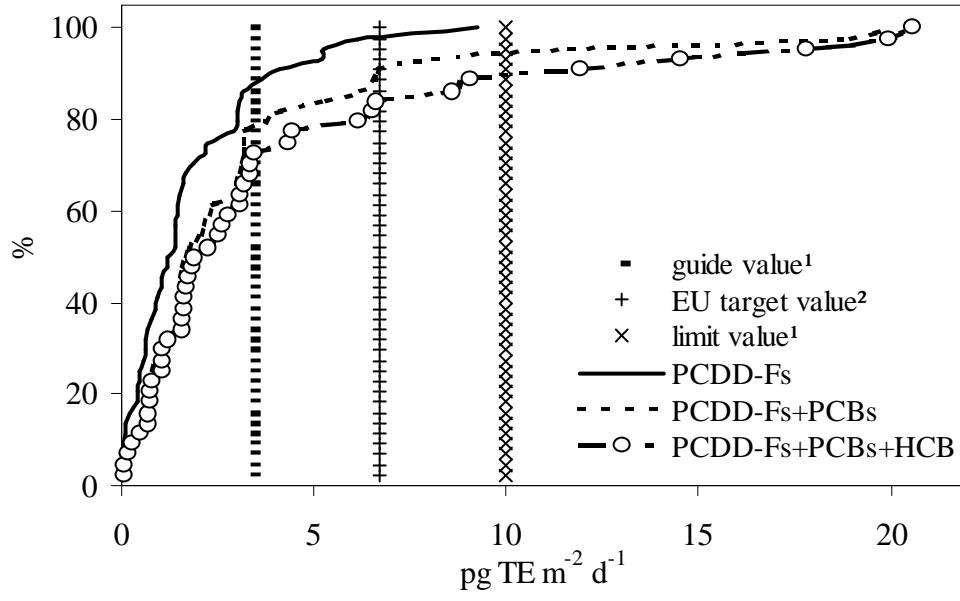
Figure captions

Figure 1. Bulk deposition sampler (modified from Bergerhoff[®]) used in the field. Right: Pyrex[®] "funnel-bottle" unit.

Figure 2. Location of atmospheric deposition sampling sites. (A=city of Venice; B=Valle Dogà; C=Valle Figheri; D=Dogaletto). Circle encloses industrial area of Porto Marghera.

Figure 3. Relative individual contribution to overall TEQs in deposition.

Figure 4. Pattern of monthly ∑PCDD/F deposition (mg TEQ) to the entire Lagoon during study period (July 1998-July 1999).

Figure 5. Comparisons of PCDD/F patterns in bulk deposition. Error bars represent one single standard deviation. Above: stations A,B,C =annual average; station D, monthly samples. Below: site D, monthly samples. [Analytical data normalised to total sum of PCDDs+PCDFs = 1000] (see text for details)

Figure 6. Plot of samples and markers in dimensional space of factor 1 and factor 3, derived from Principal Components Analysis, applied to homologue profiles of dioxins and furans.

Figure 7. Cumulative frequency of samples exceeding guidelines (recalculated from Rossini *et al.*, 2001). [1]De Fré *et al.*, 2000, [2]European Commission, 2001, EU strategy on dioxins, furans and polychlorobiphenyls.

Table 1.

Atmospheric fluxes of 2,3,7,8-substituted dioxins and furans (P_{4-8}CDD/F) in Lagoon of Venice from July 1998 to July 1999, together with information on other variables. Values below detection limit were considered equal to zero. * = 9 months sampling (November 1998 – July 1999). [1]=TE calculation made using WHO-TEF (Van den Berg *et al.,* 1998).

site	units	ΣP_{4-8}CDD/F pg m^{-2} d^{-1}	OCDD % di ΣP_{4-8}CDD/F	PCDD/PCDF	ΣTEQ[1] pg m^{-2} d^{-1}	2,3,4,7,8-CDF % di ΣTEQ
A	average	48.6	33.6	1.7	2.0	27.5
	median	35.4	36.0	1.5	0.9	32.9
	min	14.3	19.2	0.4	0.2	0.0
	max	134.6	50.1	4.3	9.2	45.7
B*	average	29.3	29.8	1.5	1.3	28.7
	median	25.4	29.9	1.1	1.4	36.7
	min	0.0	0.0	0.0	0.0	0.0
	max	61.1	51.3	4.7	3.2	50.2
C*	average	37.7	27.6	1.1	1.8	24.2
	median	30.0	25.8	1.1	1.0	32.9
	min	9.8	17.5	0.3	0.0	0.0
	max	109.2	38.1	1.9	6.2	36.0
D	average	124.1	15.0	0.5	1.9	19.8
	median	59.3	17.1	0.5	1.6	28.3
	min	29.0	1.7	0.0	0.0	0.0
	max	470.0	23.2	1.2	5.2	38.4

Table 2.

Source-related samples used for principal component analysis. EDC=ethylene dichloride, VCM=vinyl chloride monomer, PVC=polyvinyl chloride.

Code	Source-related samples	Type	Reference
urban	urban air	air	Cole *et al.,* 1999
rural	rural air	air	Cole *et al.,* 1999
PU4043	heavy ends from distillation of VCM	wastewater	Stringer *et al.,* 1995
RS1	EDC, VCM, PVC production	solid waste	Carrol *et al.,* 1996
RS2	EDC/VCM production	sludge	Carrol *et al.,* 1996
PM1	local EDC, VCM and PVC production	wastewater and sludge	this study
PM2	local VCM production	sludge	this study
PM3	local EDC/VCM production	sludge	this study
WTP	domestic water treatment plants	wastewater	this study

Table 3.

Factor loadings from principal component analysis.

	Factor 1	Factor 2	Factor 3
4CDD	-0.12	**0.81**	-0.01
5CDD	0.19	**0.90**	-0.01
6CDD	0.14	**0.88**	0.08
7CDD	0.30	0.14	**0.78**
8CDD	-0.09	-0.11	**0.92**
4CDF	**0.73**	-0.15	0.28
5CDF	**0.84**	0.18	0.20
6CDF	**0.90**	0.10	0.19
7CDF	**0.68**	0.08	-0.04
8CDF	-0.39	-0.07	**-0.85**
Expl. Var.	37.90	22.59	14.99