AIR LEVELS OF DIOXINS AT SEVESO: PATTERNS AND SOURCES

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Introduction

Seveso is well known as the site where in 1976 a wide populated area was contaminated by elevated amounts of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) isomer escaped from a chemical reactor. Studies on the consequences of the accident related exposure of the environment and population have been widely reported in the past years and epidemiological and environmental surveys are still going on for the long term follow up of the accident. However Seveso, beside the residuals of the accident, belongs to a densely populated suburban area with high concentration of small medium industries and intense traffic; it was of interest therefore to study atmospheric concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and furans (PCDFs) to gain information on the exposure of population to sources not related with the accident.

In a previous study we analysed air dioxin concentrations in zone A and B of Seveso and in high traffic area in Milan (1). Zone A was the most polluted by the Seveso accident (2,3,7,8-TCDD concentration in soil >50 $\mu g/m^2$) and it was cleaned-up by collection and disposal of contaminated soil. Zone B, affected by lower contamination (5-50 $\mu g/m^2$), was reclaimed by mixing the most contaminated points with uncontaminated underlying layers (2).

In the present study we evaluated the possible sources for atmospheric PCDDs and PCDFs in zones A and B of Seveso, investigating the presence of local sources of emission in an area with a radius of 10 km centred on Seveso. Principal Component Analysis (PCA), a multivariate method widely used to compare congener or homologue profiles of PCDDs/Fs in environmental samples (3-5), has been utilised to compare air sample profiles from Seveso and Milan with the typical profiles for the different specific emission sources.

Materials and methods

Samples and analyses were as previously described (1,6). Briefly, air samplers were working for 15 minutes every two hours for a year. Long-term air samples were collected in two locations in Seveso, corresponding to the ex zone A and B and in a reference location in Milan in a high traffic area. Samples were collected in spring, summer, autumn and winter.

A questionnaire was sent to all the 61 Municipalities in the selected area, asking for the presence of combustion sources and other known sources of PCDDs/PCDFs.

Principal Component Analysis (PCA) was utilised to evaluate results from this study and to compare such results with data arising from the literature. PCA is a multivariate data analytical technique whose main purpose is to explore and to detect patterns within a set of data. This method allows summarise the information of the original data matrix using a smallest number of variables while preserving the greatest possible amount of information. The homologue profiles and congener profiles of the Seveso and Milan air samples were evaluated by PCA in order to detect the main differences between the three sampling locations. Moreover PCA was also applied to a larger matrix containing homologue profiles of samples analysed in this study and environmental source-related samples collected from literature (7). The individual PCDD/F homologue values were normalised to the total concentration of PCDDs/Fs by expressing each

value as percentage of the sum of the total PCDD/F. Values under the limit of detection were treated as half of this limit.

Results and discussion

The average annual concentrations expressed as total toxic equivalents (∑TEQ) were 0.26, 0.35 and 0.22 pg/m^3 in Seveso zone A, B and Milan, respectively (1). Actual air dioxin values were similar or somewhat higher to those reported for urban areas of other industrialised countries (8-11) and showed a strong seasonality since PCDD/PCDF concentrations were considerably higher in Autumn/Winter than in Spring/Summer. Furthermore a high concentration peak, mainly due to tetrachlorinated dibenzofurans non 2,3,7,8-substituted, was observed in the Zone B of Seveso in autumn. The 2,3,7,8-isomer distribution of the samples did not show a significant prevalence of the 2,3,7,8-TCDD isomer in Seveso compared to Milan. The score plot of the PCA using the 2,3,7,8-substituted congeners and the homologue profiles of samples analysed in the present study did not show any "fingerprint" related to the sampling location or to the season. The score plot of the PCA using homologue profiles distinguished, along the first principal component, the sample collected in autumn in zone B from the other samples, since the high concentrations of total tetrachlorinated dibenzofurans (TCDFs) and total tetrachlorinated dibenzo-*p*-dioxins (TCDDs).

To investigate the relationships with environmental emission sources for these pollutants, source-related homologue profiles arising from the literature (7) were included in the data matrix of the PCA. The resulting score plot is shown in Figure 1. The first principal component, representing the main direction of variability of the original data, clearly discriminates two clusters: one on the left including samples related to sewage and industrial discharges, and one on the right including all combustion related samples and samples analysed in the present study. Within this cluster most of the Milan and Seveso samples are mixed with most of the samples related to municipal solid waste (MSW) incinerators and traffic emissions. Sample collected in Seveso zone B is characterised by slightly higher values of the second principal component, mainly influenced by TCDFs, and it is located between samples related to oil central heating and combustion of treated wood.

Results of the questionnaire sent to identify possible local sources of PCDDs/Fs in the area under investigation are summarised in Table 1. Several activities, including chemical industries, foundries, and a steel plant are located. Moreover, many incinerators, particularly for wood residues from furniture factories, and some main roads with high traffic levels, are also present. These results confirmed the starting hypothesis that the area is affected by several emissions sources for these pollutants, resulting in PCDD/PCDF levels that are at the upper limits of the typical concentration range found in urban air. Moreover, the highest concentrations detected in autumn in zone B and results of the comparison with source-related samples by PCA, suggest that this zone is a relapse area of local source emissions. The high density of incinerators for wood residues in the area seems to confirm such hypothesis.

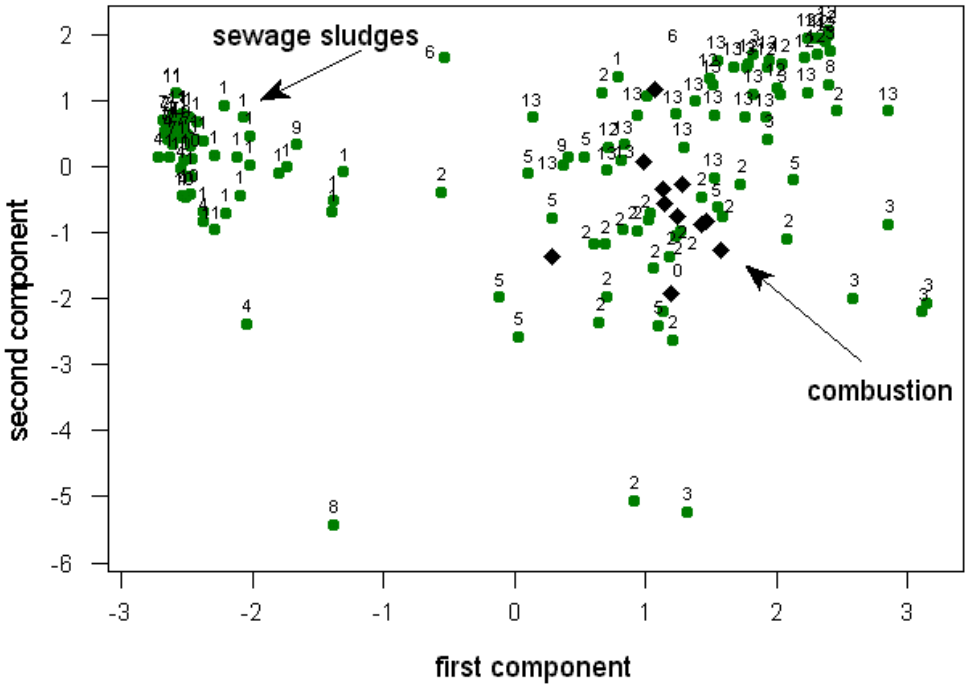

Fig. 1. Score plot of the PCA showing the first principal component versus the second one for Seveso and Milan air samples (◆) and different source related samples (●). The Seveso point with the highest value on the second component refers to Seveso zone B, autumn sample.
Legend: 1: sewage sludges; 2: MSW incinerator emissions; 3: PVC and PCB combustion; 4: residues in pentachlorophenol; 5: traffic; 6: Paper mill residues; 7: compost residues; 8: synthetic gum combustion: 9-11: dyes residues; 12: treated wood combustion; 13: soot from oil central heating.

Table 1. Activities related to PCDDs/PCDFs emissions in the area with a radius of 10 km centred on Seveso

	Number	%
Contacted Municipalities	61	100
Replies from Municipalities	41	67
MSW incinerators	1	2
Industrial incinerators	2	5
Hospital incinerators	1	2
Incinerators from paper mill effluents	0	0
Incinerators for wood residues	18	44
Incinerators for sludges	1	0
Foundries	1	2
Steel plant	14	34
Chemical industries	19	46
Others	5	12

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