Using a linear correlation as a tool for the identification of a contamination source

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Introduction

In an industrial plant inside Brescia, a city in the North-West of Italy, 150 tons of PCBs were produced in the past decades, contaminating the surrounding area.

Soil and forage samples around the industrial site were analyzed for PCB and PCDD/F congeners. In order to help identifying the source of the contamination, the analytical results were elaborated in terms of simple linear correlation of the profile, assuming that, for the same source of contamination, the concentration of a single congener is not an independent variable with respect to other congeners[1]. As a consequence, soil samples contaminated by the same source should display similar profiles and the similarity of the profiles can be ranked through correlation coefficients.

The objective of this study is to apply this approach to the contaminated soils and forages of the above mentioned case to gain information on the contamination source.

Materials and Methods

Ten soil samples (AA, AD, AI, BE, BF, BG, BO, CA, Y, R) and five forage samples (a, b, d, e, f), grown on some of the soils, were analyzed for PCBs and PCDD/Fs; they were spiked with labeled $^{13}C_{12}$ recovery standards, nine 2,3,7,8 substituted congeners of PCDD/PCDF and ten PCBs. After clean-up, these samples were injected into an Autospec HRGC/HRMS system operating at 10.000 resolution for PCDD/Fs and non-*ortho* PCBs while PCBs congeners were analyzed by HRGC/LRMS[2] .

The correlation of sample profiles is tested and the Pearson's correlation coefficient (r) is obtained: for r values higher than 0.8, the profiles considered are arbitrarily assumed to be similar; when r is 1, the profiles are coincident[3].

Results and Discussion

We considered the PCBprofile for correlation. The most contaminated soil sample (soil BO) was selected to be compared to the other soil samples.

The Pearson's correlation coefficient (r) with the other soil samples are reported in Table 1 for the 60 PCB congeners determined (Corr tot) and for the 7 indicator congeners (Corr 7PCB)[4]. Data are listed in decreasing order of the value of the Corr tot.

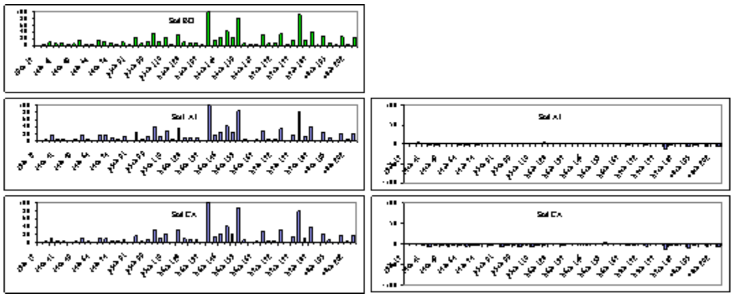
The high correlation coefficients for the profiles indicate that all samples are probably contaminated by the same PCB mixture (Table 1).

Table 1. Pearson's correlation coefficient obtained from the comparison of PCB profiles of BO soil sample with the other soils. In bold are reported the values higher than 0.8.

	AI	CA	AA	R	AD	Y	BE	BG	BF
Corr tot	**0.9940**	**0.9917**	**0.9747**	**0.9743**	**0.9723**	**0.9697**	**0.9608**	**0.9600**	**0.9075**
Corr 7 PCB	**0.9918**	**0.9886**	**0.9736**	**0.9907**	**0.9232**	**0.9569**	**0.9057**	**0.9678**	**0.9422**

In the Figure 1, the soil BO and the two best fit profiles are shown together with the graph of the profile difference.

Figure 1. PCB profile comparison: the BO sample soil and the two best fitting profiles (left side) together with their relative difference profiles (right side).



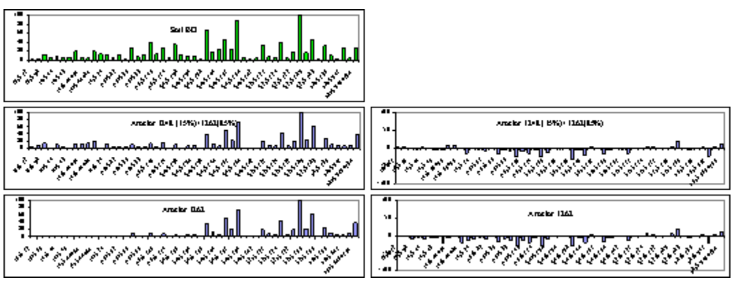
The soil profile displays a prevalence of congeners with 6 and 7 chlorine atoms, suggesting the presence of heavy mixtures, such as Aroclor 1260 or Aroclor 1264 type mixtures. When the profile correlation of soil sample BO is made with the composition profiles of industrial mixtures[5,6], including two virtual mixtures containing in the first case the 15% of Aroclor 1248 and the 85% Aroclor 1262, and in the second case a mixture with Aroclor 1248 (15%) and Aroclor 1260 (85%), the correlation coefficients reported in Table 2 are obtained.

Table 2. Pearson's correlation coefficient obtained from the comparison of PCB profiles of BO sample soil with the industrial mixtures. In bold the values between 0.8 and 1 are reported.

	Aroclor 1248 (15%)+1262(85%)	Aroclor 1262	Aroclor 1248 (15%)+1260(85%)	Aroclor 1260	Clorphen A60	Aroclor 1254	Clorphen A50
Corr tot	**0,893**	**0,883**	**0,879**	**0,871**	**0,819**	0,305	0,304
Corr 7 PCB	**0,933**	**0,962**	**0,871**	**0,898**	0,773	-0,256	-0,275

The two best fitting profiles obtained and their profile difference graphs are shown in Figure 2: the mixture containing 15% of Aroclor 1248 and 85% Aroclor 1262 provides the best correspondence with the soil profile, followed by Aroclor 1262. This correlation gives an indication that the contamination source is a heavy mixture with a minor component of lighter mixtures.

Figure 2. PCB profile comparison between the BO soil sample and the two best fitting profiles of industrial mixtures, together with their difference profiles.



A low correlation coefficient indicates significant differences in the profile.

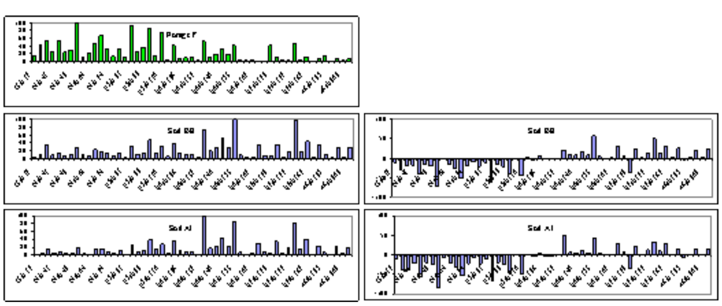
When comparing a forage (forage "f") profile with the ones of the soils in which it was grown, one could expect a good correlation: on the contrary, the value of *r* for the correlation of the "f" forage sample with the CA and the AI soil (where forage "f" was grown) samples is 0.29 and 0.36, respectively (Table 3). The other soil samples also show not significantly different *r* values. A visual inspection (Figure 3) of the profiles of the forage, the best fitting soils and their difference helps however finding the cause: the forage is richer of the more volatile congeners and poorer of the less volatile ones with respect to the soil. This suggests that the forage is contaminated not only by soil powder adhered to it, but also by PCB vapors condensed on it. Forage is indeed a summer product, and PCBs in that season easily evaporate from soil[7].

This correlation gives best results with PCB profiles. When applied to PCDD+PCDF profiles, the great prevalence of one single congener (often OCDD) over the others may give a levering effect, resulting in high values of *r* even for profiles from different sources.

Table 3. Pearson's correlation coefficient obtained from the comparison of PCB profiles of forage "f" with the soil samples.

	BE	AI	BO	AD	CA	Y	AA	BF	R
Corr tot	0.4267	0.3587	0.3330	0.3243	0.2956	0.2695	0.2078	0.1789	0.1674
Corr 7 PCB	-0.5488	-0.5236	-0.4967	-0.5474	-0.5451	-0.5850	-0.6084	-0.6330	-0.5423

Figure 3. PCB profile comparison between the forage sample (f) and the best fitting profiles of soil samples, together with their difference profiles.



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