

## INDIRECT PCDD/Fs SCREENING BY INORGANIC COMPOUNDS FPXRF ANALYSIS: A STATISTICALLY DRIVEN METHODOLOGY

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### Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are environmental contaminants detectable, in trace amount, in almost all compartments of the global ecosystem. In contrast with other chemicals of environmental concern such as PCB, PCN and polychlorinated pesticides (like DDT or PCP), PCDD/PCDFs were never intentionally produced and do not serve any useful purpose. They are highly toxic and considered among persistent organic pollutants (POPs)<sup>1</sup>. Based on the number of chlorine atoms in the chemical structure and their positions, PCDD/Fs consist of 210 congeners. Among them, 17 congeners have chlorine atoms at least in the positions 2, 3, 7, and 8 of the parent molecule: they show similar toxicological responses with the most toxic being the 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and the 2,3,7,8-tetrachlorodibenzo-p-furan (2,3,7,8-TCDF). In contaminated soils POPs emissions are often associated with the presence of inorganic compounds, such as heavy metals<sup>2,3,4</sup>. In the recent years metals contamination assessments of various sites have been performed by Field Portable X Ray Fluorescence (FPXRF)<sup>5,6</sup>. It provides significant advantages over off-site laboratory analysis: for example, low cost for each single measurement, larger number of samples to be analyzed within the same working time and fast turn-around of results; on the other hands FPXRF accuracy is negatively affected by high moisture and organic matter contents, increasing detection limits and lowering apparent concentrations<sup>5</sup>.

The aim of this study has been to examine relationships between PCDD/Fs and metals for the pollution characterization of a site in the surroundings of a former multi point source industrial facility, mainly constituted by chemical industries and ferromanganese plants<sup>7</sup>, and investigate the possibility of an indirect PCDD/Fs on-site screening by means of FPXRF metal determination.

### Materials and methods

Principal Component Analysis (PCA) is a common statistical technique used to analyze emissions of persistent organic pollutants<sup>8,9,10</sup>, although this method has rarely been used to examine the relationships between POPs and inorganic compounds. PCA is a classical statistical approach to reduce the dimension of the original dataset by transforming it to a new set of variables (called “principal components”) to summarize the features of the above mentioned original variables. Principal components are uncorrelated and ordered such that the  $k^{\text{th}}$  PC has the  $k^{\text{th}}$  largest variance among all PCs. So, the first component has the maximum variance. Successive components progressively explain smaller portions of the variance and are all uncorrelated with each other. In the present work this technique has been applied to 58 surface soil (0-10 cm) samples and 78 surface soil and subsoil (0-60 cm) samples<sup>11</sup>, taken from the above described site. For each sample the sum of 17 PCDD/F's TEQs and 6 inorganic elements (Fe, Mn, Ni, Pb, Cu, Zn) have been measured. PCDD/Fs have been analyzed by HRGC/HRMS (Trace GC Ultra/ DFS, Thermo, USA) according to EPA1613B 1994 method. Native and labelled standards were from Wellington Laboratories, Canada. Metals were analyzed by ICP-MS (Agilent, USA) according to the EPA 6020A 2007 method, after their mineralization (Ethos Touch Control, Milestone, Italy) according to EPA 3051A 2007 method. Standards were from O2Si, Charleston, USA.

Other trace metals were analyzed but their data have not been used in the present work as their concentration in the analyzed samples were close or below those of FPXRF (with respect to the different models commercially available).

Table 1 shows the smallest and largest concentration, mean, standard deviation for each inorganic and organic contaminant taken into account in the present work together with their Italian threshold limit for green areas and residential used soils. All statistical calculations and elaborations were performed using the software package SPSS v. 22.

**Table 1 Descriptive Statistics: metals and PCDD/F's congeners**

Variable	Surface soil				Surface and subsoil				Limit values
	Min	Max	Mean	Std. Deviation	Min	Max	Mean	Std. Deviation	
Fe	18.450,0	36.810,0	27.653,9	4.536,7	17.122,5	26.437,5	21.035,0	3.168,6	not reported
Mn	633,6	2.268,0	1.215,2	434,4	766,8	1.482,8	1.067,0	240,9	not reported
Ni	22,1	128,7	36,7	13,7	22,7	51,3	32,2	9,8	120
Pb	50,0	635,4	131,4	80,4	72,8	170,3	107,8	26,1	100
Cu	39,4	384,3	80,3	42,7	45,6	202,1	92,4	45,7	120
Zn	69,6	340,2	155,5	38,9	115,4	233,8	161,8	32,3	150
∑PCDD/F (TEQs)	77,6	7.380,0	911,7	1.049,8	421,7	8.811,5	2.595,9	2.852,0	10 ng/kg

Concentrations metals in ppm (mg/kg). PCDD/F (TEQs) in ng/kg

**Results and discussion:**

Principal components analysis was performed on surface soil and on surface and subsoil samples. Results are described in table 2.

**Table 2 – Principal Components Analysis: rotated component matrix and variance explained**

Variables	Surface soil		Surface and subsoil	
	PC 1	PC 2	PC 1	PC 2
Fe	0,052	0,863	-0,43	0,860
Mn	0,418	-0,607	0,431	-0,449
Ni	0,956	0,041	0,224	0,530
Pb	0,212	0,430	0,909	0,146
Cu	0,969	-0,098	0,956	-0,073
Zn	0,848	0,400	0,854	0,353
PCDD/F (TEQ)	0,880	0,024	0,741	-0,084
% variance	51	21	47	19
Cumulative % variance	51	72	47	66

Two PCs have been calculated. In surface soil and in deeper soil samples they accounted for 72% and for 66% of the cumulative variance, respectively. In surface soil, PC1 tends to show high positive correlation with Ni, Cu, Zn and PCDD/F's TEQs and PC2 presents high positive correlation with Fe and a negative correlation with Mn. Neither of the two components can perfectly "saturate" Pb in surface soil. In deeper soils, PC1 appears to be positively correlated with Pb, Cu, Zn and PCDD/F's TEQs, while Fe, and Ni show a positive correlation with PC2. Neither of the two components can perfectly "saturate" Mn in deeper soils. The relationship between original variables and PCs is graphically represented in fig. 1.

The proximity of the site to a former multi point source industrial facility suggests to represent principal components as two pollutant's emission typologies: chemical industries (PC1) and ferromanganese plants (PC2). Therefore PCDD/F's TEQs, Ni e Cu are generated from the same emission's source and they belong to the same cluster both in surface soil and in deeper soil. Multiple linear regression analysis (MLR) has been performed to realize if this "proximity" is also explained by a correlation between variables. Either an "enter" and a stepwise linear regression, in order to avoid multicollinearity between the independent variables, have been carried out considering PCDD/F's TEQs as dependent variable and Fe, Pb, Zn, Cu and Ni as explicative variables.

For both soil depths sampled, two models have been determined. Their regression coefficients ( $R^2$ ) have been reported in table 3.  $R^2$  value is significative for surface soil regression model ( $> 0,7$ ), when PCDD/F's TEQs is correlated with Cu and Mn, although Mn and dioxin/furans are not in the same cluster. The same relationship is not significative in deeper soil's samples, where, instead, 56% of PCDD/F's TEQs variance is explained by Cu, Ni and Zn. This occurs because Mn is an element less leacheable than the other metals, and tend to remain on the soil surface.

Furthermore, with the increase of the depth of the soil, linear relation intensity between PCDD/F's TEQs and metals decrease.

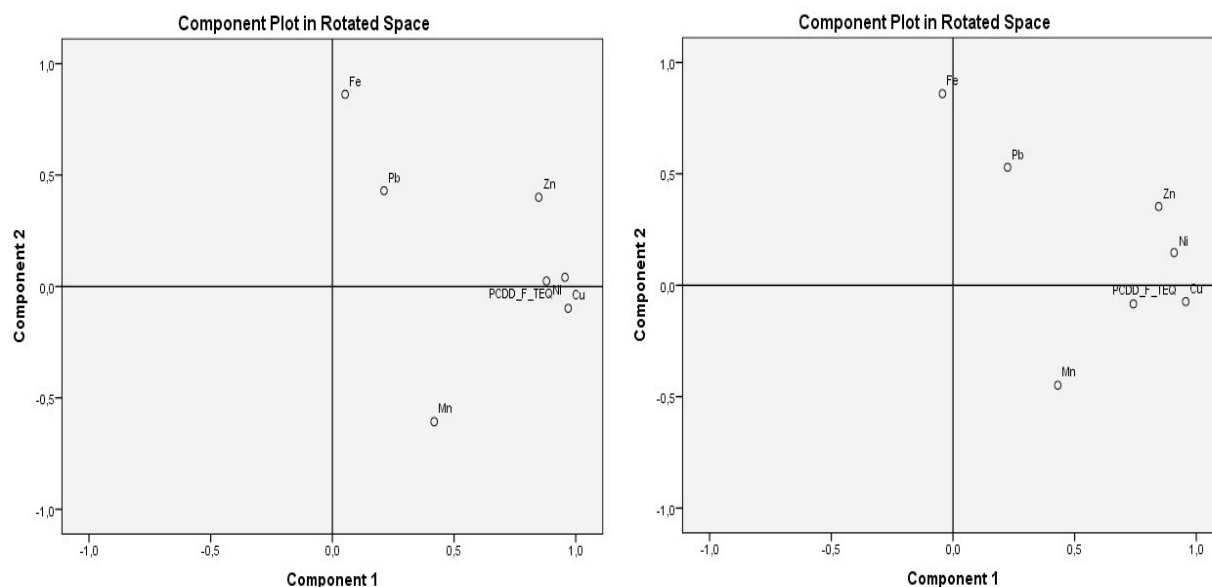


Figure 1- PCA in surface soil sample (left) and surface plus subsoil samples (right). They show similar clusters despite some variables have very different “saturation”, as shown in table 2.

Table 3 Linear regression models  
Independent Variables

Dependent variable PCDD/F's TEQs	Independent Variables	R <sup>2</sup> value
<b>Surface soil</b>		
Linear regression	Fe, Mn, Pb, Zn, Cu, Ni	0,753
Stepwise regression	Cu, Mn	0,734
<b>Surface plus subsoil</b>		
Linear regression	Fe, Mn, Pb, Zn, Cu, Ni	0,577
Stepwise regression	Cu, Ni, Zn	0,555

For the predictive purpose to be used in the indirect PCDD/F's TEQs screening, it is better to use a lower number of metals also due to the very small increase in the model precision between the “enter” and the stepwise linear regression. This choice will minimize the problems related to the FPXRF method standardization procedure. Table 4 shows the value and the significance of regression coefficients that can be used in order to set up the predictive equation for the above mentioned screening. T value is significant for B<sub>Cu</sub> and B<sub>Mn</sub>.

Table 4 Surface soil regression coefficients

		Coefficients <sup>a</sup>								
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	Correlations			
		B	Std. Error	Beta			Zero-order	Partial	Part	
1	(Constant)	-753,041	152,457		-4,939	,000				
	Cu	20,723	1,679	,843	12,346	,000	,843	,843	,843	
2	(Constant)	-395,346	215,154		-1,838	,071				
	Cu	22,219	1,751	,904	12,687	,000	,843	,852	,838	
	Mn	-,393	,172	-,163	-2,284	,026	,175	-,281	-,151	

a. Dependent Variable: PCDD\_F\_TEQ

Noteworthy Hg also was determined by ICP-MS after its stabilization with a gold solution. Its mean concentration was 2,50 ppm. This concentration is below the FPXRF's LOD and make it unsuitable for the screening procedure. Anyway MLR has also been separately performed on both soils typologies including the latter mentioned metal: it was not seen any R<sup>2</sup>'s increase for both results. Nevertheless, for the "surface and subsoil" samples it alone explains the 46% of the dependent variable variance.

### Conclusions

Principal components analysis applied to the inorganic and organic micropollutants was confirming the existence of two main sources of pollution close by the studied site. The first, due to chemicals production, is strictly correlated to the high PCDD/F's TEQ, Cu and Ni concentration in soil. The second, due to metallurgical operations, is mainly correlated to Fe. Mn, instead, is probably released into the environment from both of the above mentioned sources. Through the use of MLR method, using the stepwise variables selection procedure, it has been possible to identify a strictly linear correlation between Cu, Mn and PCDD/F's TEQs (R<sup>2</sup>=0,734) in surface soil samples. Moreover, the predictive purpose can be obtained by the application of the model's equation (PCDD/Fs TEQs= 395,346 + 22,219\*Cu-0,393\*Mn) to the Cu and Mn concentration determined on-site by the means of FPXRF. The differences of the contaminants behaviour with the soil depth has also been evaluated.

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