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PCDD/Fs AND PERSISTENT INORGANIC CONTAMINANTS IN SUPERFICIAL SOILS OF A SEMI-RURAL REGION IN NORTHERN ITALY - Land Use Evaluation -

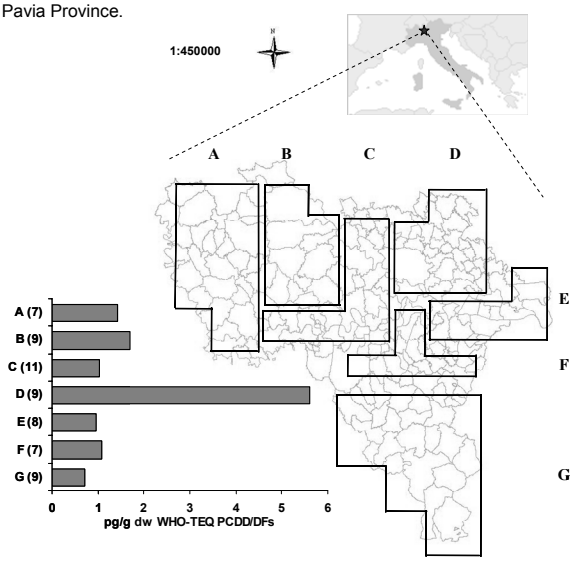
Vives I., Umlauf G., Christoph E., Mariani G., Mueller A., Ghiani M., Skejo H., Cenci R., Sena F. and Bidoglio G.

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) are, among others, persistent organic pollutants listed in the Stockholm Convention. They are released into environment through combustion emissions. Atmospheric deposition is the main route for the vast majority of PCDD/Fs entering soils. Whereas, persistent inorganic contaminants can enter into the soils by direct (eg. pesticide application) and diffuse sources (eg. atmospheric deposition from traffic emissions) or be naturally present.

Superficial soils of the semi-rural Province of Pavia (Northern Italy) were analyzed for PCDD/Fs and persistent inorganic contaminants (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Ti and Zn). The sampling sites included rural (agriculture) and light-industrialized areas to cover the whole extension of the Province and the different land uses[1,2].

Sampling and Methods

Pavia province was divided into 7 clusters for sampling (fig. 1), using the LUCASS network. Top soil samples (from 0-30 cm) were collected from 52 rural and 116 light-industrialized areas. Some bottom soil samples (from 70-100 cm) were simultaneously taken to assess background levels in Pavia Province.



(µg/g dw)	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Ti	Zn
A (7)	13	0,21	87	25	0,09	517	59	19	5208	75
B (30)	7	0,23	45	20	0,14	319	25	23	2458	70
C (41)	7	0,18	101	25	0,06	528	71	18	3424	69
D (39)	20	4,47	87	61	0,46	869	42	119	3380	609
E (28)	10	0,31	162	55	0,05	738	122	18	3902	98
F (14)	11	0,29	139	33	0,08	556	105	22	3669	89
G (9)	7	0,23	109	36	0,07	845	76	19	1928	93

Figure 1 and Table 1: Soil sample clusters in the Province of Pavia and total PCDD/Fs and persistent inorganic contaminants concentrations in soil for the different clusters (pg / g dw WHO-TEQ and µg /g dw, respectively). Between brackets, number of samples for each cluster.

The PCDD/Fs analyzed were the 2,3,7,8-chlorine substituted congeners. Analysis of PCDD/Fs were executed using HRGC-HRMS based on US-EPA 1613. Soils for trace elements were treated following the standard method ISO 11466 and analyzed using atomic absorption spectrometry, inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry.

Results and Discussion

PCDD/F congener pattern (fig. 2) found in all the samples has been previously described as a result of long-range atmospheric transport[3]. Similar pattern was found in air, precipitation, settling matter and sediments at Lake Maggiore[4,5], about 200km North of Pavia.

The cluster in the North-Eastern part of the Province (D), showed significantly higher PCDD/Fs, As and Pb mean levels ($p<0.001$) than the ones in the Southern part (cluster E, F and G). PCDD/Fs concentration in D exceeded the agriculture limits of Italian law[6], although it was not higher than the German guideline value of 40 pg/g dw I-TEQ for agriculture use without pasture[7].

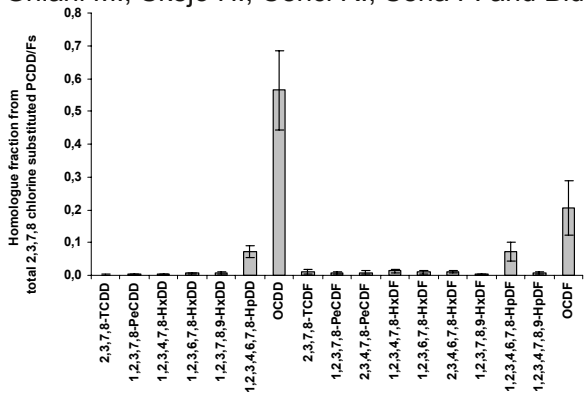


Figure 2: 2,3,7,8 chlorine-substituted PCDD/F congener profile of soil samples from Pavia Province.

Top soil PCDD/Fs levels were significantly higher than bottom soil concentrations ($p<0.0005$), whereas this was not the case for trace elements. In most of the cases the bottom soil PCDD/Fs concentration levels are at around 8-30% of the top soil levels. There was a significant positive correlation between log TOC (Total Organic Carbon) and log PCDD/Fs concentration for top soil values ($p<0.0005$).

No significant differences of PCDD/Fs and trace elements concentrations were found between areas with rural characteristics and light-industrialized sites, indicating that these values represent the baseline pollution due to atmospheric deposition independently of land use.

Principal component analysis (PCA) of PCDD/Fs and metals concentrations has provided a multivariate graphical representation of the overall pollutants distribution in the province (fig. 3). Considering only organic and inorganic levels (fig. 3a), PC1 and PC2 explain most of the cumulative variance (61 %) of the data. PC1 is mainly related to PCDD/Fs and PC2 to Zn, Cu, Cr and Ni. The samples are symbolized according the region code, showing good clustering of spatial Province distribution. Again, samples from D, characterized by the highest concentration of PCDD/Fs and some persistent inorganic contaminants, appear anomalous in relation to other sites.

PCA that plots organic and inorganic concentrations and land use explains 63% of the cumulative variance of the data by 7 principal components. PCDD/Fs, Zn and Cu are the variables with a higher effect in the model, whereas land use aspects play a minor role.

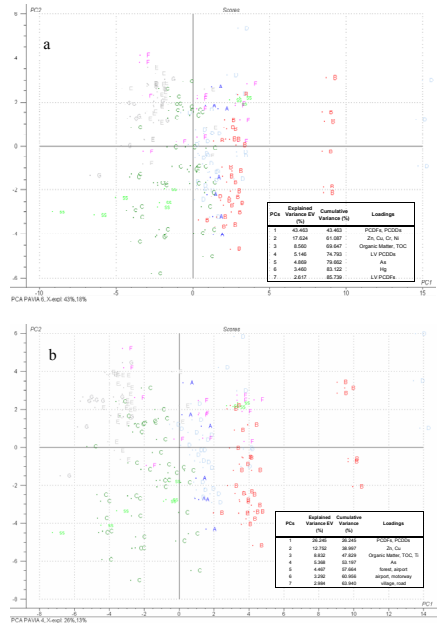


Figure 3: Plots of scores for PC1 and PC2 and tables of loadings from a) PCDD/Fs and persistent inorganic contaminants concentration data and b) concentration and land use data. Samples are labeled for region cluster code.

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Contact

Dr. Ingrid Vives

European Commission • DG Joint Research Centre

Institute for Environment and Sustainability

Tel. +39 0332 786639 •E-mail: ingrid.vives-rubio@jrc.it

ies Institute for Environment and Sustainability