SOIL CONTAMINATION WITH PCDD/Fs AS A FUNCTION OF DIFFERENT TYPES OF LAND USE IN A SEMI-RURAL REGION IN NORTHERN ITALY

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are, among others, persistent organic pollutants (POPs) listed in the Stockholm Convention[1]. They are released into the environment from many sources, such as municipal and industrial waste incineration, automobile exhaust, and as unwanted byproducts, in various chlorinated chemical formulations[2]. PCDD/Fs are, however, extremely stable to both environmental and biological degradation, they bioaccumulate, and have been shown to cause developmental and reproductive abnormalities, cancers, and endocrine disruption[3].

Atmospheric deposition is the main factor for the vast majority of PCDD/Fs entering soils. Humans are exposed to PCDD/Fs in soils through agricultural products and subsequently, these compounds are incorporated in the human body[4-6]. Soils have a great capacity to act as reservoirs for organic pollutants such as PCDD/Fs, therefore assessment of pollutants in soil provide information on regional environmental quality.

There are only few studies that describe PCDD/Fs soil concentrations in Italy and they are mainly concerned on PCDD/Fs soil levels of contaminated sites near Seveso[7] or in the vicinity of solid waste incineration plants[8,9]. The objective of the present study is to assess the PCDD/Fs contamination in soils of the semi-rural Province of Pavia, located in Northern Italy (fig. 1). The sampling sites include rural (agriculture) and light-industrialized areas, to cover the whole extension of the Province of Pavia in relation to their actual land use.

Material and Methods

Pavia province was divided into 7 clusters for sampling (fig. 1), using the Land Use Cover Area from Statistical Survey (LUCAS EUROSTAT) network. Sampling method is reported elsewhere[10].Top soil pooled samples (from 0-30 cm) were collected from 41 rural and 19 industrial areas. Bottom soil pooled samples (from 70-100 cm) were simultaneously taken to assess background levels of the 7 mentioned clusters.

The PCDD/Fs analysed were the 2,3,7,8-chlorine substituted congeners. Analyses of PCDD/Fs were executed using high-resolution gas chromatography coupled to high-resolution mass spectrometry (HRGC-HRMS) and quantification was based on isotope dilution according to US-EPA method 1613. Briefly, a mixture of 16 13C-labelled WHO-TEQ relevant PCDD/F-isomers was added to each sample prior to extraction. Soxhlet extraction was carried out with n-hexane/acetone (220:30) for 48 hours, followed by a pre-purification of the extract with sulphuric acid coated to diatomee earth. Extract purification was executed with an automated clean-up system (Power-Prep P6, FMS, USA). The chromatographic principle is based on the method published elsewhere[11]. A detailed description of the Power-Prep method and its performance is described elsewhere[12].

A gas chromatograph (Hewlett Packard 6890, Waldbronn, Germany) with split/splitless injection, coupled to a high-resolution mass spectrometer (VG Autospec Ultima, Micromass, Manchester, UK), was employed. The capillary column was 60-m long, with a 0.25 mm i.d. and 0.25 μm stationary phase film thickness (BP-DXN, SGE, Australia). The mass spectrometer operated under EI mode at 34 eV with a resolution of >10000. Two masses in the M+ isotope cluster were monitored for each analyte and each internal standard. Whenever interferences were encountered, more

masses were monitored. Dry weight concentrations of PCDD/Fs were expressed as I-TEQ and WHO-TEQ concentrations, according to the International and World Health Organization toxicity equivalent factors (I-TEF and WHO-TEF, respectively)[13,14].

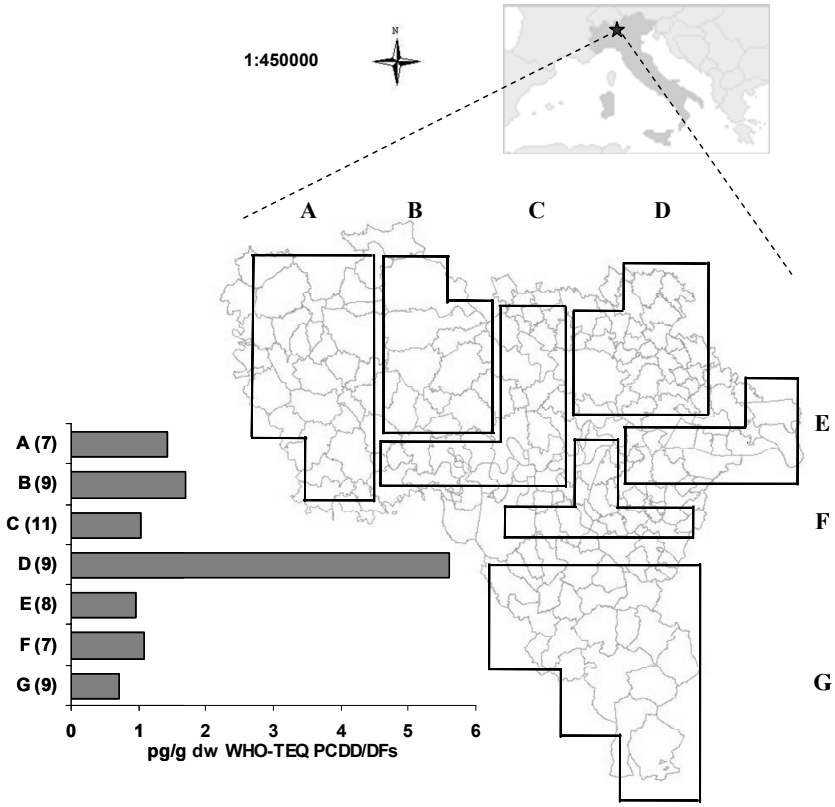

Figure 1: Soil sample clusters in the Province of Pavia and total PCDD/Fs concentrations in soil for the different clusters (pg / g dw WHO-TEQ). Between brackets, number of samples for each cluster.

Results and Discussion

OCDD/Fs dominated the 2,3,7,8 chlorine substituted congener pattern of all the soil samples (up to 80 % of the total concentration of 2,3,7,8 chlorine substituted PCDD/Fs), followed by the 1,2,3,4,6,7,8 hepta congener (fig. 2). In general, dioxin contribution was higher than furan contribution to the overall concentration. This profile has been described previously as results of long-range atmospheric transport[15]. Similar pattern was found in air, precipitation, settling matter and sediments at Lake Maggiore[16, 17], about 200km North of Pavia.

Profiles of the congener fraction of total PCDD/Fs in soil can be used to identify the existence of different pollutant sources between sites. 2,3,7,8 chlorine-substituted PCDD/F congener patterns in soil do not differ among North (clusters A, B, C and D) and South (cluster G). In terms of land use, rural and industrial areas present similar 2,3,7,8 chlorine-substituted PCDD/F congener profile in soil, dominated in all cases by the high chlorinated congeners. Probable the pattern is a result of mixing diffuse regional sources followed by long range transport and relative atmospheric deposition[18]. These results implicate that all clusters have PCDD/F input from similar sources and no significant emission source is present in that zone.

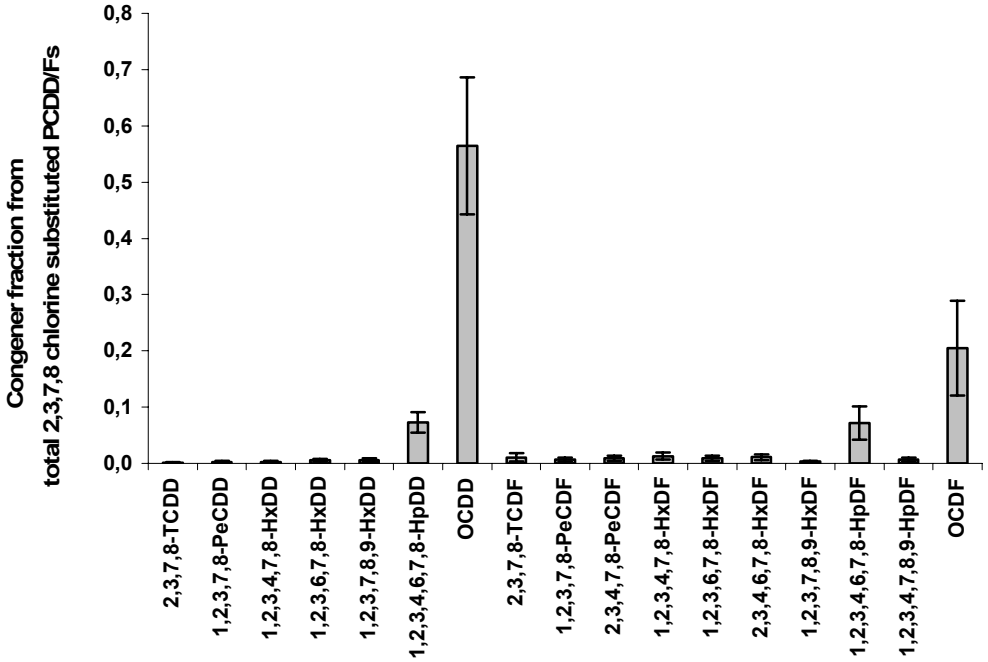

Figure 2: 2,3,7,8 chlorine-substituted PCDD/F congener profile of soil samples from Pavia Province.

Generally, the range from tetra- to octachlorinated 2,3,7,8 chlorine-substituted PCDD/Fs were detected in all the samples. Total concentrations of 2,3,7,8 chlorine-substituted PCDD/Fs in top soil samples from the Province of Pavia ranged from 0.48 to 11 pg/g dw I-TEQ (0.52-11 pg/g dw WHO-TEQ). The highest value corresponds to a site located at the North-East of the Province, up to 2 km South of one of the Milan´s airports. The clusters in the Northern part of the Province (clusters A, B, C and D) showed significantly higher mean levels ($p<0.001$) than the ones in the Southern part (cluster G). Arithmetic mean values for the Northern and Southern clusters were 1.6 and 0.62 pg/g dw I-TEQ, respectively (1.6 and 0.67 pg/g dw WHO TEQ, respectively).

Top soil levels were significantly higher than bottom soil concentrations ($p<0.0005$). Total concentrations of PCDD/Fs in bottom soil samples from the Province of Pavia (Italy) ranged from 0.086 to 0.3 pg/g dw I-TEQ (0.088-0.41 pg/g dw WHO-TEQ). In most of the cases the bottom soil concentration levels are at around 8-30 % of the top soil levels. No North/South differentiation is visible in the bottom soils.

There was a significant positive correlation between log TOC (Total Organic Carbon in soil sample) and log WHO-TEQ concentration of PCDD/Fs for the entire dataset of top soil values ($r^2=0.56$, $p<0.0005$) (fig. 3). TOC and concentrations were log-transformed as a result of the Kolmogorow-Smirnov test. Bottom soil samples show a similar trend, although there is only small number of samples to prove its significance. Normalizing PCDD/Fs concentrations with total organic carbon did not change the differences between Northern and Southern top soils.

No significant differences of PCDD/Fs soil concentrations were found between areas with rural characteristics and light-industrialized sites (arithmetic means were 1.2 and 1.2 pg/g dw I-TEQ, respectively), indicating that these

values represent the baseline pollution due to atmospheric deposition independently of land use. The obtained values are in the upper range of soil concentrations reported for agricultural soils[19-22] and in the lower range of urban/industrialized soil concentrations reported in the literature from other countries[23-26].

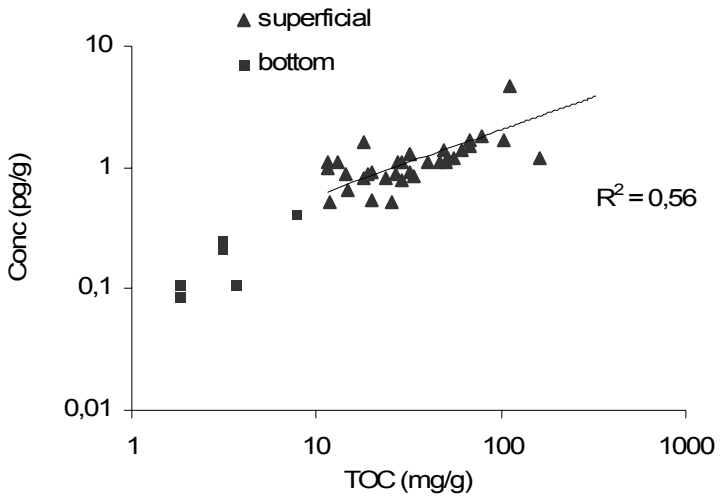

Figure 3: TOC (mg/g) vs. total PCDD/F concentrations (pg/g dw WHO-TEQ) in top and bottom soils.

At the present, in Europe there is no Directive that establishes PCDD/Fs concentrations in soil in order to regulate the possible uses of a soil. Italian law[27] on acceptable limit concentrations of PCDD/Fs in soil establishes a limit value of 10 pg/g dw TEQ for agriculture and residential use and of 100 pg/g dw TEQ for industrial uses. However, German guidelines for land use[28] recommend a more restricted limit of 5 pg/g dw I-TEQ for an unrestricted agricultural use. Only the soil concentration obtained for the North East of the Province exceeded the agriculture limits of both regulations, although it was not higher than the German guideline value of 40 pg/g dw I-TEQ for agriculture use without pasture.

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References

1. UNEP. *Final act of the conference of plenipotentiaries on the Stockholm convention on persistent organic pollutants. Document: UNEP/POPS/CONF/4.* Available from: http://irptc.unep.ch/pops, 2001.
2. UNEP. *Dioxin and furan inventories – national and regional emissions of dioxins and furans*. UNEP Chemicals, Geneva, 100p, 1999.
3. Schecter A, Birnbaum L, Ryan JR, Constable, JD. *Environ Res* in press.
4. Sweetman AJ, Alcock RE, Wittsiepe J, Jones KC. *Environ Int* 2000; 26:37.
5. Fries GF. *J Anim Sci* 1995; 73:1629.
6. Fries GF. *Rev Environ Contam Toxicol* 1995; 141:71.
7. Umlauf G, Barbiere M, Facchetti S. *Organohalogen Compd* 1999; 44:311.

8. Caserini S, Cernuschi S, Giugliano, M, Grosso M, Lonati, G, Mattaini, P. *Chemosphere* 2004; 54:1279.
9. Capuano F, Cavalchi B, Martinelli G, Pecchini G, Renna E, Scaroni I, Bertacchi M, Bigliardi G. *Chemosphere* 2005; 58:1563.
10. Cenci RM, Barbiere M, Bidoglio G, Bo F, Corace C, Cocheo V, Contini S, Dabergami D, D'Alberti F, D'Alessandro M, De Saeger E, DiNicolantonio S, Leita L, Locoro G, Leva F, Mondini C, Paracchini B, Sena F, Skejo-Andresen H, Stella S, Trincherini P, Umlauf G. EUR 20674 IT 2003.
11. Smith LM, Stalling DL, Johnson L. *Anal Chem* 1984; 56:1830.
12. Abad E, Saulo J, Caixach J, Rivera J. *J Chromatography A* 2000; 893:838.
13. North Atlantic Treaty Organization, Committee on Challenges of Modern Society. Report nº 176, August 1998.
14. van den Berg M, Birnbaum L, Bosveld ATC, Brunström B, Cook P, Feeley M, Giesy JP, Hanberg A, Hasegawa R, Liem AKD, Nolt C, Peterson RE, Poellinger L, Safe S, Schrenke D, Tillitt D, Tysklind M, Younes M, Waern F, Zacharewski T. *Environ Health Prespect* 1998; 106:775.
15. Hagenmeier H, Lindig C. and She J. *Chemosphere.* 1994; 29: 2163.
16. Castro-Jiménez J, Canuti E, Christoph E H, Eisenreich S J, Hanke G, Mariani G, Skejo H, and Umlauf G. *Organohalogen Compounds* 2005; 67: 1209.
17. Castro-Jiménez J, Mariani G, Eisenreich S J, Christoph E H, Hanke G, Canuti E, Skejo H, and Umlauf G. *Chemosphere* 2006; Submitted.
18. Hassanin A, Lee RGM, Johnston AE, Jones KC. *Chemosphere* 2006; in press.
19. Martínez K, Abad E, Rivera J. *Chemosphere* 2006; in press.
20. Rogowski DL, Yake W. *Environ Sci Technol* 2005; 39:5170.
21. Schuhmacher M, Granero S, Llobet JM, de Kok HAM, Domingo JL. *Chemosphere* 1997; 35:1947.
22. Boos R, Himsl A, Worst F, Prey T, Scheidl K, Sperka G, Gläser O. *Chemosphere* 1992; 25:283.
23. Cheng PS, Hsu MS, Ma E, Chou U, Ling YC. *Chemosphere* 2003; 52:1389.
24. Im SH, Kannan K, Giesy JP, Matsuda M, Wakimoto T. *Environ Sci Technol* 2002; 36:3700.
25. Rappe C, Kjeller LO. *Chemosphere* 1987; 16:1775.
26. Sakurai T, Kim JG, Suzuki N, Nakanishi, J. *Chemosphere* 1996; 33:2007.
27. DM 25 ottobre 1999, n. 471. Regolamento recante criteri, procedure e modalità per la messa in sicurezza, la bonifica e il ripristino ambientale dei siti inquinati, ai sensi dell'articolo 17 del decreto legislativo 5 febbraio 1997, n. 22, e successive modificazioni e integrazioni.
28. Federal Ministry for the Environment, Nature Conservation and Nuclear Safety. Handlungsempfehlungen der Bund Länder Arbeitsgruppe DIOXINE 1992.