Dioxin/Furan and Dioxin-like PCB signatures in the environmental compartments (soil, sediment, plants) of a site affected by old polluting industrial activities

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DIOXIN/FURAN AND DIOXIN-LIKE PCB SIGNATURES IN THE ENVIRONMENTAL COMPARTMENTS (SOIL, SEDIMENT, PLANTS) OF A SITE AFFECTED BY OLD POLLUTING INDUSTRIAL ACTIVITIES

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Introduction

The area of soil and sediment contamination of an old industrial site was investigated with respect to metallic trace elements (MTE) and persistent organic pollutants (PAH, PCB, dioxins/furans) potentially present and relevant in terms of risk. This paper discusses more particularly the data on dioxins/furans (PCDD/F) and dioxin-like PCB (PCB-dl) in association with the high concentrations encountered and the singular profiles of congeners with dominant furans. Local anthropized background data, acquired at the same time, are discussed for comparison. Some plant –vegetables- analyses are discussed.

Materials and methods

About 50 average surface soil samples (0-5 cm) were collected in 2007/2008 from areas of a few tens to a few hundred m², amounting to 5-9 individual subsamples sieved to 2 mm and quartered. The samples were analysed in particular for dioxins/furans, PCB-dl, and also total organic carbon (TOC). Based on the last parameter it is possible to calculate the concentration factor of the dioxins/furans with respect to the organic part of the soil known to concentrate lipophilic organic pollutants.

In addition, five surface-sediment samples were taken manually by diving with transparent Plexiglass samplers into a pond adjacent to the industrial zone. This method enables one to take account of the nature of the horizons encountered and so to favour the analysis of fine surface deposits with a low sandy fraction. The sediments are predominantly clayey silt.

Finally, in the summer of 2008, available plants (carrots, beetroots, French beans and lettuce) were also sampled from surrounding vegetable gardens. These samples were prepared (washed, peeled of the edible parts) according to a procedure oriented towards characterizing exposure to dioxins/furans, metals and PAH by indirect ingestion of home-grown plants.

HRGC/HRMS analyses (low quantification threshold) of the organic pollutants were carried out at an approved laboratory. The toxic equivalent (TEQ) is expressed according to the WHO 1997 system[1]. All the toxic congeners were quantified (> quantification thresholds) in soils and sediment; non-detected (nd) congener values are fixed at detection limit (nd=DL) for plants.

Results

Figure 1, using a logarithmic scale, shows the TEQ (PCDD/F) data of the soil, sediment and plant samples relative to dioxin concentration.

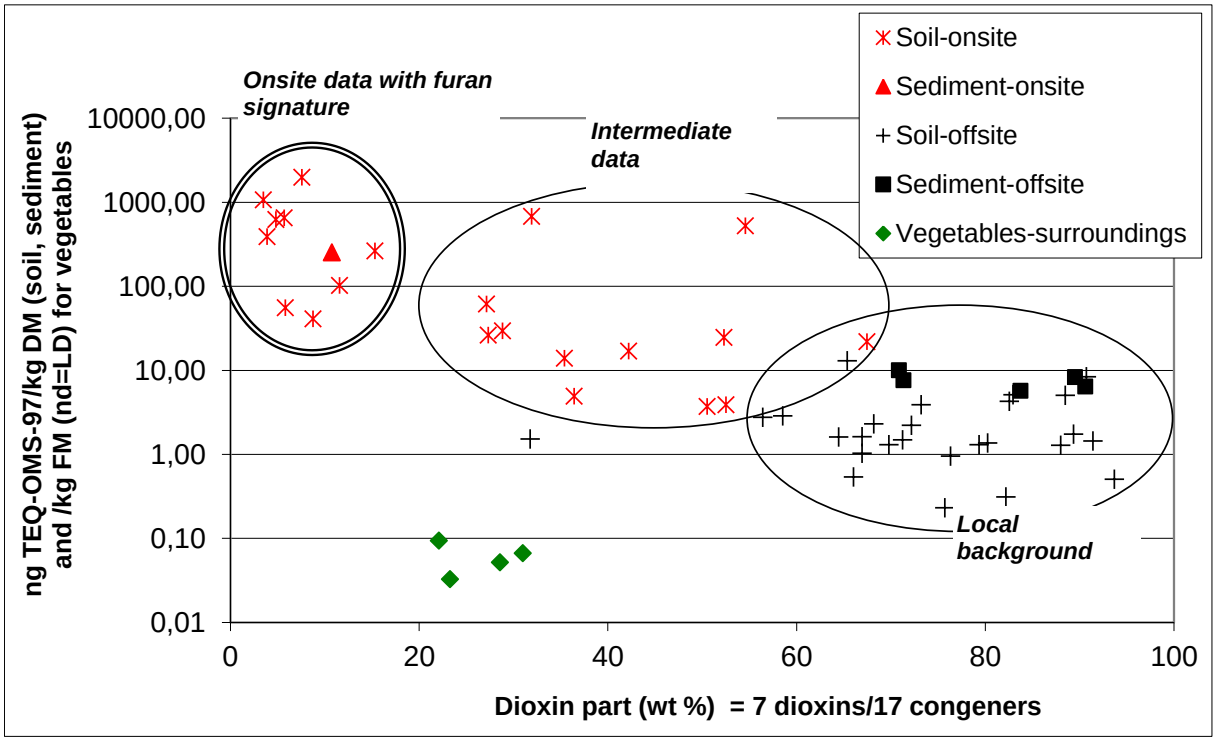

Figure 1 – Toxicity (TEQ) of the soil, sediment and plants of the polluted site and local background relative to dioxin concentration

The dioxin/furan concentrations in the onsite and offsite soil are high, well above local background. The TEQ data, expressed in ng TEQ-WHO (97)/kg DM, range from 3.7 to 1986 (median 55) on site as against a background of 0.2 to 13 (median 1.6).

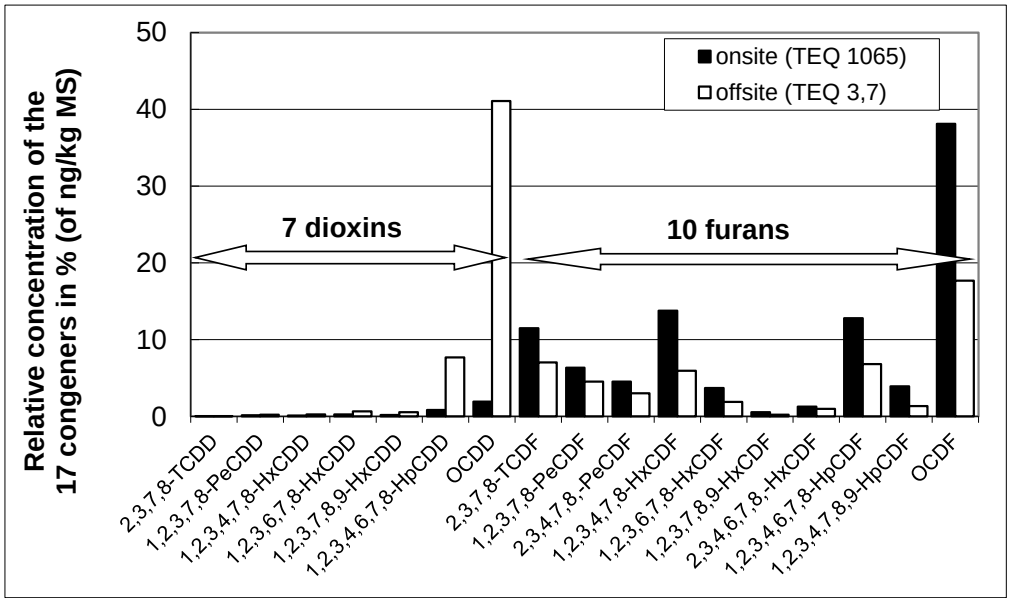

Figure 2 - Typical dioxin/furan profile of onsite and offsite soils.

The study of soil concentrations in the Pavie region of Italy[2], which used a detailed examination and quality approach, could for example serve as a comparative reference: the TEQ of 35 surface soils (0-10 to 0-30 cm) lying in the range of 0.52–11 (median 1.1) ng TEQ-WHO (97)/kg DM. These data could be also compared with selected French data of 342 surface soils[3] with median values of 1.3 and 4.7 ng TEQ-WHO (97)/kg DM.

A second characteristic of the soil and sediment samples affected by past activities concerns the respective percentages of dioxins versus furans. In particular, the soil with high TEQ has a very marked furan signature (Figure 2).
Representation of the TEQ data in terms of the TOC confirms the clear PCDD/F enrichment of organic matter in the site soil. The relative concentration of PCB-dl, however, proves to be relatively minor and probably due to distinct sources of contamination.

Lastly, the TEQ data of the dioxins/furans in vegetables, expressed in ng TEQ-WHO (97)/kg DM (nd=DL), range from 0.033 to 0.094. They are to be compared with the average French data[4] on dioxin/furan concentrations in vegetables (type not specified, 1-22 analyses) of 0.01 ng TEQ-WHO (97)/kg DM (nd=DL) or with the German values[5] of concentrations in commercial plants commercial (18 analyses) ranging between 0.003 and 0.010 ng TEQ/kg FM for summer plants and 0.03 and 0.07 ng TEQ/kg FM for winter plants.

Discussion
The onsite and offsite soils reflect a cumulative historical multi-pollutant contamination (metals not given) with possible deposits of dust (untreated at the time) and/or mixtures with production residues from the factory which functioned for nearly 180 years. The prevalence of furans is to be related to a thermal process to do with the site's historical industrial activity, and in particular with the production of bicarbonate of soda Na_2CO_3 at the beginning of the 20th century. In view of the manufacturing components (in particular NaCl and coal/lignite) and the process temperatures (900 °C and associated gradients), it appears that, at least for this process, both the ingredients and the conditions for dioxin/furan formation were present: traces of Cl, concomitant presence of aromatic compounds (pyrolysis of the lignite and coal) at temperatures known to support the formation of the dioxin/furans (250° to 400°C).

Concentrations in the summer plants near the site are also anomalous in that they fall within the published high values. They are nevertheless below the intervention level of 0.4 ng TEQ-WHO (97)/kg of gross product (DM) for vegetables fixed by European recommendation 2002/201/CE[6].

The results also illustrate the very weak degradation of these persistent organic pollutants over the years, as has been described many times before (the half-life in soil can exceed 100 years).

Discussion is currently under progress to evaluate solutions of remediation and to propose a comprehensive and integrated management of this contaminated site.

References
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