# ASSESSMENT OF PCDD/Fs, PCBs, AND HEAVY METALS IN SOIL: A MEASURE OF THE IMPACT OF THE INDUSTRIAL ZONE OF PORTO MARGHERA ON INLAND COASTAL AREAS OF ITALY

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## Introduction

Italian environmental authorities and scientists continue to address public health concerns regarding the presence of polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs), and biphenyls (PCBs), and heavy metals in the environment. The scientific community generally associates the presence of PCDD/Fs, PCBs, and heavy metals in the environment with releases from several different types of industrial activities. Anthropogenic sources of these compounds are broadly classified as combustion/incineration sources, and chemical manufacturing/ processing [(1-4)]. An important characteristic of PCDD/Fs and PCBs is the tendency to bioaccumulate in the food chain [(5)]. In 1997, IARC (International Agency for Research on Cancer) reevaluated the carcinogenicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and classified it as carcinogenic to humans, based on limited evidence in highly exposed populations and sufficient evidence in experimental animals [(6)]. IARC also considers arsenic, chromium (VI), and nickel to be carcinogenic, and cadmium and lead (inorganic) to be probable and possible carcinogens, respectively [(7)].

The presence of PCDD/Fs, PCBs, and heavy metals in the Venetian inland area may be attributed to the industrial activities of Porto Marghera; these include chemical production, metallurgy, and hazardous waste incineration [(8,9)]. Many studies have been carried out to assess the environmental conditions of the Venice Lagoon ecosystem, including those aimed at determining the presence of PCDD/Fs, PCBs, and heavy metals in sediment and biota [(10-14)]. However, few studies are available on soil levels of these chemicals in the highly industrialized area of Porto Marghera. The purpose of this project was to assess PCDD/F, PCB, and heavy metal soil levels as an important compartment of the Venice Lagoon ecosystem.

## Materials and Methods

Soil samples were collected mainly downgradient (leeward) from the central industrial zone of Porto Marghera with respect the predominant wind direction. In August and September of 1998, 108 soil samples were collected at 43 sites. Of the 108 samples, 43 surficial soil samples were analyzed by Alta Analytical Laboratory, El Dorado Hills, CA (USA) to determine concentrations of the 17 2,3,7,8-substituted PCDD/F congeners and 51 PCB congeners; the remaining 65 soil samples were analyzed by the Laboratory of Centro Agroambientale ARPAV of Castelfranco Veneto (Italy) for total and assimilable heavy metals and pedological parameters. Among the 43 sites

sampled, 34 were (downgradient) at increasing distances from the central industrial zone, 5 were from the urban area of the city of Mestre, and 4 were in agricultural areas (Torre di Mosto, Staffolo). The agricultural areas were assumed to be representative of background conditions. Six of the 43 sampling locations had not likely been rehashed or plowed for several years.

To avoid collection of non-representative samples, soil samples were collected far from the boundaries of agricultural fields, high traffic roads, disturbed areas, or recently reclaimed lands. At each sampling corner, a "hand drill" stainless steel soil auger (dutch model) was used to collect samples from a depth of 0-15 cm at each corner of a 2 x 2 meter square. Source identification was performed using Principal Components Analysis (PCA) and Hierarchical Clusters Analysis (HCA) (Pirouette, version 2.5, Woodinville, WA).

**Results and Discussion**

Heavy metal analyses indicate that while Ni, Hg, As, and Cr concentrations in soil are not influenced by sampling location, concentrations of Cd and Pb in soils collected downgradient from the central industrial zone are greater than background levels (Table 1). Concentrations of Cd and Pb from uncultivated soils are especially elevated (2-5 fold greater than background), which suggests that uncultivated soils act as a potential sink for atmospheric pollutants deposition while agricultural practices and plant uptake tend to dilute heavy metal concentrations. Along the two predominant wind directions (N/NE-S/SW and NE/SW), a negative correlation exists between Cd and Pb concentrations and downgradient distance from the central industrial zone (-0.46 and -0.42, respectively, with a p-value $<0.05$). A significant correlation was not found in the third direction (E/NE-W/SW), likely due to the biasing effect of the industrial zone of Mira. Beyond a downgradient distance of 6000 m, Cd and Pb concentrations are similar to background levels. Cd and Pb levels indicate a fallout effect from the Porto Marghera industrial zone on downgradient soils. The main sources of Cd and Pb are directly-applied soil amendments, smelting industries, waste incinerators, and fossil fuel and gasoline combustion [15].

**TABLE 1: Surficial Heavy Metal Concentrations in Venetian Coastal Inland Soils** [1]

| Sample Description | N | Cd total (mean ± sd; ppm) | Cd assim. (mean ± sd; ppm) | Pb total (mean ± sd; ppm) | Pb assim. (mean ± sd; ppm) |
|---|---|---|---|---|---|
| All samples | 41 | 0.60 ± 0.21 | 0.15 ± 0.09 | 30 ± 21 | 5.9 ± 4.3 |
| 200 - 1600 m [2] | 17 | 0.70 ± 0.24 | 0.19 ± 0.12 | 37 ± 30 | 7.1 ± 4.8 |
| 2 - 15 km [2] | 15 | 0.52 ± 0.17 | 0.11 ± 0.03 | 25 ± 9.6 | 5.8 ± 4.4 |
| Background | 4 | 0.48 ± 0.12 | 0.13 ± 0.03 | 17 ± 3.6 | 2.2 ± 1.1 |
| Urban (Mestre) | 5 | 0.62 ± 0.14 | 0.16 ± 0.05 | 30 ± 5.6 | 5.2 ± 2.0 |
| Uncultivated Soils | 5 | 0.92 ± 0.06 | 0.33 ± 0.11 | 66 ± 42 | 12 ± 5.4 |

[1] Excludes sample 41 as it is not representative of airborne fallout.

[2] Downgradient distances from the central industrial zone of Porto Marghera; estimated.

Total PCDD/F and PCB concentrations reflect a similar fallout pattern attributable to releases from the industrial zone of Porto Marghera (Table 2). Mean PCDD/F and PCB totals and TEQs in soils collected between 200 and 1600 m downgradient from Porto Marghera are several-fold greater than in distant downgradient (2-15 km) and background soils. Also consistent with the Cd and Pb data is that total PCDD/F and PCB levels are generally elevated in samples collected from uncultivated soils. Sample 41, collected from the topsoil of an old landfill, had excessively high concentrations of total PCDD/Fs (6295 ppt) and total PCBs (1255 ppb).
Each anthropogenic source of PCDD/Fs typically favors the formation and environmental release of

**TABLE 2: PCDD/Fs and PCBs in Venetian Coastal Inland Soils** [1]

| Sample Description | N | Total PCDD/Fs (mean ± sd; ppt) [2] | Total PCBs (mean ± sd; ppb) [2] | PCDD/F TEQs (mean ± sd; ppt) [3] | PCB TEQs (mean ± sd; ppt) [3] |
|---|---|---|---|---|---|
| All samples | 42 | 445 ± 543 | 10 ± 14 | 6.6 ± 8.7 | 0.70 ± 1.3 |
| 200 - 1600 m [4] | 17 | 853 ± 663 | 17 ± 18 | 13 ± 11 | 1.2 ± 1.7 |
| 2 - 15 km [4] | 16 | 157 ± 88 | 2.5 ± 1.3 | 2.3 ± 1.4 | 0.2 ± 0.5 |
| Background | 4 | 69 ± 40 | 0.9 ± 0.3 | 0.14 ± 0.06 | 0.009 ± 0.003 |
| Urban (Mestre) | 5 | 250 ± 108 | 15 ± 7.9 | 3.6 ± 2.6 | 1.3 ± 1.0 |
| Uncultivated Soils | 5 | 1134 ± 1049 | 32 ± 27 | 20 ± 16 | 2.7 ± 2.6 |

[1] Excludes sample 41 as it is not representative of airborne fallout.

[2] Non-detected congeners were assumed to equal 1/2 the reporting limit.

[3] Toxic Equivalency Quotients (TEQ) calculated using World Health Organization Toxic Equivalency Factors.

[4] Downgradient distances from the central industrial zone of Porto Marghera; estimated.

certain mixtures of PCDD/F congeners. Congener profiles associated with specific sources can help explain source contributions to environmental measurements. The dominant PCDD/F congeners in the majority of samples collected in this study are OCDF, OCDD, and 1,2,3,4,6,7,8-HpCDF. These congeners have been associated with a variety of combustion sources, including municipal solid waste incineration, industrial oil-, coal-, and wood-fired boilers, unleaded gasoline and diesel fuel combustion, sewage sludge incineration, medical waste incineration, and secondary lead and aluminum smelters [(3)]. Across all samples, TCDD averaged only 0.2%, and never more than 1.6%, of total PCDD/Fs; this is also consistent with combustion source emissions [(3)].

The pattern recognition techniques PCA and HCA reveal that samples 41, 22, 37, 38, and 40 are consistent outliers with respect to PCDD/F congener patterns compared to the remainder of the samples (Figure 1). Samples 37, 38, and 40 are the representative background samples collected in the upgradient wind direction from Porto Marghera. These samples also hold a combustion pattern of PCDD/F congeners, but are likely influenced by non-point source inputs, and possibly distant anthropogenic sources. Sample 41 is marked by enrichment of the lower-chlorinated furans relative to other samples, which may be an indication that the sample has been impacted by emissions from cement kiln incineration or secondary lead smelting. The uniqueness of Sample 22 is the absence of 1,2,3,4,6,7,8-HpCDF, leaving only OCDF and OCDD as dominant congeners; this pattern deviation cannot be explained at this time.

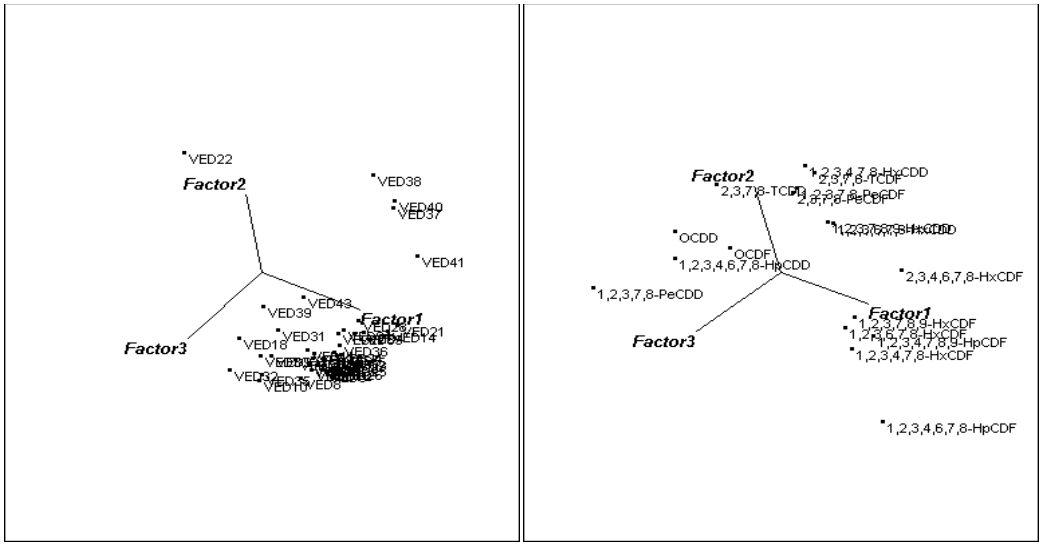


**FIG. 1: PCA scores and loadings plots of PCDD/F soil data.**

Several preliminary conclusions regarding the impact of the industrial zone of Porto Marghera on Venetian soils can be drawn from the results of this study. These include:

1. While the more distant samples downgradient from the central industrial zone of Porto Marghera are similar to background in terms of PCDD/F, PCB, Cd, and Pb concentrations, near downgradient levels are elevated. This suggests an airborne contaminant fallout effect from sources in Porto Marghera;
2. Concentrations of PCDD/Fs, PCBs, Cd, and Pb in samples collected from uncultivated soils are generally elevated. This indicates that soil disturbances (e.g., agricultural practices) can dilute contaminant concentrations and thus soil history is an important consideration when evaluating soil chemical data; and
3. PCDD/F congener patterns in inland coastal soils appear to be associated with several combustion-type sources. Soil samples showing distinctly different or unique patterns are most likely influenced heavily by specific point sources such as chemical manufacturing facilities, or, in the case of background samples, long-range transport mechanisms that favor specific congeners.

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