FINGERPRINT ANALYSIS OF PCDD/F IN SOIL SAMPLES IN THE TARANTO (PUGLIA, ITALY) AREA

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Introduction
The purpose of this study is to compare the polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/F) fingerprint found in the soil of an iron and steel factory in Taranto to the fingerpint found in the soils in the surrounding areas and with reference samples taken about 150 km from the site.

Materials and methods
Area of study and source of data. The area of study is shown in Figure 1 and includes an iron and steel plant, an area up to a distance of 15 km from the plant, and the reference area in the Lecce province (about 150 km from the plant). Data for the Taranto area were primarily from two local agencies, Agenzia Regionale per la Prevenzione e la Protezione Ambientale (ARPA) Puglia and Azienda Sanitaria Locale Taranto, and the report of the consultant to the Judge for some preliminary investigations[1]. The samples have been analyzed by different laboratories whose quality were not disclosed; the underlying data package including the selection ion current profiles were not available.

Chemical fingerprinting. The similarity of the samples has been quantified by conducting a cluster analysis and principal components analysis (PCA) on the 17 PCDD/F congeners[2]. For all analyses, congeners that were not detected in a sample were included at one-half of the reported detection limit. In order to conduct such analysis, the concentration of each congener has been transformed in percentage to the total PCDD/F concentration of the same sample.

In order to characterize the chemical fingerprint of samples in a reliable manner, cluster analysis and PCA included only samples with more than 13 congeners detected and a total PCDD/F concentration (sum of the 17 congeners, not the TEQ) greater than 50 pg/g. Samples with low concentrations for several congeners result in an unstable chemical fingerprint because small changes in a concentration create a large change in the profile. Similarly, the chemical composition of samples with very low concentrations may also be uncertain.

Soil data. We considered 36 soil samples collected inside the iron and steel facility and 51 offsite samples in the Taranto area. Sample locations are shown on Figure 1 together with concentrations for PCDD/F (TEQ$_{DF05}$). Most samples were assumed to be collected from the top 10 cm, although documentation is not complete. We also considered background soil data provided by ARPA Puglia for 21 samples collected in the Lecce area.

Results and discussion
Iron and steel plant. For the 36 iron and steel soil samples, the average and maximum PCDD/F were 7.6 pg/g and 44.8 pg/g TEQ$_{DF05}$, respectively. The maximum value for PCDD/Fs (Sample 60/1835/I/T-A) was located at the far western side of the plant, near the port and well away from the agglomeration activity.

Offsite. As can be seen on Figure 1, most of the 51 offsite soil samples were collected near the steel facility with a portion collected at a much greater distance. Most samples were collected in rural areas away from urban areas, although some samples were also collected within the towns and near busy roads. Among the 51 offsite samples, 12 were collected near a waste-to-energy facility and 1 was collected near the the facility of a company that carried on a salvage operation for PCB-containing transformers.

The analytical results are shown on Figure 1. The average and maximum TEQ$_{DF05}$ were 2.0 pg/g and 17.7 pg/g, respectively. Of the 51 offsite soil sample results for PCDD/Fs, only one was above 7 pg/g (sample Conca d'oro punto B 2009), which had a TEQ concentration of 17.7 pg/g. This sample was located outside of Massafra about 10 m from a roadside and about 100 m north of a quarry-type operation (see Figure 1).

Composition of soil. PCDD/F concentrations measured in the offsite soil are generally low, even in the industrial area of Taranto. Twenty-one soil samples collected from the area surrounding Maglie in the Lecce Province (over 150 km from Taranto) characterized the composition and variability of background conditions.

Despite the low concentrations in the offsite area, chemical fingerprint analysis was used to determine whether the composition of samples represents a consistent pattern that could be attributed to the iron and steel plant emissions. PCDD/F compositions were evaluated between samples from potential sources and soil from the offsite area. A second analysis included compositions of potential background sources from published literature. The variability in composition among the background soil samples provides perspective for the reliability of any consistent compositional differences.

Any contaminant contributions from the iron and steel facility to soil would necessarily be transported through the air, as there is no record of direct placement of material (e.g., electrostatic filter dust) from the plant. Given the low concentrations measured, there is no evidence of significant impact to soil from an industrial source.

Cluster analysis of soil. Figure 2 shows the results of the cluster analysis based on PCDD/F compositions of soil samples. The most notable result from this analysis is the heterogeneity of samples from the offsite areas, with no obvious clustering of samples representative of any single condition. The four soil samples collected from the agglomeration area of the iron and steel plant do show a consistent PCDD/F composition, as identified by the single cluster containing all of these samples (black outlined samples on Figure 2). Background samples (blue shaded samples on Figure 2Figure 2) are present in most clusters, except the first cluster (at the top of the figure) that contains the agglomeration samples. The local area soil sample containing the highest PCDD/F TEQ concentration of 17.7 pg/g (Concadoropunto B 2009, at the bottom of Figure 2) clusters most closely with a low concentration (2.7 pg/g) sample from the iron and steel plant (45/1384 29/06/2012). The Concadoropunto B sample was collected from more than 15 km north of Taranto and the iron and steel facility. There is also a background sample within the same cluster as these two samples, suggesting that any similarity in composition is likely due to common combustion sources rather than impact from a single, consistent source.

Principal component analysis of soil. Figure 3 shows results of the PCA. Similar to the cluster analysis, this analysis indicates similar PCDD/F composition among most soil. Samples from the area surrounding the iron and steel plant contain a composition similar to background conditions. Samples from the iron and steel facility are not identifiably different from background soil either, although the four samples from the agglomeration area form a tight cluster.

The soil samples from the iron and steel plant's agglomeration area contain a consistent chemical signature identified in the PCA (Figure 3) and the cluster analysis (Figure 2). Their composition is not unique enough to represent a source signature as there is a background sample with a similar composition as well as a local area sample (IAZZO TODISCO 2009).

Samples with high values for PCA Factor 1 are characterized by relatively low amounts of OCDD. The influence of OCDD is due to the very low content of this congener in the AE3T sample (7%) and samples from the agglomeration area of iron and steel plant (25−30%). The local area samples with the lowest OCDD contributions (IAZZO TODISCO 2009 at 20% and QUARANTA 2009 at 21%) are from the same location, north of the salvage operation for PCB-containing transformers. Sample 60/1835/I/T-A contains the highest PCDD/F TEQ concentration among the soil samples collected from the iron and steel plant, but it was collected from the railroad tracks along the western side of the plant. This sample is not representative of PCDD/F compositions generally found within the iron and steel facility. The other two iron and steel facility soil samples with compositions unlike background conditions (50/1558/I/T-A and 39/1109/I/T-A) contain relatively low TEQ concentrations (3.5 and 4.2 pg/g TEQ_{DF05}, respectively) and thus do not represent an area that had been impacted by any significant source of dioxins and furans.

The PCDD/F composition of samples from background and the surrounding area are likely impacted by a wide range of sources, including localized burning. Three literature sources provided PCDD/F compositions of soil affected by wildfires[3,4,5]. Samples from these studies were included in a PCA with the available soil samples from the iron and steel plant and the surrounding area, the energy-from-waste plant, and the background soil

samples collected near Maglie (Figure 4). This analysis included samples with low concentrations and undetected congeners so that all of the combustion-related samples were included. Some of the combustion-related samples had up to three congeners not detected. Results indicate the breadth of PCDD/F compositions possible due to localized brush and grassland fires since samples from the combustion literature fall on either side of the main group of samples. Some of the samples from the area around the iron and steel plant contain a PCDD/F composition that is consistent with impacts due to burning in the local area.

Acknowledgements

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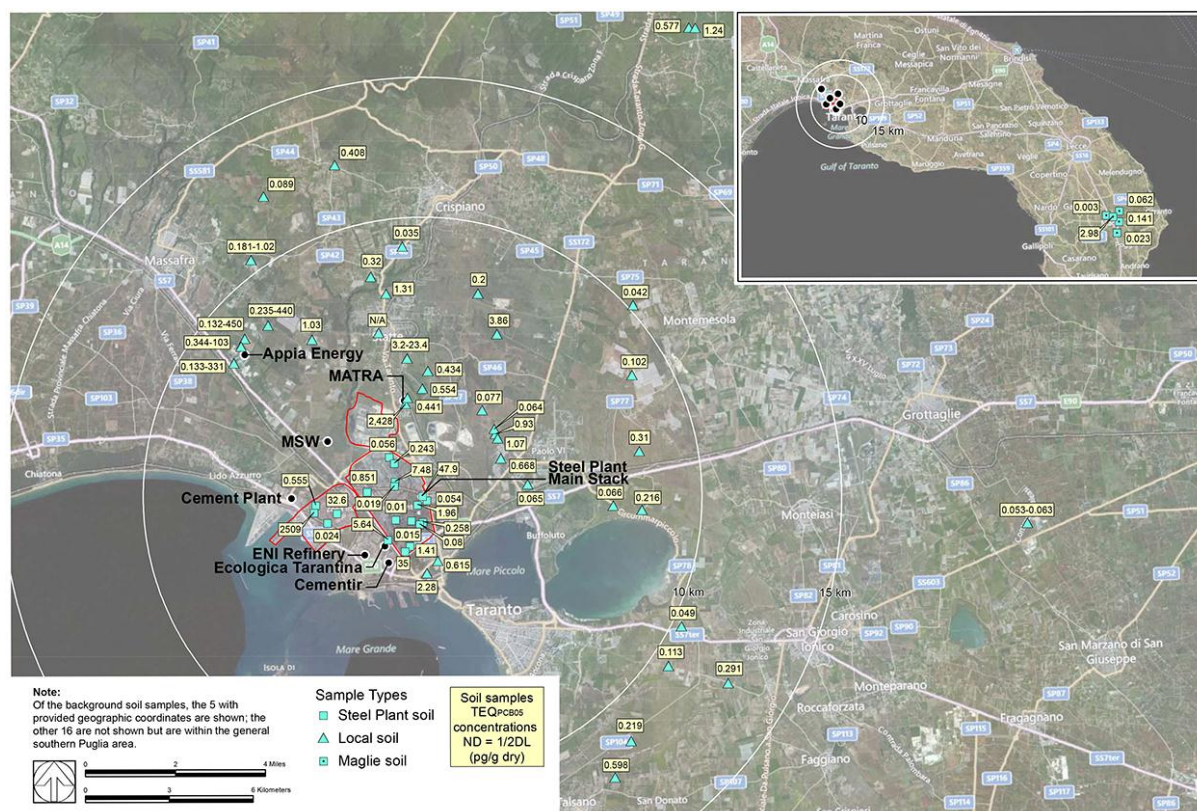
Figure 1. Sample location and total concentration of PCDD/PCDF (in pg TEQ_{DF05}/g)

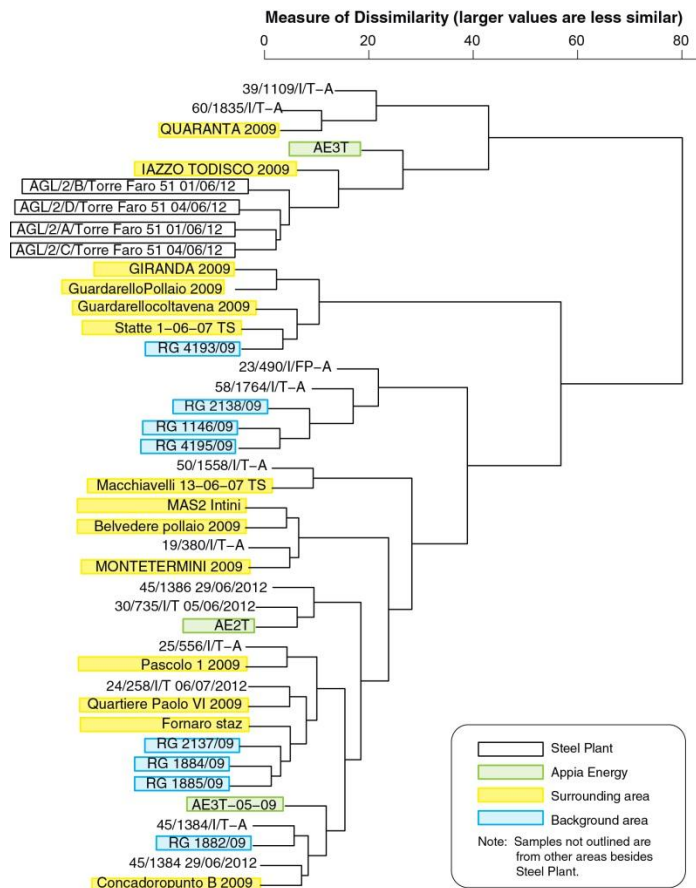**Measure of Dissimilarity (larger values are less similar)**

Figure 2. Results of the cluster analysis as applied to the soil sample data
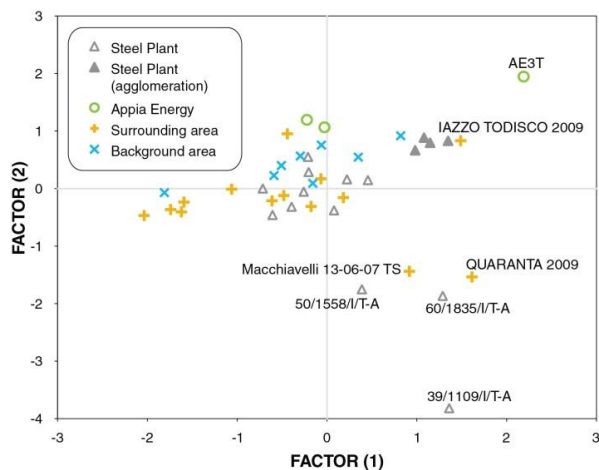

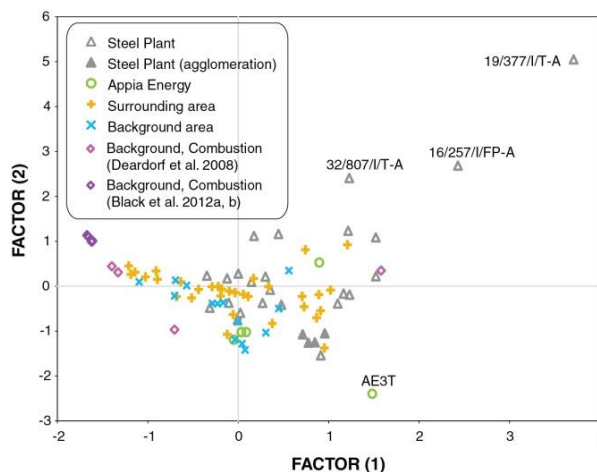Figure 3. Results of the PCA as applied to the soil sample data

Figure 4. PCA results as related to the all data available included those at very low levels of PCDD/PCDF and those with more than four congeners undetected.