IDENTIFYING PCDD/F SOURCES IN SOIL IN AN INDUSTRIAL, URBAN SETTING: TOXICITY EQUIVALENTS, CONGENER PATTERNS AND HISTORIC LAND-USE

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Introduction

Concerns regarding environmental PCDD/F levels in Newcastle, UK were raised in 1999 after a mixture of bottom and fly ash from a refuse derived fuel incinerator was found to have been applied to local allotment footpaths. These concerns prompted investigations into levels of PCDD/F in allotment footpaths and subsequently studies concerning the transfer of PCDD/Fs to soil, eggs and vegetables [1-3]. Other studies have investigated the extent of contamination from fugitive and stack emissions in an allotment site situated adjacent to the incinerator plant [4] and assessed the levels of contamination in eggs after the removal of ash [5].

In these studies the presence of a congener pattern in samples typical of that found in incinerator ash was identified. The pattern was used to establish incinerator ash or fugitive and stack emissions as the source of PCDD/F contamination. However, due to the presence of other emission sources in the same area, the studies also identified congener patterns in samples unrelated to the incinerator plant. Other studies have also used the analysis of congener patterns in environmental samples as an efficient tool in identifying the source of PCDD/F contamination in active industrial areas [6]. There are few studies, however, that have used the analysis of congener profiles to identify both contemporary and historic sources of contamination.

In the current study the aim was to identify the toxic equivalents and source of PCDD/F in soils in an urban, industrial location. The study area encompassed parts of the Tyneside region in the north east of England. Since the late 18th century this area has been a centre for heavy industry; it has also been has been described as one of the most intensely industrialized but highly populated regions of the UK [7].

Methods and Materials

Historic and current land-use survey: To establish whether any soil contamination detected was the result of fugitive and stack emissions from the incinerator, or from other industrial sources, a historical and present day land-use survey was conducted. Information concerning historic land use and the history of specific industries or areas was obtained from Newcastle City Council and the Central Library in Newcastle respectively. Information regarding contamination from current sources was obtained from the Pollution Inventory held by the Environment Agency.

Soil Survey: Based on the deposition contours predicted by dispersion modelling it was estimated that deposition of particulates (PM10) would be mainly to the north east of the incinerator. The area around the plant was therefore divided into four sectors (NE, NW, SE, SW) and into distance bands of 50m up to a distance of 750m, and thereafter into bands of 250m up to a distance of 2250m from the plant. A total of 85 mostly randomly selected sites in public open spaces were sampled. Three sites were chosen within each distance band in the NE sector, two within each band in the NW and SE sectors and one within each band in the SW sector. Within a 50m by 50m area around a chosen sampling point, three soil cores were taken (5cm in diameter and 5cm depth) from two to eight sites. Two of the soil cores were stored in glass jars at <4°C and one contributed to a composite sample for analysis.

Sample analysis: Soil samples were air-dried and sieved to <2mm. For each congener a $^{13}C_{12}$-labelled standard was added as recovery standard before extraction with toluene. For the clean-up of sample extracts a combination of neutral, acidic and basic silica, florisil, and carbopac on celite multi-columns was used. The analysis for PCDD/F was done by means of High Resolution Gas Chromatography/ High Resolution Mass Spectrometry (HRGC/HRMS) on a VG Auto Spec on two silica columns coated with DB5 res. SP2331. For each congener two isotope masses were measured. Results for PCDD/F are expressed as ng/kg of dry matter using International Toxicity Equivalents (I-TEQ). Furthermore the congener pattern of total amounts (including non-toxic congeners) of Tetra, Penta, Hexa, Hepta and Octa furans and dioxins, and the distribution pattern of 17 toxic congeners were used to determine dominant and contributing patterns. This method was used to identify likely contributing sources to contamination in each location.

Results and Discussion

There was considerable variation in the levels of PCDD/Fs which ranged from 6 to 1911ng/kg I-TEQ (Table 1). The toxic equivalents of areas in the SW sector were highest (14-1191ng/kg I-TEQ, mean 522 and median 203ng/kg I-TEQ). The mean PCDD/F levels in the SE, NE and NW sectors were 48 and 26ng/kg I-TEQ, 54 and 16ng/kg I-TEQ, 65 and 38ng/kg I-TEQ respectively.

Four main congener patterns were identified: a deposition pattern typical of urban environments; an incineration profile typical of the local waste combustion process; an OCDD dominated profile which might be characteristic of sludge, sewage or sediment; and a Furan dominated pattern in which the tetra- and penta-CDFs contributed most to the toxic equivalent. Samples exhibiting the furan dominated pattern had the highest PCDD/F levels, followed by samples with the local incineration pattern, the deposition pattern and the OCDD pattern (Table 2). Sampling sites exhibiting well-defined congener patterns were located in distinct clusters. The exception to this were sample sites with a deposition congener pattern, this profile was widespread over the whole sampling area (50% of all samples). Out of the 16 samples exhibiting the incineration pattern 3 samples exhibited elevated PCDD/F readings and these were located within the boundaries of the incinerator plant. Anecdotal evidence suggests that heaps of fly ash were stored on the site in the past and it is most likely that some windblown dispersion would have occurred. However, a further 6 samples inside the plant boundaries and 7 samples further away from the plant exhibiting this pattern did not show elevated levels of PCDD/F measured as I-TEQ.

Table 1: PCDD/F levels (ng/kg I-TEQ dm) and dominant congener profiles in soil samples

Sample ID *	PDDD/F	Dominant Profile	Sample ID	PDDD/F	Dominant Profile	Sample ID	PDDD/F	Dominant Profile
North East Sector			57, 2000	28	D	10, 300	19	O
1, 50	554	I	58, 2000	37	D	11, 300	52	D
2, 100	34	I	**North West Sector**			14, 400	27	O
3, 100	72	I	1, 50	494	I	15, 400	39	D
4, 100	90	I	2, 100	30	I	18, 500	481	F
8, 200	19	D	3, 100	121	I	19, 500	49	O
9, 200	16	I	6, 200	66	I	22, 600	7	D
10, 200	34	I	7, 200	12	D	23, 600	33	D
14, 300	38	D	10, 300	26	ocdd	26, 700	80	D
15, 300	24	O	11, 300	7	ocdd	27, 700	38	D
16, 300	62	D	14, 400	95	ocdd	30, 1000	154	F
20, 400	26	D	15, 400	19	ocdd	31, 1000	17	D
21, 400	43	O	18, 500	102	D	34, 1500	80	D
22, 400	25	I	19, 500	10	ocdd	35, 1500	72	D
26, 500	9	D	22, 600	37	D	38, 2000	40	D
27, 500	25	D	23, 600	13	ocdd	39, 2000	16	D
28, 500	15	D	26, 700	8	ocdd	**South West Sector**		
32, 600	25	D	27, 700	21	D	1, 50	84	I
33, 600	57	D	30, 1000	16	D	2, 100	54	D
34, 600	27	D	31, 1000	16	D	6, 300	39	I
38, 700	22	D	34, 1500	11	D	10, 500	435	F
39, 700	15	O	35, 1500	10	D	11, 550	308	F
40, 700	23	D	38, 2000	12	D	12, 600	1772	F
44, 1000	34	O	39, 2000	15	D	13, 650	169	F
45, 1000	13	D	**South East Sector**			14, 700	1911	F
46, 1000	16	D	1, 50	36	I	15, 750	237	F
50, 1500	38	ocdd	2, 100	31	D	16, 1000	1174	F
51, 1500	6	D	3, 100	18	I	18, 1500	69	F
52, 1500	23	D	6, 200	12	I	20, 2000	14	D
56, 2000	26	O	7, 200	56	D			

I=Incinerator profile; D=Deposition profile; ocdd=OCDD dominated profile; F=Furan dominated profile; O=Other unidentified profile; *Sample ID is composed of sample number and distance band. Sample numbers not listed were analysed for heavy metals only.

Ten samples exhibited the furan-dominated pattern, all of which occurred in the southern sectors. They appeared in a cluster along the southern bank of the river Tyne. The historic land use survey indicated that the very high levels of PCDD/F in soils to the SW and SE of the plant were most likely to be the result of graphite electrode sludges used in brine electrolysis at a chemical works between the early 1890's and 1930's. Earth movement and relocation during landscaping in the early 1970's may have contributed to re-distribution of contaminated soils. 10% of samples exhibited the OCDD dominated pattern. All but one of these came from the NW sector and were located in a distinct cluster which was identified as being the location of a culverted stream.

Table 2: PCDD/F (ng/kg I-TEQ dm) in soils with distinct congener patterns

Dominant congener pattern	N	Mean	Median	Min	Max
OCDD dominated	8	27	16	7	95
Incineration	16	108	38	12	554
Deposition	43	31	25	6	102
Furan	10	671	372	69	1911
Other	8	30	27	15	49
Across whole study area	85	121	31	6	1911

Conclusions

There was no evidence to suggest that fugitive and stack emissions made a significant contribution to the levels of soil contamination with PCDD/F outside the boundaries of the incinerator plant, however, there were some elevated levels within the plant boundaries. Clusters of hotspots, with elevated PCDD/F levels and/or distinctive congener patterns were linked to historic industrial land use dating back to approximately 1890's. The combination of measurements of current PCDD/F levels and congener patterns with surveys of historical land-use provided a powerful tool to identify both hotspots of contamination and pointers for source identification.

References

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