A SURVEY OF THE DIOXIN CONTENT OF SOILS IN WALSALL, U.K.

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ABSTRACT

The sampling strategy and analytical validation used to carry out an extensive soil survey for PCDD and PCDF levels are described. The results of the survey are discussed relative to possible source areas.

INTRODUCTION

In 1986, a national survey was commissioned by HMIP(UK) to investigate the levels of PCDDs and PCDFs ("dioxins") in rural and semi-urban British soils. The results[1] presented in 1989 showed that dioxin values were significantly elevated at some locations, among these, Walsall in the Midlands. In 1992, Walsall Metropolitan Borough Council commissioned a study of the area with a view to establish current dioxin levels in soils as well as to identify any local sources.

Walsall is situated to the north-west of Birmingham, in Central England. The area has contained, among other industrial units, three secondary non-ferrous refiners. The sampling strategy takes these into particular consideration. The analytes chosen for the study are the seventeen 2,3,7,8-chloro substituted PCDDs and PCDFs.

SAMPLING AND ANALYSIS

The sampling strategy involved two stages of sampling over four months, with roughly equal numbers of samples collected in both stages. The selection of sites for the second stage was influenced by analyte levels in samples collected during the first stage. Sampling sites were selected according to a map grid covering the whole area (fig 1) and on a radial grid and linear transects in the vicinity of the refiners. Care was taken to ensure that the sites were undisturbed areas and uninfluenced by factors such as landscaping, use of pest control chemicals, waste dumping and leaching or drainage from trees, etc.

Soils were sampled over a $100m^2$ area (10m x 10m) with 8 cores (50mm depth) taken along the diagonals of the square. Samples were stored (below 7^0C) in dioxin-free glass jars.

The soil cores were homogenised, air dried ($<22^0C$), ground and graded to yield a $\leq 2mm$ particle size. A 50g subsample was taken for the analysis which has been described in detail in earlier reports[2,3]. In brief, the analysis consisted of soxhlet extraction of samples (spiked with a series of ^{13}C labelled PCDDs and PCDFs) followed by oxidative and liquid chromatographic purification, and instrumental determination using gas chromatography (60m SP-2331) - mass spectrometry (GC-MS).

QUALITY

The variability associated with the sampling has been quantified using the results (table 1) of a number of field duplicates of three different types - spot duplicates where 2 sets of adjacent soil cores within the sampling area are taken, site duplicates where a set of soil cores are taken along the diagonals of the sampling area with a duplicate set taken along a cross-section bisecting the diagonals, and area duplicates where a second 100m^2 area is sampled adjacent to the original site.

TABLE 1. - SUMMARY OF VALIDATION DATA

1. PRECISION (COV)	NUMBER	RANGE %	AVERAGE
A. ANALYTICAL (Laboratory) DUPLICATES	4	1.4 - 17	7.2
B. ANALYTICAL (Method) REPLICATES	5	0.4 - 12	8.5
C. SAMPLING			
Spot Duplicate	2	9 - 15	12
Site Duplicate	4	6.3 - 29	18
Area Duplicate	2	42 - 102	72
2. QUALITY ASSURANCE STANDARD (COV; - Based on 6 analyses)	6	1 - 18	5
3. RECOVERY (% Extracted)			
a. All Data	103	52 - 118	84
b. Reduced Set	85	70 - 100	83
4. LIMIT OF DETECTION (Based on 10 method blanks)			
Range - 0.4ng/kg(2,3,7,8-T_4CDD) to 4ng/kg(OCDF)			

The analytical methodology has been extensively validated[2,4] and the criteria used for positive identification and quantitation of analytes have been documented[2,5]. The validation data for this study are summarised in table 1. Additionally, an internal quality assurance standard material has been continously monitored throughout the course of the analyses (table 1).

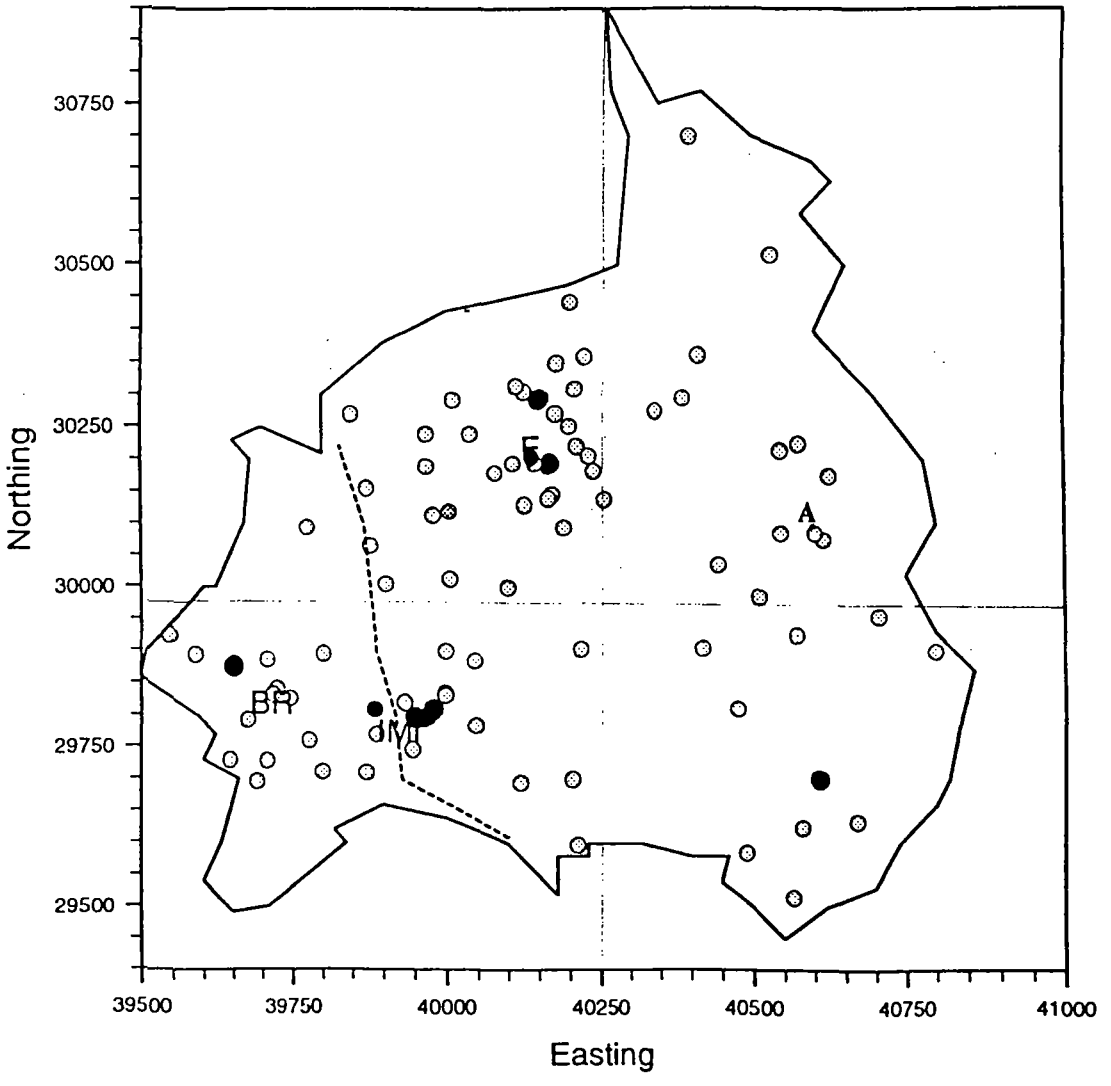

FIGURE 1. MAP OF WALSALL AREA SHOWING SAMPLE SITE LOCATION

DISCUSSION

Due to the large data sets obtained from this study and the limitations on space only condensed data (ITEQ values) and summaries are presented.

A total of 103 samples (including sampling duplicates) were analysed. The levels of dioxins ranged from 1.04 ng/kg to 209 ng/kg with a mean value of 35 ng/kg and a median of 19 ng/kg. Statistical examination of the data set indicates a subgroup comprising 90% of the samples with values ranging from 1.04 ng/kg to 77 ng/kg. This view is strengthened by the closer agreement between the mean (24 ng/kg) and median (18 ng/kg) values for this group and the similarity with the median value of the main group. All values lying outside the subgroup have been plotted on the map in bold (figure 1). The remaining sites are also shown and the refiners are indicated as IMI, E and BR. It is evident from the figure that apart from the isolated exception, the outliers from the subgroup, ie. the higher dioxin concentrations, are found in the areas around the refiners.

Spatial examination of the entire data set shows that barring the one exception, dioxin levels in the two eastern quadrants (figure 1) lie below the mean value (35 ng/kg). The higher levels are to be found in the two western quadrants which contain the refiners. Similarly, this is observed in a comparison of the mean intercept values of the samples in each of the four quadrants - NW 34ng/kg; SW 31ng/kg; NE 13ng/kg; SE 11ng/kg. Levels on average are elevated to the east of the refiners with some possible bias to the north. This is especially significant in view of the prevailing W/SW winds.

In further statistical analysis, 5 "districts" are defined, with a 2.8km diameter and centred around the 3 refiners, an outlying village (marked A in fig. 1) and the vicinity of the motorway (shown as a broken line). The two districts with the highest dioxin loading are centred on refiners IMI and E with 2-3 times the Walsall area average loading.

Examination of the data is ongoing at the present time. Further investigations of spatial/concentration factors and the significance of individual isomer data will be presented in due course.

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