

ATTACHMENT 3

BASELINE DIOXIN SURVEY

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ASEP

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DIOXIN LEVELS
in
AIR, SOIL and FOLIAGE
in the vicinity of
A PROPOSED DEVELOPMENT
at
CARRANSTOWN, Co. MEATH

**A Report to Project Management
Dublin**

September, 2000

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), commonly referred to as dioxins and furans or simply as "dioxins" are generated as by-products from various chemical manufacturing processes and from combustion processes where chlorine is present. This group of compounds has a very high toxicity to human health and consequently very low guideline values have been set for human exposure.

2. Toxic Equivalent Value (TEQ)

There are a great many different isomeric chlorinated species covered by the term "dioxins". Of these, the most toxic is the 2,3,7,8 tetrachlorodibenzo-p-dioxin. In relative terms, many other "dioxins" are much less toxic. The accepted convention is to derive a total toxic equivalent value for any sample relative to the 2,3,7,8 TCDD, which is given a TEQ of unity. This is achieved by applying the relevant agreed toxic equivalent factor to the concentration of each dioxin and furan species.

The weighting scheme proposed by NATO/CCMS (North Atlantic Treaty Organisation's Committee on Challenges of Modern Society) is the most widely accepted and is the one used in this exercise. The TEQs are tabulated below.

NATO/CCMS I- Toxic Equivalence Factors

Congener	1-TEF
2378 TCDD	1
12378 PeCDD	0.5
123478HxCDD	0.1
123678HxCDD	0.1
123789HxCDD	0.1
1234678HpCDD	0.01
OCDD	0.001
2378 TCDF	0.1
12378 PeCDF	0.5
123478 HxCDF	0.05
123678 HxCDF	0.1
234678 HxCDF	0.1
123789HxCDF	0.1
1234678 HpCDF	0.01
OCDF	0.001

3. Baseline Study

A development is proposed for a green field site, at Carranstown, Co Meath, to the south west of Drogheda. Project Management has commissioned ASEP to carry out a baseline study of dioxin levels at the site. This has involved collection of samples from ambient air, soil and vegetation from four locations around the site.

This report presents the results of the analysis of those samples.

4 Sampling Protocol

4.1 Air Samples

Sampling was carried out using a procedure based on Method TO 9A, described in the US EPA Compendium for the Determination of Toxic Organic Compounds in Ambient Air. In summary, air was sampled through a quartz fibre/polyurethane foam filter assembly using a metered high volume battery operated pump. Battery operated pumps were necessary because there was no access to mains power and the use of portable generators was discounted because of security considerations. Sampling was carried out over a seventeen-day period in order to collect between 100 and 200m³ of air. The exposed sampling media were wrapped in aluminium foil and returned to the laboratory for analysis.

4.2 Soil and Vegetation Samples

Sampling was carried out using the UK HMIP protocol. This operates on an approximate one metre square area. Five sub-samples of soil were removed from the points of a "W" shape using a corer. Surface vegetation was collected from each point and from any adjacent hedgerows, trees etc. The corer samples to an approximate depth of 15 cm with an approximate weight of 200g being taken from each point. The two sets of five sub samples were each combined to provide two composite samples, one of soil and one of vegetation which were double wrapped in heavy duty polyethylene bags and returned to the laboratory for analysis.

5 Sampling Programme

The air sampling equipment was set up by ASEP personnel at the four sites tabulated below on 22 August, 2000. Soil and vegetation samples were collected at the same time. The sites were inspected at regular intervals during the air-sampling programme which was terminated on 7 September, 2000. The sites are indicated on the outline maps of the area and photographs, which are appended.

Sampling Site Grid References

Site Reference	Grid Reference
D1	53° 40.494 N, 006° 23.535 W
D2	53° 40.688 N, 006° 23.717 W
D3	53° 40.708 N, 006° 23.420 W
D4	53° 40.672 N, 006° 23.366 W

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6 Analysis

Analysis was carried out by ENSR International, a specialist "dioxin" laboratory, based in Manchester. The analytical procedure, which is detailed below, involves a complex extraction, clean-up and concentration programme, followed by multiple ion high resolution gas chromatography - high resolution mass spectrometry, (GC/MS) using procedures based on USEPA methods 8290 and 1613, allied with UK acceptance criteria (Chemosphere, 21, 999 1990). All laboratory work is undertaken under fully documented QA/QC control, providing reproducible and traceable results under the UKAS accreditation scheme.

6.1 Extraction

Each PUF and corresponding filter pair was transferred to a Soxhlet thimble and spiked with a known amount of spike material. The soil and vegetation samples were air dried to constant weight. The soil samples were sieved through a 1mm sieve. The > 1mm fraction was retained and an aliquot of the > 1mm fraction transferred to a Soxhlet thimble. The vegetation samples were finely chopped and an aliquot of the chopped sample transferred to a Soxhlet thimble. The samples were spiked with a known amount of spike material, containing the following ¹³C isomers (*Cambridge Isotopes Laboratories mixes ED998 and EF999*)

Dioxin	Furan
2,3,7,8 TCDD	2,3,7,8 TCDF
1,2,3,7,8 PeCDD	1,2,3,7,8 PeCDF 2,3,4,7,8 PeCDF
1,2,3,4,7,8 HxCDD	1,2,3,4,7,8 HxCDF
1,2,3,6,7,8 HxCDD	1,2,3,6,7,8 HxCDF
1,2,3,7,8,9 HxCDD	2,3,4,6,7,8 HxCDF
1.2.3.4.6.7.8 HpCDD	1.2.3.4.6.7,8 HpCDF 1,2,3,4,7,8,9 HpCDF
OCDD	OCDF

The added ^{13}C mixes are used as a quantitative standard to compensate for recovery efficiency and as an internal retention time reference in the gas chromatographic analysis.

The air samples were extracted with a hexane/acetone (4:1) mixture for at least 8 hours. The Soxhlet extract was then water washed to remove the acetone and reduced in volume to ~5 ml by freeze drying.

The soil samples were Soxhlet extracted with toluene for at least 16 hours. The toluene extract was then reduced to dryness by freeze-drying and the residue re-dissolved in hexane.

The vegetation samples were extracted with hexane/acetone (4:1). The extracts were water washed to remove the acetone and reduced in volume by freeze-drying.

All the hexane extracts were then subjected to the clean-up procedure described below.

6.2 Clean-up Procedure

The clean-up is based on the method of di Domenico et al (*Anal Chem.*, 51. 735 1979) which has proved effective in removing most substances which interfere with the subsequent GC/MS analysis.

The hexane extract is put on to a pre-washed column containing, in order, anhydrous sodium sulphate, 1/2(w/w) concentrated sulphuric acid/50-100 mesh silica gel, 9/1(w/w) anhydrous sodium sulphate/sodium bicarbonate, 50-100 mesh silica gel and finally anhydrous sodium sulphate. The column is eluted with 90ml of hexane to ensure efficient elution of the PCDDs and PCDFs.

The 100ml extract volume obtained is reduced to about 2mls by freeze-drying and then transferred onto a pre-washed basic chromatography grade alumina (Woelm

Super I) column. The column is eluted with about 20mls of hexane containing 2% dichloromethane and the eluate collected.

A subsequent wash, using a 50/50 hexane/dichloromethane mixture (10 mls) is used to elute the PCDDs and PCDFs. The eluate is reduced to <1ml under a stream of clean, dry nitrogen.

Dodecane (containing a known concentration of ³⁷Cl₄ 2,3,7,8-TCDD as an overall recovery standard) is added to the sample to act as a keeper. The solution is then further reduced to the volume of the keeper.

This is then transferred into a micro-vial, which is capped and sent to the MS Laboratory.

6.3 GC/MS Analysis

6.3.1 GC Conditions

- Instrument:* HP5890 Series II, split/splitless injector at 280°C operated in splitless mode for 1 mm after injection.
- Column:* 60 m DB5 capillary column, 0.25 mm ID, 0.25 µm film thickness.
- Temperature Programme:* 190°C for 2 mins then at 2.5°C /min to 230°C, held for 1 min, then at 2.5°C/min to 250°C, held for 2 mins, then at 4°C/min to 290°C, held for 17 mins (total run time 56 mins)
- Transfer line:* 280°C.
- Helium carrier gas:* at ~1 ml/min (head pressure 29 psi)

6.3.2 MS Conditions

Instrument: VG Autospec
Resolution: > 7500 on PFK
Electron Energy: ~32eV (optimised on m/z 92 of toluene)
Operational Mode: multiple ion detection
 using the 5 groups tabulated below

Group1:TCDD and TCDF

M/z	Ion	Species
303.9016	M	TCDF
305.8987	M+2	TCDF
315.9419	M	¹³ C ₁₂ TCDF
316.9824	PFK Lock	
317.9389	M+2	¹³ C ₁₂ TCDF
319.8965	M	TCDD
321.8936	M+2	TCDD
327.8847	M	³⁷ C ₁₄ TCDD
331.9368	M	¹³ C ₁₂ TCDD
333.9338	M+2	¹³ C ₁₂ TCDD

Group 2: PeCDD and PeCDF

M/z	Ion	Species
337.8627	M	PeCDF
339.8597	M+2	PeCDF
349.9029	M	¹³ C ₁₂ PeCDF
351.9000	M+2	¹³ C ₁₂ PeCDE
353.8576	M	PeCDD
355.8546	M+2	PeCDD
365.8978	M	¹³ C ₁₂ PeCDD
366.9792	PFK Lock	
367.8949	M+2	¹³ C ₁₂ PeCDD

Group 3: HxCDD and HxCDF

M/z	Ion	Species
373.8207	M+2	HxCDF
375.8178	M+4	HxCDF
380.9760	PFK Lock	
385.8610	M+2	¹³ C ₁₂ HxCDF
387.8580	M+4	¹³ C ₁₂ HxCDF
389.8156	M+2	HxCDD
391.8127	M+4	HxCDD
401.8559	M+2	¹³ C ₁₂ HxCDD
403.8530	M+4	¹³ C ₁₂ HxCDD

Group 4: HpCDD & HpCDF

M/z	Ion	Species
407.7818	M+2	HpCDF
409.7788	M+4	HpCDF
419.8220	M+2	¹³ C ₁₂ HpCDF
421.8191	M+4	¹³ C ₁₂ HpCDF
423.7767	M+2	HpCDD
425.7737	M+4	HpCDD
435.8169	M+2	¹³ C ₁₂ HpCDD
437.8140	M+4	¹³ C ₁₂ HpCDD
442.9729	PFK Lock	

Group 5: OCDD & OCDF

M/z	Ion	Species
441.7428	M+2	OCDF
443.7398	M + 4	OCDF
453.7830	M+2	¹³ C ₁₂ OCDF
454.9728	PFK Lock	
455.7801	M+4	¹³ C ₁₂ OCDF
457.7377	M+2	OCDD
459.7348	M+4	OCDD
469.7780	M+2	¹³ C ₁₂ OCDD
471.7750	M+4	¹³ C ₁₂ OCDD

7. Data Handling

Relative response factors (RRF's) for the ¹²C and ¹³C congeners are calculated as the ratio of the sum of the areas of the two isotopic ions of the ¹³C congener to the sum of the corresponding ¹²C congener, scaled by the relative concentrations of the two species in a standard calibration mix.

The RRF's so obtained are then compared with the running mean values and, provided they do not differ by more than $\pm 15\%$ the samples are then analysed.

The unknown samples are analysed by extracting the areas and retention times of all the peaks in each mass chromatogram and transferring them to a spread sheet programme. This programme then filters the peaks on the basis of the isotopic ratios, targets the 2,3,7,8-containing congeners from retention time data and, using the RRF's derived from the calibration mix data and the amount of spike mix added, calculates the concentrations of the 2,3,7,8-containing congeners and the totals for each congener group, as well as the data on any peaks rejected on isotopic ratio grounds.

The integrated traces are then inspected to ensure that peaks are not included or rejected on the basis of an incorrect integration baseline.

These values are scaled by the amount of the original sample, when known, to give the concentrations of the various species in the sample. A TEQ is then calculated based on the concentration of the 2,3,7,8-containing congeners multiplied by the appropriate TEFs (in this case the NATO/CCMS I-TEFs) and summed.

All the resulting values are automatically compensated for extraction and clean-up efficiency by being referenced to the added spike mix concentrations. The actual recovery (for 2,3,7,8- TCDD) is obtained by comparing the areas of the ^{13}C TCDD spike and the added $^{37}\text{C}_{14}$ TCDD GC standard, scaled for relative amounts, with those obtained from a standard mix of the two compounds.

The use of more than one mass for monitoring each congener group and for monitoring the ^{13}C congeners means that in addition to mass specificity, intensity ratio measurements of the different ions can be made to detect any interference which may have occurred due to the elution of other species at or close to the retention time of the species of interest.

The criterion of similar GC retention time in the sample relative to the calibration standard is also used to aid identification and specificity. It is assumed for the 2,3,7,8-containing congener specific analyses that the sample response at the retention time of the 2,3,7,8- containing ^{13}C standard is due only to the 2,3,7,8- containing congener.

The criteria used are those of the UK Acceptance Criteria Guidelines [*Ambidge et al Chemosphere, 2*], 999 (1990)].

8. Results

Results are tabulated below giving the weights of the various isomers detected in the samples, together with the toxic equivalent value (derived from NATO/CCMS Toxic Equivalent Factors).

Weight of Dioxin/Furan in Ambient Air Samples

ASEP Ref. No.	D1	D2	D3	D4
ENSR Ref. No.	23245	23246	23247	23248
2378-TCDD	<0.002	< 0.002	< 0.002	< 0.002
Total TCDD	< 0.02	< 0.02	< 0.02	< 0.02
12378 PeCDD	< 0.002	< 0.002	< 0.002	< 0.002
Total PeCDD	< 0.02	< 0.02	< 0.02	< 0.02
123478-HxCDD	< 0.002	< 0.002	< 0.002	< 0.002
123678-HxCDD	< 0.002	< 0.002	< 0.002	< 0.002
123789-HxCDD	< 0.002	< 0.002	< 0.002	< 0.002
Total HxCDD	< 0.02	< 0.02	< 0.02	< 0.02
1234678-HpCDD	< 0.005	< 0.005	< 0.005	< 0.005
Total HpCDD	< 0.05	< 0.05	< 0.05	< 0.05
OCDD	0.01	0.01	0.02	0.02
2378-TCDF	< 0.002	< 0.002	< 0.002	< 0.002
Total TCDF	< 0.02	< 0.02	< 0.02	< 0.02
23478-PeCDF	< 0.002	< 0.002	< 0.002	< 0.002
12378 PeCDF	< 0.002	< 0.002	< 0.002	< 0.002
Total PeCDF	< 0.02	< 0.02	< 0.02	< 0.02
123478-HxCDF	< 0.002	< 0.002	< 0.002	< 0.002
123678-HxCDF	< 0.002	< 0.002	< 0.002	< 0.002
234678-HxCDF	< 0.002	< 0.002	< 0.002	< 0.002
123789-HxCDF	< 0.002	< 0.002	< 0.002	< 0.002
Total HxCDF	< 0.02	< 0.02	< 0.02	< 0.02
1234678-HpCDF	0.005	0.005	< 0.005	< 0.005
1234789-HpCDF	< 0.005	< 0.005	< 0.005	< 0.005
Total HpCDF	< 0.05	< 0.05	< 0.05	< 0.05
OCDF	< 0.01	< 0.01	< 0.01	< 0.01
I-TEQ	0.006	0.006	0.006	0.006

Note: Total refers to all isomers of the congener group ITEQ (max) calculated with "<" values at their reported limits

Dioxin/Furan Content of Soil Samples (ng/g air dried)

ASEP Ref. No.	D1	D2	D3	D4
ENSR Ref. No.	23107	23108	23109	23110
Weight loss on drying (%)	16	19	22	24
2378-TCDD	0.0002	< 0.0001	< 0.0001	< 0.0001
Total TCDD	0.015	0.002	0.001	0.003
12378 PeCDD	0.0002	0.0003	< 0.0001	< 0.0001
Total PeCDD	0.004	0.005	0.001	0.001
123478-HxCDD	0.0005	0.0004	0.0002	0.0002
123678-HxCDD	0.0002	0.0003	0.0002	0.0002
123789-HxCDD	0.0003	0.0003	0.0002	0.0001
Total HxCDD	0.007	0.006	0.004	0.004
1234678-HpCDD	0.0032	0.0030	0.0024	0.0022
Total HpCDD	0.005	0.006	0.004	0.004
OCDD	0.015	0.025	0.011	0.012
2378-TCDF	0.0003	0.0003	0.0002	0.0002
Total TCDF	0.004	0.002	0.003	0.002
23478-PeCDF	0.0004	0.0004	0.0004	0.0003
12378 PeCDF	0.0006	0.0003	0.0004	0.0004
Total PeCDF	0.005	0.003	0.003	0.003
123478-HxCDF	0.0015	0.0014	0.0005	0.0005
123678-HxCDF	0.0004	0.0003	0.0003	0.0004
234678-HxCDF	0.0003	0.0003	0.0003	0.0003
123789-HxCDF	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Total HxCDF	0.003	0.003	0.003	0.002
1234678-HpCDF	0.0044	0.004	0.0026	0.0049
1234789-HpCDF	0.0003	0.0003	0.0001	< 0.0001
Total HpCDF	0.005	0.006	0.003	0.005
OCDF	0.007	0.008	0.005	0.006
I-TEQ	0.0010	0.0009	0.0006	0.0006

Note: Total refers to all isomers of the congener group ITEQ (max) calculated with "<" values at their reported limits

Dioxin/Furan Content of Vegetation Samples (ng/g air dried)

ASEP Ref. No.	D1 VEG	D2 VEG	D3 VEG	D4 VEG
ENSR Ref. No.	23111	23112	23113	23203
Weight loss on drying (%)	77	70	71	73
2378-TCDD	< 0.0002	< 0.0002	< 0.0005	< 0.0002
Total TCDD	< 0.002	< 0.002	< 0.005	0.003
12378 PeCDD	< 0.0002	< 0.0002	< 0.0005	< 0.0002
Total PeCDD	< 0.002	< 0.002	< 0.005	0.003
123478-HxCDD	< 0.0002	< 0.0002	< 0.0005	< 0.0002
123678-HxCDD	< 0.0002	< 0.0002	< 0.0005	< 0.0002
123789-HxCDD	< 0.0002	< 0.0002	< 0.0005	< 0.0002
Total HxCDD	< 0.002	< 0.002	< 0.005	< 0.002
1234678-HpCDD	0.0007	0.0005	0.0005	0.0010
Total HpCDD	< 0.002	< 0.002	< 0.005	0.002
OCDD	0.005	0.004	0.005	0.007
2378-TCDF	0.0002	0.0002	< 0.0002	0.0005
Total TCDF	0.003	0.003	0.002	0.008
23478-PeCDF	0.0002	0.0002	< 0.0002	0.0003
12378 PeCDF	0.0001	< 0.0002	< 0.0002	< 0.0002
Total PeCDF	0.007#	< 0.002	0.002	0.003
123478-HxCDF	0.0006	< 0.0002	< 0.0002	< 0.0002
123678-HxCDF	< 0.0001	< 0.002	< 0.002	< 0.002
234678-HxCDF	< 0.0001	< 0.002	< 0.002	< 0.002
123789-HxCDF	< 0.0001	< 0.002	< 0.002	< 0.002
Total HxCDF	0.004#	< 0.002	< 0.002	< 0.002
1234678-HpCDF	< 0.0005	< 0.0002	< 0.0002	0.0010
1234789-HpCDF	< 0.0005	< 0.0002	< 0.0002	< 0.0002
Total HpCDF	< 0.005	< 0.002	< 0.002	0.001
OCDF	0.003	0.001	0.003	0.004
I-TEQ	0.0006	0.0006	0.0011	0.0007

maximum value due to interference

Note: Total refers to all isomers of the congener group ITEQ (max) calculated with "<" values at their reported limits

9. Concentrations in Ambient Air

The volumes of air sampled at the various locations are tabulated below together with the corresponding concentrations of dioxins expressed as I-TEQ(max)/m³. The volume of air is reported as dry gas at ambient temperature and pressure.

Site Ref	Sample Volume m ³ ATP	Dioxin Concentration I-TEQ (max) pg/m ³
D1	213.668	0.028
D2	130.137	0.046
D3	182.652	0.033
D4	128.518	0.046

10. Confidence Limits

The analytical measurement should have a precision of $\pm 10\%$ (from measurements of calibration standards and repeat linear injections)

11. Conclusions

Examination of the analytical results from the current study would indicate that the concentrations of the individual dioxin congeners being measured in each of the three sample matrices are at levels that are close to the limits of detection of the analytical system. The practice that has been adopted is to take all the "<" values at their reported limits so as to derive a worst case maximum value.

On this basis, the range in the soil samples is from 0.6 - 1 ng/kg and in the vegetation samples it is from 0.6 - 1.1 ng/kg of dry sample in each case. The air sample range is from 0.028 to 0.046 pg/m³.

There are only limited data on background levels in Ireland. An *Eolas*, study looking at 8 rural sites in Co Cork in 1991, showed soil levels in a range of 0.2 to 23.7 ng/kg. A *Forbairt* study was carried out in 1993/94 on behalf of Cork County Council on dioxin levels in soil and milk samples from a number of locations in Cork City and County. The level reported in soil was from 1.5 to 8.6 ng/kg TEQ.

Dioxins were also measured in soil in the Askeaton area in the course of the investigation of animal health problems. "Worst case" levels were reported in the range 1.1 – 2.0 ng/kg.

In a baseline study prior to the installation of a thermal oxidiser at Rathdrum, levels in the range 0.8 to 13.3 ng/kg were reported.

In a 1999 baseline survey for a proposed development at Kilcock in Co Kildare dioxin levels in soil samples were reported in the range 0.6 - 1.2 ng/kg.

By way of an international reference, the German Bund-Länder- Arbeitsgruppe DIOXINE shows a target value of < 5ng/kg for uncontaminated soils. HMIP data from the United Kingdom shows a range for 11 rural and 5 urban sites from 5.2 to 28.4 ng/kg.

In the Kilcock survey, dioxin levels in ambient air were reported in the range 0.003-0.007 pg/m³. That same report quotes other data from Ireland in the range 0.0002-0.08 pg/m³

However, these various data should only be compared with caution since the levels quoted are to a very large extent simply a function of the detection limits, which can vary not only between laboratories but also between samples.

In "*Dioxins in the Irish Environment, An Assessment based on levels in Cow's Milk*" Colman Concannon of the EPA's Regional Inspectorate comments on the caution necessary in making such comparisons. He refers to the uncertainty introduced by the procedure of assigning TEQs for "non-detects", quoting examples where this can produce a range of $\pm 50\%$ on reported data. He also notes that the problem is further compounded by the very large analytical uncertainties to which absolute concentrations at close to detection limits are normally subject and which are usually difficult to quantify. It is clear, he concludes that it would be unwise to place an overemphasis on comparisons of the individual values for I-TEQs.

For example, it should be noted that the approach adopted in the Kilcock report was to take "<" values at half the reported limit value for the purposes of TEQ determination.

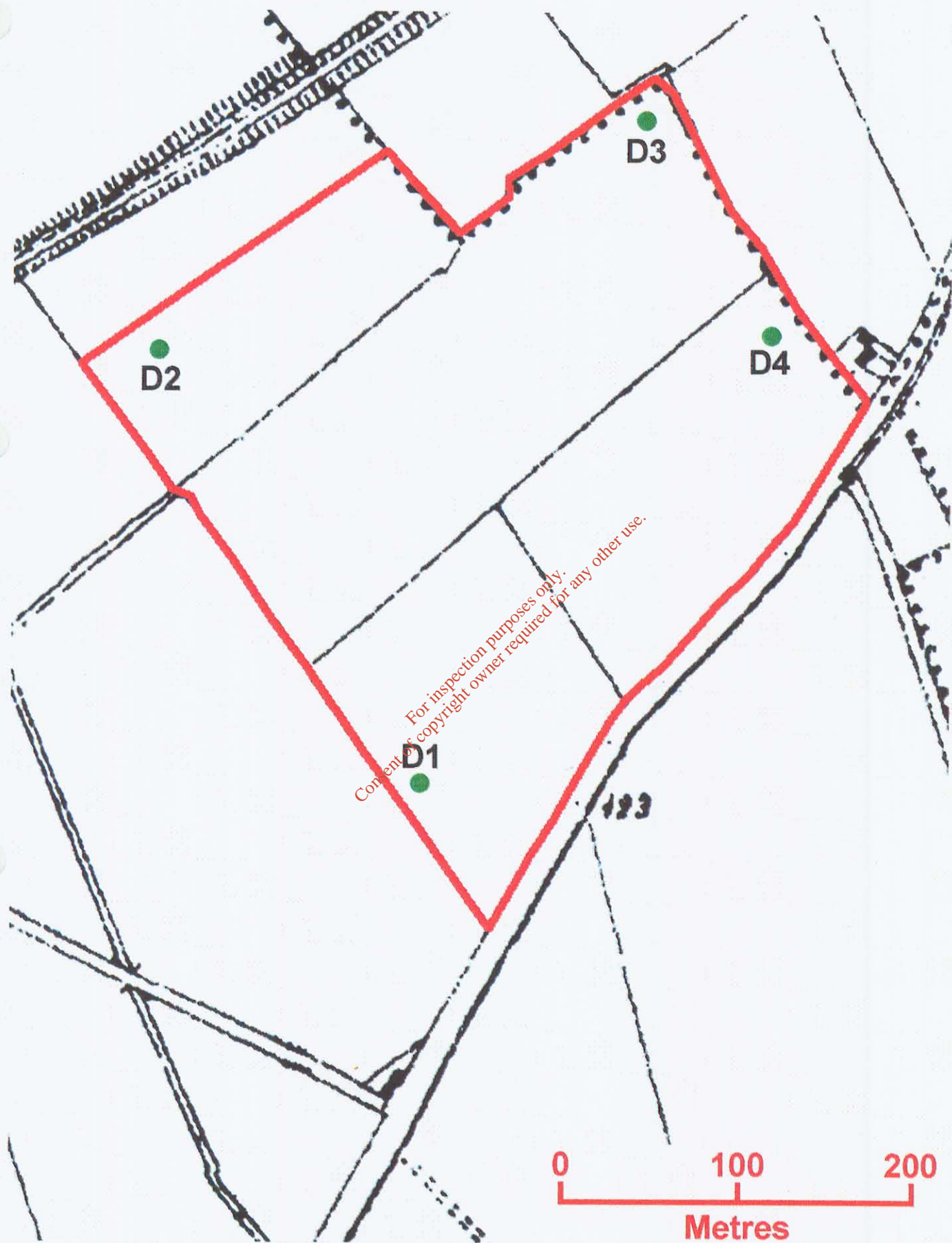
It is reasonable to conclude that the Drogheda data are within the range of background levels of dioxins in air and soils previously reported in Ireland and the vegetation data show no evidence of any accumulation from the soil.

The data from the Drogheda study provide a baseline against which to monitor the impact of the proposed development.

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Appendix: Sampling Sites



Sampling Site D1



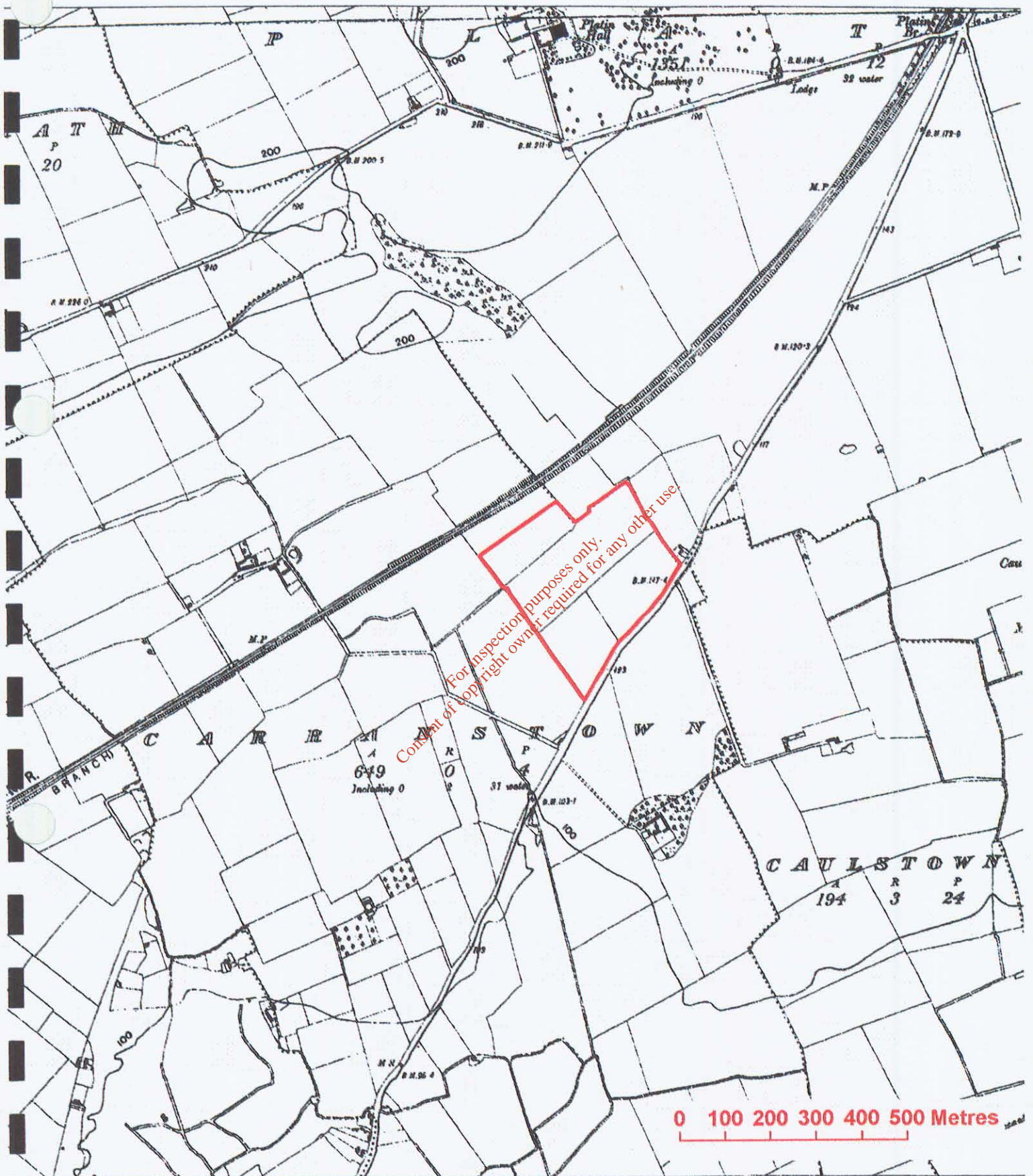
Sampling Site D2



Sampling Site D3



Sampling Site D4



Appendix: Site Location Map