

3. Land Surface Zoning for Groundwater Protection

3.1 Information and Mapping Requirements for Land Surface Zoning

The groundwater resources protection zone map is a land-use planning map, and therefore is the most useful map for the decision-making process. It is the ultimate or final map as it is obtained by combining the aquifer and vulnerability maps. The aquifer map boundaries, in turn, are based on the bedrock map boundaries and the aquifer categories are obtained from an assessment of the available hydrogeological data. The vulnerability map is based on the soils map, together with an assessment of relevant hydrogeological data, in particular indications of permeability and karstification. This is illustrated in Figure 3.

Similarly, the source protection zone maps result from combining vulnerability and source protection area maps. The source protection areas are based largely on assessments of hydrogeological data. This is illustrated in Figure 4.

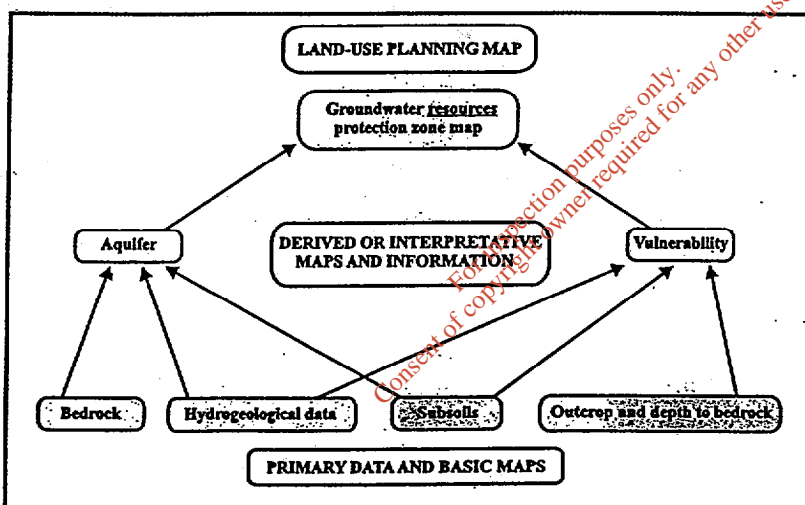


Figure 3. Conceptual framework for production of groundwater resource protection zones, indicating information needs and links

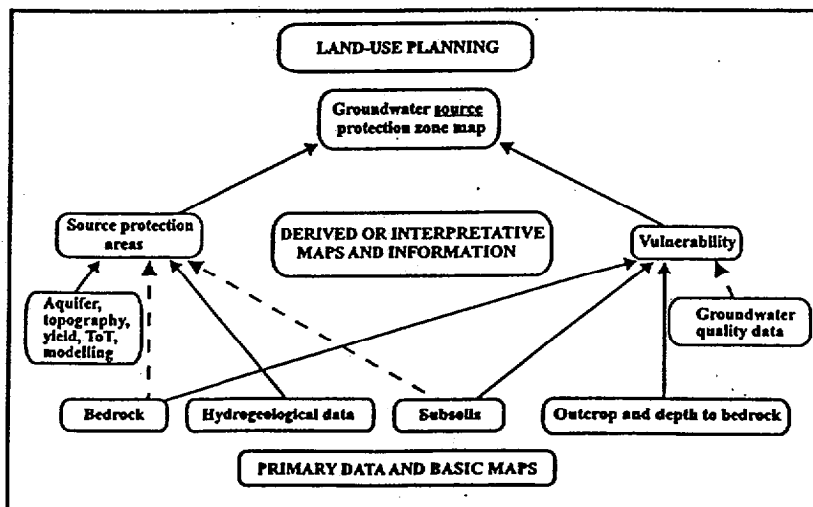


Figure 4. Conceptual framework for production of groundwater source protection zones, indicating information needs and links

3.2 Vulnerability Categories

Vulnerability is a term used to represent the intrinsic geological and hydrogeological characteristics that determine the ease with which groundwater may be contaminated by human activities.

The vulnerability of groundwater depends on: (i) the time of travel of infiltrating water (and contaminants); (ii) the relative quantity of contaminants that can reach the groundwater; and (iii) the contaminant attenuation capacity of the geological materials through which the water and contaminants infiltrate. As all groundwater is hydrologically connected to the land surface, it is the effectiveness of this connection that determines the relative vulnerability to contamination. Groundwater that readily and quickly receives water (and contaminants) from the land surface is considered to be more vulnerable than groundwater that receives water (and contaminants) more slowly and in lower quantities. The travel time, attenuation capacity and quantity of contaminants are a function of the following natural geological and hydrogeological attributes of any area:

- (i) the subsoils that overlie the groundwater;
- (ii) the type of recharge - whether point or diffuse; and
- (iii) the thickness of the unsaturated zone through which the contaminant moves.

In general, little attenuation of contaminants occurs in the bedrock in Ireland because flow is almost wholly via fissures. Consequently, the subsoils (sands, gravels, glacial tills (or boulder clays), peat, lake and alluvial silts and clays), are the single most important natural feature influencing groundwater vulnerability and groundwater contamination prevention. Groundwater is most at risk where the subsoils are absent or thin and, in areas of karstic limestone, where surface streams sink underground at swallow holes.

The geological and hydrogeological characteristics can be examined and mapped, thereby providing a groundwater vulnerability assessment for any area or site. Four groundwater vulnerability categories are used in the scheme - extreme (E), high (H), moderate (M) and low (L). The hydrogeological basis for these categories is summarised in Table 1 and further details can be obtained from the GSI. The ratings are based on pragmatic judgements, experience and available technical and scientific information. However, provided the limitations are appreciated, vulnerability assessments are essential when considering the location of potentially polluting activities. As groundwater is considered to be present everywhere in Ireland, the vulnerability concept is applied to the entire land surface. The ranking of vulnerability does not take into consideration the biologically-active soil zone, as contaminants from point sources are usually discharged below this zone, often at depths of at least 1m. However, the groundwater protection responses take account of the point of discharge for each activity.

Vulnerability maps are an important part of groundwater protection schemes and are an essential element in the decision-making on the location of potentially polluting activities. Firstly, the vulnerability rating for an area indicates, and is a measure of, the likelihood of contamination. Secondly, the vulnerability map helps to ensure that a groundwater protection scheme is not unnecessarily restrictive on human economic activity. Thirdly, the vulnerability map helps in the choice of preventative measures and enables developments, which have a significant potential to contaminate, to be located in areas of lower vulnerability.

In summary, the entire land surface is divided into four vulnerability categories - extreme (E), high (H), moderate (M) and low (L) - based on the geological and hydrogeological factors described above. This subdivision is shown on a groundwater vulnerability map. The map shows the vulnerability of the first groundwater encountered (in either sand/gravel aquifers or in bedrock) to contaminants released at depths of 1-2 m below the ground surface. Where contaminants are released at significantly different depths, there will be a need to determine groundwater vulnerability using site-specific data. The characteristics of individual contaminants are not taken into account.

Vulnerability Rating	Hydrogeological Conditions				
	Subsoil Permeability (Type) and Thickness			Unsaturated Zone	Karst Features
	High permeability (sand/gravel)	Moderate permeability (e.g. Sandy subsoil)	Low permeability (e.g. Clayey subsoil, clay, peat)	(Sand/gravel aquifers only)	(<30 m radius)
Extreme (E)	0 - 3.0m	0 - 3.0m	0 - 3.0m	0 - 3.0m	-
High (H)	> 3.0m	3.0 - 10.0m	3.0 - 5.0m	> 3.0m	N/A
Moderate (M)	N/A	> 10.0m	5.0 - 10.0m	N/A	N/A
Low (L)	N/A	N/A	> 10.0m	N/A	N/A

Notes: (1) N/A = not applicable.
(2) Precise permeability values cannot be given at present.
(3) Release point of contaminants is assumed to be 1-2 m below ground surface.

Table 1. Vulnerability Mapping Guidelines

3.3 Source Protection Zones

Groundwater sources, particularly public, group scheme and industrial supplies, are of critical importance in many regions. Consequently, the objective of source protection zones is to provide protection by placing tighter controls on activities within all or part of the zone of contribution (ZOC) of the source.

There are two main elements to source protection land surface zoning:

- Areas surrounding individual groundwater sources; these are termed source protection areas (SPAs)
- Division of the SPAs on the basis of the vulnerability of the underlying groundwater to contamination.

These elements are integrated to give the source protection zones.

3.3.1 Delineation of Source Protection Areas

Two source protection areas are recommended for delineation:

- Inner Protection Area (SI);
- Outer Protection Area (SO), encompassing the remainder of the source catchment area or ZOC.

In delineating the inner (SI) and outer (SO) protection areas, there are two broad approaches: first, using arbitrary fixed radii, which do not incorporate hydrogeological considerations; and secondly, a scientific approach using hydrogeological information and analysis, in particular the hydrogeological characteristics of the aquifer, the direction of groundwater flow, the pumping rate and the recharge.

Where the hydrogeological information is poor and/or where time and resources are limited, the simple zonation approach using the arbitrary fixed radius method is a good first step that requires little technical expertise. However, it can both over- and under-protect. It usually over-protects on the downgradient side of the source and may under-protect on the upgradient side, particularly in karst areas. It is particularly inappropriate in the case of springs where there is no part of the downgradient side in the ZOC. Also, the lack of a scientific basis reduces its defensibility as a method.

There are several hydrogeological methods for delineating SPAs. They vary in complexity, cost and the level of data and hydrogeological analysis required. Four methods, in order of increasing technical sophistication, are used by the GSI:

- (i) calculated fixed radius;
- (ii) analytical methods;
- (iii) hydrogeological mapping; and
- (iv) numerical modelling.

Each method has limitations. Even with relatively good hydrogeological data, the heterogeneity of Irish aquifers will generally prevent the delineation of definitive SPA boundaries. Consequently, the boundaries must be seen as a guide for decision-making, which can be reappraised in the light of new knowledge or changed circumstances.

3.3.1.1 Inner Protection Area (SI)

This area is designed to protect against the effects of human activities that might have an immediate effect on the source and, in particular, against microbial pollution. The area is defined by a 100-day time of travel (TOT) from any point below the water table to the source. (The TOT varies significantly between regulatory agencies in different countries. The 100-day limit is chosen for Ireland as a relatively conservative limit to allow for the heterogeneous nature of Irish aquifers and to reduce the risk of pollution from bacteria and viruses, which in some circumstances can live longer than 50 days in groundwater.) In karst areas, it will not usually be feasible to delineate 100-day TOT boundaries, as there are large variations in permeability, high flow velocities and a low level of predictability. In these areas, the total catchment area of the source will frequently be classed as SI.

If it is necessary to use the arbitrary fixed radius method, a distance of 300m is normally used. A semi-circular area is used for springs. The distance may be increased for sources in karst aquifers and reduced in granular aquifers and around low yielding sources.

3.3.1.2 Outer Protection Area (SO)

This area covers the remainder of the ZOC (or complete catchment area) of the groundwater source. It is defined as the area needed to support an abstraction from long-term groundwater recharge i.e. the proportion of effective rainfall that infiltrates to the water table. The abstraction rate used in delineating the zone will depend on the views and recommendations of the source owner. A factor of safety can be taken into account whereby the maximum daily abstraction rate is increased (typically by 50%) to allow for possible future increases in abstraction and for expansion of the ZOC in dry periods. In order to take account of the heterogeneity of many Irish aquifers and possible errors in estimating the groundwater flow direction, a variation in the flow direction (typically $\pm 10-20^\circ$) is frequently included as a safety margin in delineating the ZOC.

A conceptual model of the ZOC and the 100-day TOT boundary is given in Figure 5.

If the arbitrary fixed radius method is used, a distance of 1000m is recommended with, in some instances, variations in karst aquifers and around springs and low-yielding wells.

The boundaries of the SPAs are based on the horizontal flow of water to the source and, in the case particularly of the Inner Protection Area, on the time of travel in the aquifer. Consequently, the vertical movement of a water particle or contaminant from the land surface to the water table is not taken into account. This vertical movement is a critical factor in contaminant attenuation, contaminant flow velocities and in dictating the likelihood of contamination. It can be taken into account by mapping the groundwater vulnerability to contamination.

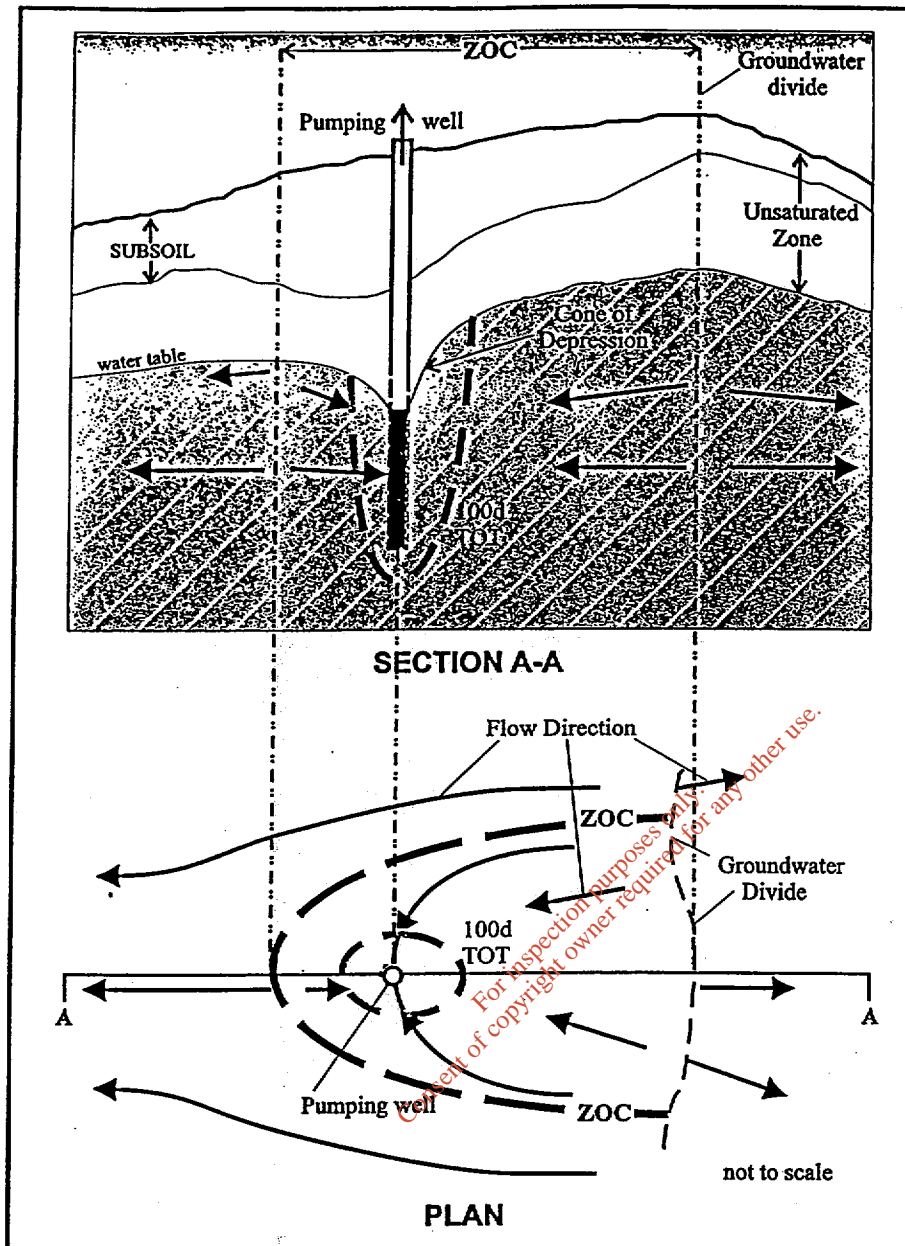


Figure 5. Conceptual Model of the Zone of Contribution (ZOC) at a Pumping Well (adapted from US EPA, 1987)

3.3.2 Delineation of Source Protection Zones

The matrix in Table 2 below gives the result of integrating the two elements of land surface zoning (SPAs and vulnerability categories) – a possible total of eight source protection zones. In practice, the source protection zones are obtained by superimposing the vulnerability map on the source protection area map. Each zone is represented by a code e.g. SO/H, which represents an Outer Source Protection area where the groundwater is highly vulnerable to contamination. The recommended map scale is 1:10,560 (or 1:10,000 if available), though a smaller scale may be appropriate for large springs.

VULNERABILITY RATING	SOURCE PROTECTION ZONE	
	Inner (SI)	Outer (SO)
Extreme (E)	SI/E	SO/E
High (H)	SI/H	SO/H
Moderate (M)	SI/M	SO/M
Low (L)	SI/L	SO/L

Table 2. Matrix of Source Protection Zones

All of the hydrogeological settings represented by the zones may not be present around each groundwater source. The integration of the SPAs and the vulnerability ratings is illustrated in Figure 6.

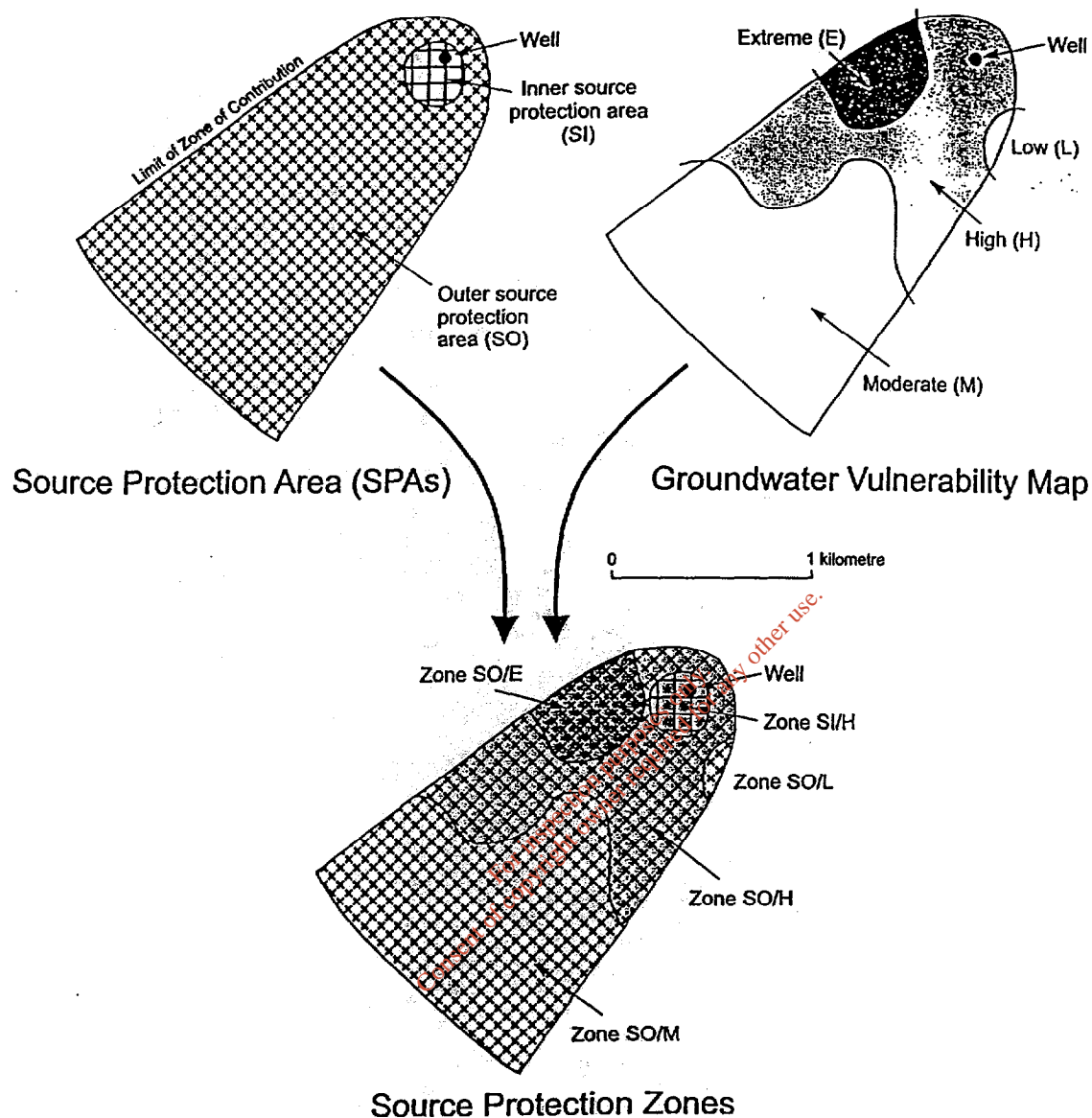


Figure 6. Delineation of source protection zones around a public supply well from the integration of the source protection area map and the vulnerability map.

3.4 Resource Protection Zones

For any region, the area outside the SPAs can be subdivided, based on the value of the resource and the hydrogeological characteristics, into eight aquifer categories:

Regionally Important (R) Aquifers

- (i) Karstified aquifers (Rk)
- (ii) Fissured bedrock aquifers (Rf)
- (iii) Extensive sand/gravel aquifers (Rg)

Locally Important (L) Aquifers

- (i) Sand/gravel (Lg)
- (ii) Bedrock which is Generally Moderately Productive (Lm)
- (iii) Bedrock which is Moderately Productive only in Local Zones (L1)

Poor (P) Aquifers

- (i) Bedrock which is Generally Unproductive except for Local Zones (P1)
- (ii) Bedrock which is Generally Unproductive (Pu)

These aquifer categories are shown on an aquifer map, which can be used not only as an element of a groundwater protection scheme but also for groundwater development purposes.

The matrix in Table 3 below gives the result of integrating the two regional elements of land surface zoning (vulnerability categories and resource protection areas) – a possible total of 24 resource protection zones. In practice this is achieved by superimposing the vulnerability map on the aquifer map. Each zone is represented by a code e.g. Rf/M, which represents areas of regionally important fissured aquifers where the groundwater is moderately vulnerable to contamination. In land surface zoning for groundwater protection purposes, regionally important sand/gravel (Rg) and fissured aquifers (Rf) are zoned together, as are locally important sand/gravel (Lg) and bedrock which is moderately productive (Lm). All of the hydrogeological settings represented by the zones may not be present in each local authority area.

VULNERABILITY RATING	RESOURCE PROTECTION ZONES					
	Regionally Important Aquifers (R)		Locally Important Aquifers (L)		Poor Aquifers (P)	
	Rk	Rf/Rg	Lm/Lg	L1	P1	Pu
Extreme (E)	Rk/E	Rf/E	Lm/E	L1/E	P1/E	Pu/E
High (H)	Rk/H	Rf/H	Lm/H	L1/H	P1/H	Pu/H
Moderate (M)	Rk/M	Rf/M	Lm/M	L1/M	P1/M	Pu/M
Low (L)	Rk/L	Rf/L	Lm/L	L1/L	P1/L	Pu/L

Table 3. Matrix of Resource Protection Zones

3.5 Flexibility, Limitations and Uncertainty

The land surface zoning is only as good as the information which is used in its compilation (geological mapping, hydrogeological assessment, etc.) and these are subject to revision as new information is produced. Therefore a scheme must be flexible and allow for regular revision.

Uncertainty is an inherent element in drawing geological boundaries and there is a degree of generalisation because of the map scales used. Therefore the scheme is not intended to give sufficient information for site-specific decisions. Also, where site specific data received by a regulatory body in the future are at variance with the maps, this does not undermine a scheme, but rather provides an opportunity to improve it.

A6.2 TRIAL PIT LOGS

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A6.3

**SAMPLING AND ANALYSIS OF SOIL SAMPLES IN THE CORK HARBOUR
AREA FOR PCDD/F, PCB AND PAH AND COMPARISON WITH EXISTING
DATA, PREPARED BY AWN CONSULTING, OCTOBER 2001.**

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TECHNICAL REPORT

**SAMPLING AND ANALYSIS OF SOIL SAMPLES IN THE
CORK HARBOUR AREA FOR PCDD/F, PCB AND PAH AND
COMPARISON WITH EXISTING DATA**

FOR

**Arup Consulting Engineers
15 Oliver Plunkett St
Cork**

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Report prepared by: **Dr Fergal Callaghan**
Our reference: **FC/01/1222SR01**
Date: **19th October 2001**

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EXECUTIVE SUMMARY

Soil sampling was conducted at 7 locations in the Cork Harbour Area and at EPA Inishcarra, with the aim of determining background PCDD/F, PCBs and PAH. Soil samples were analysed for PCDD/F, PCBs and PAH and the results compared with current data, previous data for the Cork Harbour Area and data from other countries. The conclusions of the sampling and analysis programme were as follows:

- Background soil PCDD/F concentrations were found to be very similar to those found by the EPA (at the same or adjacent sampling locations) during a soil sampling programme carried out in December 2000, with the exception of one sample in the vicinity of the Martello Tower.
- A comparison with limited previous data for the Cork Harbour Area indicates that soil PCDD/F concentrations have decreased significantly over the last decade, at a number of sites around Ringaskiddy.
- Background soil PCDD/F concentrations for the sites sampled in the Cork Harbour area are low when compared with data from other countries.
- PCB and PAH analysis data indicated that background soil concentrations for these analytes were also low.

Dr Fergal Callaghan
Senior Environmental Consultant

Niall Vaughan
Environmental Consultant

1.0 INTRODUCTION

AWN Consulting was instructed by Arup Consulting Engineers on behalf of Indaver (Ireland) Ltd to undertake surface soil sampling, dioxin, PAH and PCB analysis, reporting, interpretation and significance assessment and a comparison with existing background data for the Cork region, and a comparison between dioxin congeners.

The work was undertaken in support of a planning application for a waste to energy facility, to be located at Ringaskiddy, Cork, see Figure 1.1.

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- 5.0 DISCUSSION OF RESULTS
- 6.0 CONCLUSIONS

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2.0 LOCATION OF SAMPLING SITES AND RATIONALE FOR CHOOSING INDIVIDUAL LOCATIONS

The Environmental Protection Agency undertook a soil dioxin sampling programme in the Cork Harbour area during December of 2000, in order to determine background dioxin concentrations in soil in the area. A copy of the report and accompanying EPA memorandum is presented as Attachment 1 of this report.

The EPA undertook soil sampling at 9 locations, in the Cork Harbour area and at a control location at EPA Iniscarra, which was felt to be representative of a rural environment. The sampling locations in the harbour area are shown in Figure 2.1. The location of EPA Iniscarra is shown in Figure 2.2.

The sampling programme carried out by Awn was designed to achieve the following goals:

- Establish a background concentration for the site
- Establish a background concentration for the area downwind of the site, and in the vicinity of the site generally
- Compare monitoring data with EPA data

Soil sampling was carried out by Awn at the locations described in Table 2.1. The rationale for choosing these sampling locations is outlined in Table 2.2. The sampling locations are shown in Figure 2.3. Due to restrictions associated with the Foot and Mouth Disease outbreak, it was not possible to access the EPA sampling points which were located on farmland. The sampling programme was conducted during the month of July 2001 by Dr. Fergal Callaghan and Niall Vaughan of Awn Consulting Ltd.

AWN Sampling Point	Sampling Point Location	Closest EPA Sampling Point	Position	Sampling Date
A	Martello Tower, Ringaskiddy	EPA Sampling Point 6	51° 49.709' N 008° 18.558' W	17 th July 2001
B	IDA land overlooking Pfizer	EPA Sampling Point 7	51° 49.915' N 008° 20.091' W	18 th July 2001
C	Cuskinny Nature Reserve	EPA Sampling Point 8	51° 51.540' N 008° 15.891' W	24 th July 2001
D	Cobh Water Tower	EPA Sampling Point 9	51° 51.563' N 008° 17.181' W	4 th July 2001
E	Sample on high ground at Indaver site	EPA Sampling Point 6	51° 49.751' N 008° 18.565' W	17 th July 2001
F	Sample on low ground at Indaver site	EPA Sampling Point 6	51° 49.851' N 008° 18.191' W	16 th July 2001
G	Sample at Lighthouse, Roches Point	N/A	51° 47.585' N 008° 15.303' W	1 st July 2001
H	EPA Iniscarra	EPA Sampling Point 10	51° 54.115' N 008° 40.208' W	2 nd July 2001

Table 2.1 Location of AWN Sampling Points and nearest EPA Sampling Points

*(EPA sampling points refer to EPA memo 16th January 2001, ref. K O Brien)

Sampling Point	Sampling Point Location*
A	Compare with EPA and background in vicinity of site
B	Compare with EPA and background in vicinity of Novartis and Pfizer
C	Compare with EPA and background downwind (SW winds)
D	Background in vicinity of Cobh (downwind of SW winds from Ringaskiddy)
E	Sample on high ground above Indaver site
F	Sample on low ground at Indaver site
G	Sample downwind of Ringaskiddy of NW winds (Roches Point)
H	EPA Iniscarra - compare with EPA and regional background

Table 2.2 Rationale for choosing AWN sampling locations

NOTE

It was noted from an inspection of the windrose data from Cork Airport, for the period 1993 – 1997, that the two predominant wind directions are south westerly and north westerly. It was therefore decided to sample at Roches Point, which is south east of the industrialised area of Cork Harbour and therefore under the influence of the north west winds (see Attachment 2).

3.0 SAMPLING METHODOLOGY

The aim of the sampling programme at each site was to establish a background topsoil concentration for each particular sampling location.

US EPA guidance, as presented in the US EPA EISOPQAM, was followed in the selection and design of the sampling methodology ¹. The EISOPQAM Areal Composite Methodology was selected as the method most applicable for determining background soil concentrations for an area ². This method ensures the sample collected is representative of an area. Briefly, the methodology consists of taking a number of samples in an identical manner and of an identical size and then combining these samples to form a composite sample, which is then thoroughly mixed. A sample of this composite material is then sent for analysis.

The procedure followed by the EPA during soil sampling in the Cork Harbour area was incorporated into the sampling methodology, to ensure direct comparability between the AWN and the EPA analysis results. This procedure also followed the Areal Composite Methodology.

3.1 Sampling Depth

The investigation was designed to measure background contaminant concentrations in surface soils, which has been defined by EISOPQAM as soils between the ground surface and up to 6 to 12 inches (15 – 30cm) below the ground surface ³. Other authors, such as Hendriks et al ⁴ have taken samples of cores which are 0 – 5cm thick, whereas the team which has been working for many years on assessing the impact of the Seveso accident near Milan in Italy, has used samples of 7cm thickness ⁵.

As the aim of this study was to assess the impact of surface deposition of contaminants, it was felt that the depth used by the Seveso study team (who were studying airborne deposition and were among the first teams to actively study the impact of dioxin deposition on soil concentrations) was the most appropriate and soil samples of 7cm thickness (from the surface to 7cm below the surface) were taken. This depth was also used by the EPA during sampling in December 2000.

3.2 Sampling Pattern

The sampling on each site was carried out in a "W" Pattern. Following the EPA sampling methodology, samples were taken at 10m centres, or where this was not possible due to constraints of space on the site, at 2m or 1m centres.

The layout of the sampling grid at each sampling location (with the exception of the EPA Iniscarra site) is shown in Figures 3.1 – 3.7. The Field Record for each sampling site is presented as Attachment 3. A pictorial record of each sampling grid is shown in Figures 3.8 – 3.15.

3.3 Sample acquisition and Handling

As can be seen from the Field Records, 150 - 200 soil samples were taken at 1.5 - 4m intervals, using a 2cm diameter corer, at the sampling sites, with the sample number and sampling interval being limited by area available for sampling.

Each composite sample weighed between 5 and 6kg. Samples were thoroughly mixed in a clean plastic basin and then a 1kg and 0.5kg aliquot extracted from the mixed sample. The 1kg sample was placed in a glass jar (supplied by Alcontrol Geochem Ireland Ltd, the analytical laboratory chosen for the analysis) and the 0.5kg sample was placed in a separate glass jar. All samples were labelled Sample A, Sample B, etc and the analysis required for each sample was listed on a Geotrace Sampling and Chain of Custody Record, which is provided as Attachment 4.

The samples were collected in one batch by Alcontrol Geochem Ireland Ltd, on 27th July 2001, and couriered overnight to Alcontrol Geochem Chester Ltd, for analysis.

3.4 Analysis suite

Alcontrol Geochem Chester Ltd are a UKAS accredited laboratory and were instructed to undertake the following analysis by AWN.

- I. PCDD/F (NATO/CCMS I-TEQ)
- II. PAH (GCMS)
- III. PCB (7 EC Congeners)

Alcontrol Geochem hold UKAS accreditation for items II and III and employed Scientific Analysis Laboratories Ltd, a UK laboratory that has been awarded UKAS accreditation for PCDD/F analysis, for item I.

4.0 RESULTS OF LABORATORY ANALYSIS

The analysis results are presented as Attachment 5 of this report and have been summarised in Table 4.1.

Sample	Site Location	PCDD/F (ng/kg) ¹	PCB (µg/kg) ²	PAH (µg/kg) ³
A	Martello Tower	3.0	<1	4734
B	IDA land above Pfizer	0.55	<1	3403
C	Cushkinny Nat.Reserve	1.8	<1	16963
D	Cobh Water Tower	1.0	<1	7139
E	Ground above Indaver site	0.65	<1	4614
F	Low ground Indaver site	3.4	2	4470
G	Roches Point	1.4	<1	7264
H	EPA Insicara	<0.5	<1	3828

Table 4.1 Analysis results

- 1 NATO/CCMS I TEQ
- 2 EC7 PCB Congeners
- 3 Sum of 16 PAH

5.0 DISCUSSION OF RESULTS

The format for this Chapter of the report is as follows:

- 5.1 Issues associated with comparison of PCDD/F values
- 5.2 Analysis of measured PCDD/F values
- 5.3 Comparison with EPA testing during December 2000
- 5.4 Comparison with previous data for Cork Harbour Area
- 5.5 Comparison of measured PCDD/F values with published data for other countries
- 5.6 Comparison of PCB and PAH values with published data and relevant standards

5.1 Issues associated with comparison of PCDD/F values

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzo-*p*-furans (PCDF) are a group of tricyclic aromatic compounds, with similar chemical and physical properties and are ubiquitous in the modern environment ⁶. Mixtures of the two groups are normally referred to as PCDD/F.

The ability of chlorine atoms to substitute at various positions on the benzene ring structures of these compounds allows numerous positional isomers to be formed. In total, there are 210 positional isomers of both groups, 75 for PCDD and 135 for PCDF. The majority of these compounds are of no concern with respect to ecological and human toxicity, with the exception of 17 (7 PCDD and 10 PCDF) which have chlorine substitution in the 2,3,7,8 positions ⁷.

2,3,7,8 TCDD is the most studied dioxin and is considered to be the most toxic by far of the 17 congeners. As data began to accumulate in the 1970's and early 1980's of the toxic effects of 2,3,7,8 TCDD, a number of systems for assessing the toxicity of other PCDD/F were developed, all using the concept of Toxic Equivalence Factors (TEQ) ⁷. This concept assess the toxicity of other PCDD/F congeners and assigns a weighting compared to the known toxicity of 2,3,7,8 TCDD.

Examples of the systems which developed include the Swiss (published in 1982), German (published in 1985), Danish (published in 1984) and Canadian (published in 1983) systems ^{8,9,10,11}.

These systems applied slightly different weighting factors for calculating TEQ expressed as units of 2,3,7,8 TCDD. For instance, 1,2,3,4,6,7,8 HeptaCDD (non 2,3,7,8) was assigned a Toxic Equivalency Factor (TEF) of 0.1 by the Swiss system, but was given a TEF of 0.001 by the German system, a one hundred fold difference.

Similar differences in weightings were noted for a number of the other congeners. These differences meant that it was not possible in many instances to compare TEQ data from different countries. The NATO/CCMS system began to be more widely used through the early 1990's and the WHO also introduced a similar system ^{12,13}.

The US EPA, NATO/CCMS and the EC systems now use the same TEF Factors and the World Health Organisation has also adopted a similar system, allowing direct comparability of TEQ values ¹⁴.

The NATO/CCMS TEFs (giving a result which is defined as I-TEQ), which correspond exactly with the EC and US EPA TEFs, have been used to calculate TEQs for the PCDD/Fs measured during this study.

It is also important to examine, when comparing PCDD/F measurements acquired by different laboratories, the approach taken when adding the Toxic Equivalents. It is current best practice by UKAS laboratories to exclude values which are below the limit of detection from the calculation of toxic equivalents, however, other laboratories have assumed that any value recorded as being below the limit of detection should be assigned a value for the relevant congener of 50% of the limit of detection. This can lead to slight discrepancies between laboratories.

Discrepancies can also arise when comparing soil samples taken with a hand corer or similar instrument, as the greater the depth of the core, the greater the potential for dilution of the sample by "cleaner soil". As dioxin concentrations in soil are influenced by airborne deposition rates, a concentration gradient will exist in the soil, with the greatest concentrations in the upper layer and decreasing concentrations being measured as depth increases and the influence of surface deposition decreases.

5.2 Analysis of measured PCDD/F values

The laboratory analysis results are presented as Attachment 5 of this report. For comparative purpose, the absolute amounts of each of the 17 PCDD/F congeners and the tetra through to hepta homologues measured are presented in Table 5.1 (in ng/kg). The PCDD/F profile for each sample is also presented in pictorial fashion as Attachment 6. All concentrations are expressed in ng/kg air dried soil, unless otherwise stated.

High PCDD/F I-TEQ concentrations (relative to the other sampling sites) were reported at the Martello Tower site (Site A) and on low ground at the Indaver site (Site F), which is adjacent to the road site. However, the congener profiles of these samples are quite different, see Attachment 6. It is likely that the PCDD/F profile at Site F is strongly influenced by traffic emissions. Leaded fuel was a major source of PCDD/F emission to the environment, although it has now been phased out in Ireland, its impact on soil PCDD/F concentrations will be noted for some time. Diesel engine emissions are also another source of PCDD/F emissions. The road alongside which the sampling took place is relatively heavily trafficked by HGVs.

The congener profiles for Sites C and D (Cushkinny Nature reserve and Cobh Water Tower) are quite similar, and possibly indicative of a common source.

It is interesting to note that the measured I-TEQ values for Samples A and E and the congener profiles, are markedly different, despite the sites being relatively close. The main difference between the two sites is that Site A is at a greater elevation, being on top of the hill.

The congener profiles for Sites F and G show relatively large concentrations of OCDD, (approximately 5 – 10 times greater than the other samples), although the I-TEQ for Site F is over twice that for Site G. This is possibly indicative of a common source for a portion of the PCDD/F found at these sites.

Site H, which is the regional background, showed traces of PCDD/F, many at or below the limit of detection of 0.2 – 0.4 ng/kg (limit dependant on the congener profile) and overall the I-TEQ value was below the limit of detection of the assay.

No.	Compound	A	B	C	D	E	F	G	H
1	2,3,7,8-TCDD	0.18	N.D.	0.081	N.D.	N.D.	N.D.	0.12	N.D.
2	1,2,3,7,8-PeCDD	0.64	N.D.	0.4	0.29	0.085	N.D.	N.D.	N.D.
3	1,2,3,6,7,8-HxCDD	2.1	0.45	0.83	0.36	0.32	1.4	1.2	0.25
4	1,2,3,4,7,8-HxCDD	0.89	0.18	0.76	0.24	0.19	0.56	0.37	0.18
5	1,2,3,7,8,9-HxCDD	1.6	0.42	0.76	0.37	0.38	0.92	0.93	0.19
6	1,2,3,4,6,7,8-HpCDD	11	0.47	8.3	4.2	3.1	19	17	2.9
7	OCDD	21	18	34	15	13	150	140	14
8									
9	TCDD	12	2.9	2.5	2.2	1.2	2.2	6.9	4.5
10	PeCDD	28	1.6	6.2	1.2	1.7	2.6	2.2	1.6
11	HxCDD	28	1.6	6.3	4.1	3.5	12	16	1.8
12	HpCDD	11	3.6	8.4	3.4	2.3	19	28	2.2
13									
14	2,3,7,8-TCDF	1.2	0.35	0.97	0.58	0.44	1.6	0.77	0.15
15	1,2,3,7,8-PeCDF	1.3	0.37	0.84	0.61	0.38	1.1	0.53	0.12
16	2,3,4,7,8-PeCDF	1.8	0.41	1.2	0.81	0.47	3.6	0.73	0.12
17	1,2,3,4,7,8-HxCDF	2.3	0.52	1.1	0.79	0.56	2.7	0.84	0.19
18	1,2,3,6,7,8 HxCDF	1.8	0.33	1.2	0.53	0.41	1.7	0.72	0.16
19	2,3,4,6,7,8-HpCDF	2	0.52	0.87	0.59	0.4	2.3	0.63	0.16
20	1,2,3,7,8,9-HxCDF	0.46	N.D.	0.3	N.D.	0.11	N.D.	N.D.	N.D.
21	1,2,3,4,6,7,8-HpCDF	9.9	2.3	5.4	3.5	2.4	10	5.1	2.1
22	1,2,3,4,7,8,9-HpCDF	0.65	N.D.	0.51	0.24	0.26	N.D.	N.D.	N.D.
23	OCDF	6.7	3.4	7.7	3.1	2.4	12	8.5	27
24									
25	TCDF	17	2.7	13	6.3	4.1	32	11	0.17
26	PeCDF	12	N.D.	10	6	2.1	6.4	6	0.12
27	HxCDF	11	2.1	6	3.5	2.2	11	5.5	0.52
28	HpCDF	0.97	N.D.	N.D.	N.D.	0.17	N.D.	N.D.	N.D.
	TEQ (EC)	3	0.55	1.8	0.85	0.65	3.4	1.4	<0.5

Table 5.1 Mass of PCDD/F congeners measured in each sample and TEQ values

5.3 Comparison with EPA soil testing during December 2000

The EPA data collected during soil testing which was carried out in December 2000 and the AWN data which corresponds to similar sampling locations, is presented in Table 5.2. It should be noted that the TEFs used for the EPA analysis were not available, but as the analysis was carried out by a laboratory with UKAS accreditation for the assay, it is likely that the current NATO/CCMS TEFs were used.

EPA Sampling Location	EPA Sample	EPA		AWN		AWN Sampling Location
		I-TEQ (ng/g)	I-TEQ (ng/kg)	I-TEQ (ng/kg)	AWN Sample	
Church Area	1	0.028	28	N/A	N/A	Not applicable
Main Square	2	0.0071	7.1	N/A	N/A	Not applicable
Area beside foot field	3	0.0118	11.8	N/A	N/A	Not applicable
Cdr. Daly Area	4	0.0031	3.1	N/A	N/A	Not applicable
Foot. Pitch (dockyard)	5	0.0016	1.6	N/A	N/A	Not applicable
W. of Martello Tower	6	0.0008	0.8	3.4	A	At base of Mart. Tower
Pfizer/ADM (to s. of site)	7	0.0007	0.7	0.55	B	IDA land south of Pfizer
Ballymore (SW face field)	8	0.001	1	1.8	C	Cushkinny Nature Res.
Carrignafoy GAA Ground	9	0.001	1	1	D	Cobh Water Tower
Iniscarra WTW	10	0.0006	0.6	<0.5	H	EPA Inishcarra

Table 5.2 EPA and AWN Analysis Data and Sampling Locations

The AWN sample for the area at the base of the Martello Tower was found to contain a considerably greater PCDD/F concentration than the corresponding EPA sample, which was taken to the west of the tower. The reason for this is not clear. It may be due to the fact that the area around the Tower is slightly elevated compared to the ground to the west and that a plume is impacting on this high ground. The value recorded for the ground at the base of the Martello Tower is still relatively low, compared to background concentrations recorded for UK sites (see Section 5.5).

The AWN sample taken in the IDA land to the south of Pfizer is very similar to the value obtained by the EPA. The sample taken at Cuskinny Nature Reserve is also reasonably similar to the EPA value recorded for Ballymore.

The EPA sample for Carrignafoy GAA ground and the AWN sample for the area at the base of the Cobh Water Tower were found to have the same I-TEQ value.

The samples from Iniscarra were also found to be very similar.

It can be concluded that both data sets are in reasonably close agreement, apart from the high AWN value recorded for the area around the Martello Tower.

5.4 Comparison with previous data for the Cork Harbour area

Data previously obtained during soil sampling in Cork Harbour is presented in Table 5.3, together with the AWN and EPA data, for comparative purposes.

EPA Sampling Location	EPA 2000 I-TEQ (ng/kg)	AWN 2001 I-TEQ (ng/kg)	Eolas 1990 I-TEQ (ng/kg) ¹⁶	Cork 1994 I-TEQ (ng/kg) ¹⁷
Church Area	28	N/A	N/A	N/A
Main Square	7.1	N/A	N/A	N/A
Area beside foot field	11.8	N/A	N/A	N/A
Cdr. Daly Area	3.1	N/A	N/A	N/A
Foot. Pitch (dockyard)	1.6	N/A	N/A	N/A
W. of Martello Tower	0.8	3.4	21.6*	N/A
Pfizer/ADM (to s. of site)	0.7	0.55	23.7**	2.95***
Ballymore (SW face field)	1	1.8	N/A	N/A
Carrignafof GAA Ground	1	1	N/A	N/A
Iniscarra WTW	0.6	<0.5	N/A	N/A

NOTE

* At Martello Tower

** Near Ballybricken House

*** North of Bamaheely

Table 5.3 Comparison with previous data for Cork Harbour Area

A review of the sampling and analysis methodologies used for the Eolas survey in 1990 and the Cork County Council survey of 1994 indicates that this data can be compared with the EPA and AWN data, for the following reasons;

Firstly, the Eolas and Cork County Council samples were taken using a 2cm core diameter, to a depth of 10cm, which was very similar to the EPA and AWN sampling which was conducted to a depth of 7-8cm using a 2cm corer.

Secondly, the analysis was carried out using the 2,3,7,8 TCDD I-TEQ system which was in use at the time, and although TEFs are not given for the EOLAS analysis, the results are expressed as I-TEQ values, indicating the NATO/CCMS System has been used. TEFs are given for the Cork County Council sampling and are identical to those used for the AWN analysis.

Thirdly, a number of the sampling sites used in compiling these reports are very close to the sites used by AWN and the EPA and therefore allow direct temporal and spatial comparison of analysis data.

The values obtained for the two EOLAS samples from 1990, which correspond to the AWN and EPA sampling locations, had much higher concentrations of PCDD/F than the samples analysed in 2000 and 2001 and indicates that background PCDD/F concentrations have decreased significantly at these sites.

The sampling site for which the value shown in Table 5.3 was determined during the Cork County Council survey is some distance west of the IDA lands sampled during the EPA and AWN surveys and does not correspond directly to the Ballybricken House sample taken during the EOLAS survey, nevertheless, it provides further evidence that background soil PCDD/Concentrations have decreased significantly in the Ringaskiddy area.

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5.5 Comparison with PCDD/F data for other countries

There have been numerous studies of PCDD/F soil concentrations undertaken by many countries over the last 25 years. Comparing different studies can sometimes be difficult, especially as many studies have given total PCDD/F values rather than expressing results as I-TEQ values. Nevertheless, there is sufficient data available for comparisons to be made. With the exception of EPA Inishcarra, the sampling sites can be classed as urban, rather than rural, due to the presence of significant industrial and residential development and associated traffic levels.

A comprehensive US study, published in 1986, found 2,3,7,8 TCDD (*note not 2,3,7,8 TCDD I-TEQ*) concentrations in urban soils to range from 1 – 10 ng/kg¹⁸. The values measured by the AWN survey (which includes the other 16 congeners) found 2,3,7,8 TCDD I-TEQ values to be at the lower end of this range and the survey suggests that rural concentrations in Cork are below the limit of detection of the analysis techniques.

A study of 19 urban locations in England and Wales found 2,3,7,8 TCDD concentrations ranging from <0.5 ng/kg to 11 ng/kg¹⁹. Again, results were not expressed as 2,3,7,8 TCDD I-TEQ values, but a comparison between this data and the data obtained during the AWN survey work shows that the background soil PCDD/F concentrations for sites sampled in the Cork Harbour are at the lower end of this scale.

An investigation of the floodplain soils in the Rhine Delta (Tienhoven, Lexmond and Hagestein) in the Netherlands found soil PCDD/F concentrations, expressed as 2,3,7,8 TCDD I-TEQ values, ranging from 23 – 93 ng/kg⁴.

Measured values in the Cork Harbour area are again well below these values.

Decreasing trends in environmental PCDD/F concentrations have been noted in many developed countries throughout the 1980's and 1990's. It has been proposed that this is due to a combination of the phasing out of leaded petrol, reduction in emissions from manufacturing industries and the introduction of emission controls on incinerator emissions²⁰. From the limited monitoring data available, this trend also seems to be evident in the Cork Harbour area.

Some countries have set limits for maximum soil concentrations of PCDD/Fs. The German Government have set a limit of 40 ng/kg 2,3,7,8 TCDD I-TEQ. The growing

6.0 CONCLUSIONS

- Background soil PCDD/F concentrations were found to be very similar to those found by the EPA during a soil sampling programme carried out in December 2000, with the exception of one sample in the vicinity of the Martell Tower
- A comparison with limited previous data for the Cork Harbour Area indicates that soil PCDD/F concentrations have decreased significantly over the last decade, at a number of sites around Ringaskiddy.
- Background soil PCDD/F concentrations for the sites sampled in the Cork Harbour area are low when compared with data from other countries.
- PCB and PAH analysis data indicated that background soil concentrations for these analytes were also low.

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of crops on land which has soil PCDD/F values greater than this limit value is restricted. A second limit has also been set by the German Government, of 100 ng/kg 2,3,7,8 TCDD I-TEQ for playgrounds. If this limit is breached the playground has to be remediated.

None of the PCDD/F values measured in the AWN survey approach the lower limit value.

5.6 Comparison of PCB and PAH concentrations with relevant standards

PAH and PCB concentrations (7 EC congeners) were also analysed for the soil samples taken and these results are also presented in Attachment 5.

5.6.1 PCB

PCB concentrations were below the limit of detection of 1 µg/kg, with the exception of the sample on low ground at the Indaver site (beside the road), where 2 congeners had concentrations just above the limit of detection, giving a total PCB concentration of 2 µg/kg.

No Irish guidance is currently available for PCB contamination and in the absence of Irish Guidance, the Dutch Target and Intervention values are currently applied by the EPA in Ireland to determine if soil is classed as contaminated ²¹.

The Dutch Government have set a national target value of 20 µg/kg PCB in soil and a threshold value (the concentration above which remedial action should be considered) of 1000 µg/kg. The measured concentrations for the Cork Harbour area are below even the target value and can therefore be regarded as not significant.

5.6.2 PAH

The PAH concentrations varied across the different soil samples analysed, but all were well below the Dutch Target Value of 40,000 µg/kg ²¹. All samples were typical of background concentrations recorded for rural sites in Wales ²², which ranged from 108 – 54,250 µg/kg, with an average concentration of 2325 µg/kg. The slightly elevated concentrations noted at Cushkinny and Roches point are most likely due to the presence of peat, which is a natural source of PAH, within the soil matrix ²².

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FIGURES

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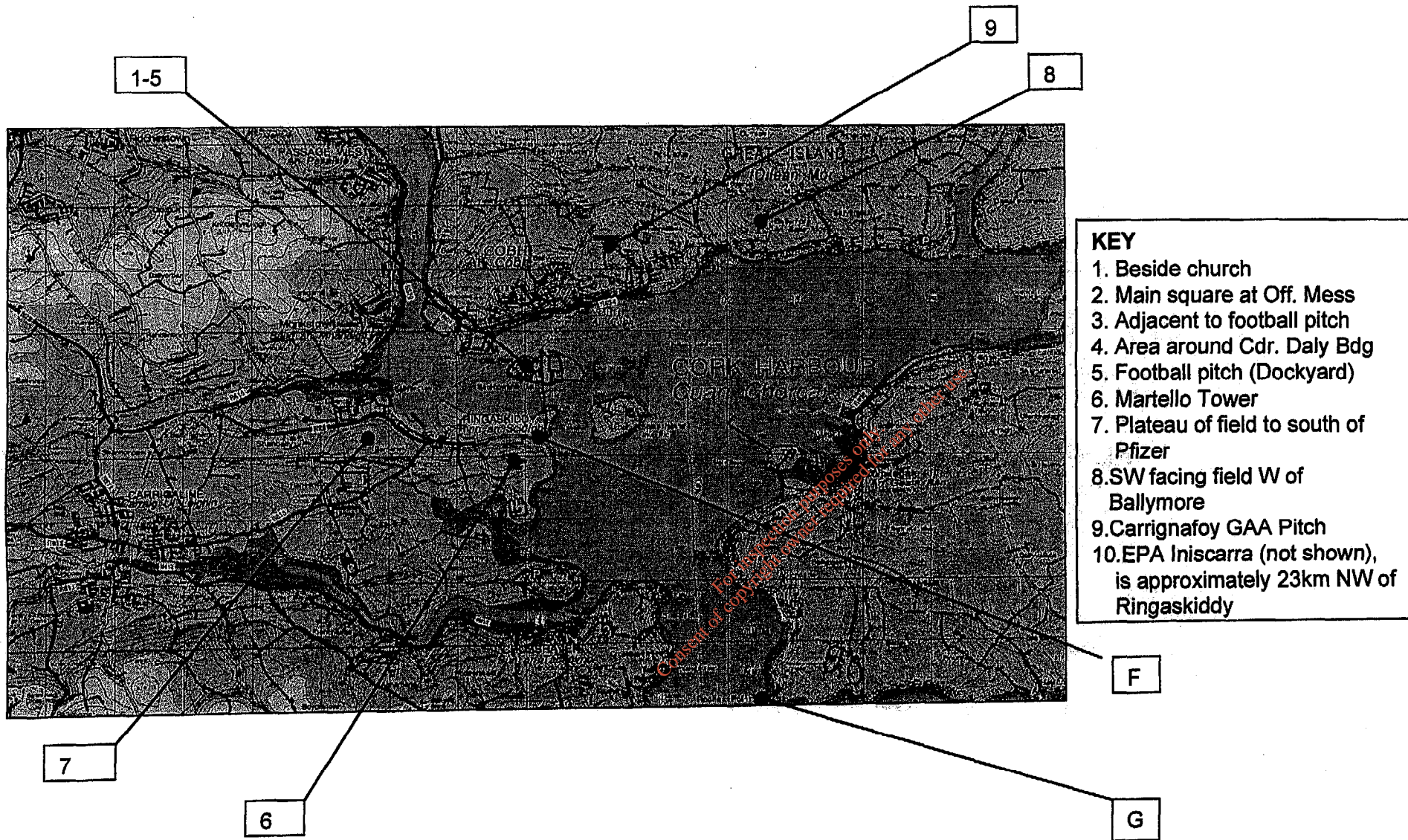
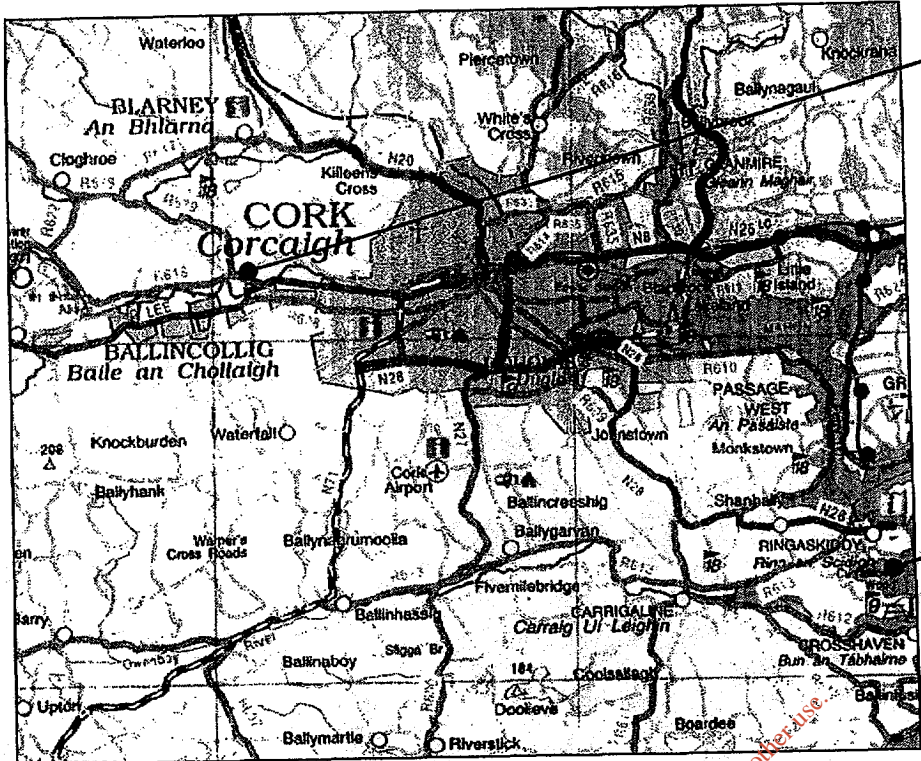


Figure 2.1 EPA Sampling Locations

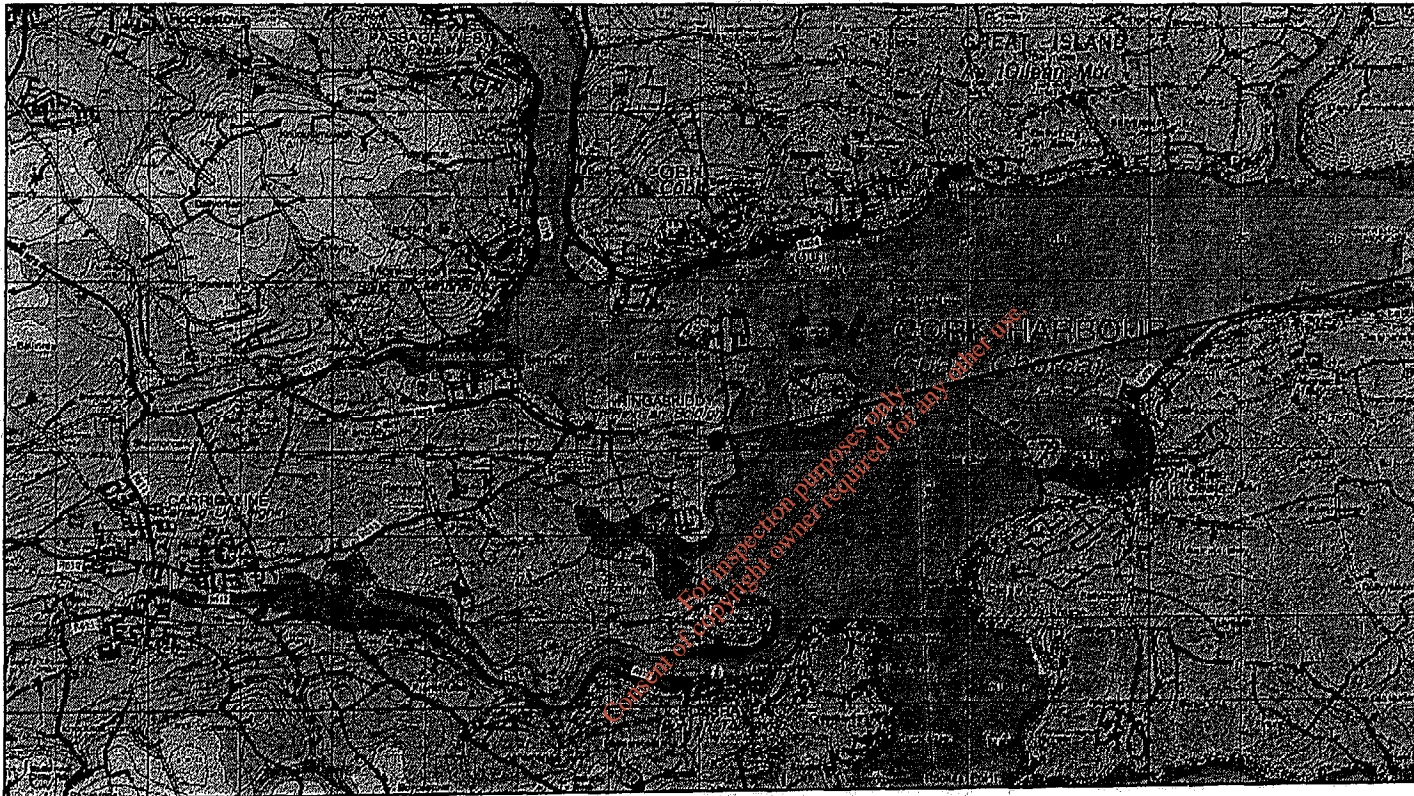
EPA Iniscarra
(EPA Sampling
Location 10)



Ringaskiddy

Figure 2.2 EPA Iniscarra (EPA Sampling Location 10) relative to Ringaskiddy

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Location of
proposed
waste to
energy
facility

Figure 1.1 Location of proposed waste to energy facility

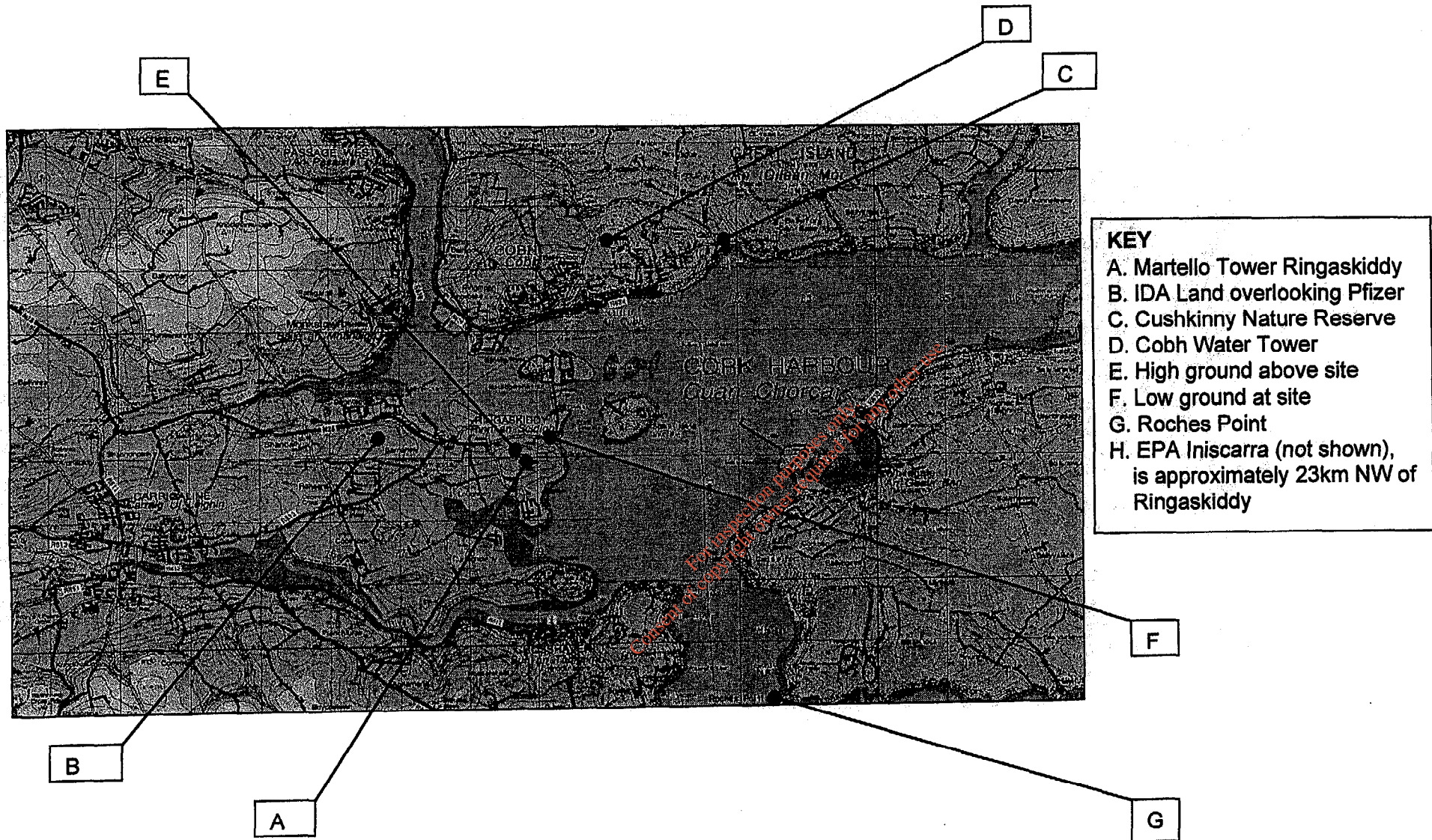


Figure 2.3 AWN Sampling Locations

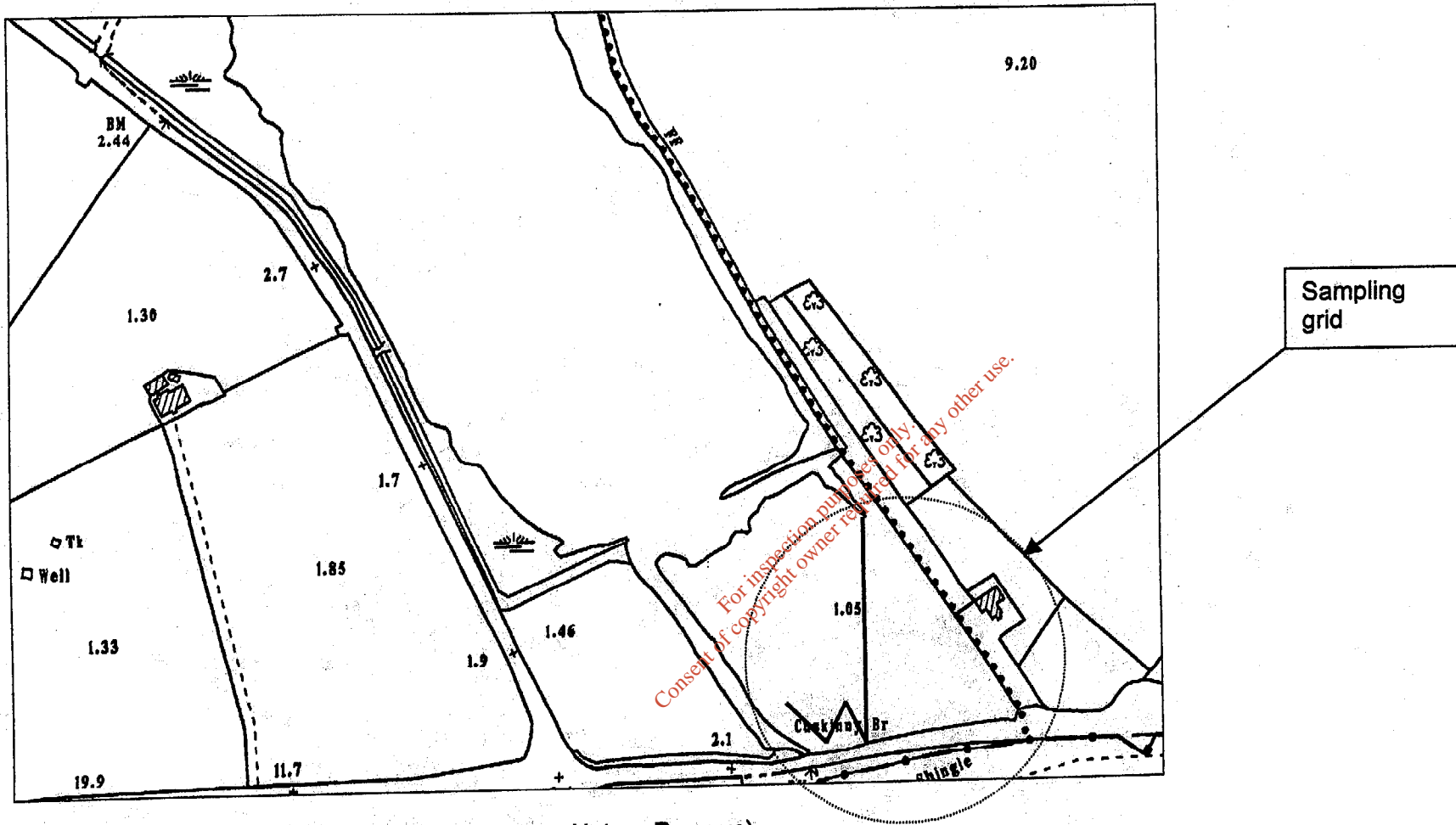


Figure 3.3 Sampling grid at Site C (Cushkinny Nature Reserve)
 Scale 1: 2500

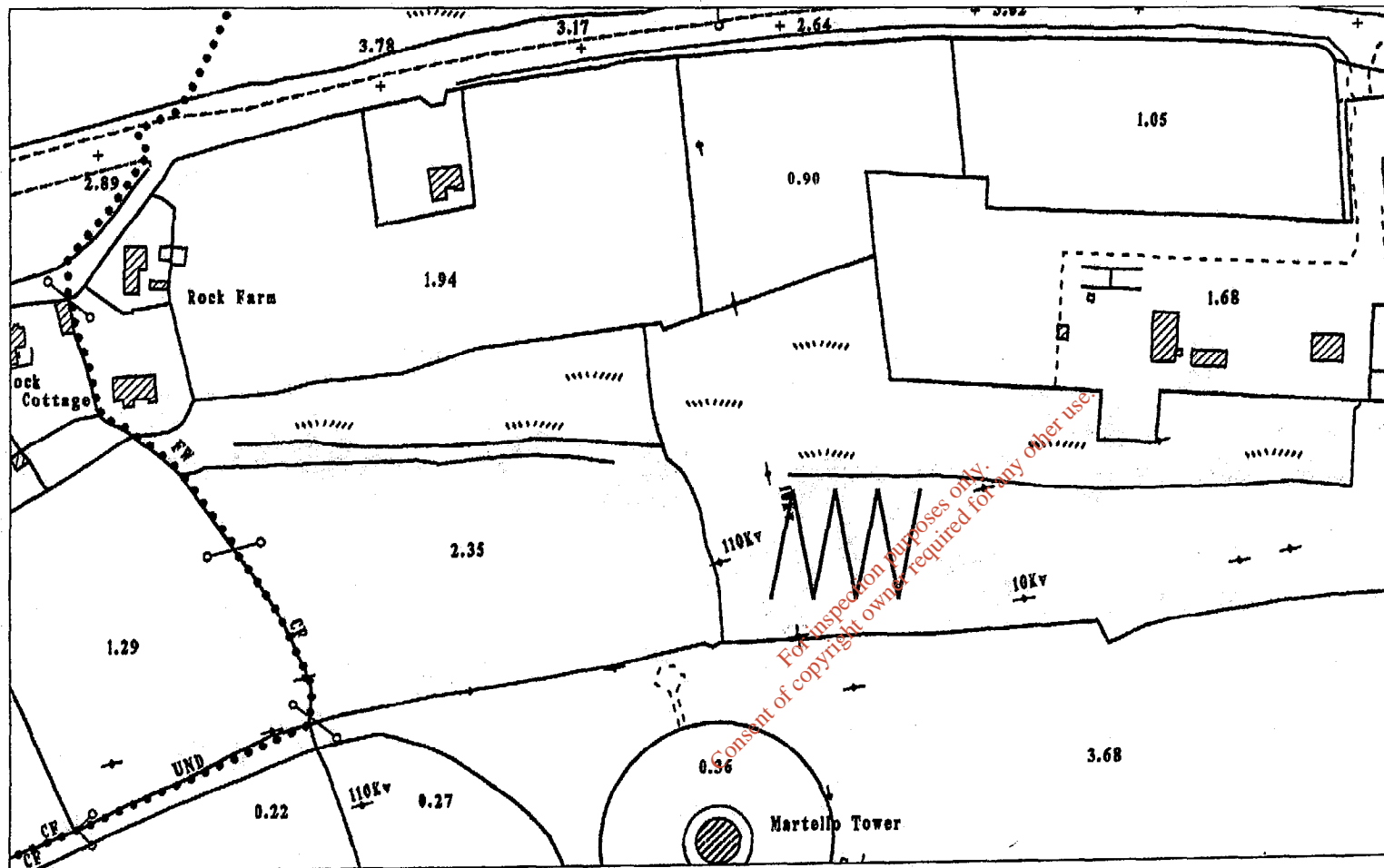


Figure 3.5 Sampling grid at Site E (High ground at Indaver Site)

Scale 1: 2500

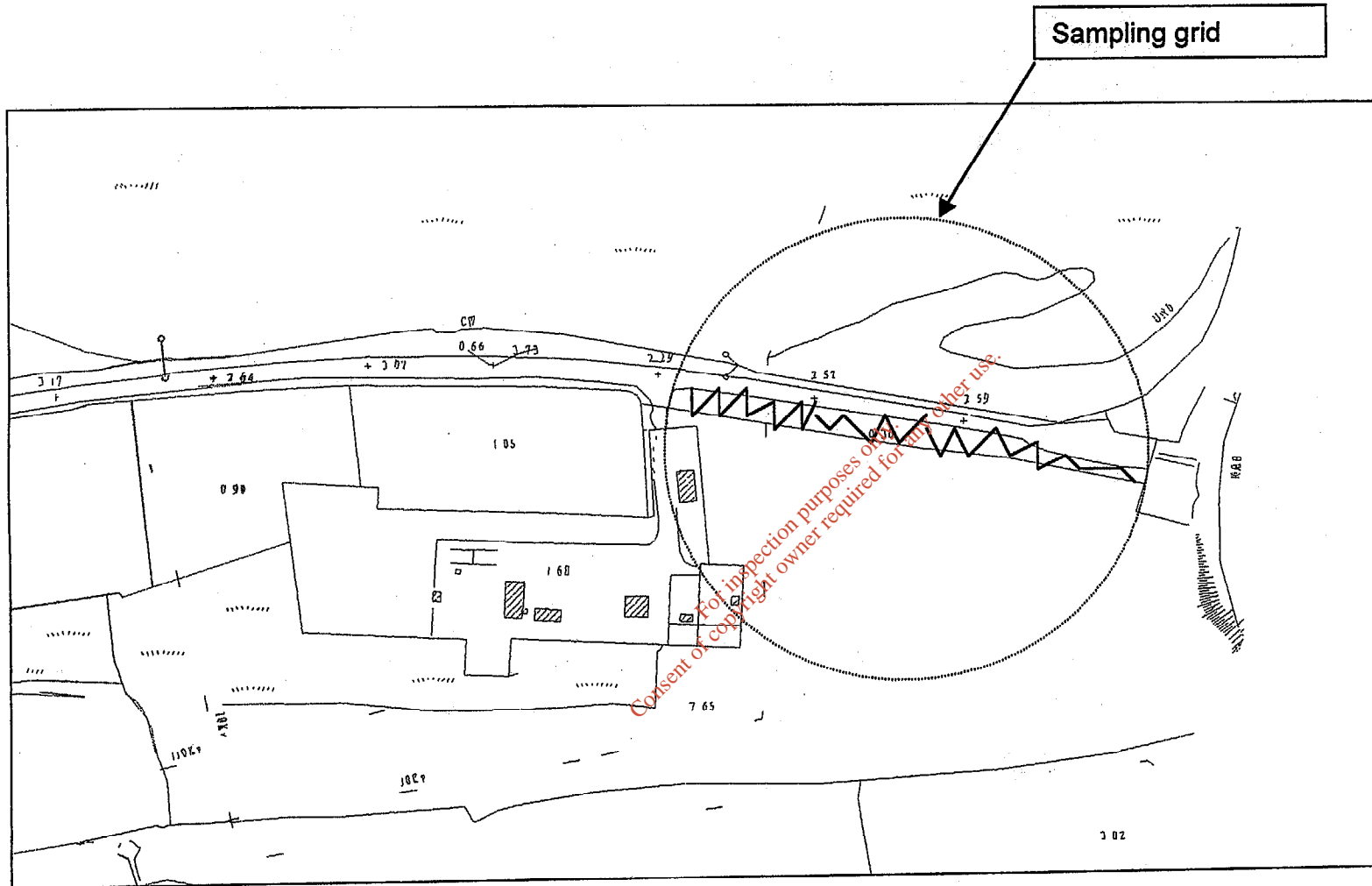


Figure 3.6 Sampling grid at Site F low ground at Indaver Site

Not to scale

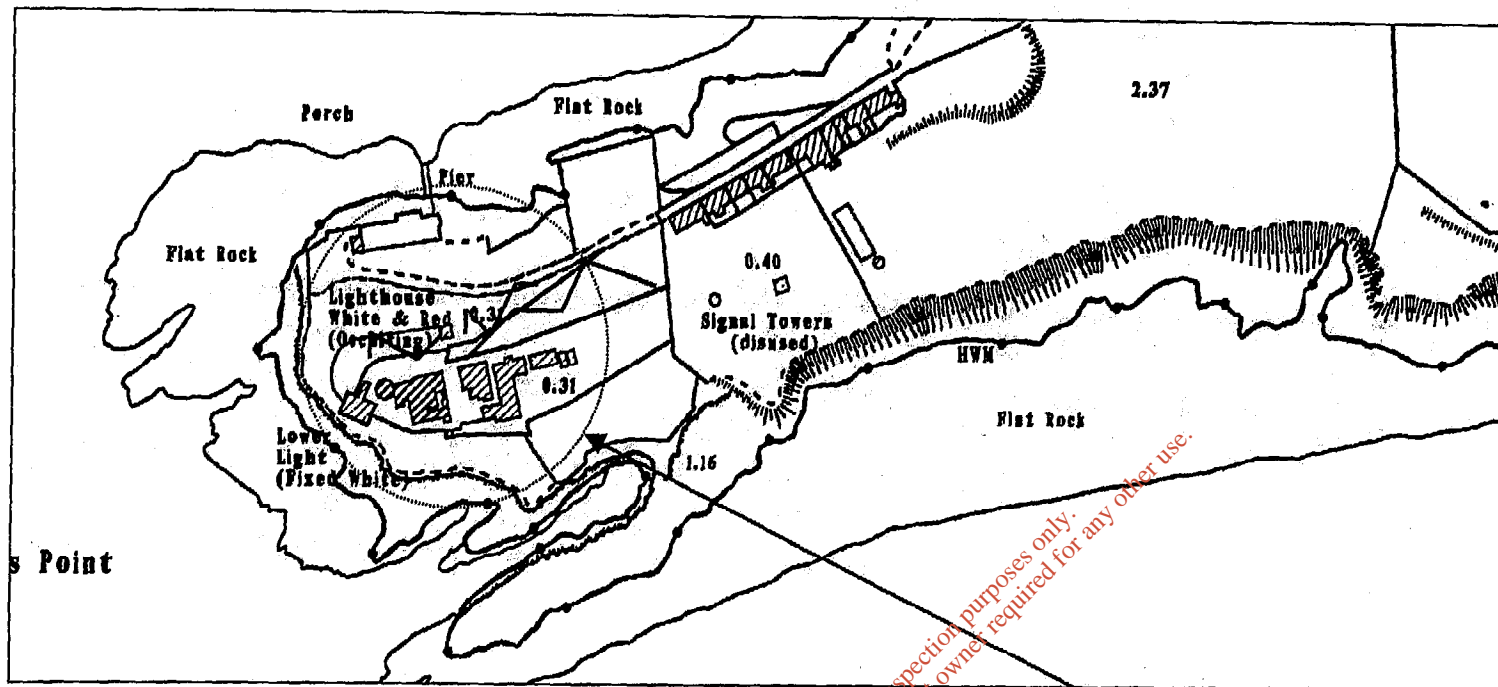


Figure 3.7 Sampling grid at Site G (Area around Lighthouse, Roches Point)
 (Grid outlined in red for clarity)

Scale 1: 2500

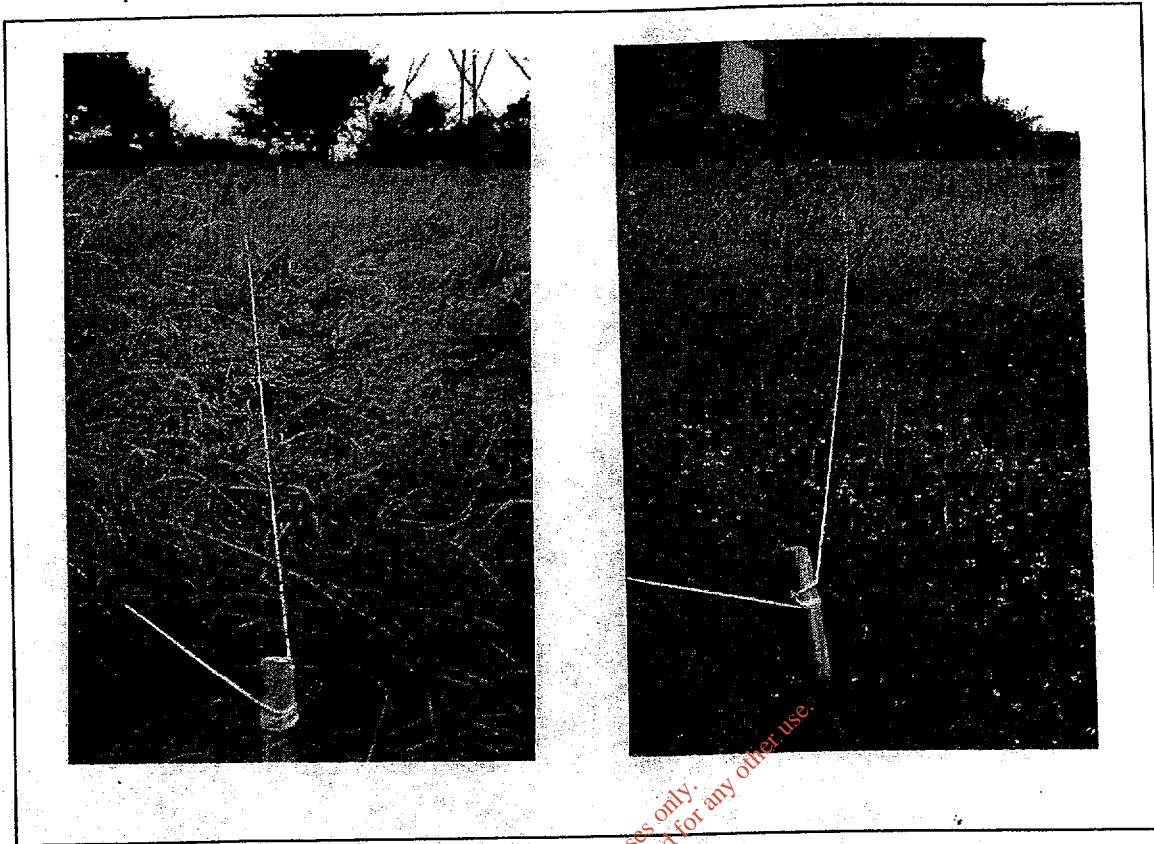


Figure 3.8 Portion of Sampling Grid at Location A

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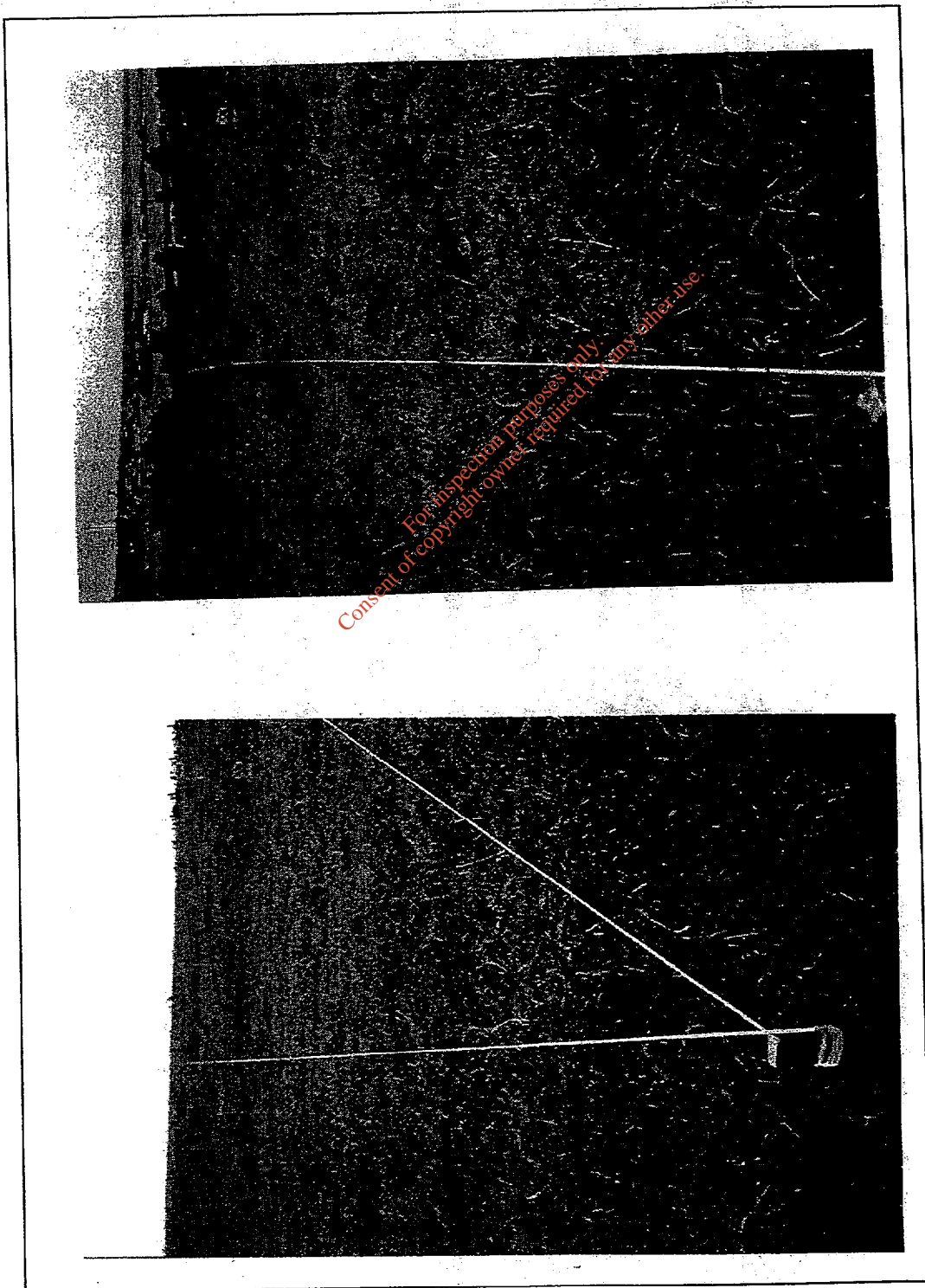


Figure 3.9 Portion of Sampling Grid at Location B

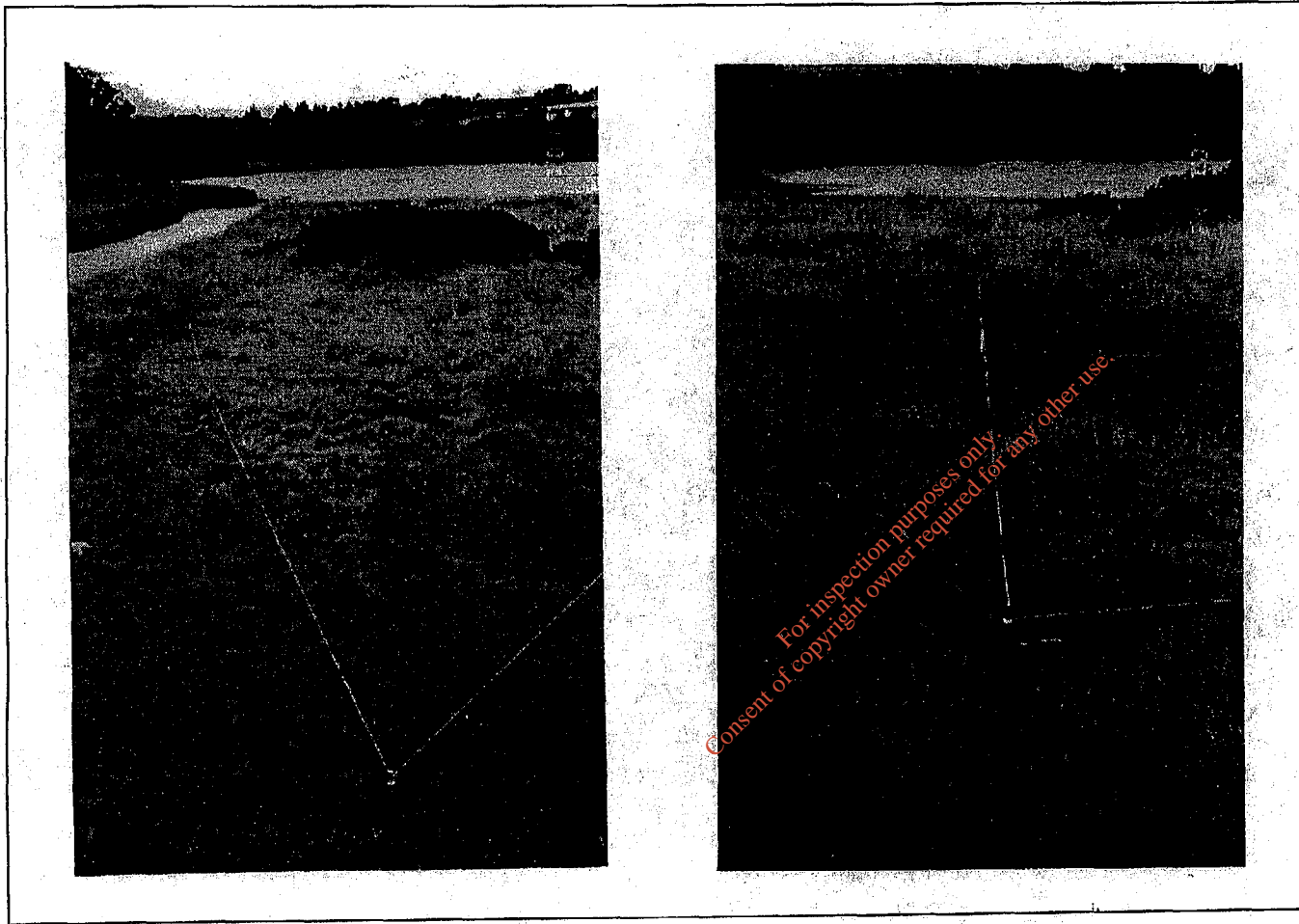


Figure 3.10 Portion of Sampling grid at Site C

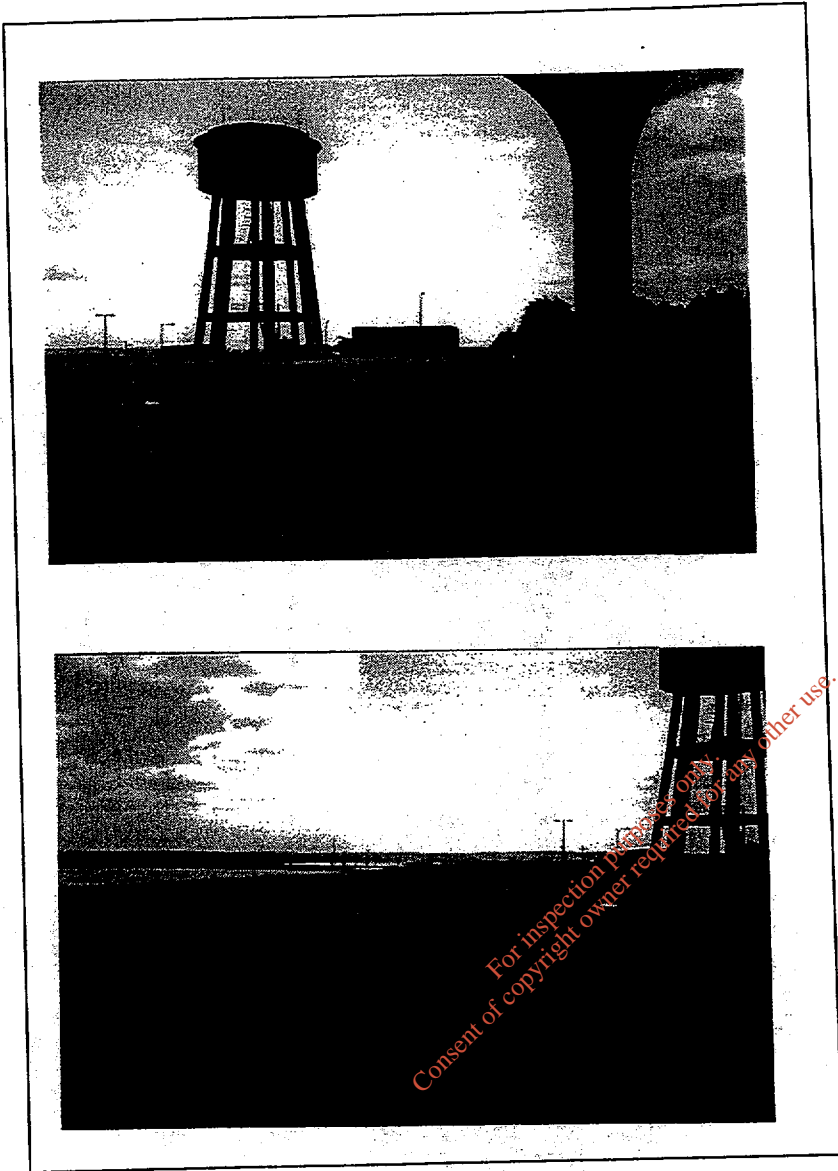


Figure 3.11 Portion of Sampling grid at Site D

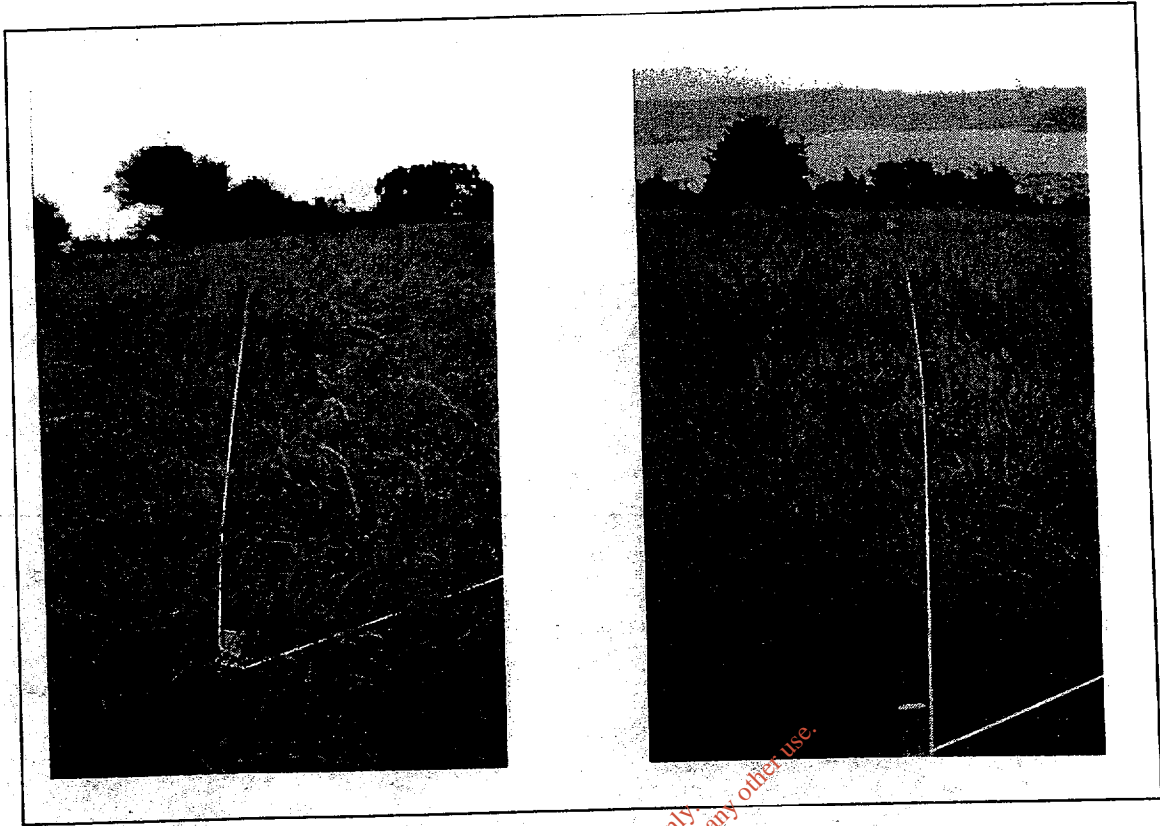


Figure 3.12 Portion of Sampling grid at Site E

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Figure 3.13 Sampling grid at Site F



Figure 3.14 Sampling grids at Site G

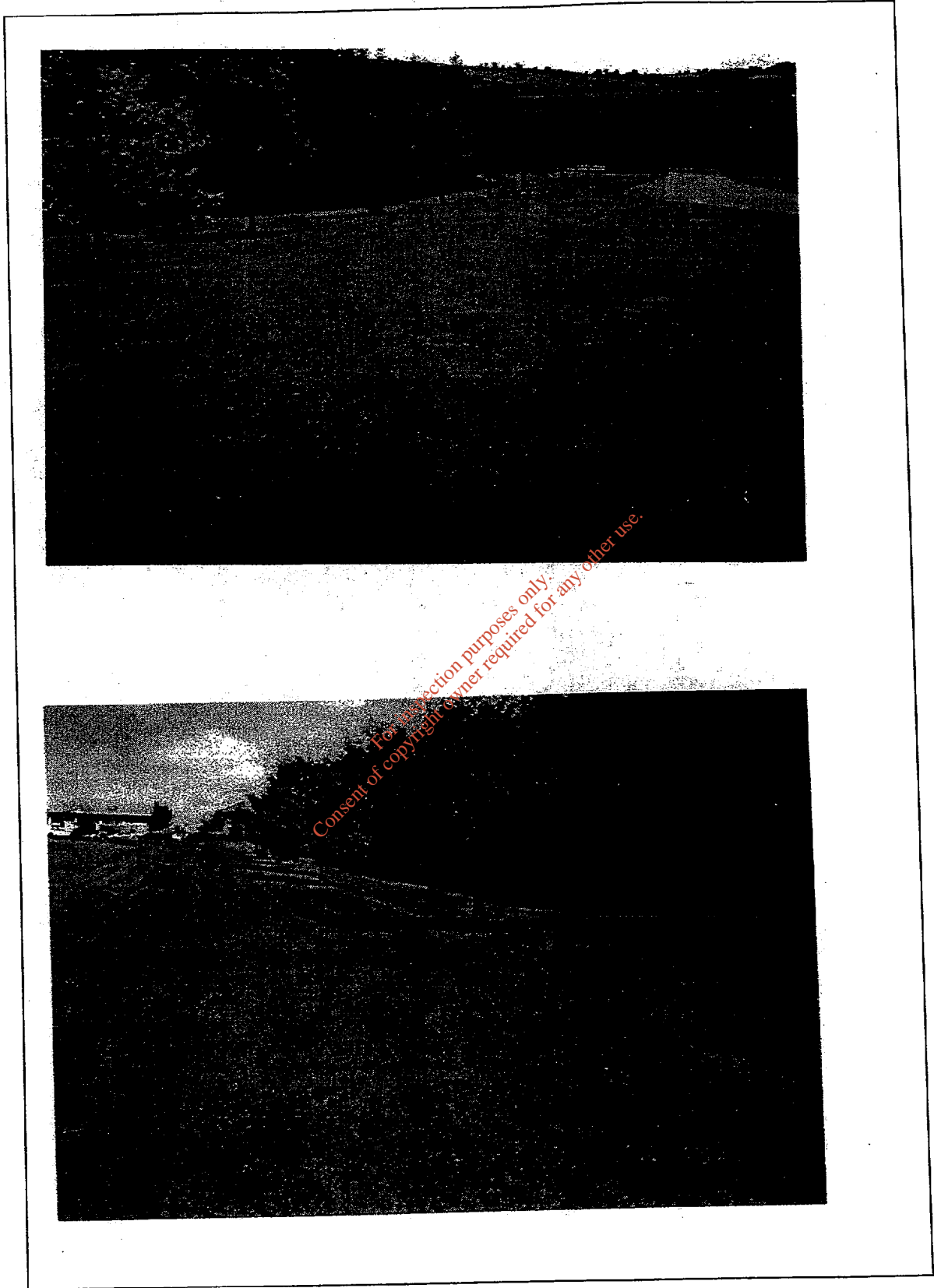


Figure 3.15 Sampling area at Site H