

# STRIVE

## Report Series No.58

# Acquisition of Essential Data for Assessments of Carbon Sequestration by Soils

## STRIVE

Environmental Protection  
Agency Programme

2007-2013

# Environmental Protection Agency

The Environmental Protection Agency (EPA) is a statutory body responsible for protecting the environment in Ireland. We regulate and police activities that might otherwise cause pollution. We ensure there is solid information on environmental trends so that necessary actions are taken. Our priorities are protecting the Irish environment and ensuring that development is sustainable.

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**EPA STRIVE Programme 2007–2013**

**Acquisition of Essential Data  
for Assessments of Carbon Sequestration  
by Soils**

**STRIVE Report**

**(2001 S/CD-(3/3))**

Prepared for the Environmental Protection Agency

by

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The EPA STRIVE Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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# Executive Summary

The major aim of this project was to provide seminal information about the nature and associations of the organic matter (OM) in Irish soils and in drainage waters with a view to establishing the extent to which Irish soils could act as sinks for carbon. It was hoped that the data could lead to the establishment of workable models for carbon sequestration in soils.

The mineral soils studied are representative of some of the major soil types in Ireland. A selection was made of both long-term grassland soils and of paired soils (i.e. soils that have been in long-term cultivation and adjacent soils that are in long-term grassland). Because of the importance of soils as sinks for carbon, and because it may be necessary to relate Irish soils to others in the context of carbon sequestration, comparisons were made with selected major soil types from outside Ireland. These soils included the International Humic Substances Society (IHSS) soil standard (a Mollisol, considered to be among the world's most fertile soils) and a Ferrisol under native forest, in grassland, and under cultivation. The latter helps in understanding how the soil organic matter (SOM) will associate with hydroxides which are known to be associated with clays in some Irish soils. Report No. 6 of the project (July–December, 2004) described the inclusion of a Terra Preta soil from the Amazon region. The Terra Pretas, or ADEs (i.e. Amazonian dark earths), are highly fertile soils found among soils of very low fertility that are characteristic of the Amazonian tropical rainforest. Char accumulations in ADEs are considered to be the source of the fertility. The project team had become aware of amazing growth enhancements for maize (*Zea mays* L.) in the University of Georgia that had resulted from amendments with chars from peanut hulls. Mollisols of the Mid-West USA partially owe their great fertility to accumulations of chars in ancient times. These observations have relevance to the current project because char additions to soil resist degradation and allow carbon credits to be made.

Eight detailed Interim Reports were submitted throughout the life of the current project. These contained extensive accounts of the large variety of techniques applied and of the results obtained. The major results and conclusions are:

- 1 The extents to which Irish soils are sinks for carbon depend on soil depth, mineral (especially colloidal) contents, drainage regimes, vegetation cover, and soil management (whether grassland or cultivated). (Detailed studies were not carried out on forested soils.)
- 2 Soil management has a critical influence on the soil carbon content, and the OM contents of the soil can be expected to be depleted by more than 50% after about 25 years of long-term cultivation. For example, Irish grassland clay loam soils with adequate drainage can be expected to have an SOM mass equivalent to that of ca. 6000 persons each weighing 85 kg standing on 1 ha of soil. If in long-term cultivation, more than half the mass of OM will be lost as CO<sub>2</sub> (from biological oxidation); the organic carbon lost in this way must be regarded as fossil C. Irish soils are predominantly in grassland and in forest and consequently have highly significant amounts of sequestered C. (This contrasts to several countries in the EU where long-term cultivation is practised, and where vast amounts of fossil carbon have been lost as a result.) The amounts of carbon lost as the result of changes in soil management will also depend on the soil texture: the SOM in a sandy loam soil (such as that at the Teagasc Research Station at Oak Park, Carlow) under grassland can be expected to be about one-third of that for a clay loam grassland soil.
- 3 To replenish the SOM in a depleted grassland soil in a temperate climate as the result of long-term cultivation will take 25–30 years if returned to grass (data are not available for Ireland). The SOM content for such grassland can be expected to return to the level that existed prior to cultivation. However, based on data from an Oak Park plot where *Miscanthus* had been grown for 13 years, this C4 plant was shown to increase the SOM by about 33% compared to the adjacent grassland. There are no data available to indicate the extent to which *Miscanthus* will sequester carbon over time in different soil types.

- 4 The addition of maize (*Zea mays* L.) stover was shown to increase the SOM content over a two-year period. The enhancement effect could be attributed to the humic substances formed as a result of the transformations of the maize residues amendments.
- 5 Biochar amendments from pyrolysis of *Miscanthus* increased soil carbon (as would be expected) and also enhanced the germination of maize seedlings and greatly enhanced maize growth over a 30-day growing period. However, the conditions used for the production of the biochar were critical in order to obtain the desired results.
- 6 Procedures were developed during the course of this study for the isolation and fractionation of SOM components. Prior to the commencement of the study, only 30–40% (at most) of the SOM could be isolated by the solvent systems recommended. The solvent systems and sequences used in this study enabled the isolation of >90% of the SOM, and novel procedures were developed to give degrees of fractionation of the organic isolates. That meant that it was possible, for the first time, to get a detailed insight into the compositions of humin, the fraction of SOM in intimate associations with the soil mineral colloids, and hence with the greatest resistance to biological transformations. By using advanced nuclear magnetic resonance (NMR) techniques, it was possible to show that humin contains small amounts of altered lignins (which are largely contained in the humic and fulvic acid fractions entrapped within, or physically associated with, the humin matrix), that it has significant amounts of peptide and saccharide components, and that its major components have an aliphatic core structure. The data obtained provide strong evidence to indicate that cutin/cutan structures are major components of the humin. Front-line advances have also been made in understanding the compositions of the humic components (humic and fulvic acids), and the project's fractionation procedures have helped greatly to advance awareness of the compositions of these humic fractions.
- 7 Previously, most studies of SOM have focused on the OM in the surface horizons. Here, the compositions of the OM to depths of 1 m in three different grassland soils, and the abundances of the OM at depths up to 1 m in several soils were examined. This generated detailed data on how the contents of the SOM change with depth, and of how the compositions change. These studies are ongoing.
- 8 The project team's data show that the surficial waters in streams reflect considerably the soils and vegetation in the watershed. However, it was possible to obtain some in-depth information about the compositions of water draining through grassland soils from lysimeter studies at Johnstown Castle, Wexford. The lysimeters had control soils, and soils treated with fertilisers and with animal urine. The data indicate that the compositions of the drainage waters resemble most closely the fulvic acids isolated from the soils at pH 7. However, there were definite differences between the compositions of the waters, as there were also for the compositions of the humic fractions from the different soils. It was evident also that the manurial treatments gave rise to significant differences in the compositions of the OM in the waters.
- 9 Modelling studies were not carried out. The data have shown that the OM contents and compositions vary between different soil types, and the contents and compositions also vary with the soil mineralogy and with the depth in the soil profile. It was concluded that more extensive data are needed before reliable models dealing with SOM reserves can be made. Thus, it is recommended that a major survey is needed to sample soils to a depth of 1 m. The SOM contents will be the priority, but parameters such as the degree of humification are significant. The humin content at different depths is also important. Once such a survey is completed, it is anticipated that there will be a good awareness of the extents of humin at depth, and of the extents to which the humic substances and humins differ at the different depths in soil profiles.

# 1 Introduction

The overall aim of this project was to provide seminal information about the nature and the associations of the organic matter (OM) in Irish soils with a view to establishing a better awareness of the extents to which different Irish soil types are sinks for carbon (C), and of the ways in which changes in management procedures might alter the capacities of the soils as carbon sinks. An understanding of the compositions of the soil organic matter (SOM) components in different Irish soils, of aspects of the structures of these components, and of the ways in which these are associated with each other and with the inorganic soil colloids, is of fundamental importance to allow predictions of how the SOM in different soils will react to environmental changes. It is considered important to have an awareness of the extents of biodegradation of SOM in Irish soils when management is changed, of the nature of the degradation processes, and of how the soils will respond to organic amendments, and produce from these transformed or humified products with a degree of resistance to degradation. Such information will allow an assessment of the extents to which different Irish soils can sequester carbon. It is hoped that the information obtained will eventually contribute to more realistic models of the abilities of Irish soils to sequester C.

Investigations of the compositions, aspects of the structures, and the properties of the dissolved organic carbon (DOC) and particulate organic carbon (POC) in soil drainage waters is considered central to understanding the compositions and amounts of OM lost in drainage waters. Relating the properties of the DOC with those of the indigenous SOM would make it possible to gain a better understanding of the reasons why more dissolved organic matter (DOM) is released from some soils than from others.

Aspects of the University of Limerick (UL) based project are relevant to other Environmental Protection Agency (EPA) supported projects led by Professor M. Jones of Trinity College Dublin (TCD) and by Professor G. Kiely of University College Cork (UCC), and so, in so far as was feasible, the Limerick-based project took account of the soils that were relevant to the studies of Professors Jones and Kiely. The TCD project involves measurements of greenhouse gases evolved from cultivated and pasture lands at the Teagasc Research Centre, Oak Park, Carlow. The UCC project measures greenhouse gases from a pasture at Dripsey, Co. Cork, and from a blanket peat at Glencar, Co. Kerry.

Detailed data have been presented in the eight Interim reports submitted to the EPA over the duration of the project. Hence, only major findings are highlighted in this Final Report.

## 2 State of the Art Before the Study Commenced

### 2.1 Soil Organic Matter Contents and Influences

The importance of the SOM to soil structure and to soil fertility is well established: soil in long-term grassland or in long-term forestry reaches a stable equilibrium. When the management is changed to long-term cultivation, biological oxidation of SOM depletes the SOM content by ca. 80% (or more, depending on the soil, temperature, moisture regime, etc.) over a period of 25–30 years. In general, studies of SOM depletion have focused on the surface soil (Johnston, 1991; Clapp et al., 2005), and it was considered that depletion as a result of cultivation took place mainly in the surface horizons. That release of carbon (as CO<sub>2</sub>) can be regarded as fossil carbon. It takes at least as long to regain the original level of SOM when management is returned to grassland or forest. There was little acceptance that carbon lost in this way is fossil carbon.

An important aim of the current research was to determine the OM components at depth in the soil profiles, and to assess how the amounts and compositions of the SOM varied with soil type, drainage regimes, etc.

### 2.2 Awareness of the Nature and Compositions of Organic Matter in Different Soils and at Different Depths in Soil Profiles

Soil organic matter was broadly classified into 'humified' and 'non-humified' material. The humified material was considered to have arisen from the biologically/chemically transformed residues of plants and animals/organisms, and with no traces of the plant or protoplasmic materials of origins. Such humified material could be regarded as humus, containing humic substances (HS). The HS were (and are) considered to be composed of humic acids (HAs), which are soluble in aqueous base but precipitated from solution at pH 1, and fulvic acids (FAs), which are soluble in aqueous media at all pH values, and the humified material, humin, which is insoluble in aqueous media at all pH values. Biological

molecules (such as peptides, saccharides, nucleic acids) and unaltered plant materials (for example, cutins, cutans), though components of the humus fraction, were not considered to be components of HS, but they could be *associated with* HS. There had been no systematic studies of the compositions of the SOM components in different soil types and at different depths.

Compositional studies of SOM had been impeded because of inadequate procedures for the isolation and fractionation of the SOM components. In general, SOM studies had been limited to the aqueous base extracts from surface soils, although considerable work had been carried out on extracts from the subsurface B<sub>h</sub> horizons of podzols. Aqueous and neutral salt solutions can extract most of the OM from the B<sub>h</sub> horizons of podzols. These materials were transported in aqueous media from the transformed OM in the surface soils and rendered insoluble by complexation with polyvalent metals in the subsurface B<sub>h</sub> horizon. Exhaustive extractions in aqueous base isolate only 30–40% of the OM of surface SOM. The residual humins were considered to compose at least 50% of the SOM.

At the start of the project, it was generally considered that HS were macromolecular (or polymeric), although there were considerations for molecular associations, rather than macromolecularity.

### 2.3 Awareness of Dissolved and Particulate Organic Matter in Waters

Because of their solubility in aqueous media, considerable advances had been made in studies of the compositions of DOM. The uses of XAD-8 ([poly]methylmethacrylate) and of XAD-4 (styrene divinylbenzene) resins have facilitated the isolation and fractionation of components of DOM. The successful applications of these resins in aquatic systems led to their introduction by the writer and colleagues for the fractionation of humic substances from soil (Hayes et al., 2008).

### 3 Organic Carbon Contents of Irish Grassland Soils and of Cultivated Soils

A list of the soils studied and of the management practices employed for these soils is given in [Table 3.1](#).

#### 3.1 Soil Organic Matter Contents to a Depth of 1 m

Initially, except where indicated otherwise in [Table 3.1](#), the soils were sampled to a depth of 20 cm. The isolates at pH 7, pH 10.6, and pH 12.6 were fractionated on the basis of charge-density differences, and also on the basis of hydrophobicity and hydrophilicity properties. At first it was considered that the material that was not extracted in the final exhaustive extraction at pH 12.6 was humin. As the urea + 0.1 molar (M) NaOH system was developed, it was evident that significantly more HAs and FAs could be extracted. The project team's detailed analyses of the fractions revealed significant differences. It was evident that the biologically transformed materials were isolated at the lower pH values, and the less transformed materials of plant and microbial origins were isolated at the higher pH values. Finally, the humin materials in intimate associations with the clays were isolated and characterised, as outlined in Sections 4.1 and 4.2 below.

**Table 3.1. Soils studied indicating the management procedures used.**

Surface soil samples
<ul style="list-style-type: none"> <li>• Cultivated (long-term) Oak Park soil (Teagasc Research Station, Oak Park, Co. Carlow).</li> <li>• Cultivated (long-term) Oak Park soil amended with maize (<i>Zea mays</i> L.). This experiment was designed to study the transformation of maize (a C4 crop enriched in <sup>13</sup>C) in the soil, to determine the extents to which organic amendments will increase SOM, and to determine the extents to which the compositions of the OM will be altered by the amendments.</li> <li>• Oak Park uncultivated (grassland) soil.</li> <li>• Oak Park soil supporting a 13-year <i>Miscanthus</i> (<i>Miscanthus x giganteus</i>) stand.</li> <li>• Soil from a blanket peat supporting a coniferous forest, near Nad, Co. Cork (site of EPA–UCC greenhouse gas experiment).</li> <li>• Blanket peat soil, site of EPA–UCC greenhouse gas experiment, Glencar, Co. Kerry.</li> <li>• Soil from pasture field in Dripsey, Co. Cork (site of the EPA–UCC grassland greenhouse gas experiment).</li> </ul>

- Knockbeg cultivated soil (Teagasc site, Knockbeg, Co. Carlow).
- Knockbeg uncultivated (grassland) soil (adjacent to cultivated field) (Teagasc site, Knockbeg, Co. Carlow).
- Clonroche cultivated soil (former Teagasc site, Clonroche, Co. Wexford).
- Clonroche uncultivated (grassland) soil (adjacent to cultivated site).
- Cashel soil (the Clifton Brown farm, near Cashel, Co. Tipperary) in long-term cultivation (barley).
- Mollisol soil (the soil standard of the IHSS, and used for comparisons and for standardisation).
- Brazilian soils (Ferrisols, including Terra Pretas [selected because of their relevance to biochar amendments to soils]), used for comparisons.
- Sand incubation (organic matter-free calcareous sand amended with maize (*Zea mays* L.) stover. This experiment set out to study the transformations of OM in the absence of indigenous SOM and to study the compositions of the products formed).

#### Soil samples taken to a depth of 1 m

- Clonakilty (Co. Cork) soil, a well-drained brown podzolic soil. Loam texture to the depth (1 m) sampled (in lysimeter studies at Teagasc Research Station, Johnstown Castle, Co. Wexford; samples were taken at 10 cm intervals to a depth of 1 m).
- Elton (Dromin, Kilmallock, Co. Limerick) soil; a moderately well-drained grey brown podzolic soil. Loam to the depth sampled (in lysimeter studies at Johnstown Castle; sampled at 10 cm intervals to a depth of 1 m).
- Rathangan (Heavenstown, Cleariestown, Co. Wexford) soil, a poorly drained gley. Clay loam texture (in lysimeter studies at Johnstown Castle; samples were taken at 10 cm intervals, 0–100 cm).
- Four brown podzolic soils from the Cahir area, Co. Tipperary. Each soil is in long-term cultivation. Samples were taken to a depth of 1 m. Samples were also taken to 1 m from the headland (uncultivated soils).
- Kinvara soil. Calcareous shallow grassland soil from Kinvara, Co. Galway.

In the course of the project team's collaboration with Drs Deirdre Fay and Karl Richards, Teagasc (who set up the lysimeter studies of grassland soils at Johnstown Castle), the importance of organic matter in soil profiles to a depth of 1 m was realised. The Interim Reports have emphasised that the SOM content of the surface soils was not a true indication of the reserves of OM at depth in the soil, and the significance of soil mineralogy and the drainage regimes was also observed. It was also recognised how these parameters influence the

compositions of the SOM components. Thus, a large body of data was amassed and presented in the Interim Reports, showing how SOM contents varied with depth in several soil profiles.

Organic carbon was determined by the Walkley-Black procedure (Allison, 1965). It was considered that the greatest losses resulting from biological oxidation would occur in the surface soils. Later it was discovered that these losses took place to a depth of at least 1 m, and so several soils were sampled to that depth, as indicated in [Table 3.1](#), with results presented in the Interim Reports. Emphasis is given here to the differences in the distributions of organic carbon (OC) at the various depths in some of the soil profiles studied and to the effects of different management practices on the OC contents.

The data in [Table 3.2](#) show the OC contents in the Oak Park soils that were the subject of EPA-sponsored projects involving the Department of Botany, TCD, and UL's Department of Chemical and Environmental Sciences. The soil is compositionally different from the other soils dealt with in this report. It is a gravelly brown earth of coarse sandy loam texture from calcareous, fluvio-glacial gravels, composed mainly of limestone with very small proportions of sandstone and granite, and is a shallow component of the Athy complex. The soil mineral content is 67% sand, 22% silt, and 11% clay. It has a low moisture-holding capacity and is prone to drought during dry periods.

Winter wheat (*Triticum aestivum* L.) has been grown in these soils for more than 30 years. Different management systems have variously been introduced, involving ploughing with straw removal since 2001 (P &

SR), ploughing with straw incorporation (P & SI) (since 2003), minimum tillage with straw incorporation since 2003 (MT & SI), minimum tillage with straw removal since 2001 (MT & SR). Miscanthus was planted in a separate part of the farm in 1994.

The data in [Table 3.2](#) indicate that SOM was lost as the result of the cultivation practices, and the losses took place at all depths down to 1 m. The different management systems were in operation for only 3 years when the samples were taken, and so definite trends resulting from the changed management practices have not been established. However, it is evident that the incorporation of straw residue is having an effect in sustaining the reserves of SOM. The results for the minimum tillage operation and straw removal compared to the ploughing operation are disappointing at this stage, and more extensive sampling will be needed before conclusions can be reached.

Results for Miscanthus are very encouraging. This C4 grass has resulted in an increase of 25% in the SOM content. The Oak Park soil, because of its relatively poor water-holding capacity, is not well suited to the growth of Miscanthus, and results for the year (2006) in which the sampling was carried out may well be disappointing because of the low Summer rainfall. It is anticipated that Miscanthus, which gives highly significant lignocellulose yields in clay loam soils, will become a highly important crop for the emerging fuel chips and biorefinery feedstocks industries. The organic matter contents have been sampled for 2 years to a depth of 1 m in the case of a clay loam soil under a Miscanthus stand. It is hoped to monitor the changes with time of the SOM contents at

**Table 3.2. Organic carbon (OC, Kg ha<sup>-1</sup> x 10<sup>4</sup>) contents at different depths in Oak Park soils subjected to different management systems.**

Depth (cm)	Uncult.	P & S R	P & S I	MT & S I	MT & S R	MIS
0–20	2.986	2.613	2.413	2.413	2.186	3.746
20–40	2.186	1.840	2.013	1.946	1.866	3.213
40–60	1.733	1.453	1.693	1.213	1.373	2.013
60–80	0.893	0.746	0.760	0.866	0.586	1.760
80–100	0.680	0.426	0.533	0.506	0.533	0.626
Totals	8.478	7.078	7.412	6.944	6.544	11.358
*OM (Estimates)	16.956	14.156	14.824	13.888	13.088	22.716
**Persons, 85 Kg equiv.	1995	1665	1744	1634	1540	2672

Uncult. = soils in grassland, not subjected to cultivation; P & SR = soils ploughed and straw removed; P & SI = soil ploughed and straw incorporated; MT & SI = minimum tillage with straw incorporation; MT & SR = minimum tillage and straw removed; MIS = soils planted to Miscanthus in 1994. \*OM is estimated by doubling the OC content. \*\*Persons, 85 kg equivalent is the number of persons averaging 85 Kg that would match the OM content in 1 ha of the soil.

**Table 3.3. Organic carbon (OC, Kg ha<sup>-1</sup> x 10<sup>4</sup>) contents at different depths in the soils under different management systems in the Cahir area of Co. Tipperary, subjected to different management systems.**

Depth	Farm 1 (Trass)			Farm 2 (Shine)		Farm 3 (O'Reilly)		Farm 4 (O'Donnell)	
	Uncult.	Cult.	Orchard 10 yrs	Uncult.	Cult.	Uncult.	Cult.	Uncult.	Cult.
0–20	2.360	1.813	2.040	4.400	1.960	3.600	2.360	3.560	2.360
20–40	2.293	1.653	1.626	1.146	0.680	1.653	1.400	1.653	1.400
40–60	1.933	1.440	1.240	1.293	0.640	0.893	0.586	0.893	0.586
60–80	0.680	0.227	0.480	0.613	0.560	0.733	0.506	0.733	0.506
Total	7.266	5.133	5.386	7.452	3.84	6.879	4.852	6.839	4.852
*SOM eq.	14.532	10.266	10.772	14.904	7.68	13.758	9.704	13.678	9.704
**Person eq.	1710	1208	1267	1753	903	1618	1142	1609	1142

\*SOM Eq. = soil organic matter equivalents, obtained by multiplying the OC contents by 2. \*\*Person eq. is the number of persons averaging 85 Kg that would match the SOM content in 1 ha of the soil.

different depths in this soil profile. However, it will take a number of years of growth in order to obtain meaningful results from new plantations.

The data in [Table 3.3](#) are for four grey brown podzolic soils near Cahir, Co. Tipperary. Each soil had been in cultivation for 30 years or more. To determine the effects of cultivation on OC contents, samples were taken from the grassland headland soils in the same field where cultivation had not taken place (uncultivated soils). Comparisons of the cultivated and uncultivated soils again emphasise how continuous cultivation and cropping results in a decrease in the OC content of the soil at each depth for all of the sites. The highest decreases (ranging from 23 to 55%) in terms of OM contents were observed in the top 20 cm of soil, but decreases were observed at all depths in the profile

down to 1 m. At Farm 1 (Trass farm), some of the cultivated land had been planted as an apple orchard in 1996. This has resulted in an increase in OC levels as the soil had not been subjected to continuous cropping for 10 years prior to sampling. However, it is likely to take a further 20 years before the lost OC is fully regained in that soil. Farm 4 (O'Donnell farm) was given organic manure amendments on a regular basis. Nonetheless, the continuous cultivation gave rise to a decrease in the OC content. Overall, the data show that from one-third to one-half of the SOM was lost arising from biological oxidation as the result of cultivation.

The data in [Table 3.4](#) show that about 63% of the SOM is in the top 30 cm of the soil in the cases of the Clonakilty and Elton soils, and that value is 83% in the case of the Rathangan soil. It is clear that there are differences

**Table 3.4. Organic carbon (OC, Kg ha<sup>-1</sup> x 10<sup>4</sup>) contents at different depths in three soil profiles and what these amounts, expressed as soil organic matter (SOM) can mean in terms of the number of persons (\*P Eq.), each weighing 85 Kg), standing on 1 ha of the soil. SOM was estimated as SOC x 2.**

Profile Depth	Clonakilty (OC)	*P Eq.	Elton (OC)	*P Eq.	Rathangan(OC)	P Eq.
0–10	6.74	<b>1586</b>	8.90	<b>2094</b>	7.23	<b>1700</b>
10–20	6.25		3.86		4.43	
20–30	3.30		2.22		1.07	
30–40	2.92		2.20		0.72	
40–50	2.55		0.92		0.43	
50–60	1.63		1.70		0.45	
60–70	0.87		1.13		0.47	
70–80	0.70		0.72		0.38	
80–90	0.65		0.72		0.32	
90–100	0.63		0.40		0.25	
Totals	26.24	<b>6174</b>	23.62	<b>5558</b>	15.75	<b>3706</b>

in the distributions of organic carbon in the different depths of soils, as will be discussed below.

The bar charts in [Figure 3.1](#) depict the fall-off with depth in the OC contents of the Clonakilty, Kinvara, Elton, and Rathangan grassland soils. (The Clonakilty, Elton, and Rathangan soils are in the lysimeter studies at Johnstown Castle.) The decreases with depth can be related to the drainage regimes in the soils: the Clonakilty soil is well drained and the grass roots penetrate deeper into the soil than in the case of the poorly drained Rathangan gley soil. The Elton soil is moderately well

drained, but it is clear that root penetration is relatively less extensive than for the Clonakilty and Kinvara soils. The SOM contents of the surface soil in the cases of the Elton and Rathangan soils are significantly greater than for the Clonakilty soil, and it can be concluded that the lesser air regimes deeper in the profiles (as the result of the poorer drainage) are major contributors to the more shallow-root penetration in the cases of the Elton and Rathangan soils. The calcareous shallow Brown Earth Kinvara soil is free draining and the negligible organic matter at depth is attributable to the lack of soil.

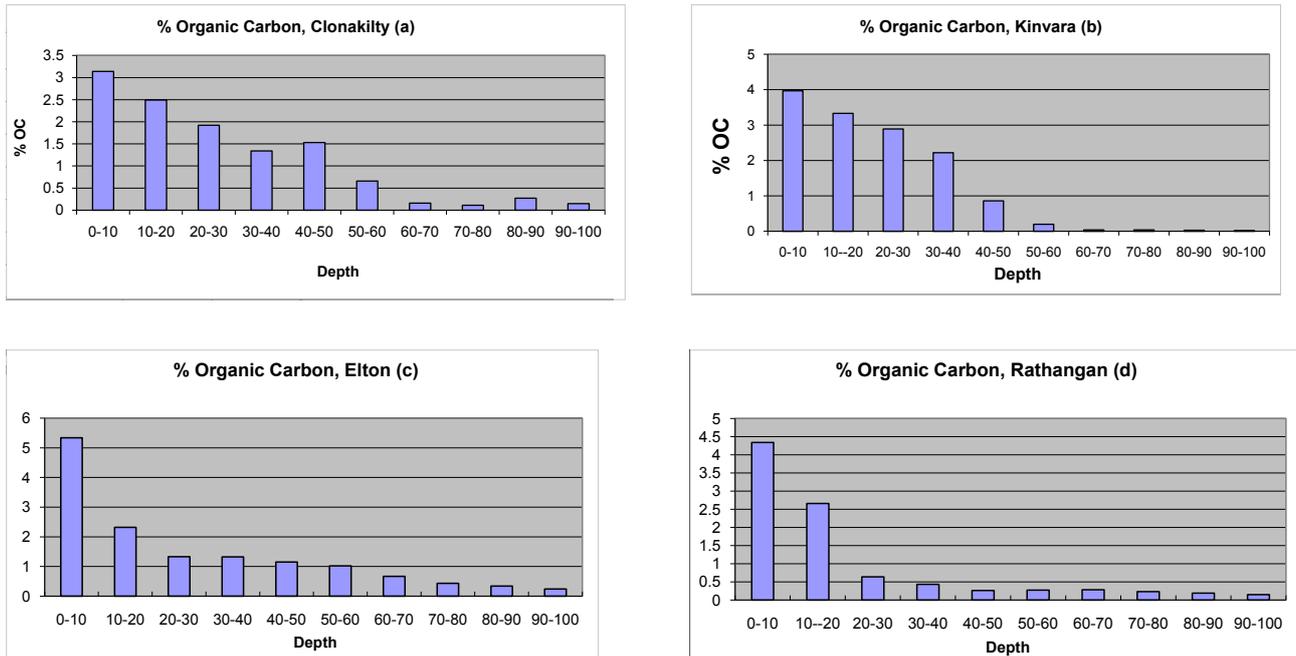


Figure 3.1. Bar chart of the organic carbon contents to a depth of 1 m in four grassland soils (a = Clonakilty; b = Kinvara; c = Elton; d = Rathangan) (see [Table 3.1](#) for a brief description of the soils).

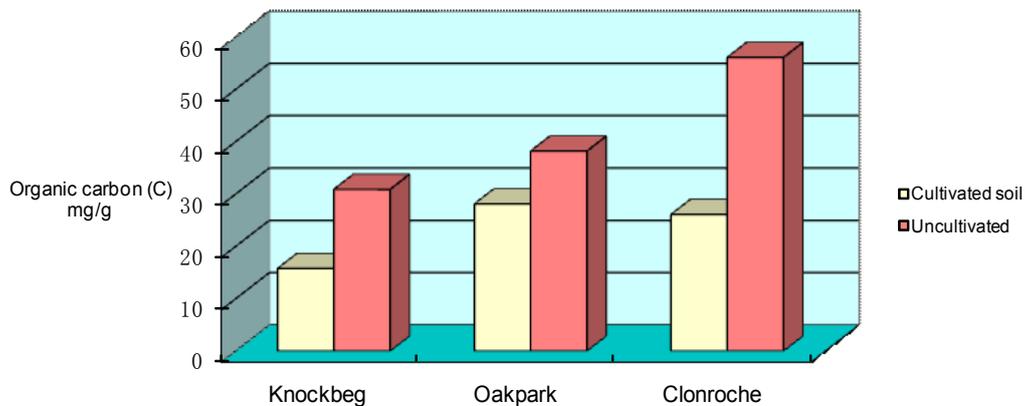


Figure 3.2. Bar charts showing how long-term cultivation has affected the organic matter contents of three Teagasc soils.

## 4 Advances Made in Awareness of Compositions of Soil Organic Matter Components

In order to be able to understand how SOM reacts in different soils and different soil environments, it is important to be aware of the conditions that give rise to the formation of the SOM and the differences in the compositions of the SOM components in different soils. There are emerging NMR techniques that provide reasonably comprehensive information about aspects of the compositions of SOM in soil. However, the effective application of the technique to whole soils is strongly influenced by the transition metals in the soil. The project team's approach was to isolate and fractionate the components of the SOM and to establish, in so far as possible, the compositions of the different components.

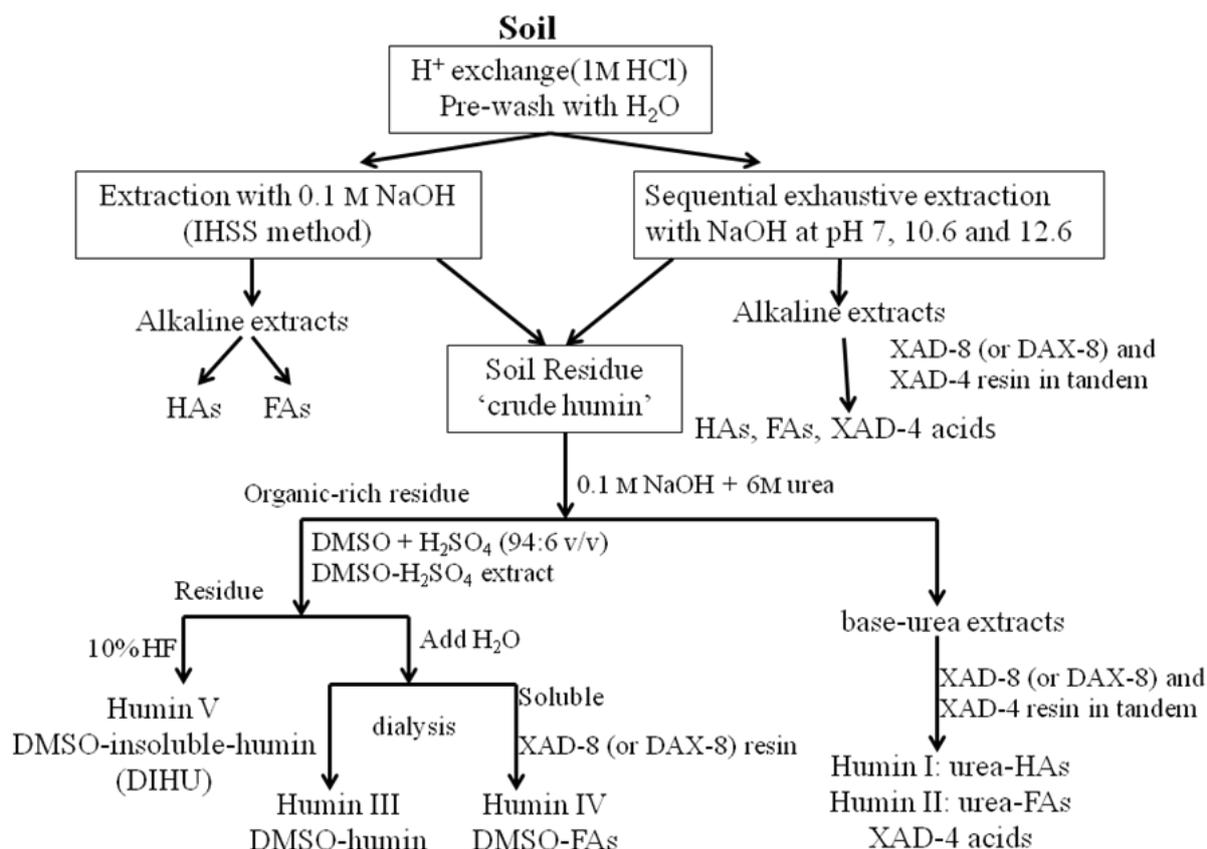
### 4.1 Isolation of Soil Organic Materials

Hayes (1985, 2006a) provided a detailed treatise on the principles and procedures (at that time) for the isolation of SOM components. He introduced the principles that should be taken into account for uses of organic solvents in soil organic studies. Hayes et al. (2008) showed that a sequential extraction process, involving charge density differences between the components of SOM, isolated fractions of different compositions, and the fraction isolated at pH 7 resembled most closely the materials in the drainage waters. However, the exhaustive extraction isolated less than 35% of the SOM. Based on the classical definitions, materials isolated in organic solvents following exhaustive extractions in aqueous media would be regarded as humin. Thus, following exhaustive extractions with 0.1 M NaOH (pH 12.6), in the aqueous sequential extractions at pH 7, pH 10.6, and pH 12.6, significant amounts of additional materials were isolated in 0.1 M NaOH + 6

M urea. That extract was similar to the isolates at pH 12.6 (Hayes, 2006a; Song et al., 2008), indicating that the urea had liberated humic components hydrogen bonded to the humin matrix, or released when the conformations of humin components were altered in the urea medium. Following exhaustive extractions in the urea system, further exhaustive extractions with a dimethylsulphoxide (DMSO) + 6% concentrated H<sub>2</sub>SO<sub>4</sub> solvent extracted most of the residual humin (up to 95% of the organic matter could be extracted in the solvent sequence described [Song et al., 2008]). The procedures used are summarised in [Figure 4.1](#). The approach has been a significant advance in the isolations of components of SOM.

### 4.2 Fractionation of Soil Organic Isolates

In the classical fractionation procedures, HAs and FAs are recovered (as indicated in Section 2.2). In the current research, a resin procedure based on that used for isolations of the HS in DOM was introduced. In this process the organic acids in base, or in base + urea, are diluted to <30 ppm, and the pH is adjusted to 2 and the solution is applied to XAD-8 and XAD-4 resins in tandem. In this way HAs and FAs are recovered from the XAD-8 resin, and XAD-4 acids are recovered from the XAD-4 resin. Any precipitates formed would not be sorbed by XAD-8 and these would wash through during the desalting process. This material is solubilised in base, the pH adjusted to 2.5, and applied to the resin as before. Significant fractionations are obtained in this way (Hayes, 2006a; Hayes et al., 2008; Song et al., 2008; Ferreira et al., 2010). Significantly greater amounts of HS fractions are recovered in this way than in the classical isolation/fractionation procedures.



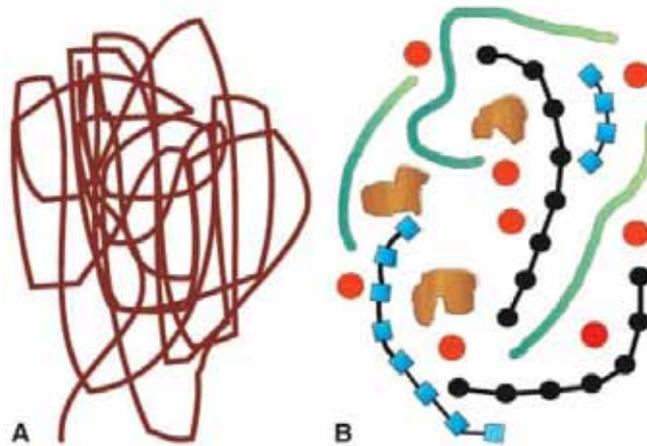
**Figure 4.1. An outline of procedures for the isolation and fractionation of humic and humin components from soils. (In this context, humin is initially considered to be the component of SOM that is not dissolved in aqueous base in the absence of organic additives. The research has shown that the urea additive isolates additional humic [HA] and fulvic acid [FA] components, labelled Humin I and Humin II, because these were not isolated in the aqueous base in the absence of the urea amendment.)**

### 4.3 Advances Made in Studies of the Compositions of Soil Organic Matter

The data have shown definite differences in the compositions of the HAs and FAs from the surface soils of different soil types (indicated in Interim Reports I–VI). A key advance was made early in the study (Simpson et al., 2002) when it was shown by diffusion ordered spectroscopy (DOSY), using liquid-state NMR, that HAs and FAs are not macromolecular but are associations of molecules, largely with molecular weights ranging between 700 and 2000 Daltons (Da). [Figure 4.2](#) depicts the random coil concept of HA macromolecular structures, which had the majority of adherents, and the molecular associations concept as deduced from DOSY data. These data showed that major components

of the mixtures were lignin-derived materials (which might be considered to be true humic components) in associations with each other and with saccharide and peptide, and aliphatic hydrocarbon (including fatty acids, long chain hydrocarbons) materials with different diffusion properties. It was concluded that associations of molecules gave pseudo-macromolecular properties. The associations were less evident in the cases of the FAs.

The introduction of the resin procedure for the isolation and the fractionation of humic substances (as indicated in several Interim Reports in the I–VI series) has greatly advanced awareness of compositions of SOM. For example, it has been possible to show in the current research definite compositional differences between samples isolated at pH 7, pH 10.6, and pH 12.6, and it



**Figure 4.2. (A) Depiction of the traditional concept of humic substances (HS) as randomly coiled macromolecules; and (B) a new concept indicating that the major components found in alkaline-extractable soil HS are relatively low molecular weight (<2,000 Daltons) molecules associated in the presence of metals to form aggregates. *Red spheres* represent generic metal cations, *black units* polysaccharides, *blue units* polypeptides, *green units* aliphatic chains, and *brown units* aromatic lignin fragments.**

became clear that the materials isolated at pH 7 are the most highly biologically oxidised. The compositions of these had distinct signals indicating biological origins. The signals for the isolates at the higher pH values suggested contributions of materials of plant origins. The NMR spectra in Appendix 2 show differences between the fractions isolated at the different pH values. Extensive analyses of the neutral sugars and amino acids contents of the different fractions have been conducted, and sugar and amino acid ratio values have been used that indicate that the components isolated at the lower pH values had origins in microbial transformation processes and those isolated at the higher pH values were derived from alterations to plant materials (Hayes et al., 2008; Ferreira et al., 2010). Dipolar dephasing (DD) NMR provided evidence for different extents of aromatic substitutions in different fractions, and chemical shift anisotropy (CSA) showed conclusively that the 60–90 ppm resonances could be attributed to the carbohydrate components. Data for such findings are contained in Interim Reports I–VI.

The XAD-4 acid, recovered from the XAD-4 resin (in the XAD-8 and XAD-4 in tandem system) were clearly components of biological origins, rich in carbohydrates and peptides, and although these materials are components of humus they should not be regarded as humic materials.

Because of its insolubility in aqueous media, humin was considered to be the intractable component of SOM. It has been recognised that humin in mineral soils has intimate associations with the soil mineral colloids, but the nature of its interactions with the mineral colloids and with anthropogenic and other chemicals could not be given appropriate attention because of the difficulties of characterising the components. It has been shown how NaOH + urea solutions isolate humic components in associations with true humin, and Appendix 2 shows that the base/urea extract gives HAs and FAs. Appendix 3 (Figure A3a) shows the extent to which, using diffusion-edited NMR, it has been possible to resolve the compositions of HAs isolated in the base/urea system. It has also been possible to get a similar resolution for several of the isolated HAs and FAs.

Applications of the DMSO + concentrated H<sub>2</sub>SO<sub>4</sub> system, developed in the project team for the isolation of SOM components, has ‘opened the door’ for understanding the compositions of humin materials. The solubilities of the components in deuterated dimethyl sulphoxide (DMSO-d<sub>6</sub>) and deuterated concentrated sulphuric acid (D<sub>2</sub>SO<sub>4</sub>) have allowed the components to be studied by <sup>1</sup>H NMR (liquid state). Appendix 3 (Figure A3b) (discussed in Interim Report VIII) indicates the natures of the materials isolated from the Mollisol. It is clear that the major components are waxes, cuticles, and lipids,

and these have significant resistances to microbial decomposition. There are also significant contributions from proteins/peptides, lipoproteins, peptidoglycans, and some altered lignin structures. (It is likely, however, that the altered lignins would be components of HA or FA materials trapped in the insoluble [in aqueous media] components of the humin matrix.) The biodegradable biological molecules are likely to be protected through their associations with the clays and with the hydrophobic (Ho), non-polar organic molecules.

As pointed out, the project team's interest in the IHSS Mollisol, from which samples for Appendices 2 and 3 (see Interim Report VIII) were taken, is because it is the IHSS soil standard, and because of the biochar it contains. The team was able for the first time to isolate the biochar component from this soil. Because (as has been noted) of its resistance to biodegradation, additions of chars to soils present definite possibilities for carbon sequestration. Furthermore, and especially important, based on studies of Terra Preta soils, chars can give rise to highly significant soil-fertility enhancement (Marris, 2006). Because of the inevitable introduction of second-generation biorefining processes, the biorefinery residues when pyrolysed will provide syngas, a bio-oil, and a biochar which could have soil-ameliorating properties (Hayes, 2006b). It is evident from the variable amplitude cross polarisation/magic angle spinning (VACP/MAS  $^{13}\text{C}$ ) NMR and DD spectra in [Figure A2](#) (Appendix 2), that Spectrum b is largely a char-derived HA that was precipitated in the pH range 2.5 to 2 ( $\text{HA}_{\text{2}}$ ) when the HA fraction isolated at pH 7 was diluted to <50 ppm and the pH slowly lowered to 2. Spectrum a is for the HA material that remained in solution in the diluted medium and was recovered from the XAD-8 resin.

The compositions of the humins isolated (in DMSO/ $\text{H}_2\text{SO}_4$ ) from a number of the Irish soils studied were examined. The solid state NMR spectrum, shown in Appendix 4 ([Figure A4](#)), for the humin isolate from the 0–10 cm layer of the Clonakilty grassland soil is typical for the humin fractions isolated. It is clear that the humin is almost entirely aliphatic, as evidenced by the strong hydrocarbon (15–40 ppm) and carbohydrate (70–105 ppm) resonances. The evidence for carbohydrate is confirmed by the distinctive anomeric carbon resonance, 105 ppm (and as highlighted by the chemical shift

anisotropy, CSA spectrum), and the DD spectrum gives evidence for a terminal methyl (15 ppm resonance). Application of Bloch Decay  $^{13}\text{C}$  NMR gave clear evidence for amorphous and crystalline methylene. Application of the relatively new technique of one- and two-dimensional High Resolution–Magic Angle spinning (HR-MAS) NMR spectroscopy provided evidence (for the first time) that cutan/cutin structures contribute to the aliphatic hydrocarbon components of humin. The evidence has been based on literature data on cutin isolated from tomatoes and cutin/cutan structures isolated from leaf cuticles. Data from HR-MAS  $^1\text{H}$ - $^1\text{H}$  TOCSY NMR have, in addition, provided evidence for: free primary alcohols; methines and methylenes in free secondary alcohols; methines attached to ester-linked mid-chain hydroxyls; methylenes attached to the oxygen (O)-side of esters between aliphatic alcohols and aromatic carboxylic acids; methines in epoxide groups, and methines in olefinic linkages.

#### **4.4 Summary of Current Awareness of Soil Organic Matter Compositions Arising from the Project Work**

The isolation of SOM components at different pH values, and using a resin fractionation procedure, has led to the isolation of humic fractions of different compositions. Further isolations in dilute base + 6 M urea have isolated a fraction which, on the basis of the classical definitions, would be classified as humin. However, this material is similar to the humic components isolated at pH 12.6 in the sequential extraction process and should not be regarded as humin. The project team has developed a procedure using DMSO + 6% concd  $\text{H}_2\text{SO}_4$  that has successfully isolated humin components (which compose >50% of the SOM). (Prior to this humin was a 'black box' term with little understanding of its compositions.)

This work has provided the definitive proof that HS extractable in aqueous media are associations of molecules. These associations are composed of lignin biodegraded substances (often the major components), saccharides, peptides, some fatty acids, and hydrocarbon moieties and metals, which can be 'cementing agents'. The cementing processes would include hydrogen and Ho bonding, and cation bridging.

The current research has shown that the compositions of HS in all soils are broadly similar, but the proportions of each component, the charge densities, and of course the abundances vary widely according to the soil type, minerals contents, and drainage regimes.

The compositions of humin materials are no longer 'mysteries'. In fact, because the component molecules are from known-type structures, they may be the easiest

components to resolve structurally. The components include minor amounts of lignin-derived structures, and these are likely to be trapped within or physically bound to the humin matrix. Other components of humin include carbohydrates (polysaccharides) and peptides. The major components are aliphatic structures, and our evidence indicates that cutin/cutan structures are important components of these.

## 5 Advances in Awareness of Compositions and Structures of Organic Matter Components of Drainage Waters

### 5.1 Waters Studied

Drainage waters were studied from the battery of lysimeters at Johnstown Castle from:

- Elton soil;
- Clonroche soil;
- Rathangan soil;
- Castlecomer soil;
- Oak Park soil.

Waters were also examined from the field lysimeters at Johnstown Castle for the:

- Elton
- Rathangan; and
- Clonakilty soils.

Finally, drainage waters were studied from:

- Forested Blanket peat soil, Moycullen, Co. Galway;
- Drainage from non-forested peat, Moycullen;
- Drainage waters from Blanket peat, Nad, Co. Cork;
- Drainage water from Blanket peat at EPA/UCC, Glencar, Kerry site.

### 5.2 Isolation of Humic Substances from Waters

The resin in tandem (XAD-8 and XAD-4) technique, outlined in Section 4.2, was used to isolate the HAS, FAs, and XAD-4 acids from the waters.

### 5.3 Studies of the Compositions of Humic Substances in Waters

The amounts of organic substances isolated from the different waters have been referred to in Interim Reports III, IV, and VI. Compositional studies have included NMR spectroscopy data, titration, and sugar and amino acid analyses. In general, the compositions of the HS in waters most closely resemble those isolated at pH 7 from the soils of the watersheds (e.g. Hayes et al., 2008). More recent studies have focused on drainage

waters from the Clonakilty, Elton, and Rathangan soils of the lysimeter studies at Johnstown Castle. Only results from the Clonakilty soil will be outlined here.

#### 5.3.1 Ultrahigh resolution FT-ICR-MS

By means of ultrahigh resolution Fourier-transform ion cyclotron mass spectrometry (FT-ICR-MS) using electrospray ionisation (ESI), it was possible to gain a molecular level understanding of the compositions of the natural organic matter (NOM) in the drainage waters.

Natural organic matter is composed of an extremely complex suite of molecules with spectra showing more than 20 peaks per nominal mass over a range of 300 mass units, and only FT-ICR-MS has the capability to resolve the thousands of individual components in the NOM samples. Many investigators have reported resolving powers of in the range of 300 000–600 000.

In order to discern the types of molecules present in the sample, the molecular formula matches can be used to construct a van Krevelen diagram that facilitates information retrieval from assigned formulas. The van Krevelen diagram plots the molar hydrogen to carbon (H/C) ratio on the Y-axis and the molar oxygen to carbon (O/C) ratio on the X-axis. Such a plot allows the elucidation of what compound classes are present and it can also lead to the identification of the reaction pathways taking place (see Appendix 5).

Clusters of peaks in high-resolution mass spectra can be structurally related to families of similar compounds. This is possible because major biomolecular components of source material, mainly the products derived from plants, occupy fairly specific locations in the plot.

Peaks located in the region with O/C ratios between 0.1 and 0.7 and H/C ratios between 0.4 and 1.7 correspond to mainly lignin-type molecules. The peaks in this area could also be derived from tannin-like molecules, since tannin molecules would have H/C and O/C ratios similar to those of lignin-type molecules. Some of the points in the diagram could also be related to condensed (e.g. dehydrated) cellulose-

type molecules. Thus, the van Krevelen diagram for Clonakilty drainage waters in Appendix 5 shows that the major contributors to the composition of the DOM in the Ho fraction (Ho, or HAs, FAs) are lignin-derived substances, and peptides, carbohydrates, and lipids, and that in addition the hydrophilic (Hi, or XAD-4 acids) fraction contains contributions from aminosugars, cellulose and tannins.

The lysimeter soils at Johnstown Castle were treated with fertiliser and bovine urine. A comparison of the van Krevelen diagrams for the Ho acid fractions from the control (no treatment) and treated Clonakilty soil showed little differences. However, the Ho acids isolated from the drainage water of the fertiliser-treated soil contained a greater contribution of aminosugars than the other fractions.

A comparison of the van Krevelen diagrams for the Ho acid fractions (hydrophobic fractions) isolated from drainage water from the Clonakilty control soil and the Rathangan control soil indicated that degraded lignin was the major component of both samples. In addition, there is evidence for the presence of biomolecules including proteins and lipids. However, the Ho acid isolated from the drainage water of the fertiliser-treated Clonakilty soil contained more aminosugars than the corresponding Rathangan sample.

### 5.3.2 Applications of NMR Spectroscopy

Appendix 6 shows the spectra for Ho acids (HAs/FAs) isolated from the Clonakilty soil drainage water. Resonances of methoxyl groups (chemical shift 56 ppm), combined with those for the pronounced O-aryl components (140–155 ppm), are characteristic of the Ho acids isolated from the control-soil drainage water and the drainage water from the soil treated with fertiliser. This combination is characteristic of 'young' humic substances, with probable origins in lignin-type components of plant residues. This corresponds well with the van Krevelen data which highlight the significant contribution of lignin to the Ho acids. Evidence for methoxyl and O-aryl is less pronounced for the Ho isolated from the drainage water of the fertiliser and bovine-urine treated soil. That would suggest that it was more highly oxidised. The methoxyl peak is rounded, suggesting resonance from peptide functionalities; these could possibly be due to inputs from the bovine urine (Byrne et al., 2010).

Note the differences between the Ho acids isolated from Rathangan (poorly drained) and Clonakilty (well-drained) soil drainage water (see Appendix 6). There are also similarities. Resonances of methoxyl groups (chemical shift 56 ppm), combined with those for the pronounced O-aryl substituents (140–155 ppm) are characteristic of the Ho acids isolated from all the samples. These are strong lignin signals. This is confirmed by FT-ICR-MS data, which highlights the strong contribution from lignin. There is strong methoxyl resonance and stronger evidence for aromatic and O-aromatic substitution by the 'stair-steps' on both peaks in the poorly drained Ho acid. This is further supported by DD data (not shown). The well-drained sample displays more carbohydrate resonance as highlighted by the CSA (not shown). These differences suggest that the Ho acid isolated from the well-drained sample has undergone more extensive transformations than that isolated from the poorly drained system. This also applied for the Ho acids isolated from the fertiliser and fertiliser and urine-treated soil drainage waters. These appear to be higher in aromatic and methoxyl resonance, suggesting incomplete transformation of lignin-type compounds. Their well-drained counterparts (from Clonakilty soil) were richer in aliphatic resonances.

### 5.3.3 Advances made in studies of organic matter in drainage waters

The data referred to in Section 5.3 refers to the most recent work carried out on the drainage waters from two of the lysimeter soils from the Johnstown Castle grassland studies. The waters in these instances had passed through the soil. This is the first time that results have been reported for FT-ICR-MS analyses of drainage waters. These results show that applications of van Krevelen plots to FT-ICR-MS data give good indications of the compositions of the organic matter in the waters, and the combinations of FT-ICR-MS and CPMAS <sup>13</sup>CNMR have given novel insights into the compositions of the DOM materials from the waters. Again, taking into account the information obtained for the soils, the data indicate a strong relationship between the DOM (which will be 90% FA materials) and the FAs isolated from the soils at pH 7.

In general, the results indicate that the OM compositions of surface waters reflect the vegetation of the site, while the compositions of the waters which drain through the soil reflect the humic components isolated at pH 7.

## **6 Conclusions**

This EPA project has 'opened many doors' to an awareness of the compositions and aspects of structures of components of SOM. It is foolhardy to consider that all humic components from all soils are the same. It is likely that the humic components from the same soil types, with similar mineralogies, and similar drainage regimes will be broadly similar. However, changes to even one of the important parameters will give rise to significant changes in the amounts and compositions of the SOM in the soil profile. Leading-edge progress has been made in understanding the sizes and associations of the humic components isolated in aqueous media, and especially in the associations and compositions of the humin materials in intimate associations with the soil mineral colloids. An understanding of humin is

very important because it composes more than 50% of the SOM. Significant amounts of humin (e.g. the carbohydrate and peptide contents) are protected by associations with the non-polar components, and/or by sorption on the clays.

The project has shown that there are significant compositional differences between the SOM at depth and in the surface soils. Study of the compositions of the OM in the deeper layers of the lysimeter soils is continuing. For example, the components at the 90–100 cm depths have been isolated and fractionated. The data show that the compositions of these deep samples are similar to those at more shallow depths in the soil profile, but the contribution of the humin fraction is greater at depth.

## **7 Future Work**

Ireland has more carbon sequestered in its soils per head of population than any other country in the EU (with the possible exception of Finland). It gets no credit for this. It can be argued that the carbon released in the long-term cultivations by other member countries is fossil C, and account should be taken of Irish stores in any carbon accrediting. The Irish case can be made more convincing should a comprehensive awareness of the SOM reserves be obtained. That will require extensive surveys to a depth of 1 m. Such surveys should determine soil organic carbon contents, and should also include some compositional studies that will indicate, at least in a broad way, the properties of Irish organic carbon reserves. If that is done Ireland will then have the most advanced information with regard

to its soil carbon, and Irish arguments to have account taken of its reserves will be more convincing.

Second-generation biorefining that uses lignocellulose substrates, including crop residues, can provide a sustainable indigenous industry for Ireland. There appears to be little future for first-generation biorefining that utilises food crops. Studies with *Miscanthus* during the course of the current project have shown that – compared with those for the grassland vegetation that it would displace – this perennial crop can enhance soil organic carbon contents significantly. It is necessary, however, to be aware of the properties of the best soils to sustain *Miscanthus*, and of the soils that will sequester most carbon under the crop.

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## **Acronyms and Annotations**

ADEs	Amazonian dark earths
CSA	chemical shift anisotropy
Da	Daltons
DOSY	diffusion ordered spectroscopy
DMSO <sup>d6</sup>	dimethylsulphoxide (deuterated)
D <sub>2</sub> SO <sub>4</sub>	deuterated concentrated sulphuric acid
DMSO	dimethylsulphoxide
DD	dipolar dephasing
DOC	dissolved organic carbon
DOM	dissolved organic matter
ESI	electrospray ionisation
FAs	fulvic acids
HAs	humic acids
Ho	hydrophobic
HS	humic substances
IHSS	International Humic Substances Society
M	molar
NMR	nuclear magnetic resonance
NOM	natural organic matter
OC	organic carbon
OM	organic matter
O/C	oxygen to carbon
POC	particulate organic carbon
SOM	soil organic matter
FT-ICR-MS	ultrahigh resolution Fourier-transform ion cyclotron mass spectrometry
XAD-4	styrene divinylbenzene
XAD-8	[poly]methylmethacrylate

# Appendix 1

## Publications arising from the Project

### *Refereed journal articles*

- Byrne, C.M.P., M.H.B. Hayes, A.J. Simpson, A. Baer, R. Kumar, E.H. Novotny, G. Lanigan, K.G. Richards, D. Fay & A.J. Simpson. 2010. Compositional changes in drainage water dissolved organic matter under different land management practices. *Water Research* **44**, 4379–90.
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- Song, G., E.H. Novotny, A.J. Simpson, C.E. Clapp & M.H.B. Hayes, 2008. Sequential exhaustive extractions, and characterisations using solid and solution state NMR, of the humic, including humin, components in a Mollisol soil. *European Journal of Soil Science* **59**, 505–516.

**A number of papers dealing with the compositions of the SOM at different depths in the soil profiles and of the relevant humin materials are in preparation.**

***Relevant book chapters***

- Michael H.B. Hayes, Guixue Song & Andre J. Simpson. 2009. Humic fractions and the nature of organic materials in intimate association with soil clays. In: D.A. Laird and J. Cervini-Silva (eds), CMS Workshop Lectures, Vol. 16, Carbon Stabilization by Clays in the Environment and Characterization Methods. The Clay Minerals Society, Chantilly, VA, pp. 1–31.
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***Refereed conference proceedings***

- Guixue Song & Michael H.B. Hayes. 2004. Isolation, fractionation, and characterization of humic substances from a maize-amended soil. Proc. 12th Intern. Conf. IHSS (San Pedro), 327–331.
- Corinna Maria Byrne, C. Edward Clapp & Michael H.B. Hayes. 2004. Transformations of plants to humic substances. Proc. 12th Intern. Conf. IHSS (San Pedro), 247–250.
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- Michael H.B. Hayes & Roger S. Swift. 2008. Humic substances in soils and in their drainage waters. Proc. 14th Meeting, International Humic Substances Society (Moscow), **Vol II**, 379–382.
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- W. Kwapinski, P. Wolfram, C. Byrne, F. Melligan, E.H. Novotny, J.J. Leahy & M.H.B. Hayes. 2010. Properties of biochar produced from *Miscanthus x giganteus* and its Influence the growth of maize (*Zea mays* L). Proc 15th International Conference IHSS, Tenerife. **Vol 1**, 95–98.
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- R. Mylotte, M.H.B. Hayes & C. Dalton. 2010. Study of estuarine sediments in Galway Bay. Proc 15th International Conference IHSS, Tenerife. **Vol 3**, 88–91.

## Appendix 2

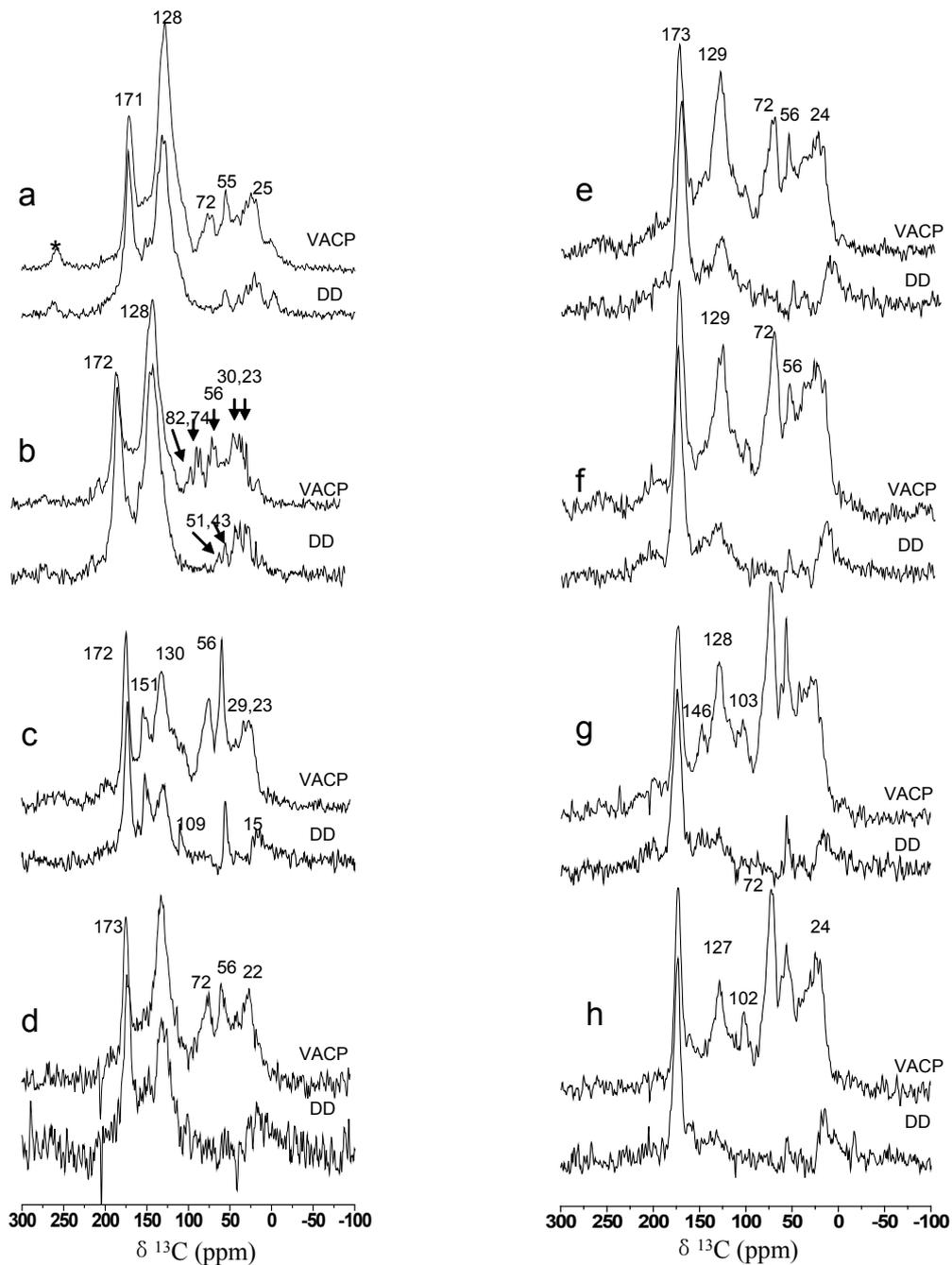
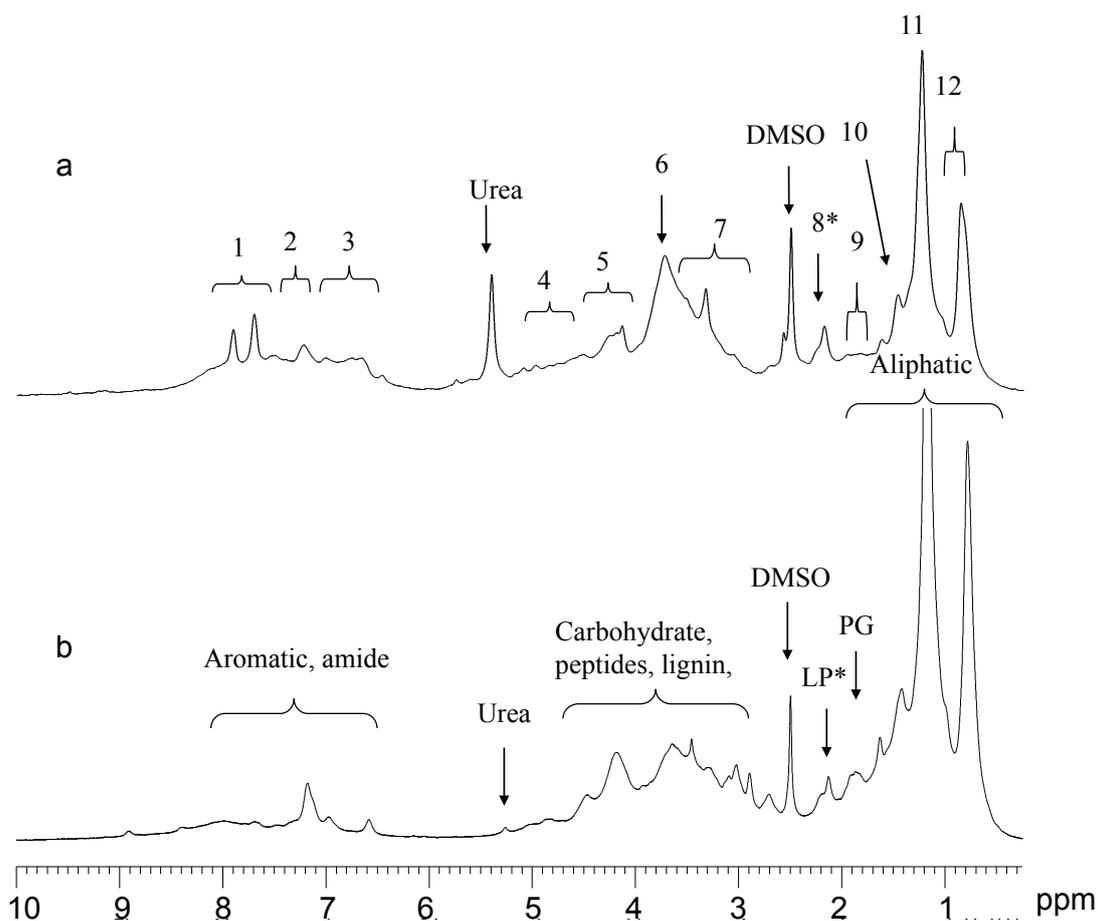


Figure A.2. Variable amplitude cross polarisation magic angle spinning (VACP/MAS)  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra (upper) and corresponding dipolar dephasing (DD) spectra (lower) for humic acid precipitate at pH 1 (HA<sub>1</sub>) (a); the humic acid that precipitated in the pH range 2 to 2.5 (HA<sub>>2</sub>) (b); from the pH 7 soil extract (see text, Sections 4.1 and 4.2); humic acids from the extract at pH12.6 (c); urea humic acids isolated in 0.1 M NaOH + 6 M urea (d); the fulvic acid isolated at pH 1 (FA<sub>1</sub>), (e); FA<sub>>2</sub> (f); fulvic acids from the extract at pH 12.6 (g); and urea fulvic acids from 0.1 M NaOH + 6 M urea (h). All humic and fulvic fractions were isolated using the XAD-8 and XAD-4 resin-in-tandem procedure (see Section 4.2) from Mollisol soil. \*Asterisk indicates side spin bands (SSB).

## Appendix 3



**Figure A.3.  $^1\text{H}$  diffusion edit nuclear magnetic resonance (NMR) of urea humic acids extracted in 0.1 M NaOH + 6 M urea (a) and dimethylsulphoxide DMSO humin extracted in DMSO + 6%  $\text{H}_2\text{SO}_4$  (b).**

Assignments in (a) refer to: 1, amide; 2, phenylalanine; 3, aromatics in lignin; 4, anomeric protons in carbohydrates; 5,  $\alpha$ -protons in proteins and peptides; 6, methoxyl in lignin; 7, other carbohydrate protons; 8\*, P-OCO-R methylene units adjacent to the carbonyl in lipoproteins; 9, N-acetyl group in peptidoglycan; 10, methylene units in an aliphatic chain  $\beta$  to an acid or ester; 11, methylene functionalities ( $\text{CH}_2$ )<sub>n</sub> in aliphatic chains; 12,  $\text{CH}_3$  (note when this peak is large relative to 11 it often indicates strong contributions from proteins). Simple assignments for spectrum (b) indicate strong contributions from: aromatic and amide functionalities, carbohydrate, peptide, and lignin-derived structures, lipoprotein (LP\*) and peptidoglycan (PG) structures, and a large contribution from aliphatic materials that would include waxes, cutins, lipids. Note: because of the addition of  $\text{D}_2\text{SO}_4$  to solubilise DMSO humin, deuterium exchanged the N-H to N-D, and so the amide resonance in the DMSO humin is strongly attenuated. \*May contain signals from lipoprotein and/or signals from fatty acids/cuticles. Refer to Simpson et al. (2007) for more details.

## Appendix 4

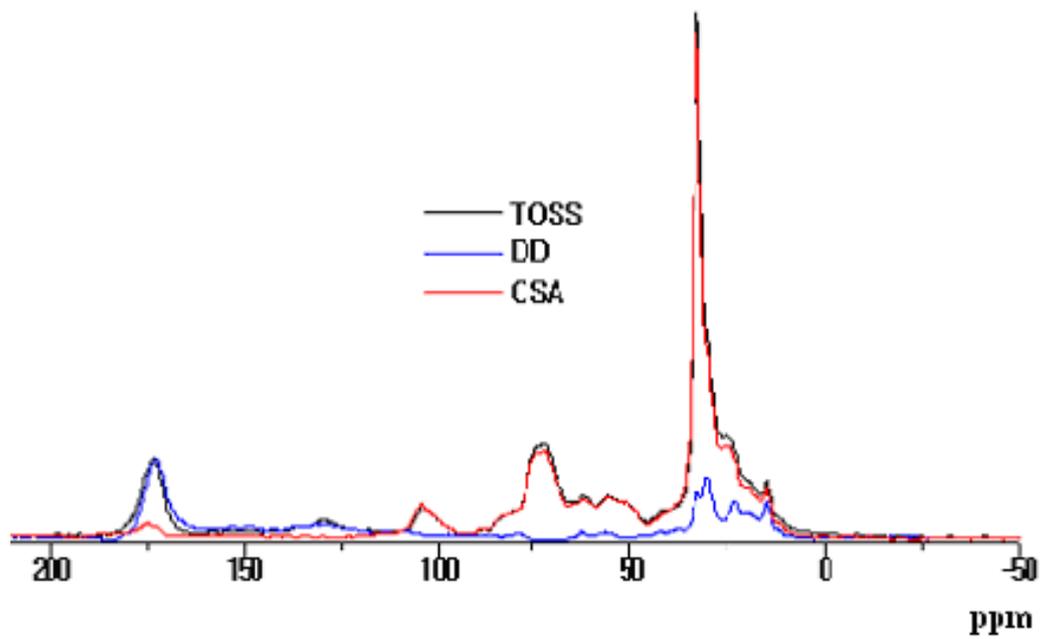


Figure A.4. Solid state CPMAS  $^{13}\text{C}$  NMR spectrum of the dimethylsulphoxide (DMSO)/ $\text{H}_2\text{SO}_4$  humin extract from the 0–10 cm layer of the Clonakilty grassland soil (see Section 4.3).

## Appendix 5

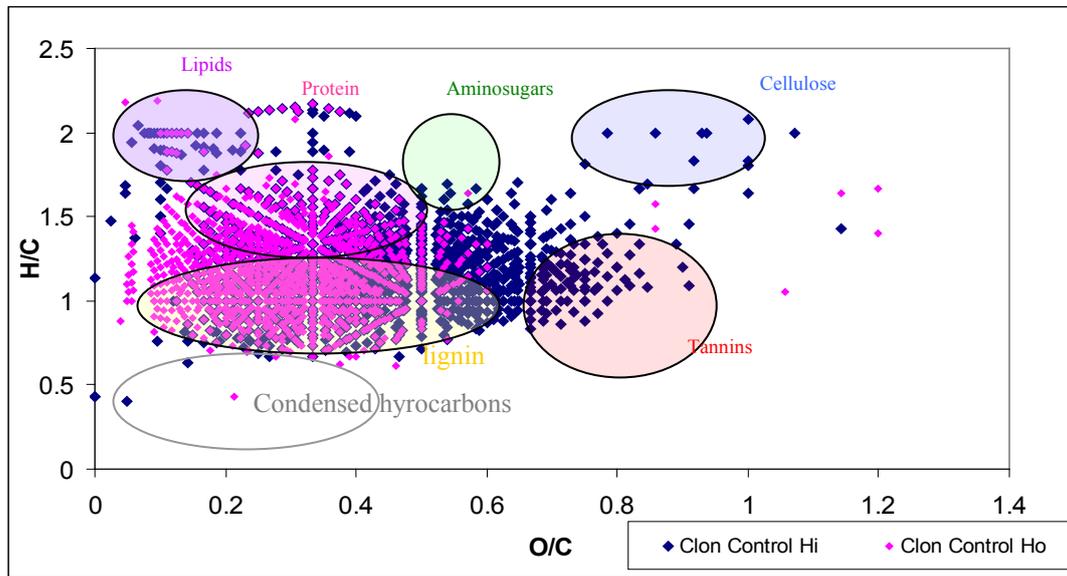
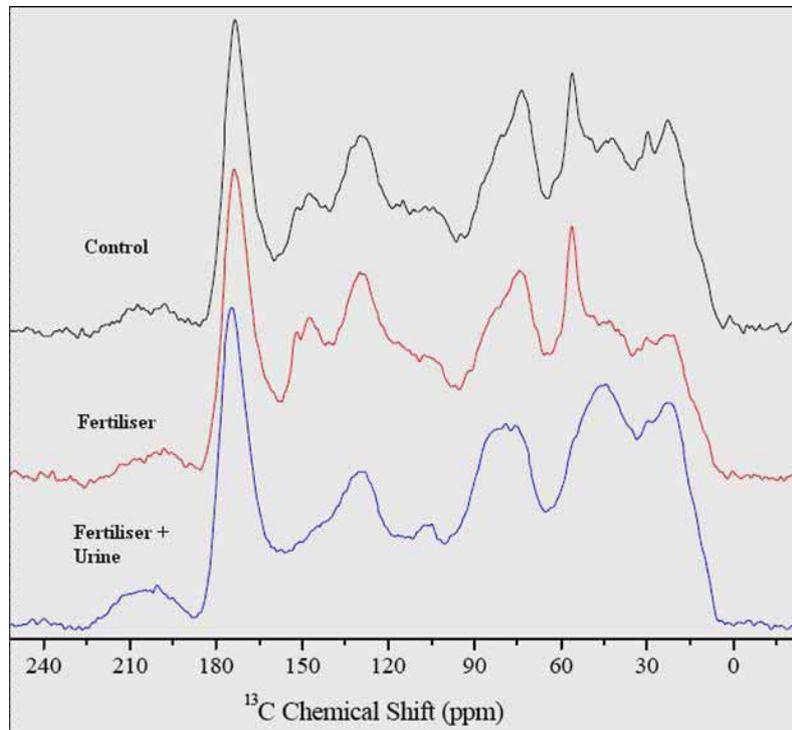


Figure A.5. Van Krevelen diagram for Clonakilty (Clon) drainage waters control hydrophobic (Ho) and hydrophilic (Hi) acids. Compound classes are represented by the circles overlain on the plot.

## Appendix 6



**B**

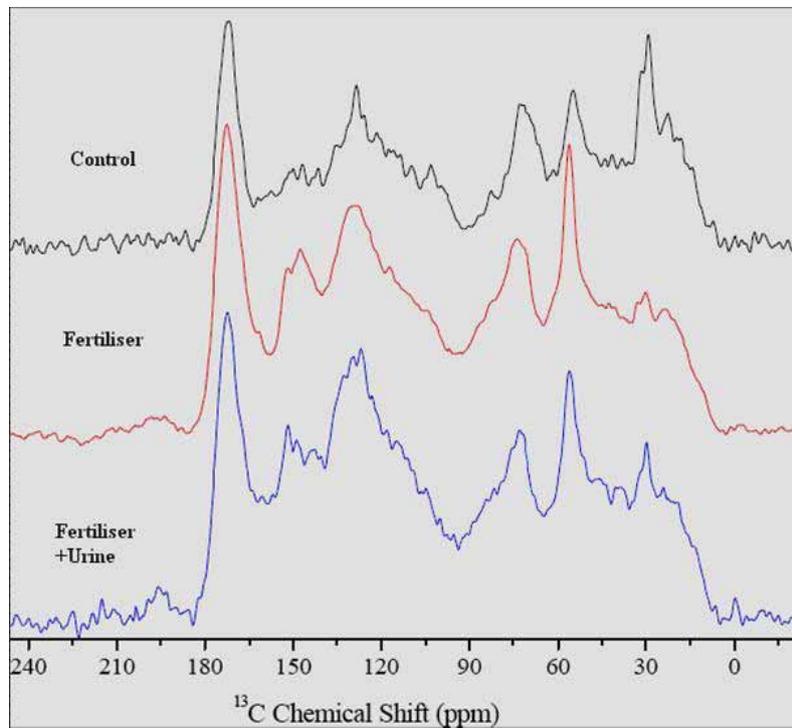


Figure A.6. Variable amplitude cross polarisation (VACP) Total Suppression of Side bands (TOSS) nuclear magnetic resonance (NMR) spectra of hydrophobic (Ho) acids (HAs and FAs) isolated from the drainage waters of the Clonakilty (A) and Rathangan (B) soils under different treatment regimes.

# An Gníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomh-nithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil agus Rialtais Áitiúil a dhéanann urraíocht uirthi.

## ÁR bhFREAGRACHTAÍ

### CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreal.
- Scardadh dramhuisse

### FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain.
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisse agus caighdeán uisce.
- Obair le húdarás áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí chomhordú a dhéanamh ar líonra forfheidhmíthe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a gníomhaíochtaí.

### MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOIL

- Monatóireacht ar chaighdeán aer agus caighdeán aibhneacha, locha, uisce taoide agus uisce talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntiú a dhéanamh.

### RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

### TAIGHDE AGUS FORBAIRT COMHSHAOIL

- Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdeán aer agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

### MEASÚNÚ STRAITÉISEACH COMHSHAOIL

- Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le plannanna bainistíochta dramhaíola agus forbartha).

### PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

### BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

### STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Gníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaímseartha, ar a bhfuil Príomhstíúrthóir agus ceithre Stíúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmíúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.

### **Science, Technology, Research and Innovation for the Environment (STRIVE) 2007-2013**

The Science, Technology, Research and Innovation for the Environment (STRIVE) programme covers the period 2007 to 2013.

The programme comprises three key measures: Sustainable Development, Cleaner Production and Environmental Technologies, and A Healthy Environment; together with two supporting measures: EPA Environmental Research Centre (ERC) and Capacity & Capability Building. The seven principal thematic areas for the programme are Climate Change; Waste, Resource Management and Chemicals; Water Quality and the Aquatic Environment; Air Quality, Atmospheric Deposition and Noise; Impacts on Biodiversity; Soils and Land-use; and Socio-economic Considerations. In addition, other emerging issues will be addressed as the need arises.

The funding for the programme (approximately €100 million) comes from the Environmental Research Sub-Programme of the National Development Plan (NDP), the Inter-Departmental Committee for the Strategy for Science, Technology and Innovation (IDC-SSTI); and EPA core funding and co-funding by economic sectors.

The EPA has a statutory role to co-ordinate environmental research in Ireland and is organising and administering the STRIVE programme on behalf of the Department of the Environment, Heritage and Local Government.