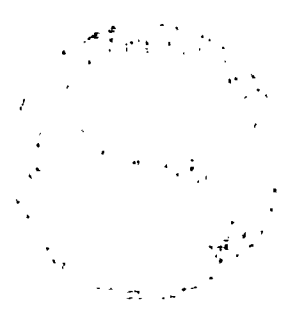


A Review of the Development of Regional Sludge
Treatment Centres and A Baseline Characterisation
of Irish Sewage Sludges.

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Submitted for a Masters of Science Degree to the Institute of
Technology, Sligo.

Supervisor: Dr. John Bartlett.




DEDICATION

I would like to dedicate this project to my parents.

DECLARATION

I confirm that the enclosed is all my own work, with acknowledged exception.

Signed:



Jane Lehany. M.Sc.

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ABSTRACT

This Study assessed the development of sludge treatment and reuse policy since the original 1993 National Sludge Strategy Report (Weston-FTA, 1993). A review of the 48 sludge treatment centres, current wastewater treatment systems and current or planned sludge treatment and reuse systems was carried out. Sludges from all Regional Sludge Treatment Centres (areas) were characterised through analysis of selected parameters.

There have been many changes to the original policy, as a result of boundary reviews, delays in developing sludge management plans, development in technology and changes in tendering policy, most notably a move to design-build-operate (DBO) projects. As a result, there are now 35 designated Hub Centres. Only 5 of the Hub Centres are producing Class A Biosolids. These are Ringsend, Killarney, Carlow, Navan and Osberstown. Ringsend is the only Hub Centre that is fully operational, treating sludge from surrounding regions by Thermal Drying. Killarney is producing Class A Biosolids using Autothermal Thermophilic Aerobic Digestion (ATAD) but is not, as yet, treating imported sludge. The remaining three plants are producing Class A Biosolids using Alkaline Stabilisation.

Anaerobic Digestion with post pasteurisation is the most common form of sludge treatment, with 11 Hub Centres proposing to use it. One plant is using ATAD, two intend to use Alkaline Stabilisation, seven have selected Thermal Drying and three have selected Composting. While the remaining plants have not decided which sludge treatment to select, this is because of incomplete Sludge Management Plans and on DBO contracts.

Analysis of sludges from the Hub Centres showed that all Irish sewage sludge is safe for agricultural reuse as defined by the Waste Management Regulations (*Use of Sewage Sludge in Agriculture*) (S.I. 267/2001), providing that a nutrient management plan is taken into consideration and that the soil limits of the 1998 (S.I. 148/1998) Waste Management Regulations are not exceeded.

TABLE OF CONTENTS

Title Page	
Dedication	ii
Declaration	iii
Acknowledgements	iv
Abstract	v
List of Contents	vi
List of Tables	ix
List of Figures	xi

LIST OF CONTENTS

CHAPTER 1.

1.0	<u>INTRODUCTION</u>	1
1.1	Introduction	2
1.2	Aims and Objectives	3
1.3	Layout of thesis	4

CHAPTER 2.

2.0	<u>SEWAGE SLUDGE TREATMENT, PRODUCTION AND DISPOSAL IN IRELAND</u>	5
2.1	Background	6
2.2	Wastewater treatment	7
	2.2.1 Preliminary treatment	9
	2.2.2 Primary treatment	9
	2.2.3 Secondary treatment	9
	2.2.4 Tertiary treatment	10
	2.2.5 Heavy Metal removal in wastewater treatment plants	10
	2.2.6 Sludge treatment	11
	2.2.6.1 Sludge treatment technologies	12
2.3	Development of sewage treatment, disposal and reuse policy in Ireland	17
	2.3.1 The effect of legislation and policy on the amount of sludge for treatment and options for disposal/reuse	20
2.4	A European perspective	21

CHAPTER 3

3.0	<u>HEAVY METALS IN SEWAGE SLUDGE</u>	24
3.1	Background	25
3.2	Sources of heavy metals in the natural environment	25
3.3	The heavy metal composition of sewage sludge	26
3.3.1	Cadmium (Cd)	27
3.3.2	Chromium (Cr)	29
3.3.3	Barium (Ba)	30
3.3.4	Copper (Cu)	30
3.3.5	Lead (Pb)	32
3.3.6	Mercury (Hg)	33
3.3.7	Nickel (Ni)	33
3.3.8	Zinc (Zn)	34
3.3.9	Arsenic (As)	35
3.3.10	Molybdenum (Mo)	36
3.3.11	Selenium (Se)	37
3.3.12	Iron (Fe)	38
3.3.13	Cobalt (Co)	38
3.4	The interaction of heavy metals in soils and sludges	39
3.5	The effects of heavy metals in plants and animals	43

CHAPTER 4

4.0	<u>MATERIALS AND METHODS</u>	47
4.1	Introduction	48
4.2	Hub Centre review	48
4.3	Sample collection, storage and preparation	48
4.4	Hach digestion method development	50
4.5	Microwave digestion method	53
4.6	Procedure for the digestion of sludge samples	54
4.7	Instrumental analysis	54

CHAPTER 5

5.0	<u>RESULTS & DISCUSSION</u>	58
5.1	Background	59
5.2	Hub Centre review	59
5.2.1	Hub Centre development from 1993 to 2003	93
5.2.2	Hub Centres producing Class A Biosolids	95
5.2.3	Sludge treatment technologies development from 1993 to 2003	96
5.3	Characterisation of Irish sewage sludge	98
5.3.1	Method development and evaluation	98
5.3.2	Analysis of sludge samples	100
5.3.2.1	Copper	102
5.3.2.2	Zinc	103
5.3.2.3	Chromium	104
5.3.2.4	Lead, Nickel, Cadmium and Mercury	104
5.3.2.5	Iron	105
5.3.2.6	Arsenic, Molybdenum, Selenium, Barium and Cobalt	105
5.4	The impact of metal contents on Biosolid reuse as a sustainable option	106
5.5	Sludge loading rates	106

CHAPTER 6

6.0	<u>CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH</u>	109
6.1	Conclusions	110
6.2	Recommendations for Further Research	111

REFERENCES	I
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APPENDICES

Appendix A	A comparison of the microwave digestion method and the Hach digestion method, using a certified reference material (C.R.M)	a-1
Appendix B	Results of heavy metal analysis	b-1

LIST OF TABLES

Table 4.1	Hub Centres/sampling locations in Ireland	49
Table 4.2	Heavy metals analysed and instrumentation selected	54
Table 4.3	ICP-MS instrument conditions	56
Table 5.1	Details of Hub Centre 1, Buncrana	61
Table 5.2	Details of Hub Centre 2, Letterkenny	61
Table 5.3	Details of Hub Centre Gweedore	62
Table 5.4	Details of Hub Centre 4, Donegal	62
Table 5.5	Results of sludge analysis for Letterkenny and Buncrana	62
Table 5.6	Details of Hub Centre 5, Sligo	63
Table 5.7	Details of Hub Centre 6, Carrick-on-Shannon	64
Table 5.8	Details of Hub Centre Derrinnumera	65
Table 5.9	Details of Hub Centre Roscommon	66
Table 5.10	Details of Hub Centre 10, Tuam	67
Table 5.11	Details of Hub Centre 15, Limerick	69
Table 5.12	Details of Hub Centre 17, Tralee	70
Table 5.13	Results of sludge analysis for Tralee	70
Table 5.14	Details of Hub Centre 18, Killarney	71
Table 5.15	Results of sludge analysis for Killarney	72
Table 5.16	Details of Hub Centre 20, Ballincollig	72
Table 5.17	Details of Hub Centre 22, Mallow	73
Table 5.18	Details of Hub Centre 23, Charleville	73
Table 5.19	Results of sludge analysis for Mallow	74
Table 5.20	Details of Hub Centre 24, Dungarvan	74
Table 5.21	Details of Hub Centre 27, Enniscorthy	75
Table 5.22	Details of Hub Centre 28, Wicklow	76
Table 5.23	Details of Hub Centre Blessington	76
Table 5.24	Results of sludge analysis for Blessington	77
Table 5.25	Details of Hub Centre 30, Ringsend	78
Table 5.26	Details of Hub Centre 32, Drogheda	79
Table 5.27	Details of Hub Centre 33, Dundalk	79
Table 5.28	Results of sludge analysis for Dundalk	80
Table 5.29	Results of sludge analysis for Monaghan	80
Table 5.30	Details of Hub Centre 34, Monaghan	81

Table 5.31	Details of Hub Centre 35, Cavan	82
Table 5.32	Results of sludge analysis for Cavan	82
Table 5.33	Details of Hub Centre 36, Longfrod	83
Table 5.34	Results of sludge analysis for Longford	83
Table 5.35	Details of Hub Centre 37, Mullingar	84
Table 5.36	Results of sludge analysis for Mullingar	84
Table 5.37	Details of Hub Centre 38, Navan	85
Table 5.38	Details of Hub Centre 39, Tullamore	86
Table 5.39	Details of Hub Centre 40, Osberstown	87
Table 5.40	Results of sludge analysis for Osberstown	87
Table 5.41	Details of Hub Centre 41, Nenagh	88
Table 5.42	Details of Hub Centre 42, Thurles	88
Table 5.43	Details of Hub Centre 43, Clonmel	89
Table 5.44	Details of Hub Centre 44, Portlaoise	90
Table 5.45	Results of sludge analysis for Portlaoise	90
Table 5.46	Details of Hub Centre 45, Kilkenny	91
Table 5.47	Details of Hub Centre 46, Carlow	92
Table 5.48	Results of sludge analysis for Carlow	92
Table 5.49	A comparison of Hub Centres recommended in the 1993 Sludge Strategy Study with the 1997 Study and subsequent reviews.	94
Table 5.50	Variable testing and selection for the Hach digestion method	99
Table 5.51	Summary of heavy metal analysis of Irish municipal sewage sludge	101
Table 5.52	Results of heavy metal analysis of industrial sludge	102
Table 5.53	Limit values for amounts of heavy metals which may be added annually to agricultural land, based on a ten year average	107
Table 5.54	Annual sludge application rates	108

LIST OF FIGURES

Figure 2.1	Typical wastewater treatment plant for population >2,000	8
Figure 2.2	Changes in municipal sludge generation and disposal/reuse patterns in Ireland between 1993 and 2005	20
Figure 5.1	Alkaline Stabilisation at Castlebar	64
Figure 5.2	Sludge storage at Tuam	67
Figure 5.3	Mesophilic Anaerobic Digestion at Tralee	70
Figure 5.4	ATAD at Killarney	71
Figure 5.5	Secondary settlement at Enniscorthy	75
Figure 5.6	Class A Biosolids generated by Thermal Drying at Ringsend	77
Figure 5.7.	Composite sludge sample from Monaghan wastewater treatment plant	80
Figure 5.8	Sludge generated by belt press at Cavan wastewater treatment plant	82
Figure 5.9	Ferric chloride dosing at Tullamore wastewater treatment plant	85
Figure 5.10	Extended aeration at Kilkenny wastewater treatment plant	91
Figure 5.11	Changes in proposed sludge treatment methods from 1993 to 2003	96

CHAPTER 1

INTRODUCTION

1.1 Introduction

Biosolids is the treated product of municipal sludge treatment that meets specified quality standards and is suitable for reuse as fertiliser in agriculture. The treatment and reuse of municipal sludge is a complex and difficult issue for Local Authorities and Government. For example, the amount of sludge for treatment is set to increase four fold between the years 1993 to 2020, due to the implementation of the Urban Wastewater Treatment Directive (91/271/EEC, that requires the installation of secondary wastewater treatment facilities for towns with populations in excess of 2000 before 2005), the Dumping at Sea Act (1996, which eliminated dumping to sea from 1999) and the Landfill Directive (1999/31/EC that prohibited the disposal of unprocessed sludge).

The Irish Government has identified agriculture as being the most suitable and desirable outlet for treated sludge (Biosolids), provided that it is consistent with the EU strategy of waste recycling, recovery and reuse. Biosolids in agriculture can supplement or replace fertilisers by providing essential nutrients and trace elements and organic matter, which are essential to improve and sustain productive soils and plant growth.

In Ireland, the application of sludge to land is carried out in accordance with Statutory Instrument 148 of 1998 (Waste Management [*Use of Sewage Sludge in Agriculture*] Regulations), which prescribes standards for the use of sewage sludge in agriculture and gives effect to European Council Directive 86/278/EEC. This was amended by the Statutory Instrument 267 of 2001 (Waste Management Regulations), which aims to avoid the accumulation of toxic substances, in particular heavy metals, which might reach excessive levels in the soil after a number of applications. The *Code of Good Practice for the Use of Biosolids in Agriculture* (FTC, 1998a) also provides very strict requirements, although not compulsory, for the treatment and use of municipal sludge. The Code requires treatment of sludges to reach an international standard (i.e. creating a Biosolids product).

Because the Government supports the land-spreading of Biosolids as being the most sustainable method of sludge management, Local Authorities, under section 22 of the 1996 Waste Management Act, are required to prepare Sludge Management Plans for their functional areas, taking particular requirements and unique characteristics of their

individual counties into consideration. Sludge Management Plans are designed to identify integrated sludge management options to facilitate treatment of municipal wastewater sludge, to produce Biosolids and to investigate options for beneficial reuse of Biosolids, while also making recommendations for the sustainable management of all non-hazardous sludges arising in each county (FTC, 1999a).

While there are many benefits associated with applying treated sludge/Biosolids to agricultural land, there are also many concerns associated with the reuse of Biosolids in agriculture, based on fear of unknown constituents, primarily heavy metals, trace organics and pathogens which could, in certain circumstances, render agriculture as an unsuitable sustainable reuse option. Fundamental to meeting the Biosolids reuse challenge is a requirement for comprehensive research into sludge characterisation (Bartlett and Killilea, 2001).

Assessing the viability of Biosolids reuse in Ireland is made particularly difficult by the autonomous nature of Local Authorities. It is not the norm to share soil, sludge or plant operating data. To form a national view, a review of all regional sludge treatment plants was necessary, with sampling and analysis of sludges from all centres.

1.2 Aims and Objectives

There were two objectives in this M.Sc. Study. The first was an assessment of the development of sludge treatment and reuse policy since the original 1993 National Sludge Strategy Report (Weston-FTA, 1993). This included a review of the 48 sludge treatment centres, current wastewater treatment systems and current or planned sludge treatment and reuse systems.

The second was the characterisation of Irish municipal sludges, using selected constituents. The set of parameters for analysis were selected using Directive 86/278/EEC (*The Use of Sewage Sludge in Agriculture and amendments*), the *Code of Good Practice for the Use of Biosolids in Agriculture* and the 'Dutch List' of parameters for assessment of soil quality. In total, 13 parameters were examined.

Samples of municipal sludge were obtained from all Regional Sludge Treatment Centres. In situations where Hub Centres were not yet established, samples were obtained from alternative wastewater treatment plants in the region. Samples of industrial sludge were obtained from Swords and Shannon. Existing analytical data were acquired from all sites.

1.3 **Layout of thesis**

The thesis document is presented in 6 chapters, as follows:

- **Chapter 1 Introduction** – describes the current situation in Ireland, benefits and challenges associated with agricultural reuse of Biosolids, the need for the research carried out in this M.Sc. Study and specific project aims/objectives.
- **Chapter 2 Sewage Sludge Treatment, Production and Disposal in Ireland** – describes wastewater and sludge treatment processes, the development of sewage treatment, disposal and reuse policy in Ireland and European perspectives on Biosolids reuse in agriculture
- **Chapter 3 Heavy Metals in Sewage Sludge** – describes sources of heavy metals in the environment, the heavy metal composition of sewage sludge, the interaction of heavy metals in soils and sludges and the effects of heavy metals in humans, animals and the environment.
- **Chapter 4 Materials and Methods** – sets out the materials and methods used for the Hub Centre Review and heavy metal analysis.
- **Chapter 5 Results and Discussion** – presents results of the Hub Centre review (which are discussed in relation to Hub Centre development, those producing Class A Biosolids, recommended sludge treatment technologies, and a comparison of Irelands sludge disposal practices), and of heavy metal analysis (discussed in relation to current limits and sludge loading rates).
- **Chapter 6 – Conclusions & Recommendations for Further Research.**

CHAPTER 2

SEWAGE SLUDGE TREATMENT, PRODUCTION AND DISPOSAL IN IRELAND

2.1 Background

The collection and treatment of wastewater produces a residual sludge that requires safe and economic disposal. In Ireland, application to agricultural land has replaced sea disposal and landfill as the preferred reuse/disposal option. This is because the application of Biosolids to agricultural land, where feasible, is considered the most desirable and economical alternative, as it recycles valuable nutrients, trace elements and organic matter present in the sewage sludge to the soil in a natural, controlled and monitored manner (Cheremisinoff, 1994; Droste, 1997; Outwater, 1994).

Worldwide, farmers are applying Biosolids to agricultural lands because they recognise the potential benefits of residual nitrogen and phosphate that Biosolids supplies to their crops and the potential savings available on fertiliser costs (Anglian Water, 1996). Despite this fact, in many countries the reuse of Biosolids is minimal, primarily because of fears associated with the reuse of sludge containing heavy metals, toxic organics and pathogens. In most countries, heavy metals (and sometimes trace organics) in Biosolids are regulated. Regulations vary from country to country, with some countries basing their regulations on what they perceive as possible to achieve, others basing theirs on risk analysis, while still others are based on the concentrations of heavy metals present in agricultural soils (Balmer, 2001).

In Ireland, sewage sludge is regulated by the Waste Management (*Use of Sewage Sludge in Agriculture*) Regulations, S.I. 148 of 1998, as amended by the Waste Management Regulations, S.I. 267 of 2001. They implement the requirements of the Council Directive 86/278/EEC (*On the Protection of the Environment, and in Particular of the Soil, when Sewage Sludge is Used in Agriculture*).

Any person using sludge as an agricultural soil amendment is required, under these regulations, to ensure that the quality of the soil, surface water and ground water is not impaired. As a result, limit concentration values for heavy metals in sludges applied to agricultural soils and receiving soils are specified for cadmium, copper, nickel, lead, zinc, mercury and chromium.

Also, under section 22 of the 1996 Waste Management Act, Local Authorities are required to prepare Sludge Management Plans for their functional areas, taking

cognisance of all non-hazardous sludge produced, and strategies for their management. Since agriculture has been identified as the most suitable sludge management option, the plans should focus on both the fertilising and soil conditioning properties of Biosolids as being the primary targets of recovery. Where agriculture does not prove suitable for the region under study, the plan should identify alternative sludge management strategies, all tailored to match local opportunities and needs (FTC, 1999a).

The range of treatment processes by which Biosolids can be produced, requirements necessary for pasteurisation, evaluation of spread-lands prior to sludge application, nutrient management planning, transportation and land-spreading of Biosolids (as outlined in the *Code of Good Practice for the Use of Biosolids in Agriculture*) should also be examined and detailed in the Sludge Management Plan (FTC, 1998a). Where some sludges in the study area are found not amenable to a specific treatment process, they should be identified and quantified in the Sludge Management Plan and options for their management explored (FTC, 1999a).

The following sections describe the process of wastewater treatment, the sources of sludge for treatment, the main technologies available for sludge treatment, the way in which national policy has developed for sludge management and what systems are used in other European countries.

2.2 Wastewater treatment

A wastewater treatment plant produces an effluent of specified quality from an influent wastewater of known composition and flow rate. The separated solids arising from the treatment of wastewaters is called sludge. The exact nature of the sludge is dependent on the type and extent of wastewater treatment and the method of sludge stabilisation (Gray, 2002).

Treated wastewater is generally discharged to surface waters, primarily rivers. The amount of treatment required depends largely upon the nature of the influent wastewater together with the water quality objectives of the receiving bodies (Gray, 2002).

Treatment processes are classified into five main groups: preliminary, primary, secondary, tertiary and sludge treatment. Figure 2.1 shows the layout of a typical wastewater treatment plant, comprising five main treatment processes. Various combinations of these treatment processes can be found to occur, depending on the population equivalent (P.E.) (i.e. loading), type and extent of treatment required etc.

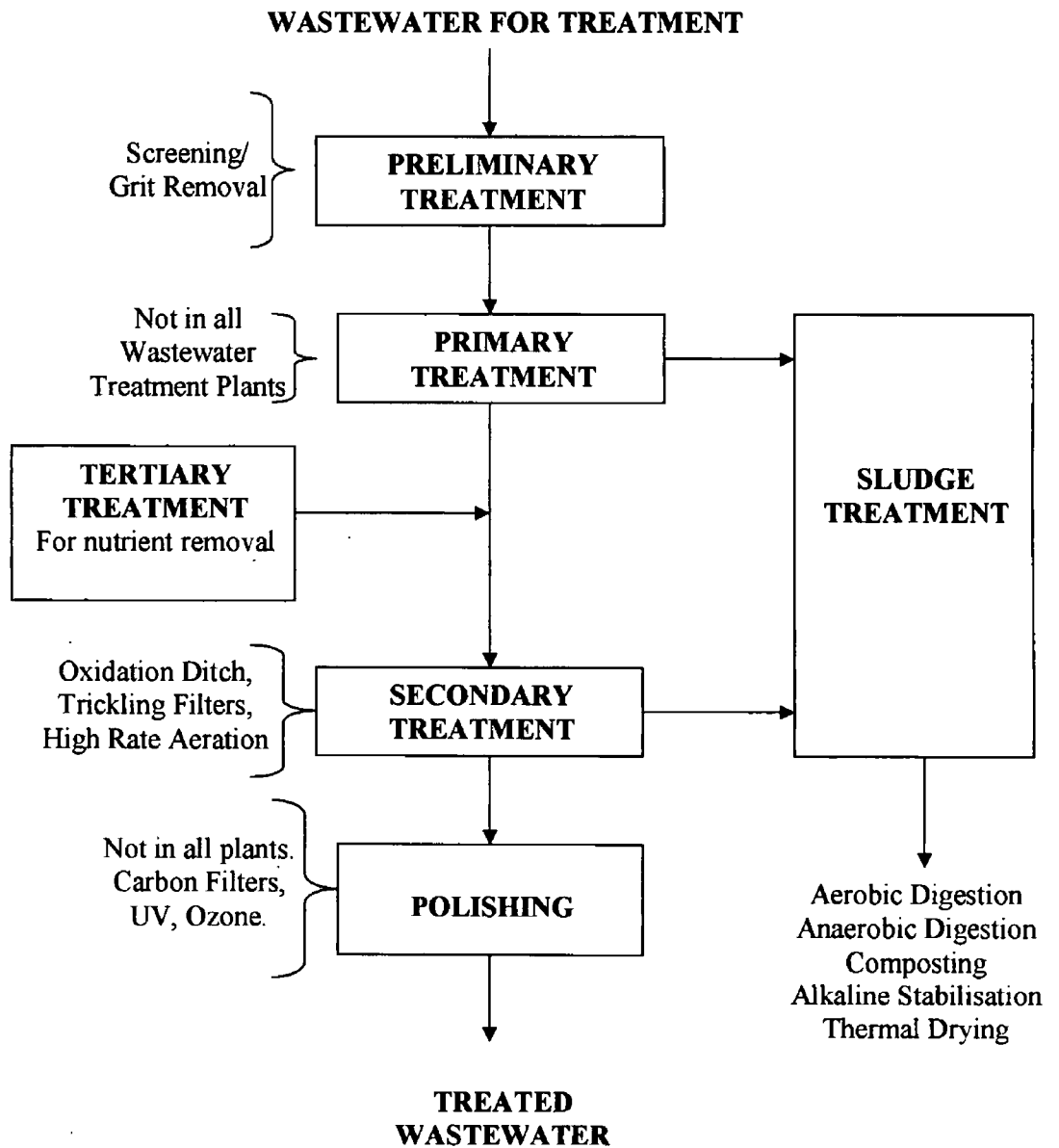


Figure 2.1 Typical wastewater treatment plant for population >2,000

2.2.1 Preliminary treatment

Preliminary wastewater treatment involves the removal of wastewater constituents that may cause maintenance or operational problems within the wastewater treatment process. Examples of preliminary operations are screens used for the removal of debris and rags, grit removal for the elimination of coarse suspended matter that may cause wear or clogging of equipment (Tchobanoglous and Burton, 1991). If there is an excessive content of fats, oils or grease in the influent wastewater, flotation units may be required, following the grit removal process. Subsequently, equalisation may be necessary where there is excessive diurnal variation in either flow rate or raw water quality to the treatment plant (Gray, 2002).

2.2.2 Primary treatment

The purpose of primary treatment is to remove organic and inorganic material by settlement of raw wastewater in sedimentation tanks. There are two main methods used. The first is physical settlement, which involves the removal of settleable-solids from suspension by gravity in the base of the tank, which can then be removed as primary sludge. The second is chemical coagulation and flocculation. This involves dosing the influent with chemical coagulants, followed by settlement where the coagulant encourages insoluble material to form flocs. These settle out in the base of the tank and are removed as primary sludge (Brett *et al.*, 1997). Primary treatment can reduce the Biochemical Oxygen Demand (BOD) by 30-40%, suspended solids by 40-70%, and faecal coliforms by up to 50% (Gray, 2002).

2.2.3 Secondary treatment

In secondary treatment, the wastewater arising from preliminary/primary treatment is mixed with a dense microbial population, under aerobic conditions. This treatment process uses microorganisms to convert soluble and colloidal organic matter into new cells, carbon dioxide and water. Nitrogen and phosphorus removal may also occur. Secondary settlement tanks are used to separate the dense microbial floc from the purified water. Secondary sludge is composed mainly of biological cells, in contrast to primary sludge, which is composed mainly of gross faecal solids. There are many different secondary biological treatment processes available, which include fixed film reactors, activated sludge systems, trickling filters and stabilisation ponds (Brett *et al.*, 1997; Gray, 2002; Tchobanoglous and Burton, 1991;).

2.2.4 Tertiary treatment

Tertiary treatment is the final polishing of the effluent, used for further removal of BOD, suspended solids, bacteria, potentially toxic elements or nutrients, to enable the final effluent to comply with discharge requirements, particularly when the standard 20:30 effluent is not sufficient.

The main methods include: (a) prolonged settlement in lagoons or irrigation onto grasslands or percolation areas. These methods require large areas of land and are suited to areas where lower operational complexity makes them preferable. Final effluents are reduced considerably in BOD, SS and COD; (b) wetlands/reedbeds are useful processes for providing effluents that are reduced considerably in levels of BOD, SS and nutrients; (c) straining through a fine mesh (i.e. microstraining), which is a treatment process used for the removal of SS from secondary effluents, particularly when low levels are required; (d) disinfection, is particularly suited for wastewater treatment plants discharging close to bathing waters. The two main forms of disinfection are ultraviolet (UV) treatment and chlorination; (e) chemical precipitation, a treatment process that involves the use of chemical precipitants (e.g. ferric chloride, aluminium sulphate or lime), which react with the soluble phosphate to produce an insoluble precipitate. It can be used either in the primary or secondary treatment processes, and is particularly suited to trickling filters where biological removal of phosphate is not considered possible (Brett *et al.*, 1997; Gray, 2002).

2.2.5 Heavy metal removal in wastewater treatment plants

The wastewater treatment process concentrates heavy metals from the influent wastewater into sludge at a concentration factor of up to 4,000 (MAFF, 1993).

According to Sengupta and SenGupta (2001), "*if heavy metals can be removed and reused in an industrial process, it would add economic justification to the solution of an environmental problem*". Unfortunately, common sludge treatment technologies cannot remove heavy metals present in sewage sludge (Wang, 1997), because according to Ukleja *et al.*, (2001), "*removal of the excessive heavy metals from sewage sludge is a complex task, technologically complicated by the fact that heavy metals accumulate as the insoluble sulphides contained in the organic waste*".

An important aspect of controlling pollution from heavy metals in municipal sewage sludge is the regulation of industrial effluent discharged to sewers (Spinosa and Vesilind, 2001). This has been shown to be extremely effective. In Germany, for example, heavy metal levels have been falling consistently over a number of years, reducing the level of concern over Biosolids as a potential source of pollutant loads to agriculture (FTC, 1998b).

2.2.6 Sludge treatment

Sludge is the concentrated by-product arising from the treatment of wastewater, which must be treated further (i.e. to produce Biosolids) to make it acceptable for reuse in agriculture. One of the main objectives of sludge treatment is to reduce the water content of the sludge prior to disposal (i.e. dewatering). Primary and secondary sludge is composed of typically 96-99% water. When sludge is composed of >90% water, it acts as a liquid, and, if directly applied to land, could cause surface runoff. Dewatering is also necessary because it reduces the total sludge volume to be handled and stored, with savings made on transport from storage facilities to land. The typical composition of solids in treated sludge generated by a belt press/centrifugation system ranges between 12-30%, and between 80-90% for sludge generated by Thermal Drying.

Another important objective of sludge treatment is the elimination or reduction of pathogens to acceptable levels, prior to disposal, so as to prevent the spread of disease. Primary sludge contains large numbers of both dead and live protozoa cysts and helminth and nematode eggs. Secondary sludge contains large numbers of bacteria and viruses. Faecal coliforms are the principal indicator organism, along with *Salmonella* species, used for evaluating the microbiological contamination of sludge. Coliforms, similar to *Salmonella* species, can cause various diseases such as internal infections, gastroenteritis and diarrhoea, and can be transmitted via the ingestion of untreated sludge, contaminated food or water (Girovich, 1996).

When untreated sludge is applied directly to agricultural lands, it has the potential of spreading microbial and viral contamination to food crops, surface and groundwater. Therefore, it is imperative that all sludge is treated to an acceptable microbiological standard prior to land reuse. In Ireland, the microbiological standards used are derived

from the USEPA Part 503 Biosolids Rule and are classified as Class A and Class B Biosolids (USEPA, 1994).

- **Class A Biosolids** - either the density of faecal coliforms in the Biosolids must be less than 1,000 most probable number (MPN) per gram total solids (dry-weight basis), or the density of *Salmonella* species bacteria in the Biosolids must be less than 3MPN per 4 grams of total solids (dry-weight basis). Either of these requirements must be met at one of the following times: when Biosolids are used or disposed, prepared for sale or give-away in a bag or other container for land application (USEPA, 1994).

- **Class B Biosolids** - values of less than 2 million MPN per gram total solids, or less than 2 million CFUs per gram of total solids are obtained at the time of use or disposal. Unlike Class A Biosolids, where pathogens are at levels below acceptable levels, Class B Biosolids may contain some pathogens. For this reason, Class B Biosolids have site restrictions, which prevent crop harvesting, animal grazing, and access by the public for specific periods of time, until such time that the pathogens levels have been further reduced (Christy, 1997; USEPA, 1994;).

2.2.6.1 Sludge treatment technologies (production of Biosolids)

There are numerous sludge treatment technologies available. Only wastewater sludge, which has undergone one of the recommended sludge treatment technologies, to accomplish a specified standard, can be classified as Biosolids. Biosolids are considered fit for agricultural reuse, depending on the remaining constituents present in the final sludge (Andersen, 2001). The six recommended sludge treatment technologies include (FTC, 1998a)

- (a) Mesophilic Anaerobic Digestion with pre or post pasteurisation
- (b) Thermophilic Anaerobic Digestion
- (c) Autothermal Thermophilic Aerobic Digestion
- (d) Composting
- (e) Alkaline Stabilisation
- (f) Thermal Drying

(a) Mesophilic Anaerobic Digestion with pre or post pasteurisation

Anaerobic digestion is the most common sludge treatment method used to reduce sludge volumes (Weemaes *et al.*, 2000). It involves the incubation of sludge under anaerobic conditions for at least 15 days at 35-55°C (Selivanovskaya *et al.*, 2001), or alternatively at least 20 days at a temperature of 25°C±3°C, where it is subject to microorganisms which break down various types of organics into simple organic compounds, methane, carbon dioxide, hydrogen and hydrogen sulphide, resulting in stable, innocuous sludge (Spinosa and Veslind, 2001).

In order to achieve Class A Biosolids, Mesophilic Anaerobic Digestion should incorporate a thermophilic phase or other pasteurising mechanism. A thermophilic phase is where a retention time of at least 1 hour is required at a temperature of greater than 70°C, or, alternatively, a retention time of 2 hours subject to a temperature of greater than 55°C. The thermophilic phase normally takes place prior to digestion (FTC, 1998a).

The advantages of Anaerobic Digestion are its many applications, in particular in the food and pharmaceutical industry (CIWEM, 1997), in addition to the calorific value of the methane gas, reduction in the mass and volume of sludge, low running costs, high loading rates that can be achieved, low nutrient requirements, and the way in which the biomass can be maintained and unfed for prolonged periods of time (Gray, 2002).

The disadvantages include long start up times, due to slow growth rate of anaerobic bacteria, highly polluted supernatant arising from anaerobic sludge thickening and dewatering, which contains suspended solids, dissolved and particulate organic materials, nitrogen and phosphorus and other compounds, thus resulting in an increased load to the wastewater treatment plant, in addition to its sensitivity to chemicals, pH variations and toxic overloads (Spinosa and Veslind, 2001). Another disadvantage of Anaerobic Digestion is the way in which nonyl phenol (NP, a detergent) accumulates during the treatment process. Di-(2-ethylhexyl)phthalate (DEHP, a plasticising agent) is not removed. Although a significant percentage of linear alkyl benzene sulphonates (LAS, surfactants) are biodegraded, residues of this substance remain, due to the large amounts initially present in the raw sludge. As a result, eco-labelling initiatives have

being prompted in a number of European countries, to influence consumer choice away from detergents containing these surfactants to alternative products (ICON, 2001).

(b) Thermophilic Anaerobic Digestion

Thermophilic Anaerobic Digestion is the same principle as Mesophilic Anaerobic Digestion, but operating at a mean retention time of 48-72 hours in temperature ranges of 50 to 55°C. A retention time of at least 1 hour is required at a temperature greater than 70°C, 2 hours at a temperature greater than 55°C, or at least 4 hours at a temperature of greater than 50°C (FTC, 1998a).

(c) Autothermal Thermophilic Aerobic Digestion (ATAD)

Aerobic Digestion is a sludge stabilisation process, where aerobic microorganisms consume the biological degradable organic components of the sludge. The objectives of Aerobic Digestion are to produce a biologically stable product while also reducing both sludge mass and volume (Bernard & Gray, 2000).

Autothermal Thermophilic Aerobic Digestion is Aerobic Digestion conducted under thermophilic conditions (50°C – 70°C) (Girovich, 1996; Snow, 1996), where all sludge is subject to a temperature greater than 55°C for at least 4 hours and a mean retention time of at least 7 days. It is an exothermic reaction. The heat released during microbial oxidation of organic matter is used to heat the sludge, in replacement for external heat (FTC, 1998a). The treatment process can achieve removal rates up to 40 percent of the biodegradable organics at very short retention times (3 to 4 days).

The main advantages of Thermophilic Aerobic Digestion over Aerobic Digestion are the high sludge treatment rates, decreased reactor volume, more effective pathogen reduction and higher volatile solids reduction (Girovich, 1996). At present, there is only one plant in Ireland producing Class A Biosolids by ATAD, which is located in Killarney, County Kerry.

(d) Composting (windrows or aerated static piles)

Composting is the biological degradation of organic matter resulting in the formation of a stable end product. As the organic material starts decomposing, it heats to temperatures in the pasteurisation range of 50 to 70°C, thereby destroying enteric

pathogens. During the treatment process, approximately 20 to 30% of volatile solids are converted to carbon dioxide and water (Tchobanglous and Burton, 1991).

It may be conducted under anaerobic or aerobic conditions, with Aerobic Composting used for municipal wastewater sludge. Aerobic Composting accelerates organic material decomposition and results in higher temperatures necessary for pathogen destruction, while, also minimising potential nuisance odours (Tchobanglous and Burton, 1991).

Composting methods include turned windrows and aerated static piles. The windrows process requires the sludge to be held at temperatures of 55°C for at least 15 days, during which time a temperature of greater than 55°C must be maintained over 5 turnings of the windrow. In aerated static piles, a temperature of greater than 55°C must be achieved and maintained uniformly for at least 3 days (FTC, 1998a).

Sludge that has been composted properly is a sanitary, nuisance free, humus-like material and can be used as a soil amendment in agriculture (Maier *et al.*, 2000), subject to limitations based on the constituents present in the sludge. Compost is beneficial for the physical properties of the soil, because it increases soil porosity, structural stability, and available water content while also reducing erosion (Pinamonti *et al.*, 1997).

However, the beneficial reuse of compost as an organic fertiliser can be limited, because, as Sidhu, (2001) reported, “*all composted Biosolids have a Salmonella re-growth potential*”. As a result, long-term storage is not recommended.

There is also some concern over the speciation and availability of metals from sludge following Composting (Lazzari *et al.*, 2000). According to Stringfellow (2001) “*both plant-available and exchangeable metals tended to increase during the active phase of composting, and decrease during maturation*”. The possible reasons for reduced metal availability during the composting process are the formation of insoluble carbonates during the thermophilic phase, adsorption of metals onto particles of alkaline materials or the formation of organo-metallic compounds (Wong *et al.*, 1997; Wong and Fang, 2000).

(e) Alkaline stabilisation

Alkaline Stabilisation involves the addition of lime to untreated sludge in sufficient quantities to raise the pH to 12 or higher. The high pH creates an environment that is not suitable for the survival of microorganisms. Therefore, the sludge will not decompose, create odours, or pose a health hazard, provided the pH is maintained at this level (Tchobanoglous and Burton, 1991).

Two methods of lime stabilisation used are (1) lime pre-treatment, which involves the addition of lime to sludge prior to dewatering, and (2) lime post-treatment, which involves the addition of lime to sludge after dewatering. Post lime stabilisation is the most cost effective method, particularly for sludges with a dry solids content of 18-30%. Either hydrated lime or quicklime can be used for post-lime stabilisation, although quicklime is favoured, as it is easier to handle and cheaper than hydrated lime (FTC, 1998a; Tchobanoglous and Burton, 1991).

Lime is added to raise the pH to greater than 12, with an accompanying rise in temperature to 70°C for 30 minutes, or, alternatively, to maintain the pH above 12 for 72 hours and to achieve a temperature greater than 52°C for at least 12 hours, followed by air drying to a dry solid content of greater than 50% (FTC, 1998a; Tchobanoglous and Burton, 1991)

Some heavy metals (e.g. Cu), having a higher affinity for organics in sewage sludge, become available in the sludge after being chemically treated. This effect is attributed to the irreversible dissolution of organically bound metals at very high pHs during processing and air-drying of the chemically-fixed sludge. While, others (e.g. Zn), have less affinity for organics and as a result become much more stable (Hsiau and Lo, 1998).

(f) Thermal Drying

The Thermal Drying process involves the evaporation of residual water from dewatered sludge to produce a solid stable product. The treatment process requires an external energy input in the form of fuel such as oil, natural gas/biogas from an anaerobic digester, or energy from the incineration of dried sludge/municipal solid waste. Thermal Drying employs one of two treatment processes, either drying by direct or indirect

contact with hot gases. The direct method involves direct contact with the drying medium, resulting in gas becoming contaminated with undesirable compounds; therefore gas scrubbing prior to recirculation is essential. A closed-loop system can be used to reduce the volume of air to be treated, which involves the recirculation of air and the use of top-up air which can be drawn from other plant components and added to the recycled air, giving an almost closed loop system. The indirect method involves the use of a heating medium, such as steam or thermal oil, and is confined to a closed loop (Girovich, 1996).

Thermal Drying technologies include flash dryers, rotary dryers, spray dryers, fluid bed dryers, disc dryers, multiple hearth dryers and multiple effect evaporators (FTC, 1998a; Tchobanoglous and Burton, 1991), with some dryers being designed to produce a granular product, (e.g. Swiss Combi system), while others require additional pelletising equipment.

The advantages of Thermal Drying are that approximately 90-95% dry solids can be achieved, and the dried sludge generated is stable, odourless and is amenable to long term storage, thereby making it easier to handle and transport. Disadvantages are the high capital investment and ongoing operating costs, the relative operational complexity of the system and the high-energy requirements (FTC, 1998a). There is one Thermal Drying plant in Ireland, situated in Ringsend, County Dublin. It is designed to cater for a population equivalent of 1.5 million and is currently in operation producing pelletised sludge, which is being used as an agricultural soil amendment.

2.3 Development of sewage treatment, disposal and reuse policy in Ireland

The Urban Wastewater Treatment Directive (91/271/EEC) required European Member States to provide secondary wastewater treatment for all towns with populations in excess of 2000, on a schedule stretching to 2005. Because many of Irelands coastal towns and cities had no secondary treatment (most disposing to sea) this meant a four-fold increase in the amount of sludge for treatment by 2005 (see section 2.3.1).

At the same time, it could be seen that landfill and dumping at sea would be removed as outlets. Existing EU legislation supported and promoted the treatment of sewage sludge

(producing Biosolids) and beneficial reuse in agriculture. In 1993, the Department of the Environment commissioned the “*Strategy Study into the Treatment and Disposal of Sewage Sludge in Ireland*”. The objective of the Study was to identify appropriate solutions for the treatment and disposal of sewage sludge, while, also complying with legislative, technical and environmental requirements. The Study can be summarised as follows (Weston-FTA, 1993):

- (a) The development of a sludge inventory on a county, regional and national basis including a review of all existing and proposed wastewater treatment schemes, while also containing all data regarding sludge production and disposal in addition to sludge classification and characterisation.
- (b) A review of all available technologies for sludge treatment and disposal, with particular emphasis on innovative technologies.
- (c) The development of realistic treatment/disposal options suitable for Irish conditions, and an evaluation of these options with specific regard to both environmental and cost considerations.

The Study recommended the establishment of 48 Hub Centres, where centralised sludge treatment/Biosolids production would be carried out. Suggestions were made for appropriate technologies in each centre.

The 1996 Waste Management Act required Local Authorities to prepare Sludge Management Plans for their functional areas.

The sludge policy and the designation of the Hub Centres were reviewed in 1997, as part of the “*Inventory of Non-Hazardous Sludges in Ireland*” (FTC, 1998c). It should be noted that, while the 1993 Study did not consider county boundaries, the 1997 review did so, with opportunities for integration to be considered as a starting point, from which a detailed sludge management plan was to emerge. As a result of boundary re-designation, and some other factors, the total number of Hub Centres were reduced from 48 to 46 (FTC, 1998c).

The “*Code of Good Practice for the Use of Biosolids in Agriculture*”, published in 1998, is another guidance document designed to facilitate the treatment and use of wastewater sludge as the most sustainable method of sludge management. It sets out

quality standards for sludge and soil, as well as good management practices for sludge and Biosolids handling (FTC, 1998a).

“Sludge Management Plans – A Guide to their Preparation and Implementation”, published in 1999, is a guidance document containing information relating to all types of sludge treatment intended to produce Biosolids, while also supplying recommendations on the selection of reuse outlets for Biosolids (FTC, 1999a).

Local Authorities are now in the process of preparing Sludge Management Plans for their functional areas. These Plans are aimed at identifying integrated sludge management options to facilitate treatment of municipal wastewater sludge, to produce Biosolids and to investigate options for beneficial reuse of Biosolids, while also making recommendations for the sustainable management of all non-hazardous sludges arising in each county (FTC, 1999a). At present (July, 2003), 14 counties have completed their Sludge Management Plans, while the remainder are in the process of finalising them. The majority of these will not be complete until 2004. This is because some plans that have yet to go to tender, while others are Design Build Operate (DBO) contracts and, as a result, are waiting on a decision by the contractors regarding the selection of specific sludge treatment technologies.

2.3.1 The effect of legislation and policy on the amount of sludge for treatment and options for disposal/reuse.

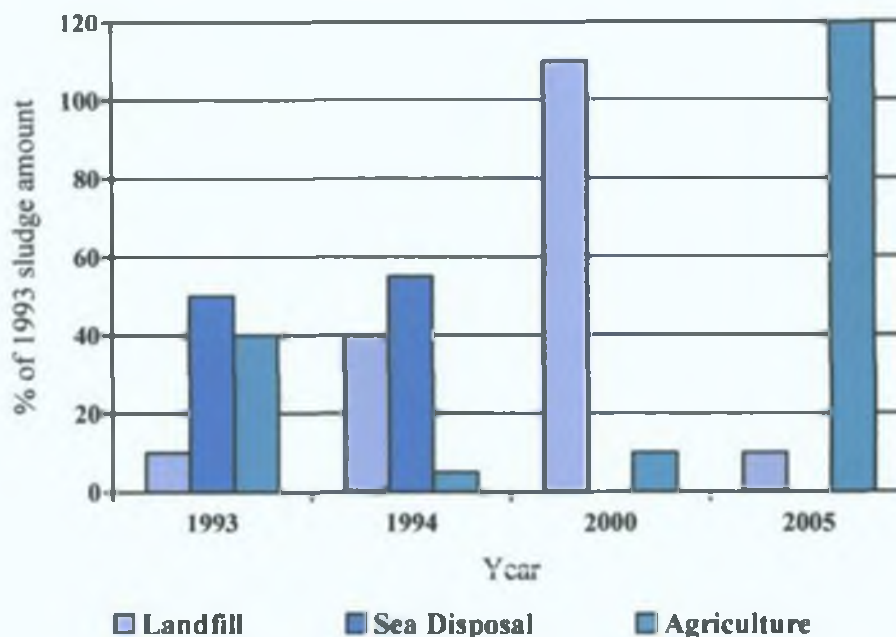


Figure 2.2 Changes in municipal sludge generation and disposal/reuse patterns in Ireland between 1993 and 2005.

Figure 2.2 shows the impact of both legislative and infrastructure developments on the quantities of municipal sludge for treatment in Ireland, and on available options for disposal/reuse.

In 1993, over 50% of sludge generated was disposed of to sea, approximately 40% was reused in agriculture, and approximately 10% was disposed of to landfill.

In 1994, the agricultural reuse option was severely restricted by implementation of the sewage sludge to agriculture regulations (except for those plants where the required treatment standard was already achieved). As a result, approximately 90% of all sludge generated was disposed of to either sea or landfill.

In 2000, the sea disposal route was eliminated by the Dumping at Sea Act. Also, by that year, the total amount of sludge for disposal had increased by 20%, as a result of the new plants built under the Urban Wastewater Directive, all of which had to be further treated to meet agricultural reuse standards. Because sufficient treatment capacity was not available, all sludge not meeting the required standard was disposed of in landfill (i.e. 90% of all sludge generated).

By 2005, due to the elimination of the landfill route, it is intended that the majority of all sludge produced will be beneficially used in agriculture, provided that it meets with required standards (Bartlett and Killilea, 2001).

2.4 A European perspective

According to Onyeche *et al.*, (2002) “*The world-wide increasing environmental awareness and its subsequent regulations have led to the application of improved technologies in wastewater purification plants*”, which has resulted in an increase in wastewater and sludge production.

In 2000, over 8.9 million tonnes of sludge was estimated in Europe, and this figure is set to increase to 14 millions tonnes by the year 2005 (Onyeche *et al.*, 2002). According to Andersen (2001) “*The debate on sludge recycling and disposal has recently been the target of growing interest*”, due to public concern relating to the potential health and environmental risks associated with using sludge in agriculture. This is because there is a public sensitivity to any process concerning sludge, arising from the faecal aversion barrier (Mathews, 1997). The public associate anything to do with faeces as potentially hazardous, particularly when, according to Mathews (1996), “*political, academic and journalistic reputations can feed off these legitimate concerns*”.

This M.Sc. Study determined that, in Ireland, several Local Authorities are land spreading the sludge at various sites. However, many farmers believe the application of sludge to land is more of a secondary issue, with their attitudes appearing negative, because they believe that there is too much animal waste to be spread on agricultural land, and that sewage sludge has a bad customer image. Alternatively, others are very optimistic about land spreading thermally dried Biosolids, originating from Ringsend,

Dublin. No concerns have yet been voiced by the food industry regarding agricultural sludge disposal, although some producers of dairy products are said to be particularly hostile towards the entire sludge issue (Andersen, 2001).

Some European countries are opposed to the reuse of Biosolids in agriculture. For example the farming community in both Finland and Luxembourg are generally hostile towards land spreading sewage sludge, mainly due to pressures associated with using animal manure. So much so, that in 1990, the Finnish Union of Agricultural Producers asked for a ban on recycling sludge to land. In 2001, they renewed their stance against the use of sludge in agriculture (Andersen, 2001).

In France, the situation was particularly controversial, where, until recently, the farmers union supported the development of recycling sludge to agriculture, on the condition that additional quality controls and an insurance fund system were set up. The situation has now changed, as farmers unions (the FNSEA and CDJA) asked for an official ban on the use of sewage sludge, because the current treatment methods used were not considered sufficient to address the risks related to the recycling of sewage sludge to agriculture (Andersen, 2001).

In 1999, the Swedish Federation of farmers (LRF) recommended that their members stop using sludge, due to concerns relating to the quality of sludge. In the Netherlands (since 1991) and Flanders (since 1999), almost all use of sewage sludge in agriculture has been prevented due to regulatory requirements (Andersen, 2001).

In other European countries, there is support for reuse. For example in the United Kingdom, the farmers association support the use of sludge in agriculture, both for economic and agronomic reasons. In Germany, opinion has recently swung in the favour of land spreading sewage sludge, due to it being considered economically viable and the potential risks associated with its reuse reduced sufficiently by the existing legislation. However, due to political developments in 2001, the debate has become increasingly controversial, with some support in favour of an increase in regulatory constraints on the land spreading of sludge. In Denmark, new regulations on the use of sewage sludge in agriculture are considered sufficiently strict to reduce risks to an acceptable level (Andersen, 2001).

In Portugal, the use of sewage sludge in agriculture is a too recent issue to generate much public debate. In some cases, farmers support the use of sludge in agriculture, based on economic and agronomic reasons. In Spain, Italy and Greece the sludge debate remains limited, due to lack of unavailable information (Andersen, 2001).

CHAPTER 3

HEAVY METALS IN SEWAGE SLUDGE

3.1 Background

Sewage sludge can retain up to 96% of all heavy metals entering wastewater treatment plants. When sewage sludge (i.e. Biosolids) containing heavy metals is applied to agricultural soils, there is the likelihood, that these elements will become concentrated in sludge-amended soils (Smith, 1996).

When considering the environmental impact of sewage sludge recycling on agricultural land the principal issue of concern is considered by many to be human health (Smith, 1996). However, others believe that phytotoxicity is the main problem (Gray, 2002).

The question is, what are the safe levels of heavy metals in soil? At what levels do they become accumulated in plants? More importantly, at what concentrations do these elements create a health hazard to both livestock and humans? The answers to these questions are complex, because the availability of heavy metals in soils is dependant upon a large number of different physical, chemical, biological and ultimately environmental factors.

The following sections describe natural and human sources of metals in the environment, the sources of metals in sludge for treatment, the profiles of 13 metals analysed in this M.Sc. Study, the way in which metals in sludge interact with soils and the effect of heavy metals on humans, animals and the environment.

3.2 Sources of heavy metals in the natural environment

Heavy metals are defined as those elements in the periodic table with a density of greater than 6 g/cm^3 (Davis, 1980). Metals, unlike organic contaminants do not have an environmental half-life, rather they persist indefinitely in the environment (Aldinger, 2002).

Heavy metals may be introduced into the environment as a result of natural weathering, erosion and atmospheric inputs in conjunction with a range of anthropogenic activities (Weigert, 1991). According to Foster and Charlesworth (1994), "*an analysis of trends in metal production and product usage suggests that the latter now makes a greater*

contribution to the total flux of heavy metals to the environment in comparison with the late 19th and early 20th centuries”.

Foster and Charlesworth (1994) reported that municipal wastewater treatment plants receive 31% of their heavy metals from domestic sources and 69% from industrial sources. Although, according to ICON (2001), “*faeces contribute 60-70% of the total load of Cd, Zn, Cu and Ni in domestic wastewater*” and approximately 30% of the input of these elements arises from mixed wastewater, composed of both domestic and industrial wastewaters. There has been a significant reduction in the inputs of metals to sewers arising from industrial discharges, because of improved trade effluent controls, and changes in the nature of traditional manufacturing industries, as well as the adoption of cleaner manufacturing technologies (Smith, 1996).

According to Gray (2001), Irish industry remains the major source of Cd, Ni and Pb, but these metals are generally present in such low concentrations that it is the domestic sources of metals (in particular Cu and Zn in conjunction with small amounts of Cd and Pb) that limit the application of sewage sludge to agricultural soils.

3.3 The heavy metal composition of sewage sludge

Sewage sludge is a valuable fertiliser resource and soil improvement material for land due to the N, P, S, Ca, Mg, K and micro-nutrients it contains, which are readily available for plant uptake, in addition to organic matter which improves the water retaining capacity and soil structure (Hasselgreen, 1998; Nyamangara, 1998; Yoshizaki and Tomida, 2000).

Sewage sludge may also contain several biologically available, potentially toxic metal contaminants (i.e. Pb, Cd, Cr, Cu, Ni, Hg, Zn) because it represents an agglomeration of pollutants originally present in the wastewater (Bodzek *et al.*, 1997; Chang *et al.*, 1995; Cole, *et al.*, 2001; Qiao & Ho, 1997; Wang, 1997). Typically, the heavy metal content of sewage sludge is 0.5-2.0% on a dry weight basis and in some cases, extremely high concentrations of up to 4% chromium, copper, lead and zinc have been reported (Sreerishnan and Tagi, 1995).

The principal elements of concern that limit the sustainable recycling of sludge to agricultural land are copper and zinc, because they potentially reduce N₂-fixation in sludge-treated soils. They reach their maximum soil concentration values in approximately 70-80 years, when sludge is applied at the annual rate of 170 kg of N/ha (Smith, 1997).

In general, metals in sludge are present in very stable, insoluble forms (Qiao, and Ho, 1997), and are organically bound, thus less available for plant uptake than the more mobile metal salt impurities found in commercial fertilisers (Frost and Ketchum, 2000). Significant factors controlling the availability of metals to crops in sludge-amended soils are both the chemical and physical properties of sewage sludge (Smith, 1996).

An evaluation of total levels of metals in sewage sludge may be useful as a global guide when characterising sewage sludge, but it is becoming more evident that the determination of specific chemical forms of heavy metals and their mode of binding in soil is very important, in order to estimate their mobility, bioavailability, and toxicity (Alonso Alvarez *et al.*, 2002; Campbell *et al.*, de Siloniz *et al.*, 2002; 1997; Fytianos *et al.*, 1998; Perez-Cid *et al.*, 1999; Perez-Cid 2001; Scancar *et al.*, 2000; Stenger, 2000; Walter *et al.*, 2002; Zhang *et al.*, 2002).

Because of the antagonistic and synergistic effects of heavy metals, complete evaluation and monitoring of sewage sludge should be performed (Joshua *et al.*, 1998), to determine the most suitable land application rates (Navas, 1998). Also, the long term effects of land treatment on normal soil functioning should also be assessed, especially since there is a body of evidence to suggest that these metals at or close to the soil limits may adversely affect important soil processes (Filcheva, 1996). The 13 metals reviewed in the following sections were those analysed in sludge samples from Regional Sludge Treatment Hub Centres.

3.3.1 Cadmium (Cd)

Cadmium has an atomic number of 48, an atomic mass of 112.4, and there are eight naturally occurring isotopes. It has a melting point of 320.9°C and a boiling point of 767°C. The main sources of cadmium are metal plating and mining wastes. Food is the most important source of cadmium in humans (Stoepler, 1991), with approximately

one third of cadmium originating from animal products and two thirds from plant products (Hapke, 1991a).

It is a non-essential element for plants, animals and man. As a result, it was considered by Dean and Suess (1985) as "*the most important contaminant because it can be accumulated from the soil by certain food plants*", while also exhibiting a toxic effect on the soil microbial activity (Moreno *et al.*, 2002). It is also believed to take precedence over all other heavy metals as being the most toxic and rate-limiting element. It is even thought to be more important than organic contaminants (especially pesticides, polychlorinated biphenyls and polycyclic aromatic hydrocarbons), based on the understanding that human intake of organic contaminants resulting from sludge application is minor, thus, unlikely to cause major health related effects (Dean and Suess, 1985)

Cadmium is found to accumulate predominantly in the kidneys. A cadmium concentration of $200\mu\text{g/g}^{-1}$ in the renal cortex can result in renal tubular dysfunction (Dean & Suess, 1985). Heavy long-term exposure to this element may produce irreversible adverse adrenal effects, particularly when there is a vitamin and protein deficiency in conjunction with bone disease (Hapke, 1991b; Stoeppler, 1991).

According to Smith (1996), results from feeding trials have shown that livestock ingestion of Cd enriched soil, at twice the statutory level, will not cause unacceptable levels in the offal, thereby constituting no major health effects, particularly when offal comprises only a small percentage of the human daily diet.

The availability of Cd in soil is dependant upon soil type, and pH (Weigert, 1991). The cadmium content, generally, is found to accumulate in the edible portions of plants to levels that may be harmful to humans, particularly if consumed over long periods of time and in large quantities, whilst having no apparent effects on the crops themselves. Cereals and potatoes represent the most important sources of dietary cadmium for the standard consumer, due to the large quantities consumed, compared to lettuce, which is found to have little human impact (Smith, 1996).

In a 1995 review, Gardiner reported that soils containing high levels of cadmium should only be used for the production of non-food crops or non-leafy foods such as grains, fruit or nuts, because the fruiting parts of plants usually contain lower metal concentrations than the vegetative parts. The cadmium content on average is found to decrease significantly in plants from roots to shoots, with many species showing significantly lower levels of cadmium in fruits rather than the shoots (Stoeppler, 1991).

3.3.2 Chromium (Cr)

Chromium (Cr) has an atomic number of 24 and an atomic mass of 51.996. It is a silvery, shiny, malleable metal with a density of 7.2g/cm^3 . Its melting point is 1860°C and its boiling point is 2670°C (Gauglhofer and Bianchi, 1991). Metal plating and mine tailings are the main sources of chromium found in the environment (Girovich, 1996).

Generally, chromium is found in soils at concentrations ranging between 10 to 90 mg/kg, with plants usually containing 0.02-14 mg/kg of chromium on dry weight basis (Stoeppler, 1991).

Chromium poisoning can cause skin disorders and liver damage, while trivalent chromium is believed to be carcinogenic (Chua, 1998).

It is found to exist in VI oxidation states, but it is only the trivalent and hexavalent chromium compounds that are of practical importance. The rate of plant uptake is strongly influenced by the oxidation state of the element (Gauglhofer and Bianchi, 1991).

Trivalent chromium is the most stable form present in nature. Chromium VI has a higher transport index and is more toxic than Cr III. Plants tend to accumulate higher concentrations of Cr III in the roots, whereas higher concentrations of Cr VI are found to dominate in the shoots (Weigert, 1991). Plants have the tendency to accumulate chromium, showing some species specificity. Animals on the other hand, are found to excrete excess chromium from their diets (Gauglhofer and Bianchi, 1991).

Soil weathering releases chromium. Lime treatment has been found to reduce the activity of Cr III and result in the increased toxicity of Cr IV, which is toxic in low

concentrations and is dependant on the pH of the soil. However, the activity of Cr IV is short lived because it is quickly reduced to Cr III (Gauglhofer and Bianchi, 1991).

3.3.3 Barium (Ba)

Barium has an atomic number of 56 and an atomic weight of 137.327. Its melting point is 727°C and its boiling point is 2143°C. Barium is a relatively abundant element in nature. Most foods contain small concentrations of this element. The toxicity of barium is associated with its solubility. Because there are no sludge data available on barium, reference is only made to its toxicological effects and exposure pathways.

Barium is not an essential element of the body, and its exposure pathways are primarily ingestion and inhalation. It is absorbed, retained and excreted in much the same way as calcium ions. The soluble forms of barium are toxic to man and the environment. Barium poisoning results in gastroenteritis, muscular paralysis, decreased pulse rate and ventricular fibrillation. Its toxicity is linked to a competitive inhibition of potassium ions and the removal of sulfate ions (Hall, 1997).

3.3.4 Copper (Cu)

Copper has an atomic number of 29 and an atomic mass of 63, its melting point is 1083°C and its boiling point is 2590°C (Scheinberg, 1991). The main environmental sources of copper are industrial discharges, mining and mineral leaching, which is dependent on weathering, drainage, oxidation-reduction potentials, the amount of organic matter in the soil, and pH.

Copper is an essential trace element, necessary for productive plant and animal growth. It is not very toxic to animals, but is found to accumulate in the liver (Hapke, 1991a). It is toxic to both plants and algae at moderate levels.

Humans absorb about 50% of dietary copper in the gastrointestinal tract, which is found to concentrate in the liver, brain and in the kidneys. Adult humans require about 2-5mg of copper per day. Children require more, depending on body weight (Scheinberg, 1991).

Oral uptake of excess copper in mammals causes local irritation, gastroenteritis and vomiting. The symptoms of acute poisoning are weakness, anorexia, dyspnoea, renal and muscular damage, and haemolytic anaemia (Hapke, 1991b).

The northern half of Ireland has been found to have elevated copper levels. It is thought that high concentrations of Fe can reduce the availability of Cu to plants and animals, and because many Irish soils contain high concentrations of Fe, it is thought to be a contributory factor of Cu deficiency in livestock. As a result, farmers often administer copper doses to livestock at regular intervals, particularly in areas where there are copper deficient soils (Coulter *et al.*, 1999; Vierboom *et al.*, 2002).

Copper deficiencies in animals can occur at 2 mg/kg, while toxicities can occur at levels greater than 20 mg/kg, with sheep being less tolerant than cattle to elevated levels of copper (Coulter *et al.*, 1999). The symptoms of copper toxicity may occur in sheep with a normal copper intake of 8-10 ppm and it is even more evident when molybdenum concentrations are below 0.5 ppm. The principal effects of excess copper experienced by animals are concerned with the liver and blood as fatal hepatitis or haemolytic anaemia (Scheinberg, 1991).

According to de Siloniz *et al.*, (2002), copper is one of the most abundant toxic heavy metals present in municipal wastewaters and sewage sludge. This is because it is ubiquitously distributed and is very easily complexed. It is involved in many metabolic processes in living organisms, some of which involve the redox potential of Cu I/Cu II (Scheinberg, 1991).

A desirable copper content of 10 mg/kg in soils is required for a good pasture. An application of copper sulphate at a rate of 10 to 20kg/ha is found to raise the copper herbage levels to between 8-10 mg/kg. One application will maintain this for many years. When the copper content of soils is adequate, application of N is found to increase the copper content of pastures, and *vice versa* (Coulter *et al.*, 1999).

3.3.5 Lead (Pb)

Lead has an atomic number of 82 and an atomic mass of 207.19. Its melting point is 327.5°C and it has a boiling point of 1740°C. Lead is a widely distributed naturally occurring non-essential element (Duffus, 1980), present in the environment in a wide range of physical and chemical forms (Southwood, 1983). Lead tends to be concentrated at point source areas due to low solubility of the compounds that are formed upon contact with the soil (Ewers and Schlipkoter, 1991a).

Its main anthropogenic sources are industry, mining, leaded petrol, plumbing and lead bearing minerals. It is found in rocks at concentrations of 10-20 ppm and is reported to be present in soil at concentrations ranging between 10 to 40 mg/kg dry weight (Ewers and Schlipkoter, 1991a). Approximately half of human lead intake is through food, with more than half originating from plant sources. The normal food chain causes a dilution factor of 1000 rather than an accumulation of the metal (Hapke, 1991a).

Absorbed lead in humans enters the bloodstream from where it is distributed to various organs and tissues. 95% of lead in the human body is bound to the erythrocytes. It is concentrated temporarily in the liver and kidney cells and thereafter in bone tissue. Under certain conditions, such as starvation, it may be released from these deposits and become reactive again in the body (Ewers and Schlipkoter, 1991a).

The acute signs of lead poisoning in animals are disorders of the central nervous system (CNS), excitement, stupor or depression, motor abnormalities, blindness. Some animals may die without showing any of these symptoms. Symptoms of severe lead poisoning in humans include abdominal pain, constipation, vomiting, asthenia, paresthesia, psychological symptoms, and diarrhoea (Ewers and Schlipkoter, 1991a).

Lead poisoning is of particular concern in children, where it causes learning difficulties. The risk of lead poisoning to children from agricultural sources is dependant on the concentration of Pb in the soil (Smith, 1996), but because lead is so immobile in the soil the only effective pathway is direct ingestion of soil (Dean & Suess, 1985).

The majority of lead particles deposited on the soil are retained and eventually mixed into the surface layers, or deeper in cultivated soils (Hutchinson & Meema, 1987),

thereby reducing its availability to organisms. Lead may be precipitated as carbonate in calcareous soils. It is retained in the soils by adsorption on hydrous oxides, notably ferric hydroxide, and adsorption is found to increase with an increase in pH (Wild, 1988).

When natural background concentrations of lead are present in the soils, only trace levels are found in plants. It is only when the concentration of lead in the soil increases, or when the binding capacity of the soil for lead decreases, that the amount of lead absorbed by plants increases. The transfer of lead from the soil to plants only happens when lead concentrations are more than 5,000 mg/kg dry matter (Hapke, 1991a).

3.3.6 Mercury (Hg)

Elemental mercury has an atomic number of 80, an atomic mass of 200.59, a melting point of -39.8°C and a boiling point of 357°C . In nature, mercury can exist in a number of different physical and chemical forms. It is present in soils at concentrations ranging from 20 to 150ppb (Von Burg and Greenwood, 1991).

Its main sources include minerals, coal combustion, pesticides, fungicides, batteries, and pharmaceutical products. The toxicological effects of mercury include neurological damage, headache, depression and birth defects (Hutchinson and Meema, 1987). Plants growing in Hg rich soils absorb only a small amount of mercury through their roots, and are usually present in the form of inorganic mercury compounds (Hapke, 1991a).

Mercury is bound to the upper topsoil (0-10cm), and only very low concentrations are found in the subsoil. It is thought that the difference is attributable to the binding of Hg by organic matter (McNab *et al.*, 1997).

However, because the availability of mercury in sludge amended soils is very low, it does not pose significant health effects (Dean & Suess, 1985; Hutchinson & Meema, 1987; Smith, 1996).

3.3.7 Nickel (Ni)

Nickel is a silver white metal, with an atomic mass of 58.71, a melting point of 1453°C and a boiling point of 2732°C . Nickel is present in the earths crust at 0.008% and its

main environmental sources are minerals and industrial discharges (Sunderman and Oskarsson, 1991).

It is normally present in food. Oral ingestion of high amounts can result in mucosal irritation followed by vomiting. After the absorption of high doses, tremors and ataxia have been reported. The absorption of nickel over prolonged periods of time results in weight loss and metabolic inhibition by disturbing carbohydrate metabolism, with liver and kidney degeneration also found to occur. Animals have a slow absorption and high excretion rate for nickel, resulting in zero accumulation (Hapke, 1991b).

The majority of nickel compounds exist as relatively soluble compounds at pH values of less than 6.5, whereas nickel exists as insoluble nickel hydroxides at pH values of greater than 6.7. The extractable nickel content of soils affects the uptake of this element by plants, which is influenced by the soils physical, chemical and biological factors (Sunderman and Oskarsson, 1991).

3.3.8 Zinc (Zn)

Zinc has an atomic number of 30 and an atomic mass of 65.39. The melting point of zinc is 419.58°C and its boiling point is 907°C. Zinc occurs in almost all minerals of the earths crust, and its anthropogenic sources include industrial waste, metal plating and plumbing. Zinc is an essential element in many metalloenzymes and aids wound healing. When present at higher concentrations it is toxic to plants (Ohnesorge and Wilhelm, 1991).

The recommended daily allowance (RDA) is 10mg/d for children and 15mg/d for adults. In medical science, zinc is usually used to promote wound healing, but can induce anaemia in cases where there is a low copper status (Ohnesorge and Wilhelm, 1991).

The ingestion of large doses of zinc by humans can cause damage to the upper alimentary canal, followed by shock symptoms. In animals, symptoms of chronic zinc toxicity include diarrhoea, subcutaneous edema, profound weakness, and jaundice (Ohnesorge and Wilhelm, 1991). Treatment is unnecessary, since replacement with food containing low zinc content results in lessening of the symptoms (Hapke, 1991b).

The toxicity of zinc to plants is generally low and is only observed in soils heavily contaminated with this element. Some plants show signs of zinc toxicity at levels of 300 mg/kg, while others, are much more resistant (Ohnesorge and Wilhelm, 1991). Levels exceeding 200 kg/ha⁻¹ of zinc were found to cause a significant reduction in corn yields (Smith, 1996).

The concentration of zinc in non-contaminated soils ranges from 10 to 300 mg/kg. In lime rich soils the availability of zinc is reduced above pH of 7.4. Zinc becomes more available at low pH with washout a possibility under acidic conditions. In Ireland, zinc has been found to range in soils from 25 to 45 mg/kg, and is found to be present in low concentrations in North Meath, Louth, Cork and Carlow (Coulter, *et al.*, 1999).

The zinc content of plants is dependant on the vegetative stage, availability of the element and type of plant species, which in turn is influenced by the geological origin of the soil. Usually, the highest concentrations of zinc are found in young plants (Ohnesorge and Wilhelm, 1991).

By increasing the availability of Zn in soils, uptake of Zn by food crops through the application of sewage sludge to agricultural land may result in a positive effect on human health, especially in females who have a lower dietary intake of Zn, compared to men of similar age (Smith, 1996).

3.3.9 Arsenic (As)

Arsenic has an atomic number of 33 and an atomic mass of 74.9216 (Leonard, 1991). Arsenic is a toxic metalloid, and it is introduced into the environment through the combustion of coal, pesticides and mine tailings (Girovich, 1996; Hutchinson and Meema, 1987).

The earth's crust and igneous rock contains approximately 3 mg/kg arsenic. The level of arsenic in the soil is approximately 7 mg/kg. Most foods contain low levels of arsenic (0.25 mg/kg), and the level of natural arsenic in plants seldom exceeds 1 mg/kg. The daily human intake of arsenic varies between 0.01 and 0.3 mg, depending on the diet. Median arsenic concentrations ranging between 0.02 to 0.06 ppm are found in normal human organs and body fluids (Leonard, 1991).

Arsenic is found to impair plant growth. An oral dose of 1 to 25 mg/kg (sodium arsenite) is considered lethal for domestic animals. It is also found to affect tissues rich in oxidative enzyme systems and is a capillary poison, resulting in hypovolemia, shock, and circulatory failure. Inorganic arsenic poisoning results in intense abdominal pain, vomiting, diarrhoea, weakness, staggering, hypothermia, and death (Leonard, 1991).

Soil texture and competing phosphates greatly influence the plant uptake of arsenic. Low levels of phosphates displace arsenic from the soil particles to increase uptake and phytotoxicity, while larger concentrations of phosphates compete with the arsenic at the root surfaces in order to decrease arsenic uptake and phytotoxicity (Leonard, 1991). According to Carbonell-Barrachina *et al.*, (1999), at near neutral pHs soluble arsenic is at its maximum, whereas under both acidic and alkaline pHs it is found to decrease.

3.3.10 Molybdenum (Mo)

Molybdenum is a silvery white metal with an atomic number of 42 and an atomic mass of 95.94. It has a boiling point of 5560°C and a melting point of 2617°C. It is present in the earth's crust at levels of approximately 1.5 ppm, and its main sources are natural sources and industrial discharges. The molybdenum concentration of herbage is found to range from 0.1 to 0.3 ppm dry matter (Davis, 1991).

It is considered an element of special concern that needs to be controlled, because cattle and other ruminants grazing on forage crops grown in high molybdenum soils can develop copper deficiencies, known as molybdenosis. This is essentially a secondary form of copper deficiency and is characterised by diarrhoea, depigmentation of hair or wool, neurological disturbances and premature death (Davis, 1991). Its availability, and consequently its potential toxicity to grazing animals, is enhanced when lime is added to the sludge and the soil pH is maintained at 6.5-7.0 (Williams, 1990).

Molybdenum poisoning can be found to occur in herbivores grazing on pastures containing large quantities of molybdenum of up to 250 mg/kg dry matter (Hapke, 1991b). Molybdeniferous soils are found to occur in County Laois. These soil series cover large parts of the county and Teagasc have indicated that 76% of the available agricultural land is used for pasture (McGlinchey, 2001). Chronic poisoning has only been reported in sheep, cattle, horses and swine and the symptoms include growth

retardation, anaemia, anorexia and coordination disorders. In cattle, hair discolouration is found to occur along with enteritis and diarrhoea (Hapke, 1991b). Plants found growing in enriched Mo soils are found to absorb high concentrations of this metal, resulting in concentrations of up to 250 mg/kg (Hapke, 1991a).

3.3.11 Selenium (Se)

Selenium has an atomic number of 34, an atomic mass of 78.96. Its melting point is 217°C and its boiling point is 685°C. Its main sources include minerals, coal, and industrial discharges. It is an essential element at low levels and a toxic element when present at high levels. The average content of selenium in the earth's crust is between 0.05-0.09 ppm. Selenium concentrations are found to vary from 0.1ug/g, in selenium deficient soils, to 1ppt in selenium rich areas (Fishbein, 1991). In County Meath, soils are found to have extremely high Se levels. The affected soils are generally low lying, poorly drained, rich in organic matter and neutral in reaction to alkali (Entec and O'Dwyer, 2001a).

The symptoms of chronic toxicity include loss of vitality, lameness, elongated and disfigured hooves, degeneration of the internal organs, and hair loss. These symptoms are commonly caused when livestock ingest vegetation containing selenium concentrations of 3 to 20 ppm (Fishbein, 1991; Hapke, 1991b).

Humans require approximately 60-120ug of selenium per day to prevent deficiency diseases. Human symptoms of selenium toxicity include bad teeth, icteroid skin, dermatitis, arthritis, gastrointestinal disturbances, hair loss, and diseased nails (Fishbein, 1991).

The concentration of selenium present in plants will vary depending on the type of species and the soil characteristics, together with the chemical form of selenium present. In acidic soils, selenium is bound as ferric selenite, which has a very low solubility, thereby reducing its availability to vegetation (Fishbein, 1991).

A lot of plants are found to convert selenium into volatile compounds, such as methyl and dimethyl selenides, with some plants being tolerant to selenium. It has strong interactions with other nutrients such as vitamins E and C. It also functions as an

antagonistic element, counteracting the toxicity of metals such as mercury, cadmium, arsenic, silver, lead, cis-platinum, and copper (Fishbein, 1991).

3.3.12 Iron (Fe)

Iron has an atomic number of 26 and an atomic mass of 55.8, its melting point is 1535°C and its boiling point is 3000°C. It is a ubiquitous element, and is the fourth-most abundant element, constituting approximately 4.7% of the earth's crust (Huebers, 1991; Weigert, 1991).

It is toxic to cells, because it catalyses the production of the hydroxyl radical which is the most potent oxidising agent that can exist in aqueous media. Iron concentrations ranging between 10 to 200mg/l of nutrient solution have been found to be toxic to plants and amounts in excess of 200mg/day, are considered toxic to man (Huebers, 1991). Levels of 2,400 mg/kg of iron may be toxic for cattle, although undesirable effects can appear at lower, sub toxic doses (Madejon *et al.*, 2002).

The availability of iron in the soil is not only dependent on the concentrations of iron present, but also on the pH and phosphate content of the soil, as well as other metals competing for its absorption (Huebers, 1991).

3.3.13 Cobalt (Co)

Cobalt has an atomic number of 27; an atomic mass of 58.93 and it belongs to the transition elements (Schrauzer, 1991). It is a component of vitamin B12 and is essential for animals and man.

Trace amounts of cobalt are found in all rocks, minerals and soils, and the average content of this element in the earth's crust is approximately 18 ppm. It is pH dependant and is found to be more mobile in acidic soils than alkaline soils (Schrauzer, 1991). The average concentration of cobalt found in Irish soils is below 10 mg/kg (Coulter *et al.*, 1999).

Ingestion of large amounts of cobalt causes gastroenteritis, liver and kidney damage. Because cobalt is excreted completely within two days, no accumulation within the

body occurs. Acute Co poisoning can be treated with EDTA (i.e. chelating agent) (Hapke, 1991 a). Plant uptake of this element is species dependant (Schrauzer, 1991).

3.4 The interaction of heavy metals in soils and sludges

Soil is a complex porous matrix with a high metal binding capacity characterised by clay, organic molecules and hydrous metal oxides. Usually, metals are present in the soil as part of the soil parent material or soil minerals, precipitated with other soil compounds, sorbed on exchange sites (i.e. metal oxides or hydroxides, clay minerals and organic matter), dissolved in the soil solution, or alternatively embodied in micro-organisms, plants or animals (Schmitt and Sticher, 1991).

Heavy metals are distributed in sludges between the liquid and solid phases, within the adsorbed and exchangeable forms or incorporated in crystalline and amorphous solids (Fytianos *et al.*, 1998). According to Fytianos *et al.*, (1998) *“The distribution ratio of the total metal content between the sludge and the water phase, depends upon the chemical properties of the metal and of the physicochemical properties of the sludge, which is dependant on the conditions employed during sludge treatment, such as pH, temperature, redox potential, presence and concentration of complexing or precipitation agents”*.

Angelidis *et al.*, (1990) found that heavy metals in sludge are found to exist in different chemical phases, these include (a) dissolved, (b) adsorbed, (c) acid-reducible, (d) oxidisable, and (e) residual. Heavy metals in both the dissolved and adsorbed phase are the most available to organisms, and metals in the oxidisable phase are also available through the food chain following sewage sludge disposal. Metals in the residual phase cannot be released because they are strongly bound to the sludge particles, thereby representing no major environmental concerns. Finally, metals in the acid reducible phase can be partially released under acidic conditions, but, in general, are significantly less available to the environment than metals in phases (a), (b) and (d).

As a result, there are considerable difficulties in interpreting the effects of heavy metal contaminated sewage sludge when applied to different soils, because the interactions

between both sludge and soil are complex (Beckett and Davis, 1979; Campbell *et al.*, 1997).

The period immediately following application of Biosolids is when Biosolid-borne metals are most available. With time, as organic decomposition rates diminish, heavy metal availability is reduced (Walter *et al.*, 2002). This is because, when sewage sludge is incorporated into the soil, it is subjected to microbial oxidation, which has the potential to release heavy metals to the soil environment and thus the food chain (Angelidis, 1990; Obrador *et al.*, 2001). The microbes complex the organic matter present in the sewage sludge. Metal ions are released which are then inorganically immobilised (Beckett and Davis, 1979).

It has been cited in several studies that the mobility, activity, and bioavailability of heavy metals in a soil/plant system is influenced by pH, temperature, redox potential, cation exchange capacity of the solid phase, competition with other metal ions, ligation by anions, clay and organic matter contents, concentrations in the soil matrix, nutrients, soil bulk density, soil moisture content, dissolved organic carbon, drainage, soil carbonates, salinity, precipitations, erosion, and land use practice (Antoniadis, 2002; Berrow and Buridge, 1991; Forste 1996; Gove *et al.*, 2001; Martinez and Motto, 2000; Page *et al.*, 1987; Richards *et al.*, 2000; Schmitt and Sticher, 1991; Weggler-Beaton *et al.*, 2000;).

According to Cornu *et al.*, (2001) metal mobility in soils "*depends on two main factors: (1) water transfer through the soil, and (2) chemical interaction of the trace metals with the solid phases of the soil (sorption/desorption, precipitation/dissolution, complexation by the organic matter)*". Whereas Smith (1996), believes that there is little potential for trace metal mobility via water percolation through the soil profile resulting in the contamination of groundwater. On the other hand, Richards *et al.*, (1998), cited several studies reporting some downward metal translocation in soil, noting a potential correlation with climate.

The most readily available elements are those present in the soil solution as either ionic state or as soluble organic matter complexes. Those that are least available are found firmly bound within soil structures. Between both of these extremes exists charged sites

on the surface of very small particles, such as organic matter, clay and silt, which are characterised by their ability to release one ion in exchange for another (Berrow and Burridge, 1991).

According to Hassen (1998), "*The binding of metals to humic complexes seems to be an important factor that potentially controls metal mobility in soil*". Heavy metals introduced into the soil can be present in various physicochemical forms (Walters and Cuevas, 1999), which are further described by Hassen (1998), "*as simple or complex ions in solution, exchangeable ions, linked to organic matter, and co-precipitated with oxides, carbonates and phosphates*", with clay minerals found to absorb far smaller quantities than other sorbents (i.e. oxides and organic material) (Schmitt and Sticher, 1991).

Since the movement of heavy metals within soils is mainly in the solution phase, chemical factors that control the distribution of metals between the solid and solution phase influence the mobility of heavy metals. Adsorption and desorption processes are some of the soil chemical reactions controlling mobility of heavy metals. Determining the metal sorption properties of soil gives a good indication of the mobility, and thus the bioavailability of these elements. It is therefore important to have an understanding of sorption properties, particularly when determining loading rates of heavy metals to soils (Barry *et al.*, 1995).

It was described by Richards, (1998), that the movement of metal species in the preferential flow paths as non-absorptive metal/organic complexes, limits the potential for interaction and adsorption in the subsoil, thereby facilitating mobility.

However, several studies, cited by Martinez and Motto, (2000), reported that pH seems to have the greatest effect of any single factor on the solubility and speciation of metals in soils. This is because pH affects the microelement uptake, thus controlling the degree to which these elements react within the soil (Artola *et al.*, 1997; Berrow and Burridge, 1991; Forste, 1996; Scancar *et al.*, 2000). In general, acidification of the soil is believed to increase the solubility of heavy metals and their availability for plant uptake or transport to ground waters (Scancar *et al.*, 2000). This happens when the pH of soil amended with sewage sludge decreases due to the production of organic acid and

nitrification (Wong *et al.*, 1998). Metal uptake is found to decrease linearly with increased soil pH, with the exception of molybdenum, which becomes more available to plants at near-neutral or alkaline pH's (Artola *et al.*, 1997; Berrow and Burrige, 1991; Forste, 1996; Scancar *et al.*, 2000).

Manganese is most sensitive to elevated pHs. This is because, with an increase in soil pH, its availability is found to decrease. This can result from the application of Biosolids treated with lime. In acidic soils, it becomes much more soluble and available to plants, and can even cause toxicity at extremely low pHs. At a pH of 6.3 manganese deficiencies can occur, which makes it the primary consideration with respect to elevating pH by using lime-treated Biosolids. In well-drained alkaline or neutral soils manganese deficiencies can also occur (Forste, 1996).

It has been reported by Moreno, (1996), that the total quantity of some metals in soil, regardless of its properties, is correlated to the quantity of metal absorbed by the plant. Copper and nickel however, showed no correlation between the soil concentrations and the quantities absorbed by the plants, implying that these metals remained bound to the organic matter in the soil, thus, preventing it from being absorbed by the plants. Madyiwa *et al.*, (2002), reported that *"it is the bioavailable metal fraction in the soil that is correlated to plant uptake"*.

Williams (1990) believed that, *"metals added to soil are firmly adsorbed onto organic matter and clay surfaces and, as such, are not subject to leaching"*. However, Gove *et al.*, (2001), suggested that a possible 'time-bomb' effect might occur, due to plant uptake and leaching of heavy metals, which would increase with time, due to the decomposition of organic matter. They also state that *"in sand and sandy soils, which are low in organic matter, metal adsorption can be expected to be low, and therefore, leaching is likely to be relatively high"*. Heavy metals remain in the soil almost indefinitely. Only in acidic soils are some metals more mobile and readily adsorbed by plants (Schmitt and Sticher, 1991; Williams, 1990).

According to Barry *et al.*, (1995); cadmium, nickel and copper were all retained to a greater extent in the 10cm surface horizon, which is most likely due to their affinity for organic matter. The greatest capacity for arsenic occurred in the 30cm horizon where

clay, Fe and Al hydrous oxides were prevalent. Hasselgreen (1998) also stated that “metals, even though relatively large amounts of sludge application (80 tonnes DS ha⁻¹) were used, stayed in the upper 10 cm of the soil layer in which the sludge was applied”, and that the soils used were slightly organic top-soils with pH values ranging between 6 and 7. Whereas, Baveye *et al.*, (1999); reported that metals of concern were significantly increased by all sludge application rates, to a soil depth of 30cm.

3.5 The effects of heavy metals in plants and animals

Metals, when present in trace concentrations, are important for the physiological functions of living tissue and regulate many biochemical processes (Chapman 1992). However, when metals are present in high concentrations in sludge, plant growth and development can be restricted (Hapke, 1991a).

According to Gardiner (1995); “*Because heavy metals are bio-accumulated and biomagnified, acceptable non-hazardous threshold levels in soils are hard to define*”. This is because the fate of toxic metal cations is largely dependant on their interactions with the inorganic and organic soil surfaces (Bragato *et al.*, 1998). It is the chemical forms of metals that greatly influence their toxicity and bioavailability within the soil environment (Chapman 1992; Fytianos *et al.*, 1998).

The amount of sewage sludge applied to agriculture is dependant upon the toxic effects of the elements present and whether their effects are additive or not (Beckett, and Davis, 1982). These effects may only become apparent in the long-term, due to the presence of organic matter and nutrients in the sludge, that may initially stimulate plant growth and the microbial activity of the soil, obscuring the onset of toxic effects (Beckett and Davis, 1979; Campbell *et al.*, 1997).

According to Mallinckrodt (1991); “*in addition to the dose, the method of uptake also determines the intensity as well as the duration of the toxic effects,*” which can cause very different symptoms. Toxic effects depend not only on the concentrations of metals present, but also on bioavailability (Renoux *et al.*, 2001) and absorption, which is a function of solubility (Filcheva, 1996). The metal fraction available to plants may not

necessarily be the same as the fraction at risk of loss by leaching to the environment (Qiao *et al.*, 2002).

According to Berrow and Burridge in 1991, “*The uptake of metals from soil by plants through their roots to their above-ground parts or under-ground storage organs depends on (1) the total amount of metals present in the soil; (2) the proportion of the total metal that is accessible to the plant roots, and (3) the ability of the plants to transfer the metals across the soil-root interface*”.

The concentration of metals in food is also dependant on the conditions under which it was produced and processed (Hapke, 1991a; ICON, 1993), together with the climate and the degree of maturity of the plant at the time of harvesting (Weigert, 1991).

Heavy metals, when present at high concentrations in soils, can cause visible injury to plants and inhibit plant growth. Healthy plants can sometimes contain metals at levels that are tolerant to plants but can be potentially toxic to grazing animals, humans or soil-microorganisms. Concentrations of 5-10 mg/kg dry matter of Mo in herbage can induce Cu deficiency in cattle; while plants can tolerate levels of up to ten times this concentration (Berrow and Burridge, 1991; Madywia *et al.*, 2002).

In the UK, Chumbley (1971) reported that the relative phytotoxicity of Zn/Cu/Ni was additive, only to be later criticised by Beckett and Davis in 1982, who stated that the toxicity of these metals was not additive, but rather they acted independently.

In general, it is unlikely that elements other than Zn, Cu and Ni will have toxic effects on crop yields, due to low concentrations present in sludge and/or because they are immobile in soil, therefore are not adsorbed by plants (Smith, 1996).

Heavy metals have intrinsic characteristics that affect microbial metabolism and reproduction. They block the enzyme systems or interfere with some essential cellular metabolite of oxidizing bacteria and protozoa. They are also known to coagulate and precipitate proteins, many of which are denatured by this action, resulting in inhibition and even cell death at some high concentrations (Dilek and Yetis 1992; Gosh and Bupp, 1992).

Human exposure to heavy metals is dependant on several different factors, including pH, soil structure, types of cultures more or less favourable to the transmission of metals, the concentration of metal components present both in the soil and in the sludge, sludge processing and land disposal methods and the food consumption habits of the individual (Stenger, 2001).

Once metals are absorbed in the body (i.e. via gastrointestinal, respiratory tract or through the skin) they enter the blood stream, prior to being rapidly distributed throughout the body. The rates of distribution are determined by the blood flow rate through the organ and the rate of ease at crossing the capillary walls and penetrating into the cells of individual tissues (Ewers and Schlipkoter, 1991b). Metal accumulation happens in specific tissues. The extent is determined by the duration of exposure together with the concentration of the metal in the organism's environment (Hapke, 1991b). The consequences of this are not only measured in terms of mortality but also in morbidity, which means that life expectancy may be reduced (Stenger, 2001).

It is important to note that the symptoms of acute and chronic metal poisoning in humans and animals can be completely different. For example, acute mercury poisoning can cause nausea, vomiting and diarrhoea, and possibly death from shock within the first 24 to 36 hours. Whereas chronic poisoning caused by the same compound causes damage primarily to the nervous system, followed by kidney damage (Mallinckrodt, 1991).

Neither Pb or Hg are absorbed by crops and thus do not pose a threat through the dietary intake of plant foods grown in sludge amended soils. The United States EPA risk assessment models suggest that the most critical pathway of exposure to Cd, Pb and Hg is through the direct ingestion of sludge by children, particularly if sludge is to be used in urban housing and in gardens (Smith, 1996).

In general, heavy metals in sludge, with the exception of cadmium are not expected to affect human health through accumulation in the food chain and fodder plants (Hani, 1991). Cadmium is of concern because plants can absorb it, with no significant effects, thereby posing a potential threat to grazing animals (Berrow and Burridge, 1991; Smith,

1996). There is little or no risk to humans when sludge containing cadmium is disposed of to forest soils or to lands that produce fodder or seed crops (Hing *et al.*, 1991).

CHAPTER 4
MATERIALS & METHODS

4.1 Introduction

This chapter sets out the methodologies used for the Hub Centre review, sample handling, storage and preservation, and procedures used for the heavy metal analysis of sludge samples collected from the Regional Sludge Treatment Centres.

4.2 Hub Centre review

A Review of the 48 Hub Centres proposed in the National Sludge Strategy Report (Weston-FTA, 1993) was carried out. This involved consultation with Local Authorities and various stakeholders, through questionnaires and telephone interviews, to identify specific factors that may enhance or limit the use of Biosolids as an agricultural soil amendment. This was followed by site visits, where representative sludge samples were collected, together with site-specific information regarding wastewater treatment processes, sludge treatment, generation, handling and disposal. The survey was subsequently updated, as not all of the proposed Hub Centres were producing Class A Biosolids at the time of the sampling survey. In some cases, Local Authorities had not finalised their Sludge Management Plans.

4.3 Sample collection, storage and preparation

5 x 1kg samples were collected in 1kg plastic PTFE containers, which were pre-acid washed with 2% HNO₃ and rinsed thoroughly with ultra pure water. Samples were then brought back to the laboratory where they were stored in dedicated freezer units, prior to analysis.

Table 4.1 outlines the areas where sludge samples were obtained for laboratory analysis. 40 locations were sampled in total, and a total of 43 samples were collected. Where treatment plants were using lime treatment, sludge samples were taken with and without lime. There were also two industrial sludge samples.

Table 4.1 Hub Centres/sampling locations in Ireland

County	Hub Centre(s) †	Sampling Location(s)
1. Donegal	(1) Buncrana	Buncrana
	(2) Letterkenny	Letterkenny
	(3) Burtonport	
	(4) Donegal	
2. Sligo	(5) Sligo	Enniscrone & Strandhill
3. Leitrim	(5) Sligo	Carrick-on-Shannon
4. Mayo	(6) Ballina	Ballina
	(7) Castlebar	Castlebar ☒
5. Roscommon	(8) Boyle	Roscommon
6. Galway	(9) Tuam	Tuam
	(10) Galway	
7. Clare	(11) Ennis	Ennis
	(12) Kilkee	Sixmilebridge
	(13) Shannon	Shannon ☐
8. Limerick	(14) Limerick	Castletroy
	(15) Newcastlewest	Newcastlewest
9. Kerry	(16) Tralee	Tralee
	(17) Killarney	Killarney
10. Cork	(18) Skibbereen	Clonakilty
	(19) Kinsale	
	(20) Ballincollig	Ballincollig
	(21) Cork	
	(22) Mallow	Mallow
	(23) Charleville	Charleville
	(24) Dungarvan	Portlaw
11. Waterford	(25) Waterford	
	(26) Wexford	
12. Wexford	(27) Enniscorthy	Enniscorthy
	(28) Wicklow	Greystones
	(29) Bray	
	(30) Ringsend	Ringsend
14. Dublin	(31) North Dublin	Swords ☐
	(32) Drogheda	Drogheda
15. Louth	(33) Dundalk	Dundalk
	(34) Monaghan	Monaghan
16. Monaghan	(34) Monaghan	Monaghan
17. Cavan	(35) Cavan	Cavan
18. Longford	(36) Longford	Longford
19. Westmeath	(37) Mullingar	Mullingar
	(39) Athlone	
20. Meath	(38) Navan	Navan
21. Offaly	(40) Tullamore	Tullamore
22. Kildare	(41) Naas/Oberstown	Oberstown
	(42) Roscrea	
23. N.R. Tipperary	(43) Thurles	Nenagh
	(44) Nenagh	Thurles
24. S.R. Tipperary	(45) Clonmel	Tipperary
25. Laois	(46) Portlaois	Portlaois
26. Kilkenny	(47) Kilkenny	Kilkenny
27. Carlow	(48) Carlow	Carlow ☒

- ☒ Samples with and without lime
 ☐ Municipal and industrial sludge samples obtained
 ☐ Industrial sludge only
 † Numbering system as per 1993 Sludge Strategy Study (Weston-FTA, 1993)

Of the original 48 Hub Centres, 11 alternative locations were selected for sampling. These were in areas that did not have any established wastewater treatment plants at the time of sampling. As a result, it was decided that, in order to obtain a general representation of the area, representative samples would be collected from the largest, most recent wastewater treatment plants built within the given area.

Samples were prepared for analysis by placing a 1kg amount onto a pre-acid washed glass tray in an oven at 100°C for 24 hours. Following this, sub-samples were incubated in a muffle furnace at 200°C for 8 hours. Samples were removed and placed in desiccators where they were left to cool. The samples were then crushed and sieved through a 2 mm sieve and stored in pre-acid washed dried containers.

Common methods for sample digestion in metal analysis for this type of material are hot plate (large volume) and microwave digestion. However, these are time consuming for large quantities of samples. In this M.Sc. Study, a new method for digestion of small quantities, based on hot plate digestion, but using the Hach heating block system, was devised.

The advantages with this system are that it can digest up to 25 samples simultaneously. It is time efficient, reliable and cost effective. The following sections describe validation of the proposed Hach digestion against the standard microwave digestion.

4.4 Hach digestion method development

The compact Hach heating block and test tube system is based on the same principle as alternative digestion methods, in that it uses a strong acid (HNO_3) and a high temperature (100°C). It replaces the standard hot plates, digestion flasks and reflux condensers.

The Hach heating block reactor can be set to maintain a temperature of between 100 to 150°C, and provides a temperature stability of $\pm 0.5^\circ\text{C}$. It consumes less than 240 watts of power and it takes approximately 40 minutes for the reactor to warm up. A thermometer is used for temperature verification. The reactor is equipped with a self-timer, and can perform unattended digestions and shut off automatically. Alternatively,

a continuous operation mode can be selected by using the rocker switch located on the reactor front panel. It is maintenance free, and is safety fused to shut down at temperatures of 195°C. It is provided with a safety shield, which can be placed around the perimeter of the reactor to provide protection from hot splattering acids.

As part of the Hach digestion method, it was necessary to optimise the method for a large array of sludge samples. Specific variables such as Hach temperature, digestion time, sample weight, time and temperature the sample was dried, in addition to the volumes of nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) were investigated. The final set of variables selected were based on the maximum recovery of a Certified Reference Material (C.R.M), together with optimum working conditions for the Hach heating block reactor. Results obtained using the Hach digestion procedure were compared to a digestion run conducted by microwave digestion. Both methods were examined for spike recovery rates and percentage recoveries of a C.R.M, to determine if any sample was lost due to the nature of the open top vessels and to compare percentage recoveries. Heavy metals were analysed by Flame Atomic Absorption Spectroscopy (FAAS) and by an external laboratory (Plasmatech) using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

(a) Materials/Apparatus

Natural matrix C.R.M of sewage sludge (Catalogue No. CRM029-050) (CRM mean values in mg/kg.dw – As [26.5], Ba [806], Cd [538], Cr [325], Co [3.07], Cu [665], Fe [8,640], Pb [227], Hg [4.17], Mo [8.77], Ni [150], Se [19.0] and Zn [847]), 1000 ppm metal standards solutions, micro pipette 100-1000µl, 20 ml glass test tubes, ultra pure water, Romil HNO₃ super purity acid (SPA) 69%, Analar Grade HNO₃ 69%, Romil H₂O₂ super purity acid (SPA) 30%, grade B volumetric pipettes, grade B graduated beakers, analytical balance (Mettler College Toledo, Type 150), cellulose nitrate Whatman filter papers 0.4µm, Millipore filtration apparatus, Hach heating block chemical oxygen demand (COD) reactor (Davidson & Hardy Ltd (25)), Inductively Coupled Plasma Mass Spectrophotometer (ICPMS) (VG Elemental Plasma Quad 1), Flame Atomic Absorption Spectrophotometer (FAAS) (Perkin Elmer 560), standard oven (100°C), muffle furnace (Carbolite at 200 °C), fume hood and dessicators.

N.B. All glassware was washed using 2% Nitric Acid and rinsed thoroughly with Ultra Pure Water.

(b) Method

1. Two 2.5g samples of a natural matrix C.R.M of sewage sludge was weighed out into crucibles and placed in a muffle furnace at 200°C. (One was heated for a period of 8 hours and the other for 24 hours, to determine if the drying time affected the recovery of metals being analysed).
2. The samples were removed and placed in a desiccator where they were left to cool.
3. 0.3g of each sample was weighed in triplicate and transferred into pre-acid washed glass test tubes.
4. 5 ml of Romil HNO₃ SPA was added to each test tube, and placed in a Hach heating block at 100°C. Triplicate blanks were prepared using the same procedure for both samples.
5. The samples were left to digest for a period of 2 hours, before 2 ml of H₂O₂ in 0.2 ml aliquots was added (N.B. H₂O₂ was added in 0.2 ml aliquots because it is a highly reactive oxidant. When added to a rich organic sample, in large aliquots, expulsion was found to occur).
6. The samples were left to react for a further 2 hours prior to making a further addition of 2 ml of Romil HNO₃ SPA.
7. A 0.5 ml aliquot of Romil HNO₃ SPA was added after 5.5 hours and left to react for a further 0.5 hours before switching off the Hach heating block.
8. The samples were removed from the Hach heating block and placed in a test tube rack where they were left to cool.
9. The samples were filtered through a Millipore filtration apparatus and rinsed with ultra pure water into Grade B 100 ml volumetrics, before been made up to the mark with ultra pure water.
10. The samples and blanks were analysed, without dilution, for Fe, Cu, Zn, Cr and Cd, using the FAAS. 1/10 dilution was made before analysing for Cu, Ni, Cr, Zn, Cd, Ba, Pb, Co, Mo, Se, As and Hg using the ICPMS.
11. All metal standard solutions were matrix matched – i.e. the same volume of HNO₃ and H₂O₂ were used.
12. All elements analysed on the FAAS were examined for spike recoveries – this involved spiking the sample with approximately 50% of the known element concentration.

4.5 Microwave digestion method

Microwave digestion is considered to have many advantages, including the increased speed and the sealed nature of the digestion technique, which significantly reduces contamination over traditional heating methodologies.

(a) Materials/Apparatus

The materials/apparatus were the same as the Hach method (see section 4.4a) except the Microwave digester apparatus (Milestone Ethos Plus) was used instead of the Hach heating block reactor and test tube apparatus.

(b) Method

1. Steps 1-3 were the same as the Hach method (see section 4.4b).
2. 7.5 ml of concentrated HNO₃ was added to the sample, followed by 2 ml of H₂O₂. The sample was left to predigest in the uncapped digestion vessel for approximately 2hrs. This was because of the H₂O₂, which is a highly reactive oxidant. If after addition this was placed immediately into the microwave unit, it could cause venting of the digestion vials through the build up of nitrous gases in the enclosed unit.
3. All vessels were then sealed and placed into the microwave unit, connected to the appropriate temperature and pressure sensors, and left to digest for approximately 25 minutes.
4. At the end of microwave digestion, the vessels were allowed to cool (to near room temperature) for a minimum period of 15 minutes. All vessels were inspected to see if they had maintained their seal throughout the process (the weight of the vessel and reagents was noted prior to and after digestion to evaluate seal integrity. If the loss in weight exceeded 1% then the sample was considered compromised. For vessels with suspected burst disks, a careful visual inspection of the disk identified compromised vessels).
5. Each digestion vessel was carefully uncapped and vented in a fume hood.
6. Steps 9 to 12 were the same as the Hach digestion method, (see section 4.4b).

4.6 Procedure for the digestion of sludge samples

The Hach digestion method was found to compare very favourably to the microwave digestion method. It was decided to use it for all sludge samples collected, because of the time advantage in analysing large numbers.

Steps 3-11 were the same as the Hach digestion procedure (see section 4.4b). Fe, Cu and Zn were analysed by the FAAS. Dilutions varied depending on the amount of analyte present. A 1/10 dilution was made prior to analysing all samples by the ICP-MS for the heavy metals selected.

4.7 Instrumental analysis

Digested samples were analysed by the FAAS, and ICP-MS. Specific instruments were chosen based on background levels of metals present in the samples and on specific sensitivities (i.e. limits of detection) of the instruments, refer to table 4.2.

Table 4.2 Heavy metals analysed and instrumentation selected

Metal(s)	Analytical Instrumentation
Arsenic (As) ¹	ICP-MS
Barium (Ba) ¹	ICP-MS
Cadmium (Cd) ¹	ICP-MS
Chromium (Cr) ¹	ICP-MS
Cobalt (Co) ¹	ICP-MS
Copper (Cu) ¹	FAAS & ICP-MS
Iron (Fe) ²	FAAS
Lead (Pb) ¹	ICP-MS
Mercury (Hg) ¹	ICP-MS
Molybdenum (Mo) ¹	ICP-MS
Nickel (Ni) ¹	ICP-MS
Selenium (Se) ¹	ICPMS
Zinc (Zn) ¹	FAAS & ICP-MS

¹Metals selected in accordance with the Dutch list, the Waste Management 1998 Regulations as amended by SI 267 of 2001 (*use of sewage sludge in agriculture*) and the USEPA 503 Rule.

² Selected because it was determined from the sampling survey that some wastewater treatment plants were using ferric chloride (FeCl) for phosphate removal.

All FAAS analysis was carried out in accordance with the Standards Methods 3030D and 3111 or 3120B (acid digestion and Flame Atomic Absorption Spectrometry). All elements analysed on the FAAS were examined for spike recoveries – this involved spiking the sample with approximately 50% of the known element concentration.

The ICP-MS standard preparation involved the following:

- **Internal standard solution:** A 10 mg/l⁻¹ multi-element (Be, Sc, Rh, and Bi) solution in 2% Nitric acid was prepared from SPEX single element 1000 µg/l⁻¹ stock standards. All standards, samples and blanks were spiked to 100 µg/l⁻¹ with this solution.
- **Calibration standards:** Multi-element calibration standards (0.5, 2.5, 5, 10, 25, 50, 100, 250 and 500 µg/l⁻¹ As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se and Zn) were prepared in 2% Nitric acid by dilution of SPEX 1000 mg/l⁻¹ certified single element standards.
- **Calibration blank:** A 2% Nitric acid calibration blank was prepared having the same matrix as the standards. All samples and standards were background corrected using this blank.
- **Reagent blank:** 10 ml of the digestion blank was diluted to volume with 2% Nitric acid.
- **Spike solutions:** The 10 mg/l⁻¹ multi-element (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se and Zn) spike solution was prepared by dilution of the 1000 mg/l⁻¹ certified single element standards. To test recoveries the reference material was spiked to a concentration of 100 µg/l⁻¹ with the above elements.
- **Calibration check standard:** The 50 µg/l⁻¹ multi-element (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se and Zn) calibration check standard was prepared from 10 mg/l⁻¹ SPEX certified multi-element standards.
- **Reslope check standard:** The 50 µg/l⁻¹ multi-element (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se and Zn) calibration standard.

Working sample preparation: Immediately prior to analysis, the digested sample was diluted by a factor of 10, spiked to 100 ppb with the internal standard solution (Beryllium, Scandium, Rhodium, Indium and Bismuth) and made up to volume with 2% nitric acid.

ICPMS Instrumentation: Elemental determinations were made using an inductively coupled plasma mass spectrometer equipped with a standard Meinhard nebulizer. The ICPMS instrument used was the VG PlasmaQuad (VG Elemental, Winsford, Uk) equipped with a high performance interface. The interface between the plasma and the mass spectrometer consists of nickel sampling microskimmer cones with orifice diameters of 1.0 and 0.75 mm respectively. The sample introduction system is comprised of a Meinhard concentric nebuliser with a standard double-pass Scott type spray chamber and surrounding water-cooling jacket.

Instrument optimisation: Prior to analysis with the ICP-MS instrument, it was evaluated for accurate mass scale calibration, short-term stability, isotopic resolution and low background count levels. Instrument response was optimised at Indium – 115 by adjustment of ion lens potentials, plasma position relative to the sampling cone and gas flow rates (nebuliser, auxiliary and plasma gas). Typical optimised instrument operating conditions are specified in table 4.3.

Table 4.3 ICP-MS instrument conditions

Incident power	1.45 kW
Plasma gas flow	12.5 l/min ⁻¹
Auxiliary gas flow	0.7 l/min ⁻¹
Nebuliser gas flow	0.830 l/min ⁻¹
Acquisition mode	Peak jumping
Dwell time	60 milliseconds
Resolution	0.8 AMU
Acquisition	1 minute

ICP-MS analytical protocol and measurements

The calibration standards were run initially, followed by samples. Each blank, sample and standard solution was measured using three by one-minute replicate acquisitions. After each aspiration, the sample introduction system was rinsed for one minute with 1% Nitric acid solution in order to avoid sample memory effects.

Quality control

The ion count at indium-115 was monitored for each solution as a check on general solution preparation and instrument performance (e.g. nebuliser blockage). The method blank, calibration blank, 50 ppb reslope standard and a 50 ppb calibration check standard was run after each batch of 15 samples in order to monitor instrument drift (if these quality checks indicated errors then analysis of the preceding samples was repeated or corrections were made to the analytical results). A CRM 029-050 was run to check for ICP-MS interferences. The reference material was spiked with $100 \mu\text{g/l}^{-1}$ with the spike solution. Limits of determination (LOD) for each isotope were based on a multiple of standard deviations of a blank solution (at least 6x standard deviation of the blank).

CHAPTER 5

RESULTS & DISCUSSION

5.1 Background

One of the most important waste management issues facing our national government today is the management of sewage sludge. Due to increasingly stringent controls on landfills, public opposition to incineration, and the ban on sea disposal, application of Biosolids (i.e. treated sludge) to agricultural land has been identified as the most suitable and desirable alternative, provided it is consistent with EC strategy of waste recycling, recovery and reuse.

The benefits associated with applying Biosolids to agricultural land are that it supplements or replaces fertilisers, by providing essential nutrients, trace elements and organic matter, which are essential to improve and maintain productive soils and plant growth. The potential constraints associated with reusing Biosolids in agriculture are the presence of heavy metal compounds, which could, depending on the concentrations present, render agriculture as an unsuitable sustainable reuse option. It is important that sewage sludge application to land is properly managed, to ensure that it does not adversely affect the environment, human and animal health.

This M.Sc. Study assessed the development of sludge treatment and reuse policy, since the original 1993 National Sludge Strategy Study (Weston-FTA, 1993), with particular reference to the selection of sludge treatment technologies. It also investigated the characterisation of sewage sludge arising from the Hub Centres.

No other study has looked at how this policy has developed and has been implemented. Because Local Authorities are autonomous, information on this topic is not routinely, or easily, collated or reviewed. This is the first time that all of the proposed Hub Centres have been visited as a group, and reviewed. It is also the first time that samples have been taken from all designated Hub Centres and comprehensively characterised using key analytical parameters. Section 5.2 focuses on the Hub Centre visits and review. Section 5.3 focuses on analytical characterisation.

5.2 Hub Centre review

The original National Sludge Strategy Study, (Weston-FTA, 1993), made predictions for up to 20 years. Progress on implementation has been slow, which has meant that

plans have changed, in the light of new circumstances, such as further study, finance and policy changes. A second study, as part of the 1997 National Non-Hazardous Sludge Study (5 years later) made reference to sewage sludge. Principally, it redrew boundaries along Local Authority lines, resulting in 2 fewer Hub Centres. It also revised projected loadings.

This M.Sc. Study is the latest (a further 5 years later) and most comprehensive study in that it looks at the current status of the building programme, the status of Sludge Management Plans (S.M.P) and whether Local Authorities have further changed plans. Most notably, there has been a move to Design Build Operate (D.B.O) projects, where contractors can select technology and reuse systems that do not concur with current national policy.

Each of the Hub Centres was visited, with information gathered on wastewater treatment processes and Sludge Management Plans. The following sub-sections set out the current status of sludge management systems with reference to earlier policies and plans.

(a) County Donegal

Buncrana, Letterkenny, Burtonport and Donegal (regions 1-4) were the proposed Hub Centres for Co. Donegal in the 1993 Sludge Strategy Report, and in the 1997 Non-hazardous Sludge Inventory. This M.Sc. Study found that the number of Hub Centres for County Donegal remained the same at 4, with changes made to Burtonport, which was replaced by Gweedore as Hub Centre. Industrial discharge arises from animal, food, fish and industrial waste. A draft Sludge Management Plan has been completed (Weston-FTA, 1993; FTC, 1998c; Holohan, 2001).

Table 5.1 Details of Hub Centre 1, Buncrana (wastewater treatment plant was built in 1990, sludge treatment [Anaerobic Digestion and sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	13,200 (total P.E of region is 26,000)	No change	Actual P.E. is 6,417, (projected P.E. is 7,000 between 2006/2020).	--
Wastewater Treatment Technology	Primary settlement	No change	No change (activated sludge is planned for 2006).	--
Recommended and/or current sludge treatment technology	Anaerobic Digestion and Sludge Dewatering in place. Recommended 1. Thickening/Anaerobic Digestion/Dewatering. 2. Thickening/Aerobic Digestion/Dewatering	No change	Anaerobic Digestion and Sludge Dewatering in place. Plans to add Thermal Drying to achieve Class A Biosolids.	Recommended in S.M.P that sludge management should address co-digestion with food industry in Greencastle.

Table 5.2 Details of Hub Centre 2, Letterkenny (wastewater treatment plant was built in 1982, sludge treatment [Aerobic Digestion and sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	22,000 (total P.E. of region is 76,000)	No change	Actual P.E. is 16,600, (projected P.E. is 37,000 between 2006/2020).	--
Wastewater Treatment Technology	Activated sludge treatment	No change	Primary settlement, extended aeration and biofiltration. (more biofiltration and activated sludge is planned between 2006/2020)	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Anaerobic Digestion/Dewatering. 2. Composting.	No change	Aerobic Digestion and sludge dewatering in place. Plans to incorporate Thermal Drying to produce Class A Biosolids.	Recommended in S.M.P that sludge management should address animal slaughtering sludges generated at Carrigans.

Table 5.3 Details of Hub Centre Gweedore (wastewater treatment plant was not established by 2002).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	N/A	--
Wastewater Treatment Technology	N/A	N/A	N/A	--
Recommended and/or current sludge treatment technology	N/A	N/A	Thermal Drying	--

Table 5.4 Details of Hub Centre 4, Donegal (wastewater treatment plant was established by 1993, no sludge treatment in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	2,460 (total P.E of region is 35,000)	No change	Actual P.E. is 5,800, (projected P.E. is 18,000 between 2006/2020).	--
Wastewater Treatment Technology	Primary settlement	No change	No change (activated sludge treatment is planned by 2006)	--
Recommended and/or current sludge treatment technology	1. Thickening/Anaerobic Digestion/Dewatering. 2. Composting	No change	Thermal Drying.	--

Table 5.5 Results of sludge analysis for Letterkenny and Buncrana (mg/kg/dw) (15/12/00)

Location(s)	Cd	Cu	Ni	Pb	Zn	Hg
Letterkenny	<1	91.3	72.2	10.6	182	<1
Buncrana	<1	55.0	45.9	27.9	207	<1
S.I. 148/1998 Legislative limits	20	1,000	300	750	2,500	16

* No results of sludge analysis were made available for Donegal.

(b) County Sligo

In the 1993 Sludge Strategy Report, Sligo (region 5) was the designated Hub Centre for both Counties Sligo and Leitrim. Because county boundaries were taken into

consideration in the 1997 Study, Sligo was only identified as the single Hub Centre for County Sligo, which was also found to remain the same in this M.Sc. Study. Sligo industrial discharge arises mainly from the agri-industrial sector. There are three industries which hold ICP licences. They are Seahan Media, Basta Hardware Ltd., and Supershore Ltd. All of their hazardous waste is disposed of via licensed contractors. The Sligo Co. Co. Sludge Management Plan is in draft form and is currently going to tender (Weston-FTA, 1993, FTC, 1998c; Jennings O'Donovan and Partners, 2002).

Table 5.6 Details of Hub Centre 5, Sligo (wastewater treatment plant was not established by 2002).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	N/A	--
Wastewater Treatment Technology	N/A	N/A	N/A	--
Recommended and/or current sludge treatment technology	1. Thickening/Anaerobic Digestion/Dewatering	N/A	Anaerobic Digestion with pre/post pasteurisation or Thermophilic Anaerobic Digestion.	--

(c) County Leitrim

In the 1993 Study, Sligo was the designated Hub Centre for both counties Sligo and Leitrim. In the 1997 Study, which took cognisance of county boundaries, Carrick-on-Shannon (region 6) was identified as the designated Hub Centre for County Leitrim. This remains the case. There is no major industrial discharge in Leitrim as Masonite treats all its own waste. The Leitrim Co. Co. Sludge Management Plan is complete (Weston-FTA, 1993; FTC, 1998c; Entec and O'Dwyer, 2002).

Table 5.7 Details of Hub Centre 6, Carrick-on-Shannon (wastewater treatment plant was built in 1986, sludge treatment [sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	3,000	No change	Actual P.E. is 3,200, (projected P.E. is 12,000 by 2020).	--
Wastewater Treatment Technology	Activated sludge treatment	No change	Extended aeration (nutrient removal is planned for 2005).	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. No sludge treatment technology recommended because it was not designated as a Hub Centre.	No change	Sludge dewatering in place. Recommends Composting.	--

* There were no results of sludge analysis made available for Carrick-on-Shannon.

(d) County Mayo

In both the 1993 and 1997 Studies, Ballina and Castlebar were the designated Hub Centres for County Mayo. The only difference was that their region codes changed from 6 and 7 in the 1993 Study, to 7 and 8 in the 1997 Study. This M.Sc. Study found that Derrinnumera is now the designated Hub Centre for Mayo. Mayo industrial discharge arises from slaughtering, food processing, fish rearing, electrical generation, Pepsi Cola, and Baxter. The Mayo Co. Co. Sludge Management Plan is complete (Weston-FTA, 1993; FTC, 1998c; FTC, 2002).



Figure 5.1 Alkaline Stabilisation at Castlebar

Table 5.8 Details of Hub Centre Derrinmera (wastewater treatment plant was not established by 2002).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	N/A	--
Wastewater Treatment Technology	N/A	N/A	N/A	--
Recommended and/or current sludge treatment technology	N/A	N/A	Thermal Drying	--

(e) County Roscommon

In the 1993 Study, Boyle (region 8) was the proposed Hub Centre for County Roscommon. In the 1997 Study, the Hub Centre was changed to Castlerea (region number 9). However, this M.Sc. Study found that Roscommon town is now the designated Hub Centre for County Roscommon. Industrial discharge arises from Kepak, Atleague, Dawn Meats, Glanbia foods, Meat processing, Green Isle Foods, Hannon's Poultry, Roscommon Mart, and Shannonside milk. The Roscommon Co. Co. Sludge Management Plan is complete (Weston-FTA, 1993; FTC, 1998c, McCarthy and Partners 2001a).

Table 5.9 Details of Hub Centre Roscommon (wastewater treatment plant was built in 1975, sludge treatment [sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	Actual P.E. is 9,550, (projected P.E. is 18,000 by 2021)	--
Wastewater Treatment Technology	N/A	N/A	Extended aeration, clarification and chemical precipitation using ferric chloride, (primary treatment is planned for the near future).	--
Recommended and/or current sludge treatment technology	N/A	N/A	Alkaline Stabilisation/Composting and or Thermal Drying.	Sludge treatment using Reedbeds or vermicomposting will be provided at all sites with a P.E. of <2000 (34 in total). The use of on site treatment will account for approx. 450tds of sludge that will not require transport or further treatment at the Hub Centre.

* There were no results of sludge analysis made available for Roscommon.

(f) County Galway

In both the 1993 and the 1997 Studies, Tuam and Galway were the proposed Hub Centres for County Galway. The only difference was that their region codes changed from 9 and 10 in the 1993 Study, to 10 and 11 in the 1997 Study. This M.Sc. Study found that Tuam is now the single designated Hub Centre for County Galway. Industrial discharge arises mainly from the agricultural food sector. Galway city sludge will be treated at the new Mutton Island plant, by anaerobic digestion with pre/post pasteurisation. As it will not import any sludges, it is not a designated Hub Centre. The Galway Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c; McCarthy and Partners, 2001b).



Figure 5.2 Sludge storage at Tuam

Table 5.10 Details of Hub Centre 10, Tuam (wastewater treatment plant was built in 1993, sludge treatment (sludge dewatering and Alkaline Stabilisation] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	8,450 (total P.E. of the region is 44,000)	No change	25,000	--
Wastewater Treatment Technology	Primary settlement, activated sludge treatment and tertiary filtration.	No change	Primary settlement, activated sludge treatment and chemical precipitation using ferric chloride.	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1.Thickening/Anaerobic Digestion/Dewatering.	No change	Sludge dewatering and Alkaline stabilisation in place. It recommends Alkaline Stabilisation and Thermal Drying.	Recommended in S.M.P that sludge management should address co-digested food industry sludge generated at Clarenbridge.

*There were no results of sludge analysis made available for Tuam.

(g) County Clare

In both the 1993 and 1997 studies, Ennis, Kilkee and Shannon were the designated Hub Centres for County Clare. The only difference was that the regions codes changed from 11, 12 and 13 in the 1993 Study to 12, 13 and 14 in the 1997 Study. This M.Sc. Study found that both counties Clare and Limerick are integrating their Sludge Management

Plans, with one Hub Centre to be built in Limerick City to treat all sludge generated from both counties. Ennis has little industrial discharge. There are two plants in Shannon. One is treating municipal waste, the other is treating industrial waste. All sludge from the industrial plant is disposed of to landfill (see table 5.11). The Clare Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c).

(h) County Limerick

In both the 1993 and 1997 Studies, Limerick and Newcastlewest were the proposed Hub Centres for Co. Limerick. The only difference was that their region codes changed from 14 and 15 in the 1993 Study, to 15 and 16 in the 1997 Study. This M.Sc. Study found, as described earlier, that Limerick will be the single Hub Centre or Counties Limerick and Clare. The Limerick municipal plant receives industrial discharge from the technological industrial park, and from a number of licensed factories e.g. Ballygowan and meat processing factories. The Limerick Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c).

Table 5.11 Details of Hub Centre 15, Limerick (wastewater treatment plant was not established in 2002)

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	N/A	--
Wastewater Treatment Technology	N/A	N/A	N/A	--
Recommended and/or current sludge treatment technology	1. Thickening/Anaerobic Digestion/Dewatering. 2. Co-composting with MSW.	No change	Undecided.	Recommended in the SMP that sludge management should address co-digestion with industrial biological sludge at Clarecastle, incorporation of industrial biological and food industrial sludges from Dromkeen and Limerick and co-digestion with food industry sludge at Askeaton.

(i) County Kerry

In the 1993 Study, Tralee and Killarney were the proposed Hub Centres for the County Kerry. They remained the same in the 1997 Study, except that the regions codes changed from 16 and 17 in the 1993 Study, to 17 and 18, in the 1997 Study. Both Tralee and Killarney were also found to be the designated Hub Centres for Kerry in this M.Sc. Study. The Kerry Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c).



Figure 5.3 Mesophilic Anaerobic Digestion at Tralee

Table 5.12 Details of Hub Centre 17, Tralee (wastewater treatment plant was built in 1998, sludge treatment [Anaerobic Digestion and sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	42,000	--
Wastewater Treatment Technology	N/A	N/A	Primary settlement, biological filtration and activated sludge treatment, (UV disinfection is planned for the near future).	--
Recommended and/or current sludge treatment technology	1. Thickening/Anaerobic Digestion/Dewatering	No change	Anaerobic Digestion and sludge dewatering in place, recommended sludge treatment technology is undecided.	Recommended in S.M.P that sludge management should address food industry sludge generated at Listowel.

Table 5.13 Results of sludge analysis (ranges for analysis) (mg/kg/dw) for Tralee, (17/01/02)

Metal(s)	Cu	Zn	Pb	Ni	Hg	Cd
Tralee	350.29 – 373.97	503.30 – 517.63	90.05 – 101.21	23.95 – 25.36	<0.01 – <0.01	3.93 – 5.07
S.I. 148/1998 Legislative limit	1,000	2,500	750	300	16	20

Table 5.14 Details of Hub Centre 18, Killarney (wastewater treatment plant was built in 1985, sludge treatment [ATAD] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	45,000 (total P.E. of region is 66,000)	No change	Currently treating 20,000 (designed for 42,000 (normally occurs during peak time i.e. Summer)	--
Wastewater Treatment Technology	Extended aeration and chemical precipitation using ferric chloride.	No change	Primary settlement, extended aeration and chemical precipitation using ferric chloride.	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Dewatering/Bio-drying. 2. Lime treatment.	No change	None because it is producing Class A Biosolids by ATAD.	Recommended in the S.M.P that sludge management should address food industry sludge located at Rathmore and industrial biological sludge generated at Killorglin.



Figure 5.4 ATAD at Killarney

Table 5.15 Results of sludge analysis for Killarney (13/06/01) (mg/kg/dw)

Metal(s)	Cu	Ni	Zn	Cd	Pb	Hg
Killarney	285	80	427	4.6	9.6	<0.1
S.I. 148/1998 Legislative limits	1,000	300	2,500	20	750	16

(j) County Cork

In the 1993 Study, there were six Hub Centres proposed for County Cork. They were Skibbereen, Kinsale, Ballincollig, Cork City, Mallow and Charleville (Rathluric) (regions 18-23). In the 1997 Study, the Hub Centres were the same except for Kinsale, which was replaced by Skibbereen/Ballincollig (regions 19-23). This M.Sc. Study found that Ballincollig, Mallow and Charleville are now the only designated Hub Centres for County Cork. Cork city, similar to Galway city, will operate as a stand-alone plant, treating sludge by anaerobic digestion with pre/post pasteurisation. Industrial discharge is been treated at Mallow, while Charleville is receiving discharge from Golden Vale. In Ballincollig, there is no industrial discharge. The Cork Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c).

Table 5.16 Details of Hub Centre 20, Ballincollig (wastewater treatment plant was established by 1993, sludge treatment [sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	18,700 (total P.E. of region is 43,000)	No change	15,000	--
Wastewater Treatment Technology	Primary settlement, biological filtration and activated sludge.	No change	No change.	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Dewatering/Bio-drying. 2. Lime Stabilisation.	No change	Sludge dewatering in place. Recommended sludge treatment technology is undecided.	Recommended in the S.M.P that sludge management should address industrial biological sludges generated at Macroom.

Table 5.17 Details of Hub Centre 22, Mallow (wastewater treatment plant was built in 1984, sludge treatment [sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	9,000 (total P.E. of region is 37,000)	No change	8,792	--
Wastewater Treatment Technology	Activated sludge treatment	No change	No change	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Anaerobic Digestion/Dewatering.	No change	Undecided	Recommended in the S.M.P that sludge management should address food-processing sludges produced in Mallow and Mitchelstown and animal slaughtering sludges.

Table 5.18 Details of Hub Centre 23, Charleville (wastewater treatment plant was built in 1982, sludge treatment [sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	15,000 (total P.E. of region is 25,000)	No change	7,500	--
Wastewater Treatment Technology	Extended aeration	No change	No change	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Anaerobic Digestion/Dewatering.	No change	Sludge dewatering in place. Recommended sludge treatment technology is undecided.	Recommended in S.M.P that sludge management should address food processing and animal slaughtering sludges generated in the region.

Table 5.19 Results of sludge analysis (mg/kg/dw) for Mallow (Nov and Dec. 1999)

Metal(s)	Cd	Cu	Ni	Pb	Zn	Hg
Mallow	<1	<1	<1	<1	<1	<1
S.I 148/1998 Legislative Limits	20	1,000	300	750	2,500	16

*There were no results of sludge analysis made available for Charleville and Ballincollig.

(k) County Waterford

In the 1993 and the 1997 Studies, Dungarvan and Waterford were the proposed Hub Centres (regions 24-25) for County Waterford. In this M.Sc. Study, it was found that Dungarvan is now the only Hub Centre for County Waterford. The Waterford Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c). It is expected that Waterford city will have a stand-alone plant, similar to Cork and Galway, but there are no firm plans at present.

Table 5.20 Details of Hub Centre 24, Dungarvan (wastewater treatment plant was not established by 2002)

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	N/A	--
Wastewater Treatment Technology	N/A	N/A	N/A	--
Recommended and/or current sludge treatment technology	1.Thickening/Anaerobic Digestion/Dewatering.	No change	Anaerobic Digestion with pre/post pasteurisation, Composting or Thermal Drying.	Recommended S.M.P sludge management should address co-digestion with food processing sludges generated at Dungarvan.

(l) County Wexford

In both the 1993 and 1997 studies, Wexford and Enniscorthy were the proposed Hub Centres (regions 26-27) for County Wexford. This M.Sc. Study found that Enniscorthy

is now the only proposed Hub Centre for the County. There is no major industrial discharge in Enniscorthy. The Wexford Co. Co. Sludge Management Plan is not ready (Weston-FTA, 1993; FTC, 1998c).



Figure 5.5 Secondary settlement at Enniscorthy

Table 5.21 Details of Hub Centre 27, Enniscorthy (wastewater treatment plant was established by 1993, sludge treatment [sludge dewatering and Alkaline Stabilisation] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	13,000 (total P.E. of region is 45,000)	No change	11,500	--
Wastewater Treatment Technology	Primary settlement	No change	Activated sludge treatment	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Windrow Composting (Open Air).	No change	Sludge dewatering and Alkaline Stabilisation in place. Recommended sludge treatment technology is undecided.	Recommended in the S.M.P that food processing sludge in Gorey should be considered for co-composting with sewage sludge.

*There were no results of sludge analysis made available for Enniscorthy.

(m) County Wicklow

In both the 1993 and 1997 Studies, Wicklow and Bray were the two Hub Centres proposed for the county (regions 28-29). It was found in this M.Sc. Study that Wicklow

and Blessington are now the two Hub Centres proposed for County Wicklow. Greystones will also produce Class A Biosolids using Mesophilic Anaerobic Digestion with pre/post pasteurisation, but is not a designated Hub Centre. The Wicklow Co. Co. Sludge Management Plan is complete (Weston-FTA, 1993; FTC, 1998c, FTC and Barry, 2002).

Table 5.22 Details of Hub Centre 28, Wicklow (wastewater treatment plant was not established by 2002)

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	8,500	--
Wastewater Treatment Technology	N/A	N/A	No change	--
Recommended and/or current sludge treatment technology	1. Thickening/Anaerobic Digestion/Dewatering	No change	Thermal Drying/Alkaline Stabilisation/Anaerobic Digestion with pre/post pasteurisation	Recommended in the S.M.P that sludge management should address industrial biological sludge at Rathdrum.

Table 5.23 Details of Hub Centre Blessington (wastewater treatment plant was established by 2002, sludge treatment [sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	1,900	--
Wastewater Treatment Technology	N/A	N/A	Extended aeration	--
Recommended and/or current sludge treatment technology	N/A	N/A	Sludge dewatering in place. Recommended sludge treatment technology is undecided.	--

Table 5.24Results of sludge analysis for Blessington (25/09/01)
(mg/kg/dw)

Metal(s)	Cd	Cu	Hg	Ni	Pb	Zn
Blessington	1	406	<1	12	29	457
S.I. 148/1998 Legislative limits	20	1,000	16	300	750	2,500

(n) County Dublin

In the both the 1993 and 1997 Studies, Ringsend and North Dublin (Baldoyle) were the two Hub Centres proposed for Co. Dublin (regions 30 and 31). This M.Sc. Study found that Ringsend is now the only Hub Centre proposed for Dublin. North Dublin, sludge is being pumped to Ringsend via undersea pipeline from Sutton pumping station. Ringsend has a big industrial catchment area and caters for all industrial discharge from the city of Dublin. The Dublin Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c).

**Figure 5.6** Class A Biosolids generated by Thermal Drying at Ringsend.

Table 5.25 Details of Hub Centre 30, Ringsend (wastewater treatment plant was built in 1906, sludge treatment [Thermal Drying] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	622,100 (total P.E. of region is 1,485,000)	No change	1.5 million	--
Wastewater Treatment Technology	Primary settlement	No change	Primary settlement and UV disinfection	--
Recommended and/or current sludge treatment technology	1. Thickening/Anaerobic Digestion/Dewatering/Thermal Drying. 2. Incineration/Co-incineration with MSW.	No change	Producing Class A Biosolids by Thermal Drying	Recommended in S.M.P that sludge management should address co-digestion with sewage sludges.

*There were no heavy metal results available for Ringsend

(o) County Louth

In both the 1993 and 1997 Studies, Drogheda and Dundalk were the two Hub Centres proposed for County Louth (regions 32-33). The Hub Centres were found to be the same for this M.Sc. Study. In Louth, the industrial discharge arises from the brewery, beef processing, drinks manufacturing, mushroom growing, cosmetics production, lime production, electrical appliances and fabric manufacturing. The Louth Co. Co. Sludge Management Plan is complete (Weston-FTA, 1993; FTC, 1998c; Tobin Environmental Services, 1999).

Table 5.26 Details of Hub Centre 32, Drogheda (wastewater treatment plant was established by 2002, sludge treatment [Anaerobic Digestion and sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	Actual P.E. is 45,000 (projected P.E. 54,000 in 2005 and 80,000 in 2020)	--
Wastewater Treatment Technology	N/A	N/A	Primary settlement, extended aeration, clarification and chemical precipitation using ferric chloride.	--
Recommended and/or current sludge treatment technology	1. Thickening/Anaerobic Digestion/Dewatering. 2. Cement Kiln Dust (CKN) Process.	No change	Anaerobic Digestion and sludge dewatering in place. Plans to use Thermal Drying to produce Class A Biosolids.	--

Table 5.27 Details of Hub Centre 33, Dundalk (wastewater treatment plant was built in 2001, sludge treatment [Anaerobic Digestion and sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	180,000 (phase 1), 240,000 (phase 2)	--
Wastewater Treatment Technology	N/A	N/A	Primary settlement, activated sludge and chemical precipitation using ferric chloride.	--
Recommended and/or current sludge treatment technology	1. Thickening/Anaerobic Digestion/Dewatering/Combined Heat and Power (CHP). 2. Agrisoil.	No change	Anaerobic Digestion and sludge dewatering in place. Plans to use Thermal Drying to produce Class A Biosolids.	--

Table 5.28Results of sludge analysis for Dundalk (Nov. 2001),
(mg/kg/dw)

Metal(s)	Cr	Ni	Cu	Zn	As	Mo	Cd	Pb
Dundalk	37	147	340	6,600	9	8	1	81
S.I. 148/1998 Legislative limits	-	300	1,000	2,500	16	-	20	750

* There were no results of sludge analysis made available for Drogheda.

(p) County Monaghan

In all three studies Monaghan was identified as the designated Hub Centre for the county (region 34). Monaghan town receives industrial discharge arising from animal slaughtering and food processing. The Monaghan Co. Co. Sludge Management Plan is ready (Weston-FTA, 1993; FTC, 1998c, FTC, 2001).

**Figure 5.7** Composite sludge sample from Monaghan wastewater treatment plant**Table 5.29**Results of sludge analysis for Monaghan (March 2002),
(mg/kg/dw)

Metal(s)	Ni	Pb	Cu	Cr	Zn	Cd	Hg
Monaghan	99.4	30.6	868.6	203	657.7	<1	1.1
S.I. 148/1998 Legislative limit	300	750	1,000	-	2,500	20	16

Table 5.30 Details of Hub Centre 34, Monaghan (wastewater treatment plant built in 1993, sludge treatment [(sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	43,833 (total P.E. of region is 57,000)	No change	18,000	--
Wastewater Treatment Technology	Primary settlement and biological filtration.	No change	Primary settlement, activated sludge, biofiltration and chemical precipitation using ferric chloride.	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Dewatering/Bio-drying. 2. Composting. 3. Anaerobic Digestion.	No change	Sludge dewatering in place. Recommends Thermal Drying and Vermicomposting to produce Class A Biosolids.	Recommended in S.M.P that sludge management should address industrial biological and food processing sludges.

(q) County Cavan

Cavan (region 35) was the proposed Hub Centre in all three studies. Cavan receives industrial discharge from PowellsTraffo (powder coating), leachate dumping, Glanbia foods, Dairy processing, Liffey Meats, Lairage Waste (Paunch contents), fat from effluent treatment plants, and timber productions. The Cavan Co. Co. Sludge Management Plan is ready (Weston-FTA, 1993; FTC, 1998c; Entec and O'Dwyer, 2001c).

Table 5.31 Details of Hub Centre 35, Cavan (wastewater treatment plant built in 1985, sludge treatment [sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	20,565 (total P.E. of region is 62,000)	No change	13,580 (P.E. is designed for 22,000)	--
Wastewater Treatment Technology	Extended aeration and chemical precipitation using ferric chloride	No change	No change	--
Recommended and/or current sludge treatment technology	Sludge dewatering. Recommended 1. N-Viro/Agri Soil Lime Treatment.	No change	Sludge dewatering. Recommended sludge treatment technology is Composting	Recommended in S.M.P that sludge management should address industrial biological, food processing and spent mushroom compost.



Figure 5.8 Sludge generated by belt press at Cavan wastewater treatment plant

Table 5.32 Results of sludge analysis for Cavan (Nov. 1999) (mg/kg/dw)

Metal(s)	Cd	Cu	Pb	Hg	Ni	Zn
Cavan	1.20	6,040.9	148.1	-	65.1	2,900.8
S.I. 148/1998 Legislative limit	20	1,000	750	16	300	2,500

(r) County Longford

Longford was the designated Hub Centre in all three Studies, (region 36). Longford industrial discharge arises from the animal slaughtering and pet food manufacturing. The Longford Co. Co. Sludge Management Plan is complete (Weston-FTA, 1993, FTC, 1998C; Entec and O'Dwyer, 2001b).

Table 5.33 Details of Hub Centre 36, Longford (wastewater treatment plant built in 1993, sludge treatment [sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	20,000 (total P.E. of region is 30,000)	No change	20,000	--
Wastewater Treatment Technology	Primary settlement and extended aeration	No change	Extended aeration and chemical precipitation using ferric chloride.	--
Recommended and/or current sludge treatment technology	1. Thickening/Dewatering. 2. Thickening/Anaerobic Digestion/Dewatering.	No change	Sludge dewatering in place. Recommended sludge treatment technology is Composting.	Recommended in S.M.P that sludge management should address industrial, biological, food and spent mushroom compost.

Table 5.34 Results of sludge analysis for Longford (Sept. 1999) (mg/kg/dw)

Metal(s)	Cd	Cu	Pb	Hg	Ni	Zn
Longford	19	0.46	<1	45	125	463
S.L 148/1998 Legislative limit	20	1,000	750	16	300	2,500

(s) County Westmeath

In the 1993 Study, Mullingar and Athlone were the two Hub Centres proposed for Co. Westmeath (regions 37, 39). In the 1997 Study, only Mullingar was proposed (region 37), which was also the same case for this M.Sc. Study. The main industrial discharge in Mullingar wastewater treatment plant arises from cattle mart effluent. The Westmeath Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c).

Table 5.35 Details of Hub Centre 37, Mullingar (wastewater treatment plant built in 1987)

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	20,000 (total P.E. of region is 30,000)	No change	20,000	--
Wastewater Treatment Technology	Extended aeration and chemical precipitation using ferric chloride	No change	No change	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Anaerobic Digestion/Dewatering	No change	Sludge dewatering in place. Recommended sludge treatment technology is undecided.	--

Table 5.36 Results of sludge analysis for Mullingar (Feb. 2000), (mg/kg/dw)

Metal(s)	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Mullingar	1.6	26.5	366.75	26.13	3.51	27.45	922.9
S.I. 148/1998 Legislative limit	20	-	1,000	750	16	300	2,500

(t) County Meath

Navan was the proposed Hub Centre (region 38) for all three studies. The main sources of industrial discharge in Navan arise from animal slaughtering, food processing, rendering, and dairy products. The Meath Co. Co. Sludge Management Plan is complete (Weston-FTA, 1993; FTC, 1998c; Entec and O'Dwyer, 2001c).

Table 5.37 Details of Hub centre 38, Navan (wastewater treatment plant was built in 1990, sludge treatment [Anaerobic Digestion, sludge dewatering and Alkaline Stabilisation] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	10,000 (total P.E. of region is 98,000)	No change	65,000	--
Wastewater Treatment Technology	Extended aeration	No change	Primary settlement, extended aeration, clarification and chemical precipitation using ferric chloride.	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Anaerobic Digestion/Dewatering	No change	Anaerobic Digestion, sludge dewatering and Alkaline Stabilisation in place. Plans to use Thermal Drying	

* There were no results of sludge analysis made available for Navan.

(u) County Offaly

Tullamore was the proposed Hub Centre in all three Studies, except the region code changed from 40 to 39 in the 1997 Study. The main industrial discharge in Offaly arises from Irish Casing Factories (meat) and meat processing industries. The Offaly Co. Co. Sludge Management is not complete (Weston-FTA, 1993; FTC, 1998c).



Figure 5.9 Ferric chloride dosing at Tullamore wastewater treatment plant.

Table 5.38 Details of Hub Centre 39, Tullamore (wastewater treatment plant built in 1986, sludge treatment [Anaerobic Digestion and sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	17,000 (total P.E. of region is 40,000)	No change	16,000	--
Wastewater Treatment Technology	Activated sludge treatment	No change	Primary settlement, biological filtration, activated sludge treatment and chemical precipitation using ferric chloride.	--
Recommended and/or current sludge treatment technology	Anaerobic Digestion and sludge dewatering in place. Recommends 1. Thickening/Anaerobic Digestion/Dewatering	No change	Anaerobic digestion and sludge dewatering in place. Recommended sludge treatment is undecided	Recommended in S.M.P that sludge management should address co-digestion with animal slaughtering sludge at Edenderry.

* There were no results of sludge analysis made available for Tullamore.

(v) County Kildare

Naas/Osberstown was the proposed Hub Centre for both the 1993 and the 1997 Studies, the only difference was that the region code changed from 41 to 40 in the 1997 Study. This M.Sc. Study found that Osberstown is the only designated Hub Centre for County Kildare. Industrial discharge to Osberstown arises from South Kildare. The Kildare Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c; Entec and O'Dwyer, 2001d).

Table 5.39 Details of Hub Centre 40, Osberstown (wastewater treatment plant built in 1981, sludge treatment [Anaerobic Digestion, sludge dewatering and Alkaline Stabilisation] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	40,000 (total P.E. of region is 161,000)	No change	80,000	--
Wastewater Treatment Technology	Primary settlement, biological filtration and activated sludge treatment.	No change	Primary settlement, activated sludge treatment and chemical precipitation using ferric chloride.	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Anaerobic Digestion/Dewatering	No change	Anaerobic Digestion, sludge dewatering and Alkaline Stabilisation. Recommends Thermal Drying.	Recommended in S.M.P that sludge management should address food processing and animal slaughtering sludges generated at Newbridge and Kildare.

Table 5.40 Results of sludge analysis for Osberstown (Oct. 01 – March 02), (ug/l)

Metal(s)	Cd	Cr	As	Cu	Pb	Al	Fe	Co
Osberstown	2	2	2	55	2	542	0.1	2
S.L 148/1998 Legislative limit	20	-	-	1,000	750	16	300	2,500

(w₁) Tipperary NR

In the 1993 Study, Nenagh, Thurles, and Roscrea were designated as Hub Centres for Tipperary NR (regions 42 – 44). In the 1997 Study, Nenagh and Thurles were the proposed Hub Centres (regions 41 and 42), which was also the case in this M.Sc. Study. The Tipperary NR Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c).

Table 5.41 Details of Hub Centre 41, Nenagh (wastewater treatment plant built in 1985, sludge treatment [sludge dewatering] in place.

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	17,000 (total P.E. of region is 37,000)	No change	18,000	--
Wastewater Treatment Technology	Extended aeration	No change	No change	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Anaerobic Digestion/Dewatering	No change	Sludge dewatering in place. Recommended sludge treatment technology is undecided.	Recommended S.M.P should address co-digestion of food processing, animal slaughtering, and industrial biological sludges in the area.

Table 5.42 Details of Hub Centre 42, Thurles (wastewater treatment plant established by 1993, no sludge treatment in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	16,640 (total P.E. of region is 30,000)	No change	8,500	--
Wastewater Treatment Technology	Extended aeration and chemical precipitation using ferric chloride.	No change	No change	--
Recommended and/or current sludge treatment technology	1. Thickening/Anaerobic Digestion/Dewatering	No change	Undecided	--

* There were no results of sludge analysis made available for Nenagh and Thurles.

(w₂) Tipperary SR

In all three studies, Clonmel was the recommended Hub Centre for Tipperary SR. The only difference was that the region codes changed from 45 to 43 in the 1997 Study. Industrial sludge generated in South Tipperary arises from animal slaughtering, rendering, tanning and fellmongering, food processing, pharmaceutical and timber production. The Tipperary SR Sludge Management is complete (Weston-FTA, 1993; FTC, 1998c; FTC, 1999b)

Table 5.43 Details of Hub Centre 43, Clonmel (wastwater treatment plant established by 2002, sludge treatment [Anaerobic Digestion and sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	N/A	N/A	Actual P.E. is 38,000 (projected P.E. is 60,000 for 2010 and 80,000 in 2018)	--
Wastewater Treatment Technology	N/A	N/A	Primary settlement and activated sludge treatment	--
Recommended and/or current sludge treatment technology	I. Thickening/Anaerobic Digestion/Dewatering	No change	Anaerobic Digestion and sludge dewatering in place. Recommended Thermal Drying to produce Class A Biosolids.	Recommended in S.M.P that sludge management should address animal slaughtering, industrial biological and food processing sludges in the region.

* There were no results of sludge analysis made available for Clonmel.

(x) County Laois

Portlaoise was the designated Hub Centre in all three Studies, except its region code changed from 46 to 44 in the 1997 Study. Industrial Discharge arises from spent mushroom compost, slaughtering industry, Randstone Ltd, Irish Forest Products, Coolrain sawmill, Smith and McLaurin Ltd. The Laois Co. Co. Sludge Management Plan is complete (Weston-FTA, 1993; FTC, 1998c; McGlinchey, 2001).

Table 5.44 Details of Hub Centre 44, Portlaoise (wastewater treatment plant built in 1981, sludge treatment [sludge dewatering] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	10,000 (total P.E. of region is 32,000)	No change	14,500	--
Wastewater Treatment Technology	Activated sludge treatment	No change	Activated sludge treatment and chemical precipitation using ferric chloride	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Composting (Windrow).	No change	Sludge dewatering in place. Anaerobic Digestion and either Composting, Thermal Drying or Alkaline Stabilisation is recommended for Portlaoise.	--

Table 5.45 Results of Portlaoise sludge analysis (mg/kg dw) (Aug. 2001)

	K	Mn	Zn	Cu	Ni	Cr	Pb	Cd	Hg	Mg	Co	Fe
Av.	3687	313	535	745	42	35	99	1.43	0.71	2565	1.6	11956
Max	5569	572	651	1666	100	74	163	2.35	2.16	3393	1.6	19265
Typical	3000	260	1700	800	80	-	500	10	6	-	-	-
S.I. 148/1998 Legislative limit	-	-	2,500	1,000	300	-	750	20	16	-	-	-

(y) County Kilkenny

Kilkenny was the designated Hub Centre in all three Studies, except the region code changed from 47 to 45 in the 1997 Study. The main sources of industrial Discharge arise from brewery waste, Textdeck (dying plant), IPODEC (i.e.waste disposal company), meat rendering plant and Honey Clover. The Kilkenny Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c).



Figure 5.10 Extended aeration at Kilkenny wastewater treatment plant

Table 5.46 Details of Hub Centre 45, Kilkenny (wastewater treatment plant built in 1990, sludge treatment [sludge dewatering and Alkaline Stabilisation] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	100,000 (total P.E. of region is 114,000)	No change	110,000	--
Wastewater Treatment Technology	Biological filtration and extended aeration	No change	No change	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended 1. Thickening/Anaerobic Digestion/Biodrying	No change	Sludge dewatering and Alkaline Stabilisation in place it recommended sludge treatment technology is undecided.	Recommended in the S.M.P that sludge management should address significant quantities of food processing sludge in Ballyragget, animal slaughtering and industrial biological sludges in the south.

* There were no results of sludge analysis made available for Kilkenny.

(z) County Carlow

Carlow was identified as the designated Hub Centre for Co. Carlow in all three studies, only difference was that their region code changed from 48 to 46 in the 1997 Study. Industrial discharge arises from Braun, electroplating industries, metal sheet fabrication industries, Greenvale Bacon factory, and Celtic Linen. The Carlow Co. Co. Sludge Management Plan is not complete (Weston-FTA, 1993; FTC, 1998c).

Table 5.47 Details of Hub Centre 46, Carlow (wastwater treatment plant was built in 1987, sludge treatment [sludge dewatering and alkaline stabilisation] in place).

	1993 Sludge Strategy Study	1997 Non Haz. Sludge Study	2001/2002 M.Sc. Study	Comment
Population equivalent (P.E)	28,250 (total P.E. of region is 79,000)	No change	31,500	--
Wastewater Treatment Technology	Activated sludge treatment	No change	No change (extended aeration, denitrification and chemical precipitation using ferric chloride is planned for the future).	--
Recommended and/or current sludge treatment technology	Sludge dewatering in place. Recommended I. N-Viro/Agri Soil Lime Treatment.	No change	Sludge dewatering and Alkaline Stabilisation in place	Recommended in S.M.P that sludge management should address animal slaughtering sludge.

Table 5.48 Results of Carlow sludge analysis (Sept. 1999), (mg/kg/dw)

Metal(s)	Cd	Cu	Pb	Hg	Ni	Zn
Cavan	<1.04	327	29.2	-	27	667
S.I. 148/1998 Legislative limit	20	1,000	750	16	300	2,500

5.2.1 Hub Centre development from 1993 to 2003

Table 5.49 compares the original designation of Hub Centres with the current situation. It also highlights those acting as full scale Hub Centres, those producing Class A Biosolids and those governed by Sludge Management Plans. There have been significant changes for a number of reasons.

In the original 1993 Sludge Strategy Report, 48 Hub Centres were proposed (Weston-FTA, 1993). The 1993 Study was not based on county boundaries. The 1997 Non-Hazardous Sludge Inventory redefined the regions along county boundary lines resulting in a total of 46 Hub Centres (FTC, 1998c). The review of Hub Centres carried out in this M.Sc. Study identified 35 current Hub Centres. The remaining sites have been reclassified since 1997, for various reasons. One of the main reasons for the most recent changes is the preparation of Local Authority's Sludge Management Plans. Some counties have reduced the number of Hub Centres, others have combined for the purpose of joint waste management plans and more have relocated Hub Centres for logistical or economic reasons.

An example is County Mayo, where the original Hub Centres of Castlebar and Ballina were reassigned as an on-site dewatering facility and a Satellite, respectively. An alternative site was designated in Derrinnumera, as the single sludge Hub Centre for County Mayo. This was because, according to FTC (2002), "*An Bord Pleanála, in lieu of the Minister, certified the EIS for the expansion and upgrade of Castlebar wastewater treatment plant subject to five conditions*" In particular, Condition number 3 stated that no sewage sludge or landfill leachate from outside the expanded Castlebar Wastewater Treatment Plant shall be transported onto the site for processing, due to the limited assimilative capacity of the river system and relative to the likely demands arising from within the Castlebar area.

Table 5.49 A comparison of Hub Centres recommended in the 1993 Sludge Strategy Study with the 1997 and subsequent reviews

County	Region Codes	1993 Hlub Centres	Region Codes	1997 Hub Centres	2003 Hub Centre	Rec. Sludge Treat. Tech.
Donegal ◀	1	Buncrana	1	Buncrana	1.Buncrana	1
	2	Letterkenny	2	Letterkenny	2.Letterkenny	1
	3	Burtonport	3	Burtonport	3.Gweedore	1
	4	Donegal	4	Donegal	4.Donegal	1
Sligo —	5	Sligo	5	Sligo	5.Sligo	2 & 1
Leitrim ◀	5	Sligo	6	C/Shannon	6.C/Shannon	3
Mayo ◀	6	Ballina	7	Ballina	7.Derrinnumera	1
	7	Castlebar	8	Castlebar		
Roscommon ◀	8	Boyle	9	Castlerea	8.Roscommon	4,3,1 *(1)
Galway ◀	9	Tuam	10	Tuam	9.Tuam	1/4 (1)
	10	Galway	11	Galway		
	11	Ennis	12	Ennis	10.Limerick	7
Clare —	12	Kilkee	13	Kilkee		
	13	Shannon	14	Shannon		
	14	Limerick	15	Limerick	10.Limerick	7
Limerick —	15	N/west	16	N/west		
	16	Tralee	17	Tralee	11.Tralee	2 & 1
Kerry —	17	Killarney	18	Killarney	12.Killarney	5
	18	Skibbereen	19	Skibbereen	13.Mallow	7
	19	Kinsale	19/20	Skibbereen/ Ballincollig	14.Charleville	7
	20	Ballincollig	20	Ballincollig	15.Ballincollig	7
	21	Cork city	21	Cork		
	22	Mallow	22	Mallow		
Waterford—	23	Charleville	23	Charleville		
	24	Dungarvan	24	Dungarvan	16.Dungarvan	2 & 1
	25	Waterford city	25	Waterford city		
Wexford —	26	Wexford	26	Wexford	17.Enniscorthy	7
	27	Enniscorthy	27	Enniscorthy		
Wicklow ◀	28	Wicklow	28	Wicklow	18.Wicklow	2 & 1
	29	Bray	29	Bray	19.Blessington	4
Dublin —	30	Ringsend	30	Ringsend	20.Ringsend	2 & 1
	31	North Dublin	31	North Dublin		
	32	Drogheda	32	Drogheda	21.Drogheda	2 & 1
Louth ◀	33	Dundalk	33	Dundalk	22.Dundalk	2 & 1
	34	Monaghan	34	Monaghan	23.Monaghan	7
Monaghan ◀	34	Monaghan	34	Monaghan	23.Monaghan	7
Cavan ◀	35	Cavan	35	Cavan	24.Cavan	3
Longford ◀	36	Longford	36	Longford	25.Longford	3
Westmeath —	37	Mullingar	37	Mullingar	26.Mullingar	7
	39	Athlone				
Meath ◀	38	Navan	38	Navan	27.Navan	2 & 1
Offaly —	40	Tullamore	39	Tullamore	28.Tullamore	7
Kildare ◀	41	Naas/Osberstown	40	Naas/Osberstown	29.Oberstown	2 & 1
NR Tipp. —	42	Roscrea	41	Neneagh	30.Nenagh	7
	43	Thurles	42	Thurles	31.Thurles	7
	44	Nenagh				
SR. Tipp. ◀	45	Clonmel	43	Clonmel	32.Clonmel	2 & 1
Laois ◀	46	Portlaois	44	Portlaois	33.Portlaois	2 & 1
Kilkenny —	47	Kilkenny	44	Kilkenny	34.Kilkenny	7
Carlow —	48	Carlow	46	Carlow	35.Carlow	4

● Operational Hub Centres, ◻ Producing Class A Biosolids, ◀ Sludge Management Plans Ready, — Sludge Management Plans not ready. 1. Thermal Drying, 2. Mesophilic Anaerobic Digestion with pre/post pasteurisation, 3. Composting, 4. Alkaline Stabilisation, 5. Autothermal Thermophilic Aerobic Digestion (ATAD), 6. Aerobic Digestion with pre/post pasteurisation, 7. Undecided (this is where Local Authorities have put forward recommended sludge treatment technologies, and are waiting on decisions regarding its selection from tenders and contractors involved in the Design Build Operate (DBO) process)

The Derrinnumera site has positive attributes, including remoteness from neighbouring houses and sensitive receptors, having a relatively good road network, and a sufficient footprint for the construction of a sludge treatment centre (FTC, 2002).

Another example was Wicklow, where, after conducting the transportation plan, it was concluded that Hub Centres should be established at both Wicklow and Blessington, while Greystones will act as a stand-alone treatment facility. It is intended that Greystones will provide sludge treatment by using Anaerobic Digestion with pre/post pasteurisation, while Wicklow will use Thermal Drying, and Alkaline Stabilisation will be used in Blessington (FTC and Barry, and Partners, 2002).

Counties Limerick and Clare are the first two counties in Ireland to integrate their Sludge Management Plans. This is where a single sludge Hub Centre will provide the required sludge treatment for both counties. It is planned for County Limerick, replacing 4 Hub Centres, three of which were located in Clare.

County Donegal has still maintained its number of Hub Centres at 4, but has relocated one of them. Burtonport has been reassigned as a Satellite and replaced by Gweedore as Hub Centre. This is because the estimated quantity of sludge produced at the Gweedore treatment works made it more economical to locate the Hub Centre thereby eliminating the need to transport the large volumes of sludge (Holohan, 2001).

5.2.2 Hub Centres producing Class A Biosolids

Only 5 of the 35 plants are currently producing Class A Biosolids. These are Killarney, Ringsend, Carlow, Navan and Osberstown. Ringsend is the only Hub Centre that is fully operational, producing Class A Biosolids, while also treating imported sludge from surrounding regions. Killarney is producing Class A sludge using ATAD, but not, as yet treating imported sludge. The remaining three plants are using Alkaline Stabilisation to produce Class A Biosolids. Carlow has been producing Class A Biosolids since 2002, when they adopted a thermal phase into their Alkaline Stabilisation treatment process. Navan and Osberstown use Alkaline Stabilisation as an interim measure to produce Class A Biosolids.

According to Local Authorities, the treatment process of Alkaline Stabilisation works well, in that it can reach and maintain the standards required. However, there are concerns about the large quantities of sludge produced. Thus, as part of Navan and Osberstown Sludge Management Plans, Thermal Drying is being proposed.

5.2.3 Sludge treatment technology development from 1993 to 2003

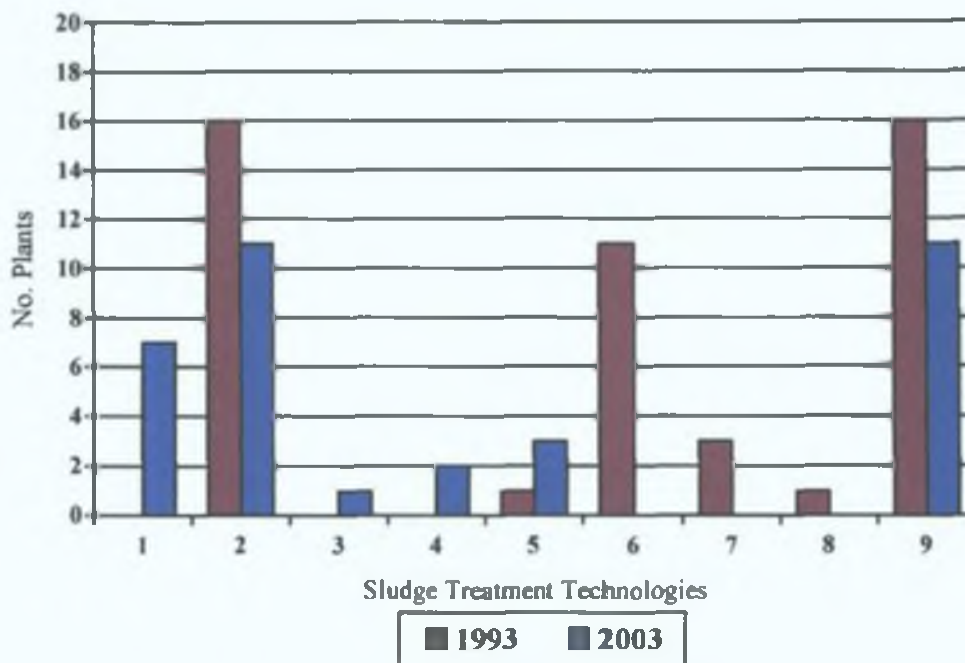


Figure 5.11. Changes in proposed sludge treatment methods from 1993 to 2003

1, Thermal Drying. 2, Mesophilic Anaerobic Digestion with pre/post pasteurisation, 3, ATAD, 4, Alkaline Stabilisation, 5, Composting, 6, Mesophilic Aerobic Digestion with pre/post pasteurisation, 7, N-Viro Agri-soil, 8, Biodrying, 9, Undecided (The exact technology could be any of the above or, alternatively, various combinations of the above. This is because, at the time of review, no single technology was identified as been the most appropriate long term solution)

It can be seen from figure 5.11, that in 1993 Mesophilic Anaerobic Digestion (16 plants) and Mesophilic Aerobic Digestion (11 plants) were recommended for the majority of the 48 designated Hub Centres.

The reason why Anaerobic Digestion was considered the most favourable option in 1993, was because it is one of the most common forms of treatment in other countries and is a good technology for treating sewage sludge, taking advantage of the energy of the methane by-product. It was also considered more economical for plants with populations in excess of 25,000 P.E. Aerobic Digestion was also considered a

favourable sludge treatment option, because it could be used to treat extended aerated sludges, which were considered unsuitable for Anaerobic Digestion. It was also considered the best environmental option for smaller treatment works (Weston-FTA, 1993).

The treatment technologies recommended in the Sludge Strategy Study were intended as a starting point, from which a detailed Sludge Management Plan was to emerge for each nominated area (Weston-FTA, 1993).

When compared to 2003, it can be seen that Mesophilic Anaerobic Digestion with post pasteurisation has become the most common sludge treatment technology, with 11 Hub Centres proposing to use it. This is where Thermal Drying is being used in many cases as the pasteurisation stage.

In the Donegal Sludge Management Plan, it has been stated that the digestion/dewatering option is not cost effective and leaves the final product as a 20-25% solid cake content, which is not an attractive material for agricultural or horticultural disposal. It also creates storage and handling problems, particularly if the final disposal route to agriculture/horticulture is unavailable for long time periods, because of, for example, poor weather conditions for land-spreading. If however, Thermal Drying is used, the final product is significantly reduced in volume and weight and is much more amenable to storage and handling. The dried Biosolids can be directed easily into either the agricultural or horticultural areas, as it can be provided in bagged form (Holohan, 2001).

Also, the County Louth Sludge Management Plan, states that the Biosolid product from the Anaerobic Digestion processes, even when dewatered, is only 30% less in volume, and has a lower nutrient content than the wastewater sludge prior to digestion. The technological combination of Mesophilic Anaerobic Digestion with Thermal Drying will produce a pasteurised Biosolids product that can be used as a beneficial fertiliser in agriculture, or in landscaping operations. Energy produced by the Anaerobic Digestion process can contribute towards the cost of Thermal Drying (Tobin Environmental Services, 1999).

Only one Hub Centre (Killarney) is using ATAD. Seven propose to use Thermal Drying, two intend to use Alkaline Stabilisation, and three have selected Composting. Also, there are 11 plants that have not decided which sludge treatment process to select, due to incomplete Sludge Management Plans, the majority of which won't be complete for at least 12 months.

Some plans have yet to go to tender. Others are Design Build Operate (DBO) contracts, and, as a result, are waiting on a decision by the contractors regarding the selection of their specific sludge treatment technologies. Local Authorities have devolved responsibility to contractors and, as a result, now play little part in the decision making process regarding the choice of technology used. It is thought that the majority of these plants will be opting for Mesophilic Anaerobic Digestion with post pasteurisation (i.e. Thermal Drying). This is because of problems envisaged with Alkaline Stabilisation, while Composting is only associated with low sludge production. ATAD and Mesophilic Aerobic Digestion have not been recommended by any of the Local Authorities.

5.3 Characterisation of Irish sewage sludges

In total, thirteen heavy metals were analysed, selected with reference to the Waste Management (*Use of Sewage Sludge in Agriculture*) Regulations 1998 (SI 148 of 1998) as amended by S.I. 267 of 2001, the Dutch List of soil contamination parameters, and US EPA 503 Rule (CFR40 Part 503), and site-specific issues.

Because of the large number of samples for analyses, an alternative digestion method (using the Hach heating block) was developed and evaluated against the standard microwave digestion method.

5.3.1 Method development and evaluation.

Method development involved optimisation of a set of selected variables, i.e. digestion temperature, digestion time, sample weight, drying temperature, and the volumes of HNO₃ and H₂O₂, (see Table 5.50). The performance of variations of the method was assessed using recovery of a standard reference spike.

Table 5.50 Variable testing and selection for the Hach Digestion method

Variable	Variable Range	Selected Variable(s)
Digestion Temp. (°C)	100°C-150°C	100°C
Digestion Time (hrs.)	0.5-6 hrs.	6hrs.
Sample Wt. (g)	0.3-0.5 g	0.3g
Time (hrs.) & Temp. (°C) Sample Dried	24-36 hrs. at 100°C, 8-24 hrs. at 200°C	24 hrs. at 100°C & 8 hrs. at 200°C
Vol. HNO ₃ (ml)	5-10ml	7.5 ml
Vol. H ₂ O ₂ (ml)	0.2-2.0ml	2 ml

A Hach temperature of 100°C was selected because at temperatures in excess of 100°C the sample was found to burn dry, with some samples more quickly than others. At a constant temperature of 100°C this problem did not arise.

The digestion time was varied between 0.5 and 6 hours. It was found that at time periods ranging from 0.5 to 2 hours, poor recovery of the reference standard was obtained. The 3 hour digestion proved favourable when temperatures in excess of 100°C was used, but because the sample was burning dry, it was decided to reduce the temperature, and increase the digestion time. It was found that after a 6-hour digestion, maximum recovery of the reference standard was obtained.

The sample weight was varied between 0.3-0.5g. Upon addition of HNO₃ to 0.4-0.5g of sample in a 20ml volume test tube, it was found that some of the sample was expelled from the test tube, due to a vigorous reaction between the sample and the acid. This did not occur at 0.3g or less.

The sample drying time and temperature was varied between 24-36hours at 100°C, followed by 200°C for time periods ranging between 8 to 24 hours. The second step, at 200°C was necessary to reduce the organic content of the sample, which increased the reaction between the HNO₃ and the sample, causing expulsion from the test tube.

The volumes of digestion chemicals tested ranged between 5-10 ml for HNO₃ and 0.2 – 2 ml for H₂O₂. It was found that additions of 7.5ml of HNO₃ and 2ml of H₂O₂ gave the best recoveries of the reference standard. At volumes below 7.5ml of HNO₃ poor recovery was found and also there was a greater potential of samples burning dry. At volumes of HNO₃ greater than 7.5ml, sample expulsion was found to occur upon

addition of H_2O_2 . Another problem associated with using volumes in excess of 7.5ml, was that the total volume of acid and hydrogen peroxide in the tube extended above the surface of the heating block, resulting in temperature variations.

H_2O_2 was used to speed up the digestion procedure. It acts as a catalyst causing a vigorous reaction that improves contact between the sample and the acid. It also changes the colour of the final sample (from a dark orange to straw yellow) improving clarity of the sample for analysis by the ICP-MS.

A range of 0.2-2ml of H_2O_2 was examined. A volume of 2ml of H_2O_2 gave the best recovery rates and colour change. Because of the vigour of oxidation, additions of H_2O_2 were made in 0.2ml aliquots.

When the optimum conditions were determined, the Hach and microwave digestion methods were compared by digestion and analysis of a certified reference material. The results are presented in Appendix A. The Hach results compared very favourably with those obtained using the Microwave method, with better reproducibility in many cases. Because the Hach method had advantages when handling large numbers of samples, it was selected for use in the main study.

5.3.2 Analysis of sludge samples

Table 5.51 and 5.52 shows summary of results of 13 heavy metals analysed in Irish municipal and industrial sewage sludge samples respectively obtained from 43 sites around Ireland (see Appendix B for the full table of heavy metal results). These 43 sites take account of the Hub Centres proposed in the 1993 National Sludge Strategy Report, with some identified variations in areas that had no established wastewater treatment plants/Hub Centres, and industrial sludges, which were obtained from Shannon Industrial Estate and Swords. The instrumentation used was the ICP-MS and the FAAS. Selection of the particular method was based on the expected heavy metal content of the sample. The ICP-MS analysed Cd, Ni, Pb, Hg, Co, As, Mo, Se Cr, and Ba and the FAAS analysed Cu, Zn and Fe. Results are reported on the mean value of triplicates, and stated in mg/kg/dw, and are presented with the legislative limits for heavy metals in sludge (Waste Management Regulations S.I. No. 148/1998) and percentage spike recoveries.

Table 5.51 Summary of heavy metal analysis of Irish municipal sewage sludge

Metal	Ranges of heavy metals found in Irish sludge (mg/kg.dw)	Legislative limits for heavy metals in sludge (Waste Management Regulations 1998) (mg/kg.dw)	% Spike recoveries
Cu	451 – 2,134	1,000	91
Zn	331 – 2,077†	2,500	90
Cd	<17	20	107
Ni	<17	300	90
Pb	15 – 168	750	117
Hg	<17	16	111
Co	<17 – 100	-	98
As	<101	-	104
Mo	<7	-	100
Fe	2,541 – 279,333	-	102
Se	<84	-	103
Ba	71 – 2,800	-	110
Cr	<167 – 1,152†	-	102

† 11,176 mg/kg.dw Zn for Dundalk (Industrial discharge), 2,001mg/kg.dw Cr for Tipperary (Industrial discharge)

It can be seen from table 5.51 that normal municipal Irish sludges are well within legislative limits for 5 of the 6 regulated metals (in Dundalk and Tipperary specific industrial discharges account for exceedences of Zn and Cr limits respectively). The Cu level in six sludges was over the limit 1000 mg/kg.dw, with one sample over 2,000 mg/kg.dw. Further details of the full set of results are given in the following sections.

Table 5.52 Results of heavy metals analysis of industrial sludge

Metal	Shannon (mg/kg.dw)	Swords (mg/kg.dw)	Legislative limits for heavy metals in sludge (Waste Management Regulations 1998) (mg/kg.dw)	% Spike recoveries
Cu	854	383	1,000	91
Zn	20,209	1954	2,500	90
Cd	56	<17	20	107
Ni	<17	<17	300	90
Pb	70	82	750	117
Hg	<17	<17	16	111
Co	385	<17	-	98
As	<101	<101	-	104
Mo	<7	<7	-	100
Fe	42,889	5,457	-	102
Se	<84	<84	-	103
Ba	1,664	290	-	110
Cr	3,545	<168	-	102

It can be seen from table 5.52 that the Shannon industrial sludge was over the legislative limits for Zn and Cd. The Swords sludge did not exceed any legislative limit.

5.3.2.1 Copper

Copper values for municipal sludge ranged from 451-2,134 mg/kg.dw. In six instances, copper was found to exceed the legislative limit of 1000 mg/kg.dw in the 1998 Waste Management (*Use of Sewage Sludge in Agriculture*) Regulations. These were Monaghan (1,345 mg/kg.dw), Newcastlewest (1,093 mg/kg.dw), Thurles (1,037 mg/kg.dw), Drogheda (1,303 mg/kg.dw), Portlaw (1,262 mg/kg.dw), and Roscommon (2,134 mg/kg.dw).

The high concentrations of copper are a result of agricultural discharge being received and treated at these plants. Copper is administered to cattle that are grazing on copper deficient soils. The literature shows that high Fe concentrations can reduce the availability of copper to both plants and animals. Because many Irish soils contain high Fe levels, it is thought to be a contributory factor of copper deficiency in livestock. This, coupled with the fact that cattle have a low absorption rate of copper in the body, means that farmers must dose their livestock at regular intervals, resulting in a high

input of this element to the environment (Coulter *et al.*, 1999; Vierboom, *et al.*, 2002). One solution would be to treat such wastewaters separately.

The Northern half of the country has high soil copper levels (Coulter *et al.*, 1999), which is also thought to contribute to the elevated levels found in Monaghan, Drogheda and Roscommon, through mineral leaching.

Copper is retained in the top 10cm of soil. It is tightly bound and not believed to negatively affect crop yields (Barry *et al.*, 1995). However, application of N is found to increase the copper content of pastures, which could lead to problems in sheep and cattle particularly at high sludge levels (Coulter *et al.*, 1999).

5.3.2.2 Zinc

Zinc levels ranging between 331 – 2,077 mg/kg.dw were obtained in municipal sludge using the FAAS. In one municipal plant (Dundalk) Zn levels of 11,176 mg/kg.dw were found.

The levels of Zn found in industrial sludge were 1,945 mg/kg.dw in Swords and 20,209 mg/kg.dw in Shannon.

In 1992, results of heavy metal analysis from nine Irish sludge samples showed that one site was found to have elevated levels of zinc (6,731 mg/kg.dw). This finding was in an area that had no obvious industrial source (McGrath, *et al.*, 2000). The two sites with elevated zinc levels above the mandatory limit of 2,500 mg/kg.dw in this M.Sc. Study are attributed to industrial discharge. The two sites were Dundalk and Shannon Industrial Estate.

Shannon Industrial Estate had high zinc levels because it caters for an industrial park that includes heavy metal industries. All sludge generated at this plant is disposed of to an on-site licensed landfill.

The Dundalk plant receives industrial discharges from cosmetics, lime production, fabric manufacturing and electrical applications industries. The elevated zinc levels are likely to originate from these industrial groups. This result was communicated to the

Local Authority, which has diverted sludge from the plant to landfill, pending further investigation.

5.3.2.3 Chromium

Chromium values obtained for Irish municipal sludges ranged between <167 and 1,152 mg/kg.dw.

Industrial sludges analysed were between <167 – 3,545 mg/kg.dw (Shannon).

Because there is no limit value set for Cr in Irish sludge, all results were compared to the USEPA ceiling concentration limit value for chromium, which is 3,000 mg/kg.dw. Only Shannon Industrial Estate exceeded this limit, at a value of 3,545 mg/kg.dw. This is because it caters for industry including electroplating industries.

5.3.2.4 Lead, Nickel, Cadmium and Mercury.

Lead, nickel and cadmium were below mandatory limits for all municipal sludge samples analysed. Cadmium was found to breach legislative limits at one industrial plant (Shannon Industrial). All sludge samples analysed for mercury were found to be less than the ICP-MS limit of detection.

- Lead was found to range between 15 and 168 mg/kg.dw. All samples were below the limit of 750 mg/kg.dw.
- Nickel was found to be below the legislative limit of 300 mg/kg.dw, with all samples less than the ICP-MS detection limit of 17 mg/kg.dw.
- Shannon Industrial Estate sludge was the only sludge sample found to exceed the legislative limit for cadmium of 20 mg/kg.dw, at 56 mg/kg.dw. This result can be explained by the industrial inputs to the plant. All others were below 17 mg/kg.dw.
- All sludge samples analysed for mercury were found to be less than the ICP-MS detection limit of 17 mg/kg.dw. When compared to the legislative limit of 16 mg/kg.dw, it is considered that all results were below this mandatory limit. Mercury is a very difficult element to analyse by multi-element analysis using the ICP-MS, because it is subject to numerous physical interferences, caused by the chemistry of Hg, which enhance the signal reading. It is therefore recommended that mercury is analysed in further studies using the hydride

generation AAS and digested using hydrochloric acid in order to achieve a lower the detection limit.

5.3.2.5 Iron

Iron values obtained in Irish sludge ranged between 2,541-279,333 mg/kg.dw. High Fe was found at plants where ferric chloride is used for phosphate removal.

European legislation does not currently limit iron in sewage sludge. However, the revision of the Directive on land application will introduce more stringent limit values for potentially toxic elements (PTEs). In the future, the use of Fe salts for phosphate removal could potentially limit the acceptability of sludge for use in agriculture, particularly when ferric precipitation is considered to also have the ability to concentrate a higher proportion of other elements in the final sludge (i.e. Cd, Ni, Pb and Zn) (ICON, 2001). Concentrations of 2,400 mg/kg.dw iron in soil may be toxic to cattle with undesirable effects appearing at lower, sub toxic doses (Madejon *et al.*, 2002).

5.3.2.6 Arsenic, Molybdenum, Selenium, Barium and Cobalt.

Arsenic, molybdenum and selenium are not governed by EU legislation therefore all results were compared to either the pollutant limit concentrations or ceiling values of the 40CFR Part 503 Rule. Barium and cobalt are not regulated by any legislation therefore limit values obtained are stated.

- Arsenic results were compared to the pollutant limit concentration of 41 mg/kg.dw as outlined in the 40CFR Part 503 Rule. All results attained were below the ICP-MS detection limit of 101 mg/kg.dw. Arsenic is subject to physical and spectral interferences using the ICP-MS, therefore it is recommended that this element be analysed in future studies using the Hydride generation AAS and digested using HCL acid in order to improve the limit of detection.
- Results for molybdenum were compared to the ceiling value of 75 mg/kg.dw in the 40CFR Part 503 Rule. All samples were below the detection limit of 7 mg/kg.dw.
- Selenium results obtained were compared to the pollutant limit of 100 mg/kg.dw in the 40CRF Part 503 Rule. All Irish values obtained were below the detection limit of 84 mg/kg.dw.

- Barium values ranged from 71 to 2,800 mg/kg.dw.
- Most cobalt values obtained were below the detection limit of 17mg/kg.dw, with the exception of Mullingar (24 mg/kg.dw), Roscommon (47 mg/kg.dw), Tipperary (36 mg/kg.dw), Shannon Industrial (385 mg/kg.dw) and Dundalk (100 mg/kg.dw).

5.4 The impact of metal contents on Biosolid reuse as a sustainable option

It can be seen from the results that, with some noted exceptions, the majority of Irish sewage sludge is safe for agricultural reuse, with reference to the 1998 Waste Management Regulations. With the 7 municipal plants (i.e. 6 for Cu and 1 for Zn) that breached legislative limits, it is considered that on site treatment of industrial wastes in each case will bring the sludge within the legislative limits.

Prior to 2001, these sludges would have been prohibited for reuse in agriculture. Legislative changes in the 2001 Waste Management Regulations (as described in more detail in section 5.5) moved from absolute sludge limits to flexible loading rates. This means that all municipal sludges are suitable for reuse. The results show that reuse of Irish municipal sludges in agriculture is a sustainable option.

5.5 Sludge loading rates

The Council Directive 86/278/EEC, (*on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture*), and its regulations set absolute limits for certain metals in sludges and soils along with a maximum tonnes dry solids per hectare (2tds/ha/yr). This left no flexibility for managing unusual site specific circumstances. The 2001 regulations changed this approach to a maximum loading per year based on a 10-year average, subject to proper nutrient management planning. The Schedule of the 1998 Regulations is amended by the substitution of the following for Part II (see table 5.53).

Table 5.53 Limit values for amounts of heavy metals which may be added annually to agricultural land, based on a ten year average (kg/ha/yr)

Heavy Metal	Limit Values
Cadmium	0.05
Copper	7.50
Nickel	3.00
Lead	4.00
Zinc	7.50
Mercury	0.10
Chromium	3.50

Balancing the nutrient requirements of the crop with nutrients in the soil is the key to good agricultural practice. The nutrient status of the soil will be evident from soil analysis, cropping and fertilisation history. Restrictions on the use of Biosolids should take account of specific planting, harvesting and grazing constraints, together with nutrients, heavy metals and hydraulic loading rates, as outlined in the legislation (FTC, 1998a)

Table 5.54 shows the annual sludge application rates obtained for Irish sludge samples analysed. Calculations are made for the seven metals regulated in the Waste Management Regulations 2001 and are based on the assumption that all sludges are applied in accordance with a nutrient management plan and that the concentration of heavy metals in soils are below the current mandatory limits.

It can be seen that, by taking this approach, higher loading rates of 3 tons per hectare per year can potentially be used in the majority of cases. Dundalk and Tipperary would be limited to 1 and 2 tonnes per hectare per year respectively (because of elevated zinc and chromium levels found).

The maximum loading rate is dictated by the limit of detection for cadmium. This is a function of sample size. It is likely that, with a larger sample size, a better limit of detection would be achieved and a higher loading rate would be permissible.

Table 5.54 Annual sludge application rate(s)(metric tons/ha/365 day period)

Sample	Cd	Cu	Ni	Pb	Zn	Hg	Cr
Ringsend	*3.00	17.00	*180.00	65.00	13.00	*6.00	*21.00
Letterkenny	*3.00	13.00	*180.00	48.00	8.00	*6.00	*21.00
Portlaois	*3.00	12.00	*180.00	103.00	7.00	*6.00	*21.00
Nenagh	*3.00	12.00	*180.00	60.00	6.00	*6.00	*21.00
Castlebar N.L.	*3.00	13.00	*180.00	123.00	12.00	*6.00	*21.00
Kilkenny	*3.00	10.00	*180.00	73.00	6.00	*6.00	19.00
Ballincollig	*3.00	14.00	*180.00	62.00	8.00	*6.00	*21.00
Navan	*3.00	12.00	*180.00	144.00	15.00	*6.00	*21.00
Castebar + L	*3.00	17.00	*180.00	202.00	23.00	*6.00	*21.00
Buncrana	*3.00	15.00	*180.00	63.00	6.00	*6.00	*21.00
Cionakilty	*3.00	14.00	*180.00	121.00	17.00	*6.00	*21.00
Carlow + L	*3.00	12.00	*180.00	122.00	18.00	*6.00	*21.00
Monaghan	*3.00	6.00	*180.00	42.00	5.00	*6.00	*21.00
Tralee	*3.00	8.00	*180.00	35.00	5.00	*6.00	14.00
Shannon D.	*3.00	15.00	*180.00	202.00	8.00	*6.00	*21.00
Tullamore	*3.00	8.00	*180.00	57.00	4.00	*6.00	*7.00
Ennis	*3.00	9.00	*180.00	79.00	11.00	*6.00	*21.00
Dundalk	*3.00	11.00	*180.00	55.00	1.00	*6.00	*21.00
Ballina	*3.00	11.00	*180.00	53.00	7.00	*6.00	*21.00
Greystones	*3.00	10.00	*180.00	66.00	6.00	*6.00	*21.00
Shannon Ind.	1.00	9.00	*180.00	57.00	0.40	*6.00	1.00
Charleville	*3.00	13.00	*180.00	273.00	10.00	*6.00	*21.00
Swords	*3.00	20.00	*180.00	49.00	4.00	*6.00	*21.00
N.C.W	*3.00	7.00	*180.00	39.00	7.00	*6.00	*21.00
Strandhill	*3.00	10.00	*180.00	103.00	8.00	*6.00	*21.00
S.M.B	*3.00	14.00	*180.00	165.00	9.00	*6.00	*21.00
Castletroy	*3.00	12.00	*180.00	116.00	10.00	*6.00	*21.00
Thurles	*3.00	7.00	*180.00	36.00	4.00	*6.00	5.00
Obserstown	*3.00	11.00	*180.00	57.00	7.00	*6.00	3.00
Drogheda	*3.00	6.00	*180.00	56.00	7.00	*6.00	*21.00
Portlao	*3.00	6.00	*180.00	39.00	15.00	*6.00	*21.00
Cavan	*3.00	12.00	*180.00	140.00	9.00	*6.00	*21.00
Longford	*3.00	16.00	*180.00	74.00	8.00	*6.00	*21.00
Carlow N.L.	*3.00	13.00	*180.00	43.00	8.00	*6.00	*21.00
C.O.S	*3.00	17.00	*180.00	26.00	8.00	*6.00	*21.00
Tipperary	*3.00	8.00	*180.00	24.00	5.00	*6.00	2.00
Roscommon	*3.00	4.00	*180.00	33.00	4.00	*6.00	8.00
Tuam	*3.00	12.00	*180.00	48.00	7.00	*6.00	*21.00
Enniscrone	*3.00	14.00	*180.00	55.00	5.00	*6.00	*21.00
Enniscorthy	*3.00	13.00	*180.00	56.00	9.00	*6.00	*21.00
Mallow	*3.00	17.00	*180.00	33.00	8.00	*6.00	*21.00
Killarney	*3.00	8.00	*180.00	36.00	4.00	*6.00	15.00
Mullingar	*3.00	8.00	*180.00	24.00	9.00	*6.00	*24.00

*Calculations are based on limits of detection. Actual loading rates may be higher if better detection limits are achieved. (Example: Ringsend Cu ASAR = $APLR/C * 0.001$ – e.g. $Cu = 7.50/446 * 0.001 = 17$ metric tons/ha/365 day period)

CHAPTER 6

CONCLUSIONS & RECOMMENDATIONS

6.1 **Conclusions**

- In the 1993 Sludge Strategy Study there were 48 designated Hub Centres. In the 1997 Non-hazardous Sludge Inventory, the number of Hub Centres was reduced to 46, this was because the Study redefined regions along county boundaries. Since 1997, Hub Centres have been reclassified for various reasons, as a result there are currently 35 designated Hub Centres. One of the main reasons was because of Local Authorities Sludge Management Plans. While some counties have reduced the number of Hub Centres, others have combined for the purpose of joint waste management plans and more have relocated for logistical or economic reasons.
- There are five Hub Centres producing Class A Biosolids. They include Ringsend, which is the only fully operational Hub Centre in Ireland, in that it is treating sludge from surrounding county regions using Thermal Drying. In addition Carlow, Navan, Osberstown are producing Class A Biosolids using Alkaline Stabilisation, while Killarney is using ATAD.
- The most common form of sludge treatment is Mesophilic Anaerobic Digestion with post pasteurisation, with 11 Hub Centres proposing to use it. This is where Thermal Drying is being used an additional pasteurisation or dewatering stage for existing anaerobic sludge treatments. Only one Hub Centre (Killarney) is using ATAD. Seven propose to use Thermal Drying, two intend to use Alkaline Stabilisation, and three have selected Composting. There are 11 plants that have not decided which sludge treatment process to select, due to incomplete Sludge Management Plans, and Design Build Operate (DBO) contracts.
- Results of sludge analysis showed that, with some noted exception, the majority of Irish sewage sludge is safe for agricultural reuse with reference to the 1998 Waste Management Regulations. With 7 municipal plants that breached legislative limits (i.e. 6 for Cu and 1 for Zn), it is considered likely that on site treatment of industrial wastes in each case will bring the sludge within the legislative limits.
- Recent changes in legislation allowing flexible loading rates also ensure that reuse of Biosolids in agriculture is a sustainable option.

6.2 Recommendations for further research

It is recommended that the following areas be studied further:

- The use of ferric chloride/sulphate in Irish wastewater treatment plants and its implication on agricultural reuse of Biosolids.
- The implications of DBO contracts on the decision making process of sludge treatment in Ireland needs to be examined.
- The determination of specific chemical forms of heavy metals and their mode of binding in soils. Also, the long-term effects of land treatment on normal soil functioning should also be assessed.

REFERENCES

Aldinger, H. (2002) The current debate on regulating the risk associated with cadmium in phosphate fertilizer in the European Union. In: 8th International Annual Conference of AFA, Cairo.

Alonso Alvarez, E. A., Callejon Mochon, M., Jimenez Sanchez, J. C. and Ternero Rodriguez, M. (2002) Heavy metal extractable forms in sludge from wastewater treatment plants. *Chemosphere*. 47, 765-775.

Andersen, A. (2001) *Disposal and recycling routes for sewage sludge, part 1 – sludge acceptance*. European Commission DG Environment. SEDE. Luxembourg.

Angelidis, M. and Gibbs, R. J. (1990) Heavy metals in urban sewage sludges, chemical forms and positive availability. In: P. L'Hermite (ed). *Proceedings of a Symposium, on Treatment and use of sewage sludge and liquid sludge agricultural wastes*, Athens. Elsevier Applied Science. London. 400-405.

Anglian Water. (1996) *A Guide to wastewater Biosolids for farmers and foresters*. Anglian Water. Lincolnshire, England.

Antoniadis, V. and Alloway, B. J. (2002) The role of dissolved organic carbon in the mobility of Cd, Ni and Zn in sewage sludge-amended soils. *Environmental Pollution*. 117, 515-521.

Artola, A., Balaguer, M. D. and Rigola, M. (1997) Use of biological sludge for heavy metal removal, pilot plant application. In: *Proceedings for the speciality Conference of the Water Environment Federation entitled Beneficial reuse of water Biosolids*. Malaga, IWA.

Balmer, P. (2001) Possibilities to improve the quality of wastewater sludges. In: *Conference proceedings of sludge management entering the 3rd Millenium, Industrial, Combined, Water and Wastewater residues*. Taipei. IWA.

Barry, G. A. Chudek, P. J., Best, E. K. and Moody, P. W. (1995) Estimating sludge application rates to land, based on heavy metal phosphorus sorption characteristics of soil. *Water Resources*. 29(9), 2031-2034.

Bartlett, J. and Killilea, E. (2001) The characterisation, treatment and sustainable reuse of Biosolids in Ireland. *Water Science and Technology*. 44(10), 35-40.

Baveye, P., McBride, M. B., Bouldin, D., Hinesly, T. D., Dahdoh, M. S. A., and Abdel-sabour, M. F. (1999) Mass balance distribution of sludge-borne trace elements in a silt loam soil following long-term applications of sewage sludge. *The Science of the Total Environment*. 227, 13-28.

Beckett, P.H.T. and Davis, R. D. (1979) The disposal of sewage sludge onto farmlands, the scope of the problem of toxic elements. *Water Pollution and Control*. 78, 419-445.

Beckett, P.H.T. and Davis, R. D. (1982) Heavy metals in sludge, are their toxic effects additive? *Water Pollution and Control*. 81, 112-119.

Bernard, S. and Gray, N. F. (2000) Aerobic digestion of pharmaceutical domestic wastewater sludges at ambient temperature. *Water Res.* 34(3), 725-734.

Berrow, M. L. and Burridge, J. C. (1991) Uptake, distribution and effects of metal compounds on plants. In: Merian E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. VCH. Weinheim. pp. 399-411.

Bodzek, D., Janoszka, B., Dobosz, C., Warezecha, L. and Bodek, M. (1997) Determination of polycyclic aromatic compounds and heavy metals in sludges from biological sewage treatment plants. *Journal of Chromatography A*. 774, 177-192.

Bragato, G., Leita, L., Figliolia, A. and de Nobili, M. (1998) Effects of sewage sludge pre-treatment on microbial biomass and bioavailability of heavy metals. *Soil and Tillage Research*. 46, 129-134.

Brett, S., Guy, J., Morse, G. K. and Lester, J. N. (1997) *Phosphorus removal recovery technologies*. Environment and Water Research Engineering Section. Imperial College of Science, Technical Medicine. Selper publications. London.

Campbell, C.D., Warren, A., Cameron, C. M. and Hope, S. J. (1997) Direct toxicity assessment of two soils amended with sewage sludge contaminated with heavy metals using a protozoan (*Colpoda Steirii*) bioassay. *Chemosphere*. 34(3), 501-514.

Carbonell-Barrachina, A.A., Jugsujinda, A., Burlo, F., Delaune, R. D. and Patrick Jr., W. H. (1999) Arsenic chemistry in municipal sewage sludge as affected by redox potential pH. *Water Res.* 34(1), 216-224.

Chang, A.C., Page, A. L. and Asano, T. (1995) *Developing human health-related chemical guidelines for reclaimed wastewater and sewage sludge applications in agriculture*. WHO, Geneva.

Chapman, D., (ed). (1992) *Water quality assessment, a guide to the use of biota, sediments and water in environmental monitoring*. 2nd edition. Cambridge, University Press Cambridge.

Cheremisinoff, P. N. (1994) *Sludge management and disposal*. Prentice-Hall Inc. New Jersey.

Christy, P. G. (1997) Lime stabilization and application of sewage sludge in the United States. In: *Proceedings for the speciality Conference of the Water Environment Federation of Beneficial reuse of water and Biosolids*. Malaga, Spain. IWA.

Chua, H. (1998) Effects of trace chromium on organic adsorption capacity and organic removal in activated sludge. *The Science of the Total Environment*. 214, 239-245.

Chumbley, C. G. (1971) Permissible levels of toxic metals in sewage used on agricultural land. *Agricultural Development Advisory Paper No. 10*. Ministry of Agriculture, Fisheries and Food.

CIWEM. (1997) *An introduction to industrial wastewater treatment and disposal*. Booklet 6.

Cole, L. J., McCracken, D. I., Grath, N., Foster, N. and Aitken, M. M. (2001) Using *Collembola* to assess the risks of applying metal-rich sewage sludge to agricultural land in Western Scotland. *Agriculture, Ecosystems and Environment*. 83, 177-189.

Cornu, S., Neal, C., Ambrosi, J., Whithead, P., Neal, M., Sigolo, J. and Vachier, P. (2001) The environmental impact of heavy metals from sewage sludge in ferralsols (Sao Paulo, Brazil) *The Science of the Total Environment*. 271, 27-48.

Coulter, B.S., McDonald, E., MacNaeidhe, F. S., Blagden, P. and Gately, T. F. (1999) *Nutrient trace element status in grassland tillage soils. A report on the chemical composition and nutrient requirements of Irish soils over a period 1989-1998*. End of Project Armis No. 4109. Teagasc, Johnstown Castle Research Centre, Wexford, Ireland. Technical Report.

Davis, B. E. (1980) Trace element pollution. In: Davis, B., (ed). *Applied Soil and Trace Elements*. J. Wiley, Chichester. 287-351.

Davis, G. K. (1991) Molybdenum. In: Merian, E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim VCH. pp. 1089-1101.

de Silonez, M. I., Balsalobre, L., Alba, C., Valderama, M. J. and Peinade, J. M. (2002) Feasibility of copper uptake by the yeast *Pichia guilliermondii* isolated from sewage sludge. *Research in Microbiology*, 153, pp. 173-180.

Dean, R.B. and Suess, M. J., (eds). (1985) The risk to health of chemicals in sewage sludge applied to land. *Waste Management and Research* 3, 251-278.

Dilek, F. B. and Yetis, U. (1992) Effects of heavy metals on activated sludge process. *Water Science and Technology*. 26(3-4), 801-813.

Droste, R.L. (1997) *Theory and practice of water wastewater treatment*. John Wiley and Sons Inc. New York.

Duffus, J. H. (1980) *Environmental toxicology*. Edward Arnold Pub.

Entec O'Dwyer. (2001a) *Meath County Council, Sludge Management Plan for County Meath*.

Entec O'Dwyer. (2001b) *Cavan County Council, Sludge Management Plan for County Cavan*.

Entec O'Dwyer. (2001c) *Longford County Council, Draft Sludge Management Strategy for County Longford*.

Entec O'Dwyer. (2001d) *Kildare County Council, Sludge Management Plan for County Kildare*.

Entec O'Dwyer. (2002) *Leitrim County Council, Sludge Management Plan for County Leitrim*.

Ewers, U. and Schlipkoter, H. W. (1991a) Lead. In: Merian, E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH.

Ewers, U. and Schlipkoter, H-W. (1991b) Intake, distribution, and excretion of metals and metal compounds in humans animals. In: Merian E. (ed)., *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH pp. 571-585.

Fehily Timoney and Company, Barry J.B. and Partners. (2002) *Sludge Management Plan for County Wicklow*. Non-technical summary.

Fehily Timoney and Company. (1998a) *Code of Good Practice for the Use of Biosolids in Agriculture, Guidelines for Local Authorities and Wastewater Treatment Plant Operators*. Prepared for the Department of the Environment and Local Government (Ireland).

Fehily Timoney and Company. (1998b) *A Study of International Practices on the Use of Biosolids in Agriculture*. Prepared for the Department of the Environment and Local Government (Ireland).

Fehily Timoney and Company. (1998c) *Inventory of Non-Hazardous Sludges in Ireland*. In association with WRc. Prepared for the Department of the Environment and Local Government (Ireland).

Fehily Timoney and Company. (1999a) *Sludge Management Plans. A Guide to their Preparation and Implementation*. Prepared for the Department of the Environment and Local Government (Ireland).

Fehily Timoney and Company. (1999b) *Sludge Management Plan for Tipperary South Riding*. Prepared for the Department of the Environment and Local Government (Ireland).

Fehily Timoney and Company. (2001) *Discussion Document – Sludge Management Plan for County Monaghan*.

Fehily Timoney and Company. (2002) *Review of Mayo Sludge Management Plan*. Prepared for: Mayo County Council, Aras an Chontae, Castlebar, Co. Mayo.

Filcheva, E., Cheshire, M. V., Campbell, C. D. and McPhail, D. B. (1996) Effect of heavy metal contamination on the rate of decomposition of sewage sludge on microbial activity. *Applied Geochemistry*. 11, 331-333.

Fishbein, L. (1991) Selenium. In: Merian E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 1153-1191.

Forste, J. B. (1996) Land Application. In: Girovich, M. *Biosolid treatment and management processes for beneficial use*. Marcel Dekker Inc. pp. 47-131. New York.

Foster, I. D. L. and Charlesworth S. M. (1994) Heavy metals in the hydrological cycle, trends and explanation. *Hydro-group working paper, No. 1*. Coventry University. England.

Frost, H.L. and Ketchum, L. H. Jr. (2000) Trace metal concentration in durum wheat from application of sewage sludge and commercial fertilizers. *Advances in Environmental Research*. 4, 347-355.

Fytianos, K., Charantoni, E. and Voudrais, E. (1998) Leaching of heavy metals from municipal sewage sludge. *Environment International*. 24(4), 467-475.

Gardiner, D.T., Miller, R.W., Badamchian, B., Azzari, A.S. and Sisson, D. R. (1995) Effects of repeated sewage sludge applications on plant accumulation of heavy metals. *Agriculture, Ecosystems and Environment*. 55, 1-6.

Gaughhofer, J. and Bianchi V. (1991) Chromium. In: Merian E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 853-879.

Girovich, Mark. J. (1996) *Biosolids treatment and management processes for beneficial use*. Marcel Dekker Inc. New York.

Gosh, S. and Bupp, S. (1992) Stimulation of biological uptake of heavy metals. *Water Science Technology*. 26(1-2), 227-236.

Gove, L. Cooke, C. M., Nicholson, F. A. and Beck, A. J. (2001) Movement of water and heavy metals (Zn, Cu, Pb, Ni) through silty loam amended with Biosolids under steady-state hydrological conditions. *Bioresource Technology* 78, 171-179.

Gray, N. F. (2001) Metal concentration – The decline of metals in Irish sewage sludge. Ireland on Show. *W and WT*. pp. 9.

Gray, N. F. (2002) *Water technology. An introduction for environmental scientists and engineers*. Bristol. Buterworth-Heinemann.

Hall, S. K. (1997) *Chemical exposure and toxic responses*. CRC Lewis Publishers. Bocaaton.

Hani, H. (1991) Heavy metals in sewage sludge and town waste compost. In: Merian E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 357-369.

Hapke, H. J. (1991a) Metal accumulation in the food chain and load of feed food. In: Merian, E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 469-481.

Hapke, H. J. (1991b) Effects of Metals on Domestic Animals. *In: Merian, E., (ed). Metals and their compounds in the environment, occurrence, analysis and biological relevance.* Weinheim. VCH. pp. 531-547.

Hasselgren, K. (1998) Use of municipal waste products in energy forestry, highlights from 15 years of experience. *Biomass and Bioenergy.* 15(1), 71-74.

Hassen, A., Jedidi, N., Cherif, M., M'Hiri, A., Boudabous, A., and van Cleemput, O. (1998) Mineralisation of nitrogen in a clayey loamy soil amended with organic wastes enriched with Zn, Cu and Cd. *Bioresources Technology.* 64, 39-45.

Hing, C. L., Zenz, D. R., and Kuchenrither, R., (editors). (1991) *Municipal Sewage Sludge Management, processing, utilization and disposal.* Vol. 4. Water Quality Management. Library of Technomic Publishing Co. Inc. Lancaster, Philadelphia.

Holohan, J. (2001) *Comhairle Chontae Dhun na nGall, Donegal County Council Draft Sludge Management Plan.*

Hsiau, P. C. and Lo, S. L. (1998) Extractabilities of heavy metals in chemically-fixed sewage sludges. *Journal of Hazardous Materials.* 58, 73-82.

Huebers, H. A. (1991) Iron. *In: Merian, E., (ed). Metals and their compounds in the environment, occurrence, analysis and biological relevance.* Weinheim. VCH. pp. 945-959.

Hutchinson, T.C. and Meema, K.M., (editors). (1987) *Lead, mercury, cadmium and arsenic in the environment.* SCOPE, Published by John Wiley and Sons Ltd.

ICON. (2001) *Pollutants in urban wastewater and sewage sludge.* Final Report. Directorate-General Environment. European Commission.

Jennings O'Donovan Partners. (2002) *Sligo Sludge Management Plan.*

Joshua, W. D., Michalk, D. L., Curtis, I. H., Salt, M., and Osbourne, G. J. (1998) The potential for contamination of soil and surface waters from sewage sludge (Biosolids) in a sheep grazing study, Australia. *Geoderma.* 84, 135-156.

Lazzari, L., Sporní, L., Bertin, P., and Pavoni, B. (2000) Correlation between inorganic (heavy metals) and organic (PCBs PAHs) micropollutant concentrations during sewage sludge composting. *Chemosphere.* 41, 427-435.

Leonard, A. (1991) Arsenic. *In: Merian, E., (ed). (1991) Metals and their compounds in the environment, occurrence, analysis and biological relevance.* Weinheim. VCH. pp. 751-775.

Madejon, P., Murillo, J. M., Maranon, T., Cabrera, F. and Lopez, R. (2002) Bioaccumulation of As, Cd, Cu, Fe and Pb in wild grasses affected by the Aznalcollar mine spill (Spain). *The Science of the Total Environment.* 290, 105-120.

Madyiwa, S., Chimbari, M., Nyamangara, J. and Bangira, C. (2002) Cumulative effects of sewage sludge and effluent mixture application on soil properties of a silty soil under a mixture of star kikuyu grasses in Zimbabwe. *Physics and Chemistry of the Earth*. 27, 747-753.

Maier, R.M., Pepper, I. L. and Gerba, C. P. (2000) *Environmental Microbiology*. USA. Academic Press. A Harcourt Science and Technology Company. San Diego.

Mallinckrodt, M. G. (1991) Acute metal toxicity in humans. In: Merian, E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 585-591.

Martinez, C.E. and Motto, H.L. (2000) Solubility of lead, zinc and copper added to mineral soils. *Environmental Pollution*. 107,153-158.

Mathews, P., (ed). (1996) *A global atlas of wastewater sludge and Biosolid use disposal*. Scientific Technical Report, No. 4. IAWQ.

Mathews, P. (1997) Practical management of Biosolids use in a European region. In: *Proceedings for the speciality Conference of the Water Environment Federation entitled Beneficial reuse of water Biosolids*. Malaga, Spain. IWA.

McCarthy, P. H Partners. (2001a) *Sludge Management Plan for County Roscommon*.

McCarthy, P. H Partners. (2001b) *Sludge Management Plan for County Laois*.

McGlinchey, G.C. (2001) *Comhairle Chontae Laois, Laois County Council. Portlaoise Main Drainage Preliminary Report. Sludge Management Plan*. MCOS COWI.

McGrath, D., Postma, L., McCormack, R. J. and Dowdall, C. (2000) Analysis of Irish sewage sludges: suitability of sludge for use in agriculture. *Irish Journal of Agriculture and Food Research* 39: pp. 73-78.

McNab N., Hughes, J. C. and Howard, J. R. (1997) Pollution effects of wastewater sludge application to sandy soils with particular reference to the behaviour of mercury. *Applied Geochemistry*. 12, 321-325.

Ministry of Agriculture, Fisheries and Food, Department of the Environment. (1993) *Review of the Rules for Sewage Sludge Application to Agricultural L (i) – Soil Fertility and Aspects of Potentially Toxic Elements*.

Moreno, J. L., Garcia, C., Hernandez, T. and Pascual, J. A. (1996) Transference of heavy metals from a calcareous soil amended with sewage-sludge compost to barley plants. *Bioresources Technology*. 55, 251-258.

Moreno, J.L., Hernez, Perez, A., and Garcia, C. (2002) Toxicity of cadmium to soil microbial activity, and the effect of sewage sludge addition to soil on the ecological dose. *Applied Soil Ecology*. 21, 149-158.

Navas, A., Bermudez, F. and Machin, J. (1998) Influence of sewage sludge application on physical and chemical properties of Gypsisols. *Geoderma*. 87, 123-135.

Nyamangara, J. (1998) Use of sequential extraction to evaluate zinc and copper in a soil amended with sewage sludge and inorganic metal salts. *Agriculture Ecosystems and Environment*. 69,135-141.

Obrador, A., Rico, M. I., Alvarez, J. M. and Novillo, J. (2001) Influence of thermal treatment on sequential extraction and leaching behaviour of trace metals in contaminated sewage sludge. *Bioresource Technology*. 76, 259-264.

Ohnesorge, F. K. and M. Wilhelm. (1991) Zinc. In: Merian, E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 1309-1343.

Onyeche, T. I., Schlafer, O., Bormann, H., Schroder, C. and Sieves, M. (2002) Ultrasonic cell disruption of stabilised sludge with subsequent anaerobic digestion. *Ultrasonics*. 40, 31-35.

Outwater, A.B. (1994) *Reuse of sludge and minor wastewater residuals*. Lewis Publishers. CRC Press.

Perez Cid, B., Fernex Albores, A., Fernex Gomez, E. and Falque Lopez, E. (2001) Use of microwave single extractions for metal fractionation in sewage sludge. *Analytica Chimica Acta*. 431, pp. 209-218.

Perez-Cid, B., Lavilla, I. and Bendicho, C. (1999) Application of microwave extraction for partitioning of heavy metals in sewage sludge. *Analytica Chimica Acta*. 378 201-210.

Pinamonti, F., Stringari, G., Gasperi, F. and Zori, G. (1997) The use of compost: its effects on heavy metal levels in soil and plants. *Resources, Conservation and Recycling*. 21, 129-143.

Qiao, L. and Ho G. (1997) The effects of clay amendment and composting on metal speciation in digested sludge. *Water Resources*. Vol. 31(5), 951-964.

Qiao, X.L., Luo, Y. M., Christie, P. and Wong, M. H. (2002) Chemical speciation and extractability of Zn, Cu Cd in two contrasting Biosolids-amended clay soils. *Chemosphere*. Article in Press.

Renoux, A. Y., Tyagi, R. D. and Samson, R. (2001) Assessment of toxicity reduction after metal removal in bioleached sewage sludge. *Water Res*. 35(6), 1415-1424.

Richards, B. K., Sttenhuis, T. S., Peverly, J. H. and McBride, M. B. (1998) Metal mobility at an old, heavily loaded sludge application site. *Environmental Pollution*. 99, 365-377.

Richards, B. K., Stenhius, T.S., Peverly, J. H. and McBride, M. B. (2000) Effect of sludge-processing mode, soil texture and soil pH on metal mobility in undistributed soil columns under accelerated loading. *Environmental Pollution*, 109, 327-346.

Scancar, J., Milacic, R., Strazar, M. and Buruca, O. (2000) Total metal concentrations and partitioning of Cd, Cr, Cu, Fe, Ni Zn in sewage sludge. *The Science of the Total Environment*. 250, 9-19.

Scheinberg, I. H. (1991) Copper. In: Merian, E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 893-909.

Schmitt, H. W. and Sticher, H. (1991) Heavy metal compounds in the soil. In: Merian, E. (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 311-333.

Schrauzer, G. (1991) Cobalt. In: Merian, E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 879-893.

Selivanovskaya, S. Yu., Latypova, V. Z., Kiyamova, S. N and Ailmova, F. K. (2001) Use of microbial parameters to assess treatment methods of municipal sewage sludge applied to grey forest soils of Tatarstan. *Agriculture Ecosystems and Environment*. 86, 145-153.

Sengupta, S. and SenGupta, A K. (2001) Chelating ion-exchangers embedded in PTFE for decontamination of heavy metal laden sludges and soils. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects*. 191,75-95.

Sidhu, J. (2001) The role of indigenous microorganisms in suppression of *Salmonella* regrowth in composted Biosolids. *Water Res.* Vol. 35, No. 4. pp. 913-920.

Smith S.R. (1996) *Agricultural recycling of sewage sludge and the environment*. WRC, UK. England. CAB International.

Smith, S. R. (1997) *Rhizobium* in soils contaminated with copper and zinc following the long-term application of sewage sludge and other organic wastes. *Soil Biol. and Biochem.* 29(9/10), 1475-1489.

Snow, K.J. (1996) Digestion. In: Girovich, M. *Biosolid treatment and management processes for beneficial use*. Marcel Dekker Inc. pp. 165-193. New York.

Page, A.L., Logan, T. G. and Ryan, J. A. (1987) *Land Application of Sewage Sludge*. Lewis Publishers.

Southwood, T. (1983) *Royal Commission on Environmental Pollution. 9th report – lead in the environment*. London. HMSO.

Spinosa, L. and Vesilind, P.A. (2001) *Sludge into Biosolids – processing, disposal and utilization*. IWA Publishing. Cornwall.

Sreekrishnan, T.R. and Tagi, R.D. (1995) A comparative study of the cost of leaching out heavy metals from sewage sludges. *Process Biochemistry*. 31(1), 31-41.

Stenger, A. (2000) Experimental valuation of food safety application of sewage sludge. *Food Policy*. 25, 211-218.

Stenger, A. (2001) Sludge and heavy metals, the consumer's perception on recycling and reuse of sewage sludge. In: *Recycling Reuse of Sewage Sludge Proceedings of the International Symposium*, organised by the Concrete Technology Unit held at the University of Dundee, Scotland, UK.

Stoeppler, M. (1991) Cadmium. In: Merian, E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 803-853.

Stringfellow, A. (2001) The influence of composting on heavy metal extractability from two sewage sludges. In: *Recycling Reuse of Sewage Sludge. Proceedings of the international symposium*, organised by the concrete technology unit held at the University of Dundee, Scotl, UK.

Sunderman, Jr, F.W. and Oskarsson, A. (1991) Nickel. In: Merian, E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 1101-1127.

Tchobanoglous, G. and Burton F. L. (1991) *Wastewater engineering – treatment, disposal and reuse*. 3rd Edition. Singapore. Metcalf and Eddy, INC, McGraw Hill, Inc.

Tobin Environmental Services Ltd. (1999) *Louth Local Authority – Louth County Council, Dundalk Urban District Council. Drogheda Corporation. Sludge Management Plan*.

Ukleja, K., Ukleja, j., Briseid, T., Mohn, H., England, G., Schuchardt, F. and Cebula, J. (2001) Biochemical removal of heavy metals from composting sludge. In: *Conference proceedings of sludge management entering the 3rd Millenium, Industrial, Combined, Water and Wastewater residues*. Taipei. IWA.

USEPA. (1994) *A Plain English Guide to the EPA Part 503 Biosolids Rule*. EPA/832/R-93/003. Technical Report.

Vierboom, M. M; Engle, T. E; Sililiano, P; and Kimberling, C. V. (2002) Effects of gestional status on apparent absorption and retention of copper and zinc in primiparous cows. *Animal Sciences Research Report*. Department of Animal Sciences, Colorado State University. pp 17-19.

Von Burg, R. and Greenwood M. R. (1991) Mercury. In: Merian, E., (ed). *Metals and their compounds in the environment. Occurrence, Analysis and Biological Relevance*. Weinheim. VCH. pp. 1045-1089.

Walter, I. and Cuevas, G. (1999) Chemical fractionation of heavy metals in a soil amended with repeated sewage sludge application. *The Science of the Total Environment*. 226, 113-119.

Walter, I., Martinez, F., Alonso, L., de Gracia, J., and Cuevas, G. (2002) Extractable soil heavy metals following the cessation of Biosolids application to agricultural soil. *Environmental Pollution*. 117, 315-321.

Wang, M. J. (1997) Land application of sewage sludge in China. *The Science of the Total Environment* 197, 149-160.

Weemaes, M., Grootaerd, H., Simoens, F. and Verstraele, W. (2000) Anaerobic digestion of ozonized Biosolids. *Water Res.* 34(8), 2330-2336.

Wegler-Beaton, K., McLaughlin, M. J. and Graham, R. D. (2000) Salinity increases cadmium uptake by wheat and Swiss chard from soil amended with Biosolids. *Australian Journal of Soil Research*. 38, 37.

Weigert, P. (1991) Metal loads of food of vegetable origin including mushrooms. In: Merian, E., (ed). *Metals and their compounds in the environment, occurrence, analysis and biological relevance*. Weinheim. VCH. pp. 449-469.

Weston-FTA Ltd. (1993) *Strategy Study on options for the treatment and disposal of sewage sludge in Ireland*. Prepared for the Department of the Environment and Local Government (Ireland).

Wild, A., (ed). (1988) *Russell's soil conditions and plant growth*. 11th Edition. England. Longman UK.

Williams, J. H. (1990) Regulations on addition of sludge-borne metals to soil and their adaptation to local conditions. In: P L'Hermite (ed). *Proceedings of a Symposium on Treatment and use of sewage sludge and liquid sludge agricultural wastes*. Athens. Elsevier Applied Science. London. 243-251.

Wong, J. W. C., Lai, K. M., Fang, M. and Ma, K. K. (1998) Effect of sewage sludge amendment on soil microbial activity and nutrient mineralisation. *Environment International*. 24(8), 935-943.

Wong, J.W.C and Fang, M. (2000) Effects of lime addition on sewage sludge and composting process. *Water Res.* 34(15), 3691-3698.

Wong, J.W.C., Fang, M., Li, G. X. and Wong, M.H. (1997) Feasibility of using coal ash residues as co-composting materials for sewage sludge. *Environ. Technol.* 18, 563-568.

Yoshizaki, S. and Tomida T. (2000) Principle process of heavy metal removal from sewage sludge. *Environmental Science and Technology*. 34(8), 1572-1575.

Zhang, F.S., Yamasaki, S. and Kimura, K. (2002) Waste ashes for use in agricultural production: II. Contents of minor and trace metals. *The Science of the Total Environment*. 286, 111-118.

APPENDICES

APPENDIX A

A comparison of the Microwave digestion method and the Hach digestion method, using a certified reference material (C.R.M)

Table A.1 A comparison of the Microwave digestion method and the Hach digestion method, using a certified reference material (C.R.M).

Analysis		Microwave Method			Hach Method		
Metals	Instrument	Mean	% C.V.	Range	Mean	% C.V.	Range
Cr	ICP-MS	450 ₍₅₎	18	367-532	486 ₍₃₎	5	462-510
Ni	ICP-MS	273 ₍₅₎	15	231-314	316 ₍₄₎	15	270-363
Cu	ICP-MS	762 ₍₅₎	20	608-917	871 ₍₄₎	14	750-993
Zn	ICP-MS	1012 ₍₄₎	18	829-1195	1089 ₍₃₎	8	998-1180
Ba	ICP-MS	1042 ₍₅₎	19	842-1243	1021 ₍₃₎	3	993-1049
Pb	ICP-MS	361 ₍₄₎	3	351-371	442 ₍₄₎	15	374-510
Co	ICP-MS	3 ₍₄₎	14	2-3	4 ₍₃₎	6	3-4
Mo	ICP-MS	12 ₍₃₎	6	11-13	14 ₍₃₎	14	12-15
As	ICP-MS	83 ₍₅₎	1	82-84	83 ₍₄₎	1	82-81
Hg	ICP-MS	17 ₍₅₎	3	16-17	17 ₍₄₎	3	16-17
Cd	ICP-MS	864 ₍₄₎	14	740-988	1035 ₍₃₎	2	1016-1053
Se	ICP-MS	<75 ₍₁₎	-	-	<75 ₍₁₎	-	-
Cr	FAAS	370 ₍₃₎	6	346-394	347 ₍₃₎	16	291-403
Cu	FAAS	810 ₍₃₎	6	760-859	779 ₍₃₎	4	748-811
Zn	FAAS	1397 ₍₃₎	18	1141-1653	1231 ₍₃₎	11	1092-1371
Cd	FAAS	723 ₍₃₎	4	693-753	705 ₍₃₎	8	649-761
Fe	FAAS	11063 ₍₃₎	1	111000-11126	10412 ₍₃₎	6	9777-11046

(No) – indicate the number of replicates analysed

APPENDIX B

Results of heavy metal analysis

Table B1 Results of heavy metal analysis of sewage sludge samples

Sample	Cu (mg/kg)	Zn (mg/kg)	Ba (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	Co (mg/kg)	Ni (mg/kg)	As (mg/kg)	Se (mg/kg)	Mo (mg/kg)	Cd (mg/kg)	Hg (mg/kg)	Fe (mg/kg)
Ringsend	446	596	117	62	<167	<17	<17	<101	<84	<7	<17	<17	2541
Letterkenny	583	898	130	83	<167	<17	<17	<101	<84	<7	<17	<17	6786
Portlaois	631	1035	362	39	<167	17	<17	<101	<84	<7	<17	<17	9206
Nenagh	643	1308	351	67	<167	<17	<17	<101	<84	<7	<17	<17	279333
Castlebar N.L.	579	620	326	32	<167	<17	<17	<101	<84	<7	<17	<17	29132
Kilkenny	771	1155	220	55	180	<17	<17	<101	<84	<7	<17	<17	26548
Ballincollig	552	948	197	64	<167	<17	<17	<101	<84	<7	<17	<17	10326
Navan	611	513	280	28	<167	<17	<17	<101	<84	<7	<17	<17	48195
Castlebar + L	447	331	192	20	<167	<17	<17	<101	<84	<7	<17	<17	11271
Buncrana	514	1299	205	64	<167	<17	<17	<101	<84	<7	<17	<17	22523
Clonakilty	526	454	165	33	<167	<17	<17	<101	<84	<7	<17	<17	10357
Carlow + L	651	422	71	33	<167	<17	<17	<101	<84	<7	<17	<17	3404
Monaghan	1345	1551	1094	95	<167	<17	<17	<101	<84	<7	<17	<17	201824
Tralee	922	1525	508	114	245	<17	<17	<101	<84	<7	<17	<17	15047
Shannon D.	502	893	424	20	<167	<17	<17	<101	<84	<7	<17	<17	10270
Tullamore	895	1914	2800	70	<167	<17	<17	<101	<84	<7	<17	<17	146864
Ennis	873	677	152	50	<167	<17	<17	<101	<84	<7	<17	<17	7193
Dundalk	711	11176	377	73	<167	100	<17	<101	<84	<7	<17	<17	34154
Ballina	681	1048	258	76	<167	<17	<17	<101	<84	<7	<17	<17	12259
Greystones	757	1238	518	60	<167	<17	<17	<101	<84	<7	<17	<17	12181
*Shannon Ind.	854	20209	1684	70	3645	385	<17	<101	<84	<7	56.46	<17	42886
Charleville	578	778	103	15	<167	<17	<17	<101	<84	<7	<17	<17	14461
*Swords	383	1054	290	82	<167	<17	<17	<101	<84	<7	<17	<17	5457
N/west	1093	1048	230	101	<167	<17	<17	<101	<84	<7	<17	<17	10409
Strandhill	778	956	155	39	<167	<17	<17	<101	<84	<7	<17	<17	7417
S/bridge	553	824	390	24	<167	<17	<17	<101	<84	<7	<17	<17	4149
Castletroy	631	756	384	34	<167	<17	<17	<101	<84	<7	<17	<17	9261
Thurles	1037	1818	482	112	726	<17	<17	<101	<84	<7	<17	<17	24742
Osberstown	667	1049	359	70	1152	<17	<17	<101	<84	<7	<17	<17	141340
Drogheda	1303	1091	379	72	<167	<17	<17	<101	<84	<7	<17	<17	29305
Portlaois	1262	510	281	102	<167	<17	<17	<101	<84	<7	<17	<17	8527
Cavan	603	843	278	29	<167	<17	<17	<101	<84	<7	<17	<17	58445
Longford	461	966	460	54	<167	<17	<17	<101	<84	<7	<17	<17	53253
Carlow N.L.	590	933	186	94	<167	<17	<17	<101	<84	<7	<17	<17	6483
C/Shannon	453	900	330	151	<167	<17	<17	<101	<84	<7	<17	<17	10199
Tipperary	960	1376	1193	164	2001	36	<17	<101	<84	<7	<17	<17	6543
Roscommon	2134	2051	652	123	462	47	<17	<101	<84	<7	<17	<17	194621
Tuam	639	1075	203	84	<167	<17	<17	<101	<84	<7	<17	<17	11983
Enniscrone	548	1376	164	72	<167	<17	<17	<101	<84	<7	<17	<17	6980
Enniscorthy	580	795	276	71	<167	<17	<17	<101	<84	<7	<17	<17	12816
Mallow	451	925	293	122	<167	<17	<17	<101	<84	<7	<17	<17	27500
Killamey	986	2077	1800	113	228	<17	<17	<101	<84	<7	<17	<17	73210
Mullingar	960	833	476	168	<167	24	<17	<101	<84	<7	<17	<17	1040

*Shannon Industrial and Swords are industrial sludge samples