An Investigation of the Trace Organic Contamination of Irish Groundwater and a Review of Current Analytical Techniques.

Presented in Part Fulfilment for the
Degree of Master in Science in Environmental Protection

by

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Dedication

to my family
Mam, who inspires us all to greatness,
Dad, for his encouragement and belief in us,
Susan, who showed us all what rewards hard work can bring
and the glorious memories of the Olympics,
Gillian, for her unfailing good humour and unlimited enthusiasm,
Mary, for her youth and the many years of friendship ahead.

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Abstract

Groundwater is a major natural resource in Ireland. It has been estimated that 30% of the drinking water supply in Ireland is provided by this source. Most of the groundwater is of a potable quality but any contamination of groundwater could lead to severe consequences. Due to the increased usage of organic compounds as well as the wide variety of organics in use, it is necessary to take protective measures to conserve this important resource. Groundwater was previously considered to be immune from contamination and for many years Irish groundwater was free from major pollution. This was due to a large extent on the fact that :

- the majority of the population lived in rural areas
- most of the urban settlements were located on the coast
- there is an abundance of water in Ireland.

The assessment of the existing data on groundwater contamination is difficult. Many aquifers have never been sampled. There is a tendency to sample only those aquifers where a problem has occurred or those at risk of contamination. There is also frequently insufficient information on the sampling conditions used and the nature of the aquifers and many wells have only been sampled once. Pollution of Irish groundwater's is no longer a possible problem but a reality. Widescale pollution is occurring as a result of industrial, agricultural and domestic carelessness. This project addresses the issues of E.C Directives EEC/76/464 (Pollution caused by certain dangerous substances discharged into the aquatic environment) and EEC/80/68 (Protection of groundwater against pollution caused by certain dangerous substances). It details the potential sources of trace organic contamination and examines the current information available on the occurrence and determination of organic contaminants in Irish groundwater, the methods for sampling and analysis of these contaminants and the value of the resulting information.

Table of Contents

List of Contents

Chapter One - Characteristics of Irish aquifers

Chapter Two - Trace Organic Contamination in groundwater

Page

Chapter Three - The extent of pollution in Ireland and procedures for sampling and analysis of trace organic contaminants

Appendices

Page

List of Figures

List of Tables

1.0 Characteristics of Irish Aquifers

1.1 Introduction

Groundwater is water which is found in saturated strata underground. These saturated strata are called aquifers. Approximately 1,140mm of rain falls in Ireland every year of which about 360mm percolates through the soil and into the aquifer, recharging the groundwater (ENFO, 1995). 50% of Irelands groundwater is considered developable but presently only about 2% of this is currently extracted. Groundwater is a major national resource and one which is virtually untapped. It has been estimated that 30% of the drinking water supply in Ireland is provided by this source. Rural areas as well as many eastern countries depend almost entirely on groundwater as a drinking water supply. Roscommon abstracts 90% of its drinking water from aquifers (Thorn,R., 1992). Most of the groundwater is of a potable nature but any contamination of groundwater could therefore lead to severe consequences. Groundwater protection is not a new idea. The large sewer in Rome, the 'cloaca maxima' built by the Emperor Tarquinius was not only constructed for aesthetic reasons but rather for the practical purposes of avoiding diseases and protecting groundwater supplies.

It has become obvious over the last few years that protecting the soil and underground water is a vital factor in protecting the environment as a whole. The extraordinary purification capacity of soil, in which we placed our confidence for so long is no longer sufficient to absorb the pollutants passing through it. Many cases of soil and groundwater contamination by petroleum products have occurred in developing and industrialised nations (Zilliox, L. 1992). Old landfill sites constitute a continuous risk for water sources. These old landfill sites (uncontrolled tips, industrial wasteland etc.) are amongst the main sources of pollution alongside fuel storage facilities, agricultural incidents and industrial effluents.

Fuels and domestic heating oil are amongst the most frequent sources as no other organic products are handled in such large volumes. Heavier products (lubricating oil, heavy fuel oils) are also causing pollution and contamination by chlorinated hydrocarbons is becoming an increasing hazard.

1.2 Geology of Irish Aquifers

50% of the country is underlain by carboniferous rock with Middle and Lower carboniferous rock aquifers being the most prolific.(Drew et. al., 1995). Both limestone's and sandstone's were deposited during the carboniferous period (345 to 280 million years ago). The carboniferous sandstone's are relatively permeable but yield small quantities of water. The limestone's underlie most of the central and west parts of Ireland and comprise the most important aquifers. They have fissure permeability, a characteristic of most of the rock types present in Ireland, the exception being the red sandstone's of Belfast and Kingscourt which have some intragranular flow. Some of the limestone's are also extensively karstified

(Thorn, R., 1991). The Burren area in Co. Clare is an example of karstification. Karstification is the process by which the secondary permeability of an aquifer is increased by the dissolution of the rock by groundwater as it permeates downwards. Limestone (calcium carbonate) is readily dissolved by weak acid solutions (rainwater) leaving large fissures in the rock allowing both water and pollutants to pass rapidly through without much attenuation. Devonian rock is common in the south and west of Ireland and in the north-west of Mayo. The Devonian period was 395 to 345 million years ago. Lower devonian rocks are generally comprised of impermeable grey-wackes, grits and shales and Upper Devonian rocks are relatively permeable e.g., old red sandstone. In general the devonian rocks are regarded as minor aquifers (Thorn, R., 1991). More than 90% of the country is overlain with Quaternary deposits (Warren, W., 1995). The Quaternary period is the most recent geological period (2 million years to the present). Quaternary deposits include glacial deposits (both tills and outwash) e.g.,, sand and gravel, peat, alluvium and coastal deposits. These sediments provide some of our major aquifers e.g., sand and gravel deposits with intragranular flow and good drainage were deposited in the Curragh area of Co. Kildare forming a reasonably well protected major aquifer. The majority of the limestone aquifers in the country are also overlain with these quaternary deposits. They are the medium through which almost all aquifer recharge in Ireland passes and they help buffer the groundwater, and as such are crucial elements in groundwater protection. These unconsolidated quaternary deposits which overlie the bedrock aquifers are very variable in thickness, extent, permeability and lithology, (reflecting their chaotic mode of deposition in the Ice Age). Areas such as the Curragh have large overburden and areas such as the Burren very little. The karstified areas of the Burren are very vulnerable to pollution as bare rock and thin or no subsoil are common. Pollutants are attenuated only slightly and move rapidly through the karst regions.

1.3 Characteristics of Irish Aquifers

Several physical features common to many Irish aquifers can leave the groundwater vulnerable to pollution. These are their unconfined nature, shallowness, the thin unsaturated zones and their mainly fissure flow. However, we do have a high rainfall which helps to attenuate pollutants by dilution and the fact that the surface water tables are shallow means that there is a rapid discharge of groundwater's to the surface which creates a localisation of pollution incidents.

Groundwater may be a good source of potable water because the rainwater must percolate through layers of soil before it reaches the aquifer thus purifying the water, removing particulates and suspended solids (Birkeland et. al., 1989). The type of soil or rock overlying an aquifer is very important from the point of view of the pollution potential of the aquifer. The type of rock formation can aid or disrupt groundwater recharge and rate of contamination. The main source of groundwater recharge is rainfall. If water is to infiltrate downwards, rock and unconsolidated sediment must be both porous and permeable. The level of soil covering the aquifer is also very important as a factor in filtering out solids. Porosity is the total volume of the rock that is taken up by openings or holes, while permeability is a measure of the capability of a rock or sediment to transmit a liquid, and is the main property controlling the rate of groundwater flow from one point to another. Large void spaces in a rock are more important than the percentage of open space. Gravel is good example of rock with high permeability, e.g.,, the sands and gravels located in the Curragh area in Co. Kildare form one of the major aquifers in the country.

1.4 Health effects of organic pollutants

Water readily dissolves a wide variety of substances which are then carried through the soil into the groundwater below. A very grave aspect of contaminated drinking water is the many health effects associated with many common organic contaminants. In Table 1, a summary of the toxic effects of common organic contaminants is shown (Watson et Al., 1993).

Table 1 - Toxic Organic Chemicals. A summary of the toxic effects of some of the most common organic contaminants found in groundwater

	Groundwater Contaminants								
Toxic Effects	Trichloro-ethene	Benzene	Toluene	Chloroform	1,1,1-Tri-chloroethane	Tetrachloro-ethene	Phenol	PCB's	Vinyl Chloride
Carcinogenicity	*	*		*	*	*		*	*
Mutagenicity					*			*	*
Teratogenicity								*	
CNS effects	*	*	*	*	*	*			*
Cardiovascular effects	*		*					*	
Kidney damage	*		*	*	*			*	*
Liver damage	*		*	*	*				
PNS effects		*							
Immunological effects		*						*	
Gastro-intestinal effects		*		*				*	
Reproductive effects								*	
Embrotoxicity				*		*		*	
Lung-Respiratory effects	*				*	*		*	
Endrocrine effects									
Blood Cell disorders	*								*
Upper Respiratory tract disorders			*			*			
Skin damage			*				*		
Visual damage									
Allergic sensitisation		*							
Eye irritation		*	*	*	*	*			*
Skin irritation	*	*	*	*	*		*		*

Polychlorinated Biphenyl Compounds (PCB's) is the generic term for the group of 209 chlorinated isomers of biphenyl. PCB's were discovered in the late 19th century and have been widely used in industry since the early 20th century. They are chemically stable, heat resistant, have a low flammability and high dielectric constants making them a popular choice in industry as dielectric fluid in electrical equipment e.g., transformers, heat transfer systems, hydraulic systems and as plasticisers. They are also highly stable, persistent in the environment, mutagenic and reportedly carcinogenic (Mc Graw -Hill, 1987).

Pesticide is a general term for a substance which is used to control pests which affect crops and animal or human health. The modern pesticides are mainly synthetic organic chemicals developed in the years since World War II (Watterson, A., 1991) (Dudley, N., 1978). The chemicals selected to kill pests are chosen because of their toxic properties which makes them efficient at killing unwanted plants, insects, rodents. There is the threat therefore that these chemicals are also potentially harmful to humans. There are two types of toxicity associated with exposure to these chemicals -acute and chronic toxicity. Acute toxicity has an immediate effect and symptoms which can include vomiting, diarrhoea, skin and eye irritation, nausea, coughing and possibly death depending of the exposure concentration. It is estimated that as many as 80,000 people each year die from pesticide poisoning, mostly in developing countries (Hurst et. al., 1991). Chronic toxicity manifests itself over a number of years and the effects are as a result of long term exposure. The concerns are about possible carcinogenic, teratogenic, mutagenic, neurological and allergic effects of humans. Amongst the pesticides which have been linked to cancer are the phenoxy herbicides, the organochlorines e.g.,, DDT and DDE, some of which may cause cancer in animals and many of which are also extremely persistent and bioaccumulative in the environment. (British Medical Association, 1992). The only pesticide which appears to have permanent effects on the reproductive system is dibromochloropropane, although other pesticides have been linked with possible reproductive effects; aldrin, captan, dieldrin, dinoseb, lindane, maneb and paraquat (Hurst et. al., 1991). Organophosphorus pesticides e.g.,, azinphos, chlorfenvinphos, are similar in principle to nerve gas and some have been linked to neurological damage, visual disturbances, gastrointestinal symptoms, liver and kidney effects, changes to the blood plasma and development of allergies. (British Medical Association, 1992) (Dudley, N., 1987). Chemicals which are suspected to be mutagens are amintriazole (also carcinogenic), captan, chlordane (also suspect carcinogen and teratogenic), dinoseb, fenitrothion, malthion, simazine and thiram. The soil fumigant 1,3-Dichloropropene has been linked to several cases of leukaemia (British Medical Association, 1992). Allergic reactions to chemicals are often not noted as they have ‘flu-like’ symptoms ; runny nose, rheumy eyes, muscle aches. Allergic reactions can occur at concentrations 20 times lower that the amounts regarded by the World Health Organisation as an acceptable intake. 2 cases of asthma have been related to organophosphorus pesticides at levels 20 times less than the acceptable level. Organophosphorus pesticides can also cause spasms by inhibition of the acetylcholinesterase enzyme (Hurst et. al., 1991). Paraquat and maneb have been associated with Parkinson's disease but no conclusive evidence has been found. (Watterson, A., 1991). Much remains unknown about the effects of pesticides but pesticides are poisons and should be treated with care.

1.5 Groundwater Contamination Mechanisms

1.5.1 Effect of Dissolved Organic Carbon on flow mechanisms

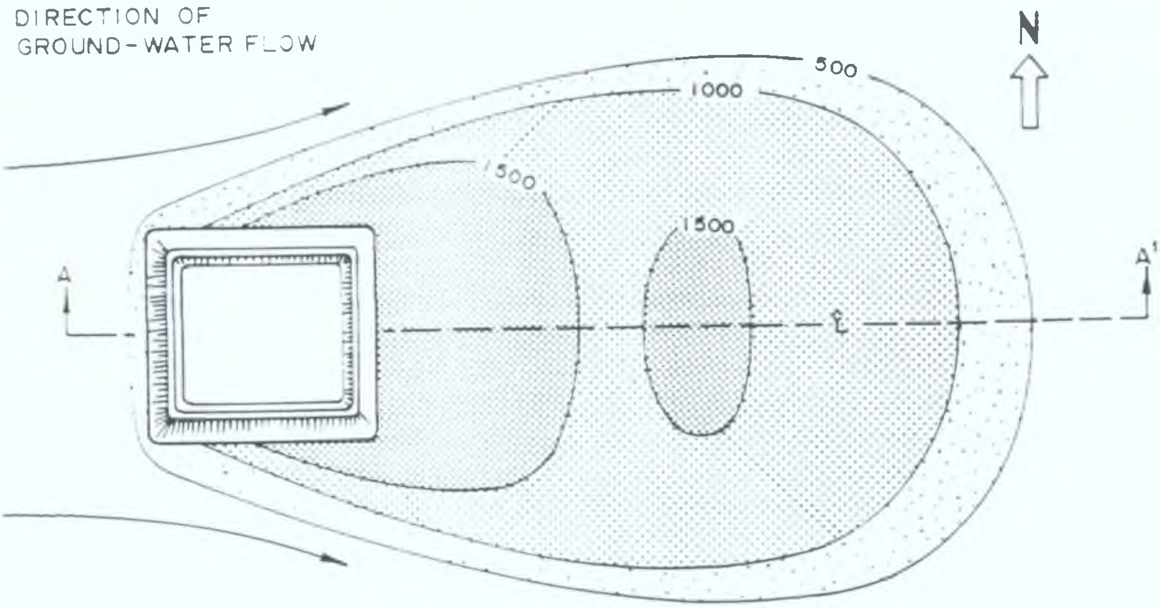
Dissolved Organic Carbon (D.O.C) in soils and aquifers is considered to be a sorbent and carrier for organic contaminants. Enhanced transport of pesticides and hydrophobic organic chemicals mediated by the presence of D.O.C in soils and other media has been documented. This enhanced mobility or leaching of the contaminant may have impact on risk assessment studies (Forst et. al., 1993). Forst et. al., have shown that the presence of oil in a leachate reduces the adsorption of organic pollutants e.g., HCH, onto soil as it passes through, in proportion to the concentration of oil present Most landfill leachates are complex mixtures which would contain at least traces of oil.

1.5.2 Mechanical Action and Dispersion

Contaminants move through an aquifer by mechanical action and by dispersion. Groundwater flow is very slow and is measured in metres per year. Therefore the implications for a polluted aquifer are very serious because the turnover time of an aquifer can be up to 10,000 years the pollutants will remain for very long periods of time after the pollution has stopped (Lester et. al., Sligo RTC manual)). In the case of a fully soluble leachate the rate of infiltration of the leachate into the aquifer eventually equals the rate of dispersion of pollutants in the groundwater, a steady state position. At the point where the leachate enters the aquifer a plume is formed and this spreads out laterally and vertically. The vertical development of the plume depends on the thickness, hydraulic gradient and permeability of the aquifer. In general the constituents of the plume move at different velocities. If there is pressure on the infiltrating leachate, increasing its flow then the rate of plume dispersal also increases. It is very important therefore to slow down leachate flow, reducing contaminant dispersal.

See Fig. 1 (Watson et. al., 1993).

Figure 1 - Spread of a leachate plume

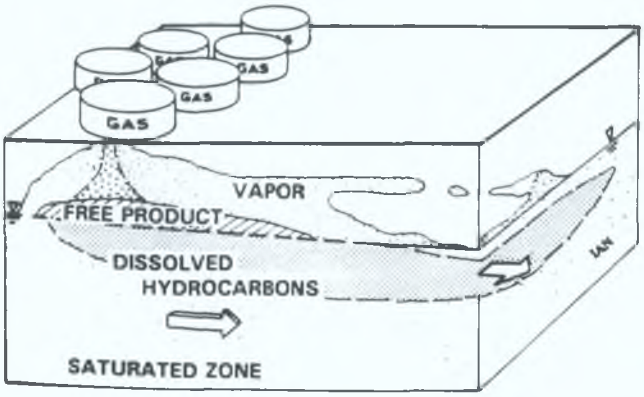


Partially soluble organic contaminants fall into two categories :

Light contaminants, those less dense than water e.g., petrol forms a transitional multi-phase plume. Initially the plume moves vertically but in the unsaturated zone volatilisation occurs creating a vapour zone. The unsaturated zone above the water table is very important for the attenuation of organic material. They can be oxidised, reduced, precipitated or volatilised in this zone. When the unvolatilised product reaches the saturated zone it then moves laterally with the main groundwater flow, initially floating on the top of the water table but with time becoming partially dissolved. It is this dissolved layer which spreads most quickly throughout the aquifer. Dilution is the main attenuation mechanism in the saturated zone.

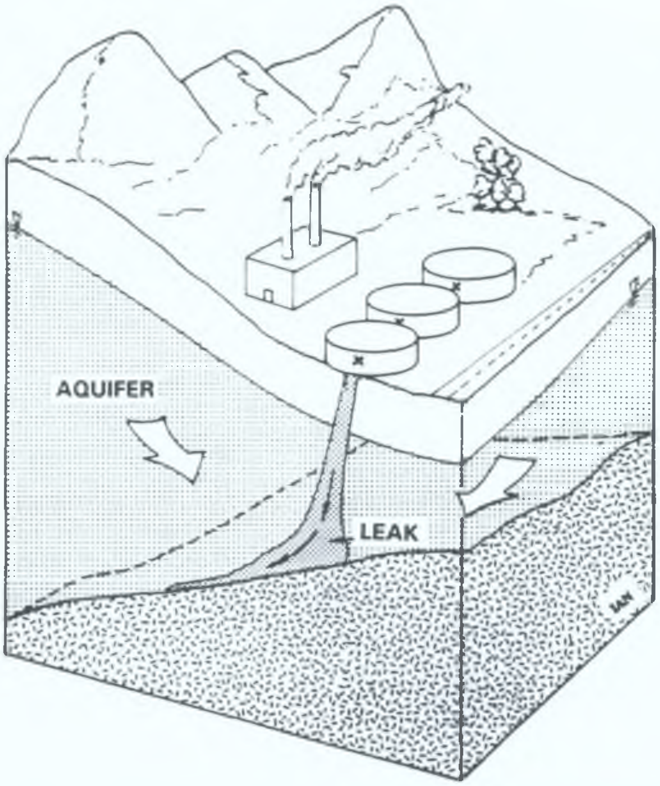
See Fig 2 (Watson et. al., 1993)

Figure 2 - Spread of low density organic compounds in water



Contaminants which are more dense than water e.g., pentachlorophenol (PCP), tetrachloroethene, hexachlorobenzene and diesel, sink to the bottom of the aquifer and migrate under gravity along the top of a low permeability layer, often this flow is against the direction of the main groundwater flow. See Figure 3 (Watson et. al., 1993).

Figure 3 - Spread of high density organic compounds in water



Contamination mechanisms can be used to describe the movement of contaminants within the aquifer and can thus help in determining the attenuation of the contaminants that occur with distance travelled. Flow net modelling can give information on the direction of the plume migration from the waste body and they allow for the rate of seepage from the disposal facility to be determined. The vertical development of the plume depends on the thickness, hydraulic gradient and the permeability of the aquifer. Predictions on the attenuation of contaminants at certain points within an aquifer material and the nature and input concentrations of contaminants using a mass chemical transport (or solute transport) equation (Watson et. al., 1993), (Ward et. al., 1990).

2.0 Trace Organic contaminants in groundwater

2.1 Introduction

The organic compounds which will be examined here fall into three main categories.

1) volatile organic compounds (VOC's)

2) semi-volatile organic compounds (SVOC's)

3) petroleum products

Petroleum products which can fall under the category of both volatile and semi-volatile compounds. Problems arising from groundwater pollution by oil have emerged as a major area for concern and as such it shall be treated separately from VOC's and SVOC's

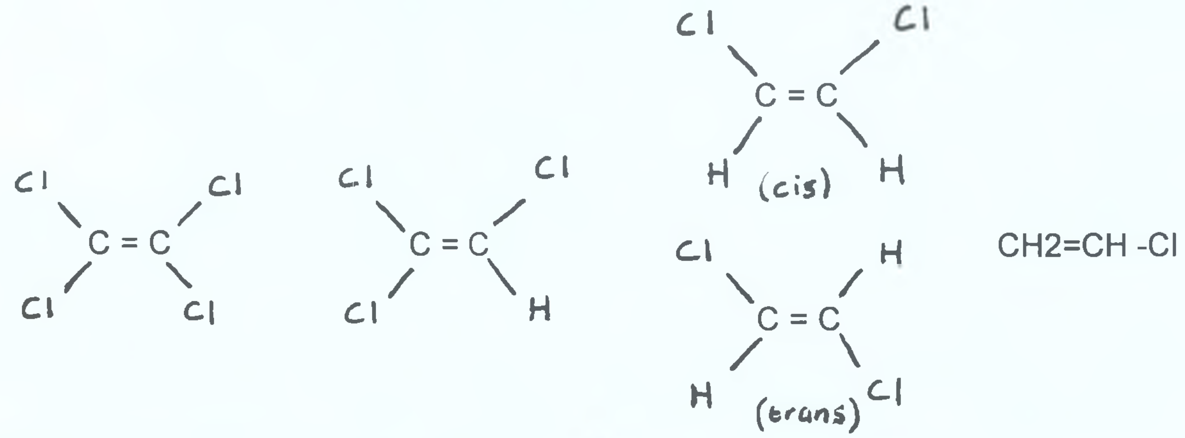
2.1.1 Volatile Organic compounds (VOC's)

VOC's are relatively low molecular weight compounds with boiling points generally up to 300ºC. Many organic solvents fall into this category and are used in a wide range of industries.

Table 2 - Physical characteristics of common organic solvents

Compound	Molecular Weight	Boiling Point (° C)	Density $^{1}{}_{n}d_{20}$
Benzene	78.11	80.1	0.874
Toluene	92.13	110.6	0.87
Xylene	106.17	138 - 142	0.8
Trichloroethene	131.39	87	1.46
Tetrachloroethene	165.85	121.1	1.62
Choroform	119.39	61	1.492
Dichloromethane	84.93	39.6	1.326
Methanol	32.04	64.5	0.971

Many of the compounds listed in Table 2 are relatively harmless at trace levels. Some however are listed as carcinogens by the World Health Organisation (WHO). Chloroform, a trihalomethane (THM) is a by-product of the chlorination of water (the other THM's are bromodichloromethane, dibromochloromethane and bromoform). The WHO has set limits of between 25-250 µg/l for total THM's and an individual limit of 30µg/l for Chloroform in drinking water (WHO, 1984). VOC's are more mobile in aquifers and less susceptible to attenuation than inorganic contaminants. They therefore spread out more in the aquifer and at high concentrations which may be dangerous to human health they persist for longer periods of time. Biotransformation of VOC's can also occur, yielding a more toxic end-product e.g., Trichloroethene a common solvent used in industry converts to Vinyl Chloride, a carcinogen (Watson et. al., 1993), (Daly, D., 1994).



Tetrachloroethene → Trichloroethene → 1,2- Dichloroethene → Vinyl Chloride
cis and trans

See Table 1 for a summary of the toxic effects of some of the most common organic contaminants found in groundwater.

2.1.2 Semi-Volatile Organic Compounds (SVOC's)

SVOC's are heavier molecular weight compounds than volatile organic compounds. They are less soluble in water than VOC's and tend to be more persistent, bioaccumulative and frequently carcinogenic e.g., Pesticides (aldrin, dieldrin, lindane), PCB's, coal-tar containing polycyclic aromatic hydrocarbons (PAH's), heavy fuels.

A list of prohibited active substances in pesticide formulations is given Table 3 (Department of Agriculture, Food and Forestry, 1996).

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[1] ${}_{n}d_{20}$ - Density measured at 20°C.

Table 3 - Active Substances used in pesticides which are banned in Ireland.

Active Substance	Date of first ban
Chlordane	1992
Aldrin	1988
DDT	1985
Dieldrin	1981
Endrin	1981
HCH (containing <99% gamma HCH)	1981
Heptachlor	1981
HCB	1981

2.1.3 Petroleum Products

The major groundwater pollution problem in Ireland is that of contamination by oil and petroleum products. This trend is similar in many of the other E.C countries. Fifty percent of all pollution damage in Hamburg is caused by mineral oil hydrocarbons (Bremer el. al., 1993). Hydrocarbons due to their high mobility have strict guidelines set out for both soil and groundwater. Under [2]EEC/76/464 hydrocarbons fall into both List 1 and List II categories.

List I - Persistent mineral oils and hydrocarbons of Petroleum origin

List II - Non-persistent mineral oils and hydrocarbons of petroleum origin.

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[2] EEC/76/464 - EUROPEAN COMMUNITIES (POLLUTION CAUSED BY CERTAIN DANGEROUS SUBSTANCES DISCHARGED INTO THE AQUATIC ENVIRONMENT)

Under [3]EEC/80/68, hydrocarbons are included as a List I substance, defined as 'Mineral oils and hydrocarbons'. No values are set out for List I or List II substances with regard to hydrocarbon material. The List I substances must be brought into law following the issue of daughter directives. There are no daughter directives currently available for hydrocarbons or mineral oils. List II materials are subject to emission limits. No limits are set for these substances in the statutory limits enabling this EC legislation. In the absence of national guidelines the Dutch VLM guidelines for soil and groundwater are commonly used. (Dutch Ministry of Housing, Physical Planning, and Environmental Protection, 1994)

Table 4 - Extract from the Dutch Guidelines for Soil and Groundwater

Parameter	Soil (mg/kg)		Groundwater (µg/l)	
	[4]S	[5]I	S	I
[6]Benzene	0.05(d)	1	0.2	30
Toluene	0.05(d)	130	0.2	1000
Ethyl Benzene	0.05(d)	50	0.2	150
Xylene	0.05(d)	25	0.2	70
Mineral Oil	50	5000	50	600

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[3] EEC/80/68 - EUROPEAN COMMUNITIES (PROTECTION OF GROUNDWATER BY POLLUTION BY CERTAIN DANGEROUS SUBSTANCES)

[4] S-value = Target value
This indicates the level for which there is sustainable soil quality. This level needs to be achieved to completely restore the functional qualities of the soil for humans, animals and plants.

[5] I-value = Intervention value
This represents the level of the concentration of contaminants in soil and groundwater above which a serious reduction or potential reduction of the 'functionality' of the soil for human beings, plants or animals occurs. Levels above the intervention value constitute a case of serious contamination.

[6] BTEX- Benzene, Toluene, Ethyl Benzene and xylene are commonly used as indicators of petrol (gasoil) contamination

Refined mineral oil, petroleum products and heating oils or rather the constituents of oil fall into the area of both. volatile and semi-volatile organics. Petrol contains benzene, toluene and low boiling point n-alkanes but its upper range goes as far as [7] $_nC_{12}$ and a boiling point of 216°C. Benzene, toluene, ethyl benzene and xylene are often used as a measure of the gasoline (petrol) content of a sample. Oils have an density ranging from 0.7 g/ml to 1 g/ml. Light products such as petrol have a viscosity less than water and heavier products , gas oils such as diesel have a viscosity greater than water. While oils and heavier petroleum products are relatively immiscible in water, lighter petroleum products such as gasoline (petrol) are sufficiently soluble to constitute a significant pollutant threat to groundwater. Petrol is unpalatable in water at levels even below 5 μg/l. The EC MAC in groundwater is however, 10 μg/l. It is difficult to achieve this detection limit for petrol unless a very large sample is taken. Petrol also contains additives which are used as octane boosters. One of these compounds Methyl Tertiary Butyl Ether (5% in regular blends and up to 15% in super blends) is highly soluble in water (up to 10 times more soluble than the other constituents in petrol). It has a taste threshold of 10 μg/l and although not very toxic it spreads rapidly in groundwater. It does allow easy identification of petrol contamination as it is readily determined below its taste threshold in a litre sample of water (Daly, D., 1994)

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[7] $_NC_{12}$ - The n refers to a straight chain hydrocarbon compound, in this case with 12 carbon atoms.

Oils are mainly insoluble but most oils are sufficiently soluble to impart a flavour or smell to the water. The more dense gas oils are also very difficult to degrade. These taste/odours are generally detected as concentrations below the levels which could be harmful (CONCAWE, 1979), (Martin. A.E., 1970).

Table 5 - Threshold Odours for petroleum products

Product	**Threshold Odour (mg/l)**
Raw petroleum	0.1 - 0.5
Refined petroleum	1 - 2
Deodorised kerosene	0.082
Commercial gasoline	0.005
Petrol (with oil additive)	0.00005
Fuel Oil	0.22 - 0.5
Heating Oil	0.3 - 0.6
Diesel Oil	0.0005
Lubricating Oil	0.5 - 25
Engine Oil	1

Water has long been subject to pollution by oil but as long as there was plenty of water available and oil was not widely used no great difficulties arose. In today's world, with an increasing population and the spread of industrialisation making heavier demands on a fixed quantity of water and using more oil the problem is now more serious. One of the major concerns in groundwater contamination is from underground storage tanks. Underground storage tanks (UST's) are used for gasoline, oils, chemicals, hazardous/toxic materials and wastes. Tanks were stored underground on the assumption that they would not leak, the consequences of which not being considered. The most common cause of leakages is from corrosion of the tank or the piping systems. Old tanks were mainly metal construction, frequently without protective coatings and often substances in the liquid contained in the tank corroded the metal. Leakages also result from punctures, external stresses, faulty construction/installation or overfilling. Tanks and piping systems have a limited lifespan and must be tested regularly to ensure safe operation (Cheremisinoff, P.N., 1992).

2.2 Existing information on groundwater quality

2.2.1 Introduction

The assessment of the existing data on groundwater quality in Ireland is very difficult because of insufficient information on sampling conditions and the nature of the aquifer sampled. Many Irish wells have only been sampled once and generally sampling and analysis only takes place when a problem occurs. Thus there is very little background data on Irish aquifers.

2.2.1.1 Stride Project 399 (Stride 399, 1993)

An E.C study, Stride 399 was a study aimed to assess trace organic contamination in Irish groundwater's. The study dealt mainly with volatile organic compounds (VOC's), taking at least two study sites from each of the 26 counties in the Republic of Ireland. Some selected sites were also monitored for semi-volatile organic compounds. Sampling sites were carefully selected in areas which had previously been polluted or where a potential source of organic contamination was located. A bias was introduced into the survey by not sampling a representative percentage of Irish groundwater's but only those aquifers where pollution has already occurred or is likely to occur.

2.2.1.2 Groundwater Protection policies

Many Local Authorities have carried out groundwater vulnerability assessments and groundwater studies for the preparation of Aquifer Protection Policies. These studies are generally carried out with the assistance of the Geological Survey of Ireland and the groundwater vulnerability maps which are produced help describe complex hydro-geological parameters in a simple format. For many of these vulnerability assessments only the electrical conductivity is measured. This is used as an indication of the quality of the groundwater in the well. Organic contamination is rarely analysed and may go unnoticed.

2.2.1.3 EPA monitoring schemes

Under E.C Directive EEC/76/464 the Environmental Protection Agency (EPA) is required to monitor the state of the environment in Ireland. In part fulfilment of the assessment of the quality of water in Ireland. a groundwater monitoring scheme has been in operation since November 1995. 300 wells are sampled for water quality on a twice yearly basis, at maximum and minimum stress times. The wells which are included are those with the highest abstractions. The samples collected are analysed for major ions only. No organic pollutant analysis is carried out on these samples. Groundwater level monitoring is carried out on some of the wells sampled. There is some sampling of locally important/poor aquifer (non-aquifer) wells for water quality, this again is based solely on the major ions.

2.2.1.4 EPA report on Pesticides in Irish Drinking Waters (EPA, 1996 (3))

A survey was carried out by the EPA on the pesticide levels in Irish drinking waters between December 1994 and December 1995. 27 Sanitary Authorities in 26 counties were monitored, 5 supplies from each with the emphasis on larger supplies but small supplies which could be considered at risk from pesticide contamination were also to be included . In total 3,300 samples were analysed. The study looked for 9 groups of pesticides :

1: BHC isomers (α-BHC, β-BHC, γ-BHC, δ-BHC)

2: aldrin, dieldrin, endrin, endrin aldehyde, Endrin ketone, isodrin.

3: Heptachlor, Heptachlor epoxide.

4: DDT and related products ; pp-DDE, op-TDE, op-DDT, pp-TDE, pp-DDT

5: Endosulphan group ; endosulphan I, endosulphan II, endosulphan sulphate

6: Organophosphorus pesticides ; diazinon, parathion, dichlorvos, dimethoate, fenitrothion, propetamphos,

7: Triazine Herbicides ; atrazine, simazine

8: Other pesticides by GC ; hexachlorobenzene, methoxyclor, trifluralin, dichlobenil.

9: Acid Herbicides and pentachlorophenol by HPLC ;2,4-D, MCPA, dichloroprop, mecoprop, MCPB, PCP.

2.2.1.5 EPA Report - The quality of drinking water in Ireland, 1993 - 1995 (EPA, 1997 (1) & (2))

The Environmental Protection Agency monitor the quality of drinking water in Ireland for a number of parameters. Groundwater is used as a potable supply in many areas of the country. The organic parameters of interest to this report are the trihalomethanes, used for chlorination purposes.

2.2.1.6 The Geological Survey of Ireland (GSI)

The GSI issues many reports which can include information on the quality of Irish soil and groundwater. Information on trace organic contamination is limited but a report issued by the GSI in 1994 on chemical pollution in Ireland (Daly, D., 1994) gave some valuable information on groundwater vulnerability and the problems associated with pesticides, landfill sites, industrial solvents and mineral oils.

2.3 Legislation relating to groundwater

2.3 1 EEC/76/464

In recent years groundwater control has come under the jurisdiction of E.C Directive 76/464 - POLLUTION CAUSED BY CERTAIN DANGEROUS SUBSTANCES DISCHARGED INTO THE AQUATIC ENVIRONMENT OF THE COMMUNITY (EEC/76/464, 1976). This Directive specifies a List I and List II of dangerous substances (See Appendix 1). Pollution by substances in List I was to be eliminated and limit values and water quality objectives were to be established for these substances. List II substances were to be controlled by establishing water quality objectives and emission values and discharges were to be subject to license. List I initially had 129 possible substances set out, there are now 132 substances on the list (See Appendix 2) and each one has to be implemented by a daughter directive. To date only 17 of these 132 dangerous substances has been issued with daughter directives, 12 of these relate to organic substances :

Hexachlorocyclohexane	[8]84/491/EEC
DDT	[9]86/280/EEC
Carbon Tetrachloride	86/280/EEC
Pentachlorophenol	86/280/EEC
“The Drins”	[10]88/347/EEC
Hexachlorobenzene	88/347/EEC
Hexachlorobutadiene	88/347/EEC
Chloroform	88/347/EEC
1,2-Dichloroethane	[11]90/415/EEC

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[8] 84/491/EEC - Council Directive on Hexachlorocyclohexane discharges -
Enabling legislation : Local Government (Water Pollution)Act S.I No 95 of 1986

[9] 86/280/EEC - Council Directive on Discharges of Certain List I substances

[10] 88/347/EEC - Council Directive on Certain List I substances (aldrin, dieldrin, endrin, isodrin, Hexachlorobenzene, Hexachlorobutadiene, Chloroform)

Trichloroethene	90/415/EEC
Tetrachloroethene	90/415/EEC
Trichlorobenzene	90/415/EEC

Article 4 of this directive (76/464/EEC) refers directly to groundwater :

- A zero emission of discharges into groundwater of substances within List I.
- Member states shall apply to groundwater the provision of this directive relating to substances belonging to the families and groups of substances in List II.
- This Directive does not apply to domestic effluents or discharges into deep saline and unusable strata.
- The provisions of this Directive no longer apply upon implementation of a separate Directive on groundwater.

2.3.2 EEC/80/68

A separate Directive on groundwater was passed by the E.C in 1980. This is E.C Directive 80/68 - PROTECTION OF GROUNDWATER AGAINST POLLUTION CAUSED BY CERTAIN DANGEROUS SUBSTANCES DISCHARGED INTO THE AQUATIC ENVIRONMENT OF THE COMMUNITY (EEC/80/68, 1980), This succeeds directive 76/464 in the area of groundwater protection. The EC Directive (80/68) sets out a List I and List II of dangerous substances and states that all direct discharges of List I substances be prohibited and all appropriate measures be taken to prevent indirect discharges of List I substances.(See Appendix 3 for List I and List II as set out in EEC/80/68) Permission may be granted to discharge List I substances directly into

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[11] 90/415/EEC - Council Directive on Certain List I substances (Dichloroethane, Trichloroethene)

groundwater if the water is not suitable for other use. Direct and indirect discharges of List II compounds shall be limited, subject to prior investigation. Under 80/68/EEC a “Direct Discharge” means the introduction into groundwater of substances in lists I and II without percolation through the soil or subsoil. “Indirect Discharge” means the introduction into groundwater of substances in Lists I and II after percolation through the soil and subsoil. It is implemented under S.I no 271 of 1992 (part iv) i.e. Local Government (Water Pollution) Regulations, 1992. There are however some differences between the Statutory Instrument and the Directive. List I and List II substances as per the Directive have been replaced by a First Schedule and a Second Schedule. (See Appendix 4) The List I and List II substances had Environmental Quality Objectives (EQO’s) and emission limits which were legally enforced by the E.C., these are not as clearly set out in the statutory instrument. Direct and Indirect discharges are also not clearly defined. Local Authorities are obliged to monitor the effects of authorised discharges on the groundwater quality.

2.3.3 EEC/80/778

Goundwater which is used as a drinking water supply is subject to regulation under 80/778/EEC (QUALITY OF WATER INTENDED FOR HUMAN CONSUMPTION) (EEC/80/778, 1980). This is implemented by the (Quality of Water Intended for Human Consumption), Regulations,1998, S.I No. 81 of 1988. Part 1 of the Schedule attached to the regulations gives the list of parameters for which [12]MAC's are set out. The organics included in this legislation are :

Table 6 - Organic parameters listed in EC Directive 80/778

	Parameter	MAC	Comment
23	Dissolved or emulsified hydrocarbons (after extraction with petroleum ether ; mineral oil	10 μg/l	
27	Other organochlorine compounds not covered by parameter 46	100 μg/l	Haloform concentrations must be as low as possible
46	Pesticides and related products - Substances considered separately Total	 0.1μg/l 0.5μg/l	Pesticides and related products means : insecticides herbicides, fungicides, PCB's, PCT's
47	Polycyclic Aromatic Hydrocarbons	0.2μg/l	

Part II of the Schedule lists the analysis requirements (pattern and frequency), while Part III gives reference methods for the analysis of the specified parameters.

2.3.4 Local Government (Water Pollution) Act, 1977

The Local Government (Water Pollution) Act, 1977 is the most important piece of legislation for the control of water pollution in Ireland. Groundwater is included in the scope of this Act. Section 3 of the Act makes it an offence to cause or allow the entry of polluting matter to water. European legislation is also introduced through the framework of the 1977 Water Pollution Act. EC directive 80/68/EEC has been

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[12] MAC - Maximum Admissible Concentration

implemented in Ireland under Local Government (Water Pollution) Regulations, 1992 - Part iv (Control of Discharges to Aquifers). Section 26 of the Act allows for the setting up of emission limits for discharges to waters and quality standards for waters based on the use of the water. Local authorities are the main body responsible for the implementation of this Act.

2.3.5 Local Government (Planning and Development) Acts, 1963 and 1976

A planning authority has authority to impose conditions attached to planning permission and as such can control pollution in proposed industrial developments. These conditions may be specified emission limits or quality standards or may require that the developer obtain a license for disposal of polluting material under the Local Government (Water Pollution) Act, 1977. Under Local Government (Planning and Development) Regulations, 1990, an Environmental Impact Assessment (EIA) is required for certain classes of activities. To date the agriculture, forestry, extractive industry, landfill operations and the chemical industry have been incorporated into the provisions of the regulations. The effect of the development both directly and indirectly on groundwater sources must be assessed.

2.3.6 EPA Act 1992

The EPA is responsible for “the state of the environment” in Ireland and is the main regulatory body for licensing, regulating and controlling activities for the purposes of environmental protection. It’s aim is to significantly strengthen the management and regulation of the environment in Ireland. Under the EPA Act, 1992 the functions for the EPA are :

- licensing of large or complex industrial and other processes with significant polluting potential on the basis of Integrated Pollution Control (with certain Best Available Technologies being specified)
- promoting environmentally sound practices through a range of guidelines, objectives and schemes.
- to give advice to public bodies on their environmental function.
- to co-ordinate environmental monitoring on a national level.

As part of IPC licensing groundwater monitoring may be required to be carried out at sites where a potential problem might arise e.g., an industrial activity using a large amount of solvents. Certain conditions are often associated with IPC licensing, aimed at protecting the overall integrity of the environment.

2.4 License Conditions

The United States Environmental Protection Agency (EPA) have compiled a list of Volatile Organic Compounds (VOC's) which covers a wide range of organics in use. (US EPA, 1988). This list comprises amongst others, aromatics such as benzene, toluene and xylenes, chlorinated solvents such as trichloroethene and tetrachloroethene and the trihalomethanes which are by-products of the chlorination of drinking water process ; Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform.

US EPA 524.2 list of compounds

Benzene	1,2-Dichloropropane
Bromobenzene	2,2-Dichloropropane
Bromochloromethane	1,1-Dichloropropene
Bromodichloromethane	trans 1,3-Dichloropropene
Bromoform	cis 1,3-Dichloropropene
Bromomethane	Ethyl Benzene
n-Butyl Benzene	Hexachlorobutadiene
t-Butyl Benzene	Isopropyl Benzene
sec-Butyl Benzene	p-Isopropyl toluene
Carbon Tetrachloride	Methylene Chloride
Chlorobenzene	Naphthalene
Chloroform	n-Propyl Benzene
Chloromethane	Styrene
2-Chlorotoluene	1,1,1,2-Tetrachloroethane
4-Chlorotoluene	1,1,2,2-Tetrachloroethane
Dibromochloromethane	Tetrachloroethene
Dibromomethane	Toluene
1,2-Dibromo-3-chloropropane	1,2,3-Trichlorobenzene
1,2-Dibromoethane	1,2,4-Trichlorobenzene
Dibromomethane	1,3,5-Trichlorobenzene
1,2-Dichlorobenzene	1,1,1-Trichloroethane
1,3-Dichlorobenzene	1,1,2-Trichloroethane
1,4-Dichlorobenzene	Trichloroethene
Dichlorodifluoromethane	Trichlorofluoromethane
1,2-Dichloroethane	1,2,3-Trichloropropane
1,1-Dichloroethane	Trichlorotrifluromethane
1,1-Dichloroethene	1,2,4-Trimethylbenzene
trans 1,2-Dichloroethene	1,3,5-Trimethylbenzene
cis 1,2-Dichloroethene	Vinyl Chloride
1,3-Dichloropropane	o-Xylene
	m,p-Xylene

The Irish EPA are making use of this comprehensive list in license proposals, requiring that the compounds listed in EPA method 524.2 be looked for in many effluent and groundwater samples for licenses. Although this list covers a wide range of compounds it is not all encompassing so the EPA may also require that a company analyse for all other solvents, or other organics which are in use in the company or plant. In this way a full complement of organics are analysed for giving a broad picture of the quality of water, with regard to organic contamination, both discharged by the company and on the aquifers on the surrounding site. A number of groundwater monitoring wells may be set out in the license. The licensee must, within a specified period of the granting of a license carry out a comprehensive hydrogeological investigation of the site. The condition of facilities for the protection of groundwater are set out. An annual environmental report on the plant must be sent to the EPA giving details of all monitoring carried out and the analytical results obtained.

2.5 Sources of pollution

2.5.1 Agriculture

Ireland is mainly an agricultural country. Intensive agriculture has meant using modern technology to help produce higher yields and bigger profits by using chemicals to kill weeds and improve growth. The price however, for this advancement is the contamination of our water supplies from these pesticides, herbicides, fungicides and insecticides. Not only are these chemicals used in intensive agriculture but they are readily available and frequently used by everyday gardeners. These chemicals are toxic and in many cases both persistent and bioaccumulative Usage of these chemicals by people who are unaware of the dangers of these compounds can have drastic results for our groundwater sources.

Table 7 - Commonly Used pesticides

Pesticide	Tradename	Usage
Atrazine	Altas Atrazine, Atrinex 80, Rose and Path Weedkiller	Professional and amateur herbicide
Paraquat	Pathclear	Amateur herbicide
Glyphosate	Roundup	Weedkiller
Chlorophenol	Preventol	Biocide
Dichlorvos	Vapona flykiller	General pupose insecticide

Because of the ‘green’ image which is portrayed in this country there is a significant lack of awareness of the environmental hazards of dealing with such chemicals. Traditional methods of disposal were to dump unused and excess agricides into the ground. In area where soil profiles are shallow there is a serious risk to groundwater from these agricides percolating through the soil. Under E.C directives it is illegal to dump hazardous chemicals without a license, however many aquifers have become contaminated needing costly remedial work. Not only are the wells being contaminated with the pesticides but they are also contaminated with the solvents used for application ; kerosene, toluene, 1,2,4-trimethylbenzene, naphthalene, solvents which themselves are dangerous pollutants.

Sheep dipping is an agricultural practice which causes contamination of groundwater supplies. Spent sheep dip is often allowed to filter into the ground. Depending of the depth and thickness of the subsoil and whether the rock has fissured or intragranular flow it is possible that the treatment chemicals will infiltrate any groundwater in the area

Treatment of the grass on golf courses is a major user of pesticides. Greens and fairways are kept free from weeds by constant application of weedkillers and copious fertilisers are added to ensure a lush growth. During heavy rains large amounts of pollutants can be transferred through the soil to aquifers.

Triazine herbicides are used in Europe as weedkillers for agriculture and for maintenance of public thoroughfares. Paillard et. al., report chronic pollution of groundwater of karstic origin by these nitrogenous pesticides up to a maximum of 10µg/l. Triazine herbicides are toxic in relatively high concentrations - the LD_{50} for rats is 1860 mg/kg (atrazine). Degradation by-products of these herbicides are however more dangerous. Atrazine is degraded to cyanuric acid which has an LD_{50} for rats of 500mg/kg. Ozone treatment can be used to partly remove simazine and atrazine from groundwater but an O_3 /H_2O_2 combination gives higher yields and less by-product formation. (Paillard et .al., 1990). In 1989 there were 460 complaints with regard to pesticides in potable waters made in the E.C, under directive 80/778 (QUALITY OF WATER INTENDED FOR HUMAN CONSUMPTION) (Vincent,G., 1990)

Some pesticides which are banned in other countries are still commercially available in Ireland. Aldicarb, a highly toxic pesticide which has been banned in the United States since 1981 is commonly used in Ireland as an insecticide in the sugar beet industry e.g., Power Aldicarb 15 (15% w/w) , Temik 10G (10% w/w). The active ingredient in Aldicarb is not itself very persistent, however its breakdown products which are equally as toxic are more persistent and more mobile that Aldicarb (Daly, D, 1995).

Pesticides causing the biggest problem in the U.K are atrazine, simazine, isoproturon, chlorotoluron and mecoprop (Crawthorne, B., 1992). Atrazine contamination of surface and groundwater's is the most problematic area. Atrazine is not used specifically in agriculture but is used for weed control and other non-agricultural applications. The E.C MAC's are set as a 'surrogate zero', meaning that none of the compound should be present. In the E.C Drinking water directive, 80/778, there is a figure of 0.5 µg/l given as the MAC for total pesticides and 0.1 µg/l for individual pesticides. The Department of Agriculture, Food and Forestry in its '*Pesticides*' book lists over 1000 currently available pesticides in Ireland. To determine a method for each individual pesticide would be costly and time consuming. A more practical approach would be to regularly monitor for the most commonly used pesticides or those used in large quantities. The main pesticides used in Ireland are atrazine, simazine, paraquat ,glyphosate chlorophenol, coumaphos, dichlorvos, isoproturon, mecoprop, lindane (γ BHC). (Dept. of Agriculture, Food and Forestry , 1996).

Another source of organic contamination from the agricultural sector is that from petroleum/mineral oil. Leaking heating oil and fuel storage tanks and spillage's from tractors/vehicles while refilling can cause pollution of aquifers.

2.5.2 The Industrial and Commercial Sector

Organic compounds containing halogens can be expected in ‘chemically polluted’ water. This group includes chloroform, trichloroethene, tetrachloroethene and trichlorobenzene. Organohalogens rarely occur naturally. The majority of halogenated organic compounds are from chemicals discharged by various industries - chemical plants, paper mills (there are agricultural related compounds such as pesticides). They are used as solvents, cleaning agents and in the production of various end-products. The presence of halogenated organic compounds must be considered undesirable because many are considered to be toxic, mutagenic and carcinogenic (See Table 1) causing health concerns. Their importance is reflected in the fact that greater than half of all priority pollutants listed by both the United States Environmental Protection Agency and the E.C (List I and List II) are halogenated organic compounds (US EPA, 1979) (EEC/76/464, 1976). The most effective solvents for grease and lacquers as well as the most effective refrigerants are represented by chlorinated hydrocarbons. Their material characteristics make chlorinated hydrocarbons some of the most frequently found contaminants of groundwater. Other organic solvents of concern are benzene, toluene and xylenes - the aromatics[13]. Toluene is used as a solvent for many pesticide formulations and xylene is used regularly in the paints industry. Phenolic compounds are aromatic compounds containing one or more hydroxy groups. Phenol is derived from ‘phene’ and old name for benzene. Phenols have a wide range of

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[13] Aromatic compounds are those which possess a cyclic configuration (a ring of carbon atoms).

uses from pesticides to food applications. Phenolics are unintentionally formed in industrial processes e.g., catechols have been determined in Kraft paper mill bleaching effluents. They are also used in antiseptic manufacture e.g., trichlorophenol (TCP). Chlorophenols such as tetrachlorophenol and pentachlorophenol are commonly used for wood treatment as antiblue stain and antisap stain agents. They are also very effective in preventing fungal deterioration of wood products. Many aquifers have been contaminated by previous or current industrial activity or by illegal dumping of waste solvent. Often the extent of contamination is not known due to the slow movement of the solvent through the aquifer. The E.C has not yet set specific levels for many of the common solvents in use.

2.5.2.1 The Pharmaceutical Industry

Ireland has a developing pharmaceutical industry which uses a wide range of solvents e.g., acetone, carbon disulphide, chloroform, dichlorobenzenes, ethanol, methanol, trichloroethene, trimethylbenzenes. A large proportion of these solvents are recovered after use, for waste minimisation and cost effective measures. Large quantities of the solvents are stored on site in tank farms. Regular checking of vessels, pipelines, valves etc. is essential to avoid leakages. Raw materials, intermediate and finished products can also be potential contaminants but in general strict controls on processes reduce risk of contamination by these materials.

2.5.2.2 Petroleum industry

Petroleum refining encompasses a wide range of products e.g.,., petrol, diesel, kerosene, mineral oils. Petroleum distillates are generally straight chain alkanes in a specific boiling point range depending on the distillate fraction. They also contain volatile, semi-volatile and high boiling organic compounds. Petrol is a low boiling point fraction and the aromatic compounds benzene, toluene, ethyl benzene and xylene are often used as indicators of petrol contamination. [14]PAH's are produced mainly from petroleum refining industry, from petrol, coal-tar, asphalt and bitumen processing. PCB's were until recently used in hydraulic fuels. The ESB also used PCB's in transformer oils.

Petrol, diesel, aviation fuel, heating oil are all stored in large tanks which are prone to leakages. It is estimated that 10% of the 1.5 million underground storage tanks in the United States have had confirmed leaks (Restek Advantage, 1994). The potential of leaks from the other 90% is a serious problem. They are often washed off surfaces as run-off and can thus cause indirect (non-point) pollution. Runoff from petrol stations is also a major non-point pollution source and can contain components of petrol and diesel such as benzene, toluene, ethyl benzenes, trimethylbenzenes and PAH's all of which can be washed into the aquifer.

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[14] PAH - Polycyclic Aromatic Compound

2.5.2.3 Pesticide production

Effluent streams from the production of pesticides can contain both active ingredients and finished products. Some of the solvents used in pesticide manufacturing are naphthalene, butyl benzenes, chlorobenzenes, ethyl benzene, toluene. Phenols are commonly used in the manufacture of pesticides to produce chlorophenol, pentachlorophenol, nitrophenol. Phenols are organoleptic materials, imparting and odour or taste to the water making it undesirable for consumption. They can also be poisonous even in small quantities, as little as 1 gram can be fatal to humans (Merck, 1983).

2.5.2 4 Adhesives Industry.

A wide range of volatile organic compounds are used in the adhesives industry ; acrylonitrile, methyl ethyl ketone (MEK), chloroethane (adhesive for plastics), 1,1- Dichloroethene, Vinyl acetate, (a polymeriser), xylenes, toluene, 4-Chloro-3-methylphenol (a preservative).

2.5.2.5 Paints and Dye Industry

Main solvents used are methyl iso butyl ketone (MIBK), methyl ethyl ketone (MEK), carbon disulphide, chlorobenzene, chlorotoluene, ethyl benzene, dichloromethane (used for paint stripping), tetrachloroethanes, trichloroethene, toluene, xylene. Trichlorobenzenes are used as dye carriers, vinyl acetate is used as polymeriser for paints and white spirits, a petroleum distillate and isopropyl benzene are used as thinners. Some PAH's are used in dye manufacturing e.g., naphthalene and anthracene.

2.5.2 6 Plastics Industry.

High molecular weight polymers are made from very toxic starting products - polyvinylchloride from vinyl chloride, a carcinogen.

Other ingredients are acrylonitrile, butyl benzene, 1,2- dichloroethane, styrene, phenols, acenaphthene and phthalates. Trimethylbenzenes are frequently used as stabilisers.

2.5.2.7 Electronics and Electrical Industry.

The electronics industry uses solvents for cleaning of components. The main solvents used are chlorinated hydrocarbons e.g., trichloroethene and tetrachloroethene. PCB's were until recently used in dielectric switches. They are no longer used but quantities of PCB's have been dumped on landfill sites and they can be a component of landfill leachate.

2.5.2.8 Commercial Sector

Dry cleaning firms use vast quantities of chlorinated solvents. Similarly photographic firms have various developing solutions and chemicals, furniture manufacturers use formaldehyde compounds in making furniture and solvents such as methyl ethyl ketone, methyl iso butyl ketone and toluene are used for spraying/lacquering the finished products.

2.5.3 Domestic Discharges

Leaking septic tanks from isolated domestic dwellings can be a major source of contamination as they are excluded from discharge licensing control. Pollution from septic tanks tends to be of a biological nature but there are a wide range of other possible polluting materials from domestic sources ;

- DIY products such as paints, varnishes, thinners, strippers containing white spirit, xylene, toluene, methyl ethyl ketone, methyl ISO butyl ketone, dichloromethane.
- Adhesives containing xylene, acetates, cyclohexane.
- Agricides such as atrazine (weedkiller), dichlorvos (insecticide - flykiller), warfarin (rat poison).
- Old fluorescent light bulbs had starter switches which contained PCB's.
- Car maintenance products such as antifreeze (ethylene glycol), engine oil, grease and rust solvents, paint sprays.

2.5.4 Landfill sites

Ireland produces approximately 28 million tonnes of waste per annum (Fitzgerald, W. 1995). Most of this waste is disposed of to landfill (93% of all municipal solid waste is landfilled). Prior to the EC directive on Toxic and Dangerous Waste (78/319/EEC) waste whether innocuous or hazardous waste was disposed of to the same landfill, in most cases the landfill being unsuitable for hazardous wastes. For a landfill to be able to cope with hazardous waste there is a minimum depth of soil cover required with a specified permeability coefficient to protect the underlying groundwater. The trend now is for a liner to be used in landfill sites which are receiving hazardous waste. Donal Daly of the Geological Survey of Ireland (G.S.I) strongly recommends against siting landfills on or near regionally important aquifers (MAJOR aquifers). It is generally accepted that 'all synthetic liners will eventually leak' and with the often unpredictable and relatively fast flow rates in major aquifers routine monitoring may not detect contaminants (Daly, D., 1996). Due to the fact that previously there was no distinction made between non-toxic and toxic waste many Irish landfills are a potential source of contamination for our groundwater. Rain falls on the landfill and passes through the waste leaching out soluble components. If the soil cover is not of sufficient depth or permeability severe contamination of the aquifer can occur. Presently there are a lack of hydrogeologically secure landfill sites in Ireland for contaminated solids, liquids and sludges (Callanan, F., 1994). Old landfills and waste disposal sites with insufficient leachate collection systems constitute a frequent risk to groundwater quality. The landfills typically contain a high organic content from municipal and industrial refuse and chemical waste. Landfills contain all the potential contaminants as set out in domestic sources as well as waste from industry and the commercial sector.

Landfill leachate then is a source of hydrocarbons (waste oils and petroleum products), solvents, pesticides, PAH's, PCB's, phenols.

3.0 Extent of pollution in Ireland and procedures for sampling and analysis of trace organic contaminants.

3.1 Introduction

The study of organic pollutants is perhaps one of the most complex issues in groundwater pollution chemistry. There is such a wide range of possible pollutants many with severe ecotoxicological effects thus making the assessment of water quality and long term trends in the aquifer very difficult.

The report from the EPA on the quality of drinking water in Ireland between 1993 and 1995 (EPA, 1997 (1) & (2)) shows that chlorinated supplies from groundwater have low trihalomethane levels in contrast to the levels found in chlorinated water supplies from surface water.

3.1.1 Pollution from agricultural sources

3.1.1.1. Teagasc in Carlow have carried out studies on the persistence in groundwater of dichlorobenil, a herbicide used for weed control (Eades, J., 1990). A contamination incident occurred in Co. Cork, in 1983 when the ground around an industrial site was sprayed with weedkiller and the runoff (on a downward slope) contaminated both the soil and groundwater of the neighbouring farm. The levels of dichlorobenil in the aquifer (which was supplying drinking water) were monitored over a three year period following the pollution incident. The concentration of dichlorobenil initially was 14 µg/l. This is 28 times the E.C MAC for total pesticides as set out in the E.C quality of water intended for human consumption regulations. The results for the monitoring Programme is given in Table 8.

Table 8 - Persistence of dichlobenil in groundwater (Co. Cork)

June 1983 - July 1986

Sampling Date		Dichlobenil level
Year	**Month**	**µg/l**
1983	8 Jun	14.0
	27 Jun	3.8
	19 Jul	0.5
	24 Aug	4.0
	23 Sept	0.2
	26 Oct	3.8
	22 Nov	4.0
	29 Dec	2.7
1984	9 Jan	4.5
	7 Feb	0.8
	2 Mar	3.4
1984	17 Apr	2.9
	22 Jun	2.4
	9 Aug	0.5
	12 Oct	3.0
1985	Jan	1.2
	Apr	1.8
	Jul	0.2
	Nov	1.4
1986	Jan	1.5
	Apr	0.1
	Jul	1.5

Three years after the pollution incident occurred the levels of pesticides in the well are still above E.C regulations for a drinking water supply, demonstrating the persistence of the pesticide.

3.1.1.2 According to a review of Irish soil published in 1995 (McGrath, D., 1995), the pesticide lindane (γ HCH) and PCB's were present in Irish soils but at reasonably low levels. DDT has been banned in Ireland in 1985 but it and its breakdown products are still present in sizeable quantities in Irish soils. In this survey organochlorine pesticide levels are also appreciable. These pollutants can be washed from the soil into the aquifer contaminating the groundwater below.

3.1.1.3 Stride 399 (Stride 399, 1994)

From the Stride Report (No. 399) on trace organic contamination of Irish groundwater's a number of sites which were contaminated were identified to be a result of agricultural processes. In terms of pesticides the study favoured analysis of phenoxy acid herbicides, triazine herbicides and organochlorine pesticides. The details are given below :

A well close to mushroom farm in Co.Mayo (MO-1) was contaminated with pesticides (2,4,5-T and lindane) and with Trimethylbenzene a solvent used for pesticide application. 1,2-Dibromo-3-chloropropane, naphthalene and trimethylbenzenes were determined at low levels (5-10 μg/l) in a well in Leitrim (LM-2) in an area where sheep grazing and dipping is carried out.

A domestic well in Waterford (WD-2) close to farmland which had been sprayed with herbicides was badly contaminated with Atrazine (16 μg/l) and Simazine (0.06 μg/l). These levels exceed the EC Drinking water directive 80/778/EEC levels for pesticides. A residential well close to tillage land in Co. Offaly (OY-2) showed volatile organics (1,2-Dibromo-3-chloropropane, naphthalene and trimethylbenzenes) at levels in excess of 30 μg/l and a residential supply and farm well in Sligo was contaminated with volatile organic compounds which are indicative of hydrocarbon contamination - a home heating oil tank on the farm had previously been found to have a leak.

3.1.1.4 From the EPA's report on Pesticides in Drinking Water (EPA, 1996 (3)) - Results of a preliminary survey, December 1994 to December 1995 over 3,300 samples were collected with only 3 samples in excess of the 0.1 μg/l level set for individual pesticides.[15] Of the 3 samples only one was a groundwater sample - this sample was from a borehole at Athboy, Co.Meath (Sample no. 92) and contained lindane at a level of 32 μg/l. This level is greatly in excess of the MAC but on re-sampling the well shortly afterwards no lindane or any other pesticides were detected. The results of the survey show that while there is no significant background levels of pesticides in the majority of Irish water supplies there may be a possibility of short-term contamination.

It can be seen that there are many non-naturally occurring organic compounds in Irish groundwater's resulting from agricultural pollution. Most of the levels detected are not dangerous but infiltration of the aquifers is occurring and as most of the wells contaminated are local supplies of water it could have repercussions on the quality of water supplied to small communities.

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[15] This MAC level for pesticides is set under EEC/80/778 - Quality of Water intended for Human Consumption, Regulations 1980.

3.1.2 Pollution from Industrial sources

3.1.2.1 Nenagh Contamination Incident, 1996 (EPA, 1996 (2))

In August 1996 an odour in the drinking water supplied to the town of Nenagh in Co. Tipperary was the first indication of contamination in the aquifer supplying the town's drinking water. The water came from a well situated in Gortlandroe, just outside the town and situated close to an industrial estate. The analysis of the water showed presence of the organics - octamethylcyclotetrasiloxane (OMCT siloxane) and 1,1,1-Trichloroethane. There was also biological contamination of the well emanating from a leaking sanitary drain on the industrial estate. After further investigation the source of the compound OMCT siloxane was traced to a possible source i.e., a leaking flange on a process effluent line. Pollution may have been by infiltration directly into the aquifer and also from the surface water drainage system which discharges directly to the main SFADCO[16] foul drain and storm water drain. 1,1,1-Trichloroethane present in cooling water from another factory was identified as a second possible source of contamination. It was also discharged to the SFADCO storm water drain. There were indications that the storm water drain and the foul water drain were leaking and the contents entering the aquifer by infiltration through the overlying soil (of low permeability). Hydrogeological investigation showed the well to be vulnerable to pollution. Levels of 1,1,1-Trichloroethane are given below and while not toxic they render the water unfit for human consumption.

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[16] SFADCO - Shannon Free Airport Development Company - the developers of the industrial estate.

Table 9 - Levels of 1,1,1-Trichloroethane in Gortlandroe well

Source	**Concentration** **1,1,1,-Trichloroethane μg/l**
Well Inflow	15
Water Supply	2.8
Tubex Discharge	8.6
Well Water after refilling and chlorination	52.6
Water Supply before chlorination	11.7

A hexane extract of the well water also showed presence phenols, phthalates and hydroxyquinoline following GC/MS analysis.

3.1.2.2 Stride Report 399

From the Stride Report No. 399 it can be seen that the main source of pollution of Irish groundwater's is from leaking fuel storage tanks and fuel spillage's. A list of the main pollutants detected as a result of contamination from industrial sites (including petrol stations and commercial premises) is given is Table 10.

Table 10 - Main organics detected in the Stride 399 project.

Benzene	1,1,1-Trichloroethane	Trichloroethene
Toluene	Freon	Dichloromethane
Ethyl Benzene	n-Butyl Benzene	Chloroform
Xylene	t-Butyl Benzene	Tetrachloroethene
Naphthalene	1,2,3-Trimethylbenzene	1,3,5-Trimethylbenzene
Bromodichloromethane	Dibromochloromethane	1,2-Dichloroethane
1,2,3-Trichlorobenzene	1,2,4-Trichlorobenzene	1,1-Dichloroethene
IsoPropyl Benzene	n-Propyl Benzene	Chlorobenzene
Styrene	naphthalene	phenanthene
anthracene	fluoroanthene	benzo(a)pyrene
pyrene	chrysene	arochlor 1016

Of the 60 nation-wide wells sampled 17 wells had organic contamination in excess of 1000 μg/l. 12 wells were polluted as a direct result of leaking fuel tanks or fuel spillage's.

e.g., Well DN-2 a major sand and gravel aquifer in south Dublin is located in an industrial area and was contaminated as a result of a diesel spillage. DN-3, a well near Dublin bay is a locally productive aquifer near fuel storage tanks, bitumen processing and wood preserving. As well as the volatile organic compounds associated with petroleum products an array of polycyclic aromatic compounds were detected (naphthalene, phenanthrene, antracene, fluoranthene, pyrene, chrysene, benzo(a)pyrene) at levels approximating 8 mg/l. PAH's being carcinogenic are List I substances under EEC/80/68 and should not be present in the aquifer. No specific daughter directive has been set out for any of the specific compounds as yet.

Halogenated organics are compounds which are frequently found in contaminated wells. Trichloroethene is a commonly used degreaser and as a solvent in the dry cleaning industry. It was found in a well in Carlow which has a history of trace organic contamination as a result of illegal dumping from nearby industry. 1,1,1-Trichloroethane, Tetrachloroethene and Chloroform were also detected in many wells. A well in Meath downgradient from a solvent recycling plant contained chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethene, dichloromethane, trichloroethene and tetrachloroethene at approximately 100 μg/l.

Significant levels of toluene (apart from levels determined as a result of petroleum product spillage's) were detected in a well adjacent to a chemical factory in Wicklow, at 96 μg/l. Xylene and naphthalene were also detected. Toluene levels in excess of 1000 g/l were found in Co. Clare from a purpose installed monitoring well immediately downgradient of a chemical plant. Some process chemicals (of phenolic and amine origins) were also detected in the well.

3.1.3 Landfill Contamination

The highest levels of trichlorobenzenes found in Irish groundwater's are associated with landfill sites (Stride 399, 1994). Trichlorobenzenes are petrol constituents, solvents and are used in dyes, coolants, lubricants, dielectric and pesticide manufacturing. Other indicators of petroleum product contamination were regularly found in wells monitored for Stride 399 : benzene, toluene, ethyl benzene, xylene, trimethylbenzenes and butyl benzenes were found in most landfill boreholes. In site Limerick-1 (LK-1) a total petroleum hydrocarbon (TPH) content of 900 μg/l was determined. Phenols were also detected in the well at LK-1 but were present at low concentrations (<1 μg/l). Chlorinated hydrocarbons were commonly detected along with toluene and naphthalene (both possibly from pesticide dumping). Some semi-volatiles were also detected e.g., Mecoprop, a pesticide was detected at 4.1 μg/l in a purpose built monitoring well on the edge of an active landfill in Dublin. Almost 30% of the samples with contamination over 1000 μg/l are contaminated as a result of landfill sites.

3.1.4 Potable Groundwater Sources

Many of the wells from the Stride report are not currently nor have ever been used as a potable water supply. Some of these wells however are domestic and public water supplies. An example of the number of the wells serving as public or domestic supplies from the Stride project are given below in categories of the contamination determined in them.[17]

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[17] The wells in the Stride report are named using the first and last letter of the county name e.g., DN denotes Dublin. The number after the letters refers to the well site - at least two wells were sampled in each county.

Table 11 - Potable supplies sampled for Stride project no. 399

Category A < 1 µg/l	Category B 1-5 µg/l	Category C 5-10 µg/l	Category D 10-100 µg/l	Category E 100-1000µg/l	Category F >1000 µg/l
LD-1	Gy-1	DL-1	CW-2	CK-4	GY-2
	KY-1	OY-2	MN-1	SO-2	WX-1
	KK-2		OY-2		
	LH-2		RN-2		
			SO-1		

From this chart it can be seen that many public and domestic water supplies have been severely contaminated by organics. The two wells with greater than 1000µg/l contamination were mainly petroleum product contamination. Well GY-2 (Galway) from a petrol station and urban runoff and well WX-1 (Wexford) was contaminated from a leaking underground storage tank. Both wells in the 100 - 1000µg/l contamination category were also contaminated as a direct result of leakage from petroleum product storage tank. Trihalomethanes (THM's) were also detected in many public supply wells. Trihalomethanes are by-products of the chlorination process and consist of chloroform, bromodichloromethane, dibromochloromethane and bromoform. The World Health Organisation has set limits in drinking water of 100 µg/l for total THM's and an individual limit of 30 µg/l for chloroform (WHO, 1984).

A well which was formerly a public supply well in Co.Roscommon (RN-2) had chloroform levels above the 30 μg/l level (Stride 399, 1994).

An important feature of Irish public water schemes is the large number of schemes (mainly borehole supplied) which supply small quantities of water. The majority of these schemes use groundwater as their source and as the water is generally of a high quality little or no treatment is required (Kilmartin, L., 1992). A lot of the water is supplied from aquifers categorised as poor/minor locally productive wells. As seen above many of the wells monitored in the Stride Project fall into this category, and many have been contaminated with organics. Water from community wells is often not chlorinated and there is a particular need to protect the sanitary quality of the water from these sources. It can also be seen however that the trace organic contamination of small community wells is a growing hazard.

Table 12 - Public Drinking Water Supplies

Source	Number	% of Total	m^3/d	% of Total
Surface	298	37	1,035,475	80.5
Groundwater	460	57.1	165,910	12.9
Surface and Groundwater	47	5.8	85,247	6.6

3.2 Analytical Techniques for trace organic contaminant analysis

There is a strong relationship between environmental problems and analytical methods. The development of more sensitive analytical methods has revealed new environmental problems and the realisation of new environmental problems has created a need for new and more sensitive analytical methods and instrumentation. The focus is on both analytical sensitivity and also specificity for environmental interpretation.

3.2.1 Separation and Detection

There are many ways of analysing volatile organic compounds. The separation of complex mixtures is generally carried out by gas chromatography with various detection systems. Gas chromatography consists of a column, coated with a polymeric substance specific for the substance(s) is question, contained in a heated oven. As the temperature of the oven, hence the column increases, the various components of a mixture to be separated by their different boiling points. The separated compounds then pass through a detector which has a specific response for the compounds. A printout gives the specific retention time for each compound and the detector response which is generally given in terms of area or height on a page.

3.2.1.1 Detectors

Identifying the compounds eluted from from the Gas chromatographic column is of utmost importance. Many different detectors are available which convert the physical and/or chemical properties of the compounds into a readable signal. These range from general purpose detectors which respond to almost any organic compound in the gas stream to selective detectors which can give information based on some element or chemical property of a group. Selective detectors by there nature provide a specific sensitive response for particular classes of compounds and can aid or complement the universal detectors. A number of detectors can be combined to provide a more exhaustive profile of a sample.

There are many different detector types in use :

Flame Ionisation Detector (FID), a general purpose detector. The flame ionisation detector enables compounds that ionise in a hydrogen (H_2) flame to be detected. This includes almost all organic compounds.

Electron Capture Detector (ECD) which is generally used for halogenated or nitro groups of compounds (insecticides pesticides, chlorinated hydrocarbons). The ECD is the most sensitive detector available for the non-destructive detection of electrophilic substances, such as chlorinated hydrocarbons.

Nitrogen/Phosphorus Detector (NPD) for nitrogen and phosphorus containing compounds such as many pesticides.

Thermal Conductivity Detector (TCD) detects a difference in the thermal conductivity between the column effluent flow (sample stream) and a reference flow (carrier gas only). A voltage proportional to this difference is produced as the output signal.

Flame Photometric Detector (FPD) for compounds containing sulphur and phosphorus. It can also be used for halogens, cyanide groups or heavy metals.

Mass Spectrometric Detector (MSD) which determines the unique mass spectrum of each compound giving an unambiguous identification.

3.2.2. Sample Introduction Techniques

The introduction of the sample into the Gas chromatograph can vary also.

Direct Injection - the sample is introduced directly onto the column. This can cause problems with matrix interference when a large amount of a compound other than those being looked for is present. The matrix interference can cause distortion of the analytes of interest making it difficult to accurately determine the quantities present.

Headspace Analysis - the sample is heated and an injection of the headspace above the sample is made - the headspace contains VOC's which are volatile at the temperature being used thus it is a useful method of isolating some of the compounds in a mixture or for eliminating matrix effects.

Purge and Trap - A helium flow is passed through the sample and this purges the volatiles onto a polymeric trap. The trap is then desorbed by heat onto the gas chromatographic column.

Solid Phase Microextraction (SPME) - A polymeric coated silica fibre is placed in contact with the sample or the sample headspace and the analytes are adsorbed onto the fibre. The analytes are then thermally desorbed off the fibre in the heated injection port of the gas chomatograph.

3.2.3 Volatile Organic Compounds (VOC's)

The US EPA has set out many methods for analysis of organic compounds amongst others. These methods have been validated and are approved methods. The main method for volatile organic compound analysis is US EPA method 524.2. This involves purging the sample with a helium gas stream and then trapping the compounds which volatilise on a packed porous polymer column with analysis by Gas chromatography/Mass Spectrometry (GC/MS). This technique has been rigorously tested and validation and recovery data is available. The method is simple to follow and provides unambiguous results. The compounds are determined both on retention time from the GC and by their mass spectra. The purge process is a method of concentrating the compounds and so low detection limits are available . An internal standard is used to reduce error from run to run in purging efficiency. The technique has some drawbacks in that the purging process carries water vapour across to the GC along with the purged volatile. A moisture control module must be used which removes the water vapour from the sample. This technique is not very effective for low boiling point polar compounds such as methanol, ethanol and acetone. The polar characteristics of these compounds mean that they act similarly to water and they are also removed to some degree in the moisture control module giving bad reproducibility and high detection limits. Another problem with the Purge and Trap method is that when the compounds are purged it is generally at room temperature. If the laboratory is not temperature controlled and the temperature fluctuates to any small degree then the efficiency of purging will increase as the temperature increases - the volatility of the compounds rises with temperature. Thus a standard calibration curve prepared when the temperature is 22°C will have a very different slope to that prepared when the temperature is 26°C. Despite its drawbacks US EPA method 524.2 is the most popular method of analysis for most volatile organic compounds.

Solid Phase Microextraction is a relatively new technique which seems to offer advantages over purge and trap as a means of introducing the analytes onto the GC column. The fused silica fibre is housed in a syringe and is available in different polymeric coatings for different analytes. Coatings such as polydimethyl siloxane (100 μm) are being using for a wide range of organic parameters. The SPME needle is placed into or just above the water sample in an enclosed vessel. The sample is agitated and the VOC's are adsorbed onto the fibre. The length of exposure and degree of agitation can affect the concentrating effect. The fibre is then placed in the heated injection port of the chromatograph and the analytes are thermally desorbed onto the GC column. Detection for a wide range of VOC's such as the US EPA Method 524.2 list of compounds is then usually carried out by Mass Spectrometry. One of the most favourable points about SPME is that is eliminates matrix effects. Only the analytes of interest are extracted thus the chromatographic trace is very easy to decipher. Studies have shown that high precision and reproducibility as well as low detection limits are easily obtained by this technique. (Zhang et. al., 1993) (Shirey, R., 1997).
Detection limits for most VOC's are in the order of 0.2 - 1 μg/. It has also been documented that adding salt to the water sample or heating the sample

can greatly improve the sensitivity of the technique. SPME seems to be a very simple, rapid and inexpensive method of sample preparation and pre-concentration which has the added benefit of being solvent free. Studies are ongoing by the US EPA and other international bodies to validate and approve SPME as a sample preparation method.

3.2.4 Total Petroleum Hydrocarbons

The American Public Health Association in its book Standard Methods for Water Analysis (APHA-AWWA-WPCF, 1989) states that TPH analysis should be carried out by liquid extraction with 1,1,2-Trichlorotrifluoroethane (Freon113) and detection by measuring a C-H bond by Fourier Transform Infra-Red spectroscopy. (F.T.I.R) Freon, a chlorofluorocarbon (CFC) gives very little background effect on the F.T.I.R so it made detection of the bond very easily. Freon is however a banned solvent and this method also used very large quantities of solvent for the extraction making it environmentally unfriendly.

One technique which is relatively solvent free is solid phase extraction (SPE). The water (usually one litre) is passed through a C18 column. The non-polar hydrocarbons are attracted to the non-polar packing material land are adsorbed onto it. The remainder of the water passes to waster. The TPH's are removed with a small volume of dichloromethane which is then concentrated to 1ml. Identification is usually by means of a gas chromatography with a general purpose flame Ionisation detector which has a very good response to hydrocarbon compounds. Each petroleum product has a distinctive gas chromatographic trace consisting of the various different n-alkanes and other compounds they are comprised of e.g., Trimethylbenzenes. Kerosene, for example has a boiling point range of 186°C to 287°C and an n-alkane range of ${}_nC_8$ to ${}_nC_{16}$. The diesel (gasoil) range is from ${}_nC_{12}$ to ${}_nC_{32}$, boiling point range from 216°C to 468°C, and so on for petrol, white spirits etc. This makes it very easy to differentiate between different petroleum fractions. Low levels of detection are obtainable because of the concentration factor of 1000, when one litre of sample is brought down to 1 ml. The technique is labour intensive as the solid phase extraction cartridges cannot be allowed to go dry. The reservoir supplying the cartridge can only hold approx. 100ml therefore it is necessary for someone to stand with the equipment constantly applying more sample to the reservoir.

One liquid extraction technique uses 1ml of n-hexane, a non-polar solvent is used to extract 960mls of water. Agitation of the sample is required. The hexane extract is then analysed by gas chromatography as before. The detection limits are still low with the concentration of 960mls to 1 ml, and it has the added advantage of using only a very small amount of solvent and being very inexpensive as it requires no extraction equipment other than a volumetric flask and a pipette for addition of the hexane. One problem with TPH analysis is that the EC MAC for TPH in drinking water (including groundwater) is 10 μg/l. Most analytical equipment e.g., GC/FID with sample concentration techniques based on a one litre sample of water have a detection limit of 30-50 μg/l. To reduce the limit of detection to the 10ug/l level at least 3 litres of water would be required, making the sampling and analysis very cumbersome. Also the water is unpalatable at levels even below 5 μg/l,(Daly, D., 1994) this means that the water might pass the EC Mac's but still is contaminated by petroleum products which are identifiable by taste. TPH analysis is usually carried out in the range $_{n}C_{12}$ to $_{n}C_{32}$, the diesel oil range. A common problem encountered in TPH analysis is the presence of interfering compounds. These are often contaminants such as phenols, phthalates or mineral oils which are also extracted. It is crucial with TPH analysis to recognise the distinctive petroleum product pattern (specific for each distillate) and to only include those peaks which belong to the petroleum product in the result.

3.2.5 Semi-Volatile organic compounds - SVOC's

Semi-volatile organic compounds are a very heterogeneous group of priority pollutants including polycyclic aromatic hydrocarbon compounds (PAH's), pesticides, polycyclic chlorinated biphenyl compounds (PCB's) and phenols.

SVOC's can be analysed as an aggregate mixture as in US EPA method 625. This involves a liquid-liquid extraction followed by gas chromatography with mass spectrometry detection. The sample is initially made basic, pH >11 for extraction of the base/neutrals and after 3 extraction's with dichloromethane the sample is acidified with the pH adjusted to pH <2. 3 extraction's with dichloromethane are again carried out to remove the acidic components. The extracts are then combined. A two litre sample of water is extracted and the extract reduced to 1 ml. Analysis by GC/MS allows for a positive identification of each compound by both retention time and by their mass spectra. Vast quantities of dichloromethane are used in the extraction process. and dichloromethane is itself a toxic carcinogenic compound. A group of researchers at the Nevada Division of Agriculture have developed a fast solvent conserving method for analysing base/neutral and acidic semi-volatile organic compounds in groundwater by solid phase extraction (SPE) (Rutland et. al., 1996). The method concentrates 400ml to 2 litre samples by passing it through an ENV-Carb SPE cartridge. The compounds are eluted separately by using eluting solvents adjusted to the correct pH. Less than 10 millilitres of total solvent is used and the limits of detection range from 0.1 - 5 ug/l for 400ml samples with most recoveries between 80 and 130 %. Analysis is often by HPLC but the extraction technique can be used with most detection systems. Similar solid phase extraction methods are being used more regularly by scientists over the traditional liquid-liquid extraction technique. (Nolan, L., 1996), (Bellar et. al., 1978) The solid phase extraction technique offers significant advantages over liquid extraction for cleanup and concentration of semi-volatile organic compounds. It is fast, efficient and uses minimal amounts of solvent and is quantitative and reproducible. It is also conducive to automation which speeds up preparation and thus analysis time. It also reduces artefact and breakdown product formation. Because of the stringent EC MAC's for pesticides in drinking water (for which many groundwater sources are used) - 0.1 µg/l of any individual pesticide and 0.5 µg/l total pesticides - it is very important to be able to positively identify the pesticide detected at low levels. This makes mass spectrometry essential to unambiguously identify the specific compound present. (Fielding et. al., 1990) There are over 1000 permitted pesticides in use in Ireland today. Certain characteristics of pesticides should be taken into account in deciding which pesticides to monitor for. These properties are :

- persistence
- likelihood to find their way into a drinking water supply
- detected previously in water

With each of the analytical techniques described a set of calibration standards must be prepared under strict quality control procedures and analysed under the same conditions as the samples. It is important to have procedures set out for dealing with samples and standards which ensure an accurate and reliable result. Good Laboratory Practice and Laboratory Accreditation are essential elements of a reliable analysis. Internal and field blanks as well as quality control and blind spike checks must be analysed in conjunction with the samples to ensure the correct result. Laboratories not adhering to a high level of quality should not in a position to produce results which are critical to Irish industry and consumers and which play and important role in ensuring the integrity of our environment.

3.3. Sampling Procedures

In order for water quality guidelines as set out in EC directives to be adhered to the collection and analysis of samples must be carried out in a methodical fashion reflecting the nature of the sample being collected. Knowledge about the nature of the water being sampled is important . The distribution and transportation of organic micropollutants in water systems are influenced by the interaction between dissolved and suspended components.

Volatilisation of organics from water is dependant on factors such as an oxygen content, temperature. Groundwater passes through a filtrate medium (soil) , therefore is low in particulates It is not influenced by atmospheric parameters and as such easily retains organic compounds. A sampling programme must be designed which clearly sets out the objectives:

- the parameters of interest
- the numerical guidelines
- the frequency of analysis

Groundwater quality is subject to seasonal fluctuations and other random variations. The sampling programmme must be designed to allow for these variations thus providing a sample which is representative of the water quality in the whole system. Sampling conditions will vary depending on the parameters of interest. It is important for the samplers to consult with the laboratory as to the sample volume required, the type of container to be used, preservation requirements, transport conditions. The reliability of the analytical result is directly coupled to the uncertainties of the sampling process, or to sample storage, preservation or pre-treatment prior to analysis. The sampling step is the first and most essential step in the analysis.(Josefsson, B., 1981) One of the biggest problems with groundwater analysis is the lack of communication between the person who requires the analysis, the sampler and the analyst.

Because of the stringency of the water quality guidelines and the fact that many of the analytes will be present at low concentrations it is critical that sample containers are entirely free of contamination. With organic analytes glass vessels are the only appropriate sampling containers. These containers must be pre-treated with a non-ionic surfactant, rinsed with tap water, rinsed with distilled water and then heated in an oven at 105°C to drive off any volatiles still remaining. The caps for these containers should be made of polytetrafluroethene (PTFE), an inert substance, to reduce the risk of loss of analyte by adhesion to the cap. A major problem occurs where samples are taken in plastic containers which allow volatile organics to diffuse through and higher boiling point organics such as those in petroleum products to stick to the container causing loss of analyte of concern and errors in the true sample result. The sample container and the lines through which the sample will be drawn should also be rinsed a few times with the water being collected before filling. Groundwater samples should only be taken after the well has been pumped sufficiently to ensure that the sample is representative of the groundwater source. It may be necessary to pump the well at a specific rate which is characteristic of the drawdown of the well. The pumping rate and the drawdown must be recorded in these cases. The sample collected should contain the sample concentration of analytes when it arrives at the laboratory for analysis as it had when it was originally sampled.

Often sample preservation techniques are necessarily employed. Microbial action, by a process called weathering can reduce petroleum hydrocarbon concentration significantly over a period of time. The shortest time between sampling and analysis is the most accurate way of obtaining a reliable result. Refrigerating the sample at 4°C is one of the best methods of short term preservation. Bellar and Lichtenberg (Bellar et. al., 1985) describe rapid biodegradation of aromatic compounds e.g., benzene, toluene and xylene in the VOC vials with PTFE seals even at low temperatures. They also describe conversion of pentachloroethene to terchloroethene. There is no single effective preservative. The best practice is to maintain the sample at 4°C and analyse it as immediately. VOC's should be analysed within 14 days of collection Absence of light can also be effective in (a) reducing microbial action and (b) reducing decomposition of light sensitive compounds such as polycyclic aromatic hydrocarbons (PAH's).

It is very important to record all conditions when taking a sample. A guide to taking water samples for organic analysis is given in Table 13.

Table 13 - Sampling Guide for Organics

Parameter	Type of Vessel	Sample Volume	Sample Preservation	Analysis Time
VOC's	Glass Vial with P.T.F.E. lined cap	50 mls	Maintain @ 4°C	Analyse within 14 days
TPH's	Glass Bottle	1 litre	Maintain @ 4° C and add 1ml of conc. acid ASAP.	Analyse within 1 month
Pesticides OCP's OPP's & PCB's	Glass bottle with P.T.F.E lined cap	2 litres (for low detection limits)	Maintain @ 4°C	Analyse within 7 days
PAH's	Amber glass bottle with P.T.F.E lined cap	1 litre	Maintain @ 4°C	Analyse within 14 days
Phenols	Polythene or glass bottle	1 litre	Maintain @ 4°C. Add 1ml of conc. acid	Analyse within 28 days

3.4 Pollution Control Approaches

A Multidisciplinary approach to groundwater pollution control is a practical option. This considers pollutant discharge, sources and control costs, pollutant dispersal and reaction in the waterway, damage reduction and the benefits of cleaner groundwater. Directive 80/68/EC itself states that provisions for discharges of List 1 compounds into groundwater can be made if the groundwater is not fit for use.

Rigid regulatory approaches often fail to yield the cleaner water it should and costs more than necessary for what it has achieved. Policy performance can be improved by

(1) remembering that water quality and not effluent purity should be the policy goal, and

(2) flexibility of approach is essential in order to exploit the advantages of various ways of producing the desired quality of water.

Gains can be realised through increased flexibility in meeting fixed water quality standards and by adopting a system of variable effluent standards. Further gains are possible through increased flexibility in setting water quality standards by balancing the advantages and disadvantages of pursuing ‘cleaner’ water. The most compelling reason for not pursuing pure water everywhere is that often the costs are prohibitive.

Point versus Non-Point Pollution Control Strategies if used effectively can help in maintaining the integrity of groundwater sources. The relative costs and water quality effects of controlling point and non-point sources of water pollution are important issues in environmental policy. The particular end use of an aquifer and the quality of water in the aquifer should both be considered in assessing the type and quantity of discharges to aquifers. EC directive 80/68 states that direct discharges of List I substances into an aquifer may be permitted providing that the groundwater is not fit for any other use. In the past point sources, particularly municipal wastewater treatment plants have been prime targets of control for environmental authorities. Since point sources of water pollutants are limited in number, regularly monitored and treatment methods are well-developed point source control is relatively easy to implement. In contrast non-point sources fall under numerous jurisdiction s. Because of the intermittent nature of pollution due to non-point sources and the large land area that may be involved it is often difficult to determine the quantity of pollutants from a particular source. Land-spreading of pesticides is one example of a non-point source where the risk of contamination could be dramatically reduced by following some application guidelines. The concentrations of pesticides applied must be strictly regulated and the times for application maybe should be restricted e.g., when heavy rains are forecast then application should be prohibited. Most water pollution from agriculture could be prevented by appropriate and effective managerial action such as when to spray pesticides, dealing with wastes, repair and maintenance containers. It is essential that regular monitoring of the groundwater in these potential problem areas is carried out. Another important factor might be to educate the users of these products of their hazards and to train them in the optimum usage and application of the chemical in question. The wide usage of trichloroethene and other chlorinated hydrocarbons makes it difficult to identify the pollution source. Solvents can cause be a major source of non-point pollution, mainly due to leakages from piping and storage systems in bad states of repair. Monitoring is often restricted to infrequent sampling and analysis of the groundwater. There is a need for a more comprehensive system to measure the impact of a factor on the groundwater quality so as to prevent or reduce contamination. Quality control on a system is very important. Frequent inspection of tanks, pipelines, connections is required with proper maintenance and repair facilities to reduce fugitive emissions thus contamination. The lifespan of most underground storage tanks is 20 years (Dynes, K., 1995) , many of the tanks in this country are at or beyond that limit without any thought to their condition. It is vital to conserving our resources that the proper maintenance and usage conditions be upheld on all storage and piping facilities in accordance with manufacturers recommendations.

Groundwater monitoring schemes - There are several groundwater monitoring schemes already in operation in the country e.g., the EPA scheme for assessing the state of the environment as required under EEC/76/464. Numerous samples are being taken but minimal analysis is carried out on the samples. The EPA scheme above samples 300 wells on a twice yearly basis, the analysis carried out is for major ions and only. These schemes provide opportunities to assess our groundwater for a wide range of parameters giving a comprehensive picture of the quality of Irish groundwater. Cost is a prohibitive factor in the number of parameters which are analysed but background information on a full suite of chemical and physical parameters e.g., organics, inorganics, metals, should be available on all major wells, especially those providing a potable water source. Regular sampling afterwards could lead to detection of contamination incident before it becomes a major problem.

A fee system for effluent discharges is a preventative measure against pollution. Effluent fees could be graded so that discharge fees become cheaper as pollution abatement techniques get more advanced. West Germany has a nation-wide effluent charge (Abwasserabgabenegaestz) based on an effluent indicator.

From the literature it can be seen that the problem with the groundwater pollution from underground and above ground fuel tanks was caused by both careless handling as well as a bad state of repair of the tanks. In the Netherlands gasoline stations must comply with strict regulations as regards soil protection, air pollution and safety. These requirements stipulate a soil investigation and if necessary remediation of the polluted site (at the owners expense) (Viveen. et. al., 1993). This would go a long way towards reducing groundwater pollution as the source of the pollution is removed.

Discussion and Conclusions

Groundwater is generally less prone to pollution than surface water as it has the natural protection of the overlying layers of soil to help attenuate pollutants. Irish aquifers are however vulnerable to pollution because of their mostly unconfined nature, the thin subsoil's, their shallowness and predominantly fissure flow. Despite this the quality of Irish groundwater is in the main of a high quality.

From a review of the data available it can been seen that trace organic contamination from agricultural sources is minimal. There have been a few pollution incidents but these seem to be of a short term nature, possibly due to weather conditions such as heavy rains. The main pesticides of concern would be the triazine herbicides due to their increased usage for pre-emergent weed control on motorways borders. While pesticides are not at present a problem our increasing usage and growing reliance on them is a cause for concern. Trends are towards intensive agriculture and the growing use of pesticides can only lead to an increase in pollution incidents. Strict controls must be laid out for the application of pesticides as with other areas of farm activities e.g. farmers must leave at least 150 metres between a well and the farmyard with animal waste, rules are set out for application of sewage sludges to land and a Code of Practise, prepared by the Department of the Environment is available for protection of waters from pollution against nitrates - this details times and methods of spreading organic and inorganic fertilisers. Similar procedures should be available for application of pesticides to vulnerable aquifer systems to prevent or reduce the risk to groundwater.

Landfill sites are a cause for concern, they were traditionally a place where waste was dumped regardless of the type of waste or the protection the land had to offer against groundwater pollution. Some wells have already been subject to contamination the main parameters determined being ; trichlorobenzenes, benzene, toluene, ethyl benzene and xylenes, naphthalene, trimethylbenzenes, butyl benzenes, trichloroethene and tetrachloroethene. Under the new Landfill Directive, new landfill sites must be designed to a high level of safety, with a provision for problems such as leachate production (leachate must be contained on the site). The containment of the leachate can be natural, where the geological strata underlying the landfill is of low permeability and adequate thickness to retain the leachate, or a synthetic liner (usually high density polyethene - HDPE) can be used or a combination of both. Ireland does not contain many areas of sufficient low permeability and required thickness of soil and bedrock so liners are required. It is generally accepted however that all liners eventually leak therefore a combination of liner and low permeability soil reduces risk of pollution. Another recommendation is that landfills should not be located on major or regionally important aquifers unless they are confined. Regular monitoring of the groundwater is also essential as it can serve as an early warning sign of a pollution problem. Under the Waste Management Act, 1996, stricter controls are being imposed on the classes of wastes which can be dumped in certain landfill sites depending on the degree of protection they afford the underlying soil and groundwater. Industry is now subject to stricter controls but domestic refuse is still a cause for concern with many household products being of a hazardous nature - control on the dumping of household waste is very difficult. An increased awareness of the potential dangers of household hazardous waste (HHW) is essential, and a national Programme of information on the risks to the environment from HHW might encourage a reduction in the volume of waste discarded thus reducing the risk of contamination of our soil and groundwater. In this current climate of sustainable development and waste minimisation and recycling the ideas of maintaining a high standard of environmental protection should be foremost. It is vital that the ideas of sustaining our environment is encouraged and promoted from a government level right down to the general public.

Industry can have a marked effect on the contamination of Irish aquifers. The industrial problems tend to be due to careless handling or lack of maintenance of facilities but are marked in that when an incident occurs it is generally a severe contamination problem. This can leave the well unfit for many uses due to excessive cleanup costs. The contamination incident at Nenagh, Co. Tipperary is one such example. The town supply was contaminated with 1,1,1-trichloroethane from nearby industrial estate leaving the town without a potable water supply. This incident could have been prevented by routine preventative maintenance of supply lines and piping and storage facilities. Lack of attention to maintenance can have disastrous consequences. The onus must be on the user/owner of a facility to make sure that all facilities are in good working order so as to ensure that no other situations like the Nenagh disaster happens again - once the pollution occurs the remedial action is often too expensive to be practical therefore pollution prevention is the goal. The industrial solvents which appear to be the most likely to cause pollution are ; the chlorinated solvents, 1,1,1-Trichloroethane, trichloroethene, tetrachloroethene, chloroform, dichloromethane, and the aromatics, toluene and xylene.

As already stated the main pollutants in Irish groundwater are oil and petroleum products, mainly leakages from storage vessels. Most underground storage tanks have a lifespan of only 20 years before requiring replacement. Routine checking and maintenance is also required on the tanks throughout their life to ensure troublefree usage periods. Periodic monitoring of groundwater resources close to petrol retail stations might be advantageous as early warning systems for potential problems. The owners of petrol stations are required by law to maintain a log on the level of petroleum products in their tanks on a daily basis. This should correlate with the volume of product sold. Any discrepancies between the two are an indication of leakage from the tank. A more vigilant check on the log books from such activities is essential, perhaps checking by the local authority on a regular basis e.g. monthly or quarterly. The main indicators of petrol contamination are the organic compounds benzene, toluene, ethyl benzene, xylene (BTEX) and naphthalene. Petroleum products can be very persistent in aquifers. Because the petroleum distillate is not exposed to the atmosphere as much as in surface waters the weathering process is not as advanced and not much breakdown of the product occurs in the unsaturated zone. Road drainage and runoff from petrol forecourts are other serious risks to our groundwater from petroleum products. All forecourts should be bunded and have drains running to a bunded area. This risk should also be carefully assessed when designing and planning new motorways and roads. Not only do petroleum products make the water unpalatable and odorous but they contain certain compounds which are themselves dangerous to human health such as benzene, toluene, xylene and naphthalene to name a few. The petroleum products are also detectable by smell and taste at levels below which they can be detected by routine analysis. It is critical to monitor for petroleum hydrocarbons as they are such a frequent cause of pollution and are so commonly used in today's society. It is important to point out that compounds may be falsely identified as petroleum hydrocarbons if a total petroleum hydrocarbon (TPH) value is calculated in an analytical result. Plasticisers from sampling vessels, and natural humic and fulvic acids may be present as well as phthalates which seem to be ubiquitous in environmental samples. These can all lead to high results. It is essential to correctly identify the compounds found as indicative of petroleum hydrocarbons to ensure that costly remedial work not carried out unnecessarily.

Polychlorinated biphenyl compounds (PCB's) which are a problem in many developed countries are not a major threat to the quality of groundwater in Ireland. The Electricity Supply Board (ESB), the main user of PCB containing transformer oil has a policy of recycling the oil as opposed to dumping the waste oil in landfill sites.

Aquifer Protection Policies which are in place in many counties play a major part in reducing and preventing contamination of groundwater. These plans which are based on the aquifer potential and the groundwater vulnerability to create groundwater protection zones are a very realistic approach to groundwater protection. They allow for certain discharges to aquifers depending on the pollution loading and the capability of the aquifer to attenuate the pollution. Following the pollution incident in Nenagh, Co. Tipperary in 1996, the Minister for the Environment, Mr. Brendan Howlin issued circular letters to all local authorities advising them that they should review their action plans for protecting drinking water supplies and responding to pollution incidents, including carrying out risk assessments on all groundwater sources used for public supplies as recommended by the EPA. The drawback of most aquifer protection policies is that they use electrical conductivity as a measure of the vulnerability of the groundwater and frequently do not monitor for any organic parameters. Routine monitoring for organic contaminants in groundwater should play a very important role in environmental monitoring and evaluation.

Many deficiencies exist with regard to the quality of Irish groundwater from the limited range of aquifers assessed, the frequency of measurements and the range of analytes assessed. Trace organic contamination is occurring, the major problems being caused with aquifers in areas associated with the petroleum industry. More vigilant monitoring of groundwater in these areas could result in a reduction of serious contamination incidents. Despite these deficiencies an review of the information on Irish groundwater would suggest that in the most part the water is of a high quality.

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Appendix 1

EEC/76/464 - Annex

List I of families and groups of substances

List I contains certain individual substances which belong to the families and groups of substances selected mainly on the basis of their toxicity, persistence and bioaccumulation, with the exception of those which are considered biologically harmless or which are rapidly converted into substances which are biologically harmless :

1. Organohalogen compounds and substances which may form such compounds in the aquatic environment,
2. Organophosphorus compounds,
3. Organotin compounds,
4. Substances in respect of which it has been proved that they possess carcinogenic, properties in or via the aquatic environment[1],
5. Mercury and its compounds,
6. Cadmium and its compounds,
7. Persistent mineral oils and hydrocarbons of petroleum origin, and for the purposes of implementing Articles 2, 8, 9 and 14 of this Directive :
8. Persistent synthetic substances which may float, remain in suspension or sink and which may interfere with any use of the waters.

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[1] Where certain substances in List II are carcinogenic, they are included in category 4 of this list.

List II of Families and Groups of Substances

List II contains :

- substances belonging to the families and groups of substances inList I for which the limit values referred to in Article 6 of the Directive have not been determined.
- Certain individual substances and categories of substances belonging to the families and groups of substances listed below.

And which have a deleterious effect on the aquatic environment, which can, however, be confined to a given area and which depend on the characteristics and location of the water into which they are discharged

Families and groups of substances referred to in the second indent

1. The following metalloids and metals and their compounds :
   1. Zinc
   2. Copper
   3. Nickel
   4. Chrome
   5. Lead
   6. Selenium
   7. Arsenic
   8. Antimony
   9. Molybdenum
   10. Titanium
   11. Tin
   12. Barium
   13. Beryllium
   14. Boron
   15. Uranium
   16. Vanadium
   17. Cobalt
   18. Thallium
   19. Tellurium
   20. Silver

2. Biocides and their derivatives not appearing in List I.

3. Substances which have a deleterious effect on the taste and/or smell of the products for human consumption derived from the aquatic environment, and compounds liable to give rise to such substances in water.

4. Toxic or persistent organic compounds of silicon, and substances which may cause the formation of such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances.

5. Inorganic compounds of phosphorus and elemental phosphorus.

6. Fluorides.

7. Ammonia and Nitrites.

Appendix 2

List of substances which could belong to List I of Council Directive 76/464/EEC

1. Aldrin
2. 2-Amino-4-chlorophenol
3. Anthracene
4. Arsenic and its mineral compounds
5. Azinphos-ethyl
6. Azinphos-methyl
7. Benzene
8. Benzidine
9. Benzyl chloride (Alpha-chlorotoluene)
10. Benzylindine chloride (Alpha, alpha-dichlorotoluene)
11. Biphenyl
12. Cadmium and its compounds
13. Carbon tetrachloride
14. Chloral hydrate
15. Chlordane
16. Chloroacetic acid
17. 2-Chloroaniline
18. 3-Chloroaniline
19. 4-Chloroaniline
20. Chlorobenzene
21. 1-Chloro-2,4-dinitrobenzene
22. 2-Chloroethanol
23. Chloroform
24. 4-Chloro-3-methylphenol
25. 1-Chloronaphthalene
26. Chloronaphthalenes (technical mixture)
27. 4-Chloro-2-nitroaniline
28. 1-Chloro-2-nitrobenzene
29. 1-Chloro-3-nitrobenzene
30. 1-Chloro-4-nitrobenzene
31. 4-Chloro-2-nitrotoluene
32. Chloronitrotoluenes (other than 4-Chloro-2-nitrotoluene)
33. 2-Chlorophenol
34. 3-Chlorophenol
35. 4-Chlorophenol
36. Chloroprene (2-chlorobuta-1,3-diene)
37. 3-Chloropropene (Allyl chloride)
38. 2-Chlorotoluene
39. 3-Chlorotoluene
40. 4-Chlorotoluene
41. 2-Chloro-p-toluidine
42. Chlorotoluidines (other than 2-Chloro-p-toluidine)
43. Coumaphos
44. Cyanuric chloride (2,4,5-Trichloro-1,3,5-triazine)
45. 2,4-D (including 2,4-D salts and 2,4-D esters)

46. DDT (including metabolites DDE and DDD)
47. Demeton (including Demeton-o, Demeton-s, Demeton-s-methyl, and Demeton-s-methyl-sulphone)
48. 1,2-Dibromethane
49. Dibutyltin dichloride
50. Dibutyltin oxide
51. Dibutyltin salts (other than Dibutyltin dichloride and Dibutyltin oxide)
52. Dichloroanilines
53. 1,2-Dichlorobenzene
54. 1,3-Dichlorobenzene
55. 1,4-Dichlorobenzene
56. Dichlorobenzidines
57. Dichlorodiisopropyl ether
58. 1,1-Dichloroethane
59. 1,2-Dichloroethane
60. 1,1-Dichloroethylene (Vinylidene chloride)
61. 1,2-Dichloroethylene
62. Dichloromethane
63. Dichloronitrobenzenes
64. 2,4-Dichlorophenol
65. 1,2-Dichloropropane
66. 1,3-Dichloroprop-2-ol
67. 1,3-Dichloropropene
68. 2,3-Dichloropropene
69. Dichlorprop
70. Dichlorvos
71. Dieldrin
72. Diethylamine
73. Dimethoate
74. Dimethylamine
75. Disulfoton
76. Endosulfan
77. Endrin
78. Epichlorohydrin
79. Ethylbenzene
80. Fenitrothion
81. Fenthion
82. Heptachlor (including Heptachlor epoxide)
83. Hexachlorobenzene
84. Hexachlorobutadiene
85. Hexachlorocyclohexane (including all isomers and Lindane)
86. Hexachloroethane
87. Isopropylbenzene
88. Linuron
89. Malathion
90. MCPA
91. Mecoprop
92. Mercury and its compounds
93. Methamidophos
94. Mevinphos
95. Monolinuron
96. Naphthalene

97. Omethoate
98. Oxydemeton-methyl
99. PAH (with special reference to : 3,4-Benzopyrene and 3,4-Benzofluoranthene)
100. Parathion (including Parathion-methyl)
101. PCB (including PCT)
102. Pentachlorophenol
103. Phoxim
104. Propanil
105. Pyrazon
106. Simazine
107. 2,4,5-T (including 2,4,5-T salts and 2,4,5-T esters)
108. Tetrabutyltin
109. 1,2,4,5-Tetrachlorobenzene
110. 1,1,2,2-Tetrachloroethane
111. Tetrachloroethylene
112. Toluene
113. Triazophos
114. Tributyl phosphate
115. Tributyltin oxide
116. Trichlorfon
117. Trichlorobenzene (technical mixture)
118. 1,2,4-Trichlorobenzene
119. 1,1,1-Trichloroethane
120. 1,1,2-Trichloroethane
121. Trichloroethylene
122. Trichlorophenols
123. 1,1,2-Trichlorotrifluoroethane
124. Trifluralin
125. Triphenyltin acetate (Fentin acetate)
126. Triphenyltin chloride (Fentin chloride)
127. Triphenyltin hydroxide (Fentin hydroxide)
128. Vinyl chloride (Chloroethylene)
129. Xylenes (technical mixture of isomers)
130. Compound not yet fully accepted.
131. Atrazine
132. Bentazone

Appendix 3

EEC/80/68

List I of families and groups of substances

List I contains the individual substances which belong to the families and groups of substances enumerated below, with the exception of those which are considered inappropriate to List I on the basis of a low risk of toxicity, persistence and bioaccumulation.

Such substances which with regard to toxicity, persistance and bioaccumulation are appropriate to List II are to be classed in List II.

1. Organohalogen compounds and substances which may form such compounds in the aquatic environment,
2. Organophosphorus compounds,
3. Organotin compounds,
4. Substances which possess carcinogenic, mutagenic or teratogenic properties in or via the aquatic environment[1],
5. Mercury and its compounds,
6. Cadmium and its compounds,
7. Mineral oils and hydrocarbons,
8. Cyanides.

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[1] Where certain substances in List II are carcinogenic, mutagenic or teratogenic, they are included in category 4 of this List.

List II of Families and Groups of Substances

List II contains the individual substances and the categories of substances belonging to the families and groups of substances listed below which could have a harmful effect on groundwater.

1. The following metalloids and metals and their compounds :
   1. Zinc
   2. Copper
   3. Nickel
   4. Chrome
   5. Lead
   6. Selenium
   7. Arsenic
   8. Antimony
   9. Molybdenum
   10. Titanium
   11. Tin
   12. Barium
   13. Beryllium
   14. Boron
   15. Uranium
   16. Vanadium
   17. Cobalt
   18. Thallium
   19. Tellurium
   20. Silver

2. Biocides and their derivatives not appearing in List I.

3. Substances which have a deleterious effect on the taste and/or odour of groundwater, and compounds liable to cause the formation of such substances in such water and to render it unfit for human consumption.

4. Toxic or persistent organic compounds of silicon, and substances which may cause the formation of such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances.

5. Inorganic compounds of phosphorus and elemental phosphorus.

6. Fluorides.

7. Ammonia and Nitrites.

Appendix 4

S.I No. 271 of 1992
First Schedule

Harmful substances

Individual substances which belong to the families and groups of substances : -

1. Organohalogen compounds and substances which may form such compounds in the aquatic environment,
2. Organophosphorus compounds,
3. Organotin compounds,
4. Substances which possess carcinogenic, mutagenic or teratogenic properties in or via the aquatic environment, including substances in the Second Schedule which possess such properties in or via the aquatic environment.
5. Mercury and its compounds,
6. Cadmium and its compounds,
7. Mineral oils and hydrocarbons,
8. Cyanides.

Second Schedule

Harmful Substances

Individual substances and the categories of substances belonging to the families and groups of substances : -

1. The following metalloids and metals and their compounds :
    1. Zinc
    2. Copper
    3. Nickel
    4. Chrome
    5. Lead
    6. Selenium
    7. Arsenic
    8. Antimony
    9. Molybdenum
    10. Titanium
    11. Tin
    12. Barium
    13. Beryllium
    14. Boron
    15. Uranium
    16. Vanadium
    17. Cobalt
    18. Thallium
    19. Tellurium
    20. Silver
2. Biocides and their derivatives not appearing in List I.
3. Substances which have a deleterious effect on the taste and/or odour of groundwater, and compounds liable to cause the formation of such substances in such water and to render it unfit for human consumption.
4. Toxic or persistent organic compounds of silicon, and substances which may cause the formation of such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances.
5. Inorganic compounds of phosphorus and elemental phosphorus.
6. Fluorides.
7. Ammonia and Nitrites.