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Further Characterisation/
Programmes of Measures

**Risk to Groundwater from Diffuse Mobile
Organics**

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Acronyms

BGS - British Geological Survey

CSO - Central Statistics Office

DAF - Department of Agriculture and Food

DCC - Dublin City Council

DED - District Electoral Division

DEFRA - Department of Food and Rural Affairs

DEHLG - Department of Environment Heritage & Local Government

DMO - Diffuse Mobile Organics

EA - Environment Agency (England and Wales)

EHS - Environment & Heritage Service (Northern Ireland)

EPA - Environmental Protection Agency (Ireland)

ERBD - Eastern River Basin District

FIPS - Forestry Inventory and Planning System

Foc - Fraction of Organic Carbon

FOCUS - Forum for Coordination of Pesticide Fate Models and Their Usage

GIS - Geographic Information System

GQS - Good Qualitative Status

GSI - Geological Survey of Ireland

GUS - Groundwater Ubiquity Score

GWB - Groundwater Body

IFS - Irish Forestry Service

K_{oc} - Partitioning Coefficient (normalised for organic carbon content)

NDSP - National Dangerous Substances Programme

NI - Northern Ireland

NRA - National Roads Authority

Acronyms (cont.)

NWGG - National Working Group on Groundwater (Ireland)

PAH - Polycyclic Aromatic Hydrocarbons

PCS - Pesticide Control Service

POM - Programme of Measures

PPA - Poorly Productive Aquifer

ROI - Republic of Ireland

SNIFFER - Scotland and Northern Ireland Forum for Environmental Research

SOC - Soil Organic Carbon

UK - United Kingdom

US - United States

USGS - United States Geological Survey

WFD - Water Framework Directive

EXECUTIVE SUMMARY

A revised national assessment of risk to groundwater from diffuse mobile organics (DMOs) has been carried out in the Irish hydrogeological context. The original Article V risk assessment that was submitted by the Environmental Protection Agency (EPA) to the European Commission (EC) in March 2005 was limited by the availability of pressure information and understanding of environmental fate and transport characteristics of DMOs. The Eastern River Basin District (ERBD) project was subsequently commissioned by Dublin City Council (DCC), on behalf of the Department of Environment, Heritage and Local Government (DEHLG), to study risk to groundwater in greater detail, with the intent of informing future monitoring needs and a Programme of Measures required by the European Union (EU) Water Framework Directive (WFD).

The basic objectives and tasks of the study were to:

- Improve the understanding of pesticide-related pressures;
- Research fate and transport characteristics of commonly used pesticides;
- In the absence of groundwater monitoring data, develop and implement a risk assessment methodology that captures both the pressure information and incorporates relevant physical factors that control leaching of pesticides from soil to groundwater.

For the purposes of the revised risk assessment, DMOs are broadly defined as pesticides. Pesticides are used in a wide array of settings, including agriculture, forestry, transportation, (urban) amenity, and industry. Detailed survey records of pesticide usage in the agriculture and forestry were obtained with the assistance of the Pesticide Control Service (PCS) and Coillte, respectively. Estimates for other sectors, including usage by local authorities, are less satisfactory, and rely on limited records, general literature, and information from interviews. Degrees and patterns of use by non-agricultural and non-forestry sectors therefore remain uncertain. Nonetheless, the available information suggests that the largest quantities of pesticides are used in the agricultural sector for pest and weed control.

Spatial mapping of pesticide usage is informed by land use activities and has been attempted in light of available records and GIS layers. The spatial resolution of mapping in the agricultural sector could be significantly improved with access to the GIS maintained by the DAF.

Systematic groundwater monitoring for pesticides has not been carried out in the past, but limited available datasets and experiences from other countries would suggest that pesticides can be expected to be detected at very low concentrations in a variety of physical settings (below the EU drinking water standard of 0.1 µg/L). Available datasets in Ireland are not sufficient to establish correlations between land uses and groundwater quality.

While pollution risk to groundwater is effectively a site-specific science, an assessment of relative risk at the national scale has been carried out by modeling

pesticide leaching for a range of physical scenarios found in Ireland, and linking the results back to the spatial distribution of the physical scenarios that were modeled. The fate and transport of pesticides in soil and groundwater is complex, requiring knowledge of how chemicals are applied (and disposed of), their chemical properties, and the physical factors that influence leaching, including rainfall, soil organic carbon content, and subsoil thickness and permeability. Many of these variables are known from existing databases and have been mapped across the country.

Results of modeling suggest the greatest risk of diffuse groundwater pollution is associated with:

- a) Pesticides that have the highest intrinsic mobility characteristics in the subsurface environment;
- b) Physical scenarios where relevant pressures (land uses) overlies areas of extreme to high groundwater vulnerability.

Pesticides with high intrinsic mobilities include triazine herbicides such as atrazine and simazine. Both (but mainly atrazine) were detected at low concentrations (<0.1 µg/L) in groundwater samples collected as part of the National Dangerous Substances Programme carried in 2006-2007. Atrazine and simazine were licensed in Ireland for use with forage maize (fodder crop) and forestry until December 2007 (but effectively banned from all sales in mid-2007 and from all use in December 2007).

Greater risk from diffuse sources would also apply where bypass flow influences vertical transport of pollutants through soils and subsoils. This cannot be mapped with certainty, and in the absence of field studies, areas where groundwater bodies are overlain by very thin soils (<1 m) are considered as surrogate indicators of bypass flow. These correspond roughly to groundwater vulnerability category "X" which has been mapped across the country by the Geological Survey of Ireland (GSI).

The fate and transport of pesticides in groundwater is subject to the properties and flow characteristics of the receiving groundwater body (aquifer). Upon reaching the groundwater table, leachates mix (dilute) with inflowing groundwater from upgradient areas, and subsequently flow in the direction of prevailing hydraulic gradients at rates which are proportional to the hydraulic properties of the aquifer.

Nearly two-thirds of Ireland is underlain by rocks that are designated as "poorly productive". These have limited storage and transmissive capacities. In this case, some of the infiltrating water (recharge) is rejected and discharges to nearby receptors (e.g. streams) via shallow flow mechanisms. Transport to streams via shallow pathways may be significantly faster than deeper groundwater pathways. Poorly productive aquifers therefore represent a particular hydrogeological situation where risk to surface water may be greater than risk to groundwater. Hydrogeological characteristics of poorly productive aquifers will be the subject of separate pilot studies by the EPA during early implementation of WFD-required monitoring in Ireland.

Recommendations on future programmes of measures broadly fall into these categories:

- Groundwater monitoring;
- Inventories/surveys of pesticide usage and applications in sectors other than agriculture and forestry;
- Spatial resolution of mapping of pesticide use;
- Fate and transport of pesticides in Irish soils – notably degradation rates for commonly used active ingredients, as well as influence of bypass flow.

Limited validation of study results is provided by sampling results from the National Dangerous Substances Programme as well as audit sampling by local authorities. However, existing data sets are insufficient and broader sampling efforts are needed. On the basis of land use patterns and distribution of physical scenarios across Ireland, groundwater sampling for validation purposes is recommended in the groundwater bodies shown in Figure ES-1.

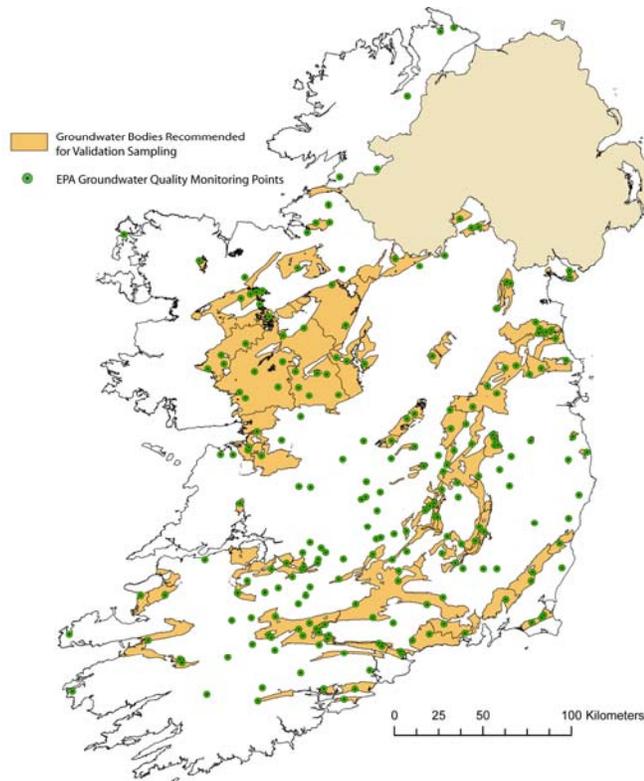


Figure ES-1: Groundwater Bodies Recommended for Validation Sampling and EPA's Monitoring Network

On the combined basis of this study and lessons learned from other countries, the EPA is carrying out a broad sweep of groundwater sampling during initial implementation of the WFD-required monitoring programme, which began in 2007. EPA is sampling the locations shown in Figure ES-1, which includes both

higher-risk and lower-risk settings. As results become available over the next two years, the monitoring programme may be appropriately scaled back.

While the revised assessment remains predictive, the study has contributed to an improved understanding of groundwater risk by: (a) developing estimates of the types and quantities of pesticides used, (b) mapping relevant sources (land uses), (c) quantifying fate and transport variables, (d) understanding which variables control pesticide leaching in the Irish context, (e) informing future monitoring activities, and (f) providing recommendations for future work that target areas of improvements.

1. Introduction

1.1 Background

In March 2005, the Environmental Protection Agency (EPA) submitted a national characterisation and analysis report on Ireland's river basin districts (RBDs) (EPA, 2005) to the European Commission (EC). The report included results of risk assessments to groundwater from diffuse and point source pressures, including diffuse mobile organics (DMOs), defined here as pesticides and polyaromatic hydrocarbons.

The reporting to the EC represented the first of many formal deliverables by the Irish government as part of its implementation of the European Union Water Framework Directive (WFD).

The DMO risk assessment was carried out at a river basin district level and results, summarised in **Figure 1**, suggested that pressures related to DMOs could pose a considerable risk to ground water at the national scale. Concerns about pesticides in groundwater mostly stem from their potential health impacts on drinking water and ecological receptors.

Importantly, the predictive risk assessment included a significant area of uncertainty, with 17% of groundwater bodies (GWBs) categorised as being "probably at risk" of failing to meet the WFD target of "good qualitative status" (GQS) by year 2015, and 18% of GWBs categorised as being "probably not at risk".

The specific criteria that were used for the DMO risk assessment were developed by the National Working Group on Groundwater (NWGG), and were based on a source-pathway-receptor model used for all Article V reporting (NWGG, 2005). In its review of the results, the NWGG concluded that the test methodology was probably overly conservative, resulting in a probable overestimate of the assessed risk. The methodology only considered the absence or presence of land use classes that would be indicative of pesticide use within a groundwater body. Actual DMO pressure information was not sufficiently available at the time, and the test did not take specific account of fate and transport characteristics that control leaching of DMOs in the subsurface. There were also no groundwater quality data available to verify the predictive risk assessment results. Pesticides have not been routinely monitored in the past.

Acknowledging these limitations, the Eastern River Basin District (ERBD) project was commissioned by Dublin City Council (DCC), on behalf of the Department of Environment, Heritage and Local Government (DEHLG), to study DMO risk to groundwater in more detail as part of the Further Characterisation phase of the WFD.

The DMO risk study is one of several similar studies that are being carried out by the various river basin district projects to better understand source-pathway-receptor issues and inform stakeholders on the subsequent selection of Programmes of Measures (POMs) and monitoring networks.

POMs are the primary mechanisms through which the objectives of the WFD will be achieved. POMs are to be implemented over successive 6-year River Basin Management Plan cycles, commencing in 2009, and will be reviewed periodically in concert with monitoring data. POMs will be designed both to improve polluted waters and to maintain good status waters according to environmental quality objectives (EQOs) and status classifications that are presently being developed by the EPA.

As part of this process, DMOs were originally defined as pesticides and polyaromatic hydrocarbons (PAHs). Following discussions with the project steering group, PAHs were deferred to the Urban Pressure Assessment project, also led by the Eastern River Basin District (ERBD) project. The DMO project therefore focuses exclusively on pesticides.

1.2 Objectives

The objectives of the revised DMO risk assessment are to:

- Summarise pesticide usage in Ireland by different sectors;
- Provide a preliminary and reasonable geographic representation of pesticide usage by sector;
- Develop a short-list of specific active ingredients, for groundwater monitoring purposes;
- Develop and implement a risk assessment methodology that captures both the pressure information and incorporates relevant physical factors that control leaching of DMOs through soils and the unsaturated zone.

To arrive at the stated objectives, a wide range of stakeholders was consulted at the project design, information collection and review stages.

Results of the DMO study have been examined jointly with the EPA to define suitable groundwater monitoring points for WFD purposes.

1.3 Steering Group

The project steering group consisted of the following organisations and individuals:

- EPA – Mr. Donal Daly, Chairperson;
- EPA – Mr. Matthew Craig;
- Pesticide Control Service (PCS) – Dr. Kenneth Conroy;
- Coillte – Mr. Micheal Keane;
- DCC and ERBD project coordinator – Mr. Ray Earle
- DCC – Ms. Imelda Avrill
- Trinity College, Dublin – Dr. Paul Johnston

Teagasc was invited on the steering group on several occasions.

The steering group had the added benefit of contacts with the British Geological Survey who presented groundwater pesticide experiences from England and Wales, and assisted in the review of this report.

1.4 Data Sources

Primary sources of data and information include:

- Pesticide Control Service of the Department of Agriculture and Food;
- The Area Aid Unit of the Department of Agriculture and Food;
- Coillte;
- Department of Agriculture and Rural Development, Northern Ireland;
- Dublin City Council;
- Geological Survey of Ireland;
- Teagasc.

Relevant literature is referenced as appropriate.

1.5 Acknowledgement

The authors wish to acknowledge the valuable inputs from the individuals on, and institutions represented by, the steering group. The authors also wish to thank the Southeastern River Basin District project for providing access to groundwater quality data associated with the National Dangerous Substances Programme.

2. Approach and Methodology

The revised risk assessment involved the following steps:

- Researching types and quantities of pesticides used by different sectors;
- Developing a spatial understanding of pesticide usage;
- Researching chemical characteristics of commonly used active ingredients;
- Short-listing active ingredients for future groundwater monitoring;
- Researching fate and transport characteristics that control leaching of pesticides from soils to groundwater;
- Modeling the leaching potential of selected active ingredients for a variety of scenarios and input parameters;
- Assessing risk to groundwater based on linkages between modeled scenarios and physical settings around the country.

Finally, the revised risk assessment resulted in the development of recommendations for future groundwater monitoring.

2.1 Types and Quantities

Numerous institutions were contacted, and usage data are derived mainly from these sources:

- Agriculture - PCS;
- Forestry - IFS and Coillte;
- Transportation - relevant transportation agencies - National Roads Authority, Iarnród Eireann, Airport Authorities - as well as local authorities;
- Urban amenity - local authorities responsible for parkland maintenance;
- Golf courses - selection of individual golf courses;
- Industry - selection of individual industries and commercial firms.

Data from Northern Ireland and other countries have been used as surrogates where necessary and appropriate, where Irish data do not exist or could not be obtained.

2.2 Mapping

Mapping of land uses that involve pesticide applications is based on the following information sources:

- European Environment Agency CORINE land cover project – Year 2000 land use coverage for Ireland.
- Central Statistics Office (CSO) – Year 2003 agricultural census returns were obtained nationally, which summarise land use data on a district electoral division (DED) level.
- Irish Forestry Service (IFS) - The 1998 Forestry and Inventory and Planning System (FIPS) relates information regarding the presence and ownership of forested land. Of particular relevance is the distinction between types of forest, as well as private and state-ownership.

The CORINE 2000 dataset provides land use data based on digitised aerial mapping to a 100m scale/resolution. CORINE has incremental layers which provide successively greater resolution of certain land use classes, but not to the extent that would allow for important differentiations in the agricultural sector, notably crop types or cropping patterns. This type of differentiation would be very useful in assessing spatial patterns of pesticide usage, since different pesticides are applied to different crop types.

The agricultural census data from 2003 represent statistical summaries of farm surveys by the DAF. The census data are collected every 4 years and provide data on crop types, quantities grown, livestock numbers, etc. The census returns are summarised and coded to the administrative boundaries of the DED.

The DAF maintains a very important GIS function, and access to this DAF mapping could significantly improve the spatial resolution of important pesticide-related land uses (notably, cropping patterns). While the project was able to obtain townland-based statistics of cropping patterns, it has not been possible to obtain DAF's associated land use coverages. It has therefore not been able possible to refine the mapping to the extent desirable.

2.3 Chemical Characteristics

Pesticides differ widely in their physico-chemical and biological characteristics and behave differently in the subsurface environment. Some chemicals are of greater concern than others, depending on their:

- Toxicity;
- Adsorption to soil and aquifer materials;
- Degradation rates.

Combined, adsorption and degradation determine the subsurface mobility of pesticides.

Adsorption indicates how strongly a chemical binds to the soil while degradation measures how long the chemical stays in its original form. A pesticide that does not adsorb to soil readily and has a slow degradation rate will have a higher potential for leaching to groundwater. Details on these processes are provided in Section 5.

The mobility of relevant active ingredients has been researched using the database of environmental information compiled by the EU-funded project FOOTPRINT (FOOTPRINT, 2006).

2.4 Short-list of Active Ingredients

A short-list of active ingredients was defined by combining usage data with chemical characteristics (notably, mobility). The short-list therefore identifies those active ingredients that would be expected to be detected in Irish groundwater, and is useful in guiding future groundwater monitoring efforts. The short-list includes active ingredients considered to be 'representative' of different land use classes and categories of chemicals, not just those that would in theory pose the greatest risk.

The short-list of active ingredients was subsequently checked against results from the National Dangerous Substances Programme (NDSP) which produced monthly pesticide data for four wells/springs in Ireland, as well as results from monitoring in the UK.

2.5 Fate and Transport

The fate and transport of pesticide migration in soils and groundwater is complex, requiring knowledge of how chemicals are applied (and disposed of), the timing of application, their chemical properties, and physical transport processes.

While pesticide leaching is a site-specific science, understanding the relative influences of important fate and transport characteristics are an important part of a risk assessment.

The major processes that determine the detections of pesticides in groundwater are well described in literature and are well understood. Mass flux from soils to groundwater involves many variables, including:

- Chemical properties - water solubility, adsorption/desorption (tendency to adhere to soil materials), and persistence (degradation).
- Soil properties - infiltration characteristics, pore size distribution, organic matter content, ion exchange capacity, hydraulic properties, soil moisture content, soil temperature, pH and oxygen status.
- Climatic factors - rainfall (rate, duration, intensity, timing), daylight and sunshine hours (photolysis).

Finally, the use of pesticides is closely related to cropping patterns. Vegetation provides uptake or assimilation in the root zone, thus reducing the quantities of pollutants available for transport to groundwater.

Pesticides are most commonly applied by spray, and can be lost to the atmosphere through volatilisation. Pesticides are also taken up by pests or crop plants, and can be degraded by microbial action and chemical reactions in the soil. They can also be transported via surface runoff or immobilised in soils through sorption

onto soil organic matter and clay minerals. A small portion of pesticides applied are also removed when crops are harvested.

Application factors that influence fate and transport include the timing, frequency, site, and amount of pesticide applied, as well as the formulation type (granules, powder or liquid) and application method.

Pesticides with higher persistence and weaker sorption properties are more readily leached, and therefore more likely to pollute groundwater. Without water to move pesticides through soils, pesticides are more likely to remain in soils (crop root zone). The physical factors that influence the movement of pesticides from soils to ground water are primarily those that control the movement of water.

Pesticide detections in ground water are considered to be more likely where groundwater vulnerability is highest, i.e., where overburden materials are thin and where permeable soils and subsoils are present. Pesticide contamination is also more likely in shallow groundwater than in deep groundwater, and where well screens are located close to the water table, however, such relations are not always true where preferential pathways exist or where vertical head gradients are significant.

2.5.1 Preferential Pathways

Preferential pathways can enhance transport of pesticides to groundwater. They are represented by macropores formed by fauna in the soil and root zones, inherent heterogeneity of subsoils, or by cracks and fractures resulting from geological processes (e.g., weathering). Poor well construction practices, and/or use of abandoned wells to dispose of waste products, can also serve to act as conduits of flow to deeper aquifers.

The role and potential impacts of preferential pathways in diffuse pollution cases are well described in the literature. A useful review of preferential pathways in the Irish context is provided by Daly (2002) who concludes that the potential for “bypass flow” would be particularly significant in areas where thickness of soils and subsoils are thin (<2 m). The groundwater vulnerability map of Ireland, reproduced in **Figure 2**, provides important clues as to where the likelihood for preferential pathways would be greatest. Areas of extreme vulnerability (categories X and E in **Figure 2**) include areas where rocks either outcrop at the surface (Category X) or are within 1 m of the ground surface (Category E), partly based on Teagasc subsoil maps (published in 2006) and partly based on recent mapping by individual river basin district projects. Additionally, the Irish Soil map of 1980 (Gardiner and Radford, 1980) provided lists of soil associations in which physical characteristics are “conducive to preferential flow”.

Although the likelihood of preferential pathways may be considered greater in extremely vulnerable areas, and areas where soils are disturbed (e.g., tillage), this does not preclude bypass flow from happening in other geological settings as well, even where thick tills and subsurface clays are present (e.g., east Meath, north Dublin, and Fingal). There are numerous case studies in the literature. Jørgensen et al (2005) describe preferential flow and pesticide transport in fractured, clay-rich tills, and Olsen (2005) reports leaching of glyphosate, a herbicide not considered to

be very mobile in the subsurface environment, via macropore flow at a monitoring site in Denmark.

2.6 Modeling

Unsaturated zone transport modeling was carried out to explore the leaching potential of important active ingredients under Irish conditions.

The combined lack of groundwater quality data and specific information on the spatial distribution of pesticide applications implies that objective criteria for defining risk to groundwater cannot be developed and that impact potential has to be assessed qualitatively until monitoring data become available. In the absence of groundwater quality data covering pesticides, modeling was deemed an appropriate alternative to understand the relative importance of physical and chemical variables that influence leaching, and to assess relative risk to groundwater at the national scale. A similar approach has been taken in Scotland and Northern Ireland (SNIFFER, 2006).

The revised risk methodology therefore included the use of a chemical fate and transport model to explore relative mass loading of selected active ingredients to groundwater for a set of representative physical scenarios. Model inputs and results were subsequently compared to the distribution of the physical scenarios across Ireland. Relative risks were determined based on the likelihood of mass loading.

Specific objectives of modeling were to:

- Evaluate the mass loading to groundwater using different combinations of physical settings (rainfall, surface and subsurface soil types, aquifer characteristics), chemicals, and land uses;
- Evaluate the relative importance of different input parameters (e.g., rainfall, soil types, chemical properties, etc.)

The results were used to study the potential spatial distribution of mass loading to groundwater, by linking model results to land use patterns and primary hydrogeological characteristics of different aquifer types across Ireland. These, in turn, have been used to select suitable groundwater monitoring locations as part of EPA's groundwater monitoring network for WFD purposes.

3. Pesticide Sources

3.1 Types and Quantities

The Pesticide Control Service (PCS) publishes and updates a list of plant protection products that may be placed on the market and used in accordance with the European Communities (Authorisation, Placing on the Market, Use and Control of Plant Protection Products) Regulations 2003. An annual report outlines applicable legislation and statutory provisions for use, sales, and marketing. The most recent publication available is dated February 2007 (PCS, 2007a).

Table 1 summarises the main activities associated with pesticide usage. Pesticides are commonly classified according to their intended target organism and their intended use - insecticides, herbicides, fungicides, growth regulators, seed treatments, nematicides, molluscicides, etc.).

3.1.1 Agriculture

Usage data for forage crops and grassland areas were obtained from the PCS for year 2003 (PCS, 2006). Usage data for arable crops were also obtained from the PCS for year 2004 (PCS, 2007b). These represent the first comprehensive national surveys of pesticide use associated with plant protection products in the ROI. The surveys are similar to those which have been carried in Northern Ireland and the rest of the UK in recent years, and are consistent with the European Commission report "Towards a Thematic Strategy on the Sustainable Use of Pesticides" (COM, 2002) which identified the need for detailed and up-to-date statistics on sales and use of pesticides at the EU level.

3.1.1.1 Grassland and Forage Crops

The PCS survey report on grassland and forage crops (PCS 2006) covers 6 main crop types:

- Grassland
- Arable silage
- Forage maize
- Fodder beet
- Fodder turnips
- Fodder kale/rape

As shown in **Figure 3**, grassland accounts for almost 70% of the total land area sprayed, followed by arable silage (20%) and forage maize (12%). Grassland also accounts for over 80% of quantities of active ingredients applied in non-arable agriculture, followed by arable silage (8%) and forage maize (7%). The breakdown of pesticide types by group and weight of active ingredient indicates that herbicides dominate. Herbicides account for 94% of the total pesticide usage, with fungicides (3%) and growth regulators (2%) representing the next largest usage classes.

Quantities of active ingredients reported in grassland and fodder production are summarised and ranked (by weight applied) in **Tables 2 and 3**, respectively. A total of 85 active ingredients were reported in the PCS grassland and fodder crops survey. MCPA alone accounted for 39% of the weight of all active ingredients applied. The nine most commonly used active ingredients were all herbicides and together accounted for 88% of the total weight of active ingredients. Atrazine, a herbicide that was used only in maize, was the fourth most commonly used active ingredient and represented 4% of the total weight of active ingredients applied.

On the basis of the totals in **Tables 2 and 3**, and hectares of crop grown, the highest total level of use (for all pesticides) by crop type was on maize (2.7 kg/ha), followed by fodder beet (2.0 kg/ha) and Swedes/turnip (1.8 kg/ha).

3.1.1.2 Arable Crops

The PCS survey report of arable crops (PCS 2007b) covers the following categories of crops:

- Cereals (winter and spring barley, wheat and oats)
- Potatoes
- Oilseed rape
- Peas
- Beans
- Sugar beet
- Lupins
- Set aside and non-food

As shown in **Figure 4**, cereals predominate, accounting for 79% of the total area of arable crops in the country, of which 42 % was spring barley and 18% was winter wheat.

All crop types received some herbicide treatment, with 100% of some crops such as winter wheat, peas, potatoes, linseed and sugar beet receiving herbicide treatment. Fungicides were applied to all crops except linseed and set-aside crops, with 100% of crops such as barley and winter wheat, potatoes, and peas receiving fungicide treatment. Use of growth regulators was mainly confined to cereal crops and non-food crops. Molluscicides were mostly limited to sugar beet and potatoes, while all crops types, except set-aside, received seed treatments.

Thus, pesticides are extensively used in arable farming. As shown in **Figure 4**, herbicides were used in the greatest quantities, representing 43.6% of the weight of active ingredients applied. Fungicides followed closely with 40.7% of the total weight of active ingredients applied.

In terms of area treated, fungicides were applied to the largest area (43.9%) followed by herbicides (27.6%), seed treatments (11.7%) and insecticides (11.1%). The latter two represent low levels of the weight of active ingredients applied, while molluscicides are used in very small quantities and on a small total area.

Spring barley and winter wheat combined accounted for over 60% of the treated area and over 50% of the weight of active ingredients applied. Potatoes accounted for 23.9% of the weight of active ingredients applied.

Tables 4 and 5 summarise and rank (by weight) total amounts of individual active ingredients used in arable crop production. A total of 128 active ingredients were reported in the PCS arable crops survey. Unlike grasslands and fodder crops, where herbicides are used in the greatest quantities, fungicides account for the greatest quantities applied on arable crops. The fungicides chlorothanil and mancozeb alone accounted for approximately 23% of the active ingredients applied (by weight).

On the basis of the totals in **Tables 4 and 5** and hectares of crop grown, the highest total level of use (for all pesticides) by crop type was on potatoes, at 27.5 kg/ha, followed by winter wheat (5.6 kg/ha) winter oats (4.1 kg/ha) and winter barley (3.7 kg/ha).

3.1.2 Forestry

The total forest estate in Ireland is just over 700,000ha or 10% of the land area. These forests are owned and managed either by the state company Coillte (56%) or by private owners (44%). Pesticide use in Irish forests is generally limited to the first 2-4 years of the life cycle of the forest where the main problem is in controlling vegetation on farmland sites. In addition, Coillte uses an insecticide on sites established after clearfelling (restock sites).

3.1.2.1 Coillte (State Forest)

Because private forestry only really began to gain importance here in the late 1980's, the age profile of forests managed by Coillte is generally older than private forests in Ireland. In recent years, most of the planting being carried out by Coillte is replanting of felled areas and the amount of farmland planting by Coillte has reduced considerably.

Pesticide use in Coillte is monitored closely and can be tracked down to individual land parcels (forest management units). In addition to following National legislation on pesticide use (through the Pesticide Control Service (PCS) of the Dept. of Agriculture and Food), Coillte is also regulated to more strict guidelines on pesticide use by its certifying body, the Forest Stewardship Council (FSC). Since 1998, Coillte's use of pesticide has reportedly dropped by 82 percent (in kg a.i./ha) (Coillte, pers. comm.). In terms of active ingredient, Coillte's use of pesticides is split almost 50/50 between herbicides and insecticides. Both are used in the establishment phase (within 2-4 years after planting), with the insecticides being used exclusively against the large pine weevil, an insect of restock sites.

Although Coillte would have 30-40,000ha in the "establishment phase" (i.e. plantations of four years old and younger) at any one time, the area on which

herbicides is applied in any one year is considerably less. Much of the vegetation control is carried out using non-pesticide methods and many sites (particularly in the uplands) do not require any vegetation control. **Figure 5** shows the actual amounts and relative proportions of pesticide use in Coillte for 2006. Four of these pesticides (alpha-cypermethrin, imazapyr, atrazine and propyzamide) will not be used after 2007.

3.1.2.2 Privately Operated

Because of the fragmented nature of private forest ownership in Ireland (average private plantation size is ~9ha), statistics on pesticide use are more difficult to estimate. In private forests, the split between conifers and broadleaves is approximately 70/30. The use of herbicides on these areas depends on site fertility, cultivation method used and tree species planted (e.g. a species like alder may not require any herbicide application because it grows so quickly in its early years whereas more slow growing species like oak may require 3-4 applications of herbicide). The total area of private forests currently in the “establishment phase” (i.e. planted between 2003-2006) is approximately 35,000ha.

The vast majority of private planting takes place on farmland sites (mostly on grassland) and many would, subsequently, require greater levels of vegetation control than upland restock sites. For the reasons mentioned above, it is difficult to get accurate estimates for herbicide use in private forests in this country. However, for the purpose of calculations, it is assumed that conifer crops receive one application and broadleaf crops receive three in the first four years of the rotation. Given these assumptions, glyphosate use in forests for 2006 is given in **Table 6**.

3.1.3 Transport

3.1.3.1 Roads

Pesticides applications along roads would be in the form of herbicides applied to verges and paths for weed control. The total length of the motorway and dual carriageway network across the country is approximately 600 km (NRA, 2006), while the total length of all national roads is approximately 5,400 km.

The NRA was contacted with regard to motorways and dual carriageways, and local authorities provided inputs on smaller roads. The NRA stated that they no longer have responsibility for maintenance of large roadways, and that this function now falls upon local authorities. The NRA produces guidance notes and procedural manuals regarding maintenance which strongly recommends against using pesticides, instead favouring a manual cutting programme.

Contact with both the NRA and a number of local authorities have yielded little or no quantitative information. Those road maintenance sections that were contacted responded that pesticides may be used occasionally but not systematically.

Table 7 summarises pesticide usage for roads obtained from DCC contractors, based on a road length of 1,090 km (about 96% of DCC roads). Roads within the DCC operational area cover a total estimated area of about 100 km², hence, the potential road density that receives pesticide application would be approximately 10 km/km².

It may be reasonable to assume that most local authorities would use similar chemicals as DCC, i.e., glyphosate and diuron. Without additional details from local authorities, it is not possible to estimate total quantities used on Irish roads. In the UK, it is reported that about 70% of major roads and 49% of minor roads receive pesticide treatment (DEFRA, 2005a).

In the UK, 80% of applications to impermeable areas, including roads, are in the form of glyphosate and diuron, commonly used in combination as a replacement chemical for atrazine and simazine which were both withdrawn for amenity use following documented groundwater pollution problems (DEFRA, 2005b).

The potential historical use of simazine and atrazine in roadway maintenance in Ireland cannot be ruled out.

Pesticides associated with road applications would enter groundwater via a variety of potential pathways, depending on how/where road verges are located in relation to road drainage features. Any pesticide applied to a hard-standing area would be prone to wash off. Where French drains or slotted kerbs exist, direct infiltration to groundwater is possible.

3.1.3.2 Rail

Iarnród Eireann makes yearly applications of glyphosate for weed control from a specially adapted train, but was unable to provide records of quantities used. The approximate national track length is 1,900 km. On the assumption that two-thirds of this is double line with an approximate treatable width of 10 metres, and one-third is single line with a treatable width of track of 6 metres, the total "treatable track" area is 1,642 hectares. At a recommended glyphosate use rate of 4 L/ha (of active ingredient), the estimated glyphosate quantities used annually is 6,567 litres of active ingredient, equivalent to 3.5 kg/km.

3.1.3.3 Airports

Dublin and Shannon airports were contacted to assess their weed and pest control operations. The Environmental Officer at Dublin airport reported that wide-scale application of pesticides is not common, and that physical cutting is used to prevent birds from feeding and nesting. Weed growth on runways, taxiways, and the apron areas are also not a problem due to sufficiently heavy traffic.

The only use of pesticide application at Dublin airport involves some spot applications in ornamental garden areas (which is reduced by the use of mulch). Routine monitoring of site surface drainage is carried out for pesticides, and the Environmental Officer reports no problems to date.

It is possible that smaller airports might use some pesticides, but this is unlikely to be a significant source in the larger context.

3.1.4 Urban Amenity

Urban footprints include land use types that are subject to pesticide applications, such as:

- Roadways

- Parklands
- Other managed open spaces (e.g., sports fields, residential lawns)

Roadways were covered in Section 3.1.3. In terms of parklands and managed open spaces, **Table 8** provides a listing of pesticides purchased by the DCC parks and landscape services section in 2004/2005. Glyphosate, diuron, simazine and dichlobenil are recurring active ingredients. The quantities listed represent those purchased, but not necessarily used.

Herbicides commonly used in domestic/residential settings include amitrole, glyphosate, paraquat/diquat, diuron, bromacil, imazapyr, ferrous sulphate, and glufosinate ammonium. Arguably the most commonly sold and used garden herbicide in Ireland is Roundup, which primarily contains glyphosate. Because of its recognised low mobility in the subsurface, glyphosate is increasingly applied as a pesticide of choice.

Without detailed sales or survey figures specifically targeted at the amenity and domestic markets, it is difficult to estimate potential quantities applied annually in Ireland.

Surveys in both the US and the UK indicate that a wide variety of pesticides are used in urban areas (USGS, 2007; DEFRA, 2005a). In the UK, herbicides (glyphosate, 2,4-D, MCPA, mecoprop, dicamba and triclopyr) generally account for 92% of all pesticides applied in the park and amenity sectors (DEFRA, 2005b).

In the US, more than 30 million kg of active ingredients are applied annually to lawns covering an estimated area of about 120,000 km², but pesticides are only regularly applied on about 50% of that area (CWP, 2000). While specific survey figures on domestic pesticide use exist in literature from urban pollution studies in the US, transposing these to Ireland is not deemed applicable: a) domestic use of agrochemicals in the US is more intensive, b) land use and development patterns are different, and c) climatic conditions are very different in many of the studied areas.

In France, a study of two semi-urban catchments near Paris indicated that 85% of all pesticides used were herbicides, and that 30% of the total was related to household usage (Blanchoud, 2004). Average annual herbicide application rates are reported as 0.9 kg per hectare (kg/ha) for road maintenance, 4 kg/ha for cemeteries, and 0.5-0.8 kg/ha for managed parklands and sports fields. The reporting does not differentiate between quantities of different herbicides, but concludes that more than 60 active ingredients were identified from surveys and sampling, and that diuron, sulfosate, glyphosate and 2,4-D are regarded as commonly used active ingredients. Overall, the French study suggested that approximately 15 kg/km² of total herbicides may be used annually by households (for lawn maintenance) in the two catchments studied (covering a total area of 154 km²).

3.1.5 Other

3.1.5.1 Commercial Facilities

Commercial facilities that store or use pesticides are garden centers and distribution centers. There are no central records available, and while some of the centres that were contacted indicated that pesticides are used, they would be expected to contribute small quantities overall.

3.1.5.2 Industry

A number of industries were approached (e.g., Roadstone), and all reported that they had no central or routine method of recording or quantifying pesticide use, and that procurement and treatment is addressed on a site-by-site basis by in-house maintenance staff.

It has not been possible to develop usable statistics from industrial facilities. Since most large-scale industrial facilities are located within or near urban fabrics, industrial pesticide usage is considered primarily an urban issue. Mapping of pesticide usage associated with individual industrial facilities, whether in urban or rural areas would require specialised surveys. Overall, such usage is expected to be a minor source compared to agriculture.

3.1.5.3 Service Organisations

Several organisations and utilities were contacted, including the Electrical Supply Board (ESB), Waterways Ireland, the Central Fisheries Board (CFB) and Office of Public Works (OPW). Records of usage or specific applications do not generally exist, but the CFB and Waterways Ireland report limited use of glyphosate and dichlobenil for weed control of aquatic plants (reeds) along canals.

3.1.5.4 Golf Courses

No relevant studies or estimates of pesticide usage on golf courses exist for Ireland. While it is not possible to estimate quantities with any level of certainty, some guidance may be offered by transposing results of UK surveys to the Irish context. Studies in the UK indicate that golf courses represent only about 2% of total pesticide use in the amenity sector (DEFRA, 2005). (Garthwaite, 1998) lists three main herbicide formulations; 2,4-D/dicamba, 2,4-D/mecoprop and fluroxypyr/mecoprop-P. In France, Blanchoud (2004) reports use of mecoprop, dichloroprop, 2,4-D and 2,4-MCPA on golf courses. In the UK, the Central Science Laboratory (CSL) estimates an average dose rate of 0.5 kg/ha of total active ingredient per application over the entirety of a golf course. This equates to a total of approximately 8,550 kg of active ingredient per year.

Table 9 lists the approved chemicals for use on golf courses in Ireland. Mecoprop-P, 2,4-D and dicamba are likely to be among the most commonly used herbicides on Irish courses, with chlorothalonil the most commonly used fungicide. Herbicide and fungicide usage would be highest on tees and greens, while insecticides (e.g., chlorpyrifos) may also be applied on greens to combat pests such as cutworm or leatherjackets.

There are an estimated 285 golf courses in Ireland, each with an average area of about 60 hectares. The estimated total "high use area" (greens, tees, fairways) is

approximately 4,600 ha. On an areal pro-rata basis, and assuming (from UK studies) that approximately 41% of active ingredient by weight consists of fungicides, 41% of herbicides, and insecticide making up the remaining 18%, a total of about 3,500 kg of herbicides and fungicides may be applied annually on golf courses in Ireland (or approximately 0.76 kg/ha for “high use areas”).

In the larger context, it would appear that golf courses represent a relatively minor input compared to other users, though localised impacts cannot be ruled out.

There are multiple references in literature on pesticide applications associated with golf courses, but studies of actual groundwater impacts are few, and tend to be focused on the US.

3.1.5.5 Sheep Dip

Pesticides and chemical substances such as xylene (a carrier product) are used in the sheep dip process, and numerous active ingredients are licensed for use. Sheep dip products are regulated by the Irish Medicines Board, and licensed active ingredients include cypermethrin, amitraz, and diazinon.

More than the application itself, waste disposal practices are of concern. In the UK, there are documented case studies where sheep dips act as point source of groundwater pollution. This has not been studied in the Irish context, but it would not be unreasonable to assume the same occurs in Ireland. Sheep dip waste products are also reportedly disposed of with slurry during seasonal landspreading.

EPA reports that sheep dip waste may be included in farm slurry that is land-spread as fertiliser material. Proper disposal of sheep dip waste is called for in the agricultural book of good farming practice (DAF, 2001).

Poor or illicit handling and disposal of pesticide products generally, through lack of care or unsuitable locations, can lead to both diffuse and point source pollution problems (e.g., Chilton et al, 2000).

3.2 Mapping

The primary land uses that involve pesticide applications and a summary of the estimated (recent) quantities applied are summarised in **Table 10**. The spatial distribution of relevant land uses are discussed below.

3.2.1 Agriculture

3.2.1.1 Grassland and Forage Crops

Grassland covers more than 50% of the total land area of Ireland. **Figure 6** shows the distribution of grassland that is silage, as percent of total grassland within a DED using the statistical information contained in the 2003 agricultural census. Overall, the total land area covered by silage is 27,217 km², or approximately 39% of the total land area of Ireland.

Site-specific mapping of pesticide applications associated with grasslands is not possible, but it is expected that they would be mostly connected with “managed” grasslands, used for animal fodder. CORINE 2000 offers a land use category for

“improved grassland”, but does not subdivide on the basis of grassland use (e.g., silage). As shown in **Figure 6**, there is a general agreement between improved grassland and DEDs with higher proportions of silage. The total land area covered by improved grasslands in year 2000 is 17,515 km², or approximately 24% of the total land area of Ireland.

Without access to the farm-level GIS maintained by the DAF, an improved spatial resolution of grassland is not possible.

The primary other animal fodder crop grown is maize, also referred to as “forage maize”. The 2003 agricultural census includes statistics on areas covered by forage maize at the DED-level, as shown in **Figure 7**. Unfortunately, the agricultural census data do not explicitly indicate where maize is grown within an individual DED.

The greatest density of maize production is in the east and southeast, although it is expanding to other areas, including the west. The Nanny catchment in particular appears to be the most intensely cultivated drainage area in Ireland. Maize is of particular interest as atrazine, a highly mobile active ingredient, was licensed for use on maize crops until the end of 2007. According to the PCS, all current registrations for products containing simazine or atrazine were revoked with effect from 30th June 2007. The current uses for both substances are under essential use criteria. The use-up period was until 31st December 2007. After these dates, the marketing, sale and/or use of any product containing either active ingredient will be illegal (PCS, 2006).

3.2.1.2 Arable Crops

Arable crops are mainly grown in the east and southeast, as shown in **Figure 8**. According to CORINE 2000, total arable land area in Ireland is approximately 5,500 km², compared to a total 36,589 km² of grassland.

Using the 2003 agricultural census data, a breakdown of dominant arable crop types has been attempted at the DED-level, as summarised in **Figure 9**. Cereals (spring and winter barley, wheat, oats) and root crops (potatoes and sugar beet) dominate. The bulk of cereal crops are grown in the east, southeast and south, while root crops are grown in the west and northwest. The dominance of cereal and root crops to the east and west respectively reflects climatic conditions.

Without access to the GIS maintained by the DAF, it is not possible to differentiate mapping between individual cereal and root crops in any given area.

3.2.1.3 Forestry

Mapping of forestry is based on the Forest Inventory and Planning System (FIPS), which is a GIS-based system operated by the IFS. The latest FIPS data available are from 1998, although a new dataset is expected to be published for 2006. This dataset is not yet available to the DMO study.

Figure 10 shows the 1998 FIPS coverage of total forestry and “young forestry”, on the basis that pesticide applications mainly apply to new and cleared plantations. On this basis, the estimated total land area where pesticides may be applied to

forestry is approximately 2,500 km². Although forestry occurs everywhere in Ireland, young forestry predominates in upland areas, (over 200 m above sea level).

As a comparison, the CORINE 2000 coverage identifies broadleaf forest, coniferous forest, and mixed forest, as shown in **Figure 10**.

3.2.1.4 Urban Amenity

The national urban coverage from CORINE 2000 is shown in **Figure 11**. As part of the national Urban Pressure Assessment POM project, built-up land uses have been refined and reclassified using county and city development plans for all towns and cities with population numbers greater than 10,000. Examples of the reclassification scheme are shown in **Figure 12**. For the 33 urban areas, the total land area associated with amenity spaces, or open managed land (e.g., parklands) is 132 km². This does not cover lawns in residential areas. On the assumption that 25% of residential land uses in urban areas are covered by lawns (and receive pesticide applications), the total estimated lawn area within the 33 largest towns is 370 km².

3.2.1.6 Other

Road, rail and airports are identified from OSI maps. It has not been possible to develop maps of industrial or commercial facilities that use pesticides.

3.2.1.7 Summary of Mapping

The spatial coverages of the most relevant sectors that consistently use pesticides have been mapped, and are considered adequate for risk assessment purposes. Additional resolution of cropping patterns in the agricultural sector would be helpful, as different pesticides are applied to different crop types. The farm-level GIS-coverage maintained by the DAF would add significant value to the mapping of agricultural areas, but is unavailable to this study. The mapping of potential agricultural usage is constrained by the resolution offered by CORINE 2000 and the DED-based agricultural census statistics. Forestry data are readily incorporated with FIPS for year 1998, and should be updated as new coverages are incorporated by the IFS.

4. Chemical Characteristics

4.1 Mobility

As described in Section 2, different chemicals have different chemical characteristics which determine the mobility of active ingredients. Mobility is primarily a function of adsorption and degradation.

4.1.1 Adsorption

Typically, as the water solubility of an active ingredient increases, adsorption of a pesticide in soil decreases, simply because water-soluble pesticides tend to stay in the soil solution. The soils organic carbon content can exert considerable influence whereby pesticide adsorption decreases as soil organic matter content decreases. In sandy soils or subsurface soils, pesticides tend to move more freely due to less adsorption. When sandy soil texture is coupled with a shallow groundwater table, risks for pesticides to contaminate groundwater are higher.

Adsorption is generally expressed as K_{oc} (mL/g or L/kg), also expressed as a soils sorption or partitioning coefficient (normalised for organic carbon content) which is empirically derived. The adsorption potential of a particular pesticide is proportional to its K_{oc} .

Adsorption coefficients can be influenced by the clay content of soils, and therefore show local variability. Clay fractions usually have higher organic carbon contents. Coquet et al (2004) demonstrated that adsorption coefficients normalised for clay content ranged between 1.6 and 17.6 litre per Kg for atrazine. Therefore, neglecting the adsorption properties of the vadose zone and relying exclusively on K_{oc} values to predict mobility may bias local risk assessments. At the local scale, information on the adsorption properties of soil/geological materials should be collected to improve the ability to predict pesticide concentrations in groundwater.

4.1.2 Degradation

Most pesticides are degraded relatively rapidly in the soil (within days to weeks) by chemical or microbiologically-mediated processes and often much more slowly below this in the subsurface (weeks or even years). Recently introduced herbicides in particular are designed to be as rapidly degraded in the soil as possible while maintaining sufficient herbicidal activity. Many older compounds can be much more persistent. Where the soil zone is bypassed, e.g. by soakaway drains, there may be little degradation before the subsurface is reached.

Soil and subsurface degradation is clearly a desirable process from the perspective of environmental safety. Persistence in soils and groundwater is inversely correlated with pesticide degradation rate. The persistence of pesticides in soil is measured by half-life ($DT_{1/2}$ or DT_{50}) - the time that it takes for a pesticide to decrease from its original concentration to half (50%) of the original concentration. The longer the half-life and persistence, the greater the likelihood a pesticide will reach groundwater.

4.1.3 Groundwater Ubiquity Score

The mobility of pesticides is frequently calculated and presented through a Groundwater Ubiquity Score (GUS) index (Gustafson, 1993), using the following equation:

$$\text{GUS} = \log(\text{DT}_{50}) \times (4 - \log(\text{K}_{oc}))$$

The GUS score incorporates only the properties of pesticides, and no information from the soil. Therefore, GUS indicates the intrinsic mobility of pesticides. Generally, a GUS score > 2.8 indicates a pesticide with high mobility (i.e., a greater risk of leaching), while a GUS score < 1.8 is indicative of less mobile constituents. By inference, a GUS score between 1.8 and 2.8 indicates moderate mobility.

To calculate GUS scores for active ingredients relevant to Ireland, the database of environmental information compiled by the EU-funded project FOOTPRINT was used. Examples of GUS computations for selected active ingredients are summarised in **Table 11**. While not exhaustive, these examples demonstrate significant range of subsurface mobilities that apply, with corresponding inferences of risk to groundwater (simply from a mobility point of view).

4.2 Indicator List of Active Substances for Monitoring

A short-list of active ingredients that are recommended for monitoring in Irish groundwater is summarised in **Table 12**. The short-list is based on usage data and relative mobilities of commonly applied active ingredients. The short-listing also takes account of certain special cases related to groundwater pathways. While extensively used, glyphosate would not be considered a high-risk ingredient given its low mobility. However, it is used extensively, including areas of extreme groundwater vulnerability.

While banned from use since 1985, an ingredient such as DDT is included on the list based on historical usage and documented persistence in soils and groundwater. In the UK and US, ingredients such as DDT and ethylene dibromide have been detected in groundwater at very low concentrations, even 30-40 years after being banned. McGrath (1998) reported trace levels of DDT and HCH (another banned substance) in soil samples from SE Ireland. It is therefore important that future groundwater monitoring be conducted with sufficiently low pesticide detection limits.

4.2.1 Check of Short-Listed Parameters in Groundwater

The short-list was checked against a limited set of groundwater quality data from Ireland and reported detections in drinking water supplies in England, Wales, and Northern Ireland (on the basis that similar pesticides are sold and used).

Pesticides have not been routinely monitored in Ireland in the past, and although audit sampling of drinking water supplies is carried out by local authorities, samples are often collected post-treatment, from taps in the distribution system. As such, they may not be representative of raw groundwater. Consultations with local authorities would indicate that pesticides are generally absent but periodically detected at concentrations below the EU prescribed (and

precautionary) norms for water intended for human consumption (as defined in the Drinking Water Directive 98/83/EC): 0.1 µg/L for individual pesticides and 0.5 µg/L for total pesticides.

EPA's drinking water quality report for the period 2006-2007 (EPA, 2007) indicates that one notification of pesticides in drinking water was received by the EPA, related to the Shinrone public water supply, a groundwater source in Offaly.

Overall, pesticides were detected in 190 of 1,342 samples collected nationally (representing 880 surface water and groundwater supplies). Only one exceedance of the 0.1 µg/l limit for individual pesticides was reported (for mecoprop) in the Clara/Ferbane groundwater supply, also in Offaly. Follow-up samples were reportedly free of the pesticide.

The majority of reported pesticide detections in the 190 samples were of the triazine herbicides atrazine (100 detections) and simazine (86 detections). These were followed by dichlorobenzil (29), terbuthlazine (19), MCPA (16), mecoprop (15), 2,4-D (10), and trichlopyr (10). 19 other specified and 23 'unspecified' pesticide detections (presumably metabolites) were also reported (EPA, 2007). While most of the water supplies in which detections were reported represent surface water sources, the samples nonetheless represent the aquatic environment and the types of pesticides detected are consistent with the types of pesticides described in Section 3.

The STRIDE project (Cullen, 1994) reported limited detections > 0.1 µg/L of triazine herbicides (atrazine and simazine) in three wells in Dublin, Waterford, and Westmeath. While sampling was limited and targeted at potential problem areas, results are nonetheless indicative of the types of pesticides that would be expected to be detected. One of the wells in which triazines was detected was collected from a shallow domestic well in an agricultural area (and located near a stream, apparently subject to surface water infiltration). Another sample was collected from a purpose-designed monitoring well located near a fuel storage site with a history of activities including timber treatment. The third well was also collected from a purpose-designed monitoring well near a historical gas storage site.

More recently (2005/2006), a monthly sampling programme of four major water supplies in Ireland was carried out as part of the NDSP. Results are summarised in **Table 13**. Triazine herbicides, notably atrazine and simazine, were detected at low concentrations (<0.1 µg/L) in a few samples. Atrazine is licensed in Ireland for use with forage maize and forestry, but is to be banned from all sales in mid- 2007 and from all use in December 2007.

Systematic pesticide monitoring has been carried out in the UK in recent years. Results indicate detections of triazine group herbicides in 5-30% of all drinking water samples analysed in England and Wales (Environment Agency, 2006). Groundwater quality reported by the Environment Agency on a wide array of wells in England and Wales are reproduced in **Table 14** and summarised in **Figure 13**. Reported exceedances of the 0.1 µg/L threshold are generally limited to atrazine and related triazines, as well as bentazone. On this basis, bentazone was

added to the Irish short-list as a precautionary measure, as it is a registered herbicide ingredient in some formulations approved for use in Ireland.

The British Geological Survey presented findings from recent groundwater studies in England and Wales (Stuart et al, 2006; Lapworth et al, 2005) to the steering group, with the following basic observations:

- An increasing number of pesticides are being detected as monitoring programmes are expanding and analytical techniques are improved;
- Defining and quantifying sources of pesticide pollution in groundwater is difficult at best;
- Point sources of pollution related to poor disposal practices probably account for a significant proportion of pesticide detections in public water supplies;
- Farm surveys in the Doncaster area of England identified use of more than 50 active ingredients over a three year period at a single, small mixed farm alone (mixed land use of sheep grazing , root crops, cereals);
- Vertical migration of pesticides through the unsaturated zone is driven by recharge and soil/subsoil conditions, and travel times, even over a few meters, are on the scale of years (notably for intergranular aquifers);
- Once in groundwater, migration of pesticides is influenced by a wide range of physical variables, and predicting movement remains subject to significant levels of uncertainty;
- Pesticide detections in shallow wells are more frequent than in deep wells.

Groundwater monitoring results in Northern Ireland include detections of triazines, MCPA, MCPP, Mecoprop and glyphosate, again at very low concentrations (EHS, 2004 and 2005). MCPA and MCPP have consistently been the most frequent pesticides to exceed regulatory standards since 1999 (EHS, 2005).

Overall, the short-listed active ingredients are in agreement with the limited results reported in Ireland and the UK, and are included as priority determinands for future EPA groundwater monitoring (under the WFD).

Results are also consistent with findings from countries such as Germany, Denmark, and the US. In the US, results of the most recent national pesticide survey conducted for the period 1998-2003 indicate that pesticides or their transformation products were detected in groundwater in more than 43 states, and that more than 140 pesticides and 20 transformation products were detected in all wells, mostly at concentrations near or below drinking water standards (USGS, 2007). In terms of water supply wells, the reported percentage of detections was approximately 26, while 6% of the wells exceeded the Federal drinking water standard of 0.1 µg/L for one or more substances.

Other US-based studies have reported the importance of including the breakdown products of pesticides (i.e., metabolites/degradates) in groundwater monitoring (Kolpin et al, 2004).

In Denmark, which relies 90% on groundwater for public water supply, pesticides and related degradation products have increasingly been detected over the past 10-15 years. The percentage of monitoring wells with reported concentrations above the EU 0.1 µg/L threshold for drinking water was approximately 10% in 2003 (Jorgensen, 2004). Pesticides and metabolites were detected in more than 40% of all wells sampled between 1998 and 2003. The triazine group of pesticides as well as the metabolite 2,6-dichlorbenzamide (BAM) are the most commonly detected compounds.

Public groundwater abstraction wells are also affected. Between 1998 and 2003, pesticides or metabolites were detected in nearly 27% of all wells, and 6% exceeded the 0.1 µg/L threshold (Jorgensen, 2004).

The Danish experience of detecting degradation products is mirrored by reports from the US which show that detection frequency increases when metabolites are included in sample analyses. Kolpin et al (2004) showed that detected concentrations varied substantially among groundwater vulnerability classes regardless of whether or not herbicide degradates were considered. However, when herbicide degradates were included, the *frequency* of herbicide compound detection within the highest vulnerability class approached 90 percent. Atrazine was the only herbicide in which the parent compound was detected more frequently than any of its metabolites.

While it may not be appropriate to compare US and EU results, a common element between reports is that pesticides and their breakdown products are detected at very low concentrations, and reported concentrations decrease rapidly (exponentially) above the 0.1 µg/L threshold. It is even suggested that where pesticide concentrations are significantly elevated, this is more likely attributed to point sources (spills, disposal practices) than diffuse sources (USGS, 2007; BGS, pers. comm.; Domagalski, 1992; Lapworth et al, 2005).

5. Fate and Transport

While chemical characteristics of pesticides and land use activities are of primary importance to groundwater risk, it is their combined effect with physical system characteristics that determine mass flux from soils to groundwater. Details on the principles of soil leaching and importance of groundwater mixing (dilution) are described below and summarised in **Figure 14**.

5.1 Principles of Leaching and Mixing

Concentrations of pesticides in groundwater are a result of leaching and mixing, and are defined by the following relationships:

$$C_{gw} = [(C_{in} \times V_{in}) + (C_{gwu} \times V_{gwu})] / (V_{in} + V_{gw})$$

Where,

C_{gw} = concentration in groundwater (M/V);

C_{in} = concentration in infiltrating water in the unsaturated zone (M/V);

V_{in} = volumetric rate of infiltrating water in the unsaturated zone (V/t);

C_{gwu} = concentration in the saturated zone from upgradient (M/V);

V_{gwu} = volumetric throughflow in the saturated zone (V/t);

V_{gw} = volume in the saturated zone beneath leaching point/area (V).

The concentration of the chemical leached from unsaturated zone soils is given by the soil-water partitioning process described in Section 4.1, and defined as:

$$C_{in} = C_s / K_d$$

Where:

C_s = concentration in soil;

K_d = soil-water partitioning coefficient;

And where,

$$K_d = F_{oc} \times K_{oc}$$

In this case,

F_{oc} = fraction of soil organic carbon (measured);

K_{oc} = organic carbon partitioning coefficient (empirically derived).

Upon reaching the water table, leachate mixes with groundwater. Mixing is a transient process, and the degree of mixing that occurs is a function of mass loading (volume, concentration, time), volumetric rate of groundwater inflow, background concentrations in groundwater, and aquifer properties.

Following mixing, pesticides migrate in groundwater under prevailing hydrogeologic conditions to discharge areas and potential receptors. During migration, dissolved pesticides are subject to attenuation processes and potential added mass flux in downgradient areas (depending on presence or absence of additional source areas along the flow path). Receptors can be surface waters, wetlands, or wells/springs.

5.2 Availability of Data Relating to Physical Variables

Most of the physical variables that influence pesticide leaching and mixing are reasonably well defined across Ireland. Many of the physical variables are available as maps or in databases created and maintained by institutions such as Met Eireann, Teagasc, GSI, and EPA.

5.2.1 Climate

Based on the equation to C_{gw} in Section 5.1, the mass flux of pesticides from soils to groundwater is proportional to infiltration rates. Thus, all other factors being constant, areas with higher effective rainfall and infiltration potential will result in areas of greater mass flux to groundwater. Using data from Met Eireann, the 30-year (1961-1990) median rainfall distribution across Ireland is depicted in **Figure 15**. The highest effective rainfall occurs in the west of Ireland and in mountainous areas elsewhere, while the driest areas are located in east and southeast.

Figure 15 also depicts the computed long-term annual median groundwater recharge, as developed under the national POM study on abstraction pressures.

5.2.2 Soils and Subsoils

Teagasc recently published new soil and subsoil maps of Ireland which contain descriptors of type, texture and drainage characteristics (Teagasc, 2006a and 2006b). Relevant information on soil organic carbon ranges and relationships with soil texture classes have been the subject of work by Zhang and Moody (2004). Soil property information is therefore reasonably well defined across Ireland.

5.2.3 Aquifers

As part of the WFD implementation in Ireland, the GSI has contributed significantly by updating its mapping of aquifer types and categories, as well as groundwater vulnerability. These have been incorporated into this study as appropriate.

5.3 Availability of Data Relating to Chemical Variables

As described in Section 4, the chemical characteristics of relevant pesticides are taken from the EU FOOTPRINT database. Uncertainties associated with the usage of pesticides involve their application timing and quantities (or rates). These are variable, and so estimates have been made based on literature and the PCS.

In the farming sector, records kept by the DAF would include surveys of pesticide applications, but such details are not available to this study. Local authorities and other relevant entities generally do not keep records of pesticide usage in any given year.

Applications are typically influenced by climate. Mild winters lead to less die-off of pests and more weeds, and use of pesticides is therefore likely to be increased over the growing season (May/June). Similarly, wet seasons may increase the incidence of fungal pathogens such as mildew.

Literature suggests that several kilograms (<10) of active ingredient per hectare may be applied to grassland and arable crops in any given year, and actual quantities will vary by region as a function of climate and site-specific conditions (e.g., pest infestations). Applications of herbicides and insecticides would be highest in the eastern and southern parts of Ireland, while fungicides would be applied in greater quantities in the root crop areas of central and western Ireland.

Groundwater pollution studies conducted by the BGS in the north of England indicated that the number of pesticides applications in any given year could vary considerably on mixed use farms, from once to more than a dozen times a year and can include a wide and variable range of active ingredients (Stuart, 2006).

6. Modeling of Pesticide Leaching

The combined lack of groundwater quality data and specific information on the spatial distribution of pesticide applications implies that objective criteria for defining risk to groundwater cannot be developed and that impact potential has to be assessed qualitatively until monitoring data become available. Modeling of pesticide leaching was deemed an appropriate alternative to explore and understand the relative importance of physical and chemical variables that influence leaching, and to assess relative risk to groundwater at the national scale. A similar approach has been taken in Scotland and Northern Ireland (SNIFFER, 2006).

The revised risk methodology therefore included the use of a chemical fate and transport model to explore relative mass loading of selected active ingredients to groundwater for a set of representative physical scenarios.

Given the site-specific nature of pollution risk, modeling can only provide insight about relative magnitudes of risk and will not necessarily result in accurate predictions at any given individual site.

The following sections summarise the selection of a model, input parameters, results, and conclusions.

6.1 Methodology

6.1.1 Model Selection

Available models currently being used by various European agencies to evaluate agri-chemical impact on the environment were reviewed, notably the SNIFFER models and the models covered by the Forum for Coordination of Pesticide Fate Models and Their Use (FOCUS), namely:

- PELMO
- PRZM
- PEARL
- MACRO

The key components of each model were reviewed for their applicability to Irish conditions, including:

- Types and quantities of pesticides used;
- Land use: crops on which the pesticides were applied (i.e., grassland, forage maize, cereal, etc.);
- Rainfall;
- Soil types.

Details on each model are provided in Appendix A, and the reviews relied upon published model descriptions, opinions, and model results rather than specific

code features. In particular, the review emphasised the following two main components:

Water Balance (Water Flow) Methodology:

From given inputs (which include climatic conditions), the selected model must adequately and realistically determine the amount of percolation that reaches the groundwater table under saturated conditions. Typically, percolation only occurs when enough infiltration is available to exceed the field capacity of the soils. Two basic approaches are typically used to model vertical water transport: capacity methods and methods using Richard's equation. Capacity approaches typically use classical water balance approaches where vertical water transport occurs only under saturated conditions when field capacity is exceeded. The rate of transport is typically based on permeability values at saturation. Richard's equation models vertical movement by using permeability changes at variable water content. As a result, some vertical migration can also occur under unsaturated conditions.

To determine the amount of rainfall that actually infiltrates the soil, the models must also accurately predict the amount of rainfall that runs off of the fields. Various approaches include use of standard curve numbers for soil/plant conditions or estimates of percent of rainfall that runs off given a particular soil type. Models typically incorporate evapotranspiration depending upon type of plants, etc.

Chemical Fate and Transport Methodology:

Once the amount of vertical water movement is solved, the models must accurately predict the concentrations of the chemical in the water at various times. Concentrations should be accurately predicted at levels of 0.1 micrograms per liter ($\mu\text{g/L}$) or less. To accurately predict chemical concentrations at these low levels, both adsorption and degradation must be adequately and correctly addressed by the models. The models reviewed have various levels of sophistication.

The simplest models use only an attenuation factor (AF). The AF is the ratio of the degradation half life to the organic-carbon normalised partition (adsorption) coefficient. The more complex models used both the degradation half life (usually first order kinetics) and a partition coefficient for adsorption. The models have various approaches to adsorption. The simplest models consider only linear adsorption while the more complex models incorporate Freundlich isotherms and two site adsorption models (equilibrium and nonequilibrium adsorption).

For the chemicals of concern, which typically degrade relatively quickly, nonequilibrium adsorption modeling is probably not necessary. The minimal level of complexity should typically be incorporation of first order kinetics for degradation and use of Freundlich equations for adsorption (FOCUS, 2006). In many cases, the Freundlich exponent may not be known for the specific soil type and chemical, so the model would result in the standard linear adsorption (i.e., $1/n$ equals one in the Freundlich equation).

6.1.1.1 Overall Recommendation for Model Selection

Because of their better predictive capabilities, use among EU countries, as well as endorsement by PCS, FOCUS models were selected over the SNIFFER models. In

the group of available FOCUS models, and in consultation with the PCS, PELMO was selected for comparative modeling of defined leaching scenarios as it uses the most widely accepted water balance approach (capacity model) and therefore predicts infiltration and chemical concentrations more accurately than other models. The model also takes into account biological degradation.

All of the PELMO chemical fate and transport modeling equations are appropriate and acceptable for this study. **Table 15** summarises the processes and approaches used by the PELMO model.

While important, macropore flow modeling using models such as MACRO is not recommended in the general FOCUS guidance.

Given the variability in natural soil conditions, water movement, degradation rates, and adsorption, accurate predictions of pesticide/herbicides concentrations near the threshold level of 0.1 µg/L are difficult. Although predicted concentration accuracies depend upon many variables, the degradation rate is especially critical.

6.1.2 Conceptual Leaching Model

A three-layer vadose (unsaturated) zone model was selected to simulate relative soil, subsurface, and aquifer conditions across Ireland. Layer one represents the topsoil composed of either: 1) a silty loam, or 2) a clay loam, each with a thickness of 10 cm. Layer two is a 90 cm thick subsoil layer below the topsoil. The properties of layer two depend upon the properties of underlying layer three (from which layer two was defined). Layer three is a variable depth layer (ranging from 0 to 900 cm thickness) located directly above the aquifer (groundwater body). The properties and thickness of this layer are dependent of the type of aquifer (permeability, karst features, etc.), the depth to the groundwater and the vulnerability categories. Selection of layer three was guided by the groundwater vulnerability mapping guidelines of the Geological Survey of Ireland (GSI), reproduced in **Table 16**. Groundwater vulnerability mapping has been completed in about half of the counties in Ireland, and areas of extreme vulnerability have been mapped by river basin district projects in counties not yet completed by the GSI. Subsequent modeling results using physical scenarios based on vulnerability categories can therefore be linked to specific locations across Ireland.

Overall, 21 physical scenarios (combination of soil/subsoil types/depths and vulnerability ratings) were selected for modeling. These are presented in Section 6.3. In addition, different combinations of rainfall scenarios, chemical and crop applications, and soil organic carbon contents for the topsoil were evaluated. The combinations of these inputs result in more than 900 simulations. However, many scenarios resulted in no leaching of pesticides through the three layers into the groundwater. Therefore, all combinations of parameters did not have to be modeled. For the various combinations of parameters that were modeled, the following results were evaluated and summarised in the results section (Section 6.5):

- Amount of water transported through the three layers into the groundwater over the simulated timeframe (total water output from the bottom of layer three expressed as millimeters of water over the simulation period);

- Amount of chemical mass transported through the three layers into the groundwater (total mass of pesticide output from the bottom of layer three expressed as grams of chemical per hectare of surface land over the simulation period);
- Amount of time to observe chemicals in the groundwater (first observed concentration of the pesticide in the water exiting the bottom of layer three expressed as years);
- Highest concentrations of pesticide observed entering the groundwater
- (highest concentration of the modeled pesticide in water exiting the bottom of layer three expressed as $\mu\text{g/L}$).

Based on evaluation of these results, conclusions were formulated (see Section 6.6).

6.1.3 Pesticides and Land Use

By considering the quantities of pesticides used, the crops/land on which the pesticide was applied, and the mobility of the pesticides in soil, six relatively mobile (high risk to groundwater) pesticides and one low risk, heavily used pesticide were selected for further evaluation. These were:

- Atrazine used on forests and grassland;
- MCPA used on grassland and arable;
- 2,4-D used on grassland, arable, urban;
- Isoproturon used on arable;
- Mecoprop used on grassland, arable, and urban;
- Chlorotoluron used on arable; (note, chlorotoluron is no longer used in Ireland, but would have been used historically. It is used as a surrogate substance for modeling purposes due to its high GUS score indicative therefore, of mobile active ingredients used in the arable sector).
- Glyphosate used on forests and urban (low risk, high use).

Further consideration of chemical properties (in particular the GUS), chemical structure, and chemical class resulted in the selection of the following pesticides and land uses for modeling:

- Atrazine on forage maize;
- MCPA on grassland;
- 2,4-D on arable, winter barley;
- Glyphosate on forest;
- Chlorotoluron on arable, winter barley

6.2 Model Input

6.2.1 Climate Data

To represent different climatic conditions across Ireland, long-term rainfall data were selected from three stations :

- Coastal wet and upland areas: Valentia (synoptic station) with a mean annual rainfall of 1,586 mm;

- Central lowland, karst areas: Glenamaddy with a mean annual rainfall of 1,037 mm;
- East, Southeast, Cork: Kilkenny (synoptic stations) with a mean annual rainfall of 868 mm.

Complete daily records between 1990 to 2005 were used. Simulations were run for 26 years, the maximum number of years allowable in the FOCUS model, and the rainfall data series was repeated for the last 10 years.

Other climate data required for the model, and their sources, are shown in **Table 17**. Monthly pan evaporation data for each station, obtained from Met Eireann, were divided by the number of days in the month to obtain daily values for use in the model. In cases where precipitation or other data were missing for a particular day, the average daily value for that month over the 16-year dataset was used.

6.2.2 Soil and Subsoil Characteristics

Soil properties available in the FOCUS model runs (Generic Guidance for FOCUS Groundwater Scenarios, Version 1.1, April 2002) were evaluated. Properties were available for the 47 soils used in nine different FOCUS scenarios. Irish soils with similar properties (grain size distribution, soil description, etc.) were categorised into groups. Average values summarised in **Table 18** were then calculated for each type of soil for use in the leaching model.

6.2.3 Chemical Properties

The chemical properties used were obtained from the FOOTPRINT Pesticide Properties Database (FOOTPRINT, 2006). The values from the database, along with the GUS values, were presented in **Table 11**. Atrazine is the active ingredient considered to be most mobile and the ingredient that is expected to leach to groundwater under the defined scenarios.

Initial model runs resulted in little or no leaching of the selected pesticides through the three soil and subsoil layers, even for atrazine. Because the modeled scenarios are based on real physical situations and input parameters of Irish soils, this would suggest that risk of pesticide leaching to groundwater is very limited.

Because simulated leaching concentrations using the FOOTPRINT chemical properties did not result in significant breakthroughs, the initial results do not allow for comparisons between scenarios. In order to be able to evaluate the relative importance of input parameters and compare results among the physical scenarios, chemical concentrations exiting the bottom of layer three (i.e., entering the groundwater) must be observed in the model results. In order to provide such results, the half life (DT_{50}) for atrazine was increased from the FOOTPRINT recommended value of 75 days to a longer half-life of 231 days. The longer value is based on reported atrazine field data from the unsaturated zone of an agricultural soil in the United States (Seybold, et al. 2001). A precedent therefore exists to use a higher DT_{50} , although it is not yet established whether this value applies in Ireland. Recent work in England on chalk aquifers suggest longer half-lives may apply (Johnson et al 2000). Simulations were continued with the higher value to

allow for a relative comparison of input parameters and physical (vulnerability) scenarios.

The degradation of all modeled compounds was assumed to produce only carbon dioxide and water (complete mineralization), although in real systems daughter products are likely. The FOCUS default adjustment factors for the subsoil degradation rate were used: the rate for layer 1 was multiplied by 1; the rate for layer 2 was multiplied by 0.5; and the rate for layer 3 was multiplied by zero (i.e., no degradation in layer 3). This adjustment reflects the typically observed decrease of degradation with depth.

Volatilisation from the infiltration water (vapor pressure or Henry's Law constants and molecular diffusion) was neglected, due to the low volatility of the pesticides and in order to be conservative (more potential mass leaching). All other chemical property parameters were obtained from the FOOTPRINT database.

6.2.4 Application Rates and Dates

The pesticide application rates and times used in the model are presented in **Table 19**, and are recommended values obtained from correspondence with PCS. It is recognised that actual application rates and timing may vary significantly from those modeled, from user to user and as a function of climatic factors. Given the uncertainties associated with application rates and times, these were kept constant for modeling purposes, in order to provide a consistent set of results which can be used to assess relative leaching risk to groundwater.

Applications on grassland normally take place between May and August while use on fodder crops is highest between March and June (PCS, 2006). For arable crops, the bulk volume of pesticides is applied between April through June (PCS, 2007b). However, pesticides may also be applied periodically in the autumn when rainfall is higher. In these circumstances, certain soil-to-groundwater pathways may be more vulnerable to leaching.

The default values in FOCUS were used for the emergence, maturity, and harvest dates for each crop. As forest land was not included in the default parameters in the FOCUS model, the database values for apple trees were used.

6.2.5 Soil Organic Carbon

Soil organic carbon (SOC) information for topsoil was reviewed from the tabulations provided by Zhang and Moody (2004). Based on these values, the SOC for topsoil (layer 1) was modeled for contents of 3%, 4.5%, and 6%. The following SOC values were selected for layers 2 and 3:

- Layer 2: 1 percent
- Layer 3: 0.5 percent for clay; 0.01 percent for sand and gravel; 0.01 percent for silt and sand

6.3 Scenarios Modeled

Based on review of the hydrogeological conditions and relevant soil/subsoil types, 20 different physical scenarios were selected for modeling to represent the variety of physical conditions across Ireland. **Table 20** provides a description of Scenarios

1 through 10. Scenarios 11 through 20 are the same except layer 1 was changed from a silty loam to a clay loam. Scenario 4a was added when initial simulations of atrazine with a faster degradation rate did not result in leaching for Scenario 4 (the thickness of layer three in scenario 4 is 900 cm and 600 cm in scenario 4a). This results in 21 physical scenarios.

6.4 Model Results

The results of the modeling are presented in **Table 21**. The table provides the following information:

- The Scenario Number, the Groundwater Vulnerability and the Chemical Modeled (columns 1, 2, and 3).
- The climate data used in the scenario (column 4, "Rain"): val = Valentia; kil = Kilkenny and glen = Glenamaddy (Section 3.1).
- Column 5, "26 yr outflow": Amount of water transported through the three layers into the groundwater over the simulated time frame (total water output from the bottom of layer three expressed as millimeters of water over 26 years).
- Column 6, "Mass": Amount of chemical mass transported through the three layers into the groundwater (total mass of pesticide output from the bottom of layer three expressed as grams of chemical per hectare of surface land over 26 years).
- Column 7, "Yr to Breakthrough": Amount of time to observe chemicals in the groundwater (first observed concentration of the pesticide in the water exiting the bottom of layer three expressed as years).
- Column 8, "Hi Conc": Highest concentrations of pesticide observed entering the groundwater (highest concentration of the modeled pesticide in water exiting the bottom of layer three expressed as $\mu\text{g}/\text{L}$).

Because of selection of the same soil/subsoil properties for the various layers, certain scenarios had identical results. Scenarios yielding the same results are provided in parentheses after the original scenario number (e.g., scenario 2 results were the same as scenario 9).

Simulated high concentrations at the groundwater table exceed the $0.1 \mu\text{g}/\text{L}$ threshold for several scenarios, but only those involving X, E and some H groundwater vulnerability categories. M and L vulnerability scenarios resulted in no breakthrough of pesticides, even when using the longer (slower) degradation rate for atrazine. X and E vulnerability scenarios resulted in the fastest breakthrough with the highest concentrations. Both the X and E vulnerability scenarios could result in impact to groundwater, but concentrations would be expected to be significantly variable depending upon the type of subsoil material present. Soil types and thickness significantly affect the breakthrough times and concentrations.

6.4.1 Sensitivity Analysis

6.4.1.1 Rainfall

The Valentia Observatory, Glenamaddy, and Kilkenny stations had average yearly precipitation values of 1,586 mm, 1,037 mm, and 868 mm, respectively. However, due to runoff, evaporation, and transpiration, not all of the precipitation reached the groundwater table. The term "effective precipitation" is the precipitation minus the pan evaporation. Additional water is consumed due to uptake by plant roots (transpiration), which is calculated by the model for different crop types. The remaining water is the infiltration or percolation. **Table 22** and **Figure 16** show the differences in transpiration for the different crop types calculated by the model. The high transpiration and less percolation of maize relative to the other vegetation types likely reflects the larger surface area of the leaves relative to the other plant types. **Table 22** also provides values for the average rainfall rate at each station and for each crop type.

Figure 17 shows the precipitation, effective precipitation, and infiltration for the Valentia Observatory Station (the crop is maize). Evaporation removes roughly one-third of the water volume, while transpiration and runoff account for an additional one-fourth.

A condition that exists in some areas, where a low permeability clay underlies layer 2 could not be accurately modeled using PELMO (see Scenarios 5 and 15 in **Table 21**). The table shows leaching of low concentrations of atrazine from layer three; however, unless preferential pathways are involved (not modeled) transport through 400 cm of clay would be difficult. In these cases, the infiltration would accumulate in layer 2 faster than it could be transmitted vertically through the clay layer (i.e., layer 3, 400 cm thick clay), resulting in lateral flow (a.k.a. interflow). The interflow would not recharge the groundwater table, but would instead flow along the clay layer until it discharges either as a spring or into a river (assuming the clay layer is continuous), or finds a subsequent pathway to groundwater. If the infiltration is reduced via interflow, no transport will occur through the layer. This occurs when rainfall from the Kilkenny station is used in Scenario 5 (lower rainfall), i.e., no leaching through layer 3 is simulated.

Out of all the parameters used, the model is the most sensitive to the infiltration rate. Therefore, the Valencia Observatory station consistently had more rapid and more significant breakthrough than for the other stations, as shown in **Figure 18**.

6.4.1.2 Chemical Properties

The most important chemical property is the degradation rate. Atrazine has the lowest degradation rate (longest half-life) of the pesticides modeled. Atrazine is the only chemical to show breakthrough (chemicals exiting the bottom of layer 3 into the groundwater). **Figure 19** shows the model scenario 1 results (90 cm of sandy loam overlain by 10 cm of silty loam) for Valentia Observatory for all selected chemicals and types of use (see **Table 19**). Scenario 1 has the most conservative conditions for leaching to groundwater (highest rainfall and no layer 3); therefore, the fact that only atrazine broke through eliminates the need to model other scenarios defined in Section 6.1.3.

6.4.1.3 Soil Organic Carbon

The SOC, along with the organic carbon partitioning coefficient (K_{oc}) of the pesticide determines the partitioning coefficient (K_d) between the soil and the infiltration water. The higher the SOC, the more pesticide is adsorbed to the soil and the lower the mass load to the groundwater. **Figure 20** shows that the effect of increasing the SOC by 50 percent (from 3 to 4.5 percent) or even 100 percent (from 3 to 6 percent) is relatively insignificant compared to other parameters.

6.4.1.4 Soil and Subsoil Characteristics

The effect of changes in subsoil composition and thickness on the breakthrough can be summarised as follows:

- The thinner the soil, the faster the breakthrough and the higher the pesticide loading and concentrations to the groundwater. These conditions are observed for X and E vulnerability classes (Scenarios 1, 2, 3 and 9 and Scenarios 11, 12, 13 and 19).
- The more permeable the layers, the faster the breakthrough and the higher the pesticide loading and concentrations to the groundwater. This is shown by the differences between Scenarios 2 and 3 (layer 3 in Scenario 2 is 200 cm of gravel/sand and layer 3 in Scenario 3 is 200 cm of clay).
- Even relatively thicker layers of low permeable materials (clay) can result in very small or zero concentrations of pesticides leaching through the layer (Scenarios 5, 7 and 8).
- Relative thick layers of high permeable materials (gravel and sand) result in significant concentrations of pesticides leaching through layer (Scenarios 10 and 20).
- The model is relatively insensitive to porosity, because "plug flow" occurs and all of the infiltration water moves through the layers.

Figures 21 and **22**, for Valentia and Kilkenny respectively, illustrate the above observations. The value of cm shown on the figure is the total depth of all layers. "L3" indicates the subsoil type for layer three.

Overall, results of sensitivity analyses indicate that:

- Rainfall is the most important variable in controlling leachate breakthrough times and concentrations. Simulated concentrations are two times higher for Valentia rainfall compared to Kilkenny rainfall. The breakthrough time is also roughly twice as fast for the higher rainfall;
- SOC has little effect on breakthrough time, however, simulated concentrations increase with lower SOC values;
- Crop types significantly influence infiltration/percolation, and therefore mass loading.

- The role of the hydrogeological setting, notably subsoil characteristics, is vital. Clayey subsoils reduce infiltration rates, increase breakthrough times and overall reduce the potential for breakthrough concentrations. The greater the subsoil thickness and clay content, the lower the pollution risk. The groundwater vulnerability mapping of the GSI provides an important indicator of pesticide leaching risk.

6.5 Dilution

Upon reaching the water table, leachate mixes with groundwater. Mixing is a transient process, and the degree of mixing that occurs is a function of mass loading (volume, concentration, time), volumetric rate of groundwater inflow, background concentrations in groundwater, and aquifer thickness.

Following mixing, pesticides migrate in groundwater under prevailing hydrogeologic conditions to discharge areas and potential receptors. During migration, dissolved pesticides are subject to attenuation processes and potential added mass flux in downgradient areas (depending on presence or absence of additional source areas along the flow path). Receptors can be surface waters, wetlands, or wells/springs.

Concentrations in groundwater resulting from mixing are subject to the equation presented in Section 5.3. Mixing is effectively a form of dilution. All factors being constant, mixing ratios can be estimated by comparing leaching (infiltration) rates and groundwater inflow rates. Different aquifers transmit groundwater at different rates, depending on aquifer properties (such as hydraulic conductivity), flow gradients, and thickness.

Mixing ratios (dilution factors) were calculated for four different aquifer types encountered in Ireland and mapped by the GSI, and applied against each of the modeled leaching results that were presented in **Table 21**. The four aquifer types considered are based broadly on the following GSI-defined aquifer categories:

Pl, Pu: poorly productive aquifers, representing about two-thirds of Ireland, and exemplified by volcanic intrusive rocks (e.g., granites), Silurian and Ordovician metasediments, Devonian Old Red Sandstone, etc.

Ll: generally unproductive fissured rocks, exemplified by Dinantian upper impure limestones.

Lm: generally productive fissured rocks, exemplified by Dinantian pure bedded limestone.

S&G: sand and gravel aquifers.

The distribution of the referenced aquifer categories is shown in **Figure 23**. Mixing ratios for karst aquifers were not attempted, as groundwater flow through karst systems are highly variable and flow does not conform to Darcy's law.

Basic calculations of Darcy groundwater flow through the four different aquifer categories are shown in **Table 23**, and are based on representative ranges of hydraulic conductivity values and gradients that were obtained from and

discussed with the GSI. Computed flows relate to unit cross-sectional areas of aquifer.

For dilution calculations, the following average groundwater flow values are suggested:

- Pl, Pu aquifers: 3 m³/yr per unit cross-sectional area
- Ll aquifers: 5 m³/yr per unit cross-sectional area
- Lm aquifer: 10 m³/yr per unit cross-sectional area
- S&G aquifers: 50 m³/yr per unit cross-sectional area

Flow values closer to the associated lower range values of hydraulic conductivity are suggested to be conservative. Higher range values would result in greater dilution.

Results of computed mixing ratios (dilution factors) are summarised in **Table 24** for each of the model runs resulting in Layer 3 breakthrough. Mixing ratios range from 3 to 158, depending on aquifer type, and are provided for indicative purposes only. Actual values will vary spatially based on site-specific hydrogeological conditions, over the ranges indicated in **Table 23**.

Table 24 also includes resultant diluted concentrations after mixing. Mixing is assumed to be instantaneous over a unit-cross-sectional area of the aquifer. In reality, mixing will occur over greater aquifer thicknesses, and would therefore result in additional dilution. The dilution presented in **Table 24** is therefore conservatively low.

Appreciable concentrations above the 0.1 µg/L threshold value only occur for atrazine, for scenarios representing vulnerability categories X, E, and H. In the case of vulnerability = H, threshold exceedances only occurred for scenarios involving the higher rainfall values (represented by Valentia).

6.6 Mixing in Poorly Productive Aquifers (PPAs)

The computed groundwater flow rates in **Table 24** are based on reasonable ranges of hydraulic conductivity and gradient values for the different aquifer types in question. In poorly productive aquifers (categories Pl, Pu, Ll), conceptual model considerations of groundwater flow characteristics have implications for fate and transport of pesticides leaching from soils.

The conceptual model of PPAs involves groundwater flow along two primary pathways:

- Deep fractures in the bedrock proper (deep groundwater flow);
- Shallow fractures near the top of the bedrock (shallow groundwater flow near the bedrock surface).

Terminology aside, the interface between the top of bedrock and subsoil materials is weathered and comprises a network of interconnected and shallow fractures which is denser than the fractures of the deep groundwater flow system. The shallow fractured zone is therefore regarded as being more transmissive than deeper bedrock, and is potentially significant to the transport of infiltrating water (and leachates) to nearby receptors (streams). Deep fractures have a finite ability to accept recharge on account of low storage and transmissive properties. Hence, recharge that is rejected from the deeper system accumulates and flows through the shallow fractured zone under prevailing gradients (which approximates topography). A detailed study of soil water and shallow groundwater flow in an upland catchment in Wales (Haria and Shand, 2004 and 2006) demonstrated that a lateral “rapid flow horizon” transported water down slope as “interflow” (at the soil–bedrock interface) whereby upper soil horizons remained largely unsaturated except along a narrow band along the stream (discharge area).

Groundwater flow systems in PPAs tend to be localised, and flow lengths between recharge and discharge zones are typically on the scale of a few hundred meters only.

Future monitoring of pesticides in groundwater associated with PPAs should therefore take account of the different (deep and shallow) pathways, as monitoring of deeper wells only may not be representative of the bulk pesticide migration.

Finally, the groundwater flow rates presented in **Table 24** are based on bulk, average hydraulic conductivity values associated with the deeper groundwater flow system. In PPAs, the transmissivity and hydraulic conductivities associated with the shallow zone are considered to be higher. The implication is greater dilution and faster travel to streams. *On this basis, risks of pesticide pollution over PPAs are considered to be greater for surface water than deep groundwater.*

Verification of the conceptual model through detailed characterisation and multi-level monitoring in PPAs is planned as part of EPA’s groundwater monitoring efforts under WFD implementation (see Section 8).

7. Conclusions

Assessing pesticide risk to groundwater involves many variables, and is effectively a site-specific science. Despite the mapping limitations, a qualitative and comparative assessment of diffuse pesticide risk at the national scale can be made by combining usage data and modeling of pesticide leaching with a range of physical scenarios found in the Republic of Ireland.

Specific mapping of usage in all sectors is constrained by lack of information on usage or lack of spatial resolution in the agricultural sector. Future studies of pesticides in groundwater would significantly benefit from access to the land use GIS maintained by the DAF (i.e., specific cropping patterns).

The types and quantities of pesticides used in the agricultural and forestry sectors are reasonably well understood. Agricultural usage is surveyed by the PCS, and forestry usage is monitored by Coillte. While total usage in sectors other than agriculture and forestry are believed to be significantly lower, records are typically not kept, and as a result, significant questions on patterns of use remain.

With the available mapping layers, areas have been identified where relevant land use practices, i.e., those that involve diffuse pesticide applications, overlie areas of extreme groundwater vulnerability. These are summarised in **Figure 24** by intersecting extreme groundwater vulnerability areas with land use areas represented by improved grassland, arable crop types (mainly cereals), and young forestry. As such, these areas would be considered to be at greater risk from diffuse pesticide pollution.

Many of the parameters that influence leaching are known from existing databases or have been mapped across the country.

On the basis of modeling results, groundwater vulnerability and land use considerations, diffuse risk to groundwater is considered greatest in the groundwater bodies shown in **Figure 25**. These groundwater bodies represent productive aquifers, as defined by the GSI, which are used extensively for public water supply. The groundwater bodies identified in **Figure 25** include areas of extreme groundwater vulnerability and land uses which involve known pesticide applications (notably agriculture and forestry). The locations of candidate public supply wells and springs that are recommended for pesticide monitoring are included in **Figure 25**.

The risk to groundwater will be enhanced by the presence of preferential pathways. These are inferred to be more significant where soils are particularly thin or absent (vulnerability category X), but cannot be ruled out in other settings as well (e.g., fractures in glacial till). Conversely, the presence of surface features such as arterial drainage are inferred to potentially decrease the risk to groundwater, as these divert water and pesticides to surface waters, and away from groundwater systems.

The lack of relevant groundwater quality data and systematic groundwater monitoring in the past does not allow for rigorous validation of predictive risk assessments. However, using limited available data sets in Ireland, pesticides have

been detected in higher-risk scenarios, and have been absent in lower-risk scenarios. This is useful as an indication (but is not conclusive) as the total available data set is simply too small.

In the larger context, risk to groundwater is considered to be limited compared to the risk to surface water for the following reasons:

- More than two-thirds of Ireland is underlain by poorly productive rocks with limited infiltration and recharge potentials. In these types of rocks, conceptual models suggest that surface runoff and shallow interflow (near the interface between overburden and top of bedrock interface) transport water quickly to rivers.
- At poorly drained sites, where slopes are high, surface runoff would be considered to be the main pathway to surface waters.
- Pesticides are applied by spray-applications, which exposes surface waters to direct spray drift.

Using reasonable ranges of input parameters representative of Irish conditions, model results of pesticide leaching would suggest that pesticides are likely to reach the water table for extreme-to-high groundwater vulnerability scenarios. Caution must be exercised because lessons from the UK and the US would suggest that pesticides can be detected where none would be expected on account of these primary factors:

- The presence of preferential pathways in the subsurface (which enhance vertical migration);
- Point sources resulting from poor pesticide disposal practices;
- Uncertainties relating to actual application rates (which are partly determined by climatic factors);
- The adsorption of certain pesticides in soils can be affected by ionic substances (minerals) which in turn may influence subsurface mobility.

Neither can be pin-pointed, (accurately) audited or mapped, thus limiting the ability to rule out risk where none would be predicted.

Land use related risk factors exist in all sectors, but is considered greatest in the agricultural and forestry contexts. On the basis of their limited geographic spread and smaller quantities of pesticides involved, risk associated with other land use factors (non-agriculture, non-forestry) is reduced.

Predicting pesticide occurrence in groundwater is scale-dependent, and the finer the scale, the greater the influence of site-specific factors. At the broader scale, reasonable predictions are possible on the basis of land uses and environmental persistence of specific types of pesticides. At the catchment scale, the differentiation of sources and variability of aquifer characteristics becomes important, while at the field scale, variability in soil and subsoil, including

preferential pathways, limiting predictive capabilities. At this scale there is no real substitute for data from monitoring.

8. Recommendations

Recommendations are many, and relate to all aspects of the source-pathway-receptor model. First and foremost, verification of risk is required through groundwater monitoring. The groundwater sampling efforts that are planned by the EPA that will be implemented as part of WFD implementation will go a long way towards verifying risk and, importantly, developing an understanding of the scale of pesticide detections in groundwater.

Source:

1. Specialised surveys and inventories of pesticide usage are recommended in non-agricultural and non-forestry sectors. This pertains mostly to usage by local authorities and national (service) organisations that routinely handle or apply pesticides (e.g., in transport/infrastructure sector).
2. Improved access to farm survey information is needed for site-specific assessment of risk to groundwater.
3. Importantly, access to DAF mapping of specific agricultural land use areas (cropping patterns) would add significant value to the assessment of pesticide risk, whether at the national or local scales.
4. The combined use of PCS usage data with the DAF GIS is expected to provide the most accurate depiction of pesticide usage patterns in the agricultural sector. The mapping presented in this study provides a reasonable representation of national patterns, but does not offer the desired resolution at local scales. As new groundwater monitoring data become available from EPA monitoring efforts, interpretation of data may necessitate an improved resolution in mapping.

Pathway:

5. Groundwater vulnerability - mapping of groundwater vulnerability in areas not yet covered by the GSI should be continued. This vital work is extremely useful to the assessment of groundwater pollution risk from any sector.
6. Bypass flow - glacial tills cover a significant portion of the country and would typically provide protection from pollution. Potential bypass flow through fractures and cracks in till-derived soils and subsoils could provide enhanced transport of pesticides and nutrients to deeper groundwater. Research on bypass flow in such "low-risk" settings should be carried out with appropriate field components.
7. Poorly productive aquifers - poorly productive rocks, as defined by the GSI, represent a special case in the hydrogeological context of Ireland. The working conceptual model is that these rock types have a finite ability to accept infiltrating water, and that a significant amount of recharge is rejected. The rejected recharge either builds up to increase the proportion of overland flow or migrates along the top of bedrock, where a weathering zone and an interconnected system of shallow

fractures allow for relatively quick transit to local discharge areas (surface water receptors). This shallow subsurface flow component is typically referred to as interflow.

While groundwater flow in poorly productive rocks is localised, the “interflow” component is potentially contributing significant pollutant loads to streams, considering that poorly productive rocks cover about two-thirds of the total land area of Ireland.

To verify this conceptual model, it is suggested that EPA’s planned pilot studies and monitoring of poorly productive aquifers at sites across the country include consideration of pesticides. Thus, final selection of EPA pilot sites should be selected with relevant land uses in mind. Alternatively, separate and targeted research may be warranted.

Receptor:

7. Systematic monitoring of groundwater quality for pesticides:

Systematic monitoring of pesticides in groundwater has not taken place in the past. With input from this study, EPA is including pesticide monitoring at a wide array of sites for both “at risk” and “not at risk” scenarios. This important and recommended action is taken in order to establish a baseline understanding of pesticide detections across Ireland. EPA’s complete groundwater monitoring network, which was established with input from all RBD projects, is presented in **Figure 26**. Pesticide monitoring began in late 2007 and will be included at each groundwater sampling station for the first two years. As results become available, some monitoring sites may be dropped, and future monitoring needs will therefore be informed by the baseline results. The short-listed pesticides from this report (i.e., those that are most likely to pose a threat to groundwater in Ireland) are all included in EPA’s groundwater monitoring programme.

Many of the groundwater sampling points are appropriately linked with surface water monitoring sites.

The work undertaken for this project should be reviewed in 12-18 months as EPA’s new monitoring results become available.

8. Research pesticide fate and transport under Irish soil conditions:

To verify and develop an improved understanding of site-specific leaching risk, research into the fate and transport of pesticides is warranted. Emphasis would be placed on establishing values of degradation and adsorption rates that are specific to Irish soils, for different soil and climatic conditions. Research would involve a limited number of controlled monitoring sites, and a selected group of variables: active ingredients, application rates, crop types, soil type, soil texture, and rainfall.

The work would involve sampling of soils, pore water and shallow groundwater, as well as column testing in laboratory conditions. The research would also involve fate and transport modeling of unsaturated zone leaching in order to calibrate leaching parameters under different physical scenarios.

The Danish Pesticide Leaching Assessment Programme (PLAP) might be an appropriate model to follow.

9. References

Anthony, Dr. Steven. Technical Note No. 2 on Priority Substances (Pesticides). Environmental Modelling and GIS Group.

Blanchoud, H., F. Farrugia, and J.M. Mouche. 2004. Pesticide Uses and Transfers in Urbanised Catchments. *Chemosphere* 55, no. 6: 905-913.

Center for Watershed Protection, 2000. The Practice of Watershed Protection: Techniques for Protecting and Restoring Urban Watersheds. Article 5: Urban Pesticides – from the lawn to the stream. 2000.

Chilton PJ, Stuart ME, Lawrence AR, Gooddy, DC, Williams RJ and Johnson AC. 2000. Assessing pesticide pollution of groundwater: current knowledge and remaining gaps. In: groundwater: Past Achievements and Future Challenges, Sililo et al. (Eds) Balkema, Rotterdam.

COM, 2002. A Thematic Strategy on the Sustainable Use of Pesticides. Commission of the European Communities. COM(2002) 349 Final. Brussels, 1.7.2002.

http://eur-lex.europa.eu/LexUriServ/site/en/com/2002/com2002_0349en01.pdf

Coquet, Y., C. Ribiere, P. Vachier, 2004. Pesticide adsorption in the vadose zone: a case study on Eocene and Quaternary materials in northern France. *Pest Management Science*, Volume 60, Number 10, October 2004, pp. 992-1000(9).

Cullen, K.T., 1994. Trace organic contaminants in Irish Groundwaters. STRIDE – Environmental Subprogramme Measures 3. Prepared for the Department of the Environment, 1994.

Daly, D., 2002. Bypass flow in Soils and Subsoils. GSI Groundwater Newsletter, No. 41, 2002. Geological Survey of Ireland.

Department of Agriculture, Food and Rural Development. Book of Good Agricultural Practice, 2001.

Department for Environment Food and Rural Affairs, 2005a. Water Quality: A Diffuse Pollution Review – Chapter 3, Sources of Diffuse Pollution. May 2005.

Department for Environment Food and Rural Affairs, 2005b. Inland Water Quality and Use: Pesticides. published online at:
www.defra.gov.uk/environment/statistics/inlwater/iwpesticide.htm

Domagalski, J.L., and N.M Dubrovsky. 1992. Pesticide residues in groundwater of the San-Joaquin Valley, California. *Journal of Hydrology*, 130, no. 1-4: p.299-388.

Environment Agency, 2006. Pesticides Report 2005: Pesticides in Rivers, Groundwater and Pollution Incidents. Environment Agency, January 2006.

Environment and Heritage Service, 2005. Regional Groundwater Monitoring Network, Northern Ireland: Review of 2004 monitoring data. A report by the Northern Ireland Drinking Water Inspectorate.

Environment and Heritage Service, 2004. Northern Ireland Drinking Water Quality 2003. A report by the Northern Ireland Drinking Water Inspectorate.

Environmental Protection Agency, 2005. The Article 5 Characterisation and Analysis of Ireland's River Basin Districts: National Summary Report (Ireland 2005). Submitted to the European Commission – March 2005.

Environmental Protection Agency, 2007. The Provision and Quality of Drinking Water in Ireland: A Report for the Years 2006-2007.

European Food Safety Authority. 2004. Opinion of the Scientific Panel on Plant Health, Plant Protection Products, and their Residues. Request on the FOCUS Groundwater Models Comparability and the Consistency of this Risk Assessment of Groundwater Contamination. September 14.

FOCUS Groundwater Scenarios in the EU Review of Active Substances, Sanco/321/2000 rev.2.

FOOTPRINT, 2006. The FOOTPRINT Pesticide Properties DataBase. Database collated by the University of Hertfordshire as part of the EU-funded FOOTPRINT project (FP6-SSP-022704). <http://www.eu-footprint.org/ppdb.html>.

Gardiner, M.J, and Radford, T., 1980. Soil Survey Bulletin No. 36. Dublin. An Foras Talúntais.

Garthwaite D. 1998. Golf Course Pesticide Usage 1994 – 1997. Central Science Laboratory Pesticide Usage Survey Group.

Generic Guidance for FOCUS Groundwater Scenarios. 2002. Version 1.1. April.

Geological Survey of Ireland, 1999. Groundwater Protection Schemes. Prepared with the Environmental Protection Agency and the Department of Environment Heritage and Local Government.

Gustafson, D. I., 1993. Pesticides in Drinking Water. Van Nostrand Reinhold, New York.

FOCUS, 2006. "Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration" Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp.

Haria AH and Shand P. Evidence for deep sub-surface flow routing in forested upland Wales: implications for contaminant transport and stream flow generation. Hydrology and Earth System Sciences 2004;8(3):334-44.

Haria, A.H., and P. Shand, 2006. Near-stream soil water-groundwater coupling in the headwaters of the Afon Hafren, Wales: Implications for surface water quality. Journal of Hydrology, Volume 331, Issues 3-4, 15 December 2006, p. 567-579.

Johnson, A., C. White, and C. Lal Bhardwaj, 2000. Potential for isoproturon, atrazine and mecoprop to be degraded within a chalk aquifer system. *Journal of Contaminant Hydrology*, Vol. 44, p. 1-18, June 2000.

Jorgensen, P.R., L.D. McKay, and J.P Kistrup, 2005. Aquifer Vulnerability to Pesticide Migration Through Till Aquitards. *Ground Water*. 2004 Nov-Dec; 42 (6-7): p. 841-855.

Jorgensen, L. F., 2004. Groundwater Monitoring 1998-2003. Geological Survey of Denmark and Greenland. December 2004. (in Danish only).

Klein Tank, A.M.G. et. al. 2002. Daily dataset of 20th-century surface air temperature and precipitation series for the European Climate Assessment. *Int. J. of Climatol.*, 22, 1441-1453. Data and metadata available at <http://eca.knmi.nl>.

Kolpin, D.W., J.E. Barbash, and R.J. Gilliom. 2002. Atrazine and metachlor occurrence in shallow groundwater of the United States, 1993-1995: Relations to Explanatory Factors. *Journal of the American Water Resources Association* 38, no. 1: p. 301-311.

Kolpin, D.W., Schnoebelen, D.J., and Thurman, E.M., 2004, Degradates provide insight to spatial and temporal trends of herbicides in ground water: *Ground Water*, v. 42, no. 4, p. 601-608.

Lapworth, D.J., D.C. Goody, M.E. Stuart, P.J. Chilton, G. Cachandt, M. Knapp, and S. Bishop. 2005. Pesticides in Groundwater: Some Observations on Temporal and Spatial Trends. *Water and Environment, Journal* 20, no. 2; p. 55-64.

McGrath, D. (1998). Persistent organochlorines in soils of the Republic of Ireland. In: British Society of Soil Science Autumn Meeting, Queen's University, Belfast, 09-Sep-1998, page 11 2024 A2

Met Eireann - The Irish Meteorological Service Online (www.met.ie).

National Climatic Data Center ds463.3 <http://dss.ucar.edu/datasets/ds463.3/>

Olsen, P., J. Kjaer, M. Ullum, and R. Grant, 2005. Leaching of Glyphosate and Amino-Methylphosphonic Acid from Danish Agricultural Field Sites. *Journal of Environmental Quality* 34, p. 608-620.

Pesticide Control Service, 2006a. Pesticide Usage Survey - Grassland and Fodder Crops 2003. The Department of Food and Agriculture, 2006.

Pesticide Control Service, 2006b. Correspondence to CDM.

Pesticide Control Service, 2007a. Annual Report - Pesticides 2007. February 2007. (<http://www.pcs.agriculture.gov.ie/Docs/Pesticides2007.pdf>)

Pesticide Control Service, 2007b. Pesticide Usage Survey - Arable Crops 2004. The Department of Food and Agriculture, 2007.

Seybolda, C.A., W. Mersie, and C. McNameeb. 2001. Anaerobic Degradation of Atrazine and Metolachlor and Metabolite Formation in Wetland Soil and Water Microcosms. *Journal of Environmental Quality* 30:1271-1277.

SNIFFER (Scotland and Northern Ireland Forum for Environmental Research). 2006. Provision of a Screening Tool to Identify and Characterise Diffuse Pollution Pressures: Phase II. Project WFD19 230/8050. January 2006.

Teagasc, 2006a. Soil map derived from interpretation of subsoils and landcover data. Spatial Analysis Unit, Teagasc. June 2006.

Teagasc, 2006b. Subsoil map derived from interpretation of stereo photographs and compilation of all existing published soil parent material/subsoil and Quaternary geology data. Spatial Analysis Unit, Teagasc. June 2006.

Stuart, M., D.C. Gooddy, A.G. Hughes, and C.R. Jackson. 2006. A Field and Modeling Study to Determine Pesticide Occurrence in a Public Water Supply in Northern England, UK. *Groundwater Monitoring and Remediation* 26, no.4. Fall 2006: 128-136.

United States Geological Survey, 2007. Pesticides in the Nation's Streams and Groundwater, 1991-2002. National Water Quality Assessment Program, Circular No. 1291.

Working Group on Groundwater, 2005. Methodology for Risk Characterisation of Ireland's Groundwater: Guidance Document No. 8.

Zhang, Dr. Chaosheng and Dr. Aidan Moody. 2004. Relevance to Ireland of EU FOCUS Scenarios for Assessing Pesticide Leaching to Groundwater. November 2004.

TABLES

**Table 1:
Pesticide Related Land Uses and Associated Activities in the Republic of Ireland**

Main Sector	Primary Use	Subsector	Activity
Agriculture – Arable	1. Seed treatment – protection from pest in field/store, prevention of germination 2. Herbicides – Clearance of crop area, pre- and post- emergence weed control, spot treatment of weed species, pre-harvest treatments and desiccation 3. Insecticides – Pre-planting pest control, prophylactic and pest-specific treatment, in-store protection 4. Fungicides – seed treatment, prophylactic and disease specific treatments	Cereal Crops	Winter wheat
			Winter barley
			Spring wheat
			Spring barley
		Root crops	Oats
	Potatoes		
	Beet		
Agriculture – Grassland	Herbicide – spot treatment for specific weeds	Livestock	Grazing
		Forage	Forage crops
			Silage
Forestry	Herbicide and Insecticides - weed and pest control	State-owned (Coillte)	Coniferous
		Private	Coniferous
			Broadleaf
Transport	Weed control	Road	
		Rail	
		Airports	
Industry	Weed control	Industrial facilities	
Urban Amenity	Weed and pest control	Open managed space	Parks
			Recreational areas
Other	Weed and pest control	Golf Courses	Golf
	Pest control	Sheep Dip	Sheep dipping

Table 2:
Quantities (kg) of Active Ingredients (or Combinations of Active Ingredients)
Applied in Overall Treatments for Grassland and Fodder Crops

Active Ingredient/Combination	CROP						Total
	Grass	Maize	Fodder beet	Silage	Swedes/ Turnips	Kale/ Rape	
Herbicides							
2,4-D	16,998						16,998
2,4-D, dicamba, triclopyr	4,774						4,774
2,4-DB, benazolin (-ethyl), MCPA	11,063						11,063
2,4-DB, linuron, MCPA	422						422
2,4-DB, MCPA	5,296			4,777			10,073
2,4-DB, mecoprop-P	1,466						1,466
aclonifen			89				89
amidosulfuron	790			25			815
asulam	5,410						5,410
atrazine		24,152					24,152
bentazone, MCPB				1,132			1,132
bromoxynil		1,557					1,557
carfentrazone-ethyl, metsulfuron (-methyl)				56			56
clopyralid		9	45				54
clopyralid, fluroxypyr, triclopyr	1,870						1,870
clopyralid, triclopyr	33						33
desmedipham, ethofumesate, phenmedipham			778				778
dicamba, MCPA, mecoprop	11,804						11,804
dicamba, MCPA, mecoprop-P	8,322			284			8,606
dicamba, mecoprop	125						125
dicamba, mecoprop-P	4,762						4,762
dichlorprop	1,461						1,461
dichlorprop, MCPA, mecoprop-P	10,688						10,688
diffenican, isoproturon				209			209
ethofumesate, metamitron, phenmedipham			9				9
ethofumesate, phenmedipham			1,178				1,178
fluzifop-P (-butyl)		6	11				17
fluroxypyr	423	108					531
fluroxypyr, triclopyr	11,185						11,185
glyphosate	73,939	2,379	91	8,605	167	334	85,515
glyphosate trimesium	426						426
haloxyfop-R			13				13
iodosulfuron-methyl-sodium				9			9
isoproturon				174			174
lenacil			571				571
MCPA	181,823			858			182,681
mecoprop	8,572			1,328			9,900
mecoprop-P	60,000			1,670			61,670
metamitron			2,882				2,882
metazachlor					193		193
metsulfuron (-methyl)	3			2			5
metsulfuron (-methyl), thifensulfuron (-methyl)				21			21
pendimethalin		7,627		626			8,253
propachlor					450	99	549
propaquizafop			30				30
pyridate		1,005					1,005
quizalofop-P			24				24
rimsulfuron		0+					0
terbuthylazine, terbutryn				2,798			2,798
thifensulfuron (-methyl)	195						195
tribenuron (-methyl)				4			4
triclopyr	568						568
trifluralin					609	44	653
triflusulfuron (-methyl)			65				65
Fungicides							
azoxystrobin				937			937
carbendazim, flusilazole			433	140			573
chlorothalonil				6,903			6,903
cyproconazole			5				5
cyproconazole, propiconazole				95			95
cyprodinil, propiconazole				118			118
epoxiconazole				925			925
epoxiconazole, fenpropimorph				129			129
epoxiconazole, kresoxim methyl				267			267
fenpropidin				1,079			1,079
fenpropimorph				357	29		386
flusilazole			14				14
mancozeb, metalaxyl					571		571
prochloraz				566			566
tebuconazole				233			233

Table 2:
Quantities (kg) of Active Ingredients (or Combinations of Active Ingredients)
Applied in Overall Treatments for Grassland and Fodder Crops

Active Ingredient/Combination	CROP						Total
	Grass	Maize	Fodder beet	Silage	Swedes/ Turnips	Kale/ Rape	
Insecticides							
bendiocarb			14				14
carbofuran		362	67		43		472
carbofuran, isofenphos					55		55
chlorpyrifos	235				52	49	336
cypermethrin				71	1	1	73
deltamethrin				0+		0+	
dimethoate				458			458
esfenvalerate			1	15			16
oxydemeton-methyl			10				10
pirimicarb					20		20
Growth regulators							
chlormequat				5,490			5,490
chlormequat, choline chloride, imazaquin				2,021			2,021
ethephon, mepiquat				892			892
Seed treatments							
carboxin, fludioxonyl, guazatine, imazalil, tebuconazole, thiram				155			155
carboxin, guazatine, imazalil, thiram				809			809
carboxin, guazatine, thiram				41			41
carboxin, thiram				96			96
fludioxonyl		13					13
fludioxonyl, guazatine				10			10
fludioxonyl, metalaxyl-M		4					4
fludioxonyl, metalaxyl, metalaxyl-M, methiocarb		83					83
guazatine				380			380
guazatine, imazalil				440			440
hymexazol			46			10	56
iprodione					7		7
metalaxyl		2					2
methiocarb		1,832	22			5	1,859
thiram			26		8	6	40
Molluscicides							
methiocarb		47	18				65
All Pesticides	422,653	39,186	6,442	45,205	2,205	548	516,239

Table 3:
Total Amounts of Active Ingredients used – In Order by Weight – for Grassland and Fodder Crops

Rank	Active Ingredient	Total kgs	Rank	Active Ingredient	Total kgs
1	MCPA	221,883	44	isoproturon	349
2	glyphosate	93,056	45	chlorpyrifos	337
3	mecoprop-P	74,598	46	ethephon	301
4	atrazine	24,152	47	thiram	293
5	2,4-D	23,458	48	simazine	269
6	mecoprop	21,761	49	carboxin	253
7	2,4-DB	18,839	50	thifensulfuron (-methyl)	238
8	triclopyr	11,450	51	tebuconazole	233
9	pendimethalin	8,253	52	metazachlor	193
10	chlormequat	7,364	53	carbendazim	191
11	asulam	7,354	54	choline chloride	143
12	dichlorprop	6,989	55	paraquat	140
13	chlorothalonil	6,903	56	kresoxim methyl	133
14	fluroxypyr	6,887	57	cyprodinil	95
15	dicamba	3,868	58	aclonifen	89
16	metamitron	2,888	59	propiconazole	82
17	methiocarb	2,007	60	cypermethrin	73
18	terbutryn	1,958	61	desmedipham	71
19	bromoxynil	1,557	62	metalaxyl	65
20	guazatine	1,359	63	triflusulfuron (-methyl)	65
21	ethofumesate	1,130	64	imazalil	62
22	epoxiconazole	1,091	65	hymexazol	56
23	fenpropidin	1,079	66	carfentrazone-ethyl	47
24	clopyralid	1,007	67	linuron	45
25	pyridate	1,005	68	cyproconazole	42
26	benazolin (-ethyl)	973	69	diflufenican	35
27	azoxystrobin	937	70	propaquizafop	30
28	amidosulfuron	920	71	quizalofop-P	24
29	terbuthylazine	839	72	pirimicarb	20
30	phenmedipham	758	73	fludioxonyl	19
31	trifluralin	653	74	metsulfuron (-methyl)	19
32	mepiquat	591	75	isofenphos	18
33	lenacil	571	76	fluazifop-P (-butyl)	16
34	prochloraz	566	77	esfenvalerate	16
35	bentazone	566	78	bendiocarb	14
36	MCPB	566	79	haloxyfop-R	13
37	propachlor	549	80	oxydemeton-methyl	10
38	carbofuran	508	81	iodosulfuron-methyl-	9
39	mancozeb	508	82	iprodione	7
40	fenpropimorph	482	83	imazaquin	4
41	dimethoate	458	84	tribenuron (-methyl)	4
42	glyphosate trimesium	426	85	metalaxyl-M	1
43	flusilazole	396		Total quantity	567,287

Table 4:
Quantities (kg) of Active Ingredients (or Combinations of Active Ingredients) Applied in Overall Treatments for Arable Crops

Active Ingredient/Combination	CROP															Total
	Spring barley	Winter barley	Spring wheat	Winter wheat	Spring oats	Winter oats	Oilseed rape	Peas	Beans	Linseed	Potatoes	Set-aside	Non-food	Lupins	Sugar beet	
Herbicides																
2,4-DB, benazolin (-ethyl), MCPA	1,181															1,181
2,4-DB, MCPA	1,587															1,587
amidosulfuron	32	8		73				13						1		127
bromoxynil, fluroxypyr, ioxynil	246															246
bromoxynil, ioxynil	1,920	97	216		288									76		2,597
carfentrazone-ethyl, metsulfuron (-methyl)	596	3		7						2						608
clopyralid			395	274												808
clodanifop																205
cyanazine																414
cycloxydim															11,137	11,137
desmedipham, ethofumesate, phenmedipham																-
dicamba, MCPA, mecoprop-P	2,791		223		277											3,291
dicamba, mecoprop-P	4,930	111		504												5,545
dichlorprop	6,276				1,270											7,546
dichlorprop-P, ioxynil	797															797
diflufenican, flurtamone								837								837
diflufenican, isoproturon		14,491		35,012										91		49,594
diquat (dibromide)								161			6,695					30
diquat (dibromide), paraquat											71					71
ethofumesate																1,674
ethofumesate, phenmedipham																10,017
fenoxaprop (ethyl)	61		45	81												187
fenoxaprop-P (ethyl)	456	82	221	459												1,218
fenoxaprop-M (isopropyl)	664	67														731
florasulam				14	2	7										23
fluaizop-P (-butyl)																202
fluroxypyr	2,621		204	1,388	60	148										4,421
glyphosate	40,733	6,084	7,834	28,596	1,720	4,236	759		542		2,458	8,012	153	56	13,481	114,664
haloxyfop-R																14
iodosulfuron-methyl-sodium	42		2	8												52
isoproturon	2,689	8,051	2,733	39,455						143				155		53,226
isoproturon , pendimethalin				26,592												26,592
lenacil																6,446
linuron											190					190
MCPA	3,529	1,183	528	848	48							1,097				7,233
mecoprop	7,759		1,044		188											8,991
mecoprop-P	82,544	619	16,609	2,803	726	3,039				97						106,437
metamitron																29,113
metribuzin											7,538					7,538
metsulfuron (-methyl)	197	2	1,656	16	16	8				1			3			1,899
metsulfuron (-methyl), thifensulfuron (-methyl)	1,125		149	42						4				1		1,321
metsulfuron (-methyl), tribenuron (-methyl)	210		104		6	17										337
paraquat	423									111	4,400					4,934
pendimethalin				1,382											50	1,432
propachlor											5					5
proprazine											3					378
propyzamide							205									205
quizalofop-P																10
rimsulfuron											5					5
simazine								1,949			3,628					5,577
sulfosulfuron																
sulphuric acid																
terbutylazine, terbutryn											147,059					147,059
thifensulfuron (-methyl), tribenuron (-methyl)	459		47						341							341
tralkoxydim	4,454	522														5,066
tribenuron (-methyl)	16,971	20	2,975	62	4	59										20,091
trifluralin (-methyl)																1,050

Table 4:
Quantities (kg) of Active Ingredients (or Combinations of Active Ingredients) Applied in Overall Treatments for Arable Crops

Active Ingredient/Combination	CROP																Total
	Spring barley	Winter barley	Spring wheat	Winter wheat	Spring oats	Winter oats	Oilseed rape	Peas	Beans	Linseed	Potatoes	Set-aside	Non-food	Lupins	Sugar beet		
Fungicides																	
azoxystrobin	6,249	1,180	2,894	8,243	273	982		47	85					6	3	19,962	
azoxystrobin, fenpropimorph	973	135	177	1,096		730								58		3,169	
benlaviy, mancozeb									167		2,225					2,392	
bromuconazole	104															104	
carbendazim	993		135	2,157					1,043							4,328	
carbendazim, flusilazole	17,623	1,613	239	730	386										3,886	24,477	
chlorothalonil	76,159	13,657	13,162	72,664		1,729		484	2,543		1,101			245	6	181,750	
chlorothalonil, flutriafol			1,631	8,808												10,439	
copper oxychloride											231					231	
cyazofamid											512					512	
cymoxanil											1,279					1,279	
cymoxanil, famoxodone											92					92	
cymoxanil, mancozeb											25,465					25,465	
cymoxanil, mancozeb, oxadixyl											4,048					4,048	
cyproconazole	48		162		18										14	242	
cyproconazole, cyprodinil	272															272	
cyproconazole, prochloraz				3,560										46		3,606	
cyproconazole, propiconazole	1,042		325	1,383	115	427										3,292	
cyproconazole, trifloxystrobin		45	286	1,261		1,201										2,513	
cyprodinil		104		1,320												1,424	
cyprodinil, propiconazole	5,196	4,173														9,369	
difenoconazole	52		101	121											107	381	
dimethomorph, mancozeb											10,496					10,496	
dimoxystrobin, epoxiconazole			75	644												719	
dithianon											356					356	
epoxiconazole	3,137	991	2,637	10,373	10	92								5		17,245	
epoxiconazole, fenpropimorph	756	179		1,538												2,473	
epoxiconazole, fenpropimorph, kresoxim methyl	797				69	152										1,018	
epoxiconazole, kresoxim methyl	8,209	1,117	1,233	1,364	179	661										12,763	
epoxiconazole, kresoxim methyl, pyraclostrobin	625															625	
famoxodone, flusilazole	727	692														1,419	
fenpropidin	5,454		1,820	1,255	51	764										9,344	
fenpropidin, fenpropimorph						72										72	
fenpropidin, propiconazole, tebuconazole	268															268	
fenpropidin, tebuconazole						116										116	
fenpropimorph	37,000	2,853	6,130	7,553	2,117	1,417								47	8	57,125	
fenpropimorph, flusilazole	1,511															1,511	
fenpropimorph, propiconazole	485															485	
fenpropimorph, quinoxifen	1,542	85	123	792	446	3,330										6,318	
fentin hydroxide											4,458					4,458	
fluazinam											11,121					11,121	
fluazinam, metalaxyl M											75					75	
fluquinconazole			161	1,251										15		1,427	
fluquinconazole, prochloraz			330	5,482												5,812	
flusilazole	2,591	885	224													3,700	
iprodione									42							42	
mancozeb				1,464					802		80,474					82,740	
mancozeb, metalaxyl							170				2,802					2,972	
mancozeb, metalaxyl M											18,689					18,689	
mancozeb, propamocarb											5,493					5,493	
mancozeb, zoxamide											14,041					14,041	
maneb											3,200					3,200	
metconazole			59	335												394	
picoxystrobin	4,974	918	62	109												6,063	
prochloraz		971	495	8,647										44		10,157	
propamocarb											221					221	
propiconazole	775	31		522		24									34	1,388	
pyraclostrobin	43	59	120	276												498	
quinoxifen	113		131						97							341	
spiroxamine	883		747			380										2,010	
spiroxamine, tebuconazole	1,594	115	1,880	9,073	1,068	2,187		53								15,970	
tebuconazole	214	6	406	1,910	207	508	62		27					24		3,364	
trifloxystrobin	1,530	397	27	470										11		2,435	

Table 4:
Quantities (kg) of Active Ingredients (or Combinations of Active Ingredients) Applied in Overall Treatments for Arable Crops

Active Ingredient/Combination	CROP															Total
	Spring barley	Winter barley	Spring wheat	Winter wheat	Spring oats	Winter oats	Oilseed rape	Peas	Beans	Linseed	Potatoes	Set-aside	Non-food	Lupins	Sugar beet	
Insecticides																
alpha-cypermethrin				37							52					89
bifenthrin	8															8
carbofuran															1,199	1,199
carbofuran, isofenphos															90	90
chlorpyrifos	2,984		109	446							26				311	3,876
cypermethrin	1,530	55	253	328	35	46			2		1					2,250
deltamethrin	40	6	4	43							903		29		27	1,052
dimethoate	3,865	686	2,475	7,860	134	950	65		29	144	1				451	16,662
esfenvalerate	395	75	109	216	9	39	1			1	55		1		2	903
lambda-cyhalothrin	11	28		20	3	13					854					929
oxydemeton-methyl	234		421	456						11	509				111	1,742
pirimicarb	134								16	15	4					169
triazamate						7										7
Growth regulators																
chlormequat	2,902	7,713	26,928	78,433	4,532	26,083									324	146,915
chlormequat, choline chloride, imazaquin		226	367	8,597												9,190
dimethipin											174					174
ethephon	553	1,037	412	358		256										2,616
ethephon, mepiquat chloride		1,020	1,944	4,299	293											7,556
maleic hydrazide											419					419
trinexapac ethyl	100	71		155	43	193								5		567
Seed treatments																
beta-cyflthrin, imidacloprid							28			40				2		70
carboxin, thiram	6,902	1,119	405	709	97	176										9,408
cymoxanil, fludioxonil, metalaxyl M								31								31
quazatine	299		2,197	6,518	90	35								28		9,167
quazatine, imazalil	10,878	1,417	29		488	1,709										14,521
imazalil											313					313
imazalil, pencycuron											346					346
imazalil, tebuconazole	38															38
imidacloprid															1,611	1,611
iprodione											4					4
methiocarb															71	71
prochloraz										1						1
propamocarb															457	457
silthiofam		64	181	665												910
thiobendazole											10					10
thiobendazole, thiram														10		10
thiram							32		618					2	190	842
Molluscicides																
metaldehyde											267					267
methiocarb		105		170			53				1,654				2,183	4,165
thiodicarb											84					84
All Pesticides	398,105	75,168	106,591	401,347	15,268	52,740	1,589	950	8,243	145	364,107	9,112	1,371	135	85,720	1,520,591

Table 5:
Total Amounts of Active Ingredients Used – In Order by Weight – for Arable Crops

Rank	Active Ingredient	Total kgs	Rank	Active Ingredient	Total kgs
1	chlorothalonil	190,776	65	carbofuran	1,259
2	mancozeb	157,295	66	fenoxaprop-P (ethyl)	1,219
3	chlormequat	155,970	67	metalaxyl M	1,141
4	sulphuric acid	147,059	68	desmedipham	1,063
5	glyphosate	116,731	69	dimethomorph	1,061
6	mecoprop-P	112,058	70	trisulfuron (-methyl)	1,050
7	isoproturon	107,852	71	silthiofam	910
8	fenpropimorph	68,157	72	esfenvalerate	850
9	metamitron	29,113	73	pyraclostrobin	831
10	epoxiconazole	24,888	74	dicamba, mecoprop-P	826
11	guazatine	22,571	75	clopyralid	808
12	flusilazole	21,203	76	famoxodone	733
13	azoxystrobin	20,795	77	flamprop-M (isopropyl)	730
14	tribenuron (-methyl)	20,485	78	pirimicarb	674
15	prochloraz	17,729	79	clodinafop	669
16	dimethoate	17,592	80	dich,lorprop-P	647
17	pendimethalin	14,727	81	flurtamone	598
18	ethofumesate	13,983	82	trinexapac ethyl	567
19	carbendazim	12,487	83	dimoxystrobin	522
20	spiroxamine	12,426	84	cyazofamid	512
21	fluzinam	11,171	85	carfentrazone-ethyl	486
22	MCPA	10,012	86	oxadixyl	482
23	fenpropidin	9,593	87	maleic hydrazide	419
24	cyprodinil	9,159	88	cycloxydim	414
25	tebuconazole	9,034	89	metconazole	394
26	mecoprop	8,992	90	difenoconazole	381
27	diflufenican	8,505	91	propaquizafop	378
28	phenmedipham	7,782	92	dithianon	356
29	dichlorprop	7,546	93	metalaxyl M	330
30	metribuzin	7,538	94	pencycuron	330
31	diquat (dibromide)	6,915	95	metaldehyde	267
32	kresoxim methyl	6,868	96	benalaxyl	262
33	lenacil	6,446	97	terbutryn	239
34	picoxystrobin	6,063	98	copper oxychloride	231
35	simazine	5,576	99	propyzamide	205
36	thiram	5,552	100	cyanazine	205
37	propiconazole	5,445	101	fluazifop-P (-butyl)	202
38	ethephon	5,162	102	linuron	190
39	mepiquat chloride	5,009	103	fenoxaprop (ethyl)	187
40	paraquat	4,977	104	dimethipin	174
41	tralkoxydim	4,976	105	lambda-cyhalothrin	131
42	carboxin	4,704	106	amidosulfuron	127
43	fluroxpyr	4,497	107	deltamethrin	120
44	fentin hydroxide	4,458	108	chlolin chloride	115
45	trifloxystrobin	4,407	109	benazolin (-ethyl)	104
46	methiocarb	4,235	110	bromuconazole	104
47	chlorpyrifos	3,850	111	terbuthylazine	102
48	maneb	3,200	112	alpha-cypermethrin	89
49	propamocarb	3,156	113	thiodicarb	84
50	cymoxanil	3,108	114	iodosulfuron-methyl-sodium	51
51	cyproconazole	2,870	115	iprodine	46
52	fluquinconazole	2,803	116	beta-cyfluthrin	35
53	metsulfuron (-methyl)	2,277	117	isofenphos	30
54	cypermethrin	2,274	118	florasulam	23
55	2,4-DB	2,272	119	imazaquin	20
56	oxydemeton-methyl	2,086	120	haloxyfop-R	15
57	quicoxyfen	1,672	121	thiabendazole	14
58	imidacloprid	1,646	122	triazamate	11
59	zoxamide	1,554	123	quizalofop-P	10
60	ioxynil	1,533	124	befenthrin	8
61	thefensulfuron (-methyl)	1,513	125	rimsulfuron	5
62	imazalil	1,467	126	fludioxonil	5
63	flutriafol	1,414	127	propachlor	5
64	bromoxynil	1,383	128	sulfosulfuron	2
				Total Quantity	1,522,655

**Table 6:
Estimated Use of Glyphosate in Forestry**

	Total Area of Forest	Estimated Area in the Establishment Phase	Use of glyphosate in 2006 (kg a.i.)
Coillte	397,675	36,376	1,015 ^[1]
Private	311,588	35,000 ^[2]	1,563 ^[3]

Note:

[1] - Actual data from Coillte records

[2] - Assumes a 30/70 ratio for conifer/broadleaf trees

[3] - Assuming conifers receive one application and broadleaves three during the establishment phase

**Table 7:
Pesticides Used for Road Maintenance by
Dublin City Council Contractors**

Contractor	Length Road Treated	Product	Active Ingredient	Amount
A	397km	Glyphosate 360	glyphosate	366 litres
		Diuron	diuron	133 litres
B	477 km	Glyphosate 360	glyphosate	79 litres
		Karmex	diuron	77kg
C	216 km	No return received		

Source: Central Laboratory, Dublin City Council

**Table 8:
Pesticide Products Purchased by Dublin City Council
for Parkland Maintenance, 2004/2005**

Area	Chemical Products (with notes)	Quantity
Northwest	No triazine products used for a number of years prior to 2004	
North Central West	None in past 2 years	
North Central East	Nomix Total (glyphosate+ diuron)	38.5 litres
(St. Anne's Park/ Par 3 Golf/Nursery)	Nomix Simflex (glyphosate + Simazine)	25.0 litres
	Ronstar (oxadiazon)	16.0 litres
	Basflex (=Basta + carrier) (glufosinate-ammonium)	40.0 litres
Central Southeast	Casoron G (dichlobenil)	1000 kg
	Suscon Green (chlorpyrifos)	10 kg
	Simflex (glyphosate + simazine)	65 litres
	Diuron	65 litres
	Basflex (=Basta + carrier) (glufosinate-ammonium)	40 litres
	Casoron G (dichlobenil)	1000 kg
	Ronstar (oxadiazon)	1 litre
	No Simazine/Atrazine used in last 2 years	
	Basta (glufosinate-ammonium)	100 litres
	Roundup (glyphosate)	80 litres
	Ronstar (oxadiazon)	20 kg
	Ronstar liquid (oxadiazon)	2 litres
	Altix 240 (triclopyr, butoxythyl ester, triclopyr acid)	5 litres
	Casoron G (dichlobenil)	1250 kg
	Basta (glufosinate-ammonium)	100 litres
	Roundup (glyphosate)	80 litres
	Casoron G (dichlobenil)	1250 kg
	South Central West	No Simazine/Atrazine products used.
South Central East	Gesatop (2.5 litres not used to date)	50 litres
Contractors:		
A	Triflex	200 litres
	Simflex (glyphosate + simazine)	150 litres
	Diuron	185 litres
	Roundup (glyphosate)	240 litres
	Casoron G (dichlobenil)	200 kg
	Cleanflex Greenway	10 litres
	Roundup Bio Active (glyphosate + carrier)	80 litres
	Enforcer (dichlorophen)	5 litres

**Table 9:
List of Approved Chemicals for Golf Courses, Ireland (2003)**

Active Ingredient	Use	Type	Generic Name
carbendazim	Fungicide	benzimidazole	methyl 1 <i>H</i> -benzimidazol-2-ylcarbamate
chlorothalonil	Fungicide	chloronitrile	2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile
fenarimol	Fungicide	pyrimidine	a-(2-chlorophenyl)-a-(4-chlorophenyl)-5-pyrimidinemethanol
iprodione	Fungicide	dicarboximide	3-(3,5-dichlorophenyl)- <i>N</i> -(1-methylethyl)-2,4-dioxo-1-imidazolidinecarboxamide
propamocarb	Fungicide	carbamate	propyl [3-(dimethylamino)-propyl]carbamate-hydrochloride
thiophanate-methyl	Fungicide	benzimidazole	dimethyl [1,2-phenylenebis(iminocarbonothioyl)]bis[carbamate]
chlorpyrifos	Insecticide	organophosphate	<i>O,O</i> -diethyl <i>O</i> -(3,5,6-trichloro-2-pyridinyl) phosphorothioate
2,4-D	Herbicide	aryloxyalkanoic acid	(2,4-dichlorophenoxy)acetic acid
clopyralid	Herbicide	pyridinecarboxylic acid	,6-dichloro-2-pyridinecarboxylic acid
dicamba	Herbicide	benzoic acid	3,6-dichloro-2-methoxybenzoic acid
dichlorophen	Herbicide	herbicide(moss)	2,2'-methylenebis[4-chlorophenol]
dichloroprop-P	Herbicide	aryloxyalkanoic acid	(2 <i>R</i>)-2-(2,4-dichlorophenoxy)propanoic acid
iron sulphate	Herbicide	-	-
MCPA	Herbicide	aryloxyalkanoic acid	(4-chloro-2-methylphenoxy)acetic acid
mecoprop-P	Herbicide	aryloxyalkanoic acid	(2 <i>R</i>)-2-(4-chloro-2-methylphenoxy)propanoic acid
triclopyr	Herbicide	pyridinecarboxylic acid	[(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid

Source: PCS

**Table 10:
Estimated Total Quantities of Selected Active Ingredients by Land Use**

Estimated Quantities (kg/yr) by Landuse									
Active Ingredient [1,7]	Managed Grassland [2]	Fodder Crops [2]	Arable Cereal [3]	Arable Root [3,8]	Arable Other [3,9]	Forestry [4]	Urban Amenity [5]	Transport [5]	Estimated Total [6]
atrazine	not licensed	24,152	not licensed	not licensed	not licensed	345	not licensed	not licensed	24,497
MCPA	181,823	858	6,136	0	1,097	n/a	n/a	n/a	189,914
2,4-D	16,998	0	0	0	0	n/a	n/a	n/a	16,998
isoproturon	0	174	52,928	0	298	n/a	n/a	n/a	53,400
mecoprop-P	60,000	1,670	106,340	0	97	n/a	n/a	n/a	168,107
glyphosate	73,939	11,576	89,203	15,939	9,522	1,015	14,371	9,693	225,258
chlorothalonil	0	6,903	177,371	1,101	3,278	n/a	n/a	n/a	188,653
mancozeb	0	0	1,464	80,474	802	n/a	n/a	n/a	82,740
chlormequat	0	5,490	146,591	0	324	n/a	n/a	n/a	152,405

Note:

[1] - Commonly used, high volume, and/or high intrinsic mobility (see Tables 11 and 12)

[2] - Source: PCS, 2006 (Pesticide Usage Survey, Grasslands and Fodder Crops)

[3] - Source: PCS, 2007b (Pesticide Usage Survey, Arable Crops)

[4] - Source: Coillte, reported values for 2006

[5] - Estimated by this study (many herbicides are likely used, but reliable estimates cannot be made)

[6] - Minimum

[7] - Does not include use in combinations of active ingredients; i.e., only individual ingredients are considered

[8] - Potatoes, sugar beet

[9] - Oilseed rape, peas, beans, set-aside, lupins, non-food

n/a = no information or no estimate possible

**Table 11:
Chemical Properties and Groundwater Ubiquity Scores
for Relevant Active Ingredients**

Active Ingredient	Type	DT ₅₀ (Days)[1]	Koc (ml/g)	GUS	Potential Groundwater Risk[2]
atrazine	Herbicide	75	100	3.75	High
triclopyr	Herbicide	39	48	3.69	High
bentazone	Herbicide	13	51	2.55	High
asulam	Herbicide	24	138	2.57	Moderate
imazapyr	Herbicide	11	125	1.98	Moderate
MCPA	Herbicide	15	74	2.51	Moderate
2,4-D	Herbicide	10	56	2.25	Moderate
isoproturon	Herbicide	12	139	2	Moderate
mecoprop-P	Herbicide	8	31	2.27	Moderate
diuron	Herbicide	75.5	1067	1.83	Moderate
glyphosate	Herbicide	12	21,699	-0.36	Low
epoxiconazole	Fungicide	354	1,802	1.90	Moderate
mancozeb	Fungicide	0.1	998	-1.00	Low
chlorothalonil	Fungicide	22	850	1.44	Low
cypermethrin	Insecticide	60	85,572	-1.66	Low
esfenvalerate	Insecticide	44	5,300	0.45	Low
chlorpyrifos	Insecticide	50	8,151	0.15	Low
DDT	Insecticide	6,200	100,000	-3.79	Low
dieldrin	Insecticide	1,400	12,000	-0.25	Low
chlormequat	Growth Regulator	10	168	1.77	Low
guazatine	Seed Treatment	500	14,150	-0.41	Low

Note:

Source of data is the FOOTPRINT database (FOOTPRINT, 2006).

[1] - DT₅₀ values listed are taken as "typical" values listed in the FOOTPRINT database.

[2] – Indicator of "leachability" (intrinsic mobility) based on chemical properties alone. GUS > 2.8, high mobility; <2.8 > 1.8, moderate mobility; <1.8, low mobility.

**Table 12:
Indicator List of Active Substances Recommended for Monitoring**

Active Ingredient	Main Use Areas	Reason for Selection
Primary[1]		
atrazine	Forage maize, forestry	High mobility, Historical use, Detected in NDSP[2], Frequently detected in drinking water supplies in England and Wales
simazine	Grassland, arable, forestry	Same family as Atrazine, detected in NDSP
MCPA	Grassland, arable, urban	High risk, high volumes, multiple formulations
2,4-D	Grassland, arable, urban	High risk, high volumes, multiple formulations
isoproturon	Arable	Widely used in arable sector, Reported in international case studies
mecoprop-P	Grassland, arable, urban	Moderate risk, high volume, multiple formulations
glyphosate	Forestry, urban, grassland, arable, transport	High volume, low risk, widespread use, increasing use
chlorothalonil	Fodder crops, arable	High volume, low risk
mancozeb	Arable	High volume, low risk
chlormequat	Fodder crops, arable	High volume, low risk
Secondary[3]		
isodrin	Arable, urban	Detected in NDSP, historical use
diuron	Grassland, arable, urban, transport	Widespread use, moderate risk
cypermethrin	Sheep dip	Licensed for sheep dip, waste disposal practices (slurry landspreading), detected in NDSP
dibutyl tin	Urban/industry	Detected in NDSP
DDT (2,4'-, 4,4'-)	Grassland, arable, urban	Historical use, high toxicity, reported in soils in Wexford
lindane	Grassland, arable, urban	Historical use, high toxicity, reported in soils in Wexford
dieldrin	Grassland, arable, urban	Historical use
bentazone	Grassland, arable, urban	Detected frequently in the UK

Note:

[1] – High volume active ingredients (including triazine group indicators)

[2] - NDSP = National Dangerous Substances Programme.

[3] – Active ingredients less widely used but included on basis of historical use and/or high toxicity

Table 13:
Pesticide Detections in Groundwater from the National Dangerous Substances Programme

Parameter	Target EQS	Limit of Detection (ug/L)	Number of Detections	Maximum Detected (ug/L) May 2005 - May 2006	No Detections (<)
Gorey					
atrazine	0.1	0.01	8	0.0173	5
isoproturon	0.1	0.01	0	<	13
mecoprop	0.02	0.02	0	<	13
MCPA	0.1	0.01	0	<	13
2,4-D	0.1	0.02	0	<	13
chlorotoluron	0.4	0.02	0	<	13
glyphosate	0.1	0.1	0	<	13
lindane	0.01	0.005	0	<	13
dieldrin	0.005	0.005	1	0.006	12
2,4'-DDT	0.01	0.002	0	<	13
4,4'-DDT	0.01	0.002	0	<	13
simazine	0.02	0.01	0	<	13
bentazone	0.1	0.02	0	<	13
Boyle					
atrazine	0.1	0.01	8	0.0316	5
isoproturon	0.1	0.01	0	<	13
mecoprop	0.02	0.02	0	<	13
MCPA	0.1	0.01	0	<	13
2,4-D	0.1	0.02	0	<	13
chlorotoluron	0.4	0.02	0	<	13
glyphosate	0.1	0.1	0	<	13
lindane	0.01	0.005	0	<	13
dieldrin	0.005	0.005	1	0.009	12
2,4'-DDT	0.01	0.002	0	<	13
4,4'-DDT	0.01	0.002	1	0.005	12
simazine	0.02	0.01	5	0.0436	8
bentazone	0.1	0.02	0	<	13
Ballinamuck					
atrazine	0.1	0.01	3	0.0137	10
isoproturon	0.1	0.01	0	<	13
mecoprop	0.02	0.02	1	0.0291	12
MCPA	0.1	0.01	0	<	13
2,4-D	0.1	0.02	0	<	13
chlorotoluron	0.4	0.02	0	<	13
glyphosate	0.1	0.1	0	<	13
lindane	0.01	0.005	0	<	13
dieldrin	0.005	0.005	1	0.0101	12
2,4'-DDT	0.01	0.002	0	<	13
4,4'-DDT	0.01	0.002	0	<	13
simazine	0.02	0.01	1	0.0139	12
bentazone	0.1	0.02	0	<	13

**Table 13:
Pesticide Detections in Groundwater from the National Dangerous Substances Programme**

Parameter	Target EQS	Limit of Detection (ug/L)	Number of Detections	Maximum Detected (ug/L) May 2005 - May 2006	No Detections (<)
Athy					
atrazine	0.1	0.01	0	<	13
isoproturon	0.1	0.01	0	<	13
mecoprop	0.02	0.02	0	<	13
MCPA	0.1	0.01	0	<	13
2,4-D	0.1	0.02	0	<	13
chlorotoluron	0.4	0.02	0	<	13
glyphosate	0.1	0.1	0	<	13
lindane	0.01	0.005	0	<	13
dieldrin	0.005	0.005	1	0.006	12
2,4'-DDT	0.01	0.002	0	<	13
4,4'-DDT	0.01	0.002	0	<	13
simazine	0.02	0.01	1	0.026	12
bentazone	0.1	0.02	0	<	13

Other Detections

Parameter	No. of Detections	Maximum Detected (ug/L) May 2005 - May 2006	No Detection (<)
Gorey			
anthracene	6	0.012	7
Boyle			
diuron	2	0.018	10
isodrin	1	0.016	11
endrin	1	0.027	11
anthracene	4	0.011	8
Ballinamuck			
anthracene	2	0.002	10
dichlorprop	1	0.023	11
Athy			
anthracene	2	0.009	10

Table 14: Summary of Detections of Pesticides in Groundwater in England and Wales: 1998-2004¹

England and Wales														
Pesticides	Total Number of Samples							Percent of Samples over 0.1 µg/l ²						
	1998	1999	2000	2001	2002	2003	2004	1998	1999	2000	2001	2002	2003	2004
Most commonly found pesticides														
atrazine	1,204	529	892	515	693	1,194	1,491	10.80	4.10	2.47	3.69	2.67	4.27	2.62
bentazone	488	285	452	347	439	995	1,483	2.25	0.40	1.55	2.59	0.23	5.03	0.88
mecoprop	622	443	629	413	619	878	1,484	1.29	9.90	0.64	1.45	3.00	0.23	0.74
clopyralid	-	-	262	423	404	500	1,394	-	-	0.24	0.50	-	-	0.43
diuron	923	350	757	421	644	988	1,560	1.63	-	1.06	3.09	1.58	0.20	0.38
simazine	1,215	533	890	508	650	1,076	1,464	0.40	0.70	1.24	1.38	1.40	0.28	0.34
chlorotoluron	926	350	715	433	727	975	1,563	0.65	0.30	1.12	0.23	0.55	0.30	0.26
pirimicarb	-	-	55	93	22	75	805	-	-	-	-	-	-	0.25
metazachlor	-	-	-	-	-	60	788	-	-	-	-	-	-	0.25
cyanazine	-	-	314	314	152	240	933	-	-	1.08	-	-	0.42	0.21
monuron	-	-	72	72	141	120	936	-	-	-	-	-	0.83	0.21
triclopyr	451	362	580	382	468	793	1,456	-	0.60	0.34	-	0.26	-	0.14
dichlorprop	535	319	506	394	455	836	1,480	-	4.70	-	-	0.22	-	0.14
terbutryn	961	286	599	384	365	492	980	0.73	0.70	0.17	-	-	-	0.1
2,4-D	580	384	564	373	560	829	1,174	-	1.56	0.18	0.27	0.18	0.24	0.09
dicamba	583	381	618	406	470	528	1,231	-	2.89	0.16	-	-	0.38	0.08
trietazine	635	274	398	301	298	707	1,194	0.47	0.40	0.25	-	0.34	-	0.08
MCPA	606	384	610	407	488	839	1,454	0.20	2.34	-	-	0.83	0.24	0.07
isoproturon	963	371	756	435	517	1,007	1,563	1.97	1.10	0.53	1.61	0.19	0.20	0.06

Source: Environment Agency, 2006

- ¹ Data shown excludes known polluted sites and pollution incidents (aim is to represent pesticide concentrations in groundwater resulting from normal application of pesticides).
- ² Levels are for illustrative purposes only - see text. In some samples the Limit Of Detection (LOD) was greater than 0.1 µg/l

Source publication: e-Digest of Environmental Statistics, Published January 2006
 Department for Environment, Food and Rural Affairs
<http://www.defra.gov.uk/environment/statistics/index.htm>

**Table 15:
Summary of Processes Simulated in the PELMO Model**

Process	Approach
Water Movement	Capacity-based water flow (tipping bucket approach) using a daily time step for all hydrological processes
Substance Movement	Convection dispersion equation based on a daily time step
Crop Simulation	Changing root zone during growing season, changing foliage (areal extent) during growing season, crop interception of water*, crop interception of substances*, foliar wash off*, foliar degradation*
Degradation in Soil	First order degradation rate, correction of rate constant with depth, soil moisture, and soil temperatures
Substance Sorption to Soil	Kd, Koc, Freundlich equation for sorption option for increase of sorption with time option for automated pH-dependence*
Substance Volatilization (from soil)	Simple model using Fick's and Henry's law
Runoff	Soil Conservation Service curve number technique
Drainage and Preferential Flow	Not simulated
Soil Erosion*	Modified Universal Soil Loss Equation
Soil Temperature	An empirical model that uses air temperatures
Plant Uptake	Simple model based on soil concentrations
Substance Applications	Applications may be foliar sprays, applied to the soil surface, or incorporated into the soil; for soil incorporated applications a variety of soil distributions can be specified
Metabolism	A sophisticated scheme with up to 8 metabolites (A = B as well as A - B - C) may be simulated simultaneously

* = typically turned off for FOCUS scenarios

**Table 16:
Groundwater Vulnerability Categories**

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

Notes:

(1) N/A = not applicable

(2) Precise permeability values cannot be given at present.

(3) Release point of contaminants is assumed to be 1 - 2 m below ground surface.

Source: Geological Survey of Ireland

**Table 17:
Climate Data Used for Modeling**

Climate Data	Units	Source
Daily Precipitation	cm/day	Met Eireann, United States National Climatic Data Center (NCDC) and European Climate Assessment and Dataset (ECA&D)
Pan Evaporation	cm/day	Daily values were calculated from monthly evaporation data provided by Met Eireann (by dividing the monthly totals by the number of days in the month)
14th Hour Temperature (2:00 pm temperature)	°C	NCDC
Daily Mean Temperature	°C	NCDC
Difference Between Min. and Max. Temperature	°C	ECA&D
Relative Humidity	Percent	Used only when calculating potential evapotranspiration using the Haude model. As actual pan evaporation data were available, the relative humidity was not required.

**Table 18:
Soil and Subsoil Characteristics**

ID No.	Location	Texture	pH	TOC %	Bulk density (gm/cm³)	Field capacity (m³/m³)	Wilting point (m³/m³)	K sat m/s x10⁻⁶
1	Layer 1 - silty loam	Silty loam	7.288	0.838	1.301	0.341	0.113	3.976
2	Layer 1 - clay loam	Clay loam	7.767	0.613	1.435	0.362	0.210	1.957
3	Layer 2 - above silt/sand	Sandy loam/loam	6.463	1.185	1.374	0.289	0.083	7.238
4	Layer 2 - above sand	Sandy loam/loam sand	5.863	1.226	1.475	0.255	0.063	10.004
5	Layer 2 - above clay	Silty clay loam	8.100	1.007	1.373	0.373	0.241	0.100
6	Layer 3 - sand/silt	Sandy loam	5.880	1.461	1.399	0.283	0.082	8.758
7	Layer 3 – sand/gravel	Sand	5.683	0.208	1.568	0.166	0.024	20.640
8	Layer 3 - clay	Silty clay loam	8.000	1.390	1.300	0.374	0.253	0.010

**Table 19:
Pesticide Application Rates Used in Modeling**

Chemical	Crop	No. Applications	Application Dates	Application Rate (kg/ha)
Atrazine	Forage maize	1	1-May	1.875*
MCPA	Grassland	2	15-April; 15-July	1.409*
2,4-D	Arable**	1	1-May	1.237*
Glyphosate	Forest	1	1-May	1.0
Chlorotoluron	Arable**	1	1-May	1.237*

Note:

* - Maximum recommended application rate, per correspondence with PCS

** - Cereal crops, generally. Application dates for winter barley may apply one month earlier (April).

**Table 20:
Model Scenarios**

Scenario	Soil/Bedrock Description	Vulnerability'	Layer 1		Layer 2		Layer 3		
			Soil thickness (cm)	Texture	Subsoil Thickness (cm)	Texture	Subsoil Thickness (cm)	Subsoil Type	Subsoil Permeability
1	Silty Loam on Bedrock/Karst	X	10	Silty loam	90	Sandy loam	0		
2	Silty Loam on Bedrock/Karst	E	10	Silty loam	90	Sandy loam	200	Gravel/sand	High
3	Silty Loam on Bedrock/Karst	E	10	Silty loam	90	Silty clay loam	200	Clay	Low
4	Silty Loam on Bedrock/Karst	H	10	Silty loam	90	Sandy loam	900	Sand/silt	Moderate
4a	Silty Loam on Bedrock/Karst	H	10	Silty loam	90	Sandy loam	600	Sand/silt	Moderate
5	Silty Loam on Bedrock/Karst	H	10	Silty loam	90	Silty clay loam	400	Clay	Low
6	Silty Loam on Bedrock/Karst	M	10	Silty loam	90	Sandy loam	900	Sand/silt	Moderate
7	Silty Loam on Bedrock/Karst	M	10	Silty loam	90	Silty clay loam	900	Clay	Low
8	Silty Loam on Bedrock/Karst	L	10	Silty loam	90	Silty clay loam	900	Clay	Low
9	Silty Loam on Sand & Gravel	E	10	Silty loam	90	Sandy loam	200	Gravel/sand	High
10	Silty Loam on Sand & Gravel	H	10	Silty loam	90	Sandy loam	900	Gravel/sand	High

Notes:

- (1) Groundwater Vulnerability X = Extra Extreme (no layer 3)
 E = Extreme
 H = High
 M = Moderate
 L = Low

**Table 21:
Model Results**

Scenario	Vulnerability	Chemical	Rain	26 yr outflow (mm)	Mass (g/ha)	Yr to Break	Hi conc (µg/L)	Layer 1 cm – soil type	Layer 2 cm – soil type	Layer 3 cm – soil type
1	X	atrazine	val	15,558	4,320	4	47.3	10-silty loam	90 sandy loam	0
	X	atrazine	kil	8,277	1,073	6	22.4	10-silty loam	90 sandy loam	0
	X	MCPA	val	24,565	0	none	0	10-silty loam	90 sandy loam	0
	X	MCPA	kil	12,555	0	none	0	10-silty loam	90 sandy loam	0
	X	2,4-D	val	23,592	0	none	0	10-silty loam	90 sandy loam	0
	X	glyphosate	val	23,662	0	none	0	10-silty loam	90 sandy loam	0
	X	chlorotoluron	val	23,592	0	none	0	10-silty loam	90 sandy loam	0
2 (9)	E	atrazine	val	15,542	3,247	4	30.3	10-silty loam	90 sandy loam	200 gravel/sand
	E	atrazine	kil	8,288	674	7	15.2	10-silty loam	90 sandy loam	200 gravel/sand
3	E	atrazine	val	15,545	365	8	4.9	10-silty loam-3 % OC	90 silty clay loam	200 clay
	E	atrazine	val	15,545	300	8	4	10-silty loam-4.5% OC	90 silty clay loam	200 clay
	E	atrazine	val	15,545	248	8	2.7	10-silty loam-6 % OC	90 silty clay loam	200 clay
	E	atrazine	kil	8,288	7.8	14	0.24	10-silty loam-3 % OC	90 silty clay loam	200 clay
4 (6)	H	atrazine	val	15,593	0	none	0	10-silty loam	90 sandy loam	900 sand/silt
	H	atrazine	kil	Not modeled	0	none	0	10-silty loam	90 sandy loam	900 sand/silt
4a	H	atrazine	val	15,546	805	6	9.2	10-silty loam	90 sandy loam	600 sand/silt
	H	atrazine	kil	8,301	53.2	11	1.4	10-silty loam	90 sandy loam	600 sand/silt
5	H	atrazine	val	15,591	13.7	13	0.28	10-silty loam-3 % OC	90 silty clay loam	400 clay
	H	atrazine	val	15,591	10.5	13	0.18	10-silty loam-4.5% OC	90 silty clay loam	400 clay
	H	atrazine	val	15,591	8.1	13	0.13	10-silty loam-6 % OC	90 silty clay loam	400 clay
	H	atrazine	glen	9,651	0.062	22	0.005	10-silty loam	90 silty clay loam	400 clay
	H	atrazine	kil	8,297	0	none	0	10-silty loam	90 silty clay loam	400 clay
6 (4)	M	atrazine	val	15,593	0	none	0	10-silty loam	90 sandy loam	900 sand/silt
	M	atrazine	kil	Not modeled	0	none	0	10-silty loam	90 sandy loam	900 sand/silt
7 (8)	M	atrazine	val	15,814	0	none	0	10-silty loam	90 silty clay loam	900 clay
	M	atrazine	kil	Not modeled	0	none	0	10-silty loam	90 silty clay loam	900 clay
8 (7)	L	atrazine	val	15,814	0	none	0	10-silty loam	90 silty clay loam	900 clay
	L	atrazine	kil	Not modeled	0	none	0	10-silty loam	90 silty clay loam	900 clay
9 (2)	E	atrazine	val	15,542	3,247	4	30.3	10-silty loam	90 sandy loam	200 gravel/sand
	E	atrazine	kil	8,288	674	7	15.2	10-silty loam	90 sandy loam	200 gravel/sand
10	H	atrazine	val	15,565	970	6	10.6	10-silty loam	90 sandy loam	900 gravel/sand
	H	atrazine	kil	8,295	75.8	10	1.8	10-silty loam	90 sandy loam	900 gravel/sand
11 (19)	X	atrazine	val	17,218	5,254	4	49.7	10-clay loam	90 sandy loam	0
	X	atrazine	kil	9,034	1,385	6	25.4	10-clay loam	90 sandy loam	0
12	E	atrazine	val	17,217	4,039	4	37.8	10-clay loam	90 sandy loam	200 gravel/sand
	E	atrazine	kil	9,058	897	6	17.1	10-clay loam	90 sandy loam	200 gravel/sand

**Table 21:
Model Results**

Scenario	Vulnerability	Chemical	Rain	26 yr outflow (mm)	Mass (g/ha)	Yr to Break	Hi conc (µg/L)	Layer 1 cm – soil type	Layer 2 cm – soil type	Layer 3 cm – soil type
13	E	atrazine	val	17,217	581	7	6.4	10-clay loam	90 silty clay loam	200 clay
	E	atrazine	kil	9,058	17	13	0.43	10-clay loam	90 silty clay loam	200 clay
14 (16)	H	atrazine	val	17,201	0.001	none	0	10-clay loam	90 sandy loam	900 sand/silt
	H	atrazine	kil	Not modeled	0	none	0	10-clay loam	90 sandy loam	900 sand/silt
15	H	atrazine	val	17,267	34.5	12	0.54	10-clay loam	90 silty clay loam	400 clay
	H	atrazine	kil	9,067	0.009	24	0.001	10-clay loam	90 silty clay loam	400 clay
16 (14)	M	atrazine	val	17,201	0.001	none	0	10-clay loam	90 sandy loam	900 sand/silt
	M	atrazine	kil	Not modeled	0	none	0	10-clay loam	90 sandy loam	900 sand/silt
17 (18)	M	atrazine	val	Not modeled	0	none	0	10-clay loam	90 silty clay loam	900 clay
	M	atrazine	kil	Not modeled	0	none	0	10-clay loam	90 silty clay loam	900 clay
18 (17)	L	atrazine	val	Not modeled	0	none	0	10-clay loam	90 silty clay loam	900 clay
	L	atrazine	kil	Not modeled	0	none	0	10-clay loam	90 silty clay loam	900 clay
19 (12)	E	atrazine	val	17,218	5,254	4	37.8	10-clay loam	90 sandy loam	200 gravel/sand
	E	atrazine	kil	9,034	1,385	6	17.1	10-clay loam	90 sandy loam	200 gravel/sand
20	H	atrazine	val	17,235	1,346	5	12.5	10-clay loam	90 sandy loam	900 gravel/sand
	H	atrazine	kil	9,063	122	9	2.4	10-clay loam	90 sandy loam	900 gravel/sand

**Table 22:
Simulated Infiltration Rates**

Chemical	Crop	Valentia		Glenamaddy		Kilkenny	
		Total Rainfall (mm/yr)	Perco-lation (mm/yr)	Total Rainfall (mm/yr)	Perco-lation (mm/yr)	Total Rainfall (mm/yr)	Perco-lation (mm/yr)
Atrazine	Forage maize	1,586	600 - 660	1,037	370	868	320 - 350
MCPA	Grassland	1,586	940	1,037	Nm	868	480
2,4-D	Arable, winter barley	1,586	910	1,037	Nm	868	Nm
Glyphosate	Forest	1,586	910	1,037	Nm	868	Nm
Chlorotoluron	Arable, winter barley	1,586	910	1,037	Nm	868	Nm

Nm = not modeled

Table 23:
Suggested Average Groundwater Flow Rates for
Different Aquifer Categories

Unit	Parameter	Aquifer Category							
		PI, Pu Lower	PI, Pu Upper	LI Lower	LI Upper	Lm Lower	Lm Upper	S&G Lower	S&G Upper
K (m/d)	Hydraulic conductivity - weathered layer	1	1	1	1	1	1	n/a	n/a
K (m/d)	Hydraulic conductivity - bedrock	0.05	0.5	0.1	1	1	10	5	50
i	Average flow gradient	0.005	0.05	0.005	0.05	0.001	0.05	0.001	0.05
A (m ² /d)	Unit cross-sectional area	1	1	1	1	1	1	1	1
Q (m ³ /day)	Darcy flow - weathered layer	0.0050	0.0500	0.0050	0.0500	0.0010	0.0500	n/a	n/a
Q (m ³ /day)	Darcy flow - bedrock layer	0.0003	0.0250	0.0005	0.0500	0.0010	0.5000	0.0050	2.5000
Q (m ³ /year)	Darcy flow - bedrock layer	0.09	9.13	0.18	18.25	0.37	182.50	1.83	912.50

Suggested Average Darcy Flow (m ³ /yr)			
PI, Pu	LI	Lm	S&G
3	5	10	50

Table 24: Simulated Leachate Concentrations, Computed Dilution, and Resulting Groundwater Concentrations

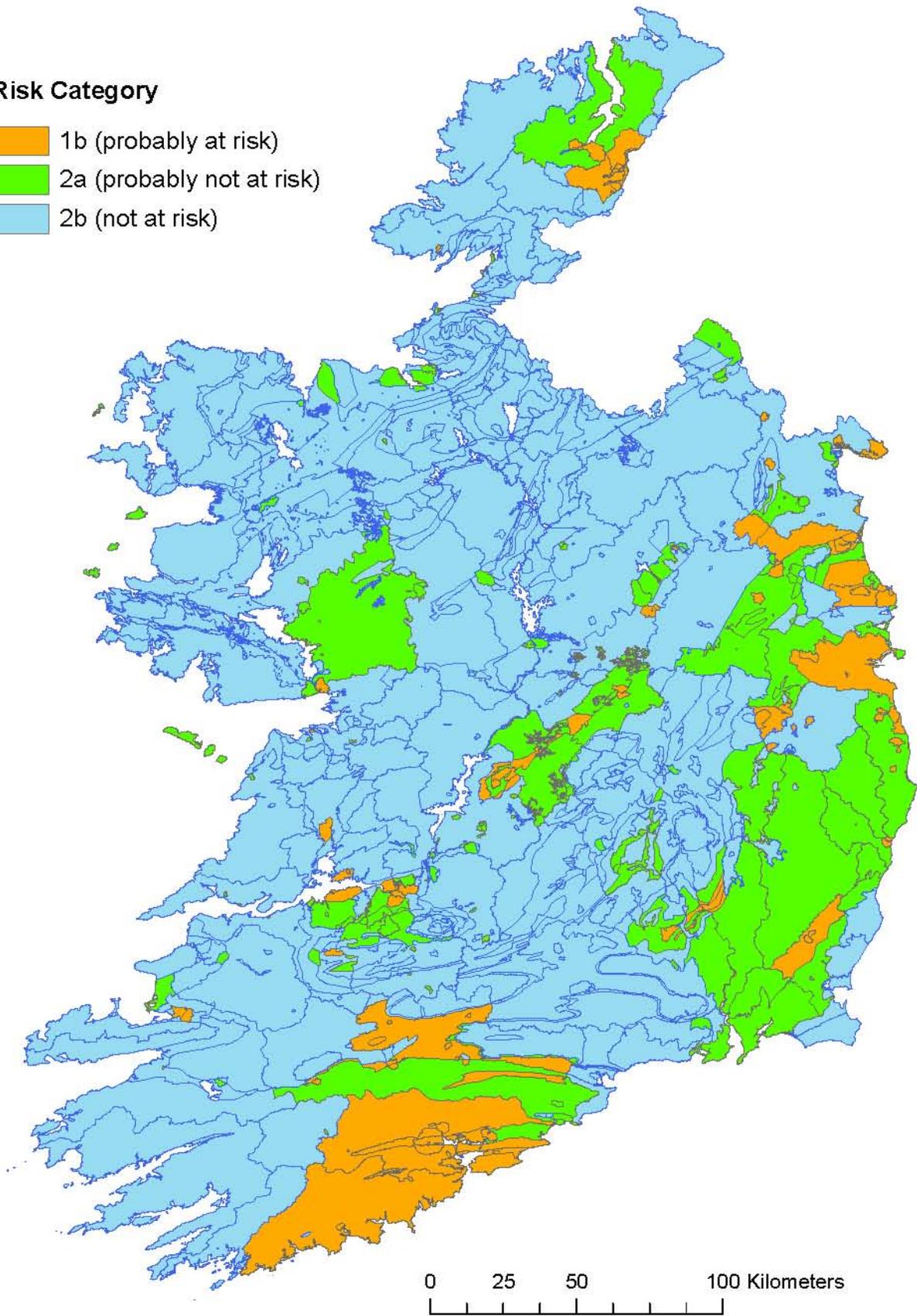
Bed Dilution	Vuln[1]	Active Ingredient	Rainfall Station	26 yr outflow (mm)[2]	Annual outflow (m3/yr) per unit area[3]	Darcy Q for PPA (m3/yr) per unit area[4]	Darcy Q for Fissured LI (m3/yr) per unit area	Darcy Q for Fissured Lm (m3/yr) per unit area	Darcy Q for S&G (m3/yr) per unit area	Dilution for PPA[5]	Dilution for Fissured LI	Dilution for Fissured Lm	Dilution for S&G	Hi conc (ug/L)[6]	Mixing Conc (ug/L) for PPA[7]	Mixing Conc (ug/L) for FI LI	Mixing Conc (ug/L) for FI Lm	Mixing Conc (ug/L) for S&G	Breakthrough after year[8]
1	X	atrazine	Valentia	15,558	0.60	3	5	10	50	6	9	18	85	47.30	7.87	5.06	2.67	0.56	4
	X	atrazine	Kilkenny	8,277	0.32	3	5	10	50	10	17	32	158	22.40	2.15	1.34	0.69	0.14	6
	X	MCPA	Valentia	24,565	0.94	3	5	10	50	4	6	12	54	0.00					none
	X	MCPA	Kilkenny	12,555	0.48	3	5	10	50	7	11	22	105	0.00					none
	X	2,4-D	Valentia	23,592	0.91	3	5	10	50	4	7	12	56	0.00					none
	X	glyphosate	Valentia	23,662	0.91	3	5	10	50	4	6	12	56	0.00					none
	X	chlorotoluron	Valentia	23,592	0.91	3	5	10	50	4	7	12	56	0.00					none
	2 (9)	E	atrazine	Valentia	15,542	0.60	3	5	10	50	6	9	18	85	30.30	5.03	3.24	1.71	0.36
	E	atrazine	Kilkenny	8,288	0.32	3	5	10	50	10	17	32	158	15.20	1.46	0.91	0.47	0.10	7
	3	E	atrazine	Valentia	15,545	0.60	3	5	10	50	6	9	18	85	4.90	0.81	0.52	0.28	0.06
	E	atrazine	Valentia	15,545	0.60	3	5	10	50	6	9	18	85	4.00	0.66	0.43	0.23	0.05	8
	E	atrazine	Valentia	15,545	0.60	3	5	10	50	6	9	18	85	2.70	0.45	0.29	0.15	0.03	8
	E	atrazine	Kilkenny	8,288	0.32	3	5	10	50	10	17	32	158	0.24	0.02	0.01	0.01	0.00	14
	4 (6)	H	atrazine	Valentia	15,593	0.60	3	5	10	50	6	9	18	84	0.00				
	H	atrazine	Kilkenny	not modeled															
	4a	H	atrazine	Valentia	15,546	0.60	3	5	10	50	6	9	18	85	9.20	1.53	0.98	0.52	0.11
	H	atrazine	Kilkenny	8,301	0.32	3	5	10	50	10	17	32	158	1.40	0.13	0.08	0.04	0.01	11
	5	H	atrazine	Valentia	15,591	0.60	3	5	10	50	6	9	18	84	0.28	0.05	0.03	0.02	0.00
	H	atrazine	Valentia	15,591	0.60	3	5	10	50	6	9	18	84	0.18	0.03	0.02	0.01	0.00	13
	H	atrazine	Valentia	15,591	0.60	3	5	10	50	6	9	18	84	0.13	0.02	0.01	0.01	0.00	13
	H	atrazine	Glenamaddy	9,651	0.37	3	5	10	50	9	14	28	136	0.01	0.00	0.00	0.00	0.00	22
	H	atrazine	Kilkenny	8,297	0.32	3	5	10	50	10	17	32	158	0.00					none
6 (4)	M	atrazine	Valentia	15,593	0.60	3	5	10	50	6	9	18	84	0.00					none
	M	atrazine	Kilkenny	not modeled															
7 (8)	M	atrazine	Kilkenny	15,814	0.61	3	5	10	50	6	9	17	83	0.00					none
	M	atrazine	Valentia	not modeled															
8 (7)	L	atrazine	Valentia	15,814	0.61	3	5	10	50	6	9	17	83	0.00					none
	L	atrazine	Kilkenny	not modeled															
9 (2)	E	atrazine	Valentia	15,542	0.60	3	5	10	50	6	9	18	85	30.30	5.03	3.24	1.71	0.36	4
	E	atrazine	Kilkenny	8,288	0.32	3	5	10	50	10	17	32	158	15.20	1.46	0.91	0.47	0.10	7
10	H	atrazine	Valentia	15,565	0.60	3	5	10	50	6	9	18	85	10.60	1.76	1.13	0.60	0.13	6
	H	atrazine	Kilkenny	8,295	0.32	3	5	10	50	10	17	32	158	1.80	0.17	0.11	0.06	0.01	10
11 (19)	X	atrazine	Valentia	17,218	0.66	3	5	10	50	6	9	16	77	49.70	8.99	5.81	3.09	0.65	4
	X	atrazine	Kilkenny	9,034	0.35	3	5	10	50	10	15	30	145	25.40	2.64	1.65	0.85	0.18	6
12	E	atrazine	Valentia	17,217	0.66	3	5	10	50	6	9	16	77	37.80	6.83	4.42	2.35	0.49	4
	E	atrazine	Kilkenny	9,058	0.35	3	5	10	50	10	15	30	145	17.10	1.78	1.11	0.58	0.12	6
13	E	atrazine	Valentia	17,217	0.66	3	5	10	50	6	9	16	77	6.40	1.16	0.75	0.40	0.08	7
	E	atrazine	Kilkenny	9,058	0.35	3	5	10	50	10	15	30	145	0.43	0.04	0.03	0.01	0.00	13
14 (16)	H	atrazine	Valentia	17,201	0.66	3	5	10	50	6	9	16	77	0.00					none
	H	atrazine	Kilkenny	not modeled															
15	H	atrazine	Valentia	17,267	0.66	3	5	10	50	6	9	16	76	0.54	0.10	0.06	0.03	0.01	12
	H	atrazine	Kilkenny	9,067	0.35	3	5	10	50	10	15	30	144	0.00	0.00	0.00	0.00	0.00	24
16 (14)	M	atrazine	Valentia	17,201	0.66	3	5	10	50	6	9	16	77	0.00					none
	M	atrazine	Kilkenny	not modeled															
17 (18)	M	atrazine	Valentia	not modeled															
	M	atrazine	Kilkenny	not modeled															
18 (17)	L	atrazine	Valentia	not modeled															
	L	atrazine	Kilkenny	not modeled															
19 (12)	E	atrazine	Valentia	17,218	0.66	3	5	10	50	6	9	16	77	37.80	6.84	4.42	2.35	0.49	4
	E	atrazine	Kilkenny	9,034	0.35	3	5	10	50	10	15	30	145	17.10	1.77	1.11	0.57	0.12	6
20	H	atrazine	Valentia	not modeled															
	H	atrazine	Kilkenny	not modeled															

- Notes:
- vulnerability category
 - calculated outflow, in mm, from model over 26-year simulation period
 - calculated annual outflow, in m, from model
 - calculated groundwater flow through poorly productive aquifer (PPA)
 - dilution factor calculated as (groundwater throughflow + infiltration)/infiltration
 - simulated high concentration
 - concentration/dilution factor
 - time of simulated breakthrough at bottom of layer 3

FIGURES

Risk Category

-  1b (probably at risk)
-  2a (probably not at risk)
-  2b (not at risk)



eastern
river basin district



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CDM

Article V Risk Assessment 2005

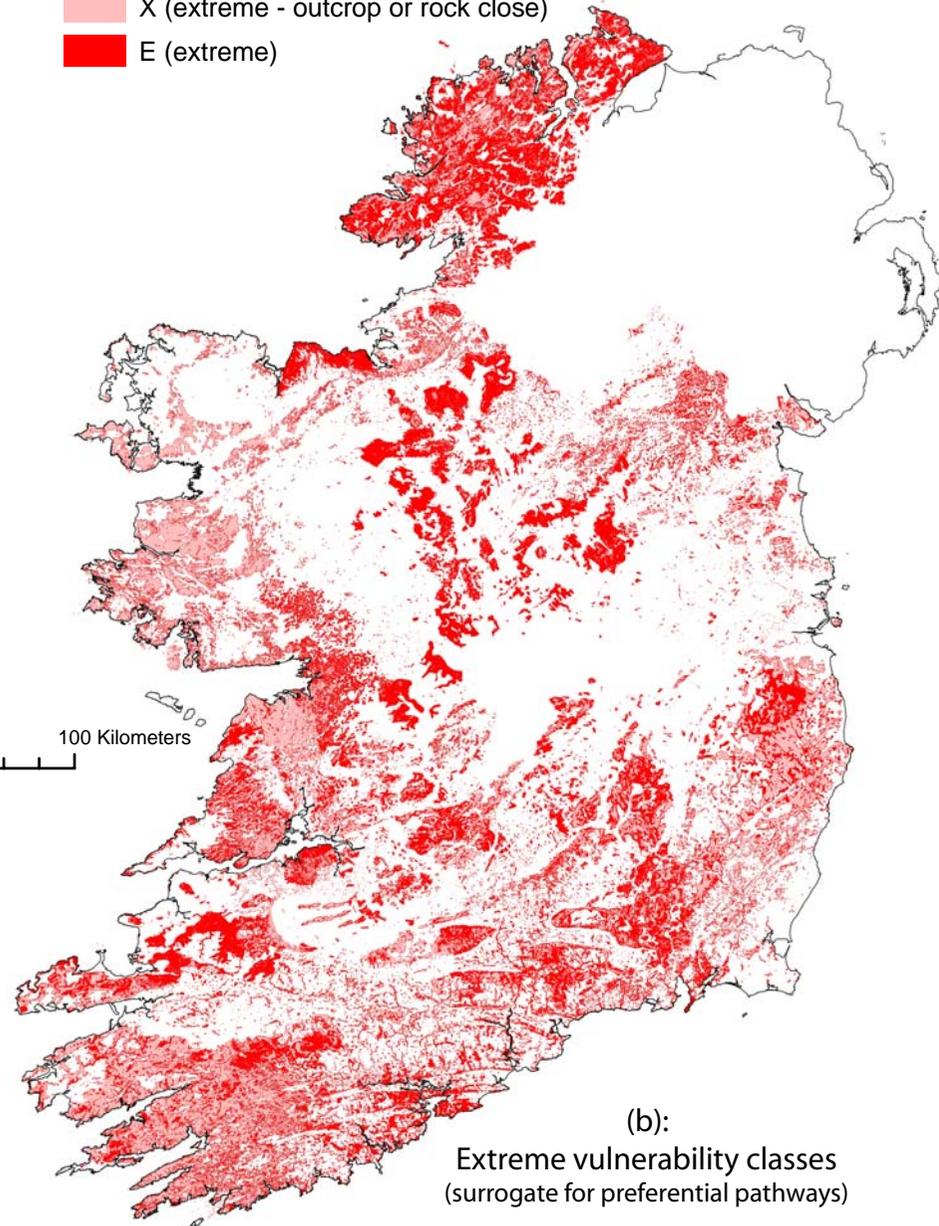
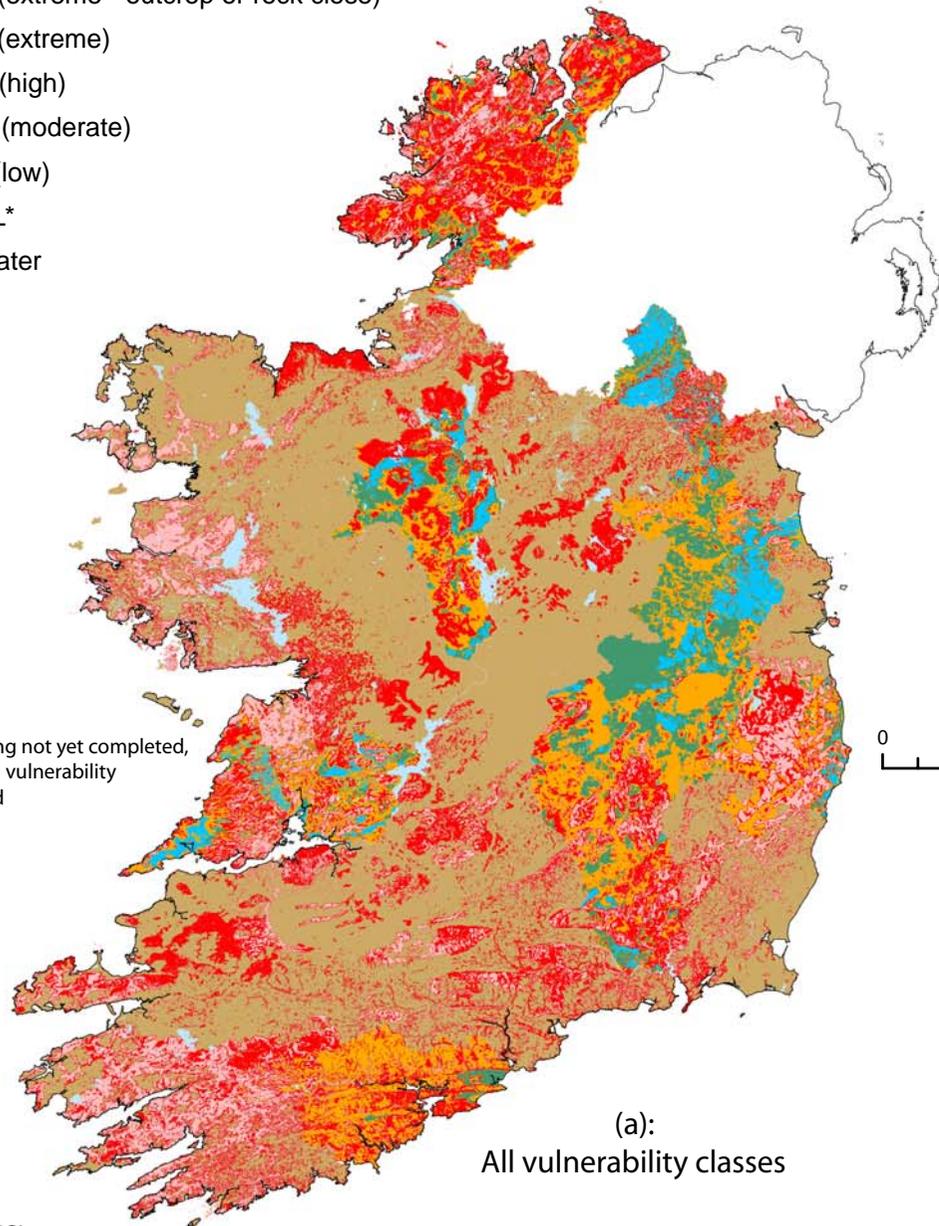
Figure
1

- X (extreme - outcrop or rock close)
- E (extreme)
- H (high)
- M (moderate)
- L (low)
- HL*
- Water

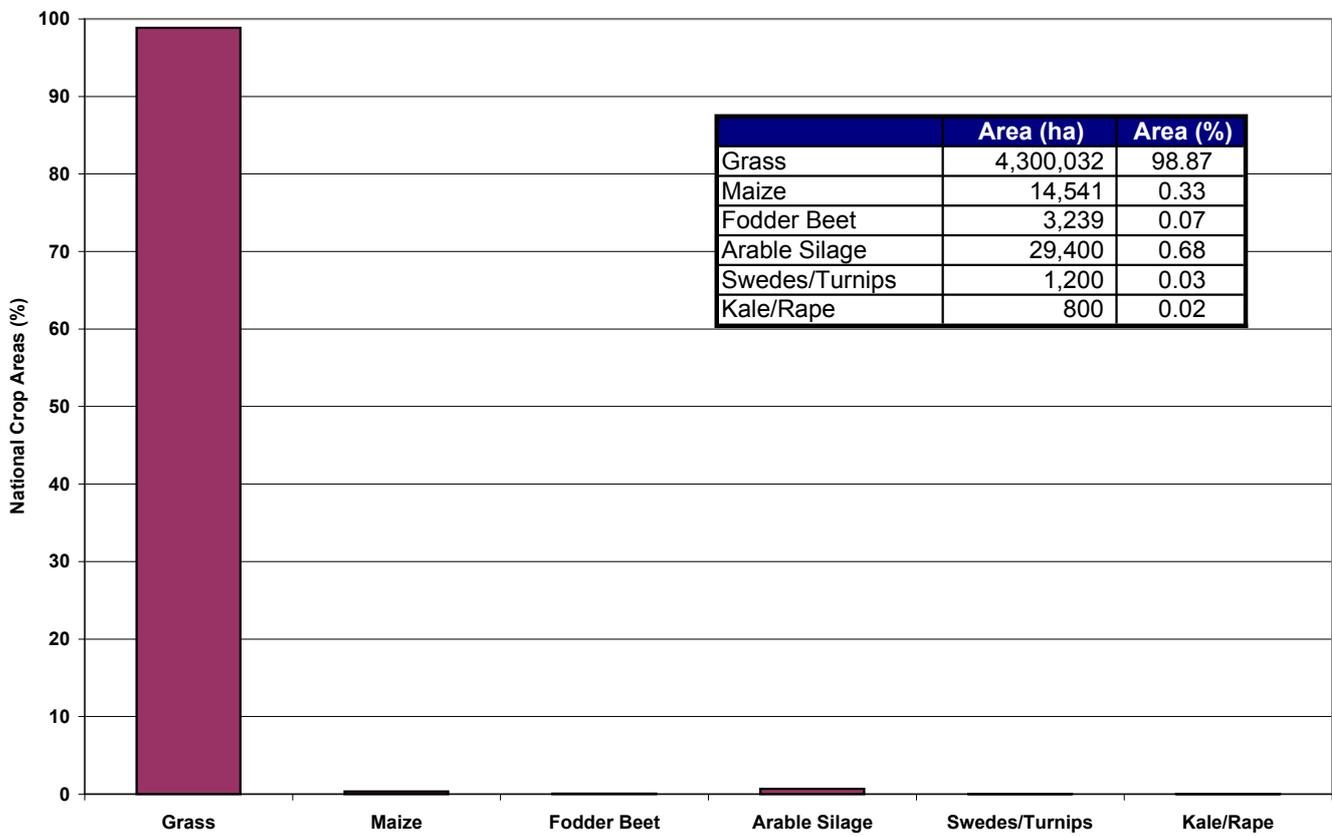
- X (extreme - outcrop or rock close)
- E (extreme)

* - mapping not yet completed, and a high vulnerability is assumed

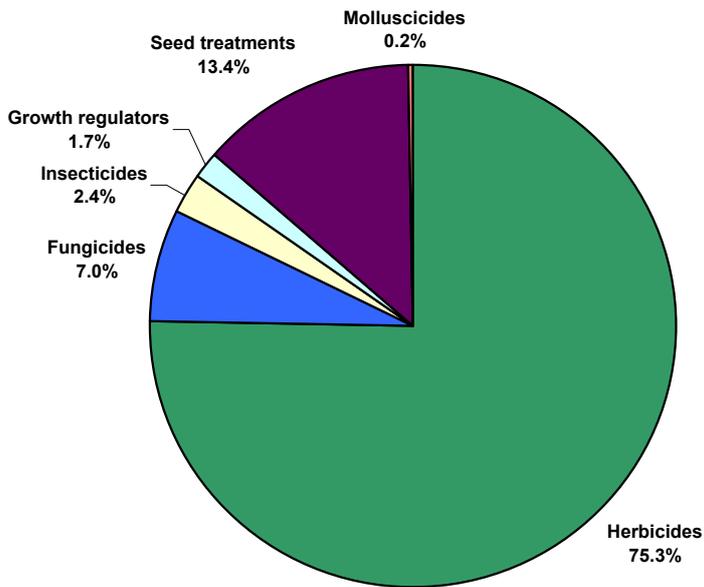
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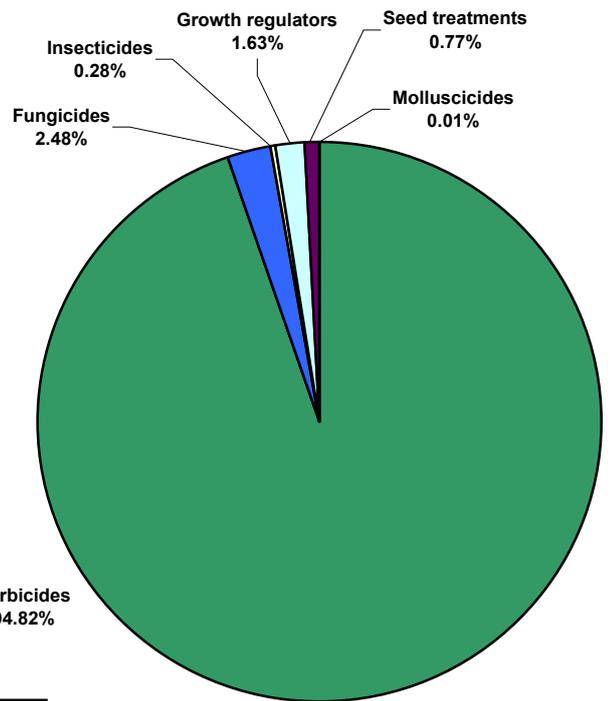
Source: GSI



National Grassland and Fodder Crop Areas (Expressed as Proportions)



Proportions of Pesticides Used by (Spray) Area Treated



Proportions of Pesticides Used by Quantities of Active Substances Applied

	Spray Hectares	Quantities Applied (Kg)
Herbicides	405,469	489,521
Fungicides	37,539	12,801
Insecticides	13,066	1,454
Growth regulators	9,272	8,403
Seed treatments	72,336	3,995
Molluscicides	1,031	65

Source: PCS, 2006

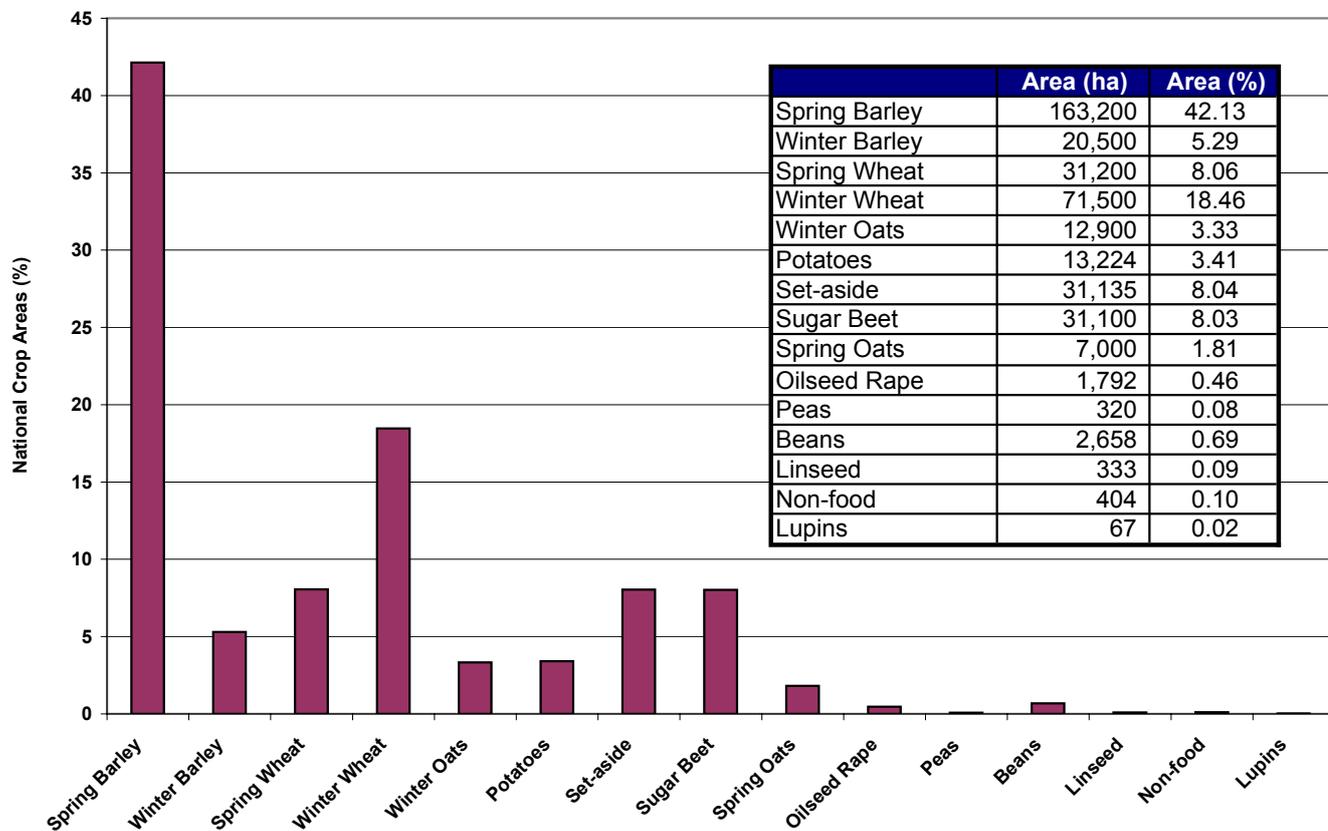


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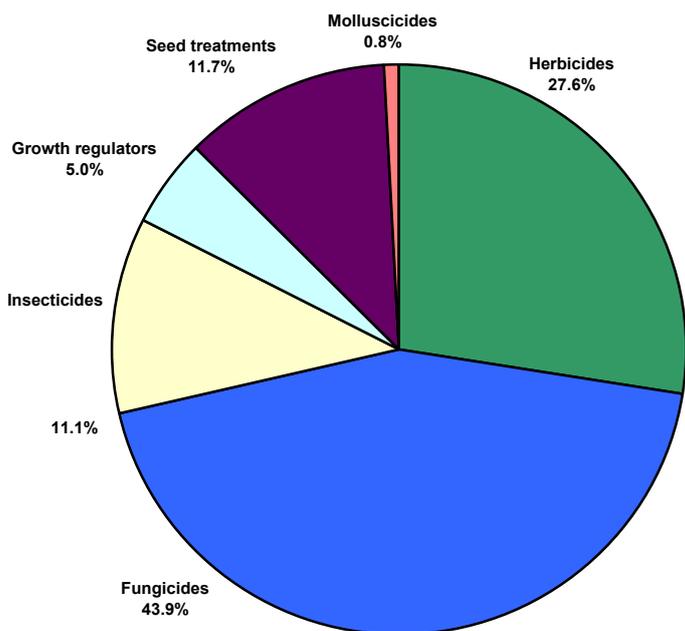


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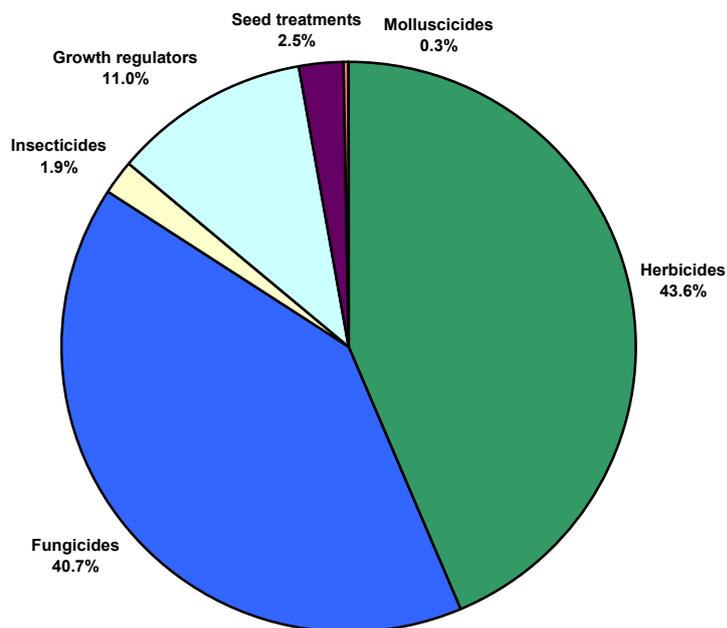




National Arable Crop Areas (Expressed as Proportions)



Proportions of Pesticides Used by (Spray) Area Treated



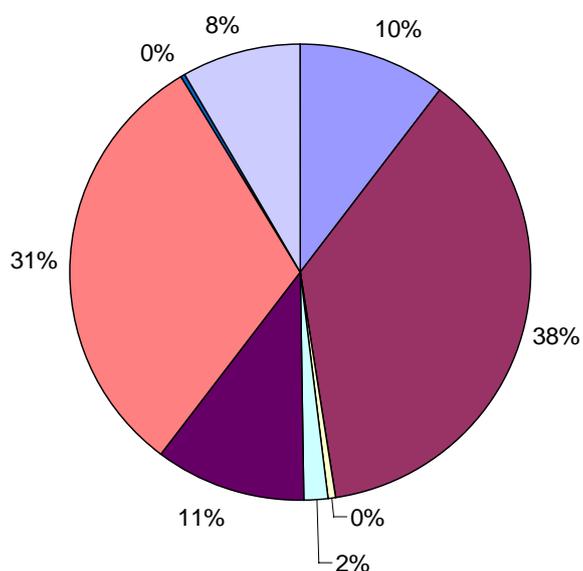
Proportions of Pesticides Used by Quantities of Active Substances Applied

	Spray Hectares	Quantities Applied (Kg)
Herbicides	1,074,171	663,238
Fungicides	1,710,235	618,612
Insecticides	431,373	28,973
Growth regulators	195,847	167,435
Seed treatments	455,610	37,810
Molluscicides	30,789	4,516
Miscellaneous	47	-

Source: PCS, 2007b

Pesticide use in Coillte 2006

■ alpha-cypermethrin
 ■ cypermethrin
 ■ imazapyr
 ■ asulam
 ■ atrazine
 ■ glyphosate
 ■ propyzamide
 ■ triclopyr



Pesticide Use (Kg active ingredient) Used by Coillte (2006)

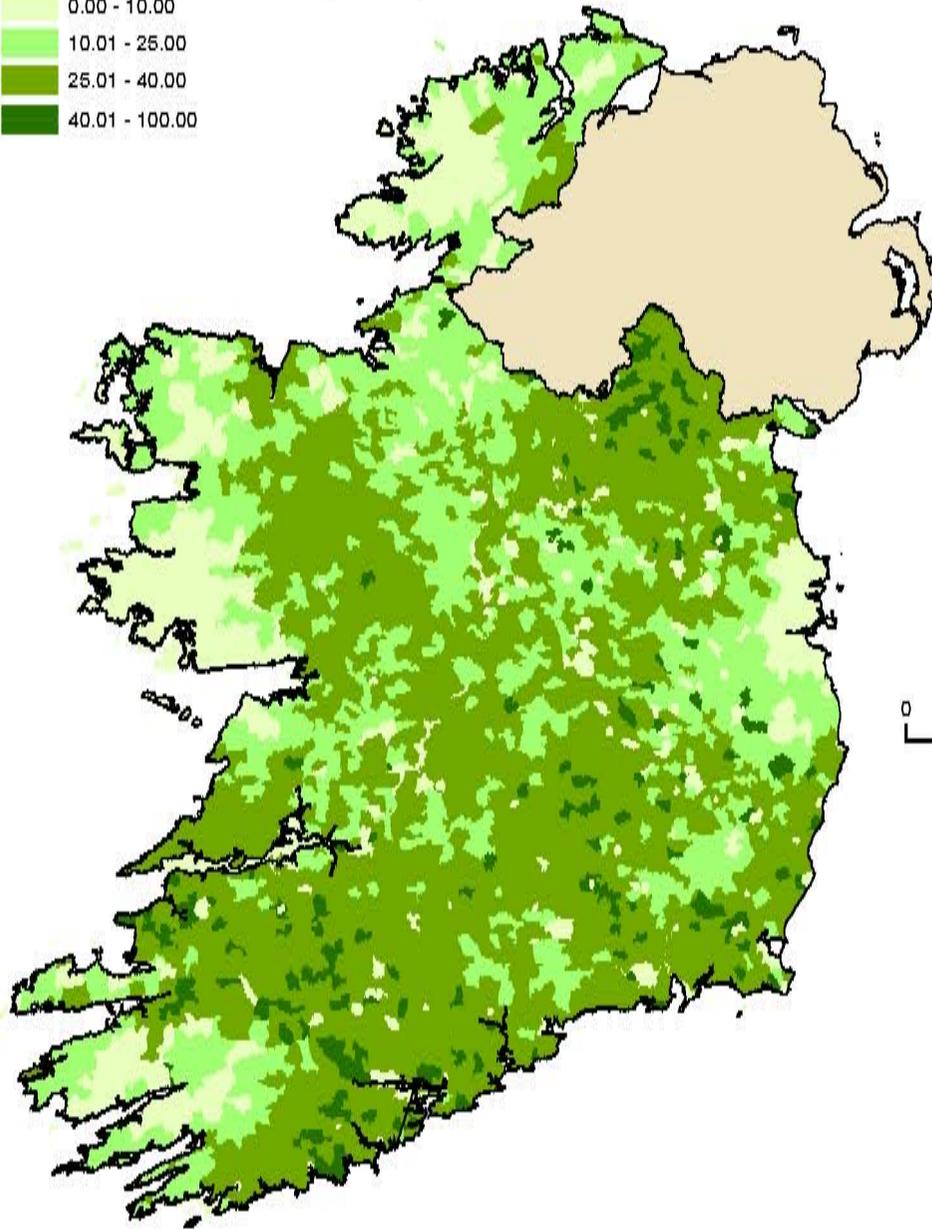
Product	Active ingredient	kg
Insecticides	alpha-cypermethrin	330.5
	cypermethrin	1216.1
Herbicides	imazapyr	14.3
	asulam	54.4
	atrazine	345.0
	glyphosate	1015.1
	propyzamide	7.6
	triclopyr	274.4

% Grassland that is Silage (Teagasc)

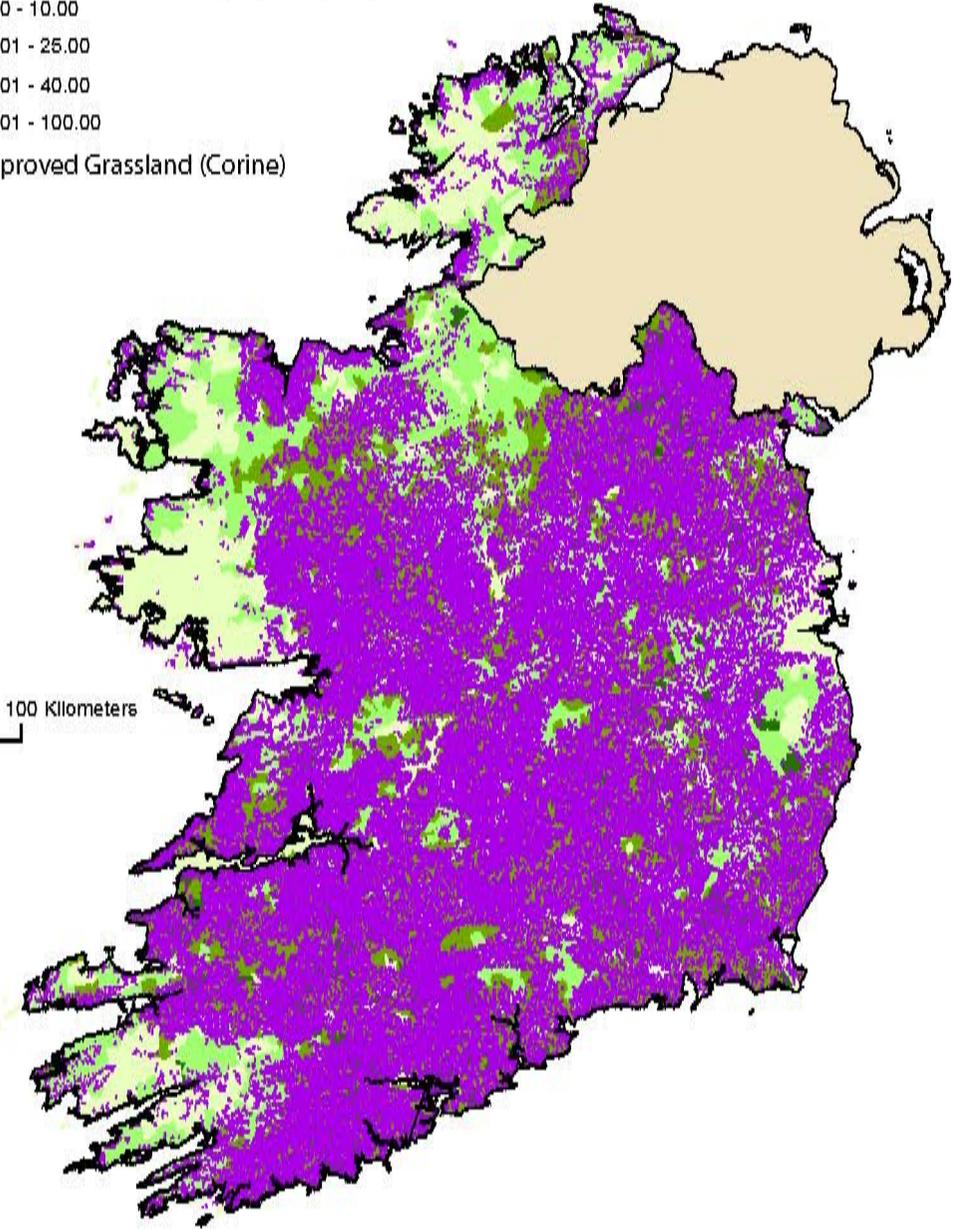
- 0.00 - 10.00
- 10.01 - 25.00
- 25.01 - 40.00
- 40.01 - 100.00

% Grassland that is Silage (Teagasc)

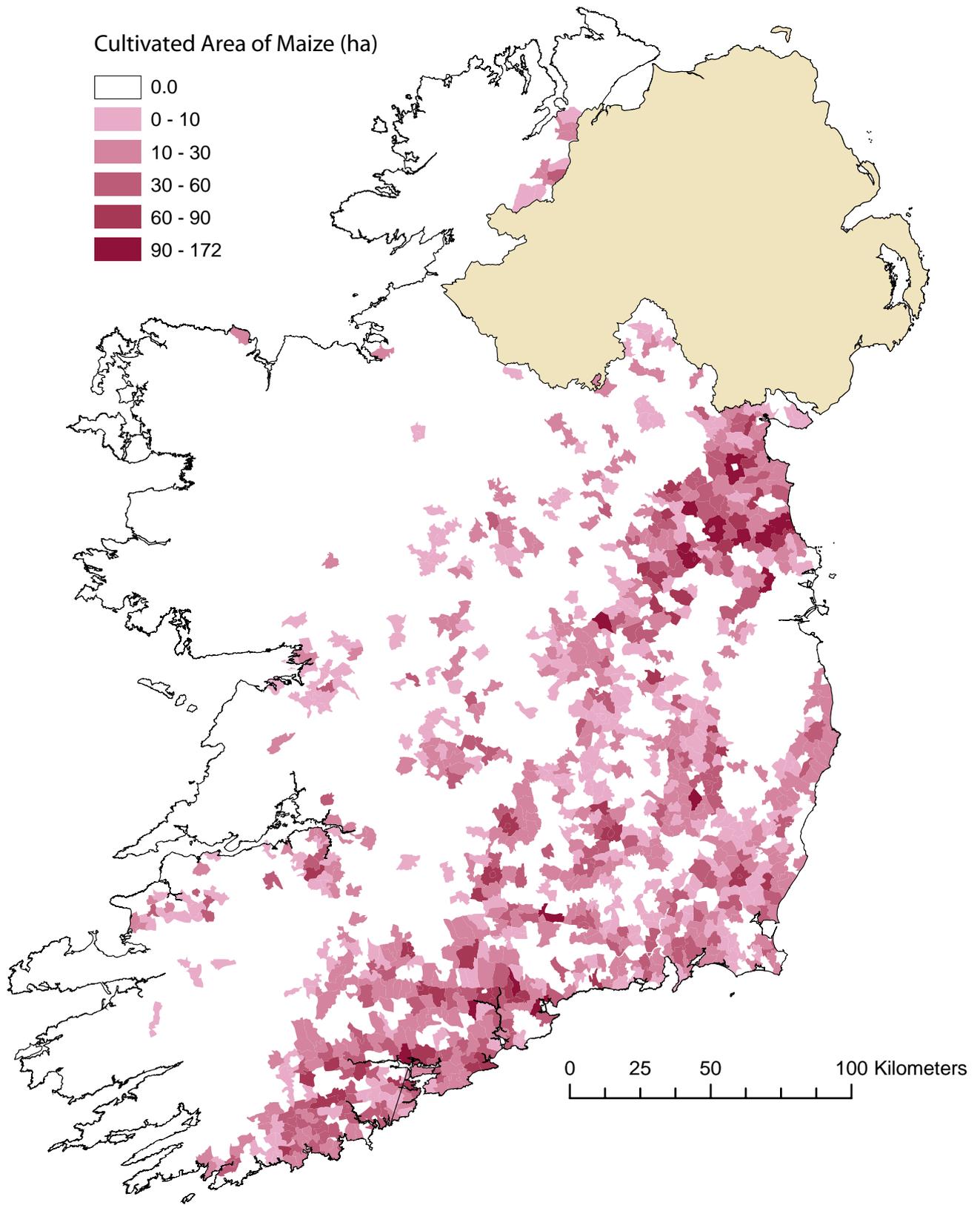
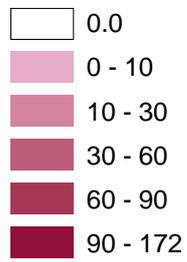
- 0.00 - 10.00
- 10.01 - 25.00
- 25.01 - 40.00
- 40.01 - 100.00
- Improved Grassland (Corine)



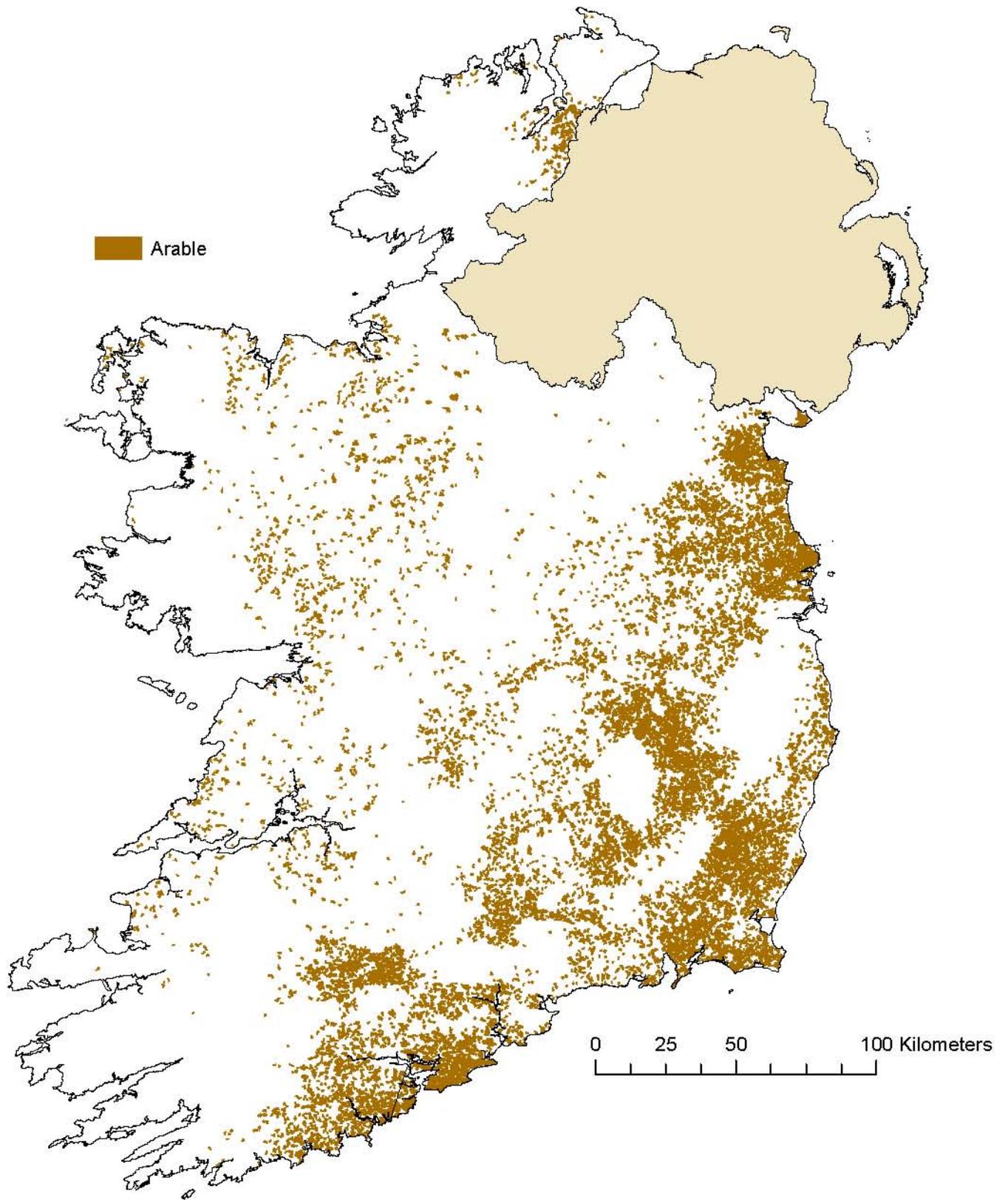
0 25 50 100 Kilometers



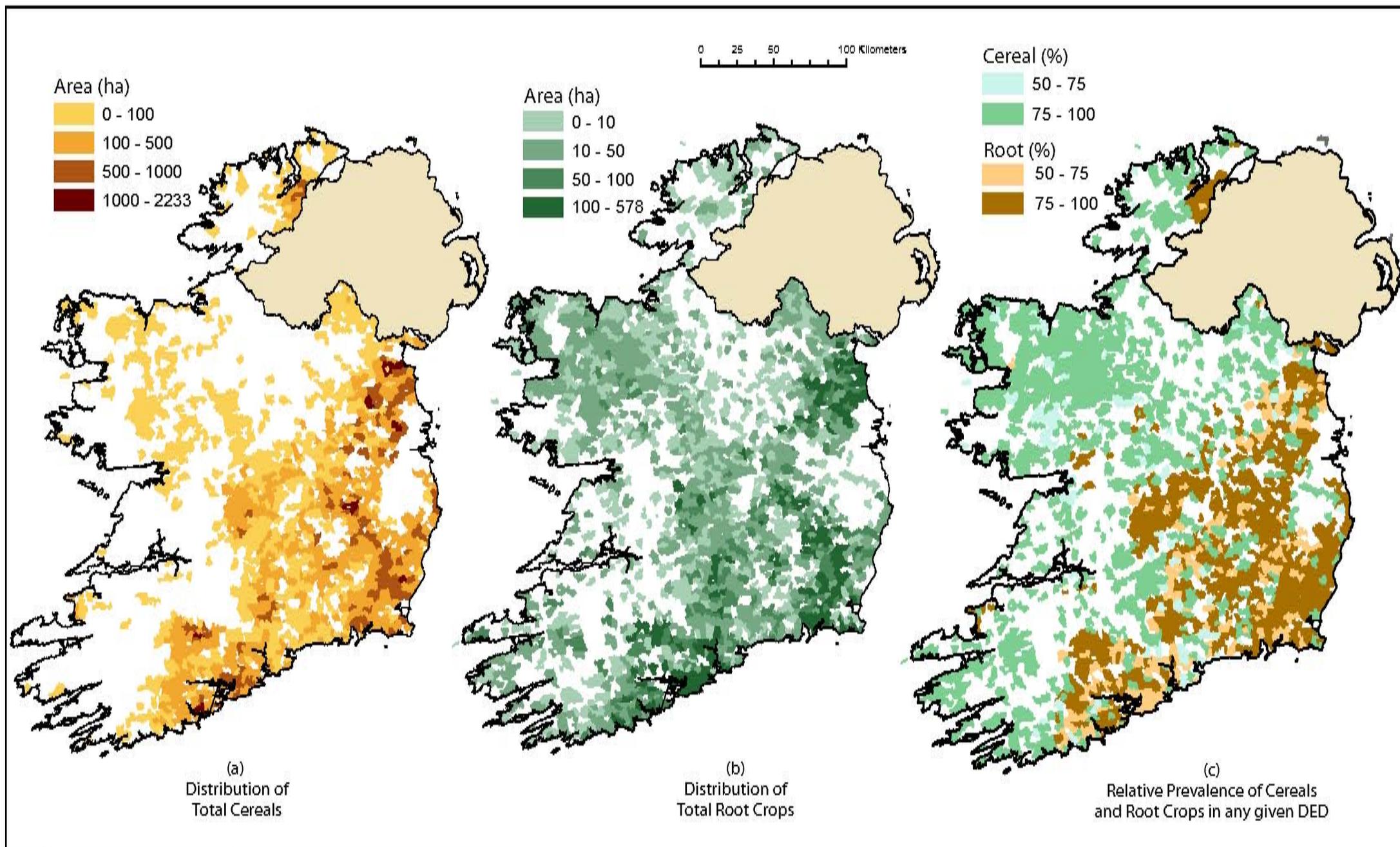
Cultivated Area of Maize (ha)



Source: Teagasc Agricultural Statistics (2003)



Source: CORINE 2000

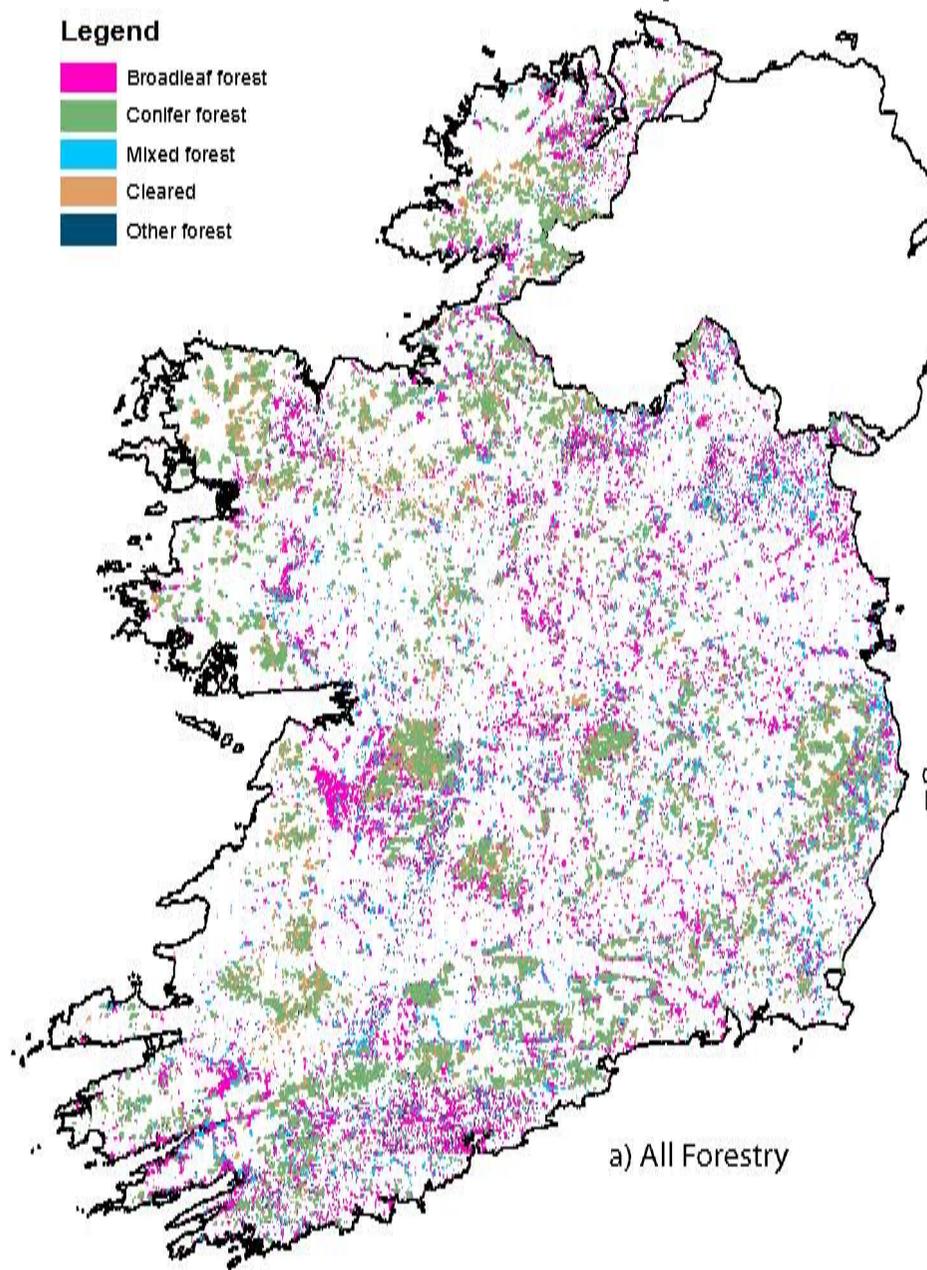


Legend

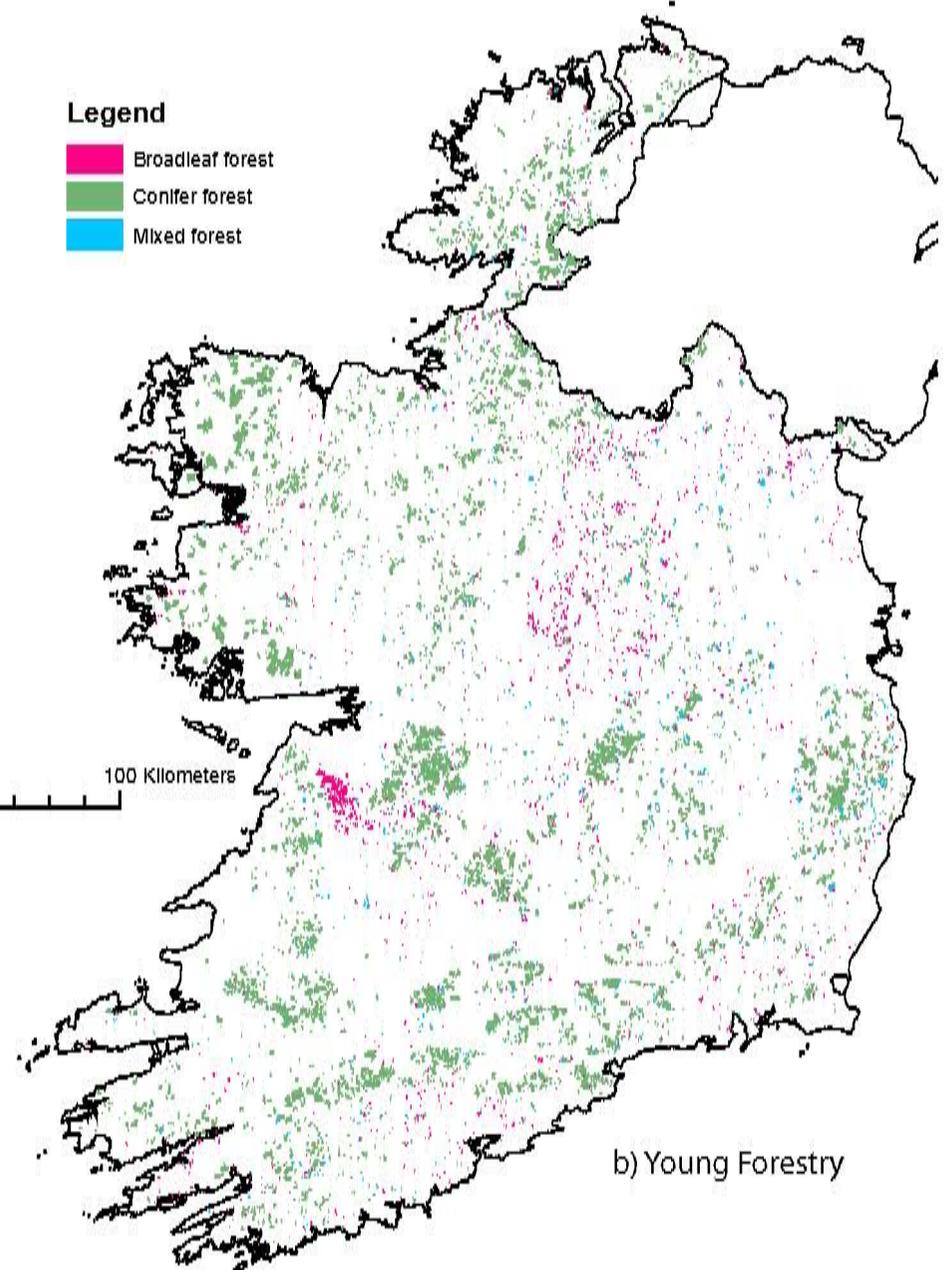
- Broadleaf forest
- Conifer forest
- Mixed forest
- Cleared
- Other forest

Legend

- Broadleaf forest
- Conifer forest
- Mixed forest

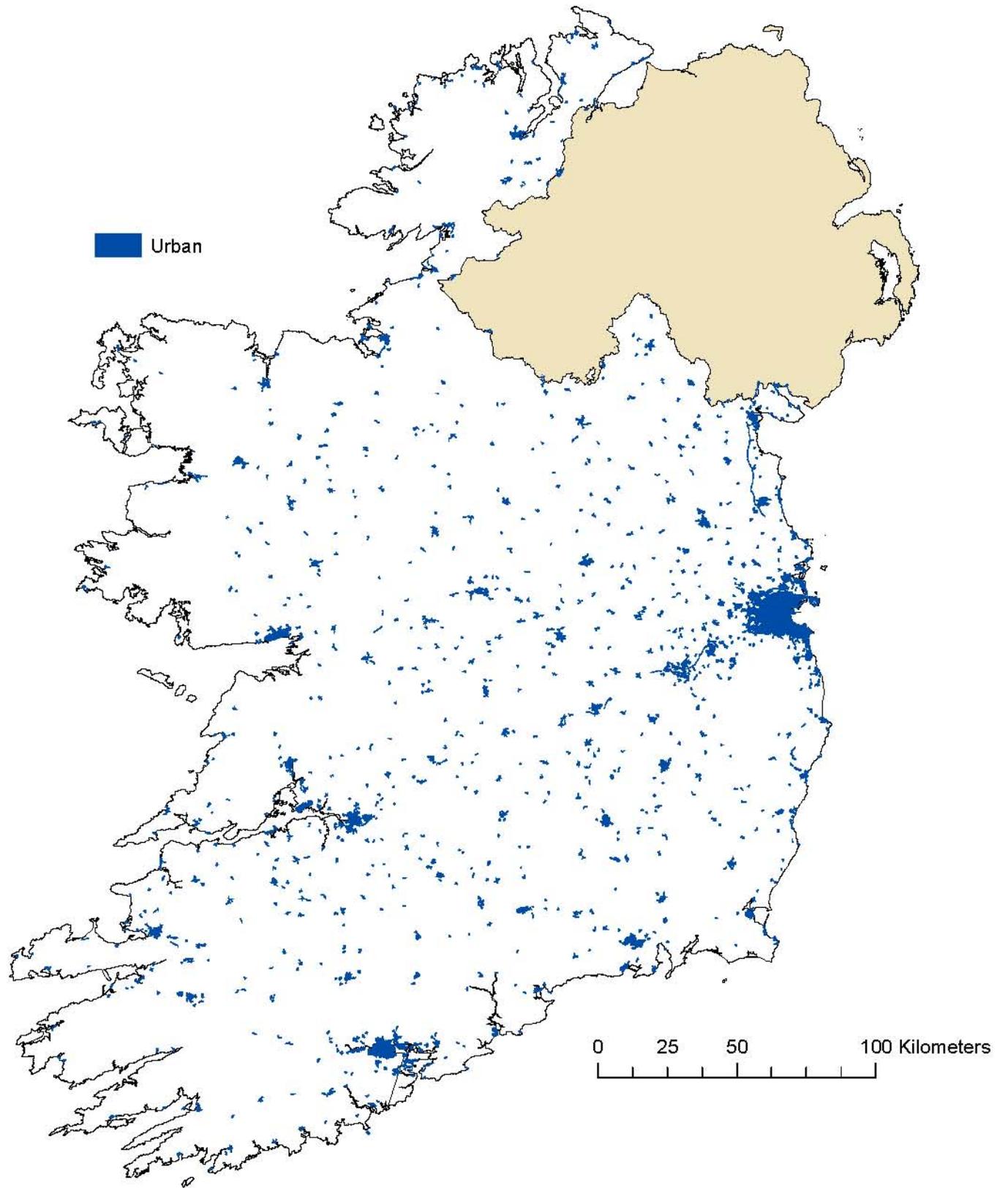


a) All Forestry



b) Young Forestry

Source: Forestry Service

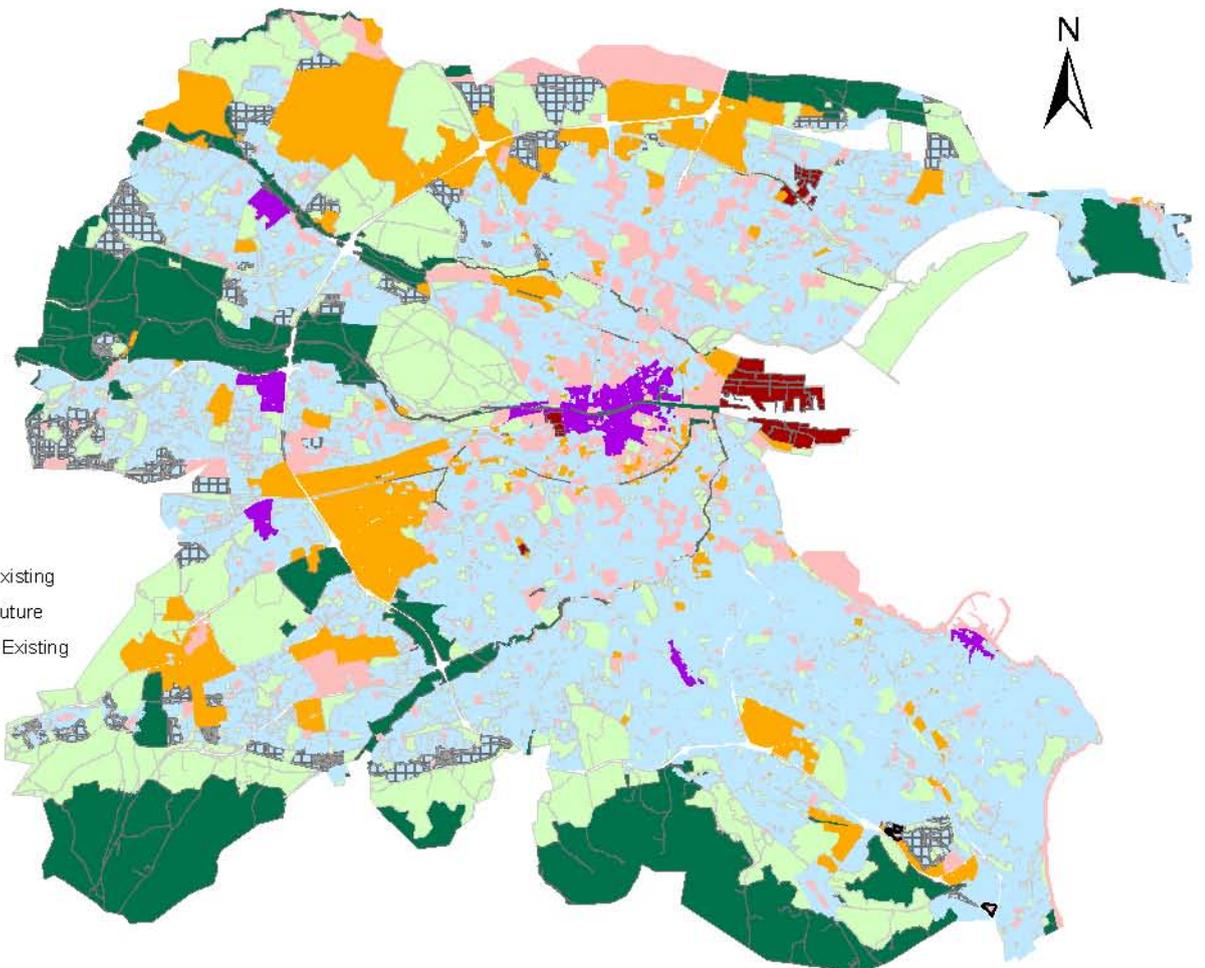


Source: CORINE 2000

DUBLIN

Legend

- Commercial Existing
- Commercial Future
- Heavy Industry Existing
- Heavy Industry Future
- Light Industry Existing
- Light Industry Future
- Mixed Use Existing
- Mixed Use Future
- Open Spaced Managed Existing
- Open Spaced Managed Future
- Open Space Unmanaged Existing
- Residential Existing
- Residential Future
- Town Centre Existing
- Town Centre Future

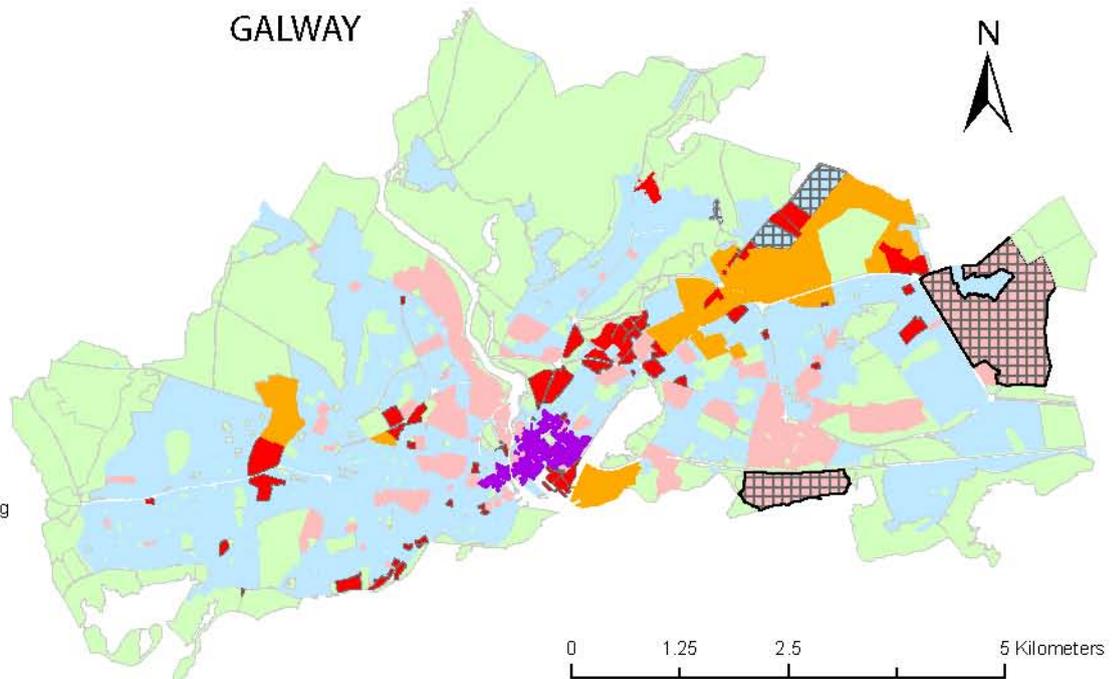


0 2.5 5 10 Kilometers

GALWAY

Legend

- Commercial Existing
- Commercial Future
- Heavy Industry Existing
- Heavy Industry Future
- Light Industry Existing
- Light Industry Future
- Mixed Use Existing
- Mixed Use Future
- Open Spaced Managed Existing
- Open Spaced Managed Future
- Open Space Unmanaged Existing
- Residential Existing
- Residential Future
- Town Centre Existing
- Town Centre Future



0 1.25 2.5 5 Kilometers



eastern
river basin district

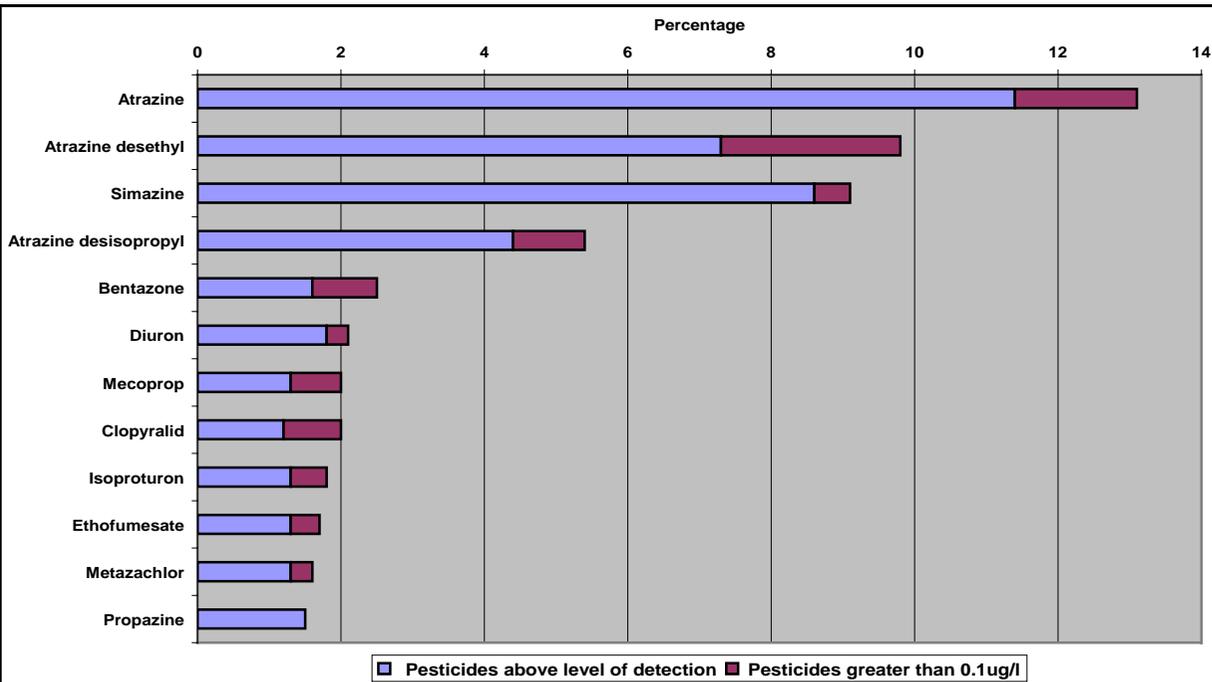


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CDM

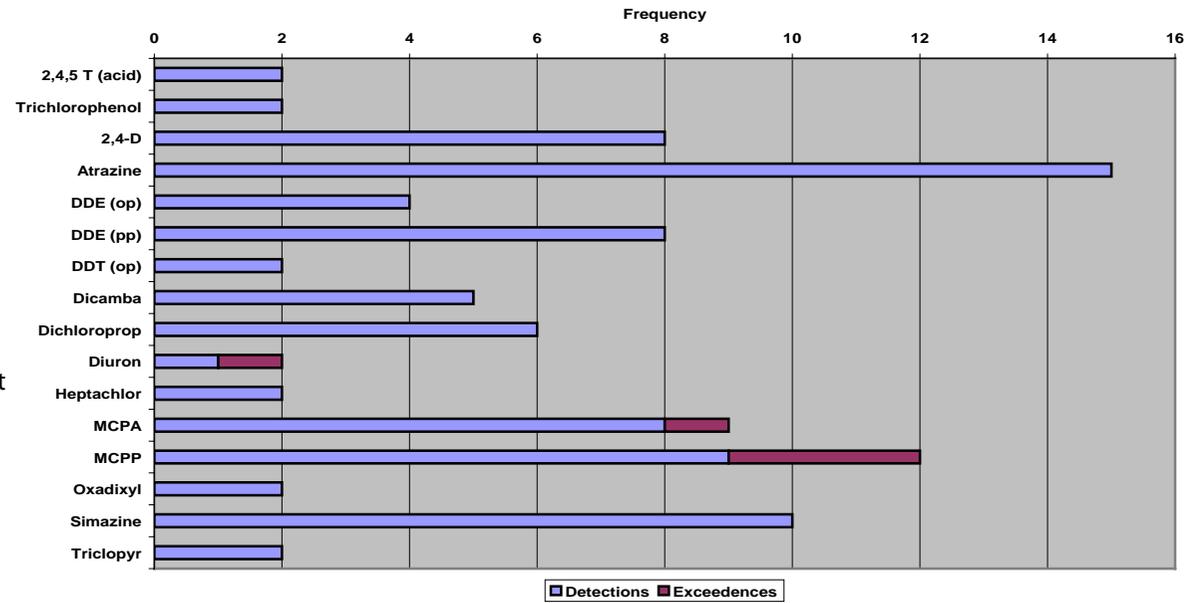
Examples of Reclassified
Urban Land Uses

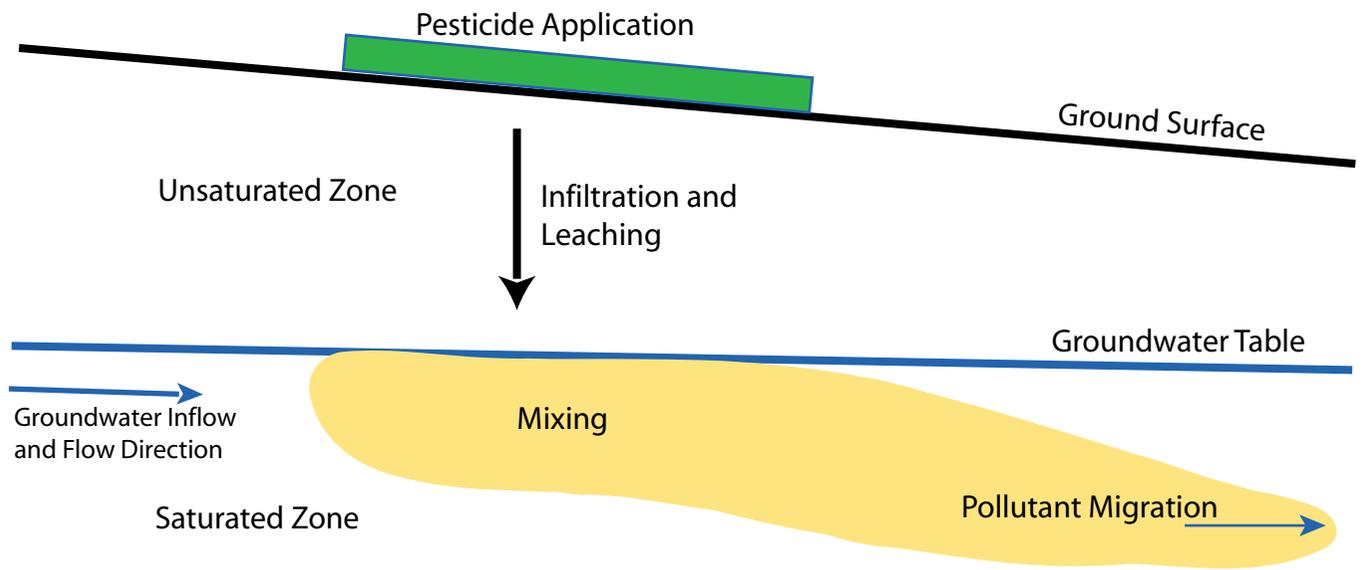
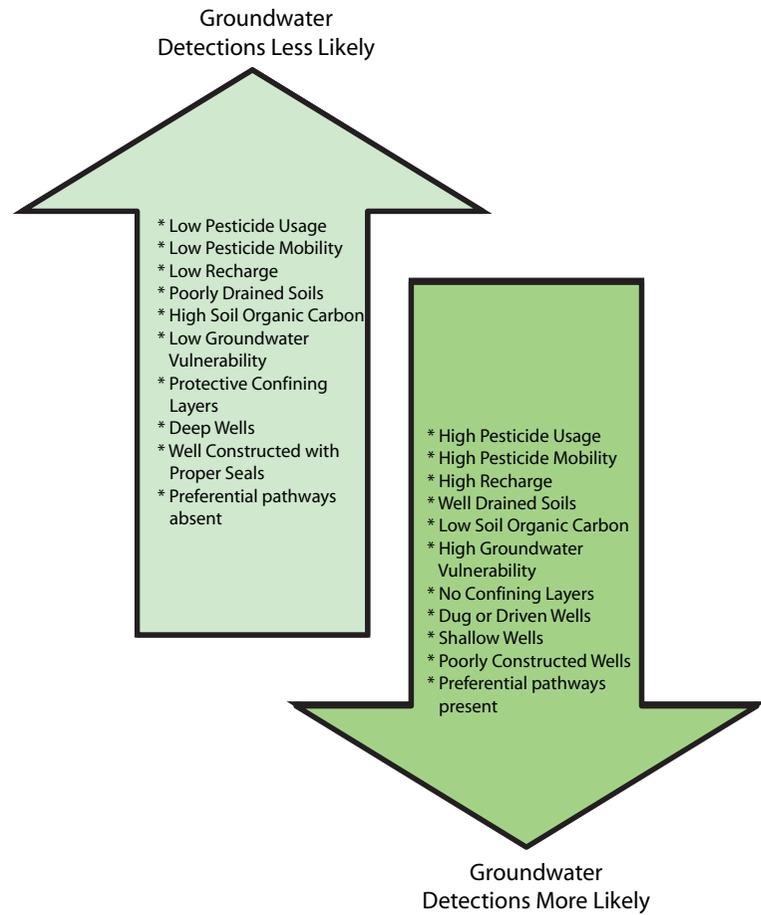
Figure
12



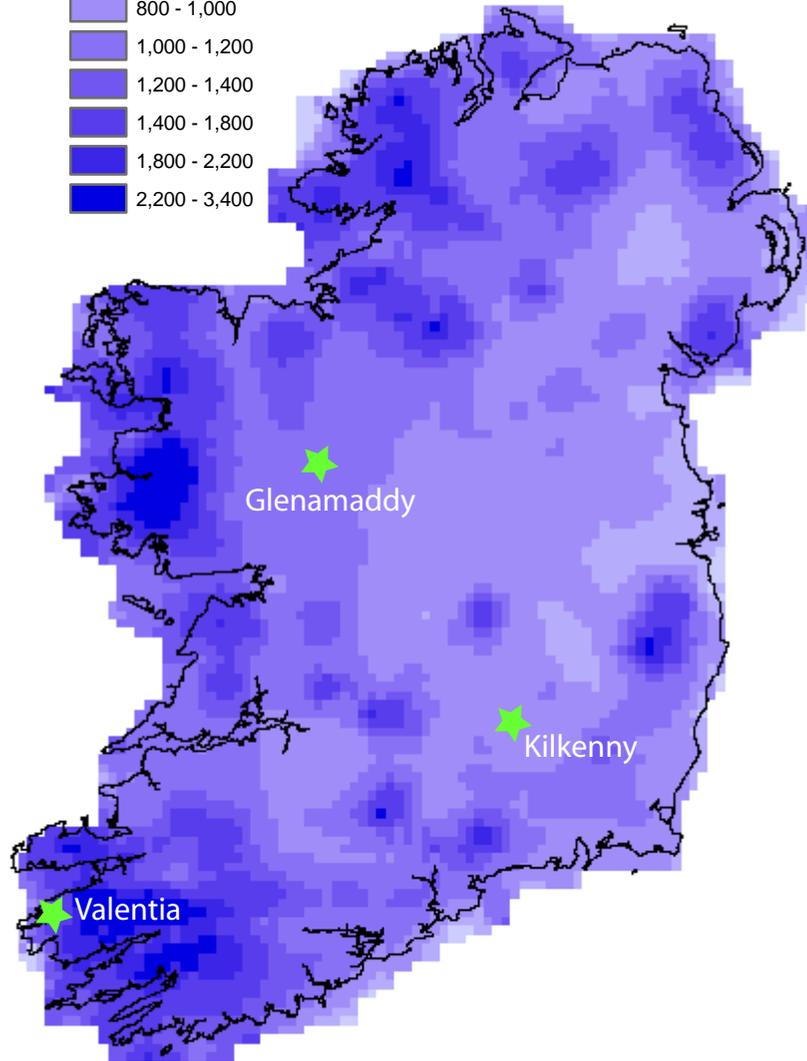
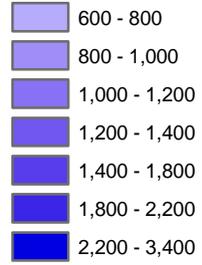
England and Wales, 2005
 Percentage Detections
 Source: Environment Agency, 2006

Northern Ireland, 2004
 Frequency of Detections
 88 sample points
 1 sample from each
 Only pesticides detected
 at more than one sample point
 are shown.
 Source: EHS, 2005





Annual Median Rainfall 1961-1990 (mm/yr)*



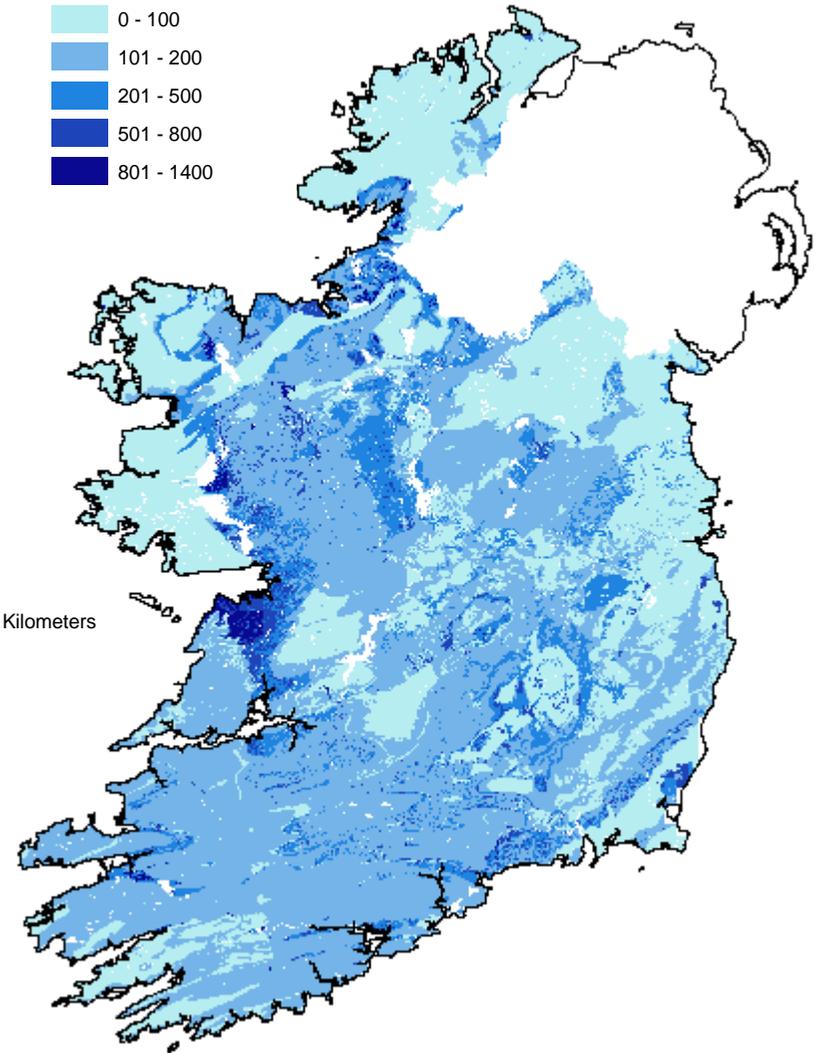
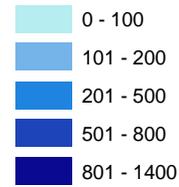
Glenamaddy

Kilkenny

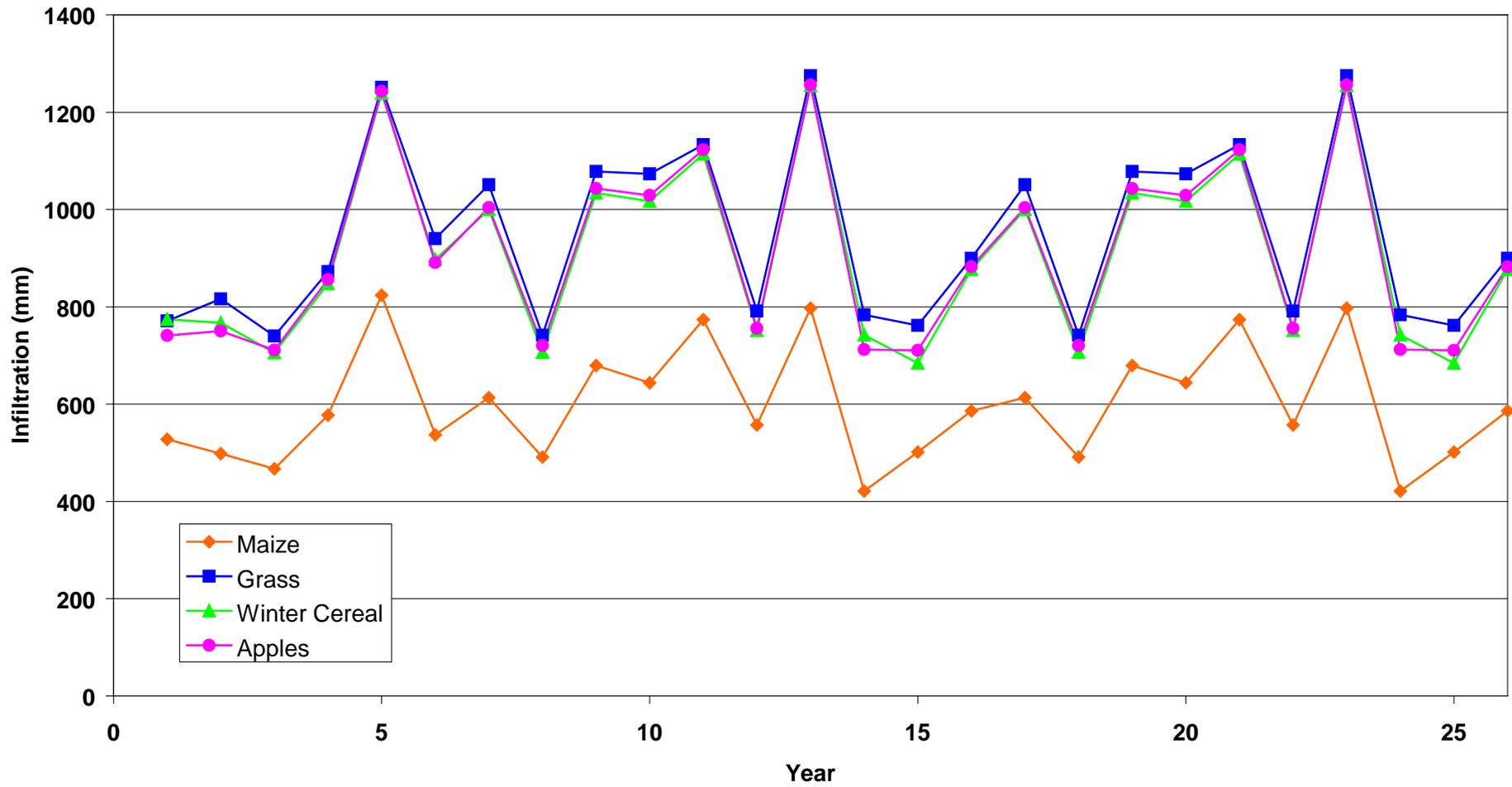
Valentia

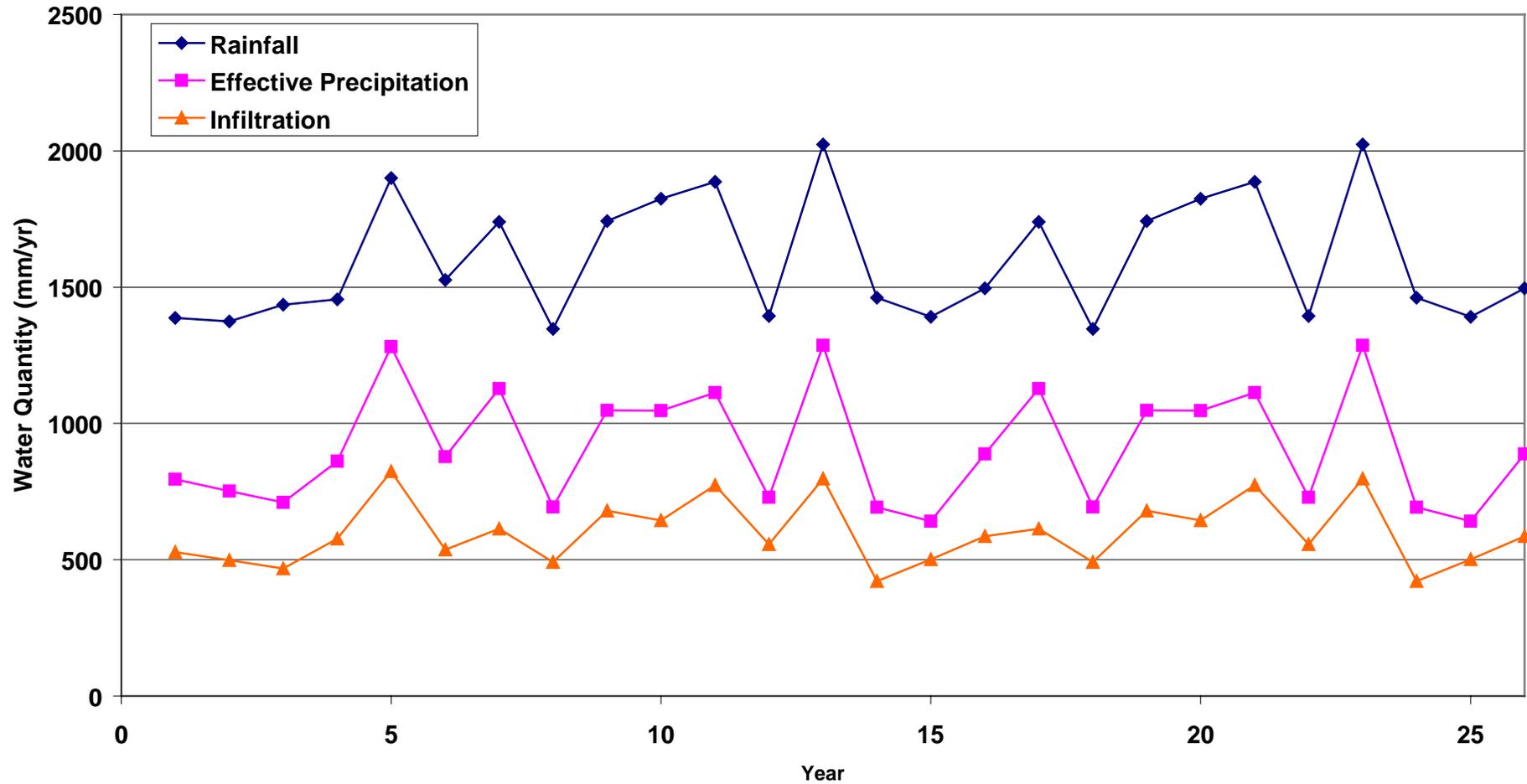
* Source: Met Eireann

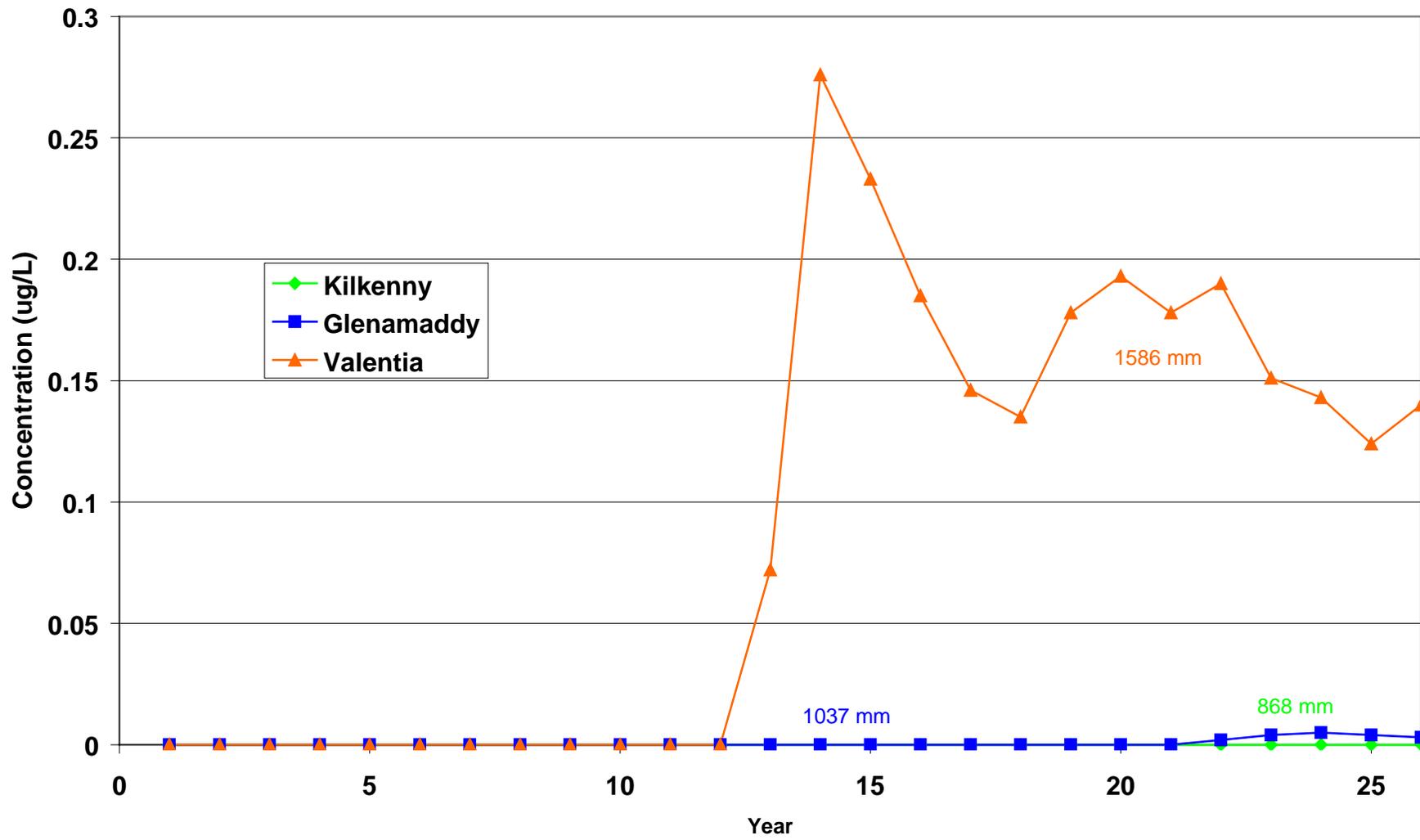
Estimated Annual Median Recharge (mm/yr)*

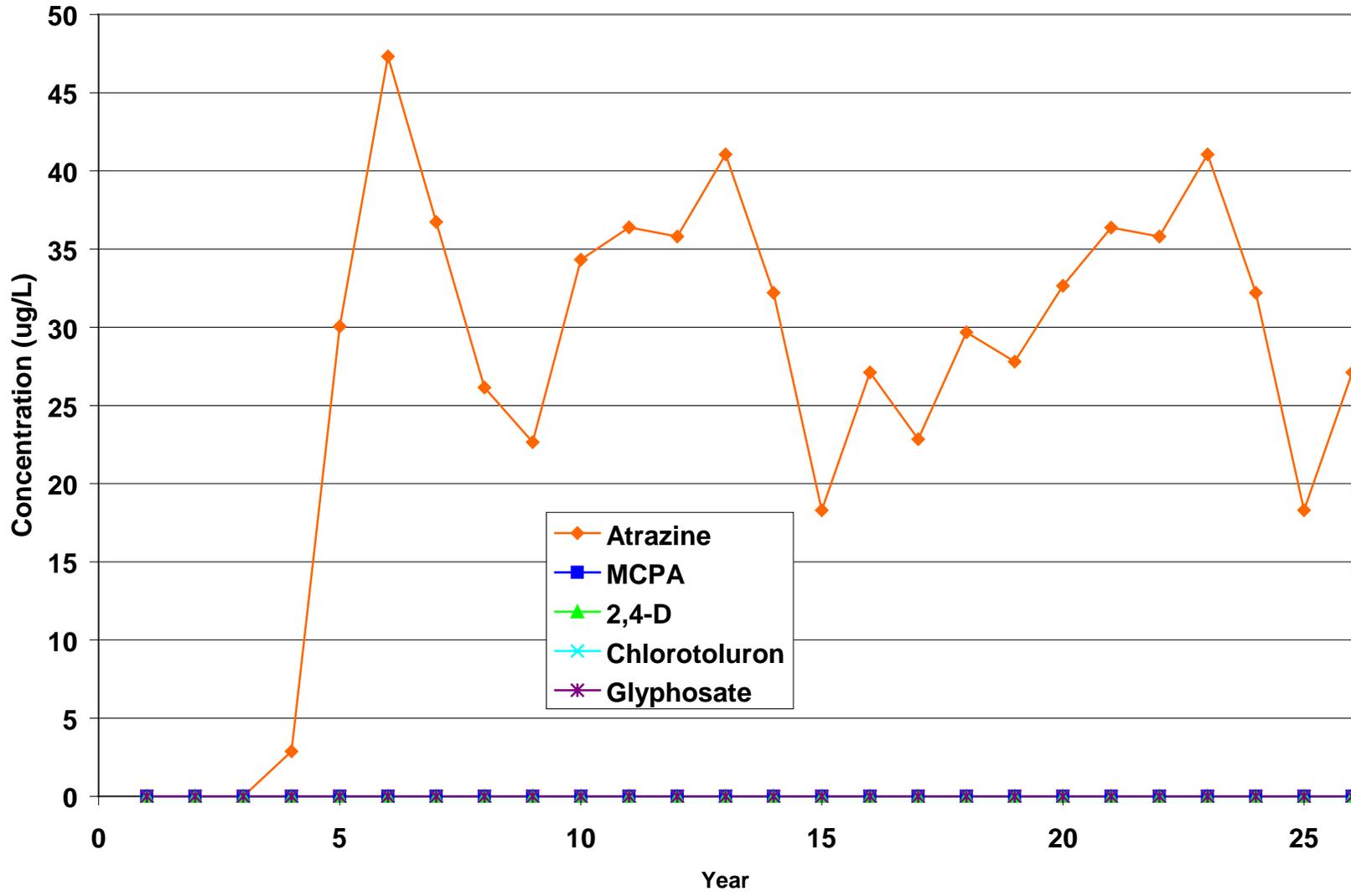


* Source: CDM - estimated with initial inputs from River Basin District projects



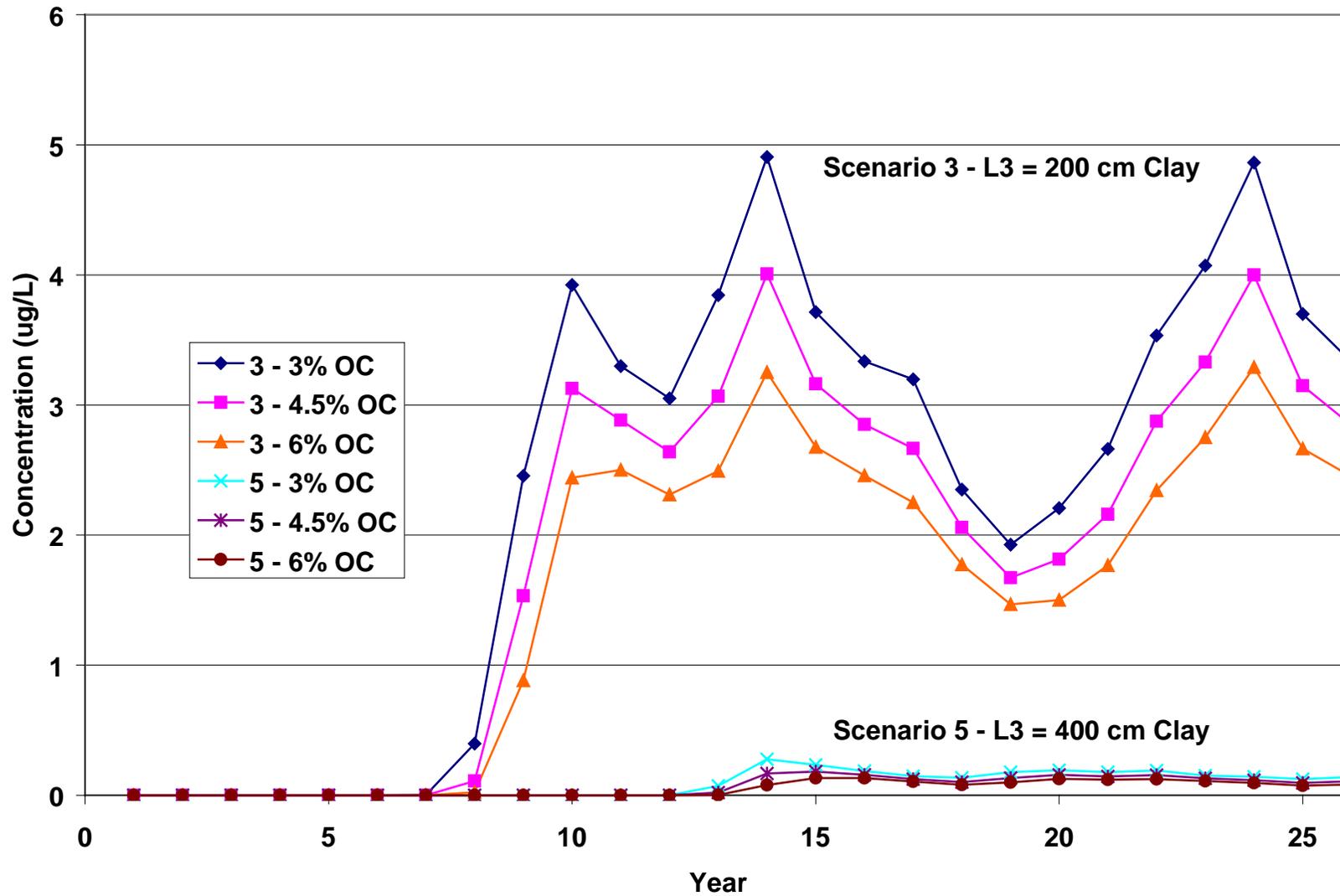


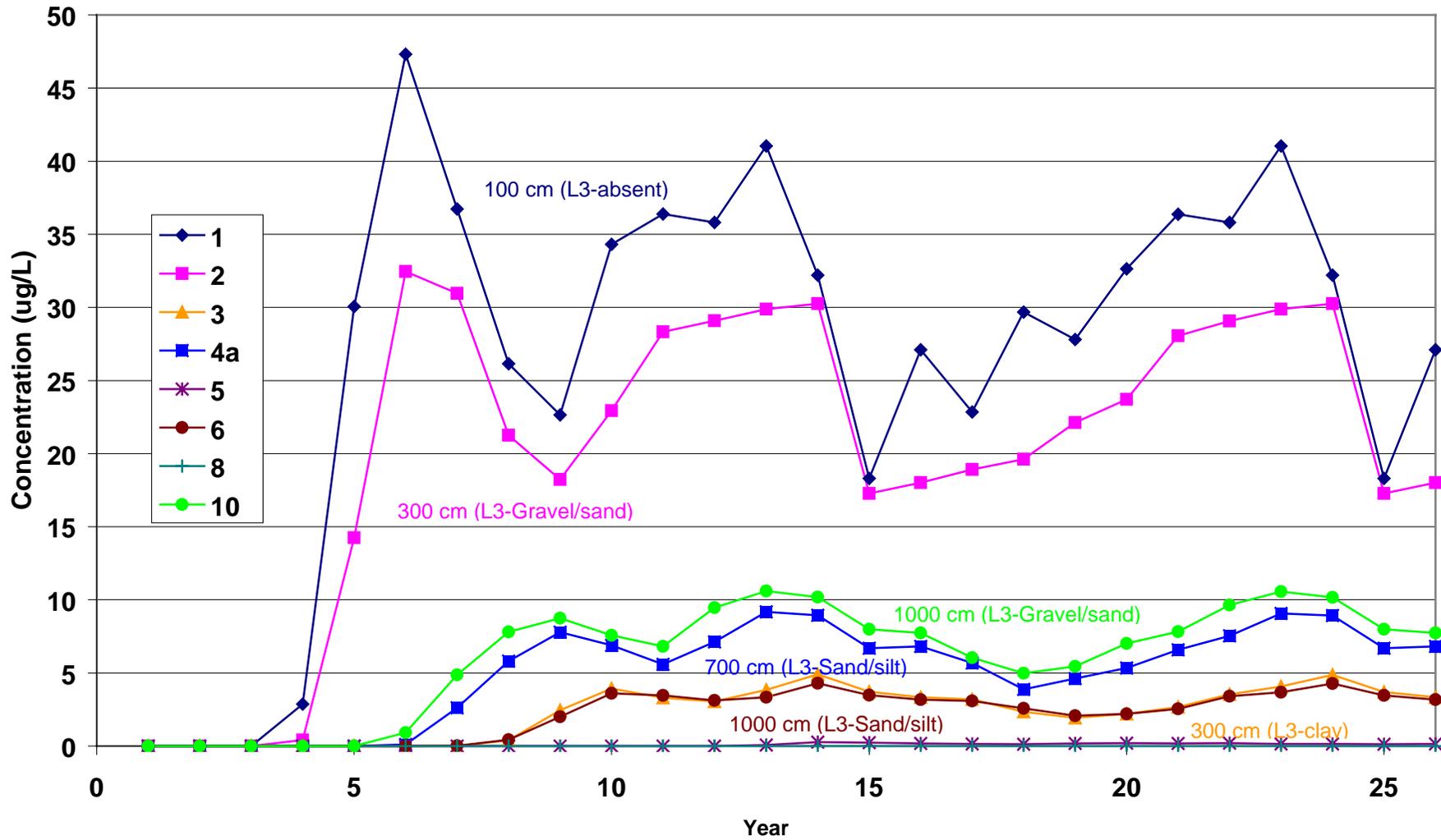




Simulated Leaching Concentrations of Different Active Ingredients for Valentia Station Rainfall Conditions

Figure 19

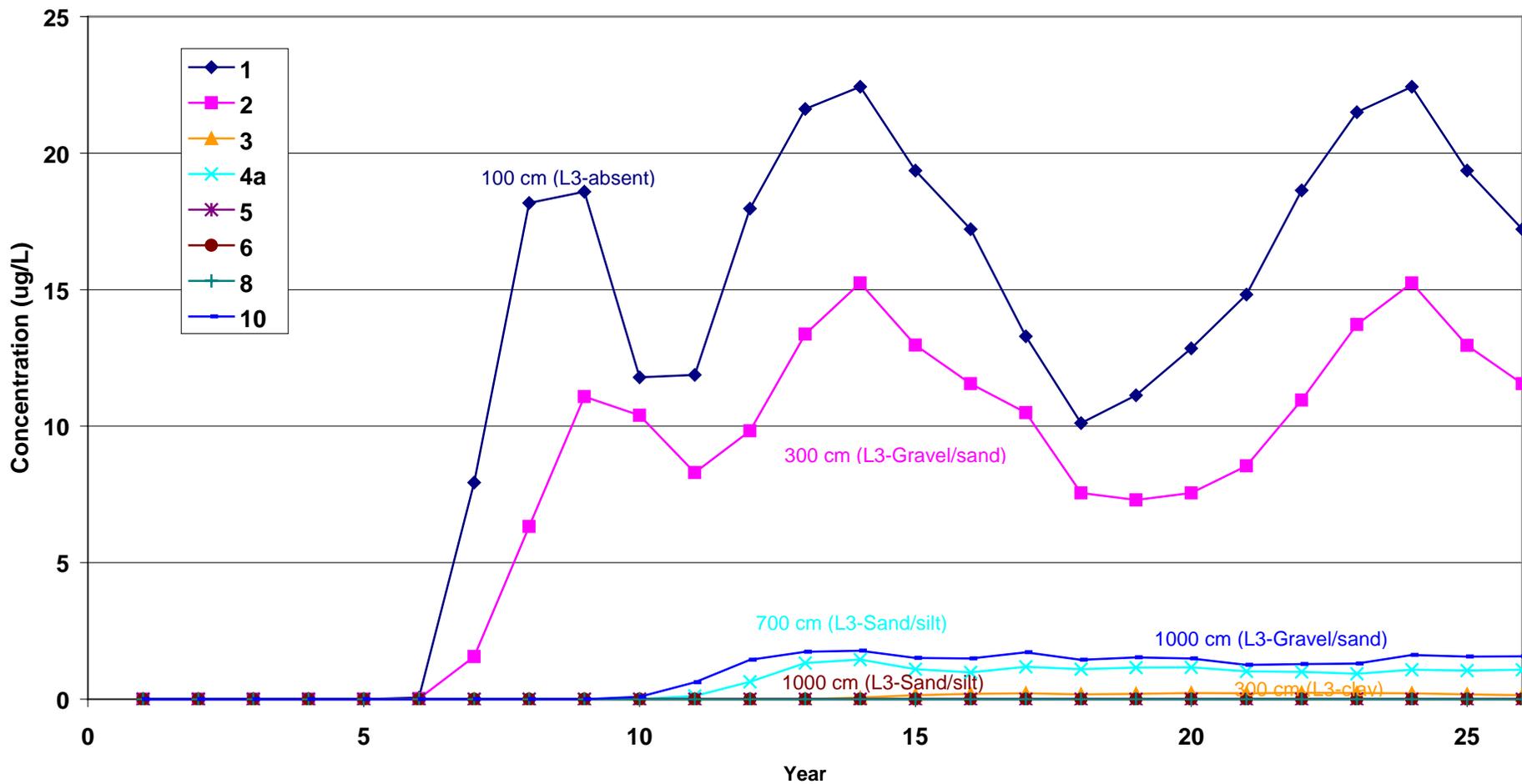




The value of cm shown is the total depth of all layers.
L3" indicates the subsoil type for layer three

Simulated Impact of Layer 3 Thickness on Atrazine Leaching Concentrations using Valentia Station Rainfall Conditions

Figure 21



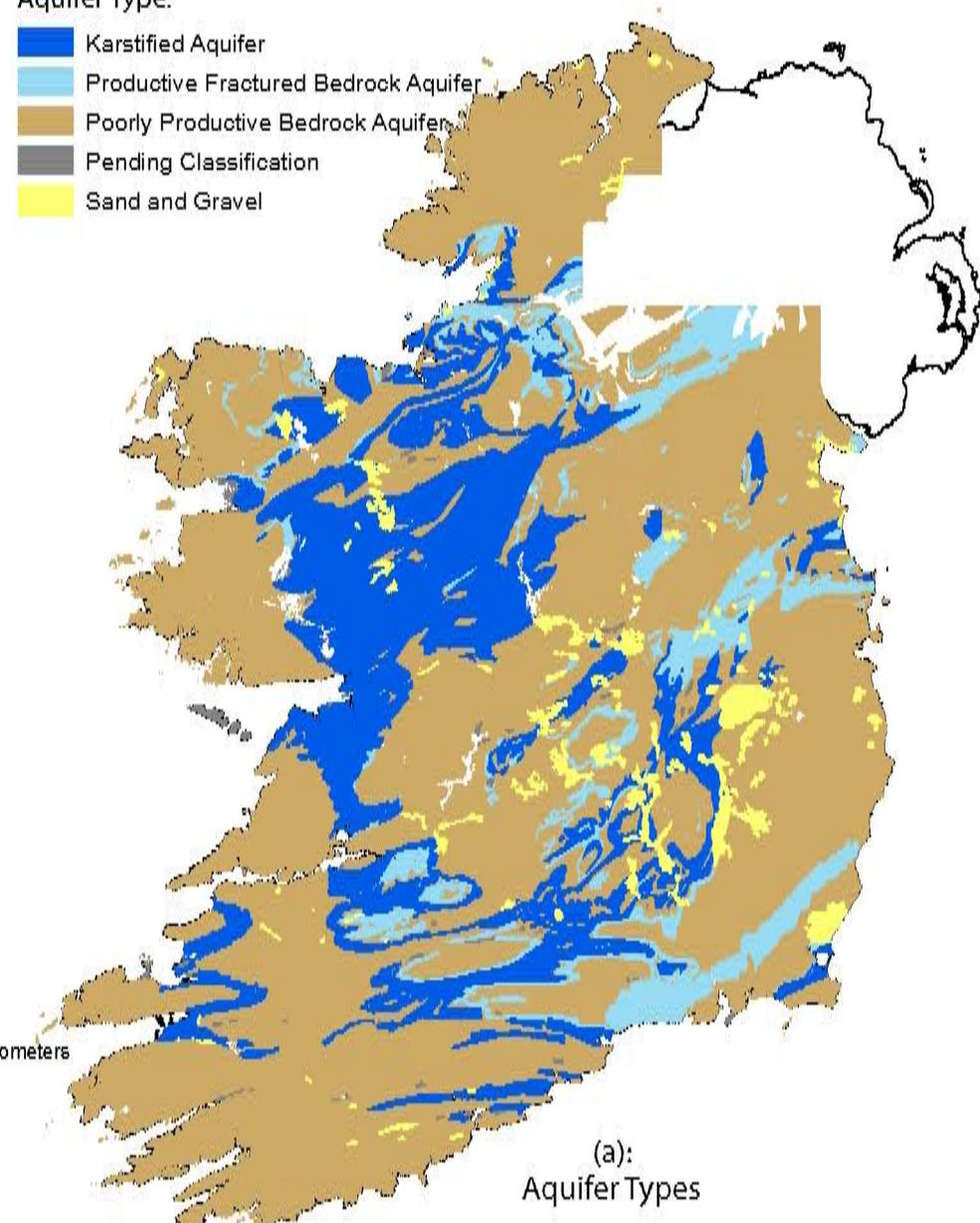
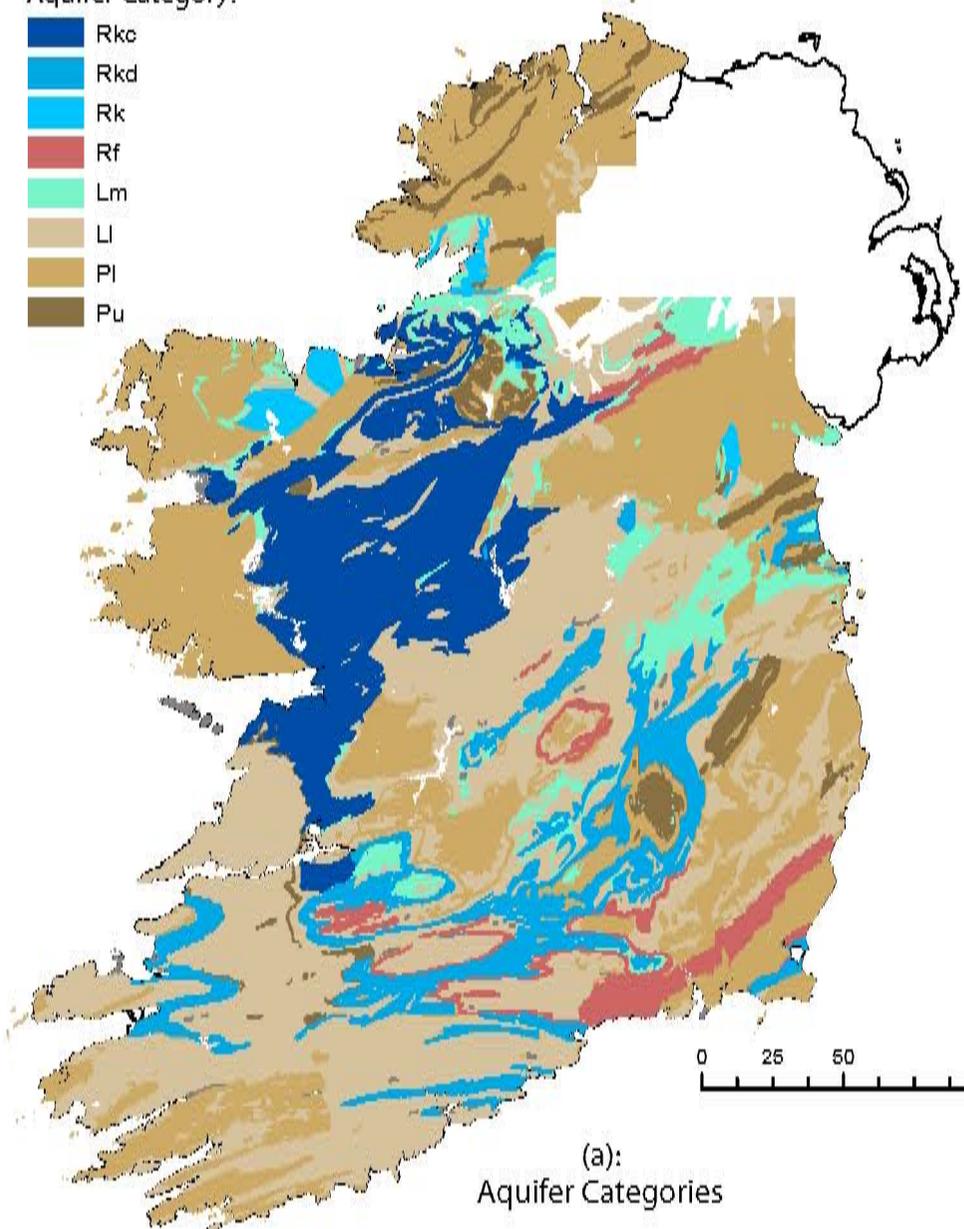
The value of cm shown is the total depth of all layers.
L3" indicates the subsoil type for layer three

Aquifer Category:

- Rke
- Rkd
- Rk
- Rf
- Lm
- Li
- Pi
- Pu

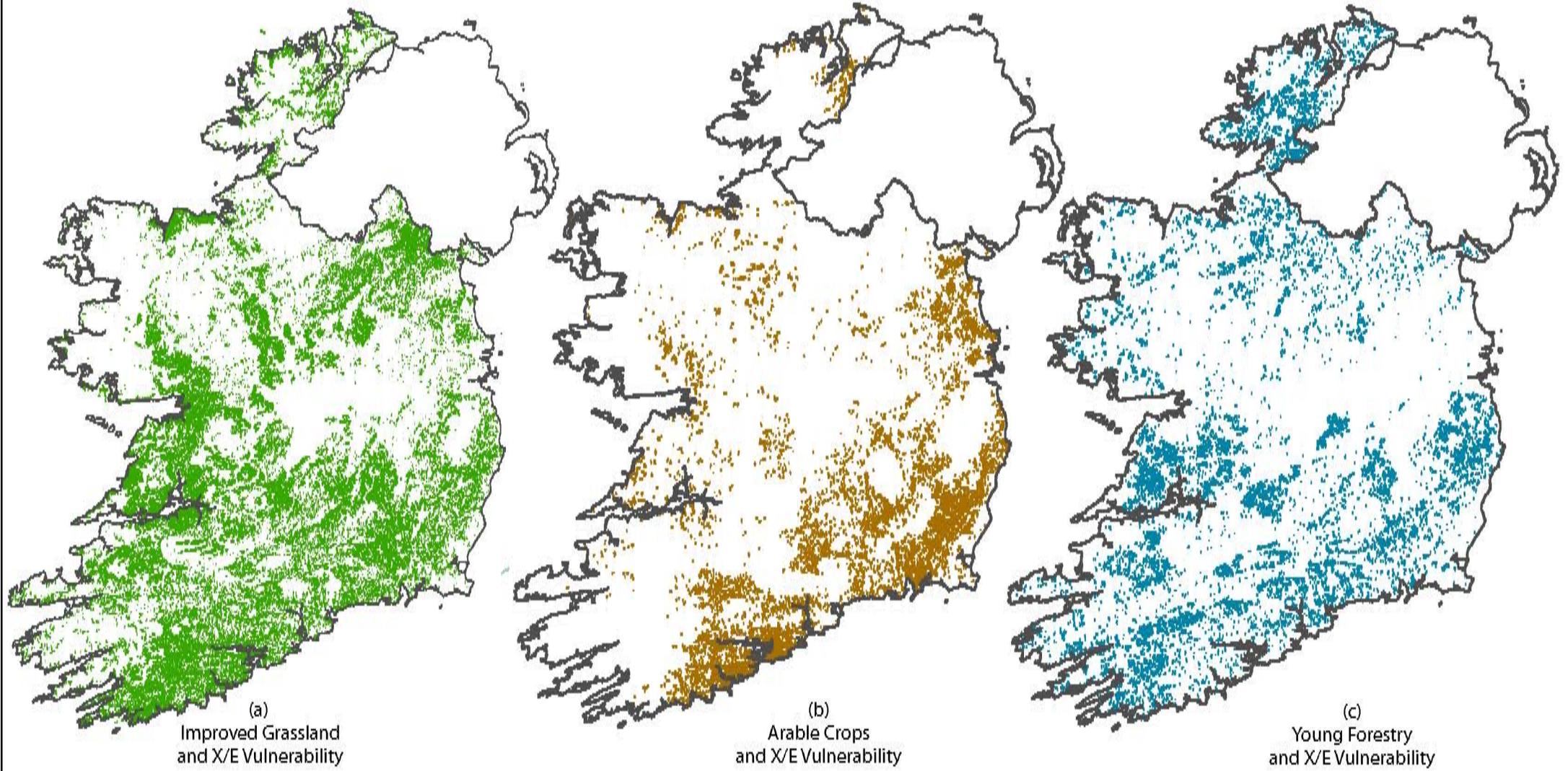
Aquifer Type:

- Karstified Aquifer
- Productive Fracture Bedrock Aquifer
- Poorly Productive Bedrock Aquifer
- Pending Classification
- Sand and Gravel

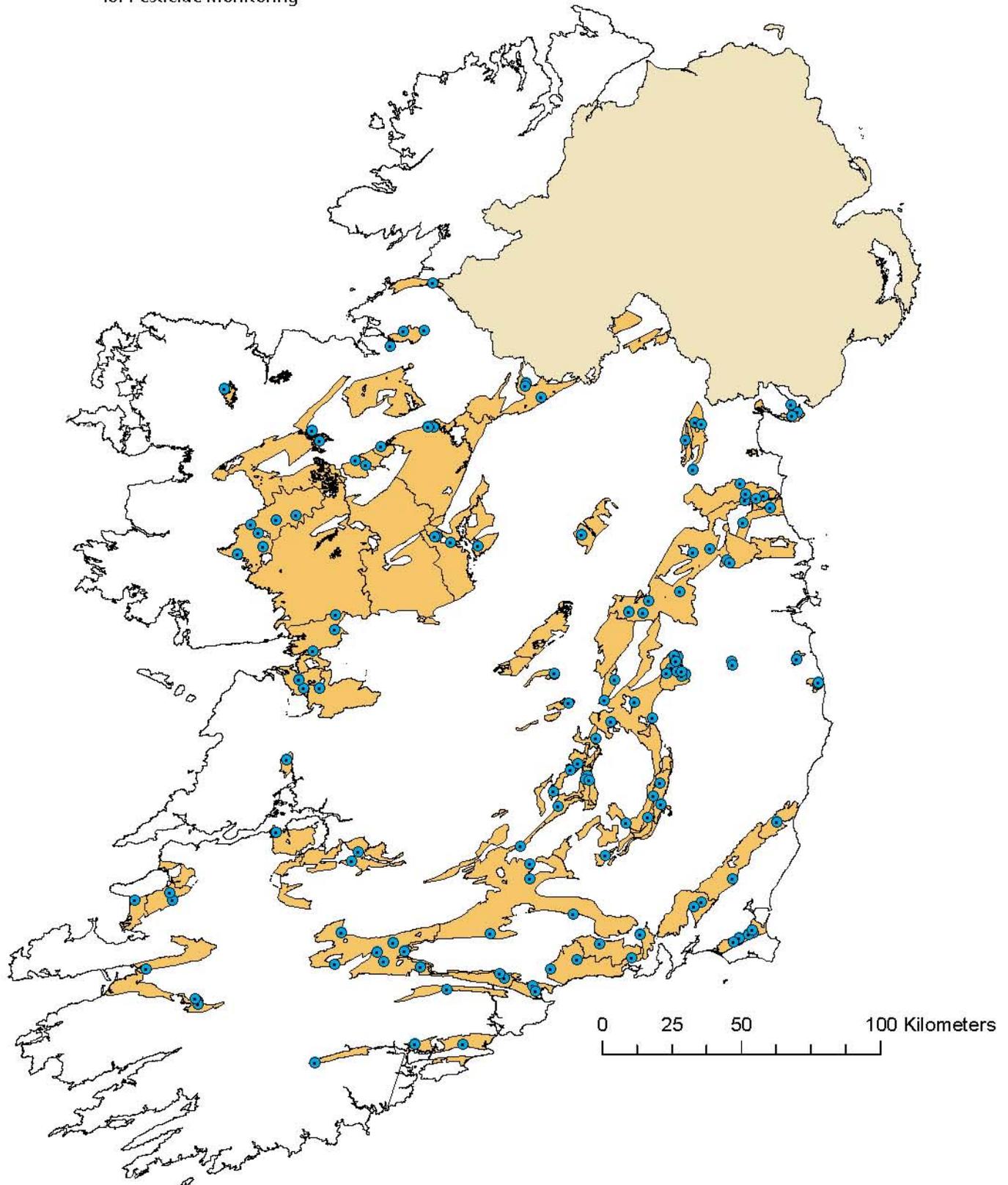


Source: Geological Survey of Ireland

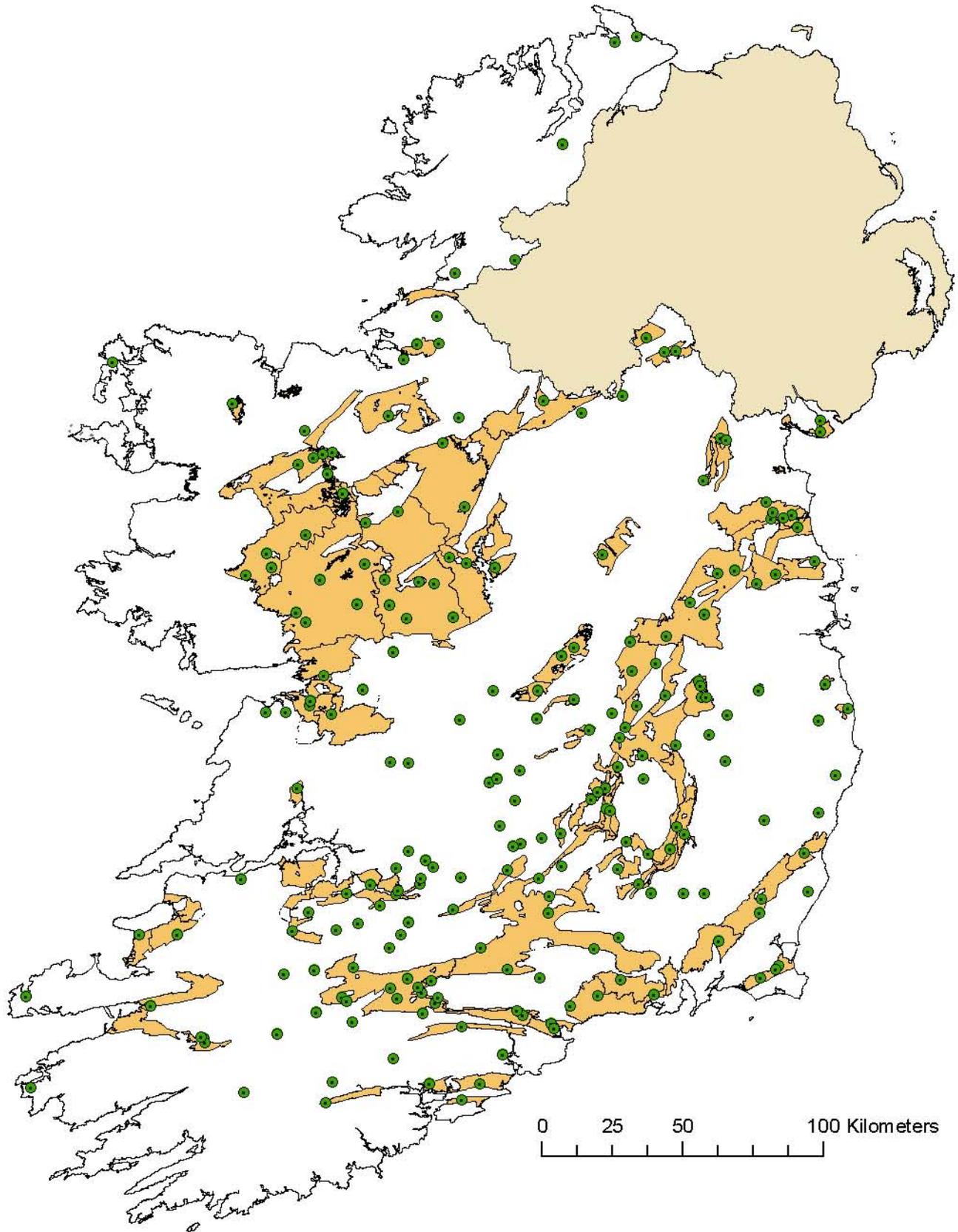
0 25 50 100 Kilometers



- Groundwater Bodies Recommended for Validation Monitoring
- Candidate Wells and Springs Recommended for Pesticide Monitoring



- Groundwater Bodies Recommended for Validation Monitoring
- EPA Groundwater Quality Monitoring Points



APPENDIX A

Model Review

1. SNIFFER

1.1 General Description

SNIFFER (Scotland and Northern Ireland Forum for Environmental Research) has recently published the document titled "Provision of a Screening Tool to Identify and Characterise Diffuse Pollution Pressures: Phase II "(SNIFFER 2006). The forum identified, selected, developed, and combined various models and methods into a systematic screening tool to assess the risk status of water bodies as the result of pollutants in the environment.

1.2 Water Balance Approach

The summary states that the model provides monthly water balance; however, the text clearly indicates that weekly water balances are performed. Weekly time steps were selected "as a level that could provide reasonable identification of which runoff mechanisms were operational at different times, whilst not being too computationally demanding for application at a national scale." Given the amount of rainfall (precipitation), weekly time steps are probably adequate (daily time steps are typically performed in more arid areas of the United States). The model partitions precipitation into three components: overland flow, sub-surface flow, and groundwater flow. Sub-surface flow appears to be the water transported horizontally under saturated conditions. Loss to groundwater is "calibrated" by use of two parameters: KV is the vertical drainage calibration parameter and KL is the lateral flow calibration parameter. KV and KL are related to the Hydrology Soil Types (HOST) for which two indices (BFI, base flow index, and SPR, standard percentage runoff) have been determined for different soil types.

Evapotranspiration rates are also calculated and include a "land use factor" to account for the influence of vegetation. All parameters are held constant for each soil type (i.e., one vertical soil compartment). Results for the various water components are summarized for each square kilometer of land surface in Scotland and Northern Ireland using 10 years of historic weather data (covers periods of dry, average, and wet years). Average 10-year groundwater percolation ranged from 50 to >450 millimeter per year (mm/yr) in Northern Ireland.

1.3 Chemical Fate and Transport Approach

The model uses an AF previously defined in the introduction (ratio of degradation to adsorption). Adsorption is assumed to be linear with no limit to capacity. Adsorption and degradation are calculated separately for the top and subsoil (two vertical compartments) taking into account differences in organic carbon content. The model simplifies soil water movement assuming that matrix flow is the dominant mechanism (preferential flow is not included). Although not stated, the model probably uses saturated permeability (hydraulic conductivity) values to determine vertical rate of flow. Pesticide loads (and concentrations) were calculated at a "threshold" depth and compared to environmental quality standards (EQS) defining good ecological status. An example EQS is 0.34 µg/L for atrazine. While results and figures were presented for surface water drainage (e.g., areas exceeding EQS), no results were presented for groundwater.

Summary of advantages and disadvantages:

Advantages include the following items:

- Relatively simple but adequate methods for water balance;
- Less computational time compared to other models (discussed below);
- Uses known and mapped parameters based on soil types;
- Other input parameters generally known (e.g., from literature);
- Number of required input parameters is less compared to other models;
- Visual presentation and identification of areas at risk shown on a one square kilometer scale over large areas.

Disadvantages include the following items:

- Only weekly water balance (probably adequate);
- Only one vertical soil compartment for water balance (may be adequate depending upon soil depth and changes with depth);
- Simplified fate and transport parameters (combined adsorption and degradation);
- Only two vertical soil compartments for fate and transport (may be adequate depending upon soil depth and types with depth);
- Preferential flow not considered;
- No results for groundwater were provided;
- No comparisons to other model results were provided.

2. PELMO

2.1 General Description

PELMO (Pesticide Leaching Model) is one of the four models evaluated and updated by the FOCUS workgroup (acronym for the Forum of the Coordination of pesticide fate models and their Use). The objective of FOCUS was to develop consensus amongst the Member States, the European Commission, and industry on the role of modeling in the EU review process of active substances. Nine models were reviewed resulting in the update and use of four models (PELMO, PRZM, PEARL, and MACRO). PELMO is similar in methods used to PRZM; therefore, PRZM was not evaluated separately. Both models are one dimensional simulating the vertical movement of chemicals in soil by chromatographic leaching.

2.2 Water Balance

PELMO (and PRZM) are "capacity" models. The vertical water flow through the soil is simulated in a stepwise approach using soil compartments that are 5 centimeter (cm) in depth (thickness). Water only moves or percolates from one compartment into the next deeper compartment when the upper compartment water content is above its field capacity. This approach is similar to the water balance in SNIFFER; however, PELMO uses daily calculations. Runoff is based on standard Soil Conservation Service curve

numbers and occurs whenever a certain amount of daily rainfall is exceeded. This rainfall amount is a dynamic parameter depending on crop stage and irrigation amount. Theoretically calculated potential evapotranspiration rates are corrected for actual rates.

2.3 Chemical Fate and Transport

PELMO (and PRZM) describe chemical movement in soil with standard convection-dispersion equations using daily time steps. With 5 cm thick soil compartments, the effective dispersion is 2.5 cm as a result of the model simulating dispersion numerically (approximately equal to 0.5 times the compartment thickness). PELMO uses first order degradation rates that are corrected in the model for temperature and moisture effects. Degradation rates can be input for each vertical compartment. However, in practice, actual rates are not known for each 5 cm compartment and therefore standard factors are applied to the topsoil degradation rate (e.g., for 0 to 30 cm the factor is 1; for 30 to 60 cm the factor is 0.5; for 60 to 100 the factor is 0.3). PELMO uses the Freundlich equation to model adsorption. The Freundlich adsorption coefficient and exponent can be separately input for each compartment or the model can adjust a single value based on organic carbon content of each compartment. If the Freundlich exponent ($1/n$) is not known, it is set at the default of 0.9. PELMO can simulate nonequilibrium adsorption using a simple increase in adsorption with time (only in the first layer). PELMO can also model up to eight transformation metabolites. Degradation rates and adsorption constants are needed for each metabolite. The resultant chemical concentrations are provided at 1 meter (m) depth (any depth can be modeled) and compared to the value of 0.1 $\mu\text{g/L}$.

Summary of advantages and disadvantages:

Advantages include the following items:

- Approved use for EU nations;
- Daily water balance;
- Detailed modeling of chemical concentrations at 5 cm intervals using both degradation and adsorption;
- Use of Freundlich adsorption;
- Ability to model metabolites;
- Ability to model nonequilibrium adsorption (probably not needed);
- Standard model runs available for use;
- Standard default parameters available .

Disadvantages include the following items:

- Numerical computation time (may be unacceptable for nationwide modeling);
- Many input parameters (must use defaults in many cases);
- Does not simulate preferential flow;

- No graphic interface to provide areawide summaries (essentially only one soil profile modeled).

3. PEARL

3.1 General Description

As previously described, PEARL (Pesticide Emission Assessment at Regional and Local scales) is one of the four models evaluated and updated by the FOCUS workgroup.

3.2 Water Balance

PEARL uses Richard's equation, which calculates the water flow through the whole soil column in a continuous, but nonlinear manner. The rate of vertical water movement depends upon the permeability at different water contents. The actual computation is performed by the Soil Water Atmosphere (SWAP) model using a finite implicit difference scheme. SWAP can handle a wide variety of hydrological boundary conditions (e.g., groundwater levels can fluctuate in response to rainfall input). During dry periods, upward flow can result from capillary rise. Runoff only occurs when the infiltration capacity is exceeded. Evapotranspiration is calculated by multiplying a reference rate with given soil and crop factors.

3.3 Chemical Fate and Transport

For PEARL, the dispersion length is set at 5 cm. This is approximately equal to the average of possible values; however, the value can be changed. For adsorption, PEARL uses a two-site Freundlich model: one equilibrium site and one kinetic (nonequilibrium) site. Degradation rates are first order and vary with water content, temperature, and soil depth (same as PELMO). Metabolites can be modeled.

Summary of advantages and disadvantages: Advantages include the following items:

- Approved use for EU nations;
- Use of the Richard's equations that enable better simulation of water movement under unsaturated conditions (because of the relatively high rainfall, modeling water movement during unsaturated may not be necessary);
- Ability to incorporate fluctuating water levels;
- Two-site Freundlich adsorption (because of relatively high degradation rates, the long-term adsorption, i.e., kinetic or non-equilibrium adsorption, may not be needed);
- Standard model runs available for use;
- Standard default parameters available.

Disadvantages include the following items:

- Numerical computation time (may be unacceptable for nationwide modeling).
- Many input parameters (must use defaults in many cases);
- Does not simulate preferential flow;

- No graphic interface to provide areawide summaries (essentially only one soil profile modeled);
- Runoff is not accurately simulated. In comparison to PELMO, the runoff quantity was less. This is because in PEARL, runoff only occurs when infiltration capacity is exceeded. This results in more infiltration and percolation;
- Chemical concentrations may be over predicted. In comparison to PELMO, the chemical concentrations at 1 meter depth were greater. This was a result of larger infiltration (less runoff) and larger dispersion. The comparison was better when the dispersion length was adjusted to 2.5 cm.

4. MACRO

4.1 General Description

As previously described, MACRO (Macropore flow simulation) is one of the four models evaluated and updated by the FOCUS workgroup. MACRO is a one-dimensional, nonsteady-state model of water flow and chemical transport in a layered soil.

4.2 Water Balance

The model simulates a high-conductivity/low-porosity macropore domain coupled to a low-conductivity/high-porosity micropore domain representing the soil matrix. Unsaturated water flow is modeled using Richard's equation in the micropores and gravity flow in the macropores using a simplified capacity type approach. Surface runoff is only included in the sense that if the surface layer is saturated, the excess water does not infiltrate.

4.3 Chemical Fate and Transport

Transport is simulated by convection-dispersion equations in the micropores, and mass flow only in the macropores. Mass exchange between the flow domains is calculated using first order rate equations and approximate, physically based expressions based on an effective aggregate half-width. Adsorption is modeled using Freundlich equations with adsorption partitioned between the micro- and macropores. Degradation is simulated using first order kinetics with separate rate coefficients for the four pools (soil and liquid, micro- and macropores). One metabolite can be simulated.

Summary of advantages and disadvantages: Advantages include the following item:

- Only model to simulate macropore flow.

Disadvantages include the following items:

- Difficult to provide specific input parameters (e.g., macropore parameters);
- Limited data to support parameterization;
- Extensive parameter requirements;
- Poorly defined estimation procedures;
- Runoff not accurately simulated;

- Actual chemical concentrations are poorly predicted;
- Not relevant to the Tier 1 assessment on the EU level (only used on one standard FOCUS model run);
- Only considers macropore flow (other forms of preferential flow not considered).

5. Opinions of Others

1. *Opinion of the Scientific Panel on Plant Health, Plant Protection products and their Residues on a request from EFSA on the FOCUS groundwater models comparability and the consistency of this risk assessment of groundwater contamination, adopted 14 September 2004:*

This opinion is typically referenced as the PPR Panel opinion. Because of the differences in the basic water balance approaches and the resultant different concentrations, the PPR panel recommends performing both PEARL and either PELMO or PRZM modeling. If the results from each model are on the same side of the threshold criteria (0.1 µg/L), no additional modeling is required. If the results are on both sides of the threshold criteria, more detailed evaluations (higher tier) are necessary. The Panel also recognized the general difficulty of modeling concentrations below 1 µg/L. Typically PEARL model concentrations were higher than either PELMO or PRZM due to higher infiltration and higher dispersion length. Therefore, the panel also made recommendations to improve the consistency between the models (e.g., using similar dispersion lengths). They concluded that MACRO was not relevant for the Tier 1 assessment on the EU level.

2. *Technical Note No. 2 on Priority Substances (Pesticides) by Dr. Steven Anthony, Environmental Modelling and GIS Group:*

This note was issued in support and description of the SNIFFER models. Statements include: The FOCUS models "require a large number of complex data and the computation time is frequently measured in hours per field site." "At the regional and national scale, risk assessments have been based on more simple, physically structured relationships..." Using MACRO, "...although the qualitative aspect or leaching was satisfactorily predicted, actual pesticide concentrations were poorly predicted. Without the opportunity for calibration, the extensive parameter requirements and poorly defined estimations procedures of the MACRO model and similar physically based models, can lead to high levels of predictive uncertainty."

3. *Generic Guidance for FOCUS Groundwater Scenarios, Version 1.1, April 2002:*

The document states that reasons for not including macropore flow include:

- Although great progress has been made in the past few years, current estimation procedures for crucial macropore flow parameters are not yet sufficiently robust in comparison to chromatographic-flow models
- Few of the normal regulatory models consider macropore flow

- Sensitive sites for chromatographic flow are usually not the sites most sensitive to macropore flow (sites most sensitive to macropore flow are often finer-textured soils with drainage systems)

Actual comparison of results of the models at one site (Chateaudun) where some experimental data were available, show that concentrations predicted by MACRO were higher (1.6 to 7 times higher) than PEARL. The exception was for the metabolite concentration of substance C. Concentrations predicted by PEARL were higher (1.3 to 10 times) than the concentrations predicted by either PELMO or PRZM.

4. PCS correspondence to CDM:

"A recent Department of Agriculture and Food-sponsored research project, in collaboration with NUI, Galway, assessed the relevance of the FOCUS scenarios for Irish environmental conditions using digital mapping. It was concluded that the conditions represented by the FOCUS scenarios are in general more vulnerable to leaching of substances to groundwater than conditions occurring in Ireland. This gives confidence that assessments conducted using the FOCUS scenarios can be reliably used to help decide whether or not an active substance used in Ireland will exceed the level 0.1 µg/L in groundwater. It therefore is considered that assessment of the leaching behavior of active substances used in plant protection products generated using the FOCUS groundwater scenarios provide a suitable approach to protect groundwater in Ireland from this potential source of contamination."