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Assessment of the vulnerability of groundwater to pesticide inputs from Irish Agriculture.

Figure 1 Installing groundwater monitoring points.

Key external stakeholders:

All farmers; Department of Agriculture, Food & Marine; Environmental Protection Agency

Practical implications for stakeholders:

This is the first specific project on pesticide occurrence in Irish groundwater. The project aimed to determine a large range of currently active and banned pesticide active ingredients and their degradation products from several locations across Ireland with contrasting physical characteristics e.g. soil type, subsoil type, and aquifer type.

The project found some active ingredients and their degradation products in groundwater at concentrations in breach permitted limits detailed in the European Union drinking water and groundwater directives. These substances were found in locations with both well drained soils, karst geology and poorly drained soils.

- **Farmers:** Pesticides occurred in karst geologies, as expected, due to little overburden material but also in poorly drained areas likely due to a delayed breakdown of pesticides.
- **Policymakers:** Mecoprop (-p), 2,4-D, and MCPA were the most frequently found active ingredients in groundwater. Degradation products were also present: usually in quantities higher than those found for active ingredients and more frequently across the catchment scale sites.
- **Scientific:** The degradation products of active ingredients were discovered in groundwater but the toxicity or persistence of these compounds is unknown.

Main results:

- The active ingredients mecoprop (-p), 2,4-D, and MCPA were frequently found both at the catchment- and national- scale (EPA data).
- The degradation products phenoxyacetic acid (PAC), dichlorbenzoic acid (DBA), and 4-chloro-2-methylphenol (4C2MP) were most frequently found in groundwater.
- Soil association, soil drainage class, subsoil type, subsoil thickness, subsoil permeability, groundwater vulnerability, and aquifer type were significantly associated with pesticide occurrence in groundwater.
- The study has highlighted that the risk of groundwater pesticide occurrence varies nationally and that mitigation measures may be required in arable farming areas dominated in high risk catchments.
- Two new analytical methods were developed to quantify for 22 substances in groundwater.

Opportunity/Benefit:

- National groundwater vulnerability databases can be used to identify areas of higher risk.
- Many compounds analysed for were not frequently detected in groundwater indicating these compounds may be less of a concern to groundwater sources e.g. bentazone and bromoxynil.

Collaborating Institutions:

Trinity College Dublin (TCD)
University College Dublin (UCD)

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1. Project background:

The widespread use of agricultural pesticide compounds has been of growing concern in the area of groundwater protection. The Drinking Water Directive (EC, 1998) and Groundwater Directive (EC, 2006) has imposed an upper limit of 0.1 µg/L for concentrations of individual pesticides (both active ingredients and degradation products) in these waters. Recent EPA reports highlighted the presence of pesticides in water samples at levels greater than 0.1 µg/L, which may have negative implications for human health. An assessment of factors influencing groundwater contamination with pesticides in Ireland was therefore urgently required. Such an assessment needed to assess the influence of pesticide mobility, adsorption, absorption and preferential flow characteristics, all of which may vary according to each pesticide's characteristics and site-specific conditions. The need for data specific to Irish agricultural conditions that can be used in a risk assessment framework to help inform policy makers of high risk compounds and regions was evident. The key objective of this research was to provide knowledge to assist in the development and implementation of policy actions to reduce the impact of pesticide usage on the environment, and in particular on groundwater quality.

2. Questions addressed by the project:

This research addressed the following questions:

- How widespread is pesticide occurrence in groundwater in Ireland?
- What pesticide compounds are most commonly detected in Irish groundwater?
- What factors influence the occurrence of pesticides in Irish groundwater?

3. The experimental studies:

Groundwater pesticide occurrence was investigated within agricultural catchments and at the national scale across Ireland. Seven intensive agricultural catchments were selected, each with different physical characteristics representing common scenarios within Ireland. Six catchments were dominated by arable farming and one by grassland. At each site monitoring points were installed to target groundwater at different depths (Figure 1). Springs, drains, and streams were also monitored where present, to gain insight into potential pesticide transport pathways. Groundwater was sampled monthly between March 2010 to March 2012, using low-flow purging methods. Water quality parameters were measured in-situ and samples collected to quantify for physico-chemical variables and pesticides.

Two in-house methods were developed using gas chromatography (GC)- and liquid chromatography (LC)-mass spectrometry (MS) and validated according to European Union legislation (SANCO/10232/2006). These methods could quantify for four organochlorine pesticides, 16 phenoxyacetic acid herbicide parent active ingredients and six of their relevant degradation products, and two benzonitrile degradation products. 22 pesticide compounds in groundwater, including degradation products, from 835 samples, were analysed throughout the study. Samples from March 2012 were also sent to an external laboratory in the UK and analysed for organophosphorous herbicides.

4. Main results:

The most frequently detected parent active ingredients in groundwater from these agricultural catchments were mecoprop and 2,4-D which were present in 35% and 26%, of all samples collected. The most frequently detected degradation products in groundwater within all seven agricultural catchments were PAC and 4-chloro-2-methylphenol (4C2MP) in 33% and 26% of samples, respectively (Figure 2). The method developed to determine mecoprop and mecoprop-p in groundwater using LC-MS was unable to differentiate between the two, thus the detection of either of these compounds is referred to as mecoprop(s). No detections of organophosphorous herbicides were found in March 2012. The most commonly detected compounds in breach of the European Union drinking water standard of 0.1 µg/L for individual compounds

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(98/83/EC) were the degradation products 2,6-dichlorobenzoic acid (DBA) and PAC. This is the first report on the widespread occurrence of these two degradation products in groundwater. The toxicity, persistence and source of these products in groundwater are unknown. The FOOTPRINT PPDB indicates that PAC degrades from MCPA and 2,4-D, DBA degrades from dichlobenil and 3,5-dichlorobenzamide (BAM), and 4C2MP degrades from MCPA, mecoprop, and mecoprop-p.

The effect of land use on pesticide occurrence was investigated by comparing pesticide occurrence on karst dominated by arable and grassland farming. The results suggest that groundwater pesticides were more associated with arable land use compared to grassland farming due to higher pesticide usage in arable areas.

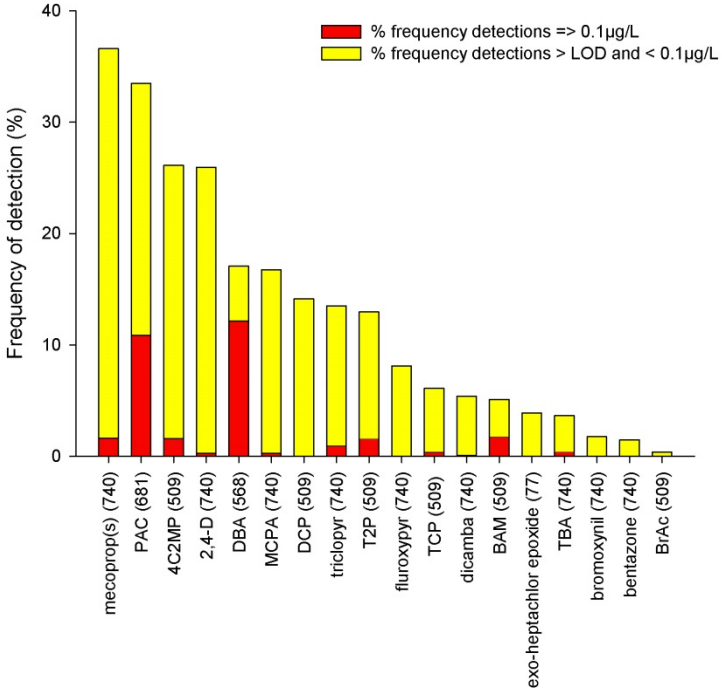

Figure 2 Percentage frequency of detection for all seven sites sampled monthly from March 2010 to March 2012. The total number of samples analysed for each compound is stated in brackets. LOD = method detection limit.

The relationship between groundwater pesticide occurrence and physico-chemical groundwater parameters was statistically evaluated. Significant positive associations were found between pesticide occurrence in groundwater and calcium, manganese, sodium, magnesium, and total nitrogen. Significant negative associations were found with redox potential, turbidity and pH. Groundwater pesticide occurrence at the national and catchment scales was found to be significantly associated with several site physical characteristics: monitoring point type, aquifer type, subsoil type, and soil drainage class were all significantly associated with pesticide occurrence at the national scale. At the catchment scale pesticides were associated with sample type, sample depth, soil association, soil texture, soil drainage class, subsoil type, subsoil thickness, subsoil permeability, aquifer type, and groundwater vulnerability. Risk of pesticide occurrence was associated with groundwater vulnerability as classified by the national methodology, providing a useful risk assessment tool. This project has highlighted that the risk of groundwater pesticide occurrence varies nationally and that mitigation measures may be required in arable farming areas dominated in high risk catchments. One high risk site of the seven studies at the catchment scale had the highest detection of compounds. This was an aerobic sand and gravel aquifer with well drained soil. The high effective porosity of the material is allowing pesticides to leach to groundwater.

At the national scale, a two year database from the Environmental Protection Agency's groundwater monitoring campaign for pesticides was analysed, reported and interpreted. The main pesticide compounds detected were MCPA and mecoprop. Comparing this national monitoring campaign with the catchment scale campaign revealed more detections during the catchment scale study (Table 1). There were also more detections in breach of the European Union drinking water standard for individual compounds during catchment scale monitoring.

Table 1 Differences in sample detection frequency between national- and catchment- scale monitoring.

Concentration category	National Scale	Catchment Scale
Number of samples analysed	845	835
≥ 0.5 µg/L	0%	8%
≥ 0.1 µg/L	3%	18%
< 0.1 µg/L	24%	41%
Non-detections	73%	41%

The overall project conclusions are summarised below:

1. The most frequently detected compounds in descending order of frequency of occurrence in Irish groundwater from catchment scale sites were: mecoprop(s), phenoxyacetic acid (PAC), 4-chloro-2-

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methylphenol (4C2MP), 2,6-dichlorobenzoic acid (DBA), MCPA, 2,4-dichlorophenol (DCP), triclopyr, and 3,5,6-trichloro-2-pyridinol (T2P).
2. Currently in Ireland mecoprop, 2,4-D, MCPA, and triclopyr are active ingredients permitted in plant protection products. Throughout the two year catchment scale monitoring campaign, the maximum observed concentrations of these four substances were 1.46 µg/L, 0.24 µg/L, 1.05 µg/L, and 0.07 µg/L, respectively.
3. Degradation products were not only found to be present in detectable concentrations in groundwater, but at concentrations in breach of the EU Drinking Water Standard for individual compounds. The most frequently detected TPs were PAC, 4C2MP, DBA, DCP, and T2P. DBA and PAC regularly exceeded the Drinking Water Standard. DBA had never been monitored for in Irish groundwater, while monitoring data for PAC in groundwater has never been published internationally. The maximum observed concentration of DBA and PAC was 120 µg/L and 4.15 µg/L, respectively.
4. The physical characteristics of zones of contribution surrounding each monitoring point which were most associated with pesticide occurrence in groundwater were the type of monitoring point, sample depth, soil association and texture, soil drainage class, subsoil type, thickness and permeability, aquifer type, and also the groundwater vulnerability index.
5. Comparing the only two available pesticide monitoring datasets on Irish groundwater for the physical characteristics most associated with pesticide occurrence revealed that monitoring point type, aquifer type, and subsoil type were associated at both monitoring scales. National scale monitoring also detected MCPA and mecoprop as some of the most frequently observed compounds. However, national scale monitoring did not quantify for any degradation products in groundwater or any other active ingredients which were frequently detected at the catchment scale (e.g. triclopyr and fluroxypyr).

European Commission (1998) 98/83/EC, Official Journal of the European Communities.
European Commission (2006) 2006/118/EC, Official Journal of the European Communities.

5. Opportunity/Benefit:

The monitoring carried out by this project represents the first analysis of pesticide groundwater quality under Irish specific conditions and can be used to assist the government in responding to EU protocols. New analytical methods were established for organochlorine, phenoxyacetic acid and benzonitrile compounds at research laboratories at Teagasc Johnstown Castle, Wexford and the Teagasc Food Research Centre, Ashtown. These may be used for future projects. New degradation products PAC, 4C2MP and DBA were widely detected in Irish groundwater monitored at the seven study sites. These compounds are relatively unknown and little is known about their toxicity or persistence in the environment in Ireland, Europe or globally. The seven sites selected and used across Ireland are now fully instrumented and could be used in the future to gain further insight into groundwater contamination. From the seven sites selected and monitored monthly, parent active ingredients from pesticide products did not exceed the 0.1 µg/L permitted limit for drinking water and groundwater as often when compared to degradation products.

6. Dissemination:

The results of the project have been presented at national and international conferences. Two papers were published and there are a further 2 papers currently under review in high impact scientific journals to date. The outputs from the project have been sent to relevant national policy makers.

Main publications:

McManus S-L, Coxon C.E., Richards K.G., Danaher M. (2013) Quantitative solid phase microextraction – Gas chromatography mass spectrometry analysis of the pesticides lindane, heptachlor and two heptachlor transformation products in groundwater, *Journal of Chromatography A*, 1284: 1– 7.
Herve Labite, Nick M. Holden, K.G. Richards, Gaelene Kramers, Alina Premrov, Catherine E. Coxon, Enda Cummins (2013) Comparison of pesticide leaching potential to groundwater under EU FOCUS and site specific conditions, *Science of the Total Environment* 463-464: 432-441.
McManus S-L, Richards K.G., Grant J., Mannix A., and Coxon C.E. (*In review*) Pesticide occurrence in Ground Water and the factors contributing to these detections in Ireland, *Journal of Environmental Monitoring and Assessment*

Popular publications:

McManus, S-L., Richards, K.G & Coxon, C.E (2009) Pesticide occurrence in Irish groundwaters. GSI groundwater newsletter, December 2009.
McManus, S-L., Richards, K.G & Coxon, C.E (2009) Investigating pesticide occurrence in groundwater in Ireland. Ireland's rural Environment: Research Highlights from Johnstown Castle, August 2009, Teagasc, Wexford.

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