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Hydrogeological characteristics influencing the occurrence of pesticides and pesticide metabolites in groundwater across the Republic of Ireland

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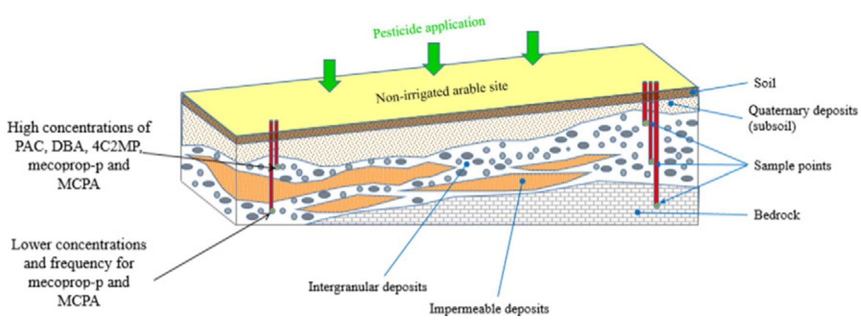
HIGHLIGHTS

- 4-chloro-2-methylphenol and phenoxyacetic acid frequently observed at higher concentrations than active ingredients
- Intergranular sand and gravel aquifers and gravel lenses within clay rich subsoil had the highest frequency of occurrence
- Only phenoxyacetic acid, triclopyr and trichlorobenzoic acid were detected above 0.1 μg/L in the artesian well
- Phenoxyacetic acid, mecoprop-p, 2,4-D and dichlorobenzoic acid were most frequently detected in groundwater.

GRAPHICAL ABSTRACT



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ABSTRACT

Pesticide contamination of water is a potential environmental issue which may impact the quality of drinking water. The full extent of pesticide contamination is not fully understood due to complex fate pathways in the subsurface. Groundwater pesticide occurrence was investigated at seven agricultural sites in different hydrogeological settings to identify where pesticide occurrence dominated in temperate maritime climatic conditions. In Ireland, six cereal dominated sites in the South East and one grassland site in the West were investigated. Soil and subsoils varied from acid brown earths with high permeability to clay and silt rich tills with lower permeability. Over a 2 year monitoring period, 730 samples were collected from a network of dedicated wells and springs across the seven sites. Multi-nested piezometers were installed in intergranular, fissured and karstic type aquifers to target shallow, transition and deeper groundwaters. Several springs were also sampled and the network included a confined aquifer. Groundwater was analysed for nine pesticide active ingredients and eight metabolites. Mecoprop and 2,4-D were the most frequently detected active ingredients above the instrument detection limit, accounting for 36% and 26% of the 730 samples collected and analysed. Phenoxyacetic acid was the most frequently detected and widespread metabolite found in 39% of samples collected at all seven sites. Where the European Union drinking water standard of 0.1 μg/L was exceeded, metabolites accounted for

Abbreviations: 4C2MP, 4-chloro-2-methylphenol; a.i., active ingredient; BAM, 2,6-dichlorobenzamide; BrAc, 3,5-dibromo-4-hydroxybenzoic acid; DBA, 3,5-dichlorobenzoic acid; DCP, 2,4-dichlorophenol; DWS, drinking water standard (0.1 μg/L); EPA, Irish Environmental Protection Agency; EU, European Union; FmWDa$_{1/2}$, fractured metasediments well-drained arable site 1 or 2; FvPDa, fractured volcanic poorly-drained arable; FvWDa, fractured volcanic well-drained arable; GSI, Geological Survey of Ireland; I/KWDa, intergranular/karst well-drained arable site; KWDa, karst well-drained arable site; KWDg, karst well-drained grassland site; Ll, locally important aquifer – bedrock which is moderately productive only in local zones; LOD, limit of detection; m bgl, metres below ground level; MS/MS, tandem mass spectrometry; ORP, oxidation-reduction potential; PAC, phenoxyacetic acid; PTFE, polytetrafluoroethylene; Rf, regionally important aquifer – fissured bedrock; Rg, gravel aquifer – regionally important; Rkc, regionally important aquifer – dominated by conduit flow; Rkd, regionally important aquifer – dominated by diffuse flow; T2P, 3,5,6-trichloro-2-pyridinol; TCP, 2,4,5-trichlorophenol; UHPLC, ultra high performance liquid chromatography.

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the majority of exceedances with 3,5-dichlorobenzoic acid (DBA) and phenoxyacetic acid (PAC) dominating. Highest detections were encountered in sites with well drained soils underlain by gravel and limestone aquifers and within gravel lenses in lower permeability subsoil. Across the seven sites pesticide detections were mostly associated with metabolites and the environmental impact of many of these is unknown as they have received little attention in groundwater previously.

1. Introduction

In Europe almost 70% of drinking water is derived from groundwater (Malaguerra et al., 2012) which can be at risk of contamination from a range of industrial and agricultural sources. In the Republic of Ireland approximately 26% of public and private drinking water supplies are from groundwater sources, with groundwater contributing up to 75% of drinking water supplies in some regions (Lucey, 2009). Groundwater has long been recognised as an important natural resource to protect and a number of European Directives have been released to protect groundwater quality from pesticides. Pesticides are widely used in modern agriculture, but some may pose risks to the environment should they reach groundwater or surface water. The European Union (EU) drinking water standard (DWS) from the Drinking Water Directive (98/83/EC) and the water quality standard for groundwater bodies under the Groundwater Directive (2006/118/EC) gives is a maximum concentration for individual pesticides of 0.1 μg/L. Not only are some parent pesticide active ingredients (a.i.) of concern in groundwater but also some of their metabolites. Metabolites are chemical substances that result from decomposition of the parent compound (Lewis et al., 2016). The parametric value of 0.1 μg/L is also used for metabolites unless the metabolite is toxicologically non-relevant. In this case the parametric value can be set up to 10 μg/L but must adhere to strict criteria as described in SANCO/221/2000 rev10. Since the Plant Protection Products Directive (91/414/EEC) was implemented, approximately 74% of a.i. have been withdrawn or banned with only 335 a.i. remaining for European use in 2010 (Cross and Edwards-Jones, 2011).

The reported extent of pesticide groundwater contamination varies between different countries and regions depending on the extent of awareness, monitoring, research, and pesticide usage. For example in America, atrazine is one of the most widely used pesticides, one of the most widely studied, and thus also the most frequently found in groundwater (Kolpin et al., 2000; Barbash et al., 2001). Although atrazine use was banned in France in 2003, both atrazine and its metabolite desethylatrazine were detected in French groundwater years after its removal from the market (Baran et al., 2008). Many studies are published each year on atrazine's presence in the environment, especially for its metabolites (Kolpin et al., 1997; Fava et al., 2007; Iker et al., 2010; Jablonowski et al., 2011). Dichlobenil is a well-known groundwater contaminant in Danish groundwater, which was deregistered in 1997 because it degrades to the metabolite 2,6-dichlorobenzamide (BAM). Dichlobenil was removed from the Irish market in 2010. The main dichlobenil metabolite BAM readily leaches into groundwater because of its mobility and persistence (Clausen et al., 2007). BAM was also found at concentrations frequently exceeding the EU drinking water standard (DWS) in Italian groundwaters (Porazzi et al., 2005) and British sandstone aquifers (White et al., 2016). There is no recent published data on the presence of either dichlobenil or BAM in groundwater from Ireland (apart from one record of dichlobenil below an industrial site (Eades, 1992)), even though BAM has been detected in groundwaters in other countries (Björklund et al., 2011). Glyphosate is a widely used herbicide across the World and its detection in shallow groundwaters in rural locations along with its main metabolite AMPA has been found by Van Stempvoort et al. (2015). A useful review on sources of AMPA can be found in Grandcoin et al. (2017).

Groundwater vulnerability influences the likelihood of a pesticide or metabolite reaching groundwater, and this term is used to conceptualise how easily groundwater can be impacted. In Ireland groundwater vulnerability is defined as the intrinsic geological and hydrogeological characteristics that determine the ease with which groundwater may be contaminated by human activities (DELG/EPA/GSI, 1999). This concept is used for a range of pollutants to provide land managers with a risk assessment tool to help protect drinking water resources. Intrinsic vulnerability depends on a number of characteristics such as travel time, groundwater depth and subsoil permeability, while the contaminant properties will play a role in specific groundwater vulnerability e.g. pesticide organic carbon coefficient which may indicate a particular pesticide's attenuation capability. The hydrological connection between the land surface and groundwater determines the vulnerability to contamination. Therefore, an aquifer which can receive recharging water and contaminants more effectively due to the connection between the overlying materials and groundwater will be more vulnerable to contamination than in a situation where the overlying materials prevent the contaminants from reaching groundwater because of their nature (Daly and Warren, 1998). However, land management practices such as irrigation and application coinciding with rainfall events can increase a pesticide's ability to leach (Menchen et al., 2017; Vendelboe et al., 2016). Substances such as pesticides are subject to complex physical, chemical, and biological transformations during their transport through the unsaturated zone and their displacement depends on the transport properties of the water-air-porous medium system (Yaron, 1989) which can complicate leaching predictions.

To aid the understanding of how pesticides from agricultural applications can leach to groundwater, a conceptual model of the pathways present should be drafted. One of the most consistent uses of pesticides in agriculture is through sprayer 'blanket' applications on fields dedicated to arable crops (e.g. spring barley). In 2010 arable land in Ireland accounted for 22% (or 273,900 ha) of the total agricultural area available (Eurostat, 2010).

The objective of this study is to evaluate exceedances of pesticide active ingredients (a.i.) and metabolite occurrence in groundwater in a range of representative hydrogeological settings across the Republic of Ireland chosen for their contrasting site characteristics. This investigation aims to indicate where the majority of pesticides and metabolites can be found across sites and also indicate which pesticides and metabolites are most frequently found in Irish groundwaters, to complement a national screening dataset published elsewhere (McManus et al., 2014b). Metabolites such as 4C2MP and PAC have until now never been analysed in groundwater and their transformation in the environment and locality in groundwater are unknown.

2. Materials and methods

2.1. Site selection

Sites were selected to represent some of the main arable agriculture, soil and hydrogeological characteristics present across Ireland. National datasets listed in Supplementary Material A were acquired and the 2006 CORINE land cover (CLC 2006) dataset from the European Environment Agency (2016) used to highlight arable land use across Ireland. A total of 398 t of a.i. was applied to the arable crop Spring barley in 2004 (Pesticide Control Service, 2007) and of this the main a.i. applied was