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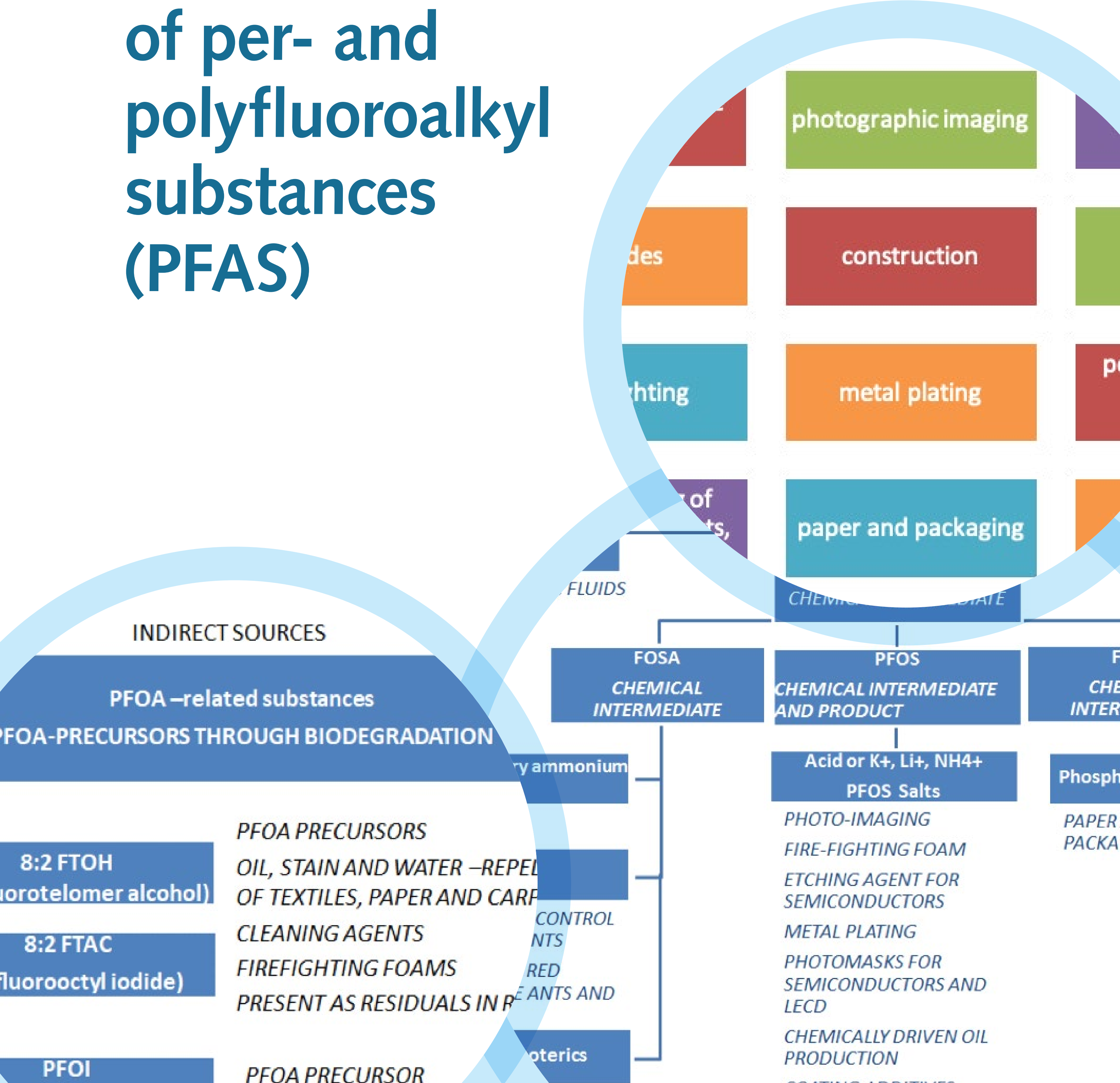
FOR WATERS

Scoping study for addressing risks to private water supplies from the presence of per- and polyfluoroalkyl substances (PFAS)



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Published by CREW – Scotland's Centre of Expertise for Waters. CREW connects research and policy, delivering objective and robust research and expert opinion to support the development and implementation of water policy in Scotland. CREW is a partnership between the James Hutton Institute and all Scottish Higher Education Institutes supported by MASTS. The Centre is funded by the Scottish Government.

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Please reference this report as follows: Ioanna Akoumianaki and Malcolm Coull 2018. Scoping study for addressing risks to private water supplies from the presence of per- and polyfluoroalkyl substances (PFAS). S600018-10. Available online at: crew.ac.uk/publications

Dissemination status: Unrestricted

Contents

Glossary

Direct PFAS sources: These refer to emissions of a specific PFAS from sites of their manufacturing, use and disposal and they can be both point and diffuse pollution sources (Buck et al 2011).

Indirect PFAS sources: Emissions of PFAS which are related to degradation of precursor compounds and formation of PFAS by chemical and/or biological transformation (Buck et al 2011).

LOD: Limit of detection of PFAS concentrations.

PFAS advisory guidelines for drinking water: Depending on context, these may refer to at least two sources of guidance: (i) the parametric values for individual PFAS (≤100ng/L) and for PFAS as a group (≤500ng/L) in drinking water proposed by the European Union (EU) (EU Recommendation 2018); and (ii) the parametric values for PFOS (400ng/l) and PFOA (4000ng/l) in drinking water recommended by the World Health Organisation (WHO) (WHO 2017).

PFAS risk to PWS indicators (in the context of this report): Spatial information that indicates the presence/absence of direct PFAS sources to a waterbody serving PWS or at selected distances from PWS.

PFAS: Per- and poly-fluoroalkyl substances.

PFAS<LOD Sites: Sites SEPA Monitored For PFAS where PFAS concentrations are < LOD.

PFAS>LOD Sites: These refer to Sites SEPA Monitored For PFAS where PFAS concentrations are >LOD.

PFOA: Perfluorooctanic acid.

PFOS: Perfluorooctane sulfonate and Perfluorooctane sulfonic acid.

Potential PFAS Source Sites: These refer to locations of direct potential PFAS sources in Scotland according to the literature review on PFAS sources in the UK and internationally.

Risk (in the context of this report as PFAS risk to PWS): The likelihood of PFAS concentrations being >LOD (PFAS>LOD) in the drinking water served by private water supplies (Rausand 2013).

Risk assessment: The term refers to analyses of what can go wrong, how likely it is for a hazardous event to happen, what its potential consequences are, and how tolerable the identified risk is (Rausand 2013). In the context of this report, this involves systematic use of available information to identify direct PFAS sources to PWS and to estimate the risk of PFAS>LOD in the drinking water served by PWS based on: experience or expert judgement; or numerical estimates for probabilities of occurrences of PFAS>LOD concentrations, sometimes with associated uncertainties.

Scoping studies (or reviews): A method used to comprehensively map evidence across a range of studies in an area, with the aim of informing future research practice, programs and policy (O'Brien et al 2016).

Sites SEPA Monitored For PFAS: Borehole sites located in rural and urban areas where SEPA measured PFAS in 2013-2016. These borehole locations were not selected to target any Potential PFAS Source Sites.

Subsurface PFAS sources: Emissions from unsaturated zones beneath PFAS-contaminated land and stream beds which are believed to be continuing sources of PFAS to the aquifer decades after cessation of PFAS use.

Executive Summary

Questions

Is there sufficient evidence for a high-level, national-scale assessment of the risk of detecting per- and polyfluoroalkyl substances (PFAS), such as perfluorooctane sulfonate (PFOS) and perfluorooctanic acid (PFOA), in private water supplies (PWS)?

Key findings

- We developed and implemented a risk-mapping method based on GIS tools, a review of available evidence on types of direct PFAS sources (i.e. related to manufacturing and use) to the water environment in Scotland, the UK and internationally, and on available PFAS data in Scotland. We showed that there is sufficient evidence to identify the locations of the majority of types of potential direct PFAS sources (hereafter reported as Potential PFAS Source Sites) in relation to the locations of all PWS. However, there is not sufficient open-access PFAS data to identify PFAS risk to PWS, i.e. whether and where PFAS concentrations are above the limit of detection (LOD) in drinking water sources to PWS.
- Groundwater PFAS concentrations from 17 Sites SEPA Monitored For PFAS (which were not sited to assess impact of Potential PFAS Source Sites on groundwater) sampled in rural and urban areas in 2013-2016 were below the advisory parametric values for drinking water recommended by the EU. However, this evidence is not sufficient for a national-scale assessment of PFAS risk to PWS.
- The GIS-based methodology developed here for mapping PFAS risk to PWS shows that:
    - o Potential PFAS Source Sites, are found in all Local Authority areas.
    - o All groundwater bodies are connected with waterbody catchments with Potential PFAS Source Sites.
    - o All Sites SEPA Monitored For PFAS are located within 5 km from the following types of Potential PFAS Source Sites: wastewater discharge points, landfill sites and sites of potentially PFAS-containing stockpiles. PFAS concentrations were above LOD in 11 out of 17 Sites SEPA Monitored For PFAS (hereafter reported as PFAS>LOD Sites); however, the site-specific causes of PFAS>LOD are uncertain.
- Review of international evidence on PFAS shows that:
    - o PFAS can be detected downstream, beneath and downgradient of direct PFAS source sites such as: airports; oil, gas and mining production sites; chemical plants; landfills; wastewater discharge points; fire-fighting foams- and biosolid-impacted land; and sites with PFAS-containing stockpiles.
    - o PFAS from direct sources may enter drinking water resources though: wastewater discharge; bank infiltration of PFAS-containing effluent to groundwater; runoff from PFAS-impacted land; leaching to groundwater from PFAS-impacted land and landfill sites; and industrial and landfill emissions to air.
    - o Groundwater is the main freshwater sink for many PFAS substances. Distribution of PFAS in groundwater depends on: presence and type of PFAS sources, PFAS chain-length and structure, geochemistry at unsaturated and saturated zones of an aquifer, and groundwater flow and velocity.

Background

The EU has proposed updates in the list and standards (i.e. parametric values) of parameters to be monitored under the Drinking Water Directive (DWD), in line with latest WHO recommendations. The EU identifies drinking water parametric values for individual PFAS (≤100ng/L) and for PFAS as a group (≤500ng/L). Upon approval of this recommendation, the parametric values for PFAS will apply to all water supplies that must be monitored under the DWD at the frequency and supply zones (or risk areas) identified following a risk assessment. In this context, the information available on the presence of PFAS in the water environment of the Scottish countryside needs to be assessed to identify PFAS risk to PWS.

GIS-based risk-mapping methodology

We assessed PFAS risk to PWS using four indicators referring to presence or absence of direct PFAS sources in relation to PWS:

(i) Presence or absence of direct Potential PFAS Source Sites in the same waterbody (surface or groundwater) as PWS, based on evidence that PFAS concentrations above the limit of detection (PFAS>LOD) are associated with direct PFAS sources within a waterbody catchment.

(ii) Presence or absence of direct Potential PFAS Source Sites within 0.5 km and 5 km (distances arbitrarily selected) from PWS, as an initial starting point for exploring PFAS risk to PWS suggested by SEPA and because direct PFAS sources out with a waterbody catchment may influence water resources through atmospheric deposition and long-distance transport along a river catchment.

(iii) Presence or absence of PFAS>LOD concentrations in data from the 17 Sites SEPA Monitored For PFAS in the same waterbody (surface or groundwater) as PWS, based on evidence that PFAS>LOD are associated with the presence of direct PFAS sources in the same waterbody catchment.

(iv) Presence or absence of PFAS>LOD concentrations in data from the 17 Sites SEPA Monitored For PFAS (or any other available locations of known PFAS concentrations in surface waters or groundwater) within 0.5 and 5 km (distances arbitrarily selected) from PWS, based on evidence that PFAS>LOD are associated with influence from direct PFAS sources emitted within the same waterbody catchment.

We must clarify that the GIS-based risk-mapping method developed here explores:

(i) Distribution of Potential PFAS Source Sites in waterbodies and Local Authority areas as baseline information collected for the first time.

(ii) Spatial relationships between Potential PFAS Source Sites and PFAS>LOD Sites to understand whether there is a consistent pattern of co-occurrence of PFAS>LOD concentrations and Potential PFAS Source Sites and potentially inform further, targeted research.

(iii) Spatial relationships between PWS and PFAS>LOD Sites to potentially inform investigative PFAS monitoring in PWS served by groundwater at PFAS>LOD Sites.

We must also explicitly clarify that the GIS-based risk-mapping method developed here:

- Does not consider that Potential PFAS Source Sites are actual direct PFAS sources to PWS.
- Does not extrapolate PFAS measurements at Sites SEPA Monitored For PFAS to the scale of groundwater waterbody, surface water waterbody, river catchment, Local Authority area, or any other regional or national scales.
- Does not account for subsurface PFAS transport pathways.
- Does not account for indirect PFAS sources.

1 Introduction

In Scotland and the EU, drinking water quality is regulated under the Council Directive 98/83/EC on the quality of water intended for human consumption (Drinking Water Directive-DWD). The revision of Annex II Part C to the DWD in October 2015 focussed attention and limited resources to hazards of local concern, by requiring risk assessments at a supply zone scale as a basis for granting deviations from the list of parameters and frequencies subject to compliance monitoring. On the 1st of February 2018, the European Commission adopted a proposal for "recasting" the DWD to improve the quality of drinking water and provide greater access and information to citizens (EU Recommendation 2018). The proposal updates the list and standards (i.e. parametric values) of parameters to be monitored in line with latest recommendations of the World Health Organisation (WHO 2017).

The update includes chemicals, which are "new" to the Directive (EU Recommendation 2018), such as:

- Per- and polyfluoroalkyl substances (PFAS) as a group.
- Individual PFAS, e.g.: perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), 8:2 flurotelomer alcohol (8:2 FTOH), 6:2 flurotelomer sulfonic acid (6:2 FTSA), perfluorobutyric acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA) and many more.

The EU Recommendation addresses the precautionary principle based on growing evidence showing the presence of various PFAS substances in drinking water. It also introduces a harmonised and feasible threshold for PFAS in drinking water among Member States. Regulating the whole PFAS group deviates from the approach recommended by the World Health Organisation (WHO), which recommended parametric values only for PFOS (400ng/l) and PFOA (4000ng/l) based on evidence that PFOS and PFOA are the most common PFAS substances in the environment (WHO 2017). Further, the parametric values in the EU Recommendation for individual PFAS differ from the guidance values for PFOS and PFOA set by several Member States.

For example, the Drinking Water Inspectorate (DWI) and Scotland's Drinking Water Quality Regulator (DWQR) in consultation with the Health Protection Agency (HPA) set health-based guidance action values only for PFOS (1000ng/l) and PFOA (5000ng/l) in drinking water and advised water companies to monitor PFOS and PFOA in supply zones where their concentrations exceed 300ng/L (DWI 2009; DWQR 2009). The German Drinking Water Commission assessed PFAS in drinking water and set a health-based guidance value for safe lifelong exposure of all population groups to the sum of PFOS and PFOA ($\Sigma_{PFOS+PFOA}$) at 300ng/L (Wilhelm et al 2008). The Italian Ministerial Decree on the PFAS contamination of drinking water in the Veneto Region (2014 cited in WHO 2016) established threshold values for PFOS at 30ng/L, and for PFOA and other PFAS at 500ng/L. The National Food Agency of Sweden (NFAS) set a non-legally binding guideline action value of 90ng/l for the sum concentration of 11 individual PFAS, i.e. PFBS, PFHxS, PFOS, 6:2 FTSA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA (NFAS 2017). For comparison, the U.S. Environmental Protection Agency (EPA) issued lifetime drinking water health advisories in 2016 at 70 ng/L for the combined concentration of PFOS and PFOA (US EPA 2016).

Upon approval of the EU Recommendation, the parametric values for PFAS will apply to all water supplies that must be monitored under the DWD at the frequency and supply zones (or risk areas) identified following a risk assessment. In Scotland, Scottish Water has the responsibility of managing, monitoring and risk assessing public water supplies, which serve approximately 97% of the resident population. The remainder of the population, predominantly in rural and remote areas, are served by private water supplies (PWS), which are the responsibility of their owners and users but are monitored by local authorities under The Private Water Supply (Scotland) Regulations 2006 as amended in 2017 (hereafter reported as The Regulations)[1].

In this context, the information available on the presence of PFAS in the water environment of the Scottish countryside needs to be assessed. Available evidence and knowledge gaps are key to informing the risk assessment for designing PFAS monitoring, as stipulated in The Regulations and the EU Recommendation (2018). This project was commissioned by the DWQR with the aim to *"develop and implement a method to provide a high-level, national risk assessment of the risks to PWS from PFAS."*

1.1 Objectives

The objectives of this study, as set out in the project specification (reproduced in italics), are:

- *A literature review of the existing information on the concentrations of PFAS in the Scottish water environment and the relevant historic and current usage and land use in Scotland. The review will cover other factors as necessary to understand the introduction, movement, and persistence of PFAS in catchments in the context of small supplies and PWS. Evidence from international examples may be used as analogues.*
- *Development of a GIS-based mapping method of potential risk for PWS from PFAS to support risk assessment.*
- *Identification of risk areas for PFAS in PWS on the basis of the literature review findings and the mapping method.*
- *Identification of numbers of PWS within risk areas by local authority and catchment scale (if suitable).*

1.2 PFC nomenclature-Terminology

This report uses the nomenclature and terminology proposed by Buck et al (2011), which has also been adopted by the wider scientific and regulatory community as well as by the United Nations (UN) Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP 2009) (hereafter reported as the Stockholm Convention), the Madrid Statement on PFAS (Blum et al 2015) the Organisation for Economic Co-operation and Development (OECD), the European Union (EU), the WHO, and the US Environment Protection Agency (US EPA). This section describes the current use of acronyms and terms applying to PFCs and PFASs.

Per- and polyfluoroalkyl substances (PFAS) and perfluorocarbons belong to the family of fluorinated chemicals, both abbreviated as PFC. The acronyms PFC and PFAS as well as the terms ‘fluorinated surfactants’, ‘fluorosurfactants’, ‘fluorinated tensides’ or ‘fluorotensides’ have been used concurrently for describing exclusively per- and polyfluoroalkyl substances. However, the Kyoto Protocol included perfluorocarbons in the substances contributing to the Greenhouse Effect using the acronym PFC (UN 1997). During the last decade the EU, the Stockholm Convention, OECD and several regulatory agencies such as US EPA use the acronym PFASs for per- and polyfluoroalkyl substances.

Buck et al (2011) clarified the difference between different types of fluorinated chemicals and recommended that:

- The acronym PFC is used to describe perfluorocarbons, which contain only C and F atoms. Examples of PFCs are the greenhouse gasses tetrafluoromethane (CF4), hexafluoroethane (C2F6), octafluorocyclobutane (C4F8) and perfluorodecalin (C10F18). Perfluorocarbons are not discussed further in this report.
- The acronym PFAS is used to describe per- and polyfluoroalkyl substances containing the perfluoroalkyl functional chain (moiety) C_nF_{2n+1}–. In perfluoroalkyl substances, fluorine has replaced all the hydrogens bonded to carbons in the alkyl chain; in polyfluoroalkyl substances, not all carbons in the chain are bonded to fluorine atoms. PFAS refers to a diverse group of

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[1] Regulations of PWS in Scotland is described in Appendix III.2.1.

substances with different properties and commercial uses. Chemical PFAS families and examples of individual PFAS are listed in Appendix I.

Buck et al (2011) also discussed additional terms referring to PFAS under the following categories:

- Degree of polymerisation. This differentiates between non-polymeric and polymeric PFASs.
- Carbon (C) chain length. There are short-chain and long-chain PFASs; generally, a perfluoroalkyl chain with seven or more C atoms, e.g., C_7F_{15}–, is ‘long’.
- Branching of the C backbone. There are linear and branched isomers of the same compound, which is of concern because this may present challenges in PFAS quantification in environmental samples.
- Acronyms for acids and their dissociated forms (anions). For simplicity, both protonated and anion forms, are referred to as ‘acids’ with the same acronym, although the anions may well predominate in environmental and biological samples. For example, both perfluorooctanoic acid and perfluoroctanoate (the anionic form) are referred to as PFOA. Likewise, both perfluorooctane sulfonic acid and the anionic perfluoroctane sulfonate are referred to as PFOS.
- Type of source. This makes a distinction between direct and indirect emission sources. Direct sources refer to emissions of a specific PFAS from sites of their manufacturing, use and disposal and they can be both point and diffuse pollution sources. Indirect sources refer to the formation of a specific PFAS by chemical and/or biological transformation of precursor substances after their release in the environment and transport to drinking water through the water cycle or to food through the food chain. Indirect PFAS sources are not further examined in relation to PFAS risk to PWS in this report.

1.3 Outline of the report

The remaining sections of this report are organised as follows:

- Section 2 outlines the literature review approach.
- Section 3 provides bitesize information on the international evidence-base on PFAS.
- Section 4 describes the available evidence on PFAS sources and occurrence in Scotland.
- Section 5 develops, implements and evaluates a GIS-based PFAS risk mapping method.

Appendix I lists names for non-polymeric and polymeric PFAS. Appendix II.1 presents the output of the computerised literature review searches. Appendix II.2 details the data-sources for GIS-based risk mapping. Appendix III provides an extensive review of available evidence on PFAS.

2.0 Literature review approach

Computerised searches were performed using web-based search engines such as Google Scholar (GS), Web of Science (WoS), Science Direct (SD), and FAOLEX. The reason for using three different search engines was to take advantage of the different benefits arising from the use of each one of them. GS enabled the detection of published peer-reviewed and grey literature (e.g. reports from government organisations, water companies or health and regulatory agencies) on the basis of full document searches including results drawn from references. WoS enabled a detection of peer-reviewed articles tagged for their high scientific impact and close relevance of their title and keywords with the search terms. In addition to the advantages referring to the WoS search engine, SD allowed for de-emphasising results from the references in a report or peer-reviewed paper. FAOLEX was used to extract information on the rational for any statutory thresholds for PFCs and PFAS in drinking water. Only articles and reports in English were selected.

The following words-phrases were used as search terms (output per search in Appendix II.1):

- Perfluorinated chemicals OR PFC OR PFAS
- Scotland
- Drinking water
- Landfill leachate OR fire-fighter foam OR wastewater OR sludge OR biosolid OR groundwater OR freshwater
- Monitoring

The findings of the review were used for compiling a list of the major usage and manufacturing activity of PFAS to identify key point and diffuse sources and industries likely to be important as direct PFAS sources to the water environment of Scotland. Concentrations in freshwater environments out with Scotland were not reviewed because these refer to local context of sources and factors influencing PFAS contamination.

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[2] Many PFASs are acids and may be present as protonated or anionic forms, or a mixture of both, depending on the pH in the environmental medium and the compound’s acid dissociation constant (pKa) (Buck et al 2011).

3.0 Background

Here, we present bitesize information based on the extensive review of peer-reviewed and grey literature in Appendix III.

3.1 General information

PFAS are a family of more than 3000 man-made chemicals that have been extensively used since the 1950s in a wide range of industrial and everyday products; however, not all of them have been studied (Appendix III.1-3). Some PFAS are persistent, biocumulative and toxic (i.e. PBT) and ubiquitous in humans, wildlife and the environment (Appendix III.1.4.)

3.2 Direct PFAS sources

The major direct PFAS sources are (Appendix III.1.5; see also Appendix III.1.8):

- Waste water discharges (effluent[3]) from wastewater treatment works (WwTW).
- Land where biosolid, i.e. treated sewage sludge or slurry, has been applied for recycling (reclamation) or as fertilizer to improve and maintain productive soils and stimulate plant growth.
- Aqueous film-forming foams (AFFF)-impacted land, such as fire-fighter training areas or areas where AFFF have been used.
- Premises such as fire stations and business sites, where PFAS stockpiles may be stored as raw materials and only if leaks occur to the surrounding ground.
- Chemical plants, where PFAS are manufactured or are used at industrial user sites.
- Oil, gas and mining production sites.
- Military bases.
- Airfields, only when storage of PFAS-containing stockpiles and use of PFAS-containing materials for training purposes are not managed in line with relevant regulations.
- Landfills.

3.3 PFAS transport: pathways from direct sources to drinking water resources

PFAS may enter water resources through the following surface transport pathways (Appendix III.7-8):

- Direct discharge of insufficiently treated wastewater from landfill leachate, airports, military bases and mixed household/industrial effluent.
- Direct discharges of trade effluent.
- Bank infiltration of PFAS-containing effluent to groundwater.
- Runoff to surface waters from PFAS-impacted land.
- Leaching to groundwater in PFAS-impacted land and landfill sites. It must be noted that the total concentrations of perfluoroalkyl acids (PFAA), which is a class of PFAS, have been found to vary from hundreds to thousands in the leachate from closed landfills (20-40 years ago) and the PFAA content of leachate in EU countries may vary from <1 to 1800 ng/L (Appendix III.1.8.2).
- As vapours emitted from pressurised equipment in chemical plants due to leaks or other unintended or irregular releases of gases.
- Emissions to the ambient air from landfill sites.

3.4 Sub-surface PFAS sources, transport pathways and sinks

Sub-surface sources (Appendix III.1.7.2):

- The unsaturated zones beneath PFAS-contaminated land and stream beds are believed to be continuing sources of PFAS to the aquifer decades after cessation of PFAS use.

Transport pathways (Appendix III.1.7.2):

- The spatial distributions of individual PFAS substances in groundwater are likely due to a combination of factors including multiple sources, PFAS chain length and structure, geochemistry at the unsaturated and saturated zones of an aquifer, presence of minerals in the soil, groundwater flow and velocity (i.e. hydraulics), and presence and transformations of PFAS precursor substances (i.e. indirect PFAS sources).
- PFAS in groundwater can travel at least 4km downgradient AFFF-impacted land.
- Short chain length PFAS (e.g. PFHxA, C6) are more mobile than long chain length PFAS (e.g. PFOS, C8) both vertically and horizontally.
- Indicatively (due to limited evidence), PFAS time-lag may range between 3 and 30 years and travel time may reach 15 years for 780 m.

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[3] The evidence reviewed in Appendix III.1.8.4 suggests that PFAS are resistant to wastewater treatment.

PFAS sinks related to drinking water quality (Appendix III. 1.7.2):

- Groundwater is the main freshwater sink for many PFAS substances.

3.5 Indirect PFAS sources

The evidence reviewed in Appendix III.1.6 shows that:

- Indirect PFAS sources refer to the formation of a specific PFAS by chemical and/or biological transformation of precursor substances after their release in the environment.
- The significance of indirect PFAS sources can only be assessed after the identification of precursor substances in the PFAS emitted from direct PFAS sources and the PFAS content in potential drinking water sources (e.g. rivers, springs, groundwater).
- Precursor substances can be transformed through aerobic and anaerobic biotransformation, which may explain the increase of PFOS and PFOA from influent to effluent, and through atmospheric degradation, which is the major source of PFAS in remote areas.
- Specific precursor substances, such as 6:2 FTSA and 8:2 FTSA, are expected to be found in AFFF-impacted groundwater.

3.6 PFAS risk to drinking water resources

A limited number of studies assessed PFAS risk to drinking water supplies.

At the river catchment scale (i.e. on average 50 Km radius) or larger scales it has been found that (Appendix III.1.8.1):

- Direct PFAS sources are significantly more abundant in river catchments and waterbody catchments with detectable PFAS (i.e. PFAS>LOD) in drinking water supplies served by surface water, spring or groundwater sources.
- PFAS may enter groundwater after infiltration in downstream regions of large river catchments when direct PFAS sources are located in their upper parts (for this see also Appendix III.1.8.4-Biosolid).
- PFAS may be detected in surface and groundwater supplies that may not located at the same river catchment as the direct PFAS sources, due to past or ongoing PFAS emissions to air.

3.7 PFAS substances as indicators of the type of direct PFAS source

Regulatory and research freshwater monitoring evidence base shows that (Appendix III.1.8):

- PFOA, PFBS, PFHxS and PFPA have been found in a wide range of everyday consumer products.
- PFBS, PFHxS, PFOA and PFOS have been found in high concentrations in contemporary landfill leachate.
- PFOS, PFOA, and PFHxS have been found in very high concentrations in biosolids.
- PFOS, PFOA and PFHxS have had widespread applications in the past (for their current regulation see Section 3.9).
- 6:2 and 8:2 FTSA have been associated with AFFF-impacted land and WwTW discharges.

3.8 Health effects of PFAS exposure in drinking water

The evidence reviewed in Appendix III.1.9 suggests that the health effects of exposure to the entire family of PFAS substances in drinking water are not well understood for three main reasons:

1. It is unclear what level of PFAS concentration in drinking water can be considered as the effect dose.
2. The health effects of PFAS have only been studied for PFOS, PFOA, PHxS and PFNA; however, it remains uncertain whether the health effects should be attributed to these particular substances or to their precursor substances.
3. Little is known about the combined toxicity due to exposure to a cocktail of individual PFAS substances under a variety of circumstances.

Adverse health effects related to PFAS exposure include (inter alia): decreased growth rate and brain development in infants and children; increased risk of bladder and kidney cancers; endocrine (hormonal) and immune systems dysfunction.

3.9 PFAS regulation

The evidence reviewed in Appendix III.2 about the regulatory measures to reduce PFAS risk to drinking water shows that the greatest challenges facing the regulatory community are:

- Lack of robust scientific evidence on PFAS content of commercial and industrial products.

- Lack of robust scientific evidence of PFAS concentrations in potential drinking water resources.
- Prohibitive cost of available technologies for the treatment of PFAS-contaminated water.

PFAS that are confirmed PBT and subject to long range transport are listed as Persistent Organic Pollutants (POPs). As of 2018:

- PFAS listed as POPs refer to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF).
- PFAS recommended for listing as POPs include perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds.
- PFAS under review by the POPs Review Committee refer to perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds.

Further information on the Stockholm Convention can be found in Appendix III.2.2. In EU, there are strict regulations in addition to the Stockholm Convention aiming to restrict the use and emissions of specific PFAS substances. For example, the REACH framework restricts the use and emissions of PFOA (Appendix III.2. 3). Further, Directive 2000/60/EC, hereafter reported as the Water Framework Directive (WFD), lists PFOS as a priority substance and has specified an environmental quality standard (EQS) value in surface waters at 0.65 ng/l (annual average) (Appendix III.2.4).

As a final note, the European Food Standard Agency (EFSA) established a Tolerable Daily Intake for PFOS at 150 ng/kg of body weight/day and for PFOA at 1500ng/kg of body weight/day, which can help identify whether exposure to PFAS in drinking water poses any health risk (Appendix III.2.5).

4.0 PFAS in Scotland's waters

4.1 Overview of PFAS data in Scotland

Substantial evidence on PFAS emissions and concentrations in the environment in Scotland and the UK is lacking. The following sources of information were found and evaluated:

1. PFAS samples collected by SEPA from 2013 to 2016 at 17 boreholes located in rural and urban areas. These borehole locations were not selected to target any potential direct PFAS sources. PFAS concentrations and composition from these samples are described in Section 4.2; see also Appendix II.2. The legislative context for the collection of these samples is reviewed in Appendix III.2.4.
2. A letter from DWQR advising Scottish Water to determine the risk for PFOS and PFOA on completed Drinking Water Safety Plans by the 30th April 2010 and describing relevant regulatory requirements (DWQR 2009). Monitoring of PFOS and PFOA concentrations in drinking water is advised where the Drinking Water Safety Plans have indicated exceedance of the threshold of 300ng/L (see Section 1.1).
3. Information on the results of the Chemical Investigation Programme (CIP2[4]), which has sampled many sites in England and Wales as well as several sites at the central belt and the East coast of Scotland (Barden 2018; Cartmell and Frogbrook n.d.). A powerpoint presentation document presented evidence that Scottish Water is assessing PFOS and PFOA in rivers upstream and downstream of water treatments works (WTW), wastewater treatment works (WwTW) and in sludge (Cartmell and Frogbrook n.d.). A recent presentation of the progress of CIP by Barden (2018) and the presentation by Cartmell and Frogbrook (n.d.) mention that PFOA and PFOS are amongst the highest ranking 10 substances of concern for removal at drinking water treatment works in the UK.
4. A comparative European peer-reviewed study[5] of PFAS concentrations in rivers and streams (Loos et al 2009), which assessed PFAS concentrations in the Rivers Clyde and Forth amongst other rivers and streams across Europe. The PFAS concentrations from these rivers were between 1 and 10ng/L, thus Rivers Clyde and Forth were neither among the most PFAS contaminated nor among the most pristine rivers of Europe.
5. A peer-reviewed study on contamination of fish in UK freshwater systems by Rose et al (2015), which assessed PFOS concentrations in brown trout and rainbow trout in the River Gryfe. The study showed that brown trout and rainbow trout specimens contained 6 and 8ng/kg of PFOS, respectively. These PFOS levels were among the lowest in fish studied across the UK.
6. Two reports on the industrial uses and emissions of Persistent Organic Pollutants (POPs) including PFOS and PFOA in the UK (Brooke et al 2004; Whiting et al 2012), both prepared for the Department for Environment Food and Rural Affairs (DEFRA), hereafter reported as the

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[4] The UKWIR (UK Water Industry Research) Chemicals Investigation Programme is the UK Water Industry's response to current and emerging legislation on trace contaminants in the water environment.

[5] A more recent review of PFOS in the environment in the Western Europe and Others Group (WEOG) region mentions range and values from rivers but no data from Scotland is reported (Harner et al 2015).

"two POPs reports for DEFRA", unless otherwise stated. The findings of the two POPs reports for DEFRA are reviewed in Section 4.3.

7. Three reports by DEFRA (describing the UK National Implementation Plan (NIP) for POPs under Regulation (EC) 850/2004 (as amended), hereafter reported as the "UK NIP reports on POPs." These provide extensive information on current PFOS and to a lesser extent PFOA with regards to: production, marketing, use and control; emission sources and release pathways; and stockpiles, compliance activity and use of alternatives in the UK. The legislative context is reviewed in Appendix III.2.2. The UK NIP reports on POPs are reviewed in Section 4.4.
8. The Scottish Pollutant Release Inventory (SPRI) for annual mass releases of PFOS to water from SEPA-regulated industrial sites. As of 2014, the SPRI database records releases above 0.1 kg of PFOS to water (SEPA 2014; SPRI-PFOS n.d.). However, it appeared that the website was either not up-to-date or there were not any PFOS releases to Scottish rivers in recent years (e.g. post-2014). The legislative context is explained in Appendix III.2.4.

4.2 PFAS concentrations in groundwater

The PFAS concentrations measured by SEPA at selected boreholes located in rural and urban areas is the only available evidence for PFAS in groundwater in Scotland. This evidence is used here to inform understanding of PFAS levels in Scotland. Given that it refers to a limited number of locations, it must be clarified that this evidence is strictly discussed at the scale of the borehole sites where the PFAS samples were collected.

This PFAS evidence from Sites SEPA Monitored For PFAS is summarised below:

- Concentrations of individual PFAS substances exceeded LOD (PFAS>LOD) in borehole samples from Angus, East Lothian, Fife, Renfrewshire, West Dunbartonshire, Moray and Scottish Borders (Table 1).
- Each sample with PFAS>LOD had a distinct compositional PFAS signature.
- Five different PFAS substances were detected (PFAS>LOD) in the borehole samples from Angus (Table 1). These were: Perfluoropentanoic Acid (PFPA); Perfluoroheptanoic Acid (PFHpA); Perfluorooctanoic Acid (PFOA); Perfluorobutane Sulfonic Acid (PFBS); and Perfluorooctane Sulfonic Acid (PFOS).
- No exceedances of LOD were observed in the borehole samples from the City of Edinburgh, Dumfries and Galloway, and South Ayrshire.
- All concentrations referring to individual PFAS substances and to PFAS as a group were below the PFAS standards (parametric values) for drinking water in the EU Recommendation (2018).

Table 1. Individual PFAS measured by SEPA in selected borehole samples and local authority where PFAS>LOD sites are located. LOD: Limit of Detection. LA: Local Authority.

PFAS group	Chemical name	LOD (ng/L)	LA where individual PFAS>LOD*
Perfluoroalkyl carboxylic acids (PFCA)	Perfluoropentanoic Acid (PFPA)	5	Angus East Lothian Fife Renfrewshire West Dunbartonshire
	Perfluoroheptanoic Acid (PFHpA)	5	Angus
	Perfluorooctanoic Acid (PFOA)	5	Angus
Perfluoroalkane sulfonic acids (PFSA)	Perfluorobutane Sulfonic Acid (PFBS)	5	Angus East Lothian Moray
	Perfluorooctane Sulfonic Acid (PFOS)	5	Angus

*No exceedances of the standards (parametric values) were reported for PFOS, PFOA and PFAS as a group in the EU Recommendation (2018) were observed.

Concentrations of individual PFAS substances varied as follows (see also Table 1):

- PFOA and PFOS (both with eight carbon chains, C8) varied between <LOD to 32.8 ng/L and <LOD-14.7 ng/L, respectively. Concentrations >LOD were detected in 7.5% of the samples for each substance; however, PFOS and PFOA were found at concentrations>LOD concurrently only in borehole samples from Angus.
- PFPA (C8) varied between <LOD to 29.2 ng/L, with concentrations >LOD in 15% of the samples. It was found in concentration>LOD in 5 out of 10 LAs sampled.
- PFBS (C4) varied between <LOD and 14.3 ng/L, with concentrations >LOD in 10% of the samples. It was found in concentration>LOD in 3 out of 10 LAs sampled.
- PFHpA (C7) exceeded LOD only once (6.89 ng/L).
- No exceedances of LOD were detected for PFDA, PFDOA, PFHpS, PFHxS, PFOSA, PFUNA.

It is difficult to explain why PFAS concentrations were below LOD in one year and above LOD in another year in the borehole samples collected by SEPA in 2013-2016. A review of international literature by Rumsby et al (2009) on PFOS and PFOA in drinking and environmental water samples reports that temporal variations in PFAS concentrations may be due to a transient source of contamination such as WwTW discharge points causing variations in PFAS concentrations with time or to sampling/analysis problems. We explored the spatial relationship between Sites SEPA Monitored For PFAS and potential transient sources (as of Rumsby et al 2009) such as CSO and wastewater discharge points and found that all Sites SEPA Monitored For PFAS are within 5 km of these sources (see Section 5.2). It must be also noted that SEPA is not aware of any issues with the PFAS analytical protocols (Huw Jones, SEPA, pers.com. September 2018). Further, the temporal variation in PFAS concentrations in the borehole samples collected by SEPA in 2013-2016 may be "due to variations along the pathway which influences the proportion of the original input at the source reaching the receptor groundwater body" (Isla Smail, SEPA, pers. com. October 2018). However, this assumption could not be tested with the available evidence.

It is also difficult to explain the distinct PFAS signature of samples with PFAS>LOD concentrations, with a mixture of both short- and long-chained PFAS substances. Plausible mechanisms that could explain this finding include: (i) different subsurface PFAS transport pathways between borehole sites (Section 3.4); (ii) potential de novo formation of long-chained substances from PFAS precursors (Section 3.5) at the borehole sites where the PFAS samples were collected from; and (iii) influence from different types of direct, historic and/or ongoing, PFAS sources (See Section 3.7) at each borehole site.

4.3 Review of the two POPs reports for DEFRA

The two PFOS reports for DEFRA concluded that the 'main PFOS release pathways to environmental media in the UK are thought to be to water', based on its historic commercial use in household goods (Brooke et al 2004; Whiting et al 2012). As of 2012, the UK estimates for annual emissions of PFOS to water and land are in the range of 300 - 800 kg to water and 5 kg PFOS to land (Whiting et al 2012). It must be noted that the influence of atmospheric deposition and landfills has not been taken into account. Whiting et al 2012 reports that the emission to surface waters from waste water treatment works represents the key emission source for PFOS to water based on model predictions, validated on a limited number of samples in two fresh-water rivers downstream of such works.

The two PFOS reports for DEFRA suggested that the main applications for PFOS in the UK are dominated by:

- Furniture stain repellent products
- Uses in Metal plating[6]
- PFOS-based fire-fighting foams[7][8]
- Products used by the photographic industry
- Semiconductors and photolithography
- Products used by Hydraulic Fluids for the Aviation Industry

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[6] In 2008, 380 kg of PFOS was sold within the UK for use in the electroplating industry (Whiting et al 2012) and in July 2008 approximately 150 kg was reported to have been used as mist suppressants. For comparison, the estimate provided in the environmental risk evaluation report for the Environment Agency for the EU in 2003 was between 8.6 – 10 tonnes for metal (Chromium) plating.

[7] As reported by Whiting et al 2012, PFOS has been used in the UK within fire-fighting foams (as part of the AFFF range) and made up approximately 6.5 percent (3M-based AFFF) of the UK provision in 1994.

[8] The UK fire service began a phase out programme shortly after this time (circa 2002/3)4 93. However, phase out at COMAH sites would be expected to be slower. The AFFF foams had a service life of approximately 12 – 15 years; therefore, it would be reasonable to assume a partial replacement of stock year on year at these sites due to usage, training etc. As of 2012, any expired stock would likely be disposed of through incineration (Whiting et al 2012).

However, these uses have also been recently phased out in the UK and therefore it is uncertain as to how important they are as ongoing sources. For example, the use of foams containing PFOS was phased out around the time that 3M ceased production in 2001 (Appendix III.1.1). The remaining fire brigade stockpiles of PFOS foams were largely consumed at the Buncefield fuel storage terminal fire in December 2005 (Whiting et al 2012). The use of fire-fighting foams in the UK, aqueous film-forming foams (AFFF) in particular, historically had two key applications: as precautionary stock at Control of Major Accident Hazards (COMAH) sites, and at fire service training sites. The AFFF foams themselves contained approximately between 1 and 2.5% PFOS wt/wt as a surfactant but, as Whiting et al (2012) estimated, the use of PFOS in AFFF has ceased since 2006. This means that residual sources of PFOS are progressively harder to locate, but also likely to be of relatively low significance compared to the quantities that may have been released in the past (Whiting et al 2012).

No information on PFOA emissions in the UK were found in the two reports to DEFRA.

4.4 UK NIP reports for POPs

The UK ratified the Stockholm Convention on 17 April 2005 and consequently submitted its first NIP in 2007 and updates were published in 2013 (DEFRA 2013), 2015 (DEFRA 2017) and 2017 (DEFRA 2017). The UK POPs Regulations 2007 (as amended) supplements the Community Regulation EC 850/2004 and designate the Competent Authority and enforcement agency for Regulation EC 850/2004 in UK jurisdictions. In Scotland, SEPA is the designated enforcer of the Stockholm Convention and associated UK legislation.

With regards to PFOS and related substances (see Appendix III.2.2), the most recent UK NIP report (DEFRA 2017) updates and summarises the evidence presented in the previous UK NIP reports, as follows:

- PFOS is not manufactured within the UK.
- The UK has used PFOS, with stockpiles and legacy waste aspects a key issue:
  - o PFOS-containing stockpiles have been notified to the Environment Agency (EA) for use as a wetting agent and mist suppressant in non-decorative hard chrome plating.
  - o Previous use of PFOS was dominated by the domestic market, particularly as a stain repellent in furniture and other furnishing items. These items which are still being used are likely to remain a source of PFOS emissions for an extended period. However, no substantiated data exists to verify current emission estimates.
- Given the difficulty in finding alternatives with comparable properties, use of PFOS and related substances in the UK still continues. This primarily relates to the use of PFOS for accepted purposes and applications exempted from restrictions (see Appendix III.2.2), i.e. within metal plating activities in the chrome industry, the use of small quantities in semi-conductor manufacture and limited applications in the photographic industry. However:
  - o Awareness raising campaigns within the industry are in place.
  - o PFOS-foams are no longer in use and several industrial holders of foams (e.g. petrochemicals industries, downstream oil industries, and aviation authorities) notified disposal of the material following the awareness campaign. However, PFOS may be present in residual forms in land resulting from PFOS-foam/water run-off occurring during past industrial incidents.
- The main environmental release PFOS pathway in the UK is believed to be to water through discharges from waste water treatment works (WwTW). Concerns have been raised about further de novo formation of PFOS within WwTW.

An earlier UK NIP report (DEFRA 2013) provided more detailed information on the use of PFOS:

- In 2011, a total 3,654kg of PFOS-containing material equating to 88kg of PFOS were notified by four manufacturing companies. These companies suggested that these quantities will diminish with increasing use of alternatives substances.
- Following a 2006 targeted campaign by the Environment Agency (EA), the Fire Rescue Service (FRS) voluntarily phased out the use of remaining stocks of PFOS-containing foam in 2011. A further campaign in 2011 identified that other industry (mainly non-FRS) continued to hold stocks of PFOS-containing firefighting foam up until the ban of its use in mid-2011. Following an awareness campaign for the need to dispose of these foams, approximately 20,000 litres of PFOS-containing foam, firewater and system flushings have been disposed of.

5.0 Mapping PFAS risk to PWS in Scotland

5.1 Risk mapping method

The risk mapping method aimed to combine three separate lines of evidence:

(i) Locations of potential direct (Glossary) PFAS sources in Scotland, hereafter reported as Potential PFAS Source Sites.

(ii) PWS locations provided by DWQR (see also Appendix II.2).

(iii) PFAS concentrations in groundwater in Scotland, which were measured by SEPA at selected boreholes located in rural and urban areas sampled from 2013 to 2016 (see Section 4.2). The borehole locations, hereafter reported as Sites SEPA Monitored For PFAS, were not selected to target any direct potential PFAS sources. This report uses the dataset from Sites SEPA Monitored For PFAS as ancillary information to help understand levels of PFAS concentrations in potential drinking water sources to PWS and to discuss potential influence from direct Potential PFAS Source Sites.

5.1.1 Identifying Potential PFAS Source Sites in Scotland

Based on the literature review of available evidence, we identified the following types of PFAS sources as relevant to the Scottish context (see Section 3, Section 4 and Appendix III):

- Wastewater discharges (effluent) from WwTW. Locations of the following wastewater categories were considered: effluent from leachate collection works; combined sewage outflows (CSOs) serving more than 2000 people; sewage and trade effluent serving 50-199, 2000-49,999 and >50K people.
- Landfill sites.
- Airfields, only when storage of PFAS-containing stockpiles and use of PFAS-containing materials for training purposes are not managed in line with relevant regulations.
- Premises such as fire stations and business sites, where PFAS stockpiles may be stored as raw materials and only if leaks occur to the surrounding ground.
- AFFF-impacted land.

Spatial information (georeferenced data) for each of these types of direct PFAS sources was sought in order to identify potential PFAS source sites in Scotland (Table 2). Data from different organisations were used such as the Scottish Environment Protection Agency (SEPA), National Air Traffic Service (NATS), the UK Airfield Guide, Scottish Fire Service, UK Fire Stations, Ordnance Survey Mastermap, and Companies House. Only data that were available at-no-cost were used. In this report, ongoing uses conditionally refer to PFAS applications still legally accepted; historic uses refer to PFAS applications that are ceased or banned (see Appendix III.2.2). The data sources explored are detailed in Appendix II.2.

Table 2. List of georeferenced PFAS risk indicators to assess PFAS risk to private water supplies (PWS). Appendix II.2 details the sources of data.

PFAS-risk indicators	Data source
PFAS>LOD sites	SEPA
Locations of High Risk Landfills (i.e. landfill locations as of 2015, with a Pollution Prevention Control permit receiving hazardous and non-hazardous waste and closed landfill locations with Waste Management License)	SEPA
Locations of WwTW	SEPA/ Ordnance Survey Mastermap
Locations of WwTW effluent monitoring by SEPA	SEPA (2017)
Locations of industries (business sites) involved in the manufacturing or processing of: carpets, outdoor textiles, paint, food packaging, paper coatings, ink, cement production, medical implant production, and metal plating	Companies House (n.d.)
Airfields	National Air Traffic Service UK Airfield Guide
Fire stations	Scottish Fire and Rescue Service, UK Fire Stations, Ordnance Survey Mastermap
Electoral wards where fire-fighting foams have been used	Scottish Fire and Rescue Service

It is recognised that land where biosolid, i.e. treated sewage sludge or slurry, has been applied for recycling (reclamation) or as fertilizer to improve and maintain productive soils and stimulate plant growth, has the potential to pose a PFAS risk to PWS. However, there is no comprehensive spatial evidence on biosolid application in Scotland. Therefore, this type of Potential PFAS Source Site was not accounted for.

The use and selection of datasets was determined in consultation with DWQR and SEPA.

5.1.2 Identifying PFAS risk indicators

Here, we define PFAS risk to PWS as the risk of any individual PFAS substance concentrations above the limit of detection (LOD) in PWS in order to address all levels of PFAS concentrations in PWS as well as potential temporal variation in PFAS concentrations from year-to-year. We assessed PFAS risk to PWS using PFAS risk indicators based on the findings of the literature review (Sections 3.6; see also Appendix III). The indicators were identified in relation to Potential PFAS Source Sites and Sites SEPA Monitored for PFAS where PFAS concentrations above the limit of detection were observed at least once during the monitoring record (PFAS>LOD Sites).

We identified the following Indicators of PFAS risk to PWS:

- Presence or absence of Potential PFAS Source Sites in the same surface or groundwater body as PWS, based on evidence that PFAS>LOD are associated with direct PFAS sources within a catchment (Section 3.6).
- Presence or absence of Potential PFAS Source Sites within a distance of 0.5 km and 5 km (which were arbitrarily selected) from PWS, regardless of waterbody boundaries. This was requested by SEPA “as an initial starting point for exploring PFAS risk to PWS” (Isla Smail, SEPA, pers. com. July 2017). PFAS risk to a PWS from Potential PFAS Source Sites located out with the waterbody catchment may be through atmospheric deposition and/or groundwater infiltration of contaminated surface water discharged upstream (see Section 3.6). It must be also noted that the boundaries of surface waterbody and groundwater bodies in Scotland do not coincide, e.g. one groundwater body may be influenced by many different surface waterbodies (Figure 1). In this context, distance may better account for influence from Potential PFAS Source Sites.
- Presence or absence of PFAS>LOD Sites in the same surface or groundwater body as PWS, based on the evidence in the literature review that PFAS>LOD are associated with the presence of direct PFAS sources in the same catchment.
- Presence or absence of PFAS>LOD Sites (or any other available locations of known PFAS concentrations in surface waters or groundwater) within 5 km (which was arbitrarily selected) from PWS, based on evidence in the literature review that PFAS>LOD are associated with the presence of direct PFAS sources in the same waterbody catchment, and given that distance may better account for influence from Potential PFAS Source Sites when one groundwater body may be influenced by many different surface waterbodies (Figure 1).

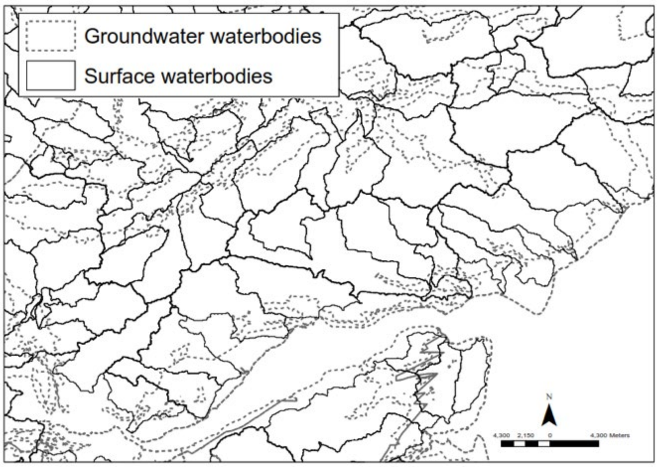

Figure 1 Boundaries of groundwater and surface water waterbodies in Tayside, Scotland. Data source: SEPA

5.1.3 Scope of the risk mapping method

It must be noted that we could not access any data on the PFAS content of emissions from Potential PFAS Source Sites. Therefore, it remains unknown which Potential PFAS Source Sites are actual direct PFAS sources. Besides, understanding whether and where direct PFAS sources pose a risk to groundwater and by extent to PWS served by groundwater sources requires knowledge of site-specific soil conditions (e.g. imperviousness, erosion risk and leaching risk) and other hydrochemical factors influencing the subsurface processes determining PFAS fate and transport (see Sections 3.4 and 3.5 and Appendix III.1.7). Exploring these lines of evidence is out with the remit of this scoping study.

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[9] Scottish groundwater bodies define areas of groundwater that behave in a similar way, both naturally and in response to pressures from human activity, as reported by the British Geological Survey (2015). BGS identified two aquifer layers: a shallow layer of superficial aquifers, and a deeper layer of bedrock aquifers. Superficial aquifers in areas of higher risk to groundwater are subdivided using surface water waterbodies. Bedrock aquifers are defined according to key groundwater flow characteristics, which are, in turn, the main drivers for differences in groundwater management approaches. In most cases, bedrock groundwater bodies follow bedrock aquifer boundaries (Dochartaigh et al 2015). In addition, the groundwater vulnerability map of Scotland shows a mosaic of classes of high vulnerability to most water contaminants to classes vulnerable to conservative contaminants (Dochartaigh

We must clarify that the mapping method developed here explores:

(iv) Distribution of Potential PFAS Source Sites in waterbodies and Local Authority areas as baseline information collected for the first time.

(v) Spatial relationships between Potential PFAS Source Sites and PFAS>LOD Sites to understand whether there is a consistent pattern of co-occurrence of PFAS>LOD concentrations and Potential PFAS Source Sites and potentially inform further, targeted research.

(vi) Spatial relationships between PWS and PFAS>LOD Sites to potentially inform investigative PFAS monitoring in PWS served by groundwater at PFAS>LOD Sites.

We must also explicitly clarify that the risk mapping method developed here:

- <u>Does not consider</u> that Potential PFAS Source Sites are actual direct PFAS sources to PWS and Scottish environment; however, knowing their locations is the first step towards a thorough PFAS risk assessment in the context of PWS.
- <u>Does not consider</u> that Sites SEPA Monitored For PFAS are actual direct PFAS sources to PWS and the Scottish environment; however, PFAS>LOD concentration in groundwater indicate influence from past or ongoing direct PFAS sources and thus exploring the presence of PWS and Potential PFAS Source Sites around PFAS>LOD Sites provides the opportunity to understand the causes of PFAS>LOD concentrations in specific groundwater locations and the risk to PWS.
- <u>Does not extrapolate</u> actual PFAS measurements at Sites SEPA Monitored For PFAS to the scale of groundwater body, surface water waterbody, river catchment, Local Authority area, or any other regional or national scales.
- <u>Does not account for</u> subsurface PFAS transport pathways (Section 3.4).
- <u>Does not account for</u> indirect PFAS sources (Section 3.5).

5.1.4 Steps to evaluating PFAS risk to PWS

Evaluating PFAS risk to PWS involved four steps.

Step 1: Potential PFAS Source Sites were mapped in relation to surface waterbody catchments (hereafter simply reported as waterbodies) and groundwater waterbodies in order to identify waterbodies with Potential PFAS Source Sites and to derive information on the distribution of Potential PFAS Source Sites in Scotland.

Step 2: PWS locations were mapped in relation to Potential PFAS Source Sites to explore the number of PWS within at 0.5 and 5 km from Potential PFAS Source Sites and provide preliminary information for risk assessment in the future.

Step 3: Sites SEPA Monitored For PFAS and PFAS>LOD Sites were mapped against Potential PFAS Source Sites to test the evidence based on the literature review that PFAS>LOD concentrations indicate influence from historic or on-going direct PFAS sources (Section 3.6).

Step 4: The number of PWS per source type and Potential PFAS Source Sites at surface and groundwater bodies and at 0.5 and 5 km and from PFAS>LOD Sites were counted to evaluate risk of PFAS>LOD concentrations in the drinking water of PWS. Given the limited number of PFAS>LOD Sites, it is not possible to identify the potential PFAS monitoring effort for each Local Authority area upon approval of the EU Recommendation (see Section 1). However, the number of PWS within 5 km from PFAS>LOD Sites were counted per Local Authority area to provide indicative information about the representativeness of the available evidence.

Step 5: Evaluation of PFAS risk to PWS involved comparing PFAS>LOD concentrations at PFAS> Sites with advisory health-based parametric values found in the literature.

It must be explicitly clarified that this approach is scoping the presence of direct PFAS source sites with the potential to cause PFAS>LOD in the drinking water of PWS. The use of data from PFAS>LOD Sites aimed to provide indicative information about the levels of PFAS concentration in potential groundwater sources to PWS and to inform a PFAS risk assessment in the future.

5.2 PFAS risk mapping results

Applying the steps described in Section 5.1.4 showed that (please also see Section 5.4.3 for the Caveats of the method):

- **Step 1**: Potential PFAS Source Sites, regardless of type of PFAS source, are found in all Local Authority areas. Besides, all groundwater bodies are spatially interconnected with waterbody catchments with Potential PFAS Source Sites.
- **Step 2**: All PWS are located within 5 km from one or more Potential PFAS Source Sites; however, PFAS risk to PWS is unknown because PFAS emissions from these sources are unknown and because PFAS concentrations in drinking water sources to PWS are unknown.

- **Step 3**:
    - 11 out of 17 Sites SEPA Monitored For PFAS are PFAS>LOD Sites.
    - Four of the Sites SEPA Monitored For PFAS are located within 5 km from the discharge point of (presumably landfill) "leachate effluent" (Figure 2a), of which those located in Angus, Renfrewshire and W. Lothian are PFAS>LOD Sites. Given that the remainder of PFAS>LOD Sites (i.e. in Scottish Borders, W. Dunbartonshire and Fife) are located out with the 5 km radius from leachate effluent discharge points and at a different groundwater waterbody than them, it is impossible to draw conclusions on whether leachate effluent discharge points functioned as direct PFAS sources for PFAS>LOD Sites. Besides, it is uncertain whether the leachate effluent is indeed contaminated with PFAS; if so, its PFAS concentration and fate (e.g. infiltration to groundwater) remain unknown.
    - All Sites SEPA Monitored For PFAS are within 5 km from a CSO serving a population >2000 people or a WwTW point discharging mixed sewage and trade effluent (Figure 2b and 2c). However, it is impossible to understand whether and where CSOs and WwTW discharge points functioned as direct PFAS sources for PFAS>LOD Sites. It is also unknown whether the effluent has infiltrated to groundwater.
    - All Sites SEPA Monitored For PFAS are within 5 km from a SEPA-regulated landfill sites (Figure 2d). However, without measurements of PFAS in groundwater beneath and downgradient a landfill site it is impossible to know whether groundwater has PFAS>LOD due to historic or ongoing leaks of landfill leachate.
    - Twelve of the Sites SEPA Monitored For PFAS are located within 5 km from Airfields (Figure 2e) and included both PFAS>LOD Sites and PFAS<LOD Sites. Therefore, it is impossible to know without measurement of PFAS concentrations in the groundwater beneath and downgradient an Airfield site whether it functioned as direct PFAS source for PFAS>LOD Sites.
    - All Sites SEPA Monitored For PFAS are located within 5 km from premises with potential storage areas of PFAS stockpiles (see fire stations in Figure 2f; business sites are not shown). However, it remains uncertain whether all or which fire stations and business sites (for which only the postcode of central offices is known) function as direct PFAS sources to groundwater.
    - Fifteen of the Sites SEPA Monitored For PFAS are located in electoral wards where fire-fighting foams have been used (Figure 2g). There was not an apparent relationship between the year of use of foams and the year PFAS>LOD concentrations were observed at PFAS>LOD Sites. This may reflect a time-lag due to transport pathways from source site to groundwater (Section 3.4). For example, in the Scottish Borders fire-fighting foams were applied in 2013 and PFOS was detected in groundwater in 2016. However, in Angus PFOS and PFOA were detected in 2013 before the application of fire-fighting foams in 2014 and 2016. Given that Sites SEPA Monitored For PFAS in Angus and Scottish Borders are within a 5 km distance from other Potential PFAS Source Sites, e.g. landfill sites, it is difficult to understand the sources of PFOS in groundwater under fire-fighting foam potentially impacted land.
- **Step 4**:
    - The number and type of sources of PWS at a radius of 0.5 and 5 km away from PFAS>LOD sites are summarised in Table 3; Table 4 and Figure 3). It must be noted that in many occasions the Type A-PWS at both 0.5 and 5 km distances from PFAS>LOD Sites were located in different groundwater bodies than PFAS>LOD Sites. However, Type A-PWS could be located at the same waterbody catchment as the Potential PFAS Source Site within 0.5 and 5 km from PFAS>LOD Sites. This can be explained by the different boundaries of surface and groundwater bodies (see Figure 1 in Section 5.1.2).
    - Overall, 276 out of 21,508 PWS were found to be within 5 Km from Sites SEPA Monitored For PFAS: 18 Type A-PWS and 258 Type B-PWS. These results show that there are very few Type A-PWS spatially related to Sites SEPA Monitored For PFAS (Figure 3a). Therefore, PFAS risk to Type A-PWS could not be reliably assessed based on the available evidence-base in Scotland. However, the study suggests that a considerable number of Type B-PWS are within 5 km from PFAS>LOD Sites (Figure 3b). It is also interesting to note that different types of Potential PFAS Source Sites occur at each Local Authority area with PFOS>LOD Sites (see also Section 5.3 for the implications of this finding).
- **Step 5**: PFAS concentrations from Sites SEPA Monitored For PFAS are all below the current advisory regulatory guidelines in UK and the EU.

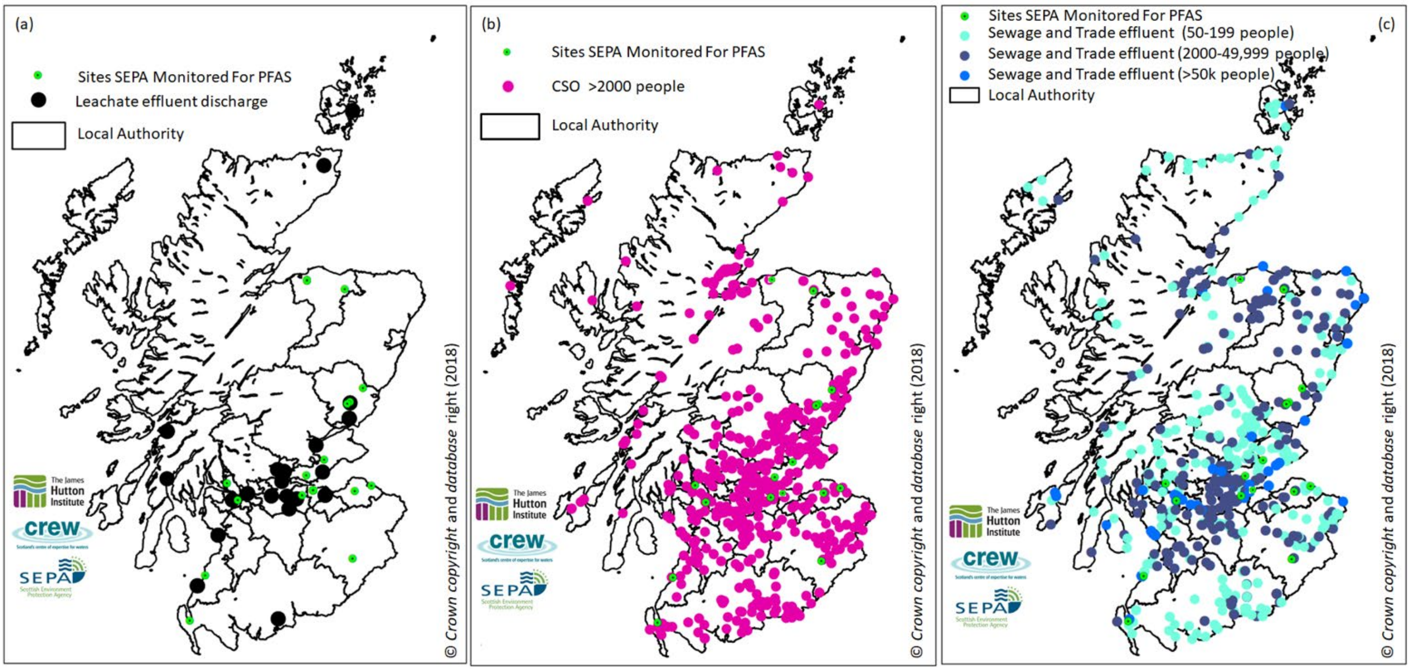

Figure 2 a-c Spatial relationship between Sites SEPA Monitored For PFAS and (a) Leachate effluent discharge points; (b) Combined Sewage Outflow (CSO) serving >2000 people; and (c) Sewage and Trade effluent discharge points. Site symbol scale equals 5 km.

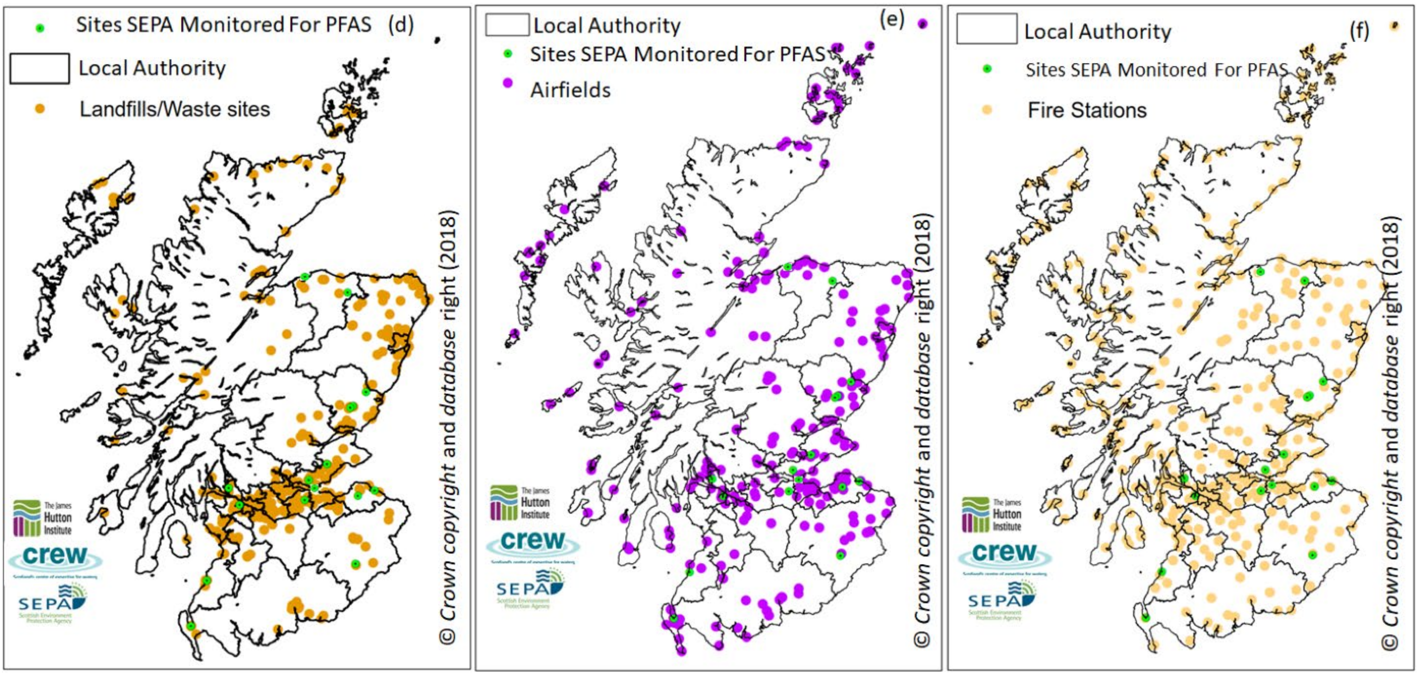

Figure 2 d-f Spatial relationship between Sites SEPA Monitored For PFAS and (d) Landfill sites; (e) Airfields; and (f) Fire stations. Site symbol scale equals 5 km.

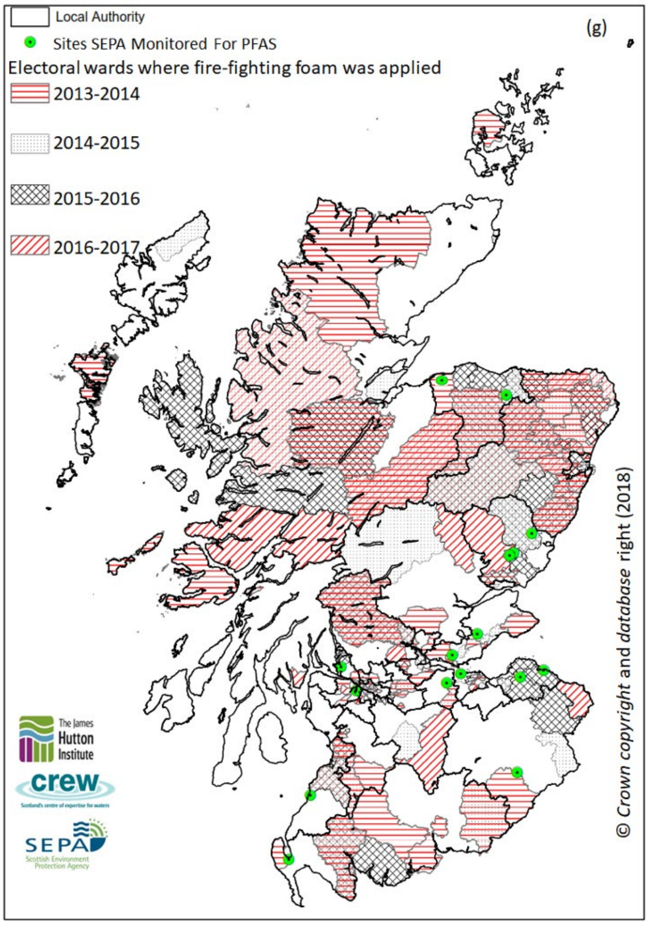

Figure 2 g Spatial relationship between Sites SEPA Monitored For PFAS and Electoral Wards where fire-fighting foam was applied in 2013-2017 Sites. Site symbol scale equals 5 km.

Table 3. Number of PWS and PFAS source sites (as of Section 2.2 and Appendix II.2) at 0.5 and 5 Km from SEPA's borehole sampling sites, where PFAS concentrations in groundwater were above LOD.

Local Authority	Location Code	Distance (km)	Type A-PWS	No. Business	No. Fire Stations	No. of WwTW	No. Landfills	No. of Airfield
Angus	334752	0.5	0	1	0	1	0	0
		5	0	3	1	2	3	1
	7817	0.5	0	0	0	0	0	0
		5	0	3	1	3	3	1
East Lothian	12905	0.5	0	2	1	0	0	0
		5	0	2	1	3	0	1
	16454	0.5	1	0	0	0	0	0
		5	1	3	1	2	1	1
Renfrewshire	125519	0.5	0	0	0	2	0	0
		5	0	32	3	7	16	4
W. Dunbartonshire	331826	0.5	0	0	0	0	1	0
		5	2	2	1	5	5	1
Scottish Borders	12918	0.5	0	2	0	0	0	0
		5	2	4	1	2	1	1
Fife	12897	0.5	0	1	0	0	1	0
		5	1	10	1	1	6	2
Moray	233010	0.5	1	0	0	0	1	0
		5	3	6	1	2	2	0

Table 4. Number of Type A-PWS and Type B-PWS per source type and local authority within a radius of 5 km from the location of SEPA's borehole sampling sites where PFAS concentrations were above LOD.

Local Authority	Type A-PWS			Type B-PWS			
	Borehole	Spring	Well	Borehole	Spring	Well	River
Aberdeenshire	0	0	0	1	1	0	0
Angus	1	1	0	0	4		2
Argyll and Bute	0	0	0	0	0	1	2
Dumfries and Galloway	0	0	2	3	3	3	2
East Lothian	1	0	0	1	1	0	0
Fife	1	0	0	5	3	0	0
Moray	1	4	1	5	52	9	3
Renfrewshire	0	0	0	0	0	1	0
Scottish Borders	0	3	0	3	83	1	6
South Ayrshire	1	1	0	0	1	0	0
W. Dunbartonshire	0	3	0	0	6	0	0

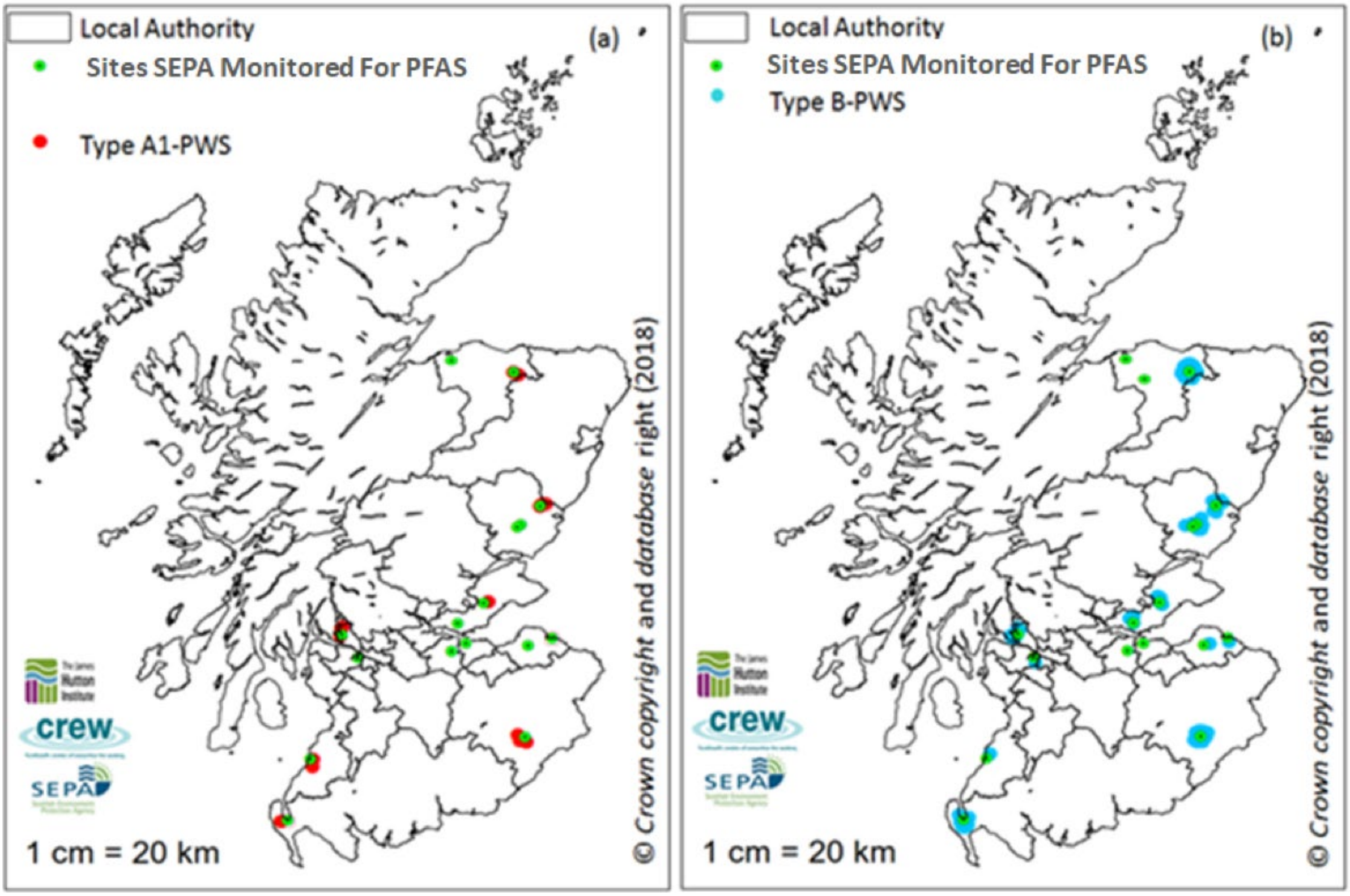

Figure 3 Type A- and Type B-PWS within 5 km from Sites SEPA Monitored For PFAS and. PWS symbol scale equals 5km. Note that all Type A-PWS are Type A1-PWS, i.e. they serve less than 100 cubic meters of water per day. Type B supplies serve less than 10 cubic meters per day or fewer than 50 people.

5.3 PFAS risk mapping: evaluation of mapping results

The PFAS risk mapping method developed here suggests that:

- It is uncertain whether and where Potential PFAS Source Sites are related to PFAS>LOD Sites because PFAS<LOD concentrations were found within 0.5 km from Potential PFAS Source Sites and at the same surface and groundwater waterbodies as Potential PFAS Source Sites.
- (As a result of the above and given that Potential PFAS Source Sites are located in all surface waterbodies, which are intersecting all groundwater waterbodies) It is uncertain which surface waterbodies and groundwater waterbodies are at risk from PFAS>LOD concentrations.
- It is uncertain what types of PFAS substances are emitted from each Potential PFAS Source Site. The implication of this finding is that identifying a fit-for-purpose approach to PFAS risk assessment on a Local Authority level must consider not only the locations of Potential PFAS Source Sites but also the different types of PFAS emitted by different direct PFAS sources.

5.4 PFAS risk mapping: evaluation of the method

The strengths, weaknesses, caveats and opportunities for improving the method are discussed below.

5.4.1 Strengths

The major strength of the method is that for the first time we mapped all potential PFAS direct sources (except biosolid-impacted land) in Scotland. This can inform future monitoring to verify whether PFAS are emitted from the mapped sources and assess risk to the water environment and drinking water sources to PWS.

5.4.2 Weaknesses

The major weakness of the method is that it relies on any available PFAS data from groundwater or surface water waterbodies to assess whether Potential PFAS Source Sites function as actual direct PFAS sources. The available PFAS dataset from the 17 Sites SEPA Monitored For PFAS is very limited to enable any national-scale, science-based, PFAS risk assessment based on the mapping of Potential PFAS Source Sites in relation to PWS. Therefore, levels of PFAS contamination in the Scottish water environment and PFAS risk to PWS remain largely unknown. See also Section 5.4.3.

5.4.3 Caveats

Practically, the findings of the risk mapping exercise refer to PFAS risk to the PWS located within a distance of 5km from SEPA's PFAS sites and not to PWS in general. **Any generalisations must be avoided and interpreted with caution for the following reasons:**

1. Lack of data on PFAS emissions from potential PFAS source sites. Potential PFAS Source Sites are found in all local authority areas of Scotland, in both urban and rural areas. However, the identification of PFAS source sites was based on literature data from elsewhere; even the data referring to the UK most likely refer to emissions in England. Therefore, it remains uncertain whether PFAS emissions from potential source sites pose a risk to the freshwater environment and by extent to PWS in rural areas in Scotland.
2. Insufficient PFAS data in the rural freshwater environment. Sites SEPA Monitored For PFAS refer to borehole sampling stations located in the vicinity of urban areas and lowland rural areas. This means that these sites are not representative of the Scottish upland rural environment, where the majority of PWS are found. Besides, it must be borne in mind, that based on international evidence, PFAS have been found in remote areas and that historic PFAS sources are still causing freshwater contamination decades after cessation of their emissions. Therefore, the levels of PFAS contamination out with (downgradient and downstream) Sites SEPA Monitored For PFAS remain unknown.
3. Lack of measurement of PFAS precursor substances. FOSA, the only PFAS precursor measured by SEPA under their groundwater monitoring programme, was not detected in any of the samples in groundwater; however, both PFOS and PFOA, which can derive abiotically and biotically from FOSA were detected in three borehole locations. This raises questions for PFOS sources because this substance has very few strictly regulated uses nowadays. It also shows the limitations of the available evidence to identify direct PFAS sources and to predict risk of contamination based on historic or ongoing contamination with PFAS precursor substances.
4. Imprecise information related to the actual location of Potential PFAS Source Sites and PWS. For example, the locations of business sites refer to the postcode of central offices and not necessarily to the actual site of use, storage and disposal of PFAS-containing raw materials. Further, WwTW discharge points were not known; instead, unverified locations of treatment plants and SEPA's effluent monitoring sites were used. Finally, the PWS locations refer to premises and not to the water intake points whereas in many cases PWS and

SEPA's PFAS sites were located at different groundwater bodies.

5. Lack of information on groundwater flow paths and velocity as well as on the geochemistry of the unsaturated and saturated zones of the aquifers where Sites SEPA Monitored For PFAS. This information may be available to SEPA or BGS and it is expected to be site-specific. Nevertheless, examining the distance from a Potential PFAS Source Site without factoring in surface water or groundwater flow direction is maybe a worst-case scenario to assess the spread of contaminated surface water groundwater plumes. However, this approach is not consistent with the actual processes shaping the distribution of PFAS contaminants.
6. Presence of multiple potential PFAS source sites in the vicinity of Sites SEPA Monitored For PFAS. The problem with this approach is that it precludes the identification of the key source of water PFAS contamination. For example, in Angus PFAS>LOD Sites are within 5 km from discharge points of landfill leachate, a CSO, a landfill and an airfield. Given the interannual variability observed in PFAS samples from Sites SEPA Monitored For PFAS, the presence of multiple sources further perplexes the assessment of PFAS risk to PWS.
7. Unaccounted PFAS sources such as biosolid application. For example, approximately 70,000 tonnes of sewage sludge are spread on land each year in Scotland (Scottish Government 2016). However, it remains unknown whether this practise poses a PFAS risk to the water environment, and, if so, where it is spread. Evidence from elsewhere shows that biosolid-impacted land posed a PFAS risk to water resources (see Appendix III.1.8.4).

5.4.4 Opportunities for improvement

Ground-truthing of Potential PFAS Source Sites as direct PFAS sources may improve the available evidence. For example, consultation with stakeholders (e.g. Scottish Water, landfill managers, FRS) can help to verify whether the locations identified are posing a historic or ongoing PFAS risk to PWS. In this context, SEPA or Scottish Water could evaluate whether the WwTW maps (Figure 2a-c) are correct and whether the effluent or sludge/biosolid from some WwTW contains PFAS (see Section 4.1 on CIP2 programme). Further, consultation with FRS will provide evidence on the content of fire-fighting foams to verify whether their use poses an ongoing risk and what individual PFAS substances are expected to be found in areas where they are used. Finally, PWS monitoring or surface water and groundwater sampling in relation to actual PFAS source sites will help to develop an evidence-based assessment of PFAS risk to PWS.

In the face of this evidence, it is not possible to either assess overall PFAS risk to PWS or identify the source of PFAS>LOD in samples from Sites SEPA Monitored For PFAS. The GIS-based method developed here could be used to inform a national scale PFAS risk assessment. The literature review showed that investigating direct sources of PFAS to water supplies to inform control measures and policy requires sampling specific for each type of Potential PFAS Source Sites and at locations that are downstream and, in groundwater, beneath and downgradient and at selected distances from source sites (e.g. Weber et al 2017; Hu et al 2016; Houtz et al 2016; WHO et al 2016; see also Appendix III.1.7 and III.1.8).

6.0 Concluding remarks

We developed and implemented a GIS-based method to provide a high-level, national-scale assessment of the PFAS risk to PWS, i.e. the risk of detecting PFAS in private water supplies. We developed PFAS risk indicators related to presence or absence of direct potential PFAS sources based on the available evidence-base in Scotland and internationally about types of sources, introduction, movement, and persistence of PFAS in catchments in the context of small supplies, i.e. in rural areas.

The key findings are summarised below.

- We developed and implemented a risk-mapping method based on GIS tools, a review of available evidence on types of direct PFAS sources (i.e. related to manufacturing and use) to the water environment in Scotland, the UK and internationally, and on available PFAS data in Scotland. We showed that there is sufficient evidence to identify the locations of the majority of types of potential direct PFAS sources (hereafter reported as Potential PFAS Source Sites) in relation to the locations of all PWS. However, there is not sufficient open-access PFAS data to identify PFAS risk to PWS, i.e. whether and where PFAS concentrations are above the limit of detection (LOD) in drinking water sources to PWS.
- Groundwater PFAS concentrations from 17 Sites SEPA Monitored For PFAS (which were not sited to assess impact of Potential PFAS Source Sites on groundwater) sampled in rural and urban areas in 2013-2016 were below the advisory parametric values for drinking water recommended by the EU. However, this evidence is not sufficient for a national-scale assessment of PFAS risk to PWS.
- The GIS-based methodology developed here for mapping PFAS risk to PWS shows that:

    - Potential PFAS Source Sites, are found in all Local Authority areas.
    - All groundwater bodies are connected with waterbody catchments with Potential PFAS Source Sites.
    - All Sites SEPA Monitored For PFAS are located within 5 km from the following types of Potential PFAS Source Sites: wastewater discharge points, landfill sites and sites of potentially PFAS-containing stockpiles. PFAS concentrations were above LOD in 11 out of 17 Sites SEPA Monitored For PFAS (hereafter reported as PFAS>LOD Sites); however, the site-specific causes of PFAS>LOD are uncertain.
- Review of international evidence on PFAS shows that:
    - PFAS can be detected downstream, beneath and downgradient of direct PFAS source sites such as: airports; oil, gas and mining production sites; chemical plants; landfills; wastewater discharge points; fire-fighting foams- and biosolid-impacted land; and sites with PFAS-containing stockpiles.
    - PFAS from direct sources may enter drinking water resources though: wastewater discharge; bank infiltration of PFAS-containing effluent to groundwater; runoff from PFAS-impacted land; leaching to groundwater from PFAS-impacted land and landfill sites; and industrial and landfill emissions to air.
    - Groundwater is the main freshwater sink for many PFAS substances. Distribution of PFAS in groundwater depends on: presence and type of PFAS sources, PFAS chain-length and structure, geochemistry at unsaturated and saturated zones of an aquifer, and groundwater flow and velocity.

Challenges related to lack of PFAS data in potential drinking water sources to PWS can be tackled by PFAS measurements in selected locations in drinking water sources to PWS, which are downstream and beneath and downgradient the Potential PFAS Source Sites identified in this project.

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CREW is a Scottish Government funded partnership between
the James Hutton Institute and Scottish Universities.