Developing a groundwater watch list for substances of emerging concern: a European perspective

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Abstract

There is growing concern globally about the occurrence of anthropogenic organic contaminants in the environment, including pharmaceuticals and personal care products. This concern extends to groundwater, which is a critical water resource in Europe, and its protection is a priority to the European Commission, the European Union (EU) Member States and national agencies across Europe. Maintaining good groundwater status supports improved public health, economic growth and sustains groundwater dependant ecosystems. A range of measures have been introduced for regulating several substances that have impacted groundwater (e.g. nitrate and pesticides). However, these measures only cover a small fraction of anthropogenic substances that could pollute groundwater. Monitoring for these unregulated substances is currently very limited or not carried out at all. Therefore, a coordinated European-wide approach is needed to identify, monitor and characterise priority substances or groups of substances that have the potential to pollute groundwater. This evidence base is critical for policy development and controls on these currently unregulated substances. The European Commission highlighted this as a need during the review of the EU Groundwater Directive Annexes in 2014, when the requirement to develop a Groundwater Watch List (GWWL) was established. This paper describes the approach that has been developed through a voluntary initiative as part of the EU CIS Working Group Groundwater to establish the voluntary EU GWWL. The process for developing the GWWL is one that has brought together researchers, regulators and industry, and is described here for the first time. A summary of the key principles behind the methodology is presented as well as results from pilot studies using per- and polyfluoroalkyl substances and pharmaceuticals. These explore and support the viability of the GWWL process, an important step towards its adoption and its future use for groundwater protection across Europe.
1. Introduction

Over the last two decades there has been a growing interest in the occurrence and fate of unregulated organic contaminants in groundwater globally (Focazio et al 2008, Loos et al 2010, Lapworth et al 2012, Sui et al 2015). Regulation of some key organic substance groups, such as pesticides, has been in place for over 20 years in the EU (e.g. European Commission 1998, 2006a). However, the vast majority of anthropogenic organic compounds, although covered by the ‘prevent and limit input to groundwater’ requirements of the European Commission Groundwater Directive (EC GWD) (European Commission 2006a), have only recently been recognised, are poorly understood (Loos et al 2010, Lapworth et al 2012) and frequently are effectively unregulated. These include substances used for a range of purposes including human and animal health, personal care, industrial manufacturing, food production and fire suppression (Richardson and Kimura 2017). Most of these compounds are currently not sufficiently monitored in groundwater and are unregulated globally (Küster and Adler 2014, Lamastra et al 2016, Hartmann et al 2018). These compounds are often referred to as substances or compounds of emerging concern, or ‘emerging organic contaminants’ (EOC) (Stuart et al 2012) and include groups such as pharmaceuticals, veterinary medicines, surfactants, plasticisers as well as substances used in personal care products. The term ‘EOC’ is used to cover not only newly developed compounds but also compounds newly discovered in the environment, often due to analytical developments (Richardson and Ternes 2017) and compounds that have only recently been categorised as potential contaminants that are therefore unregulated. For example pesticides and poly-aromatic hydrocarbons would fall outside of this scope.

There is a real conundrum at present regarding the approach to gather evidence of EOC occurrence in groundwater: on one hand there is insufficient monitoring data to underpin and inform development of European groundwater regulation, whilst on the other hand there is no formal requirement to monitor for anthropogenic organic substances that might be of potential concern. To date limited evidence gathering has taken place for the occurrence of EOCs in groundwater, particularly compared to surface water, and what is available is often restricted to a few EU member states (MS) (Lapworth et al 2012, Lopez et al 2015, Lamastra et al 2016). The current situation has resulted in a lack of adequate evidence on many anthropogenic organic substances in groundwater to adequately inform EU policy on this topic (Hartmann et al 2018).

At the same time there is growing public interest and concern in the environmental and potential health impact of EOCs (Daughton 2010). This has been recently exemplified by the high profile public debate on fate of micro-plastics, and plasticisers, as well as the build-up of anti-microbial resistance in the environment (Levy and Marshall 2004, Andrade 2011). At the heart of this discourse is the need for robust evidence to feed into policy development with respect to monitoring and protection of the environment, including drinking water resources. Given the vast array of potential contaminants and significant methodological/cost constraints, risk assessment and monitoring needs to be prioritised, e.g. using the persistence-mobility-toxicity approach (Berger et al 2018) to target substances or substance groups which are of particular concern in terms of human and ecosystem health (Küster and Adler 2014). There are still analytical challenges for many groups of substances, for example many per- and polyfluoroalkyl substances (PFAS) and metabolites of parent compounds, but recent developments in analytical methods makes the task of screening for very large numbers of organic compounds possible and more cost-effective (Richardson and Ternes 2017).

The objective of this paper is to show how in the absence of a policy for substances of emerging concern in groundwater, and in the face of insufficient data, a group of states, agencies and researchers have come together to try and fill this important policy gap on a voluntary basis, while at the same time addressing the science gap. This paper describes, for the first time, how the process of developing a European groundwater watch list (GWWL), a list of selected priority compounds for groundwater monitoring, has been initiated, and outlines the current state of discussion regarding the GWWL methodology, which has been developed through interactions with a range of key stakeholders across Europe. Two groups of compounds are described as pilot studies, PFAS and pharmaceutical substances, are used as exemplars for how the proposed GWWL process may work to prioritise monitoring of substances of emerging concern in groundwater in Europe. These two groups were selected due to their widespread use and environmental persistence and due to a higher level of monitoring in groundwater for these compounds. This voluntary process for EOCs in groundwater is the first of its kind, as far as the authors are aware, and will also be of interest to the science and policy community beyond Europe.

2. Approach for developing a European GWWL

2.1. Environmental governance context

Kuhlmann (2001) summarises the European environmental governance context as ‘a process through which a socio-political community achieves binding decisions in the face of conflicting interests. The processes of consensus-building, decision making or even implementation of decisions are not merely determined by state actors or formal governments … it is the interaction of societal and state actors that defines problems, builds up the necessary degree of consensus on problems and solutions, consolidates conflicting interests and (pre-)determines...
political decisions’. The precautionary principle is one important dimension in the European approach to risk regulation on the one hand, while on the other hand a trend towards greater scientific rigour through formal risk assessments to justify environmental decisions at the national and international level exists (Vogel 2003, Küster and Adler 2014, Hartmann et al 2018), which is often favoured by industry. Since the 1970s research and innovation policies in Europe have moved from a national to a transnational arrangement in part due to closer regulation, greater internal and external trade and competition (Kuhlmann 2001).

It is widely acknowledged that environmental policy in US and Europe has often suffered from poor effectiveness (Commission for European Cooperation (CEC) 1999, Jordan 2002). Newig and Fritsch (2009) state that ‘As a response [to poor effectiveness] two key strategies have been proposed and pursued: (i) to adapt the level and spatial scale of governance of the environmental problems and; (2) to enhance participation of non-state, civil society actors in environmental decision making’. Both of these have been implemented through the Water Framework Directive (WFD) (2006), and the Public Participation Directive (PPD 2003, 2003/35/EC) which have promoted more collaborative forms of environmental governance (see figure 1). This has resulted in a multi-partner approach (e.g. Leydesdorff and Etzkowitz) to formulating environmental policy in Europe and elsewhere involving a number of actors including those from research, industry, government and civil society. It is in this governance context that the voluntary GWWL was initiated (in 2015) and the ongoing GWWL methodology has been developed (2015–present).

In the EU many environmental policy instruments have embraced voluntary initiatives, in part due to the growing complexity and administrative costs of traditional command-and-control approaches (Börkey and Lévêque 2000). The principal of voluntary submission of data by MS, as part of gathering information to inform new policy, is embedded in the WFD and GWD review process. Also, the consideration of the expertise of stakeholders such as industry has been shown to be advantageous for policy making procedures. The GWWL as a voluntary initiative can be seen as an extension of this well-established practice.

2.2. Chronicle of science and policy that has initiated the voluntary GWWL process

A chronicle of how the science and policy developed towards an agreement by EU MS to develop a GWWL is summarised in figure 1. In the European Union (EU) Water Framework Directive (WFD) (EC 2000) is the overarching water legislation. It aims to protect water resources (quality and quantity) and sets environmental objectives to ensure that all EU water bodies achieve good status, provided exemptions do not apply. For groundwater it covers chemical and quantitative status. The European Groundwater Directive, (European Commission 2006a) and the review of its Annexes in 2014 (European Commission 2014), is a ‘daughter directive’ of the WFD. It specifically defines the objectives for preventing or limiting inputs of pollutants to groundwater and establishes groundwater quality standards for nitrate and pesticides (Annex I), as well as listing further substances for which threshold values should be set by EU MS if they are putting groundwater bodies at risk of failing their good status objective (Annex II).

A number of benchmark papers (Loos et al 2010, Lapworth et al 2012, Stuart et al 2012) drew attention to the occurrence of EOCs in European groundwater at nanogram-microgram/L concentrations and highlighted the need for more systematic monitoring of EOCs in groundwater. However, the published studies mostly have small sample sizes or looked at very limited groups of compounds and had limited geographical coverage. These papers in part provided the context for developing the voluntary GWWL in Europe. The purpose of the GWWL is to produce high-quality Europe-wide monitoring data on substances that have not routinely been considered and that may be of concern because they pose a risk, or potential risk, of groundwater bodies not achieving their environmental objectives.

In contrast to groundwater, there has been recent progress on monitoring EOCs in surface waters (Barbosa et al 2016), driven principally by the development of the ‘surface water watch list’ (SWWL). Unlike the voluntary GWWL process, the SWWL is a mandatory process established by the 2013 amendment to the EU Environmental Quality Standards Directive (2008/105/EC), EC (2008a, 2015). The SWWL was instigated to gather EU-wide monitoring data ‘for the purpose of supporting future prioritisation exercises in accordance with Article 16(2) of Directive 2000/60/EC...’. Table S1 is available online at stacks.iop.org/ ERL/14/035004/mmedia provides a brief comparison between the SWWL and GWWL regarding their purpose, decision process and reporting protocols.

The formal starting point of the GWWL development process followed the review of the GWD Annexes, which took place in 2014 (European Commission 2014). Prior to this, a public consultation took place in 2013 on the review of Annex I and II of the GWD. A stakeholder conference, and associated preparatory work was carried out by the WFD Common Implementation Strategy Working Group Groundwater in 2011 (CIS-WFD 2011), which drew attention to the need to consider a wider number of groups of emerging organic contaminants. Although the issue was highlighted as part of the review of the GWD Annexes, it was determined that ‘not enough information is available to set new groundwater quality standards in Annex I to that Directive for any pollutants’ and that ‘the need to obtain and respond to new information
on other substances posing a potential risk should be acknowledged. Therefore, a watch list for pollutants of groundwater should be established... to increase the availability of monitoring data on substances posing a risk or potential risk to bodies of groundwater, and thereby facilitate the identification of substances, including emerging pollutants, for which groundwater quality standards or threshold values should be set.

The European Commission aims to ensure the improvement of data availability, and consider works and results for the 'fitness check' of the WFD, daughter directives and Floods Directive in 2019.

3. Methods

3.1. Data collection and analysis of evidence

The evidence reported in this paper on the development of the GWWL methodology was collected through personal participant observation as part of the GWWL working group. The pilot studies presented in this paper provide more detailed examples of how the GWWL approach may work in practice and has been able to road-test the voluntary approach required for data sharing and participation if the GWWL process is to be a success. All the pilot study data on groundwater occurrence reported in this paper was obtained voluntarily from MS (on PFAS and pharmaceuticals) and were collected through structured survey questionnaires.

A European-wide team of researchers, regulators, industry and European Commission representatives participated directly in the development of the GWWL methodology as a voluntary group. This process has taken place since 2014 and was facilitated by 5 two-day workshops in Berne (September 2015), Luxembourg (October 2015), Vienna (June 2016), Paris (March 2017) and Brussels (September 2017). Representatives (including all co-authors in this paper) participated directly in this process; drafting text, discussing and debating inclusion of material, proposing new material, obtaining feedback from the working group, editing the methodology text directly and commenting on subsequent versions of the draft methodology (CIS-WG 2018). The GWWL voluntary group also designed and sent out the pilot study questionnaire collaboratively and collated results. A template as an EXCEL table was sent to participating countries (PC) in order to gather information on groundwater occurrences of pharmaceuticals and PFAS in a standardised form. The first pilot study on pharmaceuticals revealed that different names are used by PC to qualify a unique substance. Feedback on this first pilot study highlighted the need for a unique code for each substance. Moreover, the template enabled the collection occurrence data in a predefined form. This collated

Figure 1. Chronicle of science, policy and legislation that has led to the voluntary GWWL process.
information from organisations participating in the GWWL process as well as MS and organisations not participating directly in the GWWL voluntary group. The template for the PFAS questionnaire and can be found here: https://circabc.europa.eu/sd/a/12c16174-a560-497d-ac88-3ec56171993c/PFC-Template.xlsx.

All material associated with the methodology development, various drafting meetings are also hosted as open access files and folders in the same directory on the EU circabc website (https://circabc.europa.eu/w/browse/8804bf88-0c0-4890-80e4-4e1a3b682cf2). This survey questionnaire template was emailed to relevant regulators in MS to collate summary statistics on PFAS occurrence in groundwater. Data from a total of 12 MS were collated. Summary results were collated from the questionnaire survey and were used for the analysis presented in section 4.1. Further details on the quality assurance (QA) for collecting and assessing returned survey data is described in the supplementary information. Further details on the process and participation in data collection and analysis of results for the pharmaceuticals case study are reported in Marsland and Roy (2016). No site specific information was collated as part of this process and results were summarised and reported so that country level information was anonymised.

3.2. Co-development of the GWWL methodology between researchers, regulators and industry
Unlike for the SWWL, EU MS are currently not legally bound to implement a GWWL process. Instead the European Commission has adopted a voluntary mechanism. Therefore, to make it successful, there was a need to demonstrate the benefits of the GWWL to attract and build participation among MS. This was achieved through the existing networks of scientists, regulators and industry across Europe which has a track record of effective professional collaboration within the European Commission WFD CIS Working Group on Groundwater. The GWWL process was initiated in 2014 and brought together over ten EU stakeholders (including representatives from the following sectors: environmental regulation, industry—including R&D and environmental research) with the specific aim of developing a methodology for producing an initial GWWL. From the outset there was a common vision amongst the GWWL voluntary group to work towards a robust methodology which balances both the broad agreement on the need for improved groundwater chemical monitoring across Europe and the burden of monitoring and regulation for each member state (CIS-WG 2018). This was discussed by MS at the EU conference on the review of the Annexes I and II of the GWD (European Commission 2013a) and agreed at the CIS-WG meeting in Greece in 2014. A number of key ingredients facilitated the process of drafting the current GWWL methodology:

- Critical mass in term of countries/organisations (8 countries were represented including MS largely comprising policy makers and regulators, researchers and industry) represented on the GWWL voluntary group, which helped to give the process legitimacy;
- High level of commitment from voluntary participants;
- Openness among all stakeholder participants, respect for input from all sides and acknowledgement of competencies and good-will;
- Previous track record of inter- and intra-country cross-sector collaboration on this topic;
- A mutual commitment to finalise the GWWL methodology, aided by regular face-to-face meetings to co-author and refine the draft methodology;
- Willingness of MS/and associated countries (AC) to share relevant experience and existing data sets with GWWL voluntary group.

From the outset the process of drafting the GWWL methodology aimed to be highly consultative. Considerable time and effort was made to ensure that the different opinions within the drafting group and the wider EU CIS Groundwater Working Group were represented. Both national and European-wide stakeholders, e.g. the EU and multi-national associations/companies, were involved in the process and ensured that a pragmatic and balanced methodology was developed. ‘The cooperative nature of the methodology development process enabled industry to play an important part in identifying data sources and data availability issues as well as initiating discussions on GWWL deselction criteria’—quote from an industry representative. Throughout the drafting process the evolving GWWL methodology has been shared and communicated with both the EU and other national entities to gather feedback and input and all relevant documentation is openly available on the EU website: https://circabc.europa.eu.

The voluntary nature of the process was helpful in facilitating a GWWL voluntary group that achieved considerable ‘buy-in’ to the methodology and will aid the future development and implementation of the GWWL. ‘The mutual benefits of sharing existing groundwater monitoring data and of a coordinated approach to summarize evidence were clear from the outset’ quote from GWWL voluntary group participant. The GWWL voluntary group brought to the table relevant recent experience from national programmes for monitoring anthropogenic substances in groundwater. These included examples from national monitoring programmes in England and Wales (Manamsa et al 2016), France (Lopez et al 2015), Germany (Bergmann et al 2011, LAWA 2016), Italy (Meffe and de Bustamante 2014), Netherlands (KWR 2017), Spain
Insights were gained from the different approaches employed by national surveys and methodologies, including those from the United States (e.g. US-EPA United State Environment Protection Agency 2009), and the EU data sets formed the basis for pilot studies for groups of groundwater anthropogenic substances that were prioritized by the GWWL voluntary group.

3.3. The process of establishing a GWWL for Europe

The process for establishing a GWWL required current knowledge from across Europe to be brought together for the first time on: detections of anthropogenic substances in groundwater, their physico-chemical properties, chemical usage and production as well as information on toxicity. This process, as currently proposed, is summarised in figure 2. This process can be used to rank and prioritise anthropogenic substances based on (i) groundwater monitoring data, (ii) theoretical environmental exposure, mobility and persistence and (iii) toxicity, i.e. the relative risk they pose in the groundwater environment. Considerable time was spent by the GWWL voluntary group debating and agreeing on the specific methodology, including 6 two-day meetings dedicated to this task between 2015–2017, where text was reviewed and redrafted, ‘line-by-line’ through a collaborative processes.

3.3.1. Prioritisation based on existing monitoring data on occurrence in groundwater

An initial step comprises the collection of monitoring data on substances already detected in groundwater (see figure 2). Detection of anthropogenic substances in groundwater demonstrates that a substance has the ability to reach the water table, and if it is a potentially hazardous pollutant, has the potential to cause a detrimental impact to groundwater quality or its associated receptors. This first step uses aggregated data provided voluntarily by national agencies compiled in an agreed format. As well as collating quantitative results (from accredited methods/laboratories), in some cases so-called semi-quantitative data was also collated (also from accredited laboratories), for example methods which use target based screening approaches with two-point calibrations and isotopically labelled internal standards (e.g. Manamsa et al 2016). The intention is that these data are provided on a regular basis to grow the database and generate the most up-to-date information on anthropogenic substances occurrence in groundwater across Europe. Based on data collated in step I, a list of substances of
specific concern are identified (column I), this is ranked based on both the frequency of detection reported in groundwater as well as the number of countries with detections to generate ranked list I (figure 2). The experience gained undertaking the pilot studies which only considered pharmaceuticals and PFAS was very useful in developing a reporting protocol for step I. The Supplementary Information details the proposed data capture and QA for the existing monitoring data used in the pilot GWWL studies.

3.3.2. Prioritisation based on persistence and mobility data
To assess the potential for substance entry into groundwater, both the persistence and mobility of substances have to be considered. These are the most relevant properties for identifying substances that can easily leach through the unsaturated zone and reach the aquifer (Stuart et al 2012), and is also relevant for substance only recently marketed and used in the environment which may as yet have not reached groundwater. This step, figure 2, generates a list of compounds (ranked list II) with proven and/or a theoretical capacity to leach to, and be transported in, groundwater based on their physio-chemical properties:

- The mobility of a substance is defined by its potential to move conservatively with water and not be sorbed to organic and (clay) minerals or oxides (ranking based on the ionic form of the molecules for polar and charged compounds).

- The persistence of a substance in the subsurface is expressed by its half-life in soil or water depending on the physico-chemical conditions of the environment. (the REACH classification depends on this), see supporting information and Burger et al (2018).

In general, substances with a high persistence (expressed as dissipation half-life time, DT50) and a low adsorption coefficient (defined via sorption coefficients, \(K_{oc}\) or \(K_{ow}\)) have a high potential to leach to groundwater. A substance will be considered as having the potential for groundwater exposure if at least one of the indicators of persistence and at least one of the indicators of mobility satisfy the proposed criteria, see CIS-WG (2018), these substances are then ranked based on the environmental mobility and/or persistence criteria to generate ranked list II (figure 2). Substances identified as possible pollutants can also be ranked depending on their theoretical potential to reach groundwater. The suggested prioritisation procedure is a classical point system ranking, detailed in CIS-WG (2018). Sub-scores are assigned to each available indicator for persistence and mobility. A global groundwater exposure score is calculated based on these sub-scores. Substances that have the highest potential to reach GW are those with the highest groundwater exposure score. The ranking of substances according to their properties is completed by considering additional factors, such as the amount of a substance released to the environment and its use-pattern. The results from the two initial ranked lists of compounds are combined to generate ranked list III (figure 2).

3.3.3. Prioritisation based on hazard-toxicity
A combination of ranked List III with the hazard potential of the considered substances, figure 2, adds potential toxicity and bioaccumulation hazards. This produces an integrated ranked list of chemicals (ranked list IV) that are considered to pose a potential concern for groundwater and the ecosystems that rely on it. In this step, the highly ranked substances from ranked list III, are further prioritised taking into account relevant toxicity criteria, i.e. toxicity and other relevant properties, e.g. persistent, bioaccumulative, and toxic (PBT), vPvB (very persistent and very bioaccumulative), carcinogenicity-mutagenicity-reprotoxicity (CMR) or endocrine disrupting (ED) potential (Dulio and Slobodnik 2015). Substances are ranked depending on their significance as a hazard to human health and/or the environment. The prioritisation is based on the calculation of a ‘hazard’ score that merges the three indicators PBT, CMR and ED. The detailed scoring system used and source of this information is detailed in CIS-WG (2018). Any new development/revision in the assessment of ED properties should be taken into account in the dynamic process of this step. The collection of available toxicity data is a large ongoing task and is the main focus of future activities for developing the GWWL methodology. This step has the greatest uncertainty due to the paucity of data for some compounds.

3.3.4. GWWL substance selection
The GWWL is designed to be dynamic and updated based on improved criteria and input data for ranking substances based on occurrence, mobility/persistence and toxicity. The outcome of the integration of toxicity will be a list of substances ranked (list IV) according to their potential to harm the environment, human health or the potential use of groundwater. For substances with a high or medium potential (based on the final ranking scheme outlined in figure 2—see supporting information and CIS-WG (2018) for further details on scoring approaches) to compromise the WFD/GWD objectives, an assessment of the data availability is then undertaken to feed into the EU assessment of whether ‘enough information is available to set new groundwater quality standards in Annex I of the Groundwater Directive’. Currently an equally balanced scoring approach for the three scoring criteria has been agreed. If a substance is highly ranked in list IV but there is insufficient monitoring data for decision making available, the substance goes to the GWWL to prioritise further monitoring and the collect sufficient data. To keep the Watch List process...
manageable it was agreed to limit the number of substances on the GWWL (e.g. 30 substances).

If there are many substances remaining on the integrated List IV with identical or very similar scores further selection should be based on an enhanced expert judgement. Besides the integrated score additional information may also be taken into account if this is available. For example, the amount of a substance released to the environment and its use-pattern. If there are different groups of substances e.g. pharmaceuticals and PFAS in List III it might be reasonable to select high ranked representative(s) of each group of substances. The final selection of substances will be carried out by a group of experts mandated by the EU Working Group Groundwater. MS/AC will be asked to monitor and report GWWL substances on a voluntary basis commencing in 2019 (CIS-WG 2018).

3.3.5. Selection of substances or group of substances for the review of the GWD (Annexes I and II)

The summary and assessment of available monitoring data will show whether a substance is of ‘potential concern’. If this is the case these substances will go to a list of substances to be considered by the European Commission in the next review of Annexes I and II of the GWD, and shall support European Commission revising the GWD and WFD and identify substances that should be regulated in the future. There are a series of technical and political decisions which need consideration as a result of the new data generated by the GWWL e.g. (i) if it should be considered for Annex I or II, (ii) political decisions based on technical recommendations, (iii) political desire as well as cost implications.

3.3.6. Deselection of substances from the GWWL process

For substances on the GWWL, as soon as sufficient monitoring data are available to confirm that they are, or, are not a pollutant of ‘potential concern’ they can be integrated in to the GWD Annex I/II process or removed from further consideration on the GWWL. If a substance is considered of potential concern it may be subsequently put on the ‘List facilitating Annex I and II review process of the GWD’. This means that sufficient monitoring data are available and there is no need to keep them on the GWWL.

If a substance is monitored in several countries (e.g. 8 MS/AC) over a sufficiently long period and at a sufficient number of appropriate monitoring sites, and if there are no or only a very small proportion of detections, there needs to be a mechanism to deselected the substance from the GWWL and allow space for other new substances to be added to the GWWL (see figure 2). If a substance is ranked high in list IV but is not detected then it could also be argued that there is a need for low-frequency monitoring to continue, however, based on the methodology outlined in figure 2, this substance would be removed from the GWWL to make room for substances for which there is currently inadequate monitoring. There are a number of plausible scenarios whereby detections in groundwater may be on a long-term upward trend but where the GWWL monitoring has shown (e.g. over a 3–5 year monitoring period) that currently a particular substance is not a concern for groundwater. This issue of a potential long lag between contamination at the surface and occurrence in groundwater will need to be considered as part of the longer-term review of the GWWL, for example, it may be possible in some circumstances for a compound to be included again in the GWWL if there is a change and sufficient detections start to increase over a long period of time. This of course does not preclude ongoing voluntary monitoring on a lower frequency basis by MS/AC. For example, if the substance can be monitored as part of broad screening method which is employed for GWWL monitoring purposes then the cost of ongoing monitoring for this deselected substance will be negligible.

4. Results and discussion

4.1. Pilot studies on pharmaceuticals and PFAS in groundwater

Undertaking the two pilot studies was important to test the initial methodology, provide a sense check for the type of information required and to learn from the process through undertaking initial pilot studies using some generally better characterised substances of emerging concern.

4.1.1. Motivation for using pharmaceuticals and PFAS as pilot studies

The discovery of pharmaceutical products (PPs) within the environment is relatively recent and is reflected in the growing body of literature since the 1990s (Mompleat et al 2009). Studies on the occurrence, sources and fates of PPs in groundwater are more limited compared to surface and waste waters (Jurado et al 2012, Lapworth et al 2012, Lopez et al 2015, Sui et al 2015). However, PPs have been researched to a greater extent than many other anthropogenic substances groups and therefore data are available to inform and pilot step I and II assessment through the GWWL process. While risks to human health are considered low, as drinking water concentrations are typically more than 1000-fold below minimum acute therapeutic doses (MTD), the toxicity of PP mixtures on aquatic organisms (Clevers 2003, Cizmas et al 2015) and resistance formation for e.g. antibiotics (Levy and Marshall 2004) are areas of growing concern.

PFAS are used for a range of purposes including textile stain guards, grease-proof papers, fluoropolymer manufacture, coatings, and aqueous film-forming foams. The family of PFAS compounds is very large and includes >6, 000 compounds (Buck et al 2011). Of
these substances, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the most studied compounds regarding their potential widespread effects on the environment (Lindstrom et al 2011, Herzke et al 2009, Guelfo and Adamson 2018). PFOS has been classified as persistent organic pollutants (POPs) under the Stockholm Convention (2001), a global treaty to protect human health and the environment. PFOS is covered by EU REACH Annex XVII (European Commission 2006b) and European Commission 2006c, and while regulation of PFOS in textile products is in place, no such European-wide limits are currently in place for other PFAS. However, the European Chemical Agency suggested a comprehensive ban of PFOA in September 2015 with a limit value of 0.2 micrograms/L (European Chemical Agency (ECHA) 2015).

EU-wide environmental quality standards (EQS) were set for PFOS and its derivatives in surface freshwater, coastal and transitional water (European Commission 2013b). Surface water monitoring data from across the EU shows the widespread occurrence of PFAS, with frequent exceedance of the EQS for PFOS (0.65 ng L$^{-1}$) (Pistocchi and Loos 2009, CONCAWE 2016, Lindim et al 2016). In most EU countries no regulatory standards have been set for groundwater. Given the ubiquitous nature and persistence of PFAS and their potential impact on human health and the environment, and hence the chemical status of groundwater bodies (European Commission 2006a), PFAS were an obvious choice for the pilot study.

4.1.2. Summary results for pharmaceuticals and PFAS in groundwater

Following a request for data made by the GWL voluntary group in 2015, twelve PCs submitted data sets for pharmaceuticals, results were compiled and reported by Marsland and Roy (2016). This exercise revealed the need for consistency in substance identification and the importance of using the chemical abstract service (CAS) numbers as a unique identifier for each substance rather than substance name. Preliminary assessment of the data revealed a wide range in the reported limits of quantification (LoQ), raising questions over the consistency of reporting and interpretation of these values by different laboratories. The subsequent data request for PFAS learned from this initial data request and provided a more structured format for reporting.

4.1.2.1. Pharmaceuticals

Summary results for pharmaceutical substances reported from five or more PC are summarised in figure 3. A very wide range of pharmaceutical substances (in total approximately 300 different substances) have been monitored in groundwater by PCs and were reported by Marsland and Roy (2016). However, there appear to be differences between PCs on what substances are included in this category, and therefore some substances are under-represented in the collected data. Carbamazepine was the most widely analysed pharmaceutical substance by PCs, followed by diclofenac. Carbamazepine was also frequently detected above the LoQ (at 12% of sites), but
diclofenac had relatively low detection rate (1%). As a percentage of sites monitored, paracetamol was the most frequently detected substance (24%) with diatrizoic acid, primidon, ibuprofen and clofibric acid also frequently detected in groundwater.

4.1.2.2. PFAS
As a result of learning from the pilot study on pharmaceuticals the voluntary data request for the second pilot study on PFAS started with a simple questionnaire and list of substances clearly identified by its CAS no, name and chemical formula. The list comprised 53 substances. Monitoring data for twenty eight different PFAS compounds were reported by PCs. PFOS and PFOA were analysed and found in groundwater by all the twelve PCs. The results revealed a detection rate above the LoQ at > 20% of sites (23% and 27% respectively). As a percentage of sites monitored, perfluorobutanoic acid (monitored by five PCs) was the most frequently quantified perfluorinated compound in groundwater (46% of 1189 sites). Two PFAS, 1H, 1H, 2H, 2H-perfluorocanesulfonic acid (H4-PFDeS -8:2 FTS) and 6:2 fluorotelomer phosphate diester (6:2 diPAP) were monitored by only one PC but with a detection rate equal or above 10% of sites. These last substances should be of high interest for other EU MS and AC to verify their occurrence in groundwater.

Figure 4 shows the comparison between PFAS scoring results from list I assessment based on existing monitoring data and list II assessment based on theoretical groundwater leaching/mobility data. The global analysis reveals that highly ranked PFAS from the step I assessment are also highly ranked for the list II assessment and vice versa for low ranked PFAS. This validates the criteria selected to assess groundwater exposure to PFAS. In contrast, two substances; Perfluorodecane Sulfonate (PFDS) and Perfluorotetradecanoic Acid (PFTeDA) had leaching sores of 0.5

| Score | No of MS/PC |
|-------|-------------|
| 1     | 12          |
| 0.8   | 10          |
| 0.6   | 8           |
| 0.4   | 6           |
| 0.2   | 4           |
| 0.0   | 2           |

| Score results step I | Score results step II | No of MS/PC that submitted data |
|----------------------|-----------------------|---------------------------------|
|                     |                       | 12                              |
|                     |                       | 10                              |
|                     |                       | 8                               |
|                     |                       | 6                               |
|                     |                       | 4                               |
|                     |                       | 2                               |

| Score | No of MS/PC |
|-------|-------------|
| 1     | 12          |
| 0.8   | 10          |
| 0.6   | 8           |
| 0.4   | 6           |
| 0.2   | 4           |
| 0.0   | 2           |


but clearly more data are needed to confirm this. Perfluorobutanoic acid (PFBA) is ranked high in list I and II, however, there are significantly fewer countries that have reported for this compound compared to PFOA and PFOS due to differences in analytical methods/suites used between PCs.

The initial ranking and selection process (as far as ranked list III) has been tested for two groups of compounds: pharmaceuticals and PFAS. These first test groups revealed the difficulties with collecting comprehensive and homogenous data on theoretical groundwater leaching potential and hazard properties. For example, there is the issue of inconsistent approaches to hazard assessments as well as missing information for some measures of mobility which mean that these two elements have greater uncertainty compared to the groundwater occurrence criteria for these test groups. In some cases using read-across values from substances with very similar chemical structures or using modelling techniques such as quantitative structure-activity relationships (QSAR) have been shown to be robust and pragmatic options to fill data gaps where experimental hazard data is not available (Alves et al. 2018, Nendza et al. 2018). Further information is currently being gathered to make an initial assessment for ranked list IV possible and is the focus of future work for the GWWL Working Group. In some cases input data for the multi-core calculations sometimes exist, but are not currently accessible and may be commercially sensitive. Stronger collaboration with toxicologists and more comprehensive hazard data, and better access to this data, are essential to fill existing data gaps (Dulio et al. 2018) required for step IV (ranking based on hazard). Indeed, for example another challenge is access to comprehensive manufacturing and usage data for PFs in EU MS. Similarly, better PFAS mobility data, and persistence properties for some pharmaceuticals and PFAS would clearly benefit the process.

5. Conclusions and future outlook

The GWWL concept has been developed within the framework of the EU WFD CIS Working Group on Groundwater though intense collaboration between EU MS, industry, other stakeholder representatives and the European Commission. The current multi-party approach ensures that inputs and concerns from all sectors (EU/national administrations, academia and industry) are considered for the selection of substances for the GWWL and the assessment of monitoring data, groundwater exposure potential, and hazard. Deliberate steps have been taken to ensure that the GWWL concept is in line, as far as possible, with the EU SWWL process and other EU research networks focussed on the selection of potential anthropogenic substances (Dulio et al. 2018). For example, some GWWL participants are also involved in the NORMAN network for emerging substances. Progress made during the reflective process were regularly presented to the NORMAN network during its General Assembly in Vienna (2016) and Leipzig (2017) and in specific Working Group 1 ‘prioritisation of emerging substances’ meetings in Berlin (2015) and Paris (2016). Moreover, the WG-1 co-ordinator of NORMAN network on prioritisation of emerging substance participated in GWWL methodology development process and provided advice on the ranking and selection process for emerging substances.

As a first outcome, the results of the pharmaceuticals and PFAS pilot studies serve as a starting point for the identification of substances to be considered for the first GWWL substances list, if (1) they are subsequently sufficiently highly ranked in list III of the selection procedure and (2) sufficient monitoring data are lacking. The current pilot studies have demonstrated that a voluntary data request for potentially monitored substances has generated useful results and shows that the process of voluntary monitoring is already being undertaken within many MS and AC (figures 3 and 4). Also, it was demonstrated that there is a willingness by MS/AC to deliver data voluntarily. The results generated on prioritisation for PFAS compounds based on exposure mapped on to the existing monitoring data well (see figure 4). However, further work is needed to refine the methodology based on the prioritization in list IV, relating to substance hazard, and will be the focus of future work. Based on this current methodology, substances—including emerging substances—posing a risk will be flagged up that (1) exhibit sufficient monitoring data at the European level to directly assess their relevance for a potential inclusion into Annex I/II of the GWD (European Commission 2006a) or (2), do not show adequate European-wide monitoring data in this regard, but can be prioritized according to their potential environmental release, groundwater contamination potential, and defined hazard criteria for inclusion in the GWWL leading to a priority monitoring by national agencies.

The prioritisation methodology has been initially explored with substance groups for which considerable monitoring data were already available (e.g. pharmaceuticals and PFAS). This methodology is thus suitable to screen the selected substance groups for suspected substances of concern, for which via the GWWL monitoring procedure a sound base of groundwater monitoring data can be produced. Via the GWWL process, PC will also receive advice on how to improve their surveillance monitoring for anthropogenic substances on a voluntary basis and for informing water managers and policy makers (e.g. setting threshold values). Finally, this process will enable evidence-based decisions on inclusion of substances in the revision process for Annex I/II of the EU GWD. In order to achieve compatibility with the EU GWD revision cycle, the GWWL process cycle has been designed to be aligned as far as possible with the WFD evaluation process.
The mandate for a voluntary GWWL was discussed and completed by the EU Working Group Groundwater (Vienna, October 2018) with the intention of setting up the first GWWL in 2019. The GWWL process will be reviewed and revised, based on the experience and results from the first six-year river basin management planning cycle, aiming to streamline and improve—i.e. in terms of future substance groups to be considered, the data collection and substance prioritisation process. It is hoped that a well-designed GWWL process will help PC to concentrate their limited resources available for groundwater monitoring on the most relevant anthropogenic substances and will contribute to ensuring that European citizens continue to benefit from high-quality groundwater as their principal drinking water resource in the future.

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