Pesticides and their metabolites in European groundwater: comparing regulations and approaches to monitoring in France, Denmark, England and Switzerland

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Abstract

Pesticides, i.e. plant protection products (PPP), biocides and their metabolites, pose a serious threat to groundwater quality and groundwater dependent ecosystems. Across large parts of Europe these compounds are monitored in groundwater to ensure compliance with the European Water Framework Directive (WFD), the Groundwater Directive (GWD) and Drinking water Directive (DWD). European regulation concerning the placing of PPP on the market includes groundwater monitoring as a higher tier of the regulatory procedure. Nevertheless, the lists of compounds to be monitored vary from one directive to another and between countries. The implementation of monitoring strategies for these directives and other national drivers, differs across Europe. This is illustrated using case studies from France, Denmark (EU member states), England (part of the EU up to January 2020) and Switzerland (associated country). The collection of data (e.g. monitoring design and analytical approaches) and dissemination at national and European level and the scale of data reporting to EU is country-specific. Data generated by the implementation of WFD and DWD can be used for retrospective purposes in the context of PPP registration whereas the post-registration monitoring data generated by the product applicants are generally only directly available to the regulators. This lack of consistency and strategic coordination between thematic regulations is partly compensated by national regulations. This paper illustrates the benefits of a common framework for regulation in Europe but shows that divergent national approaches to monitoring and reporting on pesticides in groundwater makes the task of assessment across Europe challenging.

1. Introduction

Pesticides are used throughout the world, particularly in agriculture, to secure good crop yields. Groundwater pesticide contamination is a major threat to aquifer quality status globally (Foster and Chilton, 2021), and often results in complex mixtures of pesticides and their degradation products in groundwater sources used for water supply (Lapworth et al., 2006; Gimsing et al., 2019; Baran et al., 2021). In Europe, groundwater is the most important drinking water resource for many countries (e.g. up to 100% in Denmark or Austria, 80% in Switzerland and around 70% in France – EurEau, 2021). Pesticides may also affect groundwater ecosystem services based on microbial activities (e.g. denitrification, Michel et al., 2021) and other groundwater dependant ecosystems such as wetlands, lakes and rivers (McKnight et al., 2012).

There is a wide range of different frameworks used globally for regulating pesticide use (Pelaez et al., 2013) and protecting groundwater bodies as well as different approaches undertaking groundwater monitoring. EU legislation divides pesticides into plant protection products (PPP) and biocides used for non-food or feed purposes. This can lead to confusion as PPP and biocides are not subject to the same regulations. The regulation EC N°1107/2009 for PPP was updated and consolidated in March 2021 and the regulation EU N°528/2012 for biocides was updated and consolidated in June 2021. The latter apply without prejudice to REACH regulation n°1907/2006. Similarly, active substances used in PPP and/or biocides are first approved at EU level. In a second stage, EU countries authorise the placing on the market of PPP or biocides products containing those active substances on their territory and ensure compliance with EU rules. European Commission decisions on approval and non-approval are published in the Official Journal of the European Union; information being also available on two websites ("EU pesticides database" and "information on biocides" on the European commission and ECHA – European Chemicals Agency - websites, respectively). Regarding PPP, it is therefore possible to know if an active substance has uses allowed in the different Member States (MS - even if it is recommended to check the national databases) and to access the information regarding environmental risk and notably risk of transport into groundwater. In May 2021, at EU level in the context of PPP, 469 active substances are approved and 61 pending (i.e. waiting for a decision). It should be noted that active substances of PPP are classified in 21 categories and correspond to organic and inorganic compounds as well as fungi and/or viruses.

The ECHA database for biocides contains a list of 366 active substances (corresponding to 21 product-types – May 2021)) of which 169 are approved at EU level as biocides. It should be noted that an active substance can show properties for being both a PPP and a biocide but can be authorised for only one of the cases (e.g. diuron, clothianidine or warfarin not yet approved as PPP but approved as biocide).

A cross comparison between the 2 databases is not trivial making difficult to identify which compounds are both an active substance of PPP and a biocide.

Although EU regulation encourages the use of less harmful active substances, pesticides are still intensively used and therefore may pose human health or environmental risks. The presence of pesticides or their metabolites in groundwater throughout the world is regularly highlighted either in regional (Fisher et al., 2021; Moreau et al., 2019) or national studies (Bexfield et al., 2021; Close et al., 2021; Kiefer et al., 2020; Hintze et al., 2020; Kotal et al., 2021; Lapworth et al. 2015; Lopez et al., 2015; Stuart et al., 2012). Several large-scale monitoring studies have been carried out in Europe more than a decade ago (Loos et al., 2009; 2010) and to our knowledge there has been no such campaign recently. Therefore, having a precise vision of the status of groundwater with respect to pesticides and their metabolites at the European scale is not trivial.

Driven by a strong regulatory context, considerable effort is put into focused monitoring of the quality of groundwater in Europe with respect to pesticides and their metabolites compared to other regions (Donley 2019, Pelaez et al., 2013). Major environmental directives (Water Framework Directive 2000/60/EC, WFD - and associated Groundwater Directive 2006/118/EC - GWD, and Drinking Water Directive 98/83/EC, recently revised EU 2020/2184, DWD) and the European Regulation (EC) No. 1107/2009 concerning the placing of PPP on the market require the implementation of groundwater monitoring. However, the heterogeneity of datasets through Europe regarding groundwater and the lack of knowledge to support the risk assessment were highlighted by European Environment Agency (EEA) as key obstacles to improve regulation and management of groundwater resources (Mohaupt et al., 2020). Very recently, a European wide collection and analysis of existing monitoring data on non-relevant pesticide metabolites (nrM) has been carried out in the frame of the WFD CIS task “Voluntary Groundwater Watch List” (cf. chapter 3).

There are common challenges across Europe with respect to pesticide contamination in groundwater. The UN (United Nations) Sustainable development goals related to water resources and specifically pollution (targets 3.9, 6.3 and 15.1) are also a common driver for progress in this area. The challenge of pesticide contamination in groundwater needs to be understood at a regional level, e.g. a large number of pesticides are authorised and used across large area in Europe with an agricultural footprint, to enable feffective solutions for improved groundwater protection and management. Societal drivers for improved status of environmental waters extend beyond national boarders, and this has implications for the authorisation and use of PPPs and the trade of food products and goods between countries. More timely sharing of data can direct monitoring and interventions in one region and can inform activities in another region. Highly divergent approaches and implementation of regulation and monitoring at different administrative levels make this task more challenging. Having a common framework really helps, particularly one which is flexible to country specific issues.

While this paper is focussed on Europe, this is not a unique challenge for Europe, indeed regional, national and state regulation for monitoring of pesticide use and groundwater contamination is also highly divergent for other regions such as North America and Asia and Africa (Li 2018; Pelaez et al., 2013; Donley 2019; Bexfield et al., 2020; Bhushan 2006; Gupta et al., 2018; K'oreje et al., 2020).

With a focus on Europe, which has a strong common regulatory framework, this paper examines the current practices in terms of groundwater pesticide monitoring and dissemination of information for use by stakeholders. To the best of our knowledge, there has been no published study that compares and contrasts the different approaches and how these are effectively operationalised in different countries in Europe.

Thus, a selection of four European countries is used to illustrate common practice as well as divergent approaches to pesticide sampling, analysis and reporting of groundwater pesticide contamination. The two different monitoring setups i.e. general monitoring (linked to environmental directives) and targeted monitoring studies (for use in the authorization procedure of PPPs) are addressed. These examples discuss to what extent a common vision for groundwater protection from contamination by PPP on a European scale can be realised. Comparing two EU countries (FR, DK) and two non-EU countries (EN, CH) enables insights to a broader range of approaches and the development of new ideas for future European procedures related to pesticide assessment in groundwater.

After a brief presentation of the regulatory context, a meta-analysis of the different approaches covering several aspects including regulatory context, the analytical challenges and the specific monitoring campaigns and developments compared and contrasted for the first time in this paper. Three themes are investigated in detail: i) the implementation of groundwater monitoring and data collection, ii) which substances are actually monitored and their occurrence in groundwater, and iii) approaches to early warning and surveillance for pesticides and metabolites.

2. Methods

Based on the examples of three EU member states (MS) (France, FR; Denmark, DK - EU MS; England, EN part of the EU up to January 2020 - so the regulatory framework in place still very much represents the EU framework) and one associated country (Switzerland, CH – AC - contributes quite closely and actively to the EU groundwater framework discussions),we will illustrate the practices both in terms of groundwater monitoring and dissemination of information and its use by decision makers. Note that in the context of PPP registration operating in the EU, France, Denmark and England belong(ed) respectively to the southern, northern and central zone, according to the zonal system (3 zones) of PPP authorisation. Regulatory zones are supposed to have comparable agricultural practices, and comparable plant health and environmental (including climatic) conditions. For comparison, Switzerland was chosen as an example of a well-established associated European country.

This work was not intended to be exhaustive regarding groundwater monitoring across Europe, but rather to show the similarities and disparities in practices to illustrate to what extent a vision on a European scale can be proposed and implemented. Our work focuses on raw groundwater and considers both pesticides and metabolites. In this paper, the term “metabolite” corresponds to "*any metabolite or a degradation product of an active substance, safener or synergist, formed either in organisms or in the environment*" according to the Article 3(32) of Plant Protection Regulation EC n°1107/2009. A guidance document exists on the assessment of the relevance of metabolites in groundwater of substances regulated under council directive EC/91/414 replaced by EC n°1107/2009 (Sanco/221/2000 –rev.10). The revised version of DWD (Directive (EU) 2020/2184 entered in to force on 12 January 2021) refers to EC n°1107/2009 regarding the definition of metabolites (point 32 of Article 3) and the relevance of metabolites for water intended for human consumption.

Following DW and GWD, concentrations of pesticides and relevant metabolites may not exceed 0.1 µg/L for a single of those compounds (in the case of aldrin, dieldrin, heptachlor and heptachlor epoxide, the parametric value shall be 0.03 µg/L) and 0.5 µg/L for the total concentration of those compounds. Swiss legislation fixes a 0.1 µg/L limit for drinking water and groundwater. Except for Denmark, no limit value has been defined for non-relevant metabolites when looking apart from single compound specific cases. In Denmark, all metabolites of pesticides, with a few exceptions, are considered to be relevant in accordance with the uniform principle in Article 29 of Regulation 1107/2009/EC, even compounds found to be non-relevant in the EU must not be detected in Danish groundwater in concentrations exceeding the EU parametric drinking water limit of 0.1 µg/L.

3. Regulatory context in European Union, England and Switzerland

The DWD, adopted in 1998, concerns the quality of water intended for human consumption. This directive has recently been revised (Directive (EU) 2020/2184) and the MS shall bring into force the laws, regulations and administrative provisions necessary to comply with Articles 1 to 18, Article 23 and Annexes I to V by 12 January 2023. Water quality monitoring is mandatory in this context (first type of general monitoring). A list of parameters (including inorganic and organic compounds, odour, colour etc.) that shall be monitored has been established including non-specific terms “pesticides” and “total pesticides”. This directive states that “only those pesticides, which are likely to be present in a given supply, need be monitored”.

WFD adopted in 2000 and its daughter directive GWD adopted in 2006 require that all MS ensure that all surface waters are in good chemical and ecological status and groundwater bodies are in good chemical and quantitative status. Programmes and plans to achieve the status required are to be included in river basin management plans. In this context, MS were obliged to design monitoring programmes to provide a comprehensive overview of groundwater chemical and quantitative status that were to be operational (objective) by the end of 2006. This corresponds to the second type of general monitoring. WFD thus provided an overarching approach to water management including European and national prioritization of pollutants.

Recently (in 2014), a European wide and voluntary 'Groundwater Watch List' (GWWL) process was launched by the European Commission in the frame of the Common Implementation Strategy CIS of the WFD. The objective of the "watch list for pollutants of groundwater" is "to increase the availability of monitoring data on substances posing a risk or potential risk to bodies of groundwater" "(Recital 4 of the revised GWD). The GWWL should "facilitate the identification of substances, including emerging pollutants, for which groundwater quality standards or threshold values should be set". The most important output of the GWWL process is the identification of substances present in groundwater based on sufficient monitoring data available. These substances integrate the "List facilitating Annex I and II review process of the GWD" and support the EC review of the GWD by identifying substances or groups of substances that may be considered for future regulation via the GWD (Lapworth et al., 2019). Up to now three data collections on Pharmaceuticals (Amec Foster Wheeler, 2016), PFAS (WFD CIS 2020) and nrM (WFD CIS 2021) have been carried out.

The WFD (article 18) also requires the MS to report data on pesticides to the EU Commission (performed every 6 years - A mid-term review of the implementation of the Programmes of Measures is also carried out). Within this framework, the Commission must publish a report to the European Parliament and to the Council on the implementation of this Directive after each update of the River Basin Management Plans (see https://ec.europa.eu/environment/water/water-framework/impl_reports.htm).

Within the DWD, to ensure a comparable reporting, countries report to European Environment Agency every three years for a limited number of compounds (actually ten active substances namely atrazine, bentazone, bromacil, diuron, isoproturon, MCPA, mecoprop, simazine, S-metolachlor and terbuthylazine, one metabolite (atrazine-desethyl), and total pesticides concentrations including also other national monitored pesticide beside the short list) (Mohaupt et al., 2020).

At EU level, 469 active substances of PPP are currently approved, but the number of national approvals is country-dependent (Figure 1). Thus, only 85 active substances are commonly approved in the four selected countries. More generally, we observe that only 26 active substances are allowed in all the 28 recent MS (Figure 2), whereas 24 active substances have an approval in only one MS. Each MS must therefore consider its specificity in terms of use e.g., fenpicoxamide appears specific to France, metosulam to England (in May 2021).

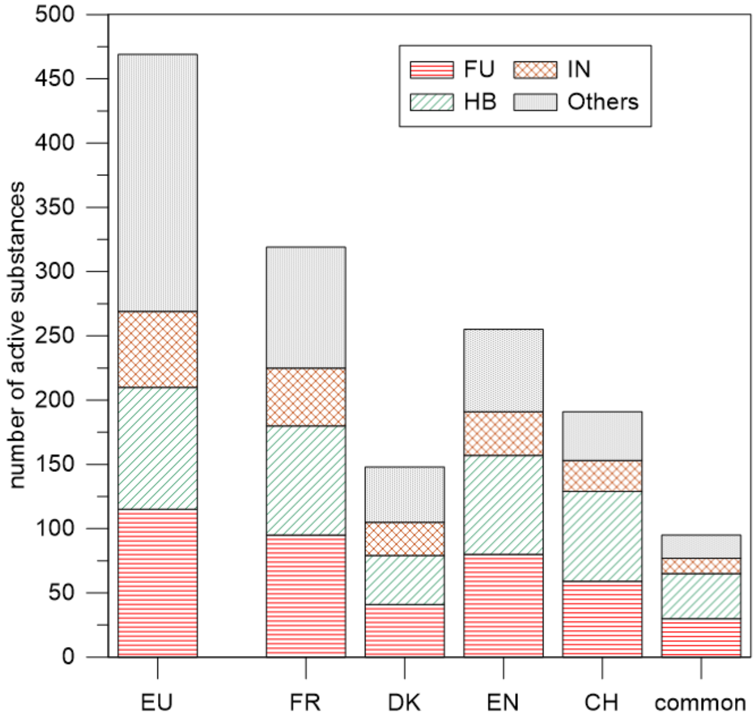

Figure 1. Number of active substances of plant protection products approved at European level (EU) and simultaneously by the countries France (FR), Denmark (DK), England (EN) and Switzerland (CH) added with the number common for these four countries and their respective categories: fungicide only (FU), herbicide only (HB), insecticide only (IN) and others than FU, HB and IN (source: EU Pesticide database, May 2021).

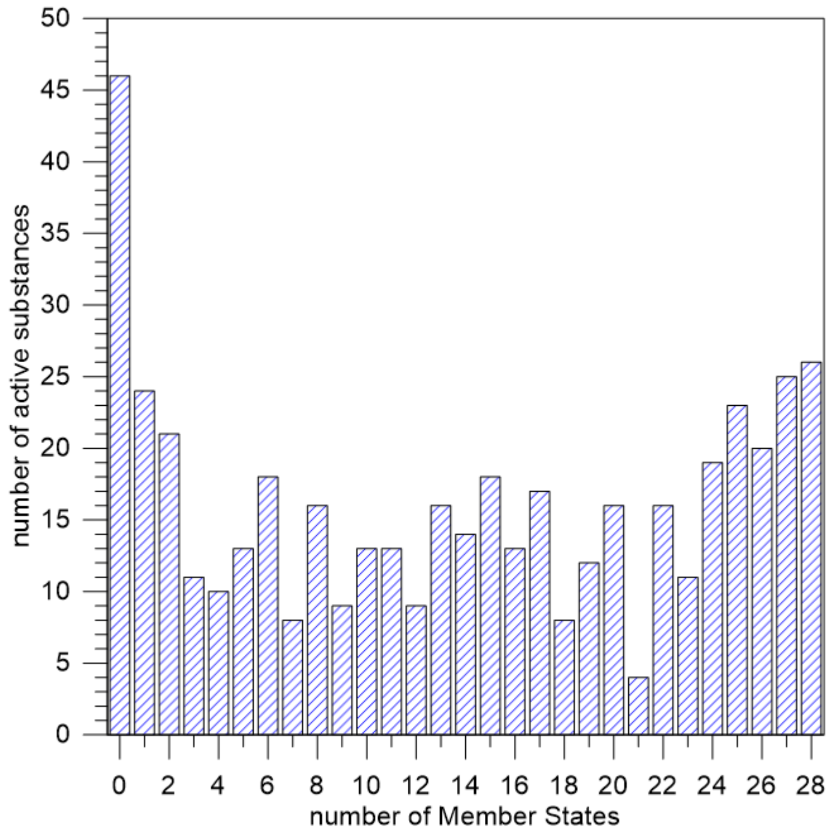

Figure 2. The relationship between the number of active substances of plant protection products being approved at European level (469) and the number of member states having authorised use.

Associated countries have adopted and implemented EU legislation, in a whole, in part or not at all, as Switzerland, within their national legislation on a voluntary basis. EU legislation covering environmental regulation was transposed into UK law when UK left the EU, and new bodies such as UK REACH set up to authorise PPP. It is likely that UK legislation will continue to adhere to EU principles despite leaving the EU. However, how this will be implemented in the long term is a matter at the national level and there is potential for deviation from EU regulations in the medium and long term. For example, in the UK this may affect how groundwater pesticide quality data is collected and on what substances it is collected for in England, Scotland, Wales and Northern Ireland in the future. In Switzerland, these issues are considered by the specific Swiss legislations (e.g. Environment and water protection legislation; Food safety and drinking water legislation), which are updated regularly.

In addition, regulation (EC) No 1107/2009 concerning the placing of PPP on the market, which came into force on 14 June 2011 includes groundwater monitoring as the highest tier option (Tier 4) in the regulatory groundwater assessment of PPP in EU (See Gimsing et al., 2019 for description of registration procedure). In this case targeted monitoring is employed with a different purpose than general monitoring previously described above. Briefly, the registration is based on risk assessment regarding both human and ecosystem health's. The first-tier groundwater assessment is addressed by using FOCUS groundwater models with nine different soil and weather scenarios to represent different parts of Europe. The models are used to simulate the requested pattern of use and predict concentrations in groundwater for the pesticide active substance and its metabolites. If the active substance or one of its metabolites fails the first-tier groundwater risk assessment, higher tier approaches may be possible. In this context, groundwater monitoring performed by applicants is not systematically requested by the national authorities. Nevertheless, registrants have been conducting monitoring studies with currently registered pesticide active substances and their metabolites with an increasing frequency over years (Gimsing et al., 2019). Data are then provided by the PPP producers to regulators to which there is generally no public access. However, in some cases, results are published by the PPP producers (e.g. Pinoxaden and its metabolites – McManus et al., 2021).

4. Results and Discussion

a. Implementation of groundwater monitoring and data collection

National scale

France

In France, the water law of December 16, 1964 (law n° 64-1245) organizes water management at the basin level with the creation of six water agencies in mainland and four offices in overseas territories, and basin committees. As early as the middle of the 90's, the will to structure a national database appeared (see supplementary material S1 for details). Thus, ADES a national open-access database on groundwater, was created. This base contains data from 314 networks (i.e. wells and/or springs), mainly sanitary and environmental monitoring networks, covering both quantitative (groundwater levels) and qualitative aspects. To date, it contains over 102 million water analyses from about 77,000 quality observation points (vs. 4,900 for groundwater level monitoring).

To answer the WFD and GWD objectives, existing networks were adapted from 2007 to 2009 to ensure a wide and patrimonial vision of groundwater quality leading to an increase of the number of monitored wells (~2 400) distributed on the 575 (on 645) Groundwater bodies – GWBs) delineated and monitored and analyses (see for example atrazine at national scale, Baran et al., 2021). Despite the existence of a core list established at national level (Act 2015, JORF 2015), monitored compounds varied across the country, several water agencies managing the monitoring.

With respect to drinking water, the French Public Health Code specifies the conditions for verifying the conformity of water to quality standards (sanitary surveillance). A control is carried out by a laboratory approved by the Ministry of Health at regional or departmental level (eighteen regional agencies of health).

In addition, drinking water producers carry out self-controls; unfortunately, these data are not necessarily shared and are generally poorly stored. Each producer of data uploaded in ADES is responsible of its quality.

Denmark

In Denmark, the national groundwater monitoring programme (GRUMO), was initiated in 1988 (see Supporting material S1 for more historic information). GRUMO's aim was to monitor the effect of the Danish Environmental legislation launched in 1987 on general agricultural regulations in relation to the nutrient load (the phosphorus and nitrate load) of the aquatic environment wastewater plants and secondly to ensure the supply of good quality drinking water to the population. GRUMO was hence designed to provide information on the quality of the groundwater in selected catchments estimated to be representative for Denmark. The monitoring has since been adapted continuously based on improved knowledge and varying administrative needs, including the fulfilment of the reporting obligations under the coming EU directives as the Nitrates directive 1991 (91/676/EEC), which is yearly. When deciding which compounds were to be analysed in GRUMO, pesticides were included already in 1990. As a consequence of the GRUMO results, also waterworks were from 1996 obligated to monitor both waters directly sampled from water works wells (groundwater) and the water tap (drinking water) for pesticides. The list of compounds to be analysed in GRUMO is adjusted at least every 6th year to account for environmental political priorities and legislation. If needed, screening studies under GRUMO are organized annually.

Danish drinking water is solely based on almost untreated groundwater (only aeration and filtration were permitted following a decision by the Danish parliament). This quality is highly valued by the citizens of Denmark, and thus the increased number of detections of pesticides and their degradation products in the groundwater collected within the framework of GRUMO posed a strong wish to determine the source/cause for these detections. Did the compounds originate from agricultural practices (diffuse sources), point sources or accidental spills? To answer this question, the Geological Survey of Denmark and Greenland, GEUS, together with Aarhus University came up with the idea to setup up an early warning monitoring system to monitor at six fields, representative of Danish conditions as regards soil types and climate, whether pesticides being applied on agricultural fields in accordance with regulation and the way of farmers, would cause unacceptable leaching of pesticides and/or selected metabolites.

In 1998, the Danish Parliament provided funding until the end of 2001 for the establishment and operation of the Danish Pesticide Leaching Assessment Program (PLAP; http://pesticidvarsling.dk/?lang=en) including five agricultural fields (both sandy and loamy soils) being management according to regulation though always applying the maximum allowed dose of pesticides, when testing the coherent potential leaching. The two main objectives of the PLAP-system are hence to: i) evaluate if approved pesticides and/or their degradation products leach to the groundwater in concentrations above the permitted limit and ii) prepare and inform about the scientific foundation for optimising the Danish authorities' approval and regulation procedures for pesticides based on the collected monitoring data. The PLAP is still ongoing, delivering yearly reports documenting the results (see http://pesticidvarsling.dk/?lang=en), including six fields, and managed headed by the Geological Survey of Denmark and Greenland (GEUS) in close cooperation with the Department of Agroecology (AGRO) at Aarhus University, as sub supplier, the Department of Bioscience (BIOS) at Aarhus University and the project owner the Danish Environmental Protection Agency (EPA).

The same year of the initiation of the PLAP in Denmark, the DWD came into force followed by the WFD and later GWD. Each of these directives gave rise to a changed monitoring strategy within GRUMO, which has become more distributed and resulted in increased surveillance. To date, the monitoring concerns 689 GWBs on the 2,050 delineated (Thorling et al., 2021).

While pesticides are authorised for use within the EU, it is crucial for Denmark's drinking water quality to evaluate the knowledge acquired by the European Food Safety Authority (EFSA) if there is even the smallest indication of a leaching risk of pesticides and/or their degradation products (Rosenbom et al., 2015). This knowledge is applied in the yearly selection of compounds to be monitored in PLAP. If a metabolite or a pesticide appears in high concentrations in groundwater collected from underneath the PLAP-fields, this knowledge is included when updating the list of compounds to be monitored in GRUMO and the result of the national monitoring will finally appear in the Jupiter database (see Supplementary material).

England

Overall, around 30% of drinking water in England is from groundwater, this figure is much higher for parts of southern England where it is closer to 100%. In the United Kingdom, a number of pieces of legislation and associated regulatory tools have sought to directly or indirectly protect groundwater from pesticide (and other) pollution (see supplementary material Table S1). Whilst the UK was a member of the European Union, the WFD and GWD were the overarching regulatory drivers for groundwater monitoring. Although the UK has now left the European Union, the devolved nations will continue to adhere to the principles contained within these directives. This is reflected in the recent UK Environment Bill (UK Government, 2020a), the EU Withdrawal Agreement Act 2020 (UK Government, 2020b), the UK Government's 25-year environment plan (UK Government, 2018) and domestic legislation that (directly and indirectly) requires groundwater protection. The responsibility for monitoring pesticides in groundwater bodies, reporting on status and trends and making this information available sits with the devolved organisations within each country, *i.e.* the Environment Agency in England.

The delineation of groundwater management units (i.e. GWBs) for the purpose of groundwater-quality monitoring and reporting is based on the knowledge acquired from development of a robust hydrogeological conceptual model of the given unit. The conceptual model informs the design of a monitoring network that is proportional to nature and scale of pollution risk. Various guidance documents set out recommendations for developing conceptual models (UKTAG, 2007, EC, 2007) as well the Environment Agency's Operational Instruction 924_08. The Environment Agency's designation of GWBs has followed this conceptual model approach and currently identifies 272 GWBs across England.

England's National Groundwater Quality Monitoring Network (GWQMN) currently has around 2,500 wells that are monitored, with a minority of these being water company owned sites. The current monitoring network is greatly dependent on third-party owned sites. These include public water supply sites, licensed industrial abstractions and unlicensed private abstractions. In relation to pesticides the purpose of the GWQNM is to:

- assist in characterisation of groundwater bodies and risk assessment, including natural quality (baseline) assessment and detection of pollutants;
- establish the chemical status of groundwater bodies and identify anthropogenically induced trends in pollutant concentrations;
- assist in the design of programmes of measures to protect groundwater from deterioration and/or restore to good status;
- evaluate the effectiveness of programmes of measures including trend reversal.

The GWQMN in England, in terms of the number of sites, analytical capabilities and approach, has evolved with time and was very recently (early 2021) the subject of a periodic review to assess current capabilities against current objectives and future drivers and requirements.

England's groundwater quality data visibility has greatly improved in recent years, and groundwater quality monitoring data is regularly uploaded to the NGWQM database and there is web access to water quality data including pesticides and metabolites in waters (https://environment.data.gov.uk/water-quality/view/landing). Water company data can also be obtained, but this requires a separate application, and is not publicly available in the same way due to issues of confidentiality/security. Devolved nations publish status reports on a regular basis, which includes information on pesticide occurrence in groundwater.

Switzerland

Since 2002 the Swiss NAQUA National Groundwater Monitoring provides a nation-wide picture of the situation and evolution of the groundwater resources in terms of both quality and quantity (FOEN/BAFU, 2019). The results including those for pesticides and their metabolites are summarised and made available annually on the website of the Federal Office for the Environment FOEN (Link: Pesticides in groundwater (admin.ch)) and regularly published in national reports (FOEN/BAFU, 2019). The data of the Swiss surface water and groundwater monitoring are stored and managed in a centralised water database at FOEN.

The joint federal-cantonal monitoring programme NAQUA records the state of and changes in the groundwater resources at more than 600 monitoring sites in Switzerland. The natural conditions and the impact of human activity on the typical aquifers of Switzerland are monitored.

The purpose of the National Groundwater Monitoring is to:

- document the situation and development of groundwater quality and quantity at national level;
- detect the occurrence of problematic substances at an early stage and to systematically follow up any undesirable developments;
- check the effectiveness of protective measures already adopted and identify the need for further measures;
- characterise and classify the most important groundwater resources in Switzerland.

NAQUA forms the basis for nationally coordinated protection of groundwater as a natural resource in Switzerland and ultimately helps to protect the public from harmful substances. As Switzerland collaborates closely with the EU on environmental matters, the collected data are reported to different organisms as the European Environment Agency as a member or on a voluntary base (e.g. IGRAC, IAEA).

The Swiss legislation requires the federal government to collect data on environmental pollution (Constitution Art. 65, Environmental Protection Act, Art. 44), water quality and hydrologic conditions in Switzerland (Water Protection Act (WPA) Art. 57) and to inform the public of the results (Environmental Protection Act Art. 10e, WPA Art. 50 & Art. 57). The NAQUA National Groundwater Monitoring carries out these federal functions in relation to groundwater.

According to Art. 58 of the WPA, the cantons shall carry out any further surveys which may be necessary for the enforcement of this Act. The cantons shall furthermore establish an inventory of water supply installations and groundwater resources on their territory. The inventory shall be available to the public unless the interests of national defence require secrecy.

According to Art. 6 of Federal Act on Freedom of Information in the Administration (Freedom of Information Act) "any person has the right to inspect official documents and to obtain information about the content of official documents." Exceptions apply.

Comparison across the four countries and European scale

For these four countries, databases, generally created long years ago, ensure storage of raw groundwater quality monitoring data mainly collected in the framework of GWD and DWD. National portals provide access to data from other networks. In contrast, data provided by products applicants is typically restricted to national regulatory agencies . Here Denmark via the presence of PLAP are less sensitive to this lack of access regarding the national regulation of PPPs with its links to the GWD and DWD.

Data accessibility via national portals is free or via request, depending on the country. The information are provided in relation with other metadata: information on the geological context, the aquifer and/or the groundwater body, characteristics of the well tapping the sampled water etc.

At European scale, IPCheM Portal (https://ipchem.jrc.ec.europa.eu/) is the European Commission's reference access point for chemical monitoring in various media (environmental, human bio-monitoring, food and feed, products and indoor air) allowing searching, accessing and retrieving chemical occurrence data collected and managed in the EU. The platform has been developed to fill the knowledge gap on chemical exposure and its burdens on health and the environment. Several types of database exist including e.g. Waterbase, which is the generic name given to the EEA's databases on the status and quality of Europe's rivers, lakes, groundwater bodies and transitional, coastal and marine waters, on the quantity of Europe's water resources, and on the emissions to surface waters from point and diffuse sources of pollution. Its creation is based on the INSPIRE Directive 2007/2/EC which aims to create a European Union spatial data infrastructure for the purposes of EU environmental policies and policies or activities which may have an impact on the environment. According to the data type (notably raw data versus aggregated data), data access could be restricted, public or limited to the owner. In some cases, it is therefore possible to find raw and more detailed information at national level than in the European database.

b. Monitored pesticide substances and occurrence in groundwater

National scale

France

In France, a national regulatory decree (under revision) sets the guidelines (minimum required) for groundwater monitoring in terms of frequency of measurements, number of points per km^2 and lists of parameters to be measured, a "core list" (Act 2015 published in JORF, 2015 and its modified version of 2018, JORF 2018). Three types of monitoring's are defined: i) regular (every year – 2 times /year for unconfined aquifers - all points of the networks), ii) photographic analysis (once per WFD cycle – all points), and iii) complementary analysis (quarter of the sites of the monitoring program). The list of parameters is monitoring type dependent. A distinction is also made between mainland and the overseas territories. Of the 227 parameters included as a minimum requirement, 115 are active substances of PPP, 21 metabolites and 2 compounds being both active substance and metabolite (Figure 3 – supplementary materiel Table 2). Half of the 138 compounds (69) originate from a currently authorised pesticide, the other half (69) can be related to former uses. Some water agencies carry out a much more exhaustive monitoring (up to 651 molecules for France, 106-612 per river basin depending on the water agency – status report of 2013) in order to cover for instance specific uses (e.g. crops with limited geographical extension). While this more comprehensive research is important to get a more complete picture of groundwater quality, it makes analysis of the data at the national level more challenging.

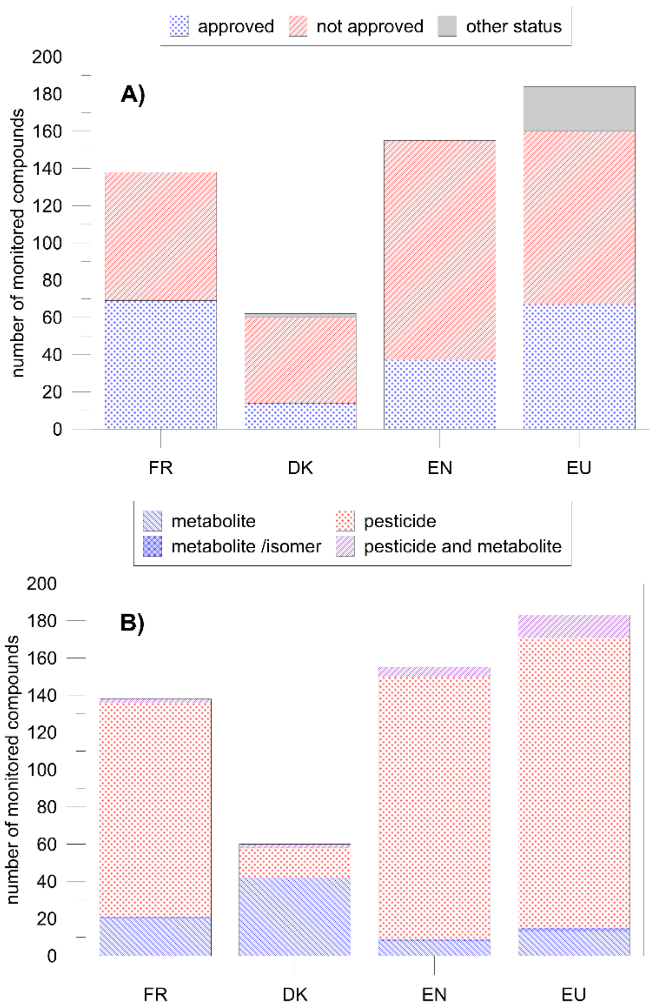

Figure 3. Distribution of substances monitored (minimum required) within the WFD by **A)** status (compounds are or originated from an approved active substance or not approved active substance according to national status in May 2021 or not known) and **B)** distinguishing metabolite and pesticide by the countries France (FR), Denmark (DK), England (EN) and at European level (EU – data from Mohaupt and al., 2020)

With respect to drinking water, the minimum frequency of sampling and analyses is determined by the volume of water distributed or produced each day within a supply zone (~ 32,000 wells tapping groundwater). Among the 54 parameters, the generic term "pesticides and (relevant) metabolites" is used, and it is recommended that monitoring should be adapted to regional context (Direction Générale de la Santé, 2020). The Ministry of Health states given the number of authorized (or formerly authorized) pesticides, it is necessary to target the analysis for pesticides, according to their potential occurrence in water and the risks for human health and adapted based on local use. DWD monitoring is consequently heterogeneous between regions.

Identifying "only those pesticides which are likely to be present in a given supply" is challenging due to the limited availability of data on pesticides used in specific areas relevant to a given water source (Kotal et al., 2021). This issue is obviously not unique to France. To establish their monitoring program, French regional health agencies can use SIRIS-Pesticides (Le Gall et al., 2007), a decision support tool that classifies active substances according to their potential to reach surface water and groundwater in relation to local uses when known. Two weaknesses of this tool are well known: pesticides withdrawn from the market and metabolites are not considered.

The latest national report (ADES data of 2018, Ministère de la transition écologique, 2020) highlights that 46% of 760 analysed substances were quantified at least once: 48% of them are authorized, 5% are degradation products (metabolites) of authorized substances, 37% are banned substances and 9% are metabolites of banned substances. Almost 80% of the 2,340 measuring points of the groundwater quality monitoring networks were found to have at least one pesticide detected. It should be noted that this assessment includes all the compounds analysed and not only those of the core list established within WFD, which for example does not include the metabolites of metazachlor and dimetachlor. The metabolites of atrazine and dimetachlor, present in 55% of the monitoring sites, are the most frequently quantified compounds. Among the active substances authorized in 2020, the metabolites of metolachlor, metazachlor and dimetachlor, as well as the parent substances bentazone, chlortoluron or glyphosate, are among the most quantified compounds in the country. Despite their ban or market withdrawal for almost two decades, some compounds (atrazine, sodium chlorate, simazine, alachlor, oxadixyl, chloridazon), as parent substance or as metabolites, are among the most quantified compounds in the country. The French West Indies (oversea territory) are affected by historical pollution by chlordecone, an insecticide historically used on bananas banned since 1993.

Denmark

In the GRUMO, the current list of compounds to be monitored for water chemistry regarding pesticides excluding screening and verification (https://www.retsinformation.dk/eli/lta/2021/1110 and https://mst.dk/media/210472/grundvandsbilag-pr-febr-2021.pdf in Danish) encompasses 63 compounds of which 16 are pesticides, 43 are metabolites, two are both pesticide and metabolite, and two are synthesis impurities (Figure 3 - supplementary materiel Table 2). Only 15 compounds of the 61 compounds (not counting the two impurities) are or originate from a currently authorised pesticide, whereas 46 of the 60 compounds can be related to former uses. The outcome of the monitoring, which is published in Thorling et al. (2021), reveals that the five most detected compounds in 2019 in the water from (i) GRUMO's wells are:

- DPC (desphenylchloridazon; 25.7% with detections and 12.4% exceeding 0.1 µg/L),
- N,N-DMS (N,N-dimethylsulfamid; 23.8% with detections and 3.2% exceeding 0.1 µg/L),
- 1,2,4-triazole (16.1% with detections and 2.9% exceeding 0.1 µg/L),
- MDPC (methyldesphenylchloridazon; 15.1% with detections and 4.4% exceeding 0.1 µg/L)
- BAM (2,6-dichlorobenzamide; 11.1% with detections and 2.8% exceeding 0.1 µg/L)

and (ii) water works wells are:

- N,N-DMS (N,N-dimethylsulfamid; 28.6% with detections and 7.4% exceeding 0.1 µg/L),
- DPC (desphenylchloridazon; 22.5% with detections and 6.7% exceeding 0.1 µg/L),
- BAM (2,6-dichlorobenzamide; 15.8% with detections and 1.5% exceeding 0.1 µg/L),
- dimethachlor ESA (9.0% with detections and 2.1% exceeding 0.1 µg/L)
- MDPC (methyldesphenylchloridazon; 5.0% with detections and 0.8% exceeding 0.1 µg/L).

The list of compounds is seen as dynamic where compounds seldom or never found are removed, and new compounds added.

Eighteen of the 62 compounds have previously been tested in PLAP (Rosenbom et al., 2021) where only seven are either an authorised pesticide (bentazone, glyphosate and MCPA) or a metabolite of an authorised pesticide (1,2,4-triazole, AMPA, metamitron-desamino and N,N-DMS). Among the last 11 compounds included in the PLAP, six degradation products (diketo-metribuzin, desamino-metribuzin, PPU IN70941, PPU-desamino IN70942, CGA62826 and CGA108906) of three pesticides applied to potato plants (metribuzin, rimsulfuron and metalaxyl-M) were included in GRUMO caused by their long-term leaching being documented in PLAP.

With the drinking water in Denmark solely being based on largely untreated groundwater, PLAP has not been the only action initiated by the Danish Government to protect the quality of the groundwater. In 2019, "Vandpanelet" (The Water Panel) was commissioned to act upon threats against the groundwater and hereby the drinking water and coordinate actions against such threats towards the water supply. Two surveys of groundwater quality were conducted in 2019 (415 compounds included) and 2020 (23 compounds detected in the 2019 screening and 76 new compounds; https://mst.dk/media/211541/fagligt-notat-om-resultater-af-massescreening-2020.pdf). The Water panel agreed with the Danish EPA's on the inclusion of six compounds (the pesticide monuron, CGA369873 and CGA373464 (metabolites of dimethachlor), TFMP (metabolite of fluazifop-P-butyl), tsulfinylacetic acid (metabolite of acetochlor) and TFA (metabolite of many pesticides containing a CF3 group) in the pesticide list presented in Appendix 2 of Executive Order on Drinking Water (https://www.retsinformation.dk/eli/lta/2021/1110) and GRUMO (https://www.ft.dk/samling/20201/almdel/MOF/bilag/470/2368151/index.htm). This means that from 1 July 2021, the water supplies must control the drinking water for those six compounds as well.

England

A number of analytical suites which cover 155 pesticide and metabolite compounds (141 pesticides, 9 metabolites and 5 being both pesticide and metabolite) are used for quantifying pesticides (1-organo-nitrogen pesticides, 2-organo-chloride pesticides, 3-acid pesticides and 4-uron/urocarb pesticides, 5-pyrethroids, 6- Discretionary pesticides and other organics (e.g. tralkoxydim, flutriafol and propiconazole). Only 37 compounds are or originate from a currently authorised pesticide, whereas 118 compounds can be related to former uses (Figure 3 – supplementary materiel Table 2).

A dedicated suite of pesticide compounds (n=42) were used as part of WFD reporting. Accredited data collected by the 6 pesticide suites is supplemented by broad screening scan methods (GCMS and LCMS) which also contain pesticide and metabolites. Presently around 40% of the GWQMN sites are sampled and analysed on an annual basis for the dedicated pesticide suites (1-5). Repeat sampling is undertaken to different extents (typically annual or quarterly) depending on the vulnerability of the particular groundwater body, its current status in terms of pesticide pollution and the pesticide occurrence trends.

In 2019 of the 271 groundwater drinking water protection areas (DWPA) in England, 7 (in the Thames and Anglian river basin districts) were classified as of poor chemical status due to pesticide pollution. Non statutory safeguard zones (SGZs) were established around 31 (11%) groundwater DWPA's due to concerns over pesticide pollution (EAE, 2019). Historical pesticide monitoring data collected between 1998-2005 shows the frequency of detections for the 15 most commonly detected pesticides in groundwater exceeding 0.1 µg/L in the GWQMN to be less than 11% and more typically less than 1% for individual pesticides (DERFA, 2010). In 2005 atrazine was still the second most frequently detected pesticide (behind bentazone) but detections exceeding 0.1 µg/L were low (1.3%) and had fallen significantly since 1998 which had a figure of 10.3 % exceedances. Contaminated groundwater can take many decades to recover, particularly where unsaturated zones are deep, such as within parts of the Chalk aquifers of Southern England, even when the inputs of the chemicals cease (e.g. Lapworth and Gooddy 2006). For example, the pesticides atrazine and simazine were both withdrawn from use in the UK in 2003, but they continue to be detected in groundwater due to very slow degradation rates (EAE, 2019). Recent data (EAE, 2019), show that the most frequently detected pesticides in groundwater are bentazone (2.7 % SGZs), metaldehyde (1.5 % SGZs) atrazine (1% SGZs) and mecoprop-P (<1% SGZs), which were all (apart from atrazine) approved for use at the time.

Lapworth et al., (2018) summarises results from groundwater surveillance monitoring in England (n=7473, 2009-2017) using targeted semi-quantitative scanning methods. Using GC-MS methods the most frequently detected pesticides and metabolites were atrazine (9.4 % of samples), desethyl atrazine (6.4 %), simazine (4.7 %), emphasising the issue of legacy contamination from banned pesticides, followed by BAM (metabolite of dichlobenil, 2.8 %), metaldehyde (2.5 %) and oxadixyl (2 %). In contrast, from a smaller sample (n=249) the more sensitive LCMS method showed that pesticides dominated the top 50 detected compounds with detection frequencies >60 % for the following compounds, deisopropylatrazine > desethylatrazine > simazine > atrazine. Notable detection frequencies were also reported for diuron (50 %), clothianidin (33 %), bentazone (28 %), monuron (25%) and isoproturon (22%).

Switzerland

Residues of PPP, i.e. their active substances as well as their degradation products, occur at over half of the groundwater monitoring sites across Switzerland. In intensive arable farming areas, residues of PPP are detected at over 90% of the monitoring sites. According to the Waters Protection Ordinance (WPO), groundwater should not contain persistent synthetic substances in general. For groundwater that is used for drinking water or is intended as such, there is also a limit value ('numerical requirement') of 0.1 micrograms per litre (µg/L) for active substances of pesticides. In addition, the groundwater – after basic treatment, where appropriate – must meet the requirements of legislation on foodstuffs. This legislation also prescribes a maximum value of 0.1 µg/L for metabolites of pesticides classified as relevant.

In recent years, the concentrations of active substances of PPP have exceeded the limit value (0.1 µg/L) at around 2% of the NAQUA monitoring sites. The three active substances of PPP that exceeded the limit value at multiple monitoring sites every year between 2014 and 2019 are bentazone, metolachlor and atrazine. After the approval of atrazine was revoked in 2007, the concentrations of this compound in groundwater are by now gradually decreasing.

Metabolites have also been widely detected in elevated concentrations. The concentrations of various metabolites of metolachlor have risen in recent years. In 2019, four metabolites of this herbicide (metolachlor NOA 413173, metolachlor-ESA, metolachlor-OXA, metolachlor CGA 368208) were found in groundwater in concentrations above 0.1 µg/L. Metabolites of the beet herbicide chloridazon are also widespread in groundwater. In particular, the metabolite DPC is widely found in groundwater in concentrations of more than 0.1 µg/L. Furthermore, metabolites of the fungicide chlorothalonil were detected for the first time in groundwater in Switzerland during a NAQUA pilot study in 2017. The metabolites chlorothalonil R471811 and/or chlorothalonil R417888 exceed at more than 50% of the monitoring sites 0.1 µg/L in groundwater on the Swiss Plateau.

Comparison across the four countries

In the four countries, analysis is performed by a national laboratory or several public or private laboratories. In all cases, quality assurance is taken into account, based in particular on the directive EC 2009/90, to guarantee the reliability of the data (see supplementary material S3).

In France and Denmark, monitoring programmes for WFD are constrained by the duration of public procurements i.e. the list cannot be revised every year in relation for example with new pesticide approvals. In France, the implementation by several agencies leads to heterogeneity in monitoring for both GWD and DWD even if core lists are defined. By contrast, in Switzerland and England, the list is revised regularly if necessary. We can also mention that for the four countries, the delay between the measurement of a pesticide and the publication of a synthesis report driven by different bodies depending on water governance is about two years (collecting, storing, processing and using the data). In all the four countries, the lists of monitored compounds are different with the DWD targeting the compounds prone to be present and the WFD wanting to have a broader view. Even if the prioritization criteria are different, the existence of information on uses is essential to establish these lists. Although data on PPP sales by country may be available, even on a more regional scale, this scale is not necessarily suitable for defining targeted monitoring at the catchment/well level. On the other hand, farmers in EU countriesare obliged to register their practices (PPP -Art. 67 of regulation EC N°1107/2009 and biocides). These data are not directly accessible but should be available (for at least 3 years) to the competent authority on request. Third parties such as the drinking water industry, retailers or residents, may request access to this information by addressing the competent authority. To our knowledge, this request is not generally made.

For the four countries, among the list of pesticides, the compounds searched for are mainly active substances or metabolites of PPPs and few are biocides. Less environmental data, less well characterised uses could explain the low monitoring of biocides.Through expanded monitoring, it appears that groundwater contamination is due to presence of legacy pesticides and their metabolites as well as pesticides currently in use and their metabolites. However, the number of metabolites included in regular monitoring remains low and their detection in groundwater can be linked to extended or more specific campaigns. Atrazine is probably the best-known case of legacy groundwater contamination in Europe, but it is not unique. Persistence of active substance and/or metabolites in GW several years after the last application can be due to several factors (Baran et al., 2021), including a long-term release of the substance from soil and/or a long residence time (i.e. low rate of replenishment). For the latter, knowledge on aquifer hydrodynamic is needed but in many cases, remains limited. More generally metabolites are seldom monitored in the existing regulatory contexts. Yet, data is available on their risk of leaching to groundwater through scientific reports of the EFSA or the European Union publicly available for active substances (re)approved recently. In this respect, Denmark stands out with 42 metabolites monitored, selected based on the above-mentioned documents, versus 21 for France (core list) and 8 for England (Figure 3).

European scale

The Waterbase – Water quality database includes a large volume of concentration measurement data reported by countries to the European Environment Agency. Data include observations on sampling dates (so called 'disaggregated'), data and aggregated data (including yearly mean, minimum, maximum and Limit of Quantification of pesticide concentrations). Therefore, there are many data sources for pesticides, but the availability of comparable data across Europe is rather limited and except for triazine metabolites, monitoring of metabolites is scarce (Mohaupt et al., 2020). Within the WFD, the data on 184 distinct pesticides were extracted from Waterbase (Mohaupt et al., 2020 – data 2007-2017), covering a total of 16,886 groundwater monitoring sites in 26 countries. According to the authors, 156 compounds are pesticides, 12 are both pesticide and metabolite, 13 are metabolites and three are "others" (Figure 3 – supplementary material Table 2). Only 67 of the 187 compounds are or originate from a currently authorised pesticide, whereas 93 can be related to former uses and 24 not having information on their status. The comparison with FR, DK and EN shows that 353 compounds are considered but that only 11 are present in all four lists (Supplementary material Table 2). The European report does not highlight the compound identified in each country with high occurrence and in particular metabolites mentioned in one or more of the four countries (e.g. metabolites of metolachlor, dimethachlor, chlorothalonil and chloridazon).

To answer the issue of non-relevant metabolites on a European scale, a study on nrM as defined within the EC n°1107/2009 has very recently been carried out in the frame of the CIS GWD Groundwater Watch list (GWWL) activity (WFD GWD 2021). MS and AC were asked to provide available monitoring data on 53 selected nrM in groundwater across Europe. 29 MS/AC responded and 17 countries provided groundwater data on the nrM compounds in the related questionnaire. nrM were widely detected in European groundwater above limits of quantification. The percentage of detections in groundwater were highest for DPC (31.7%), Metolachlor ESA (30.0%), N,N-DMS (24.4%), MDPC (23.7%), Metazachlor ESA (21.0%) and Dimethachlor CGA 369873 (20.7%).

Regarding drinking water, in 2015 a draft list with 21 DWD pesticides and metabolites of concern has been established by compiling voluntary contributions from nine MS sent to European Commission DG Environment. From one contribution including around 700 compounds, only the 25 highest ranked compounds with over 50,000 analyses have been considered. Compounds indicated by at least four

MS have been included in a short list (an extended list has also been established including compounds indicated by less than four MS). The six metabolites mentioned are: AMPA (Aminomethylphosphonic acid), desethyl-atrazine, desethyl-terbuthylazine, desisopropylatrazine, Metazachlor ESA, MDPC and 15 active substances: atrazine, bentazone, chloridazon, diuron, glyphosate, hexazinone, isoproturon, MCPA, mecoprop/mecoprop-P, metalaxyl/metalaxyl-M, metamitron, metazachlor, metribuzine, simazine, terbuthylazine.

c. Early warning / surveillance prospective and contributions from research

National scale

France

Regarding drinking water production there is an ongoing campaign performed at national scale on 48 pesticides, and three compounds being both metabolite and pesticide as well as explosives and others compounds (Direction Générale de la Santé, 2020a). This campaign concerns ~ 300 sampling points including surface and groundwater, raw and treated and distributed water/site. If most of the selected compounds have already been analysed, others are not usually monitored and will provide new information on their occurrence (e.g. on metabolites M2 and M3 of pinoxaden or pethoxamide-MET100, MEYT101 and MET-42).

As part of WFD activities**,** the French Ministry of Ecology and the French National Agency for Water and Aquatic Environments have initiated in 2010 a national reconnaissance study of 411 emerging (or poorly monitored) contaminants of various possible origins (e.g., pharmaceutical products, industrial compounds, personal care products and 103 active substances or metabolites of pesticides). The results (but also results obtained in the overseas territories, not published), highlighted the presence of parent molecules that, in many cases, are no longer on the market and their metabolites. These results were taken into account during the revision of the act (2015; 18 active substances or metabolites linked with legacy or current uses have been added in the mandatory surveillance.

Later, according to WFD, in 2016, France set up the “prospective surveillance network” managed by French ministry of Ecology and French office of biodiversity (Staub et al., 2019). This surveillance programme aims to ensure “the efficient and effective design of the future monitoring programme”. Although focused on contaminants of emerging concern, this approach will also increase knowledge on pesticides and metabolites. It includes several components such as the implementation of explanatory campaigns (at this stage surface and coastal waters / in preparation groundwater) or the validation of innovative tools for monitoring (bioassays, passive sampling, etc.). The use of high-resolution mass spectrometry (HRMS) was recently applied at national scale for surface waters complementary to conventional quantitative analyses. Indeed, HRMS enables a comprehensive screening whereas triple quadrupole analyser allows only a pre-define list of molecules to be analysed.

Denmark

Since the initiation of PLAP in 1999 in Denmark, this early warning system has documented and warned the Danish EPA about pesticides and/or their metabolites being prone to leaching to the groundwater after the pesticide has been applied to a well-characterised agricultural field included in PLAP in accordance with regulation.

In general, compounds (pesticides and/or their metabolites) are selected for being monitored in PLAP following three categories: (i) newly registered PPP that are assessed to have a high application potential in amount per application or area wise. The purpose of this is to provide an early warning regarding compounds leaching to the groundwater; (ii) Old PPP that have already been applied in high quantities in large parts of the agricultural land through time; iii) approved pesticides, which in connection with first approval, reapproval or new knowledge obtain are assessed to have a high leachability of the pesticide itself or it degradation products. For the category i and iii, the establishment of a method of analysis is often required, which is conducted based on analytical standards provided by the producer of the pesticide included for test in PLAP. Like in France, possibilities of improving the identification of leacher with HRMS is evaluated.

As early warning systems, the PLAP fields (sandy soils having a short distance to the 1-2 m fluctuating groundwater or loamy soils being tile drained in approximately one meter depth and having 3-5 m of fluctuating groundwater) were selected to reduce the vertical and lateral transport of the compounds within the saturated and unsaturated zones.

The value of PLAP can be exemplified by the action taken regarding metalaxyl-M. Metalaxyl-M and its two metabolites CGA 62826 and CGA 108906 were included in PLAP as the EU-evaluation of metalaxyl-M from 2002 presented results, revealing pronounced leaching of the two metabolites. When the national approval of metalaxyl-M in Denmark occurred in 2007, the Danish EPA was aware of the metabolites and requested their inclusion as part of monitoring. At one of the PLAP fields, CGA 108906 was detected in groundwater samples 6 ½ years after the spraying in July 2010, highest concentration being 0.34 µg/L. After the first years of detections in PLAP, metalaxyl-M was banned in Denmark in December 2013. In 2014, it was included in both the revised analysis program of GRUMO and in the Danish Waterworks quality control of groundwater used for drinking water purposes and detected (Thorling et al., 2021) not only in sandy agricultural areas where potatoes are grown but also loamy agricultural areas, which could be caused by metalaxyl-M also being applied as seed dressing. Further, results from PLAP were sent to EFSA to be considered in the re-evaluation of metalaxyl-M in EU.

England

In England there is a twin approach of using quantitative analytical suites with limited numbers of compounds and HRMS screening techniques for surveillance. Dedicated pesticide monitoring suites are used for regulatory reporting purposes, historically for WFD reporting and to assess river basin status and trends, using accredited and dedicated quantitative suites (see earlier section 3.2). This is informed and supplemented by surveillance monitoring for organic compounds in groundwater (n=1526), including for pesticides and metabolites (n=796), using high resolution broad screening GCMS and LCMS methods (e.g. Lapworth et al., 2015; 2018, Manamsa et al., 2016). For these campaigns, groundwater samples were collected by the Environment Agency England and analysed by the NLS using a target-based, multi-residue GCMS methods, which are semi-quantitative.

More recently, LC-MS-MS-time of flight methods with vastly improved detection limits (typically an order of magnitude lower) compared to GCMS methods have been used for surveillance purposes (Lapworth et al., 2018). GC x GC TOF-MS methods are also being developed which extend detection limits and the range of compounds compared to conventional GCMS methods (e.g. Mohler et al., 2020) and these techniques are also being considered for surveillance monitoring in England. There has been a growing reliance on multi-residue screening techniques, which are semi-quantitative, to undertake surveillance monitoring and the large database of results going back as far as 2009 provides a significant resource for groundwater pesticide and metabolite occurrence data for England. These screening techniques are a flexible and versatile tools and when standards become available for new compounds these can be rapidly added to the existing extensive database of pesticide compounds and they will continue to be an important surveillance tool in the future.

To date there has been a focus on the use of grab samples for surveillance monitoring, passive sampling techniques have not been routinely deployed for groundwater monitoring purposes in England. Surveillance monitoring is used to supplement and inform other monitoring undertaken by other dedicated quantitative methods and for formal reporting. The process of monitoring and reporting national data collected as part of the GWQMN is devolved (England, Wales, Scotland, Northern Ireland), and there are broadly consistent approaches, at least for England and Wales.

Switzerland

In Switzerland, a target screening study covered more than 180 pesticides (active substances, safeners, synergists of PPP only) and approximately 70 metabolites in 2017. A suspect screening approach was also applied with a special focus on pesticide metabolites being most of the time more polar than the parent compound (Kiefer et al., 2019). In this study, 31 groundwater samples (9 springs and 22 abstraction wells regularly monitored within the Swiss National Groundwater Monitoring NAQUA) were sampled. The suspect screening identified with variable degree of confidence, additional 19 metabolites including those of chlorothalonil, dimethachlor, metolachlor, nicosulfuron and terbuthylazine.

Recent field studies concluded furthermore, that the anionic chlorothalonil metabolites R471811 and R417888, frequently detected in Swiss groundwater, do not accumulate in soil due to their very high mobility (Hintze et al., 2021). Therefore, soil and unsaturated zone is frequently not expected to act as long-term source unlike for metabolites of chloridazon. These chloridazon metabolites (Hintze et al., 2020) seem to have a longer residence time in soils and are thus expected to impact groundwater over longer times scale and can also show some retardation in aquifers.

In Switzerland, a common process to prioritize pesticide metabolites for the cantonal and federal monitoring is currently set up. The process will be based on monitoring results, research results (e.g. screening studies), the pesticide substance approval list, and the outcomes of evaluation studies (e.g. groundwater contamination risk score e.g. Korkaric et al., 2022).

Comparison across the four countries

Denmark stands out for its specific site-based monitoring, but all four countries tend to increase the list of molecules searched. For the four countries, actions are implemented for going beyond the regulatory monitoring related to WFD and DWD, in terms of compounds monitored and types of sampling. Thus, broad screening campaigns are undertaken more or less regularly to try to highlight the occurrence of compounds that more readily leach to groundwater, notably metabolites. These campaigns correspond either to *suspect* or non-*targeted* screenings based on HRMS.

Thus, HRMS allows identifying compounds and provides a level of confidence on target and non-target screening based on mass accuracy (Soulier et al., 2016), samples may be raw water, extracts of water or extracts of passive samplers. HRMS is therefore relevant to identify new compounds in groundwater, but it should be remembered that physico-chemical properties range of organic compounds detected or identified with this technique is limited by sample pretreatment, chromatographic or ionization conditions (Reemtsma et al., 2013b; Soulier et al., 2016). HRMS followed by a suspect screening appears also a solution to overcome the lack of analytical standards (not always commercially available notably for metabolites) even if uncertainty on molecule identification remains and can only be overcome by standard injection (Schymanski et al., 2014).

This pitfall can be overcome thanks to the obligation of producers of PPP to make available non-marketed analytical standards for the metabolites of the active molecules they market, provided that the market, if requested, for example if they are needed for official control (Commission Regulation (EU) 284/2013 of 1 March 2013 – section 5). This obligation has been met in the case of specific research projects (Kiefer et al., 2019; Reemtsma et al., 2013 a,b) or specific environmental monitoring projects (PLAP). However limits exist: i) the standard may no longer be available (e.g. “old” dossier), ii) producers of PPP will probably not be able to provide in the long term or for all laboratories and iii) working with only one standard is not completely in line with the French recommendations (and probably also applied in other countries) (COFRAC recommendation based on ISO 17025 regarding the need to prove accuracy of calibration) to perform a cross-analysis of two standard solutions from different suppliers or preparations.

5. Conclusions, Perspectives and Future Outlook

Characterising groundwater contamination by pesticides and their metabolites is paramount to ensure resource protection and mitigate potential effects on human and ecosystems health. The strong regulatory framework in European Union (WFD, GWD, DWD, regulation EC N°1107/2009) facilitates a high level of groundwater quality monitoring, especially for pesticide / active substances (and in particular PPPs - versus biocides) and to a lesser extent, their metabolites. However, with regard to this regulatory framework, two types of monitoring exist: general monitoring and targeted monitoring with different implementations, different objectives and different data dissemination, monitoring data. Thus monitoring data obtained in the case of targeted monitoring (regulation EC N°1107/2009), generally has limited access to regulators.

National networks (i.e. general monitoring) were created or strengthened in the context of the WFD and GWD, leading to a great production of data on groundwater quality. To convert such data into insights on actual and potential exposure combinations at the European scale, is not trivial and demands a vision for future detailed assessment of the status of groundwater with respect to pesticides and their metabolites. This pitfall in assessment of data is in part due to the lack of consistency and strategic coordination between different pieces of legislation e.g. thematic regulations as illustrated by the four countries described here.

Nevertheless, data clearly reveal that groundwater contamination is caused by pesticides (parent compounds) with both past or current uses and their metabolites. Moreover, metabolites of "recently" (re-)approved active substances of PPP, prone to leached to groundwater, are known thanks to EC n°1107/2009 regulation, but they are only rarely monitored. However, at the national level, specific campaigns make it possible to highlight these compounds. The challenge is then to share the information at the European level, this includes difficulties in sharing raw data, variable detection/quantification limits etc.

The impact of pesticide use on groundwater can persist for a very long time because i) in some areas there is a deep unsaturated zone and low renewal rate of the groundwater and ii) the active substances or their metabolites can be stored and released from soils and unsaturated zone over several years or decades. These compounds can also be preferentially, and rapidly, transported to depth of lower degradation than in the plough layer. These aspects must be better taken into account in the PPP regulatory procedures including leaching assessment to the surface and groundwater. The variability in soils and climate within EU calls for a differentiated regulation based on improved knowledge regarding dominant processes controlling the leaching of compounds from the soil surface to the groundwater obtainable via target high-quality early-warning monitoring systems, which addresses the representability of a water sample taking consideration of high-resolution geological models. Today, in accordance with the EC n°1107/2009 regulation, the assessment of the leaching risk of pesticides and metabolites to groundwater are conducted applying nine mostly unvalidated virtual FOCUS groundwater scenarios. Here the lack of field data (Vanderborght et al., 2011) and spatial representation in soil-related parameters (hydraulic, chemical, physical and microbial) (Rosenbom et al., 2014 and 2015) have been obstacles for improvement of the assessment. Adding to this, the scenarios have significant drawbacks such as: i) being one-dimensional, ii) applying climate from 1960-1990, iii) not accounting for fluctuating groundwater table, iv) having limited or no inclusion of preferential flow and transport. With "A Century of Denial: Preferential and Nonequilibrium Water Flow in Soils" by Beven, 2018) and numerous studies suggesting considerable preferential solute transport through soils being the rule more than the exception – this process needs to be addressed in future leaching assessments of PPP to the groundwater (Beven and Germann, 2013; Beven, 2018; Nimmo, 2021; Nimmo et al., 2021). Better knowledge of soil contamination could also be useful, but to date there is no regulatory framework at EU level for this.

To assess the representability of a groundwater sample, detailed hydrogeological knowledge is needed. Today, the hydrogeological understanding of many aquifers / groundwater bodies is limited, therefore hydrogeological knowledge must be strengthened to support and underpin improved conceptualisation and subsequent monitoring. WFD and GWD provide a framework for this that needs to be strengthened. Similarly, the long-term fate and preferential transport of pesticides and their metabolites are poorly documented and are not considered in European pesticide regulations; this point appears as a weak point of current pesticide regulation. Thus, the development, improvement and evaluation of new models and/or scenarios for predicting leaching of pesticides and metabolites, which can be applied in a premarket stage appears necessary.

In the three studied EU/recent EU countries, the implementation of European directives (WFD, GWD and DWD) is managed at different scales (regional or national) by one or several stakeholders. Each country has its own dissemination strategies with freely accessible databases including raw data as opposed to the European database including sometimes only aggregate data. In addition, the above-mentioned directives have different objectives, leading to different monitoring strategies. For instance, DWD determines the list of compounds to be monitored in the context of drinking water production considering that "only pesticides which are likely to be present in a given supply need to be monitored". On the other hand, importantly, drinking water is not the only issue of GWD. Indeed, there are other groundwater dependant water bodies and ecosystems for which the presence of pesticides and their metabolites is significant. A broader remit than just 'drinking water' needs to be considered for monitoring/regulating pesticides regarding groundwater.

Furthermore, whatever the regulatory context, the issue of the effects of mixtures arises even for compounds which might be considered individually to be of low toxicity. Therefore, broad surveillance is justified as a first approach.

However, establishing exhaustive lists of compounds to be monitored remains challenging and should be tackled at different scales (from regional to European levels), considering country-specific uses, for both biocide and PPP. For the latter and, with agriculture being highly variable within EU level, a large panel of national authorisations and uses of active substances exists within EU. Thus, the monitoring needs to address these heterogeneous conditions and cannot be conducted referring to a unique list for EU to get a comprehensive view. A method for establishing country-specific lists could be defined in order to have harmonized practices and to make pesticide monitoring more cost-effective and more reliable.

It is essential that once information is acquired, it is made available using FAIR (Findable, Accessible, Interoperable, Reusable) principles to the various potential users (regulators, scientists, other stakeholders etc.) even if they operate within different regulatory frameworks. Thus, data acquired under WFD or DWD, should be made available as raw data (and not aggregate data) to regulators acting in the context of EC n° 1107/2009 as part of a re-approval of an active substance. Reciprocally, data coming from EC n° 1107/2009 registration should be better taken into account to implement the surveillance within the context of WFD and DWD.

Making data available requires evaluation of its quality, and delimitation of the potential limitations of its use. From an analytical point of view, Directive 2009/90/EC provides a framework that can ensure this. HRMS is being developed for environmental applications but also has limitations (e.g. extraction of polar compounds or ionization) and must be subject to quality assurance procedures that have yet to be created. More generally, development of innovative tools and analytical methods to detect and measure complex mixtures (including metabolites) in groundwater remains essential. Of equal importance, specifically for metabolites, the lack of commercially available analytical standards is a strong technical limitation for routine monitoring.

In conclusion, there is a need to harmonize monitoring protocols including sampling and conservation, assessment of the representativeness of the monitored point, analytical aspects as well as data management to allow appropriate assessment of national and regional data. These points highlight the necessity of sharing expertise and the necessity of improved uptake of research results in creation or revision of technical guidances, databases management etc. There is also a need to further develop methodology and guidance on how to select compounds of relevance. Sharing knowledge and expertise on these different aspects is essential to optimise surveillance by adapting it to the specificities of each country but guaranteeing a possible comparison.

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