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

3

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15 **Keywords:** Water Framework Directive; plant protection product; Drinking Water Directive; early
16 warning; analytical issue; groundwater monitoring

17 **Abstract**

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

36 1. Introduction

37

38 Pesticides are used throughout the world, particularly in agriculture, to secure good crop yields.
39 Groundwater pesticide contamination is a major threat to aquifer quality status globally (Foster and
40 Chilton, 2021), and often results in complex mixtures of pesticides and their degradation products in
41 groundwater sources used for water supply (Lapworth et al., 2006; Gimsing et al., 2019; Baran et al.,
42 2021). In Europe, groundwater is the most important drinking water resource for many countries (e.g.
43 up to 100% in Denmark or Austria, 80% in Switzerland and around 70% in France – EurEau, 2021).
44 Pesticides may also affect groundwater ecosystem services based on microbial activities (e.g.
45 denitrification, Michel et al., 2021) and other groundwater dependant ecosystems such as wetlands,
46 lakes and rivers (McKnight et al., 2012).

47 There is a wide range of different frameworks used globally for regulating pesticide use (Pelaez et al.,
48 2013) and protecting groundwater bodies as well as different approaches undertaking groundwater
49 monitoring. EU legislation divides pesticides into plant protection products (PPP) and biocides used for
50 non-food or feed purposes. This can lead to confusion as PPP and biocides are not subject to the same
51 regulations. The regulation EC N°1107/2009 for PPP was updated and consolidated in March 2021 and
52 the regulation EU N°528/2012 for biocides was updated and consolidated in June 2021. The latter
53 apply without prejudice to REACH regulation n°1907/2006. Similarly, active substances used in PPP
54 and/or biocides are first approved at EU level. In a second stage, EU countries authorise the placing on
55 the market of PPP or biocides products containing those active substances on their territory and ensure
56 compliance with EU rules. European Commission decisions on approval and non-approval are
57 published in the Official Journal of the European Union; information being also available on two
58 websites (“EU pesticides database” and “information on biocides” on the European commission and
59 ECHA – European Chemicals Agency - websites, respectively). Regarding PPP, it is therefore possible to
60 know if an active substance has uses allowed in the different Member States (MS - even if it is
61 recommended to check the national databases) and to access the information regarding
62 environmental risk and notably risk of transport into groundwater. In May 2021, at EU level in the
63 context of PPP, 469 active substances are approved and 61 pending (i.e. waiting for a decision). It
64 should be noted that active substances of PPP are classified in 21 categories and correspond to organic
65 and inorganic compounds as well as fungi and/or viruses.

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

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

72 Although EU regulation encourages the use of less harmful active substances, pesticides are still
73 intensively used and therefore may pose human health or environmental risks. The presence of
74 pesticides or their metabolites in groundwater throughout the world is regularly highlighted either in
75 regional (Fisher et al., 2021; Moreau et al., 2019) or national studies (Bexfield et al., 2021; Close et al.,
76 2021; Kiefer et al., 2020; Hintze et al., 2020; Kotal et al., 2021; Lapworth et al. 2015; Lopez et al., 2015;
77 Stuart et al., 2012). Several large-scale monitoring studies have been carried out in Europe more than
78 a decade ago (Loos et al., 2009; 2010) and to our knowledge there has been no such campaign recently.
79 Therefore, having a precise vision of the status of groundwater with respect to pesticides and their
80 metabolites at the European scale is not trivial.

81 Driven by a strong regulatory context, considerable effort is put into focused monitoring of the quality
82 of groundwater in Europe with respect to pesticides and their metabolites compared to other regions
83 (Donley 2019, Pelaez et al., 2013). Major environmental directives (Water Framework Directive
84 2000/60/EC, WFD - and associated Groundwater Directive 2006/118/EC - GWD, and Drinking Water
85 Directive 98/83/EC, recently revised EU 2020/2184, DWD) and the European Regulation (EC) No.
86 1107/2009 concerning the placing of PPP on the market require the implementation of groundwater
87 monitoring. However, the heterogeneity of datasets through Europe regarding groundwater and the
88 lack of knowledge to support the risk assessment were highlighted by European Environment Agency
89 (EEA) as key obstacles to improve regulation and management of groundwater resources (Mohaupt et
90 al., 2020). Very recently, a European wide collection and analysis of existing monitoring data on non-
91 relevant pesticide metabolites (nrM) has been carried out in the frame of the WFD CIS task "Voluntary
92 Groundwater Watch List" (cf. chapter 3).

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

105 While this paper is focussed on Europe, this is not a unique challenge for Europe, indeed regional,
106 national and state regulation for monitoring of pesticide use and groundwater contamination is also
107 highly divergent for other regions such as North America and Asia and Africa (Li 2018; Pelaez et al.,
108 2013; Donley 2019; Bexfield et al., 2020; Bhushan 2006; Gupta et al., 2018; K'oreje et al., 2020).

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

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

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

128

129 2. Methods

130

131 Based on the examples of three EU member states (MS) (France, FR; Denmark, DK - EU MS; England,
132 EN part of the EU up to January 2020 - so the regulatory framework in place still very much represents
133 the EU framework) and one associated country (Switzerland, CH – AC - contributes quite closely and
134 actively to the EU groundwater framework discussions), we will illustrate the practices both in terms of
135 groundwater monitoring and dissemination of information and its use by decision makers. Note that
136 in the context of PPP registration operating in the EU, France, Denmark and England belong(ed)
137 respectively to the southern, northern and central zone, according to the zonal system (3 zones) of
138 PPP authorisation. Regulatory zones are supposed to have comparable agricultural practices, and

139 comparable plant health and environmental (including climatic) conditions. For comparison,
140 Switzerland was chosen as an example of a well-established associated European country.

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

153 Following DW and GWD, concentrations of pesticides and relevant metabolites may not exceed 0.1
154 µg/L for a single of those compounds (in the case of aldrin, dieldrin, heptachlor and heptachlor
155 epoxide, the parametric value shall be 0.03 µg/L) and 0.5 µg/L for the total concentration of those
156 compounds. Swiss legislation fixes a 0.1 µg/L limit for drinking water and groundwater. Except for
157 Denmark, no limit value has been defined for non-relevant metabolites when looking apart from single
158 compound specific cases. In Denmark, all metabolites of pesticides, with a few exceptions, are
159 considered to be relevant in accordance with the uniform principle in Article 29 of Regulation
160 1107/2009/EC, even compounds found to be non-relevant in the EU must not be detected in Danish
161 groundwater in concentrations exceeding the EU parametric drinking water limit of 0.1 µg/L.

162

163 3. Regulatory context in European Union, England and Switzerland

164

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

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

181 Recently (in 2014), a European wide and voluntary 'Groundwater Watch List' (GWWL) process was
182 launched by the European Commission in the frame of the Common Implementation Strategy CIS of
183 the WFD. The objective of the "watch list for pollutants of groundwater" is "to increase the availability
184 of monitoring data on substances posing a risk or potential risk to bodies of groundwater" "(Recital 4
185 of the revised GWD). The GWWL should "facilitate the identification of substances, including emerging
186 pollutants, for which groundwater quality standards or threshold values should be set". The most
187 important output of the GWWL process is the identification of substances present in groundwater
188 based on sufficient monitoring data available. These substances integrate the "List facilitating Annex I
189 and II review process of the GWD" and support the EC review of the GWD by identifying substances or
190 groups of substances that may be considered for future regulation via the GWD (Lapworth et al., 2019).
191 Up to now three data collections on Pharmaceuticals (Amec Foster Wheeler, 2016), PFAS (WFD CIS
192 2020) and nrM (WFD CIS 2021) have been carried out.

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

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

204 At EU level, 469 active substances of PPP are currently approved, but the number of national approvals
205 is country-dependent (Figure 1). Thus, only 85 active substances are commonly approved in the four
206 selected countries. More generally, we observe that only 26 active substances are allowed in all the 28
207 recent MS (Figure 2), whereas 24 active substances have an approval in only one MS. Each MS must

208 therefore consider its specificity in terms of use e.g., fenpicoxamide appears specific to France,
209 metosulam to England (in May 2021).

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

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

236

237 4. Results and Discussion

238 a. Implementation of groundwater monitoring and data collection

239 *National scale*

240 **France**

241

242 In France, the water law of December 16, 1964 (law n° 64-1245) organizes water management at the
243 basin level with the creation of six water agencies in mainland and four offices in overseas territories,

244 and basin committees. As early as the middle of the 90's, the will to structure a national database
245 appeared (see supplementary material S1 for details). Thus, ADES a national open-access database on
246 groundwater, was created. This base contains data from 314 networks (i.e. wells and/or springs),
247 mainly sanitary and environmental monitoring networks, covering both quantitative (groundwater
248 levels) and qualitative aspects. To date, it contains over 102 million water analyses from about 77,000
249 quality observation points (vs. 4,900 for groundwater level monitoring).

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

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

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

263

264 *Denmark*

265 In Denmark, the national groundwater monitoring programme (GRUMO), was initiated in 1988 (see
266 Supporting material S1 for more historic information). GRUMO's aim was to monitor the effect of the
267 Danish Environmental legislation launched in 1987 on general agricultural regulations in relation to the
268 nutrient load (the phosphorus and nitrate load) of the aquatic environment wastewater plants and
269 secondly to ensure the supply of good quality drinking water to the population. GRUMO was hence
270 designed to provide information on the quality of the groundwater in selected catchments estimated
271 to be representative for Denmark. The monitoring has since been adapted continuously based on
272 improved knowledge and varying administrative needs, including the fulfilment of the reporting
273 obligations under the coming EU directives as the Nitrates directive 1991 (91/676/EEC), which is yearly.
274 When deciding which compounds were to be analysed in GRUMO, pesticides were included already in
275 1990. As a consequence of the GRUMO results, also waterworks were from 1996 obligated to monitor
276 both waters directly sampled from water works wells (groundwater) and the water tap (drinking water)
277 for pesticides. The list of compounds to be analysed in GRUMO is adjusted at least every 6th year to

278 account for environmental political priorities and legislation. If needed, screening studies under
279 GRUMO are organized annually.

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

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

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

309 While pesticides are authorised for use within the EU, it is crucial for Denmark's drinking water quality
310 to evaluate the knowledge acquired by the European Food Safety Authority (EFSA) if there is even the

311 smallest indication of a leaching risk of pesticides and/or their degradation products (Rosenbom et al.,
312 2015). This knowledge is applied in the yearly selection of compounds to be monitored in PLAP. If a
313 metabolite or a pesticide appears in high concentrations in groundwater collected from underneath
314 the PLAP-fields, this knowledge is included when updating the list of compounds to be monitored in
315 GRUMO and the result of the national monitoring will finally appear in the Jupiter database (see
316 Supplementary material).

317

318 *England*

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

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

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

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

352

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

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

363

364 *Switzerland*

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

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

375 The purpose of the National Groundwater Monitoring is to:

- 376 • document the situation and development of groundwater quality and quantity at national level;
- 377 • detect the occurrence of problematic substances at an early stage and to systematically follow up
378 any undesirable developments;

379 • check the effectiveness of protective measures already adopted and identify the need for further
380 measures;

381 • characterise and classify the most important groundwater resources in Switzerland.

382 NAQUA forms the basis for nationally coordinated protection of groundwater as a natural resource in
383 Switzerland and ultimately helps to protect the public from harmful substances. As Switzerland
384 collaborates closely with the EU on environmental matters, the collected data are reported to different
385 organisms as the European Environment Agency as a member or on a voluntary base (e.g. IGRAC, IAEA).
386 The Swiss legislation requires the federal government to collect data on environmental pollution
387 (Constitution Art. 65, Environmental Protection Act, Art. 44), water quality and hydrologic conditions
388 in Switzerland (Water Protection Act (WPA) Art. 57) and to inform the public of the results
389 (Environmental Protection Act Art. 10e, WPA Art. 50 & Art. 57). The NAQUA National Groundwater
390 Monitoring carries out these federal functions in relation to groundwater.

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

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

398

399 *Comparison across the four countries and European scale*

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

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

409

410 At European scale, IPChem Portal (<https://ipchem.jrc.ec.europa.eu/>) is the European Commission’s
411 reference access point for chemical monitoring in various media (environmental, human bio-
412 monitoring, food and feed, products and indoor air) allowing searching, accessing and retrieving
413 chemical occurrence data collected and managed in the EU. The platform has been developed to fill

414 the knowledge gap on chemical exposure and its burdens on health and the environment. Several
415 types of database exist including e.g. Waterbase, which is the generic name given to the EEA's
416 databases on the status and quality of Europe's rivers, lakes, groundwater bodies and transitional,
417 coastal and marine waters, on the quantity of Europe's water resources, and on the emissions to
418 surface waters from point and diffuse sources of pollution. Its creation is based on the INSPIRE
419 Directive 2007/2/EC which aims to create a European Union spatial data infrastructure for the
420 purposes of EU environmental policies and policies or activities which may have an impact on the
421 environment. According to the data type (notably raw data versus aggregated data), data access could
422 be restricted, public or limited to the owner. In some cases, it is therefore possible to find raw and
423 more detailed information at national level than in the European database.

424

425 **b. Monitored pesticide substances and occurrence in groundwater**

426 *National scale*

427 *France*

428 In France, a national regulatory decree (under revision) sets the guidelines (minimum required) for
429 groundwater monitoring in terms of frequency of measurements, number of points per km² and lists
430 of parameters to be measured, a “core list” (Act 2015 published in JORF, 2015 and its modified version
431 of 2018, JORF 2018). Three types of monitoring's are defined: i) regular (every year – 2 times /year for
432 unconfined aquifers - all points of the networks), ii) photographic analysis (once per WFD cycle – all
433 points), and iii) complementary analysis (quarter of the sites of the monitoring program). The list of
434 parameters is monitoring type dependent. A distinction is also made between mainland and the
435 overseas territories. Of the 227 parameters included as a minimum requirement, 115 are active
436 substances of PPP, 21 metabolites and 2 compounds being both active substance and metabolite
437 (Figure 3 – supplementary materiel Table 2). Half of the 138 compounds (69) originate from a currently
438 authorised pesticide, the other half (69) can be related to former uses. Some water agencies carry out
439 a much more exhaustive monitoring (up to 651 molecules for France, 106-612 per river basin
440 depending on the water agency – status report of 2013) in order to cover for instance specific uses
441 (e.g. crops with limited geographical extension). While this more comprehensive research is important
442 to get a more complete picture of groundwater quality, it makes analysis of the data at the national
443 level more challenging.

444 With respect to drinking water, the minimum frequency of sampling and analyses is determined by the
445 volume of water distributed or produced each day within a supply zone (~ 32,000 wells tapping
446 groundwater). Among the 54 parameters, the generic term “pesticides and (relevant) metabolites” is
447 used, and it is recommended that monitoring should be adapted to regional context (Direction
448 Générale de la Santé, 2020). The Ministry of Health states given the number of authorized (or formerly

449 authorized) pesticides, it is necessary to target the analysis for pesticides, according to their potential
450 occurrence in water and the risks for human health and adapted based on local use. DWD monitoring
451 is consequently heterogeneous between regions.

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

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

474 *Denmark*

475 In the GRUMO, the current list of compounds to be monitored for water chemistry regarding pesticides
476 excluding screening and verification (<https://www.retsinformation.dk/eli/lta/2021/1110> and
477 <https://mst.dk/media/210472/grundvandsbilag-pr-febr-2021.pdf> in Danish) encompasses 63
478 compounds of which 16 are pesticides, 43 are metabolites, two are both pesticide and metabolite, and
479 two are synthesis impurities (Figure 3 - supplementary materiel Table 2). Only 15 compounds of the
480 61 compounds (not counting the two impurities) are or originate from a currently authorised pesticide,
481 whereas 46 of the 60 compounds can be related to former uses. The outcome of the monitoring, which
482 is published in Thorling et al. (2021), reveals that the five most detected compounds in 2019 in the
483 water from (i) GRUMO’s wells are:

- 484 • DPC (desphenylchloridazon; 25.7% with detections and 12.4% exceeding 0.1 µg/L),
- 485 • N,N-DMS (N,N-dimethylsulfamid; 23.8% with detections and 3.2% exceeding 0.1 µg/L),
- 486 • 1,2,4-triazole (16.1% with detections and 2.9% exceeding 0.1 µg/L),
- 487 • MDPC (methyl-desphenylchloridazon; 15.1% with detections and 4.4% exceeding 0.1 µg/L)
- 488 • BAM (2,6-dichlorobenzamide; 11.1% with detections and 2.8% exceeding 0.1 µg/L)

489 and (ii) water works wells are:

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

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

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

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

518

519 *England*

520 A number of analytical suites which cover 155 pesticide and metabolite compounds (141 pesticides, 9
521 metabolites and 5 being both pesticide and metabolite) are used for quantifying pesticides (1-organo-
522 nitrogen pesticides, 2-organo-chloride pesticides, 3-acid pesticides and 4-uron/urocarb pesticides, 5-
523 pyrethroids, 6- Discretionary pesticides and other organics (e.g. tralkoxydim, flutriafol and
524 propiconazole). Only 37 compounds are or originate from a currently authorised pesticide, whereas
525 118 compounds can be related to former uses (Figure 3 – supplementary material Table 2).

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

533 In 2019 of the 271 groundwater drinking water protection areas (DWPA) in England, 7 (in the Thames
534 and Anglian river basin districts) were classified as of poor chemical status due to pesticide pollution.
535 Non statutory safeguard zones (SGZs) were established around 31 (11%) groundwater DWPA's due to
536 concerns over pesticide pollution (EAE, 2019). Historical pesticide monitoring data collected between
537 1998-2005 shows the frequency of detections for the 15 most commonly detected pesticides in
538 groundwater exceeding 0.1 µg/L in the GWQMN to be less than 11% and more typically less than 1%
539 for individual pesticides (DERFA, 2010). In 2005 atrazine was still the second most frequently detected
540 pesticide (behind bentazone) but detections exceeding 0.1 µg/L were low (1.3%) and had fallen
541 significantly since 1998 which had a figure of 10.3 % exceedances. Contaminated groundwater can take
542 many decades to recover, particularly where unsaturated zones are deep, such as within parts of the
543 Chalk aquifers of Southern England, even when the inputs of the chemicals cease (e.g. Lapworth and
544 Goody 2006). For example, the pesticides atrazine and simazine were both withdrawn from use in
545 the UK in 2003, but they continue to be detected in groundwater due to very slow degradation rates
546 (EAE, 2019). Recent data (EAE, 2019), show that the most frequently detected pesticides in
547 groundwater are bentazone (2.7 % SGZs), metaldehyde (1.5 % SGZs) atrazine (1% SGZs) and mecoprop-
548 P (<1% SGZs), which were all (apart from atrazine) approved for use at the time.

549 Lapworth et al., (2018) summarises results from groundwater surveillance monitoring in England
550 (n=7473, 2009-2017) using targeted semi-quantitative scanning methods. Using GC-MS methods the
551 most frequently detected pesticides and metabolites were atrazine (9.4 % of samples), desethyl
552 atrazine (6.4 %), simazine (4.7 %), emphasising the issue of legacy contamination from banned

553 pesticides, followed by BAM (metabolite of dichlobenil, 2.8 %), metaldehyde (2.5 %) and oxadixyl (2
554 %). In contrast, from a smaller sample (n=249) the more sensitive LCMS method showed that pesticides
555 dominated the top 50 detected compounds with detection frequencies >60 % for the following
556 compounds, deisopropylatrazine > desethylatrazine > simazine > atrazine. Notable detection
557 frequencies were also reported for diuron (50 %), clothianidin (33 %), bentazone (28 %), monuron
558 (25%) and isoproturon (22%).

559 *Switzerland*

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

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

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

583

584 *Comparison across the four countries*

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

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

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

621

622 *European scale*

623 The Waterbase – Water quality database includes a large volume of concentration measurement data
624 reported by countries to the European Environment Agency. Data include observations on sampling
625 dates (so called ‘disaggregated’), data and aggregated data (including yearly mean, minimum,
626 maximum and Limit of Quantification of pesticide concentrations). Therefore, there are many data
627 sources for pesticides, but the availability of comparable data across Europe is rather limited and
628 except for triazine metabolites, monitoring of metabolites is scarce (Mohaupt et al., 2020). Within the
629 WFD, the data on 184 distinct pesticides were extracted from Waterbase (Mohaupt et al., 2020 – data
630 2007-2017), covering a total of 16,886 groundwater monitoring sites in 26 countries. According to the
631 authors, 156 compounds are pesticides, 12 are both pesticide and metabolite, 13 are metabolites and
632 three are “others” (Figure 3 – supplementary material Table 2). Only 67 of the 187 compounds are or
633 originate from a currently authorised pesticide, whereas 93 can be related to former uses and 24 not
634 having information on their status. The comparison with FR, DK and EN shows that 353 compounds
635 are considered but that only 11 are present in all four lists (Supplementary material Table 2). The
636 European report does not highlight the compound identified in each country with high occurrence and
637 in particular metabolites mentioned in one or more of the four countries (e.g. metabolites of
638 metolachlor, dimethachlor, chlorothalonil and chloridazon).

639 To answer the issue of non-relevant metabolites on a European scale, a study on nrM as defined within
640 the EC n°1107/2009 has very recently been carried out in the frame of the CIS GWD Groundwater
641 Watch list (GWWL) activity (WFD GWD 2021). MS and AC were asked to provide available monitoring
642 data on 53 selected nrM in groundwater across Europe. 29 MS/AC responded and 17 countries
643 provided groundwater data on the nrM compounds in the related questionnaire. nrM were widely
644 detected in European groundwater above limits of quantification. The percentage of detections in
645 groundwater were highest for DPC (31.7%), Metolachlor ESA (30.0%), N,N-DMS (24.4%), MDPC
646 (23.7%), Metazachlor ESA (21.0%) and Dimethachlor CGA 369873 (20.7%).

647 Regarding drinking water, in 2015 a draft list with 21 DWD pesticides and metabolites of concern has
648 been established by compiling voluntary contributions from nine MS sent to European Commission DG
649 Environment. From one contribution including around 700 compounds, only the 25 highest ranked
650 compounds with over 50,000 analyses have been considered. Compounds indicated by at least four
651 MS have been included in a short list (an extended list has also been established including compounds
652 indicated by less than four MS). The six metabolites mentioned are: AMPA (Aminomethylphosphonic
653 acid), desethyl-atrazine, desethyl-terbuthylazine, desisopropylatrazine, Metazachlor ESA, MDPC and
654 15 active substances: atrazine, bentazone, chloridazon, diuron, glyphosate, hexazinone, isoproturon,
655 MCPA, mecoprop/mecoprop-P, metalaxyl/metalaxyl-M, metamitron, metazachlor, metribuzine,
656 simazine, terbuthylazine.

657 c. Early warning / surveillance prospective and contributions from research

658 National scale

659 *France*

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

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

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

685

686 *Denmark*

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

691 In general, compounds (pesticides and/or their metabolites) are selected for being monitored in PLAP
692 following three categories: (i) newly registered PPP that are assessed to have a high application

693 potential in amount per application or area wise. The purpose of this is to provide an early warning
694 regarding compounds leaching to the groundwater; (ii) Old PPP that have already been applied in high
695 quantities in large parts of the agricultural land through time; iii) approved pesticides, which in
696 connection with first approval, reapproval or new knowledge obtain are assessed to have a high
697 leachability of the pesticide itself or its degradation products. For the category i and iii, the
698 establishment of a method of analysis is often required, which is conducted based on analytical
699 standards provided by the producer of the pesticide included for test in PLAP. Like in France,
700 possibilities of improving the identification of leacher with HRMS is evaluated.

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

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

717

718 *England*

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

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

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

745

746 *Switzerland*

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

755 Recent field studies concluded furthermore, that the anionic chlorothalonil metabolites R471811 and
756 R417888, frequently detected in Swiss groundwater, do not accumulate in soil due to their very high
757 mobility (Hintze et al., 2021). Therefore, soil and unsaturated zone is frequently not expected to act as
758 long-term source unlike for metabolites of chloridazon. These chloridazon metabolites (Hintze et al.,
759 2020) seem to have a longer residence time in soils and are thus expected to impact groundwater over
760 longer times scale and can also show some retardation in aquifers.

761 In Switzerland, a common process to prioritize pesticide metabolites for the cantonal and federal
762 monitoring is currently set up. The process will be based on monitoring results, research results (e.g.

763 screening studies), the pesticide substance approval list, and the outcomes of evaluation studies (e.g.
764 groundwater contamination risk score e.g. Korkaric et al., 2022).

765

766 *Comparison across the four countries*

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

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

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

793

794 5. Conclusions, Perspectives and Future Outlook

795

796 Characterising groundwater contamination by pesticides and their metabolites is paramount to ensure
797 resource protection and mitigate potential effects on human and ecosystems health. The strong

798 regulatory framework in European Union (WFD, GWD, DWD, regulation EC N°1107/2009) facilitates a
799 high level of groundwater quality monitoring, especially for pesticide / active substances (and in
800 particular PPPs - versus biocides) and to a lesser extent, their metabolites. However, with regard to
801 this regulatory framework, two types of monitoring exist: general monitoring and targeted monitoring
802 with different implementations, different objectives and different data dissemination, monitoring
803 data. Thus monitoring data obtained in the case of targeted monitoring (regulation EC N°1107/2009),
804 generally has limited access to regulators.

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

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

819 The impact of pesticide use on groundwater can persist for a very long time because i) in some areas
820 there is a deep unsaturated zone and low renewal rate of the groundwater and ii) the active substances
821 or their metabolites can be stored and released from soils and unsaturated zone over several years or
822 decades. These compounds can also be preferentially, and rapidly, transported to depth of lower
823 degradation than in the plough layer. These aspects must be better taken into account in the PPP
824 regulatory procedures including leaching assessment to the surface and groundwater. The variability
825 in soils and climate within EU calls for a differentiated regulation based on improved knowledge
826 regarding dominant processes controlling the leaching of compounds from the soil surface to the
827 groundwater obtainable via target high-quality early-warning monitoring systems, which addresses
828 the representability of a water sample taking consideration of high-resolution geological models.
829 Today, in accordance with the EC n°1107/2009 regulation, the assessment of the leaching risk of
830 pesticides and metabolites to groundwater are conducted applying nine mostly unvalidated virtual
831 FOCUS groundwater scenarios. Here the lack of field data (Vanderborght et al., 2011) and spatial
832 representation in soil-related parameters (hydraulic, chemical, physical and microbial) (Rosenbom et

833 al., 2014 and 2015) have been obstacles for improvement of the assessment. Adding to this, the
834 scenarios have significant drawbacks such as: i) being one-dimensional, ii) applying climate from 1960-
835 1990, iii) not accounting for fluctuating groundwater table, iv) having limited or no inclusion of
836 preferential flow and transport. With “A Century of Denial: Preferential and Nonequilibrium Water
837 Flow in Soils” by Beven, 2018) and numerous studies suggesting considerable preferential solute
838 transport through soils being the rule more than the exception – this process needs to be addressed
839 in future leaching assessments of PPP to the groundwater (Beven and Germann, 2013; Beven, 2018;
840 Nimmo, 2021; Nimmo et al., 2021). Better knowledge of soil contamination could also be useful, but
841 to date there is no regulatory framework at EU level for this.

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

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

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

865 However, establishing exhaustive lists of compounds to be monitored remains challenging and should
866 be tackled at different scales (from regional to European levels), considering country-specific uses, for
867 both biocide and PPP. For the latter and, with agriculture being highly variable within EU level, a large

868 panel of national authorisations and uses of active substances exists within EU. Thus, the monitoring
869 needs to address these heterogeneous conditions and cannot be conducted referring to a unique list
870 for EU to get a comprehensive view. A method for establishing country-specific lists could be defined
871 in order to have harmonized practices and to make pesticide monitoring more cost-effective and more
872 reliable.

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

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

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

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905 **FIGURES CAPTIONS**

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

911
912 Figure 2. The relationship between the number of active substances of plant protection products
913 being approved at European level (469) and the number of member states having authorised use.

914
915 Figure 3. Distribution of substances monitored (minimum required) within the WFD by **A)** status
916 (compounds are or originated from an approved active substance or not approved active substance
917 according to national status in May 2021 or not known) and **B)** distinguishing metabolite and
918 pesticide by the countries France (FR), Denmark (DK), United England (EN) and at European level (EU
919 – data from Mohaupt and al., 2020)

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924 [9aa7-9964bbe8312d/library/a1e23792-6ecd-4b34-b86c-dcb6f1c7ad1c/details](https://circabc.europa.eu/ui/group/9ab5926d-bed4-4322-9aa7-9964bbe8312d/library/a1e23792-6ecd-4b34-b86c-dcb6f1c7ad1c/details) or **pilot study**
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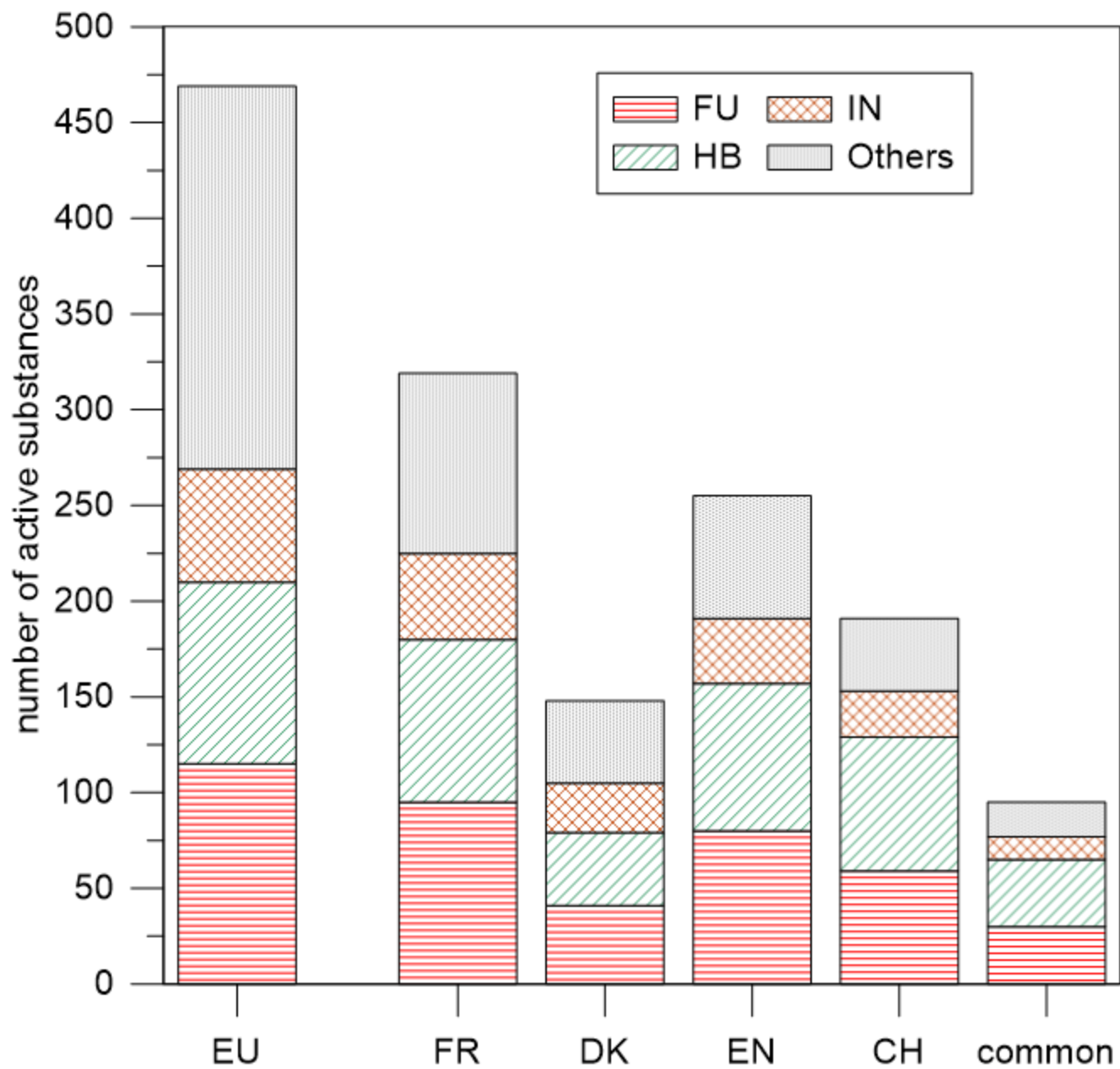
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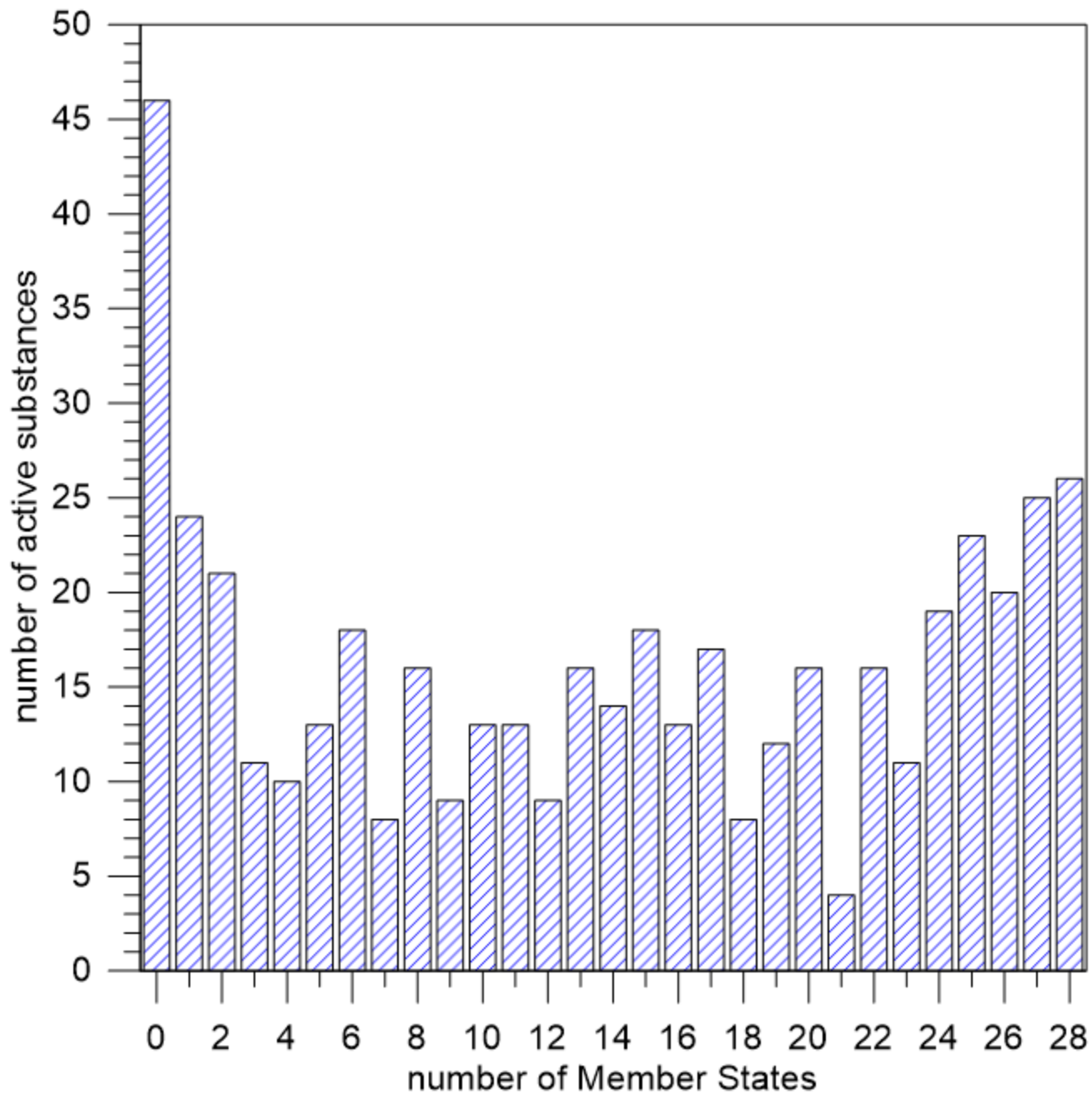
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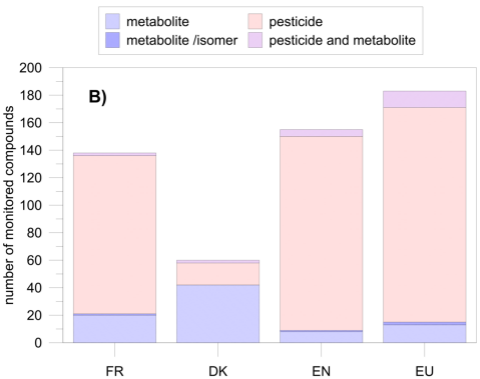
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EU Regulatory context

Data collection and sharing – Monitoring implementation

Analytical aspects

Pesticides and metabolites in European groundwater

Analysed compounds and occurrence

Early warning and prospective surveillance

Case studies:
FR, DK, EN, CH



European Union