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1 **Pesticides in groundwater at a national scale (France): Impact of regulations,**
2 **molecular properties, uses, hydrogeology and climatic conditions.**

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8

9 **Abstract**

10 Contaminants in groundwater are a major issue worldwide. Temporal trends of such occurrences in
11 French groundwaters were evaluated for several active substances of pesticides belonging to
12 different chemical classes, to identify key factors explaining groundwater contamination. Our study
13 relied on exploitation of a French national database (ADES, created in the mid-1990s and remarkable
14 for the available data, including over 88 million analyses). Temporal changes in the frequency of
15 exceeding a reference value of 0.1 µg/L for several substances were determined at yearly and
16 monthly scales. Such trends were examined by distinguishing different periods according to changes
17 in regulations (new approval, withdrawal, or dose reduction), and were combined with data on
18 effective rainfall as a proxy for groundwater recharge, on aquifer lithology, and on sales of active
19 substances as a proxy for actual applications. A review of monthly data shows that a rapid transfer of
20 pesticides with contrasting physico-chemical properties can occur after application in many aquifers,
21 regardless of their lithology. For substances such as metolachlor, showing a sharp increase in sales, a
22 clear relationship exists between quantities sold and frequency of exceeding the reference value. For
23 other active substances, such as isoproturon or chlortoluron, frequencies of exceedance are
24 governed by both sales and effective rainfall. Finally, the occurrence of active substances in
25 groundwater several years after their withdrawal from the market is explained by at least three

26 major mechanisms: the transfer time from soil into groundwater, processes of remobilization from
27 soil and/or unsaturated zone, and no or low degradation in the saturated zone. While these
28 processes are well documented for atrazine and different types of aquifers, they can be virtually
29 unknown for other active substances.

30

31 1. Introduction

32 In many countries, groundwater is a major resource for drinking-water production, requiring a good
33 initial sanitary quality. In addition to this sanitary aspect, environmental preoccupations are growing
34 as well. This is the context in which, at a European level, the Water Framework Directive (WFD) and
35 its subsidiary directives (European Commission, 2000, 2006) aim at limiting contaminant pressure,
36 reducing content trends and avoiding new contaminations. Several programmes of measures have
37 been designed to reach these objectives, but evaluating their efficacy can be difficult, especially
38 within the physical realm of groundwater. This is especially due to the fact that transfer times of
39 solutes in water between soil and groundwater, and within the aquifer itself, can take many years or
40 even decades.

41 Among the contaminants of human-made origin for agricultural or other use, pesticides are a
42 major source of groundwater contamination in the WFD sense. During a French survey in 2013, 203
43 out of 589 aquifers were in a poor chemical condition, 88 of which for the single “pesticides”
44 parameter and 63 for the two parameters “pesticides” and “nitrate”. The presence of pesticides in
45 groundwater can be due to diffuse or point pollution. Concerning the first, the pesticide transfer to
46 groundwater is affected by several factors, such as the properties of the active substance and of the
47 soil, in turn affecting sorption and degradation processes. Though such transfer is well studied for
48 soil, it remains poorly understood within the deeper unsaturated zone—below 1 to 2 m—and in the
49 saturated. However, this knowledge is essential for evaluating the risk of groundwater contamination
50 and the resilience of aquifers in terms of such contamination.

51 The risk of groundwater contamination by pesticides has been evaluated for many years,
52 using for instance screening methods based on leaching-risk indices that consider the physical
53 properties of a pesticide (adsorption, solubility, etc.), integrating or not the soil characteristics.
54 Numerous indices exist and can be compared, though the results obtained by different methods may
55 seem contradictory (Akay Demir et al., 2019). Similarly, numerous qualitative (e.g., overlay-index
56 methods), quantitative and statistical methods have been developed for estimating the intrinsic or
57 specific vulnerability of an aquifer (Machiwal et al., 2018). Moreover, modelling approaches of
58 varying complexity can be used. In Europe for instance, EC Regulation 1107/2009 concerning the
59 marketing of plant-protection products, the risk of transfer to groundwater is partly based on
60 modelling (Gimsing et al., 2019).

61 In addition, groundwater-quality monitoring data can be used for evaluating the degree
62 and/or the evolution of contamination, or for identifying the situations most at risk. Contrary to the
63 results from indicators or modelling, monitoring data provide a real image of groundwater conditions
64 and are not subject to biases related to conceptualization of the model or the indicator. However,
65 monitoring data can only be used for molecules that are known to occur and are searched for in
66 groundwater. Moreover, only a limited number of publications exists on the presence of pesticides
67 mentioned in the 1st and 2nd Watch List on European Surface and Groundwaters (Pietrzak et al.,
68 2019), and that surveillance of groundwater quality may be incomplete for certain pesticides.

69 Generally, when using monitoring data, the temporal evolution of groundwater quality is
70 estimated either by comparing data from monitoring points at different dates, ignoring what
71 happened between those dates (Kolpin et al., 2004: 86 wells in Iowa, three comparisons between
72 two dates;), or by more continuous monitoring over a shorter period of one or several years
73 (Guzzella et al. 2005, McManus et al., 2014). The latter often covers a restricted number of points
74 (Lapworth et al., 2006: 14 wells over a year in a given hydrogeological context, McManus et al.,
75 2017), or, more exceptionally, is more intensive (De Guzman et al., 2005: 175 sites monitored over

76 seven years, or 10,054 samples). Still, short-term monitoring poses the problem of how
77 representative the data are in terms of water use and aquifer recharge.

78 Groundwater-quality data can be examined in the light of various factors that may influence
79 contaminant transfer, such as molecular properties (Worall and Kolpin, 2004), uses in a context of
80 substitution of the active substance (de Guzman et al., 2005), environmental data such as the
81 hydrogeological setting (Fonseca et al., 2019; Mas et al., 2020), or the hydrodynamic context
82 (Lapworth et al., 2006). In most cases, however, the number of observations is relatively small and
83 generally concentrated in a small enough geographic area for drawing site-specific conclusions.

84 We, however, propose to examine—at a national scale and using multi-year monitoring data
85 since the mid-1990s—the evolution of groundwater quality in France. This evolution may be due to
86 changes in pesticide use as driven by regulatory evolution, but also to changes in the hydrogeological
87 and climatic context. As far as we know, this is the largest dataset ever used for this type of exercise.

88 2. Materials and methods

89 2.1. Groundwater-quality database

90 In France, since the mid-1990s, the Ministry for the Environment has set up a national open-access
91 database coordinated by the French Geological Survey (BRGM) on groundwater, called ADES
92 (<https://ades.eaufrance.fr/>). This base contains data from sanitary and environmental monitoring
93 networks, covering both quantitative (groundwater levels) and qualitative aspects. Today, it contains
94 over 88 million water analyses from about 75,000 observation points.

95 Launched in 2007 and fully operational in 2009, the monitoring networks were structured to
96 answer the WFD objectives and its directive EC 2006/118 on “The protection of groundwater against
97 pollution and deterioration”. Creating these networks i) increased the number of analyses, ii)
98 stabilized the number of monitored wells and iii) obtained a wider and patrimonial vision, earlier
99 pesticide monitoring tended to focus on known or suspected contaminated areas. However, as the

100 monitoring was not steered by a single national entity, the monitored substances were not the same
101 everywhere.

102 Today, this groundwater surveillance covers 26,055 monitoring points over 589 groundwater
103 bodies. As not all 2019 data had been entered into the ADES database when preparing this paper, we
104 decided to restrict ourselves to 1996-2018 high-quality data.

105 2.2. Molecules studied

106 The ADES database contains the results of concentration measurements for several hundreds of
107 active substances. A selection was thus made of the most frequently quantified active substances in
108 French groundwater. As the monitoring of metabolites is generally more recent and less
109 homogeneous, we focused on the active substances for this review of data over a longer time span.
110 Other criteria retained for covering different situations, included evaluation of national regulations
111 (and thus of uses), chemical classes, and crops to protect. The main information is summarized in
112 Table 1. We retained atrazine, metolachlor, isoproturon and chlortoluron, all frequently detected
113 during a national campaign (Lopez et al., 2015). In addition, molecules with a similar use in cropping
114 terms were selected as well, such as dimethenamid and acetochlor that are much used on maize, like
115 metolachlor. The retained molecules covered the following situations:

- 116 • Substances for which permitted dose levels were reduced over time: atrazine (1990, 1997
117 and withdrawn in 2003), isoproturon (2004 and withdrawn in 2017), chlortoluron (2004);
- 118 • Substances no longer authorized for part of the study period: atrazine (withdrawn in 2003,
119 terbuthylazine (last use in June 2003 except for grapevines with last use in June 2004);
- 120 • Substance authorized for the first time during the study period: acetochlor (introduced in
121 2000, withdrawn with last use in June 2013);
- 122 • Substances whose isomeric ratio was modified in the commercial product: (S)-metolachlor,
123 and dimethenamid-(P), leading to a reduction in doses applied per hectare. For both
124 molecules, some French laboratories provide only an overall analysis that may, or may not,

125 be accompanied by a complementary analysis for distinguishing isomers. By convention,
126 here, the generic term metolachlor or dimethenamid is used for sales and analytical results
127 of both isomers.

128 In addition to the changes connected with French marketing authorizations, our study covered
129 different types of use, i.e. crops. It included molecules with different application dates throughout
130 the year, molecules belonging to different chemical classes (substituted ureas, triazines,
131 chloroacetamides) and those with different physico-chemical properties and GUS indexes (Gustafson,
132 1989) (Table 1). Schematically, isoproturon and chlortoluron are herbicides with similar GUS indexes,
133 used for straw cereals (post-sprouting). The chloroacetanilides studied are mainly used as maize
134 herbicides, with metolachlor (the most mobile according to the GUS index) *versus* acetochlor and
135 dimethenamid, which have comparable values. Atrazine was used on maize but also as a general
136 weedkiller, and terbuthylazine was used on maize as well as on grapevines.

137

138 2.3. Soil use and crops of interest

139 French data for 2015 in the agricultural parcel register (Ministry for Agriculture data) list the surfaces
140 occupied per crop type. Processing these data with a Geographic Information System (GIS) defined
141 the percentage of surface occupied by a crop of interest for a specific groundwater body. For this
142 study, a 'crop of interest' is a crop that may have received applications of one of the active
143 substances studied, but only majority use of such a substance was considered. Groundwater bodies
144 below a minimum 'crop of interest' surface were specifically examined for these molecules, this
145 arbitrary limit being set to ensure a minimum of potential substance application over the water body
146 (Table 1).

147

148 2.4. Pesticide and herbicide sales

149 In France, since 2009 and following national regulations, all distributors of crop-protection products
150 must declare their annual sales figures for nation-wide monitoring. These data are stored in the

151 National Crop Protection Products Sales database (BNV-D). The information is available at a
152 departmental (provincial) scale. A limit to using these data is set by the fact that sales are referenced
153 by the municipality of the sales point. More recently, the referencing has changed to the municipality
154 where the buyer is headquartered, which may differ from where a substance is actually used. It is
155 thus clear that such data can only be used at a national or departmental scale, or over large surfaces,
156 as using such data at a local scale may introduce a strong bias. Faced with such uncertainties on
157 where the substances were used and possible geographical discrepancies between sales and actual
158 use, we decided to aggregate the data by year for the whole of France in order to highlight the main
159 trends. As said before, 2019 data were not available when our work started.

160 2.5. Frequency of exceeding the reference value

161 In order to characterize the temporal evolution of groundwater quality, we had to define reference
162 criteria. For a given contaminant and water body, several laboratories may have intervened over
163 time, or the same laboratory may have modified its analytical methods, causing changes in the
164 quantification limit over time. Similarly, the quantification limit is molecule dependent. For these
165 reasons, we decided not to consider the quantification frequency (occurrence *sensu stricto*), but a
166 common frequency of exceeding a reference value for most substances. The adjusted method, like a
167 common threshold for computing frequencies, allows unbiased comparison among compounds
168 (Kolpin et al. 1998). We retained a value of 0.1 µg/L as this exceeds the quantification limits of many
169 laboratories for most substances (more than one hundred referenced in ADES had a maximum limit
170 of quantification over 0.1 µg/L for the study period) without being too high to mask temporal
171 variations in concentration. Comparison with other threshold values close to this value showed that
172 we could compare the trends regardless of the retained threshold value, even though the
173 frequencies of exceedance in absolute values obviously will be different (S.figure 1). Moreover,
174 though not being our initial decisional criterion, the 0.1 µg/L value is that retained in the European
175 Drinking Water and Water Framework directives.

176 The frequency of exceeding the 0.1 µg/L value was examined at yearly and monthly scales, and
177 compared with data on effective rainfall, hydrogeological context and soil use. When possible, it was
178 also compared with sales figures for active substances. All these data were available for the period
179 2008-2018.

180 2.6. A standard for groundwater bodies

181 Groundwater bodies are the evaluation units of the Water Framework Directive; they are defined as
182 a distinct volume of groundwater within one or several aquifers, their boundaries being based on
183 hydrogeological criteria and, if necessary, anthropic pressures. Such groundwater bodies are defined
184 by six types of hydraulic functioning (alluvial, sedimentary, volcanic edifice, intensely folded,
185 basement, locally impermeable), by their condition (confined or unconfined) and by other attributes.
186 Of the 589 groundwater bodies recorded in a 2013 French database, 117 are in an alluvial domain,
187 299 in a sedimentary environment, 1 in a volcanic edifice, 36 in folded rocks, 51 in a locally
188 impermeable aquifer, and 85 in basement rocks. We examined the groundwater quality data by type
189 of associated lithology, and—at the scale of specific water bodies—also in terms of surface crop
190 types.

191 2.7. Effective rainfall

192 In France, the SAFRAN hydrological model was developed by MétéoFrance in order to distribute of
193 water-resource data at a national scale. This atmospheric forcing model allows the interpolation and
194 extrapolation of precipitation data, considering especially terrain effects. The model provides
195 national coverage with an 8x8 km grid, and is used operationally for hydrological monitoring and
196 estimating flowrates for all of metropolitan France. In our case, annual effective rainfall data were
197 available for the period 1958-2019. Using these data allowed linking the evolution of groundwater
198 quality with climatic context, effective rainfall being used as a proxy for groundwater recharge. For
199 the period 1996-2018, the annual average was 411 mm.

200 3. Results and discussion

201 3.1. Impact of the withdrawal, reduction in permitted levels and marketing of active 202 substances

203 3.1.1. The case of triazines

204 Figure 1 shows at the scale of France, for atrazine and terbuthylazine, and for groundwater bodies
205 with a crop of interest, the frequency of exceeding 0.1 µg/L per year (1996-2018), distinguishing
206 between years with authorized use and years after market withdrawal. The effective rainfall is shown
207 by the size of the symbol, as is the number of analyses per year.

208 For atrazine, the frequency of exceeding 0.1 µg/L was highest (near 20%) before the 1997
209 dose reduction and restriction to agricultural use only. For the first years shown, the number of
210 analyses was smaller than during the last decade, and it should be remembered that early
211 monitoring often favoured the potentially most affected sectors. Unfortunately, before 2003 no sales
212 data are available for comparing uses and the frequency of exceeding threshold values, which might
213 explain the strong reduction between 1996 and 2003, the year that atrazine use was halted. After
214 that date, the frequency further diminished in a significant, but not continuous, manner. In some
215 cases, the frequency of exceedance increased when the year was more humid than the preceding
216 one(s), such as 2012 vs. 2011, or 2016 vs. 2015). For more recent years and over 15 years after it was
217 taken off the market, atrazine continues to be quantified (>0.05%) in many aquifers, still with values
218 over 0.1 µg/L, regardless of whether all of a territory is considered, or just the water bodies with at
219 least 10% maize crops on surface. This presence in groundwater, notwithstanding no new input, was
220 demonstrated for several areas with differing hydrogeological contexts in France (Morvan et al. 2006;
221 Baran et al. 2007), but also in Germany (Tappe et al. 2002), Italy (Guzzela et al., 2005) Ireland
222 (McManus, 2014), Belgium (Hakoun et al., 2017) and Slovenia (Koroša et al., 2016), all countries
223 where atrazine use was forbidden at different dates. This time lag can be caused by several
224 phenomena that may be superimposed, of which we will discuss the three main ones, for atrazine
225 but also for other molecules that will be discussed hereafter. A fourth phenomenon could be the use

226 of residual stocks after the bans, but given the national scale and the long duration of the
227 observations, this hypothesis is not considered to be significant and will not be discussed hereafter.

228 The first of the three possible phenomena, the presence in groundwater where use was
229 stopped can be explained by a long transfer time of the substance through the soil and the
230 unsaturated and saturated zones that may take years or decades (Chen et al., 2019; Gourcy et al.
231 2009; Gutierrez and Baran, 2009). A transfer time is dependent upon hydrodynamic phenomena and
232 specific interactions between a molecule and soil/subsoil constituents. For atrazine in the
233 unsaturated zone of till materials, retardation was observed and attributed to sorption (Helmke et
234 al., 2005). Long-term atrazine storage in a karst aquifer (Chalk) was found 20 years after
235 discontinuing its use, due to slow transfer through the matrix (Hillebrand et al. 2014) and the
236 heterogeneity of atrazine percolation through matrix and fractures in the unsaturated zone of a
237 chalky aquifer was demonstrated (Chen et al., 2019b). For an unconfined chalky aquifer, a correlation
238 between water-level fluctuations and atrazine concentration was observed even several years after
239 market withdrawal (Hakoun et al., 2017).

240 A second phenomenon that might explain atrazine presence in groundwater several years
241 after the last applications, is the possible remobilization of atrazine from the soil during several
242 decades. In fact, the analysis of solid samples from a lysimeter (Jablonowski et al., 2009), or from an
243 agricultural parcel (Vonberg et al. 2014) has shown the persistence of the mother-molecule in soil for
244 over 20 years after its last application and its possible leaching. Similarly, Caprile et al. (2017)
245 detected atrazine in all lysimeter-drainage up to three years after its application raising questions
246 about a possible increase in groundwater contamination due to the persistence of atrazine, several
247 years after its last application.

248 Finally, a third phenomenon that could explain this persistence of atrazine in groundwater
249 long after its last use, is that the molecule degrades very slowly in the saturated zone. In alluvial-
250 deposits and fluvioglacial sediments, degradation is very slow (Guzzella et al., 2005). For different

251 aquifer materials, laboratory experiments under saturated and stagnant-water conditions showed
252 that atrazine degradation was limited, with an estimated half-life of 206 to 710 days (Schwab et al.
253 2006). A lag effect on atrazine degradation or terbuthylazine aging in aquifer sediment, probably
254 attributable to low sorption, was demonstrated as well (Johannesen and Aamand, 2003). Low to no
255 atrazine mineralization was observed under different redox conditions (Larsen and Aamand, 2001).
256 Working on groundwater samples collected in seven observation wells and a spring-water sample
257 from the same sandy aquifer, doped at a low dose (1 µg/L), atrazine (and isoproturon) had become
258 mineralized (>14% and 21-58%, respectively) after 385 days in one of the wells (Janniche et al.,
259 2012).

260 For terbuthylazine, (Fig. 1), whether for data covering all of France, or concerning only water
261 bodies overlain by ground covered with at least 2% grapevines, the frequency of exceeding the
262 0.1 µg/L threshold was highest in 1997-1998, before its market withdrawal. For these years, as for
263 atrazine, the number of analyses was rather small, and it is possible such research was restricted to
264 areas where the molecule was expected. Since 1998, this frequency of exceedance shows an overall
265 decrease, but cannot be compared with sales figures, which are unavailable. However, for the years
266 2001 and 2004 and areas covered by >2% grapevines, the frequency slightly increased; both years
267 followed years with more rainfall than before. The overall frequency decrease was quite marked
268 between 1998 and 2005, after which it slowed down. The frequency of exceedance, for the last years
269 and since moratorium on its use in 2003, was around 0.05% nation-wide and 0.2-0.6% for areas with
270 vineyards. As expected in view of the relatively specific, though not exclusive, use on grapevines, the
271 calculated frequency of exceedance is clearly higher when only water bodies below vineyards are
272 considered, *versus* all French data.

273 As for atrazine, several factors can explain such occurrences several years after use was
274 halted. A recent review of terbuthylazine showed that studies of its occurrence are limited, especially
275 for groundwater (Tasca et al., 2018), thus limiting the possibilities for comparing our results with
276 other studies. Based on a lysimeter experiment (1 m² surface area, 2 m depth), it was shown that

277 terbuthylazine was not detected in leachates, but that 743 days after its application, it could still be
278 quantified in the first 30 cm of soil (Schuhmann et al., 2019). The hypothesis of a remobilization from
279 soil is plausible, but may be limited. However, it was shown by other experiments on soil lysimeters
280 that increasing the time between substance application and the first rain reduces the leached flux
281 (Milan et al., 2015); they also showed that, between years, reducing the leached water volume
282 reduces the terbuthylazine flux. Concerning degradation, biodegradation of terbuthylazine was
283 demonstrated by an autochthonous bacterial community in groundwater microcosms, but for high
284 concentrations (100 mg/L), the high residual concentration at the end of the experiment raises the
285 question of whether degradation will be significant at low environmental concentrations (Barra
286 Caracciolo et al. 2010). Moreover, no mineralization of terbuthylazine was observed in Chalk
287 (Kristensen et al., 2001).

288

289 3.1.2. Herbicides of the chloroacetamides class used on maize

290 Figure 2 shows for acetochlor, metolachlor and dimethenamid—for France as a whole and for
291 groundwater bodies with at least 10% of their surface covered by maize crops—the number of cases
292 where the 0.1 µg/L value is exceeded. It distinguishes years with authorized use from those after
293 withdrawal of the molecule from the market (the case of acetochlor) and also considering effective
294 rainfall. For the three molecules, the low number of analyses at the start of monitoring can explain
295 the high frequencies of exceedance, the research being possibly targeted in “critical” areas. For all
296 three molecules, sales data were available for the period 2008-2018 (Fig. 3). It is likely that the 2013
297 market withdrawal of acetochlor caused increased sales and use of dimethenamid and metolachlor
298 (Fig. 3).

299 For the three molecules, a general relationship exists between quantities sold and frequency
300 of exceedance (Fig. 3). The greater frequencies of exceedance of metolachlor compared to other
301 molecules of the same class are probably related to greater applied quantities at the national scale,
302 but also to a higher GUS index (Table 1) indicating a higher mobility toward groundwater.

303 In detail, between 2008 and 2012, acetochlor sales increased by about 10%, the frequency of
304 exceedance increasing 3-fold (Fig. 3). In 2012 and 2013, the conjunction between a possibly greater
305 use related to using up existing stocks before market withdrawal and a higher effective rainfall
306 (414 and 524 mm in 2012 and 2013 respectively), might explain the increase in frequency of
307 exceedance compared to 2011. After 2013, this frequency of exceedance strongly decreased,
308 indicating that the substance reached groundwater less frequently, which is consistent with a
309 moratorium on use even though the quantification work did not stop entirely. The highest
310 frequencies of exceedance of dimethenamid correspond to the year with highest sales (2013 to
311 2018), *versus* a group of points corresponding to the years 2008 to 2012. Metolachlor sales increased
312 by 30% between 2012 and 2014, but a smaller increase was noted since 2008. Generally speaking,
313 the frequency of exceedance correlates with sales for the period 2008-2016, but 2017 and 2018 do
314 not follow this trend. Several hypotheses may explain the difference between these two years.
315 Effective rainfall is considered at the scale of a year, but a different distribution of precipitation over
316 the year may cause different leaching patterns. In addition, the available data concern sales and not
317 real applications, which can be different. Despite the large sales and relatively high rainfall, 2018 had
318 a rather low frequency of exceedance compared to the overall trend. This may be explained by two
319 factors: the sales may have been greater because of an impending change in taxation, applications
320 not necessarily following sales. Or, in view of the presence of metolachlor metabolites in
321 groundwater, major stewardship actions may have affected the use of the active substance, such as
322 dose reduction, no application in certain sectors, etc.

323 In addition to sales, it is clear that the climatic context as represented by effective rainfall,
324 also plays a major role in the frequency of exceedances, as shown by comparing two years with
325 similar sales volumes but different rainfall volumes. For instance for dimethenamid, the high
326 effective rainfall of 2013 (524 mm) might explain the frequency that was slightly higher than in 2014,
327 2015 and 2016, despite lower sales. For metolachlor, for comparable sales between 2009 and 2012,
328 the frequency of exceedance was higher for 2012, which also had a higher effective rainfall

329 (414 mm). In 2010, however, with a similar effective rainfall to that of 2012, the frequency of
330 exceedance was smaller. For quite similar sales figures, 2017 (rather dry year at 309 mm) had a lower
331 frequency of exceedance than 2016, more humid at 444 mm. This relation between amount of
332 precipitation and transfer through soil had already been demonstrated by local studies for acetochlor
333 (Newcombe et al., 2005).

334 Regarding the three phenomena discussed above that could explain the persistence of an
335 active substance in groundwater (remobilization, delayed transfer time and no degradation in
336 saturated zone), information on the behaviour and transfer of dimethenamid to groundwater is rare.
337 It is not detected in the Chalk aquifers of England and France, but it is observed in New Zealand, the
338 small doses sometimes being advanced as a factor for explaining the low detection (Lapworth et al.,
339 2015; Moreau et al., 2019).

340 The persistence of acetochlor in groundwater after its withdrawal could be due to a possible
341 remobilization as acetochlor was still detected in soils 344 days after application (Baran et al., 2004),
342 in lysimeter leachates up to nine years after its last application (Caprile et al., 2017) or in drainage
343 networks over three months (Woodward et al. 2019). A remobilization of metolachlor from soil is
344 likely to occur, as demonstrated by its detection in lysimeter leachates up to three years after an
345 application (Schuhmann et al., 2019). Rainfall characteristics might explain inter-annual differences
346 of the results.

347 Concerning transfer in the unsaturated zone below soil, for four geological materials, the
348 adsorption of acetochlor is limited or non-measurable for limestone (Janniche et al. (2010).
349 Concerning the transfer time of metolachlor in the unsaturated zone, it was shown that a lag effect is
350 possible for fluvioglacial deposits (Sidoli et al., 2016; 2020), or for alluvial aquifer (Baran and Gourcy,
351 2013), because of interactions between the molecule and the solid matrix. Based on the multi-year
352 monitoring of seven sites, it was shown that the presence of metolachlor in groundwater is limited,
353 in particular because of degradation (Rose et al., 2018). However, the data also show that there are

354 site-specific alterations to metolachlor's fate, related to climate, soil type, and hydrologic
355 characteristics.

356 Regarding degradation in the saturated zone, no acetochlor degradation was found over a
357 period of two years in 14 aquifer sediments, but in five other sediment samples, acetochlor had an
358 estimated half-life of 9 to 19 years (Janniche et al., 2010). They state that this mineralization can
359 occur under both anaerobic and aerobic conditions. Working on groundwater samples from seven
360 observation wells and from a spring in a sandy aquifer, and using quartz sand as substratum, no
361 acetochlor mineralization was found after 385 days (Janniche et al., 2012). As far as we know, no
362 work has been done on geological material from the saturated zone, for evaluating the degradation
363 of metolachlor within an aquifer.

364

365 3.1.3. The case of substituted ureas on wheat: isoproturon and chlortoluron

366 Whether for chlortoluron or isoproturon during the period 1996-2018 (Fig. 4), the data from
367 France as a whole as well as from areas where water bodies are overlain by at least 10% wheat-crop
368 surfaces, show similar trends for a given molecule in the frequency of exceeding the 0.1 µg/L
369 threshold, though the frequency is higher for the second. Considering sales volumes for the period
370 2008-2018 in addition to the effective rainfall, the importance of climatic context was confirmed for
371 both molecules (Fig. 3B). In the case of isoproturon, for 2010, 2013 and 2016 with similar sales, the
372 frequencies of exceedance were higher for the wettest year (2013); the same is true for the years
373 2014 and 2011. For chlortoluron, for 2012 and 2013 with similar sales figures, the frequencies of
374 exceedance were higher for the wetter year (2013) as was observed for other molecules. Similarly,
375 even though the chlortoluron sales figures for 2009 and 2011 were higher than those for 2008, the
376 frequency of exceedance was higher for the wettest year (2008). Year 2017 stands out for its high
377 frequency with respect to rainfall and sales. The two molecules isoproturon and chlortoluron have a
378 similar leaching profile with a GUS index of 2.6 and quite similar sales figures compared to other
379 active substances; in this respect, it should be stressed that since 2004 only one or the other

380 substance can be applied on a plot during a single year. Study of the entire dataset, however, does
381 not show a clear structural trend as was seen for chloroacetamides, and other factors should be
382 considered. Herbicides for wheat can be bought for application during sprouting, but are also used
383 during tillering if required by the conditions. This means that application can take place under quite
384 different climatic conditions and it is known that delay between application and significant rainfall
385 events impacted the leaching flux of these two molecules (Walker et al., 2005) though differently
386 according to the type of molecule studied and the application periods (Nolan et al. 2008). Detailed
387 examination of rainfall distribution during a year may explain the observed differences, especially as
388 application periods can differ strongly from one year to the next, varying from spring to autumn.

389 Regarding transfer time into groundwater, five-year monitoring in a Chalk aquifer showed
390 that isoproturon and chlortoluron occurrence in shallow groundwater correlates with application,
391 and that concentrations in samples collected during periods of inflow are higher than those in native
392 groundwater samples, suggesting rapid infiltration (Goody et al., 2001). Experiments with
393 reconstituted columns of saturated glaciofluvial sediment and of gravel from an aquifer, showed that
394 isoproturon was adsorbed with a lag effect similar to that of bromide. This was likely due to
395 interaction with organic matter in the matrix and with mineral surfaces (Tuxen et al., 2000). Despite
396 possible rapid transfer, a lag effect in transfer to the aquifer was also observed in some cases.

397 Concerning the persistence of isoproturon in groundwater, Larsen and Aamand (2001) noted
398 little or no mineralization of isoproturon under different redox conditions, suggesting that the
399 degradation could be co-metabolic and that it could not have been started by microorganisms
400 because of a low organic carbon content. After a lag phase, a mineralization of isoproturon (less than
401 5% after 258 days) occurred in Chalk, with large variations in both rate and extent (Kristensen et al.,
402 2001). Working on groundwater samples from seven observation wells and a spring in an aquifer
403 with a quartz-sand substrate, isoproturon at relatively low grades of around 1 µg/L was mineralized
404 in water from one of the wells (21-58% after 385 d) and in the spring water (25–41%) (Janniche et al.,
405 2012).

406 For the various molecules studied that belong to different chemical classes (triazines,
407 chloroacetamides and substituted ureas), variations in sales figures—that may become zero after
408 withdrawal from the market—and variations in effective annual rainfall, partly explain the variability
409 in frequencies of exceeding the value 0.1 µg/L.

410

411 3.2. Transfer paths: the impact of hydrogeology

412 3.2.1 Studying distribution patterns at a monthly scale

413 The apparent relation between frequency of exceedance and annual effective rainfall
414 indicates that, even though we studied groundwater—generally implying long transfer times—rather
415 than surface water, relatively rapid transfer can occur from surface to aquifer in the weeks after
416 applying an active substance. We studied the distribution of frequencies of exceedance at a monthly
417 scale, selecting water bodies with an overlying crop of interest. For molecules whose use changed
418 over time, we also distinguished between years with a reduction in authorized use, or pre- and post-
419 withdrawal years.

420 For atrazine and terbuthylazine that were withdrawn from use in mid-2003 and mid-2004,
421 respectively, study of the monthly distribution distinguished the years with and without use (Fig. 5).
422 For acetochlor, the distinction was made since 2000 (market entry), and before and after 2013 (final
423 use of remaining stocks) (Fig. 5). In addition to the fact that the frequencies of exceedance decreased
424 after the moratorium on use, the monthly detection patterns varied for atrazine, terbuthylazine and
425 acetochlor during and after their periods of use.

426 For atrazine before 2003, the frequency of exceedance increased from April to August
427 following the application periods for maize (during sprouting), but also during autumn when aquifer
428 recharge restarted, resulting in a frequency of exceedance during November that was close to that of
429 the application periods. After 2003, the frequencies of exceedance no longer showed this seasonal
430 variation. For terbuthylazine, during the years of use, the frequencies of exceedance generally

431 increased from March till July, during weeding of the vineyards. After market withdrawal, the
432 frequency of exceedance was relatively stable throughout the year and much lower than before.

433 Acetochlor was applied when maize was sprouting (March-May). As for atrazine, the monthly
434 distribution of frequencies of exceedance was different during the years of use (2000-2013) and
435 without use (>2013). During years of use, the frequencies were highest in June, related to the
436 application periods, and increased again in autumn and early winter to reach a maximum in
437 February, related to recharge. After market withdrawal, the frequencies of exceedance decreased
438 and no longer showed the earlier seasonality and range of variations, with whole months without
439 exceedance.

440 These examples, covering two chemical classes (triazines, chloroacetamides) for which use
441 was forbidden several years ago, confirm that rapid transfer can occur from soil to aquifer in
442 connection with application periods and that this partially contributes during the year to exceeding
443 the 0.1 µg/L value.

444 For substituted ureas (Fig. 6, chlortoluron and isoproturon), still used but with dose
445 restrictions since 2004, the frequencies of exceedance are higher in the November-January and
446 February-March periods, corresponding to two potential application periods (early autumn or winter
447 / sprouting or tillering of wheat) and aquifer recharge. This was more obvious before dose
448 restrictions, but is still visible. Distribution patterns of these molecules, whose applications are at
449 different periods than those of the three discussed above, also suggest rapid transfer to groundwater
450 related to application periods and to leaching during aquifer recharge.

451 For metolachlor (Fig. 7), the applications on maize during sprouting (March to May) explain
452 the increase in frequencies of exceedance during springtime until August. The other increase in such
453 frequencies (November-January) is concomitant with aquifer recharge from winter rains. For a fluvio-
454 alluvial aquifer, monthly monitoring has shown that metolachlor could be quantified in groundwater
455 in the weeks after its application, but also when recharge began again (Baran and Gourcy, 2013). For

456 dimethenamid (Fig. 7), this temporal structuring is much less clear, doubtlessly because of the much
457 lower number of cases when the 0.1 µg/L value was exceeded.

458 Regardless of the situation (chemical class, moratorium on use, dose reduction or no major
459 change, and application date), the monthly distribution of frequencies of exceedance shows that
460 rapid transfer to groundwater during the application period is possible. For certain molecules, a
461 higher frequency of exceedance also exists outside the application periods, related to increased
462 aquifer recharge during autumnal rains (in France) and provided the molecule remains ready to be
463 mobilized.

464

465 3.2.2. Transfer affected by lithology

466 Hereafter, we examine the frequencies of exceedance by aquifer lithology in more detail, in
467 order better to understand the transfer dynamics of the various molecules. None of the volcanic-rock
468 aquifers were concerned by exceeding any of the reference values for the investigated molecules, a
469 fact that may relate to a limited number of analyses as such rocks cover only a small part of France.

470 a) Transfer patterns observed for chloroacetamides

471 For chloroacetamides (Fig. 8), we see that exceedance of the 0.1 µg/L value does not
472 necessarily concern the same aquifer types. For acetochlor (Fig. 8) over the years when this molecule
473 was used, frequencies of exceedance were observed for three types of aquifer, with different
474 seasonal effects. For basement-rock aquifers, even though the number of analyses is smaller than for
475 the other lithologies, we see exceedance throughout the year. The strongest ones, in June and
476 August, close to the application period, are also seen in alluvial and sedimentary aquifers. The latter,
477 however, are not or little impacted during the rest of the year. In February, the frequency of
478 exceedance is highest and only concerns the basement aquifers.

479 For metolachlor (applied to maize during the period 1996-2018, Fig. 8), the analyses mainly
480 covered alluvial aquifers, mostly in sedimentary and basement environments. Most exceedance

481 occurred in sedimentary formations and alluvial aquifers. In contrast to acetochlor, basement
482 aquifers are thus of less concern. Dimethenamid (Fig. 8) shows an intermediate situation to both
483 preceding substances, with basement-rock aquifers tending toward exceedance especially in
484 February and December, alluvial aquifers during spring and summer, and sedimentary-rock aquifers
485 showing exceedance throughout the year and in particular in autumn.

486 Even though the three chloroacetamides do not have the same physico-chemical properties
487 (Table 1) and the quantities used nation-wide are different (though permitted levels per hectare are
488 comparable), the observed differences described above probably are also affected by different
489 regional contaminant pressures. Study of the sales figures by province (data not included here)
490 shows that in Brittany (mostly underlain by basement rock) the total sales for acetochlor and
491 metolachlor are comparable, whereas in most other French departments—and thus for different
492 lithologies—metolachlor sales generally are much higher than acetochlor.

493 **b) Transfer patterns observed for chlortoluron and isoproturon**

494 For chlortoluron and isoproturon over the period 2004-2016 and water bodies with over 10%
495 of their surface area covered in wheat crop (Fig. 9), most analyses concern sedimentary aquifers.
496 However, different types of aquifer contribute to the frequency of exceedance. For both molecules,
497 the increase in frequency of exceedance during autumn and winter essentially concerns sedimentary
498 aquifers for which recharge in France generally starts in early autumn and continues until March-
499 April, depending upon the year. However, a difference between the two molecules appears for
500 March and April. More local investigations show the importance of application dates, for instance
501 due to regional differences between sowing dates, that may explain why more aquifers are affected
502 by isoproturon than by chlortoluron during this period.

503 **c) Transfer patterns observed for triazines (atrazine and terbuthylazine)**

504 For atrazine, in water bodies with over 10% of surface area covered by maize crop during the
505 period 1997-2003 (Fig. 10A), exceedance mostly concerns alluvial and sedimentary aquifers, and to a

506 lesser extent basement ones. For alluvial and sedimentary domains, the frequencies of exceedance
507 are rather constant throughout the year, except for summer when the contribution from alluvial
508 aquifers is greater. For August, the smaller number of analyses in sedimentary aquifers might explain
509 this feature, but this is not the case for other months, such as July, which indicates that this temporal
510 variability is caused by aquifer type.

511 Finally, for terbuthylazine where the number of analyses is much smaller than for the other active
512 substances studied (Fig. 10B), we see a large variety of affected aquifer types, especially in folded-
513 rocks in which other molecules were not concerns. This is probably due to the fact that vineyards in
514 France have a strongly heterogeneous, mostly on slopes rather than in alluvial plains.

515 The different examples described here show that, for a given molecule, the temporal
516 variability of frequencies of exceeding 0.1 µg/L in groundwater depends upon the type of aquifer, but
517 that this distribution is also molecule-dependent. In addition to the physico-chemical properties of
518 molecules, we need more precise data on real substance use in order better to understand the
519 relative importance of the hydrogeological context and of a molecule in these observations. Such an
520 approach would have a greater regional/local interest, but depends upon the availability of data on
521 local-use.

522

523 4. Conclusions –

524 We analysed monitoring data on groundwater quality in France at a national scale over a period
525 of more than twenty years. This provided insight into the short- and medium-term impact of changes
526 in regulations governing pesticide use (withdrawal, dose reduction, or new marketing authorization),
527 on the frequency of exceeding the reference value of 0.1 µg/L. The persistent exceedance of
528 molecules in groundwater after withdrawal is probably related to a conjunction of several factors,
529 such as (1) limited degradation of active substances within the unsaturated and saturated zones; (2)
530 long transfer times in the unsaturated zone and a long residence time; and (3) the possible

531 remobilization of active substances from the unsaturated zone—especially soil—over periods that
532 may last several years. Each of these three phenomena was well documented for atrazine,
533 confirming their importance, but several reference data were lacking for other molecules.
534 Understanding of how molecules remobilize within the soil - and the unsaturated zone as a whole –
535 over the short- to long-term, thus needed improvement.

536 In this context, the climatic setting and the type of aquifer both play a role that is at least as
537 important as the use and properties of the molecules. Any evaluation of evolution trends should thus
538 consider the hydrodynamic context, at least in a qualitative sense, when comparing two non-
539 consecutive years. The examples discussed here illustrate the time lag between changes in
540 contaminant pressure and the impact on water quality, both at an annual scale and for shorter
541 periods, in particular during recharge. An understanding of this time lag is primordial for better
542 aquifer management, and especially for a more qualified assessment of action programmes and/or
543 recommendations for the marketing of active substances.

544 We showed that a long observation period is indispensable for interpreting and evaluating
545 the impact of management actions since there is a long - depending on hydrogeological context - lag
546 time between the implementation of measures and effects on groundwater quality. Withdrawing a
547 substance is not in itself a guarantee for a rapid groundwater quality improvement. An assessment of
548 the impacts of management actions or regulation changes should also consider the metabolites
549 related to the active substances of interest, provided there is sufficient available data.

550 Our work has also shown the remaining difficulties in data interpretation. Even though recent
551 dose reductions for, e.g., isoproturon and chlortoluron probably were beneficial in reducing
552 substance transfer to groundwater, it is difficult fully to appreciate their impact on current
553 concentrations just by working on data collected at a nation-wide scale. France can rely on a
554 remarkable database regarding groundwater quality, but more local data on actual use are necessary
555 for a reliable evaluation. Today, even though the national databases have been greatly enriched over

556 the past decade, for fully understanding the real impact of mitigation measures it is necessary to
557 collect, make available and cross-check new data. These spatialized data are particularly important
558 for active substances applied on crops that are unequally distributed throughout France, and it would
559 be pertinent to develop a similar approach that is aimed at a more local scale when data become
560 available. We showed that for such specific cases a national approach may be insufficient. A better
561 understanding of substance use, i.e. of the real quantities applied, would lead to even better results.

562 Despite these limitations, the data examined at a national scale have proven to be of great
563 value. They form a solid foundation for reforming long-term groundwater monitoring, in particular
564 when considering variations in context, such as contaminant pressure or aquifer type.

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571

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726 aquifer properties with molecular descriptors. *Journal of Hydrology*, 293: 191-204.

727

728 Figure captions

729

730 Figure 1: Frequency of exceeding the 0.1 µg/L value for atrazine (A) and terbuthylazine (C) at national
731 scale, and for groundwater bodies with a crop of interest: >10% maize for atrazine (B), >2%
732 grapevines for terbuthylazine (D). Number of analyses for the period 1996-2018. Circle size
733 proportional to effective rainfall. Hollow symbol corresponds to year with national authorization of
734 use; full symbol corresponds to year after molecule withdrawal.

735 Figure 2: Frequency of exceeding the 0.1 µg/L value for acetochlor (A), metolachlor (C) and
736 dimethenamid (E) at national scale, and for groundwater bodies with an overlying crop of interest
737 (>10% maize) (B-D-F right). Number of analyses for the period 1996-2018. Circle size proportional to
738 effective rainfall. Hollow symbol corresponds to year with national authorization of use; full symbol
739 corresponds to year after acetochlor withdrawal.

740 Figure 3: Sales vs. frequency of exceeding the 0.1 µg/L value at national scale for A: dimethenamid
741 (DMT), acetochlor (ACT) and metolachlor (MET); and B: isoproturon (IPU) and chlortoluron (CLT), per
742 year for the period 2008-2018. Circle size proportional to effective yearly rainfall.

743 Figure 4: Frequency of exceeding the 0.1 µg/L value for chlortoluron (A) and isoproturon (C) at
744 national scale, and for groundwater bodies with a crop of interest (>10% wheat) (B and D). Number
745 of analyses for the period 1996-2018. Circle size proportional to effective rainfall. Hollow symbol
746 corresponds to years before applied dose reduction; full symbol corresponds to year after applied
747 dose reduction.

748 Figure 5: Monthly distribution of frequency of exceeding 0.1 µg/L and number of analyses for years
749 with use (hollow symbol) and years after withdrawal (full symbol) for atrazine (A), terbuthylazine (B)
750 and acetochlor (C). Arrows correspond to potential application period (for years with authorized use)

751 Figure 6: Monthly distribution of frequency of exceeding 0.1 µg/L and number of analyses for years
752 before dose reduction (hollow symbol) and years after dose reduction (full symbol) for chlortoluron(
753 A) and isoproturon (B). Arrows correspond to the potential period of application.

754 Figure 7: Monthly distribution of frequency of exceeding 0.1 µg/L and number of analyses for
755 metolachlor (A) and dimethenamid (B). Arrows correspond to the potential period of application.

756 Figure 8: Monthly frequency of exceeding 0.1 µg/L. Period of: A) acetochlor use 2000-2013, B)
757 metolachlor use 1996-2018, and C) dimethenamid use 1996-2018. Number of analyses per type of
758 aquifer (groundwater bodies with maize over >10% of the area).

759 Figure 9: Monthly frequency of exceeding 0.1 µg/L of chlortoluron (A) and isoproturon (B) and
760 number of analyses per type of aquifer. Period 1996-2018 and groundwater bodies with wheat crop
761 >10% of the area.

762 Figure 10: (A) Monthly frequency of exceeding 0.1 µg/L of atrazine and number of analyses per type
763 of aquifer (period 1996-2003 and groundwater bodies with maize crop >10% of the area). (B)
764 Monthly frequency of exceeding 0.1 µg/L of terbuthylazine and number of analyses per type of
765 aquifer (period 1996-2004 and groundwater bodies with grape vines >2% of the area).

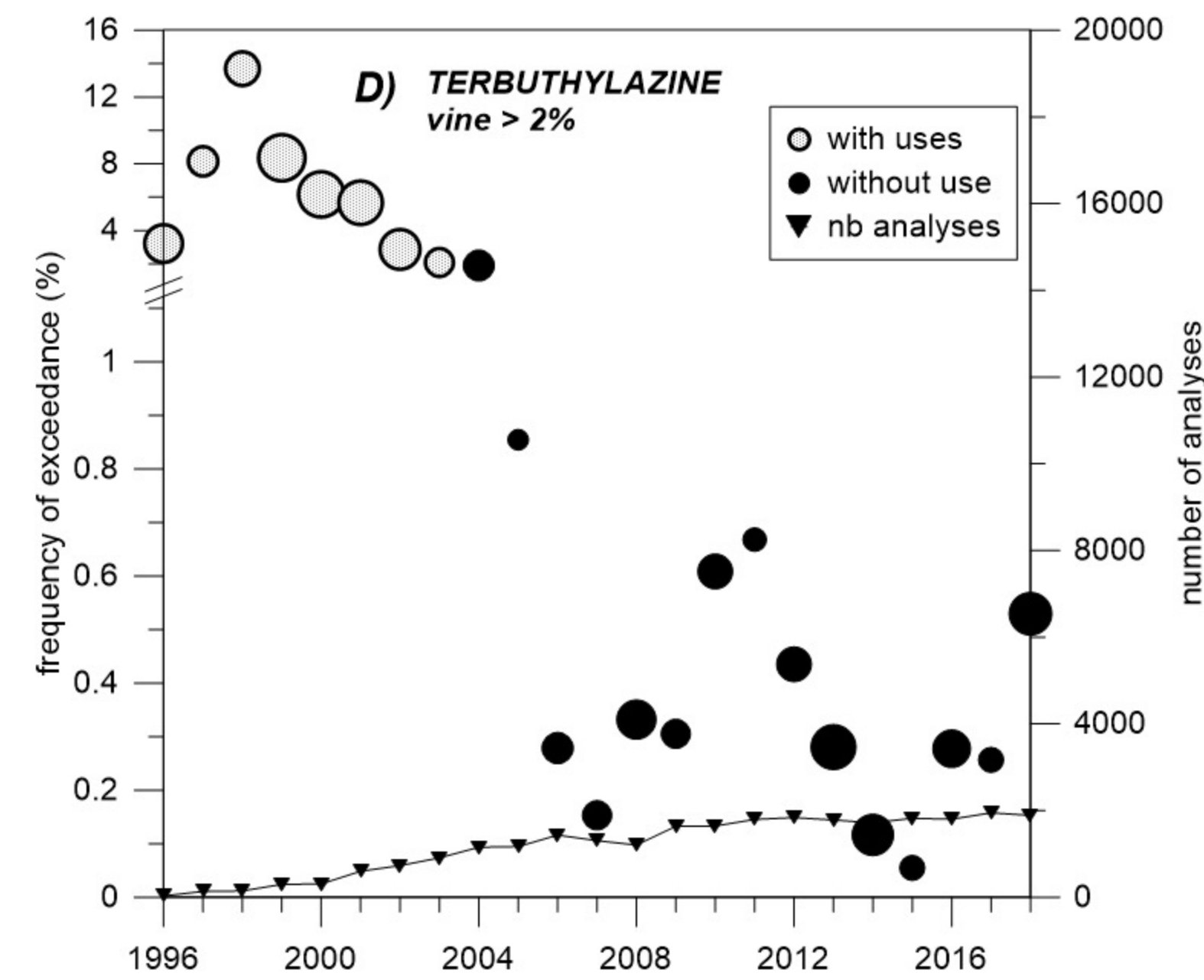
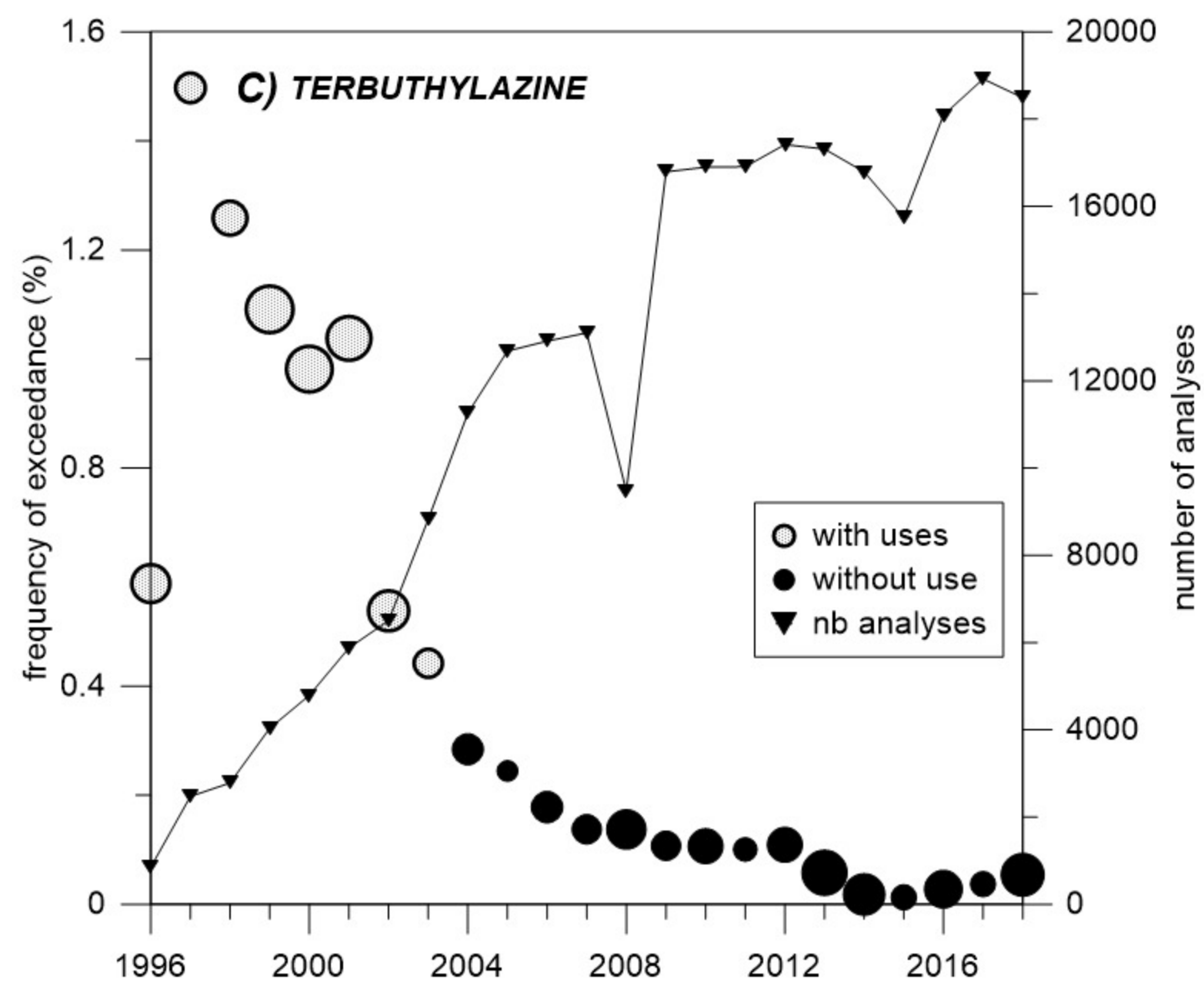
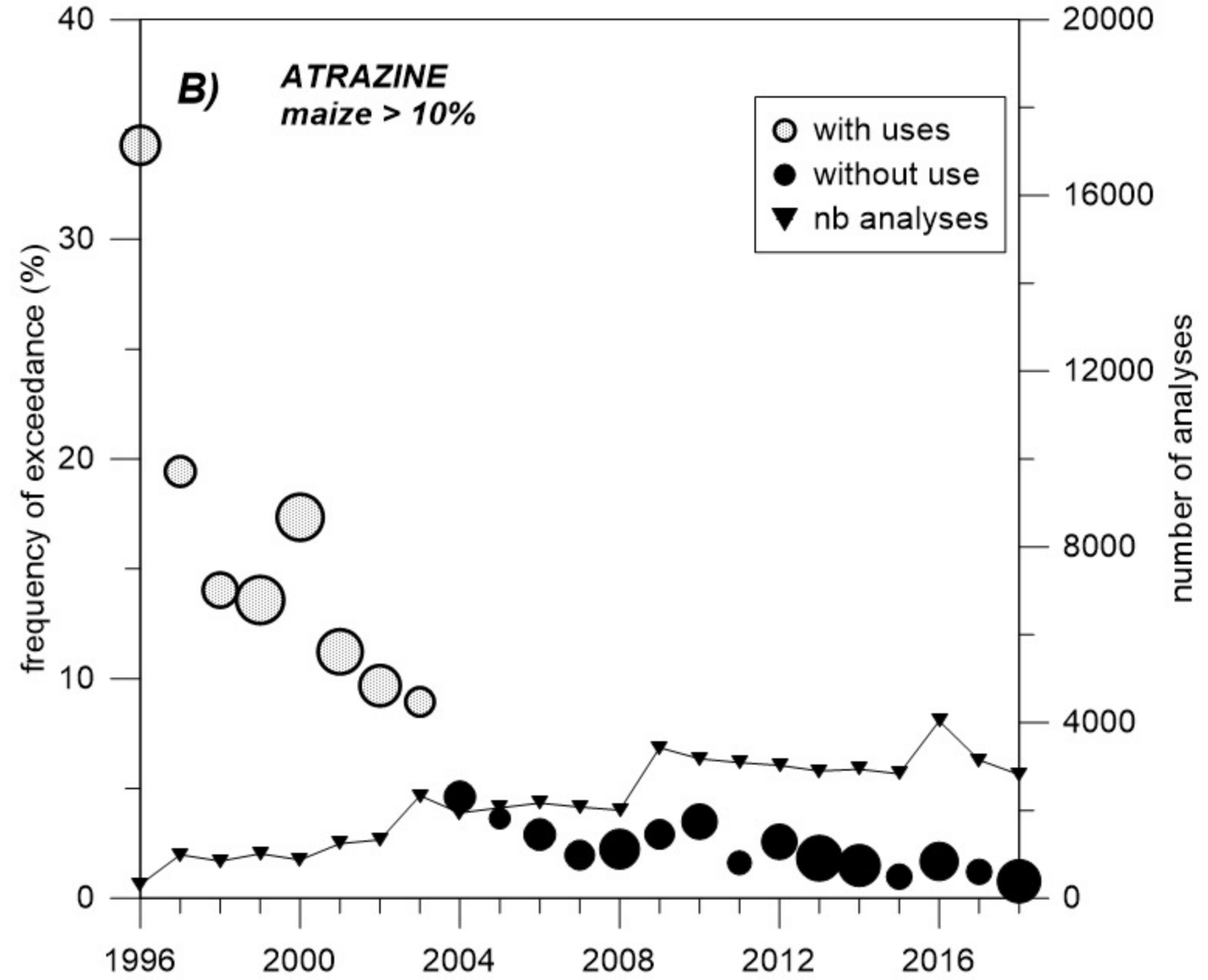
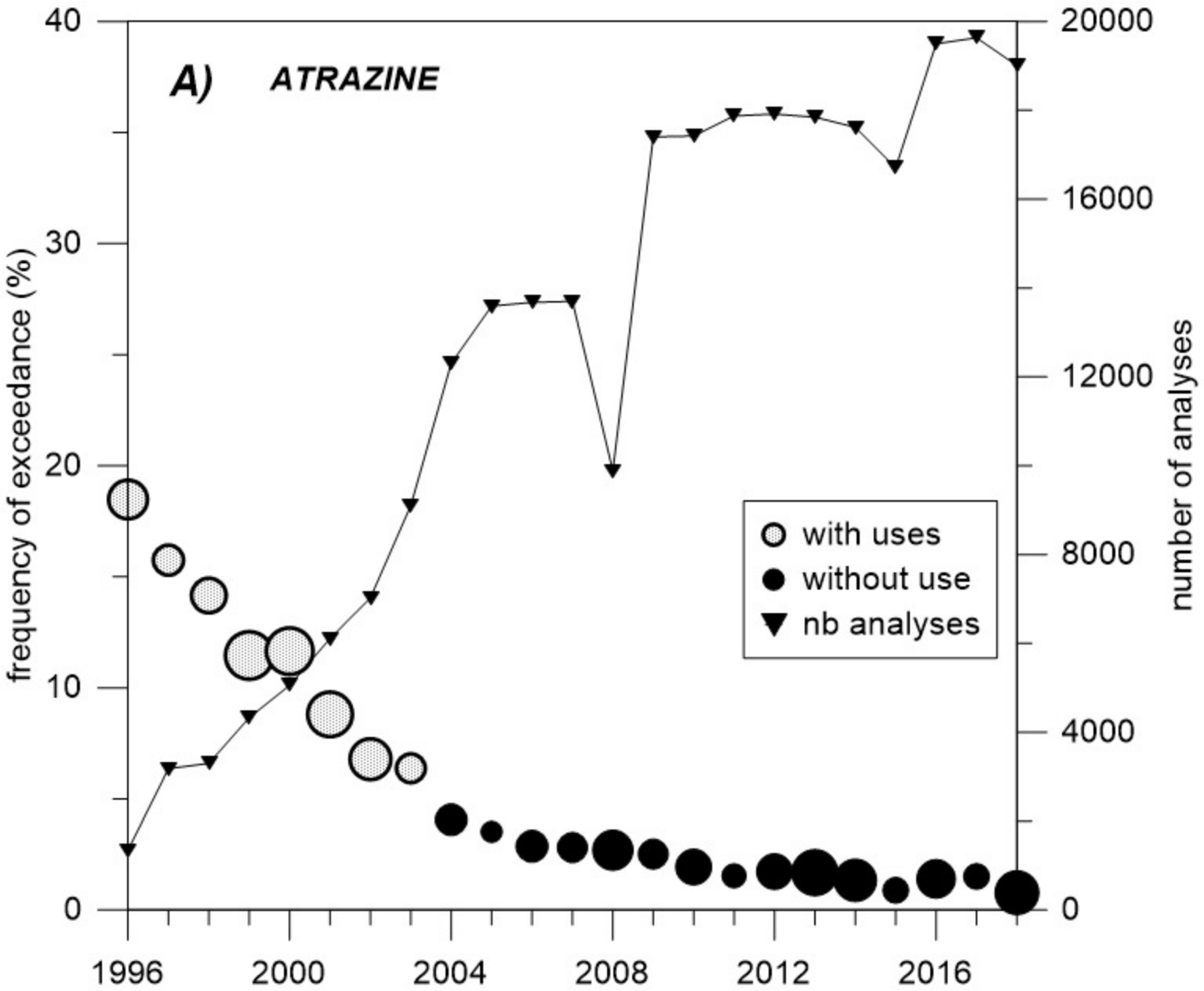
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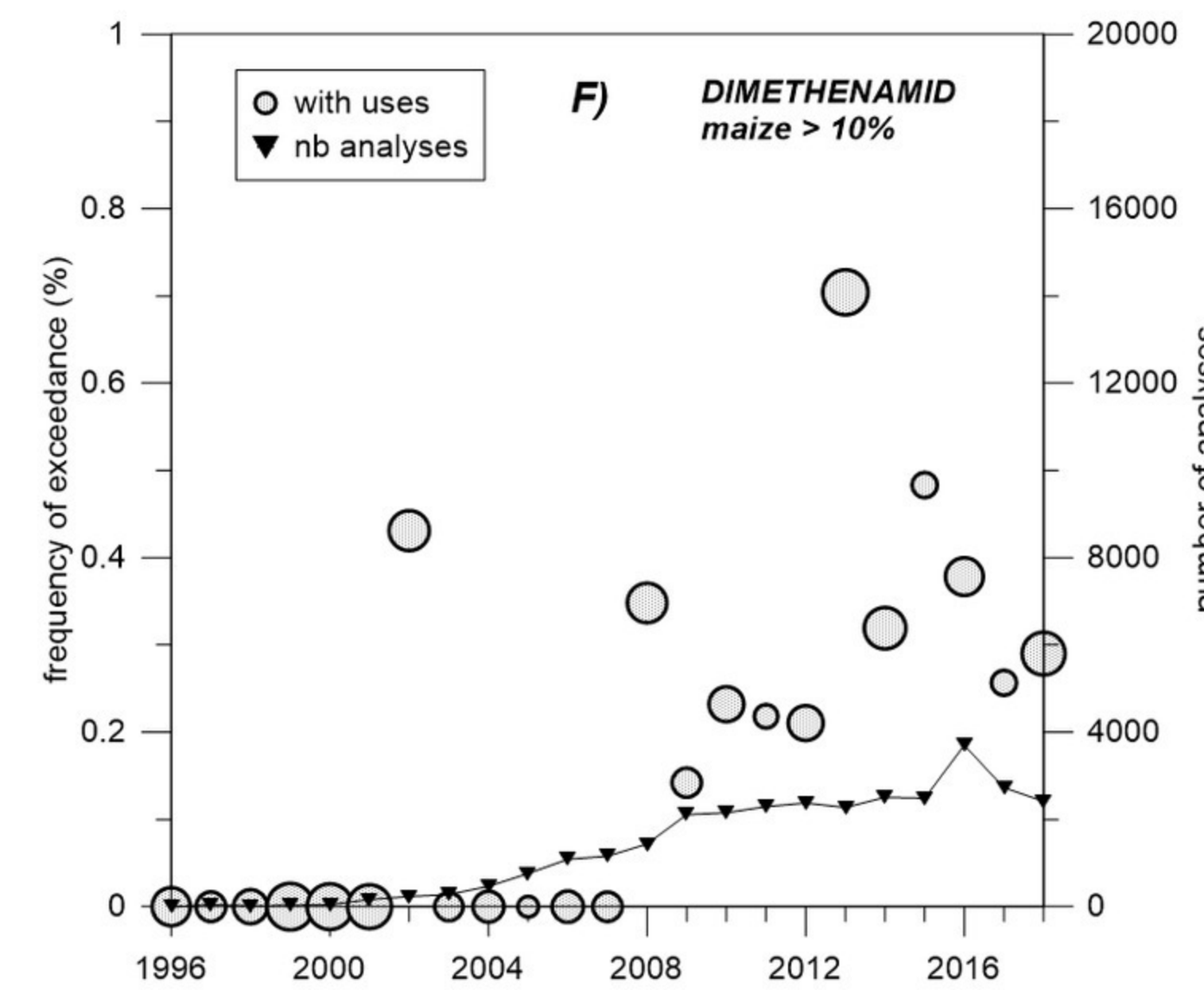
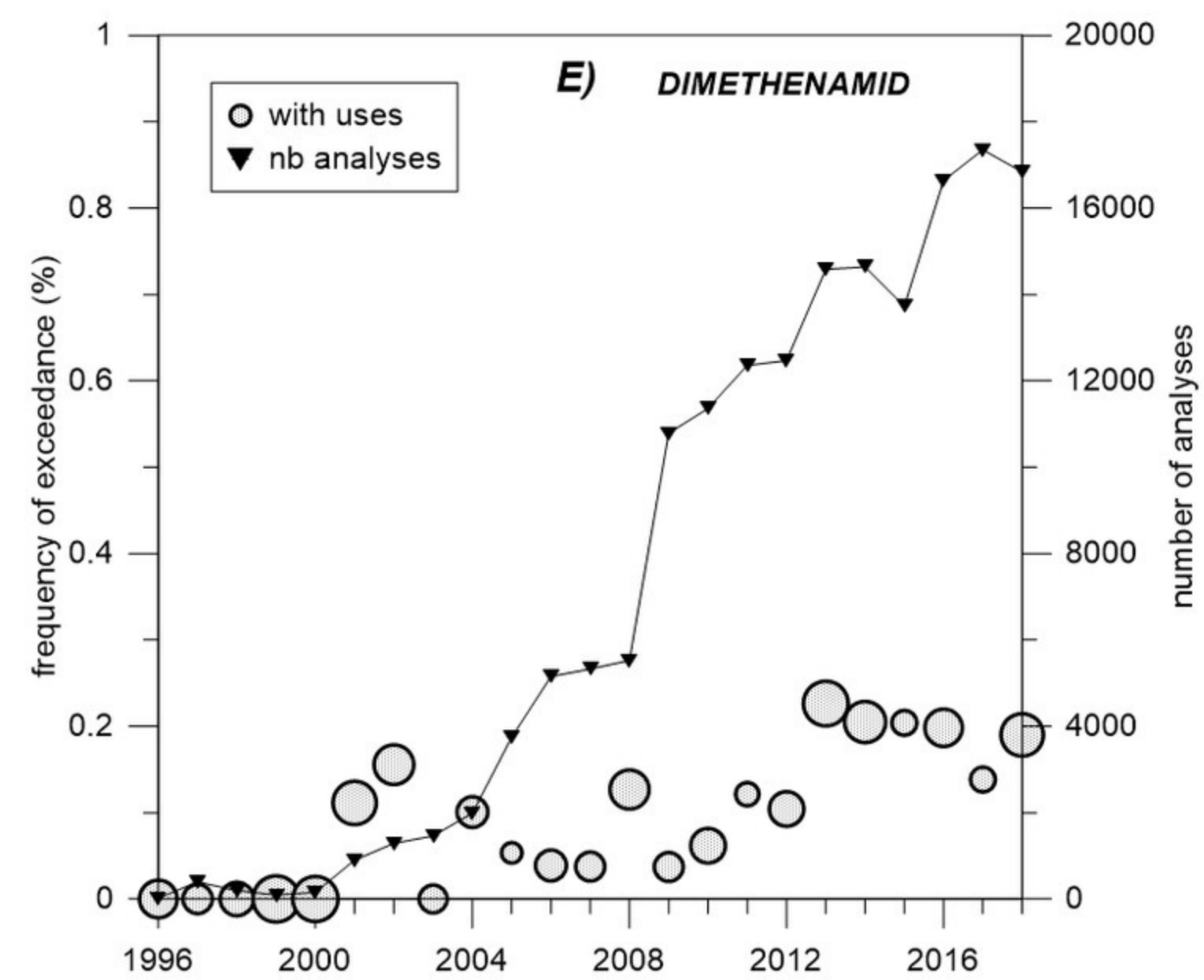
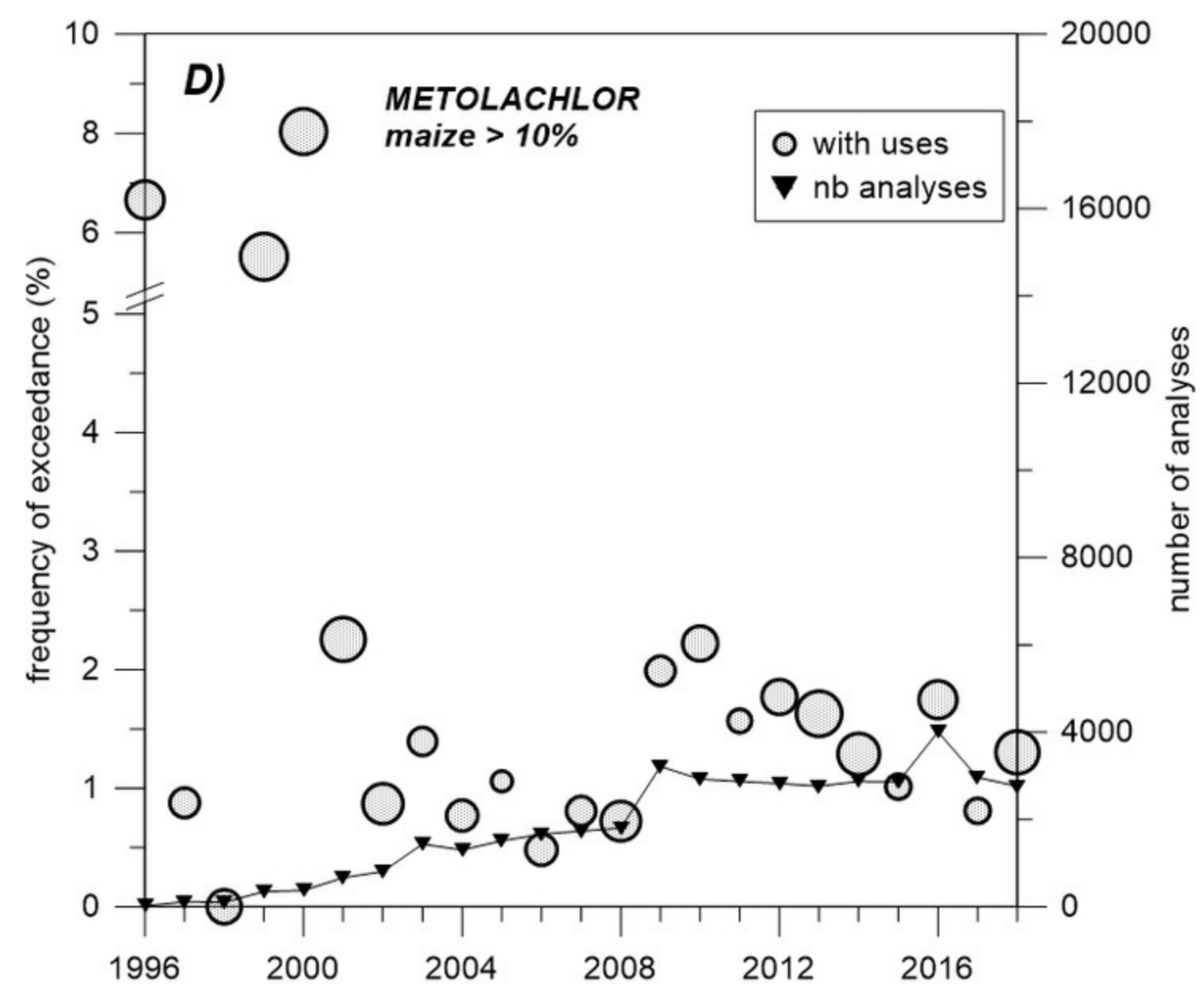
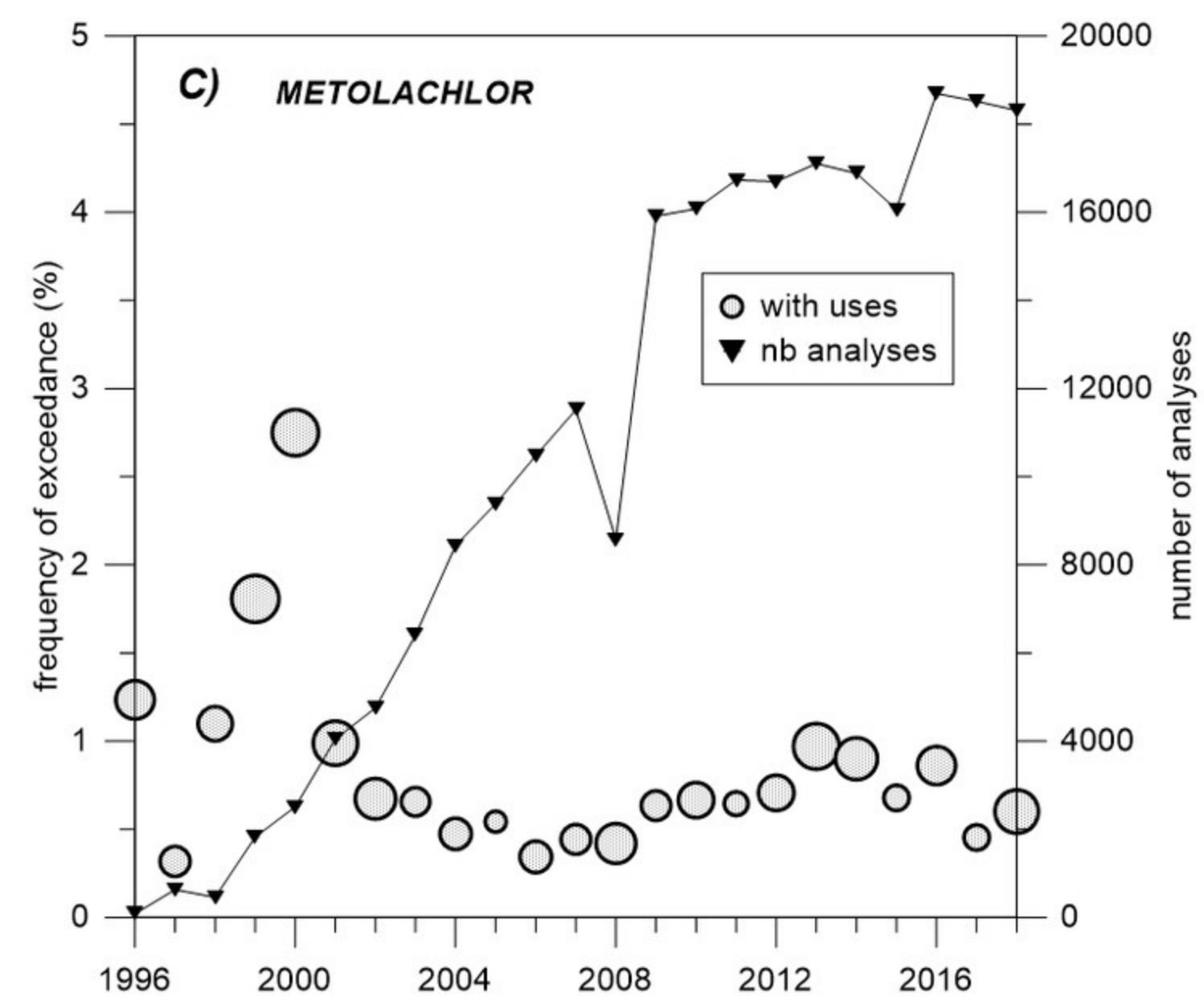
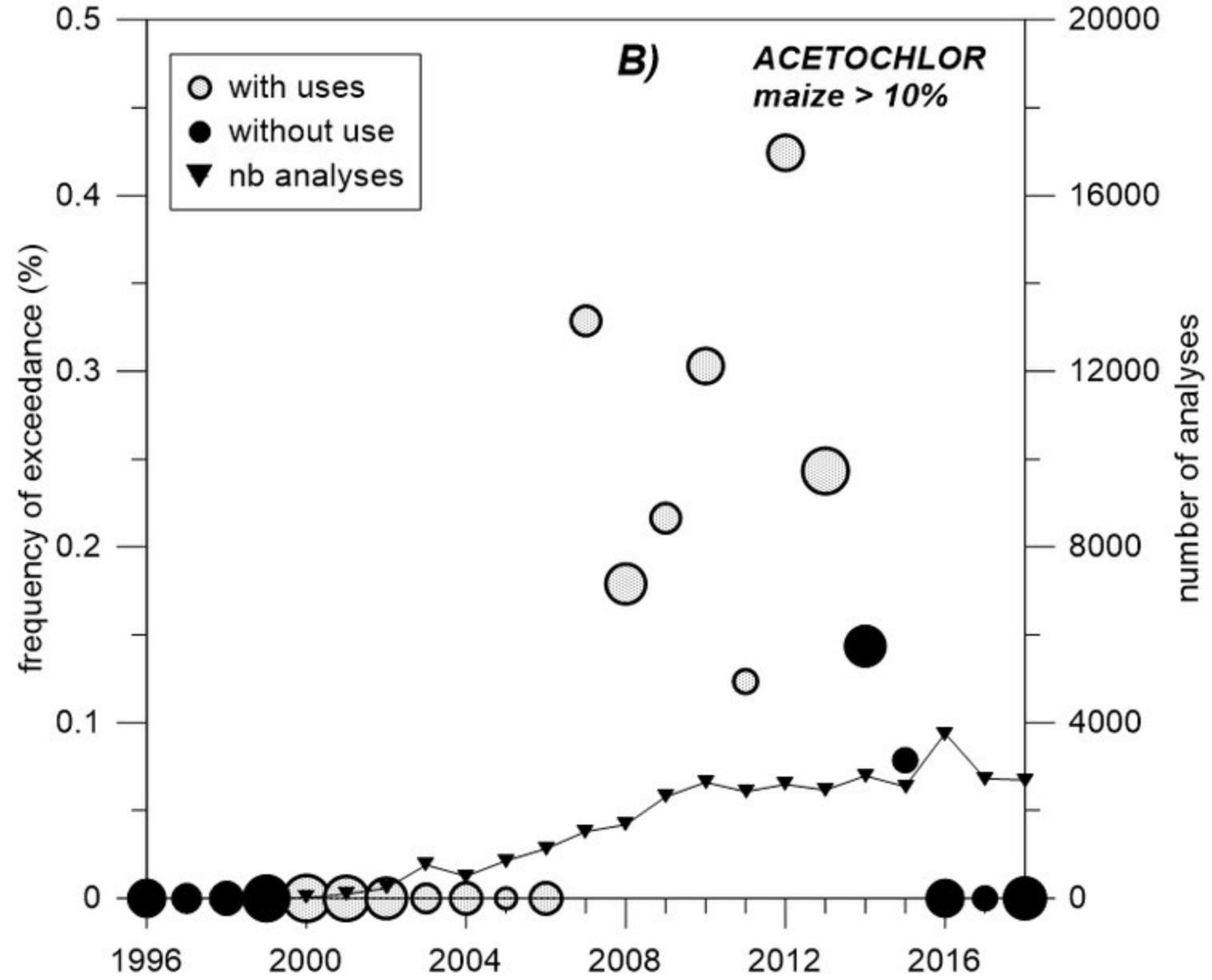
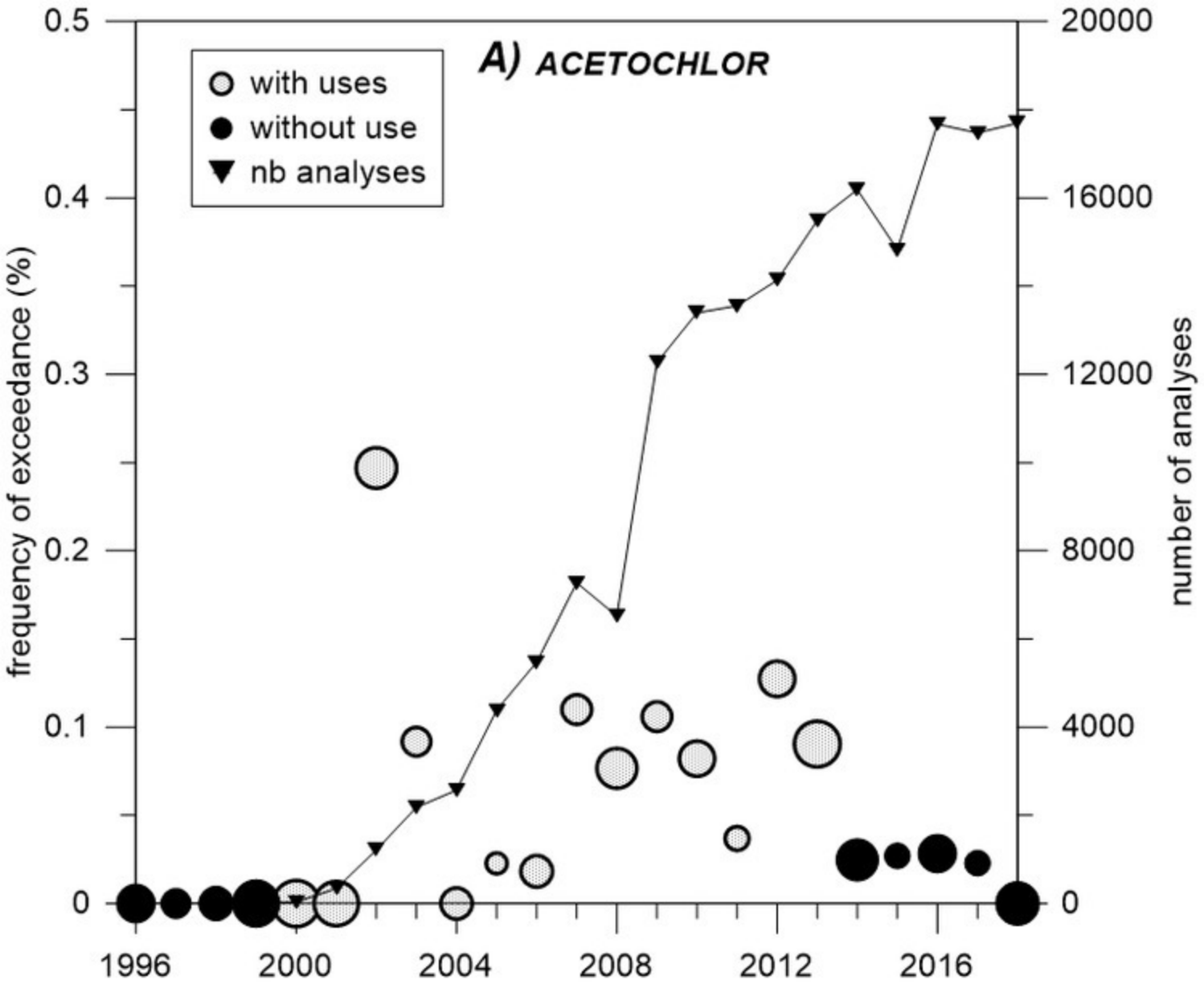
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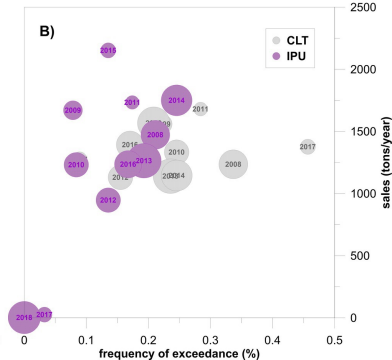
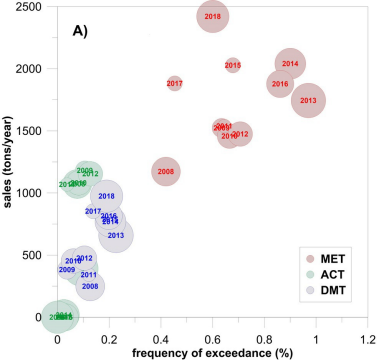
768 **Table caption**

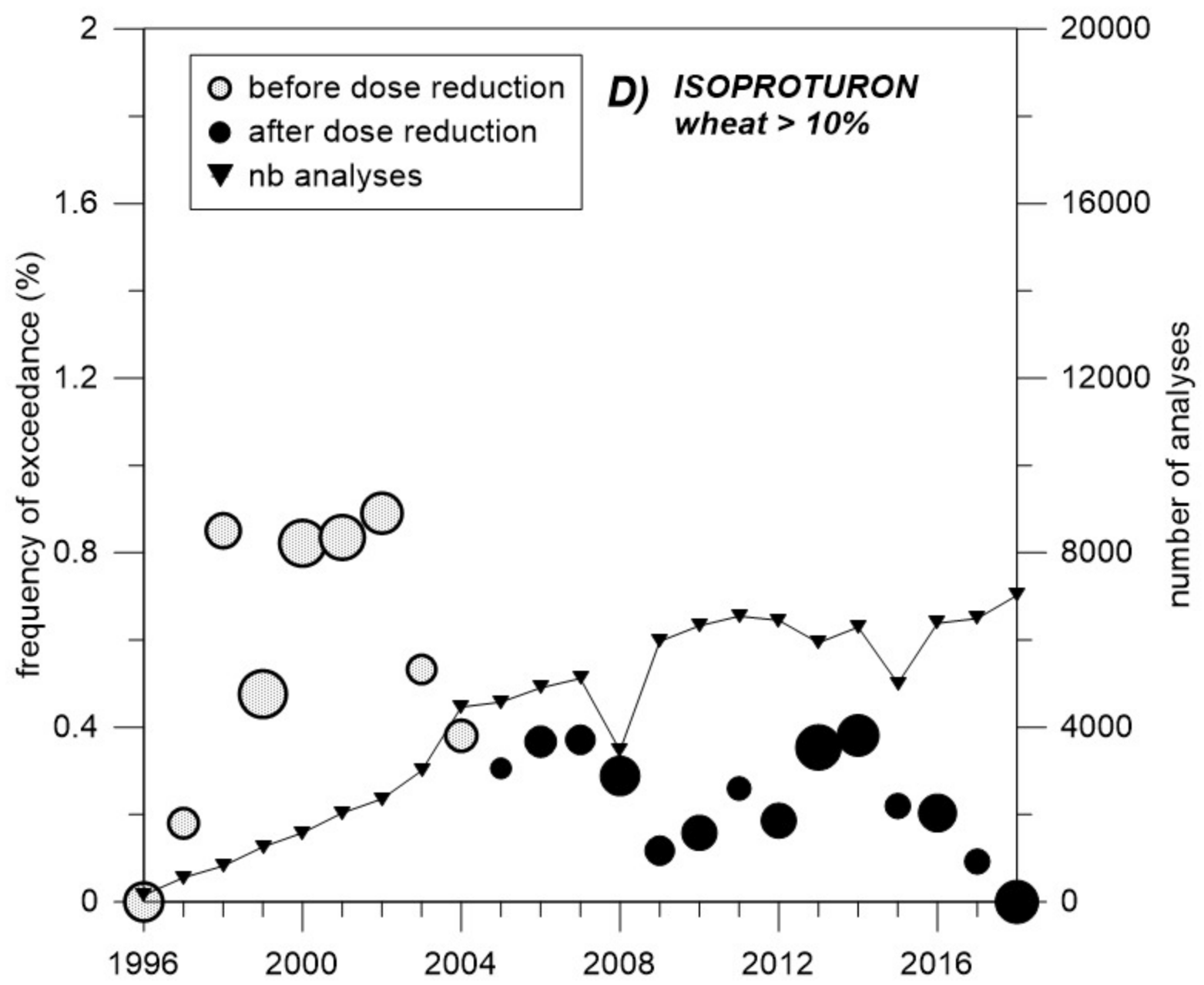
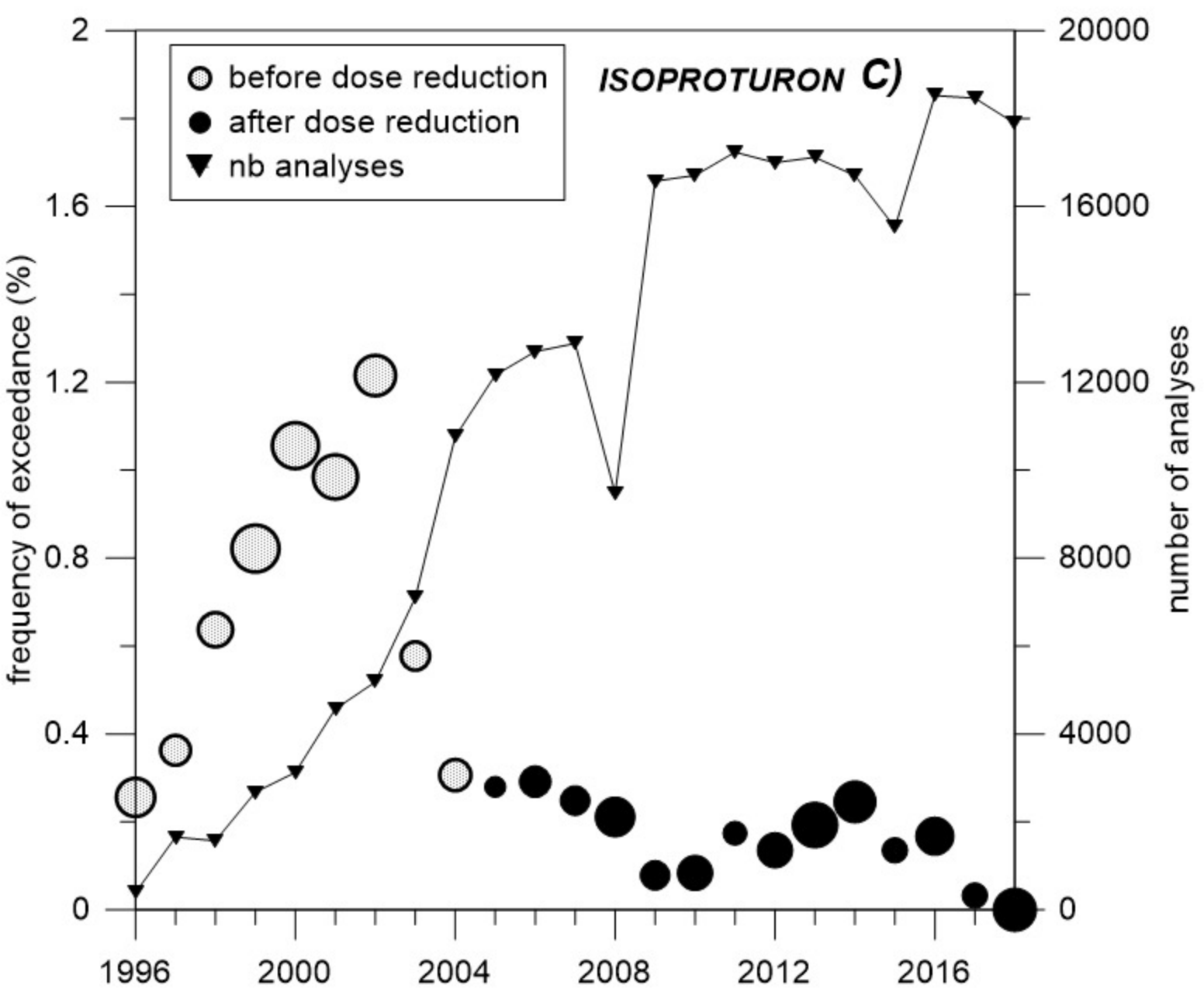
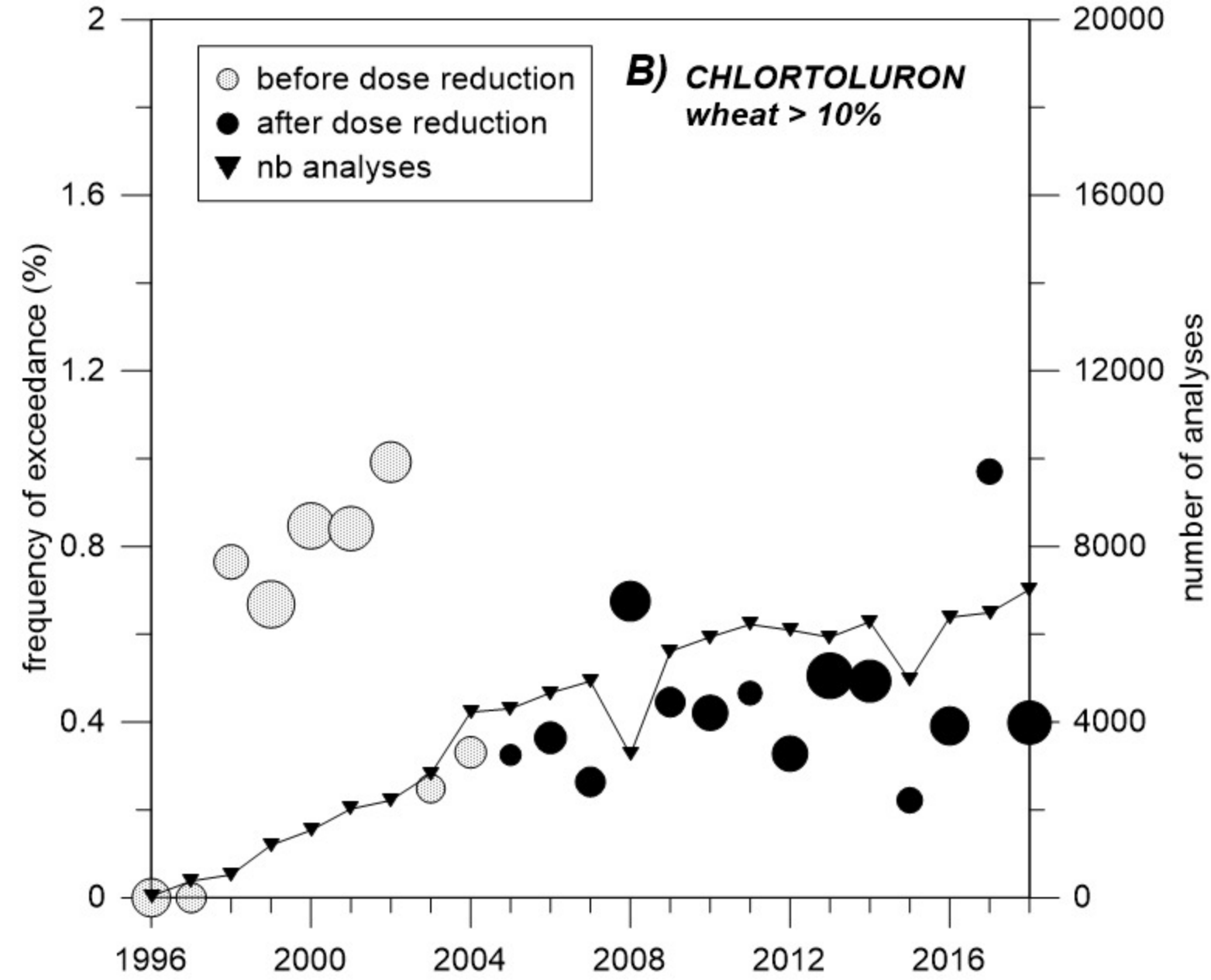
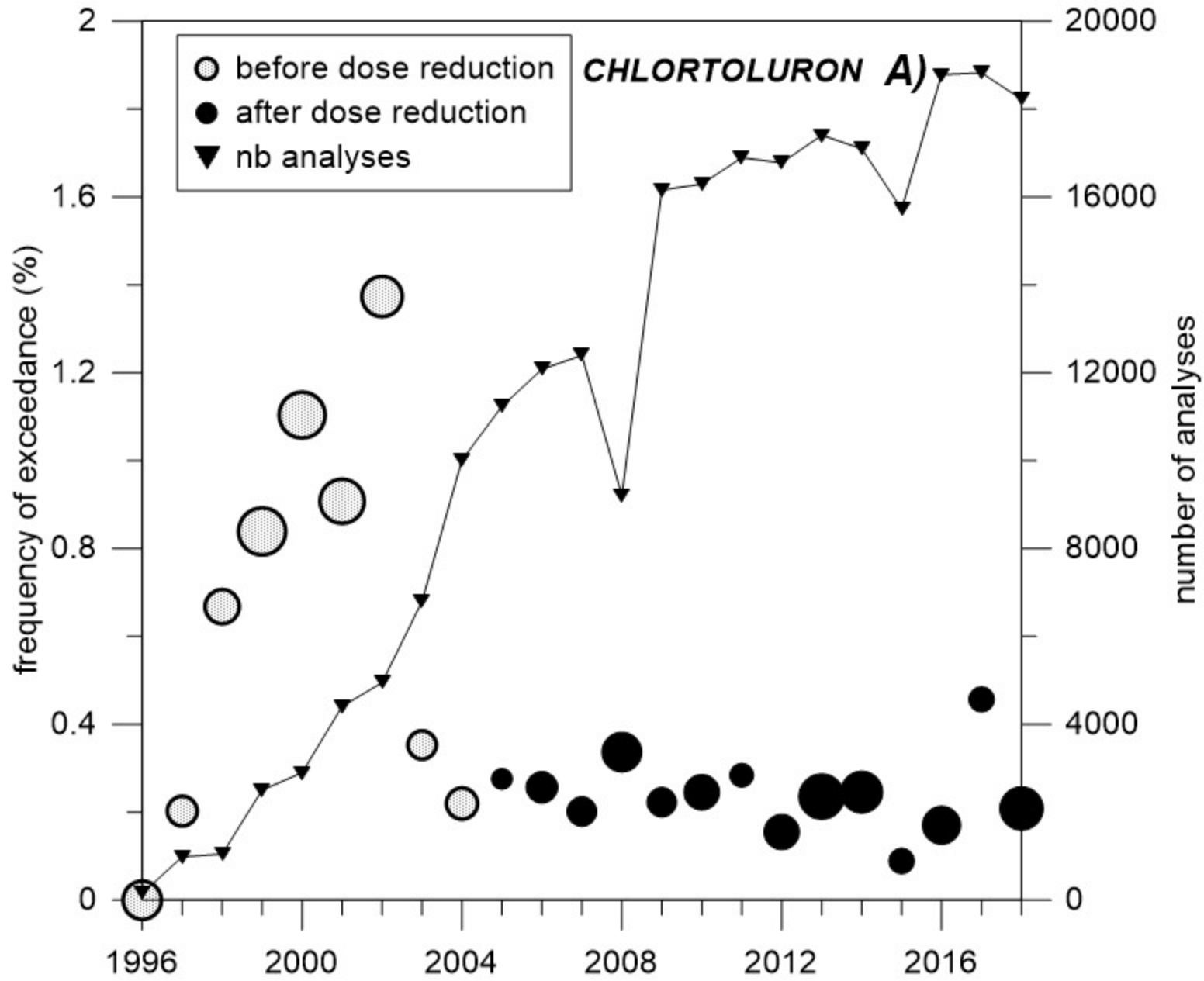
769 Table 1: General information on studied active substances (chemical class, half-life DT50 in soil,
770 adsorption coefficient Koc, GUS leaching potential index, crops having major uses and status
771 (Approved – non approved) at national scale

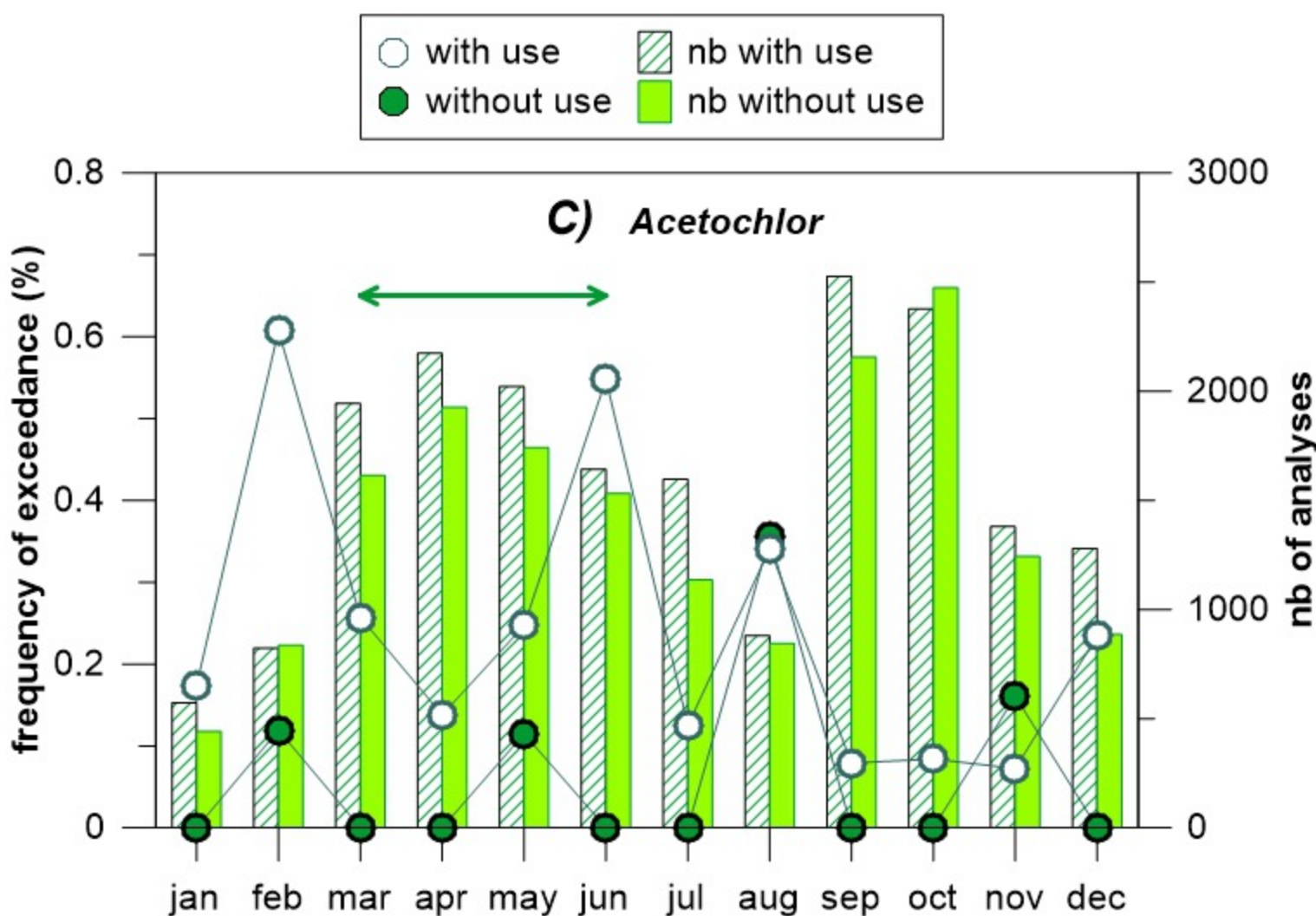
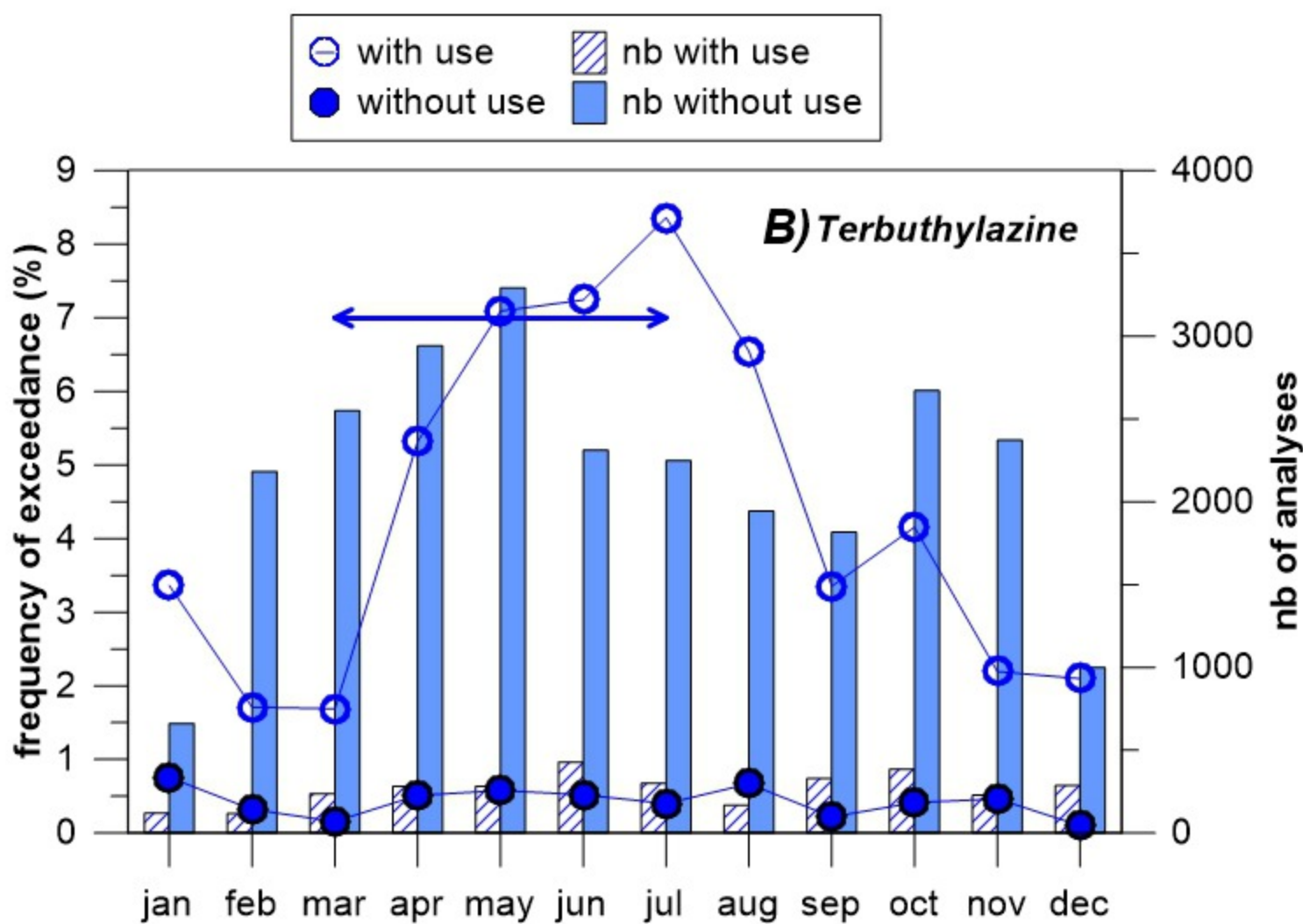
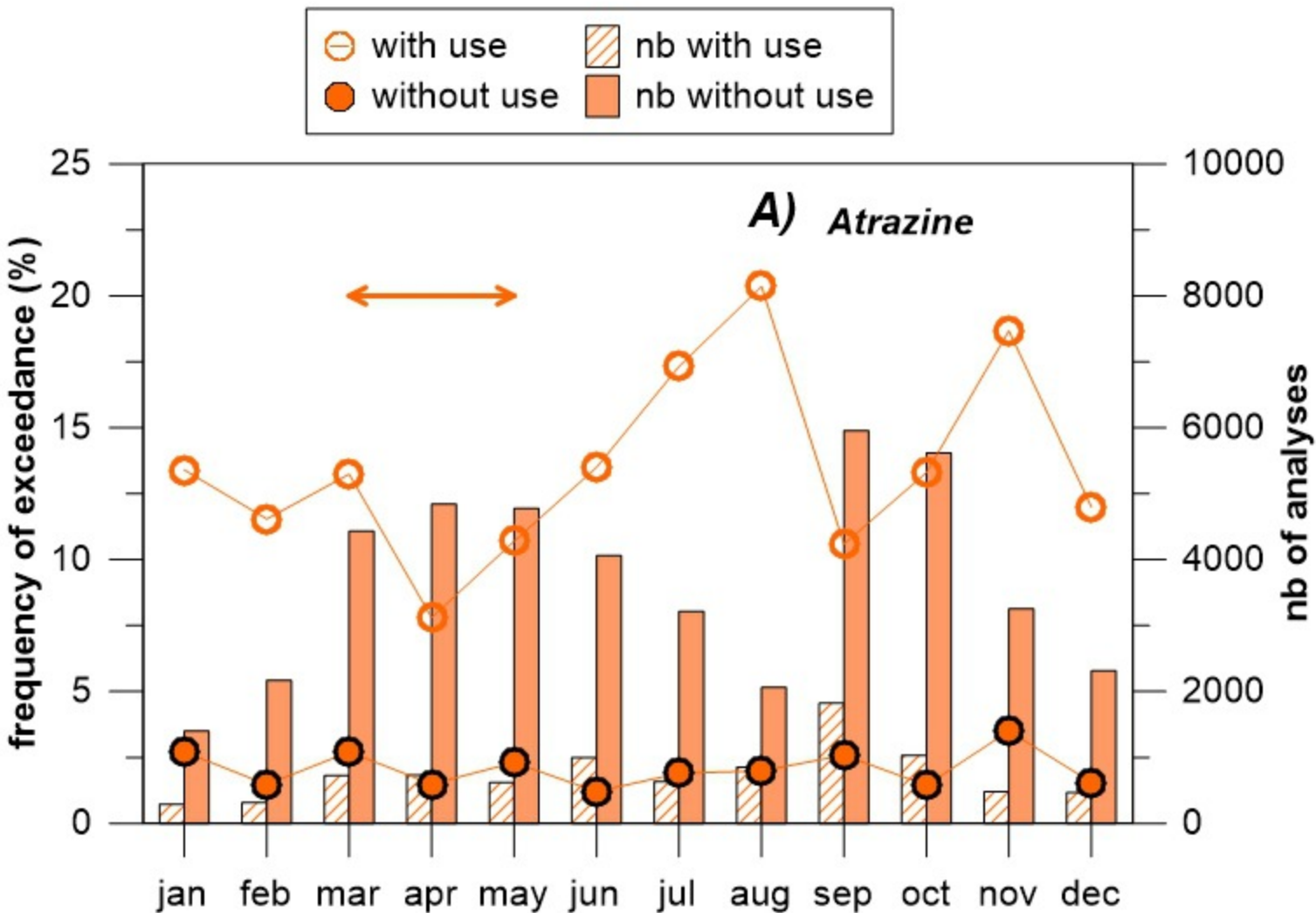
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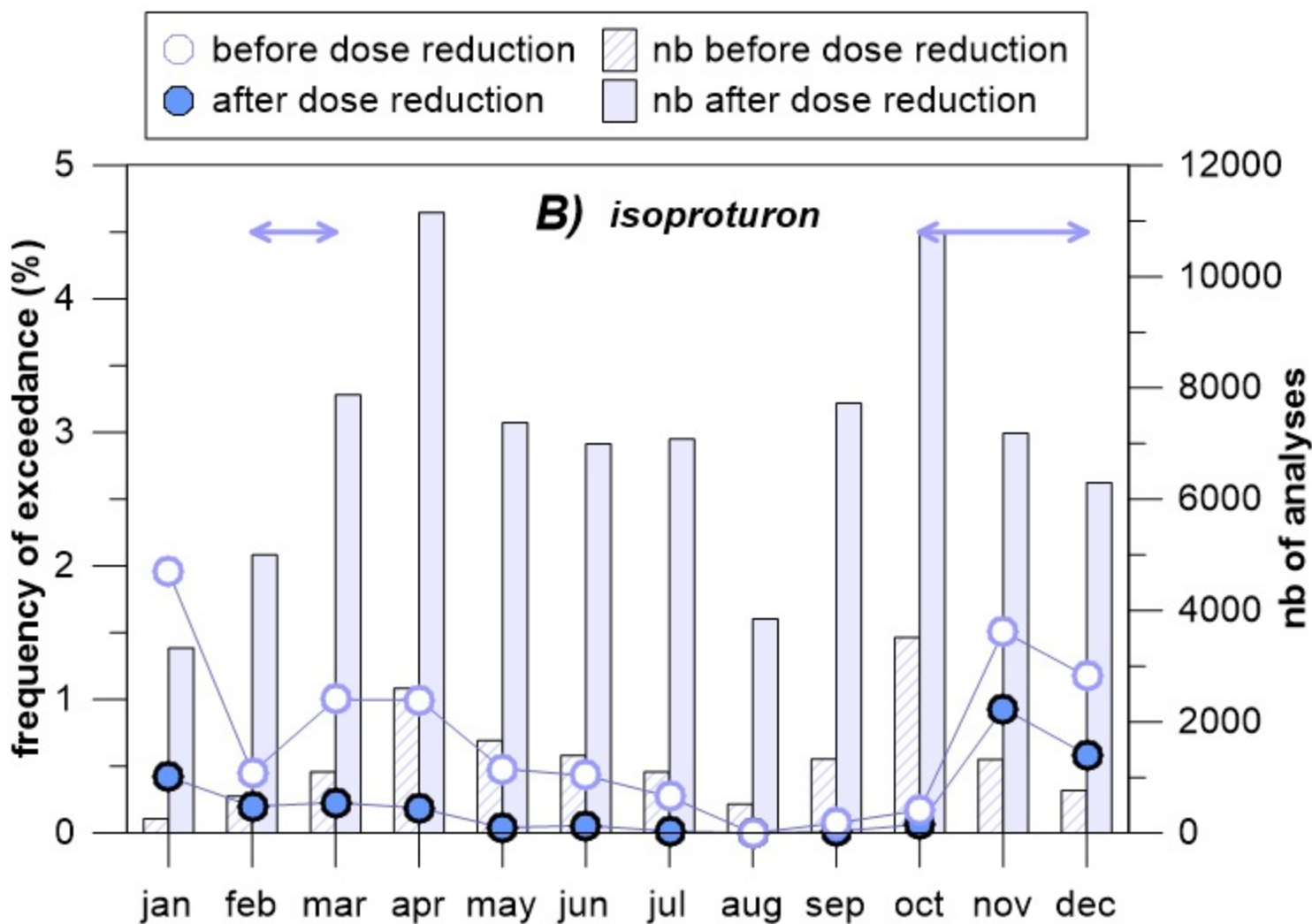
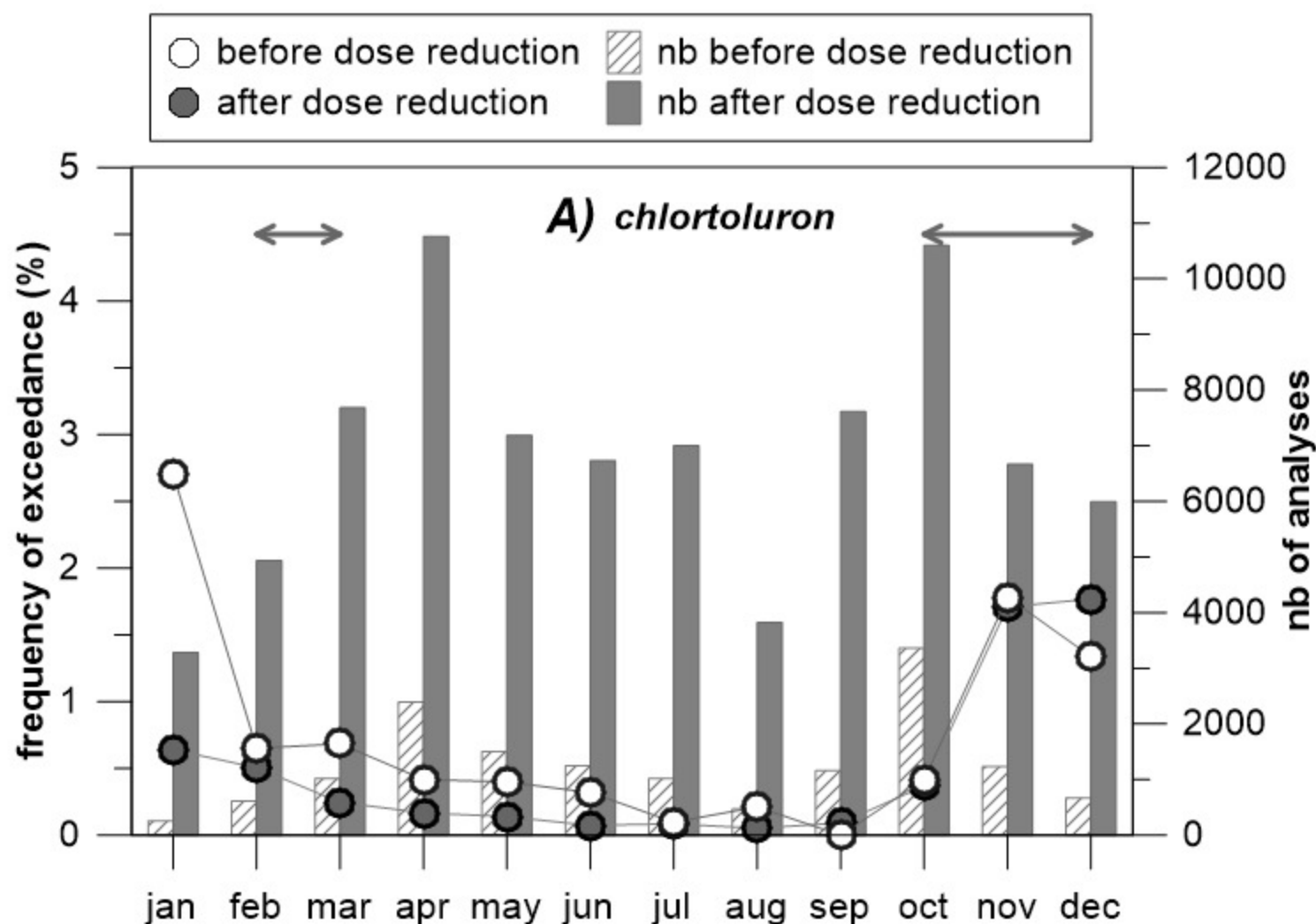


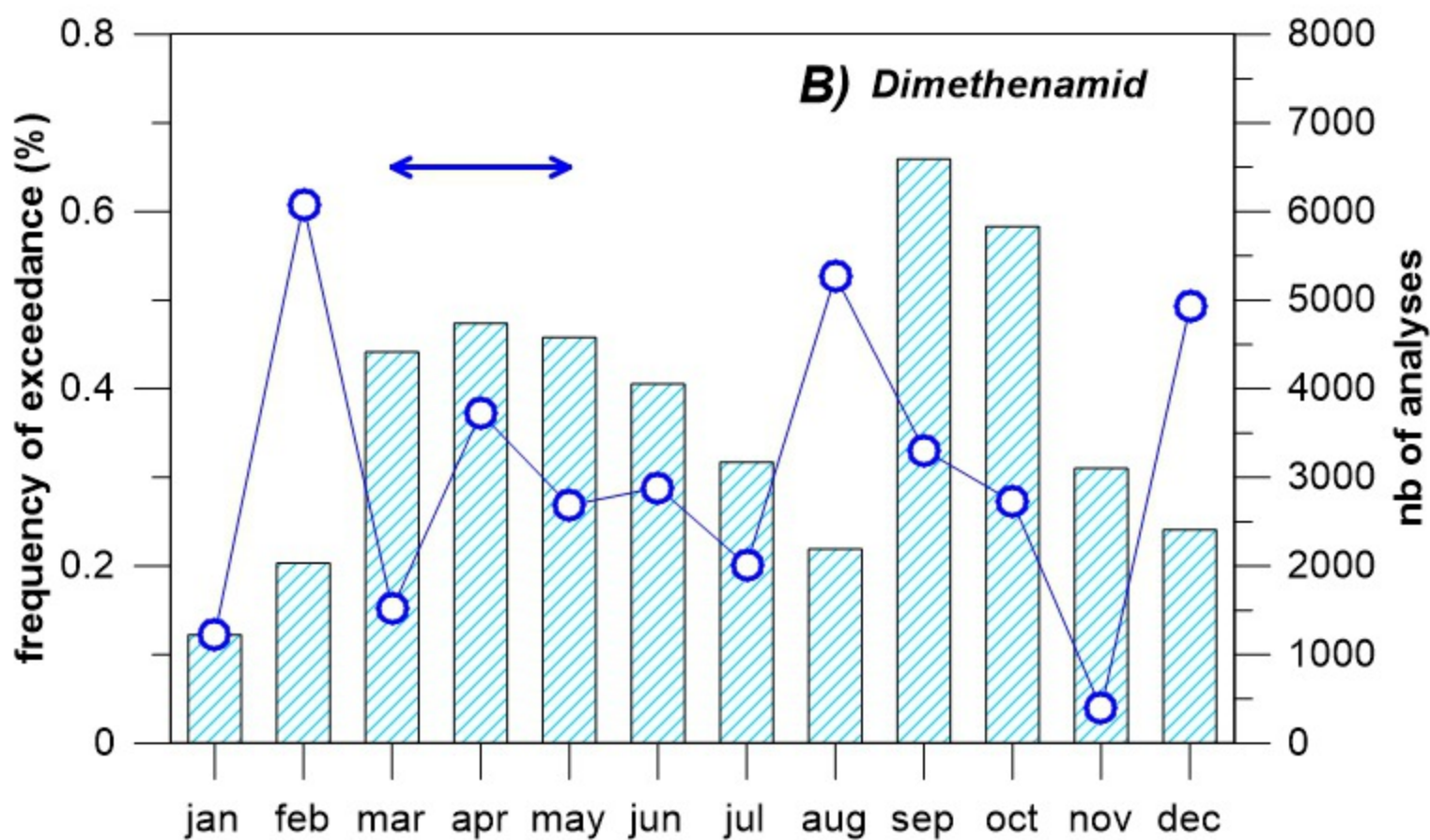
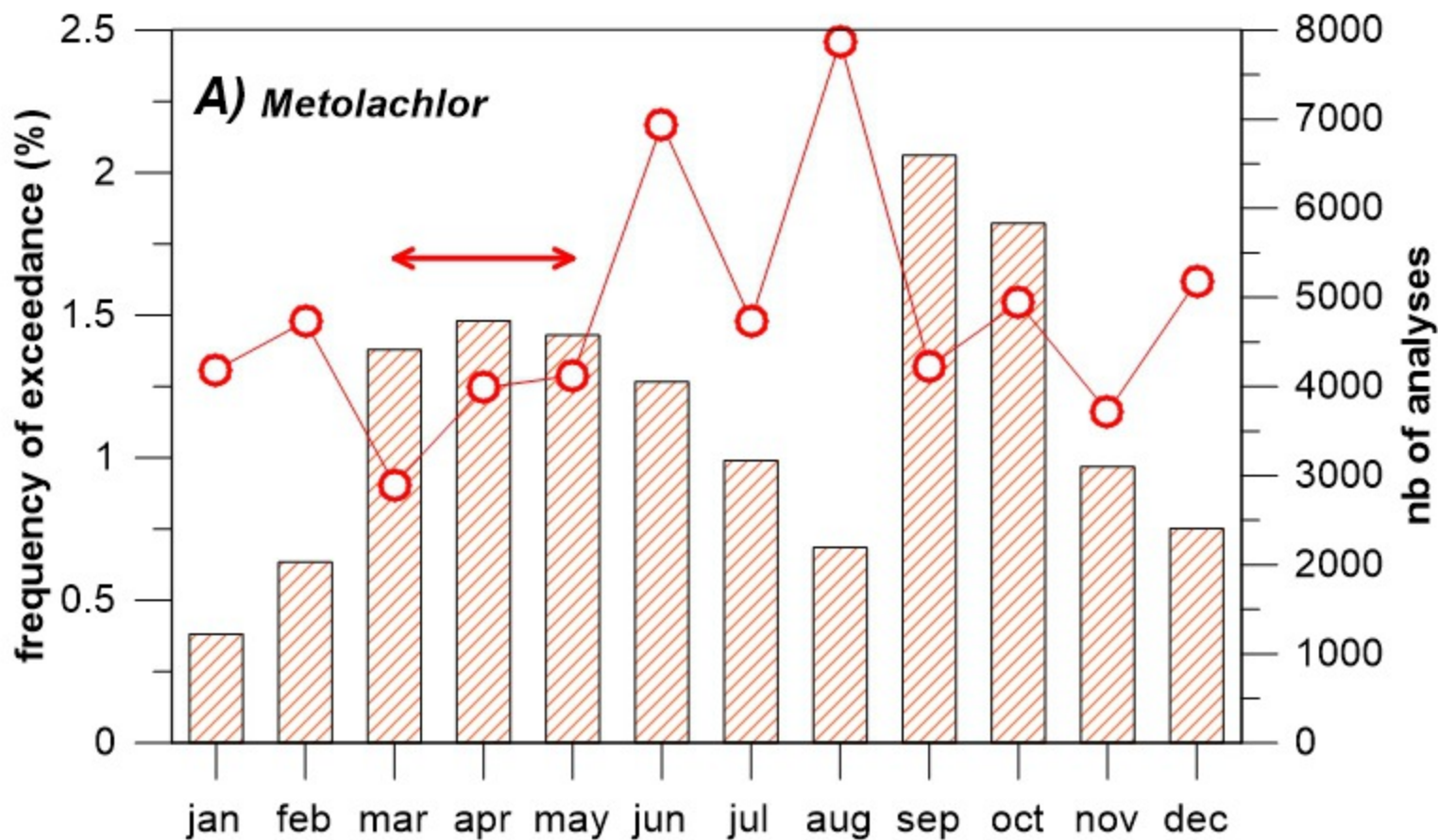




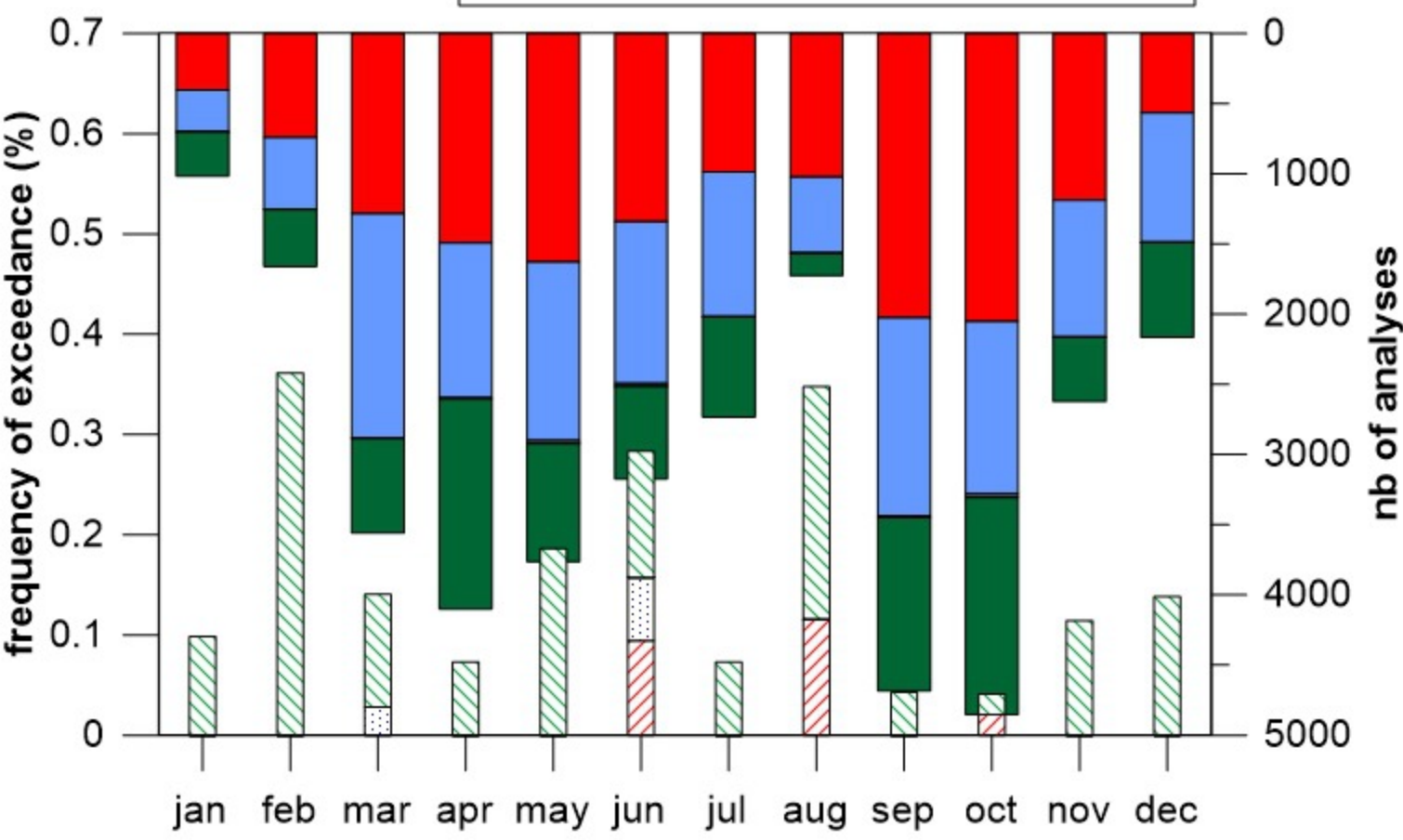




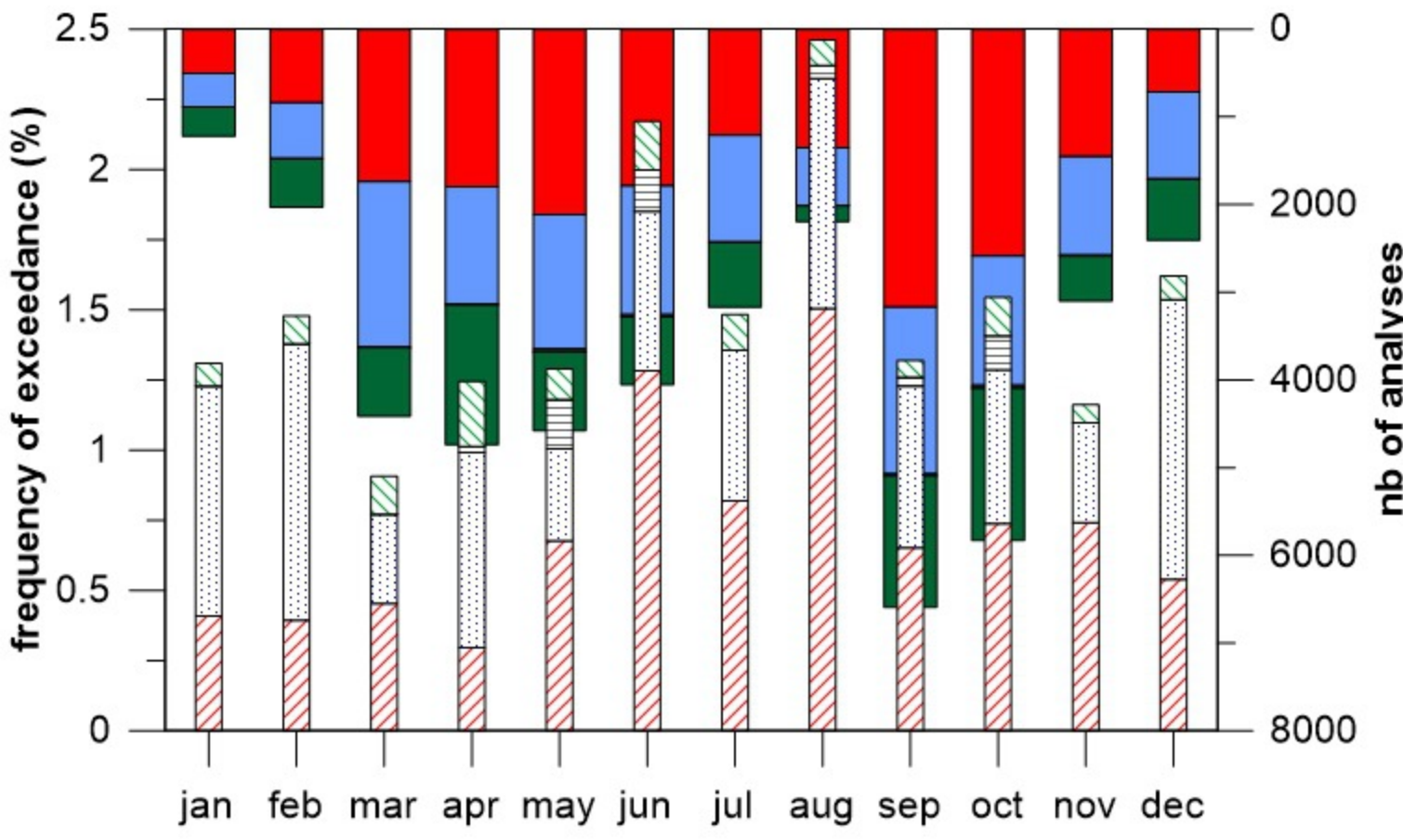




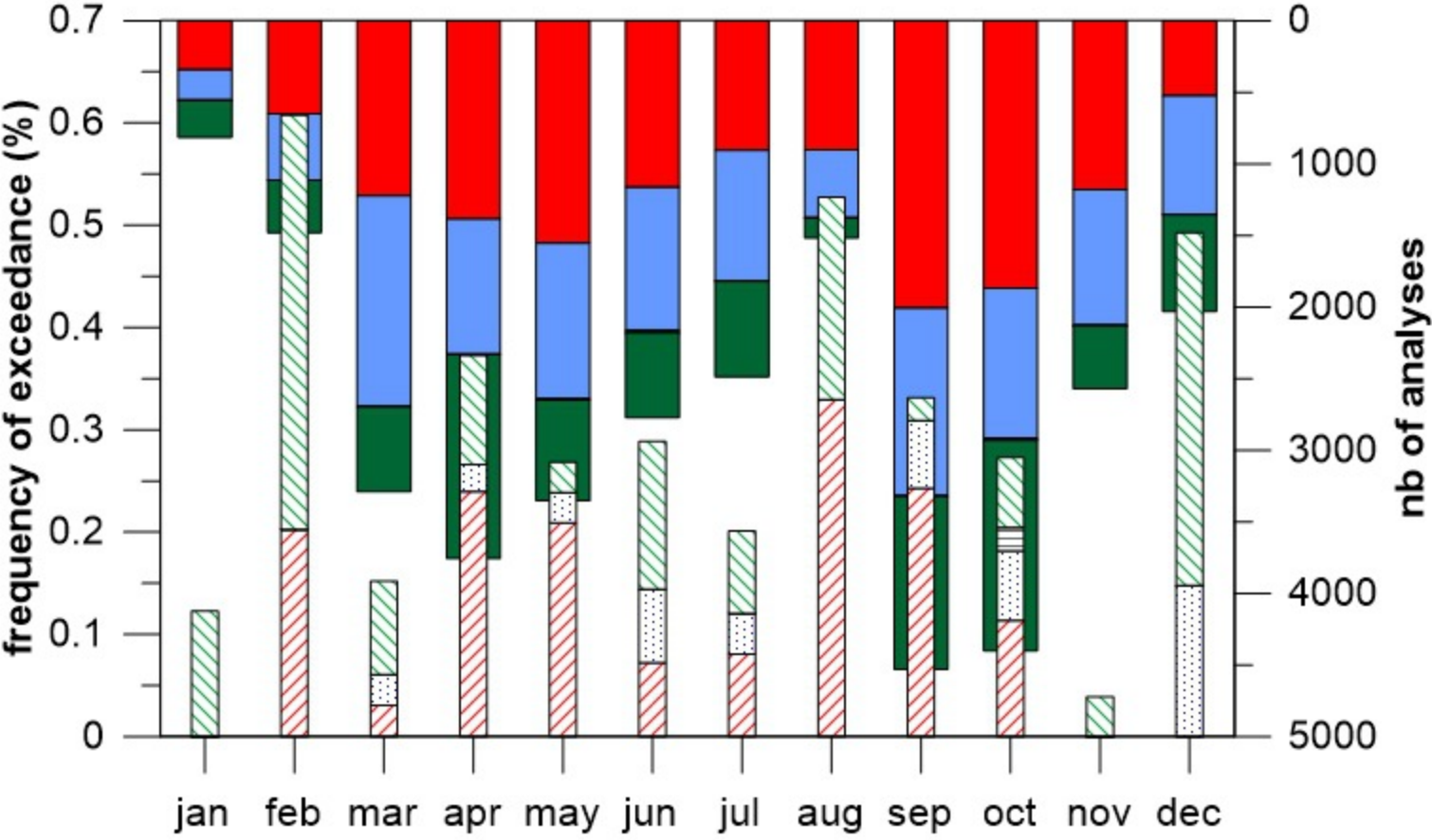
A)
Acetochlor



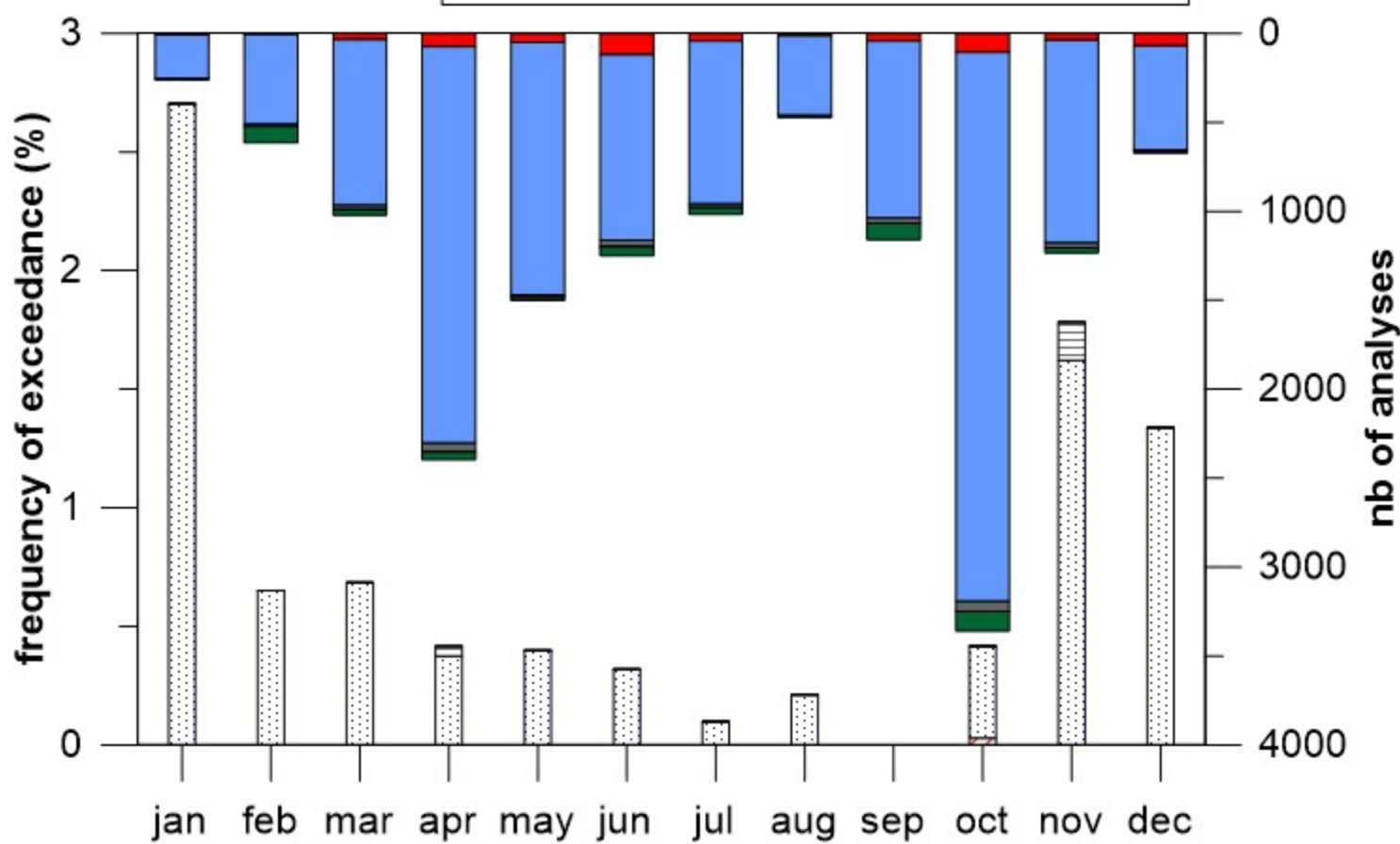
B)
Metolachlor



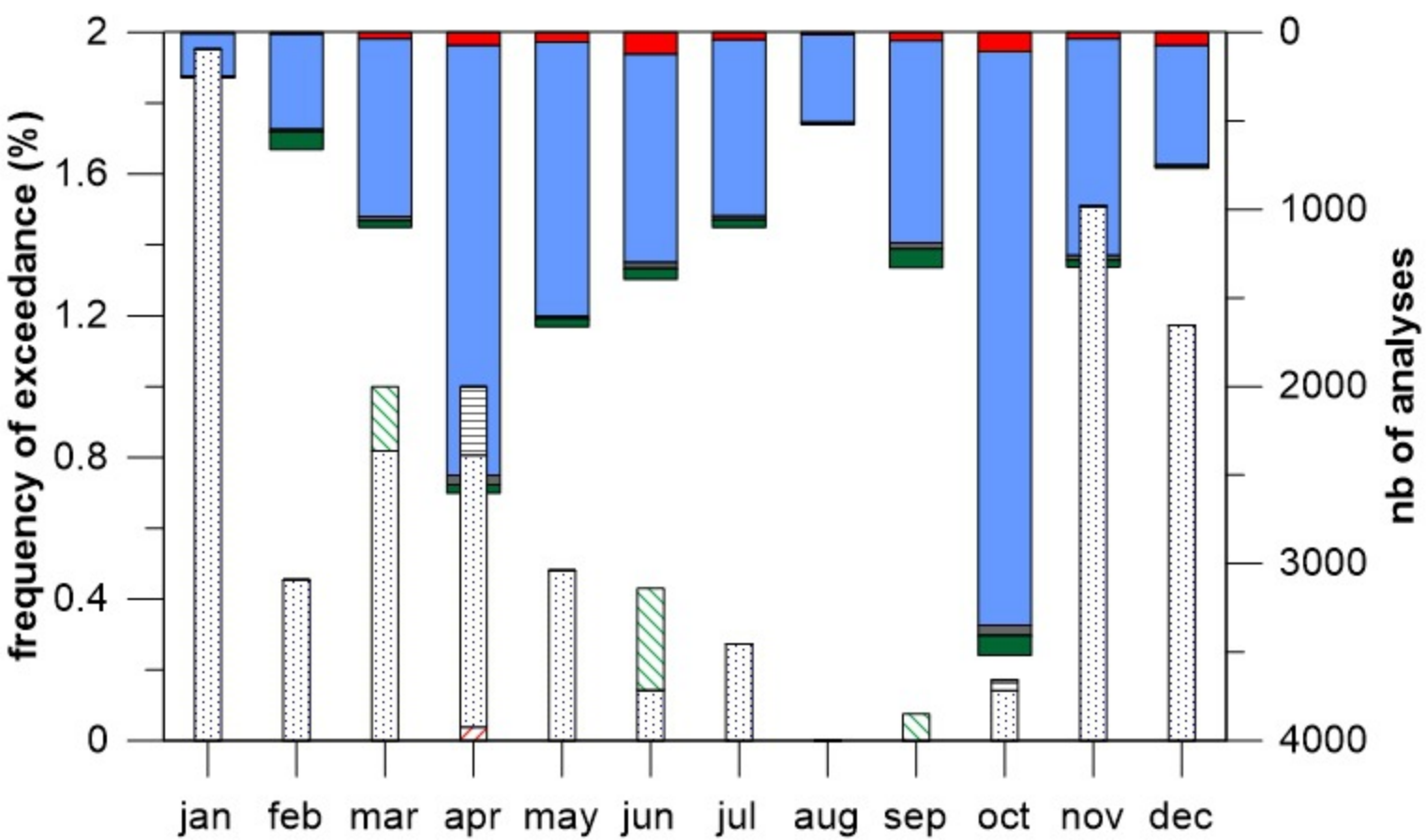
C)
Dimethenamid



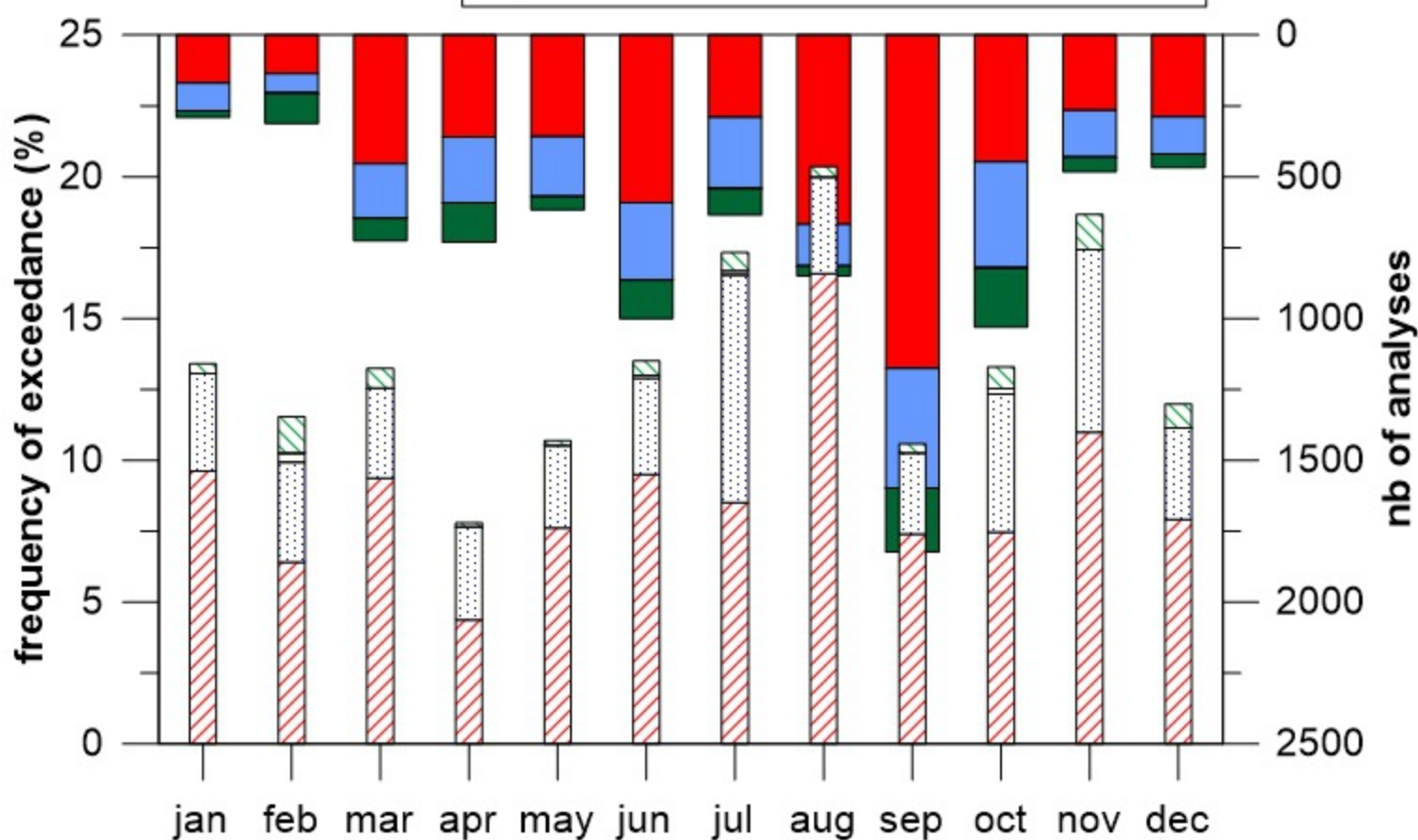
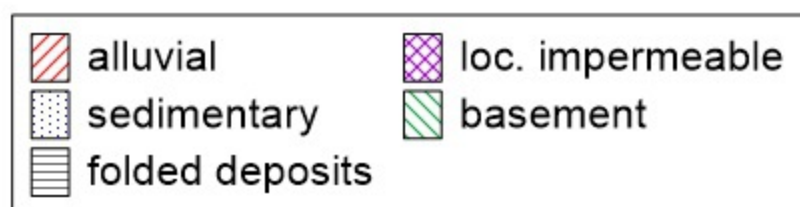
A)
Chlortoluron



B)
Isoproturon



A)
Atrazine



B)

Terbutylazine

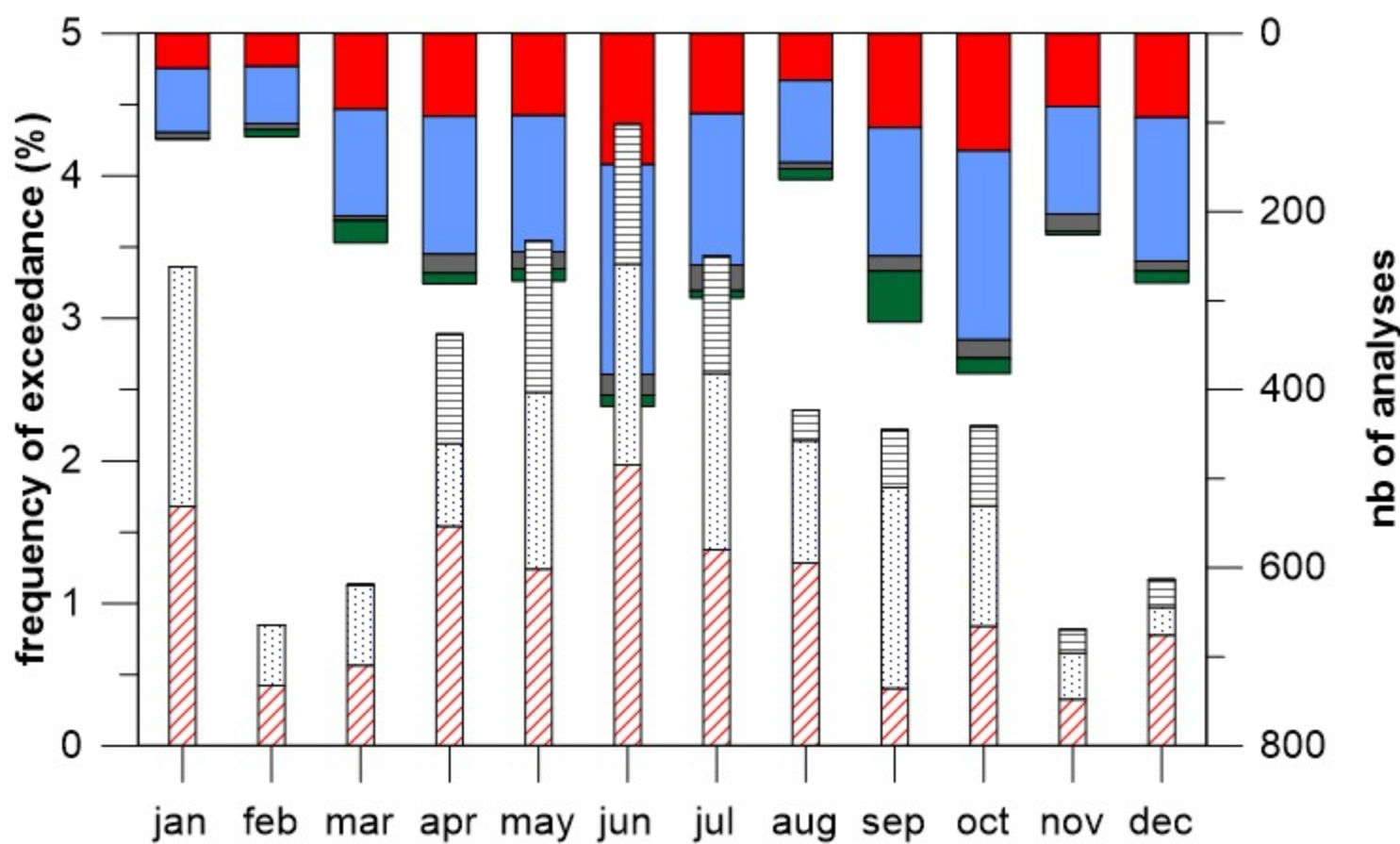
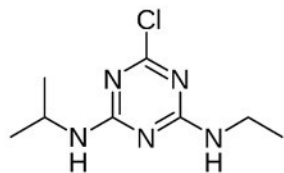


Table 1: General information on studied active substances (chemical class, half-life DT50 in soil, adsorption coefficient Koc, GUS leaching potential index, crops having major uses and status (Approved – non approved) at national scale, and crops of interest and minimum surfaces retained for data study.

Active substance	Chemical class	DT ₅₀ (days) ⁽¹⁾	Koc ⁽¹⁾	GUS ⁽¹⁾	Major uses (Crop of interest and minimum surface retained)	National status
atrazine	triazine	Lab studies DT ₅₀ range 28-150 days	k _{foc} range 70-429 mL g ⁻¹ , 1/n range 1.04=1.10, Soils = 13	2.57	Maize (maize > 10 %)	Approved in 1959. Historical agricultural and non-agricultural uses; only agricultural use since 1997 with dose reduction (2.5 -> 1.5 (1990) -> 1 kg a.s./ha ⁽²⁾). Withdrawal from Annex I in 2003 (final date of use 30 SEP 2003)
terbuthylazine	triazine	EU 2017 dossier lab studies DT ₅₀ range 38.2-167 days	K _{foc} range 151-333 mL g ⁻¹ , 1/n range 0.88-0.98, Soils=9	2.19	Grapevine, maize, orchards (ornamental crops) Currently: maize (grapevines > 2%)	Withdrawal from Annex I in 2003. Last application 30 JUN 2004. Re-approved in 2017 only for maize
acetochlor	chloracetamide	EU dossier lab studies DT ₅₀ range 3.4-29 days,	K _{foc} range 74.0-600 mL g ⁻¹ , 1/n range 0.79-2.16, Soils=13 K _{foc} range 74.0-600 mL g ⁻¹ , 1/n range 0.79-2.16, Soils=13	1.67	Only maize (maize > 10 %)	Approved in 2000; voluntarily withdrawn from Annex I in June 2013 ⁽³⁾ . (final date of use 23 JUN 2013)

metolachlor	chloracetamide	FSA 2018 lab studies DT ₅₀ (normalised) range 10.3-221 days,	K _{foc} range 112-368 mL g ⁻¹ , ¹ / _n range 0.887-1.002, Soils=12	2.32	Maize, sunflower, beet root (maize > 10 %)	Approved as metolachlor since 30 DEC 2003 ⁽⁴⁾ . Replaced by S-metolachlor. Switch accompanied by permitted dose reduction. (e.g. on maize 3.072 kg a.s./ha in 2000, 1.5 to 1.92 kg a.s. /ha today)
dimethenamid	chloracetamide	EU dossier Lab studies DT ₅₀ range 8-67 days,	K _{foc} range 90-474 mL g ⁻¹ , ¹ / _n range 0.92 - 1.07, Soils=10	1.39	Maize, beet root, rapeseed (maize > 10 %)	Introduced in Europe in 1996. Approved as dimethenamid since June 2008 ⁽⁵⁾ . Replaced by dimethenamid-P. Switch accompanied by dose reduction (e.g. 1..4 kg a.s/ maize ha in 2008 -> 0.85 kg a.s./ ha today)
isoproturon	urea	EU dossier lab studies DT ₅₀ range 7.2-18.2 days	K _{foc} range 36-241 mL g ⁻¹ , ¹ / _n range 0.66-0.94, Soils = 21; Literature mean: kf = 3.0 mL g ⁻¹ , K _{foc} = 155 mL g ⁻¹ , ¹ / _n = 1.02, Soils = 33	2.61	Cereals (wheat crops > 10%)	Dose reduction in 2004 ⁽⁶⁾ 1.8 -> 1.2 kg a.s. / ha, single application per campaign for isoproturon or chlortoluron Banned since 30 SEP 2017 ⁽⁷⁾
chlortoluron	urea	EU dossier Lab studies DT ₅₀ range 52-66 days	K _{oc} range 108-384 mL g ⁻¹ , Soils=6	2.62	Cereals (wheat crops > 10%)	Dose reduction in 2004 ⁽⁶⁾ 2.5 -> 1.8 kg a.s. / ha, single application per campaign for isoproturon or chlortoluron. Proposed as alternative after isoproturon withdrawal

- (1) From ppdb - Lewis, K.A., Tzilivakis, J., Warner, D. and Green, A. (2016). *An international database for pesticide risk assessments and management. Human and Ecological Risk Assessment: An International Journal*, 22(4): 1050-1064. DOI: 10.1080/10807039.2015.1133242
- (2) French Official Journal 15 February 1997 and 4 July 1997 (in French)
- (3) Official journal of the European Union. Commission implementing regulation (EU) N° 1372/2011 of 21 December 2011 concerning the non-approval of the active substance acetochlor, in accordance with regulation (EC) N° 1107/2009 of the European Parliament and of the Council concerning the placing of plant protection products on the market, and amending Commission decision 2008/934/EC
- (4) French Official Journal 18 August 2002 (in French)
- (5) Official journal of the European Union. Official journal of the European Union. Commission decision of 22 December 2006 concerning the non-inclusion of dimethenamid in Annex I to Council Directive 91/414/EEC and the withdrawal of authorizations to plant protection products containing that substance 2006/1009/CE
- (6) Official journal of the European Union. French Official Journal 18 February 2004
- (7) Official journal of the European Union. Commission implementing regulation (EU) N° 2016/872 of 1 June 2016 concerning the non-renewal of the active substance isoproturon, in accordance with regulation (EC) N°1107/2009 of the European Parliament and of the Council concerning the placing of plant protection products on the market, and amending Commission implementing regulation (EU) N°540/2011.

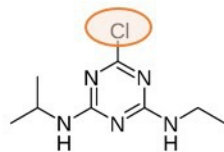


Selected active substances

atrazine, terbuthylazine, acetochlor, metolachlor, dimethenamid, isoproturon, chlortoluron



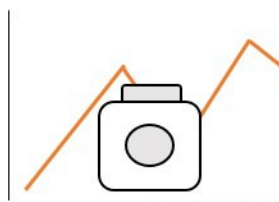
~26 000 observation points in groundwater (1996-2018)



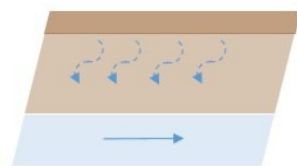
Molecular properties



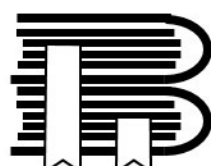
Effective rainfall



Sales of active substance



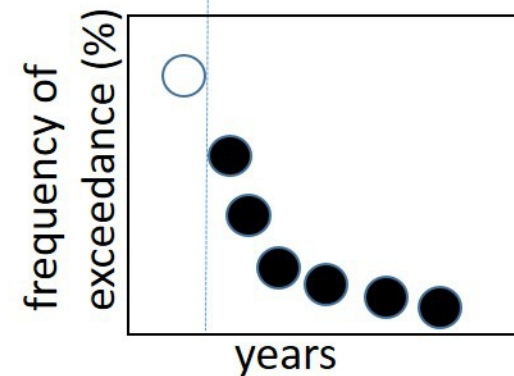
Aquifer lithology



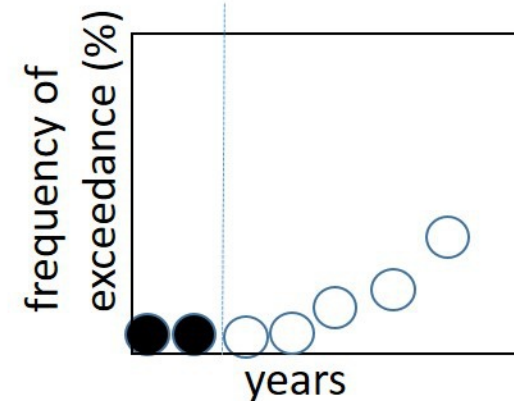
Regulation

Explaining key factors

Active substance withdrawn



Active substance authorization



Explained Pesticides trends in Groundwater