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RAW WATER DATABASE OF PLANT PROTECTION PRODUCTS

2022 ANALYSIS

Gemeinsam
die Zukunft sichern!

Zusammenarbeit von
Wasserversorgung und
Pflanzenschutzmittelindustrie
in Deutschland

Cooperation to protect drinking water resources

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SUMMARY

The water industry associations (BDEW, DVGW, VKU) and the Plant Care Industry Association (Industrieverband Agrar e. V. – IVA) began collaborating at the Water Industry / Plant Protection Industry Round Table in 2009. The key elements of the agreement "Gemeinsam die Zukunft sichern" (Securing the future together) were to share information on a regular basis, to work together to solve problems, and to operate a database on the presence of plant protection products (PPP) in raw water resources.

The Raw Water Database of Plant Protection Products (RWDB PPP) was established by the DVGW-Technologiezentrum Wasser (German Water Centre – TZW) and is operated collaboratively by the German Association of Energy and Water Industries (Bundesverband der Energie- und Wasserwirtschaft e. V. – BDEW), the German Technical and Scientific Association for Gas and Water (Deutscher Verein des Gas- und Wasserfaches e. V. – DVGW) and IVA. The database provides a national overview of the exposure situation in raw water. The current analysis of the Raw Water Database, including the latest survey results, is described in this brochure entitled "Raw Water Database of Plant Protection Products – 2022 Analysis". The results of the 2019 survey are summarised in the brochure "Plant protection products in a nutshell", which has been available on the TZW website since March 2021. The website also contains detailed information on how the Raw Water Database works and the nature of the collaboration between water companies and PPP manufacturers.

The RWDB PPP includes more than 97,000 analyses of plant protection products from over 8,400 raw water abstraction points of around 1,200 water companies throughout Germany. The Raw Water Database contains analyses of more than 500 parameters, including 400 PPP active substances and over 100 degradation products (metabolites).

In 6,803 (99%) of the total of 6,878 raw water abstraction points (RWAPs) investigated in the period from January 2010 to the end of 2022, the latest measured concentrations for all the active substances under investigation were below the threshold value of 0.1 µg/L set out in the Groundwater Ordinance (GrWV). 73 (1%) RWAPs exhibited exceedances. For five RWAPs, the exceedances were attributed to approved active substances; for 68 RWAPs, there were exceedances for active substances that are no longer approved.

In 3,574 (54%) of the total of 6,577 RWAPs investigated in the period from January 2010 to the end of 2022, the latest measured concentrations for all relevant metabolites and those currently classified as non-relevant metabolites under investigation were below 0.1 µg/L. At 3,003 (46 %) RWAPs the concentration was above 0.1 µg/L. At 2,481 RWAPs, the latter was due to metabolites of authorised active substances, at 1,474 RWAPs this was due to metabolites of active substances that are no longer approved.

The Water Industry / Plant Protection Industry Round Table has set itself the following goals:

- Identification of criteria characterising areas sensitive to the leaching of PPP active substances.
- Development of proposals for local restrictions on the use of PPP active substances that become conspicuous in particularly sensitive areas.
- Review and, where applicable, improvement of the implementation of direction for use "NG301" of the Federal Office of Consumer Protection and Food Safety (BVL) for non-relevant metabolites (degradation products).
- Early detection of new problematic active substances and/or areas of use.
- Continuation of the RWDB PPP, including the survey of water companies on the analytical results of plant protection products every three years.
- Shortening and simplification of the procedure for clarifying findings.
- Encouragement of agriculture to provide public drinking water suppliers with data on the use of plant protection products in drinking water catchment areas.
- Exchange of information on the occurrence of transformation products of active substances in water treatment.

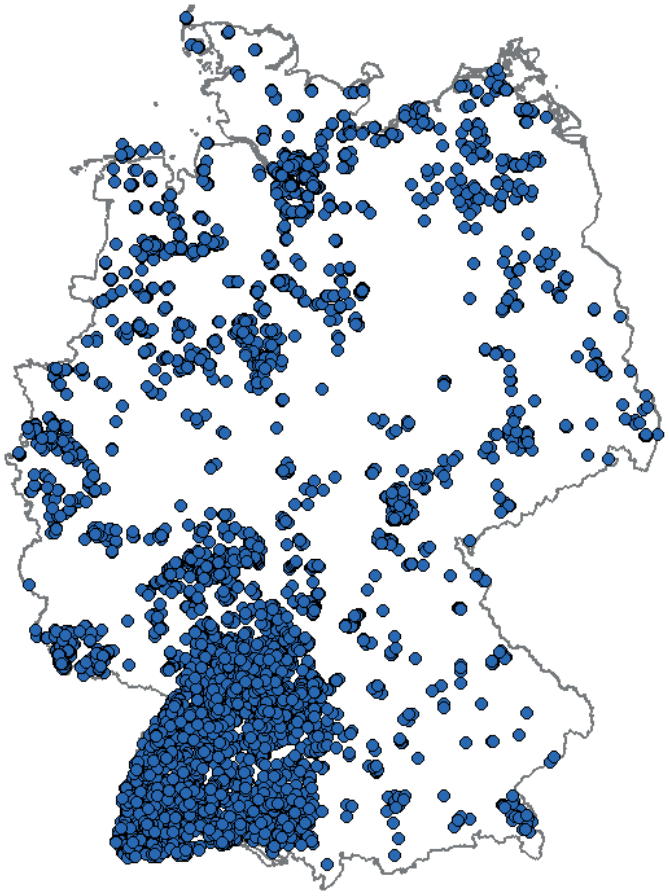
The Round Table is currently developing proposals on how to restrict the use of certain plant protection products in water protection areas in the near term.

INTRODUCTION

Dr. Claudia Castell-Exner (DVGW) | Andrea Danowski (BDEW) | Dr. Mark Winter (IVA)

A key element of the agreement "Gemeinsam die Zukunft sichern" (Securing the future together) between the water industry and manufacturers of plant protection products (PPPs) is to establish and operate the Raw Water Database of Plant Protection Products (RWDB PPP) on the occurrence of plant protection products in raw water resources. The RWDB PPP, operated collaboratively by BDEW, DVGW and IVA, provides a national overview of the exposure situation in raw water.

Since the start of the project, around 1,200 water companies have provided 97,000 analysis data from more than 8,400 raw water abstraction points (RWAPs) for the RWDB PPP (Figure 1), providing an overview of the exposure situation of drinking water resources from groundwater. Around 400 PPP active substances and more than 100 metabolites have been recorded. The RWDB PPP only includes findings from RWAPs that are in use (i.e. no upgradient groundwater quality monitoring wells or other monitoring wells).



● Raw water abstraction points with PPP analyses

Source: Data provided by water companies participating in the Raw Water Database of Plant Protection Products project; Administrative boundaries: © GeoBasis-DE / BKG 2020 (data amended)

Figure 1: The raw water abstraction points included in the RWDB PPP provide an overview of raw water quality in Germany. The high density in Baden-Württemberg is due to the import of data from the Groundwater Database, which has been used there for 30 years. (Raw Water Database of Plant Protection Products [RWDB PPP], as of 06/2023)

The 2019 survey results on the occurrence of PPP in raw water are presented in the brochure "Plant protection products in a nutshell", which is available on the TZW website (Raw Water Database Water Supply Pesticides | TZW). The website also contains a detailed description of how the Raw Water Database works and the nature of the collaboration between the water industry and PPP manufacturers.

The current analysis of the RWDB PPP, based on the latest survey results, is presented in this paper entitled "Raw Water Database of Plant Protection Products – 2022 Analysis".

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FINDINGS FOR APPROVED PPP ACTIVE SUBSTANCES IN RAW WATER

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A total of 288 PPP active substances are currently approved in Germany (as of July 2023[1]). The Raw Water Database of Plant Protection Products (RWDB PPP) contains data on 108 approved active substances and 291 active substances that are no longer approved. This chapter provides an overview of the findings in raw water with regard to approved active substances. The RWDB PPP also contains data on 109 metabolites; those findings are analysed in the following section.

To provide an overview of the findings, a selection was first made of active substances for which the latest value available in the Raw Water Database is above the limit of quantification at one or more raw water abstraction points (RWAPs) from the start of the database in 2010 to the end of 2022. In another query of the database, the active substances were selected that were measured above the limit of quantification in raw water in the period 2020 to 2022.[2] The RWAPs in this second query were (still) actively sampled during this period. The first type of database query included monitoring points where the last sampling took place some time ago and which had been abandoned before the last survey. Only substances that were approved in at least one of the evaluation periods used here were shown. Tables 1 and 2 show the findings for active substances.

The question of which active substances were detected above the respective threshold values in accordance with the Groundwater Ordinance (GrWV) in groundwater used as raw water for drinking water production is of considerable importance to water companies, manufacturers and agriculture. These values are therefore also shown in the tables.

The latest measured value recorded in the database as of 13/06/2023 is above the limit of quantification[3] for 20 approved active substances or active substances that until recently were approved[4] (Table 1). The frequency of findings exceeding the limit of quantification for the active substances recorded is in the single-digit percentage range at most. The number of RWAPs with values above 0.1 µg/L is in the single-digit parts-per-thousand range at most. In 6,803 (99%) of the total of 6,878 RWAPs investigated in the period from January 2010 to the end of 2022, the latest measured concentrations for all the active substances under investigation were below the threshold value of 0.1 µg/L set out in the Groundwater Ordinance (GrWV). 73 (1%) of the abstraction points exhibited exceedances. For five RWAPs, the exceedances were attributed to approved active substances; for 68 RWAPs, there were exceedances for active substances that are no longer approved.

For individual active substances, the situation is as follows: for the no longer approved active substance bentazone – a herbicidal active substance used mainly in cereals and maize to control weeds – the latest measured value exceeded the threshold value in accordance with the Groundwater Ordinance (GrWV) at 14 of the 5,936 RWAPs sampled in total. For mecoprop – a herbicide to control weeds in cereals – it was exceeded at three of the 5,132 abstraction points; for the oilseed rape herbicide metazachlor, two of the 6,206 abstraction points were affected (Table 1).

[1] https://www.bvl.bund.de/DE/04_Pflanzenschutzmittel/01_Aufgaben/02_ZulassungPSM/01_ZugelPSM/psm_ZugelPSM_node.html

[2] Median of the annual medians

[3] Limit of quantification (LOQ): is the lowest concentration of a substance that can be quantitatively determined with a certain precision. The limit of detection (LOD), which is below the LOQ, denotes the measured variable at which the substance can just be detected reliably (available: a yes/no decision). Both properties depend on the instrument used, the method available, and the substance to be analysed

[4] Bentazone: last approved up to 31/01/2018, period of grace: 31/07/2019. Chloridazon: last approved up to 31/12/2018, period of grace: 30/06/2020

Table 1: Findings of approved[5] active substances with the latest value above the limit of quantification (LOQ) with analyses in the period 2010 to 2022 (number of raw water abstraction points [RWAPs, groundwater], as of 13/06/2023)

Active substances	No. of RWAPs with analyses	No. of RWAPs with the latest value					Maximum latest value in µg/L	Threshold value in µg/L	Threshold value[6]
		≥ LOQ ≤ 0.1 µg/L	> 0.1 µg/L ≤ 1 µg/L	> 1 µg/L ≤ 3 µg/L	> 3 µg/L ≤ 10 µg/L	> 10 µg/L			
Bentazone**	5936	76	14				0,44	0,1	TV in acc with GrwV
Mecoprop (MCPP)*	5132	18	3				0,51	0,1	TV in acc with GrwV
Metazachlor	6206	8	2				0,61	0,1	TV in acc with GrwV
Metolachlor*	5567	9					0,07	0,1	TV in acc with GrwV
Chloridazon**	4795	7					0,08	0,1	TV in acc with GrwV
Terbuthylazine	6165	7					0,05	0,1	TV in acc with GrwV
Boscalid	948	5					0,053	0,1	TV in acc with GrwV
Metalaxyl	4328	5					0,054	0,1	TV in acc with GrwV
Dichlorprop (2,4-DP)*	4885	5					0,06	0,1	TV in acc with GrwV
MCPA (4-chloro-2-methyl phenoxy acetic acid)	4980	5					0,04	0,1	TV in acc with GrwV
Metconazole	513	3					0,1	0,1	TV in acc with GrwV
Glyphosate	2451	3					0,053	0,1	TV in acc with GrwV
Clopyralid	939	2					0,02	0,1	TV in acc with GrwV
Metribuzin	2633	2					0,08	0,1	TV in acc with GrwV
Chlortoluron	4998	2					0,05	0,1	TV in acc with GrwV
Bifenox	844	1					0,005	0,1	TV in acc with GrwV
Flufenacet	1341	1					0,07	0,1	TV in acc with GrwV
Ethofumesate	1805	1					0,02	0,1	TV in acc with GrwV
Metamitron	2213	1					0,025	0,1	TV in acc with GrwV
Metobromuron	2406	1					0,05	0,1	TV in acc with GrwV

[5] Approval status: October 2022; for the current status, see https://apps2.bvl.bund.de/psm

[6] TV in acc with GrwV: threshold value in accordance with the Groundwater Ordinance (GrWV)

* Mecoprop-P, dichlorpropP and S-metolachlor are currently approved

** Bentazone: last approved up to 31/01/2018, period of grace: 31/07/2019. Chloridazon: last approved up to 31/12/2018, period of grace: 30/06/2020

In the analysis for the period 2020 to 2022 (Table 2), analyses are available for significantly fewer RWAPs (a maximum of 2,070 RWAPs). For this reason, there are also fewer positive findings and fewer findings exceeding 0.1 µg/L. In the analysis for this three-year period, there are measurement results above the limit of quantification for 17 instead of 20 active substances compared to the analysis for the whole period. Again, the highest frequencies were found for the active substances bentazone and mecoprop. However, the exceedance of the threshold value of 0.1 µg/L is limited to the active substance bentazone with a maximum mean concentration of 0.5 µg/L.

The further spectrum of active substances with positive findings differs in composition and order of frequency of findings. While the six active substances MCPA, clopyralid, flufenacet, ethofumesate, metamitron and metobromuron do not appear in the second analysis, dimethenamid, tritosulfuron and quinmerac are only found in this list. Twelve other substances appear in both analyses, but in different positions in the order of frequency of findings.

Table 2: Findings of approved[7] active substances above the limit of quantification in the period 2020 to 2022 (number of raw water abstraction points [RWAPs, groundwater], as of 13/06/2023)

Active substances	No. of RWAPs with analyses	No. of RWAPs with median					Maximum latest value in µg/L	Threshold value in µg/L	Threshold value[8]
		≥ LOQ ≤ 0.1 µg/L	> 0.1 µg/L ≤ 1 µg/L	> 1 µg/L ≤ 3 µg/L	> 3 µg/L ≤ 10 µg/L	> 10 µg/L			
Bentazone**	2070	24	9				0,51	0,1	TV in acc with GrwV
Mecoprop (MCPP)*	1430	8					0,087	0,1	TV in acc with GrwV
Boscalid	457	6					0,053	0,1	TV in acc with GrwV
Metribuzin	909	5					0,04	0,1	TV in acc with GrwV
Chloridazon**	1764	5					0,05	0,1	TV in acc with GrwV
Metconazole	305	3					0,1	0,1	TV in acc with GrwV
Chlortoluron	1791	3					0,05	0,1	TV in acc with GrwV
Dimethenamid	623	2					0,053	0,1	TV in acc with GrwV
Metolachlor*	1652	2					0,055	0,1	TV in acc with GrwV
Metazachlor	1869	2					0,036	0,1	TV in acc with GrwV
Bifenox	378	1					0,005	0,1	TV in acc with GrwV
Tritosulfuron	438	1					0,025	0,1	TV in acc with GrwV
Quinmerac	502	1					0,039	0,1	TV in acc with GrwV
Glyphosate	1130	1					0,053	0,1	TV in acc with GrwV
Dichlorprop (2,4-DP)*	1277	1					0,055	0,1	TV in acc with GrwV
Metalaxyl	1337	1					0,02	0,1	TV in acc with GrwV
Terbuthylazine	2093	1					0,02	0,1	TV in acc with GrwV

[7] Approval status: October 2022, for the current status, see https://apps2.bvl.bund.de/psm

[8] TV in acc with GrwV: threshold value in accordance with the Groundwater Ordinance (GrWV)

* Mecoprop-P, dichlorpropP and S-metolachlor are currently approved

** Bentazone: last approved up to 31/01/2018, period of grace: 31/07/2019. Chloridazon: last approved up to 31/12/2018, period of grace: 30/06/2020

FINDINGS FOR METABOLITES
IN RAW WATER

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To provide an overview of the findings, a selection was first made of metabolites for which the latest value is above the limit of quantification at one or more raw water abstraction points (RWAPs) from the start of the database in 2010 to the end of 2022. In another query of the database, the metabolites were selected that were measured above the limit of quantification in raw water in the period 2020 to 2022.[9] The RWAPs in this second query were (still) actively sampled during this period. The first type of database query included monitoring points where the last sampling took place some time ago and which had been abandoned before the last survey. Only substances that were approved in at least one of the evaluation periods used here were shown. Tables 3 and 4 show the findings for metabolites.

In 3,574 (54%) of the total of 6,577 RWAPs investigated in the period from January 2010 to the end of 2022, the latest measured concentrations for all the relevant and non-relevant metabolites under investigation were below 0.1 µg/L. At 3,003 (46%) RWAPs the concentration was above 0.1 µg/L. At 2,481 RWAPs, the latter was due to metabolites of authorised active substances, at 1,474 RWAPs this was due to metabolites of active substances that are no longer approved.

For the metabolites of active substances that are or were until recently approved[10], the latest values of 29 parameters in total were at or above the limit of quantification (Table 3). The most frequent detections were of trifluoroacetic acid (TFA), with positive findings at 2,181 RWAPs, and of the two degradation products of the sugar beet herbicide chloridazon: desphenyl-chloridazon and methyl-desphenyl-chloridazon were at or above the limit of quantification at 1,769 and 1,034 RWAPs, respectively. Compared to active substances, significantly more non-relevant metabolites are above the limit of quantification (up to 73% for TFA, 38% for desphenyl-chloridazon, and 20% for CGA 354743 of S-metolachlor) as a percentage of the number of RWAPs sampled in each case.

The situation of the metabolites with the most frequent findings is described in more detail below. Trifluoroacetic acid (TFA, a breakdown product of several active substances and precursors, including from non-agricultural sources) was above 0.1 µg/L at 2,088 RWAPs, above 3 µg/L at 67 RWAPs, and above 10 µg/L at 14 RWAPs (Table 3). Desphenyl-chloridazon was above 0.1 µg/L at 1,241 RWAPs, above 3 µg/L at 67 RWAPs, and above 10 µg/L at one abstraction point. Five metabolites of S-metolachlor were found (CGA 354743, CGA 351916, NOA 413173, CGA 357704, CGA 368208); all except CGA 368208 were found at concentrations above 0.1 µg/L in more than 10% of the RWAPs under investigation. For CGA 354743, this was the case at 231 RWAPs; the concentration was above 3 µg/L at two abstraction points. CGA 351916 was detected at concentrations above 0.1 µg/L at 192 RWAPs and above 3 µg/L at one abstraction point. Methyl-desphenyl-chloridazon exceeded 0.1 µg/L at 519 RWAPs and 3 µg/L at one abstraction point. Three metabolites of metazachlor were

[9] Median of the annual medians
[10] Chloridazon: last approved up to 31/12/2018, period of grace: 30/06/2020

found (BH 479-8, BH 479-4 and BH 479-12); BH 479-8 was found at concentrations above 0.1 µg/L in more than 10% of the RWAPs under investigation. This figure corresponds to 279 RWAPs, 19 of which exhibited a value above 1 µg/L. BH 479-4 was detected at concentrations above 0.1 µg/L at 125 RWAPs and above 1 µg/L at two abstraction points.

In the analysis for the period 2020 to 2022 (Table 4), there are significantly fewer RWAP analyses than in the analysis for the whole period (a maximum of 1,771 RWAPs). For this reason, there are also fewer positive findings and fewer findings exceeding 0.1 µg/L.

In the analysis for this three-year period, there are findings for a similar number of substances as in the analysis for the whole period, with measurement results above the limit of quantification for 26 instead of 29 metabolites. In total, 23 metabolites were detected at concentrations above 0.1 µg/L at RWAPs. The number of RWAPs affected ranges from one to 597 RWAPs, depending on the parameter.

The range of parameters is almost identical to the overall analysis, except that the dimethachlor metabolite CGA 373464, the metalaxyl-M metabolite CGA 62826 / NOA 409045 and the nicosulfuron metabolite UCSN do not appear in the second analysis. The order of frequency of findings between the two analyses varies significantly less for metabolites than for active substances.

In the analysis for the three-year period, the highest frequency of findings in the highest concentration class above 10 µg/L is also for findings of TFA and desphenyl-chloridazon, with a comparable number of RWAPs affected. The highest concentration is 20 µg/L for TFA and approximately 12 µg/L for desphenyl-chloridazon, which are above the respective threshold values. The concentration threshold of 3 µg/L is also exceeded by the second chloridazon metabolite methyl-desphenyl-chloridazon (which, with a maximum of more than 6 µg/L, is also above the HRIV). The metabolites metolachlor sulfonic acid, metazachlor sulfonic acid, and metolachlor acid are also detected in the concentration range between 1 and 3 µg/L. All other metabolites also exhibit findings in the concentration range between 0.1 µg/L and 1 µg/L. Only the metabolites CGA 368208 of S-metolachlor, CGA 108906 of metalaxyl, and desethyl-terbuthylazine were not detected at concentrations above 0.1 µg/L in this analysis.

Table 3: Findings of metabolites of approved[11] active substances with the latest value above the limit of quantification (LOQ) with analyses in the period 2010 to 2022 (number of raw water abstraction points [RWAPs, groundwater], as of 13/06/2023)

Metabolites	No. of RWAPs with analyses	No. of RWAPs with the latest value					Maximum median in µg/L	Threshold value in µg/L	Threshold value[12]
		≥ LOQ ≤ 0.1 µg/L	> 0.1 µg/L ≤ 1 µg/L	> 1 µg/L ≤ 3 µg/L	> 3 µg/L ≤ 10 µg/L	> 10 µg/L			
Trifluoroacetic acid	2970	93	1577	430	67	14	20	10[13]	UBA recom
Desphenyl-chloridazon (metabolite B)*	4635	528	925	248	67	1	11,88	3	HRIV
Metabolite CGA 380168 / CGA 354743 of S-metolachlor (metolachlor sulfonic acid)	1898	153	177	52	2		6,2	3	HRIV
Methyl-desphenyl-chloridazon (metabolite B1)*	4333	515	493	25	1		6,31	3	HRIV
Metabolite CGA 51202 / CGA 351916 of S-metolachlor (metolachlor acid)	1871	128	175	16	1		4,6	3	HRIV
Metabolite BH 479-8 of metazachlor (metazachlor sulfonic acid)	2125	255	260	19			2,3	3	HRIV

[11] Approval status: October 2022; for the current status, see https://apps2.bvl.bund.de/psm

[12] UBA recom: recommendation by the Federal Environment Agency (UBA); HRIV: health-related indicator value; aux TV: auxiliary threshold value for non-relevant metabolites without an HRIV classification; TV in acc with GrwV: threshold value in accordance with the Groundwater Ordinance (GrWV)

[13] Toxicologically based guidance value: 60 µg/L

* Chloridazon: last approved up to 31/12/2018, period of grace: 30/06/2020

Metabolites	No. of RWAPs with analyses	No. of RWAPs with the latest value					Maximum median in µg/L	Threshold value in µg/L	Threshold value[12]
		≥ LOQ ≤ 0.1 µg/L	> 0.1 µg/L ≤ 1 µg/L	> 1 µg/L ≤ 3 µg/L	> 3 µg/L ≤ 10 µg/L	> 10 µg/L			
Metabolite NOA 413173 of S-metolachlor	1206	77	125	9			2,5	3	HRIV
Saccharin / tribenuron metabolite IN-00581	2149	195	25	4			2,07	1	aux TV
Metabolite BH 479-4 of metazachlor (metazachlor acid)	2033	209	123	2			1,98	3	HRIV
Metabolite CGA 369873 (dimethachlor) = metabolite N479H160 (metazachlor)	1235	83	91				0,99	1	HRIV
Metabolite CGA 357704 of S-metolachlor	600	40	61				0,94	1	HRIV
Metabolite M27 of dimethenamid-P and dimethenamid	665	36	36				0,43	3	HRIV
Metabolite CGA 354742 of dimethachlor (dimethachlor sulfonic acid)	1667	47	20				0,67	3	HRIV
2,6-dichlorobenzamide (fluopicolide-M01)	4063	88	15				0,99	3	HRIV
Metabolite CGA 368208 of S-metolachlor	468	38	12				0,31	1	HRIV
Metabolite SYN 545666 of terbuthylazine	11	5	5				0,18	1	aux TV
Metabolite BH 479-12 of metazachlor	516	25	4				0,22	1	HRIV
Metabolite CGA 50266 of dimethachlor (dimethachlor acid)	1589	12	4				0,2	3	HRIV
Metabolite CGA 108906 of metalaxyl	474	18	3				0,15	1	HRIV
Metabolite CGA 324007 of terbuthylazine	61	2	3				0,29	1	aux TV
Metabolite M2 of flufenacet	499	4	2				0,16	1	HRIV
Nicosulfuron metabolite ASDM	12	2	2				0,2	1	aux TV
Metabolite M23 of dimethenamid-P and dimethenamid	175	21	1				0,21	3	HRIV
AMPA (aminomethylphosphonic acid)	1800	5	1				0,12	1	aux TV
Metabolite CGA 373464 of dimethachlor	16	0	1				0,34	1	HRIV
Metabolite CGA 62826 / NOA 409045 of metalaxyl-M	619	0	1				0,25	1	HRIV
Desethylterbuthylazine	4684	8					0,09	0,1	TV in acc with GrwV
Nicosulfuron metabolite AUSN	11	3					0,09	1	aux TV
Nicosulfuron metabolite UCSN	8	1					0,051	1	aux TV

Table 4: Findings of metabolites of approved[14] active substances above the limit of quantification in the period 2020 to 2022 (number of raw water abstraction points [RWAPs, groundwater], as of 13/06/2023)

Metabolites	No. of RWAPs with analyses	No. of RWAPs with median					Maximum median in µg/L	Threshold value in µg/L	Threshold value[15]
		≥ LOQ ≤ 0.1 µg/L	> 0.1 µg/L ≤ 1 µg/L	> 1 µg/L ≤ 3 µg/L	> 3 µg/L ≤ 10 µg/L	> 10 µg/L			
Trifluoroacetic acid	1108	67	370	159	55	13	20	10[16]	UBA recom
Desphenyl-chloridazon (metabolite B)*	1771	193	368	135	38	1	11,88	3	HRIV
Methyl-desphenyl-chloridazon (metabolite B1)*	1681	213	246	8	1		6,31	3	HRIV
Metabolite CGA 380168 / CGA 354743 of S-metolachlor (metolachlor sulfonic acid)	759	63	77	20			2,6	3	HRIV
Metabolite BH 479-8 of metazachlor (metazachlor sulfonic acid)	921	142	126	4			2,6	3	HRIV
Metabolite CGA 51202 / CGA 351916 of S-metolachlor (metolachlor acid)	764	33	71	4			1,35	3	HRIV
Metabolite BH 479-4 of metazachlor (metazachlor acid)	856	96	50				0,941	3	HRIV
Metabolite NOA 413173 of S-metolachlor	440	32	42				0,9	3	HRIV
Metabolite CGA 369873 (dimethachlor) = metabolite N479H160 (metazachlor)	465	44	35				0,31	1	HRIV
Metabolite CGA 357704 of S-metolachlor	109	12	24				0,49	1	HRIV
Metabolite M27 of dimethenamid-P and dimethenamid	197	16	15				0,39	3	HRIV
Metabolite CGA 354742 of dimethachlor (dimethachlor sulfonic acid)	750	18	10				0,52	3	HRIV
Metabolite SYN 545666 of terbuthylazine	10	5	5				0,18	1	aux TV
2,6-dichlorobenzamide (fluopicolide-M01)	1140	17	4				0,17	3	HRIV
Metabolite BH 479-12 of metazachlor	113	7	3				0,19	1	HRIV
Metabolite CGA 324007 of terbuthylazine	59	2	3				0,25	1	aux TV
Metabolite M2 of flufenacet	121	2	2				0,16	1	HRIV

[14] Approval status: October 2022; for the current status, see https://apps2.bvl.bund.de/psm

[15] UBA recom: recommendation by the Federal Environment Agency (UBA); HRIV: health-related indicator value; aux TV: auxiliary threshold value for non-relevant metabolites without an HRIV classification; TV in acc with GrwV: threshold value in accordance with the Groundwater Ordinance (GrWV)

[16] Toxicologically based guidance value: 60 µg/L

* Chloridazon: last approved up to 31/12/2018, period of grace: 30/06/2020

Metabolites	No. of RWAPs with analyses	No. of RWAPs with median					Maximum median in µg/L	Threshold value in µg/L	Threshold value[15]
		≥ LOQ ≤ 0.1 µg/L	> 0.1 µg/L ≤ 1 µg/L	> 1 µg/L ≤ 3 µg/L	> 3 µg/L ≤ 10 µg/L	> 10 µg/L			
Nicosulfuron metabolite ASDM	3	1	2				0,15	1	aux TV
Metabolite M23 of dimethenamid-P and dimethenamid	70	8	1				0,21	3	HRIV
Saccharin / tribenuron metabolite IN-00581	123	4	1				0,112	1	aux TV
Metabolite CGA 50266 of dimethachlor (dimethachlor acid)	701	4	1				0,2	3	HRIV
Nicosulfuron metabolite AUSN	3	2	1				0,115	1	aux TV
AMPA (aminomethylphosphonic acid)	781	2	1				0,12	1	aux TV
Metabolite CGA 368208 of S-metolachlor	121	12					0,096	1	HRIV
Metabolite CGA 108906 of metalaxyl	112	6					0,082	1	HRIV
Desethyl-terbuthylazine	1477	2					0,02	0,1	TV in acc with GrwV

ANALYSIS OF ACTIVE SUBSTANCES THAT ARE NO LONGER APPROVED AND THEIR METABOLITES

In addition to the findings on approved active substances and their metabolites presented above, the RWDB PPP also contains data on "historical" active substances and their degradation products, i.e. active substances whose approval expired long ago, but which, due to their properties and application practice, were able to enter groundwater and are therefore still included in many investigation programmes today. This pool of data is analysed below using the example of the herbicidal active substance atrazine and its metabolites. For this active substance, a sufficiently consistent database is available at the RWAPs, which also allows statistically reliable statements to be made about the long-term development of the concentration in groundwater over the last three decades.

Table 5 shows the analysis of the findings according to the latest measured value available in the RWDB PPP for the active substance atrazine and its two main metabolites, desethylatrazine and desisopropylatrazine. More than 30 years after it was banned, atrazine can still be found in about 2% of RWAPs. In fact, the threshold value of the Groundwater Ordinance (GrWV) of 0.1 µg/L is even exceeded in almost 0.1% of RWAPs.

Table 5: Findings based on the latest value of the active substance atrazine and its two main metabolites, desethylatrazine and desisopropylatrazine (number of raw water abstraction points [RWAPs, groundwater] with analyses in the period 2010 to 2022, as of 13/06/2023)

Parameter	RWAPs with analyses	Latest value ≥ LOQ < 0.075 µg/L	Latest value ≥ 0.075 µg/L < 0.1 µg/L	Latest value ≥ 0.1 µg/L	Maximum latest measured value [µg/L]
Atrazine	6180	124	6	7	0,29
Desethylatrazine	6077	276	20	18	0,95
Desisopropylatrazine	5968	41	0	1	0,15

Table 6 shows a comparison of the findings over the three previous decades, from the ban on use to the present day, for almost 1,100 consistent monitoring wells, i.e. raw water abstraction points, for which measured values for atrazine and desethylatrazine were available for all three periods. It can be seen that the exceedances of the 0.1 µg/L threshold value for atrazine and desethylatrazine decrease only gradually over three decades, first from 16 and 23% to 4 and 8% and then to 0 and 2%, respectively, demonstrating the much-cited "long memory of groundwater".

Table 6: Comparison of findings of atrazine and desethylatrazine for consistent RWAPs over the three decades since the ban (raw water abstraction points [RWAPs, groundwater] with analyses, median of the annual medians, as of: November 2021)

	Atrazine			Desethylatrazine		
	1991 - 2000	2001 - 2010	2011 - 2020	1991 - 2000	2001 - 2010	2011 - 2020
No. of RWAPs < LOQ	912	967	1052	820	884	981
No. of RWAPs ≥ LOQ < 0.075 µg/L	153	114	37	199	156	72
No. of RWAPs ≥ 0.075 µg/L < 0.1 µg/L	6	7	3	18	13	12
No. of RWAPs ≥ 0.1 µg/L	21	4	0	30	14	2
Total	1092	1092	1092	1067	1067	1067

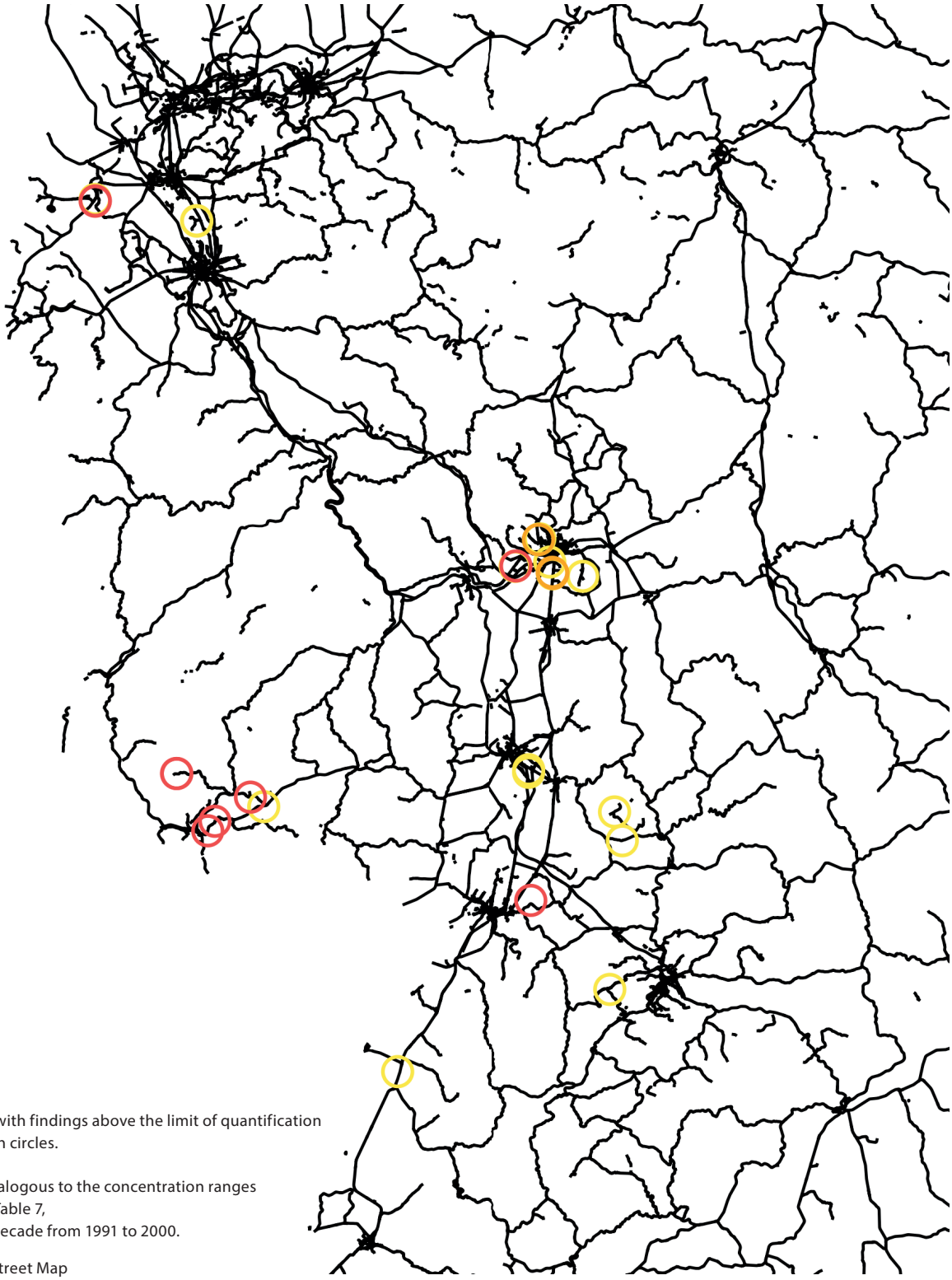
A further analysis examined the possibility of an association between the findings of the herbicidal active substances atrazine and bromacil. Since bromacil was only used on railway tracks, this relatively mobile substance can be seen as an "indicator" for other active substances that were also applied to this target area. Historical data from the RWDB PPP was therefore to be used to test the hypothesis that findings of atrazine in raw water could originate from rail applications. To this end, the spatial proximity of common atrazine and bromacil detection sites to tracks was examined as a baseline. Due to the many influencing factors and the lack of detailed hydrogeological and pedological information on the catchment areas of the individual RWAPs, a detailed analysis of the causes would require further studies.

An examination of the database for the co-occurrence of atrazine and bromacil shows that the probability of a simultaneous positive finding over all three ten-year periods under investigation is about 12%. However, there was no evidence to suggest that this was more pronounced in the first decade or for monitoring wells with high concentrations of atrazine.

As a first rough test of the hypothesis that the associated findings originate from entries at railway tracks, the RWAPs that exhibited common findings were assessed on an individual basis (Table 7). Geographic information system (GIS) analysis showed that railway tracks were located within a 5-km radius of the affected RWAPs in each case (Figure 2). This can be seen as a confirmation of the above hypothesis that the findings of atrazine in the respective raw water originate from track applications. However, this would need to be supported by further evaluation on a case-by-case basis.

Table 7: Findings at RWAPs with positive findings of atrazine and bromacil over the three decades since the ban of atrazine (raw water abstraction points [RWAPs, groundwater] with analyses, median of the annual medians, as of: June 2022)

	1991 - 2000	2001 - 2010	2011 - 2020
Number of RWAPs with positive findings of atrazine and bromacil	28	29	14
of which			
Atrazine ≥ LOQ < 0.075 µg/L	16	25	10
Atrazine ≥ 0.075 µg/L < 0.1 µg/L	3	2	2
Atrazine ≥ 0.1 µg/L	9	2	2



The 28 RWAPs with findings above the limit of quantification are marked with circles.

Colouring is analogous to the concentration ranges for atrazine in Table 7,
query period: decade from 1991 to 2000.

Source: Open Street Map

Figure 2: Raw water abstraction points (RWAPs) in the vicinity of railway tracks with findings of atrazine and bromacil

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GLOSSARY

Limit of quantification and limit of detection:
The limit of quantification (LOQ) is the lowest concentration of a substance that can be quantitatively determined with a certain precision. The limit of detection (LOD), which is below the LOQ, denotes the measured variable at which the substance can just be detected reliably (available: a yes/no decision). Both properties depend on the instrument used, the method available and the substance to be analysed.

Health-related indicator value (HRIV):
The Federal Institute for Risk Assessment (BfR) and the Federal Environment Agency (UBA) set these precautionary health-related indicator values (in German: HRIV = Gesundheitlicher Orientierungswert (GOW)) for a lifelong intake based on the information available on the respective substance. If additional data is available, e.g. from longer-term subchronic studies, higher guideline values can be established. Toxicologists distinguish between lifelong exposure to a substance (health-related guidance value) and exposure that is tolerated for a shorter period (action value). Precautionary health-related assessments also take into account possible combination effects of several substances, special high-risk groups (e.g. infants), accumulation in the body, the prevention of contamination, and the possibilities of reducing or removing substances during drinking water treatment. Substances that have not undergone a full toxicological assessment are evaluated on the basis of existing data from a precautionary health-related perspective. The HRIV is derived in the process. Depending on the mode of action, the value is set in a range from 0.01 to 3.0 µg/L. The HRIV is set at such a low level that even a lifelong intake of the substance concerned will not give rise to health concerns. Although HRIVs cannot be explicitly substantiated in terms of health, they are toxicologically very conservative estimates, which can therefore also be substantiated in terms of drinking water hygiene. Exceeding them by a factor of 3 to 10 in the short to medium term (10 years) is a cause for concern for drinking water hygiene, but not for health. However, measured values of > 3 µg/L to 10 µg/L are unacceptable in the long term; any values exceeding 10 µg/L are generally unacceptable.

Sources: https://www.umweltbundesamt.de/themen/wasser/trinkwasser/trinkwasserqualitaet/toxikologie-des-trinkwassers

https://www.umweltbundesamt.de/sites/default/files/medien/5620/dokumente/gowpflanzenschutzmetabolite-20211109_0.pdf

(List of HRIV for NRM of PPP active substances, version as updated in November 2021)

Limit value:
Limit values are maximum concentrations for natural substances, residues of active substances, and environmental contaminants in food products, consumer products and environmental media that have been politically defined (legally binding) in laws and ordinances. They have proven effective in regulating exposure to chemicals and many other potentially noxious substances in all areas of the human environment. Active substances and relevant metabolites of plant protection products must not exceed the maximum concentrations of 0.1 µg/L (per individual substance) and 0.5 µg/L

Source: https://www.umweltbundesamt.de/sites/default/files/medien/377/dokumente/grenzwerte_leitwerte.pdf

Guidance value:
Toxicologically substantiated guidance values can be determined for specific substances and substance quantities, depending on the toxic potential, if they are fully assessable. Substances that can only be partially assessed due to incomplete data and for which only a health-related indicator value (HRIV) is available can be assessed using a guidance value if the toxicological database is complete. Guidance values may only be exceeded temporarily up to the level of an action value.

Source: https://www.umweltbundesamt.de/sites/default/files/medien/377/dokumente/grenzwerte_leitwerte.pdf

Parameter value:
Concentration value of a substance that is set for the purpose of monitoring it.

Threshold value:
Concentration of a pollutant, group of pollutants, or indicator of pollution in groundwater or the value of a pollution indicator in groundwater set to protect human health and the environment.

Source: https://www.gesetze-im-internet.de/grwv_2010/GrwV.pdf

Environmental quality standard:
A wide range of substances are discharged into water bodies from households, industry, commerce, transport and agriculture. As analytical techniques continue to improve, ever smaller concentrations of all kinds of substances are detected in water bodies. The EU Water Framework Directive requires that these substances be assessed with regard to their significance for environmental protection and, in some cases, health protection, and that environmental quality standards (EQS) be set where appropriate. The EU Water Framework Directive groups substances into those with EU-wide significance and those with local significance for surface waters. Consequently, environmental quality standards are set and monitored across the EU or on a national level.

Source: https://www.umweltbundesamt.de/themen/wasser/gewaesser/fluesse/ueberwachung-bewertung/chemisch#textpart-1

Precautionary action value:
A provisionally acceptable precautionary action value (PAV) with regard to drinking water hygiene. For non-relevant metabolites (NRM) of PPP active substances, this value is 10 µg/L. Deviation from the HRIV for a limited period with exemption(s) from the competent public health department. Implementation of mitigation measures according to the action plan.

Source: https://www.umweltbundesamt.de/sites/default/files/medien/377/dokumente/grenzwerte_leitwerte.pdf

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https://www.umweltbundesamt.de/sites/default/files/medien/5620/dokumente/gowpflanzenschutzmetabolite-20211109_0.pdf
[Translation: Health-related indication value (HRIV) for non-relevant metabolites (NRM) of active substances from plant protection products (PPP)]

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IMPRINT

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The brochure "Raw Water Database of Plant Protection Products – 2022 Analysis" can be downloaded from the website of the DVGW-Technologiezentrum Wasser (German Water Centre – TZW):

Scan the QR code
and download this
(24-page) brochure
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The "Plant protection products in a nutshell" brochure can also be downloaded from the TZW website. The website also contains all information concerning the Raw Water Database and the work of the Round Table:
https://tzw.de/en/projects/project-details/detail/raw-water-database-water-supply-pesticides