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PLANT PROTECTION PRODUCTS
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Zusammenarbeit von
Wasserversorgung und
Pflanzenschutzmittelindustrie
in Deutschland

Cooperation to protect drinking water resources:
Viewpoints, experiences, measurement results – solutions and goals for the future

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SUMMARY

The water industry associations (BDEW, DVGW, VKU) and The Plant Care Industries 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, work together to solve problems, and operate a data base on the presence of plant protection products (PPP) in raw water resources.

The Raw Water Database Water Supply was established by the DVGW-Technologiezentrum Wasser (German Water Centre – TZW) and has been operated by it in collaboration with the German Association of Energy and Water Industries (Bundesverband der Energie- und Wasserwirtschaft e. V. – BDEW), IVA and the German Association of Local Utilities (Verband kommunaler Unternehmen e. V. – VKU) since 2012. The database provides a national overview of the current exposure situation in raw water. It includes around 74,000 analyses of plant protection products from over 7,150 raw water abstraction points of 1,150 water companies throughout Germany. The Raw Water Database contains analyses of 296 approved substances, 87 active substances that are no longer approved, and 90 degradation products (metabolites). In 5,431 (96%) of the total of 5,659 raw water abstraction points investigated in the period from January 2010 to March 2020, the measured concentrations for all PPP active substances and metabolites under investigation were below the limit value for drinking water or the health-related indicator value (HRIV; in German: HRIV = Gesundheitlicher Orientierungswert (GOW)). 228 (4%) abstraction points exhibited exceedances. Exceedances of the limit value for drinking water by individual active substances were in the low parts-per-thousand range at most. In the case of individual non-relevant metabolites, exceedances of the HRIV were in the low single-digit percentage range at most.

The data shows that the problem area revolves around a few active substances and non-relevant metabolites at a comparatively small number of raw water abstraction points. The water industry associations and IVA collaborate on-site with the water companies concerned in order to clarify the findings and to develop action for reducing inputs. During the peak phase in the fourth year of the project (2016), 47 "areas requiring action" of 20 water companies received joint support with regard to eight substances. At the beginning of 2019, eight remaining areas requiring action were still receiving support.

Combined with the actions developed, the Raw Water Database is evolving from a data recording tool to an early warning system to help support the water companies affected, ensuring the quickest possible rehabilitation of contaminated raw water.

Three different kinds of case studies from areas requiring action and the analysis results of the Raw Water Database are described in detail in "Plant protection products in a nutshell". The brochure also highlights aspects of cooperation that are important for the Round Table, as well as future challenges.

Following a reorientation of the work of the Round Table in 2019, these future objectives were set:

1. Identification of criteria characterising sensitive areas with regard to the leaching of PPP active substances.
2. Development of proposals for local restrictions on the use of active substances that become conspicuous in particularly sensitive areas. This would enable farmers in other areas to continue to use these active substances.
3. 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).
4. Early detection of new problematic active substances and/or areas of use.
5. Continuation of the Raw Water Database, including a survey of water companies on the analytical results of plant protection products every three years.
6. Shortening and simplification of the procedure for clarifying findings.
7. Encouragement of agriculture to provide public drinking water suppliers with data on the use of plant protection products in drinking water catchment areas.
8. Exchange of information on the occurrence of transformation products of active substances in water treatment.

INTRODUCTION

Dr. Claudia Castell-Exner (DVGW) | Dr. Friedrich Dechet (IVA)

Under the guiding principle

"We tackle problems as if we were 'one company' that produces both top-quality plant protection products and drinking water"

the water industry associations (BDEW, DVGW, VKU) and IVA began collaborating at the Water Industry / Plant Protection Industry Round Table in 2009.

BDEW, DVGW, VKU and IVA set themselves the goal of

1. using coordinated and tested methods to detect conspicuous findings of plant protection products (PPPs) as well as relevant and non-relevant metabolites, and to prevent exceedances of the limit value of 0.1 µg/L (Drinking Water Ordinance – TrinkwV) or the health-related indicator value (HRIV; in German: HRIV = Gesundheitlicher Orientierungswert (GOW)).

2. clarifying the cause of input and initiating the rehabilitation of drinking water resources in areas exhibiting contamination by plant protection products.

3. monitoring new PPP active substances by conducting systematic monitoring programmes in selected pilot areas.

The activities of the Round Table have achieved their purpose once limit values and HRIVs are no longer exceeded by PPP active substances and their metabolites in raw water from drinking water extraction plants – this is the common understanding.

Besides the regular exchange of information and collaboration to solve problems, the key elements of the agreement "Gemeinsam die Zukunft sichern" (Securing the future together) were to establish and operate a database on the occurrence of PPPs in raw water resources (Raw Water Database Water Supply). This Raw Water Database contributes to the identification of drinking water abstraction areas exhibiting contamination by PPPs and the targeted introduction of actions that help improve the quality of raw water ("areas requiring action").

The DVGW-Technologiezentrum Wasser (German Water Centre – TZW), acting in the capacity of the contractor and operator of the database, notifies the participating water companies in the event that anomalies are detected during the analysis of the data they reported. Conversely, water suppliers can put their questions directly to the association contact persons mentioned below or to TZW. Figure 1 shows the interaction between the Round Table, the Raw Water Database and local water companies.

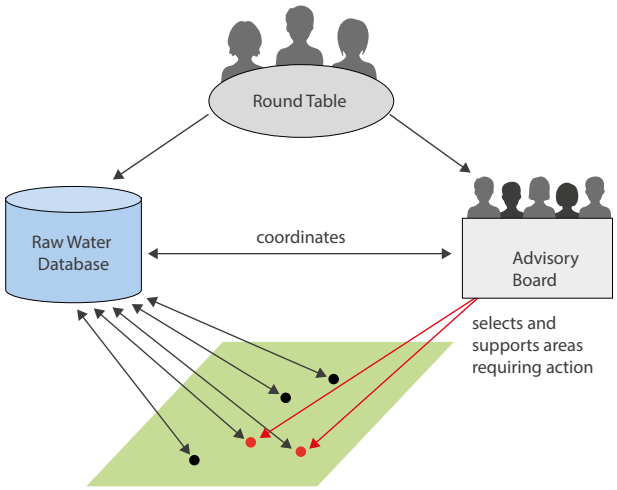
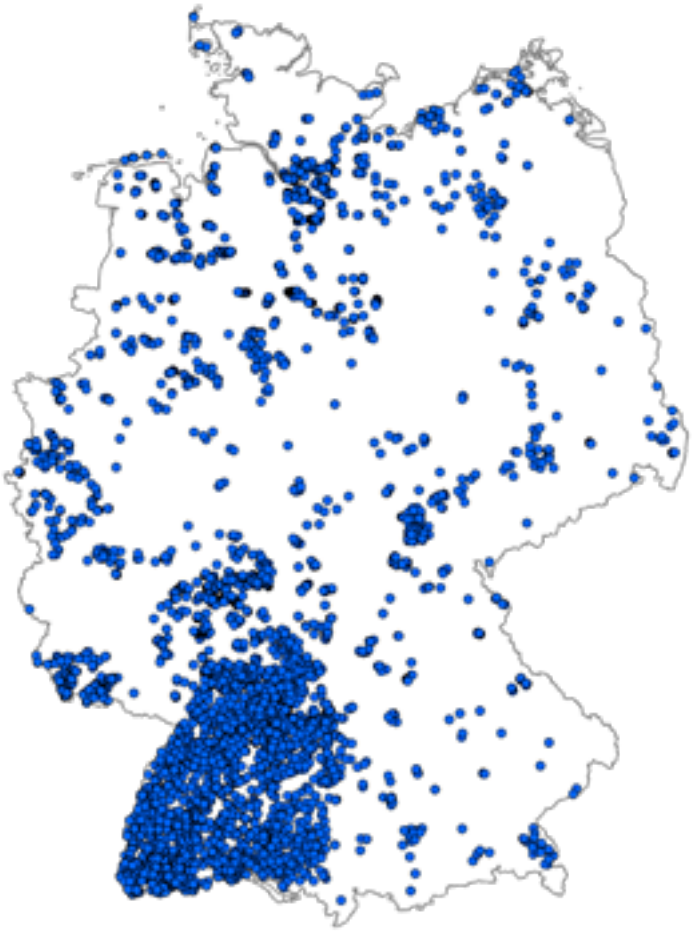


Figure 1: The flow of information between water companies, the Raw Water Database Water Supply and the Water Industry / Plant Protection Industry Round Table

Since the start of the project, around 1,150 water companies have voluntarily provided almost 74,000 analysis data from more than 7,150 raw water abstraction points for the Raw Water Database (Figure 2). The Raw Water Database provides an overview of the exposure situation of drinking water resources. 383 PPP active substances and 90 metabolites have been recorded. The Raw Water Database exclusively includes raw water abstraction points that are in use (i. e. no upgradient groundwater quality monitoring wells or other monitoring wells). It therefore provides a picture of raw water extracted from groundwater resources that is actually used for the provision of drinking water.



Raw Water Database Water Supply, as of 11/2020
● Raw water abstraction points with PPP analyses

Source: Data provided by water companies participating in the Raw Water Database Water Supply project. Administrative boundaries: © GeoBasis-DE / BKG 2020 (data amended)

Figure 2: The raw water abstraction points included in the Raw Water Database Water Supply allow a comprehensive analysis 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 25 years.

In principle, all water companies with conspicuous findings related to PPP active substances and their metabolites can contact members of the Round Table to receive support from the water industry associations and IVA member companies. In concrete terms, this means that the exposure situation is analysed on site together with the water companies; where necessary, actions are initiated to improve the quality of raw water. The steps involved in this process are outlined below. If the Round Table recommends systematic monitoring, the manufacturers cover half of the costs incurred.

First action: step up monitoring

A systematic monitoring programme is established taking into account the framework conditions related to soil science and hydrogeology as well as agricultural use. The elements of systematic monitoring are:

- Selection of the relevant active substances and metabolites in terms of actual use
- Selection of the raw water abstraction points
- Scope and point in time of the monitoring programme
- Sampling and chemical analysis
- Evaluation and assessment of results

Second action: initiate activities on the ground

- Collection of key information on the catchment area in the form of a fact sheet
- Improvement of information sharing to people in the catchment area who decide on the use of active substances and who apply PPPs
- Intensification of advice in the catchment area (e. g. with regard to compliance with the directions for using the PPP and special provisions)
- Area-specific minimisation concepts for reducing the discharge of substances taking into account agronomic measures
- Change in product use, e. g. restrictions on application, limitation of quantities, substitution, rotation of active substances

Actions in an area requiring action can follow the timeline of the example given below (Table 1).

The Round Table has since been able to help several water supply companies to address the contamination issues related to their drinking water resources in dialogue with PPP manufacturers, users and the official advisory system, and to initiate actions to improve the quality of the raw water.

For more information, please contact the contact persons from the participating associations:

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Table 1: Sequence of actions in an area requiring action

Period	Action
January/February 2012	First contact to water companies / discussion of the questions: Contamination? Causes? Assessment? Rates of application? Area inspection ...
March 2012	In consultation with plant protection services, agriculture, agricultural trade: advisory concept with recommendations for active substance management, planning of the compliance survey, systematic monitoring of potential routes of entry
End of 2012 / early 2013	PPP industry funds 50% of monitoring costs
Autumn 2013	Readjustment of monitoring, joint decision to continue the project
Autumn 2016	Approval of the measured concentrations

VIEWPOINT OF THE WATER INDUSTRY

Dr. Claudia Castell-Exner (DVGW) |

Professor Dr.-Ing. Frieder Haakh (special-purpose association Landeswasserversorgung, Stuttgart)

Water companies face a complex set of conflicting demands: consumers justifiably place the highest demands on the quality of drinking water, given that it is a natural product; ideally, it should be "naturally pure" and "free of anthropogenic influences". The No. 1 food should be fit for consumption and available all day, every day. A closer look at drinking water resources shows that they are exposed to a variety of risks due to inputs of pollutants; in many places, these resources are measurably compromised. These pollutants include plant protection products and their degradation products. Concentrations above limit values or so-called health-related indicator values (HRIVs) show that the legal rules and their enforcement are not sufficient everywhere to adequately ensure the necessary protection of resources.

Water companies are in a position where they must provide their customers with top-quality drinking water, despite not being the cause of the problem of excessively high concentrations of PPPs in drinking water resources. The public is very sensitive to pesticide residues in drinking water, and often customers do not differentiate between the contamination of drinking water resources and the pristine quality of drinking water – no easy task when it comes to communication. The protection of drinking water resources has the highest priority – an approach that is by nature long term. After all, the officially approved production of drinking water is in place for generations to come.

In view of the inadequate legal protection of drinking water resources on the one hand and the urgent need to avoid further contamination with PPP active substances and their metabolites on the other, contact was sought with PPP manufacturers, with the aim of involving them in solving the problem as part of their product stewardship. Adopting the motto *"Gemeinsam die Zukunft sichern"* (Securing the future together), the stakeholders managed to develop an understanding of the concerns of the water industry on the one hand and the need to use plant protection products on the other. The joint activities have achieved their purpose once limit values and HRIVs are no longer exceeded by PPP active substances and their metabolites in drinking water resources.

A two-stage approach is pursued: first, specific problems are solved locally at sites where excessive concentrations of PPP active substances and metabolites are measured in drinking water resources. In a second, preventive stage, future problems are to be averted through close cooperation with PPP manufacturers by means of systematic monitoring and early detection. The most effective instrument for protecting water in this connection is prevention, i. e. the avoidance of PPP emissions into the aquatic environment. The catalyst for successful collaboration is an overlap of interests, which provides a basis for concrete cooperation in problem-solving.

VIEWPOINT OF MANUFACTURERS OF PLANT PROTECTION PRODUCTS

Dr. Friedrich Dechet (IVA) | Dr. Herbert Resseler (Syngenta Agro)

The predominant form of agriculture practised under current agronomic conditions, which produces affordable food, feed and renewable raw materials, requires the use of environmentally safe plant protection products and the responsible handling of these substances.

In connection with the protection of drinking water resources, it is important to know how these products behave in soil. The regulation is very clear for active substances and relevant metabolites: if the approval assessment shows that the limit value of 0.1 µg/L is exceeded in groundwater, the product cannot be authorised. In the case of non-relevant metabolites (NRM), i. e. metabolites without comparable properties as the active substance, the European guidance document SANCO/221/2000 recommends tolerating up to 10 µg/L of these NRM in groundwater. This guidance value is simultaneously a target value that must be complied with in the authorisation procedure.

Moreover, lower values apply in Germany, at least for drinking water: since 2008, the Federal Environment Agency (UBA) has recommended so-called health-related indicator values (HRIVs) of 1 or 3 µg/L to regulate non-relevant metabolites in drinking water. For a few years now, however, there have been calls to extend these indicator values, applicable to drinking water, to the entire groundwater as binding limit values. In view of raw water treatment and undivided groundwater protection, this is understandable from the perspective of the water industry. Until now, however, it is unclear which scientific criteria are to be applied if these indicator values are to be understood as a substitute for higher and strictly scientifically based guidance values: if all non-relevant metabolites were to be regulated to a maximum of 1 µg/L in groundwater, it would no longer be possible to use several PPPs in line with current agricultural practice. The fact that this could lead to the overuse of the remaining PPPs, with adverse consequences, is not readily discussed: even now, agriculture is facing transregional resistance problems in parts of Germany – as well as severe climate-induced yield losses. Nor would this create additional safety for humans and the environment.

The plant protection industry is therefore in a quandary. Plant protection products may only be authorised if there is evidence that degradation occurs within an acceptable period of time. However, degradation also necessarily results in the formation of degradation products. The rule (under the laws of nature) is that degradation in soil reduces toxicity, but also makes the molecule smaller, resulting in greater mobility in the aqueous phase and therefore potentially more leaching. Furthermore, limit values are currently being lowered at a rate that outstrips the ability to adapt products accordingly.

One way to solve this dilemma would be to adopt an alternative, i. e. scientifically more robust, threshold value approach, which would have to be discussed with the water industry and the authorities. This alternative would be an additional element alongside previously introduced measures, such as HRIVs in drinking water and direction for use NG301, which IVA is in favour of extending to active substances in particularly sensitive areas. This would mean that these active substances, which are important for agriculture, could still be used outside particularly sensitive areas (or inside such areas, albeit in smaller quantities), while getting closer to the goal of being able to ensure even better protection of raw water for the purpose of supplying the public with drinking water.

In view of the intensive use of land in such a populous country as Germany, it is evident that the protection of drinking water reserves requires measures that go beyond the requirements of area-wide water protection, depending on the natural site conditions: the greater the requirements for regulating trace substances, the more precisely the use of their parent substances must be adapted to the relevant local or regional environmental conditions. Anything else would be a spurious solution to the detriment of agriculture. After all, environmental requirements similar to those applicable to agriculture do not yet exist for non-agricultural emitters (e. g. sewerage, industry) in peri-urban areas.

Under these circumstances, abandoning the use of synthetic organic PPPs in agricultural practice is not a realistic option either, unless extensive additional areas are to be ploughed up in Germany or abroad. Extensive farming methods that consciously avoid the use of synthetic organic herbicides and mineral fertilisers, but use other plant protection products (such as copper and pyrethrins) to control fungi and pests instead, produce only around half the yield per hectare of intensive farming. This would inevitably have negative consequences for meeting food needs and conserving resources such as land, energy and areas of refuge. At this point, water protection would indirectly compete with the protection of biodiversity in agricultural landscapes and adjacent areas. Moreover, organic farming is not possible everywhere due to the lack of a market. We consider it unsustainable to ignore these interrelationships in the face of a population that continues to grow at an increasing rate.

The efficient actions identified by the water industry and PPP manufacturers should be closely interlinked with the authorisation of PPPs, expert and competent agricultural advisory services, and the monitoring of groundwater and drinking water. The whole of society has a responsibility to reconcile the protection of the environment and drinking water with the necessary land use – agriculture being one such use. Neither one nor the other can have absolute priority. The Water Industry / Plant Protection Industry Round Table is the best example of how pragmatic collaboration can succeed to this end.

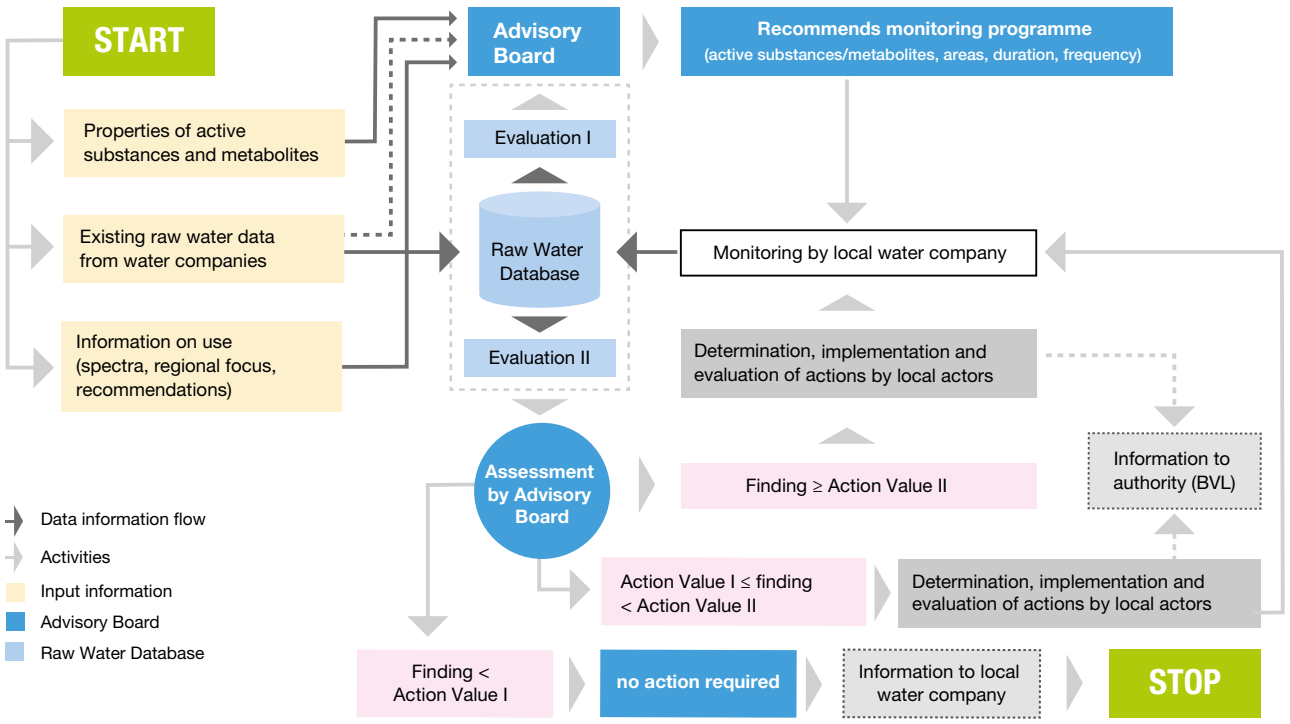
THE RAW WATER DATABASE WATER SUPPLY

Joachim Kiefer (TZW) | Thilo Fischer (TZW)

Since the start of the Raw Water Database Water Supply project in 2012, around 1,150 water companies have voluntarily provided 74,000 analysis data from more than 7,150 raw water abstraction points for the database. Compliance with data protection and strict confidentiality are key requirements for this. Data is only published in anonymous form to prevent conclusions being drawn about individual raw water abstraction points. For the first time, the database provides reliable data on the number of drinking water abstraction areas affected and an overview of areas where actions are initiated ("areas requiring action"). As a result, information on the exposure situation of raw water in public water supplies with PPP active substances and their metabolites has been pooled in one place for the whole of Germany.

In the event of conspicuous findings, the water company affected receives on-site rehabilitation support from the water industry associations and IVA or the manufacturer of the active substance concerned. Consequently, the Raw Water Database is a targeted and efficient water protection tool. During the peak phase in the fourth year of the project (2016), 47 areas requiring action of 20 water companies received joint support with regard to eight substances. At the beginning of 2019, eight areas requiring action were receiving support.

Figure 3 below shows the activities related to the Raw Water Database and in the areas requiring action.



Source: DVGW-TZW

Figure 3: The flow of information between water companies, the Raw Water Database and the corresponding Advisory Board of the Round Table. Action Value I is 75% of the respective limit value or HRIV (in German: HRIV = Gesundheitlicher Orientierungswert (GOW)) for the active substance or non-relevant metabolite. Action Value II corresponds to the respective limit value or HRIV.

FINDINGS FOR
APPROVED ACTIVE SUBSTANCES IN RAW WATER

Joachim Kiefer (TZW) | Thilo Fischer (TZW)

A total of 296 PPP active substances are currently approved in Germany (as of January 2019[1]); data for these substances is available in the Raw Water Database Water Supply, along with 87 active substances which are no longer approved. 90 metabolites have been recorded. To provide an overview of the findings, a selection was made of active substances for which the latest value is above the limit of quantification at one or more raw water abstraction points (RWAP) and which were approved at the beginning of the last survey period. The question of which active substances were detected above the respective limit and guidance values in groundwater used as raw water for drinking water production is of considerable importance to water suppliers, manufacturers and agriculture. For this reason, the Water Industry / Plant Protection Industry Round Table defined so-called action values[2]. If these action values are exceeded, certain actions have been defined for the areas concerned.

Tables 2 and 3 show the findings for active substances and metabolites, respectively. The most recent measured value recorded in the database as of 29 May 2019 is above the limit of quantification for 30 active substances and 32 metabolites[3]. Findings exceeding the limit of quantification for the active substances recorded are in the single-digit percentage range at most. The number of raw water abstraction points with values above Action Value I (= 0.075 µg/L) is in the single-digit parts-per-thousand range at most. In 5,431 (96%) of the total of 5,659 raw water abstraction points investigated in the period from January 2010 to March 2020, the measured concentrations for all the parameters under investigation were below the limit value for drinking water or the health-related indicator value (HRIV). 228 (4%) abstraction points exhibited exceedances.

Exceedances of the limit value for drinking water were in the low single-digit parts-per-thousand range at most (with reference to the individual active substance). Exceedances of the HRIV are in the lower single-digit percentage range at most (with reference to the individual non-relevant metabolite).

For individual active substances, the situation is as follows: for the active substance bentazone, a herbicidal active substance used mainly in cereals and maize to control weeds, the latest measured value exceeded Action Value II at twelve of the 4,884 raw water abstraction points sampled in total; for Mecoprop, a herbicide to control weeds in cereals, it was exceeded at four of the 4,229 points; for the oilseed rape herbicide Metazachlor, two of the 5,080 abstraction points were affected (Table 2 / Figure 4). For the beet herbicide Chloridazon, one of the 3,916 raw water abstraction points was above Action Value I. In the case of active substances and relevant metabolites, Action Value II corresponds to the limit value of 0.1 µg/L stipulated in the Drinking Water Ordinance.

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

[2] Action Value I is 75% of the respective limit value or HRIV, in German: HRIV = Gesundheitlicher Orientierungswert (GOW), for the active substance or non-relevant metabolite. Action Value II corresponds to the respective limit value or HRIV.

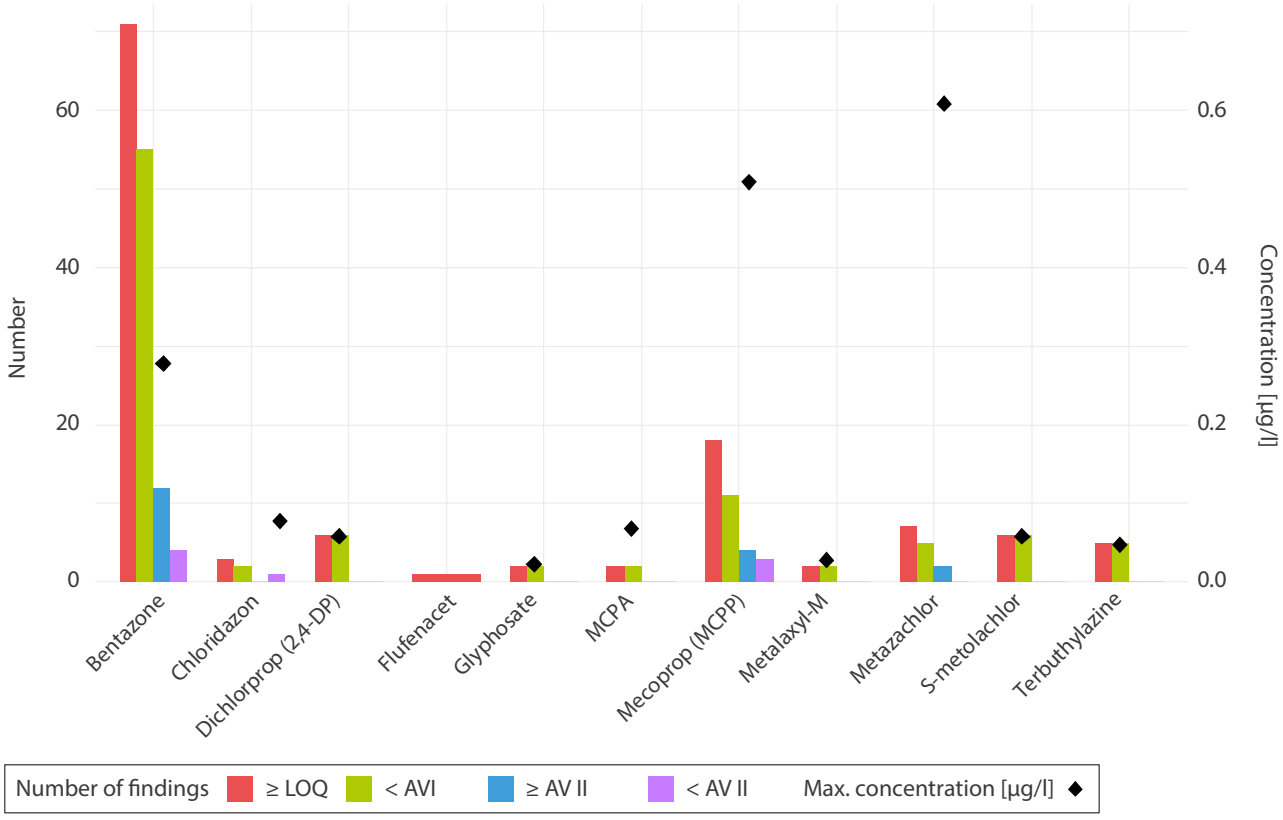
[3] Limit of quantification (LOQ): is the lowest concentration of a substance that can be quantitatively determined with a certain precision. The limit of detection (LOD), which is below the LOQ, denotes the measured variable at which the substance can just be detected reliably (available: a yes/no decision).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

Table 2: Findings of active substances with the latest value above the limit of quantification (LOQ) or below/above action values (AW) (number of raw water abstraction points (RWAP, groundwater) with analyses from 2010, as of April 2019)

Active substances	RWAP with analyses	Latest value ≥ LOQ	Latest value ≥ LOQ < AV I	Latest value ≥ AV I < AV II	Latest value ≥ AV II	AV I [µg/L]	AV II [µg/L]	Maximum latest value [µg/L]
Bentazone	4884	71	55	4	12	0.075	0.1	0.28
Mecoprop (MCPP)	4260	18	11	3	4	0.075	0.1	0.51
Metazachlor	5103	7	5	0	2	0.075	0.1	0.61
Dichlorprop (2,4-DP)	4121	6	6	0	0	0.075	0.1	0.06
S-metolachlor	4142	6	6	0	0	0.075	0.1	0.06
Terbuthylazine	5085	5	5	0	0	0.075	0.1	0.05
Chloridazon	3961	3	2	1	0	0.075	0.1	0.08
Glyphosate	1265	2	2	0	0	0.075	0.1	0.025
Metalaxyl-M	3548	2	2	0	0	0.075	0.1	0.03
MCPA (4-chloro-2-methyl-phenoxy acetic acid)	4173	2	2	0	0	0.075	0.1	0.07
Flufenacet	988	1	1	0	0	0.075	0.1	0.07
Metamitron	1553	1	1	0	0	0.075	0.1	0.025
Metobromuron	1889	1	1	0	0	0.075	0.1	0.05

LOQ: limit of quantification | AV: action value | RWAP: raw water abstraction point

Authorisation status: beginning of 2018; for the current status, see
https://www.bvl.bund.de/DE/Arbeitsbereiche/04_Pflanzenschutzmittel/01_Aufgaben/02_ZulassungPSM/01_ZugelPSM/psm_ZugelPSM_node.html



LOQ: limit of quantification | AV: action value

Figure 4: Findings of active substances with the latest value above the limit of quantification (LOQ) or below/above action values (AV) (number of raw water abstraction points (RWAP, groundwater) with analyses from 2010, as of April 2019)

FINDINGS FOR METABOLITES

Joachim Kiefer (TZW) | Thilo Fischer (TZW)

For metabolites, the latest values of 25 parameters in total were at or above the limit of quantification. The two degradation products of the sugar beet herbicide Chloridazon were detected most frequently (Table 3 / Figure 5): Desphenyl-chloridazon and Methyl-desphenyl-chloridazon were at or above the limit of quantification at 1,455 and 886 raw water abstraction points, respectively.

The metabolite BH 479-8 of Metazachlor, an oilseed rape herbicide, was the third most frequently detected substance in this group of metabolites, with 314 findings at or above the limit of quantification. Compared to the active substances, significantly more non-relevant metabolites are above the limit of quantification (up to 40% for Desphenyl-chloridazon) as a percentage of the number of raw water abstraction points sampled in each case.

Desphenyl-chloridazon was at or above Action Value II at 60 raw water abstraction points. Trifluoroacetic acid (TFA, a breakdown product of several active substances, including from non-agricultural sources) was above Action Value II at 28 abstraction points (Table 3). The metabolite CGA 357704 was above Action Value II at seven raw water abstraction points; the metabolite CGA 354743 exceeded it at one abstraction point. Both metabolites are transformation products of the maize herbicide S-metolachlor. The metabolite BH 479-4 of Metazachlor was above Action Value II at one raw water abstraction point. The more recent of these active substances, such as Metazachlor and Metolachlor, were approved pre-1980.

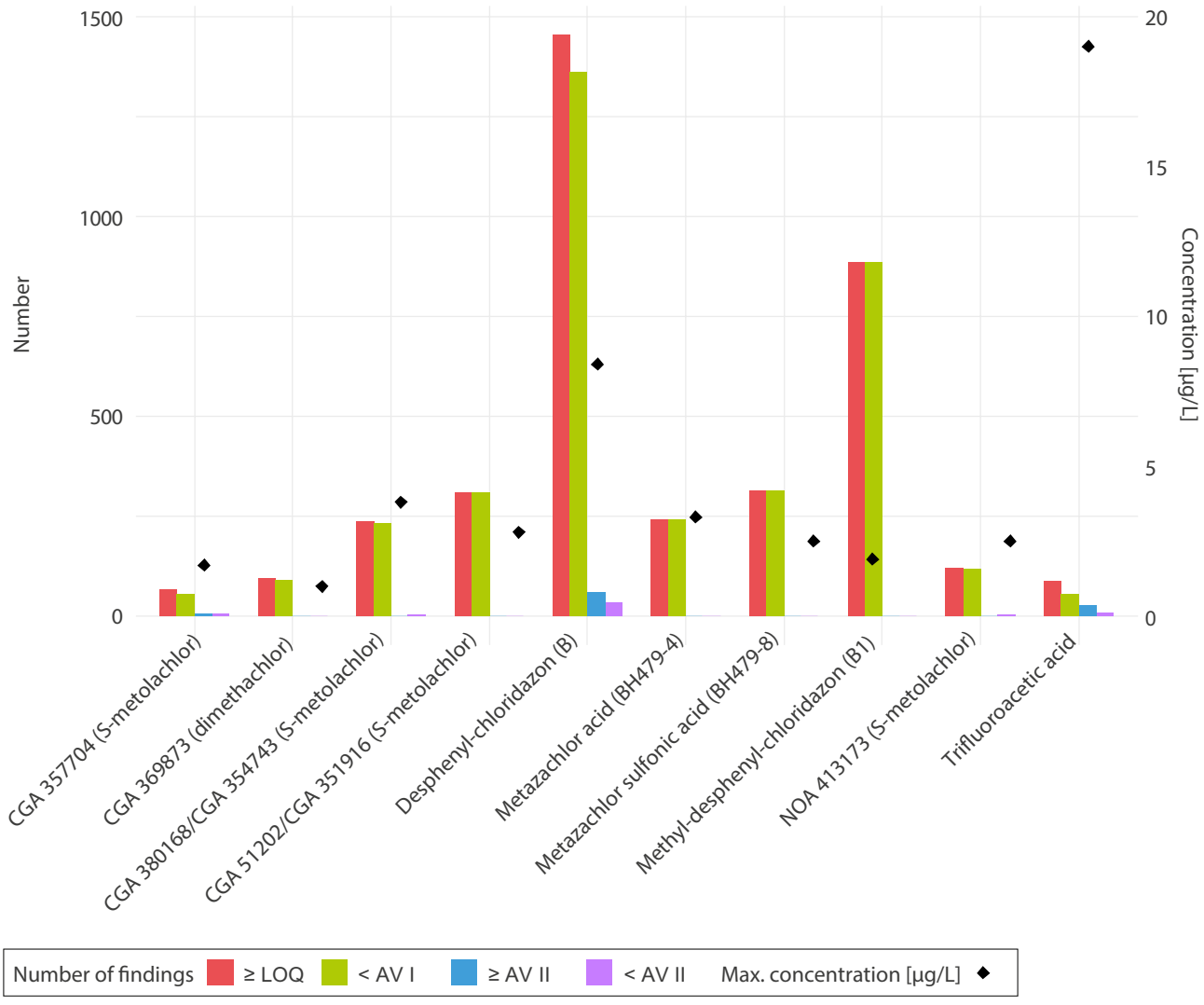
Table 3: Findings of metabolites with the latest value above the limit of quantification (LOQ) or below/above action values (AW) (number of raw water abstraction points (RWAP, groundwater) with analyses from 2010, as of April 2019)

Metabolites	RWAP with analyses	Latest value ≥ LOQ	Latest value ≥ LOQ < AV I	Latest value ≥ AV I < AV II	Latest value ≥ AV II	AV I [µg/L]	AV II [µg/L]	Maximum latest value [µg/L]
Desphenyl-chloridazon (metabolite B)	3683	1455	1361	34	60	2.25	3	8.4
Trifluoroacetic acid (TFA)	226	89	53	8	28	2.25	3	19
Metabolite CGA 357704 of S-metolachlor	446	68	54	7	7	0.75	1	1.7
Metabolite BH 479-4 of metazachlor (metazachlor acid)	1214	241	240	0	1	2.25	3	3.3
Metabolite CGA 380168 / CGA 354743 of S-metolachlor (metolachlor sulfonic acid)	1235	238	233	4	1	2.25	3	3.8
Methyl-desphenyl-chloridazon (metabolite B1)	3411	886	886	0	0	2.25	3	1.9
Metabolite BH 479-8 of metazachlor (metazachlor sulfonic acid)	1265	314	313	1	0	2.25	3	2.5
Metabolite CGA 51202 / CGA 351916 of S-metolachlor (metolachlor acid)	1379	311	310	1	0	2.25	3	2.8
Metabolite NOA 413173 of S-metolachlor	679	121	119	2	0	2.25	3	2.5
Metabolite CGA 369873 of dimethachlor	672	93	92	1	0	0.75	1	0.99
2,6-dichlorobenzamide	3444	86	86	0	0	2.25	3	0.80
Metabolite M27 of dimethenamid-P and dimethenamid	373	43	43	0	0	2.25	3	0.66
Metabolite CGA 354742 of dimethachlor (dimethachlor sulfonic acid)	895	40	40	0	0	2.25	3	0.94
Metabolite CGA 368208 of S-metolachlor	313	36	36	0	0	0.75	1	0.22
Metabolite BH 479-9 of metazachlor	98	18	1	1	16	0.075	0.1	1.9
Metabolite BH 479-12 of metazachlor	348	17	17	0	0	0.75	1	0.16
Metabolite CGA 108906 of metalaxyl-M	359	14	14	0	0	0.75	1	0.19
Metabolite CGA 50266 of dimethachlor (dimethachlor acid)	902	13	13	0	0	2.25	3	0.13
Metabolite M23 of dimethenamid-P and dimethenamid	107	12	12	0	0	2.25	3	0.07
Desethyl-terbuthylazine	3856	8	7	1	0	0.075	0.1	0.09
Metabolite M2 of flufenacet	348	2	2	0	0	0.75	1	0.06
ASDM* metabolite of nicosulfuron	8	1	0	1	0	–	–	0.09
AMPA* (aminomethylphosphonic acid)	977	1	0	1	0	–	–	0.09
UCSN* metabolite of nicosulfuron	8	1	1	0	0	–	–	0.05
Metabolite CGA 321113 of trifloxystrobin	46	1	1	0	0	0.75	1	0.03
Metabolite CGA 62826 / NOA 409045 of metalaxyl-M	495	1	1	0	0	0.75	1	0.03

LOQ: limit of quantification | AV: action value | RWAP: raw water abstraction point

*AMPA, ASDM and UCSN are non-relevant metabolites that have not yet been assigned an HRIV (see also the *Bericht zur Grundwasserbeschaffenheit – Pflanzenschutzmittel – Berichtszeitraum 2012 bis 2016* of the German Working Group on Water Issues of the Federal States and the Federal Government)

Authorisation status: beginning of 2018; for the current status, see
https://www.bvl.bund.de/DE/Arbeitsbereiche/04_Pflanzenschutzmittel/01_Aufgaben/02_ZulassungPSM/01_ZugelPSM/psm_ZugelPSM_node.html



LOQ: limit of quantification | AV: action value

Figure 5: Findings of metabolites with the latest value above the limit of quantification (LOQ) or below/above action values (AV) (number of raw water abstraction points (RWAP, groundwater) with analyses from 2010, as of April 2019)

THE AUTHORISATION PROCEDURE FOR PLANT PROTECTION PRODUCTS

Dr. Herbert Resseler (Syngenta Agro) | Dr. Friedrich Dechet (IVA)

Plant protection is comprehensively regulated by the EU. In Germany, EU law is implemented primarily through the Plant Protection Act (*Pflanzenschutzgesetz* – PflSchG) and several ordinances. The Plant Protection Act regulates the authorisation, marketing and use of plant protection products. Before a plant protection product can be used in practice, the active substance must be approved at EU level and the plant protection product must be authorised nationally. In the approval assessment of PPP active substances, the parameter value of 0.1 µg/L from the EC Drinking Water Directive is used when assessing possible entries into groundwater. This value applies to PPP active substances and their relevant metabolites (degradation products). In case of expected concentrations above this parameter value, authorisation of the plant protection product cannot be granted.

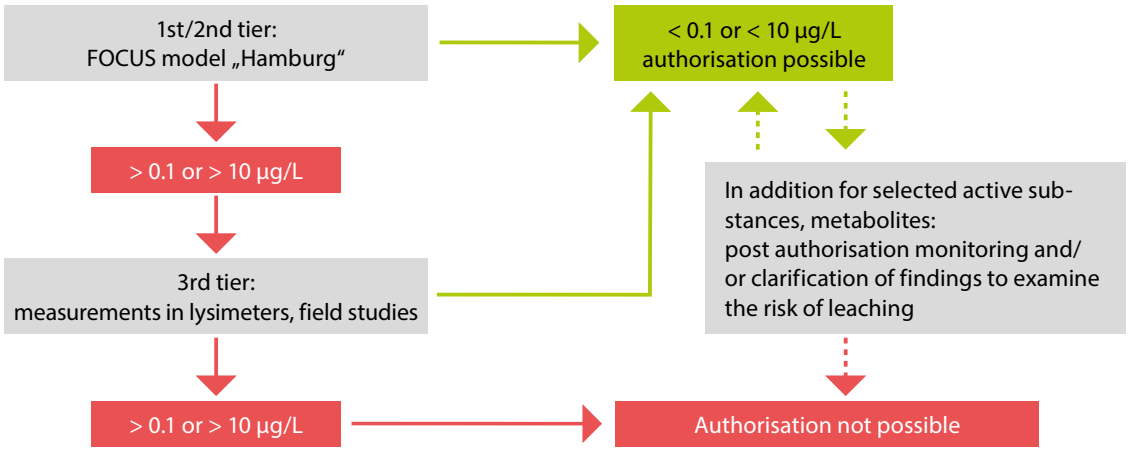
As a basis for the assessment, it is possible to use not only concentrations of the active substances under review that have been predicted for groundwater or leachate using computer models, but also analysis values measured under field conditions in leaching studies conducted over several years. In the case of a computer-based prediction, the expected concentration of a PPP active substance in the leachate is simulated by means of officially defined soil and climate scenarios as well as chemical properties (e. g. degradation rate and bond strength in soil).

Other important input parameters for estimating the expected concentration of the relevant plant protection product are

- the application rate that reaches the soil (depending on the growth stage of the treated crop and the crop characteristics),
- the timing of application (e. g. autumn or spring) and
- the frequency of application

all of which are fed into the computer model.
This simulates the substance's tendency to translocate with the leachate in soils with different susceptibility to leaching and under adverse weather conditions in Europe (Figure 6).

Assessment of the leaching potential of plant protection products



Active substances and **"relevant metabolites" (RM)** under plant health legislation: **0.1 µg/L**
"Non-relevant metabolites" (NRM) under plant health legislation: **10 µg/L**
Realism and complexity of tests increase at higher tiers.

Figure 6: Risk assessment of inputs to groundwater

The basis for assessment is a simulated concentration that is chosen so conservatively that it covers about 90% of all temporally and spatially possible application situations.

If the model calculation predicts an exceedance of the maximum tolerable limit of 0.1 µg active substance/L in the leachate at a soil depth of one metre, an experimental verification must be conducted before authorisation can be obtained. Field experiments are then conducted under adverse conditions to investigate the leaching of the substance under consideration. This involves measuring concentrations of the active substance and its metabolites in the leachate collected or in groundwater.

The approval/authorisation assessment of the active substance / plant protection product is conducted on the basis of the concentrations of the active substance and its metabolites relevant to the assessment. Defined limit and threshold values may not be exceeded.

It is important to note the assumption in this context that plant protection products are used for the intended purpose and properly applied. The effects of accidents with pesticide sprayers, filling or disposal errors or incorrect applications cannot be reviewed in the authorisation procedure. In this case, regulatory or penal measures must be taken. Special site conditions in hydrogeologically sensitive areas, such as open karst areas, are not assessed either. The manufacturers expressly point out that products with a higher tendency to leach should not be used, e. g. on karst areas.

If limit and guidance values are exceeded in groundwater as a result of the use of authorised products, the Federal Office of Consumer Protection and Food Safety (BVL) requires the authorisation holder to clarify the findings in the event of a validated finding of the active substance of an authorised plant protection product or of a metabolite of the active substance. According to established technical rules, a measurement result is (only) considered to be verified following a second, independent analysis with the same finding. A request for the clarification of findings can be made via a report form, explained in detail, on the BVL website (https://www.bvl.bund.de/DE/Arbeitsbereiche/04_Pflanzenschutzmittel/01_Aufgaben/09_Gesundheit-Naturhaushalt/02_SchutzNaturhaushalt/03_Fundaufklaerung/Fundaufklaerung_node.html). Experts commissioned by the manufacturer assess the facts based on the analysis results, the information available on the monitoring well and the surrounding area, and by conducting a site visit. The report on the results of the clarification of findings is discussed with the water company. If there is an accumulation of findings, restrictions on use can be imposed.

This means that the active substance can retain its approval and remain available to farmers, albeit with a modified (reduced) application profile, even in the case of product applications that have caused anomalies in practice following authorisation. On request, the entire active substance approval can also be reviewed by the authorities.

When assessing metabolites of plant protection products, the classification of metabolites into “relevant” and “non-relevant” metabolites plays a crucial role, because relevant metabolites are treated like the actual active substance in the assessment. The following criteria have been established to determine the relevance of a metabolite:

- A metabolite is considered relevant if it has a biological activity, a pesticide effect, like the active substance or if it is toxic or genotoxic.

- For non-relevant metabolites, there is no legally defined limit value; however, a recommendation is given in an EU-wide guidance document[4]: in the interests of preventive groundwater protection, an annual average concentration of 10 µg/L should not be exceeded for these metabolites. In Germany, a verified exceedance of 10 µg/L in groundwater also triggers a clarification of findings, as described above.

[4] https://food.ec.europa.eu/system/files/2016-10/pesticides_ppp_app-proc_guide_fate_metabolites-groundwtr.pdf

HOW DO PLANT PROTECTION PRODUCTS FIND THEIR WAY INTO GROUNDWATER?

Dr. Herbert Resseler (Syngenta Agro) | Dr. Friedrich Dechet (IVA)

In spite of strict approval assessments (described in the previous section "The authorisation procedure for plant protection products"), active substances and metabolites may be discharged into groundwater due to factors such as gross misconduct, improper use or accident situations.

Such cases cannot be avoided, no matter how strict the authorisation procedure, because it is not possible to simulate such real-life situations in trials/models. A point source is a typical case. This can occur when plant protection products are handled incorrectly, where there is short-circuiting of groundwater, e. g. at a groundwater well that is used for irrigation purposes or for filling the plant protection sprayer. Sites where threshold values are exceeded must be taken seriously and the cause of input must be clarified and remedied quickly in order to prevent further contamination. Conversely, not every finding need be a direct cause for great concern as long as permissible threshold values are not exceeded and no upward trend is observed. After all, modern analytical technology is able to detect even the smallest quantities of applied plant protection products that are well below the threshold values.

Unfortunately, accidents with filled pesticide sprayers that are serious from a water protection perspective do occur, e. g. when a tractor ends up a ditch, causing the spray agent tank to leak. Accidents involving spray loss can affect farmers from any type of agriculture, irrespective of whether they practise conventional, integrated or organic farming. Another "irregular" type of entry can occur when plant protection products are applied in extremely karst areas, where, after a few centimetres of soil, fissures reach down to groundwater. According to good agricultural practice, certain plant protection products should not be applied to "bare" soil in such areas.

If point sources cause a plant protection product to enter drainage inlets (gullies), ditches or surface waters due to runoff from treated areas, it may, in areas with bank filtration, enter groundwater and find its way into drinking water resources.

To further minimise the risk of point sources, in particular, IVA regularly conducts demonstration and training activities for opinion leaders and farmers with the support of experts from chambers of agriculture. The section "Actions to reduce the entry of plant protection products into water bodies" contains further information on how to avoid emissions.

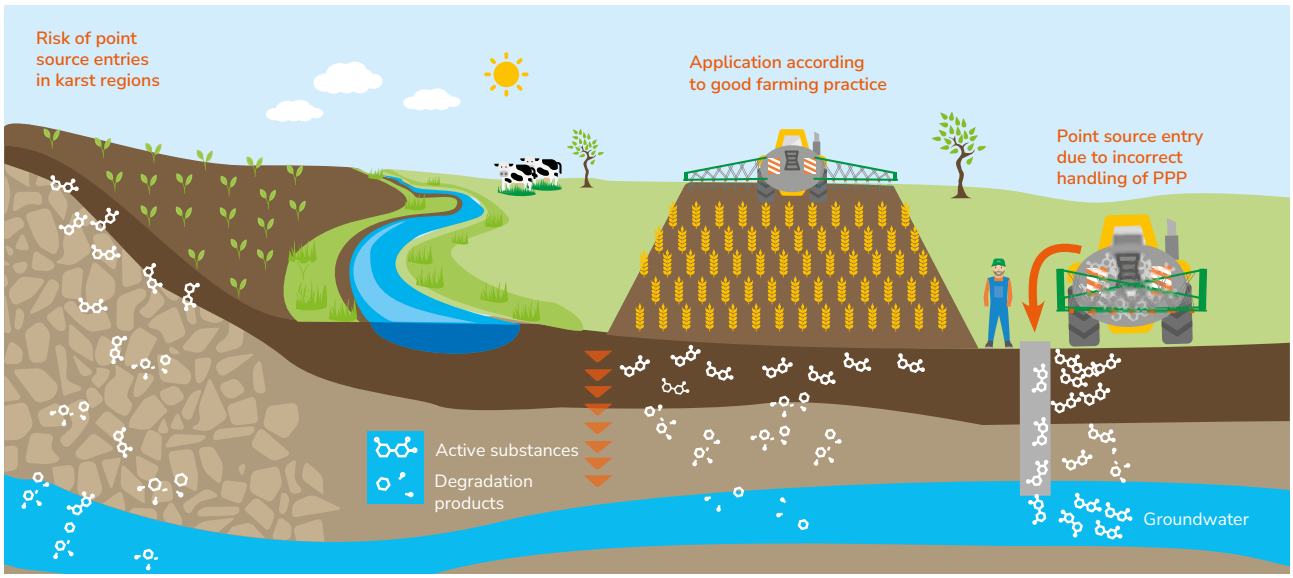


Figure 7: Causes of input that can lead to leaching with subsequent exceedance of limit values in groundwater

ACTIONS TO REDUCETHE ENTRY
OF PLANT PROTECTION PRODUCTS INTO WATER BODIES

Dr. Marco Reitz (Syngenta Agro) | Dr. Volker Laabs (BASF SE)

There are several ways in which plant protection products can enter water bodies. However, there is a wide range of practical measures available to prevent this from happening. Some of these actions, such as avoiding point source contamination by cleaning the sprayer correctly, are recommended universally and for all plant protection products. For other actions, it is important to ensure that the selected actions are appropriate to the region (landscape, soil, climate) and the farm concerned, and tailored to address the problem locally. In water protection areas in particular, it may be necessary to adopt farming approaches that go beyond normal "good agricultural practice".

With the objective of providing support to farmers and advisory services on water protection, the European Crop Protection Association (ECPA; since 2021 CLE = CropLife Europe) launched the TOPPS project (www.topps-life.org) in 2005. The project now operates in 23 European countries, working with a large number of partners.

The aim of the project is to raise awareness of water protection in the use of plant protection products and to promote actions that help reduce the input of plant protection products into water bodies. TOPPS brochures and flyers provide guidance on aspects such as risk diagnosis for the different entry routes of plant protection products into water; they also describe a variety of agricultural measures to protect water.

Table 4: Actions to reduce the risk of runoff

Measure categories	General measures	Measures for very low risk	Measures for low risk	Measures for moderate risk	Measures for high risk
Soil management	Reduce surface soil compaction, reduce subsoil compaction, increase humus content, improve soil structure	Prepare rough seedbed	Establish optimised tramlines, farm contours in parallel	Establish in-field earth walls/bunds, reduce tillage intensity	Reduce tillage intensity (direct drilling)
Cropping practices	Use crop rotation (summer/winter planting)	Grow catch crops, establish extensive vegetation	Grow catch crops	Enlarge headlands, use double sowing for areas at higher risk, use annual cover cash crops	Practise strip cropping
Vegetated buffer strips		Manage field access areas, use riparian buffer strips		Use edge-of-field buffer zones, shorten slope length using in-field buffer strips	Establish talweg buffers, establish buffers in the form of hedges/woodlands
Retention systems				Use edge-of-field earth walls/bunds	Build fascines, establish vegetated ditches, establish artificial wetlands / retention basins
Adapted use of PPP			Adapt application timing	Adapt product selection and application rate	
Optimised irrigation	Use modern technologies, adapt timing and rate of irrigation				

Source: TOPPS

In the event of known water quality problems involving plant protection products in a catchment area, a methodological approach should be used to

a) record all relevant entry routes to the contaminated water body,
b) diagnose the risks for each entry route, and
c) define appropriate protective measures for each of the risk areas/points identified.

This can best be done through the Agricultural Advisory Service in cooperation with the farmers and the water company. Risk mitigation measures can then be defined in a local body, e. g. an existing water cooperation.

A number of actions for the protection of drinking water resources are presented below as examples. A wide range of additional measures are described in the relevant TOPPS brochures, which are available from IVA for download or free of charge in printed form (TOPPS-Projekt | Industrieverband Agrar (iva.de)).

Cleaning of sprayers:

After application, plant protection product remnants may accumulate on the outer surfaces of the sprayer or remain in the sprayer as residues. Cleaning the sprayer on the farmyard may cause residues to enter water bodies via farm drains or the sewerage system. The problem is that the plant protection products cannot be degraded in soil before reaching the water cycle. For this reason, sprayers should generally be cleaned on the field, or at least on a vegetated area. There has been considerable technical progress in the internal cleaning of sprayers in recent years, making it much easier to clean them on the field. Older sprayers can be retrofitted with a continuous internal cleaning system, while automated internal cleaning should be considered when purchasing a new sprayer. Alternatively, a separate cleaning area can be established on the farm, where resulting residues of plant protection products are collected. In this area, technical solutions have also been developed specifically for the treatment of PPP residues, e. g. evaporation systems (Figure 8) and biofilters (Figure 9).

Source: Syngenta Agro GmbH

Source: Bayer CropScience Deutschland GmbH

Figures 8 and 9: Systems for handling effluent produced when cleaning sprayers

Source: TOPPS

Figure 10: Concentrated runoff

Rotation of active substances:

Switching between different PPP active substances has been practised in agriculture for a long time to prevent the onset of resistance to a particular active substance. This practice also offers an important advantage for water protection. The classic approach taken when an active substance becomes locally conspicuous is to completely avoid its use in that area. The active agent is usually replaced by another one (i. e. a complete substitution), which can often lead to problems with the substitute active substance at a later stage. Rotation of active substances involves the active substance concerned remaining in use in an area, albeit at a lower level of application, while ensuring that it is alternated with other active substances. As a result, individual active substances are used less frequently in the area. This significantly reduces the probability that guidance and limit values will be exceeded. Besides taking into account resistance strategies, however, economic aspects and the predominant crops and crop rotations in the area must also be considered. Any plans to rotate active substances should therefore always be agreed with the Agricultural Advisory Service.

Prevention of erosion:

The runoff of plant protection products from the field after precipitation is one of the main entry routes into water bodies. This entry route can be considerably reduced by vegetated riparian buffer strips. In addition, actions should also be taken directly in the field to prevent erosion. No-tillage and reduced tillage play an important role in this respect. The soil structure is disturbed less, making it less susceptible to erosion. Technology, however, also offers new solutions in this area. In potato cultivation, for example, the risk of erosion can be minimised by using devices to construct micro-dams between ridges. These tools, which can be attached to the planter, create small dams at right angles to the rows of potatoes. As a result, water can no longer simply run off during precipitation or irrigation but remains in the field.

Inputs of plant protection products into water bodies continue to present a challenge to water companies, as well as to farmers and PPP manufacturers. Water protection and pest management goals can nevertheless be achieved in the vast majority of areas if the existing toolbox of proven and practicable water protection action is applied flexibly and, above all, consistently in the catchment area. This requires that farmers are informed of existing water quality problems and can understand how they can contribute to local problem-solving. Targeted promotion of individual measures via official programmes or the water company should also be considered. Efficient and expedient planning, implementation and monitoring of water protection measures can usually only be achieved jointly in collaboration with farmers, pest management consultancy, and water companies.

REGULATORY FRAMEWORK
TO MINIMISE THE ENTRY OF PLANT PROTECTION PRODUCTS INTO GROUNDWATER

Steffi Rentsch (Bayer CropScience Deutschland GmbH)

Impeccable water and drinking water quality constitutes preventive consumer protection and is ensured by extensive legal provisions. In this context, a number of regulations, such as the Drinking Water Ordinance, the Ordinance on the Protection of Groundwater, and the Plant Protection Act, are interlinked. These legal acts define, among other things, limit values, threshold values or guidance values for PPP active substances and their degradation products (see also the section "The authorisation procedure for plant protection products" and the glossary).

Drinking Water Ordinance: limit value for PPP active substances and their **relevant metabolites** of **0.1 µg/L** or **0.5 µg/L** in total
https://www.gesetze-im-internet.de/trinkwv_2001/BJNR095910001.html#BJNR095910001BJNG000201310

Groundwater Ordinance: threshold value for PPP active substances and their **relevant metabolites** of **0.1 µg/L** or **0.5 µg/L** in total
https://www.bmuv.de/gesetz/verordnung-zum-schutz-des-grundwassers

Groundwater protection is also, in principle, taken into account in the authorisation of plant protection products:
"Plant protection products are only authorised if it can be excluded that, when used for the intended purpose and properly applied, active substances and their metabolites could have a harmful effect on groundwater." (BVL website)

A risk assessment is carried out as part of the authorisation procedure. This risk assessment also includes the potential entry of active substances or their degradation products into groundwater (see the section "The authorisation procedure for plant protection products"). Consideration is given, among other things, to ensuring that the limit value defined in the Drinking Water Ordinance for PPP active substances and their relevant metabolites can be complied with if the product is used for the intended purpose.

Based on this assessment, additional special requirements for the protection of groundwater can be imposed for the plant protection product concerned: so-called NG requirements, where "NG" stands for "nature protection groundwater".

Examples of groundwater protection requirements:

NG346: The maximum application rate of 1000 g active substance X per hectare must not be exceeded for the same area within 3 years – even in combination with other plant protection products containing this active substance.

NG325: Other products containing the active substance Y are not to be used additionally within the same calendar year on the same area.

NG402: Between treated areas with an incline of more than 2% and surface water – except only occasionally but including periodically water-bearing surface water – there must be a buffer strip under complete plant cover. The buffer strip's protective function must not be impaired by the use of implements. It must be at least 10 m wide. This border is not necessary if:

- sufficient catching systems are available for the water and soil transported by runoff, which do not flow into surface water or are not connected with the urban drainage system or
- the product is used for mulch or direct drilling methods.

NG405: Not to be used on drained surfaces.

Risk mitigation requirements regulate aspects such as maximum quantities of a certain active substance per area and year, or permit the use of the product for a specific period only, at times when there is not increased groundwater recharge due to winter precipitation. Some plant protection products may not be used on certain soil types or on drained areas; for others, special regulations apply with regard to vegetated riparian buffer strips.

Such restrictions help ensure the reduction of expected concentrations in groundwater. The application rate can generally be reduced, e. g. by carrying out fewer treatments or by applying the product at a later stage of the crop's development, resulting in only a small amount reaching the soil. Application can be limited to certain times, e. g. spring application only, when the rate of degradation is high due to elevated temperatures and less leachate is produced owing to high evaporation rates. Degradation products of plant protection products that do not exhibit biological activity similar to the active substance and that are toxicologically harmless are referred to as "non-relevant metabolites". These substances are regulated under plant health legislation, but not in the Drinking Water Ordinance. According to plant health legislation, a guidance value of 10 µg/L in groundwater is applicable to these breakdown products (see also the section "The authorisation procedure for plant protection products").

However, the Drinking Water Ordinance states: "Drinking water must not contain concentrations of chemical substances that give rise to concerns for impacts on human health." (Section 6(1) of the Drinking Water Ordinance).

For the assessment of non-relevant metabolites of plant protection products in drinking water, the Federal Environment Agency (UBA) therefore developed a recommendation (in cooperation with the Federal Institute for Risk Assessment (BfR)); this recommendation is based on compliance with so-called health-related indicator values (HRIVs; in German: *HRIV = Gesundheitlicher Orientierungswert* (GOW)) (see References).

HRIVs are precautionary values and may be replaced by a higher drinking water guidance value representing a tolerable lifetime intake of the substance concerned, provided more extensive toxicological data is submitted.

A short-term exceedance of the HRIV does not automatically imply a hazard to health. It is first and foremost a problem related to drinking water hygiene that requires certain measures, such as increased monitoring or research into the causes of contamination.

For this reason, the recommendation of UBA and BfR provides for the toleration of exceedances of the HRIV up to a value of 10 µg/L in the short and medium term (up to 10 years). It is at the discretion of the relevant health authority to make use of this option.

If PPP active substances or their degradation products are detected in raw water above the relevant limit, guidance or indicator values, the water company concerned has the option of informing the Federal Office of Consumer Protection and Food Safety (BVL).

More detailed information can be found on the BVL website under the heading "Clarification of findings in the event that PPP active substances or their relevant and non-relevant metabolites exceed limit values and guidance values in groundwater". A report form is provided on the website for this purpose (https://www.bvl.bund.de/SharedDocs/Downloads/04_Pflanzenschutzmittel/Meldeformular_Fundaufkl%C3%A4rung_Grundwasser.html). The authorisation authorities can, for example, request the authorisation holder to clarify findings; they may also order post-authorisation monitoring or impose specific additional risk mitigation requirements.

Criteria for the initiation of a procedure for clarifying findings

BVL requires the authorisation holder to clarify findings if there is a validated finding of the active substance of an authorised plant protection product or a metabolite of the active substance exceeding the limit or guidance value in groundwater applicable under plant health legislation:

- 0.1 µg/L for active substances and relevant metabolite (limit value)
- 10.0 µg/L for non-relevant metabolites (guidance value)

One example of such a requirement is the direction for use "NG301-1 Not to be used in water protection areas or catchment areas of drinking water supply works", which are published in the *Bundesanzeiger* (Federal Gazette) by BVL. The Water Industry / Plant Protection Industry Round Table takes the view that this direction for use can be extended to include active substances.

The prerequisite for submitting a report to BVL is that certain criteria are met (see text box "Criteria for listing and possibility of reporting").

After reviewing the facts, the authority may issue restrictions on the use of certain plant protection products to protect groundwater resources used for the production of drinking water. The water protection areas and catchment areas of drinking water supply works to which the restrictions on use apply are published in an announcement in the Federal Gazette and on the BVL website.

Direction for use NG301-1

Criteria for listing and possibility of reporting:
To be included in the table, water protection areas and catchment areas for the production of drinking water must submit a corresponding report. The prerequisite for inclusion is that at least one non-relevant metabolite (NRM) of a PPP active substance has been detected in groundwater or raw water, and that these four criteria are met:

- exceedances of 3.0 µg/L at a raw water abstraction point and/or of 10.0 µg/L at an upgradient groundwater quality monitoring well such that
- concentrations of the same substance above the guidance value were detected in 3 measurements at intervals of no less than 6 months within 3 years,
- the latest exceedance is no more than 6 months before the date it was reported, and
- that it is probable that the entry into groundwater is due to the proper and intended agricultural use and not to structural deficiencies or defects at the raw water abstraction point(s) or upgradient groundwater quality monitoring well(s), and that sampling, sample transport and analytical determination of the substances were carried out according to the current state of the art.

APPROACH TAKEN BY THE WATER INDUSTRY / PLANT PROTECTION INDUSTRY ROUND TABLE

The primary objective of the Round Table is to provide water companies affected by conspicuous findings with a speedy and proven solution on site. In concrete terms, this means that the exposure situation is analysed on the ground together with all stakeholders and the water companies. To this end, evaluations of the Raw Water Database Water Supply and comparisons with empirical data from other areas can contribute to the analysis. An essential element is to clarify the cause of the findings as quickly as possible. The joint planning of systematic monitoring, taking into account the soil and hydrogeological conditions and agricultural use, can be another element.

The manufacturers pay half of the costs incurred by the monitoring activities recommended by the Round Table. Other steps could include gathering important information on the catchment area and improving the flow of information to people who advise and decide on PPP applications in the catchment area. In certain cases, it has proved useful to set up a local round table at the water company, enabling representatives of agriculture, the Agricultural Advisory Service and the manufacturer to participate and monitor the progress of the project on site. As a result, possible action to improve the quality of raw water can be discussed together and, where applicable, communicated more efficiently.

THE CASE OF
STADTWERKE GÜTERSLOH

Anke Femmer (Stadtwerke Gütersloh)
Burkhard Linneweber (Landwirtschaftskammer NRW – Chamber of Agriculture of North Rhine-Westphalia)
Ulrich Peterwitz (Gelsenwasser AG)
Marco Reitz (Syngenta Agro)

Stadtwerke Gütersloh – rotation of active substances on sandy sites

Problem:

Non-relevant metabolites (especially S-metolachlor sulfonic acid) were found in concentrations of less than 1 µg/L up to 3 µg/L, depending on the abstraction area, in the raw water of several water abstraction areas of Stadtwerke Gütersloh. The upgradient groundwater quality monitoring wells also exhibited considerably higher concentrations.

Characterisation of the water abstraction areas:

The water protection areas concerned exhibit mainly light sandy soils with a high groundwater level. Vertical wells pump water from the first groundwater level from a depth of 15-25 m. Accounting for 30 to 40% of arable land, maize is a dominant crop in the District of Gütersloh, where the active substance S-metolachlor was used intensively until the mid-2000s and to a lesser extent thereafter. Some of the investigations into non-relevant metabolites at Stadtwerke Gütersloh therefore focused on the degradation products of S-metolachlor; these investigations were stepped up again from 2012 onwards under expert supervision and with funding from the PPP manufacturers as part of the measures taken in the context of cooperation with the Water Industry / Plant Protection Industry Round Table.

Description:

To find a solution, a local Advisory Board was set up in 2012, which included the water company, representatives of the Chamber of Agriculture of North Rhine-Westphalia and members of the Round Table, as well as the local agricultural trade. The Advisory Board meets once a year at the invitation of Stadtwerke Gütersloh to discuss progress and further action in the area. To assess the development in the water protection areas, a groundwater monitoring programme was set up with the financial participation of the PPP manufacturers; this monitoring programme covers not only raw water abstraction points, but also several upgradient groundwater quality monitoring wells. Samples are taken and analysed in summer and winter.

The rotation of active substances was introduced by the Agricultural Advisory Service of Stadtwerke Gütersloh and the Plant Protection Adviser of the Chamber of Agriculture of North Rhine-Westphalia in 2013 as a first measure to minimise risk and reduce inputs. As part of this active substance management, mainly three herbicide strategies were recommended in maize in rotation, including a variant with S-metolachlor. The aim was, and is, to alternate the use of different active substances on the same area.

It has since been shown that, under the given conditions, even single applications of S-metolachlor can lead to significantly elevated levels of non-relevant metabolites in the upper aquifer after 3 to 4 years. Based on this experience, from 2019 onwards it was refrained from recommending the use of products containing S-metolachlor on the light sandy sites that dominate in the water catchment areas. Since 2019, the authorisation holder Syngenta has also generally advised against the use of products containing S-metolachlor on such sites (light sandy soils in combination with a high groundwater level and high winter precipitation). The area continues to rotate active substances, but without S-metolachlor. This is to prevent the problem from recurring in the future with a different active substance.

Implementation in agriculture:

In North Rhine-Westphalia, the Chamber of Agriculture attaches great importance to providing farmers with neutral advice on production technology. The Chamber of Agriculture's own experimentation enables it to give neutral, fee-based advisory recommendations on plant cultivation and plant protection to farmers, in contrast to the commercial sales advice provided by trade and industry. These recommendations enjoy a high level of acceptance on the ground. It was also of considerable advantage for the implementation of the measures that Stadtwerke Gütersloh has its own Agricultural Advisory Service.

In spite of extensive advisory coverage in the area, it was hugely important to involve not only farmers, but also agricultural contractors and the agricultural trade. Given that the advisers were able to liaise directly with the stakeholders, they were able to explain to the agricultural players the problems faced by the water companies, and to point out to farmers the risk of the potential loss of active substances if the situation in the water protection areas failed to improve. The gentle pressure exerted by advisers was maintained over the years, and continues to this day. Farmers, contractors and traders working in the area were provided with free information by means of conferences, letters and, most notably, by highly popular field visits, which were held in small groups three to four times each spring. From the advisory perspective, the procedure can be considered a success. The recommendations to rotate active substances and to refrain from using S-metolachlor are being implemented by farmers.

The problem of the occurrence of non-relevant metabolites in raw and pure water considered here will remain a major issue for Stadtwerke Gütersloh in the future. However, the actions have led to initial demonstrable successes, also in groundwater.

THE CASE OF DEGENFELD

Dr. Folkert Bauer (BASF SE) |
Prof. Dr.-Ing. Frieder Haakh
(special-purpose association Landeswasserversorgung, Stuttgart)

Bentazone regional report: the "Degenfeld" water protection area

What problems needed to be solved?
Due to the exceedance of the SchALVO (Regulation on Protected Areas and Compensatory Payments) limit value for PPP active substances […] of 0.1 µg/L in spring waters by Bentazone, the Degenfeld water protection area, covering around 140 hectares, was classified as a "SchALVO PPP rehabilitation area" as of 1 January 2011. The protected area, located south of the town Schwäbisch-Gmünd in the Suebian Jurassic karst, is considered vulnerable to Bentazone, because the main aquifer is located directly below the topsoil, which is typical for karst.

What actions were developed with the participating partners?
Together with the Lower Water Authority, the Agriculture Division of Ostalbkreis District Office, the manufacturer and the farmers concerned, the interconnections were discussed and the further course of action was mutually agreed. The aim was to ensure that, once the area had been successfully rehabilitated and the SchALVO requirements lifted, it would not become conspicuous again as a result of (excessively) high concentrations of Bentazone. Measures that went beyond the SchALVO requirements were agreed on:

- The involvement of other potential polluters, i. e. drawing the attention of weekend house owners to the problem and requesting them not to use plant protection products containing Bentazone, e. g. to treat weeds on driveways;
- Intensification of spring water monitoring to two or three sampling dates per year;
- Collection and analysis of soil samples by the agricultural technical service;
- Agreement between the public utility companies and the manufacturer on sharing the costs of the intensive monitoring programme;
- Regular provision of information to stakeholders and data transparency;
- Advice on alternative active substances and active substance splitting.

How is it possible to assess the effectiveness of the actions?
There is a close correlation between precipitation and spring discharge. The average total spring discharge is approximately 347,000 m^3/a (11 L/s). Groundwater recharge can be assumed to be around 250 mm (corresponding to 350,000 m^3/a for 140 ha). There is no exact data on the storage volume of the aquifer, but a usable specific storage volume of up to 5% and a thickness of around 50-150 m can be approximately assumed. This results in a usable storage volume of up to 700,000 m^3. The spring discharge therefore yields a mean residence time (MRT) of 700,000 m^3/ 347,000 m^3/a = 2.02 years and, assuming complete mixing ("stirred tank model"), a half-life (HL) = ln(2) * MRT = 1.4 years.

Assuming an exponential decrease in Bentazone contamination (Figure 11), a half-life of comparable magnitude can be determined from model fitting, resulting in a calculated storage volume of around 770,000 m^3. The clearly discernible downward trend from autumn 2011 onwards suggests that the SchALVO limit value will not be exceeded in the long term. This directly proves the effectiveness of the ban on using the active substance.

What experience was gained with stakeholders during the implementation and execution of the actions?
One of the key challenges was to raise awareness among farmers of the adverse impact of their actions on groundwater. The case in question involved the use of a more mobile herbicide (Bentazone) on a site susceptible to leaching, such as karst – despite the fact that the manufacturer had clearly stated, in the presence of users, that it should not be applied. What is clear from this is that the result of any action taken to resolve the problem hinges on the willingness of agriculture to implement the measure.

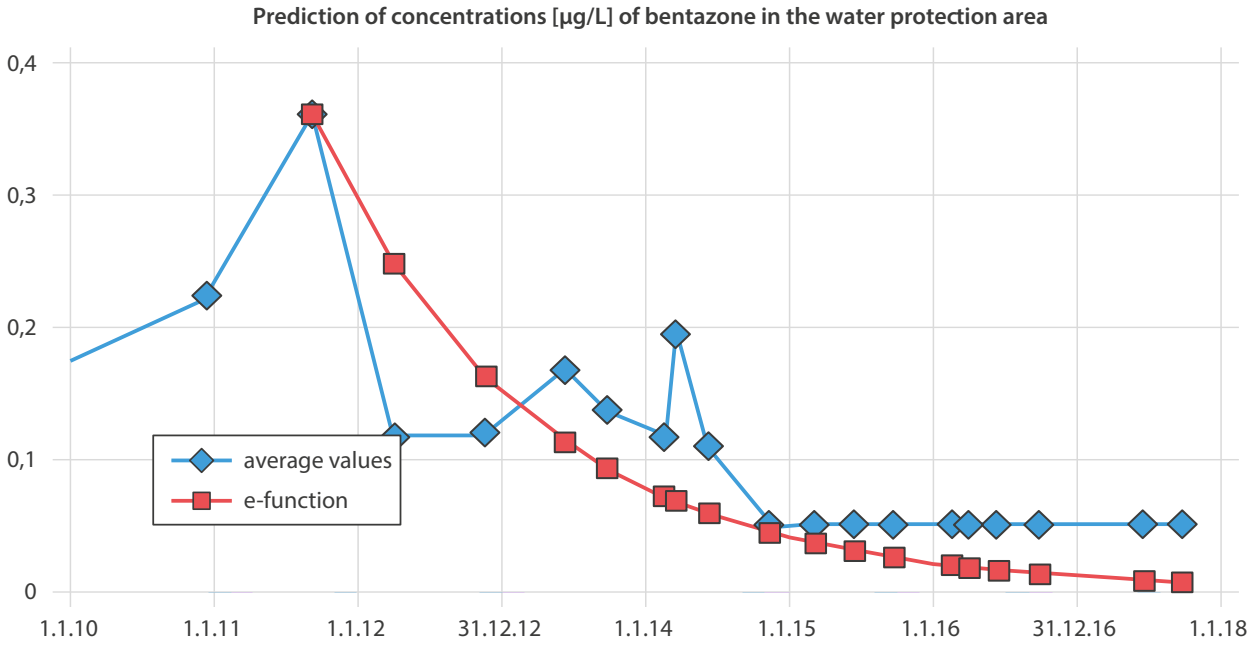


Figure 11: Mean values of Bentazone concentrations and the mathematically expected exponential decline

What should be changed / done differently with regard to the effectiveness of the actions?

The approach taken by the Water Industry / Plant Protection Industry Round Table in its role as intermediary between agriculture and the water industry was very effective. Since the Round Table represents both sides equally (in this case, represented by Professor Dr. Haakh, special-purpose association Landeswasserversorgung, Stuttgart, and Dr. Bauer, BASF) and is neutral, it was easier for each party to understand the other's sensitivities in a less biased way. This enabled a swift solution to be found that was acceptable to all.

It is generally desirable to establish such an intermediary role for similar issues in the set of conflicting demands between the water industry and agriculture. It makes communication easier, contributes to mutual understanding, and generates additional third-party expertise. By doing so, the intermediary eases the burden on water companies in their day-to-day business and provides practical assistance in solving the problem.

THE CASE OF TECHNISCHE WERKE DER STADT ÖHRINGEN

Andrea Danowski (BDEW) | Horst Geiger (Technische Werke Öhringen, Water Supply Division) | Dr. Folkert Bauer (BASF SE)

Technische Werke of the town of Öhringen, Water Supply Division, detected non-relevant metabolites of the beet herbicide Chloridazon in raw water from three drinking water abstraction areas. In two areas, water is extracted from the top groundwater level of a pore aquifer at a depth of around 3 m. In the third area, water is extracted from the fourth groundwater level of a pore aquifer with early-stage karstification and with little impact on surface water at a depth of around 60 m. The respective mean groundwater recharge rate is 50-120 mm/a. The water protection area Zone III of the third area measures 787.7 ha, that of the other two 74 and 36.7 ha. The area of Zone II is 28.6, 4.8 and 3.9 ha, respectively. The well from which deep water is extracted is the largest and therefore most important source of raw water for Technische Werke Öhringen.

Soon after the Technologiezentrum Wasser (German Water Centre – TZW) asked whether the water company would be willing to cooperate, an initial discussion was held at Technische Werke with the German Association of Energy and Water Industries (BDEW) and BASF, the authorisation holder of Chloridazon. The participants were introduced to the idea, principles and working practices of the Water Industry / Plant Protection Industry Round Table, which is based on voluntary cooperation with an equal sharing of costs, with no obligations for the water company.

Based on the problem situation, the participants managed to devise a form of cooperation during the first meeting. This included a clarification of the cause of entry, possible actions derived from this, and an estimate of the work involved.

The aim was to solve the problems faced by the water company concerned without significantly disrupting its day-to-day business.

The responsible contact person from the water company in Öhringen obtained information about the range of crops grown, the proportion of arable land in the water abstraction areas, the cultivation history, the plant protection products used, as well as the practice of cleaning sprayers and dealing with spray liquid residues on the ground. He granted access to water analysis data, maps (e. g. soil map, geological maps, water table contour maps) and geological reports. In close consultation with the public utility companies, the cooperation partners evaluated and contextualised the available information and data to determine the cause of contamination; they then summarised the data, treated confidentially, in a report. BASF covered half of the costs incurred for additional water sampling (if, however, a limit value is exceeded in drinking water or groundwater, i. e. 0.1 µg/L for active substances and relevant metabolites, or 10 µg/L for non-relevant metabolites, the authorisation holder covers all costs incurred within the clarification of findings imposed by law).

A total of two follow-up meetings were held on site in addition to a telephone conference; during these talks, the results of the work steps previously agreed between the cooperation partners were discussed and further steps were planned. This allowed flexibility in adapting the approach, such as monitoring a particular area at closer intervals in the case of a data gap, or taking soil samples to determine the texture and content of organic matter in an effort to make a more accurate assessment of a site's susceptibility to leaching.

In the case of Öhringen, the dominant hydrogeological situation in the drinking water abstraction areas concerned (groundwater-rich shell limestone and Lettenkeuper with a layer of loess/loess loam, which is thin in places), the substance properties of the non-relevant metabolites of Chloridazon (highly persistent, low sorption capacity), and the absence of the parent substance Chloridazon in the raw water formed the starting point for analysing the cause of discharge.

The information gathered from different fields and disciplines (hydrogeology, hydrology, solute transport, soil science, agriculture, water supply) enabled the participants to rule out the more improbable cause of input and to gradually get closer to the most plausible cause. Analysis parameters such as E. coli, turbidity, other PPP active substances and their degradation products, slurry and wastewater parameters provided additional valuable information on the cause of the entry of the substances under consideration into raw water.

Taking an overall view of all available information and analysis data, inputs from point sources could be largely ruled out for all three drinking water abstraction areas. It is highly probable that the entry of non-relevant metabolites of Chloridazon into groundwater was due to proper and correct use of the product, i. e. leaching from treated agricultural areas.

The actions derived from this included compensation payments to farmers willing to refrain from using Chloridazon from Technische Werke Öhringen, as well as a joint information event for farmers from the abstraction areas concerned, organised by Technische Werke, which was very well attended. In addition to the Round Table presentation and the description of the problem situation by BDEW and Technische Werke, the BASF representative explained that the abstraction areas concerned were highly vulnerable due to hydrogeological and substance-specific factors and urged users to refrain from applying Chloridazon.

Ultimately, with the support of TZW, Technische Werke Öhringen applied to BVL for a ban on the use of Chloridazon in the affected drinking water abstraction areas in the context of NG301. This ban was listed on 29 January 2018 and published on 16 February 2018.

It must be noted that the Chloridazon metabolites are still detectable, even though it can be proven that the parent substance is no longer in use. It must therefore be assumed that Chloridazon metabolites have a long residence time in these soils.

OUTLOOK AND CHALLENGES
FROM THE WATER COMPANIES' PERSPECTIVE

From the water companies' perspective, one of the main challenges is to establish coherence between drinking water legislation, water protection legislation, and regulations on the emissions side – in this case, plant health legislation – in legislation and enforcement so as to minimise entries of plant protection products to water bodies and reduce the need for repairs in waterworks by means of treatment.

Coherence means that the permissible emissions and the requirements concerning drinking water quality are compatible and that, for example, there are no exceedances of limit values and HRIVs resulting from the use of plant protection products. This goes beyond the consideration of the situation from a purely legal perspective. After all, it also concerns specific use in water protection areas, advisory services, official monitoring and control. The great commitment of all those involved in the Water Industry / Plant Protection Industry Round Table to solving problems by working together on the ground has led to success in the past, but will remain a challenge in the future.

It will be necessary to ensure the greater involvement of other stakeholders such as farmers and agricultural authorities.
A major obstacle to a direct solution to the problem is the current lack of transparency in the application rates of plant protection products (PPPs) on agricultural areas and in the degradation behaviour of plant protection products (PPP metabolites). Such data is the basis for efficient monitoring by the water company in the catchment area of its drinking water abstraction plants in the sense of "incoming goods inspection" and – if necessary – for promising rehabilitation planning. The Advisory Services are likewise in urgent need of this data, so as to be able to avert the threat of the exceedance of limit values, e. g. by splitting active substances.

As the water industry sees it, the issue of non-relevant metabolites of plant protection products has not yet been addressed satisfactorily. There is a regulatory gap on the emissions side, given that the legislator has no generally applicable instruments to limit emissions that take effect when the HRIV is exceeded. The only tools available in this context are the Round Table's action programmes and the restrictions on the use of certain plant protection products, introduced in 2015 by the Federal Office of Consumer Protection and Food Safety (BVL), to protect groundwater resources used for drinking water production (NG301).

Further classifications, such as the "provisionally relevant metabolites" published by UBA in April 2019, do not solve the problem. In the case of conspicuous findings, it must be possible to directly limit emissions – this is the only way to ensure water protection. There is currently no regionally applicable tool or legally binding definition of sensitive areas, e. g. karst areas, to prevent PPP problems from arising at the regional level in the first place. The "Water protection area requirement" of the Federal Biological Research Centre (now the Federal Office of Consumer Protection and Food Safety (BVL)), which was known well into the 1990s, can serve as a "blueprint" for mapping the vulnerability of drinking water resources in this case.

Another challenge is the urgent need to regulate ubiquitous PPP metabolites, such as trifluoroacetic acid (TFA). The aim in this case is not to assess the origin of the metabolite, but its properties, and to set threshold values or environmental quality standards in the context of the Water Framework Directive.

Following the principle that the most efficient water protection is always precautionary and therefore seeks to avoid emissions in the first place, the fundamental question of whether there are other, more groundwater-compatible farming systems must also be asked. Experience shows that organic farming is the only system so far that reliably succeeds in protecting drinking water resources.

Furthermore, the "task of plant protection" begins long before the direct use of chemical plant protection products. The EU postulates the priority of integrated pest management over chemical pest management. In practice, however, farmers often resort directly to chemical crop protection. Last but not least, the "National Action Plan on Sustainable Use of Plant Protection Products" is becoming a wasted opportunity to develop chemical plant protection into a tool for sustainable water protection. In particular, there is a lack of ambitious implementation of concrete risk and input reduction targets.

BDEW, DVGW and VKU are counting on the Round Table and are open to continuing the previous successful cooperation in the future. This is often also controversial, which is in the nature of things. And yet it is coupled with the willingness of both sides to repeatedly take as the starting point for discussions the shared motto "We tackle problems as if we were 'one company' that produces both top-quality plant protection products and drinking water".

OUTLOOK AND CHALLENGES
FROM THE PERSPECTIVE OF PPP MANUFACTURERS

We, the manufacturers of plant protection products, are sure of one thing: in view of future challenges related to water protection, we remain committed to the concept that has proven its worth ever since the Water Industry / Plant Protection Industry Round Table was established – namely, open exchange, shared information and constructive cooperation with our partner, the water suppliers.

In concrete terms, this means maintaining options for the use of plant protection products that are oriented towards water protection. In the process, mutual coordination (where possible and expedient) will also lead to clarity in informing policymakers and the public in the future.

The challenge we see here is to identify actions that provide the water company with a local solution, while at the same time ensuring that farmers suffer no further loss of methods of control, jeopardising their livelihoods. This must be seen in light of the fact that agriculture in Germany and Europe has fewer plant protection products and methods of genetic engineering at its disposal than its global competitors; it must also meet more requirements.

Even though it is not directly relevant to water supplies, as the natural partner of agriculture, we feel it is our duty to point out the consequences of such displacement effects. After all, good beer needs a combination of two things: pure water and sufficient barley that is suitable for brewing. Raw materials for food that is not produced here grow elsewhere, sometimes in ecologically more sensitive areas.

A common credo was, and is, that the protection of drinking water resources in accordance with natural site conditions necessitates measures that go beyond the requirements of area-wide water protection. We remain committed to this, also in the future. In our opinion, however, this also means that measures required in water protection areas need not extend beyond those protected areas. Shaping and communicating this properly is an ambitious yet worthwhile goal. The successful work undertaken in the areas requiring action has shown that we are able to effectively apply local bespoke solutions together in practice.

MEMBERS OF THE ROUND TABLE
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Andrea Danowski (BDEW, Berlin)
Frieder Haakh (special-purpose association Landeswasserversorgung, Stuttgart)
Markus Penning (Oldenburgisch Ostfriesischer Wasserverband, Brake)
Ulrich Peterwitz (Gelsenwasser AG, Gelsenkirchen - until July 2022)
Carsten Schmidt (RheinEnergie AG, Cologne)
Nadine Steinbach (VKU, Berlin – until Dezember 2019)

The Plant Care Industries Association (IVA):
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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/gesundheitlicher-orientierungswert-gow

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

Listing of HRIV (= GOW) 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 (total of substances) laid down as binding precautionary limits in the Drinking Water Ordinance.

(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)

Area requiring action:
If action values are exceeded, the Water Industry / Plant Protection Industry Round Table recommends case-specific actions for the affected region, aimed at reducing entries and ensuring that limit and guidance values are met again as soon as possible; the Round Table also accompanies these actions in the area requiring action. Examples of actions taken in the area include: systematic monitoring, clarification of conspicuous findings, advisory services, changes in agricultural practices and/or the use of products. The process and coordination are described in detail in this brochure, both in general terms and by using case studies.

Action value:
A threshold value set by the Water Industry / Plant Protection Industry Round Table which, when exceeded, results in the recommendation of certain actions being introduced in water protection areas (area requiring action). This value is not to be confused with the precautionary action value (PAV).

Action Value I:
is 75% of the respective limit value or HRIV for the active substance or non-relevant metabolite.

Action Value II:
corresponds to the respective limit value or HRIV.

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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p. 30 Öhringen town; p. 33 font

IMPRINT

December 2020:
Plant protection products in a nutshell (Translation of the German original text)

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The brochure "Plant protection products in a nutshell" and a flyer (synopsis) can be downloaded from the website of the DVGW-Technologiezentrum Wasser (German Water Centre – TZW). 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

Scan the QR code and download this (40-page) brochure or click here.

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