Special Chemistry Monitoring Programme 2017

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Special Chemistry Monitoring Programme 2017

Summary

In the Special Monitoring Programme 2013, many "new" substances were detected. This showed that it is important to integrate new analytical methods and to constantly question the current monitoring programme. As a result, the ICPR decided to carry out a new special monitoring programme in 2017 which, in addition to target analysis, should also examine the possibilities of non-target analysis.

For the substance list for target analysis, 88 substances were determined based on new ICPR findings and experiences. As no laboratory was able to measure all of these substances, the study was carried out in five different laboratories. The non-target analysis was the subject of two Master's theses, with a focus on detecting unknown sources and the prioritisation of detected masses.
In the Special Monitoring Programme 2017, samples were taken at 21 measuring points. Non-target analysis was implemented at all 21 measuring points and target analysis at 15 measuring points. Of these 21 measuring points, 10 were already examined in the Special Monitoring Programme 2013. 4 samples were taken per measuring point, between March and September. Sampling took place as far as possible as a mix taken over a week, according to the flow time model "in the flowing wave[1]". The complex sample logistics were coordinated and carried out by the German Federal Institute of Hydrology.

As a result of non-target analysis, fexofenadine was added to the list of 88 substances for target analysis, meaning that 89 substances were ultimately examined. 58 substances were detected at least once and seven substances that showed an ever greater limit of detection. The Schwarzbach and Emscher tributaries were heavily polluted, averaging the highest concentrations. For 14 substances, the maximum concentration was above 1 µg/L.

From interpretation of the data, it is also noticeable that the concentration distribution between the Rhine and its tributaries and the load profile along the Rhine demonstrate clear differences. Substances such as valsartanic acid, which show an increase in load along the Rhine, are probably discharged via municipal waste water treatment plants. Substances such as 2,2,6,6-tetramethyl-4-piperidinone, which are noticeable with a peak load and declining or constant load, are most likely to come from point sources (i.e. industrial discharges). In total, it was possible to classify 35 of the 51 substances detected in the Rhine. For the remaining substances, the number of positive results was sometimes too low, or a clear classification through concurrent effects was not possible.

The data set on the investigated substances is not large, meaning that inclusion in the Rhine Chemistry Monitoring Programme should be discussed. To this end, the selection of substances from the target analysis should be carried out depending on the measured concentrations and the number of findings above the limit of detection. Based on these two criteria, a point scheme with a maximum score of 200 has been developed. The substances that received at least 100 points were examined more closely and, where possible, recorded with data on the results and toxicological values. The resulting recommendation of the SANA expert group is that the substances dicyandiamide, melamine, guanylurea, oxypurinol, valsartanic acid, fexofenadine, 2,2,6,6-tetramethyl-4-piperidinone, pyrazole, triphenylphosphine oxide and 1H-1,2,4-triazole must be included. For a further 15 substances, inclusion in the monitoring programme would be preferable if this is possible within the framework of an existing method. It must be noted that some of these substances cannot be integrated into the existing methods of previous Rhine monitoring; therefore a separate method with the necessary outlay is needed.

[1] With the aim to sample the same water mass at different places throughout the flow.

The non-target evaluation was carried out within the framework of two Master's theses, which, due to the enormous amount of time required, only examined the samples of the March campaign. The focus of the work lay on the recognition of unknown sources or unknown substances in the Rhine, as well as the prioritisation of detected masses or the testing of an analysis method not previously used in surface water monitoring. Both studies showed that hotspots for industrial discharges are located at the measuring points Weil am Rhein, Worms, Koblenz and Duisburg. The generated feature lists (feature: combination of mass and associated retention time) are a good basis for further clarification and can be made available to the monitoring stations. In addition, it was possible to identify two previously unknown substances - the antihistamine fexofenadine and the vermifuge praziquantel - and, in the case of fexofenadine, also to find the source. The gas chromatographic method newly developed in one of the Master's theses can provide a valuable addition to conventional methods in selected situations, but cannot replace them. This means that the previous method can still be considered the most suitable.

The results of the Special Monitoring Programme 2017 increase the level of knowledge about the Rhine, in particular about the occurring micropollutants, discharge sites and background information. The findings have an effect on the Rhine Chemistry Monitoring Programme and highlight the importance of further efforts in the field of non-target analysis, also in the structuring of the Rhine Monitoring Programme.

1. Introduction

In the ongoing Rhine Chemistry Monitoring Programme (ICPR Technical Report No. 222), the monitoring data on around 200 substances are continuously documented. On the basis of regional monitoring programmes and the timely monitoring of the Rhine at selected Rhine measuring points, there are findings on a further 200 substances.

The Special Monitoring Programme 2013 (ICPR Technical Report No. 221) of the ICPR demonstrated that new analysis methods and a targeted selection of measuring points can provide a current overview of the occurrence and concentration level of previously unrecorded substances. This means that additional knowledge is available to the states, so they can classify evidence of these "new" substances in the Rhine and, where necessary, adapt the Rhine Chemistry Monitoring Programme in accordance with the current load situation of the Rhine.

The Special Monitoring Programme 2017 pursued a broader analytical approach in comparison with the Special Monitoring Programme 2013, as not only substances from the target analysis were investigated, but the load situation of the Rhine was also to be determined within the framework of non-target screening. For this report, target analysis is understood to be the determination and quantification of known chemical species - after calibration with appropriate standards. Non-target analysis is understood to be the detection of substances without prior limitation, as far as they are detectable with the analytical method employed.
In the target analysis, substances were initially selected which were either contained in the facultative Rhine Chemistry Monitoring Programme, or which had already been detected in the Rhine catchment, but were not comprehensively analysed. Building on this, substances were added or removed on the basis of expert surveys (e.g. due to insufficient analytical methods). In response to findings from the non-target screening of the Special Monitoring Programme, fexofenadine was added to the ongoing target analysis programme, ultimately resulting in a list of 89 substances. A large proportion of the list of substances for target analysis comprises industrial chemicals that presumably originate from point sources, and about which there was previously a low level of knowledge with regard to loads in the Rhine - in terms of their spatial distribution and concentration.

Particularly due to the very complex data analysis required, non-target analysis is not yet feasible in a routine examination. For this reason, selected samples of the Special Monitoring Programme 2017 were subjected to non-target analysis within the framework of two Master's theses. The Master's theses were carried out at the German Federal Institute of Hydrology (BfG) and at the Swiss Federal Institute of Aquatic Science and Technology (Eawag). In addition to the classic LC-HRMS screening (Liquid Chromatography-High-Resolution Mass Spectrometry), GC-DBDI-HRMS screening-technology (Gas Chromatography-Dielectric Barrier Discharge Ionisation-High-Resolution Mass Spectrometry) was also used, with the aim of examining to what extent the recorded substance range could be extended through additional methods. In order to make the best use of the limited capacities available, the focus of both Master's theses was on the detection of load hotspots and sources along the Rhine, and less on the identification of unknown substances.

The information obtained should be used to adapt the Rhine Chemistry Monitoring Programme where necessary, and to provide recommendations for the analysis of the Rhine, specific to measuring points.

2. Measuring points and sampling

In order to enable a comparison between the two Special Monitoring Programmes, the 10 measuring points of the Special Monitoring Programme 2013 were re-examined. In addition to this, there were a further eleven measuring points (see Table 1, in **bold**), with six of these measuring points being examined exclusively in the context of non-target analysis. Thus, 21 measuring points were examined in the Special Monitoring Programme 2017. Non-target analysis was implemented at all 21 measuring points and target analysis at 15 measuring points. As there is no previous knowledge of non-target analysis and the findings can be very heterogeneous, a comparison between measuring points is very important - also with regard to possible sources of discharge, meaning that more measuring points were sampled.

Four samples were taken per measuring point (20.03.-01.04., 15.05.-27.05., 10.07.-22.07. 18.09.-30.09., see table, Appendix 2); meaning that a total of 60 samples were examined within the framework of the target analysis. As far as possible, mixed samples were taken over the course of a week from the individual measuring stations along the Rhine; as far as possible in accordance with the flow time model "in the flowing wave".

Table 1: Measuring points for the Special Monitoring Programme 2017

Measuring point	**Rhine km**	**Target analysis**	**Non-target analysis**
Brugg - Aar	103		x
Rekingen - Rhine	100		x
Weil am Rhein	171	X	x
Karlsruhe/Lauterbourg	359	X	x
Mannheim (Neckar)	426	X	x
Worms (left bank of the Rhine)	443	X	x
Worms (right bank of the Rhine)	443	X	x
Kornsand (right bank of the Rhine)	482		x
Schwarzbach (Hesse)	475	X	x
Bischofsheim (mouth of the Main)	497	X	x
Mainz	499		x
Koblenz - Rhine	590	X	x
Koblenz - Moselle	592	X	x
Bad Honnef	640	X	x
Düsseldorf-Flehe (right bank of the Rhine)	732		x
Duisburg (left bank of the Rhine)	779		x
Dinslaken (mouth of the Emscher)	798	X	x

Measuring point	Rhine km	Target analysis	Non-target analysis
Lobith	863	X	x
Bimmen	865	X	x
Maassluis	1026	X	x
Kampen	994	X	x

2.1 Insights for future monitoring programmes (especially regarding logistics)

The logistics of sampling and, in particular, sample shipment depend strongly on the type and number of substances to be analysed by target analysis and the number of participating laboratories. In the Special Monitoring Programme 2017, substances were analysed at 15 measuring points using target analysis from five different laboratories. Here, the volumes per sampling point required by the individual laboratories differed significantly (from 100 mL at LANUV laboratory, BfG, up to 3 L at TZW laboratory) according to the species spectrum covered. In order to minimise the number of sample packages to be shipped, and thus avoid damage during transport, the samples from the individual measuring points in each of the four campaigns were initially collected at the BfG in Koblenz and then simultaneously sent to the individual analysis laboratories. The sample bottles and the transport crates were provided to the measuring points by the BfG, prior to the four campaigns. In addition, the BfG assumed responsibility for the return of the transport crates and the rinsing and preparation of the sampling bottles for the next monitoring campaign. This procedure was a great outlay for the BfG, but is indispensable in terms of quality assurance. Almost all of the samples were sent to the analysis laboratories within the intended timeframe. Overall, there were only isolated losses due to glass breakage during transport. As it is very likely that the spectrum of analysis will be very different in future monitoring programmes and therefore a large number of analytical methods will be necessary that cannot be performed by a single laboratory; the procedure of the 2017 Special Monitoring Programme should be further built upon.

In addition, in the future, the personnel and transport costs, which were assimilated by the BfG for the Special Monitoring Programme 2017 (transport 4 k€, material consumption ~2 k€, excluding personnel costs), should be included in the cost planning for other special monitoring programmes, and the costs assigned to the respective measuring point operators. The allocation of sample logistics or the use of existing shipping structures should also be taken into consideration, as there is no assurance that a single institute - such as the BfG in the case of the Special Monitoring Programme 2017 - can provide the human resources for the very complex logistics.
In order to minimize the logistical effort, a small number of measuring laboratories and a detailed examination of the necessary sampling points are generally advisable.

3. Target analysis

With regard to target analysis, substances were quantified for which determination requires particularly sensitive analytical procedures that are not routinely used by all measuring point operators. The list of substances includes 88 (+ fexofenadine) substances, the measurement of which, with a correspondingly low limit of detection, required 15 different analytical methods. Two methods used GC-MS processes; the remaining methods were based on LC-MS methods with or without enrichment, different columns, etc. The details of the analysis can be found in appendix 3.3.

The resulting data are subject to measurement uncertainty, which is essentially characterised by sampling, transport and analytical determination. Furthermore, the inclusion of regional conditions around the measuring points is important for interpreting

the data, e.g. knowledge of industrial sources, inflows of waste water treatment plants, influences of tributaries.

3.1. Evaluation according to frequency and concentration

The 15 measuring points were each sampled and examined four times between March and September 2017. In total, 5340 data points were generated, which can be found in detail in Appendix 3.1.

Of the 89 substances examined, 58 were detected at least once as being greater than the limit of detection (LOD) (see Table 2). Accordingly, 31 substances were not detected. 33 substances were detected in at least half of the studies and seven in all studies as greater than the LOD. The range of substances that have always been found, is large. Along with guanylurea and valsartanic acid, the following can be detected in all 60 samples of the four measurement campaigns: pharmaceutical metabolites, with dicyandiamide, a nitrification inhibitor in agriculture (partly also used in the chemical industry, increased concentrations here through industrial discharger), and industrial chemicals (melamine and phosphoric acid triethylester), an analgesic (phenazone) and the insect repellent DEET.
For 14 substances, the maximum concentration was ≥ 1 µg/L, another 29 had a maximum between 0.1 and 1 µg/L.

16 of 89 substances could be detected in at least one of the samples as being over the orientation value of the international warning and alarm plan for the Rhine (orientation value for biocides, PPP and pharmaceuticals 0.3 µg/L, other substances 3 µg/L) (**in bold** in Table 2). It must be noted that mixed samples, taken over a week, were examined within the scope of the monitoring programme, meaning that under certain circumstances the concentration was even higher in the daily average.

Table 2: Positive findings from the target analysis of the Special Monitoring Programme 2017 across all measuring points and sampling; sorted in descending order in accordance with the number of findings greater than the limit of detection (LOD).

Substance*	**LOD in µg/L**	**Number > LOD**	**MV >LOD in µg/L**	**Max in µg/L**	**90 quantile in µg/L**	**50 quantile in µg/L**
Guanylurea	0.05	60	4.6	**60**	8.8	0.84
Dicyandiamide (cyanoguanidine)	0.02	60	2.0	**46**	2.1	0.61
Melamine	0.025	60	2.3	**21**	3.2	1.5
Valsartanic acid	0.005	60	0.58	**4.8**	1.2	0.26
Phosphoric acid triethyl ester (TEP)	0.01	60	0.25	**4.0**	0.44	0.085
Phenazone	0.001	60	0.024	0.28	0.045	0.010
DEET	0.002	60	0.027	0.23	0.055	0.013
Oxypurinol	0.03	59	1.7	**15**	4.5	0.58
Pregabalin	0.005	59	0.056	**0.61**	0.076	0.031
Cyclamate	0.005	59	0.082	0.38	0.16	0.058
Hydrochlorothiazide	0.01	57	0.23	**1.7**	0.93	0.036
Denatonium cation	0.005	56	0.046	0.33	0.14	0.018
Tris(butoxyethyl) phosphate (TBEP)	0.01	55	0.036	0.15	0.066	0.024
Carboxy acyclovir	0.02	54	0.17	1.1	0.34	0.076
Fexofenadine	0.002	54	0.1	**0.84**	0.19	0.048
Ethyltriphenylphosphonium cation	0.001	53	0.025	0.24	0.043	0.014
Gabapentin-lactam	0.02	52	0.12	1.0	0.236	0.045

Substance*	**LOD in µg/L**	**Number > LOD**	**MV >LOD in µg/L**	**Max in µg/L**	**90 quantile in µg/L**	**50 quantile in µg/L**
Clopidogrel acid	0.005	52	0.030	0.17	0.09	0.013
Olmesartan	0.01	51	0.089	**0.79**	0.22	0.026
Torasemide	0.003	51	0.026	0.18	0.10	0.008
TMDD (Surfynol 104)	0.1	50	0.55	**4.4**	0.65	0.23
Tris (1,3-dichloroisopropyl) phosphate (TDCP)	0.01	47	0.022	0.16	0.031	0.014
Triphenylphosphine oxide (TPPO)	0.01	46	0.23	**3.9**	0.23	0.033
9-CA-acridines	0.01	44	0.046	0.26	0.11	0.016
Atenolol acid	0.01	42	0.097	0.80	0.14	0.019
Pyrazole	0.05	41	0.98	**4.3**	2.3	0.18
Phosphoric acid triisobutyl ester (TiBP)	0.02	41	0.038	0.15	0.049	0.026
Bisoprolol	0.005	39	0.057	**0.67**	0.14	0.007
2,2,6,6-tetramethyl-4-piperidinone	0.1	35	0.79	**13**	0.62	0.13
Methyltriphenylphosphonium cation	0.002	35	0.10	0.99	0.19	0.010
Diphenylphosphine oxide (DPPO)	0.01	34	0.059	0.28	0.084	0.016
2,4-dichlorobenzoic acid	0.10	30	10	**150**	8.6	0.07
Diphenylphosphonic acid (DPPA)	0.01	30	0.11	0.45	0.14	0.008
AMPS	0.01	28	0.025	0.10	0.024	0.00
Tetrapropylammonium cation	0.005	27	0.045	0.22	0.054	0.00
1H-1,2,4-Triazole	0.1	26	0.23	0.45	0.29	0.00
Phosphoric acid tris (2-chloroethyl) ester (TCEP)	0.03	25	0.085	0.23	0.12	0.00
Tetrabutylammonium cation	0.01	24	0.098	0.37	0.18	0.00
(Methoxymethyl) triphenylphosphonium cation	0.01	19	0.094	0.42	0.044	0.00
Terbutryn sulfoxide	0.01	19	0.029	0.076	0.039	0.00
Tetracarbonitrilpropen	0.02	17	0.038	0.079	0.039	0.00
Tri-n-butyl phosphate (TnBP)	0.02	16	0.052	0.15	0.048	0.00
4-hydroxy-diclofenac (4-OH-DCF)	0.005	14	0.022	0.047	0.024	0.00
Dimethomorph	0.005	13	0.010	0.027	0.007	0.00
14-Hydroxyclarithromycin (= 14R-Erythromycin)	0.01	10	0.047	0.120	0.034	0.00
Cefuroxime	0.01	8	0.05	0.097	0.018	0.00
Acyclovir	0.02	7	0.032	0.052	0.023	0.00
Atenolol	0.02	5	0.11	0.16	0.000	0.00
Duloxetine	0.003	4	0.008	0.015	0.000	0.00
Uvinul 4050H	0.15	3	0.21	0.22	0.000	0.00
Triphenylphosphine sulphide (TPPS)	0.01	3	0.049	0.072	0.000	0.00
Boscalid	0.025	3	0.030	0.030	0.000	0.00
tributylphosphine oxide	0.01	2	0.012	0.012	0.000	0.00
Thiacloprid	0.01	1	0.020	0.020	0.000	0.00
Acetamiprid	0.005	1	0.017	0.017	0.000	0.00
Simvastatin	0.01	1	0.013	0.013	0.000	0.00
Opipramol	0.01	1	0.011	0.011	0.000	0.00
Dimoxystrobin	0.001	1	0.001	0.001	0.000	0.00

*The substances that were never detected as greater than LOD are listed in Appendix 3.2.

As part of the special monitoring programme, in addition to the Rhine, the most important tributaries were sampled. All of these tributaries are characterized by a high proportion of wastewater (Emscher up to 100% wastewater) compared to the Rhine (approx. 5% wastewater in Basel). Substances that are discharged via a municipal waste water treatment plant should therefore have a higher concentration in the tributaries than in the Rhine. If this approach is applied to the concentrations found, it is possible to draw conclusions about the sources of discharge of substances.

For a comparison between the Rhine and the tributaries, avoiding extreme values, the ratio of concentration 90 quantiles (RQ90) is useful (Figure 1). Of the total of 58 quantitatively detected substances, only for the following five substances: 2,2,6,6-tetramethyl-4-piperidinone (RQ90 = 0.7), pyrazole (RQ90 = 0.4), tetrabutylammonium cation (RQ90 = 0.27), AMPS (RQ90 = 0.99), tetracarbonitrilpropen (RQ90 = 0), is the 90 quantile of the tributaries smaller than in the Rhine; ethyltriphenylphosphonium cation and tetrapropylammonium cation are almost identical with the RQ90 of 1.1. This can only be explained by industrial discharge along the Rhine.

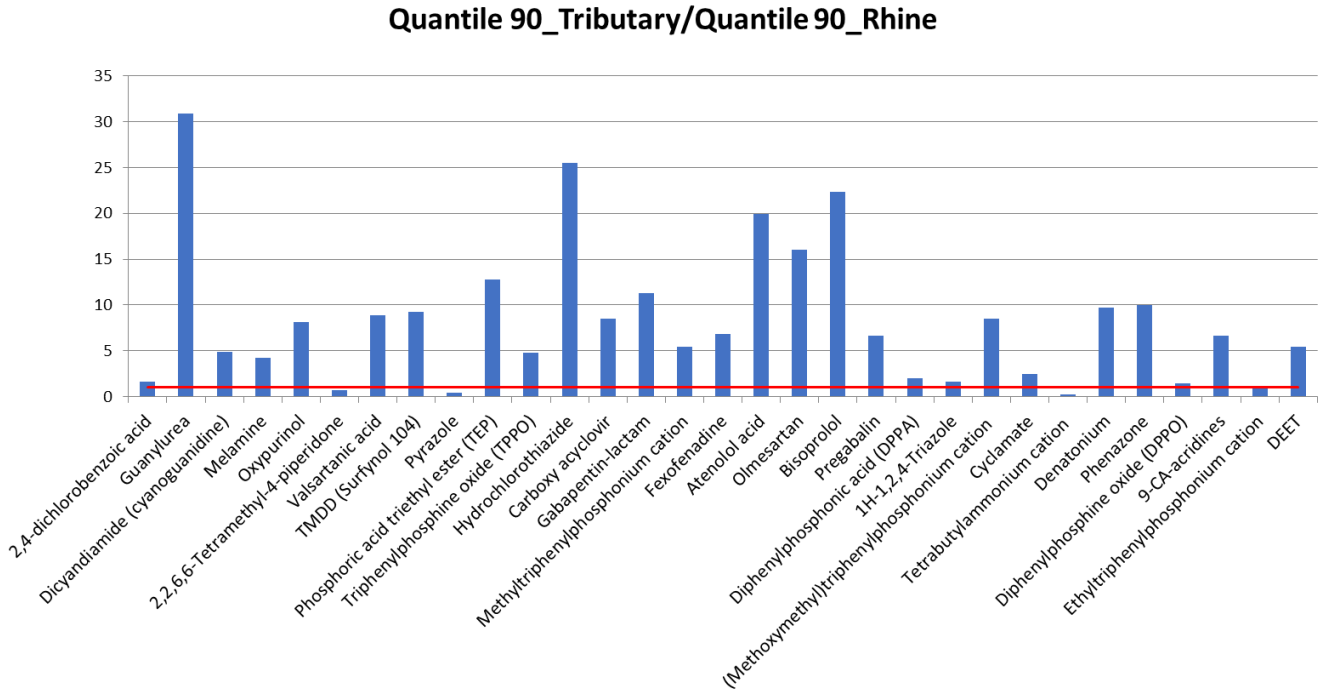

Fig. 1: Concentration 90 quantile ratio between tributaries and Rhine over all measuring stations and sampling. Represented here are the first 31 substances, sorted by descending max. concentration. The red line corresponds to the ratio 1.

Using as a basis the commonly known use of the substances examined, the finding is mainly industrial chemicals and plasticisers with a RQ90 of less than five. Decomposition products of commonly used drugs such as oxypurinol, valsartanic acid, atenololic acid, gabapentin lactam, which cannot be assigned to a point source, have RQs greater than 8. The two ratio values of more than 20 of guanylurea and bisoprolol can be explained by high findings, especially in the Schwarzbach and the Emscher. In the case of hydrochlorothiazide, the concentration in the Main is also noticeable. The RQ of 2.4 for the sweetener cyclamate should also be noted. As it is a wastewater-borne substance, a higher RQ would have been expected. Whether the very good decomposition of cyclamate in waste water treatment plants (and later in the surface water itself) is responsible for this or additional effects play a role, cannot be clarified clearly.

It should be noted that point discharges in an inflow, such as fexofenadine, are not captured with this categorisation, because the discharge is masked by the high level of wastewater in the Main.

3.2. Sources

Due to the approach of sampling in the flowing wave, a comparison of the concentration or loads along the course of the river is possible. Substances with a municipal origin and low decomposition behaviour must accumulate along the Rhine according to the proportion of wastewater. In contrast, industrial point sources should be notable through peak loads near the source and persistent or decreasing loads corresponding to the substance-specific decomposition behaviour and further dilution through downstream tributaries. To illustrate the course, a heat map of the cumulated loads was selected for the four samples along the Rhine (Fig. 2). The discharge data for calculating the loads were provided by the measuring point operators (Appendix 2). As the Lobith sampling point is located directly in the discharge of the Emmerich waste water treatment plant, and is therefore not representative for the current study, the Lobith site in the heat map was not taken into account.

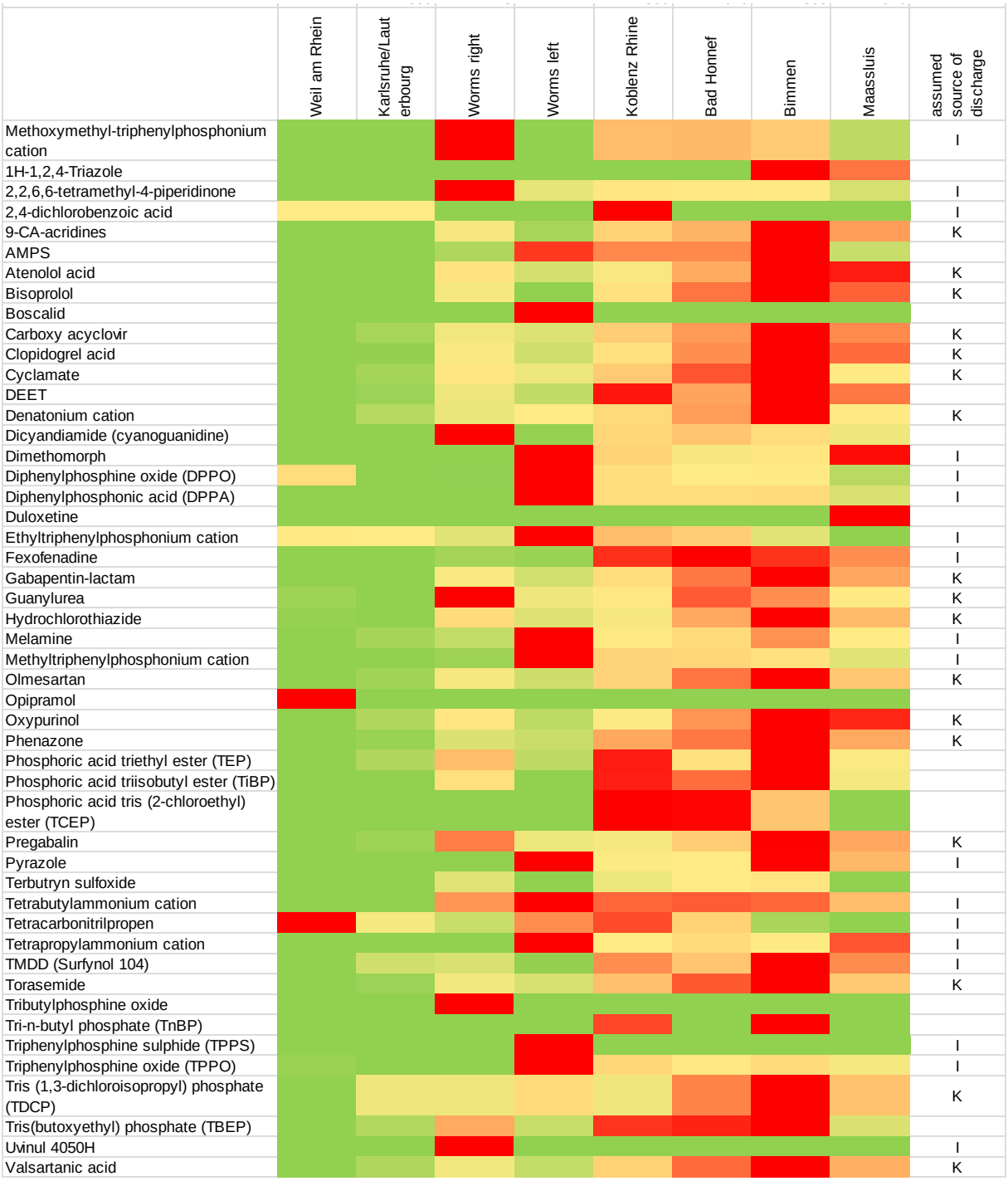

Fig. 2: Heatmap of the cumulated daily loads of the four samples from the Rhine sampling points; assumed discharge source K = municipal discharge, I = industrial source. (Colour scaling according to increasing load - from green to yellow, orange to red, where green = low load, red = high load, reference values are per substance)

Based on the colour coding (green = low load, red = high load), load progressions are well represented using the heat map. It should be noted that the two sampling lines of the measuring point Worms do not capture the Rhine as a whole, and in Maassluis, only random samples were taken. Despite these limitations, the courses do provide useful insight.

Taking into consideration valsartanic acid, which was also chosen within the context of the Master's thesis of the BfG as a reference substance for a municipal discharge (Chapter 4.1), here there is clearly an increasing load along the course of the river. Similar courses can be observed with the substances designated "K". Tetracarbonitrile propene, which is discharged into the Rhine shortly before Basel due to industrial production, is a typical example of the load course after industrial point discharge. Overlaps of discharges from industrial point sources and the use of the products (diffuse inflows or entry via waste water treatment plants) make interpretation difficult. For example, fexofenadine (antihistamine) as a new substance from non-target screening (see Chapter 4) has a background load of municipal origin, but is mainly discharged by a point source into the Main. This point source dominates the load course downstream, meaning that the designation "industrial discharge" must be made.

Substances with few findings in the vicinity of the LOD must be interpreted with caution due to increasing analytical uncertainty and therefore were not assigned to the two categories, municipal (K) or industrial (I) discharge. For example, in the case of phosphoric acid tris (2-chloroethyl) ester, the daily loads in Koblenz are about 10 kg and are thus only 2.5 times higher than when referring to the LOD.

3.3. Prioritisation of results - consequences for the Rhine Chemistry Monitoring Programme

In order to prioritise the results of the Special Monitoring Programme 2013, the maximum concentrations and detection frequency were drawn upon. Due to the fact that within the framework of the Special Monitoring Programme 2017 many industrial chemicals and partially heavily polluted inflows were included in the testing programme, this approach can only be applied with caution to the Special Monitoring Programme 2017. Concentration maximums are dominated by the heavily polluted inflows, and point discharges in upstream sections of the Rhine are weighted higher than discharges close to the mouth, due to the detection frequency alone.
Nonetheless, the adjusted criteria (see Table 3) from 2013 have been selected for a baseline assessment and the substances have been prioritised according to these evaluation criteria (see Table 4). For the criterion of maximum concentration, the heavily polluted Emscher and Schwarzbach tributaries were not taken into account, as these accounted for about three quarters of the max. concentration and therefore this criterion would not be relevant for the Rhine. For pharmaceuticals and pesticides, a 10-fold lower value was chosen for prioritisation due to the largely better (eco)toxicological evaluation basis, based on maximum concentrations. Based on these two criteria, a maximum of 200 points can be achieved (points concentration + points findings on percentage basis > limit of detection).

Table 3. Criteria for the calculation of the evaluation points

Concentration (µg/L)			**Percentage results > Limit of detection (LOD)**		
Pharmaceuticals/ pesticides	other chemicals	Points			Points
≥ 0.1	≥ 1	100	100%	> LOD	100
≥ 0.075	≥ 0.75	75	75-99%	> LOD	75
≥ 0.05	≥ 0.5	50	50-74%	> LOD	50
≥ 0.03	≥ 0.3	30	30-49%	> LOD	30
≥ 0.01	≥ 0.1	10	10-29%	> LOD	10
<0.01	0.01 - 0.1	1	1-10%	> LOD	1

Tab. 4: Evaluation points for all substances (shown starting from 10 points)

Substance	max. concentration in µg/L (without Emscher and Schwarzbach)	Conc. points	A[1] > LOD	Percent greater than LOD	H[2]-points	Total
Dicyandiamide (cyanoguanidine)	46	100	52	100	100	200
Melamine	5.8	100	52	100	100	200
Guanylurea	3.2	100	52	100	100	200
Oxypurinol	2.3	100	51	98	75	175
Valsartanic acid	0.96	75	52	100	100	175
Fexofenadine	0.84	100	46	88	75	175
Hydrochlorothiazide	0.22	100	49	94	75	175
2,2,6,6-Tetramethyl-4-piperidone	13	100	28	54	50	150
Pyrazole	4.3	100	33	63	50	150
TMDD (Surfynol 104)	0.85	75	42	81	75	150
Pregabalin	0.091	75	51	98	75	150
Olmesartan	0.089	75	43	83	75	150
DEET	0.058	50	52	100	100	150
2,4-dichlorobenzoic acid	57	100	22	42	30	130
Phenazone	0.046	30	52	100	100	130
Phosphoric acid triethyl ester (TEP)	0.20	10	52	100	100	110
Cyclamate	0.33	30	51	98	75	105
Triphenylphosphine oxide (TPPO)	0.71	50	38	73	50	100
Carboxy acyclovir	0.29	10	46	88	75	85
Gabapentin-lactam	0.18	10	44	85	75	85
Tris(butoxyethyl) phosphate (TBEP)	0.099	10	47	90	75	85
Torasemide	0.028	10	43	83	75	85
Denatonium	0.069	1	48	92	75	76
Ethyltriphenylphosphonium cation	0.056	1	46	88	75	76
Clopridogrel acid	0.036	1	44	85	75	76
Tris(1,3-dichlor-isopropyl)phosphate (TDCP)	0.031	1	39	75	75	76
Diphenylphosphonic acid (DPPA)	0.45	30	23	44	30	60
Tetrabutylammonium cation	0.37	30	16	31	30	60
1H-1,2,4-Triazole	0.33	30	18	35	30	60
Diphenylphosphine oxide (DPPO)	0.28	10	29	56	50	60
Methyltriphenylphosphonium cation	0.27	10	31	60	50	60
Tetrapropylammonium cation	0.22	10	27	52	50	60
Bisoprolol	0.026	10	31	60	50	60
Atenolol acid	0.087	1	34	65	50	51
9-carboxy-acridine	0.080	1	36	69	50	51
Phosphoric acid triisobutyl ester (TiB	0.062	1	33	63	50	51
Phosphoric acid tris (2-chloroethyl) ester (TCEP)	0.12	10	17	33	30	40
AMPS	0.10	10	24	46	30	40
Tetracarbonitrilpropen	0.079	1	17	33	30	31
Boscalid	0.030	30	3	6	1	31
(Methoxymethyl)triphenylphosphonium cation	0.18	10	15	29	10	20
Dimethomorph	0.027	10	12	23	10	20
Uvinul 4050H	0.22	10	3	6	1	11
Tri-n-butyl phosphate (TnBP)	0.088	1	9	17	10	11
Terbutryn sulfoxide	0.043	1	14	27	10	11
Acyclovir	0.023	10	1	2	1	11
4-hydroxy-diclofenac (4-OH-DCF)	0.012	1	6	12	10	11
Cefuroxime	0.011	10	1	2	1	11
Opipramol	0.011	10	1	2	1	11
Triphenylphosphine sulphide (TPPS)	0.072	1	4	6	1	2
14-Hydroxyclarithromycin (= 14R-Erythromycin)	0.013	1	2	4	1	2
Tributylphosphine oxide	0.012	1	1	2	1	2

[1] - Number of measurement values with greater limit of detection; [2] - frequency

In the case of the substances in Table 4, which in total have at least 100 points, inclusion in the measurement program must be discussed. The majority of this group of 18 compounds consists of pharmaceuticals or pharmaceutical metabolites with a total of eight substances. The maximum concentration listed corresponds to the maximum concentration across all measurements, but without the heavily polluted Emscher and Schwarzbach waters. Further evaluation should also be based on this reduced data set.

In principle, new substances should only be included in a regular monitoring programme if the following conditions apply:

- A substance was detected within the framework of the special monitoring programme at at least one of the measuring points above the limit of detection.
- If a substance has been detected at one of the measuring points above the limit of detection, it must be checked whether 1/3 of the orientation value of the international warning and alarm plan for the Rhine has been exceeded and/or if the substance or the concentration detected in the context of the special monitoring programme is to be classified as critical in terms of ecotoxicology (if known).
- In the case of exceeding 1/3 of the orientation value and/or ecotoxicological relevance, the substance should be included in the regular monitoring programme. However, substances that originate from point sources as industrial chemicals should only be included from the discharge source, to minimise effort and analysis costs.

Dicyandiamide, melamine, guanylurea and pyrazole have been rated with ≥ 150 points in accordance with the underlying evaluation scheme. The four substances are very polar, and cannot be captured by the commonly used chromatographic methods. Here, special analysis is therefore required, which as a rule entails additional time, personnel and cost outlays for the measuring point operators.

Fexofenadine was rated with 175 points according to the underlying evaluation scheme. Research following the Special Monitoring Programme 2017 has shown that the predominant discharge source is an industrial plant on the Main. The specialist authority HLNUG from Wiesbaden commented on this as follows:
"The discharge of fexofenadine via the central waste water treatment plant of an industrial large-scale discharger into the Main is known to the relevant water authority and was re-approved in 2017 after thorough examination of the relevance to water of this substance within the framework of an approval procedure for the alternative production of fexofenadine in accordance with the BImSchG [Federal Immission Control Act]. A concrete monitoring value was not determined according to the risk assessment (biodegradable, PEC/ PNEC <1). However, in order to further minimise the discharge of fexofenadine, operational trials on behalf of the emitter were carried out successfully, and these are expected to be implemented in mid-2019, leading to the further relief of the Main." (Email: E. Saller dated 30.11.2018 to Uwe Kunkel). With regard to these findings, for the control of measures, monitoring or inclusion in the monitoring programme only in Mainz is appropriate.

2,4-Dichlorobenzoic acid is noteworthy as a target in Schwarzbach and above all in the samples from Koblenz (Rhine and Moselle). The further concentration course with negative findings in Bad Honnef is not plausible, meaning that the data would first need to be checked before inclusion in the monitoring programme would be appropriate.

The preliminary assessment of SANA on the inclusion, and further information, ecotoxicological findings, data on further test results at the individual measuring stations,

etc. for the substances that were rated with 100 or more points, are given in Appendix 3.4.

On the basis of these data, the inclusion of the substances (see Appendix 3.4) in the Rhine Chemistry Monitoring Programme must be checked by the ICPR. In particular, the ecotoxicological data must be checked before inclusion in the Rhine Chemistry Monitoring Programme.

Substances with more than 100 points, which do not obligatorily need to be included but can be incorporated into existing methods, can be included in the facultative Rhine Chemistry Monitoring Programme.

4. Non-target analysis

Non-target analysis offers the opportunity to identify previously unknown substances. In order to also detect regionally recorded substances, which may possibly only be identified there, the number of measuring points below catchment areas with a higher density of potentially relevant point sources has been increased. Due to the enormous outlay for non-target analysis at 21 different measuring points and the time limitations of a master's thesis, only the samples from the March campaign have been evaluated in detail thus far. The further campaigns will only be used as a reference or as confirmation of anomalies in the March campaigns. An in-depth non-target evaluation of the May, July and September campaigns is not planned.

4.1. Master's thesis on the BfG / LC-ESI-HRMS analysis

In this thesis (Gemüth 2017 [2]), samples were analysed at the 21 measuring points of the March campaign with the aid of the LC-HRMS method developed by the BfG, as per Schlüsener et al. (2015) [3]. The result of the non-target analysis is a feature list consisting of the high-resolution mass, retention time (RT) and the intensity of the chromatographic peaks. Each feature can stand for an unknown chemical substance. The change in intensity is proportional to the change in the concentration of the substance. The intensity of the selected features can be observed over different samples; here across the entire course of the Rhine, in order to determine trends. Where a feature in the Master's thesis was sufficiently striking, the aim was to attempt to further explore it in future studies, and thus provide reinforcement of the data basis for further measures.

Figure 3 shows the number of determined features of the individual measuring stations along the course of the Rhine. The average number of features in the Rhine is 2,250 (red line). Tributaries with a high anthropogenic influence show a significantly increased feature count. With over 25,000 possible unknown substances, the Emscher was still significantly ahead of the Schwarzbach, with over 13,000 features found.

[2] Gemüth, T. (2017) Identifizierung von Schadstoffen und ihrer Quellen im Rheinlängsverlauf mittels hochauflösender Massenspektrometrie gekoppelt mit Flüssigkeitschromatographie [Identification of pollutants and their sources in the course of the Rhine by means of high-resolution mass spectrometry coupled with liquid chromatography] (LC-HRMS/MS) (available at the BfG and the ICPR)

[3] Schlüsener M. P., Kunkel U., Ternes T. A. (2015) Quaternary Triphenylphosphonium Compounds: A New Class of Environmental Pollutants Environ. Sci. Technol., 49 (24), pp 14282–14291

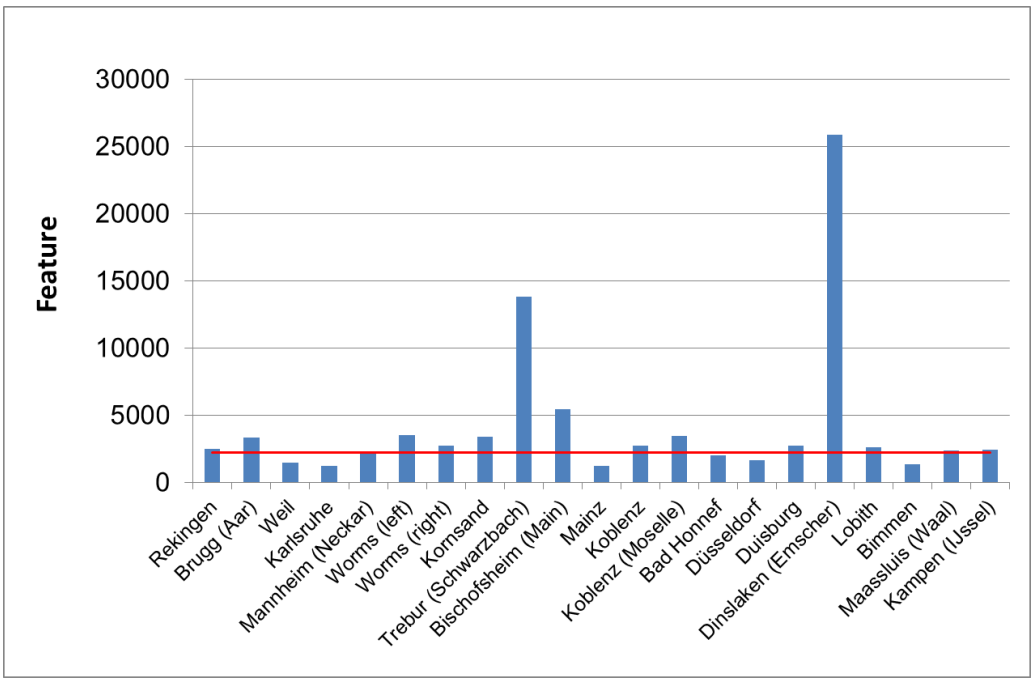

Fig. 3: Number of determined features of the individual measuring stations along the course of the Rhine. The red line shows the average value of all measured features in the Rhine from 2250.

In order to identify newly discharged substances in the Rhine at individual stations, prioritisation was carried out by comparing the feature lists with the preceding measuring point. The tributaries were compared with the comparatively unpolluted samples from the Rekingen measuring station. The lists thus obtained were sorted by intensity and the TOP 35 of the positive and negative ionisation of each measuring station was examined more closely. These TOP 35 have been classified into categories: category A (point source municipal waste water treatment plant) and category B (point source industrial waste water treatment plant) where a relation was found to a municipal wastewater indicator substance such as carbamazepine (positive ionisation) or valsartanic acid (negative ionisation). This categorisation could not be carried out for the tributaries, as when comparing the tributaries with Rekingen, the TOP 35 mainly showed only substances with an increased incidence in municipal wastewater (category A). Category A features have a similar course to the comparative substances (Figure 4).

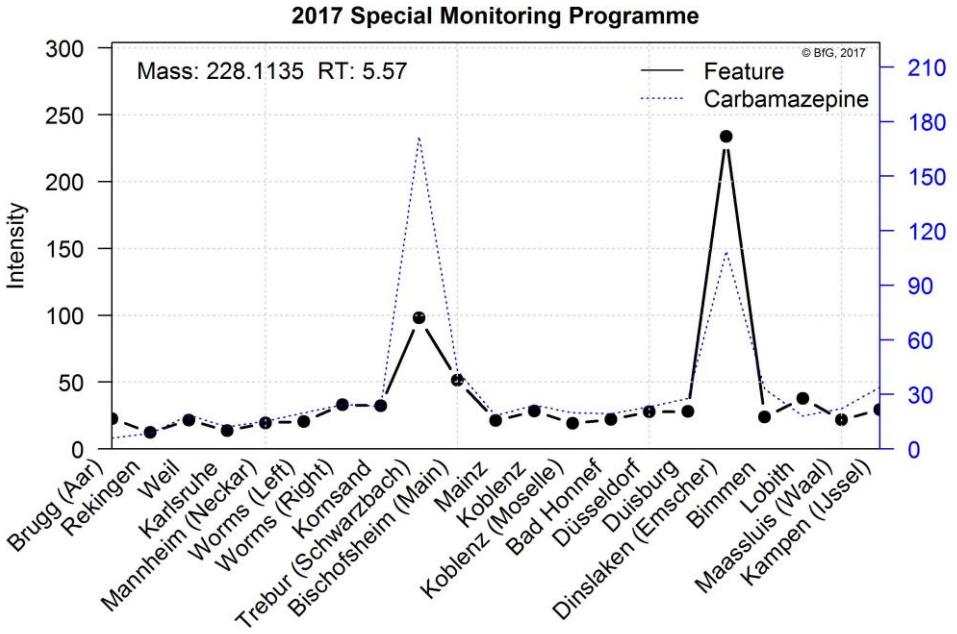

Fig. 4: Exemplary representation for features of category A (municipal waste water treatment plant) in comparison to carbamazepine.

Features of category B (Figure 5) have a high point intensity at a measurement point that is close to the source of the discharge. After that, the intensity drops and shows a constant or slightly decreasing trend. The intensity along the course of the Rhine is unlike the reference substance carbamazepine. Tributaries usually show no discharge.

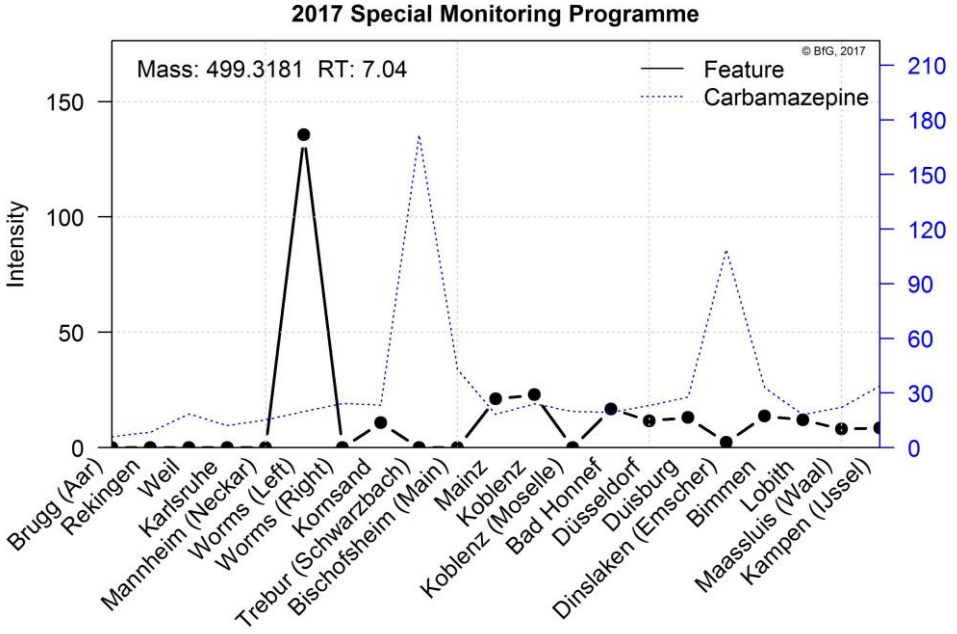

Fig. 5: Exemplary representation for features of category B (point discharge, not municipal waste water treatment plant) in comparison to carbamazepine.

Evaluation of the TOP 35 categorisation revealed that on average 40% of all TOP 35 features can be assigned to categories A (16%) or B (24%). In Figure 6, Lobith station

shows the highest number of Category A features (33). This is due to the Emmerich waste water treatment plant, which discharges into the Rhine immediately before the measuring station on the same side of the river. By contrast to this, Bimmen, which is located on the opposite side of the river, shows no new discharges in the Rhine. The highest signs of category B can be found in Worms on the left bank of the Rhine (63), Duisburg (40) and Weil (36). Before these measuring stations, there must therefore be dischargers that emit new substances into the Rhine, which as a rule are not discharged via municipal waste water treatment plants. The aim in future studies is to use the prioritised features of Category B to determine the underlying chemical substances and allocate them to a discharger.

Conclusion:

It should be noted that with the help of non-target analysis in combination with sampling along the Rhine, discharge types of previously unknown substances can be isolated. In the samples of the March campaign (sampling within 3 weeks), the main discharge points of substances into the Rhine at a single point are each directly before the measuring stations Weil, Worms and Duisburg. Identification of the prioritised features is planned for the coming years and will be carried out by the BfG (M. Schlüsener). After identification of the unknown substances, the concentration in the Rhine can subsequently be determined, to initiate evaluations. The non-target analysis shows that it is a highly effective instrument of water monitoring, with the help of which not only the occurrence, but also the discharge location and or originator of the pollution can be determined.

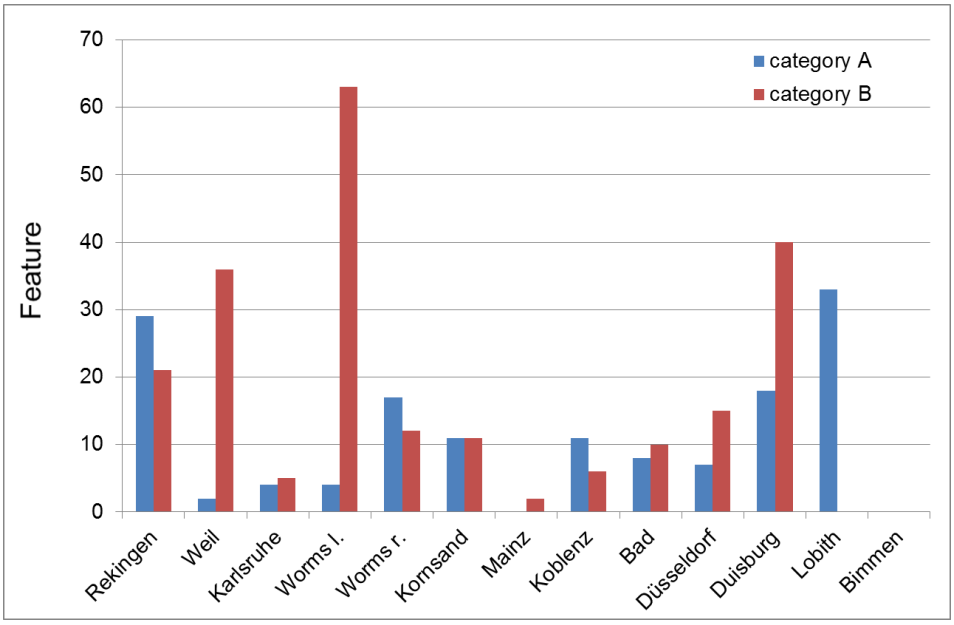

Fig. 6: TOP 35 features of both types of ionisation along the course of the Rhine, which can be assigned to category A or B (for details see Master Thesis Gemüth 2017 [4]).

[4] Gemüth, T. (2017) Identifizierung von Schadstoffen und ihrer Quellen im Rheinlängsverlauf mittels hochauflösender Massenspektrometrie gekoppelt mit Flüssigkeitschromatographie [Identification of pollutants and their sources in the course of the Rhine by means of high-resolution mass spectrometry coupled with liquid chromatography] (LC-HRMS/MS) (available at the BfG and the ICPR)

4.2. Master's thesis on EAWAG and AUE-BS / GC-DBDI-HRMS analysis

In addition to the non-target results from the Master's thesis at the BfG, a second Master's thesis at Eawag examined the extent to which the detectable spectrum of substances in the non-target analysis can be extended through another analysis technique. To this end, a technique was used in which, after gas chromatographic separation, the analytes are ionised in a plasma source (DBDI - Dielectric Barrier Discharge Ionisation) and then detected in a high-resolution mass spectrometer (Orbitrap technology). As, during this process, molecular ions (usually protonated) are formed analogously to the conventional LC-ESI-HRMS screening, this analytical technique is fundamentally suitable for further non-target analysis, in particular for non-polar, thermostable and volatile substances. The GC-DBDI-HRMS method was initially developed and optimised in several steps. To increase detection sensitivity, an enrichment stage, by means of solid phase extraction (SPE), was also implemented. The substance spectrum that can be detected with this method was evaluated with a test set-up spanning 390 substances. 49% of the tested substances could be detected by the method. All other analytes were undetectable due to their thermal instability and temperatures during gas chromatographic separation.
Analogously to the non-target analysis using LC-HRMS (Master's thesis at the BfG), 16 samples of the Rhine and its main inflows from the March campaign were investigated using the newly developed GC-DBDI-HRMS method. It was thus possible to quantify 31 target substances, including triethyl phosphate and tetraglyme with maximum concentrations of 1,700 ng/L and 310 ng/L. Even substances that have not yet been analysed in the routine study on the Rhine were successfully quantified. In this way, praziquantel was detected in the Schwarzbach with a maximum concentration of 680 ng/L. Cross-comparisons with already existing measurements in the Rhine showed a good conformity with, and underscoring of the suitability of, the developed method for quantitative analysis.
Analogously to the non-target analysis using LC-ESI-HRMS, a feature list was generated from the recorded GC-DBDI-HRMS data, consisting of the high-resolution mass, the retention time (RT) and the intensity (area) of the gas chromatographic peaks. The peak areas of the 1,765 detected non-target features along the Rhine (inflows were not studied) were visualised - when normalised - against a surrogate standard in a heatmap to identify local hotspots (Figure 7). A noteworthy number of unknown substances (features) were identified in the samples of the stations Worms left, Worms right and Koblenz. The substance clusters framed in blue in Figure 7 show the unknown features for each measurement station, which are recommended for complex substance identification.

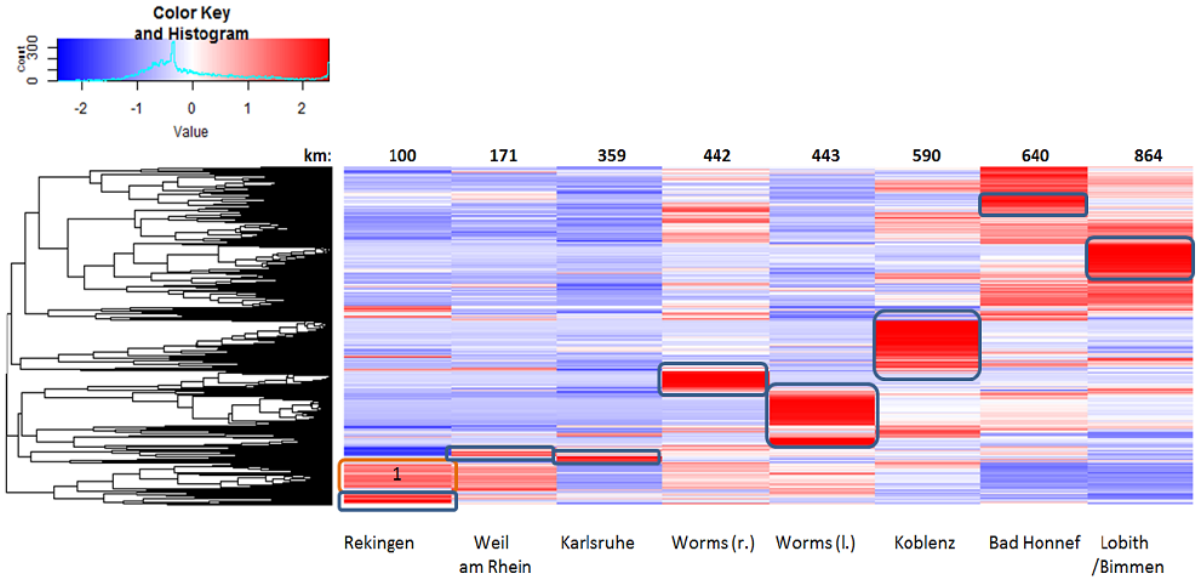

Fig. 7: Heatmap of 1,756 features along the Rhine.

Conclusion:

The developed GC-DBDI-HRMS method is suitable for both the sensitive quantification of target substances and for the identification of unknown substances (non-target feature). Together with the very good gas chromatographic resolution, the method can be a valuable addition to the conventional LC-ESI-HRMS analysis in selected situations; without being able to replace it. The routine use of this method in the monitoring of the Rhine in addition to the LC-ESI-HRMS method is therefore in principle possible, but is not considered urgently necessary due to the limited additional benefit.

4.3 Conclusions from non-target analysis for monitoring programmes and measuring point selection

The two non-target methods used in the Special Monitoring Programme 2017 within the framework of the Master's theses provided valuable additional insight compared to pure target analysis. It was possible to identify thus far only isolated new substances potentially relevant to the Rhine, which occur in high concentrations at many measuring points. This, however, was not the main focus of the two Master's theses. The focus of the theses lay rather on the recognition of unknown sources or unknown substances in the Rhine, as well as the prioritisation of detected masses (Master's thesis BfG) or the testing of an analysis method not previously used in surface water monitoring (Master's thesis Eawag). Here, it became apparent that the previously used LC-HRMS is the method of choice for the investigation of polar to medium-polar substances.

The Master's theses focused on the one hand on an extensive suspect screening (targeted examination of the sample according to an existing list of substances) and on the other, mainly on the detection of substances that are predominantly registered in the Rhine via individual industrial point sources. This approach discriminates against substances that are per se (almost) ubiquitous in the Rhine, but are not yet included on any suspect list (substance list with details on the exact mass and partially on retention time), i.e. precisely the actual non-targets. Nevertheless, with the increased concentrations of the antihistamine fexofenadine in the Main and the vermifuge praziquantel in the Schwarzbach, two substances were identified that were not expected (in increased concentrations) in the Rhine.

Overall, the two Master's theses confirmed that in addition to the background pollution with substances from municipal waste water treatment plants, there are some (known) hotspots in the lower reaches of larger industrial plants, where a large number of known and, above all, unknown substances are introduced into the Rhine. In the samples of the March campaign, these especially include Weil am Rhein, Worms (left, right), Duisburg and partly Koblenz. These findings should be considered in the planning of future monitoring programmes, and in the selection of measuring points in the course of optimising timely water monitoring. In the future, if possible, primarily LC-HRMS procedures for timely water monitoring should be used at the prioritised measuring points in order to quickly and effectively record unknown discharges and, if necessary, initiate corresponding reduction measures.

For a recommendation on the use of non-target analysis in the timely, future water monitoring of the Rhine, reference is made to the document "Recommendations for an efficient and contemporary non-target screening with LC/ESI/HRMS/MS along the river Rhine". This document sets out the proposals of the EG SANA to implement a harmonised measurement and evaluation process based on the LC-HRMS method. In addition to the results of the ring trial on non-target analysis conducted within the ICPR, this document also included the findings of the two Master's theses carried out as part of the Special Monitoring Programme 2017.

5. Conclusion

In the Special Monitoring Programme 2017, through the division into a target and non-target component and sampling in the flowing wave, it was possible to increase the level of understanding and standard of knowledge about the Rhine, in particular with regard to the occurring micropollutants, discharge locations and background information on discharge.
Of the 89 measured target substances, 58 were detected as positive at least once. Of the 51 substances detected in the Rhine, 18 are likely due to industrial discharges. Based on a prioritisation of the number of findings and concentration, the following ten substances are recommended for inclusion in the Rhine Chemistry Monitoring Programme: dicyandiamide, melamine, guanylurea, oxypurinol, valsartanic acid, fexofenadine, 2,2,6,6-tetramethyl-4-piperidinone, pyrazole, triphenylphosphine oxide and 1H-1,2,4-triazole.
The focus of the non-target component (2 Master's theses) was the capturing and categorisation of the observed features (combination of mass and associated retention time). The hotspots for industrial discharge sources are located at the stations Weil am Rhein, Worms, Koblenz and Duisburg. This means that at these stations, non-target analysis with LC-HRMS should be used as a priority.

Appendix 1: Target list (89 substances)

Substance	CAS No.	Use	AA-EQS* (PNEC) [µg/L]	Comment	Laboratory
14-Hydroxyclarithromycin (= 14R-Erythromycin)	116836-41-0	Metabolite of the antibiotic clarithromycin		Clarithromycin on EU Watchlist	TZW
1H-1,2,4-Triazole	288-88-0	Basic framework of pesticides and fungicides, nitrification inhibitor			TZW
2,2,6,6-Tetramethyl-4-piperidinone	826-36-8	UV stabilizer, pharmaceutical content			TZW
2,4-dichlorobenzoic acid	50-84-0	Intermediate in the production of pharmaceuticals, pesticides, etc.			TZW
3-trifluoromethylaniline	98-16-8	Intermediate in the production of pharmaceuticals, pesticides, etc.			AUEBS
4'-Hydroxydiclofenac	64118-84-9	Metabolite/TP of diclofenac			BfG
9-carboxy-acridine	5336-90-3	TP of carbamazepine metabolites			BfG
Acetamiprid	160430-64-8	Insecticide		EU Watchlist	AUEBS
Acyclovir	59277-89-3	Antivirals			BfG
Carboxy acyclovir	80685-22-9	TP of acyclovir			BfG
Aclonifen	74070-46-5	Pesticide	0.12	Priority substance, ICPR 2014 checklist	TZW
Allopurinol	315-30-0	Gout medication			BfG
Oxypurinol	2465-59-0	Metabolite/TP of diclofenac			AUEBS
Amlodipine	8815042-9	Antihypertensives			BfG
Amoxicillin	26787-78-0	Antibiotic		EU Watchlist	BfG

Substance	CAS No.	Use	AA-EQS* (PNEC) [µg/L]	Comment	Laboratory
AMPS	15214-89-8	Additive in many products			AUEBS
Atenolol	29122-68-7	Beta blocker			BfG
Atenolol acid	56392-14-4	Metabolite/TP of atenolol and metoprolol			BfG
Bifenox	42576-02-03	Herbicide	0.012	Priority substance, ICPR 2014 checklist	TZW
Bifenoxsäure	53774-07-5	TP of Bifenox			TZW
Bisoprolol	66722-44-9	Beta blocker			AUEBS
Boscalid	188425-85-6	Fungicide			LANUV
Butyltriphenyl-phosphonium	1779-51-7 (as bromide)	industrial chemical			BfG
Cefaclor	53994-73-3	Antibiotic			TZW
Cefuroxime	64544-07-6	Antibiotic			TZW
Chloroxylenol	88-04-0	Disinfectant			TZW
Chlorpropham	101-21-3	Herbicide			BfG
Clopidogrel acid	144457-28-3	Metabolite of clopidogrel, platelet inhibitor			AUEBS
Clothianidin	210880-92-5	Insecticide	0.44 (PNEC)	EU Watchlist	LANUV
DEET	134-62-3	Repellent			BfG
Denatonium	3734-33-6 (as benzoate)	Bitter substance			BfG
Dicyandiamide (cyanoguanidine)	461-58-5	Nitrification inhibitor, industrial chemical (intermediate)			TZW
Dimethomorph	110488-70-5	Fungicide			AUEBS
Dimoxystrobin	149961-52-4	Fungicide	0.03		AUEBS

Substance	CAS No.	Use	AA-EQS* (PNEC) [µg/L]	Comment	Laboratory
Diphenylphosphine oxide (DPPO)	4559-70-0	Industrial chemical			BfG
Diphenylphosphonic acid (DPPA)	05/03/1707	Industrial chemical			BfG
Duloxetine	116539-59-4	Antidepressant			AUEBS
Ethyltriphenyl-phosphonium	1530-32-1 (as bromide)	Industrial chemical			BfG
Etrimfos	38260-54-7	Pesticide	0.004		AUEBS
Phenazone	60-80-0	Inflammatory inhibitors			AUEBS
Fexofenadine	83799-24-0	Antihistamine		Non-target analysis	BfG
Flurtamone	96525-23-4	Pesticide	0.2		AUEBS
Gabapentin-lactam	64744-50-9	TP of Gabapentin			BfG
Guanylurea	141-83-3	Metabolite/TP of metformin			TZW
Hydrochlorothiazide	58-93-5	Antidiuretic			AUEBS
Icaridin	119515-38-7	Insecticide			AUEBS
Lincomycin	154-21-2	Antibiotic			TZW
Melamine	108-78-1	Intermediate in plastic production			TZW
Methiocarb	2032-65-7	Insecticide		EU Watchlist	AUEBS
Methoxymethyl triphenylphosphonium	4009-98-7 (as chloride)	Industrial chemical			BfG
Methylaminoantipyrin	519-98-2	Metabolite of metamizole			BfG
Methyltriphenyl-phosphonium	1779-49-3 (as bromide)	Industrial chemical			BfG
Cyclamate	139-05-9 (as sodium-salt)	Sweetener			AUEBS

Substance	CAS No.	Use	AA-EQS* (PNEC) [µg/L]	Comment	Laboratory
Nevirapine	129618-40-2	Antivirals			BfG
Nicosulfuron	111991-09-4	Herbicide	0.009		AUEBS
Nitenpyram	150824-47-8	Insecticide	0.045 (PNEC)		LANUV
Olmesartan	144689-24-7	Antihypertensives			AUEBS
Omethoate	06/02/1113	Insecticide	0.004		AUEBS
Opipramol	315-72-0	Antidepressant			BfG
Pentoxifylline	06/05/6493	Anticoagulant and inflamation inhibitor			BfG
Phosphoric acid triethyl-ester (TEP)	78-40-0	Flame retardants, plasticiser			UBAAT
Phosphoric acid triiso-butyl ester (TiBP)	126-71-6	Plasticiser			UBAAT
Phosphoric acid-triphenyl ester (TPP)	115-86-6	Flame retardants, plasticiser			UBAAT
Phoxim	14816-18-3	Insecticide	0.008		UBAAT
Pregabalin	148553-50-8	Antiepileptic			AUEBS
Pyrazole	288-13-1	Intermediate in the production of pharmaceuticals, pesticides, etc.			LANUV
Repaglinide	135062-02-1	Antidiabetic			BfG
Simvastatin	79902-63-9	Statin			AUEBS
Phosphoric acid tris (2-chloroethyl) ester (TCEP)	51805-45-9	Plasticiser			UBAAT
Terbutryn sulfoxide	-	TP of Terbutryn		Terbutryn priority substance	BfG
Tetrabutyl ammonium	1112-67-0 (as chloride)	Industrial chemical			BfG

Substance	CAS No.	Use	AA-EQS* (PNEC) [µg/L]	Comment	Laboratory
Tetrabutyl phosphonium	2304-30-5 (as chloride)	Industrial chemical			BfG
Tetracarbonitrilpropen	36589-04-5	Industrial chemical			AUEBS
Tetrapropyl ammonium	5810-42-4 (as chloride)	Industrial chemical			BfG
Thiacloprid	111988-49-9	Insecticide	0.03 (PNEC)	EU Watchlist	LANUV
Thiamethoxam	153719-23-4	Insecticide		EU Watchlist	LANUV
TMDD (Surfynol 104)	126-86-3	Surfactant			TZW
Topramezone	210631-68-8	Herbicide			AUEBS
Torasemide	56211-40-6	Antihypertensives			AUEBS
Triphenylphosphine oxide (TPPO)	791-28-6	Industrial chemical			BfG
Triphenylphosphine sulphide (TPPS)	3878-45-3	Industrial chemical			BfG
Triallate	2303-17-5	Herbicide		EU Watchlist	TZW
Tributylphosphine oxide	814-29-9	Industrial chemical			AUEBS
Tri-n-butyl phosphate (TnBP)	126-73-8	Plasticiser			UBAAT
Tris(1,3-dichlor-isopropyl) phosphate (TDCP)	13674-87-8	Flame retardants			UBAAT
Tris(2-butoxyethyl) phosphate (TBEP)	78-51-3	Plasticiser			UBAAT
Uvinul 4050H	124172-53-8	UV stabiliser			BfG
Valsartanic acid	164265-78-5	TP of valsartan (and other sartans)			AUEBS
Zidovudine	30516-87-1	Antivirals			BfG

*Environmental Quality Standard (EQS), expressed as an annual average (AA-EQS) for above-ground waters without transitional waters pursuant to the Surface Waters Ordinance (OGewV) of 20.06.2016

Appendix 2: Sampling point with sampling times, discharge, framework conditions

Rhine km	Sampling point	ROUND	Sample generation	Start	End	Storage during sampling	Storage after sampling	Discharge [m³/s]
100	Rekingen - Rhine	1	time proportional	19.03.2017 24:00	26.03.2017 24:00	4°C	4°C	350
		2	time proportional	15/05/2017	22/05/2017	4°C	4°C	495
		3	time proportional	10.07.2017 0:00	16.07.2017 24:00	4°C	4°C	412
		4	time proportional	18.09.2017 0:00	24.09.2017 23:59	6°C	4°C	580
103	Brugg - Aar	1	time proportional	20.03.2017 10:20	27.03.2017 14:10			293
		2	time proportional	15/05/2017	22.05.2017 14:00		4°C	322
		3	time proportional	10/07/2017	17/07/2017		4°C	300
		4	time proportional	18/09/2017	24/09/2017			145
171	Weil am Rhein - Rhine	1	Discharge proportional	21.03.2017 8:00	28.03.2017 8:00	4°C	4°C	1010
		2	Discharge proportional	16.05.2017 8:00	23.05.2017 8:00	4°C	4°C	1140
		3	Discharge proportional	11.07.2017 8:00	18.07.2017 8:00	4°C	4°C	900
		4	Discharge proportional	19.09.2017 8:00	26.09.2017 8:00	4°C	4°C	960
359	Karlsruhe/Lauterbourg - Rhine	1	time proportional	23/03/2017	29/03/2017	4°C	chilled	1180
		2	time proportional	18/05/2017	25/05/2017	4°C	chilled	1246
		3	time proportional	13/07/2017	20/07/2017	4°C	chilled	895
		4	time proportional	21/09/2017	27/09/2017	4°C	chilled	1013
426	Mannheim - Neckar	1	time proportional	24/03/2017	30/03/2017	4°C	chilled	102
		2	time proportional	19/05/2017	26/05/2017	4°C	chilled	95
		3	time proportional	14/07/2017	21/07/2017	4°C	chilled	58
		4	time proportional	22/09/2017	28/09/2017	4°C	chilled	50
443	Worms (right) - Rhine	1	Discharge proportional	24/03/2017	30/03/2017	4°C	4°C	1311
		2	Discharge proportional	19/05/2017	26/05/2017	4°C	4°C	1373
		3	Discharge proportional	14/07/2017	21/07/2017	4°C	4°C	963
		4	Discharge proportional	22/09/2017	28/09/2017	4°C	4°C	1074
443	Worms (left) - Rhine	1	Discharge proportional	24/03/2017	30/03/2017	4°C	4°C	1311
		2	Discharge proportional	19/05/2017	26/05/2017	4°C	4°C	1373
		3	Discharge proportional	14/07/2017	21/07/2017	4°C	4°C	963
		4	Discharge proportional	22/09/2017	28/09/2017	4°C	4°C	1074
475	Trebur - Schwarzbach	1	time proportional	25.03.2017 0:00	01.04.2017 0:00	17°C	7°C	
		2	time proportional	20.05.2017 0:00	27.05.2017 0:00	25°C	7°C	
		3	time proportional	15.07.2017 0:00	22.07.2017 0:00	27°C	7°C	
		4	time proportional	23.09.2017 0:00	30.09.2017 0:00	17°C	7°C	
482	Kornsand-Rhine	1	Random sample	06.04.2017 15:00				
		2	Random sample	23.05.2017 12:00	-	24°C	4°C	
		3	Random sample	19.07.2017 15:00	-	24°C	4°C	
497	Bischofsheim - Main	1	time proportional	25.03.2017 0:00	01.04.2017 0:00	4°C	4°C	191
		2	time proportional	20.05.2017 0:00	27.05.2017 0:00	4°C	4°C	154
		3	time proportional	15.07.2017 0:00	22.07.2017 0:00	4°C	4°C	133
		4	time proportional	23.09.2017 00:01	30.09.2017 00:01	4°C	4°C	134
499	Mainz - Rhine	3	Discharge proportional	15/07/2017	21/07/2017	4°C	4°C	1112

Rhine km	Sampling point	ROUND	Sample generation	Start	End	Storage during sampling	Storage after sampling	Discharge [m³/s]
590	Koblenz Rhine	1	time proportional	26.03.2017 0:00	01.04.2017 24:00	4°C	4°C	1530
		2	time proportional	21/05/2017	27/05/2017	4°C	4°C	1566
		3	time proportional	16.07.2017 0:00	23.07.2017 0:00	4°C	4°C	1087
		4	time proportional	24/09/2017	01/10/2017	4°C	4°C	1214
592	Koblenz - Moselle	1	time proportional	26.03.2017 0:00	01.04.2017 24:00	4°C	4°C	211
		2	time proportional	21/05/2017	27/05/2017	4°C	4°C	90
		3	time proportional	16.07.2017 0:00	23.07.2017 0:00	4°C	4°C	48
		4	time proportional	24/09/2017	01/10/2017	4°C	4°C	64
640	Bad Honnef - Rhine	1	time proportional	26.03.2017 0:00	01.04.2017 24:00	6-8 °C	6-8 °C	1825
		2	time proportional	21.05.2017 0:00	27.05.2017 23:59	5-10 °C	6-8 °C	1678
		3	time proportional	16.07.2017 0:00	23.07.2017 0:00	5-10 °C	6-8 °C	1169
		4	time proportional	24.09.2017 00:00	30.09.2017 24:00	5-10°C	6-8°C	1317
732	Duesseldorf - Rhine	2	time proportional	22.05.2017 08:00	29.05.2017 8:00	6-8 °C	6-8 °C	1677
		3	time proportional	17.07.2017 8:00	24.07.2017 8:00	6-8 °C	6-8 °C	1210
779	Duisburg - Rhine	1	Random sample	06.04.2017 11:00				
		2	Random sample	29.05.2017 11:00	-	24°C	4°C	1450
		3	Random sample	24.07.2017 11:10	-	22.5 °C	4°C	1290
		4	Random sample	26.09.2017 14:35	-	20°C	4°C	1450
798	Dinslaken - Emscher	1	time proportional	28.03.2017 07:00	04.04.2017 7:00	6-8 °C	6-8 °C	13
		2	time proportional	23.05.2017 08:00	30.05.2017 8:00	6-8 °C	6-8 °C	11
		3	time proportional	18.07.2017 8:00	25.07.2017 8:00	6-8 °C	6-8 °C	19
		4	time proportional	27.09.2017 8:00	04.10.2017 8:00	6-8 °C	6-8 °C	15
863	Lobith - Rhine	1	time proportional	29.03.2017 0:00	05.04.2017 0:00	5°C	5°C	1847
		2	time proportional	24.05.2017 0:00	30.05.2017 23:59	5°C	5.4°C	1593
		3	time proportional	19.07.2017 00:00	25.07.2017 23:59	5°C	5°C	1210
		4	time proportional	27.09.2017 00:00	03.10.2017 23:59	5°C	5°C	1395
865	Bimmen - Rhine	1	time proportional	29.03.2017 0:00	04.04.2017 23:59	9°C	9°C	1857
		2	time proportional	24.05.2017 0:00	30.05.2017 23:59	7.3°C	4°C	1672
		3	time proportional	19.07.2017 00:00	25.07.2017 23:59	8.5 - 11.5 °C	4°C	1272
		4	time proportional	27.09.2017 00:00	03.10.2017 23:59	8°C	9°C	1431
994	Kampen - IJssel	1	Random sample	11.04.2017 13:30	-			289
		2	Random sample	08.06.2017 13:35	-			321
		3	Random sample	01.08.2017 13:35	-			326
		4	Random sample	24.10.2017 13:34	-			257
1026	Maassluis - Nieuwe Waterweg	1	Random sample	06.04.2017 05:05	-			1194
		2	Random sample	01.06.2017 13:04	-			1141
		3	Random sample	27.07.2017 10:29	-			1107
		4	Random sample	02.11.2017 14:50	-			1092

* Sampling at the points Trebur, Kornsand, Duisburg took place without cooled sampler.

Appendix 3.1 Target results of the monitoring campaign

Rhine km	Sampling point	Round	(Methoxymethyl)triphenyl-phosphonium cation	14-Hydroxyclarithromycin (= 14R-Erythromycin)	1H-1,2,4-Triazole	2,2,6,6-Tetramethyl-4-piperidone	2,4-dichlorobenzoic acid	3-trifluoromethylaniline	4-OH-diclofenac	9-CA-acridines	Acetamiprid	Aclonifen	Acyclovir	Allupurinol	Amlopidine	Amoxicillin
	LOQ in µg/L		0.01	0.01	0.1	0.1	0.1	0.1	0.005	0.01	0.005	0.01	0.02	0.1	1	0.3
171	Weil am Rhein - Rhine	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	<LOQ	0.82	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
359	Karlsruhe/ Lauterbourg - Rhine	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	<LOQ	0.39	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	<LOQ	0.16	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
426	Mannheim (Neckar)	1	<LOQ	<LOQ	<LOQ	<LOQ	0.14	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	0.18	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.017	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	0.016	<LOQ	<LOQ	0.19	0.17	<LOQ	<LOQ	0.058	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	0.15	<LOQ	<LOQ	<LOQ	**0.005**	0.080	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
443	Worms (right) - Rhine	1	0.13	<LOQ	<LOQ	13	<LOQ	<LOQ	<LOQ	0.012	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	0.033	<LOQ	<LOQ	1.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	2.9	<LOQ	<LOQ	<LOQ	0.015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	1.1	<LOQ	<LOQ	<LOQ	0.021	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
443	Worms (left) - Rhine	1	<LOQ	<LOQ	<LOQ	0.18	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	0.18	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	0.23	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.010	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
475	Trebur - Schwarzbach	1	0.42	0.064	0.37	0.22	150	<LOQ	0.030	0.13	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	0.22	0.044	0.38	0.5	14	<LOQ	0.043	0.068	<LOQ	<LOQ	0.025	<LOQ	<LOQ	<LOQ
		3	0.31	0.021	0.4	0.37	1.4	<LOQ	0.014	0.13	<LOQ	<LOQ	0.027	<LOQ	<LOQ	<LOQ
		4	0.26	0.035	0.45	0.2	9.4	<LOQ	0.045	0.26	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
497	Bischofsheim - Main	1	<LOQ	0.013	0.13	0.1	4.2	<LOQ	0.010	0.035	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	0.13	<LOQ	1.4	<LOQ	0.012	0.021	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	0.12	0.59	<LOQ	**0.005**	0.057	<LOQ	<LOQ	0.023	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	0.13	<LOQ	0.39	<LOQ	0.011	0.063	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
590	Koblenz - Rhine	1	0.034	<LOQ	<LOQ	0.61	57	<LOQ	<LOQ	0.013	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	0.016	<LOQ	<LOQ	0.18	20	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	0.19	12	<LOQ	<LOQ	0.017	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	8.5	<LOQ	<LOQ	0.020	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
592	Koblenz - Moselle	1	<LOQ	<LOQ	<LOQ	<LOQ	4.1	<LOQ	<LOQ	0.012	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	<LOQ	2.5	<LOQ	<LOQ	0.016	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	<LOQ	3.8	<LOQ	<LOQ	0.038	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	0.14	1.6	<LOQ	<LOQ	0.061	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
640	Bad Honnef - Rhine	1	0.032	<LOQ	<LOQ	0.41	<LOQ	<LOQ	<LOQ	0.011	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	0.011	<LOQ	<LOQ	0.17	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	0.16	<LOQ	<LOQ	<LOQ	0.017	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.020	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
798	Dinslaken - Emscher	1	<LOQ	0.072	0.22	<LOQ	3	<LOQ	0.047	0.14	<LOQ	<LOQ	0.031	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.12	0.29	0.57	2.9	<LOQ	0.025	0.13	<LOQ	<LOQ	0.024	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.034	0.23	0.74	1.3	<LOQ	0.029	0.11	<LOQ	<LOQ	0.052	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.059	0.17	0.79	1.6	<LOQ	0.024	0.15	0.017	<LOQ	0.042	<LOQ	<LOQ	<LOQ
863	Lobith - Rhine	1	0.026	<LOQ	0.29	0.42	1.1	<LOQ	<LOQ	0.015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	0.011	<LOQ	0.2	0.16	0.75	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	0.23	0.19	0.5	<LOQ	<LOQ	0.023	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.011	0.14	<LOQ	0.55	<LOQ	<LOQ	0.027	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
865	Bimmen - Rhine	1	0.026	<LOQ	0.33	0.4	<LOQ	<LOQ	<LOQ	0.012	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	**0.010**	<LOQ	0.14	0.11	<LOQ	<LOQ	<LOQ	**0.01**	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	0.23	0.14	<LOQ	<LOQ	<LOQ	0.021	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	0.16	<LOQ	<LOQ	<LOQ	<LOQ	0.023	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
994	Kampen - IJssel	1	0.018	<LOQ	0.27	0.57	<LOQ	<LOQ	<LOQ	0.019	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	0.011	<LOQ	0.16	0.13	<LOQ	<LOQ	<LOQ	0.012	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	<LOQ	0.21	<LOQ	<LOQ	0.025	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	0.11	<LOQ	<LOQ	<LOQ	**0.006**	0.029	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1026	Maassluis - Nieuwe Waterweg	1	0.014	<LOQ	0.24	0.24	<LOQ	<LOQ	<LOQ	0.019	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	0.25	0.12	<LOQ	<LOQ	<LOQ	0.012	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	0.13	<LOQ	<LOQ	<LOQ	0.016	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	0.11	<LOQ	<LOQ	<LOQ	<LOQ	0.015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Rhine km	Sampling point	Round	AMPS	Atenolol	Atenolol acid	Bifenox	Bifenox acid	Bisoprolol	Boscalid	Butyltriphenylphosphonium cation	Carboxy acyclovir	Cefaclor	Cefuroxime	Chlorpropham	Chloroxylenol	Clopridogrel acid
	LOQ in µg/L		0.01	0.02	0.01	0.003	0.01	0.005	0.025	0.01	0.02	0.1	0.01	0.01	0.04	0.005
171	Weil am Rhein - Rhine	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**0.006**
359	Karlsruhe/ Lauterbourg - Rhine	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.027	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.020	<LOQ	<LOQ	<LOQ	<LOQ	**0.007**
426	Mannheim (Neckar)	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.031	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	0.036	<LOQ	<LOQ	0.014	<LOQ	<LOQ	0.083	<LOQ	<LOQ	<LOQ	<LOQ	0.016
		3	<LOQ	<LOQ	0.058	<LOQ	<LOQ	0.011	<LOQ	<LOQ	0.17	<LOQ	<LOQ	<LOQ	<LOQ	0.023
		4	<LOQ	<LOQ	0.070	<LOQ	<LOQ	0.016	<LOQ	<LOQ	0.17	<LOQ	<LOQ	<LOQ	<LOQ	0.035
443	Worms (right) - Rhine	1	<LOQ	<LOQ	0.013	<LOQ	<LOQ	**0.007**	<LOQ	<LOQ	0.057	<LOQ	<LOQ	<LOQ	<LOQ	**0.007**
		2	<LOQ	<LOQ	0.013	<LOQ	<LOQ	**0.005**	<LOQ	<LOQ	0.036	<LOQ	<LOQ	<LOQ	<LOQ	**0.007**
		3	0.015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.047	<LOQ	<LOQ	<LOQ	<LOQ	**0.007**
		4	<LOQ	<LOQ	0.015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.067	<LOQ	<LOQ	<LOQ	<LOQ	0.014
443	Worms (left) - Rhine	1	0.012	<LOQ	0.012	<LOQ	<LOQ	<LOQ	0.03	<LOQ	0.055	<LOQ	<LOQ	<LOQ	<LOQ	**0.007**
		2	0.015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.026	<LOQ	<LOQ	<LOQ	<LOQ	**0.005**
		3	0.046	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.040	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	0.02	<LOQ	0.012	<LOQ	<LOQ	<LOQ	0.03	<LOQ	0.036	<LOQ	<LOQ	<LOQ	<LOQ	**0.010**
475	Trebur - Schwarzbach	1	0.023	0.021	0.13	<LOQ	<LOQ	0.67	<LOQ	<LOQ	0.73	<LOQ	0.017	<LOQ	<LOQ	0.055
		2	<LOQ	<LOQ	0.15	<LOQ	<LOQ	0.16	<LOQ	<LOQ	0.26	<LOQ	0.041	<LOQ	<LOQ	0.13
		3	0.012	<LOQ	0.14	<LOQ	<LOQ	0.12	<LOQ	<LOQ	0.31	<LOQ	<LOQ	<LOQ	<LOQ	0.13
		4	<LOQ	<LOQ	0.18	<LOQ	<LOQ	0.14	<LOQ	<LOQ	0.64	<LOQ	0.022	<LOQ	<LOQ	0.17
497	Bischofsheim - Main	1	0.017	<LOQ	0.057	<LOQ	<LOQ	0.026	<LOQ	<LOQ	0.29	<LOQ	<LOQ	<LOQ	<LOQ	0.021
		2	0.03	<LOQ	0.051	<LOQ	<LOQ	0.025	<LOQ	<LOQ	0.092	<LOQ	0.011	<LOQ	<LOQ	0.027
		3	0.1	<LOQ	0.037	<LOQ	<LOQ	**0.010**	<LOQ	<LOQ	0.14	<LOQ	<LOQ	<LOQ	<LOQ	0.021
		4	0.024	<LOQ	0.087	<LOQ	<LOQ	0.024	<LOQ	<LOQ	0.14	<LOQ	<LOQ	<LOQ	<LOQ	0.031
590	Koblenz - Rhine	1	0.016	<LOQ	0.015	<LOQ	<LOQ	**0.006**	<LOQ	<LOQ	0.078	<LOQ	<LOQ	<LOQ	<LOQ	**0.008**
		2	0.02	<LOQ	<LOQ	<LOQ	<LOQ	**0.006**	<LOQ	<LOQ	0.039	<LOQ	<LOQ	<LOQ	<LOQ	**0.006**
		3	0.023	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.050	<LOQ	<LOQ	<LOQ	<LOQ	**0.008**
		4	<LOQ	<LOQ	0.019	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.055	<LOQ	<LOQ	<LOQ	<LOQ	0.011
592	Koblenz - Moselle	1	<LOQ	<LOQ	0.010	<LOQ	<LOQ	**0.007**	<LOQ	<LOQ	0.093	<LOQ	<LOQ	<LOQ	<LOQ	0.013
		2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.14	<LOQ	<LOQ	<LOQ	<LOQ	0.025
		3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.03	<LOQ	0.12	<LOQ	<LOQ	<LOQ	<LOQ	0.014
		4	<LOQ	<LOQ	0.034	<LOQ	<LOQ	**0.01**	<LOQ	<LOQ	0.18	<LOQ	<LOQ	<LOQ	<LOQ	0.033
640	Bad Honnef - Rhine	1	0.014	<LOQ	0.019	<LOQ	<LOQ	**0.008**	<LOQ	<LOQ	0.087	<LOQ	<LOQ	<LOQ	<LOQ	**0.009**
		2	0.016	<LOQ	**0.01**	<LOQ	<LOQ	**0.006**	<LOQ	<LOQ	0.038	<LOQ	<LOQ	<LOQ	<LOQ	**0.007**
		3	0.024	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.051	<LOQ	<LOQ	<LOQ	<LOQ	**0.008**
		4	<LOQ	<LOQ	0.017	<LOQ	<LOQ	**0.006**	<LOQ	<LOQ	0.057	<LOQ	<LOQ	<LOQ	<LOQ	0.013
798	Dinslaken - Emscher	1	0.023	0.15	0.61	<LOQ	<LOQ	0.24	<LOQ	<LOQ	1.1	<LOQ	0.048	<LOQ	<LOQ	0.12
		2	0.017	0.15	0.56	<LOQ	<LOQ	0.22	<LOQ	<LOQ	0.76	<LOQ	0.07	<LOQ	<LOQ	0.11
		3	<LOQ	0.087	0.49	<LOQ	<LOQ	0.15	<LOQ	<LOQ	0.7	<LOQ	0.094	<LOQ	<LOQ	0.092
		4	<LOQ	0.16	0.8	<LOQ	<LOQ	0.21	<LOQ	<LOQ	0.93	<LOQ	0.097	<LOQ	<LOQ	0.14
863	Lobith - Rhine	1	0.011	<LOQ	0.026	<LOQ	<LOQ	0.014	<LOQ	<LOQ	0.11	<LOQ	<LOQ	<LOQ	<LOQ	0.016
		2	0.017	<LOQ	0.015	<LOQ	<LOQ	**0.008**	<LOQ	<LOQ	0.047	<LOQ	<LOQ	<LOQ	<LOQ	**0.010**
		3	0.052	<LOQ	0.035	<LOQ	<LOQ	**0.010**	<LOQ	<LOQ	0.079	<LOQ	<LOQ	<LOQ	<LOQ	0.013
		4	<LOQ	<LOQ	0.038	<LOQ	<LOQ	0.013	<LOQ	<LOQ	0.090	<LOQ	<LOQ	<LOQ	<LOQ	0.018
865	Bimmen - Rhine	1	0.013	<LOQ	0.019	<LOQ	<LOQ	**0.01**	<LOQ	<LOQ	0.12	<LOQ	<LOQ	<LOQ	<LOQ	0.014
		2	0.014	<LOQ	0.026	<LOQ	<LOQ	**0.006**	<LOQ	<LOQ	0.055	<LOQ	<LOQ	<LOQ	<LOQ	**0.009**
		3	0.055	<LOQ	0.021	<LOQ	<LOQ	**0.005**	<LOQ	<LOQ	0.076	<LOQ	<LOQ	<LOQ	<LOQ	**0.009**
		4	<LOQ	<LOQ	0.024	<LOQ	<LOQ	**0.008**	<LOQ	<LOQ	0.075	<LOQ	<LOQ	<LOQ	<LOQ	0.014
994	Kampen - IJssel	1	0.022	<LOQ	0.033	<LOQ	<LOQ	0.015	<LOQ	<LOQ	0.12	<LOQ	<LOQ	<LOQ	<LOQ	0.018
		2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.070	<LOQ	<LOQ	<LOQ	<LOQ	**0.010**
		3	<LOQ	<LOQ	0.040	<LOQ	<LOQ	**0.009**	<LOQ	<LOQ	0.093	<LOQ	<LOQ	<LOQ	<LOQ	0.015
		4	0.012	<LOQ	0.054	<LOQ	<LOQ	0.013	<LOQ	<LOQ	0.11	<LOQ	<LOQ	<LOQ	<LOQ	0.036
1026	Maassluis - Nieuwe Waterweg	1	<LOQ	<LOQ	0.026	<LOQ	<LOQ	**0.010**	<LOQ	<LOQ	0.11	<LOQ	<LOQ	<LOQ	<LOQ	**0.01**
		2	0.024	<LOQ	0.025	<LOQ	<LOQ	**0.007**	<LOQ	<LOQ	0.067	<LOQ	<LOQ	<LOQ	<LOQ	0.019
		3	<LOQ	<LOQ	0.035	<LOQ	<LOQ	**0.006**	<LOQ	<LOQ	0.074	<LOQ	<LOQ	<LOQ	<LOQ	0.011
		4	<LOQ	<LOQ	0.028	<LOQ	<LOQ	**0.008**	<LOQ	<LOQ	0.077	<LOQ	<LOQ	<LOQ	<LOQ	0.012

Rhine km	Sampling point	Round	Clothianidin	Cyclamate	DEET	Denatonium	Dicyandiamide (cyanoguanidine)	Dimethomorph	Dimoxystrobin	Diphenylphosphine oxide (DPPO)	Diphenylphosphonic acid (DPPA)	Duloxetine	Ethyltriphenylphosphonium cation	Etrimfos	Fexofenadine	Flurtamone
	LOQ in µg/L		0.01	0.005	0.002	0.005	0.02	0.005	0.001	0.01	0.01	0.003	0.001	0.003	0.002	0.001
171	Weil am Rhein - Rhine	1	<LOQ	0.019	0.011	<LOQ	0.061	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.056	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.043	**0.009**	<LOQ	0.11	<LOQ	<LOQ	0.031	<LOQ	<LOQ	0.036	<LOQ	0.012	<LOQ
		3	<LOQ	0.054	0.011	<LOQ	0.097	<LOQ	<LOQ	0.081	<LOQ	<LOQ	0.014	<LOQ	0.013	<LOQ
		4	<LOQ	0.032	**0.007**	<LOQ	0.083	<LOQ	<LOQ	0.043	<LOQ	<LOQ	**0.009**	<LOQ	**0.006**	<LOQ
359	Karlsruhe/ Lauterbourg - Rhine	1	<LOQ	0.031	**0.010**	**0.005**	0.07	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.046	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.051	**0.010**	**0.005**	0.12	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.034	<LOQ	0.011	<LOQ
		3	<LOQ	0.05	0.012	**0.006**	0.1	<LOQ	<LOQ	0.019	<LOQ	<LOQ	0.013	<LOQ	0.013	<LOQ
		4	<LOQ	0.029	**0.006**	**0.008**	0.081	<LOQ	<LOQ	0.015	<LOQ	<LOQ	0.011	<LOQ	**0.006**	<LOQ
426	Mannheim (Neckar)	1	<LOQ	0.034	**0.009**	**0.006**	0.067	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.045	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.33	0.019	0.031	11	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**0.001**	<LOQ	0.021	<LOQ
		3	<LOQ	0.11	0.058	0.056	46	0.014	<LOQ	0.019	<LOQ	<LOQ	0.034	<LOQ	0.035	<LOQ
		4	<LOQ	<LOQ	0.043	0.069	18	<LOQ	<LOQ	0.014	<LOQ	<LOQ	0.029	<LOQ	0.0212	<LOQ
443	Worms (right) - Rhine	1	<LOQ	0.076	0.011	0.011	1.6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.029	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.1	0.012	0.011	1.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.026	<LOQ	0.016	<LOQ
		3	<LOQ	0.056	0.018	0.014	5.6	<LOQ	<LOQ	0.018	<LOQ	<LOQ	0.013	<LOQ	0.017	<LOQ
		4	<LOQ	0.013	0.012	0.018	3.2	<LOQ	<LOQ	0.015	<LOQ	<LOQ	0.011	<LOQ	0.010	<LOQ
443	Worms (left) - Rhine	1	<LOQ	0.04	**0.010**	0.013	0.073	<LOQ	<LOQ	0.17	0.2	<LOQ	0.043	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.079	0.011	**0.010**	0.12	0.02	<LOQ	<LOQ	0.060	<LOQ	0.051	<LOQ	0.013	<LOQ
		3	<LOQ	0.052	0.015	0.023	0.12	<LOQ	<LOQ	0.28	0.43	<LOQ	0.034	<LOQ	0.014	<LOQ
		4	<LOQ	0.064	**0.007**	0.021	0.13	<LOQ	<LOQ	0.17	0.45	<LOQ	0.022	<LOQ	**0.007**	<LOQ
475	Trebur - Schwarzbach	1	<LOQ	0.04	0.036	0.14	0.16	<LOQ	<LOQ	0.12	0.26	**0.006**	0.020	<LOQ	0.48	<LOQ
		2	<LOQ	0.25	0.055	0.16	0.22	**0.009**	<LOQ	<LOQ	0.050	0.015	0.035	<LOQ	0.17	<LOQ
		3	<LOQ	**0.005**	0.058	0.18	0.12	<LOQ	<LOQ	0.17	0.31	<LOQ	0.061	<LOQ	0.14	<LOQ
		4	<LOQ	0.079	0.044	0.33	0.12	<LOQ	<LOQ	0.23	0.21	<LOQ	0.240	<LOQ	0.13	<LOQ
497	Bischofsheim - Main	1	<LOQ	0.12	0.019	0.022	0.83	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.16	<LOQ
		2	<LOQ	0.18	0.027	0.030	1.5	<LOQ	**0.001**	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.51	<LOQ
		3	<LOQ	0.21	0.046	0.035	0.18	**0.008**	<LOQ	0.017	<LOQ	<LOQ	<LOQ	<LOQ	0.84	<LOQ
		4	<LOQ	0.07	0.024	0.043	0.25	<LOQ	<LOQ	0.016	<LOQ	<LOQ	**0.002**	<LOQ	0.61	<LOQ
590	Koblenz - Rhine	1	<LOQ	0.049	0.013	0.011	0.71	<LOQ	<LOQ	0.022	0.041	<LOQ	0.029	<LOQ	0.049	<LOQ
		2	<LOQ	0.097	0.015	0.012	0.76	**0.006**	<LOQ	<LOQ	<LOQ	<LOQ	0.031	<LOQ	0.053	<LOQ
		3	<LOQ	0.054	0.018	0.017	1.7	<LOQ	<LOQ	0.057	0.082	<LOQ	0.020	<LOQ	0.08	<LOQ
		4	<LOQ	0.025	0.012	0.020	0.99	<LOQ	<LOQ	0.041	0.087	<LOQ	0.013	<LOQ	0.070	<LOQ
592	Koblenz - Moselle	1	<LOQ	0.084	**0.007**	**0.008**	0.052	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.074	0.015	0.032	0.12	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.022	<LOQ
		3	<LOQ	0.11	0.027	0.025	0.13	0.027	<LOQ	0.017	<LOQ	<LOQ	<LOQ	<LOQ	0.027	<LOQ
		4	<LOQ	0.064	0.024	0.037	0.088	<LOQ	<LOQ	0.015	<LOQ	<LOQ	**8E-04**	<LOQ	0.018	<LOQ
640	Bad Honnef - Rhine	1	<LOQ	0.068	**0.010**	0.012	0.62	<LOQ	<LOQ	<LOQ	0.02	<LOQ	0.028	<LOQ	0.055	<LOQ
		2	<LOQ	0.064	0.012	0.013	0.69	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.028	<LOQ	0.056	<LOQ
		3	<LOQ	0.072	0.017	0.016	1.8	**0.005**	<LOQ	0.056	0.083	<LOQ	0.014	<LOQ	0.089	<LOQ
		4	<LOQ	0.037	**0.009**	0.019	1.2	<LOQ	<LOQ	0.036	0.091	<LOQ	0.011	<LOQ	0.060	<LOQ
798	Dinslaken - Emscher	1	<LOQ	0.038	0.097	0.15	2.7	<LOQ	<LOQ	<LOQ	0.067	<LOQ	**0.001**	<LOQ	0.24	<LOQ
		2	<LOQ	0.06	0.23	0.3	0.59	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**0.001**	<LOQ	0.33	<LOQ
		3	<LOQ	0.38	0.17	0.13	0.69	<LOQ	<LOQ	0.020	0.13	<LOQ	<LOQ	<LOQ	0.18	<LOQ
		4	<LOQ	0.051	0.1	0.24	0.79	<LOQ	<LOQ	0.018	0.13	<LOQ	**0.002**	<LOQ	0.15	<LOQ
863	Lobith - Rhine	1	<LOQ	0.074	0.011	0.015	0.65	<LOQ	<LOQ	<LOQ	0.043	<LOQ	0.018	<LOQ	0.049	<LOQ
		2	<LOQ	0.082	0.012	0.014	0.63	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.021	<LOQ	0.047	<LOQ
		3	<LOQ	0.24	0.023	0.024	1.4	**0.006**	<LOQ	0.046	0.093	<LOQ	0.010	<LOQ	0.074	<LOQ
		4	<LOQ	0.046	0.013	0.027	0.7	<LOQ	<LOQ	0.033	0.079	<LOQ	**0.009**	<LOQ	0.055	<LOQ
865	Bimmen - Rhine	1	<LOQ	0.052	**0.010**	0.013	0.66	<LOQ	<LOQ	<LOQ	0.019	<LOQ	0.018	<LOQ	0.049	<LOQ
		2	<LOQ	0.051	0.014	0.016	0.62	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.023	<LOQ	0.044	<LOQ
		3	<LOQ	0.13	0.019	0.020	1.4	**0.006**	<LOQ	0.048	0.088	<LOQ	0.012	<LOQ	0.073	<LOQ
		4	<LOQ	0.036	**0.010**	0.023	0.76	<LOQ	<LOQ	0.035	0.08	<LOQ	**0.009**	<LOQ	0.049	<LOQ
994	Kampen - IJssel	1	<LOQ	0.041	0.011	0.016	0.26	<LOQ	<LOQ	<LOQ	0.06	<LOQ	0.021	<LOQ	0.073	<LOQ
		2	<LOQ	0.044	0.014	0.019	0.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.015	<LOQ	0.048	<LOQ
		3	<LOQ	0.16	0.029	0.023	0.38	**0.007**	<LOQ	0.056	0.074	<LOQ	0.014	<LOQ	0.031	<LOQ
		4	<LOQ	0.069	0.012	0.027	0.26	<LOQ	<LOQ	0.034	0.063	<LOQ	**0.007**	<LOQ	0.053	<LOQ
1026	Maassluis - Nieuwe Waterweg	1	<LOQ	0.045	0.010	0.013	0.3	**0.006**	<LOQ	<LOQ	0.016	<LOQ	0.012	<LOQ	0.044	<LOQ
		2	<LOQ	0.099	0.028	0.018	0.39	<LOQ	<LOQ	<LOQ	0.025	**0.007**	0.016	<LOQ	0.09	<LOQ
		3	<LOQ	0.098	0.018	0.014	2	0.013	<LOQ	0.029	0.032	<LOQ	**0.010**	<LOQ	0.033	<LOQ
		4	<LOQ	0.023	**0.007**	0.023	0.89	**0.005**	<LOQ	0.027	0.036	**0.005**	**0.004**	<LOQ	0.039	<LOQ

Rhine km	Sampling point	Round	Gabapentin-lactam	Guanylurea	Hydrochlorothiazide	Icaridin	Lincomycin	Melamine	Methiocarb	Methylaminoantipyrine	Methyltriphenylphosphonium cation	Nevapirin	Nicosulfuron	Nitenpyram	Olmesartan	Omethoate
	LOQ in µg/L		0.02	0.05	0.01	0.01	0.01	0.025	0.003	0.1	0.002	0.01	0.025	0.01	0.01	0.005
171	Weil am Rhein - Rhine	1	<LOQ	0.64	0.017	<LOQ	<LOQ	0.23	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.5	0.011	<LOQ	<LOQ	0.32	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.43	0.011	<LOQ	<LOQ	0.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.41	0.014	<LOQ	<LOQ	0.26	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
359	Karlsruhe/ Lauterbourg - Rhine	1	<LOQ	0.46	0.017	<LOQ	<LOQ	0.43	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.47	0.011	<LOQ	<LOQ	0.48	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.24	<LOQ	<LOQ	<LOQ	0.61	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.38	0.014	<LOQ	<LOQ	0.66	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.013	<LOQ
426	Mannheim (Neckar)	1	0.018	0.54	0.019	<LOQ	<LOQ	0.38	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	0.079	1.6	0.083	<LOQ	<LOQ	1.6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.038	<LOQ
		3	0.18	2.5	0.044	<LOQ	<LOQ	3.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.039	<LOQ
		4	0.17	2.4	0.1	<LOQ	<LOQ	1.9	<LOQ	<LOQ	0.052	<LOQ	<LOQ	<LOQ	0.074	<LOQ
443	Worms (right) - Rhine	1	0.024	1.3	0.051	<LOQ	<LOQ	0.71	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.017	<LOQ
		2	0.029	0.85	0.034	<LOQ	<LOQ	0.87	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.019	<LOQ
		3	0.040	0.83	0.019	<LOQ	<LOQ	1.1	<LOQ	<LOQ	**0.002**	<LOQ	<LOQ	<LOQ	0.014	<LOQ
		4	0.041	0.81	0.034	<LOQ	<LOQ	0.75	<LOQ	<LOQ	**0.009**	<LOQ	<LOQ	<LOQ	0.021	<LOQ
443	Worms (left) - Rhine	1	0.020	0.92	0.03	<LOQ	<LOQ	1.8	<LOQ	<LOQ	0.061	<LOQ	<LOQ	<LOQ	0.013	<LOQ
		2	0.018	0.79	0.026	<LOQ	<LOQ	2.2	<LOQ	<LOQ	0.27	<LOQ	<LOQ	<LOQ	0.013	<LOQ
		3	0.020	0.61	0.016	<LOQ	<LOQ	5.8	<LOQ	<LOQ	0.22	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	0.022	0.68	0.032	<LOQ	<LOQ	3.1	<LOQ	<LOQ	0.19	<LOQ	<LOQ	<LOQ	0.015	<LOQ
475	Trebur - Schwarzbach	1	0.57	16	1.7	<LOQ	<LOQ	2.7	<LOQ	<LOQ	0.25	<LOQ	<LOQ	<LOQ	0.79	<LOQ
		2	0.58	10	0.92	<LOQ	<LOQ	2.5	<LOQ	<LOQ	0.34	<LOQ	<LOQ	<LOQ	0.44	<LOQ
		3	0.64	3.8	0.64	<LOQ	<LOQ	2.7	<LOQ	<LOQ	0.49	<LOQ	<LOQ	<LOQ	0.53	<LOQ
		4	1	8.7	1.4	<LOQ	<LOQ	1.8	<LOQ	<LOQ	0.99	<LOQ	<LOQ	<LOQ	0.5	<LOQ
497	Bischofsheim - Main	1	0.062	3.2	0.16	<LOQ	<LOQ	2.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.047	<LOQ
		2	0.089	2.1	0.18	<LOQ	<LOQ	2.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.064	<LOQ
		3	0.12	1.9	0.12	<LOQ	<LOQ	3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.057	<LOQ
		4	0.13	2.9	0.22	<LOQ	<LOQ	2.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.089	<LOQ
590	Koblenz - Rhine	1	0.026	0.94	0.038	<LOQ	<LOQ	1.2	<LOQ	<LOQ	0.012	<LOQ	<LOQ	<LOQ	0.022	<LOQ
		2	0.029	0.6	0.023	<LOQ	<LOQ	1.1	<LOQ	<LOQ	0.054	<LOQ	<LOQ	<LOQ	0.017	<LOQ
		3	0.035	0.61	0.017	<LOQ	<LOQ	2.1	<LOQ	<LOQ	0.041	<LOQ	<LOQ	<LOQ	0.015	<LOQ
		4	0.039	0.72	0.031	<LOQ	<LOQ	1.3	<LOQ	<LOQ	0.041	<LOQ	<LOQ	<LOQ	0.02	<LOQ
592	Koblenz - Moselle	1	0.026	0.67	0.029	<LOQ	<LOQ	0.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.026	<LOQ
		2	0.095	0.31	<LOQ	<LOQ	<LOQ	0.66	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.069	<LOQ
		3	0.091	0.94	<LOQ	<LOQ	<LOQ	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.063	<LOQ
		4	0.10	1.4	0.037	<LOQ	<LOQ	1.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.05	<LOQ
640	Bad Honnef - Rhine	1	0.032	1	0.04	<LOQ	<LOQ	1.1	<LOQ	<LOQ	0.012	<LOQ	<LOQ	<LOQ	0.018	<LOQ
		2	0.033	0.55	0.027	<LOQ	<LOQ	1.2	<LOQ	<LOQ	0.045	<LOQ	<LOQ	<LOQ	0.021	<LOQ
		3	0.045	0.55	0.018	<LOQ	<LOQ	2	<LOQ	<LOQ	0.036	<LOQ	<LOQ	<LOQ	0.023	<LOQ
		4	0.044	0.69	0.043	<LOQ	<LOQ	1.2	<LOQ	<LOQ	0.034	<LOQ	<LOQ	<LOQ	0.029	<LOQ
798	Dinslaken - Emscher	1	0.29	59	1.6	<LOQ	<LOQ	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.25	<LOQ
		2	0.44	60	1.5	<LOQ	<LOQ	13	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.22	<LOQ
		3	0.14	21	0.97	<LOQ	<LOQ	11	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.17	<LOQ
		4	0.23	44	1.7	<LOQ	<LOQ	6.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.24	<LOQ
863	Lobith - Rhine	1	0.042	1.8	0.067	<LOQ	<LOQ	1.5	<LOQ	<LOQ	**0.009**	<LOQ	<LOQ	<LOQ	0.029	<LOQ
		2	0.045	0.76	0.035	<LOQ	<LOQ	1.6	<LOQ	<LOQ	0.038	<LOQ	<LOQ	<LOQ	0.028	<LOQ
		3	0.056	1.4	0.056	<LOQ	<LOQ	2.5	<LOQ	<LOQ	0.028	<LOQ	<LOQ	<LOQ	0.062	<LOQ
		4	0.055	1.6	0.091	<LOQ	<LOQ	1.7	<LOQ	<LOQ	0.025	<LOQ	<LOQ	<LOQ	0.039	<LOQ
865	Bimmen - Rhine	1	0.036	0.98	0.053	<LOQ	<LOQ	1.4	<LOQ	<LOQ	**0.009**	<LOQ	<LOQ	<LOQ	0.025	<LOQ
		2	0.050	0.15	0.028	<LOQ	<LOQ	1.5	<LOQ	<LOQ	0.036	<LOQ	<LOQ	<LOQ	0.023	<LOQ
		3	0.052	0.73	0.034	<LOQ	<LOQ	2.2	<LOQ	<LOQ	0.030	<LOQ	<LOQ	<LOQ	0.027	<LOQ
		4	0.049	0.81	0.069	<LOQ	<LOQ	1.5	<LOQ	<LOQ	0.026	<LOQ	<LOQ	<LOQ	0.037	<LOQ
994	Kampen - IJssel	1	0.050	1.2	0.055	<LOQ	<LOQ	1.6	<LOQ	<LOQ	0.017	<LOQ	<LOQ	<LOQ	0.026	<LOQ
		2	0.046	0.09	0.011	<LOQ	<LOQ	1.3	<LOQ	<LOQ	0.023	<LOQ	<LOQ	<LOQ	0.023	<LOQ
		3	0.066	0.71	0.038	<LOQ	<LOQ	1.4	<LOQ	<LOQ	0.021	<LOQ	<LOQ	<LOQ	0.021	<LOQ
		4	0.061	1.4	0.14	<LOQ	<LOQ	1.7	<LOQ	<LOQ	0.018	<LOQ	<LOQ	<LOQ	0.046	<LOQ
1026	Maassluis - Nieuwe Waterweg	1	0.033	1.1	0.027	<LOQ	<LOQ	1.2	<LOQ	<LOQ	**0.009**	<LOQ	<LOQ	<LOQ	0.018	<LOQ
		2	0.062	0.51	0.046	<LOQ	<LOQ	1.6	<LOQ	<LOQ	0.042	<LOQ	<LOQ	<LOQ	0.028	<LOQ
		3	0.038	1	0.024	<LOQ	<LOQ	2.3	<LOQ	<LOQ	0.013	<LOQ	<LOQ	<LOQ	0.016	<LOQ
		4	0.042	0.82	0.068	<LOQ	<LOQ	1.5	<LOQ	<LOQ	0.011	<LOQ	<LOQ	<LOQ	0.031	<LOQ

Rhine km	Sampling point	Round	Opipramol	Oxypurinol	Pentoxifylline	Phenazone	Phosphoric acid triethyl ester (TEP)	Phosphoric acid triisobutyl ester (TiBP)	Phosphoric acid triphenyl ester (TPP)	Phosphoric acid tris (2-chloroethyl) ester (TCEP)	Phoxim	Pregabalin	Pyrazole	Repaglinide	Simvastatin	Terbutryn sulfoxide
	LOQ in µg/L		0.01	0.03	0.01	0.001	0.01	0.02	0.1	0.03	0.05	0.005	0.05	0.01	0.01	0.01
171	Weil am Rhein - Rhine	1	0.011	0.088	<LOQ	**0.002**	0.053	<LOQ	<LOQ	<LOQ	<LOQ	0.011	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.13	<LOQ	**0.002**	0.032	<LOQ	<LOQ	<LOQ	<LOQ	0.011	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.094	<LOQ	**0.002**	0.02	<LOQ	<LOQ	<LOQ	<LOQ	0.012	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	**0.003**	0.03	<LOQ	<LOQ	<LOQ	<LOQ	**0.005**	<LOQ	<LOQ	<LOQ	<LOQ
359	Karlsruhe/ Lauterbourg - Rhine	1	<LOQ	0.24	<LOQ	**0.002**	0.065	<LOQ	<LOQ	<LOQ	<LOQ	0.02	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.22	<LOQ	**0.003**	0.046	<LOQ	<LOQ	<LOQ	<LOQ	0.014	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.26	<LOQ	**0.003**	0.034	<LOQ	<LOQ	<LOQ	<LOQ	**0.008**	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.058	<LOQ	**0.002**	0.036	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
426	Mannheim (Neckar)	1	<LOQ	0.21	<LOQ	**0.003**	0.06	0.02	<LOQ	<LOQ	<LOQ	0.011	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	1.7	<LOQ	0.013	0.12	0.042	<LOQ	<LOQ	<LOQ	0.091	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	1.6	<LOQ	0.021	0.15	0.044	<LOQ	0.063	<LOQ	0.057	0.11	<LOQ	<LOQ	0.043
		4	<LOQ	0.85	<LOQ	0.017	0.2	0.032	<LOQ	0.045	<LOQ	0.033	0.076	<LOQ	<LOQ	0.038
443	Worms (right) - Rhine	1	<LOQ	0.55	<LOQ	**0.005**	0.073	0.032	<LOQ	<LOQ	<LOQ	0.046	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.52	<LOQ	**0.006**	0.11	0.022	<LOQ	<LOQ	<LOQ	0.036	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.57	<LOQ	**0.006**	0.046	<LOQ	<LOQ	<LOQ	<LOQ	0.021	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.2	<LOQ	**0.005**	0.092	<LOQ	<LOQ	<LOQ	<LOQ	0.011	<LOQ	<LOQ	<LOQ	**0.01**
443	Worms (left) - Rhine	1	<LOQ	0.17	<LOQ	**0.004**	0.063	<LOQ	<LOQ	<LOQ	<LOQ	0.021	2.5	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.24	<LOQ	**0.005**	0.041	<LOQ	<LOQ	<LOQ	<LOQ	0.028	3	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.19	<LOQ	**0.004**	0.048	<LOQ	<LOQ	<LOQ	<LOQ	0.015	4.3	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.3	<LOQ	**0.006**	0.041	<LOQ	<LOQ	<LOQ	<LOQ	0.022	0.053	<LOQ	<LOQ	<LOQ
475	Trebur - Schwarzbach	1	<LOQ	8.6	<LOQ	0.078	0.43	0.064	<LOQ	0.064	<LOQ	0.12	0.08	<LOQ	0.013	<LOQ
		2	<LOQ	4.7	<LOQ	0.037	0.43	0.049	<LOQ	0.16	<LOQ	0.046	0.17	<LOQ	<LOQ	0.052
		3	<LOQ	6.5	<LOQ	0.044	0.52	0.064	<LOQ	0.23	<LOQ	0.05	0.93	<LOQ	<LOQ	0.053
		4	<LOQ	4.5	<LOQ	0.045	0.53	0.072	<LOQ	0.13	<LOQ	0.037	0.28	<LOQ	<LOQ	0.063
497	Bischofsheim - Main	1	<LOQ	1.2	<LOQ	0.017	0.079	0.031	<LOQ	<LOQ	<LOQ	0.074	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	1.5	<LOQ	0.045	0.085	0.062	<LOQ	0.034	<LOQ	0.044	0.06	<LOQ	<LOQ	<LOQ
		3	<LOQ	2.3	<LOQ	0.046	0.12	0.03	<LOQ	0.04	<LOQ	0.034	0.13	<LOQ	<LOQ	0.022
		4	<LOQ	1.2	<LOQ	0.031	0.099	0.023	<LOQ	0.033	<LOQ	0.028	0.081	<LOQ	<LOQ	0.022
590	Koblenz - Rhine	1	<LOQ	0.34	<LOQ	**0.006**	0.045	0.025	<LOQ	<LOQ	<LOQ	0.035	0.49	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.58	<LOQ	**0.009**	0.07	0.039	<LOQ	0.061	<LOQ	0.026	0.6	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.47	<LOQ	0.011	0.14	0.031	<LOQ	0.11	<LOQ	**0.008**	0.83	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.14	<LOQ	**0.007**	0.14	0.04	<LOQ	0.12	<LOQ	**0.006**	<LOQ	<LOQ	<LOQ	**0.01**
592	Koblenz - Moselle	1	<LOQ	0.23	<LOQ	**0.003**	0.041	0.021	<LOQ	0.046	<LOQ	0.034	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	1.6	<LOQ	**0.009**	0.094	0.026	<LOQ	0.054	<LOQ	0.053	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	1.6	<LOQ	0.013	0.12	0.027	<LOQ	0.069	<LOQ	0.033	0.08	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.52	<LOQ	**0.006**	0.19	0.026	<LOQ	0.079	<LOQ	0.016	0.077	<LOQ	<LOQ	0.023
640	Bad Honnef - Rhine	1	<LOQ	0.62	<LOQ	**0.007**	0.084	0.036	<LOQ	0.051	<LOQ	0.038	0.45	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.34	<LOQ	**0.008**	0.058	0.026	<LOQ	0.056	<LOQ	0.013	0.56	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.47	<LOQ	**0.01**	0.042	<LOQ	<LOQ	0.076	<LOQ	0.012	0.83	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.48	<LOQ	**0.009**	0.05	0.021	<LOQ	0.06	<LOQ	0.014	<LOQ	<LOQ	<LOQ	0.013
798	Dinslaken - Emscher	1	<LOQ	15	<LOQ	0.13	4	0.053	<LOQ	0.077	<LOQ	0.61	0.16	<LOQ	<LOQ	<LOQ
		2	<LOQ	14	<LOQ	0.28	0.69	0.042	<LOQ	0.13	<LOQ	0.31	0.2	<LOQ	<LOQ	<LOQ
		3	<LOQ	6.4	<LOQ	0.13	2.1	0.15	<LOQ	0.18	<LOQ	0.46	0.31	<LOQ	<LOQ	0.05
		4	<LOQ	3.9	<LOQ	0.18	1.9	0.045	<LOQ	0.13	<LOQ	0.2	0.19	<LOQ	<LOQ	0.076
863	Lobith - Rhine	1	<LOQ	1	<LOQ	0.011	0.13	0.029	<LOQ	<LOQ	<LOQ	0.061	2.3	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.96	<LOQ	0.013	0.066	0.039	<LOQ	<LOQ	<LOQ	0.04	1.3	<LOQ	<LOQ	<LOQ
		3	<LOQ	1.2	<LOQ	0.017	0.16	0.027	<LOQ	<LOQ	<LOQ	0.037	2.8	<LOQ	<LOQ	0.013
		4	<LOQ	1.1	<LOQ	0.013	0.11	0.024	<LOQ	<LOQ	<LOQ	0.034	0.38	<LOQ	<LOQ	0.014
865	Bimmen - Rhine	1	<LOQ	0.53	<LOQ	**0.009**	0.089	0.034	<LOQ	<LOQ	<LOQ	0.045	2.5	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.58	<LOQ	**0.01**	0.086	0.022	<LOQ	0.034	<LOQ	0.017	1.3	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.96	<LOQ	0.013	0.094	0.038	<LOQ	<LOQ	<LOQ	0.025	3.2	<LOQ	<LOQ	0.012
		4	<LOQ	0.66	<LOQ	**0.01**	0.063	0.035	<LOQ	<LOQ	<LOQ	0.018	0.48	<LOQ	<LOQ	0.013
994	Kampen - IJssel	1	<LOQ	0.91	<LOQ	0.011	0.12	0.029	<LOQ	<LOQ	<LOQ	0.042	1.9	<LOQ	<LOQ	<LOQ
		2	<LOQ	0.51	<LOQ	**0.01**	0.077	<LOQ	<LOQ	<LOQ	<LOQ	0.016	1.1	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.55	<LOQ	0.013	0.12	0.024	<LOQ	<LOQ	<LOQ	0.015	1.8	<LOQ	<LOQ	0.016
		4	<LOQ	0.99	<LOQ	0.013	0.11	<LOQ	<LOQ	<LOQ	<LOQ	0.037	0.53	<LOQ	<LOQ	**0.01**
1026	Maassluis - Nieuwe Waterweg	1	<LOQ	0.73	<LOQ	**0.007**	0.083	0.025	<LOQ	<LOQ	<LOQ	0.043	1.7	<LOQ	<LOQ	<LOQ
		2	<LOQ	1.4	<LOQ	0.014	0.072	0.026	<LOQ	<LOQ	<LOQ	0.039	1.3	<LOQ	<LOQ	<LOQ
		3	<LOQ	0.79	<LOQ	**0.009**	0.084	<LOQ	<LOQ	<LOQ	<LOQ	0.02	0.7	<LOQ	<LOQ	<LOQ
		4	<LOQ	0.42	<LOQ	**0.009**	0.07	<LOQ	<LOQ	<LOQ	<LOQ	0.013	0.3	<LOQ	<LOQ	<LOQ

Rhine km	Sampling point	Round	Tetrabutylammonium cation	Tetrabutylphosphonium cation	Tetracarbonitrilpropen	Tetrapropylammonium cation	Thiacloprid	Thiamethoxam	TMDD (Surfynol 104)	Topramezone	Torasemide	Trialate	Tributylphosphine oxide	Tri-n-butyl phosphate (TnBP)	Triphenylphosphine sulphide (TPPS)
	LOQ in µg/L		0.01	0.005	0.02	0.005	0.01	0.01	0.1	0.01	0.003	0.01	0.01	0.02	0.01
171	Weil am Rhein - Rhine	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	0.079	<LOQ	<LOQ	<LOQ	0.13	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	0.054	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
359	Karlsruhe/ Lauterbourg - Rhine	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.14	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	0.045	<LOQ	<LOQ	<LOQ	0.13	<LOQ	**0.003**	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	0.029	<LOQ	<LOQ	<LOQ	0.16	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
426	Mannheim (Neckar)	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.65	<LOQ	0.014	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.46	<LOQ	0.021	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.023	<LOQ	<LOQ	<LOQ	<LOQ
443	Worms (right) - Rhine	1	0.16	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.11	<LOQ	**0.004**	<LOQ	<LOQ	<LOQ	<LOQ
		2	0.012	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.16	<LOQ	**0.005**	<LOQ	<LOQ	<LOQ	<LOQ
		3	0.023	<LOQ	0.022	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**0.006**	<LOQ	0.012	<LOQ	<LOQ
		4	<LOQ	<LOQ	0.026	<LOQ	<LOQ	<LOQ	0.13	<LOQ	**0.007**	<LOQ	<LOQ	<LOQ	<LOQ
443	Worms (left) - Rhine	1	0.37	<LOQ	<LOQ	0.017	<LOQ	<LOQ	<LOQ	<LOQ	**0.003**	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	0.22	<LOQ	<LOQ	0.1	<LOQ	**0.004**	<LOQ	<LOQ	<LOQ	0.029
		3	0.18	<LOQ	0.061	0.061	<LOQ	<LOQ	<LOQ	<LOQ	**0.004**	<LOQ	<LOQ	<LOQ	0.072
		4	<LOQ	<LOQ	0.033	**0.010**	<LOQ	<LOQ	<LOQ	<LOQ	**0.005**	<LOQ	<LOQ	<LOQ	0.047
475	Trebur - Schwarzbach	1	0.051	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.24	<LOQ	0.18	<LOQ	0.012	0.029	<LOQ
		2	0.027	<LOQ	<LOQ	<LOQ	0.02	<LOQ	0.27	<LOQ	0.11	<LOQ	<LOQ	0.12	<LOQ
		3	0.030	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.26	<LOQ	0.12	<LOQ	<LOQ	<LOQ	<LOQ
		4	0.050	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.39	<LOQ	0.12	<LOQ	<LOQ	0.15	<LOQ
497	Bischofsheim - Main	1	<LOQ	<LOQ	<LOQ	0.13	<LOQ	<LOQ	0.51	<LOQ	0.015	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	0.061	<LOQ	<LOQ	0.67	<LOQ	0.022	<LOQ	<LOQ	0.031	<LOQ
		3	<LOQ	<LOQ	<LOQ	0.015	<LOQ	<LOQ	0.65	<LOQ	0.025	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.85	<LOQ	0.028	<LOQ	<LOQ	<LOQ	<LOQ
590	Koblenz - Rhine	1	0.24	<LOQ	<LOQ	0.019	<LOQ	<LOQ	0.15	<LOQ	**0.005**	<LOQ	<LOQ	0.021	<LOQ
		2	<LOQ	<LOQ	<LOQ	0.053	<LOQ	<LOQ	0.25	<LOQ	**0.006**	<LOQ	<LOQ	0.031	<LOQ
		3	0.012	<LOQ	0.051	**0.006**	<LOQ	<LOQ	0.23	<LOQ	**0.007**	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	0.043	<LOQ	<LOQ	<LOQ	0.3	<LOQ	**0.007**	<LOQ	<LOQ	<LOQ	<LOQ
592	Koblenz - Moselle	1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.13	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.3	<LOQ	**0.008**	<LOQ	<LOQ	0.024	<LOQ
		3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.1	<LOQ	**0.010**	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.26	<LOQ	**0.009**	<LOQ	<LOQ	<LOQ	<LOQ
640	Bad Honnef - Rhine	1	0.20	<LOQ	<LOQ	0.020	<LOQ	<LOQ	0.13	<LOQ	**0.006**	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	0.047	<LOQ	<LOQ	0.14	<LOQ	**0.006**	<LOQ	<LOQ	<LOQ	<LOQ
		3	0.040	<LOQ	0.038	0.017	<LOQ	<LOQ	0.13	<LOQ	**0.009**	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	0.027	<LOQ	<LOQ	<LOQ	0.23	<LOQ	**0.009**	<LOQ	<LOQ	<LOQ	<LOQ
798	Dinslaken - Emscher	1	0.082	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	4.4	<LOQ	0.1	<LOQ	<LOQ	0.071	<LOQ
		2	0.023	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.3	<LOQ	0.12	<LOQ	<LOQ	0.031	<LOQ
		3	0.015	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.1	<LOQ	0.085	<LOQ	<LOQ	0.033	<LOQ
		4	0.029	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.6	<LOQ	0.1	<LOQ	<LOQ	0.031	<LOQ
863	Lobith - Rhine	1	0.19	<LOQ	<LOQ	0.026	<LOQ	<LOQ	0.29	<LOQ	**0.008**	<LOQ	<LOQ	0.048	<LOQ
		2	<LOQ	<LOQ	<LOQ	0.037	<LOQ	<LOQ	0.32	<LOQ	**0.008**	<LOQ	<LOQ	<LOQ	<LOQ
		3	0.0208	<LOQ	0.027	0.011	<LOQ	<LOQ	0.26	<LOQ	0.013	<LOQ	<LOQ	0.052	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.4	<LOQ	0.011	<LOQ	<LOQ	0.088	<LOQ
865	Bimmen - Rhine	1	0.19	<LOQ	<LOQ	0.020	<LOQ	<LOQ	0.22	<LOQ	**0.007**	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	0.037	<LOQ	<LOQ	0.38	<LOQ	**0.007**	<LOQ	<LOQ	0.049	<LOQ
		3	0.022	<LOQ	0.026	0.011	<LOQ	<LOQ	0.3	<LOQ	**0.01**	<LOQ	<LOQ	0.026	<LOQ
		4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.41	<LOQ	**0.009**	<LOQ	<LOQ	<LOQ	<LOQ
994	Kampen - IJssel	1	0.24	<LOQ	0.028	0.010	<LOQ	<LOQ	0.43	<LOQ	**0.008**	<LOQ	<LOQ	<LOQ	<LOQ
		2	0.011	<LOQ	<LOQ	0.035	<LOQ	<LOQ	0.17	<LOQ	**0.007**	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	0.032	0.017	<LOQ	<LOQ	0.2	<LOQ	0.014	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	0.062	<LOQ	<LOQ	0.32	<LOQ	0.011	<LOQ	<LOQ	<LOQ	<LOQ
1026	Maassluis - Nieuwe Waterweg	1	0.12	<LOQ	<LOQ	0.022	<LOQ	<LOQ	0.14	<LOQ	**0.005**	<LOQ	<LOQ	<LOQ	<LOQ
		2	<LOQ	<LOQ	<LOQ	**0.010**	<LOQ	<LOQ	0.46	<LOQ	**0.009**	<LOQ	<LOQ	<LOQ	<LOQ
		3	<LOQ	<LOQ	0.02	0.2	<LOQ	<LOQ	0.3	<LOQ	**0.007**	<LOQ	<LOQ	<LOQ	<LOQ
		4	<LOQ	<LOQ	<LOQ	0.032	<LOQ	<LOQ	0.2	<LOQ	**0.008**	<LOQ	<LOQ	<LOQ	<LOQ

Rhine km	Sampling point	Round	Triphenylphosphine oxide (TPPO)	Tris (1,3-dichloroisopropyl) phosphate (TDCP)	Tris(butoxyethyl) phosphate (TBEP)	Uvinul 4050H	Valsartanic acid	Zidovudine
	LOQ in µg/L		0.01	0.01	0.01	0.15	0.005	0.03
171	Weil am Rhein - Rhine	1	<LOQ	0.011	0.016	<LOQ	0.046	<LOQ
		2	0.014	<LOQ	<LOQ	<LOQ	0.052	<LOQ
		3	0.020	<LOQ	0.015	<LOQ	0.065	<LOQ
		4	0.023	<LOQ	<LOQ	<LOQ	0.06	<LOQ
359	Karlsruhe/ Lauterbourg - Rhine	1	<LOQ	0.014	0.015	<LOQ	0.062	<LOQ
		2	<LOQ	0.012	0.012	<LOQ	0.087	<LOQ
		3	0.012	**0.01**	0.018	<LOQ	0.13	<LOQ
		4	0.019	<LOQ	<LOQ	<LOQ	0.13	<LOQ
426	Mannheim (Neckar)	1	<LOQ	<LOQ	0.015	<LOQ	0.083	<LOQ
		2	<LOQ	0.012	0.099	<LOQ	0.46	<LOQ
		3	0.015	0.031	0.064	<LOQ	0.88	<LOQ
		4	0.015	0.022	0.06	<LOQ	0.79	<LOQ
443	Worms (right) - Rhine	1	<LOQ	0.021	0.03	0.19	0.12	<LOQ
		2	<LOQ	<LOQ	0.029	0.22	0.17	<LOQ
		3	0.015	0.013	0.024	0.22	0.28	<LOQ
		4	0.018	<LOQ	0.012	<LOQ	0.23	<LOQ
443	Worms (left) - Rhine	1	0.71	**0.01**	0.016	<LOQ	0.074	<LOQ
		2	0.16	0.013	0.019	<LOQ	0.11	<LOQ
		3	0.25	<LOQ	0.014	<LOQ	0.15	<LOQ
		4	0.23	0.018	<LOQ	<LOQ	0.16	<LOQ
475	Trebur - Schwarzbach	1	0.27	0.033	0.044	<LOQ	4.8	<LOQ
		2	0.94	0.033	0.12	<LOQ	3	<LOQ
		3	2.3	0.026	0.081	<LOQ	3.7	<LOQ
		4	3.9	0.032	0.036	<LOQ	3.2	<LOQ
497	Bischofsheim - Main	1	<LOQ	0.019	0.038	<LOQ	0.25	<LOQ
		2	<LOQ	0.018	0.041	<LOQ	0.51	<LOQ
		3	<LOQ	0.023	0.019	<LOQ	0.96	<LOQ
		4	0.011	0.016	0.02	<LOQ	0.77	<LOQ
590	Koblenz - Rhine	1	0.15	0.015	0.03	<LOQ	0.12	<LOQ
		2	0.022	0.011	0.031	<LOQ	0.17	<LOQ
		3	0.075	<LOQ	0.037	<LOQ	0.31	<LOQ
		4	0.075	<LOQ	0.016	<LOQ	0.23	<LOQ
592	Koblenz - Moselle	1	<LOQ	**0.01**	0.033	<LOQ	0.077	<LOQ
		2	<LOQ	0.016	0.017	<LOQ	0.51	<LOQ
		3	<LOQ	0.016	0.013	<LOQ	0.71	<LOQ
		4	<LOQ	0.019	0.028	<LOQ	0.54	<LOQ
640	Bad Honnef - Rhine	1	0.091	0.022	0.034	<LOQ	0.12	<LOQ
		2	0.016	<LOQ	0.027	<LOQ	0.19	<LOQ
		3	0.067	0.016	0.029	<LOQ	0.35	<LOQ
		4	0.055	0.012	0.014	<LOQ	0.33	<LOQ
798	Dinslaken - Emscher	1	0.041	0.16	0.14	<LOQ	0.81	<LOQ
		2	0.014	0.035	0.054	<LOQ	1.6	<LOQ
		3	0.055	0.03	0.11	<LOQ	1.5	<LOQ
		4	0.12	0.07	0.15	<LOQ	1.2	<LOQ
863	Lobith - Rhine	1	0.113	0.011	0.024	<LOQ	0.16	<LOQ
		2	0.019	<LOQ	0.026	<LOQ	0.23	<LOQ
		3	0.074	0.018	0.034	<LOQ	0.45	<LOQ
		4	0.083	0.026	0.022	<LOQ	0.4	<LOQ
865	Bimmen - Rhine	1	0.075	0.018	0.033	<LOQ	0.16	<LOQ
		2	0.024	0.02	0.024	<LOQ	0.23	<LOQ
		3	0.087	0.014	0.029	<LOQ	0.4	<LOQ
		4	0.082	0.019	0.023	<LOQ	0.36	<LOQ
994	Kampen - IJssel	1	0.044	0.015	0.03	<LOQ	0.22	<LOQ
		2	0.021	<LOQ	<LOQ	<LOQ	0.22	<LOQ
		3	0.1	0.013	0.023	<LOQ	0.49	<LOQ
		4	0.075	0.011	0.021	<LOQ	0.4	<LOQ
1026	Maassluis - Nieuwe Waterweg	1	0.055	0.015	0.023	<LOQ	0.11	<LOQ
		2	0.096	0.011	0.018	<LOQ	0.33	<LOQ
		3	0.051	0.011	0.011	<LOQ	0.33	<LOQ
		4	0.052	0.013	0.011	<LOQ	0.27	<LOQ

Colour code:
0.0001 - 0.01
0.01 - 0.1
0.1 - 1
1 - 200

Appendix 3.2: 31 Target substances that could not be detected above the limit of detection (LOD)

Substance	LOD µg/L	Substance	LOD µg/L
3-trifluoromethylaniline	0.1	**Methiocarb**	0.003
Aclonifen	0.01	**Methylaminoantipyrine**	0.1
Allupurinol	0.1	**Nevapirin**	0.01
Amlopidine	1	**Nicosulfuron**	0.025*
Amoxicillin	0.3*	**Nitenpyram**	0.01
Bifenox	0.003	**Omethoate**	0.005*
Bifenox acid	0.01	**Pentoxifylline**	0.01
Butyltriphenylphosphonium cation	0.01	**Phosphoric acid triphenyl ester (TPP)**	0.10
Cefaclor	0.1	**Phoxim**	0.05*
Chlorpropham	0.01	**Repaglinide**	0.01
Chloroxylenol	0.04	**Tetrabutylphosphonium cation**	0.005
Clothianidin	0.01	**Thiamethoxam**	0.01
Etrimfos	0.003	**Topramezone**	0.01
Flurtamone	0.001	**Triallate**	0.01
Icaridin	0.01	**Zidovudine**	0.03
Lincomycin	0.01		

*LOD is greater than 1/3 of the EQS according to the WFD or 3 x the required LOD according to the watch list

Appendix 3.3: Method descriptions for analytical target methods

Tab.: Listing of method used per substance and whether own ISTD was used in quantification

Substance	Method	own ISTD	Substance	Method	own ISTD	Substance	Method	own ISTD
14-Hydroxyclarithromycin	7		Denatonium	2	x	Phosphoric acid triethyl ester (TEP)	14	
1H-1,2,4-Triazole	6	x	Dicyandiamide (cyanoguanidine)	6	x	Phosphoric acid triisobutyl ester (TiBP)	14	
2,2,6,6-Tetramethyl-4-piperidone	12	x	Dimethomorph	1		Phosphoric acid triphenyl ester (TPP)	14	
2,4-dichlorobenzoic acid	13	x	Dimoxystrobin	1		Phoxim	15	
3-trifluoromethylaniline	1		Diphenylphosphine oxide (DPPO)	3		Pregabalin	1	x
4-Hydroxydiclofenac	2	x	Diphenylphosphonic acid (DPPA)	3		Pyrazole	5	x
9-carboxy-acridine	2	x	Duloxetine	1	x	Repaglinide	3	
Acetamiprid	1	x	Ethyltriphenyl-phosphonium cation	2	x	Simvastatin	1	x
Acyclovir	2	x	Etrimfos	1		Phosphoric acid tris (2-chloroethyl) ester (TCEP)	14	
Carboxy acyclovir	2	x	Phenazone	1	x	Terbutryn sulfoxide	3	
Aclonifen	1		Fexofenadine	2	x	Tetrabutylammonium cation	2	x
Allopurinol	2		Flurtamone	1		Tetrabutylphosphonium cation	2	x
Oxypurinol	1	x	Gabapentin-lactam	2	x	Tetracarbonitrilpropen	1	
Amlodipine	2		Guanylurea	8	x	Tetrapropylammonium cation	2	x
Amoxicillin	2		Hydrochlorothiazide	1	x	Thiacloprid	4	
AMPS	1		Icaridin	1		Thiamethoxam	4	
Atenolol	1	x	Lincomycin	7		TMDD (Surfynol 104)	12	x
Atenolol acid	1	x	Melamine	9	x	Topramezone	1	
Bifenox	11		Methiocarb	1		Torasemide	1	x
Bifenox acid	10		Methoxymethyl-triphenylphosphonium	2	x	Triphenylphosphine oxide (TPPO)	3	

Substance	Method	own ISTD	Substance	Method	own ISTD	Substance	Method	own ISTD
			cation					
Bisoprolol	1	x	Methylaminoantipyrin	3		Triphenylphosphine sulphide (TPPS)	3	
Boscalid	4		Methyltriphenyl-phosphonium cation	2	x	Triallate	10	
Butyltriphenyl-phosphonium cation	3		Cyclamate	1	x	Tributylphosphine oxide	1	
Cefaclor	7		Nevirapine	3		Tri-n-butyl phosphate (TnBP)	14	
Cefuroxime	7		Nicosulfuron	1	x	Tris(1,3-dichlor-isopropyl)phosphate (TDCP)	14	
Chloroxylenol	12	x	Nitenpyram	4		Tris(2-butoxyethyl)phosphate (TBEP)	14	
Chlorpropham	3		Olmesartan	1		Uvinul 4050H		
Clopidogrel acid	1		Omethoate	1		Valsartanic acid	1	x
Clothianidin	4		Opipramol	3		Zidovudine		
DEET	2	x	Pentoxifylline	3				

List of individual methods

	Method 1			Method 2		
Sample preparation:	Filtration:	Yes	over glass fibre filter	Filtration:	Yes	over glass fibre filter
	Centrifugation:	No		Centrifugation:	No	
	pH-value:	set to 6.5-7		pH-value:	as sample	
Sample volume:	0.5 L			Injection volume		
Enrichment:	Yes	SPE	Self-made cartridge (Oasis HLB/ ENV+, ZT-WAX, ZT-WCX)	No		
Enrichment factor:			1000		Enrichment factor:	
Direct injection	No			Yes		
Injection volume:	20 µL			Method 1: 80 µL; Method 2: 100 µL; Method 3: 50 µL		
Column:	Waters XBridge, C18 3.5 µm, 2.1 mm x 50 mm			Zorbax Eclipse Plus C18 column (2.1 × 150 mm, 3.5 µ		
Eluent:	Water/0.1% HCOOH (A) / MeOH/0.1% HCOOH (B)			ACN/water per 0.1% HCOOH		
Column temp .:	25 °C			30°C		
LCMS measurement:	LC-HRMS/MS	Mass range:	115-1000	LC-MS/MS	Mass range:	SMRM
		Ionisation:	heated ESI		Ionisation:	ESI
		Quantification:	via fullscan (resolution 60000 at m/z 400)		Quantification:	SMRM trace
		MS/MS:	data dependent		MS/MS	Yes

	Method 3			Method 4		
Sample preparation:	Filtration:	Yes	over glass fibre filter	Filtration:	No	
	Centrifugation:	No		Centrifugation:	No	
	pH-value:	as sample		pH-value:	no setting	
Sample volume:	Injection volume			Injection volume		
Enrichment:	No			No		
		Enrichment factor:			Enrichment factor:	
Direct injection	Yes			Yes		
Injection volume:	100 µL			100 µL		
Column:	Zorbax Eclipse Plus C18 column (2.1 × 150 mm, 3.5 µm)			Synergi Hydro RP 2.5 µm, 100 x 3 mm		
Eluent:	ACN/water per 0.1% HCOOH			A: 2.5 mmol/l HCOONH4/0.005 v% HCOOH / water		
				B: 2.5 mmol/l HCOONH4+ 0,005 V% HCOOH / MeOH		
Column temp .:	30°C			40°C		
LCMS measurement:	LC-HRMS/MS	Mass range:	100-1200	LC-HRMS/MS	Mass range:	
		Ionisation:	ESI		Ionisation: ESI pos	
		Quantification:	Full scan		Quantification: MRM	
		MS/MS	data dependent		MS/MS	

	Method 5			Method 6		
Sample preparation:	Filtration:	No		Filtration:	No	
	Centrifugation:	No		Centrifugation:	No	
	pH-value:	no setting		pH-value:	neutral	
Sample volume:	Injection volume			1 mL		
Enrichment:	No			None		
		Enrichment factor:			Enrichment factor:	
Direct injection	Yes			Yes		
Injection volume:	90 µL			100 µL		
Column:	Synergi Hydro RP 2.5 µm, 100 x 3 mm			Thermo Hypercarb, 150 x 2.1 mm, 5 µM		
Eluent:	A: 0.05 V% HCOOH / Water			A: Water + 0.1% HCOOH		
	B: 0.05 V% HCOOH / ACN			B: MeOH + 0.1 % HCOOH		
Column temp .:	40°C			40 °C		
LCMS measurement:	LC-HRMS/MS	Mass range:		LC-MS/MS	Mass range:	
		Ionisation: ESI pos			Ionisation:	ESI pos
		Quantification: MRM			Quantification:	MRM
		MS/MS			MS/MS	Yes

	Method 7			Method 8		
Sample preparation:	Filtration:	No		Filtration:	No	
	Centrifugation:	No		Centrifugation:	No	
	pH-value:	neutral		pH-value:	neutral	
Sample volume:	1 mL			1 mL		
Enrichment:	None			None		
		Enrichment factor:			Enrichment factor:	
Direct injection	Yes			Yes		
Injection volume:	100 µL			40 µL		
Column:	Phenomenex Kinetex 100 x 2.1 mm, 2.6 µm			TCI Dual ODS CX15, 150 x 2 mm, 5µm		
Eluent:	A: Water + 0.1% HCOOH + 0.2 mM HCOONH4			A: Water + 50 mM HCOONH4 with HCl at pH3		
	B: MeOH + 0.1 % HCOOH			B: ACN		
Column temp .:				40 °C		
LCMS measurement:	LC-HRMS/MS	Mass range:		LC-HRMS/MS	Mass range:	
		Ionisation:	ESI pos		Ionisation:	ESI pos
		Quantification:	MRM		Quantification:	MRM
		MS/MS	Yes		MS/MS	Yes

	Method 9			Method 10		
Sample preparation:	Filtration:	No		Filtration:	No	
	Centrifugation:	No		Centrifugation:	No	
	pH-value:	neutral		pH-value:	neutral	
Sample volume:		1 mL			1 mL	
Enrichment:	None			None		
		Enrichment factor:			Enrichment factor:	
Direct injection	Yes			Yes		
Injection volume:	40 µL			100 µL		
Column:	Phenomenex Luna, 150 x 3 mm, 3 µm			Waters Xbridge C18, 75 x 2.1 mm, 2.5 µm		
Eluent:	A: Water + 0.1% HCOOH			A: Water + 2mM NH4-acetate		
	B: MeOH + 0.1 % HCOOH			B: MeOH + 2 mM NH4-acetate		
Column temp .:	40 °C			40 °C		
LCMS measurement:	LC-HRMS/MS	Mass range:		LC-HRMS/MS	Mass range:	
		Ionisation:	ESI pos		Ionisation:	ESI
		Quantification:	MRM		Quantification:	MRM
		MS/MS	Yes		MS/MS	Yes

	Method 11			Method 12		
Sample preparation:	Filtration:	No		Filtration:	No	
	Centrifugation:	No		Centrifugation:	No	
	pH-value:	neutral		pH-value:	neutral	
Sample volume:	20mL				500mL	
Enrichment:	Yes			Yes		
		Enrichment factor: 160			Enrichment factor: 2500	
Direct injection	No			No		
Injection volume:	80 µL			2 µL		
Column:	Waters Xbridge C18, 75 x 2.1 mm, 2.5 µm			Restek RTX 502.2. 30 m x 250 µm		
Eluent:	A: Water + 2mM NH4-acetate					
	B: MeOH + 2 mM NH4-acetate					
Column temp .:	40 °C			up to 270 °C		
LCMS measurement:	LC-HRMS/MS	Mass range:		GC-MS	Mass range:	
		Ionisation:	ESI pos		Ionisation:	EI
		Quantification:	MRM		Quantification:	
		MS/MS	Yes		MS/MS	No

	Method 13			Method 14		
Sample preparation:	Filtration:	No		Filtration:	No	
	Centrifugation:	No		Centrifugation:	No	
	pH-value:	2		pH-value:	no setting	
Sample volume:	500mL			500 mL		
Enrichment:	Yes			Yes		fl/fl extraction with dichloromethane
		Enrichment factor: 2500			Enrichment factor: 1000	
Direct injection	No			Yes		
Injection volume:	2 µL			10 µL		
Column:	Agilent DB5 MS, 30 m x 0.32 mm, 1 µm			Zorbax Eclipse Plus C18 column (2.1 × 150 mm, 3.5 µr		
Eluent:				ACN/water per 0.2% HCOOH		
Column temp .:	up to 270 °C					
LCMS measurement:	GC-MS	Mass range:		LC-HRMS/MS	Mass range:	
		Ionisation:	EI		Ionisation: ESI	
		Quantification:			Quantification: MRM??	
		MS/MS	No		MS/MS	
	Method 15					
Sample preparation:	Filtration:	No				
	Centrifugation:	No				
	pH-value:	neutral				
Sample volume:						
Enrichment:	None					
		Enrichment factor:				
Direct injection	Yes					
Injection volume:	20 µL					
Column:	Acquity BEH C18 Column (1.7µm; 2.1 x 50mm; Waters)					
Eluent:	A: Water + 0.01% glacial acetic acid					
	B: MeOH + 0.25 mM NH4-acetate					
Column temp .:						
LCMS measurement:	LC-HRMS/MS	Mass range:				
		Ionisation:	ESI			
		Quantification:	MRM			
		MS/MS	Yes			

Appendix 3.4 Substance evaluation table - suggestion for inclusion in the monitoring programme

Substance	max. concentration (without Emscher and Schwarzbach)	Conc points	> LOD	Percent > LOD	H*-points	Total .	Maximum (without Emscher, Schwarzbach)	Assessment	Comment	Analyt. Measurability*	toxicological values	Left
Dicyandiamide (cyanoguanidine)	46	100	52	100	100	200	Neckar	obligatory from Worms	Special analysis - industrial chemical and nitrification inhibitor, also in the Rhine > 3 µg/L	**1**		
Melamine	5.8	100	52	100	100	200	Worms left	obligatory	special analysis	**1**	AA-EQS: 525 µg/L MAC-EQS: 6000 µg/L	https://www.rivm.nl/bibliotheek/rapporten/2018-0077.pdf
Guanylurea	3.2	100	52	100	100	200	Main	obligatory	Special analysis, also in the Rhine > 3 µg/L	**12**	GOW 1 µg/L	https://www.umweltbundesamt.de/sites/default/files/medien/374/dokumente/liste_der_nach_gow_bewerteten_stoffe_201802.pdf
Oxypurinol	2.3	100	51	98	75	175	Main	obligatory	Exceeding the set limits	**2**	GOW 0.3 µg/L	https://www.umweltbundesamt.de/sites/default/files/medien/374/dokumente/liste_der_nach_gow_bewerteten_stoffe_201802.pdf
Valsartanic acid	0.96	75	52	100	100	175	Main	obligatory	constant background load up to 0.5 µg/L	**2**	GOW 0.3 µg/L	https://www.umweltbundesamt.de/sites/default/files/medien/374/dokumente/liste_der_nach_gow_bewerteten_stoffe_201802.pdf
Fexofenadine	0.84	100	46	88	75	175	Main	obligatory for Mainz	Background value at 0.02 µg/L	**2**		
Hydrochlorothiazide	0.22	100	49	94	75	175	Main	if possible include	only Main otherwise no exceeding of 0.1 µg/L	**2**		
2,2,6,6-tetramethyl-4-piperidinone	13	100	28	54	50	150	Worms right	obligatory from Worms	Industrial chemical	**3/2**		
Pyrazole	4.3	100	33	63	50	150	Worms left	obligatory from Worms	Industrial chemical	**1/2**	GOW 3 µg/L	https://www.umweltbundesamt.de/sites/default/files/medien/374/dokumente/liste_der_nach_gow_bewerteten_stoffe_201802.pdf
TMDD (Surfynol 104)	0.85	75	42	81	75	150	Main	if possible include	Industrial chemical, Karlsruhe-Max. at 0.6 µg/L since 2014, GC-MS substance	**3/2**		
Pregabalin	0.091	75	51	98	75	150	Neckar	if possible include		**2**		
Olmesartan	0.089	75	43	83	75	150	Main	if possible include		**2**	GOW 0.3 µg/L	https://www.umweltbundesamt.de/sites/default/files/medien/374/dokumente/liste_der_nach_gow_bewerteten_stoffe_201802.pdf
DEET	0.058	50	52	100	100	150	Neckar	if possible include	in Basel always comes in waves with exceedances of 0.1 µg/L	**2**		
2,4-dichlorobenzoic acid	57	100	22	42	30	130	Koblenz Rhine	if possible include	Data insufficient, industrial chemical	**1/2**		
Phenazone	0.046	30	52	100	100	130	Main	do not include	Background load significantly below 0.1 µg/L		GOW 0.3 µg/L	https://www.umweltbundesamt.de/sites/default/files/medien/374/dokumente/liste_der_nach_gow_bewerteten_stoffe_201802.pdf
Phosphoric acid triethyl ester (TEP)	0.20	10	52	100	100	110	Neckar	do not include	Measurement values LANUV and LUBW significantly below 1 µg/L, detectable everywhere			

Substance	max. concentration (without Emscher and Schwarzbach)	Conc points	> LOD	Percent > LOD	H*-points	Total .	Maximum (without Emscher, Schwarzbach)	Assessment	Comment	Analyt. Measurability*	toxicological values	Left
Cyclamate	0.33	30	51	98	75	105	Neckar	if possible include	Sweetener	**2**		
Triphenylphosphine oxide (TPPO)	0.71	50	38	73	50	100	Worms left	obligatory	Industrial chemical, relevant for sediment	**2**		
Carboxy acyclovir	0.29	10	46	88	75	85	Main	if possible include		**2**		
Gabapentin-lactam	0.18	10	44	85	75	85	Main	if possible include	in the Rhine <0.1 µg/L	**2**	GOW 1 µg/L	https://www.umweltbundesamt.de/sites/default/files/medien/374/dokumente/liste_der_nach_gow_bewerteten_stoffe_201802.pdf
Tris(butoxyethyl) phosphate (TBEP)	0.099	10	47	90	75	85	Main	do not include			13 µg/L (MPC)	https://rvszoeksysteem.rivm.nl/stof/detail/1308
Torasemide	0.028	10	43	83	75	85	Main	do not include				
Denatonium cation	0.069	1	48	92	75	76	Neckar	do not include				
Ethyltriphenyl-phosphonium cation	0.056	1	46	88	75	76	Weil am Rhein	if possible include	toxicologically relevant, industrial chemical, from Basel	**2**		
Clopidogrel acid	0.036	1	44	85	75	76	Neckar	do not include	Main decomposition product of clopidogrel			
Tris(1,3-dichlor-isopropyl)phosphate (TDCP)	0.031	1	39	75	75	76	Neckar	do not include			10 µg/L	https://circabc.europa.eu/sd/a/7fe29322-946a-4ead-b3b9-e3b156d0c318/Monitoring-based%20Exercise%20Report_FINAL%20DRAFT_25nov2016.pdf
Diphenylphosphonic acid (DPPA)	0.45	30	23	44	30	60	Worms left	do not include	Industrial chemical			
Tetrabutylammonium cation	0.37	30	16	31	30	60	Worms left	do not include	Industrial chemical			
1H-1,2,4-Triazole	0.33	30	18	35	30	60	Bimmen	obligatory	special analysis is discussed as a relevant metabolite	**1**		
Diphenylphosphine oxide (DPPO)	0.28	10	29	56	50	60	Worms left	do not include	Industrial chemical			
Methyltriphenyl-phosphonium cation	0.27	10	31	60	50	60	Worms left	if possible include from Worms	toxicologically relevant, industrial chemical	**2**		
Tetrapropylammonium cation	0.22	10	27	52	50	60	Worms left	do not include				
Bisoprolol	0.026	10	31	60	50	60	Main	do not include			0.1 µg/L	Derived tolerance in drinking water for adults: http://www.umweltbundesamt.at/fileadmin/site/publikationen/REP0623.pdf
Atenolol acid	0.087	1	34	65	50	51	Main	if possible include	Continuous load	**2**		
9-carboxy-acridine	0.080	1	36	69	50	51	Neckar	if possible include	Values in the Rhine <0.05 µg/L	**2**	GOW 0.1 µg/L	https://www.umweltbundesamt.de/sites/default/files/medien/374/dokumente/liste_der_nach_gow_bewerteten_stoffe_201802.pdf

Substance	max. concentration (without Emscher and Schwarzbach)	Conc points	> LOD	Percent > LOD	H*-points	Total .	Maximum (without Emscher, Schwarzbach)	Assessment	Comment	Analyt. Measurability*	toxicological values	Left
Phosphoric acid triisobutyl ester (TiBP)	0.062	1	33	63	50	51	Main	do not include			0.1 µg/L	JRC 2016: https://circabc.europa.eu/sd/a/7fe2932 2-946a-4ead-b3b9- e3b156d0c318/Monitoring- based%20Exercise%20Report_FINAL %20DRAFT_25nov2016.pdf
Phosphoric acid tris (2-chloroethyl) ester (TCEP)	0.12	10	17	33	30	40	Koblenz Rhine	do not include			4 µg/L	JRC 2016: https://circabc.europa.eu/sd/a/7fe2932 2-946a-4ead-b3b9- e3b156d0c318/Monitoring- based%20Exercise%20Report_FINAL %20DRAFT_25nov2016.pdf
AMPS	0.10	10	24	46	30	40	Main	do not include	relevant to drinking water, occurs shore-soil passage			
Tetracarbonitrilpropen	0.079	1	17	33	30	31	Weil am Rhein	do not include	Industrial chemical, stable in the water phase, discharge before Basel			
Boscalid	0.030	30	3	6	1	31	Worms, Moselle	do not include			12 µg/L	http://www.oekotoxzentrum.ch/expertenservice/qualitaetskriterien/qualitaetskriterienvorschlaege-oekotoxzentrum/
Methoxymethyl-triphenylphosphonium cation	0.18	10	15	29	10	20	Worms right	if possible include	toxicologically relevant, industrial chemical	**2**		
Dimethomorph	0.027	10	12	23	10	20	Moselle	do not include				
Uvinul 4050H	0.22	10	3	6	1	11	only in Worms right	do not include				
Tri-n-butyl phosphate (TnBP)	0.088	1	9	17	10	11	Lobith	do not include			11 µg/L	JRC 2016: https://circabc.europa.eu/sd/a/7fe2932 2-946a-4ead-b3b9- e3b156d0c318/Monitoring- based%20Exercise%20Report_FINAL %20DRAFT_25nov2016.pdf
Terbutryn sulfoxide	0.043	1	14	27	10	11	Neckar	if possible include	possibly toxicologically relevant	**2**		
Acyclovir	0.023	10	1	2	1	11	Main	do not include	only once pos. detected		GOW 0.3 µg/L	https://www.umweltbundesamt.de/sites/default/files/medien/374/dokumente/liste_der_nach_gow_bewerteten_stoffe_201802.pdf
4-hydroxy-diclofenac (4-OH-DCF)	0.012	1	6	12	10	11	only Main pos.	do not include				
Cefuroxime	0.011	10	1	2	1	11	Main	do not include				
Opipramol	0.011	10	1	2	1	11	Weil am Rhein	do not include				

GOW = The GOW is considered to be the German precautionary level in drinking water and drinking water resources and/or in waters from which untreated water is extracted for drinking water. This entails a general precautionary measure for demonstrable non-genotoxic substances for which data on oral toxicity, immunotoxicity and germ cell damaging potential do not lead to a value lower than 1 µg/L (GOW_4) (cf. UBA, 2003). As such, it also applies to components of combinations of simultaneously acting substances.

* Measurability: 1- single substance analysis (special analysis), 2 - measurement with existing LC/MS methods possible, 3 - measurement with existing GC/MS methods possible, 3/2 - measurement with existing GC/- or LC/MS methods, 1/2 - measurable only by adapting existing LC/MS methods