

Development and Evaluation of the Rhine Water Quality 2009 - 2012

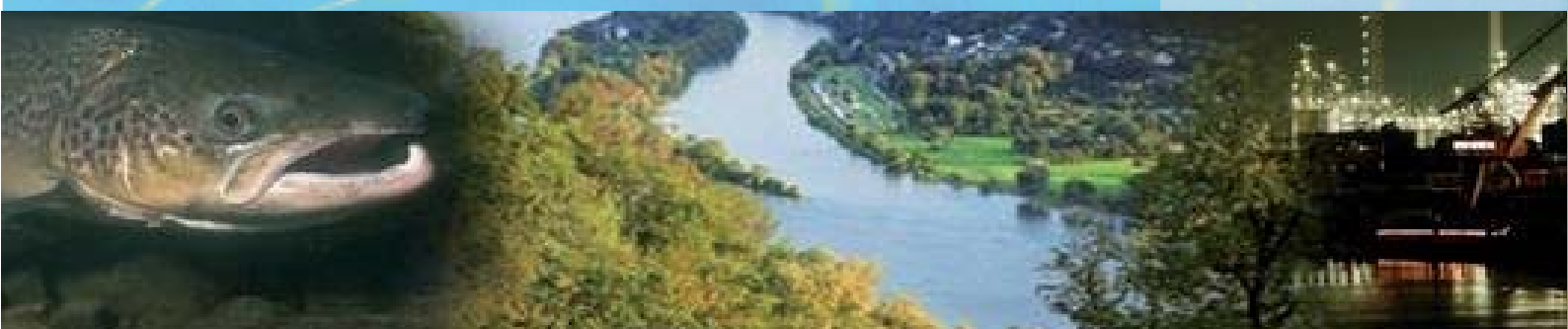


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1. Introduction

So far, in the Rhine catchment, different international water quality evaluation systems were applied: (i) The EU Environmental Quality Standards (EQS) for priority substances, (ii) the environmental standards for substances relevant for the Rhine catchment (EQS Rhine) derived according to the same rules as the EQS and (iii) the ICPR target values applied to the main stream. With a view to a future harmonization of Rhine water quality evaluation, the following principal rules are to be followed:

- a) Substances for which EU-wide EQS or Rhine EQS exist will be evaluated on the basis of the annual average EQS concentration for inland surface waters.
- b) Additionally, the maximum values of the annual substance measurement series will be compared to the values of the Directive 98/83/EC "Water for human consumption" and evaluated, even though the international main monitoring stations are not located in the water body used for drinking water production. In cases of values in excess of national standards which are stricter than the values of the Directive 98/83/EC, these will be explained in the text.
- c) Dissolved heavy metal contents (filtered sample) as well as total heavy metal contents (non-filtered sample) may be measured and the measurement values may be compared to the EQS.
- d) For substances of the List of Rhine Substances 2011 (ICPR, technical report 189 on www.iksr.org), for which only target values exist, the ICPR target value will continue to be applied and the evaluation will be done as usual (in three steps).
- e) For substances, for which there are neither EQS nor ICPR target values, a graphical evaluation will be made for four years based on four concentration levels.

The report at hand is based on the measurement data of the period 2009-2012. In sub-chapter 2.1 of the report at hand the validated measurement values will be compared to the EQS and EQS Rhine and, as far as substances are concerned, for which no EQS and EQS Rhine are available, to the target values for the international monitoring stations Weil am Rhein, Lauterbourg-Karlsruhe, Koblenz/Rhein and Koblenz/Moselle, Bimmen and Lobith. Sub-chapter 2.2 includes a separate comparison of the validated measurement values with values of the Directive 98/83/EC "Water for human consumption" and sub-chapter 2.3 includes a comparison with national evaluation standards beyond those of the EU-wide EQS. Finally, sub-chapter 2.4 illustrates the concentration development of substances, for which no evaluation standards exist in graphs. Chapter 3 is a summary of the most important results.

2. Development of Water Quality

2.1 Comparison of monitoring values with international evaluation standards (EQS, EQS Rhine, ICPR target values)

Introduction

During the past years, the ICPR Member States have invested much work into the analysis of different substances occurring in surface waters.

Apart from Switzerland, the Member States also carried out this work as part of the implementation of the EU Water Framework Directive (WFD). The results achieved may thus easily be re-used, in order to represent the Rhine water quality at different monitoring stations (i.e. Weil am Rhein, Lauterbourg-Karlsruhe, Koblenz, Bimmen and Lobith).

2.1.1 EQS

This chapter deals with measurements of water samples (total) and samples of suspended matter. All substances dealt with in this chapter belong to the so-called list of priority substances agreed upon at EU level (substances of the list figuring in Directive 2008/105/EC). For these substances, EU environment quality standards have been agreed upon. This chapter compares the measurement results (annual mean values) of 2009, 2010, 2011 and 2012 in surface waters to the above mentioned standards. The annual mean values have been calculated according to Article 5 of the Directive 2009/90/EC. The report at hand does not take into account the EQS of the Directive 2013/39/EU. For some new priority substances measurement values are already available, and are presented in chapter 2.4 of the report at hand.

All in all, 40 substances are represented in such manner. In seven cases, the EQS refer to the sum of different, conspecific substances (isomers). For example, instead of indicating individual results, the sum of six BDE is indicated.

Results

The 40 substances (and groups of substances) are classified in four categories: heavy metals, polycyclic aromatic hydrocarbons (PAH), plant protection agents and other substances.

Heavy metals

At the 6 monitoring stations under consideration, the four heavy metals cadmium, lead, mercury and nickel respect the MAV-EQS during all four years (see table 2.1.1.1). The analysis of the biota EQS for mercury is not part of this report. Biota will equally be analysed within an ICPR pilot programme starting in 2014/2015.

Polycyclic aromatic hydrocarbons (PAH)

A comparison of the mean average values with the existing standard (Table 2.1.1.1) clearly indicates that the sum of benzo(ghi)perylene and indeno(1,2,2-dc)pyrene is regularly above the standard. Considering that the occurrence of these substances in surface waters is above all due to atmospheric deposition, it is expected that, at most monitoring stations, in particular this sum of PAH will in future remain in excess of the standard.

For other PAH, among others benzo(a)pyrene, the sum of benzo(b)fluoranthene and benzo(k)fluoranthene, partly also fluranthene, anthracene and naphthalene it is clear that the few water samples deliver few relevant data. Often, these substances could not be analysed in the water phase in a manner permitting a comparison of the result with the standard. For these cases it was decided to convert the analysis results in suspended matter into the water phase and to compare these calculated values with the current standard in water (see Annex 2).

Table 2.1.1.1: Survey table for heavy metals and PAH aimed at evaluating the Rhine water quality based on EQS (mean annual value)

Sub-stance name	EQ S	Weil am Rhein				Lauterbourg-Karlsruhe				Koblenz/Rhine				Bimmen				Lobith			
		2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012
Heavy metals																					
Cadmium	< 0.08-0.25	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.01	< 0.01	0.01	0.012	0.04*	0.03*	0.04*	0.033*	<0.05	<0.05	<0.05	<0.05
Lead	7.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.2	< 0.2	< 0.2	0.6	0.5	0.4	0.39	1.7*	1.45*	1.7*	1.2*	< 0.1	< 0.1	< 0.1	< 0.1
Mercury	0.05	< 0.01	< 0.01	< 0.01	< 0.005	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	< 0.002	< 0.002	< 0.002	0.01*	< 0.01*	0.007*	0.005*	0.001	< 0.001	< 0.001	0.006
Nickel	20	0.81	0.64	<0.5	0.55	0.6	0.7	0.59	0.54	2.2	0.7	1.2	0.53	2.1*	2.1*	2.0*	1.8*	1.2	1.2	1.2	1.0
Polycyclic aromatic hydrocarbons (PAH)																					
Anthracene	0.1	< 0.005	< 0.005	< 0.005	0.0017	< 0.0025	< 0.0025	< 0.0025	< 0.0025	< 0.01	< 0.01	< 0.01	< 0.01	-	-	0.0037	0.0016	< 0.01	< 0.01	< 0.01	< 0.004
Fluoranthene	0.1	< 0.01	< 0.01	0.003	0.011	0.004	0.005	0.003	0.003	< 0.01	< 0.01	< 0.01	< 0.01	0.009	0.03	0.017	< 0.01	< 0.01	< 0.01	0.010	0.0097
Naphthalene	5.4	< 0.005	0.007	0.007	0.002	0.007	0.005	0.004	0.005	< 0.01	< 0.01	< 0.01	< 0.01	<0.05	-	0.02	<0.05	< 0.1	< 0.1	< 0.1	< 0.03
Benzo(a)pyrene	0.05	< 0.005	< 0.005	0.001	0.003	< 0.0025	< 0.0025	0.004	< 0.0025	0.004	0.005	0.003	0.003	0.005	0.009	0.009	0.006	< 0.01	< 0.01	< 0.005	0.002
Benzo(b)fluoranthene*	0.03	0.007	0.008	0.002	0.006	0.002	0.001	0.003	0.002	0.005	0.007	0.005	0.006	0.007	0.013	0.013	0.008	0.014	0.015	0.016	0.011
Benzo(ghi)perylene*	0.002	0.008	0.009	0.0045	0.0046	0.0019	0.0029	0.0019	0.0015	0.007	0.008	0.005	0.005	0.0013	0.018	0.016	0.008	0.015	0.017	0.016	0.009

Legend

Dark blue	Below EQS
Light blue	Converted from measurements of suspended matter to total water (see Annex 2); below EQS
Red	In excess of EQS
<	The mean annual value is below the limit of quantification, for Lobith below the limit of reporting
*	Values in Bimmen for total heavy metal
-	No measurement data available
Q	The analysis of the biota EQS for mercury is not part of this report.
Benzo(b)fluoranthene*	Sum benzo(b)fluoranthene + benzo(k)fluoranthene
Benzo(ghi)perylene*	Sum benzo(ghi)perylene + indeno(1,2,3-cd)pyrene

Table 2.1.1.1: Survey table for heavy metals and PAH aimed at evaluating the Rhine water quality based on EQS (mean annual value)

Name of the substance	EQS	Koblenz/Moselle			
		2009	2010	2011	2012
	µg/l				
Heavy metals					
Cadmium	< 0.08–0.25	0.02	< 0.01	< 0.01	0.014
Lead	7.2	0.6	0.4	< 0.2	0.53
Mercury ^Q	0.05	< 0.002	< 0.002	0.002	0.0025
Nickel	20	2.6	0.9	1.4	1.1
Polycyclic aromatic hydrocarbons (PAH)					
Anthracene	0.1	< 0.01	< 0.01	< 0.01	< 0.01
Fluoranthene	0.1	< 0.01	< 0.01	< 0.01	< 0.01
Naphthalene	2.4				
Benzo(a)pyrene	0.05	0.005	0.01	0.008	0.008
Benzo(b)fluoranthene*	0.03	0.006	0.015	0.016	0.017
Benzo(ghi)perylene*	0.002	0.008	0.017	0.016	0.013

Legend:

Dark blue	Below EQS
Light blue	Converted from measurements of suspended matter to total water (see Annex 2); below EQS
Red	In excess of EQS
<	The mean annual value is below the limit of quantification
Q	The analysis of the biota EQS for mercury is not part of this report.
Benzo(b)fluoranthene*	Sum benzo(b)fluoranthene + benzo(k)fluoranthene
Benzo(ghi)perylene*	Sum benzo(ghi)perylene + indeno(1,2,3-cd)pyrene

Table 2.1.1.2: Survey table for plant protection agents aimed at evaluating the Rhine water quality based on EQS (mean annual value)

Substance name	EQS	Weil am Rhein				Lauterbourg-Karlsruhe				Koblenz/Rhine				Bimmen				Lobith			
		µg/l	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011
Plant protection agents																					
Alachlor	0.3	< 0.005	< 0.005	< 0.005	< 0.005	< 0.001	< 0.001	< 0.001	< 0.001	< 0.05	< 0.05	< 0.05	< 0.05	< 0.025	< 0.025	< 0.025	< 0.025	< 0.01	< 0.01	< 0.01	< 0.01
Atrazine	0.6	0.008	0.006	0.005	0.005	0.007	0.007	0.007	0.005	< 0.02	< 0.02	< 0.02	< 0.02	< 0.025	< 0.025	< 0.025	< 0.025	< 0.01	< 0.01	< 0.01	< 0.01
Chlorfen- vinphos	0.1	< 0.005	< 0.005	< 0.005	< 0.005	< 0.001	< 0.001	< 0.001	< 0.001	< 0.05	< 0.05	< 0.05	< 0.05	< 0.01	< 0.025	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Chlorpyrifos	0.03	< 0.005	-	-	-	< 0.001	< 0.001	< 0.001	< 0.001	-	-	-	-	< 0.01	< 0.025	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cyclodien pesticides	0.01	<0.0000 6	<0.0002	<0.00003	0.00003	< 0.003*	< 0.003*	< 0.003*	< 0.003*	-	-	-	-	< 0.0003	< 0.0001	< 0.0003	< 0.005*	< 0.0005*	< 0.0005*	< 0.001*	< 0.0005*
Total DDT	0.025	0.00007	0.00005	0.00001	0.00008	< 0.0025*	< 0.0025*	< 0.0025*	< 0.0025*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	0.00008	0.00008	0.0002	< 0.005*	< 0.001*	< 0.001*	< 0.001*	< 0.0003*
p, p'-DDT	0.01	<0.0000 4	<0.00006	<0.00001	0.00003	< 0.0025	< 0.0025	< 0.0025	< 0.0025	< 0.01	< 0.01	< 0.01	< 0.01	< 0.00002	< 0.00002	< 0.00002	< 0.005	< 0.001	< 0.001	< 0.0001	< 0.0001
Simazine	1	-	< 0.005	< 0.005	< 0.005	0.003	0.0026	0.003	0.0022	< 0.02	< 0.02	< 0.02	< 0.02	< 0.025	< 0.025	< 0.025	< 0.025	< 0.01	< 0.01	< 0.01	< 0.01
Diurone	0.2	0.005	0.005	0.007	0.006	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.025	< 0.025	< 0.025	< 0.025	0.01	< 0.01	< 0.01	< 0.01
Endosulfan	0.005	< 0.002*	< 0.002*	-	-	< 0.0025*	< 0.0025*	< 0.0025*	< 0.0025*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	-	-	-	< 0.01*	< 0.0005*	< 0.0005*	< 0.001*	< 0.0005*
Hexachloro- cyclohexane	0.02	< 0.002*	< 0.002*	-	-	< 0.0025*	< 0.0025*	< 0.0025*	< 0.0025*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.0003	< 0.0001	< 0.0001	< 0.005*	0.001	0.001	0.0009	0.0009
Isoproturon	0.3	0.005	0.007	0.005	0.006	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.025	< 0.025	< 0.025	< 0.025	0.02	0.02	0.02	0.015
Trifluralin	0.03	< 0.005	< 0.005	< 0.005	< 0.005	< 0.001	< 0.001	< 0.001	< 0.001	< 0.05	< 0.05	< 0.05	< 0.05	< 0.02	< 0.02	< 0.02	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01

Legend

Dark blue	Below EQS
Light blue	Converted from measurements of suspended matter to total water (see Annex 2); below EQS
Red	In excess of EQS
Grey	The limit of reporting (Lobith) and the limit of quantification (for the other monitoring stations) are above the EQS
<	The mean annual value is below the limit of quantification, for Lobith below the limit of reporting
*	All individual values are below the limit of quantification, for Lobith below the limit of reporting
-	No measurement data available
Cyclodien pesticides	Sum aldrin, dieldrin, endrin, isodrin
Total DDT	Sum p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD
Endosulfan	Sum alpha- and beta-endosulfan
Hexachlorocyclohexane	Sum alpha-, beta-, gamma-, delta-HCH

Table 2.1.1.2: Survey table for plant protection agents aimed at evaluating the Rhine water quality based on EQS (mean annual value)

Name of the substance	EQS µg/l	Koblenz/Moselle			
		2009	2010	2011	2012
Plant protection agents					
Alachlor	0.3	<0.05	<0.05	<0.05	<0.05
Atrazine	0.6	< 0.01	< 0.01	< 0.01	< 0.01
Chlorofenvinphos	0.1	< 0.02	< 0.02	< 0.02	< 0.02
Chloropyrifos	0.03	< 0.01	< 0.01	< 0.01	< 0.01
Cyclodien pesticides	0.01	-	-	-	-
Total DDT	0.025	0.0003	0.0002	0.0003	0.006
p, p'-DDT	0.01	0.0001	0.00003	0.00008	0.0003
Simazine	1	< 0.01	< 0.01	< 0.01	< 0.01
Diurone	0.2	<0.05	<0.05	<0.05	<0.05
Endosulfan	0.005	< 0.01*	< 0.01*	< 0.01*	< 0.01*
Hexachlorocyclohexane	0.02	-	-	< 0.01*	< 0.01*
Isoproturone	0.3	< 0.04	< 0.04	< 0.04	0.04
Trifluralin	0.03	< 0.02	< 0.02	< 0.02	< 0.02

Legend:

Dark blue	Below EQS
Light blue	Converted from measurements of suspended matter to total water (see Annex 2); below EQS
Grey	The limit of quantification is above the EQS
<	The mean annual value is below the limit of quantification
*	All individual values are below the limit of quantification
-	No measurement data available
Cyclodien pesticides	Sum aldrin, dieldrin, endrin, isodrin
Total DDT	Sum p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD
Endosulfan	Sum alpha- and beta-endosulfan
Hexachlorocyclohexane	Sum alpha-, beta-, gamma-, delta-HCH

Plant protection agents

Table 2.1.1.2 shows that no values are in excess of the standard. However, in some cases measurement results of the suspended matter analysis have been converted to values for the water phase. Afterwards the converted value has been compared to the standard applicable to the water phase. Even then there are no values in excess of the standard.

Furthermore, in many cases results turned out to be lower than the limit of reporting. Since this limit of reporting is lower than the standard, the statement remains true that the no values are in excess of the standard.

The case of endosulfan points out that the limit of reporting at the Lobith monitoring station and the limit of quantification at the other monitoring stations is in excess of the standard (represented as values in greyed cells). As a matter of principle, in these cases it is not possible to determine whether values are in excess of or below the standard. Since, at the neighbouring monitoring stations, values remain distinctly behind the standard for endosulfan, it is assumed that endosulfan also remains behind the standard in the other cases.

Other substances

In most cases the data of the other substances (Table 2.1.1.3) remain behind the standard. However, some substances require particular attention. This concerns substances the methods of analysis for which are not sufficiently sensitive to be able to check the respect of the standard in the water phase. Almost all data concerning tributyltin and BDE are based on measurement results of the analysis in suspended matter.

Most of the measurement results for DEHP are below the limit of reporting for the Lobith monitoring station and below the limit of quantification of the other monitoring stations. However, these limits of reporting or limits of quantification are not near a third of the standard, as required by the Directive QA/QC (2009/90/EC).

The case of pentachlorobenzene shows that at some monitoring stations the limit of reporting or the limit of quantification is in excess of the standard (represented as values in greyed cells). In these cases not possible to determine whether values are in excess or below the standard. Since, at the neighbouring monitoring stations, values remain distinctly behind the standard for pentachlorobenzene, it is assumed that pentachlorobenzene also remains behind the standard in the other cases.

Table 2.1.1.3: Survey table for the other substances aimed at evaluating the Rhine water quality based on EQS (mean annual value)

Sub- stance name	EQS	Weil am Rhein				Lauterbourg-Karlsruhe				Koblenz/Rhine				Bimmen				Lobith			
		µg/l	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011
Other substances																					
Benzene	10	< 0.25	< 0.25	< 0.25	< 0.25	< 0.02	< 0.02	< 0.02	< 0.02	< 0.1	< 0.1	-	-	<0.05	<0.05	<0.05	<0.05	0.01	< 0.01	< 0.01	0.01
BDE	0.0005 = 0.5 ng/l	0.010	0.006	0.005	0.013	< 3	0.018	0.006	0.009	0.029	0.038	0.021	0.018	0.12	0.16	0.12	0.08	<0.5	0.15	0.33	0.10
1,2-dichloroethane	10	< 0.04	< 0.04	< 0.04	< 0.04	< 0.03	< 0.03	< 0.03	< 0.03	< 0.1	< 0.1	-	-	<0.05	<0.05	< 0.1	< 0.1	0.01	< 0.01	0.01	< 0.01
Dichloromethane	20	< 0.04	< 0.04	< 0.04	0.046	< 0.03	< 0.03	< 0.03	0.056	< 0.1	< 0.1	-	-	< 5	< 5	< 5	<0.05	< 10	< 10	< 10	< 10
Trichloromethane	2.5	0.07	<0.05	<0.05	0.035	0.03	0.02	0.02	0.02	< 0.1	< 0.1	-	-	<0.05	<0.05	<0.05	<0.05	0.02	0.02	0.012	0.012
Tetrachloromethane	12	0.005	0.004	0.0032	0.002	< 0.01	0.01	< 0.01	< 0.01	< 0.1	< 0.1	-	-	<0.05	<0.05	<0.05	<0.05	< 0.01	< 0.01	< 0.01	< 0.01
Tetrachloroethylene	10	0.033	0.026	0.026	0.021	0.04	0.03	0.03	0.03	< 0.1	< 0.1	-	-	<0.05	<0.05	<0.05	<0.05	0.03	< 0.01	0.016	< 0.01
Trichloroethylene	10	0.004	0.005	0.004	0.004	< 0.02	< 0.02	< 0.02	< 0.02	< 0.1	< 0.1	-	-	<0.05	<0.05	<0.05	<0.05	< 0.01	< 0.01	< 0.01	< 0.01
DEHP	1.3	<0.5	< 0.1	0.015	0.015	<0.5	<0.5	<0.5	< 0.2	<0.5	<0.5	<0.5	< 0.2	0.021	0.033	0.021	0.015	< 1	< 1	< 1	< 1
Hexachlorobenzene	0.01	0.00025	0.00014	0.00001	0.00004	< 0.002	< 0.002	0.002	< 0.002	< 0.01	< 0.01	< 0.01	< 0.01	0.0003	0.0003	0.0004	0.00024	< 0.001	< 0.001	< 0.0005	< 0.0002
Hexachlorobutadien	0.1	< 0.02	< 0.001	< 0.001	< 0.001	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	<0.05	<0.05	<0.05	< 0.01	< 0.005	< 0.005	0.002
4-nonyl-phenol	0.3	< 0.01	-	-	< 0.01	-	< 0.011	< 0.011	< 0.011	0.033	0.067	0.032	0.030	<0.05	0.06	0.07	0.07	< 0.1	< 0.1	-	< 0.1
Octylphenol	0.1	0.039	0.025	< 0.03	< 0.01	< 0.006	< 0.006	< 0.006	-	0.010	0.016	0.015	0.03	0.01	0.02	0.04	0.013	< 0.005	< 0.005	< 0.005	< 0.005
Pentachlorobenzene	0.007	0.0001	0.0001	0.00001	0.00004	< 0.0025	< 0.0025	< 0.0025	< 0.0025	<0.05	<0.05	<0.05	<0.05	0.00006	0.00006	0.00008	< 0.005	< 0.0001	< 0.0001	< 0.0001	0.00006
Pentachlorophenol	0.4	-	-	-	-	< 0.006	< 0.006	< 0.006	< 0.006	< 0.1	< 0.1	-	-	-	-	-	-	< 0.1	< 0.1	< 0.1	< 0.1
Tributyltin-cation	0.0002 = 0.2 ng/l	0.03	0.05	0.016	0.05	-	-	-	0.02	0.05	0.05	0.03	0.09	0.02	0.099	0.08	0.05	0.13	0.10	0.198	0.07

Sub-stance name	EQS	Weil am Rhein				Lauterbourg-Karlsruhe				Koblenz/Rhine				Bimmen				Lobith			
		2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012
Trichlorobenzenes	0.4	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	-	< 0.01*	< 0.01*	< 0.01*	< 0.01*	-	< 0.05*	< 0.05*	< 0.05*	< 0.01* / 0,05*	< 0.01* / 0,05*	< 0.01* / 0,05*	< 0.01* / 0,05*

Legend

Dark blue	Below EQS
Light blue	Converted from measurements of suspended matter to total water (see Annex 2); below EQS
Red	In excess of EQS
Grey	The limit of reporting (Lobith) and the limit of quantification (for the other monitoring stations) are above the EQS
<	The mean annual value is below the limit of quantification, for Lobith below the limit of reporting
*	All individual values are below the limit of quantification, for Lobith below the limit of reporting
-	No measurement data available
BDE	Sum of congeners of the numbers 28, 47, 99, 100, 153 and 154. Values in ng/l
Tributyltinication	Values in ng/l
Trichlorobenzenes	Sum of the three isomers

Table 2.1.1.3: Survey table for the other substances aimed at evaluating the Rhine water quality based on EQS (mean annual value)

Name of the substance	EQS µg/l	Koblenz/Moselle			
		2009	2010	2011	2012
Other substances					
Benzene	10	< 0.1	< 0.1	-	-
BDE	0.0005 = 0.5 ng/l	0.090	0.16	0.12	0.17
1,2-dichlorethane	10	< 0.1	< 0.1	-	-
Dichloromethane	20	< 0.1	< 0.1	-	-
Trichloromethane	2.5	< 0.1	< 0.1	-	-
Tetrachloromethane	12	< 0.1	< 0.1	-	-
Tetrachloroethylene	10	< 0.1	< 0.1	-	-
Trichloroethylene	10	< 0.1	< 0.1	-	-
DEHP	1.3	<0.5	<0.5	<0.5	< 0.2
Hexachlorobenzene	0.01	< 0.01	< 0.01	< 0.01	< 0.01
Hexachlorbutadiene	0.1	< 0.01	< 0.01	< 0.01	< 0.01
4-nonylphenol	0.3	< 0.025	0.058	< 0.025	< 0.025
Octylphenol	0.1	0.026	0.024	0.016	0.013
Pentachlorobenzene	0.007	<0.05	<0.05	<0.05	<0.05
Pentachlorophenol	0.4	< 0.1	< 0.1	-	-
Tributyltin-cation	0.0002 = 0.2 ng/l	0.06	0.05	< 0.04	0.06
Trichlorobenzenes	0.4	< 0.01*	< 0.01*	< 0.01*	< 0.01*

Legend

Dark blue	Below EQS
Light blue	Converted from measurements of suspended matter to total water (see Annex 2); below EQS
Grey	The limit of quantification is above the EQS
<	The mean annual value is below the limit of quantification
*	All individual values are below the limit of quantification
-	No measurement data available
BDE	Sum of congeners of the numbers 28, 47, 99, 100, 153 and 154. Values in ng/l
Tributyltin-cation	Values in ng/l
Trichlorobenzenes	Sum of the three isomers

2.1.2 EQS Rhine

Introduction

During the last years and apart from the priority substances described in the section above, the other substances relevant for the Rhine were analysed at the monitoring stations Weil am Rhein, Lauterbourg/Karlsruhe, Koblenz, Bimmen and Lobith.

This chapter deals with measurements of water samples (total). For all substances presented in this chapter, the ICPR has determined so-called Environmental Quality Standards for the Rhine (Rhine-UQN). This chapter compares the measurement results (mean annual values) of 2009, 2010, 2011 and 2012 in surface waters to these standards.

All in all, 12 substances are represented.

Results

The substances belong to three categories: heavy metals, plant protection agents and other substances. When the EQS Rhine are respected, the mean annual value has a blue background.

Heavy metals

As clearly shown in the tables, the measured mean annual values for heavy metals are always below the standard for dissolved heavy metals.

In some cases there are no monitoring values to assess, eg. arsenic in Lauterbourg-Karlsruhe.

As far as zinc is concerned, the values seem to have been in excess of the standard at the Bimmen monitoring station several times. However, only the total content in water is available; since zinc is not in excess of the standard at the other monitoring stations it is to be supposed that the values would equally fall below the standard at the Bimmen monitoring station if the measurement was made in dissolved contents.

Plant protection agents

Data show that, in most cases, values are not in excess of the standard. For some monitoring stations data are lacking. This is true of dichlorvos at the monitoring stations Weil am Rhein and Koblenz-Moselle and for dimethoate at the monitoring stations Weil am Rhein, Koblenz/Rhine and Koblenz/Moselle.

Furthermore, the limit of reporting (Lobith) and the limit of quantification (at the other monitoring stations) in particular for dichlorvos are above the applicable EQS. Therefore, no statement is possible with respect to the question whether the values for dichlorvos are in excess or fall below the EQS. Thus, the mean annual values appear against a grey background.

Other substances

There are no data available for dibutyltin in the water phase. Therefore it was decided to work with values converted from suspended matter. On this basis, the values fall below the EQS in those cases, in which data are available.

At some monitoring stations data are missing: this is true of 4-chloroanilin at the monitoring stations Bimmen and Koblenz/Moselle.

In order to be able to check the EQS Rhine for ammonium N, indications concerning pH and temperature are required. Since these data are not available everywhere, ammonium N is evaluated in chapter 2.1.3. Annex 3 includes a preliminary evaluation of data for ammonia.

Table 2.1.2.1: Survey table for EQS Rhine (mean annual value)

Sub- stance name	EQS- Rhine µg/l	Weil am Rhein				Lauterbourg-Karlsruhe				Koblenz/Rhine				Bimmen				Lobith			
		2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012
Heavy metals																					
Arsenic	BC + 0.5	-	0.80	0.84	0.75	-	-	-	-	-	0.71	0.89	0.79	1.0*	0.87*	0.97*	1.1*	1.0	0.80	0.79	0.78
Chromium	BC + 3.4	-	0.29	0.25	0.19	0.31	0.21	0.29	0.21	0.67	0.25	0.27	0.71	1.7*	1.3*	1.5*	1.3*	<0.5	<0.5	<0.5	<0.5
Zinc	BC + 7.8	-	< 1	< 1	< 1	< 2	< 2	< 2	< 2	3.5	3.7	2.9	3.8	13*	11.9*	13.4*	11.0*	4.6	4.4	4.3	3.8
Plant protection agents																					
Bentazone	73	< 0.01	0.0011	0.0011	< 0.001	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.025	< 0.025	< 0.025	< 0.025	< 0.01	< 0.01	< 0.01	< 0.01
Chloroto- lurone	0.4	< 0.01	< 0.005	0.002	0.004	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.025	< 0.025	< 0.025	< 0.025	0.01	0.02	0.010	0.010
Dichlorvos	0.006	-	-	-	-	< 0.001	< 0.001	< 0.001	< 0.001	<0.05	<0.05	<0.05	<0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005	< 0.005	< 0.005	< 0.005
Dichloro- prop	1.0	< 0.01	< 0.005	< 0.005	< 0.005	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.025	< 0.025	< 0.025	< 0.025	<0.05	<0.05	<0.05	<0.05
Dimethoate	0.07	< 0.01	< 0.005	-	< 0.001	< 0.002	< 0.002	< 0.002	< 0.002	-	-	-	-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
MCPA	1.4	< 0.01	0.004	0.006	< 0.005	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.025	< 0.025	< 0.025	< 0.025	<0.05	<0.05	<0.05	<0.05
Mecoprop	18	0.012	0.011	0.015	0.01	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.025	< 0.025	< 0.025	< 0.025	<0.05	<0.05	<0.05	<0.05
Other substances																					
4- chloroaniline	0.22	< 0.02	< 0.02	< 0.02	< 0.02	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.5	-	-	-	< 0.01	< 0.01	< 0.01	< 0.01
Dibutyltin- cation	0.09	0.0004	0.001 1	0.000 25		-	-	-		0.0004	0.0003	0.0002	0.0003	0.000 07	0.000 8	0.000 7		0.000 3	0.000 4	0.000 3	0.000 3

Legend

Dark blue	Values are below the EQS Rhine
Light blue	Converted from measurements of suspended matter to total water (see Annex 2); below EQS-Rhine
Grey	The limit of reporting (Lobith) and the limit of quantification (for the other monitoring stations) are above the EQS-Rhine
<	The mean annual value is below the limit of quantification, for Lobith below the limit of reporting
*	Values in Bimmen for total heavy metal and total arsenic
-	No measurement data available
BC	Background Concentration: As: BC=1 µg/l; Cr: BC=0.38 µg/l; Zn: BC=3 µg/l (Rhine), 1 µg/l (other waters)

Table 2.1.2.1: Survey table for EQS Rhine (mean annual value)

Name of the substance	EQS-Rhine	Koblenz/Moselle			
		2009	2010	2011	2012
	µg				
Heavy metals					
Arsenic	BC + 0.5	-	1.3	1.2	1.2
Chromium	BC + 3.4	0.73	1.2	< 0.2	0.54
Zinc	BC + 7.8	3.1	3.3	2.4	7.7
Plant protection agents					
Bentazone	73	< 0.03	< 0.03	< 0.03	< 0.03
Chlorotolurone	0.4	0.041	0.046	< 0.04	< 0.04
Dichlorvos	0.006	-	-	-	-
Dichloroprop	1.0	< 0.03	< 0.03	< 0.03	< 0.03
Dimethoate	0.07	-	-	-	-
MCPA	1.4	< 0.03	< 0.03	< 0.03	< 0.03
Mecoprop	18	< 0.03	< 0.03	< 0.03	< 0.03
Other substances					
4-chloroaniline	0.22	-	-	-	-
Dibutyltin-cation	0.09	0.0003	0.0004	0.0003	0.0003

Legend

Dark blue	Values are below the EQS Rhine
Light blue	Converted from measurements of suspended matter to total water (see Annex 2); below EQS-Rhine
<	The mean annual value is below the limit of quantification
-	No measurement data available
BC	B ackground C oncentration: As: BC=1µg/l; Cr: BC=0.38 µg/l; Zn: BC=3 µg/l (Rhine), 1 µg/l (other waters)

2.1.3 Comparison with target values

Under the "Rhine Action Programme", target values were derived for individual substances/sum parameters, which have largely been substituted by the EQS or the EQS Rhine (this is not true of the target value for the asset meriting protection "sediments"). These target values are recommendations. They refer to the percentile 90 of an annual series at the six reference monitoring stations. Following the rules for interpretation, there are three groups of results.

During the past years, the achievement of the target has regularly been documented in "target alignments" taking into consideration the past monitoring year as well as a longer lapse of time (e.g. ICPR reports no. 159, 180 and 193). With respect to the asset worth protection "sediments", all heavy metals analysed, including those for which EQS exist for the water phase and/or biota are represented below. Table 2.1.3.1 includes a summary representation.

Heavy metal contents of suspended matter

For **arsenic**, only the values at Weil am Rhein and Lobith were not below half of the target value 2009 and 2011. In 2012, the 90 percentile value at the mouth of the Moselle was only just above half of the target value, so that, for the first time in many years, a classification in the 2nd class of results was required. On the long term, the values are permanently distinctly below the target values at all monitoring stations.

Since 1995, the values for **chromium** have been near the target values at all monitoring stations. During the past years, a trend towards lower values is determined at the monitoring stations Weil am Rhein, Koblenz, Bimmen and Lobith. These findings were also confirmed in 2009-2012.

For the target alignments 1990-2008, **copper** still had to be classified in the 1st group of results (values in excess of the double target value in Lobith). During the following period, 2009-2012, all values are again within the range of the target values. It is striking that values for 2012 along the Rhine are lower than in the preceding years.

In the meantime, and except for Lobith (values more than double of the target values in 2009 and 2011) the situation for **mercury** and **cadmium** is satisfactory (however, see chapter 2.1.1 concerning mercury). Both at Weil am Rhein and at the mouth of the Moselle, even values below half of the target values were registered during the period under report.

The general situation for **lead** and **nickel** is satisfactory. While nickel values were all within the target values, those for lead on the Upper and Middle Rhine were almost all below half the target value.

For some years, the **zinc** pollution has been falling (see ICPR report no. 193). This trend did not continue during 2009-2012. In particular, comparatively high values were determined in 2011. On the Lower Rhine, the contamination with zinc was measured to the double of the target values on the Lower Rhine - in 2011, at Bimmen and Lobith it was even above three times the target value (table 2.1.3.1). For the first time, this value was below the double target value in Bimmen in 2012.

Group of PCB (Table 2.1.3.1)

PCB are found all over the world and thus belong to the ubiquitous contaminants. Until the 1980s, they were used in transformers, electric condensers, in hydraulic systems as hydraulic fluids and as softeners in plastics all over the Rhine catchment. Since the Stockholm Convention of 2001 there is a worldwide ban on PCB.

During the past target alignments, the compound **PCB 153** was considered more closely as a representative and example for the PCBs. Regularly, values were distinctly in excess of the target values at several monitoring stations, among others in Weil am Rhein in 2003/2004. Contrary to these older values, the values for PCB 153 during 2009-2012 were comparatively low, and in 2009 and in 2011, they were even below half the target value. Until Lauterbourg-Karlsruhe the PCB value was near the target value, but from the Middle Rhine (Koblenz) and downstream, the double of the target value was topped up to several times. Just as for heavy metals, the particularly high values in 2011 are conspicuous (values about 7 times in excess of the target value in Bimmen and Lobith and 6 times in excess of the target value at the mouth of the Moselle). The high values at these monitoring stations are mainly due to the former use of PCB in hydraulic fluids in mining. The sharp fall in concentrations at Bimmen in 2012 is just as conspicuous. For the first time, values were below the double of the target value.

The situation for **PCB 28** and **PCB 54** is slightly better. Most values were within the range of the target value or even below half of the target value. In 2009 and 2011, values above the double target value were only measured in Lobith.

The situation for **PCB 101** and **PCB 118** is not quite as good. While, on the Upper Rhine, the Middle Rhine and in the Moselle values were in the range of the target values or even below half the target value, values above double of the target value were registered in Lobith and Bimmen.

The situation of **PCB 138** is comparable to the poor situation of PCB 153: values are, almost everywhere, in excess of the double of the target value, in 2010 this even applies to Weil am Rhein and Koblenz. However, in 2012 for the first time values at Bimmen were below the double of the target value.

Finally, it can be established that the situation for **PCB 180** is comparatively good until Koblenz, and that, apart from the known contaminations at Bimmen and Lobith - as for PCB 153 - more serious contaminations are registered at the mouth of the Moselle, where, in 2011, values were almost 4 times in excess of the target values.

For all PCBs and due to their ubiquitous spreading and high persistence no trend towards improvement can be made out.

Ammonium-N (Table 2.1.3.1)

The positive trend registered for ammonium-nitrogen during 1990 to 2006 (see ICPR report no. 193) is continuing. In 2012, at most Rhine monitoring stations, values were even below half of the target value (3rd group of results). Only in Lobith and at the mouth of the Moselle monitoring values were still in the range of the target values (2nd group of results), but remained below the target value.

We may summarize that the problem of ammonium in the Rhine has been solved.

Table 2.1.3.1: Survey Table on the Evaluation of Rhine Water Quality based on ICPR Target Values (90 percentile)

Substance name	TV	Unit	Weil am Rhein				Lauterbourg-Karlsruhe				Koblenz/Rhine				Bimmen				Lobith			
			2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012
Heavy metals																						
As	40	mg/kg	20.1	18.3	20.5	19	17	15	16.4	13.8	16	17	17	14	18	19	19.4	16.4	24	20	22	16.9
Cr	100	mg/kg	63	58	66	62.7	75	76	77	79	65	71	67	59.1	60	63	65	54	95	81	98	74.2
Cu	50	mg/kg	62	59	57	57	77	69	94	62	84	75	74	58	76	84	100	69	100	89	90	71
Cd	1	mg/kg	0.46	0.44	0.54	0.54	0.70	0.50	0.50	0.50	0.60	0.65	0.72	0.52	1.3	1.6	1.3	1.0	2.4	1.5	2.3	1.5
Hg	0.5	mg/kg	0.45	0.25	0.32	0.23	0.41	0.39	0.36	0.30	0.38	0.35	0.36	0.42	0.51	0.7	0.64	0.44	1.2	0.66	1.1	0.61
Ni	50	mg/kg	51	46	47	50	56	54	51	53	50	47	49	45	48	80	76	44	54	53	53	51
Pb	100	mg/kg	39	38	43	35	51	43	54	44	49	48	47	43	72	103	78	55	120	84	119	83
Zn	200	mg/kg	213	214	215	210	310	266	380	324	299	310	324	267	433	411	434	358	558	489	600	509
Group of PCB																						
PCB 28	0.1	ng/l	<0.05	<0.094	<0.017	0.012	<0.022	<0.03	<0.016	<0.04	0.036	0.052	0.02	0.031	0.068	0.073	0.11	0.052	0.21	0.099	0.30	0.095
PCB 52	0.1	ng/l	<0.05	<0.094	<0.017	0.023	0.026	<0.03	<0.017	<0.04	0.042	0.054	0.024	0.033	0.082	0.085	0.20	0.062	0.17	0.13	0.32	0.11
PCB 101	0.1	ng/l	<0.05	0.11	<0.017	0.056	0.042	0.067	0.028	0.10	0.074	0.105	0.073	0.074	0.17	0.17	0.39	0.11	0.29	0.22	0.43	0.17
PCB 118	0.1	ng/l	<0.05	<0.094	<0.017	0.049	<0.022	<0.03	<0.018	<0.04	0.061	0.08	0.039	0.043	0.11	0.11	0.24	0.08	0.21	0.18	0.31	0.17
PCB 138	0.1	ng/l	0.064	0.26	0.027	0.11	0.053	0.073	0.048	0.11	0.13	0.203	0.098	0.082	0.27	0.39	0.63	0.18	0.32	0.27	0.45	0.26
PCB 153	0.1	ng/l	<0.05	0.12	0.024	0.098	0.058	0.073	0.052	0.095	0.16	0.23	0.137	0.18	0.23	0.36	0.71	0.198	0.48	0.38	0.69	0.35
PCB 138	0.1	ng/l	0.064	0.26	0.027	0.11	0.053	0.073	0.048	0.11	0.13	0.203	0.098	0.082	0.27	0.39	0.63	0.18	0.32	0.27	0.45	0.26
PCB 180	0.1	ng/l	<0.05	<0.094	0.025	0.056	0.024	<0.04	0.022	<0.04	0.10	0.14	0.069	0.11	0.12	0.197	0.46	0.12	0.198	0.198	0.25	0.22
Other substances																						
NH4-N	200	µg/l	79	88	71	62	60	77	50	50	80	90	72	70	130	120	110	98	160	130	139	103

Legend

Red:	Failure to meet target value (TV) or distinct transgression (>2*TV)
Yellow	Values monitored near the target values (½TV<x<2xTV).
Green:	Target value met or value distinctly below target value (<½TV).

Table 2.1.3.1: Survey Table on the Evaluation of Rhine Water Quality based on ICPR Target Values (90 percentile)

Name of the substance	TV	Unit	Koblenz/Moselle			
			2009	2010	2011	2012
Heavy metals						
As	40	mg/kg	17	19	20	20.2
Cr	100	mg/kg	75	91	74	76.5
Cu	50	mg/kg	86	86	85	91
Cd	1	mg/kg	0.86	1.0	0.78	0.74
Hg	0.5	mg/kg	0.25	0.24	0.84	0.30
Ni	50	mg/kg	63	64	58	59
Pb	100	mg/kg	86	100	94	73
Zn	200	mg/kg	482	525	479	478
PCB group						
PCB 28	0.1	ng/l	0.023	0.057	0.03	0.15
PCB 52	0.1	ng/l	0.045	0.10	0.06	0.14
PCB 101	0.1	ng/l	0.079	0.19	0.19	0.17
PCB 118	0.1	ng/l	0.059	0.13	0.097	0.13
PCB 138	0.1	ng/l	0.14	0.30	0.33	0.39
PCB 153	0.1	ng/l	0.194	0.43	0.63	0.48
PCB 180	0.1	ng/l	0.10	0.33	0.38	0.34
Other substances						
NH4-N	200	µg/l	110	110	140	154

Legend

Red	Failure to meet target value (TV) or distinct transgression (>2*TV)
Yellow	Values monitored near the target values ($\frac{1}{2}$ TV<x<2xTV).
Green:	Target value met or value distinctly below target value (< $\frac{1}{2}$ TV).

Longstanding survey

The longstanding survey represents the development at the monitoring stations along the main stream during 1990 to 2012.

Table 2.1.3.2: Longstanding survey of the evaluation of the Rhine water quality based on ICPR target values (TV) 1990-2012

Substance	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	
Heavy metals																								
Arsenic																								
Chromium																								
Copper																								
Cadmium																								
Mercury																								
Lead																								
Nickel																								
Zinc																								
Other substances																								
PCB																								
Ammonium nitrogen																								

Legend	
	Failure to meet target value or distinct transgression.
	Values monitored near the target values.
	Target value met or value considerably below target value

2.2 Comparison of monitoring values with values of the Directive 98/83/EC "Water for human consumption"

Since water from the Rhine is also used for producing drinking water for some 30 million people, chapter 2.2 compares the monitoring values with standards for surface waters used for drinking water production (according to the Directive 98/83/EC) applicable in the European Union.

According to Table 2.2.1, during the period under consideration, the maximum values of individual substances during one monitoring year are in excess of the quality requirements of the Directive 98/83/EC (Directive Drinking Water Production) or they correspond to these values.

In the Rhine tributary Moselle, at Koblenz, chlorotoluene is in excess of this quality requirement in 2009, 2010, 2011 and 2012, while the value is reached and thus respected at Lobith.

The result of the check of pesticides in the list of priority substances according to the Directive 2008/105/EC only pointed out values in excess at the monitoring stations Bimmen, Lobith and Koblenz/Moselle (see Table 2.2.1)

Table 2.2.1: Survey Table of Annual Maximum Values for the Comparison with the Values of the Directive 98/83/EC

Substance name	Directive /98/83 /EC µg/l	Weil am Rhein				Lauterbourg-Karlsruhe				Koblenz/Rhine				Bimmen				Lobith			
		2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012	2009	2010	2011	2012
Heavy metals																					
Arsenic	10	-	0.91	1.1	0.87	-	-	-	-	-	1.0	1.1	1.5	1.5*	1.3*	1.8*	2.3*	1.3	1.1	0.94	0.78
Chromium	50	-	0.39	0.33	0.46	0.39	0.40	0.60	0.38	5.3	1.0	0.90	4.9	3.3*	2.3*	5.8*	6.1*	<0.5	<0.5	<0.5	<0.5
Copper	2000	1.6	2.1	1.2	1.5	1.5	1.8	1.7	1.5	6.6	2.5	4.5	2.8	5.2*	5.3*	5.6*	8.4*	2.6	2.4	2.1	2.2
Plant protection agents																					
Bentazone	0.1	< 0.01	0.005	0.009	0.005	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.025	< 0.025	< 0.025	< 0.025	0.02	0.01	0.02	< 0.01
Chlorotolurone	0.1	< 0.01	0.007	0.016	0.031	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.026	0.065	0.052	0.076	0.06	0.09	0.10	0.07
Dichlorvos	0.1	-	-	-	-	< 0.001	< 0.001	< 0.001	< 0.001	<0.05	<0.05	<0.05	<0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005	< 0.005	< 0.005	< 0.005
Dichlorprop	0.1	0.014	< 0.005	< 0.005	< 0.005	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.025	< 0.025	< 0.025	< 0.025	<0.05	<0.05	<0.05	<0.05
Dimethoate	0.1	< 0.01	< 0.005	-	0.004	< 0.002	< 0.002	< 0.002	< 0.002	-	-	-	-	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Diurone	0.1	0.018	0.008	0.014	0.11	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.025	< 0.025	< 0.025	< 0.025	0.03	0.02	0.02	0.02
Isoproturone	0.1	0.019	0.035	0.029	0.046	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.053	0.12	0.11	0.092	0.08	0.17	0.05	0.11
MCPA	0.1	0.014	0.009	0.018	0.023	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.025	< 0.025	< 0.025	< 0.025	<0.05	<0.05	<0.05	<0.05
Mecoprop	0.1	0.073	0.045	0.073	0.062	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.027	< 0.025	< 0.025	< 0.025	<0.05	<0.05	<0.05	<0.05
Other substances																					
Ammonium nitrogen	390	90	95	100	85	70	80	60	70	90	150	84	202	170	150	120	240	250	180	200	188
4-chloroaniline	0.1	< 0.02	< 0.02	< 0.02	< 0.02	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.5	-	-	-	< 0.01	0.02	0.012	0.014

Legend

Dark blue	Values below those of the Directive 98/83/EC
Red	Values above those of the Directive 98/83/EC
Grey	The limit of reporting (Lobith) and the limit of quantification (for the other monitoring stations) are above the values of the Directive 98/83/EC
<	The values of the Directive 98/83/EC are below the limit of quantification, for Lobith below the limit of reporting
*	Values in Bimmen for total heavy metal
-	No measurement data available

Table 2.2.1: Survey Table of Annual Maximum Values for the Comparison with the Values of the Directive 98/83/EC

Name of the substance	Directive /98/83/EC	Koblenz/ Moselle			
		2009	2010	2011	2012
	µg/l				
Heavy metals					
Arsenic	10	-	2.3	1.9	3.9
Chromium	50	3.0	4.6	0.50	3.0
Copper	2000	3.0	3.5	4.1	6.2
Plant protection agents					
Bentazone	0.1	0.04	0.09	< 0.03	0.07
Chlorotolurone	0.1	0.21	0.22	0.29	0.17
Dichlorvos	0.1	-	-	-	-
Dichloroprop	0.1	< 0.03	< 0.03	< 0.03	< 0.03
Dimethoate	0.1	-	-	-	-
Diurone	0.1	0.096	0.094	0.29	0.13
Isoproturon	0.1	0.096	0.083	0.31	0.27
MCPA	0.1	< 0.03	0.032	< 0.03	0.096
Mecoprop	0.1	< 0.03	< 0.03	< 0.03	< 0.03
Other substances					
Ammonium nitrogen	390	170	230	190	283
4-chloroaniline	0.1				

Legend

Blue	Values below those of the Directive 98/83/EC
Red	Values above those of the Directive 98/83/EC
<	The values of the Directive 98/83/EC are below the threshold of measurement
*	Value for total heavy metal
-	No measurement data available

2.3 Comparison of monitoring values with more strict national evaluation standards

Switzerland

The requirements for water quality are determined in the Regulations on Water Protection (GSchV), annex 2. For surface water and ground water they include numerical as well as general requirements. In particular, annex 2 stipulates that the water quality of surface waters must be such that, after applying adequate treatment methods, requirements of food law must be met. The water quality of groundwater used for drinking water production must be such that, after applying simple treatment methods, the water meets the requirements of food law. Thus, the Regulations on Water Protection directly point to the Food Law determining the numerical requirements of the Regulations of the Swiss Home Office on foreign substances and ingredients in food stuff (Swiss Regulation on Foreign Substances and Ingredients (FIV)). A comparison of the assessment scale of the Swiss FIV with the Directive 98/83/EC shows that largely, the same quality criteria apply in Switzerland. In a few cases, the values of the Swiss regulation are slightly lower, but remain in the same order of magnitude (cadmium: CH 3 µg/l, EU 5 µg/l; copper: CH 1 mg/l, EU 2 mg/l; nitrate: CH 40 mg/l, EU 50 mg/l). For volatile chlorinated hydrocarbons (1 µg/l) the Regulations on Water Protection are stricter than the EU regulation (trichloroethene 10 µg/l).

Thus, in Switzerland, only drinking water threshold values for chlorinated hydrocarbons are stricter than those of the Directive 98/83/EC.

France

The Directive 2000/60/EC of the European Parliament and the Council of 23 October 2000 establishing a framework for Community action in the field of water policy has been transposed into French Environmental Protection Act, in particular into the Articles L.211 and R.212 to 213.

A decree of 25 January 2010 determines methods and criteria for the description of the different classes of the ecological state, the chemical state and the ecological potential of surface waters, applying Articles R.212-10, R.212-11 and R.218 of the Environmental Protection Act. This decree also takes into account the requirements of the Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy and the Commission Decision of 30 October 2008 establishing the values of the Member State monitoring system classifications as a result of the intercalibration exercise. With respect to the quality of water for human consumption, the values determined in the Directive 98/73/EC of the Council of 3 November on the quality of water for human consumption apply.

In France, no drinking water limit values are stricter than those of the Directive 98/83/EC.

Germany

The Regulation on Surface Waters (OGewV) of 20 July 2011 (BGBl. I S. 1429) implements the Directive 2000/60/EC of the European Parliament and the Council establishing a framework for Community action in the field of water policy, last modified by the Directive 2009/31/EC and the Directive 2008/105/EC on environmental quality standards in water policy.

According to § 7 of the OGewV, the German federal states must identify surface water bodies used for drinking water production and avoid a deterioration of their quality. In Germany, no drinking water limit values are stricter than those of the Directive 98/83/EC.

Netherlands

For drinking water intakes from surface waters, the standards of the decision on quality requirements and water body surveillance 2009¹ (Bkmw) and the standards of the drinking water regulation² (Dwr) apply. The Bkmw includes requirements to be met by the state (water management), while the Dwr concerns quality requirements applicable to a resource from which drinking water works take water. The Bkmw 2009 includes guidance values (commitments to result) for water intakes and target values (commitments to action) for surface water bodies.

For the purpose of the management plan for 2015-2021, Rijkswaterstaat and RIWA have produced a document pointing out the supra-regional substance problems related to substances relevant for drinking water in the Dutch arms of the Rhine in the Rhine delta and possible countermeasures (Supra-regional supplement, regional document Rhine delta, 11 December 2013). Several parameters, among others plant protection agents and pharmaceuticals are in excess of the quality requirements. In particular, the drinking water regulation includes communication values for some specified substances (MTBE, diglyme) and for "other substances of anthropogenic origin which might put drinking water supply at a risk" (1 µg/l).

2.4 Development of substance concentrations, for which no evaluation criteria exist

Apart from substances, for which an environment quality standard (EQS) according to the Directive 2008/105/EC or an ICPR target value exists, further organic trace components are measured within the Rhine Monitoring Programme Chemistry. In the following, these substances are evaluated for the monitoring years 2009 to 2012 and for the ICPR monitoring stations Weil am Rhein, Lauterburg-Karlsruhe, Koblenz/Rhein, Bimmen, Lobith and Koblenz/Moselle.

2.4.1 Test criterion

As no comparisons with target values or EQS are possible for the substance concentrations found, the mean annual value and the maximum value of the year (based on individual measurements) will be represented in a graph. With respect to the determining mean annual value (MW), the measurement values were divided into the following four levels of concentration (categories):

1st level: MW at all measurement stations below 0.01 µg/l (10 ng/l)

2nd level: MW between 0.01 and < 0.1 µg/l

3rd level: MW between 0.1 and 1.0 µg/l

4th level: MW above 1.0 µg/l

The mean annual value is decisive for the representation in a graph. The maximum value is even represented, when the numerical value is outside the scale of the corresponding level.

For reasons of consistency it is necessary to introduce a further level, the so-called level 0. A substance is classified in this category if, after data interpretation, no MW is in excess of the threshold of measurement and monitoring stations indicate different thresholds of measurement above or below/equal to 0.01 µg/l for this substance.

¹ Bkmw 2009. Decision of 30 November 2009 concerning rules for the implementation of the environmental targets of the Water Framework Directive (Decision on quality requirements and water body monitoring 2009). State journal of law of the Kingdom of the Netherlands 2010, no. 15

² Drinking water regulation. Regulation of the Secretary of State for Infrastructure and Environment of 14 June 2011, no. BJZ2011046947 on details concerning certain topics with respect to the supply with drinking water, industrial water and water for households (drinking water regulation). Dutch Official Gazette no. 10842 of 27 June 2011

2.4.2 Evaluation

The evaluation is based on the Rhine Monitoring Programme Chemistry with 13, resp. 26 individual values per substance. At individual measurement stations, some of the substances presented here are also subject to daily surveillance so that such a measurement series may also lead to higher maximum values than what is presented here. If daily values were available for the purpose of this report, they have been taken into account and are indicated in a footnote.

All in all, some 80 substances have been evaluated, among them 5 priority substances (PS, indicated in colour) for which an EQS exists since August 2013. According to the amending Directive 2013/39/EU, reporting on these substances is only obligatory as of 2018.

Table 2.4.2.1 represents the distribution of substances with respect to the levels of concentration. It is striking that, between 2009 and 2012, the mean annual value of no substance was above 1 µg/l (4th level). Most substances were found at the 1st concentration level that is with mean annual values below 10 ng/l. Due to the situation of data, none of the 19 substances of level "0" can be classified in one of the other levels.

For technical reasons, substances were even classified in level 1, when a threshold of measurement up to 0.05 µg/l was indicated for individual monitoring stations and the mean value as well as the maximum value of the annual series was below this threshold of measurement.

Few substances, for which values were only available at one monitoring station were not integrated into the table of substances below, as no preliminary classification is possible.

Table 2.4.2.1: Distribution of organic trace compounds on the defined levels of concentration (related to the mean annual value of six monitoring stations during 2009 to 2012)

	Classification criteria	Number	PS
Level 0	Insufficient data	19	
1st level	Concentrations below 0.01 µg/l	35	4
2nd level	Concentration between 0.01 and 0.1 µg/l	14	1
3rd level	Concentration between 0.1 and 1.0 µg/l	11	-
4th level	Concentration above 1.0 µg/l	-	-

Legend: **PS** = new priority substance according to Directive 2013/39/EU

Table 2.4.2.2: Classification of trace substances in levels of concentration
(Nr = Number of graph in Annex 1)

Classification of trace substances in levels of concentration					
No.	level 3	No.	level 1	No.	level 0
	Plant protection agents		Pharmaceuticals		Plant protection agents
1	AMPA	27	Clofibric acid	66	Dinitro-ortho-cresol (DNOC)
		28	Erythromycin	67	Dinoseb
	Other substances	29	Roxythromycin	68	Dinoterb
2	Aniline			69	Metazachlor
3	Amidotrizoe acid		Plant protection agents	70	Tebuconazole
4	ETBE	30	Chloridazon		
5	MTBE	31	iso-Chloridazon		Other substances
6	Iopamidole	32	Diazinon	71	Acenaphthene
7	Iopromide	33	Disulfoton	72	Anthranilic acid iso-propylamide (AIPA)
8	Diglyme	34	Desethylatrazine	73	Dibutylphthalate
9	Triglyme	35	Linuron	74	1.2-dichlorobenzene
10	Tetraglyme	36	Methabenzthiazuron	75	1.3-dichlorobenzene
11	TCPP	37	Metoxuron	76	2.6-dichloro-aniline
		38	Mevinphos	77	2.4-/2.5-dichloranilin compound
		39	Monolinuron	78	2.6 dimethylanilin
	Level 2	40	Pyrazofos	79	Musk xylene
	Pharmaceuticals	41	Terbutylazin	80	Nitrobenzene
12	Bezafibrate	42	Tolclofos-methyl	81	N,N-Diethylaniline
13	Carbamazepine	43	2,4,5-T	82	N,N-Dimethylaniline
14	Clarithromycin	44	Triazofos	83	2-nitrotoluene
15	Diclophenac			84	TCEP
16	Ibuprofen		Other substances		
17	Metoprolol	45	Acenaphthylene		
18	Soltalol	46	7H-Dodecafluorheptanoate (HPFHpA)		
19	Sulfamethoxazole	47	Perfluorpentanoate (PFPA)		
		48	Perfluorohexanoic acid (PFHxA)		
	Plant protection agents	49	Perfluoroheptanoic acid (PFHpA)		
20	Glyphosate	50	Perfluorooctanoic acid (PFOA)		
21	Metolachlor	51	Perfluorononanoic acid (PFNA)		
		52	Perfluorodecanoic acid (PFDA)		
	Other substances	53	Perfluoroundecanoic acid (PFUnA)		
22	PFBA (perfluorobutanoic acid)	54	Perfluorododecanoic acid (PFDoA)		
23	Perfluorobutanesulfonic acid (PFBS)	55	2H, 2H-perfluorodecanoic acid (PFDA)		
24	TPPO	56	2H,2H,3H,3H-Perfluoroundecanoic acid		

Classification of trace substances in levels of concentration					
No.	level 3	No.	level 1	No.	level 0
25	HHCB (galaxolid)	57	1H,1H,2H,2H-Perfluorooctanesulfonic acid (H4PFOS)		
26	PFOS	58	Perfluorohexane sulfonic acid (PFHxS)		
		59	Perfluorodecyle sulfonic acid (PFDS)		
		60	Perfluorooctanesulfonamide (PFOSA)		
		61	Tetrabrombisphenol A		
			Concerning level 1 (new priority substances)		
			Plant protection agents		
		62	Cypermethrin		
		63	Irgarol (Cybutryn)		
		64	Heptachlor/heptachlor epoxide		
		65	Terbutryne		

2.4.3 Conclusion

The classification according to the described groups/levels of concentration shows which substances were found in the Rhine between 2009 and 2012 in what concentrations. According to data of 2012, among the new priority substances according to the Directive 2013/39/EU PFOS is in excess of the EQS. For the other substances, the limits of quantification must be adapted to the analytical methods in order to be able to check on the respect of the EQS.

3. Summary and outlook

The different international water quality evaluation systems applicable to the Rhine catchment: (i) the EU environmental quality standards (EQS), (ii) the environmental quality standards for the Rhine catchment (EQS Rhine) and (iii) the ICPR target values have been brought together into one comprehensive evaluation concept.

For 39 priority substances, groups of substances or sum total parameters of the Directive 2008/105/EC the values monitored at the international main monitoring stations Weil am Rhein, Lauterbourg/Karlsruhe, Koblenz Rhine, Bimmen and Lobith and Koblenz Moselle between 2009 and 2012 were **below** the Environmental Quality Standards.

Among the substances the values of which are below the EQS figure heavy metals, almost all polycyclic hydrocarbons (PAH), plant protection agents.

The only priority substance **in excess** of the EQS during almost the entire period mentioned and at all monitoring stations mentioned is benzo(ghi)perylene. Atmospheric deposition is the main input pathway into surface water of this substance mainly originating from incineration processes. It is expected that transgression of the EQS will continue at most monitoring stations.

During 2009-2012, the river-specific substances also called **substances relevant for the Rhine**, for which EQS Rhine have been derived following the rules of the WFD, were **below** the **EQS Rhine** at all monitoring stations.

Under the "Rhine Action Programme", **target values** were derived for 77 individual substances/sum parameters. These target values are recommendations. Since, for 9 substances, no EQS or EQS-Rhine exist for the sediments as asset of protection, the target values continue to be applied as international evaluation standard for water quality. Among these substances, measurements for heavy metals, zinc, mercury, cadmium and PCBs along the Lower Rhine are **distinctly above** the target values. While, for 3 heavy metals, measurements at all monitoring stations are near the target values, those of ammonium-N and lead are partly near and partly above the target values. The positive trend registered for ammonium-nitrogen during 1990 to 2006 (see ICPR report no. 193) is continuing. We may summarize that the problem of ammonium-N in the Rhine has been solved.

Since water from the Rhine is also used for producing drinking water for some 30 million people, the monitoring values for 12 substances are also compared to standards for surface waters used for **drinking water production** (according to the Directive 98/83/EC) applicable in the European Union. Among these substances, the values of the plant protection agents chlorotoluene and diuron are **above** the drinking water values at the mouth of R. Moselle, those for isoproturon are **in excess of** drinking water values at two monitoring stations along the Rhine as well as at the monitoring station Koblenz-Moselle.

Apart from substances, for which an EQS or an ICPR target value exists, some 80 further organic trace components are measured within the Rhine Monitoring Programme Chemistry. In a graph for the monitoring years 2009 to 2012 and at the ICPR monitoring stations Weil am Rhein, Lauterburg-Karlsruhe, Koblenz/Rhein, Bimmen, Lobith and Koblenz/Moselle these substances have been evaluated for 4 levels of concentration.

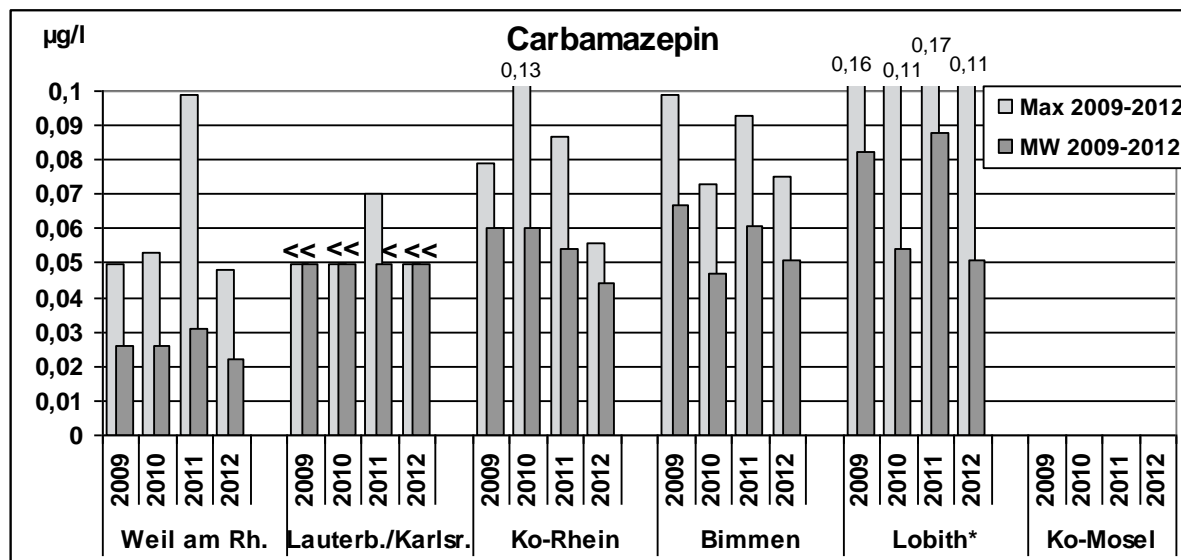
Table 2.4.2.1 represents the distribution of substances with respect to the levels of concentration. It is striking that between 2009 and 2012, the mean annual value of no substance was classified in the 4th level, most were classified in the 1st level, 19 substances were at level "0". Due to the situation of data, none of the latter substances can be classified in one of the other levels.

Among the Rhine bordering countries Switzerland, France, Germany and the Netherlands only Switzerland applies slimit values for drinking water (for volatile chlorinated hydrocarbons) than those of the Directive 98/83/EC.

Legend and graphs for substances without evaluation criteria

Legend for Figures 1 to 84

Carbamazepine is used as an example to explain the contents of the graphs.



The graphs represent the maximum value and, overlapping towards the front - the mean value of an annual measurement series for 6 monitoring stations during the period 2009-2012.

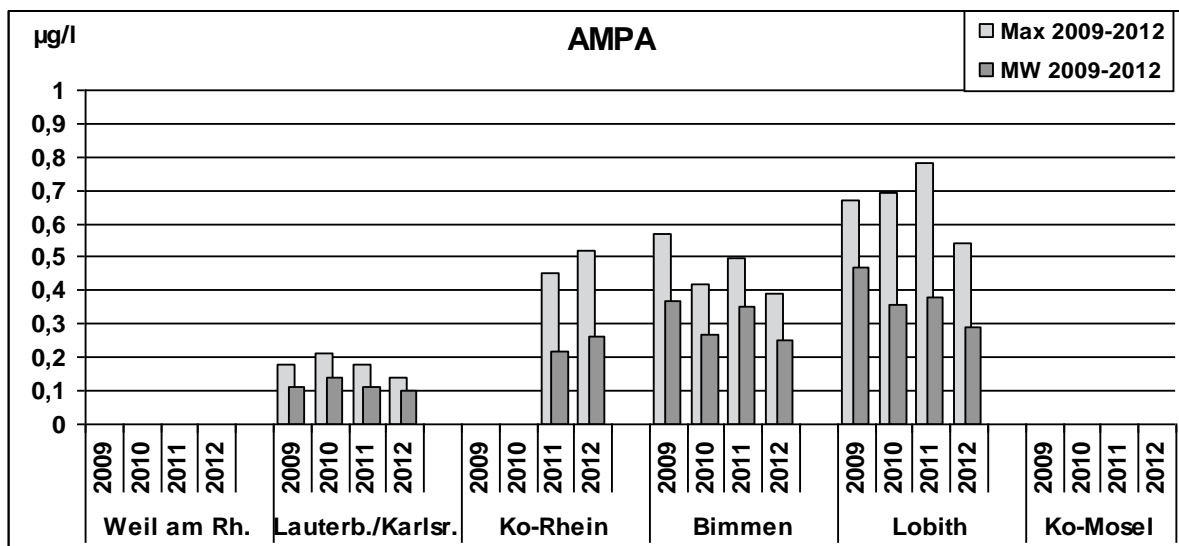
If the maximum value is in excess of the scale given, the numeric value figures above the bar.

"<" above the bar means: the mean value of all monitoring values or the maximum values is lower than the limit of quantification or the reporting limit at the monitoring station concerned.

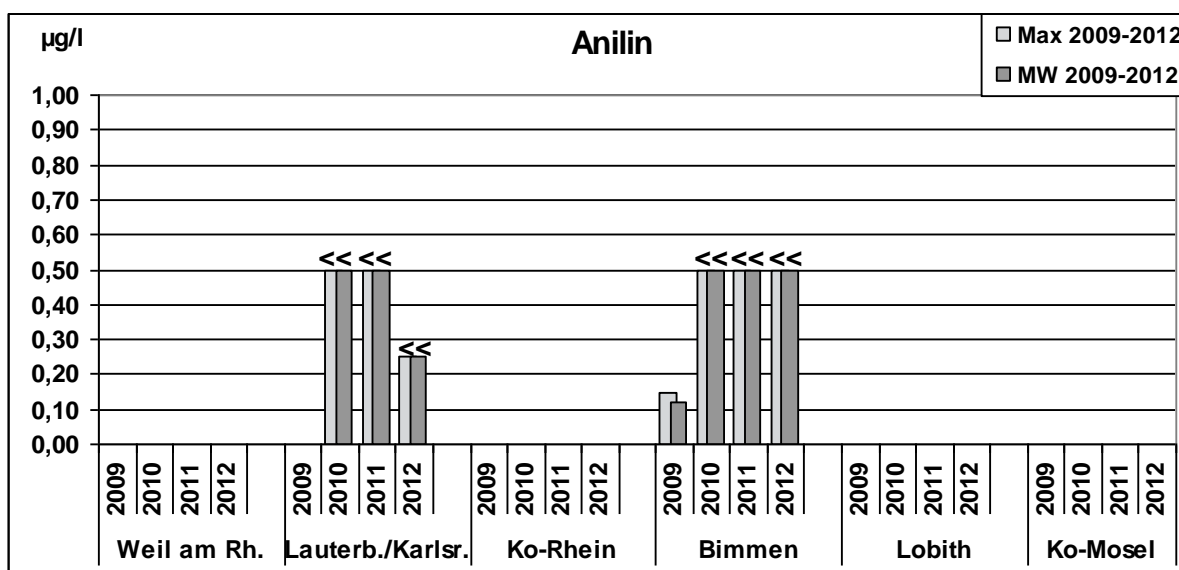
The Lobith monitoring station is marked with an asterisk, if RIWA-data (Dutch association of river water works) were used for this monitoring station.

11 substances of the concentration level 3

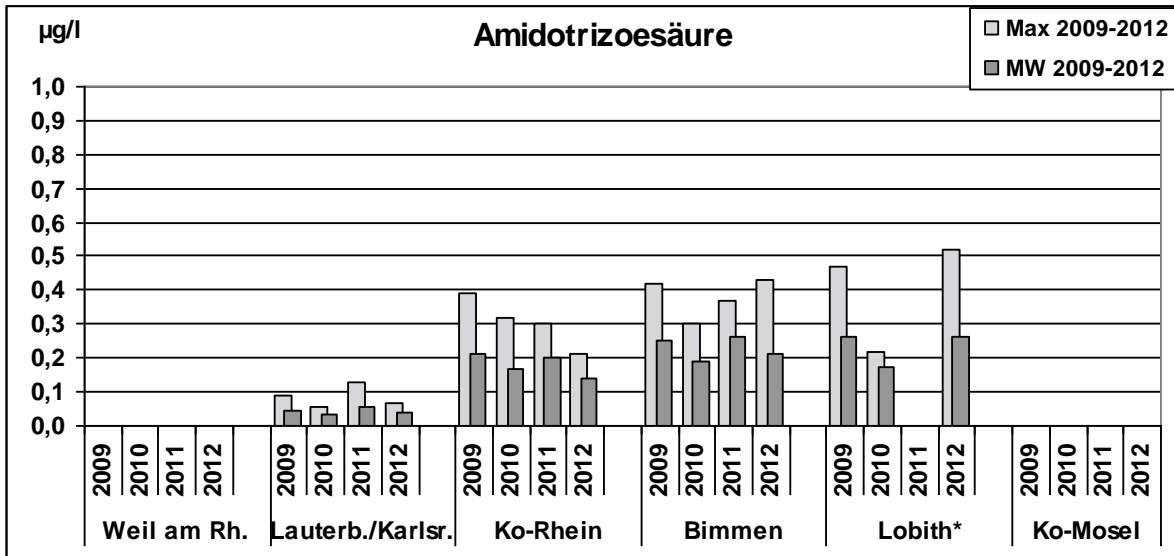
Graph 1 AMPA: Maximum (max) and mean (MW) values between 2009 and 2012



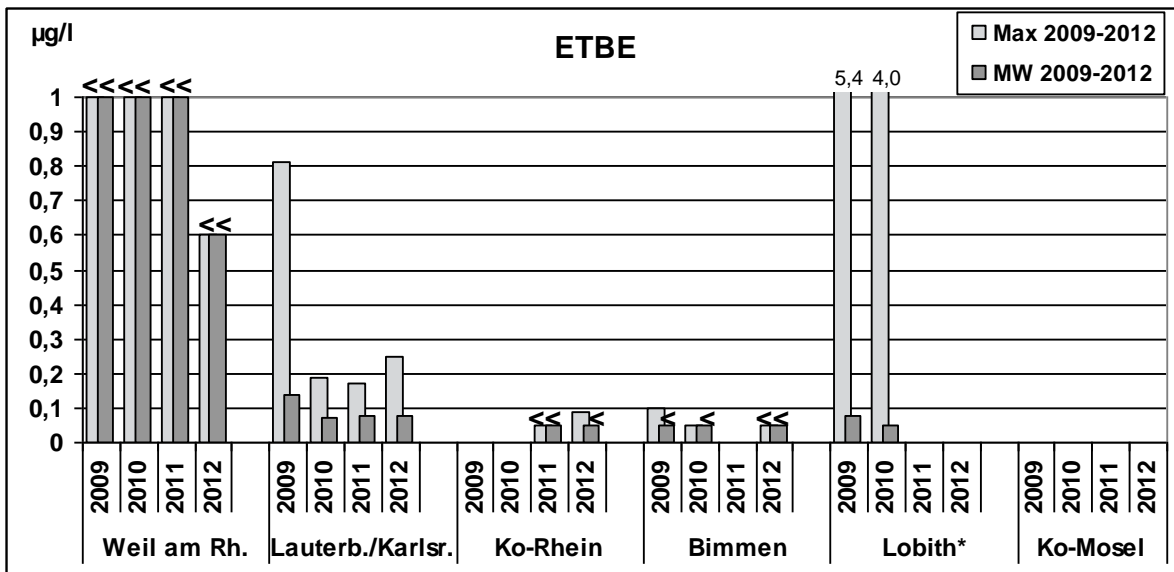
Graph 2 Aniline: Maximum (max) and mean (MW) values between 2009 and 2012



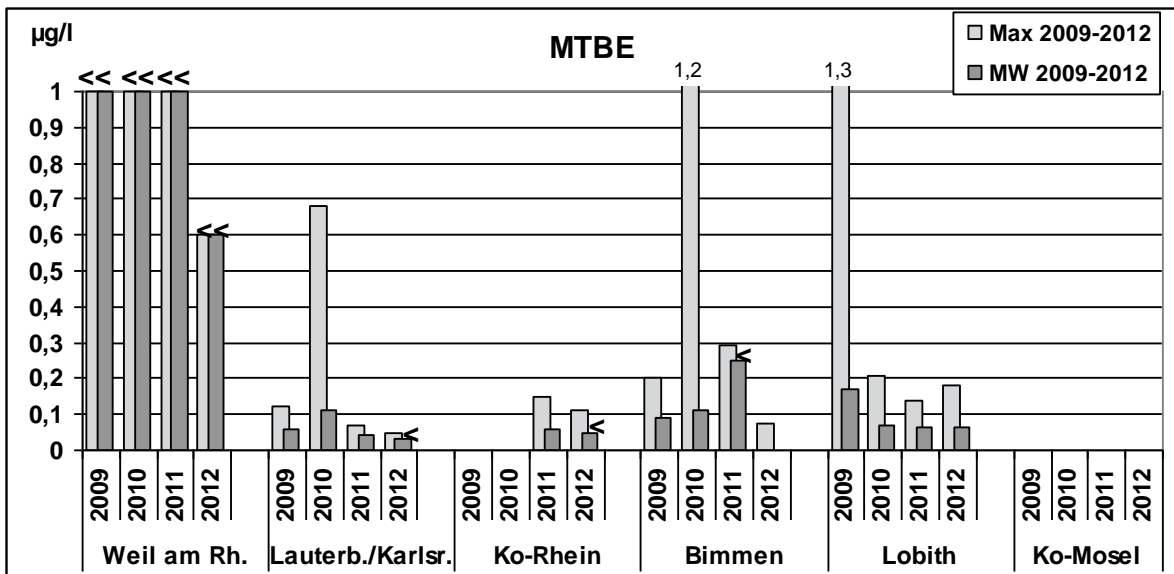
Graph 3 Amidotrizoee acid: Maximum (max) and mean (MW) values between 2009 and 2012



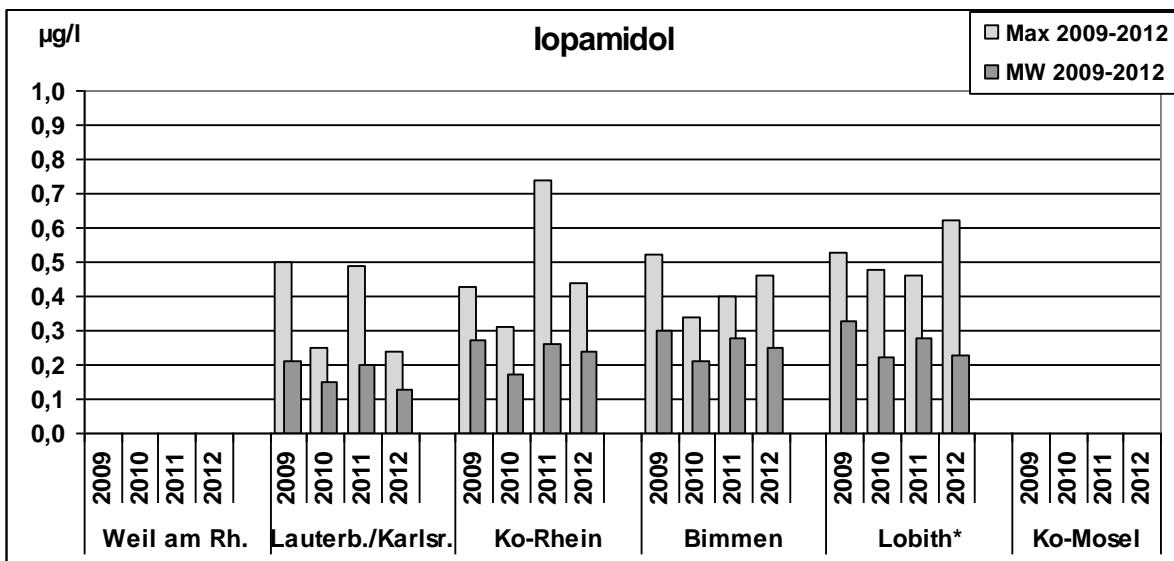
Graph 4 ETBE: Maximum (max) and mean (MW) values between 2009 and 2012



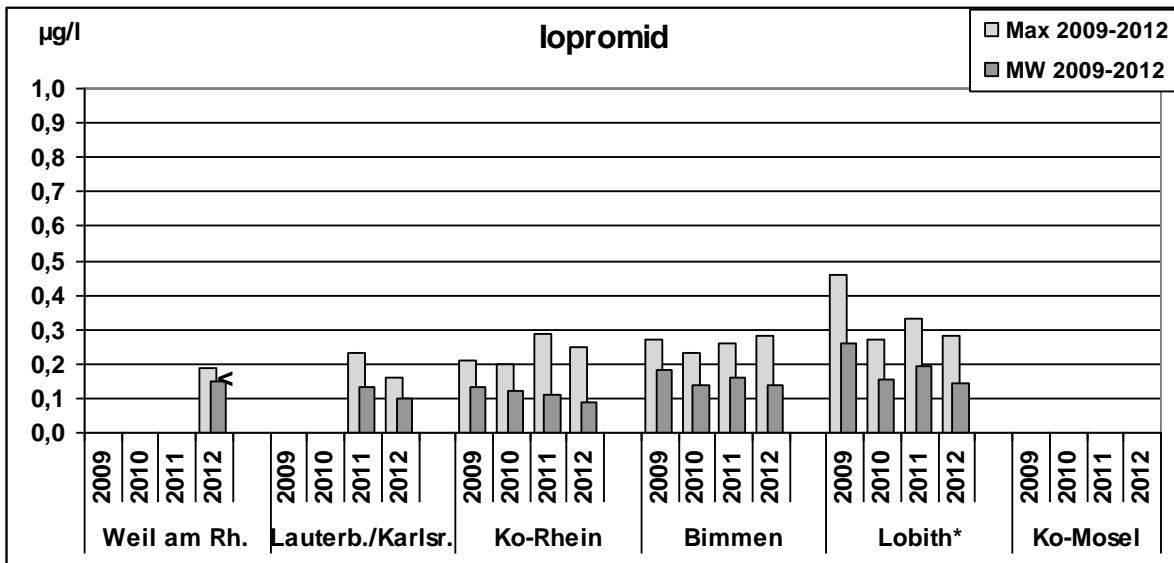
Graph 5 MTBE: Maximum (max) and mean (MW) values between 2009 and 2012



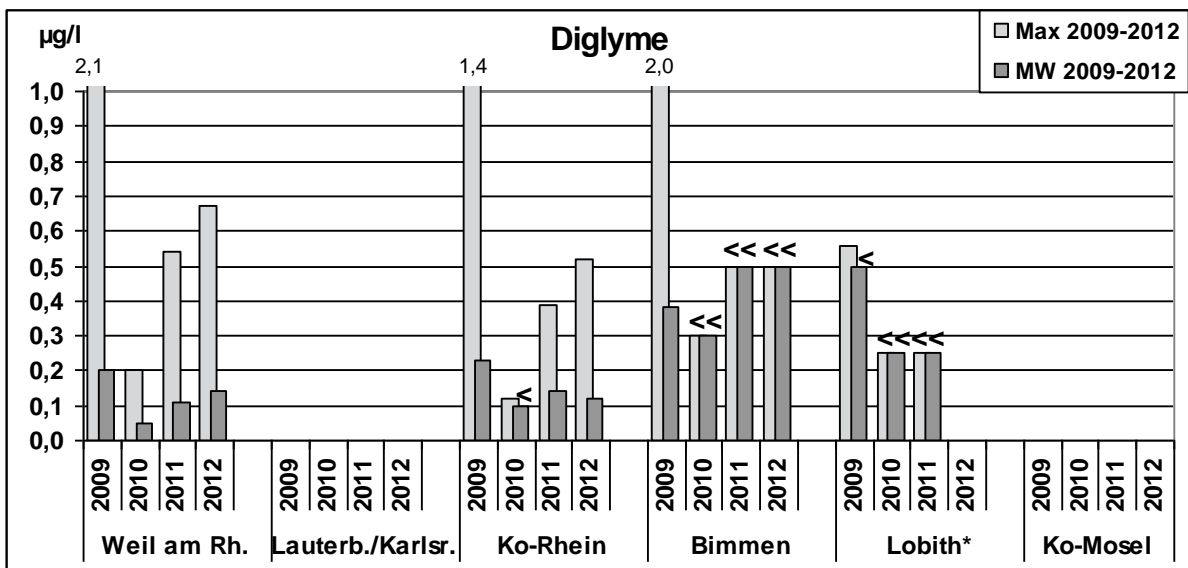
Graph 6 Iopamidole: Maximum (max) and mean (MW) values between 2009 and 2012



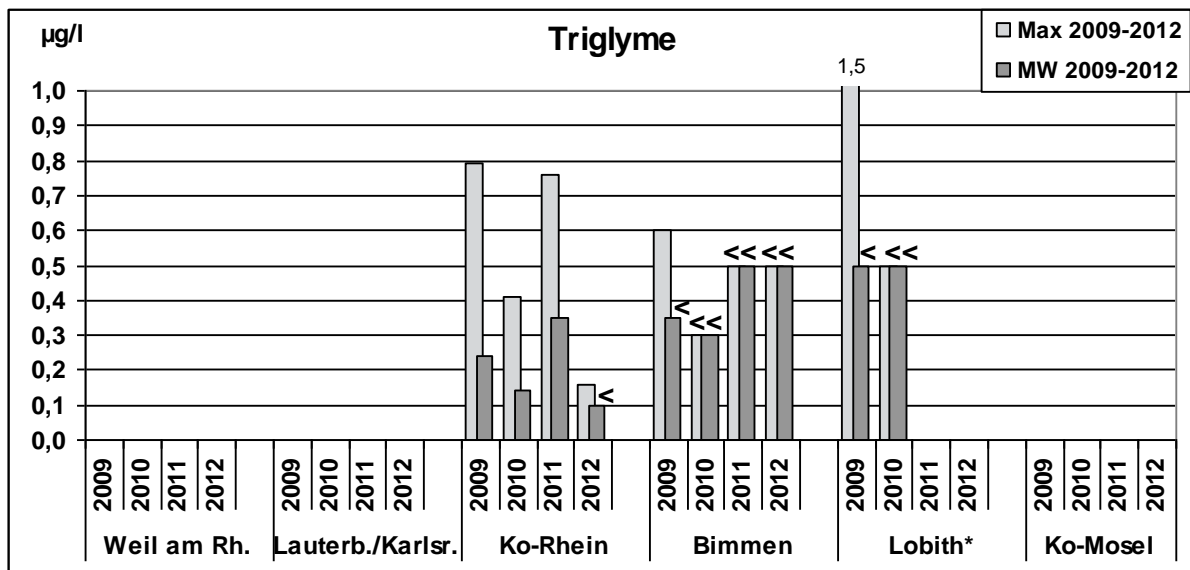
Graph 7 Iopromide: Maximum (max) and mean (MW) values between 2009 and 2012



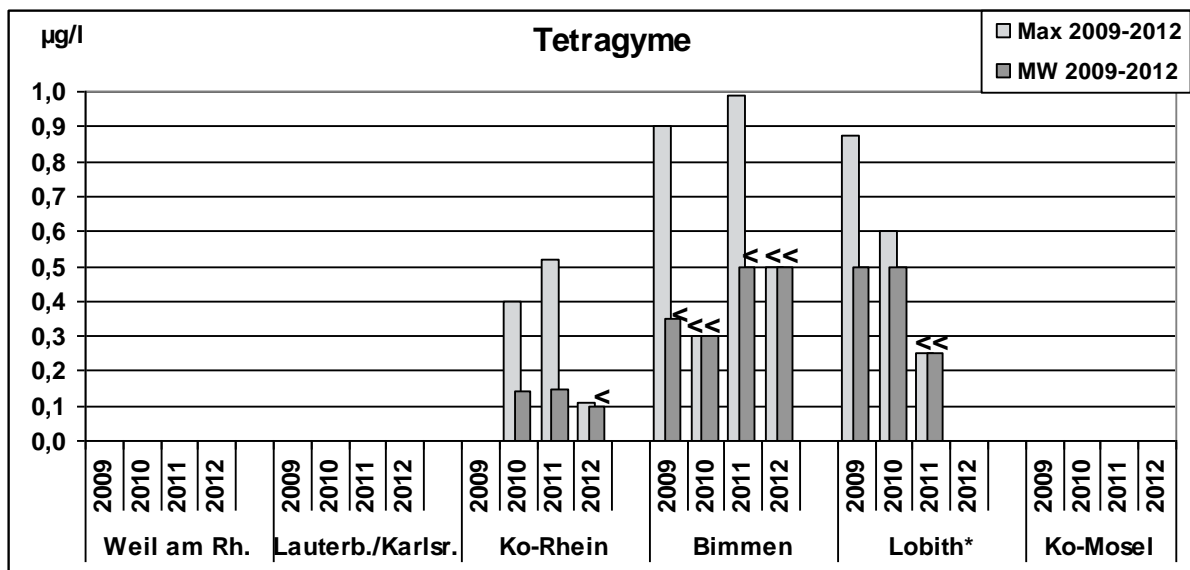
Graph 8 Diglyme: Maximum (max) and mean (MW) values between 2009 and 2012



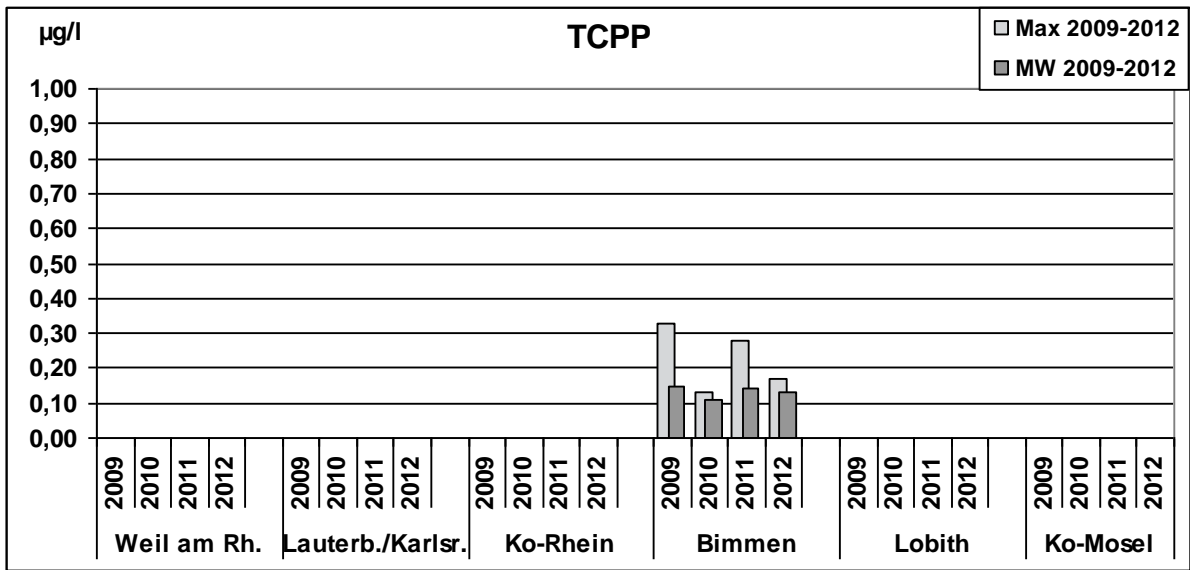
Graph 9 Triglyme: Maximum (max) and mean (MW) values between 2009 and 2012



Graph 10 Tetraglyme: Maximum (max) and mean (MW) values between 2009 and 2012

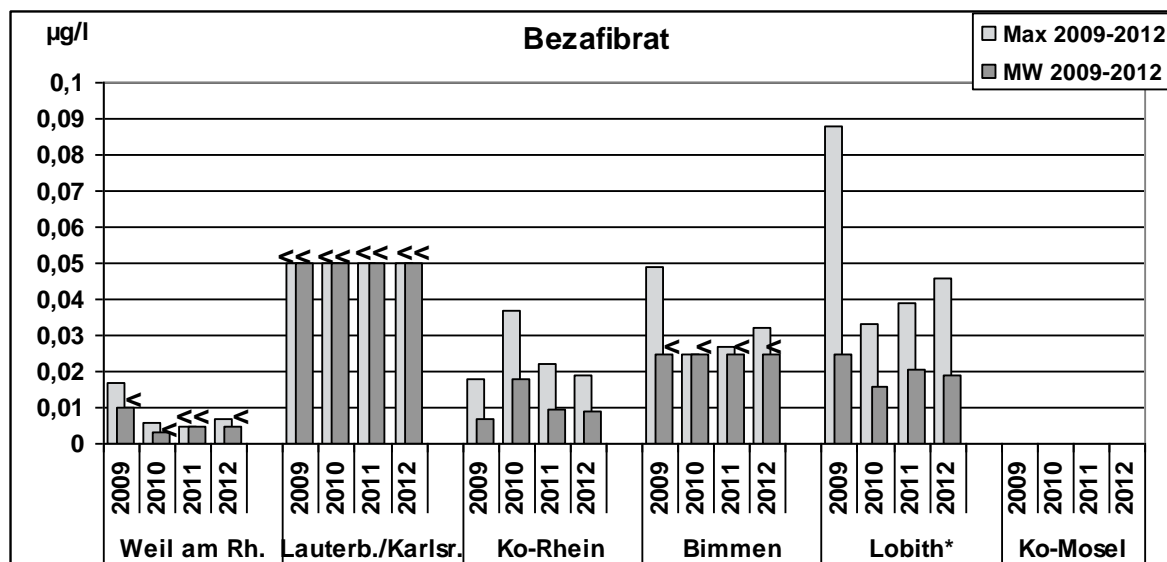


Graph 11 TCPP: Maximum (max) and mean (MW) values between 2009 and 2012

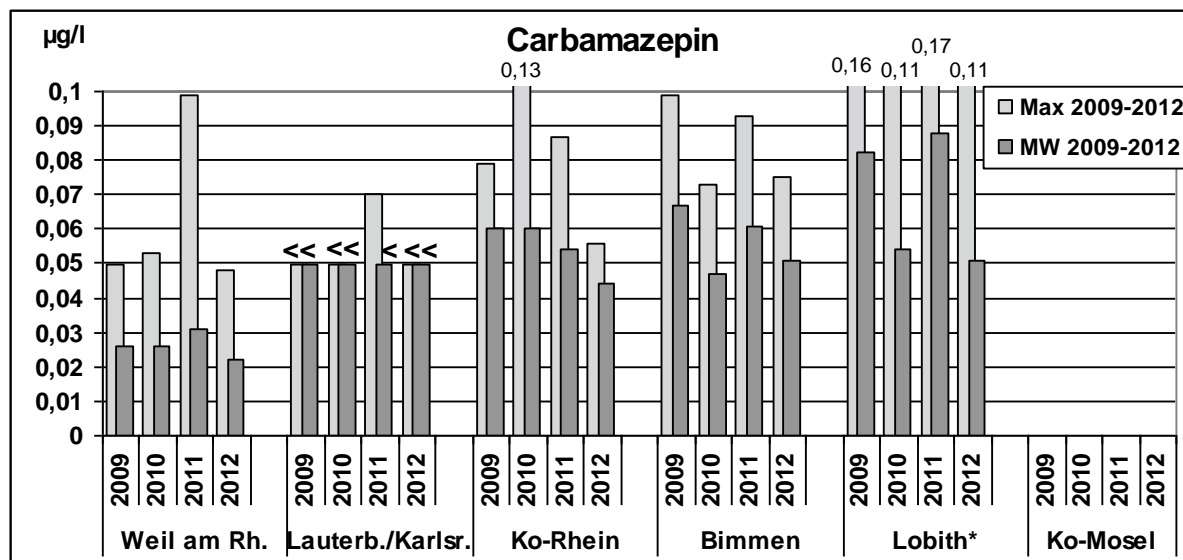


14 substances belonging to the concentration level 2 (+ 1 new priority substance)

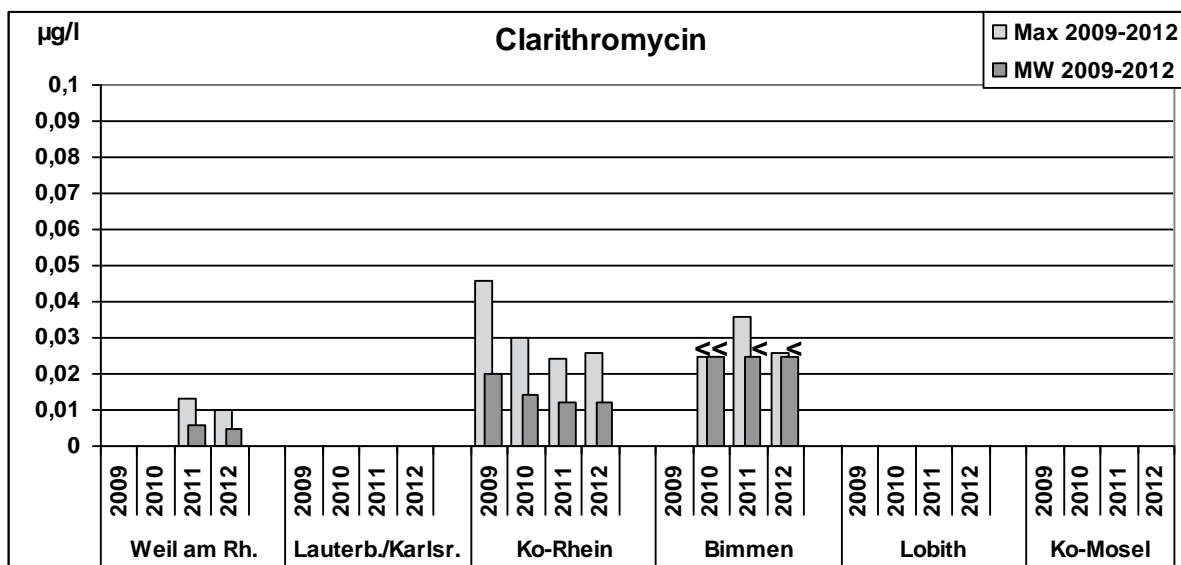
Graph 12 Bezafibrate: Maximum (max) and mean (MW) values between 2009 and 2012



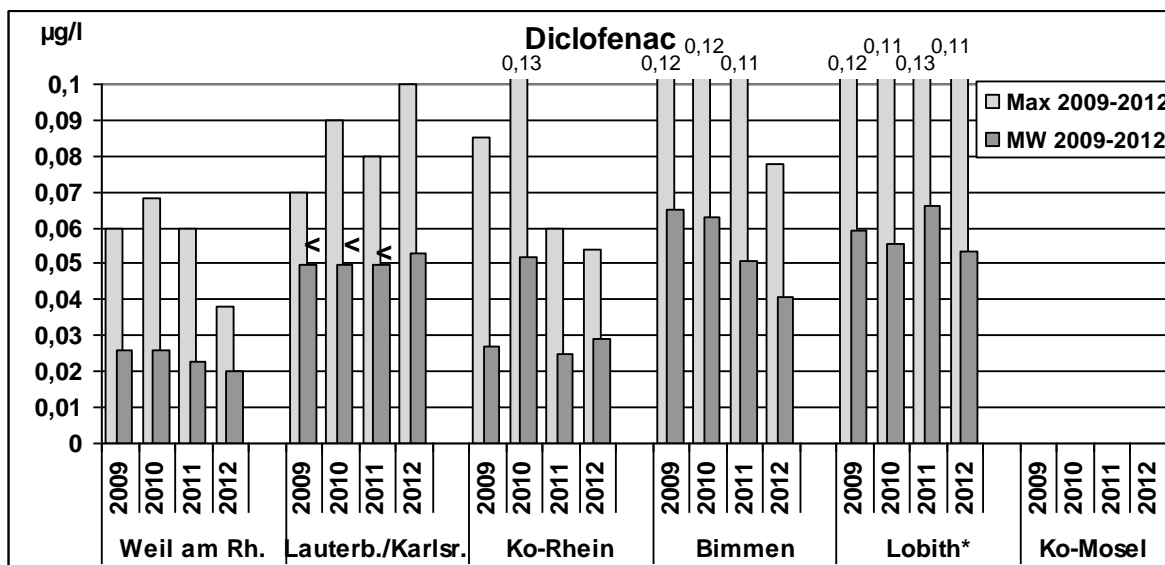
Graph 13 Carbamazepin: Maximum (max) and mean (MW) values between 2009 and 2012



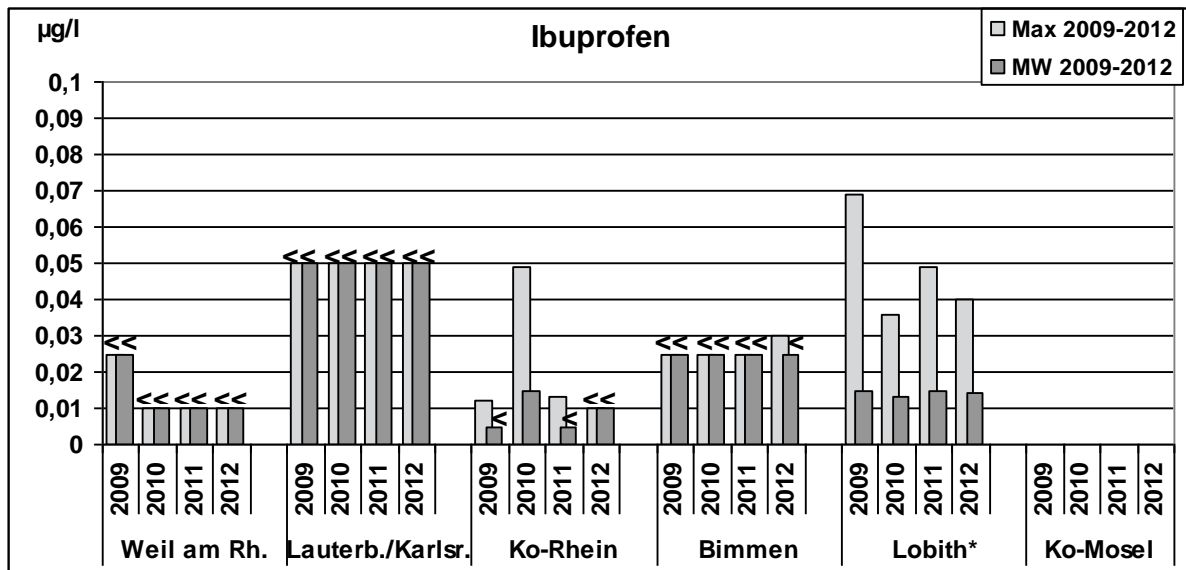
Graph 14 Clarithromycin: Maximum (max) and mean (MW) values between 2009 and 2012



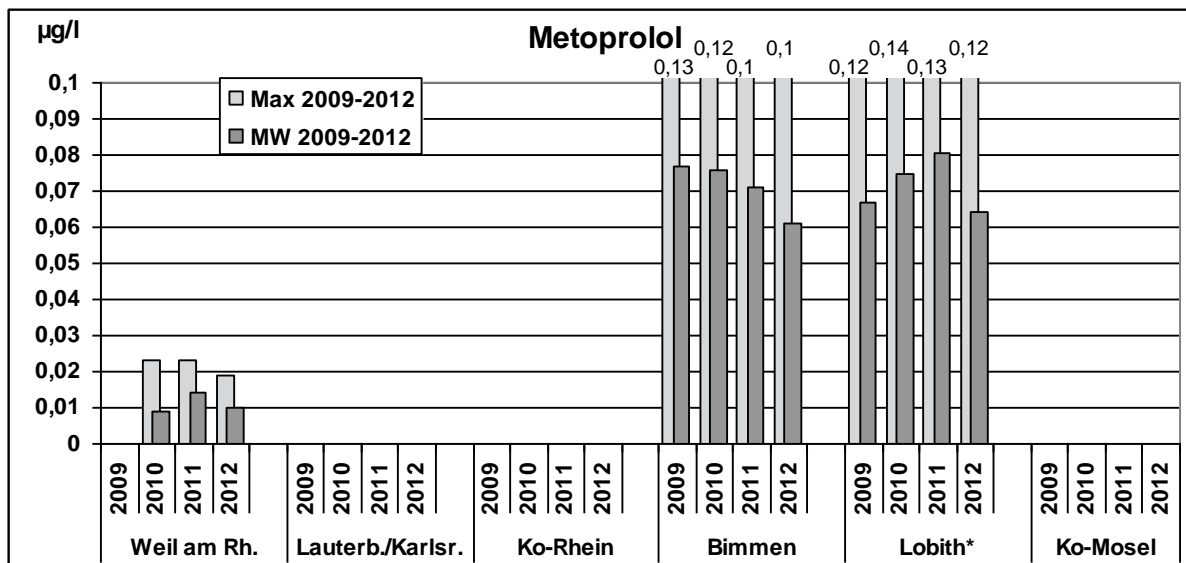
Graph 15 Diclofenac: Maximum (max) and mean (MW) values between 2009 and 2012



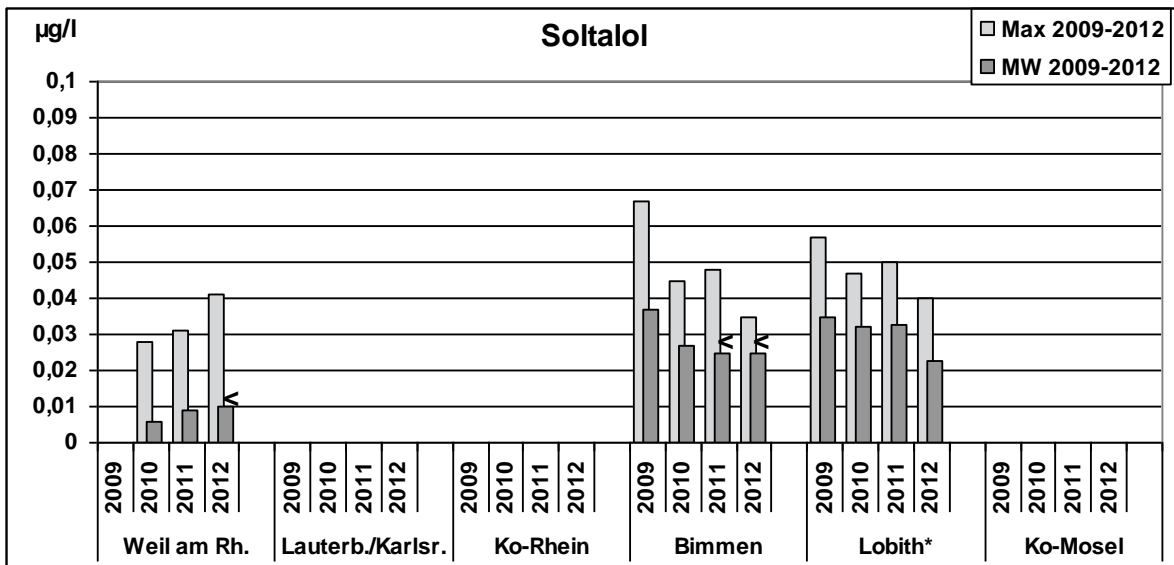
Graph 16 Ibuprofen: Maximum (max) and mean (MW) values between 2009 and 2012



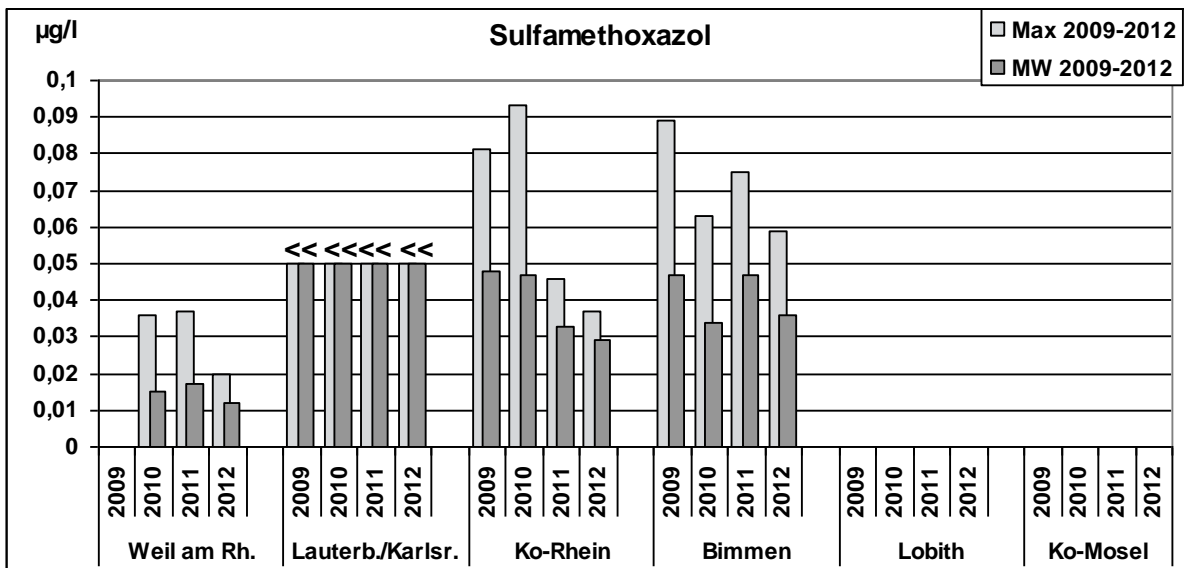
Graph 17 Metoprolol: Maximum (max) and mean (MW) values between 2009 and 2012



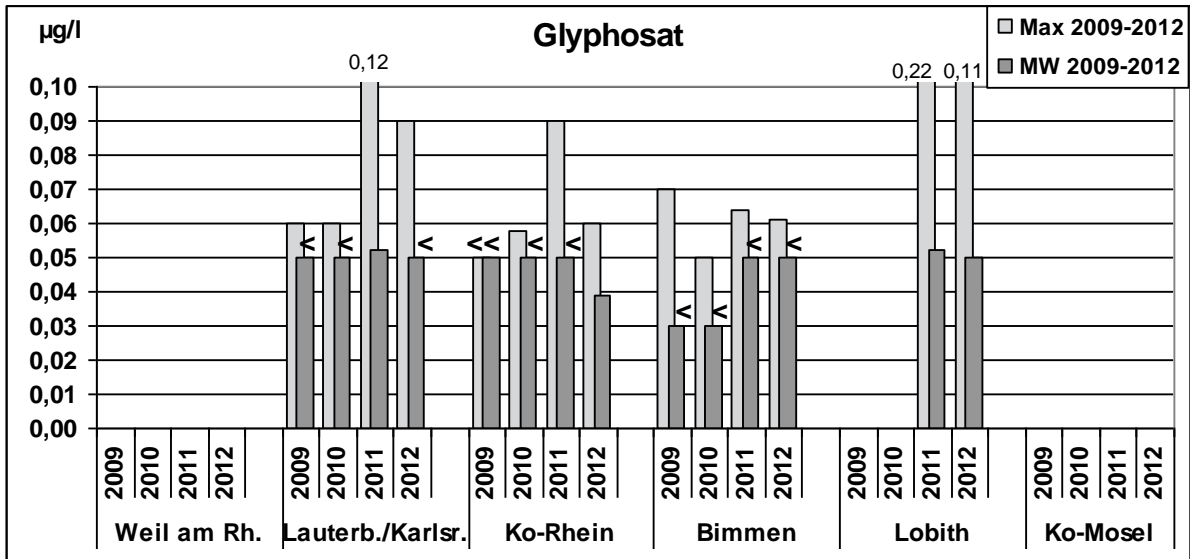
Graph 18 Soltalol: Maximum (max) and mean (MW) values between 2009 and 2012



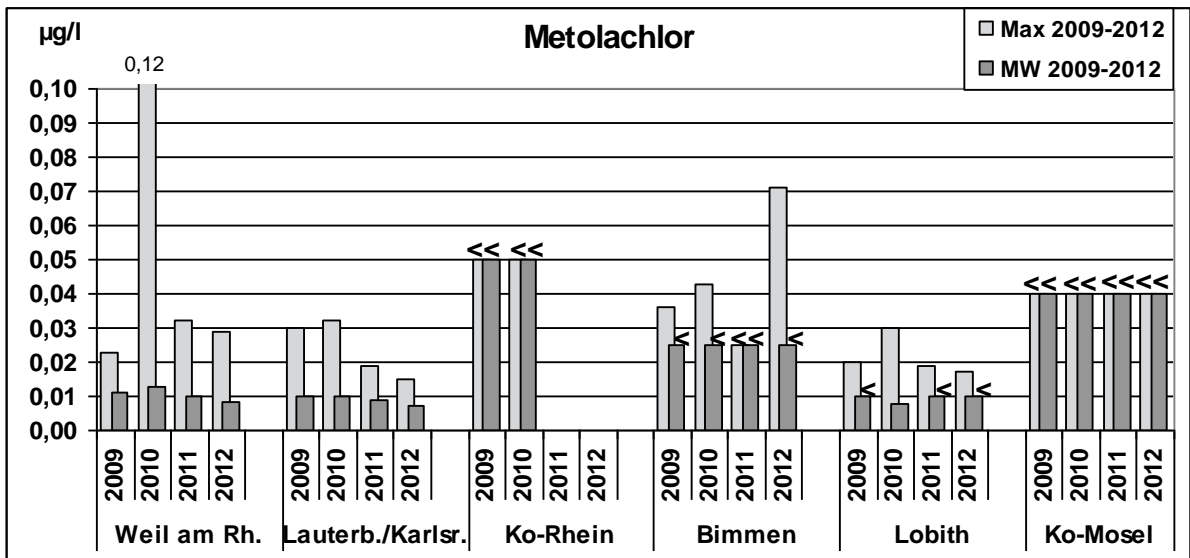
Graph 19 Sulfamethocazole: Maximum (max) and mean (MW) values between 2009 and 2012



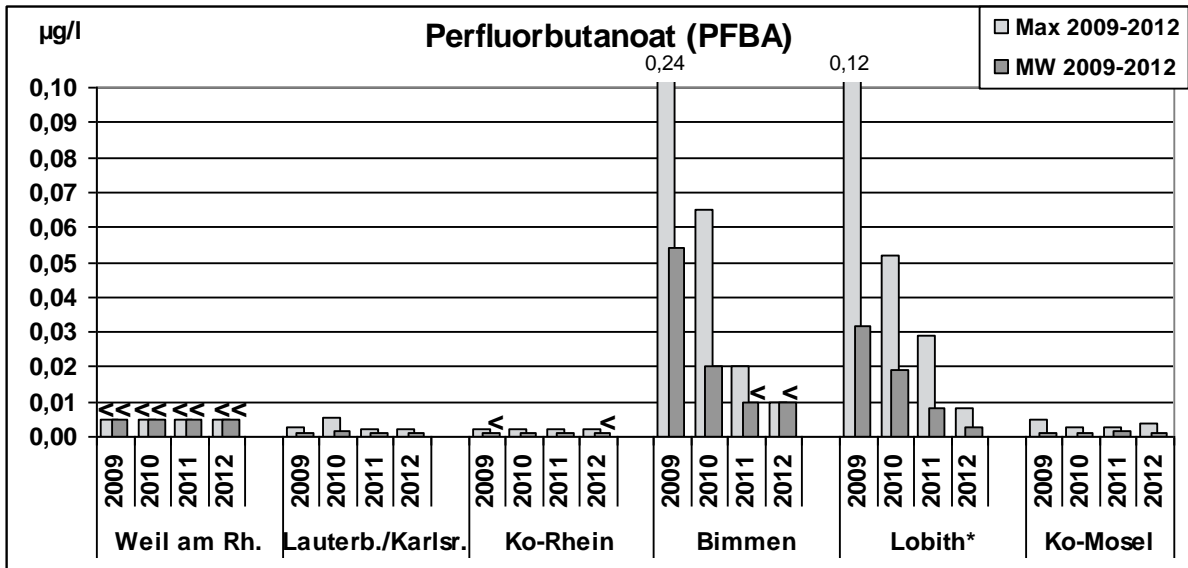
Graph 20 Glyphosate: Maximum (max) and mean (MW) values between 2009 and 2012



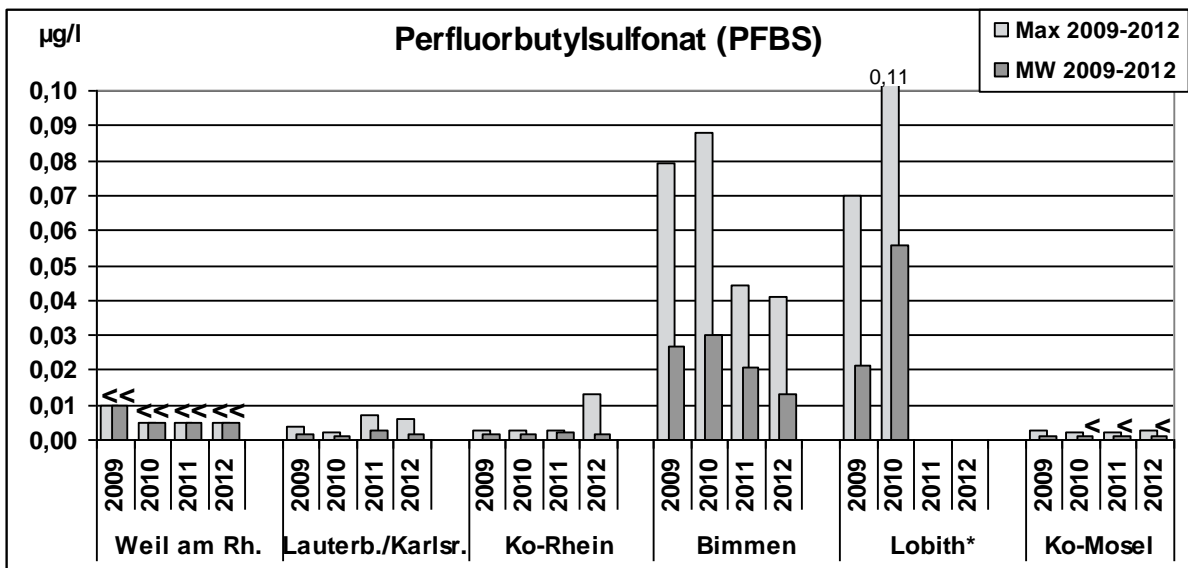
Graph 21 Metolachlor: Maximum (max) and mean (MW) values between 2009 and 2012



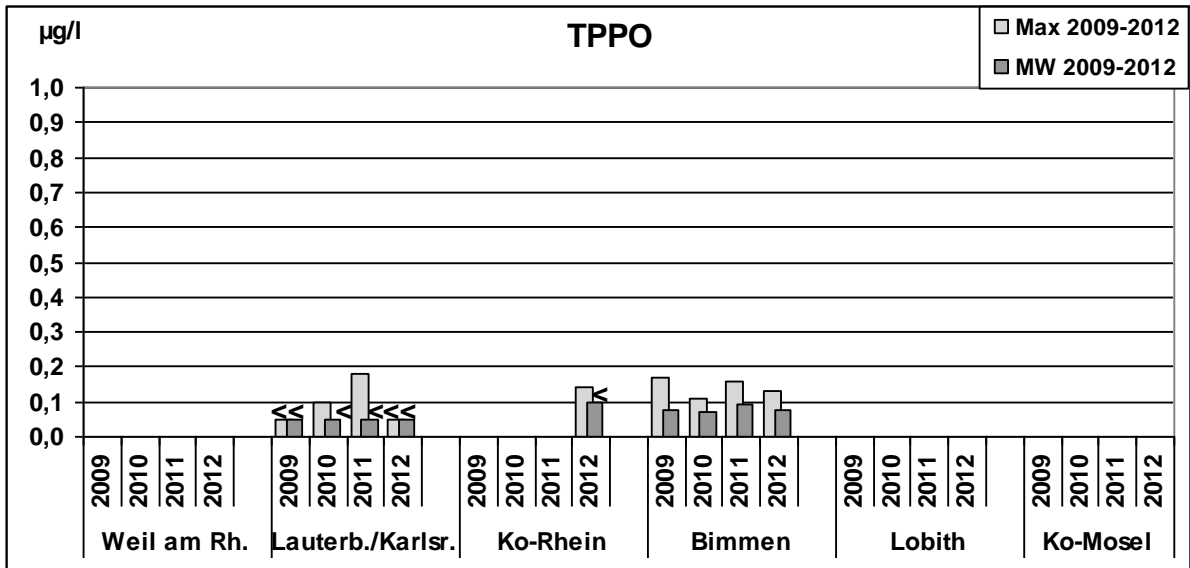
Graph 22 PFBA: Maximum (max) and mean (MW) values between 2009 and 2012



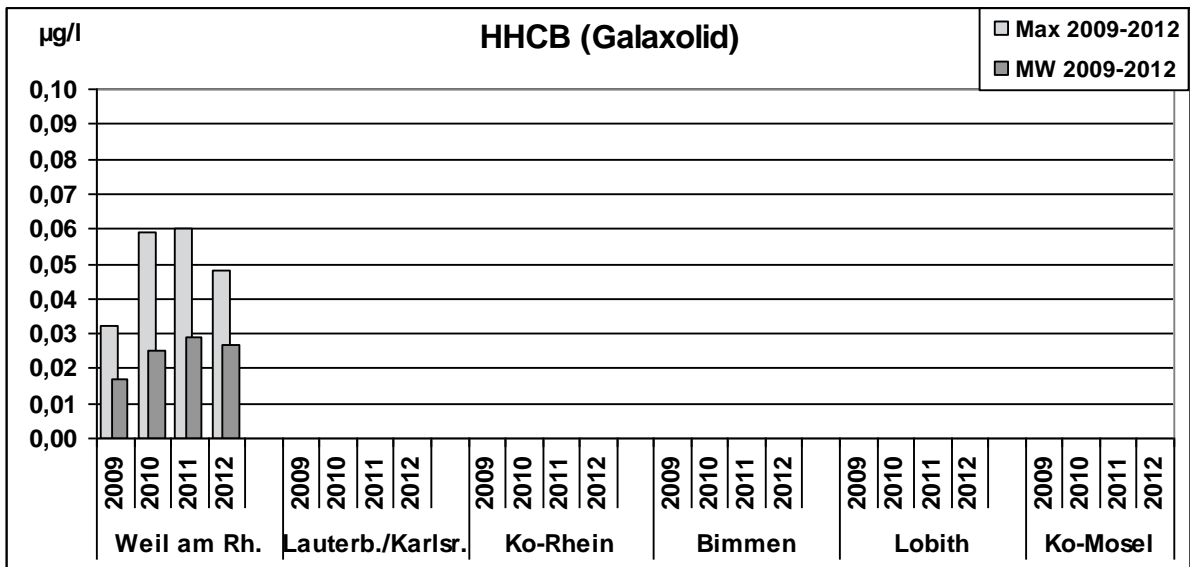
Graph 23 PFBS: Maximum (max) and mean (MW) values between 2009 and 2012



Graph 24 TPPO: Maximum (max) and mean (MW) values between 2009 and 2012

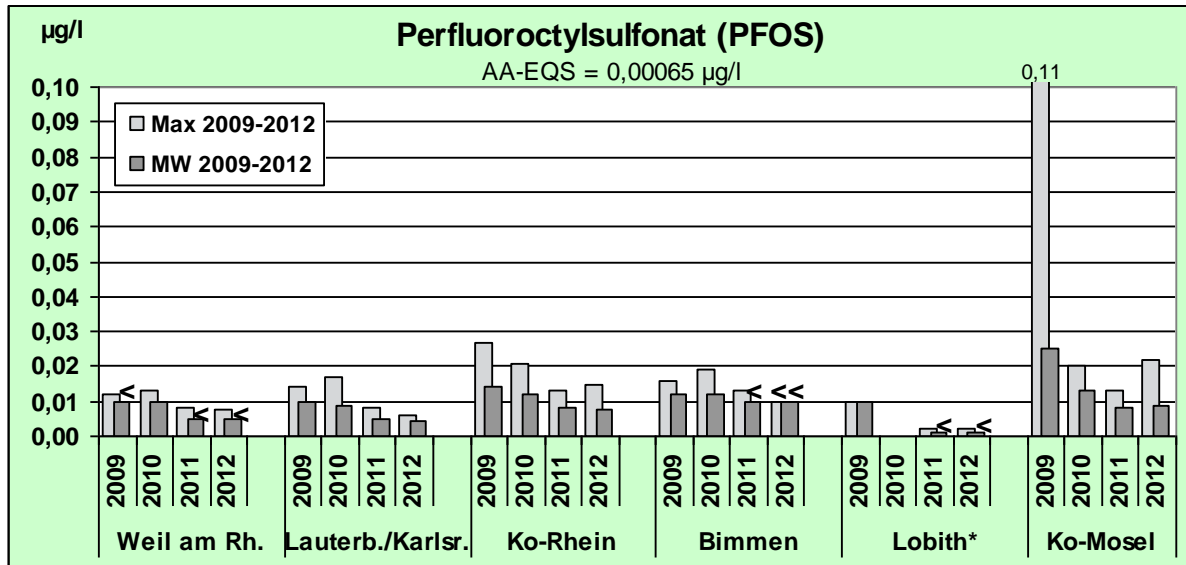


Graph 25 HHCB (Galaxolid): Maximum (max) and mean (MW) values between 2009 and 2012



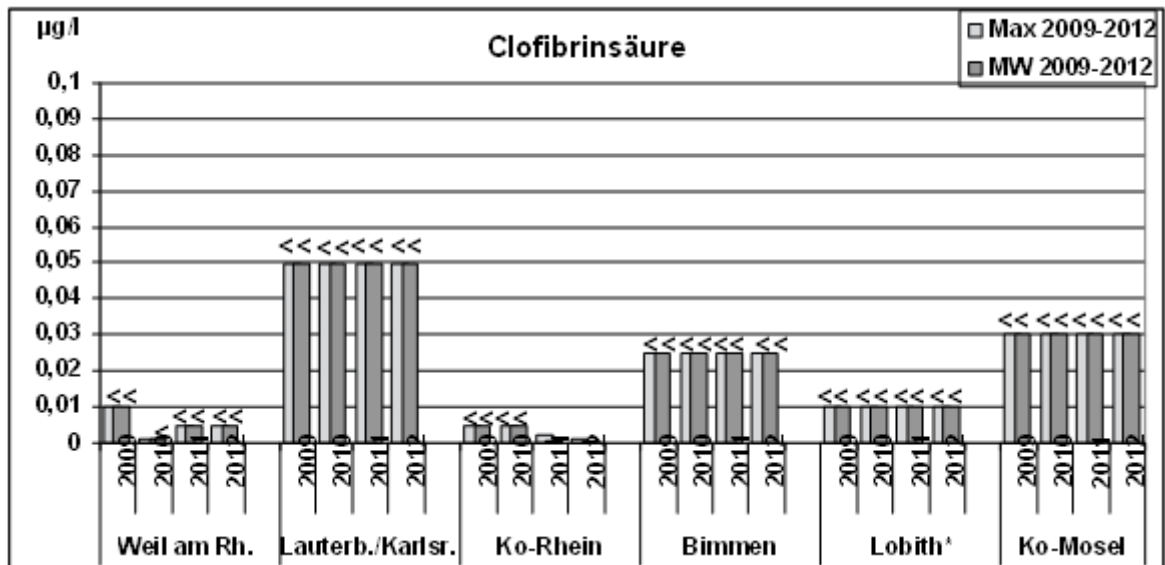
New priority substance according to Directive 2013/39/EU

Graph 26 PFOS: Maximum (max) and mean (MW) values between 2009 and 2012

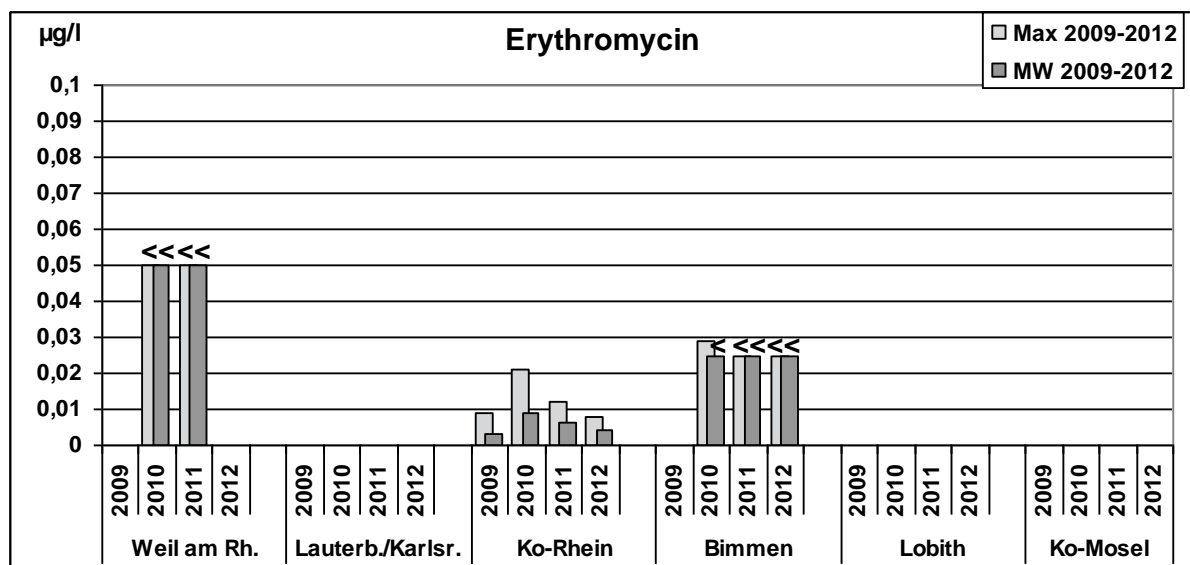


5 substances belonging to the concentration level 1 (+ 4 new priority substances)

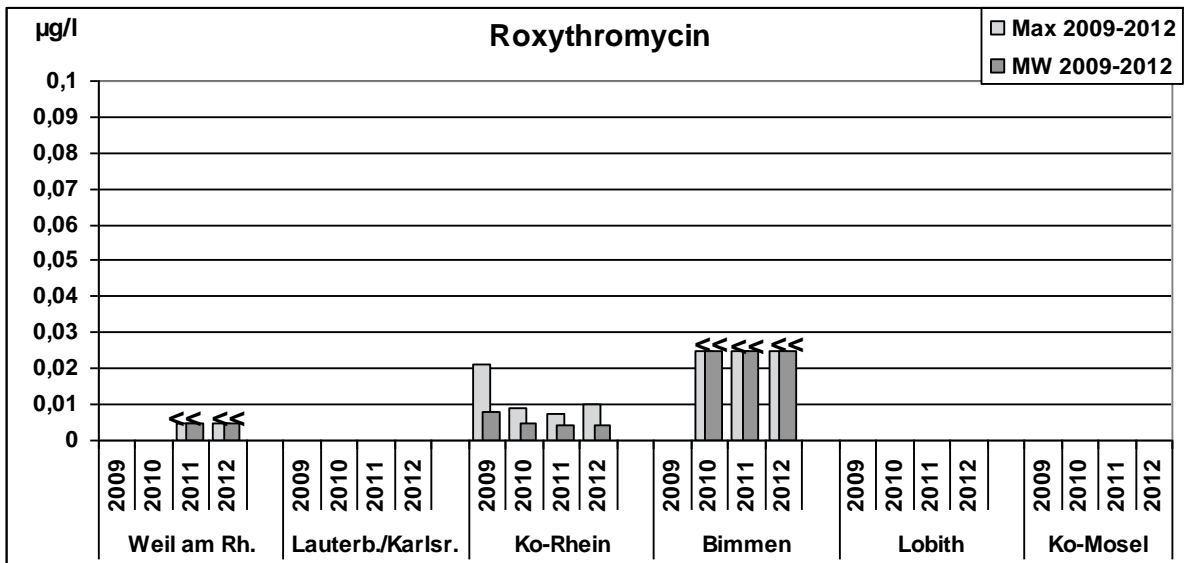
Graph 27 Clofibric acid: Maximum (max) and mean (MW) values between 2009 and 2012



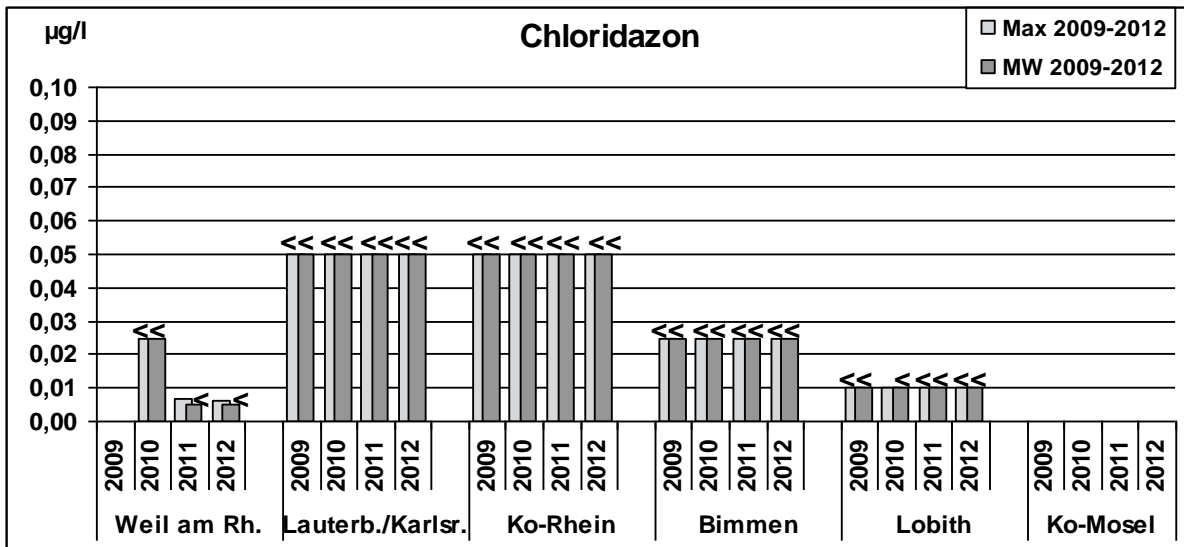
Graph 28 Erythromycin: Maximum (max) and mean (MW) values between 2009 and 2012



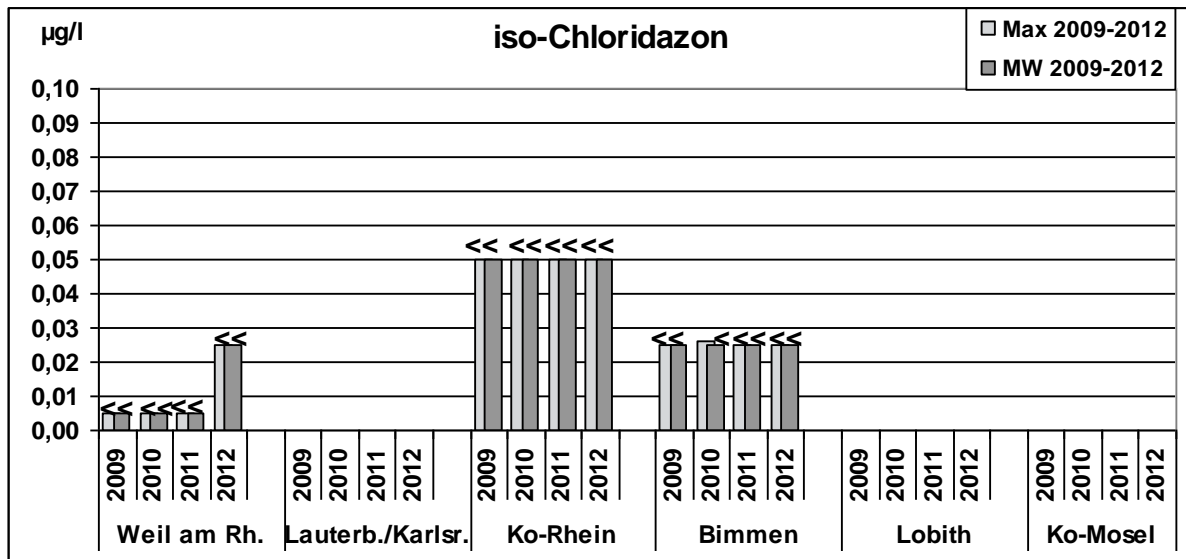
Graph 29 Roxythromycin: Maximum (max) and mean (MW) values between 2009 and 2012



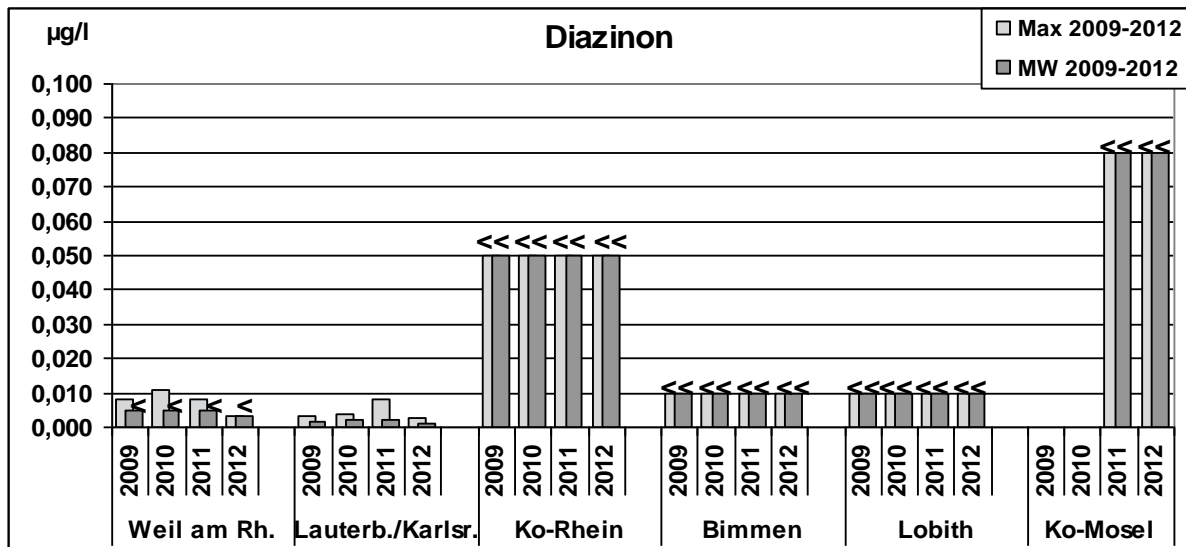
Graph 30 Chloridazon: Maximum (max) and mean (MW) values between 2009 and 2012



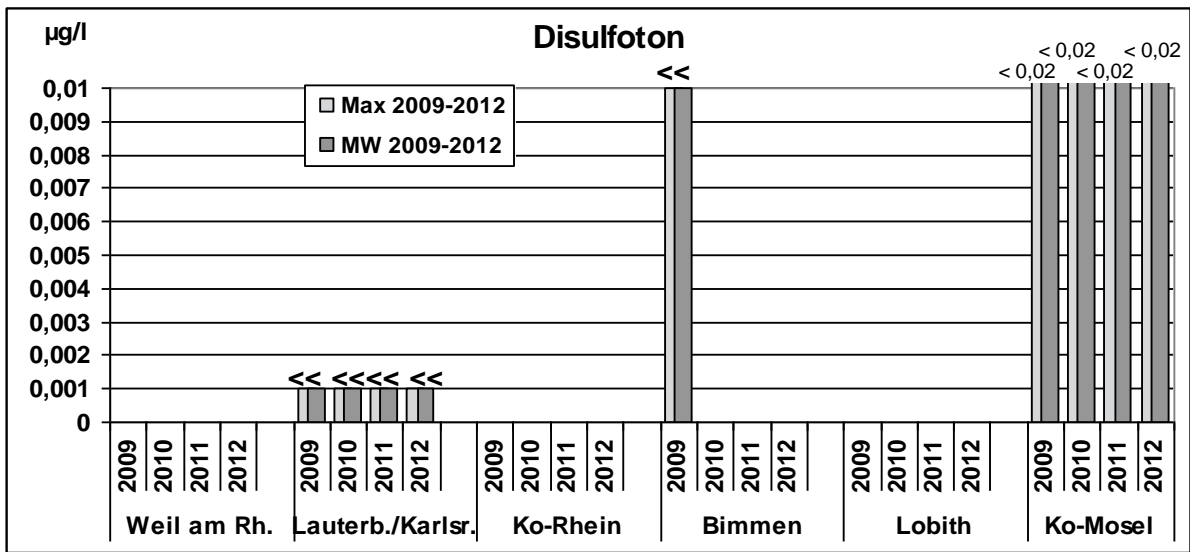
Graph 31 iso-Chloridazon: Maximum (max) and mean (MW) values between 2009 and 2012



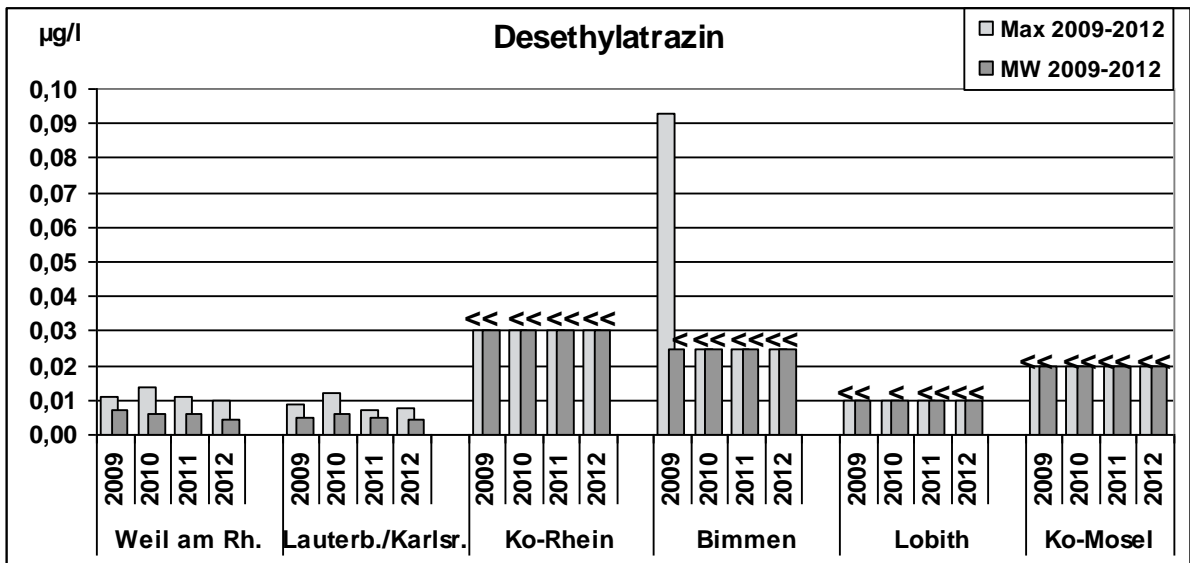
Graph 32 Diazinon: Maximum (max) and mean (MW) values between 2009 and 2012



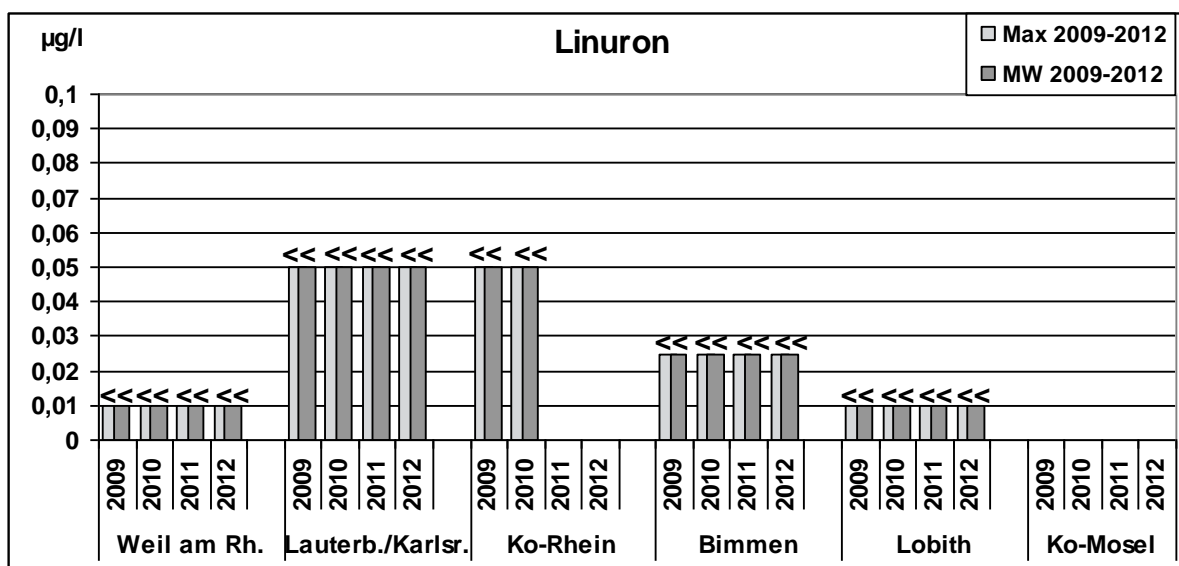
Graph 33 Disulfoton: Maximum (max) and mean (MW) values between 2009 and 2012



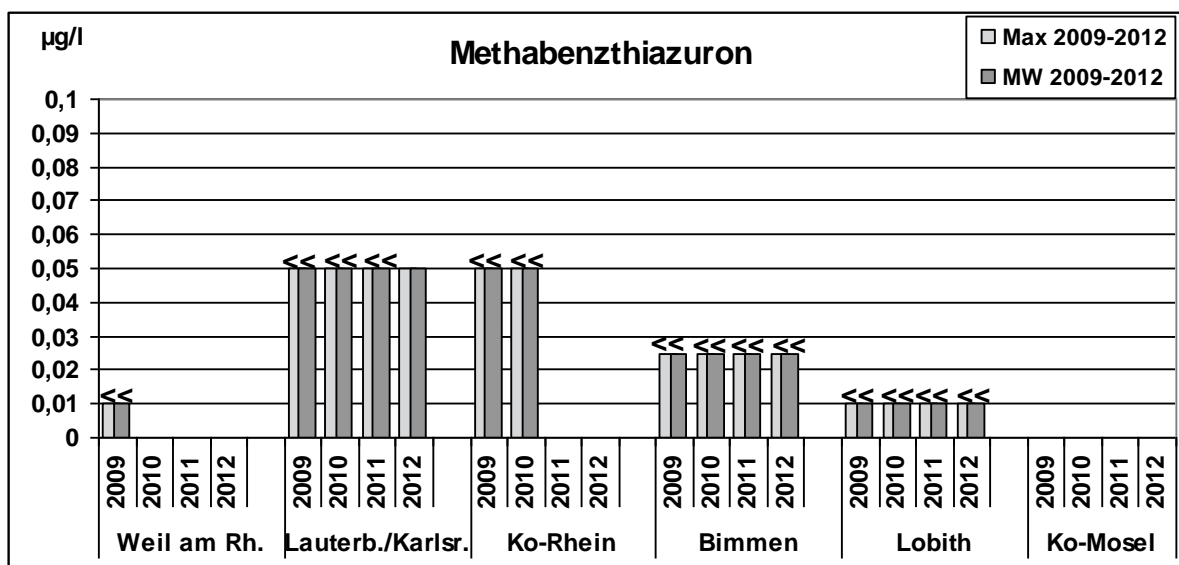
Graph 34 Desethylatrazin: Maximum (max) and mean (MW) values between 2009 and 2012



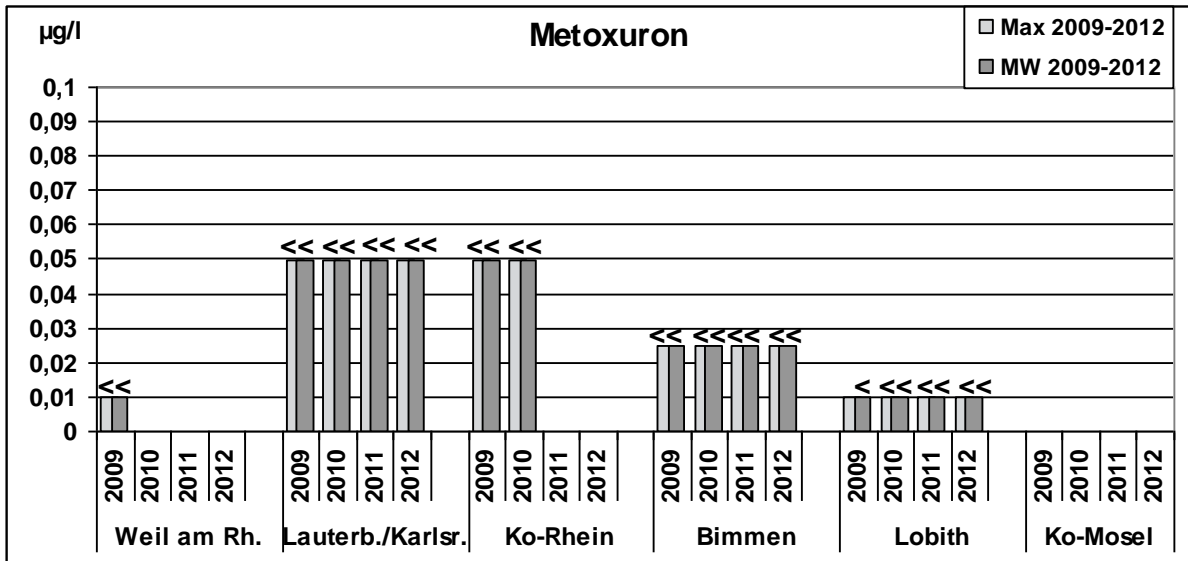
Graph 35 Linuron: Maximum (max) and mean (MW) values between 2009 and 2012



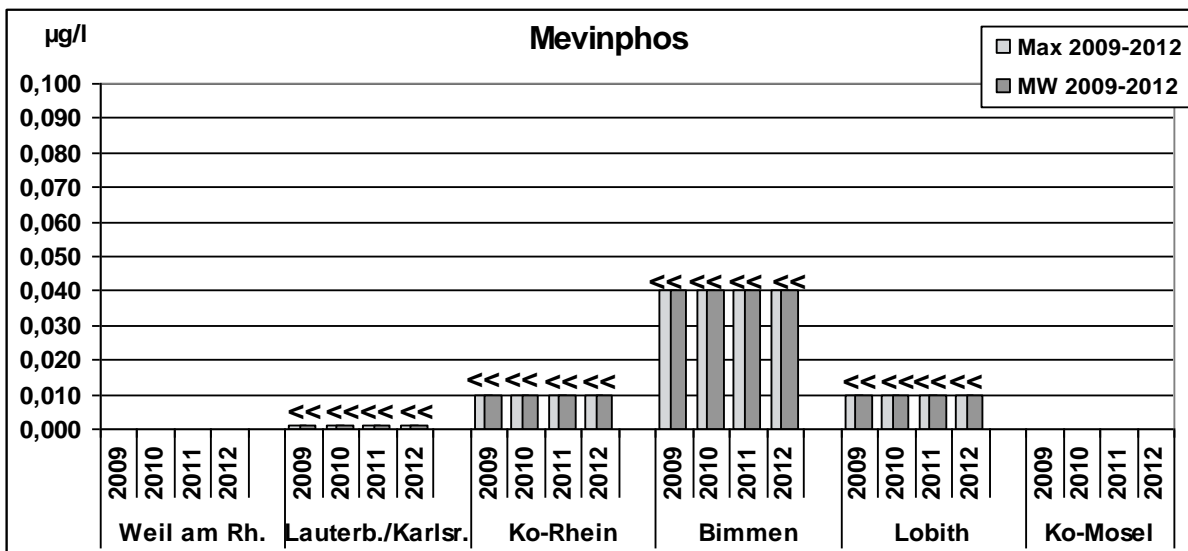
Graph 36 Methabenzthiazuron: Maximum (max) and mean (MW) values between 2009 and 2012



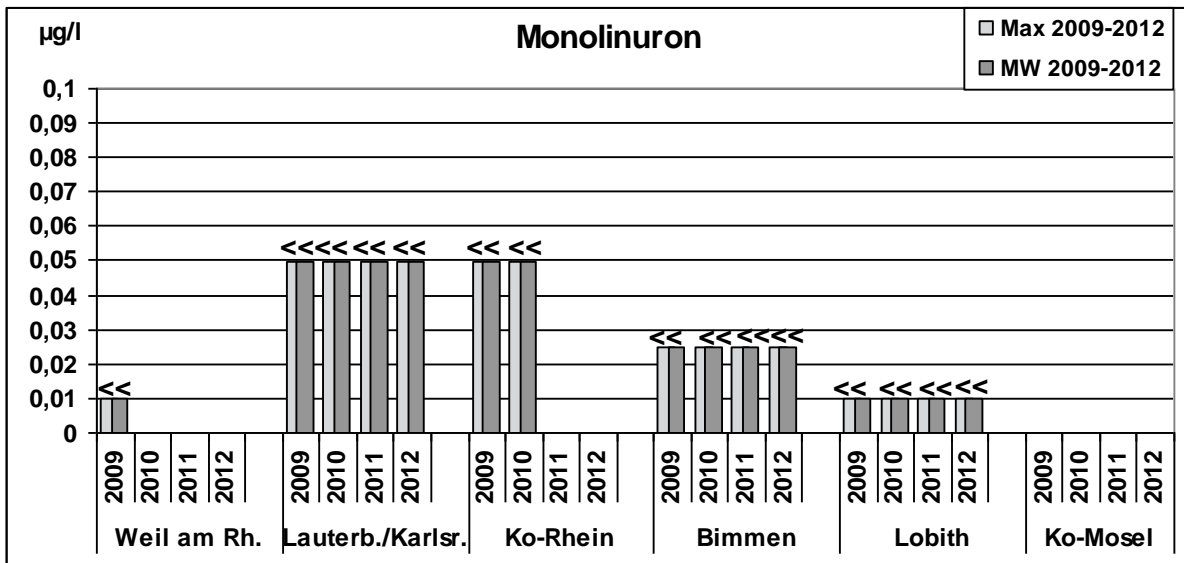
Graph 37 Metoxuron: Maximum (max) and mean (MW) values between 2009 and 2012



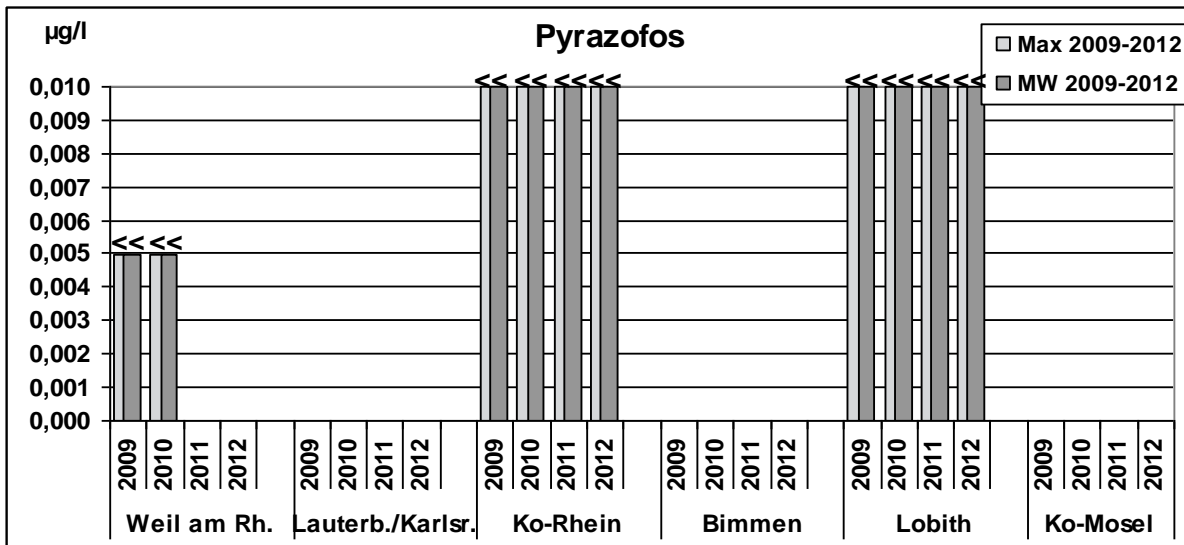
Graph 38 Mevinphos: Maximum (max) and mean (MW) values between 2009 and 2012



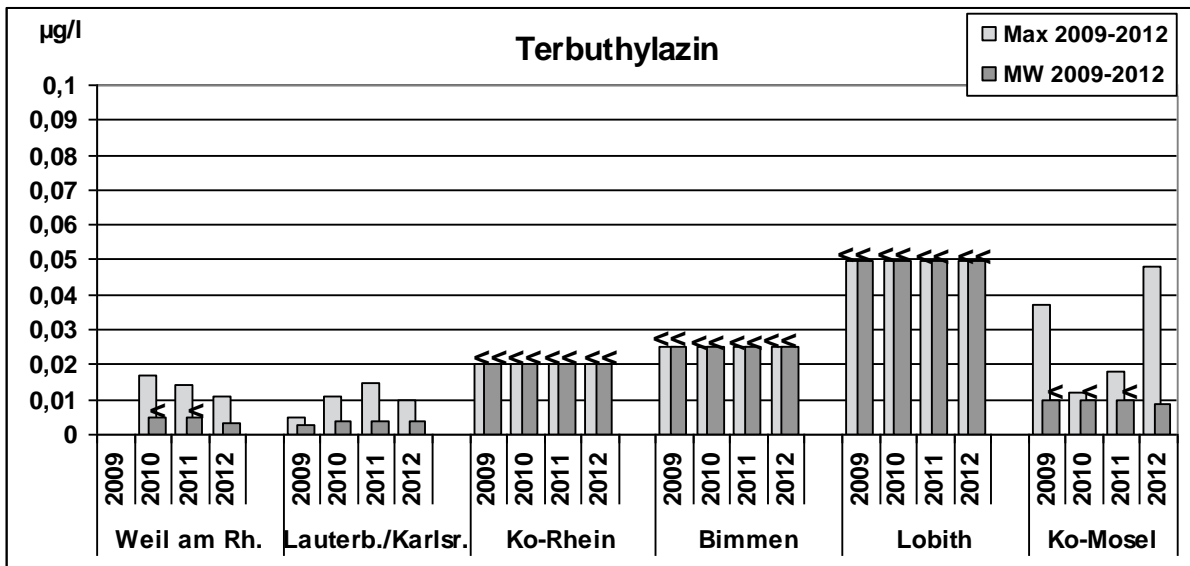
Graph 39 Monolinuron: Maximum (max) and mean (MW) values between 2009 and 2012



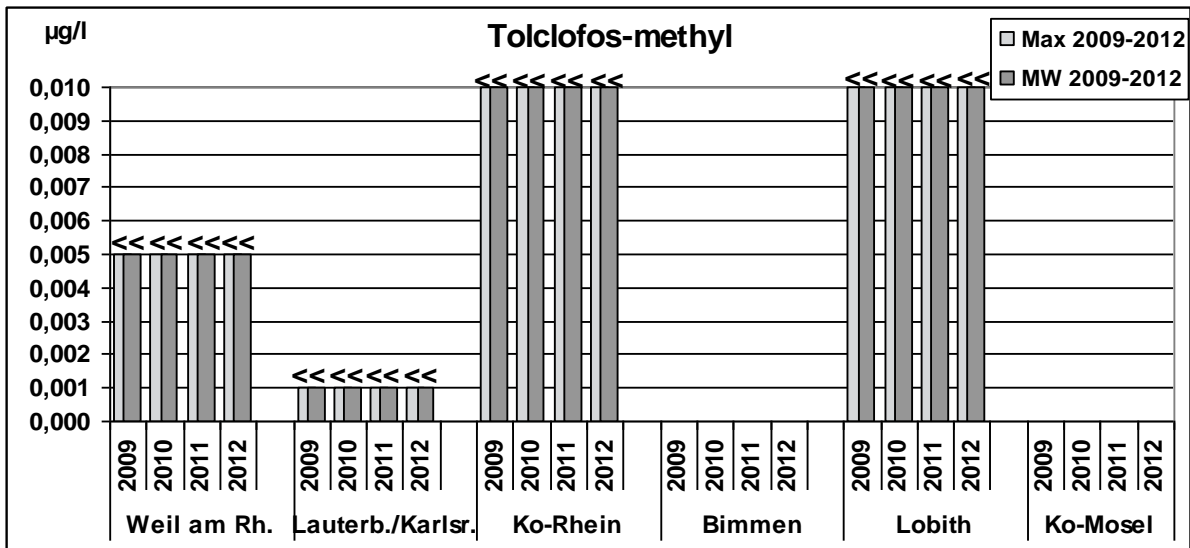
Graph 40 Pyrazofos: Maximum (max) and mean (MW) values between 2009 and 2012



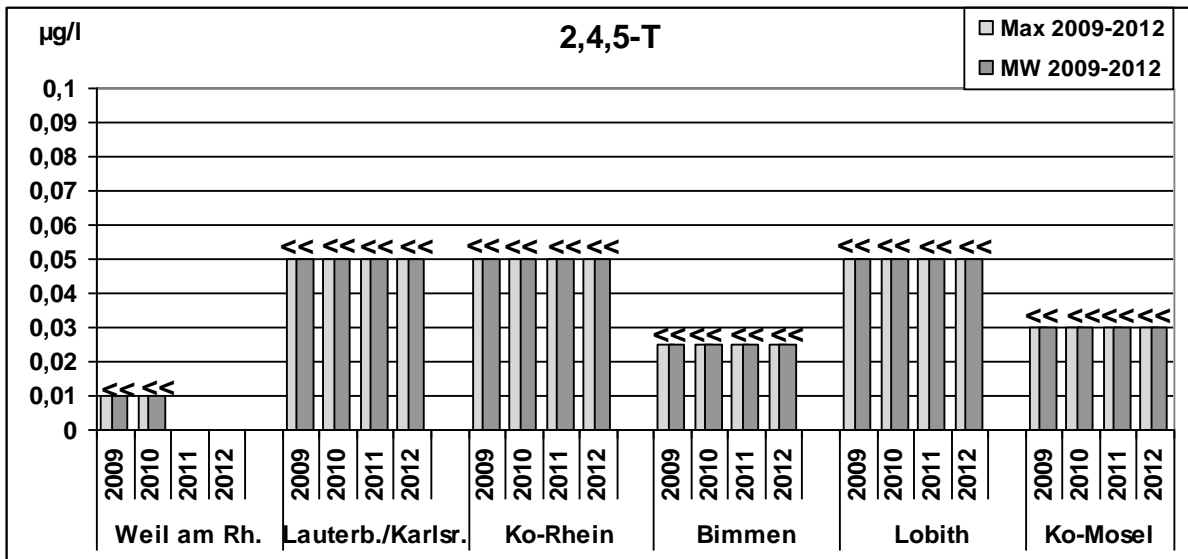
Graph 41 Terbutylazine: Maximum (max) and mean (MW) values between 2009 and 2012



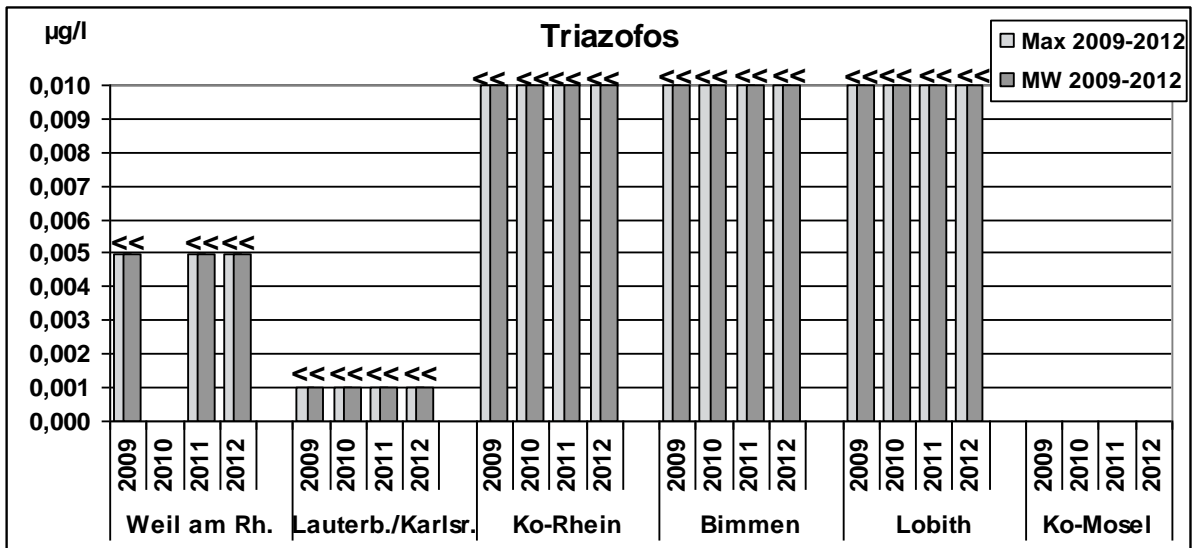
Graph 42 Tolclofos-methyl: Maximum (max) and mean (MW) values between 2009 and 2012



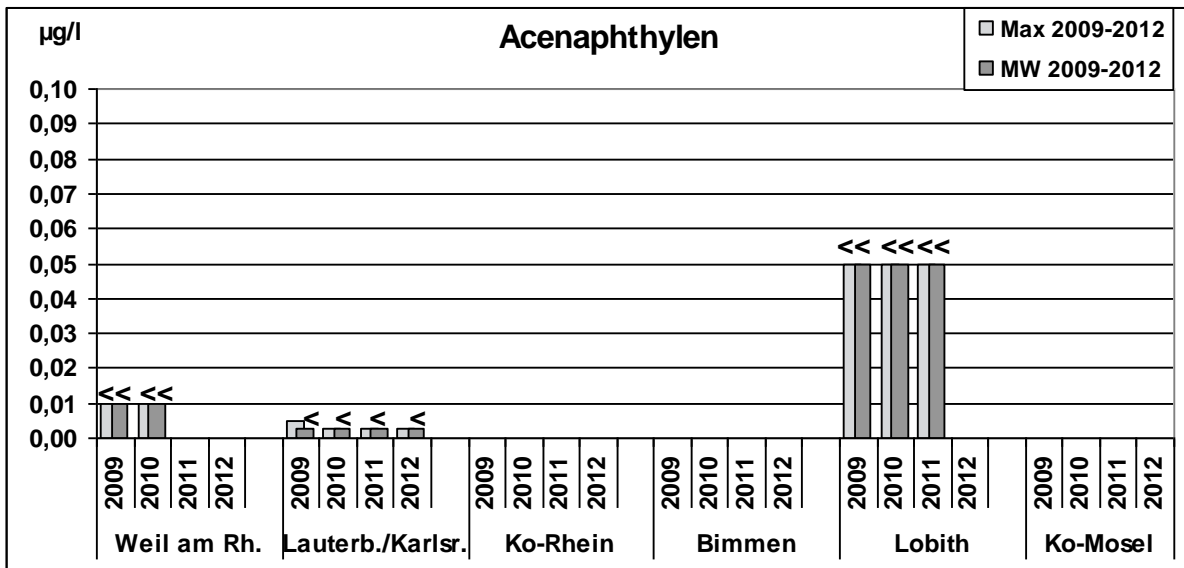
Graph 43 2,4,5-T: Maximum (max) and mean (MW) values between 2009 and 2012



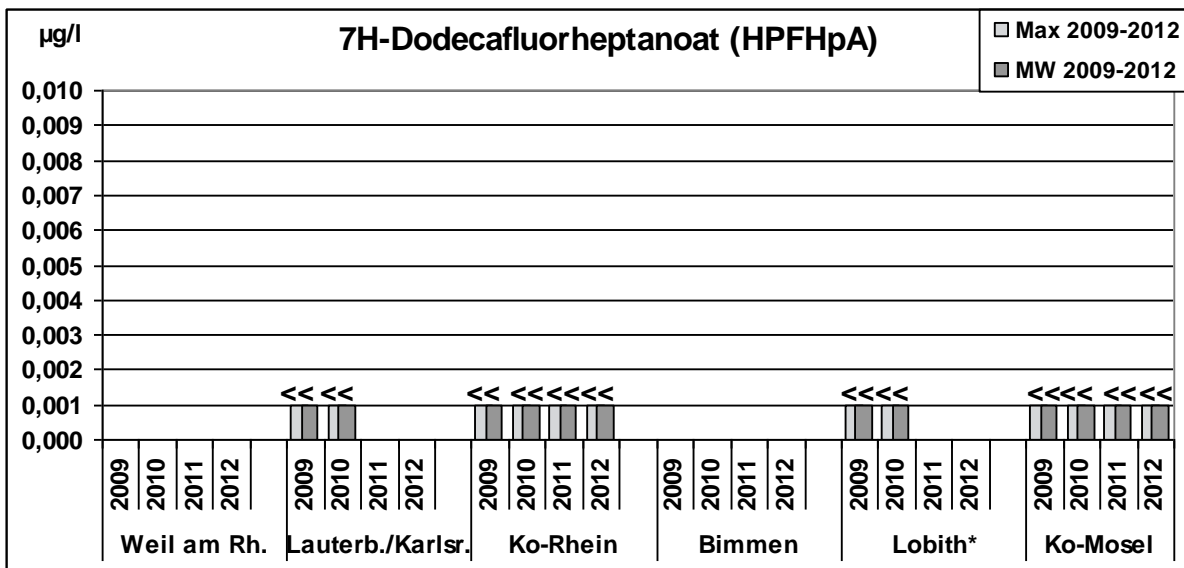
Graph 44 Phosphorothioic acid O,O-diethyl O-(1-phenyl-1H-1,2,4-triazol-3-yl) ester: Maximum (max) and mean (MW) values between 2009 and 2012



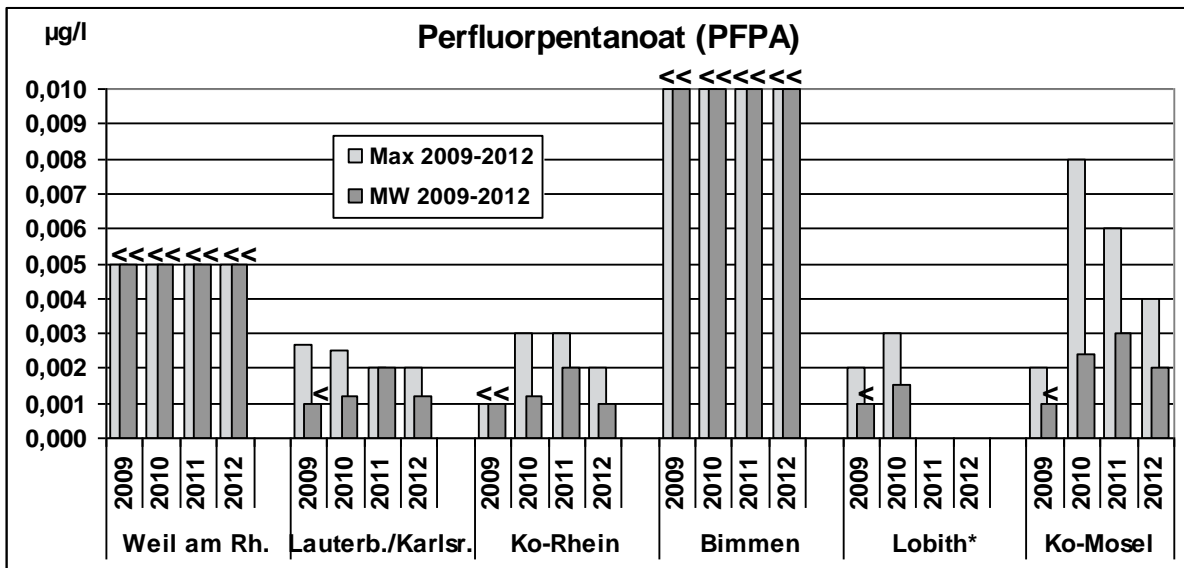
Graph 45 Acenaphthylen: Maximum (max) and mean (MW) values between 2009 and 2012



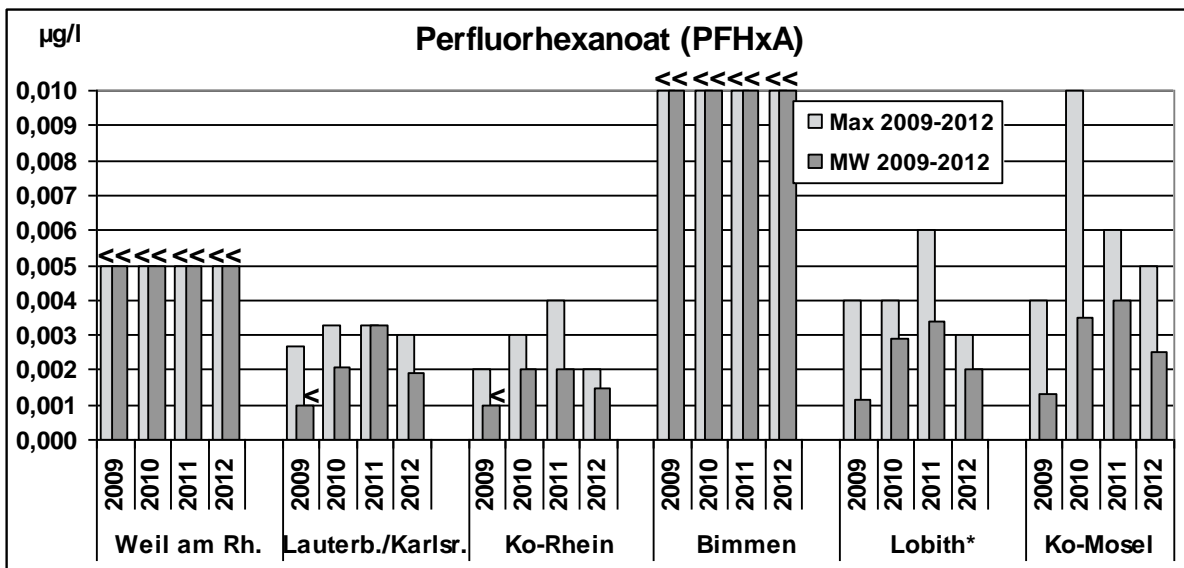
Graph 46 Dodecafluoroheptanoate: Maximum (max) and mean (MW) values between 2009 and 2012



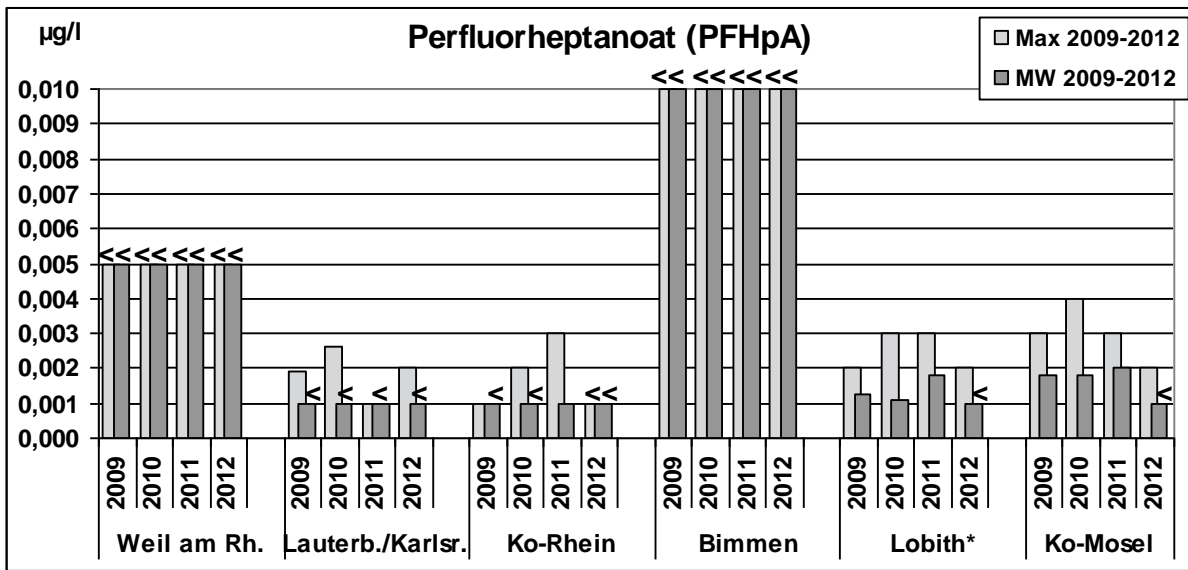
Graph 47 Perfluorpentanoate: Maximum (max) and mean (MW) values between 2009 and 2012



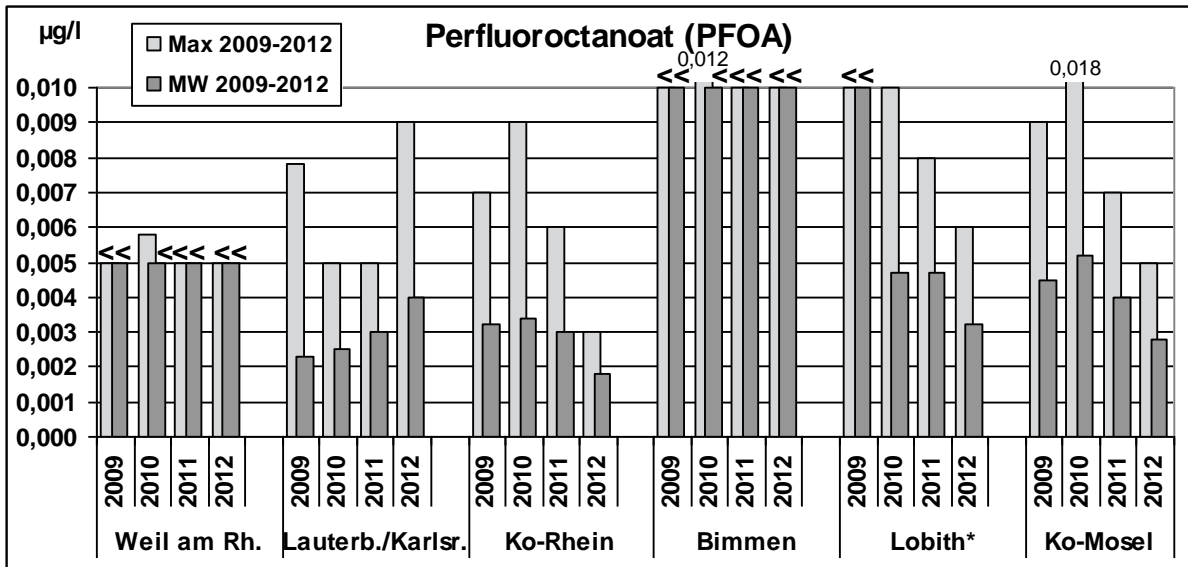
Graph 48 Perfluorhexanoic acid: Maximum (max) and mean (MW) values between 2009 and 2012



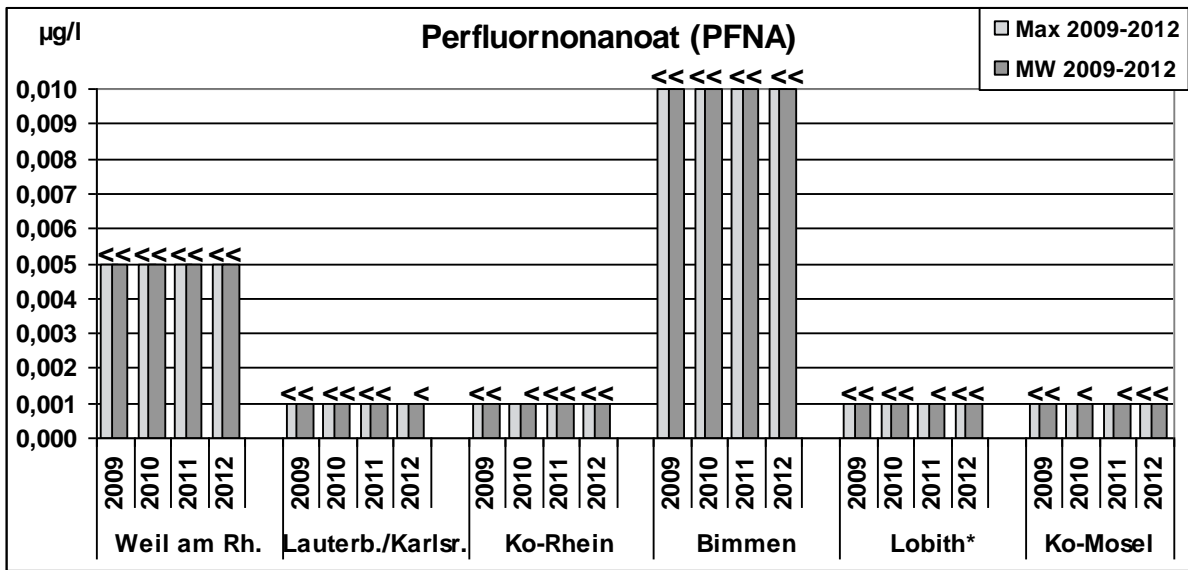
Graph 49 Perfluoroheptanoate: Maximum (max) and mean (MW) values between 2009 and 2012



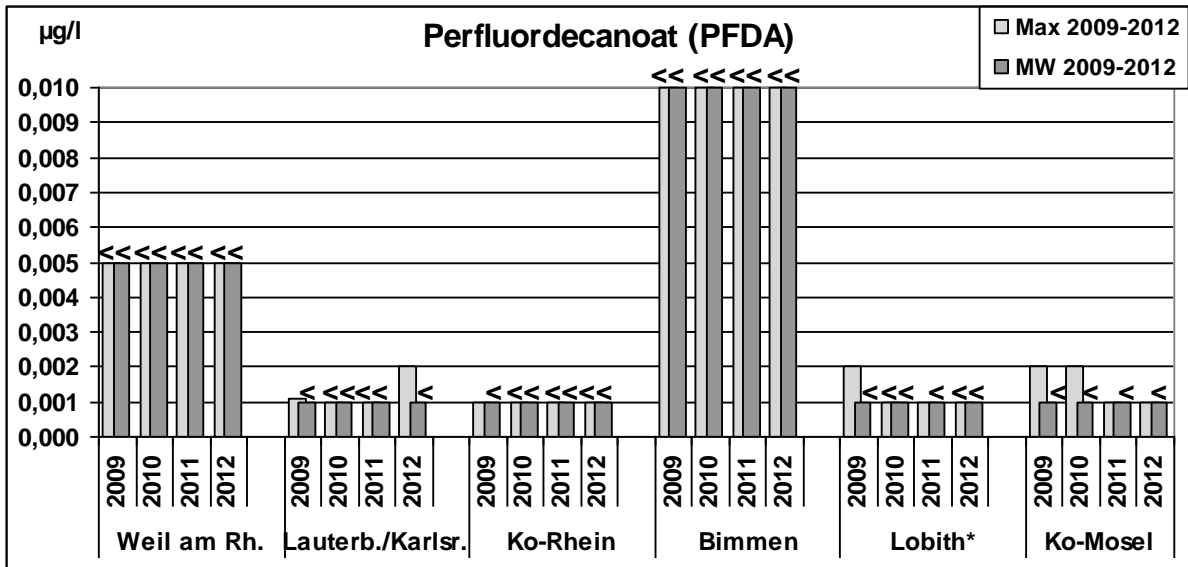
Graph 50 Perfluorooctanoate: Maximum (max) and mean (MW) values between 2009 and 2012



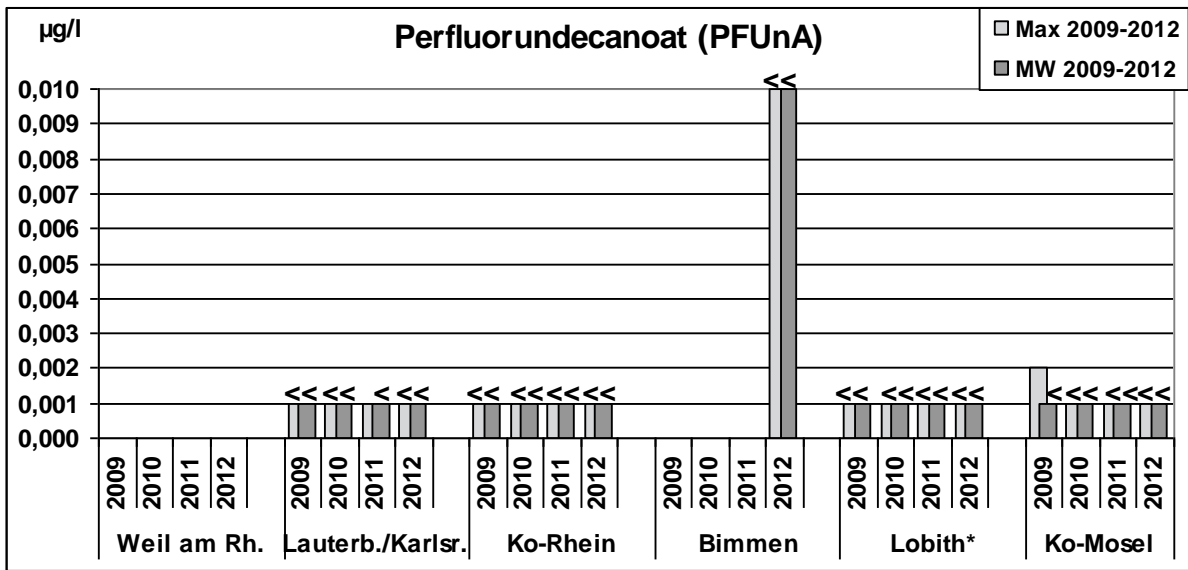
Graph 51 Perfluorononanoate: Maximum (max) and mean (MW) values between 2009 and 2012



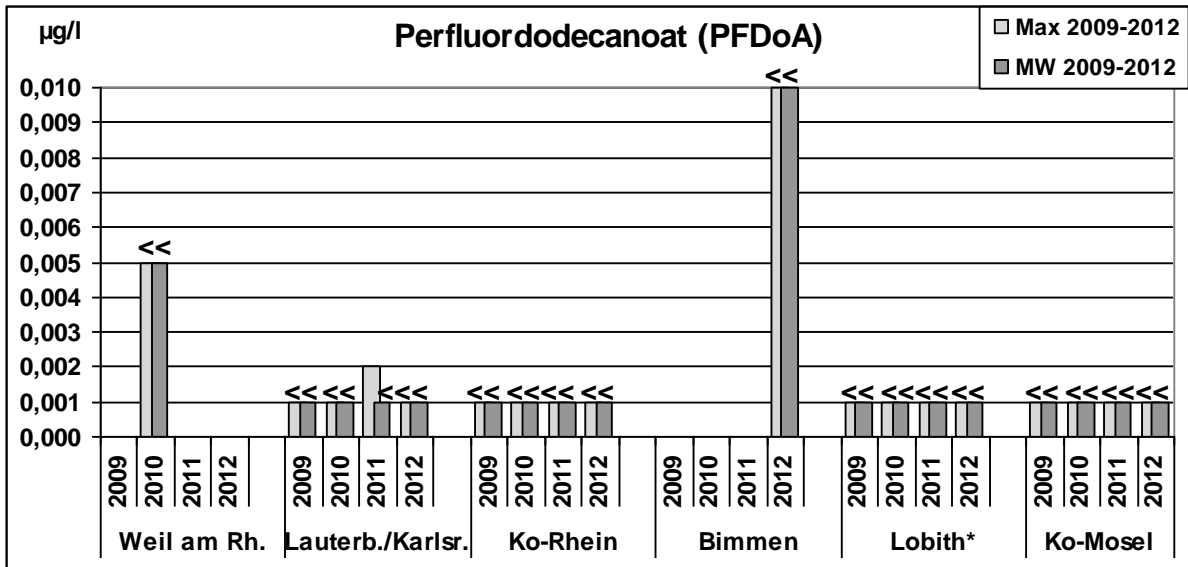
Graph 52 Perfluorodecanoate: Maximum (max) and mean (MW) values between 2009 and 2012



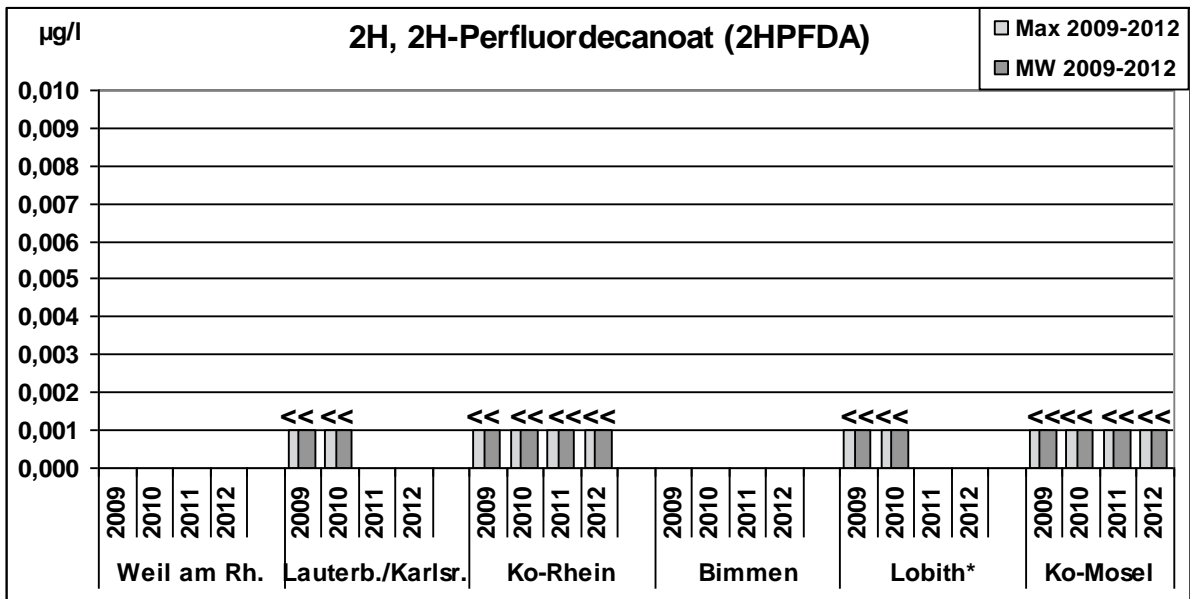
Graph 53 Perfluorundecanoate: Maximum (max) and mean (MW) values between 2009 and 2012



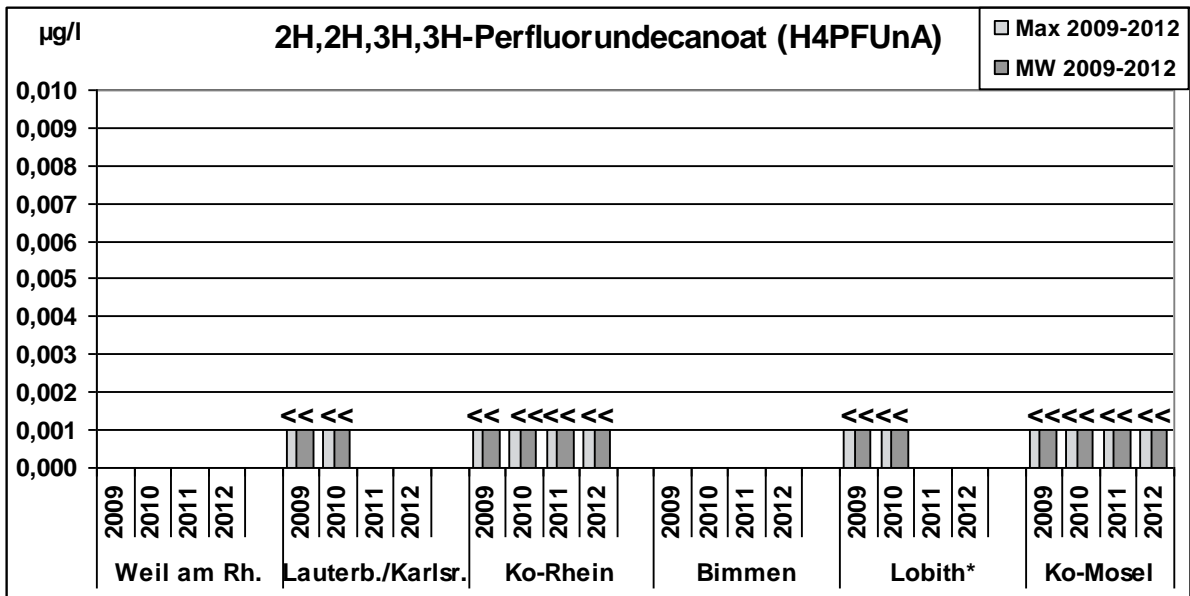
Graph 54 Perfluordodecanoate: Maximum (max) and mean (MW) values between 2009 and 2012



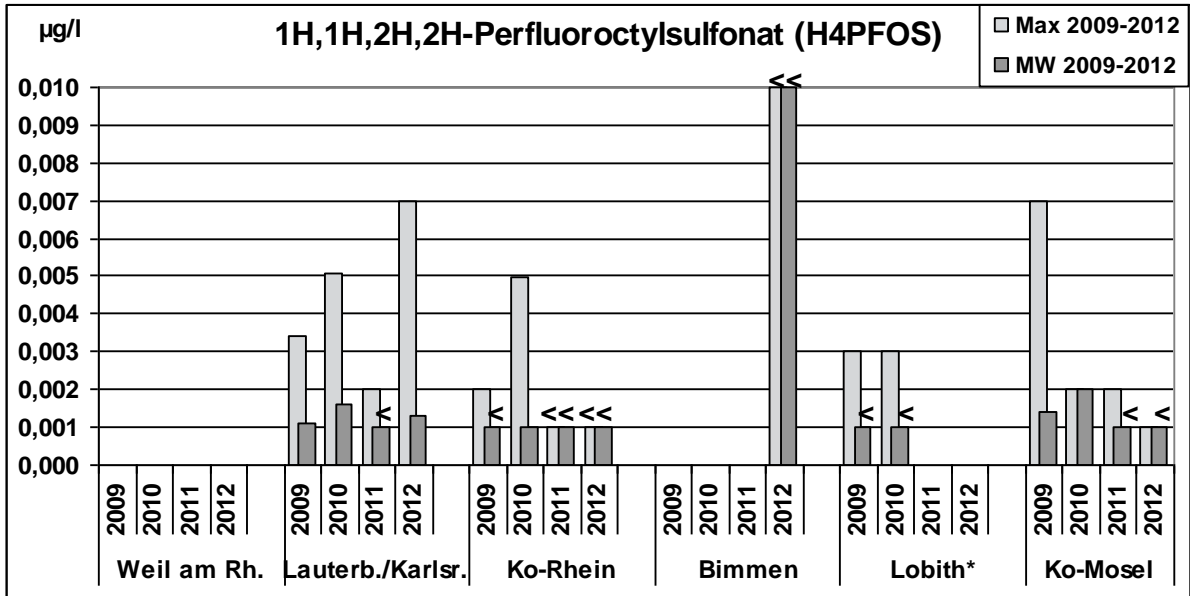
Graph 55 2H,2H-Perfluorodecanoate: Maximum (max) and mean (MW) values between 2009 and 2012



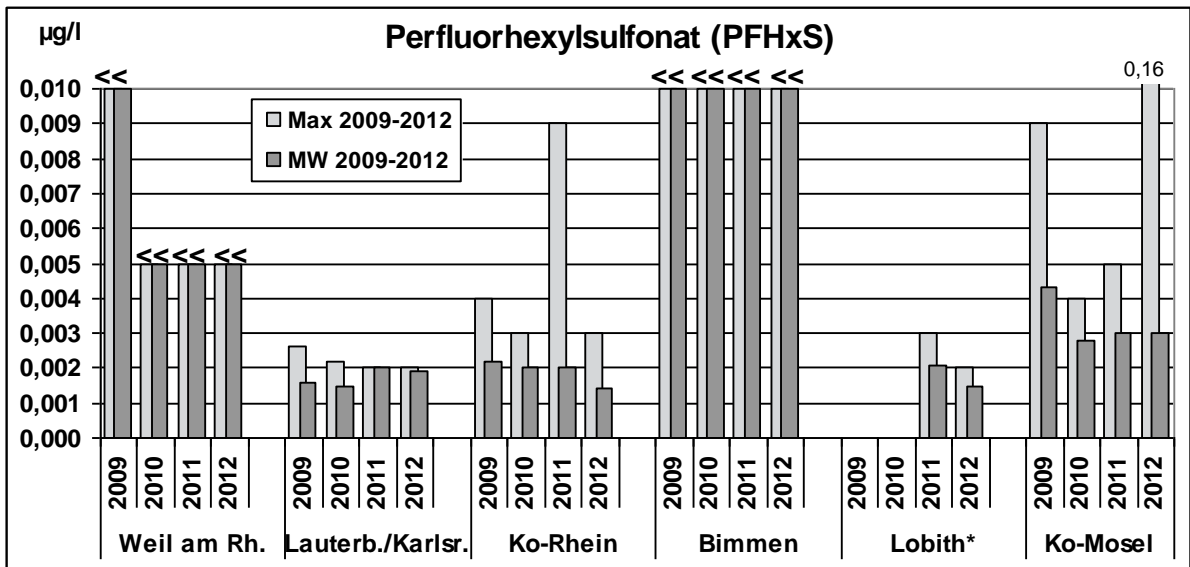
Graph 56 2H,2H,3H,3H-Perfluorundecanoate: Maximum (max) and mean (MW) values between 2009 and 2012



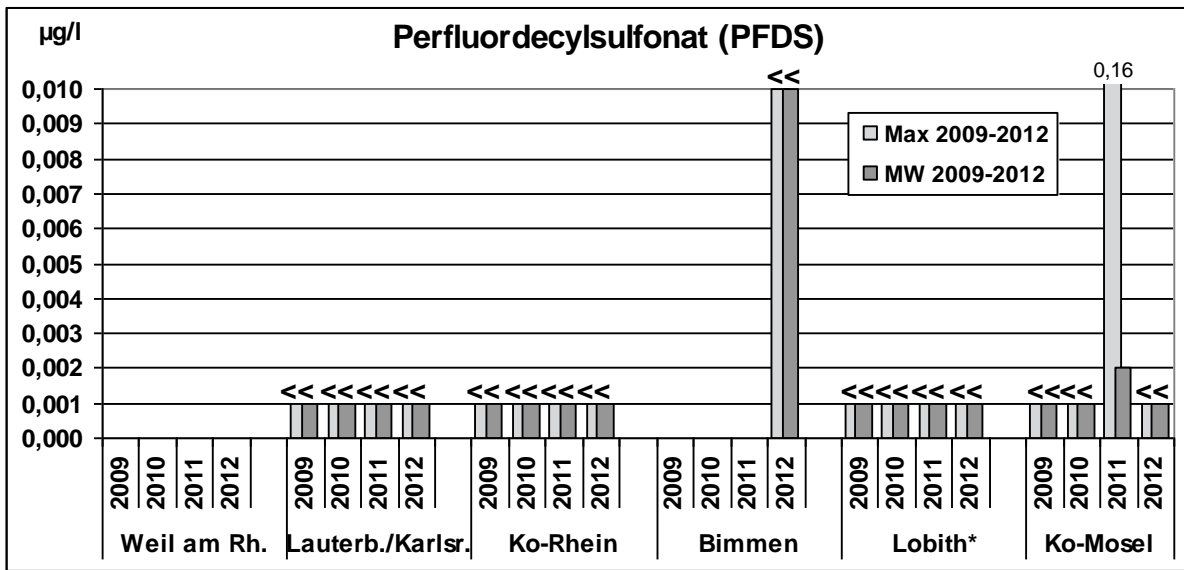
Graph 57 1H,1H,2H,2H-perfluorooctyl-1-sulfonic acid Maximum (max) and mean (MW) values between 2009 and 2012



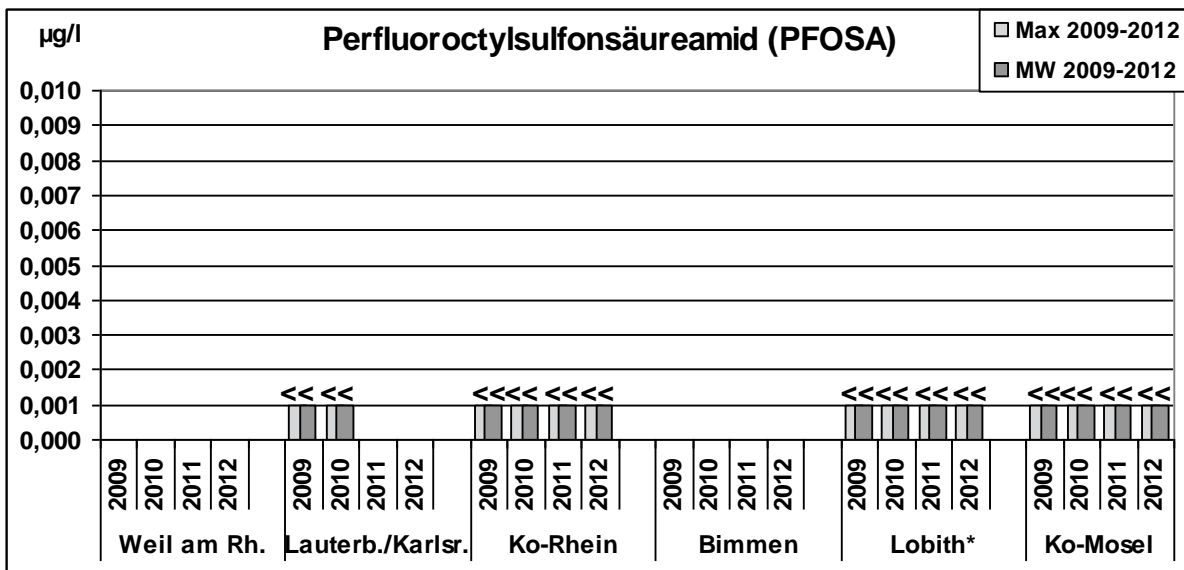
Graph 58 Perfluorooctanoate: Maximum (max) and mean (MW) values between 2009 and 2012



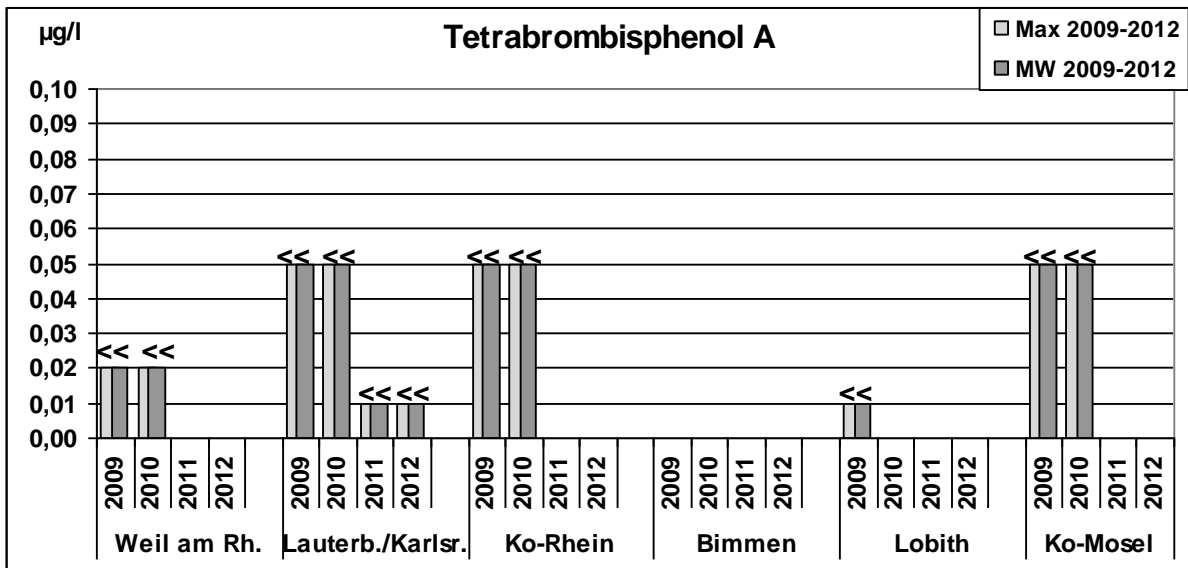
Graph 59 Perfluorodecyle sulfonic acid: Maximum (max) and mean (MW) values between 2009 and 2012



Graph 60 Perfluorooctanesulfonamide: Maximum (max) and mean (MW) values between 2009 and 2012

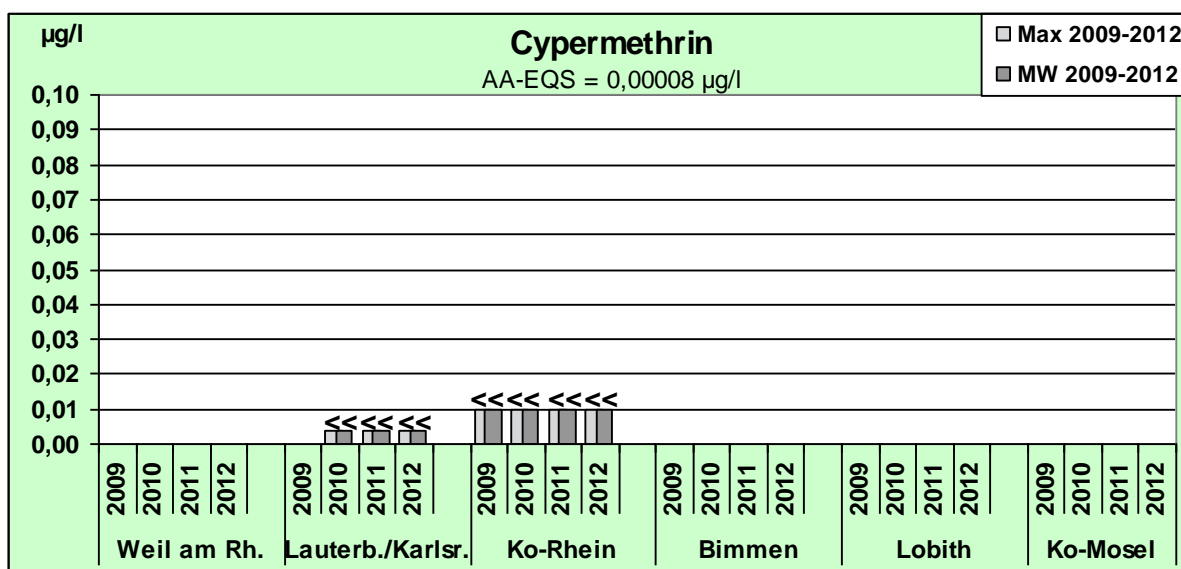


Graph 61 Tetrabrombisphenol A: Maximum (max) and mean (MW) values between 2009 and 2012

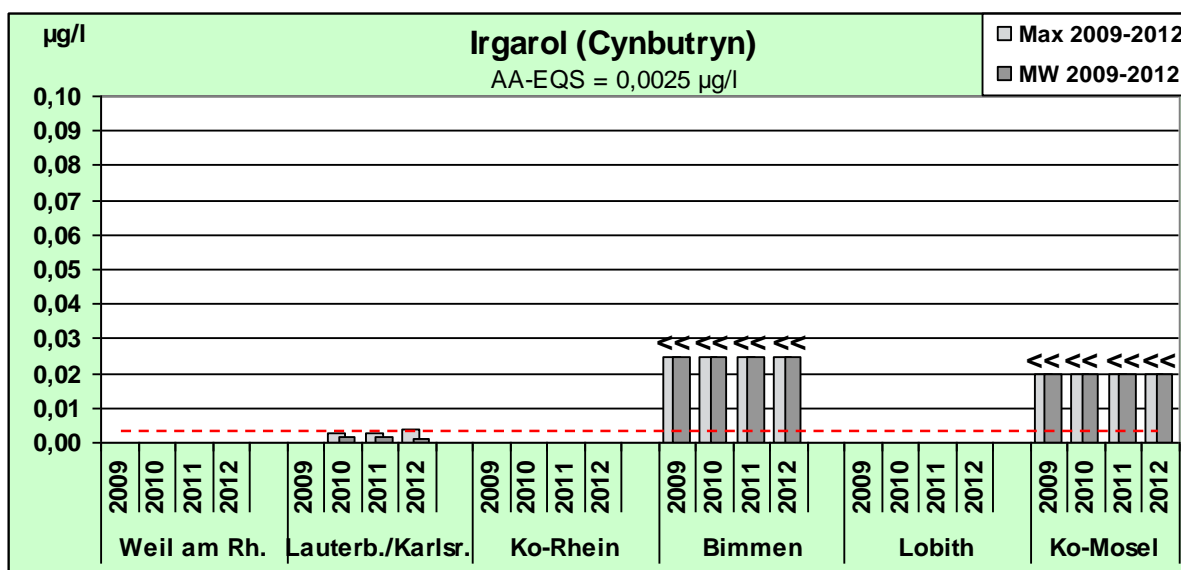


4 New priority substance according to Directive 2013/39/EU

Graph 62 Cypermethrin: Maximum (max) and mean (MW) values between 2009 and 2012

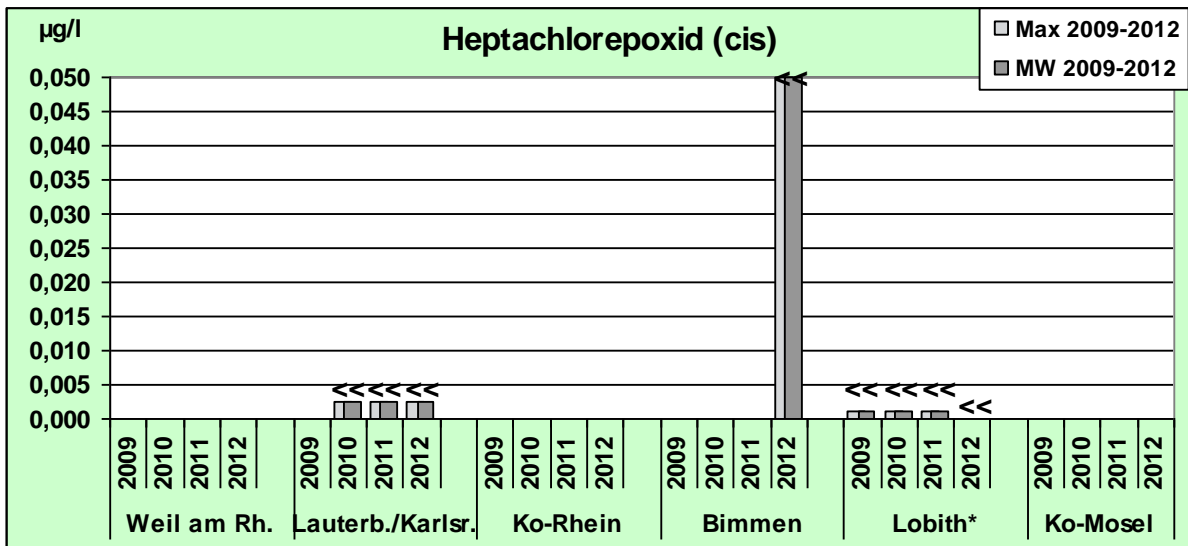
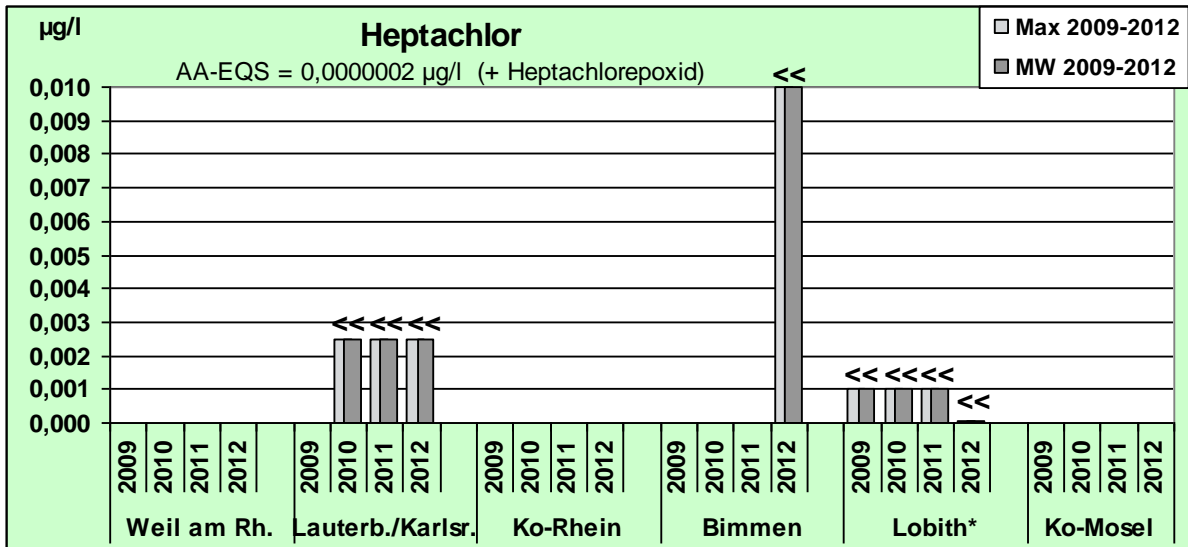


Graph 63 Cybutryn: Maximum (max) and mean (MW) values between 2009 and 2012

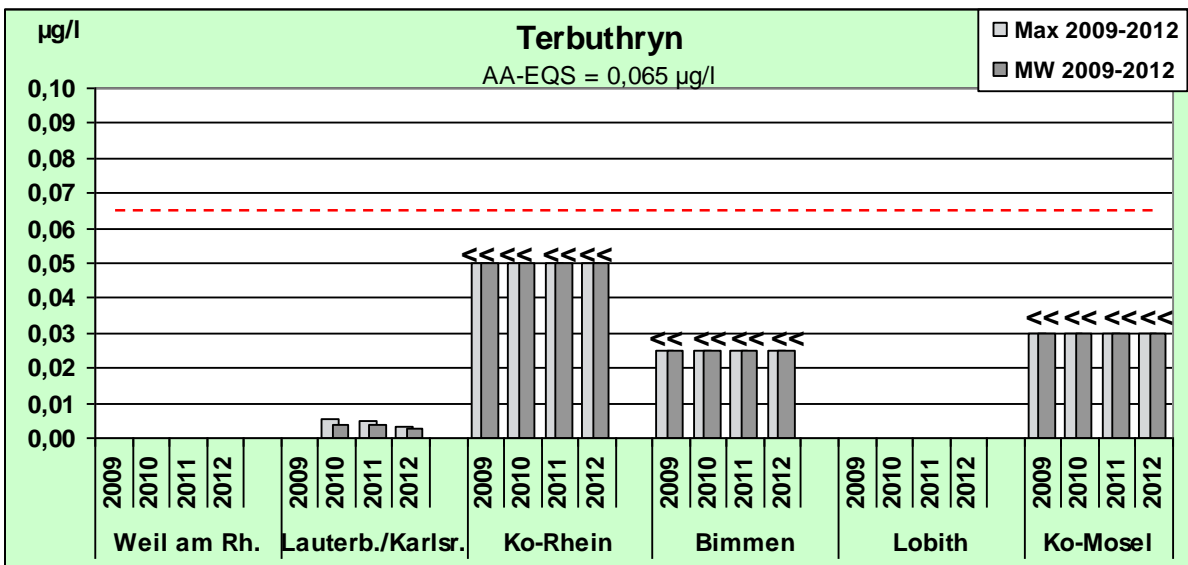


Red line: new EQS (0.0025 µg/l)

Graph 64 a/b Heptachlor/Heptachlorepoxid: Maximum (max) and mean (MW) values between 2009 and 2012



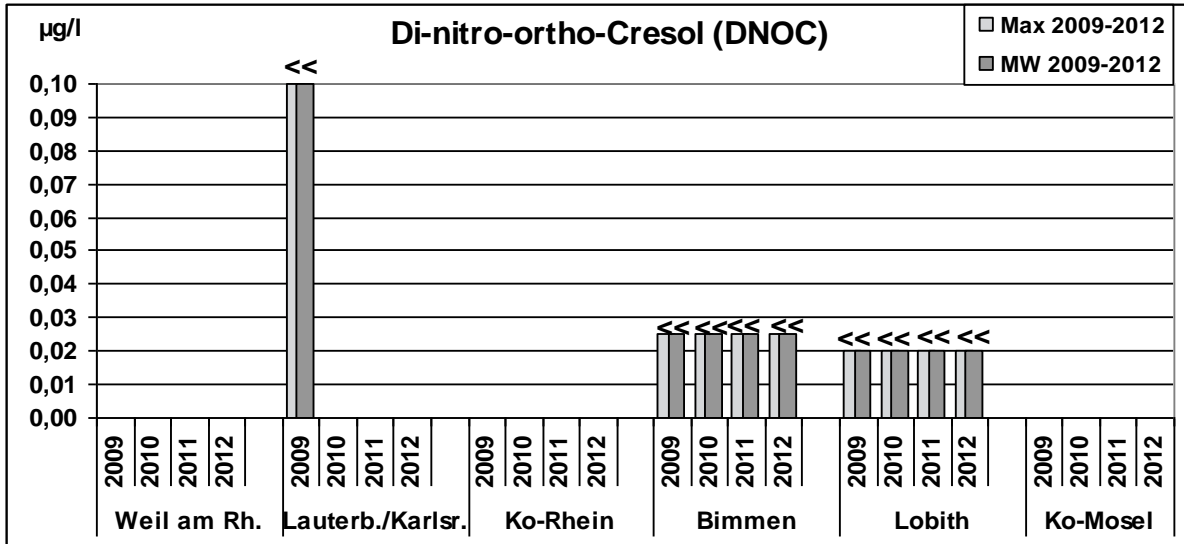
Graph 65 Terbutryn: Maximum (max) and mean (MW) values between 2009 and 2012



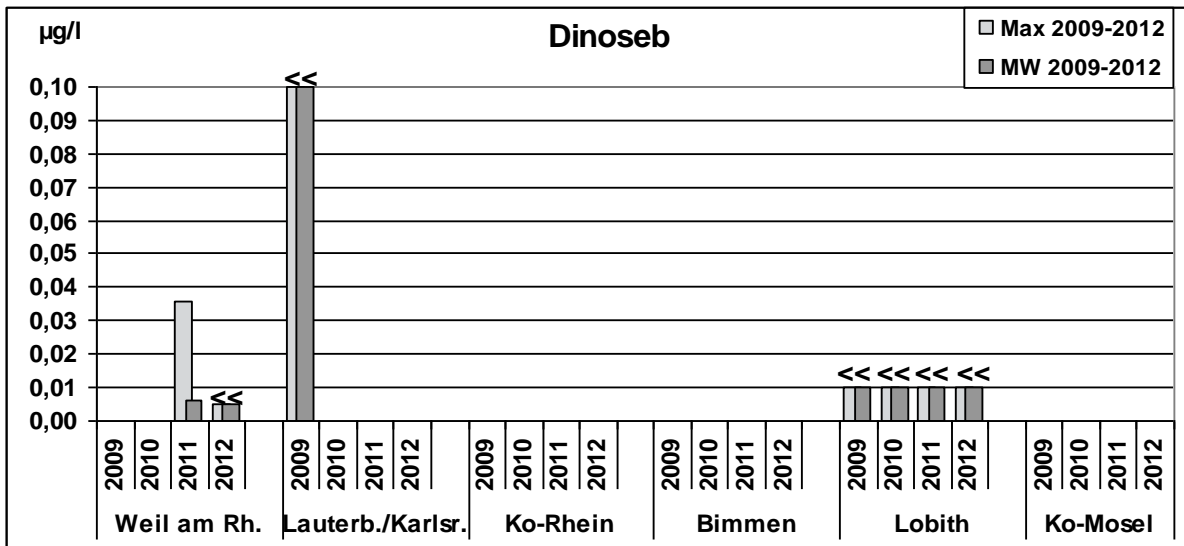
Red line: new EQS (0.065 µg/l)

19 substances of the concentration level 0

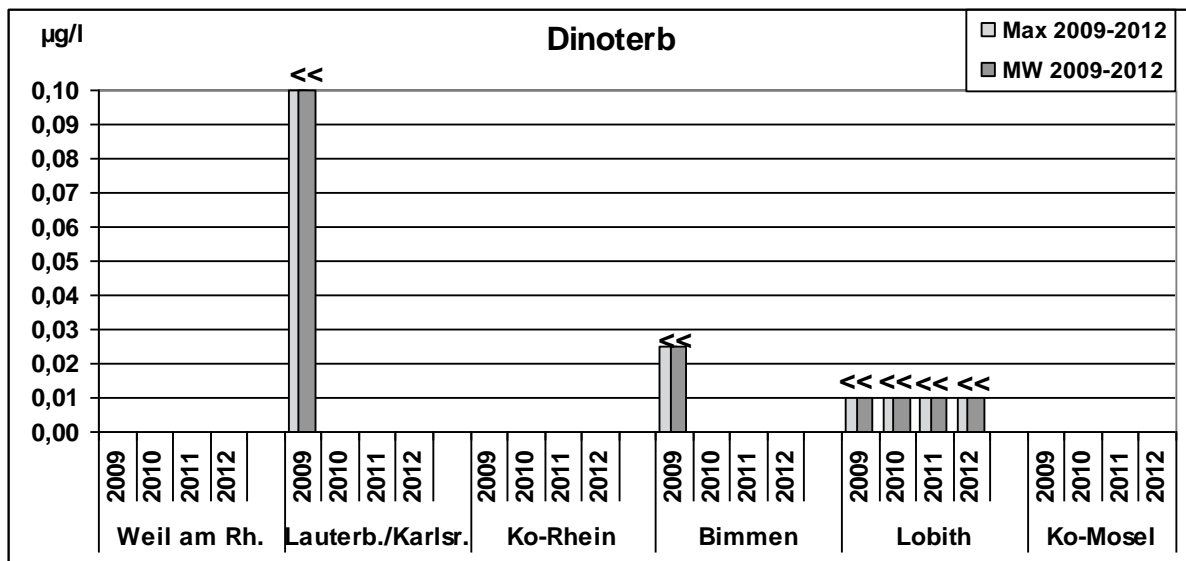
Graph 66 Di-nitro-ortho-Cresol: Maximum (max) and mean (MW) values between 2009 and 2012



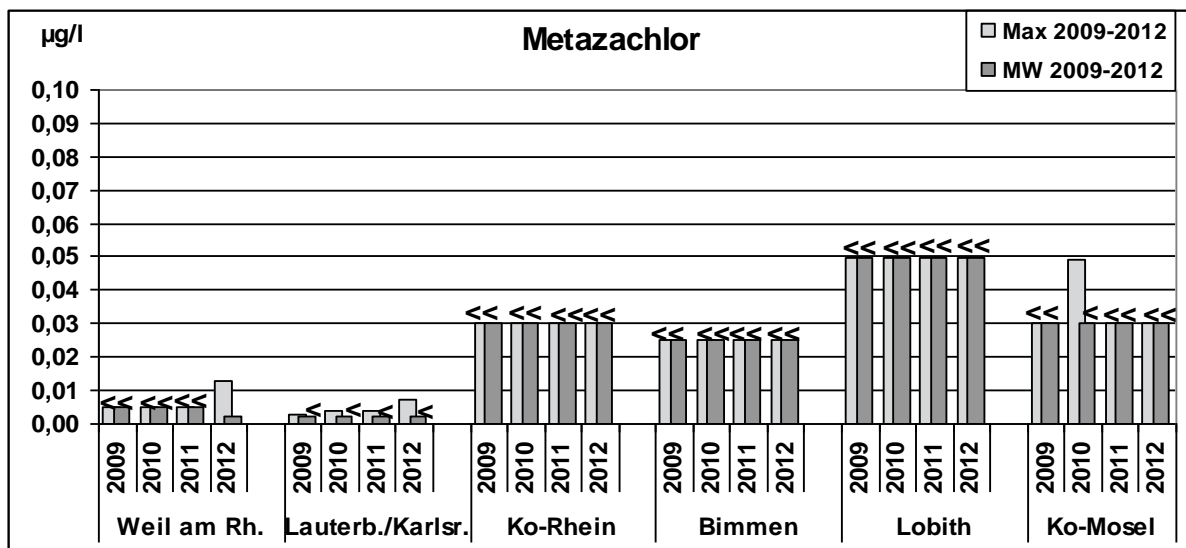
Graph 67 Dinoseb: Maximum (max) and mean (MW) values between 2009 and 2012



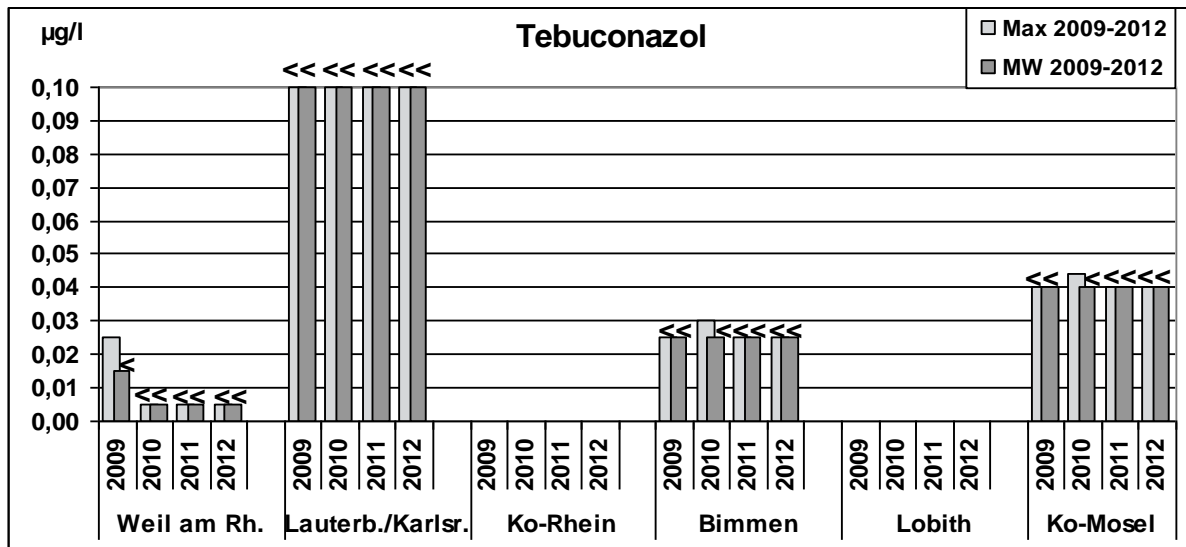
Graph 68 Dinoterb: Maximum (max) and mean (MW) values between 2009 and 2012



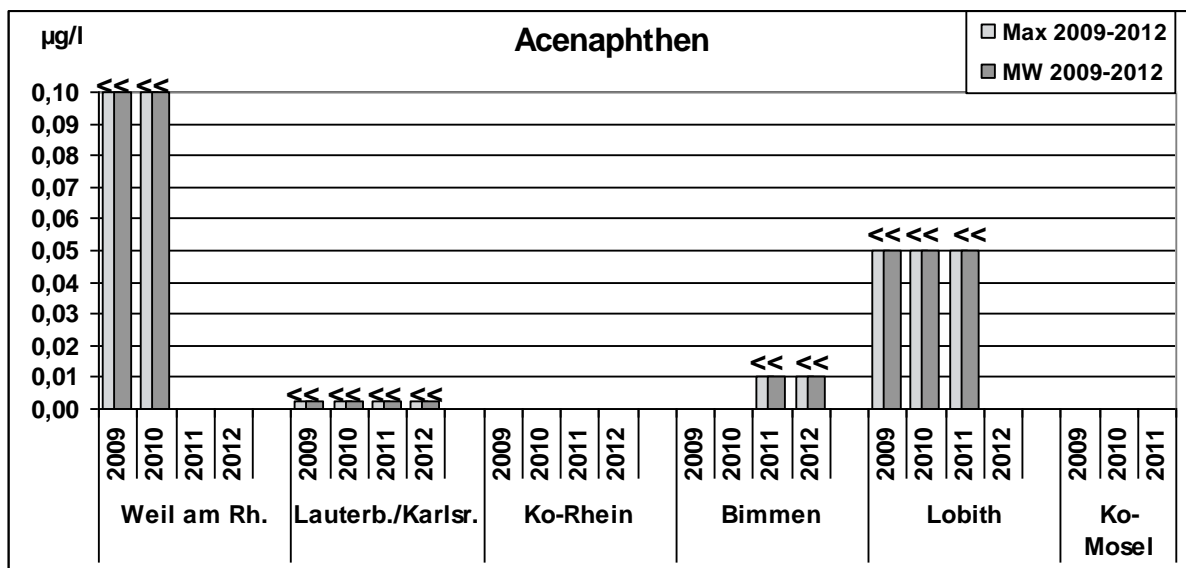
Graph 69 Metazachlor: Maximum (max) and mean (MW) values between 2009 and 2012



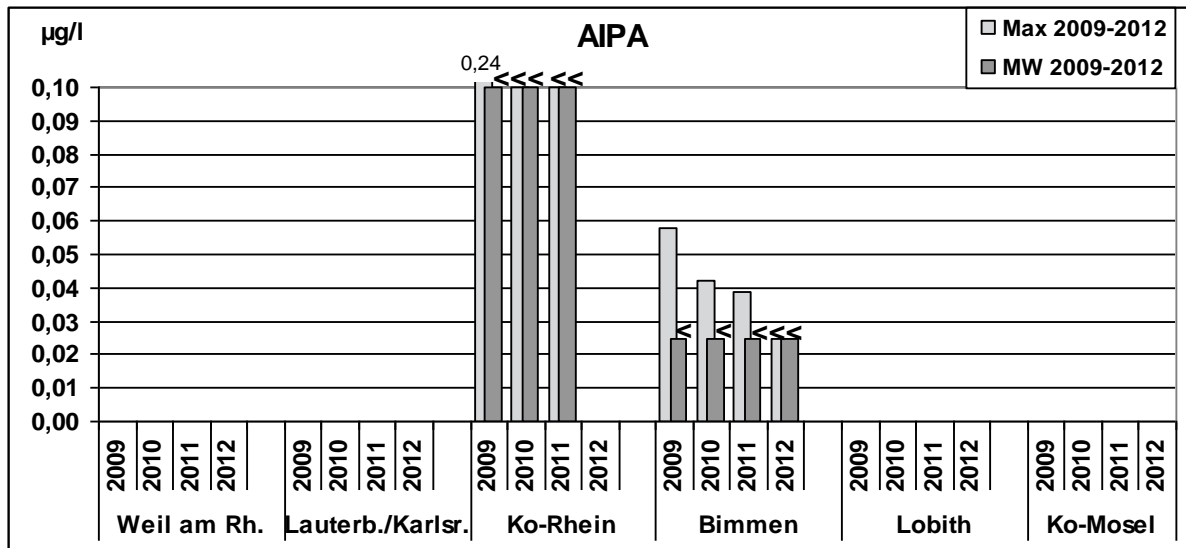
Graph 70 Tebuconazole: Maximum (max) and mean (MW) values between 2009 and 2012



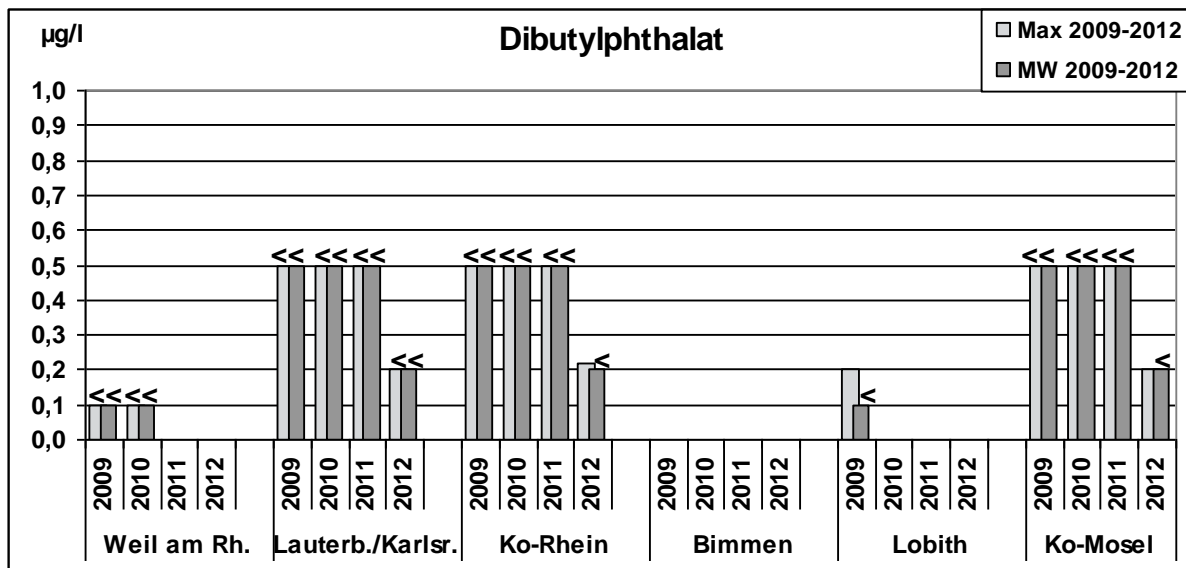
Graph 71 Acenaphthene: Maximum (max) and mean (MW) values between 2009 and 2012



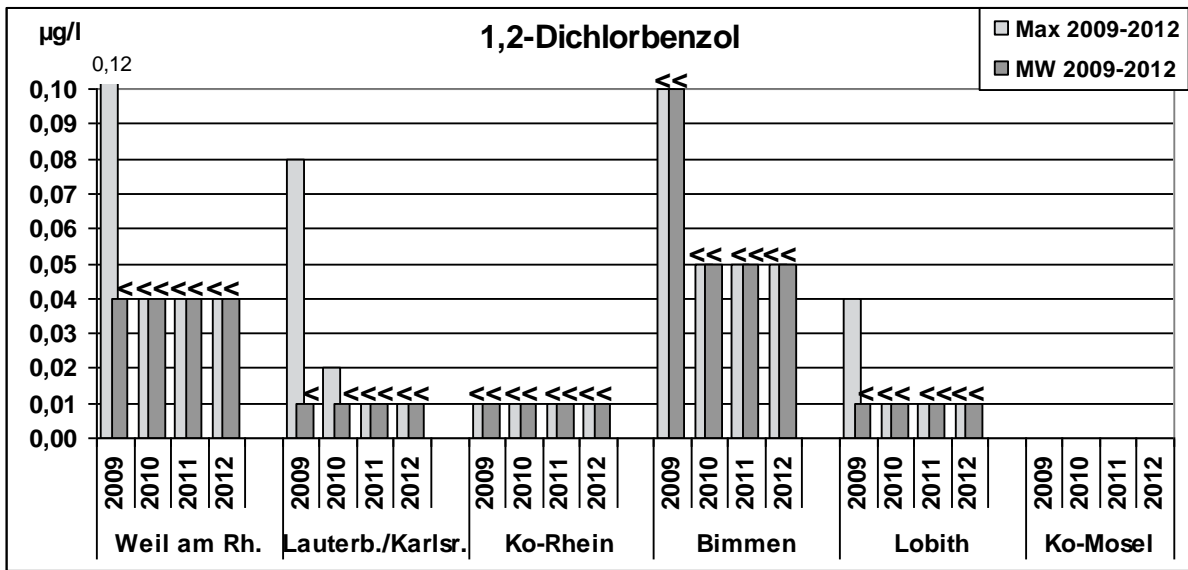
Graph 72 AIPA: Maximum (max) and mean (MW) values between 2009 and 2012



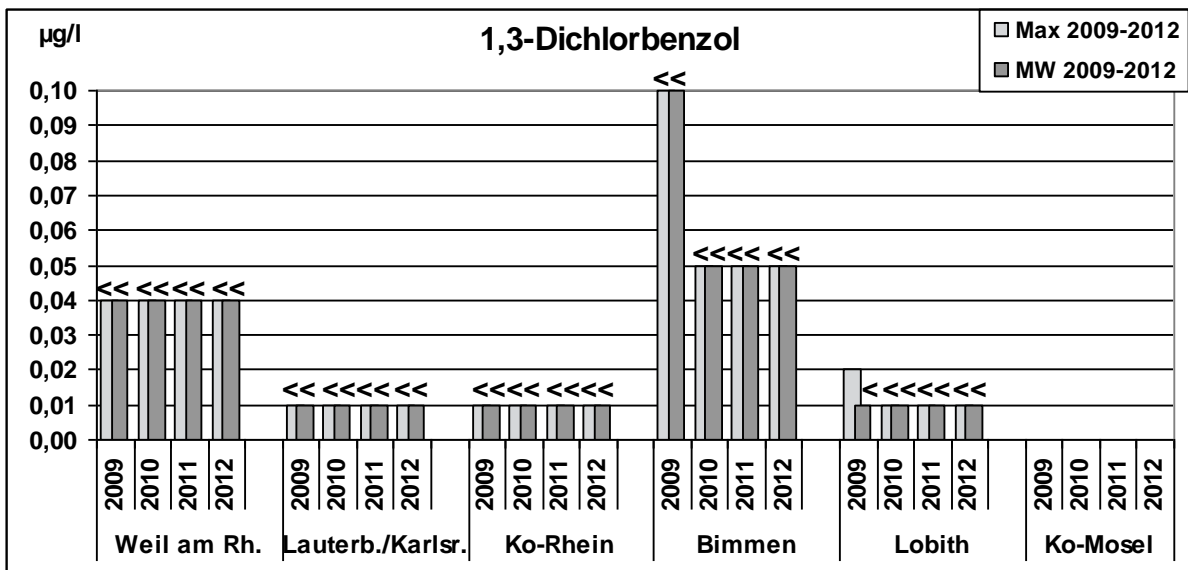
Graph 73 Dibutylphthalat: Maximum (max) and mean (MW) values between 2009 and 2012



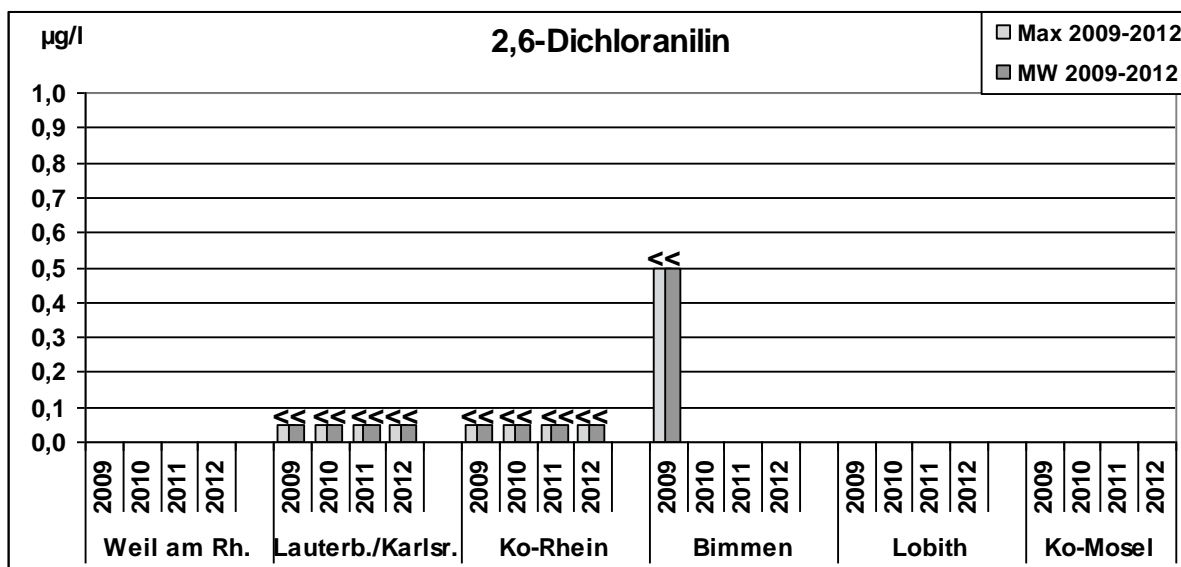
Graph 74 1.2-dichlorobenzene Maximum (max) and mean (MW) values between 2009 and 2012



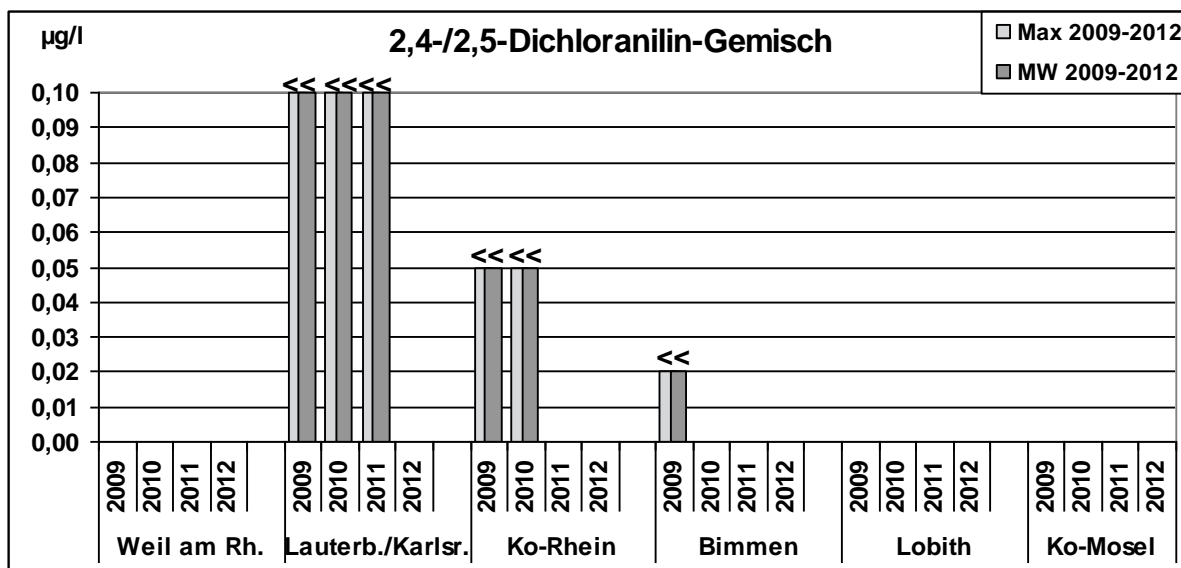
Graph 75 1.3-dichlorobenzene Maximum (max) and mean (MW) values between 2009 and 2012



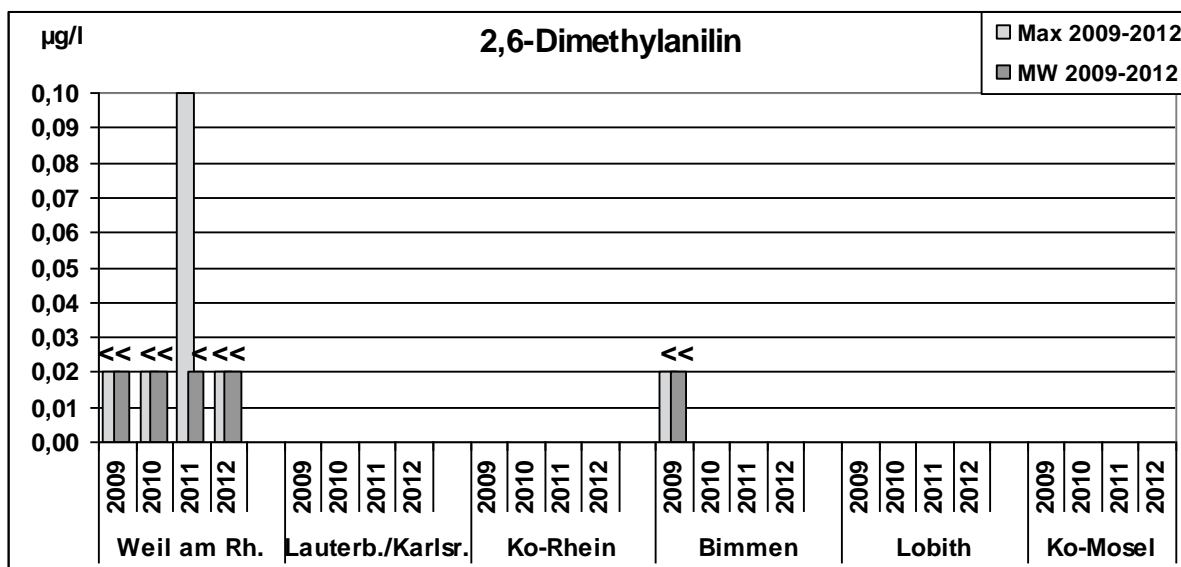
Graph 76 1.3-dichloranilin Maximum (max) and mean (MW) values between 2009 and 2012



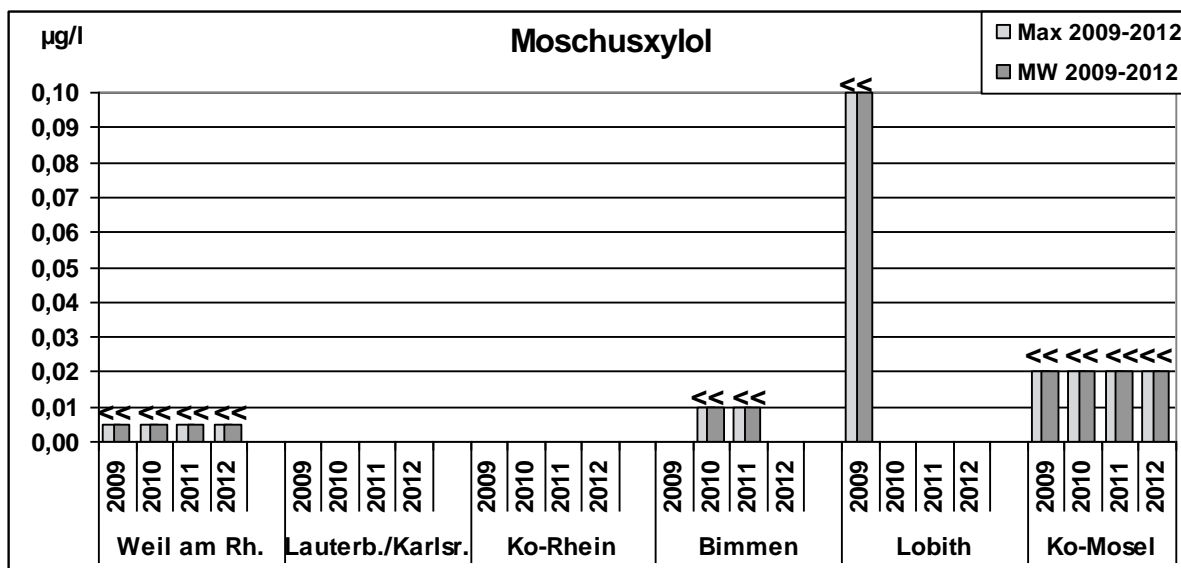
Graph 77 2.4-/2.5-dichloranilin compound Maximum (max) and mean (MW) values between 2009 and 2012



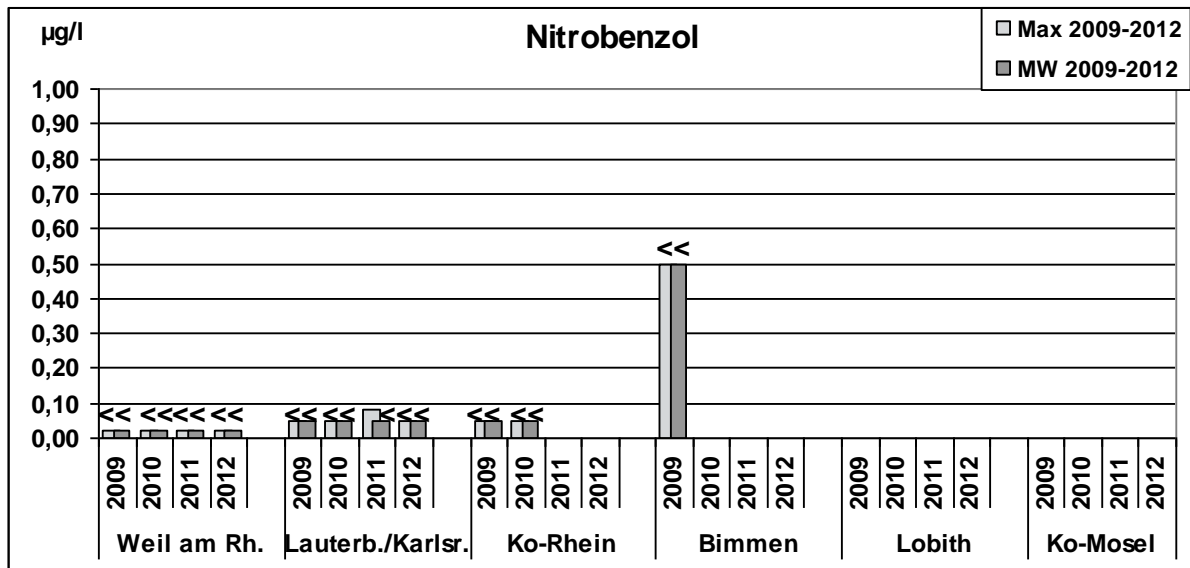
Graph 78 2.6-dimethylaniline: Maximum (max) and mean (MW) values between 2009 and 2012



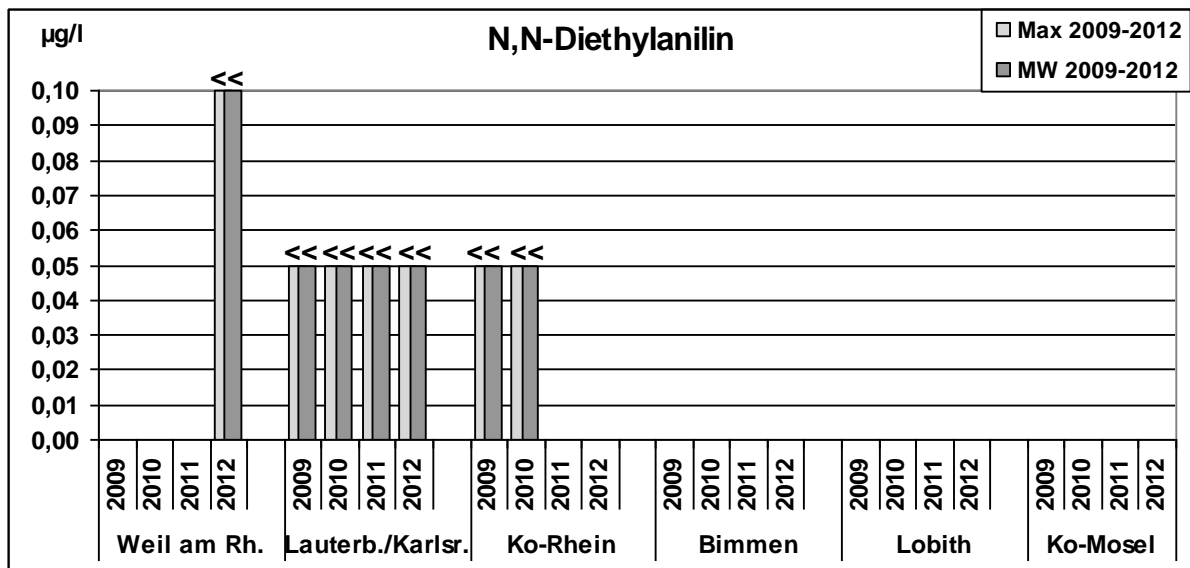
Graph 79 Musk xylene: Maximum (max) and mean (MW) values between 2009 and 2012



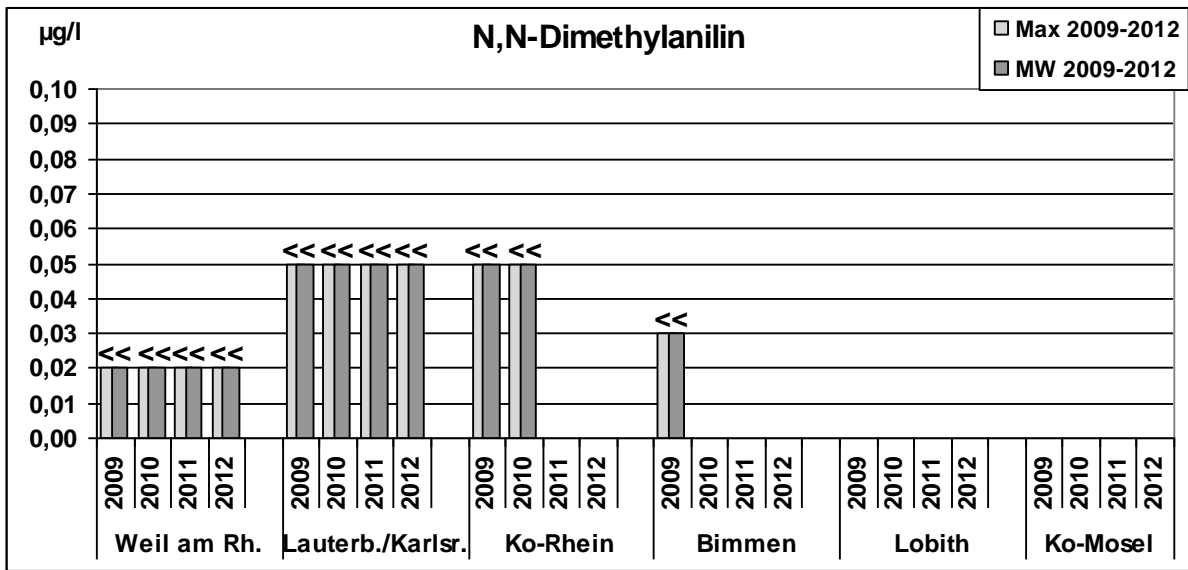
Graph 80 Nitrobenzene: Maximum (max) and mean (MW) values between 2009 and 2012



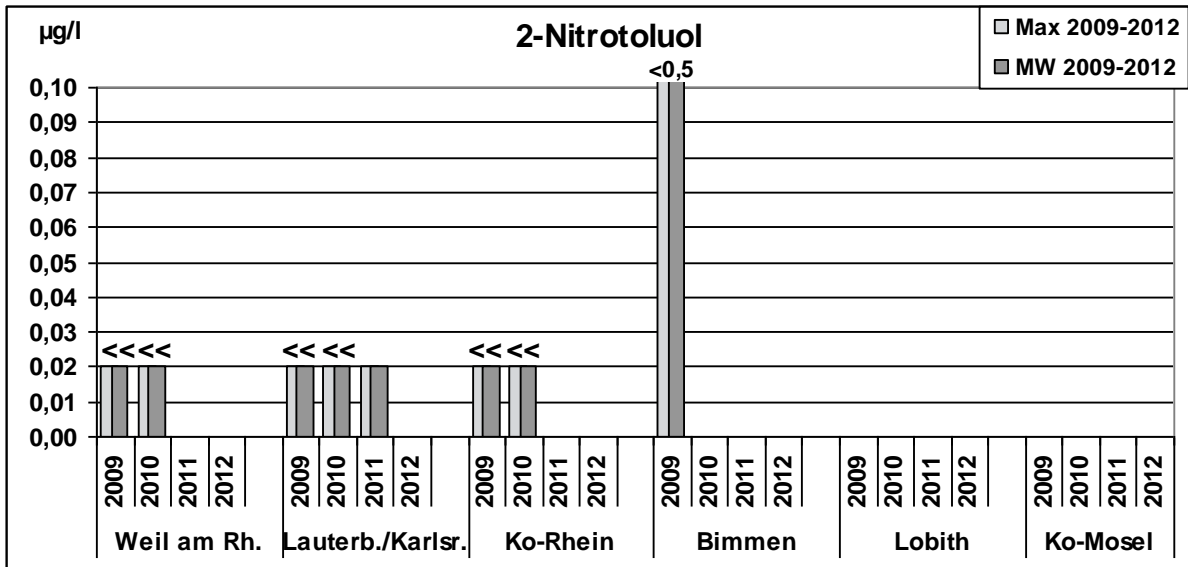
Graph 81 N,N-diethylaniline: Maximum (max) and mean (MW) values between 2009 and 2012



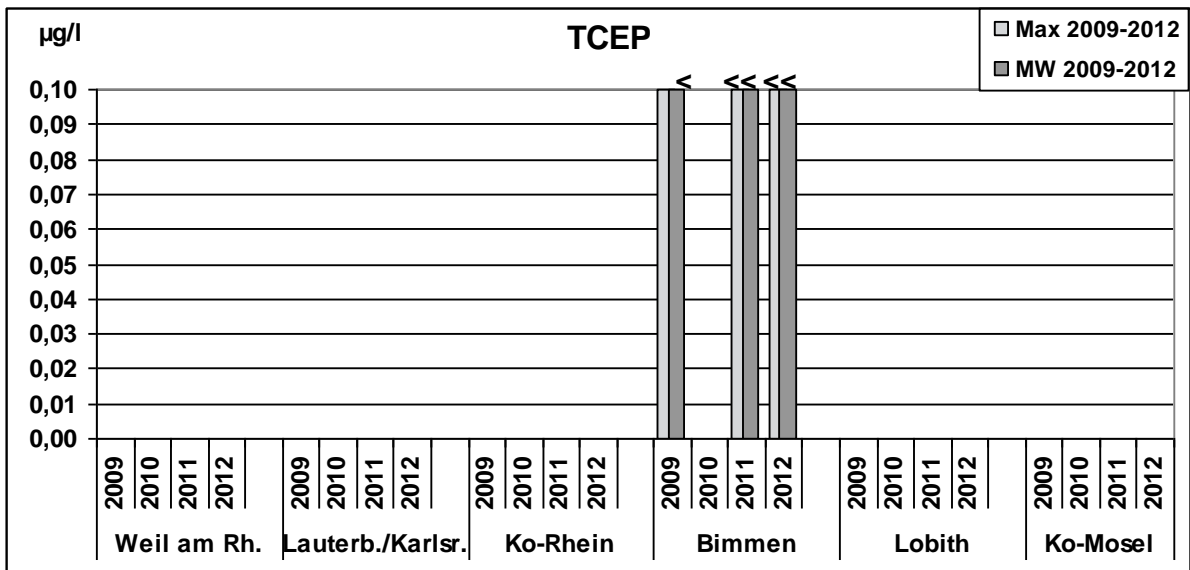
Graph 82 N,N-dimethylaniline: Maximum (max) and mean (MW) values between 2009 and 2012



Graph 83 2-nitrotoluene: Maximum (max) and mean (MW) values between 2009 and 2012



Graph 84 TCEP: Maximum (max) and mean (MW) values between 2009 and 2012



Conversion into total contents.

The conversion method described was used for substances marked in light blue in the Tables of the report at hand.

Table 1: Formula for calculating the total content of partly dissolved and partly adsorbed substances.

$C_{Ti} = 2 (Si \times C_{Si}) \times 10^{-6}$ <p>Remark: The 50- or 90-percentile and mean annual concentration (MAV) are calculated based on C_{Ti}-values</p>	C_{Ti} = Total content on the day of sampling in $\mu\text{g/l}$ Si = Suspended matter content on the day of sampling in mg/l C_{Si} = Pollutant content of suspended matter on the day of sampling in $\mu\text{g/kg}$
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Table 2: Formula for calculating the total content of predominantly adsorbed substances

$C_{Ti} = (Si \times C_{Si}) \times 10^{-6}$ <p>Remark: The 50- or 90-percentile and mean annual concentration (MAV) are calculated based on C_{Ti}-values</p>	C_{Ti} = Total content on the day of sampling in $\mu\text{g/l}$ Si = Suspended matter content on the day of sampling in mg/l C_{Si} = Pollutant content of suspended matter on the day of sampling in $\mu\text{g/kg}$
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Example for a conversion of ammonium-N values for a comparison with the guidance value for ammonia.

For a transitional period, a comparison was made between the monitoring values of ammonium N with the ICPR target value for ammonium N (Chapter 2.1.3). In this annex, and preparing future reports on the development and evaluation of Rhine water quality, the conversion of ammonium N measurement values to the ammonium share is explained and compared to the guidance value for ammonia (ICPR report 164).

For all stations mentioned in the Table except for Weil am Rhein, the Rhine Monitoring Programme Chemistry also indicates the water temperatures (WT) and the pH-values at the time of NH₄-N (E14) random sampling. For the period 2009-2011, results for daily random samples taken at the Bimmen monitoring station are available for all three parameters.

In addition, for the monitoring station Weil am Rhein, annual average values were additionally calculated based on daily mean water temperature and pH values on the day of sampling. The values are indicated in brackets.

The calculation method is based on ICPR recommendations for a guidance value of 5 µg/l for NH₃ (ICPR report no. 164).

Conclusion: at all monitoring stations considered, the annual mean values calculated on the basis of the E14 random samples are distinctly below the guidance value set to 5 µg/l. The highest mean annual values were found in 2011 with 1.8 µg/l at the monitoring stations Bimmen and Koblenz-Moselle.

The comparison of the results at Bimmen for 2009-2011 of daily random samples with random samples taken every fortnight does not indicate any significant difference. The calculation of mean annual values based on mean daily temperature and pH-value (instead of the values at the time of sampling) does not result in any significant difference compared to available data for Koblenz-Rhine and Koblenz-Moselle in 2012.

Ammonium-N Guidance value for ammonia	Monitoring station	Mean annual value in µg/l NH ₃			
		2009	2010	2011	2012
5 µg/l (NH ₃)	Weil am Rhein	(1.6)	(1.6)	(1.7)	(1.4)
	Lauterbourg/Karlsruhe	1.4	0.67	0.54	0.80
	Koblenz	0.79	0.91	0.70	0.88
	Bimmen	1.6	1.3	1.8	1.6
	Lobith	1.0	1.3	1.1	0.95
	Koblenz-Moselle	1.2	1.8	1.8	0.87

Annex 4

Definition of the limit of quantification and of the reporting limit

"Limit of quantification" (according to Directive 2009/90/EC) means a stated multiple of the limit of detection at a concentration of the determinand that can reasonably be determined with an acceptable level of accuracy and precision. The limit of quantification can be calculated using an appropriate standard or sample, and may be obtained from the lowest calibration point on the calibration curve, excluding the blank;

"Reporting limit" (only used in NL)

In the Netherlands, reporting limits are used instead of limits of quantification. The reporting limit is directly derived from the lowest concentration of a chemical parameter which is measurable by a laboratory (in the Netherlands, this is called the limit of detection). The lowest concentration (limit of detection) is determined by means of experiments and corresponds to thrice the absolute standard deviation of random noise. The reporting limit is not determined by means of experiments. The reporting limit is always a value near the lowest measurable concentration (limit of detection), is however indicated as a rounded value corresponding to the lowest concentration (limit of detection) or a higher value.