Danube Transnational Programme

Danube Hazard m3c

Deliverable D.T2.3.1
Catalogue of management measures
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1. Introduction

1.1 Background

Several projects related to emissions to water, carried out in recent years for the European Commission (EC) (Roovaart, J., et al., 2013) and the EEA (ETC/ICM 2017, EEA 2018a, EEA 2018b) show serious problems regarding a sound implementation of the management cycle. Especially the preparation of the pressures and impact analysis, the risk assessment and the elaboration of an appropriate detailed Programme of Measures (POMs) remains rather weak in some countries, so also often in the Danube region. Deficient aspects include:

- very little reporting on diffuse sources;
- low use of model application to support parts of the management cycle, such as the impact and risk analyses as a precondition to create the POM

Especially, the use of models can prepare significant improvement of the above-mentioned deficits in the assessment of the management cycle items (in case input data are quantitatively and qualitatively sufficient). If reliable models are setup, they can avoid high costs and spatial constraints of monitoring and are suitable instruments to:

- bridge information gaps
- provide regionalized system analyses with quantification of pathways and sources
- give better insights in the role of diffuse pollution and the specific pathways
- calculate the effect of scenarios (e.g. of mitigation measures).

Consequently, in this project, modelling (among others) plays an important part and is prepared on two spatial and content-specific scales.

On the one hand side, the emission model MoRE (Modelling of Regionalized Emissions, Fuchs et al., 2017), representing a spatial medium-scale Tier III – pathway oriented approach (Technical Guidance Document, No 28) is established in seven pilot regions and four countries (Romania, Bulgaria, Hungary, Austria) representing the typical natural and socio-economic gradient in the Danube Catchment (WP T2). All pilot regions can be used as "Role Model" for further application in the Danube region and thus strengthening the implementation of the management cycle in the countries with pilot regions and beyond that in the other Danube countries with similar conditions. Detailed results achieved in the pilots, e.g. with respect to i. improved data availability, ii. the understanding of system behavior, or iii. the implementation of new modelling approaches for specific substances or pathways, should feed directly into the evaluation of hot spots of pollution and an risk assessment, which clearly addresses substances, which exceed the EQS from European and from national legislation.

One aim of the modelling in pilot regions is to provide i. a model framework, which considers specific conditions in seven pilot regions in Bulgaria, Romania, Hungary and Austria (Del. 2.1.1 and Del. 2.1.2) ii. Adapt the model approaches for the substances listed below (when reasonable and possible) (Del. 2.1.1 and Del. 2.1.2) iii. Prepare a system analyses for the pilot regions and iv. Evaluate, based on a risk analyses, a catalogue of measures, which is Taylor-made to the specific conditions and adopted to needs but also opportunities in the pilot regions.

The modelled substances were selected before the start of the project, represent chemicals, which are of major relevance in the Danube Basin, and should be also of high relevance in the pilot regions:

- Perfluorooctanesulfonic acid (PFOS), Perfluorooctanoic acid (PFOA) (industrial chemicals)
- 16 EPA Polycyclic aromatic hydrocarbons (PAHs, industrial chemicals, and combustion by-products)

- Mercury (Hg), Cadmium (Cd), Copper (Cu), Nickel (Ni), Lead (Pb), Zinc (Zn), and Arsenic (As) (metals)
- Diclofenac and Carbamazepine (pharmaceuticals)
- 4-tert-Octylphenol (industrial chemical)
- Nonylphenol (industrial chemical)
- Bisphenol A (industrial chemical)
- Metolachlor (herbicide) including Metolachlor-ESA and Metolachlor-OA (metabolites)
- Tebuconazole (fungicide) (Del. 1.2.2, 2020).

If necessary, measures will address the agricultural and the industrial sector, mining sites as well as the urban and rural wastewater management.

In the following Deliverable, a short overview on the results from the risk assessment is prepared, followed by a description of relevant pathways, which account for a high proportion of the exceedance of the EQS and resulting from this the proposed mitigation measures.

2. Results from the risk assessment

In the WFD the risk analyses is a prerequisite for setting measures. If there is a risk that the target will not be met, appropriate measures must be taken and implemented. The EU countries use results from there nation-wide monitoring approaches and support the results (if available) with model results. From the monitoring approaches, the often 12 fold monthly measurements are used to calculate mean annual concentrations, which are compared to the EU and additionally to the nation-wide prescribed EQS.

In the Danube Hazard m3c project, a specific monitoring approach of surface waters was designed, which should on the one hand guarantee optimal results with respect to annual concentration and load calculations (needed among others for the validation of the model results) and on the other hand should avoid extreme high costs from countless analyses. Due to these objectives, the monitoring approach in surface water was designed, by:

- Preparing bimonthly composite samples from weekly grab samples during average flow conditions (low flow to mean flow and even discharges above MQ).
- Considering event flow conditions (with flood peaks often representing the highest 10 % discharges of a long-term series) by automatic sampling (OT1.2 Demonstration of harmonized and cost effective monitoring).

It was discussed, that the monitoring of the composite samples would be a good representation of the sampling that is routinely performed in the different Danube countries. These are usually carried out according to a fixed, regular schedule and only postponed at short notice, when extreme events hinder accessibility or jeopardize representative sampling. Consequently, the six bimonthly composite samples were used to calculate mean annual concentrations on each of the 20 monitoring sites. In case of analytics detect probes below the limit of detection (LOD), they have been calculated as LOD/2.

This is explicitly mentioned here, because specific calculations made in "OT1.2 Demonstration of harmonized and cost effective monitoring" that do not correspond to the considerations made above and have not been made for a risk assessment, can produce deviating results.

Results for risk assessment, which should reproduce the applied methodology, are demonstrated in Table 2-1.

For PFOS in nine sub-catchments from five pilot regions an exceedance of EQS was calculated. This includes pilot regions with an increased anthropogenic activities, like Wulka and Zagyva and Somesul Mic downstream the point emission of the large WWTP of Cluj Napoka, but also at the outlet of the pilots Ybbs and Vit (pilots mainly characterized by extended natural areas), where mean annual concentration were only very slightly above the EQS of 0,00065 µg/l.

The pesticide s-Metolachlor is regulated under the "National List of Substances" in Hungary with 0,2 µg/l. In Koppany, an example of catchments with intensive agricultural use, mean annual concentration were calculated from monitoring results, which are significantly higher. In no other country with pilot regions, a Quality standard for s-Metolachlor exists. However, no concentrations nearly as high as in Koppany could be measured in any other catchment area.

The Viseu pilot region was selected to understand more about the influence of abandoned mining, which has an important impact in many regions of the Danube River Basin. Obviously, the distinct influence of abandoned mining is reflected in the conditions in surface waters, with significantly elevated levels of heavy metal pollution, especially from cadmium, copper and zinc. While cadmium concentration exceed the EQS prescribed in the Directive 2013/39/EU (which also regulates PFOS), zinc and copper overshoot the national regulation.

Country/National regulation	Pilot region	Station	Sub-catch-ment ID	Substances (PS and National substance	Substances (new PS proposals)	Substance group	EQS [µg/l]	Proposed new EQS [µg/l]	Source of EQS	Monitored mean conc [µg/l]*	Factor conc/EQS
AT	Wulka	AWM	12001	PFOS	-	Industry	0,00065	-	Directive 2013/39/EU	0,00398	6,1
AT	Wulka	AWN	12003	PFOS	-	Industry	0,00065	-	Directive 2013/39/EU	0,00354	5,4
AT	Wulka	AWE	12002	PFOS	-	Industry	0,00065	-	Directive 2013/39/EU	0,00404	6,2
AT	Wulka	AWN	12003	-	PFOA	Industry	-	0,0044	new proposal PS list	0,00284	0,6
AT	Wulka	AWE	12002	-	PFOA	Industry	-	0,0044	new proposal PS list	0,00461	1,0
AT	Wulka	AWM	12001	-	Bisphenol A	Industry	1,6	0,000034	national substance List/new proposal PS list	0,03	0,019; 882,353
AT	Wulka	AWN	12003	-	Bisphenol A	Industry	1,6	0,000034	national substance List/new proposal PS list	0,0152	0,01; 447,059
AT	Wulka	AWE	12002	-	Bisphenol A	Industry	1,6	0,000034	national substance List/new proposal PS list	0,0883	0,055; 2597,059
AT	Wulka	AWM	12001	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	0,64566	16,1
AT	Wulka	AWN	12003	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	0,0695	1,7
AT	Wulka	AWE	12002	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	0,642	16,1
AT	Ybbs	AYL	11001	PFOS	-	Industry	0,00065	-	Directive 2013/39/EU	0,00073	1,1
AT	Ybbs	AYH	11005	-	Bisphenol A	Industry	1,6	0,000034	national substance List/new proposal PS list	0,01	294,1
AT	Ybbs	AYU	11002	-	Bisphenol A	Industry	1,6	0,000034	national substance List/new proposal PS list	0,00103	30,3
AT	Ybbs	AYL	11001	-	Bisphenol A	Industry	1,6	0,000034	national substance List/new proposal PS list	0,01	294,1
HU	Koppany	HKH	21001	s-Metolachlor	-	Pesticides	0,2	-	national substance List	11,537	57,7
HU	Koppany	HKT	21002	s-Metolachlor	-	Pesticides	0,2	-	national substance List	5,761	28,8
HU	Koppany	HKH	21001	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,0115	338,2
HU	Koppany	HKT	21002	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,0119	350,0
HU	Koppany	HKH	21001	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	0,6536	16,3
HU	Koppany	HKT	21002	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	0,2401	6,0
HU	Zagyva	HZN	22004	PFOS	-	Industry	0,00065	-	Directive 2013/39/EU	0,00091	1,4
HU	Zagyva	HZT	22005	PFOS	-	Industry	0,00065	-	Directive 2013/39/EU	0,00143	2,2
HU	Zagyva	HZH	22002	PFOS	-	Industry	0,00065	-	Directive 2013/39/EU	0,00133	2,0
HU	Zagyva	HZN	22004	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,0304	894,1
HU	Zagyva	HZT	22005	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,0399	1173,5
HU	Zagyva	HZH	22002	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,01	294,1
HU	Zagyva	HZ6	22001	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,00602	177,1
HU	Zagyva	HZN	22004	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	0,1636	4,1
HU	Zagyva	HZT	22005	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	1,3558	33,9
HU	Zagyva	HZH	22002	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	0,2505	6,3
HU	Zagyva	HZ6	22001	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	0,2523	6,3
RO	Viseu	RVC	32003	Cadmium	-	Heavy Metals	0,25 (class 5)	-	Directive 2013/39/EU	5,524	Min: 22,1
RO	Viseu	RVV	32001	Cadmium	-	Heavy Metals	0,25 (class 5)	-	Directive 2013/39/EU	0,7801	Min: 3,1
RO	Viseu	RVC	32003	Copper	-	Heavy Metals	10 (class 3)	-	national substance List	36,977	Min: 3,7
RO	Viseu	RVV	32001	Copper	-	Heavy Metals	10 (class 3)	-	national substance List	15,97	Min: 1,6
RO	Viseu	RVC	32003	Zinc	-	Heavy Metals	73 (class 3)	-	national substance List	1572,124	Min: 21,5
RO	Viseu	RVV	32001	Zinc	-	Heavy Metals	73 (class 3)	-	national substance List	174,384	Min: 2,4
RO	Viseu	RVC	32003	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,0164	482,4
RO	Viseu	RVV	32001	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,0147	432,4
RO	Somesul Mic	RSD	31001	PFOS	-	Industry	0,00065	-	Directive 2013/39/EU	0,00096	1,5
RO	Somesul Mic	RSU	31003	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,01	294,1
RO	Somesul Mic	RNR	31002	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,1	2941,2
RO	Somesul Mic	RSD	31001	-	Bisphenol A	Industry	-	0,000034	new proposal PS list	0,0153	450,0
RO	Somesul Mic	RSU	31003	-	-	-	-	-	-	-	-
RO	Somesul Mic	RNR	31002	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	0,0907	2,3
RO	Somesul Mic	RSD	31001	-	Diclofenac	Pharmaceuticals	-	0,04	new proposal PS list	0,3391	8,5
BG	Vit	BVD	41001	PFOS	-	Industry	0,00065	-	Directive 2013/39/EU	0,00073	1,1
BG	Vit	BVB	41005	-	Bisphenol A	Industry	1	0,000034	national substance List/new proposal PS list	0,01	0,01; 294,118
BG	Vit	BVC	41004	-	Bisphenol A	Industry	1	0,000034	national substance List/new proposal PS list	0,01	0,01; 294,118
BG	Vit	BVD	41001	-	Bisphenol A	Industry	1	0,000034	national substance List/new proposal PS list	0,01	0,01; 294,118

* calculated from 6 bimonthly composite samples at low and mean flow conditions

Table 2-1: Risk assessment considering all monitored substances and outlook to possible further risk in future (proposed new substances and proposed EQS).

Table 2-1 furthermore gives a first impression of future challenges, which might arise from new substances and EQS proposed in the revised Directive 2013/39/EU. For PFOA, but especially for Bisphenol A and Diclofenac a large number of overshootings of the EQS are evaluated that would affect each of the selected pilot areas.

Although, the model performance in reproducing PFOS concentration in 20 monitoring sites shows a good fit (Figure 2-0-1), the low EQS of 0,00065µg/l makes a modelled risk assessment a serious challenge. From nine sub-catchments with exceedances calculated from the monitoring program, the model could only reproduce five. Few further sub-catchments were addressed to exceed the EQS in the 34 sub – catchments based on modelling results. All of them were situated in the Wulka pilot catchment, which is affected strongest by PFOS pollution.

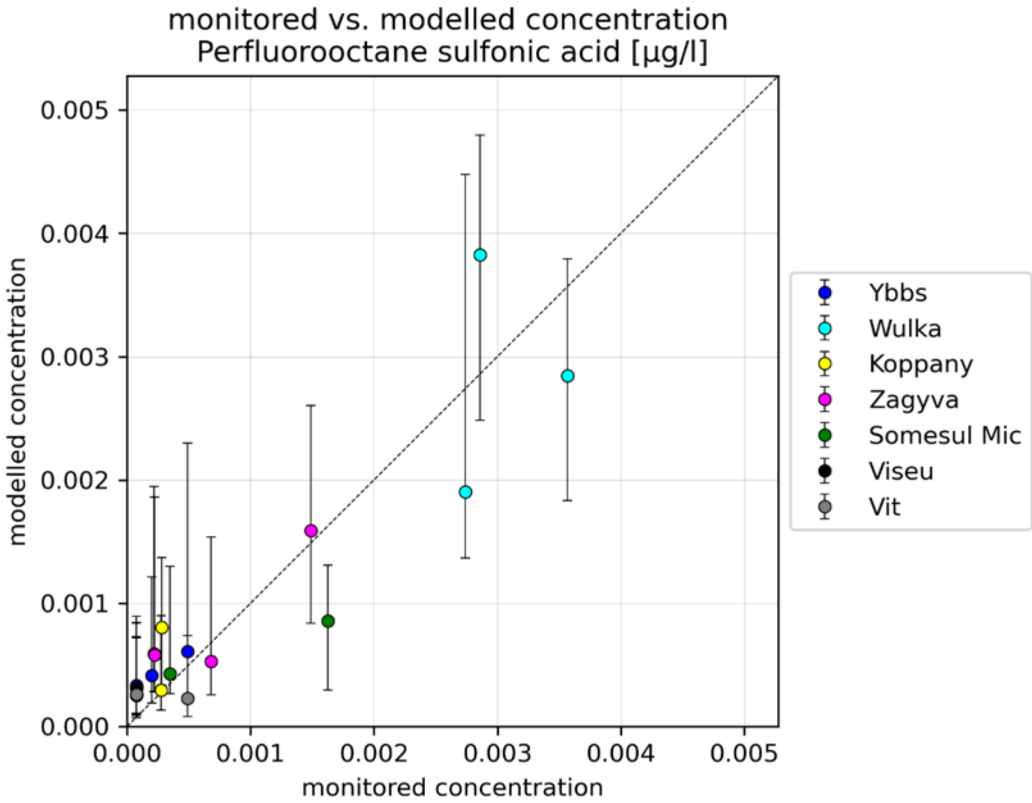


Figure 2-0-1: Monitored versus modelled PFOS concentrations in 20 sub-catchments [µg/l].

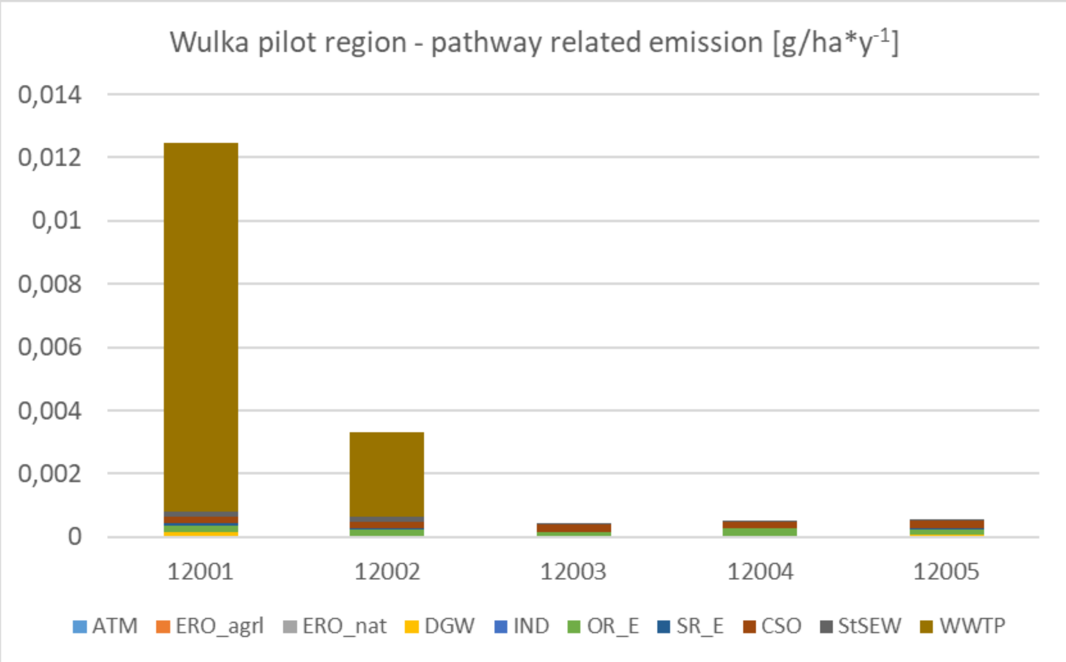
Also for the heavy metals cadmium, copper and zinc a good or sufficient model performance could be established. In addition to the exceedances indicated by monitoring, the model results also calculate exceedances of cadmium and zinc in the non-monitored catchment area of Viseu (ID 32002).

3. Pathway evaluation

3.1 PFOS

The highest PFOS concentrations in all pilot regions were found in the Wulka pilot region. Especially in the more downstream sub-catchments 12001, 12002 and 12003 the measured concentration exceed the EQS by factor five to six. In the more upstream sub-catchments model results compute an exceedance of factor 1,3 only. In Zagyva the monitored exceedance of EQS is much smaller. The factors range between 1,4-2,2 (sub-catchment 22001, 22002, 22004 and 22005). In the catchment, which is not monitored (22003) the model calculates an undercutting of the EQS with factor 0,91.

Figure 3-0-1 expresses the shares of different pathways in g/ha*y^{-1} for each sub-catchment of pilotregion Wulka and Zagyva.



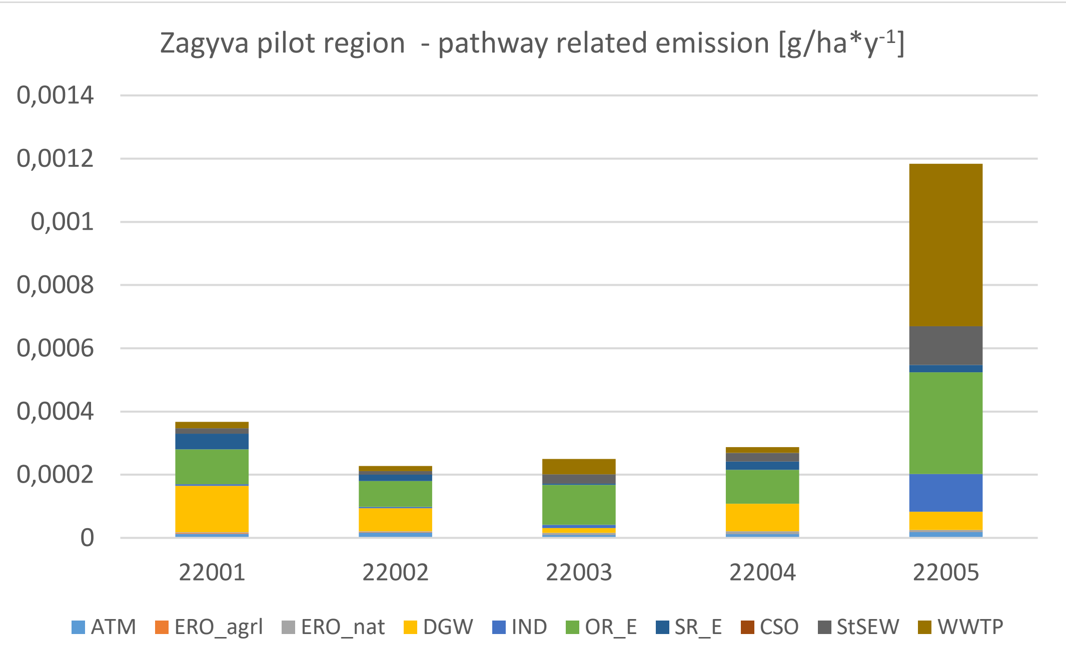


*Figure 3-0-1: Area specific Loads [g/ha*y^{-1}] in sub-catchments of pilot regions Wulka and Zagyva.*

In general the area – specific loads in the Wulka sub-catchments with operating point sources are an order of magnitude higher, than in Zagyva and clearly dominate the PFOS inputs. Emission from sewer systems compared to the point sources have only a minor influence. In Zagyva the upstream sub-catchment ID 22005, obviously has a strong influence on the downstream parts of the river, with area-specific emission being fivefold higher than in the other parts of the pilot catchment.

Specific situation in Wulka catchment: In the Wulka catchment the treatment plants under investigation have a capacity of 54.000 p.e. (12002) and 110.000 p.e. (12001) and are equipped with nutrient removal (N and P). In both sub-catchments emission from WWTPs represent the dominant pathway with more than 60% (12002) and more than 80% in 12001. In the other sub-catchments, the emission from combined sewer overflows play a dominant role. For catchments, 12002 and 12001 the focus on possible mitigation measures to reduce PFOS emissions can be placed on the reduction of inputs from wastewater treatment plants. Information from the Swedish EPA (2017) point out, that the purification capacity of PFOS can be increased to 75 % by using activated carbon. The expansion of the large wastewater treatment plant of Wulkatal with an advanced purification stage is in line with actual proposals from the revised UWWTD presented for discussion with the member states. Here, a fourth treatment stage on municipal wastewater treatment plants >100,000 p.e. to be implemented by 2035 is proposed. For municipal WWTPs >10.000 EW – 100.000 p.e. in catchments with risk, the fourth treatment stage is proposed to be implemented by 2040.

In catchment 12003 (with sewer being treated at plant "Wulkatal" in 12001) and the other two upper catchments high shares of PFOS emission stem from combined sewer overflows (more than 40% of the total emission). Scenario results from an earlier study (STOBIMO Spurenstoffe, https://info.bml.gv.at/themen/wasser/wasserqualitaet/fluesse_seen/stobimo-spurenstoffe.html) increasing the solids retention before discharge in storm water overflow and combined sewer overflow, point out only a slight reduction for PFOS (as a consequence of its system behavior). However, a higher share of storm water retained in the systems and transferred to the purification at the wastewater treatment plant would be a promising measure to reduce PFOS in those catchments. Again, the proposed measure is based on proposals from the revised UWWTD, which discusses integrated management plans for municipal Wastewater for settlement areas > 100.000 p.e. (2030) as well as possible integrated management plans for municipal Wastewater for settlement areas > 10.000 – 100.000 p.e. (2035) in case of a risk.

Proposal for potential mitigation measures: Advanced wastewater treatment at treatment plant "Wulkatal" (100.000 p.e.) and "Eisenstadt" (54.000 p.e.). Adsorption stage (activated carbon) for municipal wastewater treatment plants.

Increased retention capacity of combined sewer overflow and treatment on the plant "Wulkatal".

Specific situation in the Zagyva catchment: In the investigated region, model results underestimate the PFOS concentration in 22004 and 22002. Emissions from separate sewer systems overflows have a significant share of the total PFOS emission in the Zagyva pilot region. Further significant shares of total PFOS emission are calculated from groundwater, which resulting from a high proportion of the water balance at low concentrations. In the Zagyva pilot region almost in all sub-catchment, municipal WWTPs and even industrial direct dischargers are present. However, their total share on the PFOS emission in the catchments is only around 15%. Only in the upstream catchments (22005), the share of municipal and industrial wastewater is in a magnitude of more

than 40% with a clear dominance of the municipal wastewater, having a significant share on the net discharge in this catchment.
While Information from the Swedish EPA (2017) point out, that the purification capacity of PFOS can be increased to 75 % by using activated carbon, a reduction of PFOS emission from storm-water discharges from separate systems is not easy to achieve. Scenario results from an earlier study (STOBIMOSpurenstoffe,2019, increasing the solids retention before discharge in storm water overflow and combined sewer overflow, point out only a slight reduction for PFOS (as a consequence of its system behavior).
Proposal for potential mitigation measures: Advanced wastewater treatment at the municipal treatment plant in sub-catchment 22005 > 10.000 p.e.. Adsorption stage (activated carbon) for municipal wastewater treatment plants. The proposed measure is in line with proposals from the revised UWWTD, which discusses construction of a 4th purification stage for municipal wastewater for settlement areas > 10.000 – 100.000 p.e. (2040) in case of a risk.

Ybbs, Somesul Mic and Vit

The catchment outlet of Ybbs (ID 11001), Somesul Mic (ID 32001) and Vit (ID 41001) also show slight exceedances of the PFOS EQS (factor 1,1, 1,5 and 1,1).

Specific situation in Ybbs catchment: The dominant share of the low PFOS emission in the upstream sub-catchments stem from groundwater and surface runoff, which do lead to surface water concentrations significantly below the EQS (results from monitoring and modelling results). The increase of PFOS concentration in catchment 11001, which leads to an exceedance of the EQS by factor 1,1 is mainly related to an increased influence from WWTPs (>10.000 p.e.), industrial direct dischargers and emission from rainwater discharges via separate sewer systems in this more urban area. However, the monitoring of one WWTP ("Oberes Urltal") in the sub-catchment gives evidence, that effluent concentration are in the range of the LOD (0,0015 µg/l) or below and therefore shows only a slight potential for further significant and effective reductions of PFOS. With respect to modelling, which underestimates the PFOS concentration in sub-catchment 11001, around 20% of PFOS emission stem from storm-water overflows and from municipal WWTP effluents and around 25% from industrial wastewater.

Information from the Swedish EPA (2017) point out, that the purification capacity of PFOS can be increased to 75 % by using activated carbon. A reduction of PFOS emission from storm-water overflows is not easy to achieve. Scenario results from an earlier study (STOBIMO Spurenstoffe, 2019), increasing the solids retention before discharge in storm water overflow and combined sewer overflow, point out only a slight reduction for PFOS (as a consequence of its system behavior).

Proposal for potential mitigation measures: Advanced wastewater treatment at treatment plants in sub-catchment 11001 > 10.000 p.e.. Adsorption stage (activated carbon) for municipal wastewater treatment plants. Advanced wastewater treatment for industrial direct dischargers.

Specific situation in Somesul Mic: While in the analitical unit 31001 the dominant share of the PFOS emission stems from the Wastewater Treatment Plants and a further serious share from combined sewer systems and stormwater overflows other pathways are more relevant in the more rural upstream regions and in the sub-catchment of the tributary Nadas. Here surface-runoff and groundwater and interflow are much more important. However, these emission do not result in an exceedance of PFOS EQS in the upstream catchments. This finding is also supported by the model results in the other sub-catchments, which calculate concentration well below the EQS in all other sub-catchments.

Data of PFOS from municipal WWTP in Romania (as well as many other European countries) are sparse. In the Somesul Mic catchment three waste water Treatment Plants (Cluj Napoca, Apahida and Tetarom III (Jucu)) were monitored in the project (3x influent and effluent weekly composite sample). In order to increase the robustness of the assessment, the project adds data from different Danube countries in a data base that will be used for a possible evaluation of measures.

As a result, the focus can be laid on the inputs from the outlet catchment area and concentrate on improving the purification capacity of the large Waste Water Treatment Plant of Cluj Napoca. The treatment plant has a capacity of 414.000 p.e. and a load of 366.867 p.e. and is equipped with nutrient removal stage (N and P).

Information from the Swedish EPA (2017) point out, that the purification capacity of PFOS can be increased to 75 % by using activated carbon. Moreover, the expansion of the large wastewater treatment plant of Cluj Napoca with an advanced purification stage is in line with actual proposals from the revised UWWTD for micro-pollutants presented for discussion with the member states. Here, a 4 treatment stage on municipal wastewater treatment plants >100,000 p.e. to be implemented by 2035 is proposed.

Proposals for potential mitigation measures: Advanced wastewater treatment for municipal wastewater treatment plants with a capacity of > 100.000 p.e.. Concrete: Adsorption stage (activated carbon) at the large treatment plant of Cluj Napoca. Beneath a serious further reduction of PFOS, this would have a large additional positive effect on a huge number of organic and inorganic pollutants and the water quality of Somesul Mic downstream Cluj Napoca.

Specific situation in Vit catchment: In the Vit catchment the dominant pathways for PFOS emission are groundwater and surface runoff. Direct emission from untreated wastewater via sewer systems discharging into surface water is another significant pathway. Treatment of untreated wastewater is a measure with a valuable effect, not only with respect to decrease PFOS concentrations. Due to the only slight exceedance of the EQS of factor 1,1 the treatment of wastewater in the pilot region can be a sufficient measure to undershoot the PFOS EQS in sub-catchment 41001.

Proposal for potential mitigation measures: Currently, a lot of research for removing of PFOS from water is done worldwide. The repair of the sewerage system, construction of well-operated small wastewater treatment plants and optimization of existing wastewater treatment plants can have a positive impact over the reduce of PFOS concentrations in surface waters.

3.2 Heavy metals

In the Viseu pilot region monitored concentration of cadmium, copper and zinc show extreme high values. The highest emission are related to the upstream sub-catchment ID 32003, where direct discharges from abandoned mining sites could be monitored. Exemplarily, the emission of copper [kg/y] and the share of pathways is presented in Figure 3-2. In sub-catchment 32002 similar geological conditions are present. In the model approach, this leads to high emission from groundwater. However, among 50% of all emissions of copper in the Viseu pilot region stem from direct discharges from abandoned mining sites.

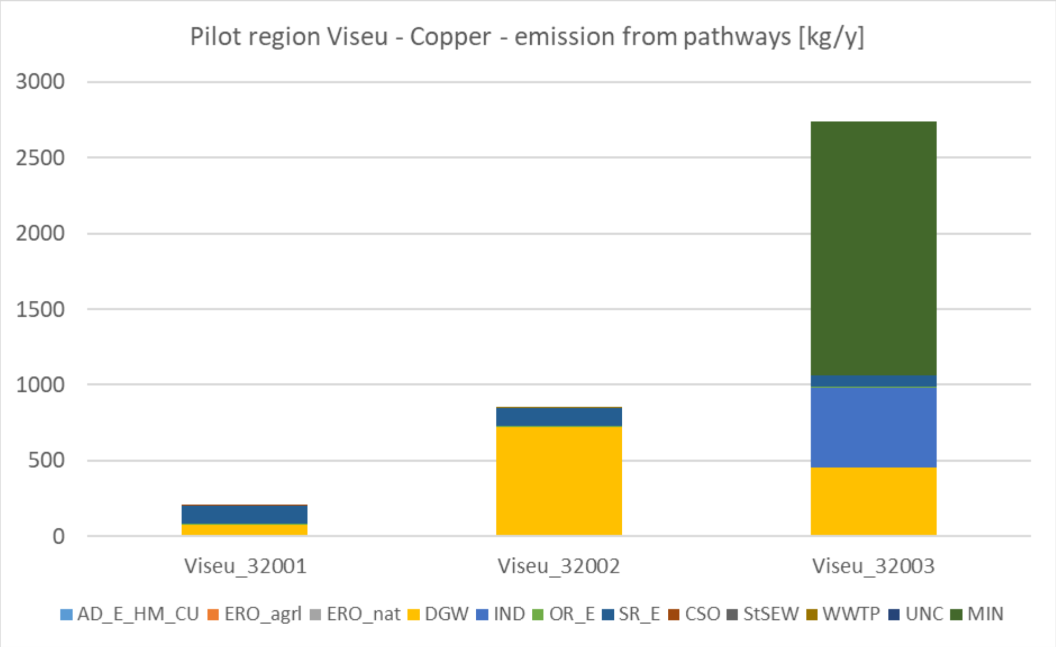


Figure 3-2: Copper emission [kg/y] in sub-catchments of the Viseu pilot region.

Specific situation: As mentioned above, the catchment under investigation is heavily influenced by former mining activities. In soil probes partly high concentration were found with respect to Cadmium, Zinc and even Copper. Concentrations in Waste Water Treatment Plant effluents were still high, when influenced by mining (32003), with Cu and Zn in a range of 1 or 0,5 mg/l and Cd with 0,04 mg/l. Untreated mining water, also monitored in this project in five different well known effluents shows the highest concentrations. Here mean Cu and Zn concentrations range in a magnitude of 0,6-4 mg/l and 2 to 35 mg/l, while Cd concentration were found in a range of 0,01 to 0,1 mg/l. One serious problem was the estimation of a valid mean discharge from abandoned mining sites. Rough estimates lead to the assumption of 0,054 m^3/s from all five effluents, which is slightly higher, than the treated effluent from one mining site (0,037 m^3/s).

Of course, these estimations and the model results prepared so far underlie significant uncertainties! Nevertheless, using maximum literature data of groundwater concentrations from mining influenced area still leads to a significant underestimation of dissolved concentrations of Cd, Cu and Zn monitored in the surface water in sub-catchment 32003. This leads to the assumption, either that the discharge of untreated mining water is underestimated or that serious amounts of Cd, Cu and Zn are emitted from unknown, untreated diffuse discharges of abandoned mining sides, from pits, pump sumps, entering the surface water system by percolation, interflow and via small temporary trickles. Of course, a combination of both effects is also possible.

Despite the serious uncertainties, it becomes clear, that the influence of abandoned mining is a significant threat to surface waters in the Viseu pilot region. At least 60% of emission of Cu and Zn and 40% of Cd stem from untreated, but well known discharges of abandoned mining in sub-catchment 32003. For Cu even the discharge of the treated mining influenced wastewater has still a serious share of the total emission of more than 20%.

In 32002 and 32001 the dominant pathways of dissolved heavy metals are groundwater and with minor influence surface runoff.

Proposals for potential mitigation measures:

In a first step the untreated well known abandoned mining effluent should be treated. In Treatment Plants, transfer coefficients into the sewage sludge can be subject to large variations for heavy metals. In a literature study Diepold, 2020 found mean transfer coefficients of 0,72 (Cd), 0,79 (Cu) and 0,66 (Zn). After optimization, in actual treatment plants an even better purification could be managed, with: 96% (Cd), 90% (Cu) and 86% (Zn) (Diepold, 2020). Similar purification rates could be achieved in mining waters (e.g. Gallagher et al., 2012). With respect to Cu even the existing treatment needs to be significantly improved (which is partly true for Cd and Zn).

The construction of the WWTPs should be planned on base of a detailed register including even suspected contaminated sites and diffuse sources of mining influenced water, percolating to smaller ditches and creeks. Even diffuse runoff from those areas should be collected and treated.

Short – term perspective: Cleaning of abandoned mining water from well-known and diffuse runoff.

Target value: Reduce Cd, Cu and Zn concentrations by 96%, 90% and 86%.

Mid-term/Long-term perspective: Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment).

Target value: Reduction of groundwater emission by 50%.

3.3 Pesticides

In the Koppany pilot region s-Metolachlor significantly exceed the EQS from the National Substance List of 0,2 µg/l.

Specific information of Koppany catchment: Concentrations of s-Metolachlor in arable soils show increased values in five from six composite samples. In all four samples of suspended matter from high flow events, the concentrations of s-Metolachlor were increased, too; in atmospheric deposition only in May and June s-Metolachlor concentrations were analyzed above the limit of detection. All findings give evidence of transport by erosion and surface runoff being at least periodically of relevance. All samples from WWTP were below the limit of detection.

The water balance in Koppany is dominated by subsurface- and base flow with around 60%; Surface runoff has a share of around 10%. Effluent from Waste Water Treatment Plants share in a magnitude of 5% in 21001 and around 25% in 21002.

Proposal for potential mitigation measures: Proposed Mitigation measure I: Source control - reduction of s-Metolachlor application by 50% on all relevant crops. Proposed mitigation measure II: reduction of erosion from arable land by 50%.

3.4 Conclusions

The detailed analyses conducted in chapter 3, point out the decision for specific mitigation measures. On the one hand, the effectiveness of measures was taken into account, on the other hand even the practicability was considered. Results for this analyses stem from monitoring and modelling. The considerations and interpretations leads to a proposal of measures for all pilot regions, which is summarized in a catalogue of measures.

4. Catalogue of measures

Country/ National regulation	Pilot region	Station	Sub-catch-ment ID	Substances (PS and National substance list)	Catalogue of Measures
AT	Wulka	AWM	12001	PFOS	Advanced wastewater treatment at treatment plant "Wulkatal" (100.000 p.e.): Adsorption stage (activated carbon) for municipal wastewater treatment plants.
AT	Wulka	AWE	12002	PFOS	Advanced wastewater treatment at treatment plant "Eisenstadt" (54.000 p.e.): Adsorption stage (activated carbon) for municipal wastewater treatment plants.
AT	Wulka	AWN	12003	PFOS	Increased retention capacity of combined sewer overflow and treatment on the plant "Wulkatal".
AT	Wulka	-	12004	PFOS	Increased retention capacity of combined sewer overflow and treatment on the plant "Wulkatal".
AT	Wulka	-	12005	PFOS	Increased retention capacity of combined sewer overflow and treatment on the plant "Wulkatal".
AT	Ybbs	AYL	11001	PFOS	No specific further measures.
HU	Zagyva	HZH	22002	PFOS	No specific further measures.
HU	Zagyva	HZN	22004	PFOS	No specific further measures.
HU	Zagyva	HZT	22005	PFOS	Advanced wastewater treatment at the municipal treatment plant > 10.000 p.e.: Adsorption stage (activated carbon) for municipal wastewater treatment plants.
RO	Somesul Mic	RSD	31001	PFOS	Advanced wastewater treatment at the large treatment plant of Cluj Napoca with a capacity of > 100.000 p.e.: Adsorption stage (activated carbon) for municipal wastewater treatment plants.
BG	Vit	BVD	41001	PFOS	Repair of the sewerage system; Construction of well-operated small wastewater treatment plants; Optimization of existing wastewater treatment plants.
RO	Viseu	RVV	32001	Cadmium	1. Short – term: Cleaning of abandoned mining water from well-known and diffuse runoff. 2. Mid-term/Long-term: Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment).
RO	Viseu	-	32002	Cadmium	1. Short – term: Cleaning of abandoned mining water from well-known and diffuse runoff. 2. Mid-term/Long-term: Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment).
RO	Viseu	RVC	32003	Cadmium	1. Short – term: Cleaning of abandoned mining water from well-known and diffuse runoff. 2. Mid-term/Long-term: Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment).
RO	Viseu	RVV	32001	Copper	1. Short – term: Cleaning of abandoned mining water from well-known and diffuse runoff. 2. Mid-term/Long-term: Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment).
RO	Viseu	RVC	32003	Copper	1. Short – term: Cleaning of abandoned mining water from well-known and diffuse runoff. 2. Mid-term/Long-term: Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment).
RO	Viseu	RVV	32001	Zinc	1. Short – term: Cleaning of abandoned mining water from well-known and diffuse runoff. 2. Mid-term/Long-term: Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment).
RO	Viseu	-	32003	Zinc	1. Short – term: Cleaning of abandoned mining water from well-known and diffuse runoff. 2. Mid-term/Long-term: Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment).
RO	Viseu	RVC	32003	Zinc	1. Short – term: Cleaning of abandoned mining water from well-known and diffuse runoff. 2. Mid-term/Long-term: Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment).
HU	Koppany	HKH	21001	s-Metolachlor	1. Source control: reduction of s-Metolachlor application by 50% on all relevant crops. 2. reduction of erosion from arable land by 50%.
HU	Koppany	HKT	21002	s-Metolachlor	1. Source control: reduction of s-Metolachlor application by 50% on all relevant crops. 2. reduction of erosion from arable land by 50%.

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DANUBE RIVER BASIN MANAGEMENT PLAN (UPDATE 2021): Nutrient Emission Modelling with MONERIS. ANNEX 5.

Deliverable D.T2.1.1 (2021): Datasets containing basic input data for pilot regions.

Deliverable D.T2.1.2 (2021): Technical documentation of the model setup in the pilot regions.

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