Danube Transnational Programme

Danube Hazard m3c

Output T2.2
Report on improved system understanding as basis for adapted transnational emission modelling at DRB scale
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AUTHORS AND CONTRIBUTING PARTNERS

Name co-author	Contributing partner
Oliver Gabriel	Environment Agency Austria (Umweltbundesamt), AT
Marianne Bertine Broer	Environment Agency Austria (Umweltbundesamt), AT
Thomas Rosmann	Environment Agency Austria (Umweltbundesamt), AT
Clemens Steidl	Environment Agency Austria (Umweltbundesamt), AT
Steffen Kittlaus	TU Wien, AT
Matthias Zessner	TU Wien, AT
Ottavia Zoboli	TU Wien, AT
Nikolaus Weber	TU Wien, AT
Adrienne Clement	Budapest University of Technology and Economics, HU
Máté Krisztián Kardos	Budapest University of Technology and Economics, HU
Zsolt Jolánkai	Budapest University of Technology and Economics, HU
Katalin Mária Dudás	Budapest University of Technology and Economics, HU
Galina Dimova	Bulgarian Water Association, BG
Radoslav Tonev	Bulgarian Water Association, BG
Dimitar Mihalkov	Bulgarian Water Association, BG
Dimiter Alitchkov	Bulgarian Water Association, BG
Ioana Nedelea	National Administration "Romanian Waters", RO
Corina Boscornea	National Administration "Romanian Waters", RO
Mugurel Sidau	National Administration "Romanian Waters", RO
Elvira Marchidan	National Administration "Romanian Waters", RO
Jos van Gils	Deltares (sub-contractor of ICPDR)
Sibren Loos	Deltares (sub-contractor of ICPDR)
Adam Kovacs	International Commission for the Protection of the Danube River (ICPDR)

Responsible for the Output: Oliver Gabriel (Environment Agency Austria)

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1. Introduction

With the introduction of the Water Framework Directive (WFD, 2000/60/EEC), trace substances are included in the water status assessment, with priority substances and nationally relevant substances (other substances or river basin specific pollutants RBSP) being highlighted in particular.
According to the Directive, Member States are obliged to present national reports on the status of water bodies and the possibilities for improvement in management plans (Art. 13) and programs of measures (Art. 11). They are required to report an inventory of emissions, discharges and losses of priority substances. Such information give insights on significant pressures but also on the success of measures to reduce emissions and indicate whether further efforts may be needed to achieve good chemical status.
Several projects related to emissions to water, carried out in recent years for the European Commission (EC) (Roovaart, J., et al., 2013a/b) and the EEA (ETC/ICM 2017, EEA 2018a, EEA 2018b) show serious problems regarding consistency, completeness and quality of the EU reported emission data. More specific, the EEA reports have shown:

- Very little reporting on diffuse sources;
- Limited (incomplete) reporting on urban wastewater treatment plant (UWWTP) effluents (not all UWWTPs, not all relevant pollutants);
- Unclear quality of emission data of industrial sources (not all facilities, not all relevant pollutants);
- Inconsistent reporting in time and space (no comparable and consistent time ranges and not all river basin districts reported) (Joost van den Roovaart et al., 2020).

In the current Danube River Basin Management Plan (DRBMP) and national plans of the Danube region, this topic is heavily underrepresented, mostly owing to substantial knowledge gaps and to the lack of system understanding as well as institutional capacity regarding hazardous substances emissions pathways and effective management options.
While often concrete information on point source emission are available or at least comparatively easy to calculate, diffuse pollution can only be described by model approaches. Models are important tools for the comprehensive consideration of complex areas, for the understanding of processes, the assessment and evaluation of the emission behavior and estimation of the efficiency of measures.
They can provide spatially differentiated fundamental insights of loads emitted to water bodies from different sources and pathways, can contribute to a pressure and impact assessments also for catchments that have not been monitored and investigated in detail, and evaluate measures with regard to their effectiveness.
If reliable models are setup, they can avoid high costs and spatial constraints of monitoring and are suitable instruments to:

- Bridge information gaps,
- Give support to establish a risk assessment,
- Provide regionalized system analyses with quantification of pathways and sources,
- Calculate the effect of scenarios (e.g. of mitigation measures).

In the Interreg Danube Transnational Programme project "Tackling hazardous substances pollution in the Danube River Basin by Measuring, Modelling-based Management and Capacity building" (short title: Danube Hazard m^{3}c) in seven pilot regions all over the Danube emission modelling was performed with the emission model MoRE (Modelling of Regionalized Emissions). Pilot regions represent several specific landscape areas, like the alps

(Ybbs), the Pannonian lowlands (Wulka, Zagyva, Koppány), Transylvania (Someșul Mic) including the Eastern Carpathians (Vișeu) and the Balkan mountains (Vit) and distinctive characteristics with respect to climate, hydrology, land-use and pollution pressure. They cover aspects of "natural background", "intensive agricultural use", "high share of treated wastewater", "high share of untreated wastewater", "rural wastewater management" and "abandoned mining". The Modelling period is from 2016 – 2021, which guarantees a high degree of topicality. Consequently, the modelled pilot regions can be used as "Role Model" for further model applications in the Danube region.
In Output T2.1 the adapted MoRE model is provided together with a sound technical documentation, describing model approaches in flow charts and with a detailed description of input data.
In this Output information of improved system understanding based on modeling results are at the center of the investigations. Results were presented for different substance groups, like industrial chemicals (PFAS), Heavy metals and Pharmaceuticals. The substance group of Pesticides was added and a first modelling approach applied.
Based on evaluations in pilot regions model results give detailed information on:

- The delineation and characterization of sub-catchments,
- The water and sediment balance,
- The model validation,
- A regionalized pathway analyses,
- The role of emission models in risk analyses,
- The role of emission models to develop a catalogue of measures,
- The quantification of mitigation measures by scenario analyses.

Before the model results are presented and discussed in detail, the technical setup, the used approaches and the input data needs are shortly introduced.

2. Model setup and model algorithms

"Modeling of Regionalized Emissions" (MoRE) is a model for the regionalized pathway analysis of substance emission into surface waters (Fuchs et al., 2017) based on sub-catchments with a size of around 100 km^2. The fluxes of different substances from various sources that reach surface waters via different input pathways are calculated with the help of empirical approaches (Kittlaus et al., 2021). The model calculates the emissions via different input paths (see Figure 2-1).

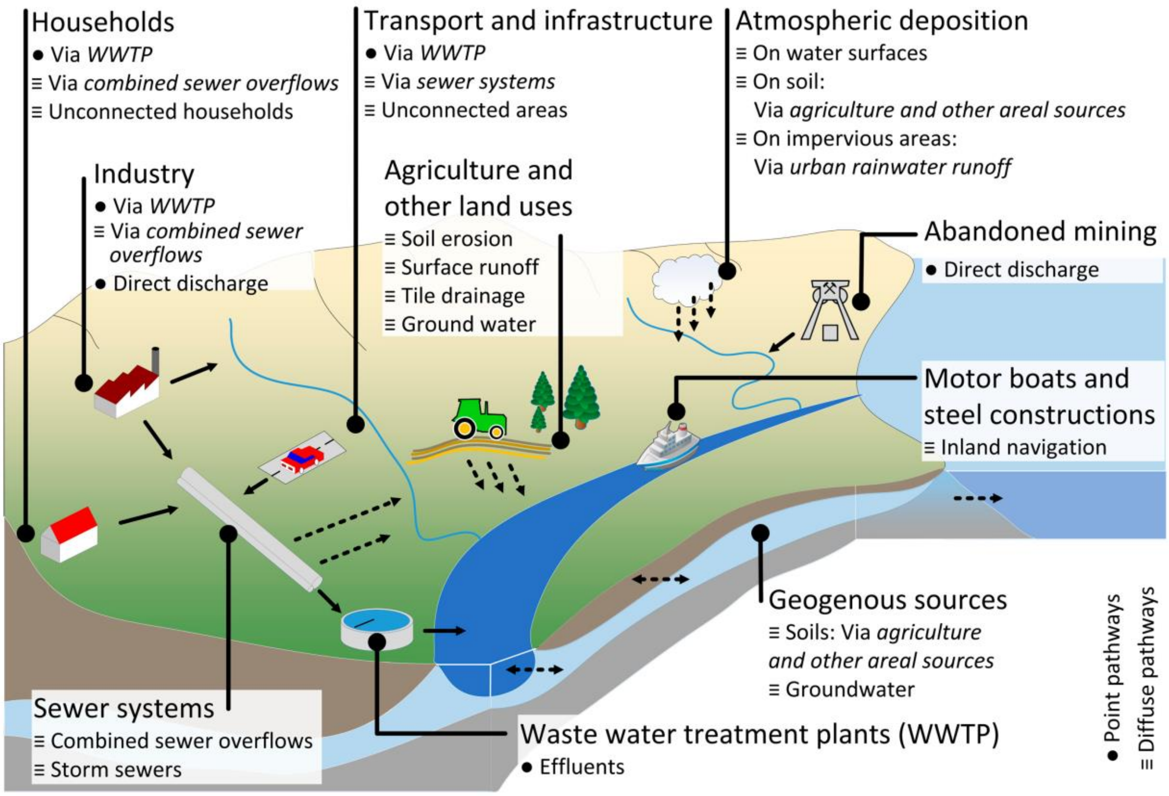

Figure 2-1: Substance emission pathways of current MoRE applications, arranged by source type (Fuchs et al., 2017)

The modelling approach considers annual time steps for hydrological sub-catchments. Consequently, for each catchment or sub-catchment related to the variation of time-dependent input data, like hydrological data, climatic data, erosion or point source emission total emissions reaching the surface are calculated for each modelled substance. The model also takes into account the retention (sedimentation or degradation/gassing) of substances. Consequently, a substance load in the water body can be calculated for each sub-catchment at the area outlet. A plausibility check of the modelled water body loads is possible by means of a comparison with the loads obtained from observations (Amann et al., 2019).
In general the model approaches used for the pilot regions includes the following pathways:

- Municipal Wastewater Treatment Plants > 2.000 PE,
- Industrial Wastewater Treatment Plants,
- Sewer systems not connected to Wastewater Treatment Plants (Bulgaria),
- Combined storm water overflows (combined system),
- Storm water overflow (storm sewer),
- Country roads and highways,

- Atmospheric deposition (direct on water surfaces),
- Surface runoff,
- Erosion (agricultural areas, natural areas (forests), open areas (mountainous)),
- Drainage (Tile drainages),
- Groundwater.

In a further step, annual concentration can be calculated using the total load and the total discharge at each outlet point of a catchment or sub-catchment.
Additionally, for river basins influenced by abandoned mining, a first data base was evaluated and implemented in the model to calculate Heavy Metal emission in the Viseu catchment (See Chapter Abandoned mining).
In this model application two new substance groups were implemented: fungicides and herbizides. For both substances the standard model approach, was chosen. Due to the monitoring and the establishment of the database in the scope of the project, the data availability was sufficient to model all the relevant pathways for pesticides.
A second approach was setup and tested. This one is based on culture specific application rates and empiric transfer functions. A detailed description is given in O.T2.1, Appendix II.
Furthermore, two new approaches to calculate pesticide emissions and concentrations (s-Metolachlor and Terbuconazole) were developed or implemented. See chapter
Not all pathways are relevant for all substances. E.g. in case of Pharmaceuticals, the quantified pathways are reduced to point sources (municipal and industrial), to sewer systems and to groundwater indirectly influenced by leaking sewers or other IAS, like septic tanks.
Following, a detailed description on the used approaches to quantify emissions from the different pathways is prepared.

2.1 Specification of model setup and model algorithms

In the following chapters, the technical documentation of the model will be described in detail. The technical documentation itself consists of flowcharts to give an overview of the calculation steps. In the MoRE model, the calculation is organized as follows:
For the emissions for each substance group, a so-called algorithm stack is created. Each algorithm stack consist of different algorithms, in general each algorithm describes one possible pathway. Each algorithm consists of all the needed formulas to calculate the emissions for this substance group for this particular pathway.
For instance for the PAH emissions, the algorithm stack consists of different algorithms, each describing one pathway. The algorithm “Emissions > PAH emissions via waste water treatment plants” consist of the following formulas:

- PAH- emissions via municipal wastewater treatment plants (point source),
- PAH-emissions via small wastewater treatment plants,
- Total PAH emissions via municipal wastewater treatment plants.

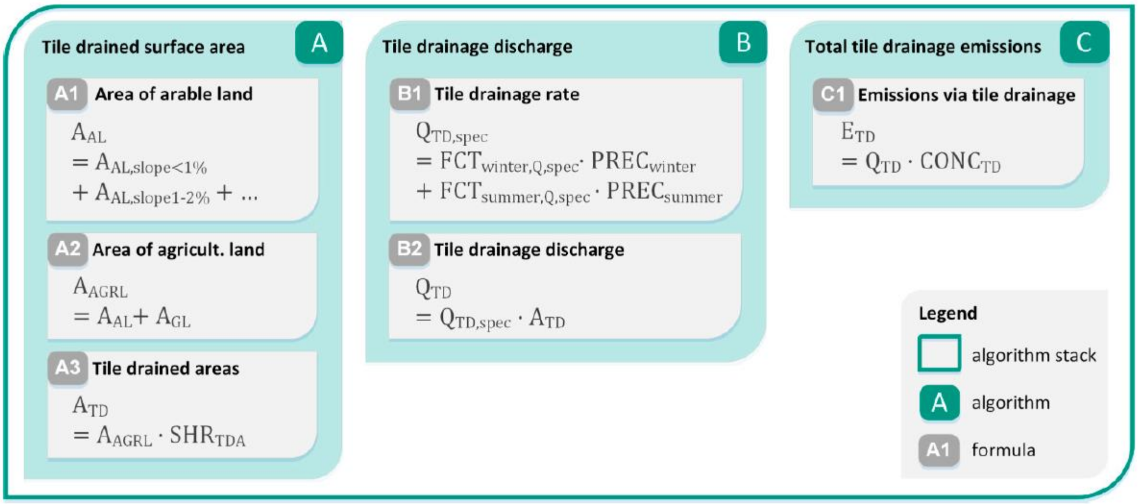

Figure 2-2: Example of the hierarchic implementation of the modelling approaches in MoRE (Fuchs et al., 2017) A: Area; SHR: share; Q: Discharge; FCT: factor; PREC: Precipitation; E: Emissions; CONC: concentration. Subscripts: TD: tile drainage; TDA: tile drained area; AGRL: agricultural area; AL: arable land; GL: grassland; spec: specific.

In Figure 2-2, the hierarchic approach for the emissions from tile-drained areas is displayed. In this case the algorithm stack "Emissions from tile drainages" consists of three algorithms: Tile drained surface areas, tile drained discharge and total tile drainage emissions, which all consists of one or more formulas. In addition to the emission pathways, also the land-use balance, the fine solids balance and the water balance have their own algorithm stack. In some cases, an entire algorithm stack is represented in one flowchart (land use balance, water balance and fine solids balance), in all other cases the flowcharts are organized by pathways and substance. If the calculations for a specific pathway are the same for different substances, the flowcharts are (exemplarily) only given for one substance in Appendix_III of Output_T2.1 Harmonized MoRE Model.

In the MoRE model, there are different types of input variables. Constants are the same for each analytical unit and each year and include for instance enrichment ratios and the effects of measures in percentage. In this model version, 600 constants are implemented.

Analytical unit variables are defined for each analytical unit, but are (assumed) constant over time, i.e. content of hazardous substances in soil and rock and the percentage of inhabitants (not) connected to sewer systems. In total 180 analytical unit variables are present in the model.

Periodical analytical unit variables are the most used variables in the MoRE model and include for instance all hydrological and climate data, and almost all substance specific data. There are 1,700 periodical analytical unit variables.

For this project the base MoRE model with already implemented approaches from different projects (Amann et al., 2019 and Fuchs et al., 2020) was used. When the existing approaches were still applicable they were kept as they were and only were translated into an English version, for instance for most of the diffuse sources. When the approaches were transformed, a quality check was done for all existing algorithms and formulas and corrections (if necessary) implemented.

In Figure 2-3 model metadata of periodical analytical unit variables is presented. On the left hand site, the modular model structure is shown.

In Figure 2-4 formulas are presented, which are used to calculate the emission from different pathways.

The MoRE model consist of around 500 formulas, which are always applied on an entire substance group. Each formula has a result variable. For each result variable it is possible to have more than one formula in the model, however only one formula can be active. In this model, if new formulas are constructed, the old formulas are kept inactive in the model, to ensure flexibility for other applications.
These 500 formulas are compiled in approximately 120 algorithms and 20 algorithm stacks.

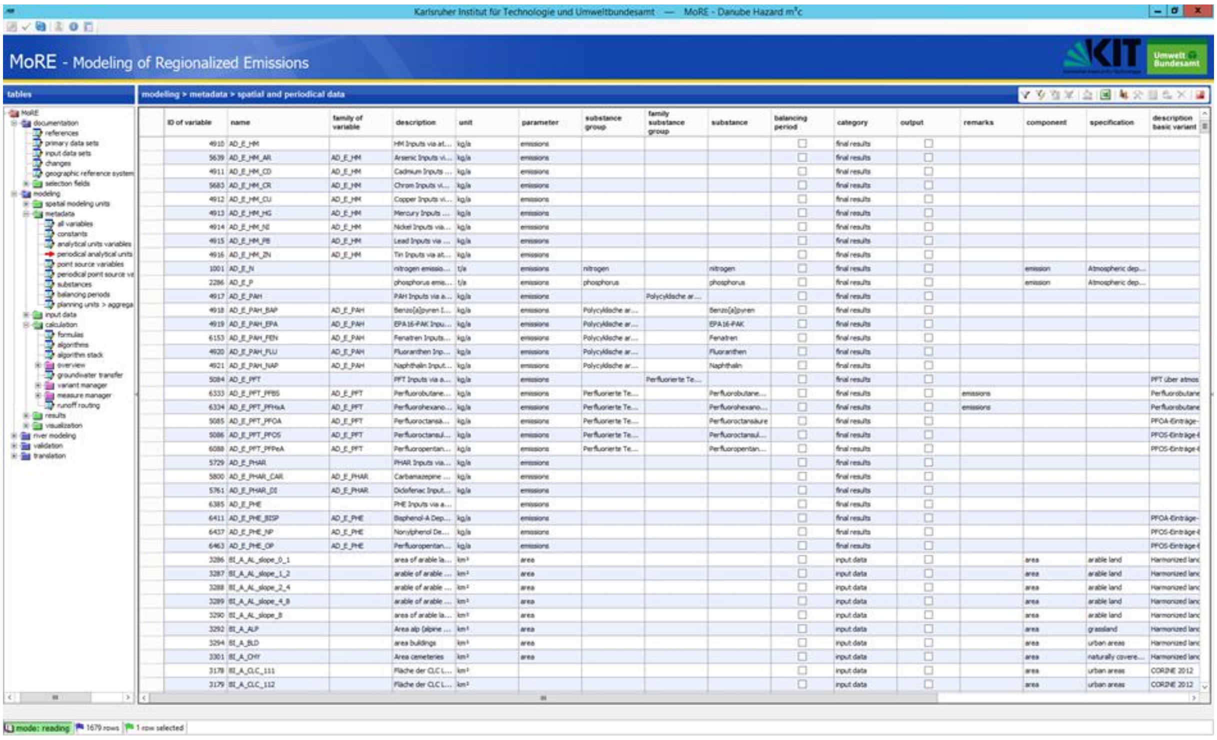

Figure 2-3: Screenshot from the MoRE model which shows the metadata some periodical analytical unit variables.

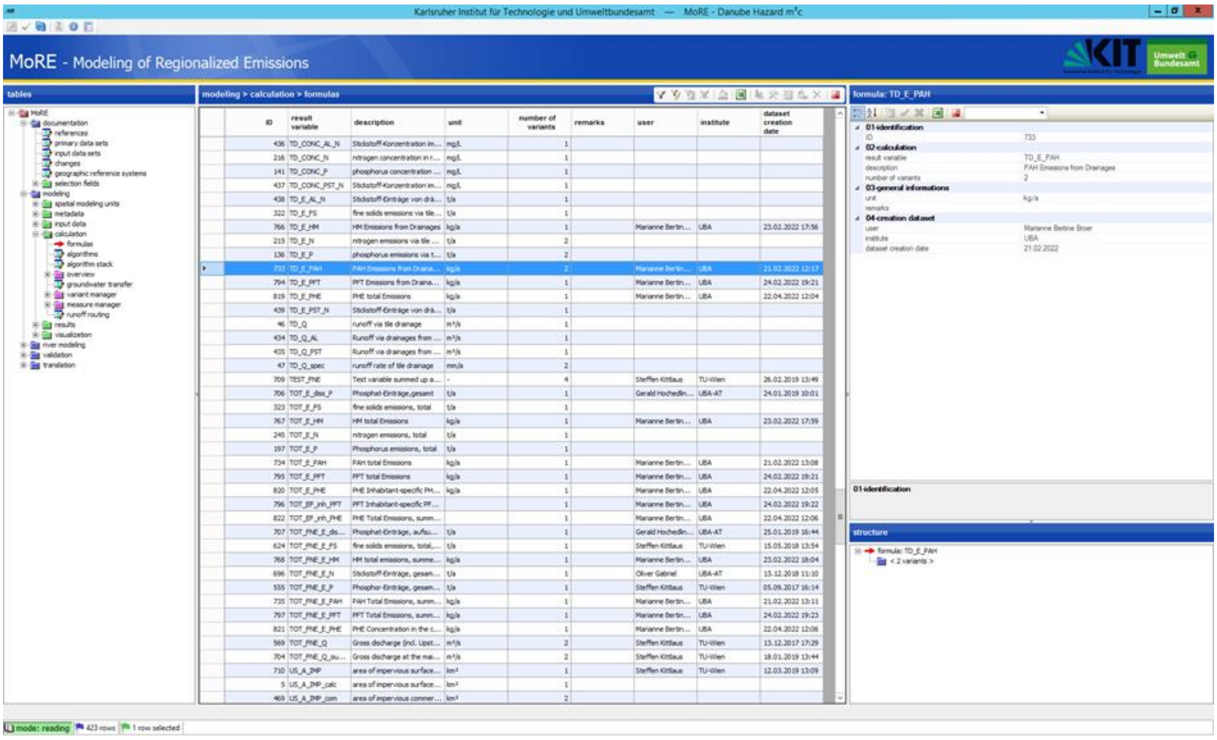

Figure 2-4: Overview of the formula-view in the MoRE model.

2.2 Implemented approaches

The implemented approaches can be divided in four main groups. The general calculations, which include common approaches of landuse, water balance and the fine solids balance, which can be checked for plausibility. The second and third group, which describes point source- and diffuse pathways addressed and quantified in the model approach and the fourth group with information on the calculation of total emission, retention in surface water and the calculation of loads and concentration in the surface waters.

2.2.1 General calculations

2.2.1.1 Land use

In general, the *area calculation* algorithm stack was used from the base model, if there are changes made, this will be stated in the text. The flowcharts represent the model used in this project.

The *area calculation* algorithm stack consists of six algorithms, which will be described briefly in this paragraph.

Land use: In this algorithm, all the land use categories are summed up and the difference between the sum of land uses and the area of the AU is calculated. This algorithm was adapted to incorporate all the land use classes used in the CORINE land cover layer
Agricultural areas: in this algorithm the percentage of agricultural land is calculated for each AU. In a first check, the landuse data was evaluated in all sub-catchments on consistency. It was found that the balances are closed and reproduce reasonable results.

Tile drained areas: The tile areas are calculated by multiplying the agricultural and pasture area with the percentage of tile drained area in each AU.

Areas contributing to the formation of surface runoff: This area comprises the following land uses: Agricultural areas, natural areas, open areas, not impervious urban areas and non-urban roads that are not discharging into a water body.

Areas contributing to groundwater recharge: This area excludes the following land uses: Agricultural areas, natural areas, open areas impervious urban areas and non-urban roads that are not discharging into a water body. Waster surfaces, tile drained areas, open mining, impervious urban areas non-urban roads that are not discharging into a water body.

The last algorithm *urban impervious area(total)* concerning land use calculates the total urban impervious area.

The flowcharts for this algorithm stack can be found in Appendix_III of Output_T2.1 Harmonized MoRE Model named 01_Land_use.

2.2.1.2 Water balance

The *water balance algorithm stack* consists of 11 algorithms, where the first algorithm comprises the entire *area calculation* algorithm stack.

The algorithm *runoff from precipitation on water surfaces* calculates the runoff from precipitation directly on water surfaces.

Drainage runoff is calculated from the tile drained area and the precipitation in each AU.

The algorithm *Runoff from areas and inhabitants not connected to sewer systems* is an adaption of the MoRE model to accommodate the situation in Bulgaria and calculated from the runoff from areas and inhabitants not connected to a sewer system from the impervious area not connected to a sewer system, the actual precipitation, the inhabitants not connected to a sewer system and the water consumption.

Runoff from areas, inhabitants commercial areas only connected to sewer systems is an adaption of the MoRE model to accommodate the situation in Bulgaria and calculated the runoff from commercial areas and inhabitants. The calculations are based on areas only connected to a sewer system, the actual precipitation, the inhabitants only not connected to a sewer system and the water consumption and the discharge from commercial areas only connected to a sewer system.

Runoff from sewer systems (combined sewers and storm sewers) calculates the total discharge from sewer systems.

The algorithm, *runoff from non-urban road* is calculated based on the area of non-urbans roads discharging into surface waters, yearly precipitation and a discharge coefficient for non-urban roads.

The algorithm *runoff from Point Sources (WWTP+ID)* is taken from the basic MoRE model, the discharge from the point sources, which comes directly from the input data is aggregated to the AU

Runoff from unsealed areas (surface runoff) is calculated as the sum of the discharge from mountainous areas and areas covered by vegetation.

The algorithm *runoff from ground water and inter flow* is adapted from the basic MoRE model. The runoff from groundwater and interflow is calculated as the difference between the total runoff and the sum of all the water balance components described above.

Runoff, total sums up all the different components of the water balance described above. In a first check the water balance was evaluated in all sub-catchments on consistency. It was found that the balances are closed and reproduce reasonable results.

The flowchart for this algorithm stack can be found in Appendix_III of Output_T2.1 Harmonized MoRE Model named 30_Water_balance.

2.2.1.3 Fine solid balance

In order to calculate the substance inputs via the input of eroded soil and rock material, it is first necessary to model the soil erosion and sediment input process. For this purpose, empirical approaches are used, which were finally calibrated at suspended sediment measuring points in Austria and mainly in alpine and pre-alpine regions to determine suspended solids loads from open areas (forests), mountainous areas and glaciers (Amann et al., 2019). While glaciers play no role in the pilot regions, there are extended areas of forests in most pilots, while mountainous areas are only relevant in the Vit catchment and have only a small share in the Viseu catchment.
Comparing model results with suspended solids loads calculated from the monitoring approach applied in this project (see Output T1.2) the modelled suspended solids loads

showed a huge overestimation. On the one hand, the approach developed in Austria could not simply be transferred to the natural conditions in the other pilot regions. On the other hand, the period in which measurements were carried out in most pilot regions (2021-2022) had a particularly low discharge period, while others, such as the Ybbs, were characterized by a particularly intensive flood event. To take these circumstances into account, the constant inputs from natural areas and mountainous areas of 0.2 t/ha·a^{-1} deposited available from older model versions were also used and applied in Vit, Viseu and Somesul Mic.

In order to be able to model and calibrate the entire transport of suspended solids, the (only comparatively small) solid inputs via sewer systems (combined sewer overflows and storm sewers in the separation system), drainage systems and municipal wastewater treatment plants were also calculated.

In addition to the fundamentally high inputs from the natural areas, the long-term average soil erosion of agricultural land calculated by using the Revised Universal Soil Loss Equation (RUSLE) was calculated and imported into the model as input data (Basic input data). While these information are available in Hungary and Austria in the form of nationwide long-term soil erosion maps or own calculations which are based on the Invekos data, in Romania and Bulgaria an alternative data set (JRC-ESDAC) was used and prepared by the responsible project partners (Basic input data). In the Vit pilot region, this approach leads to unexpected high soil loss rates especially from pastures but even from arable land. The soil loss from pastures was reduced to a constant value of 0.8 t/ha·a^{-1}. The soil loss from arable land was corrected using typical soil loss rates from the Ybbs upstream sub-catchments, which are most comparable to the Vit catchment.

In the model, the R-factor of the soil erosion equation is varied with the hydrological characteristics of the current calculation year: The sum of summer precipitation (PRECsummer, May-October) compared to the long-term mean is used as a proxy for precipitation intensity (Fuchs et al., 2010, Deumlich and Frielinghaus 1993/1994). The coefficients of this empirical function for calculating the precipitation correction of the R-factor (ER_PRECcorr) were taken from Fuchs et al. (2020):

$$ER\_PREC_{corr} = \frac{(0{,}02 \cdot PREC_{summer})^{1{,}7} - 6{,}88}{(0{,}02 \cdot PREC_{summer\_longterm})^{1{,}7} - 6{,}88} \qquad \text{(Equation 1)}$$

Only a small amount of the soil removed from the land reaches water bodies. Much of the removed material is redeposited in shallower areas of the surface or sediments in flow paths before reaching the water bodies. To represent this process in the model, the so-called Sediment Delivery Ratio is calculated and multiplied with the soil erosion. The sediment Delivery Ratio (SDR in %) is calculated according to Venohr et al. (2011) as a function of the mean slope in the area (SLP in %) and the share of cropland in the total area (SHR_{AL} in %):

$$SDR = 0{,}0066884 \cdot (SLP - 0{,}25\,)^{0{,}3} \cdot (\,SHR_{AL} + 20\,)^{1{,}5} \qquad \text{(Equation 2)}$$

Thus, the sediment input from agricultural land (SED_{AGRL} in t/a) is calculated as follows:

$$SED_{AGRL} = (SL_{AL} \cdot A_{AL} + SL_{PST} \cdot A_{PST}) \cdot ER\_PREC_{corr} \cdot \frac{SDR}{100} \qquad \text{(Equation 3)}$$

With:
SL_{AL} = soil erosion from cropland (t/km²/a)
A_{AL} = cropland (km²),

SL_{PST} = soil erosion from grassland (t/km²/a)
A_{PST} = grassland area (intensive + extensive in km²).

The sediment input from naturally covered areas (SED_{NAT} in t/a) in the Austrian approach (applied for Ybbs, Wulka, Koppany and Zagyva) is calculated as a function of the mean slope in the area.

$$SED_{NAT} = 0{,}05 \cdot e^{0{,}07 \cdot SLP} \cdot A_{NAT} \cdot ER\_PREC_{corr} \qquad \text{(Equation 4)}$$

With: A_{NAT} = area of naturally covered surfaces (km²)

Sediment inputs from mountainous open areas (SED_{MNT} in t/a) are calculated by multiplying the specific rates by the associated area.

A concentration of 145 mg/l was calculated for solids inputs via combined sewer overflows and 35 mg/l solids for inputs from storm sewers in the separate system (Amann et al., 2019). The inputs are calculated by multiplication with the runoff volumes.

Inputs from municipal wastewater treatment plants were calculated to be 10 mg/l solids and inputs via drainage systems were calculated to be 100 mg/l (Stone and Krishnappan, 2002).

All calculations concerning the fine solid balance were adapted from the basic MoRE model and adjusted in the way described. A balance check of the modelled and monitored fine solids was applied, which shows reasonable results (5.2).

The flowchart for this algorithm stack can be found in Appendix_III of Output T2.1 Harmonized MoRE Model named 90_Fine_solids_balance.

2.2.2 Point sources

In this chapter, a short introduction on the calculated pathways from point sources is presented. Flowcharts (in the Appendix) give detailed information on the calculation procedure and the used algorithms and data. Exemplarily they are established for PAHs.

2.2.2.1 Urban Wastewater Treatment plants

For plants with a capacity of 2,000 PE or more, the calculation of trace substance inputs from municipal wastewater treatment plants is initially performed at the level of the individual plant by multiplying the concentration by the annual wastewater volume. Having a located discharge point, the load of each plant is assigned to one sub-catchment. Subsequently, the loads of all plants in an analysis area are summed up.
If data from treatment plants < 2,000 PE are available, calculated loads (summed up wastewater discharge aggregated per sub-catchment x concentration) are added to the loads from plants > 2,000 PE (see flowchart 09_WWTP_PAH in Appendix_III of Output T2.1 Harmonized MoRE Model).

Substance specific concentrations of discharges from WWTPs were provided from the established database and the own monitoring results of the project (Substance specific input data)

2.2.2.2 Direct discharges from industrial Treatment Plants

Similar to the municipal treatment plants, the discharge from industrial treatment plants is aggregated to a sub-catchment. Each industrial WWTP discharge is multiplied with a substance specific concentration. The loads of all industrial Treatment Plants are summed up (see flowchart 08_ID_PAH in Appendix_III of Output T2.1 Harmonized MoRE Model). Substance specific concentrations of discharges from WWTPs were provided from the established database and the own monitoring results of the project. (Substance specific input data)

2.2.2.3 Urban systems

The calculation of urban systems can not clearly be addressed to either point source nor to diffuse pollution. Sewer systems without treatment but with a defined discharge point can be addressed as point sources, while most of the other pathways included in this approach are related to the specific to the diffuce pathways. The calculation of these pathways was modified with respect to the specific conditions in the pilot catchments and therefore is presented in detail in chapter Adapted urban systems.
(See flowchart 11_US_PAH in Appendix_III of Output T2.1 Harmonized MoRE Model).

2.2.2.4 Abandoned mining sites

To represent the situation in the Viseu Pilot area a new type of point source was introduced in the MoRE model: Abandoned mining site. The emissions from abandoned mining sites are calculated in the same manner as the emissions from WWTPs or industrial discharges. For abandoned mining only heavy metal emissions are calculated. (See flowchart 16_AM_HM in Appendix_III of Output T2.1 Harmonized MoRE Model).

2.2.3 Diffuse sources

In this chapter, a short introduction on the calculated pathways from diffuse sources is presented. Flowcharts (in the Appendix_III of Output T2.1 Harmonized MoRE Model) give detailed information on the calculation procedure and the used algorithms and data. Exemplarily they are established for PAHs.

2.2.3.1 Emissions via atmospheric deposition onto water surfaces

This pathway describes the input of trace substances from the air into water bodies by wet and dry deposition directly onto the water surface. Substance specific concentrations of atmospheric depositions were provided as country-specific input data from the established database and the own monitoring results of the project. (Substance specific input data).
The emission via atmospheric deposition to the water surfaces are calculated by multiplying the deposition rate by the water surface area.
Other impacts of atmospheric deposition e.g. on soils or on paved areas are not separately calculated but are integrated e.g. in soil concentrations (erosion pathway), concentration in surface runoff (surface runoff pathway), and concentrations in combined sewer overflow and storm sewer (sewer systems pathway).

Substance specific concentrations of atmospheric deposition were provided from the established database and the own monitoring results of the project. (Substance specific input data).

An example (PAHs) of the flowchart for this algorithm can be found in Appendix_III of Output T2.1 Harmonized MoRE Model as 02_AD_PAH.

2.2.3.2 Emissions via erosion

This pathway describes the input of particulate-bound trace substances during soil erosion by surface precipitation runoff. The modeling is based on the solids balance. The soil emission to surface waters are multiplied by a trace substance concentration in the soil. For example, for inputs from agricultural land (ER_E_{AGRL} in kg/a):

$$ER\_E_{AGRL} = \frac{(SL_{AL} \cdot C_{SOIL\_AL} \cdot A_{AL} + SL_{PST} \cdot C_{SOIL\_PST} \cdot A_{PST})}{1000} \cdot ER\_PREC_{corr} \cdot \frac{SDR}{100} \qquad \text{(Equation 5)}$$

where:
SL_{AL} = Soil erosion of arable land (t/km²/a)
C_{SOIL_AL} = Trace substance concentration in topsoil on arable land (mg/kg)
A_{AL} = Arable land (km²)
SL_{PST} = Soil erosion of grassland (t/km²/a)
C_{SOIL_PST} = trace element concentration in topsoil on grassland (mg/kg)
A_{PST} = grassland area (intensive + extensive in km²)
ER_PREC_{corr} = precipitation correction of R-factor
SDR = sediment input ratio (%).

For the substance groups heavy metals the process of substance enrichment due to the accumulation of fine material during the transport process on agricultural land is also modeled. For this purpose, a substance enrichment factor (ENR) is added to the equation. This is calculated according to Auerswald (1989) as a function of the specific long-term soil removal on arable land (SL_{AL_lt} in t/ha/a):

$$ENR = 2{,}53 \cdot {SL_{AL\_lt}}^{-0{,}21} \qquad \text{(Equation 6)}$$

The ENR calculated in this way is limited to 1 at the bottom and 4.5 at the top.
The inputs from agricultural land are thus calculated for heavy metals as follows:

$$ER\_E_{AGRL} = \frac{(SL_{AL} \cdot C_{SOIL\_AL} \cdot A_{AL} + SL_{PST} \cdot C_{SOIL\_PST} \cdot A_{PST})}{1000} \cdot ER\_PREC_{corr} \cdot \frac{SDR}{100} \cdot ENR$$

(Equation 7)

For erosive inputs from naturally covered areas, the sediment input (from the solids balance) is multiplied by the trace metal concentration in the topsoil of naturally covered areas provided from the established database and the own monitoring results of the project.
For heavy metals, sediment inputs from mountainous open areas (from the solids balance) are multiplied by the heavy metal contents of the rocks.

Information on basic input data (calculation of erosion from arable land) is presented in Basic input data. An example of the flowchart for this algorithm can be found in Appendix_III of Output T2.1 Harmonized MoRE Model named 06_ER_PAH.

2.2.3.3 Emissions via tile drainage

This pathway describes the input of trace substances from agricultural drainage pipes. The calculation is made by multiplying the trace substance concentration and drainage runoff (from the runoff balance). The calculation of the drained areas in the different pilot regions is presented in Basic input data. Concentrations of trace substances related to drainage runoff are very sparse. For this reason, groundwater concentrations are used as an approximation. Since a clear specification is not possible due to the missing concentrations in the drainages, the loads from drainages and those from the other subsurface inflows (groundwater as baseflow and interflow) are presented together.

The flowchart for this algorithm can be found in Appendix_III of Output T2.1 Harmonized MoRE Model named 03_TD_PAH.

Since concentration data in drainage runoff are often not available for hazardous substances, concentrations of subsurface runoff (groundwater baseflow and interflow) will be used for drainages (Substance specific input data).
For this application, the emissions from tile drainages and groundwater were treated as one pathway as the same concentrations were used for both.

2.2.3.4 Emissions via surface runoff

This pathway describes the input of dissolved trace substances in surface precipitation runoff. It is calculated by multiplying the concentration of trace substances and the surface runoff volume. The flowchart od this algorithm can be found in in Appendix_III of Output T2.1 Harmonized MoRE Model named 10_SR_PAH.
Since concentration data in surface runoff are often not available for hazardous substances, concentrations of atmospheric deposition will be used to enable a first approximation.

2.2.3.5 Emissions via groundwater and interflow

This pathway describes the input of trace substances by underground transport via groundwater (baseflow and interflow), which enters the water body by exfiltration or by spring discharges. The calculation is made by multiplying the concentration of trace substances and the groundwater discharge (from the discharge balance). Substance specific concentrations of groundwater (baseflow and interflow) were provided from the established database and the own monitoring results of the project. (Substance specific input data).

Since there is currently no meaningful way to distinguish the input pathways due to a lack of substance-specific data in the drainages, the whole input of underground emission (baseflow, interflow and drainage flow) is presented as one pathway.
The flowchart for groundwater (baseflow and interflow) can be found in Appendix_III of Output T2.1 Harmonized MoRE Model named 07_GW_PAH.

2.2.3.6 Emissions via roads outside of settlements

This pathway describes the input of trace substances by precipitation runoff from rural roads and highways, in case the runoff is not leaking after flowing over the embankment, but being collected and discharged directly into the surface water after passing a retention basin. The calculation is proceeded by multiplying the concentration of trace substances and the road runoff (from the runoff balance).

There are only very few measurements of trace substances available in the database (Substance specific input data). The flowchart for this algorithm can be found in Appendix_III of Output T2.1 Harmonized MoRE Model named 12_OR_PAH.

2.2.4 Total emissions, retention and river load

In this chapter, a short introduction on the calculated total emission, retention and river loads is presented. Flowcharts (in the Appendix) give detailed information on the calculation procedure and the used algorithms and data. If substance specific approaches are described, they are exemplarily established for PAHs.

2.2.4.1 Total emissions

The calculation of total emission to the surface waters in a sub-catchment is a simple addition of all emissions from pathways (point and diffuse sources) calculated with the model approach. In total this are (here again as an example for PAHs):

- ID_E_PAH (industrial point sources),
- WWTP_E_PAH (municipal point sources),
- AD_E_PAH (atmospheric deposition),
- TD_E_PAH (tile drainages),
- ER_E_PAH (erosion from agricultural areas, natural areas (wood), open areas (regions without vegetation) is calculated separate and then totaled,
- US_E_PAH (urban systems, here are combined systems and storm water system calculated and totaled),
- OR_E_PAH (country roads and freeways),
- SR_E_PAH (surface runoff),
- GW_E_PAH (underground discharge from baseflow and interflow).

The flowchart for this algorithm can be found in Appendix_III of Output T2.1 Harmonized MoRE Model named 13_TOT_PAH. In the case of heavy metals, also the pathway abandoned mining is added to the total emissions.

2.2.4.2 Retention in tributaries and main rivers

Not the total load of substances discharged into the water body is transported directly to the outlet of the catchment. Processes of retention and degradation act on the trace substances. Since the trace substances modeled in this project all have high persistence in the aquatic environment, degradation processes were considered negligible and were not modeled. However, trace substances that tend to adsorb to particles are deposited by sedimentation of particles in slow-flowing stream segments and especially in flow-through lakes and impoundments, and then removed from the system, by either sediment removal or flushing and deposition during floods. To represent this process, the retention approaches developed for phosphorus in MONERIS were used (Venohr et al., 2011).

The retention approach distinguishes between main and tributary waters. For the tributaries, the retention factor is calculated as a combination of two different retention approaches: The retention approach according to the discharge donation (Rq_trib) is calculated as follows (Amann et al., 2019):

$$R_{q\_trib} = \frac{1}{1+8,77\cdot\left(\frac{Q_{net}\cdot 1000}{A}\right)^{-1}} \qquad \text{(Equation 8)}$$

With:
Qnet = net discharge (m³/s)
A = area of the analysis area (km²)

The retention factor according to the hydraulic load for tributaries (RHL_trib):

$$R_{HL\_trib} = \frac{1}{1+15,91\cdot\left(\frac{Q_{net}\cdot 365\cdot 24\cdot 60\cdot 60}{A_{WS\_trib}\cdot 1000\cdot 1000}\right)^{-1}} \qquad \text{(Equation 9)}$$

with AWS_trib = water area of rivers and lakes at tributaries (km²)

The retention factor for tributary waters (Rtrib) is calculated as the mean value of these two retention factors.

$$R_{trib} = \frac{R_{q\_trib} + R_{HL\_trib}}{2} \qquad \text{(Equation 10)}$$

For the main watercourses, only the retention factor main river is calculated according to the hydraulic load (RHL_mr):

$$R_{HL\_mr} = \frac{1}{1 + 15{,}91 \cdot \left(\frac{Q_{net} \cdot 365 \cdot 24 \cdot 60 \cdot 60}{A_{WS\_mr} \cdot 1000 \cdot 1000}\right)^{-1}} \qquad \text{(Equation 11)}$$

with AWS_mr = water area of rivers and lakes in the main watercourse (km^2)

The retention factors calculated in this way for tributaries and main courses are then used for the water load calculation.

The flowchart for this algorithm can be found in Appendix_III of Output T2.1 Harmonized MoRE Model named 82_RM_Retention.

2.2.4.3 River loads and concentrations

While no retention by sedimentation is assumed for the polyfluorinated surfactants and for Carbamazepin and Diclofenac due to their rather good solubility, the water loads for heavy metals and pesticides are calculated including retention.
Assuming that point sources and combined sewer overflows are predominantly found on the mainstream in the downstream parts of a catchment area, retention is applied only to the remaining diffuse input pathways and the load flowing from upstream areas. The load from tributary waters (Ltrib in kg/yr) is calculated as:

$$L_{TRIB} = (E_{TOT} - E_{WWTP} - E_{ID} - E_{CSO}) \cdot R_{trib} \qquad \text{(Equation 12)}$$

where E_{TOT} = total inputs (kg/a)
E_{WWTP} = inputs from wastewater treatment plants (kg/a)
E_{ID} = inputs from direct industrial dischargers (kg/a)
E_{CSO} = inputs via combined sewer overflows (kg/a) and
R_{trib} = retention factor for tributaries.

The load from upstream catchments discharging into a downstream catchment (L_{upstr} in kg/a) is calculated according to:

$$L_{upstr} = R_{HL\_mr} \cdot \sum_{Upstream\_areas} L \qquad \text{(Equation 13)}$$

with R_{HL_mr} = retention factor main river after hydraulic loading
L = water load (here of the upstream areas, in kg/a).

The total load from an area (L in kg/a) is then calculated as:

$$L = L_{upstr} + L_{TRIB} + E_{WWTP} + E_{ID} + E_{CSO} \qquad \text{(Equation 14)}$$

This load and the gross discharge (Q_{brutto} in m³/s) are used to calculate the mean annual water body concentration at the outlet of the analysis area (C in µg/L):

$$C = \frac{L \cdot 1000 \cdot 1000}{Q_{brutto} \cdot 365 \cdot 24 \cdot 60 \cdot 60} \quad \text{(Equation 15)}$$

The flowchart for this algorithm can be found in Appendix_III of Output T2.1 Harmonized MoRE Model.

2.2.4.4 Modelling of dissolved heavy metals

For heavy metals the EQS is defined for dissolved metals, therefore in addition to the total emissions and concentration also the dissolved emissions and concentrations have to modelled. For the pathways industrial point sources, abandoned mining, atmospheric deposition, tile drainages, groundwater and surface runoff it is assumed that all emissions are from dissolved metals.
For the pathways erosion, urban systems and country roads and freeways the dissolved metal emissions were calculated with the liquid partition coefficient and the fine solid concentration in the pathway in the following way:

$$E_{diss} = E_{tot} \cdot \frac{1}{1 + \frac{KD \cdot C_{FS}}{1000 \cdot 1000}} \quad \text{(Equation 16)}$$

For Copper, Cadmium, Mercury, Nickel, Lead and Zinc the liquid partition coefficient was taken from a previous project (Amann et al., 2019). For Arsenic and Chrome the liquid partition coefficient was calculated from the monitoring data, according to the method described in Clara et. Al (2014).

2.2.5 Adapted approaches

2.2.5.1 Adapted water balance

The existing water balance was adapted for two different cases, which will be described briefly in the following paragraph.

In previous versions the groundwater and tile drainage pathways were separated, however for hazardous substances no measurement data on tile drainages was available, therefore the groundwater concentration was used as substitute for the tile drainage concentration .Both pathways where summed up and treated as one pathway, which is also in line with the DSHM Model and ensures an easier comparison.

The second case where the water balance had to be adjusted was in the Somesul Mic pilot area. In this pilot area ground water infiltration takes place in the downstream sub catchment, which was not included in the water balance. To mimic the effect of groundwater infiltration, two additional analytical units where created. One analytical unit represents the ground waterbody where the groundwater is infiltration and is located next to the old catchment outlet. The second catchment represent only the large WWTP in Cluj Napoca, because this WWTP is situated very close to the catchment outlet and therefore the assumption is made that the outflow from the WWTP will nog infiltrate into the ground water body. From the old catchment outlet the river flow is splitted with the split function in MoRE between the artificial groundwater body and the new catchment outlet containing the WWTP. The net discharge of the old catchment outflow was adjusted to reflect the adapted model situation.

2.2.5.2 Adapted urban systems

Background

In the model structure, several options were implemented to calculate emission from urban systems, expressing the wide variety of available input data for different model applications in different countries (especially Germany and Austria in the model base version). However, the existing approaches were based on conditions with more than 95% of PE connected to sewer systems and to a wastewater treatment plant and on collected data in a well-organized database, like the Emission Register for Surface waters Emreg-OW in Austria, which is operated since 2009 (following the so called “Kläranlagendatenbank” operating since 2000).

In this project, implementation and information of wastewater management in some pilots, is beyond the standards already implemented in the model. Therefore, the approaches must be adapted to the specific conditions, the available data and the information prepared from experts, e.g. rating the state, especially the tightness, of sewer systems.

For the modelling of the urban systems in the pilot regions first an inventory on possible cases and the available data in the pilot regions was prepared. For each pilot region/country, the best possible modelling approach was chosen, predominantly based on the available data. In the following paragraphs, each individual modeling approach will be described in detail.

Because MoRE prepares a flexible model environment, both the structure of the urban systems as well as the data availability in the different pilot regions where the key criteria in adapting of existing and the construction of new algorithms.

The urban system is divided into several pathways, which might not be relevant in all pilot areas. Table 2-1 shows an overview of the relevant pathways in the different countries. As can be seen, there is a big difference in the relevant paths ways, which makes the modeling approach more complex.

Table 2-1: Overview of the pathways within the urban systems and their relevance in the different countries.

Urban System Pathway	BG	RO	HU	AT
Septic tanks (not water tight)	X			
Septic tanks (water tight)		X	X	
Inhabitants connected only to the sewer system	X			
Separate sewer systems		X	X	X
Combined sewer systems	X	X		X

To calculate the load for each substance for each pathway both the discharge and the concentrations of the modelled substances should be known, however this is not the case for every relevant pathway for all countries. Therefore, the model approaches where adapted taking both the additional pathways in respect to the base model and the data avialibilty in the different countries into account.

Data Availability

<u>Bulgaria (Vit)</u>

For Bulgaria, only the inhabitants and the inhabitant specific water consumption are available for all agglomerations. For some agglomerations, the connection rate to the sewer system is available. There is one working WWTP in Glogovo, however there is no data available on discharge from this WWTP.

Romania (Somesul Mic, Viseau)
For Romania, the following information on urban systems is available:
- Length of storm sewers & combined sewers
- inhabitant specific water consumption
- storage volume of stormwater overflow tanks in combined sewer systems
- inh (not)connected to sewer systems and WWTP

Hungary (Zagyva, Koppány)
For Hungary, the following information on urban systems is available:
- inhabitant specific water consumption
- storage volume of stormwater overflow tanks in combined and seperate sewer systems
- storage volume of stormwater overflow tanks in combined sewer systems, area-specific
- inh (not)connected to WWTP and sewer systems
- percentage of inhabitant load that is transported from septic tanks to waste water treatment plants

Austria (Ybbs, Wulka)
For Austria the following information on urban systems is available:
- Length of storm sewers, combined sewers & sewage sewers
- inhabitant specific water consumption
- inh (not)connected to WWTP and sewer systems
- percentage of inhabitant load that is transported from septic tanks to waste water treatment plants
- Surface potentials for hazardous substances from previous project

Approach

Bulgaria (Vit)
A described in paragraph **Data Availability** the situation regarding the sewer systems differs from the situation in the other pilot regions and therefore requires a tailor-made approach.

Loads from sewer systems, who are connected to a WWTP
For inhabitants who are connected to a WWTP, the discharge will be estimated from the inhabitant specific water consumption. It is assumed are well maintained and therefore no significant losses are occurring in the sewer systems. The concentration from the treated WW will be obtained from a WWTP just outside of the pilot area, alternatively the measurement from the Romanian pilot areas might be used as an estimate. All sewer systems connected to a WWTP in the pilot area are combined systems. The runoff via combined sewer overflows is calculated according to existing methods already present in the model.

Loads from sewer systems, which are not connected to a WWTP
For inhabitants who are connected to a sewer system, the discharge will be estimated from the inhabitant specific water consumption minus losses in the sewer system, which will be estimated based on some measurements in the catchment. It is assumed that the leaked untreated WW reached the groundwater, the concentration have to be estimated by multiplying the concentration of the untreated waste water by a decay factor from literature research. The concentrations of the untreated waste water will be obtained from

measurements in the catchment. Additionally the surface run-off from urban areas might also reach the sewer systems. The concentrations from surface run-off will be estimated from measurements in the catchment during wet conditions. The discharge from surface run-off will be calculated from yearly precipitation.

Inhabitants not connected to a sewer system

In the VIT catchment a lot inhabitants are not connected to a sewer system and make use of a Septic tank. The amount of water into the septic tanks is calculated from the inhabitant specific water consumption. It is assumed that water is leaking from the septic tank into the underground, the concentration has to be estimated by multiplying the concentration of the untreated WW by a decay factor from literature research. The sludge in the septic tanks has to be transported to a WWTP, it is assumed that this takes place once a year. It is also assumed that in agglomerations with less than 2000 inhabitants, septic tanks are used.

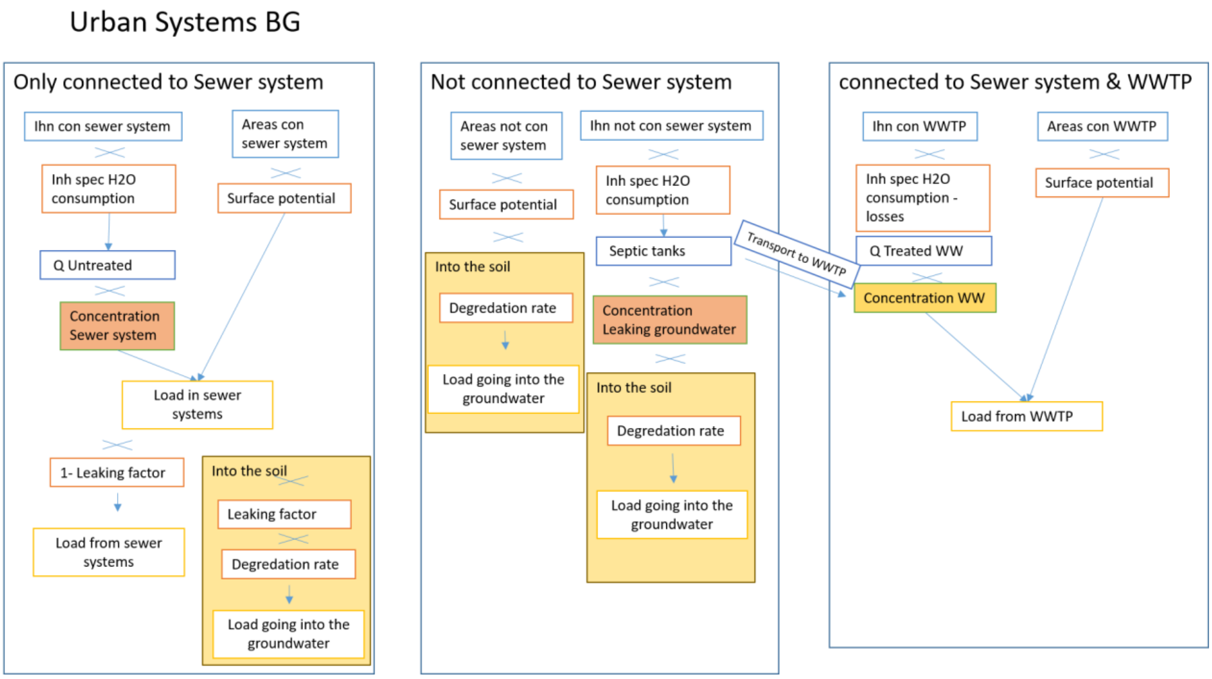

Figure 2-5: Schematic overview of the urban systems for Bulgaria.

Romania and Hungary (Somesul Mic, Viseau; Zagyva, Koppány)

For Romania and Hungary, sufficient data is available to separate the different pathways (storm water systems, combined sewer systems) in the urban systems.

In Romania and Hungary, households are either connected to a sewer system where the WW is transported to a WWTP or households have a septic tank.

Inhabitants not connected to a sewer system

All inhabitants who are not connected to the sewer system have a septic tank. It is assumed that the Septic tanks in Romania and Hungary are not leaking any sludge to the groundwater and that the sludge in the septic tanks is transported to a WWTP once a year. It is also assumed that in agglomerations with less than 2000 inhabitants, septic tanks are used.

Loads from inhabitants connected to a sewer systems and WWTP

From information from local experts following assumptions are made: every household connected to the sewer system is also connected to a WWTP, The sewer systems are well maintained and no sludge is leaking into the soil. The runoff via combined sewer overflows is calculated according to existing methods already present in the model.

The discharge from the WWTP is available from the UWWTP. The concentrations of the hazardous substances will be determined from measurements in the scope of this project.

<u>Stormwater systems</u>
As information on storm water systems is available, the discharge from the storm water will be calculated from the annual precipitation, the concentrations in the storm water will be obtained from a previous Austrian Project SCHTURM or from measurements in the scope of this project.

<u>Austria (Ybbs, Wulka)</u>
For Austria the approach as described in Deliverable_DT2.1.1 in paragraphs 2.3.8 Sewer System & 2.3.9 Municipal Waste Water Treatment Plants.

2.2.6 New approaches

2.2.6.1 Abandoned mining

The new approach for abandoned mining is described in Abandoned mining sites.

2.2.6.2 Pesticides

In this model application two new substance groups were implemented: fungicides and herbizides. For both substances the standard model approach, was chosen. Due to the monitoring and the establishment of the database in the scope of the project, the data availability was sufficient to model all the relevant pathways for pesticides.
A second approach was setup and tested. This one is based on culture specific application rates and empiric transfer functions. A detailed description is given in O.T2.1, Appendix II.

2.2.6.3 Chromium and Arsenic

The heavy metals Chromium and Arsenic where added to the substance group heavy metals and calculated accordingly. The input data was taken from monitoring and the database in the developed in the scope of the project.

2.2.7 Load and concentration calculation from monitoring results

The model validation is practiced by comparing measured results and modeled results. This can be done on base of loads or concentrations. The model calculates emission for each delineated sub-catchment and routes it to the surface water. Using the pre-defined runoff tree, the emission are cumulated. While for some specific substance groups retention by sedimentation is considered for other substance groups not (Retention in tributaries and main rivers). The total annual load is simply related to the total annual runoff for each outlet of a sub-catchment to calculate mean annual concentration.
In the Danube Hazard m3c based on the monitoring results, mean annual loads and concentration were calculated on base of a one year monitoring (2021-2022). Available data refer to bimonthly composite samples from weekly random samples taken only during defined flow conditions (low flow to mean flow). Additionally, event flows were sampled. Sampling of events starts at flows, which were higher than Q10. Consequently, two data sets were produced. Both datasets of this stratified sampling approach were used to calculate most realistic annual loads and concentrations based on time intervals represented by the measured concentrations. A detailed description of the method and the results from the annual load and concentration calculation is presented in OT1.2 Demonstration of a harmonized and cost-effective measurement concept for the monitoring of HS river pollution and of HS emission pathways in 7 pilot regions.

Annual load calculation refers to the monitoring period of the bimonthly composite samples from 04/2021 to 04/2022. However, model results can be only calculated based on annual time-steps. For a best fit the monitored data were equated with the year 2021.
In almost all cases (heavy metals, pharmaceuticals, pesticides) the load calculation was used for validation. For PFAS validation orientates on the mean annual concentrations, driven by several exceedances of the Environmental Quality Standard (EQS) of PFOS, which makes a risk assessment and the evaluation of measures useful.

2.2.8 Model validation

The model needs a number of substance specific input data from different technical and natural compartments:

- Municipal and industrial wastewater (municipal: raw and treated wastewater),
- Abandoned mining sites,
- Combined sewer systems,
- Storm sewers,
- Atmospheric deposition,
- Surface runoff (paved and unpaved areas),
- Soils,
- Drainages,
- Groundwater.

Often those data sets are basic and not sufficient for regionalization or for thematic disaggregation.
Due to the database developed by the project, there are new options for validation of the model results (OT.1.1). Several queries provide datasets of substance specific input data with different levels of spatial or thematic aggregation. Among these are country specific data with often large datasets (e.g. from Germany, Austria and Hungary or Romania), data sets, which refer to different landuse classes, or to specific wastewater treatment stages or size classes. Additionally, the inventory established in the pilot regions from project specific investigations was made available. This data set of course should lead to the best model validation, being most specific, but counteracts the meaning of the model approach, which should, on the base of generalized datasets, provide valid results in a multitude of river catchments, with often no information on substance specific data available. Consequently, the pilot region related data set was not used pilot-specific, but only on a generalized level, with all information from seven pilot regions included. An exception is the information on point sources. However, this is practiced in the model approach anyway.
All data from the data base queries were provided as 10, 25, 50, 75 and 90 percentiles so that even with respect of weighting the results a large number of opportunities for validation was provided. As a result of the huge number of possible input data sets a validation routine was established:

- In a first step the model was parameterized with data sets that represent a high degree of certainty (high number of measurements combined with high share of data above the limit of determination,
- Using always the median (c50) as base version,
- Implementing two versions considering uncertainties of input data:
    - Best case version (using the 25 percentile)
    - Worst case version (using the 75 percentile)
- Comparison of modelled and monitored results
- Establishing a “best fit” version, in which:

- Original chosen data sets could be changed
- Statistical values could be varied.

The establishment of the best fit variant by varying different data sets and statistical values demonstrates either the possibility of achieving a good model fit with the available data sets or the need for further, more detailed data, in case the model fit was weaker or bad. Thus, it also contributes to data analysis and the identification of gaps in knowledge and the need for action.

The technical implementation of the model variants in the model structure is described in the following chapter.

2.2.9 Implementation of model variants

To implement variants in the MoRE model, several steps have to be taken, which will described briefly in the following paragraphs.

First for all substance specific variables additional variants have to be implemented, this has to be done in the metadata. After that all variables that have variants have to be defined in the variant manager, see Figure 2-6.

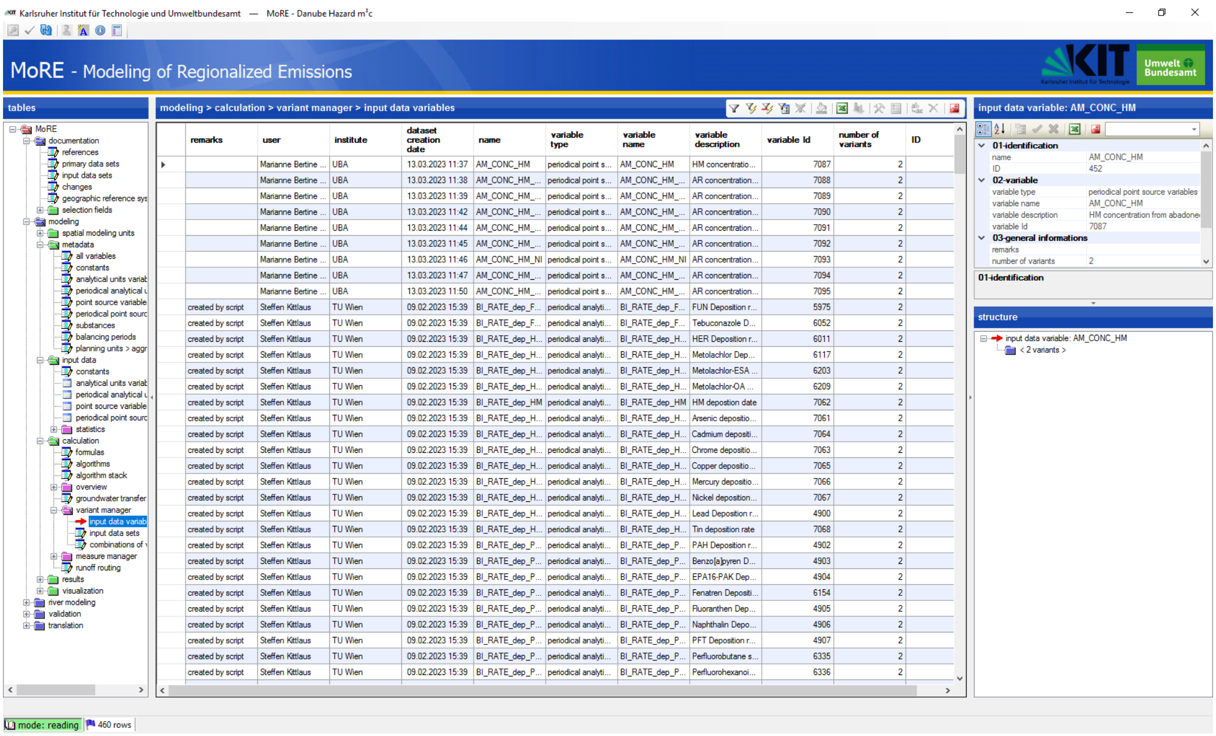

Figure 2-6: Screenshot of the variant manager in MoRE.

All variables containing variants are combined into input data sets, in this case Best-Case for the 25% percentile data and Worst-Case for the 75% percentile, which then have to be added to combinations of variants of input data.

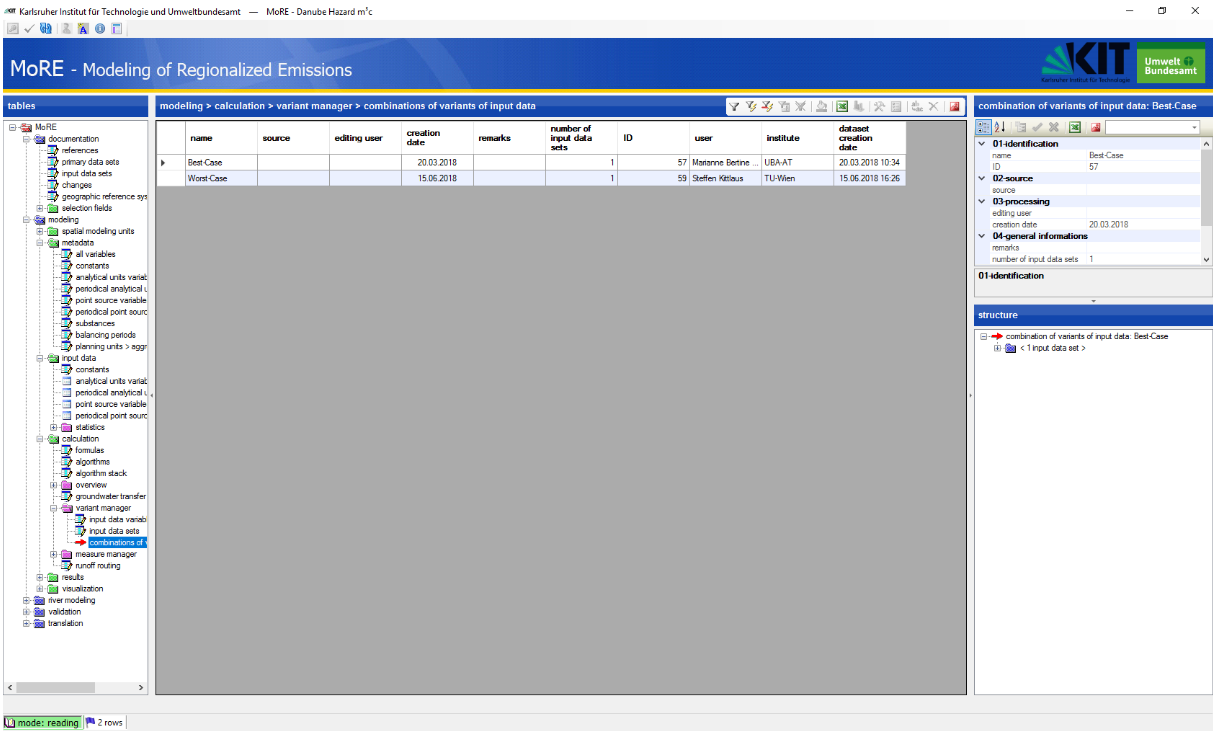

Figure 2-7: Screenshot of the variant manager in MoRE.

The calculation of the variants has to executed directly with the selection of the algorithm stack.

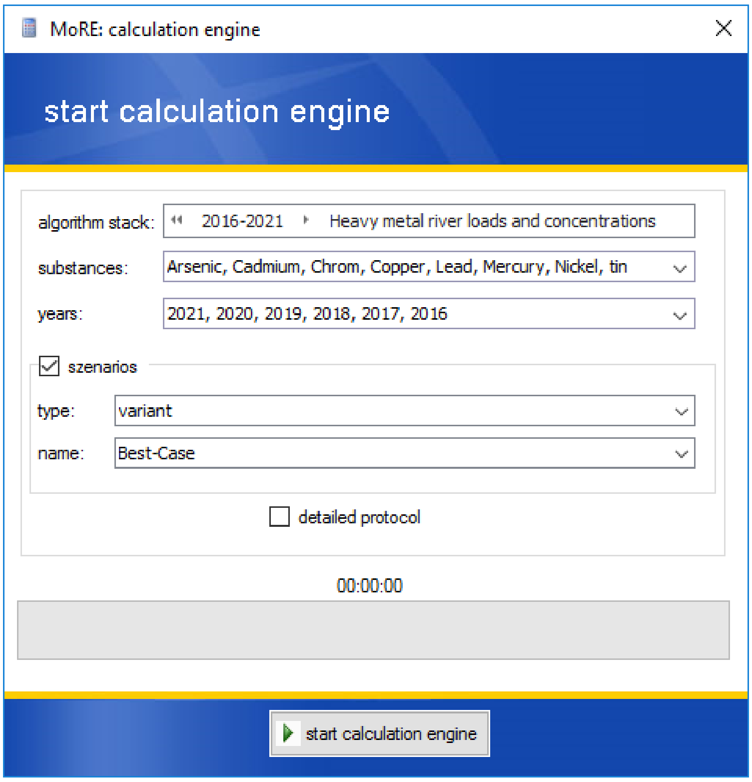

Figure 2-8: Selection of a variant in the MoRE calculation engine.

3. Input data

To run the model a large amount of input data for each delineated sub-catchment are obligatory. In general the needed input data can be subdivided in:

- Basic input data
- Substance specific input data.

Both types of input data will be described in the following paragraphs.

3.1 Basic input data

Basic input data subsume all kind of background information on the physical characterization of each sub-catchment and are not substance concentrations or substance-specific turnover or removal rates. In general these data represent GIS data (e.g. specific land use polygons or lines records), but also time series for precipitation or runoff available at specific locations can build these databases. In the latter case, punctual information often have to be interpolated by geo-statistical methods like kriging to produce a valid mean value for the analytical unit of the model: the sub-catchment. In some cases, even geo-statistical methods have to be applied to develop the needed data. This is especially the case if regionalization becomes difficult, because input data are not distributed over the whole area of interest and information are sparse or lacking in specific sub-catchments.

Basic input data includes easily determined morphological data, such as the mean elevation and the mean slope of a sub-catchment or on the other hand information on land use and hydrology, as well as, for example, the soil loss from agricultural areas derived from complex calculation methods.

The basic data were compiled from a variety of different data sets for each of the seven pilot regions and are aggregated at the level of the sub-catchment. In general the model output is adopted to annual time steps, nevertheless for some pathways, the temporal information has to be prepared on other frequencies, such as monthly values (e.g. precipitation) or long-term data sets (e.g. soil loss). Of course, even data sets with a higher temporal resolution can be used as input data set and be aggregated to the needed time-step.

Because the model structure is flexible, which means that pathways can be added or retired and modelled pathways can be modified and adapted to available information, the data set and the model algorithms can change within different model applications. With respect to data sampling this should clarify, that the description of a basic data set to start the model is meaningful on the one hand, but it should be acknowledged that the definition of these datasets is not final. On the contrary, the prescribed input data needs to be evaluated with respect to the prevailing data situation because the input data set as well as the model algorithms can be modified and balanced during an iterative determination.

Furthermore, it is worth mentioning that once a parameterization of all required input data has been done, updating or modeling further study periods by far does not require updating all data sets, but essentially only those that change annually.

3.2 Model basic input data requirements

Based on already applied model applications a list of basic input data was compiled.

Overall Basic input data necessary for a first setup of the model in the pilot regions can be summarized under several main classes with number of datasets necessary in brackets:

- Analytical Unit (1),
- Topography (1),
- Landuse (16),
- Drainages (1),
- Meteorological data (2),
- Hydrological data (1),
- Erosion (2),
- Sewer system (13*),
- Point sources – municipal (5),
- Point sources – industrial (1).

While most of the basic input data are obligatory for the actual model setup, some are only optional. This is especially true for the input data describing emissions from sewer systems. For this pathway, different approaches are implemented in the model and can be used with respect to the data availability. On the other hand that means that not all of the 13 datasets have to be available in each pilot region.
From Table 3-1 it can be seen that besides area related basic input data some basic input data are related to other units, like time series, rates, shares and specific statistical data. For each country in which pilot regions are situated the data availability, transparency and data management is on a different level, but does show a typical gradient within the Danube region, which makes the results valuable and representative for the whole region.

Table 3-1: Overview of the basic input data needed in the MoRE model.

Actual input data code	**Name**	**Description**	**Unit**	**Source**
Analitical Unit (AU)	**Topography/Area**	**Delineation of Analytical Units**		
BI_A	Area	Area of analytical units	km²	(x)
BI_ELEVA	Digital Elevation Model	Mean hights of subcatchments	m	(x)
Landuse	**Landuse data set**	**Landuse categories in actual version**	**km²**	
BI_A_AL_slope_0-1	Arable land	5 slope classes: 0-1; 1-2; 2-4; 4-8; >8 % (if available)	km²	(x)/(x,t)
BI_A_PST	Pastures	Greenland, meadows	km²	(x)/(x,t)
BI_A_WS_mr	Water surface	Main river (also lakes; reservoirs)	km²	(x)/(x,t)
BI_A_WS_trib	Water surface	Tributaries (also lakes; reservoirs)	km²	(x)/(x,t)
BI_A_FOR	Naturally covered areas	Woods; scrubland	km²	(x)/(x,t)
BI_A_O	Open areas	Mountainous area without vegetation; beaches; dunes	km²	(x)/(x,t)
BI_A_OPM	Surface mining	Mining areas	km²	(x)/(x,t)
BI_A_URB	Settlements	Total urban areas	km²	(x)/(x,t)
BI_A_IMP	Impervious urban area	Paved areas inside urban areas: settlements; industrial estates; car parks….	km²	(x)/(x,t)
BI_A_WL	Wetlands	Area of Bog; swamp; floodplains	km²	(x)/(x,t)
BI_A_OR	Country roads	Paved road area; not included in settlements	km²	(x)/(x,t)
BI_A_REM	Other remaining areas	Other areas not listed above	km²	(x)/(x,t)
Drainages	**Melioration cadastre**			
TD_SHR_a_td_agrl	Tile drained areas	From arable land and pastures	km²	(x)

Actual input data code	Name	Description	Unit	Source
Meteorological Data	**Climatic data**			
AD_EVAPO_lt	Evapotranspiration	Longterm mean annual evapotranspiration	mm	(x)/(x,t)
BI_PREC_apr	Precipitation	Monthly values	mm	(x)
Hydrological data	**River Discharges**			
BI_Q_net	Net runoff	Modelling period; annual data	m3/s	(x)
Erosion	**Soil loss**			
ER_agrl_SL_spec_lt_AL	Soil loss	Soil loss from arable land (optional from 5 slope classes)	t/(ha·a)	(x)/(x,t)
ER_agrl_SL_spect_lt_PST	Soil loss	Soil loss from pastures	t/(ha·a)	(x)/(x,t)
Sewer sytem	**Statistical Data about inhabitants and waste water system (partly from UWWTD)**			
BI_INH	Number of inhabitants	Populaltion	inh	(x,t)
US_cso_VOL_spec_SOT	Stormwater overflow	Storage volume of stormwater overflow tanks in combined sewer systems, area-specific	m³/ha	(x)/(x/t)
US_L_CS	Combined sewers	Length of combined sewers	km	(x)/(x/t)
US_L_SS	Stormwater sewers	Length of stormwater sewers	km	(x)/(x/t)
US_SHR_inh_con_tot	Connection rate	Percentage of inhabitants that are connected to sewer systems	%	(x)/(x/t)
US_SHR_inh_conWWTP_tot	Connection rate	Percentage of inhabitants that are connected to sewer systems and waste water treatment plants	%	(x)/(x/t)
US_SHR_inh_nss_tot	Connection rate	Percentage of inhabitants that are not connected to sewer systems	%	(x)/(x/t)
US_INHC_H2O	Water consumption	Inhabitant specific water consumption	l/(inh·d)	
US_nss_SHR_inhl_towwtp_sept		Percentage of inhabitant load that is transported from septic tanks to waste water treatment plants	%	(x)/(x/t)
US_Q_spec_COM		Runoff rate for commercial waste water	l/(ha·s)	
Point source data (one value for each treatment plant)	**Urban wastewater (partly from UWWTD)**			
WWTP_ps_INH_conWWTP	Connection rate	Number of inhabitants that are connected to sewer systems and waste water treatment plants (point sources)	Inh	(x)/(x/t)
WWTP_ps_CP	Capacity	Capacity of the waste water treatment plant (point sources)	PE	(x)
WWTP_ps_PE	Load	Nominal load of waste water treatment plant (point sources)	PE	(x,t)
WWTP_ps_TS	Treatment type	Current treatment type of waste water treatment plant (point sources)	-	(x)/(x/t)
WWTP_ps_Q	Discharge	Runoff via waste water treatment plant (point sources)	m³/a	(x/t)
Industrial wastewater				
ID_ps_Q	Discharge	Runoff via industrial direct dischargers	m³/a	(x/t)

(x,t) = function of space and time; (x) = function of space; (c) = function of space using homogeneous values per country.

3.3 General description of basic input data

A detailed description of the basic input data sets used in this model application can be found in Appendix I Deliverable D.T2.1.1 Basic input data of Output T2.1 Harmonized MoRE Model.

3.4 Substance specific input data

In general, the substance specific input data was obtained from database created in this project, which also contains the monitoring data. The process of choosing which data is used for each input variable is described in Model validation.
To aid with the creation of the MoRE input files extractions for each substance group where made from the database. For each variant for each substance group MoRE input files were created, which can be found in Appendix I, also the model results for the corresponding model runs can be found in this Appendix.

3.4.1 Data for abandoned mining

3.4.1.1 Abandoned mining point sources

In the scope of the Danube Hazard project 6 point sources from abandoned mining were sampled in the Viseu catchment. The data from these Samples was directly used as input data for the MoRE model. One of the six sampling points was an industrial direct discharge and the other 5 sampling points were untreated waste water. The Heavy metal concentrations measured at these sampling points where used as concentrations for the abandoned mining point sources.
See Table 3-2 for an overview of the used concentrations.

Table 3-2: Overview of the basic input data needed in the MoRE model.

untreated mining effluent [µg/l]	**Median**	**Perz 25**	**Perz 75**
As	5.0570	3.8776	6.0315
Cd	29.6800	17.9520	43.0604
Cu	1239.6162	511.3307	2366.8000
Pb	36.5304	22.0198	67.1250
Zn	11665.0700	3407.1783	23763.5950
Ni	28.9803	14.1657	47.0904
Cr	1.4991	1.2414	2.0830
Hg [ng/l]	4.5250	2.3925	7.5175

3.4.1.2 Abandoned mining diffuse sources

For both upstream sub-catchments in the Viseu pilot area the soils, background mining rock and groundwater concentrations for Cadmium, copper and Zinc were adjusted.
To get an indication of the concentration of heavy metals in groundwater and background mining rock a literature research was done, with a focus on Romania and Bulgaria. The used literature dated from the years 2003 to 2011.
For the concentrations used in the Viseu catchment please see Table 3-3.

Table 3-3: Overview of the basic input data needed in the MoRE model.

	Cd	Cu	Zn
groundwater	**µg/l**	**µg/l**	**µg/l**
Median	1.4	6.8	177
Perz 25	0.2	5	95
Perz 75	2.3	9.9	370
Background mining rock	**mg/kgTM**	**mg/kgTM**	**mg/kgTM**
Mean	1.2	39.35	95.1

The input data for the heavy metal concentrations of the the Soils in the two upper catchments from Viseu were taken from the sampling campaign within the scope of the Danube Hazard Project. The used concentrations are displayed in Table 3-4.

Table 3-4: Heavy metal concentrations in soils in the Viseu Catchment.

	Pasture			Arable land			Forest		
mg/kgTM	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**
As	10.390	7.836	12.104	13.961	11.867	16.055	18.522	7.537	39.500
Cd	93.237	67.454	123.194	0.299	0.209	0.389	0.446	0.133	0.934
Cu	21.453	15.183	32.826	23.048	22.648	23.448	37.403	10.390	83.800
Pb	25.137	13.895	31.451	28.637	24.269	33.005	56.628	25.858	98.000
Zn	82.594	58.374	120.129	92.671	84.098	101.243	148.375	51.332	313.000
Ni	39.030	27.215	56.396	49.444	38.514	60.374	27.049	17.194	33.600
Cr	93.237	67.454	123.194	108.105	92.733	123.478	85.811	78.832	94.400

3.5 Missing or inadequate data

During the modelling conducted in the scope of this project it became clear that some input data is not available or is not available in the right quality.

Erosion data for Bulgaria and Romania
For this project for Bulgaria and Romania erosion data from JRC were used, which especially in the VIT catchment resulted in very high erosion rates. For Romania the erosion rates in both catchments where reasonable, however for both countries it is advised that a countrywide erosion model should be developed.

Inventory of the abandoned mining sites in the Viseu Catchment
In this model application the abandoned mining sites are represented by point sources, however this is a simplification of the real situation. At this moment there is no knowledge of diffuse emissions from the abandoned mining. Furthermore, the runoff of the well-known and monitored abandoned mining effluents should be collected.

Investigation of the sewer systems in the Vit catchment
For the Vit Catchment very few information on the sewer systems and the connected households was available. All information used in the current model application for the urban systems in the Vit pilot area is based on expert judgement, because official information was not available.

Data on storm sewers for Pesticides
For the Pesticides no data from storm sewers was available.

Land use data: roads outside of settlements

For this model application the CORINE landcover data set was used, which resulted in very large areas for roads outside settlements, which subsequently resulted in very high emissions from that pathway. When using the CORINE landcover data set, special attention has to be paid to this aspect.

4. Delineation and characterization of catchments and sub catchments

The spatial units used in the MoRE model are sub catchments, who are preferable around 100 km^2 or comparable in size. To ensure a possibility to validate the model it is important that as many as possible outlets points of sub catchments coincide with discharge and water quality measurement. In order to reach these objectives the delineation of the sub catchments was updated in respect to the delineation in the project proposal. In the following two chapters, first the delineation process and second the changes made will be described.
By updating the delineation of the catchments, it was also ensured that in all seven pilot areas the same method was used.

4.1 Delineation method

This method delineates catchments from a Digital Elevation Model (DEM) with existing ArcGIS functions from the Watershed toolbox. The following input data is needed:

- DEM (raster data),
- Water network (raster data),
- Outlet points (vector data).

The first step is to push the water network into the DEM. This is done by lowering the raster cells representing the water network by a small amount, only the cells of the water network are lowered.

The next steps will be listed as bullet points:

- The prepared DEM is filled with the ArcGIS spatial analyst function fill, this results in a filled DEM.
- From this filled DEM, the flow direction is calculated, the results is a raster file with the flow direction. The flow direction represent the way in which water would flow from one raster cell to an adjacent cell.
- The flow direction water is used to calculate the flow accumulation, which represent how many cell flow into a particular raster cell, the result is a raster file with the flow accumulation.
- The outlet points and the snap distance together with the flow accumulation are used as input for the function snap pour points to distinguish the cells with the highest accumulated flow within the specified distance from the outlet points. This results in a raster with the outlet points.
- The flow direction and outlet points rasters are used as input data for the Watershed function, which calculated the watersheds belonging to the predefined outlet points. The watershed raster is converted into watershed polygons.
- The raster based watershed borders are smoothed.

4.2 Delineation and characterization of pilot regions

Seven pilot regions characterizing representative conditions in the Danube basin were selected for detailed investigations with respect to monitoring and modelling Figure 4-1. Two pilots are situated in Austria (Ybbs and Wulka) and represent a typical pre-alpine (Ybbs) and one Pannonian catchment (Wulka), with agricultural use, and moderate to high anthropogenic activities. Two pilots in Hungary (Koppany and Zagyva), which are also situated in the

Pannonian landscape represent catchments with intensive agricultural use (Koppany) and increased industrial and anthropogenic activities 8Zagyva). Furthermore, two pilots in Romania (Somesul Mic and Viseu) were selected. Somesul Mic (in Transylvania) is characterized by a steep upstream to downstream gradient with natural areas in the upper and mid river reach and the large settlement Cluj Napoca with more than 320.000 inhabitants in the downstream region. Viseu is a catchment in the Carpathians, which is characterized by large areas of forest but especially by traditional mining with several abandoned mining sites determine the water quality.
In Bulgaria one pilot region is investigated. The Vit catchment in the Balkan region is characterized by natural conditions and an extensive anthropogenic use.

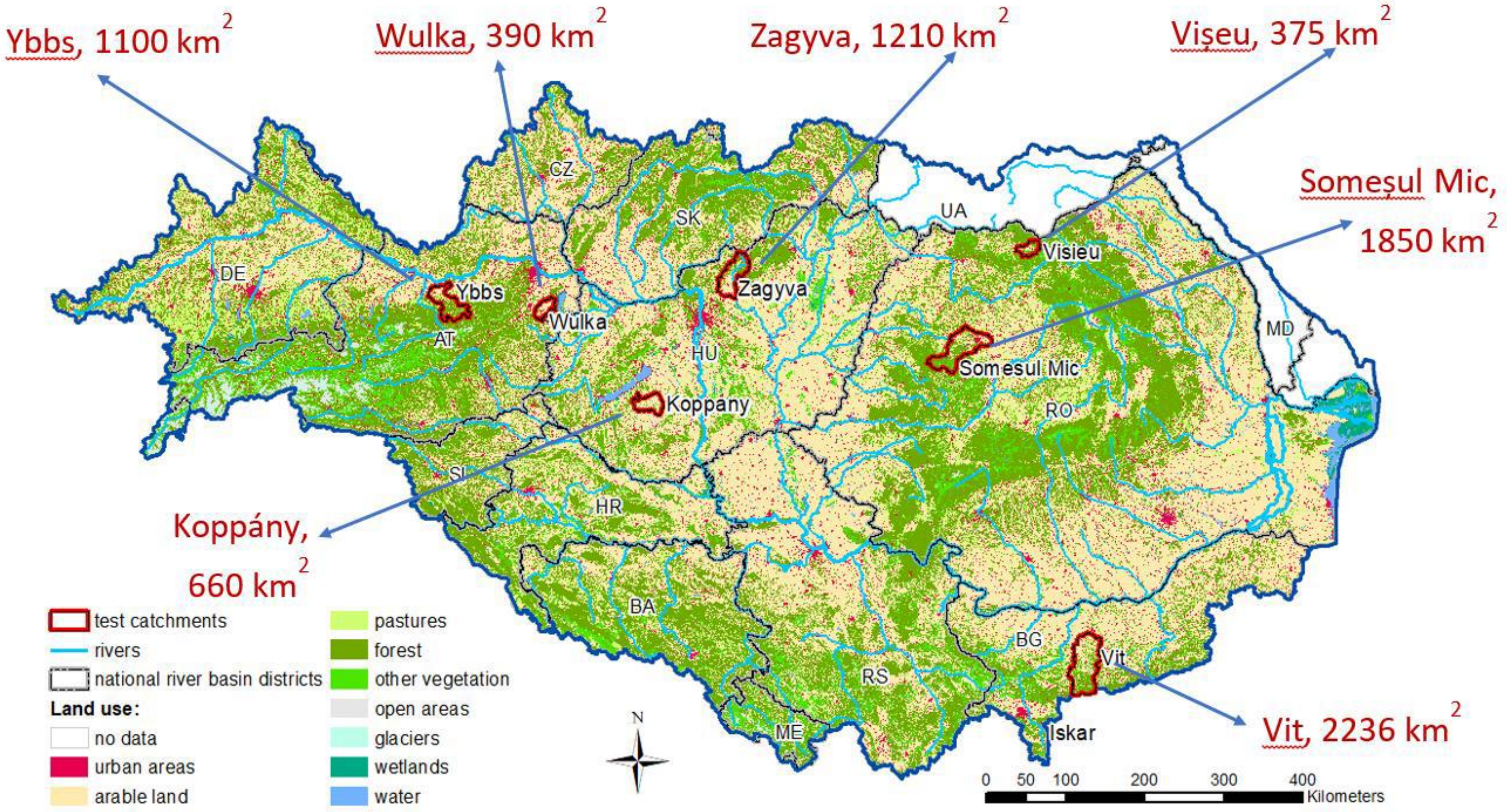

Figure 4-1: Location and size of the pilot regions across the Danube River basin.

Figure 4-1 expresses the final catchment delineation in the pilot regions, the sub-catchments, their ID, the catchment hierarchy (ToID), the area, the summed area considering the discharge tree and the mean average elevation.
In total in seven pilot regions distributed among four countries, 34 sub-catchments were delineated. The seize of the sub-catchments varies from 41.4 to 666.8 km^2 and have a mean seize of 232.3 km^2. The mean elevation varies from 169.7 m a A. in a Wulka sub-catchment to 1276.9 m a A. in a Viseau sub-catchment.

Table 4-1: Overview of Sub Catchments for all Pilot regions.

Sortier_N	State	Riversystem	Catchment	ID MORE	TOID MORE	Rivername	Area [km^2]	Summed Area [km^2]	Mean Elevation [m a A]
1	AT	Danube	Ybbs	11001	11000	Ybbs	224,4	1111,9	396,0
2	AT	Danube	Ybbs	11002	11001	Url	158,7	158,7	439,0
3	AT	Danube	Ybbs	11003	11001	Ybbs	112,5	728,8	599,0
4	AT	Danube	Ybbs	11004	11003	Kleine Ybbs	111,8	111,8	684,0
5	AT	Danube	Ybbs	11005	11003	Ybbs	71,0	504,5	728,6
6	AT	Danube	Ybbs	11006	11005	Ybbs	118,3	433,5	842,4
7	AT	Danube	Ybbs	11007	11006	Ybbs	199,4	315,2	945,1
8	AT	Danube	Ybbs	11008	11007	Ybbs	115,7	115,7	1039,1
9	AT	Danube	Wulka	12001	12000	Wulka	41,4	383,0	169,7
10	AT	Danube	Wulka	12002	12001	Eisbach	66,8	66,8	226,9
11	AT	Danube	Wulka	12003	12001	Nodbach	62,4	62,4	200,1
12	AT	Danube	Wulka	12004	12001	Wulka	136,8	212,3	260,1
13	AT	Danube	Wulka	12005	12004	Wulka	75,5	75,5	386,3
14	HU	Danube	Koppany	21001	21000	Koppany	389,3	658,4	170,4
15	HU	Danube	Koppany	21002	21001	Koppany	269,1	269,1	196,4
16	HU	Danube	Zagyva	22001	22000	Zagyva-patak	411,3	1200,2	215,1
17	HU	Danube	Zagyva	22002	22001	HerXdi-Bér-patak	180,2	180,2	221,2
18	HU	Danube	Zagyva	22003	22001	Zagyva-patak	376,7	608,8	306,8
19	HU	Danube	Zagyva	22004	22003	Zagyva-patak	157,7	157,7	336,6
20	HU	Danube	Zagyva	22005	22003	Tarján-patak	74,4	74,4	304,8
21	RO	Danube	Somesul	31001	31000	Somesul Mic	528,0	1959,7	441,4
22	RO	Danube	Somesul	31002	31001	Nadas	290,3	290,3	508,2
23	RO	Danube	Somesul	31003	31001	Somesul Mic	285,4	1141,4	619,8
24	RO	Danube	Somesul	31005	31003	Somesul Mic	210,4	521,0	896,9
25	RO	Danube	Somesul	31006	31003	Somesul Mic	335,1	335,1	1228,0
26	RO	Danube	Somesul	31004	31005	Somesul Rece	310,5	310,5	1238,5
27	RO	Danube	Viseu	32001	32000	Viseu	145,3	378,0	991,4
28	RO	Danube	Viseu	32002	32001	Viseu	133,3	133,3	1276,9
29	RO	Danube	Viseu	32003	32001	Tisla	99,4	99,4	1205,2
30	BG	Danube	Vit	41001	41000	Vit	548,0	2206,3	234,4
31	BG	Danube	Vit	41002	41001	Vit	666,8	1658,3	335,8
32	BG	Danube	Vit	41003	41002	Vit	524,7	991,5	583,6
33	BG	Danube	Vit	41004	41003	Cherni Vit	161,1	161,1	1032,6
34	BG	Danube	Vit	41005	41003	Beli Vit	305,7	305,7	1053,1

4.2.1 Ybbs pilot region

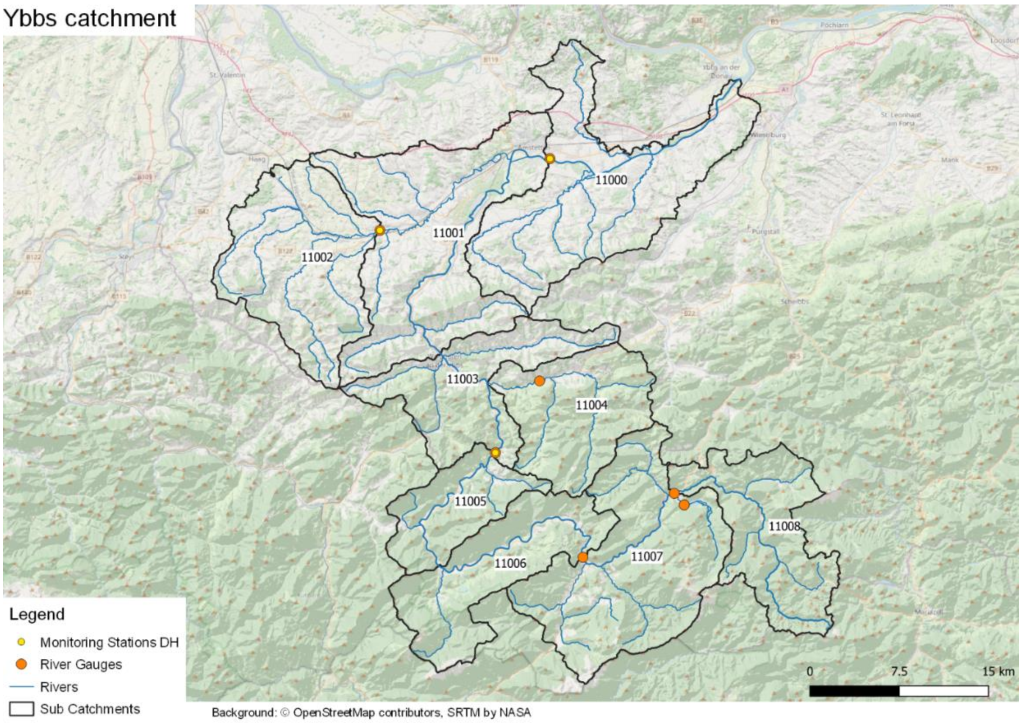

Figure 4-2: Ybbs catchment divided in 8 sub-catchments.

The Ybbs catchment was divided in 7 sub-catchments to make optimal use of the discharge measurements. Monitoring stations were associated with existing gauging stations. Conceptual, this allows gaining concrete information from the measurable part of the outlet catchment (11001), from a tributary with increased agricultural use (11002) and from the largely unaffected regions in the upper reaches (11005).
Point sources (Figure 4-2: Ybbs catchment divided in 8 sub-catchments) are of minor relevance in the Ybbs catchment. In total seven treatment plants are operated, the largest with 18,000 PE in the outlet catchment 11001. Here also two industrial treatment plants are located.
The pilot region shows a clear upstream downstream gradient, with wide natural areas in the upper reaches and increasing anthropogenic use in the direction of the outlet. In total Ybbs is a moderately populated pilot region (compared to the other pilot regions) with extended forests, pastures and a growing share of agricultural land in the downstream sub-catchments (especially in the Url sub-catchment, 11002). The pilot region is characterized by a high long-term runoff.

Table 4-2: Characteristic values in the Ybbs pilot region.

Pilot region	Catchment Area [km^2]	Mean Elevation [m]	Population density [Inh/km^2]	Arable land [%]	Arable land > 4% slope [%]	Pasture [%]	Forest [%]	Urban Area [%]	Runoff [mm]
Ybbs	1111.9	685.8	68	11.8	8.2	24.9	58.7	0.4	811

4.2.2 Wulka pilot region

The Wulka pilot was divided into 5 sub-catchments to make optimal use of the discharge measurements in the catchment. The monitoring stations are not exactly situated at the outlets of the sub-catchments. The monitoring station located in 12000 refers to the outlet of the modelled region in 12001 (main river). The station in sub-catchment 12001 refers to the tributary Eisbach 12002. That in 12003 to the tributary Nodbach.

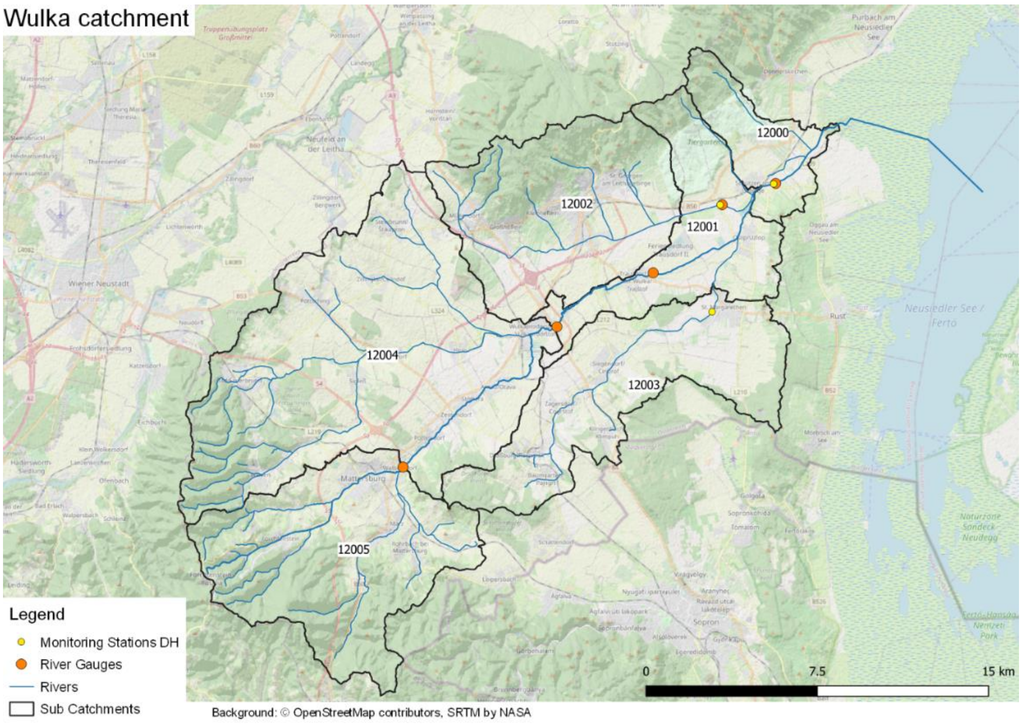

Figure 4-3: Wulka catchment, subdivided into five sub-catchments.

In the Wulka catchment the Wastewater Treatment Plants under investigation have a capacity of 54,000 PE (12002) and 110,000 PE (12001) and are equipped with nutrient removal (N and P).
Arable land and forests is dominating in the upstream catchment (12005). In the rest of the pilot region, the degree of urbanization is comparable. The population density is moderate, but compared to the other pilots in the upper third. The long-term runoff is low and comparable to the low specific runoff of the pilot regions in Hungary.

Table 4-3: Characteristic values in the Wulka pilot region.

Pilot region	Catchment Area [km^2]	Mean Elevation [m]	Population density [Inh/km^2]	Arable land [%]	Arable land > 4% slope [%]	Pasture [%]	Forest [%]	Urban Area [%]	Runoff [mm]
Wulka	383	259.6	163	50.9	21.2	1.9	38.3	3.3	66

4.2.3 Koppany pilot region

For the Koppany catchment was delineated into two sub-catchments. At each sub-catchment outlet one monitoring station is situated at a gauging station, to guarantee the model validation of each sub-catchment.

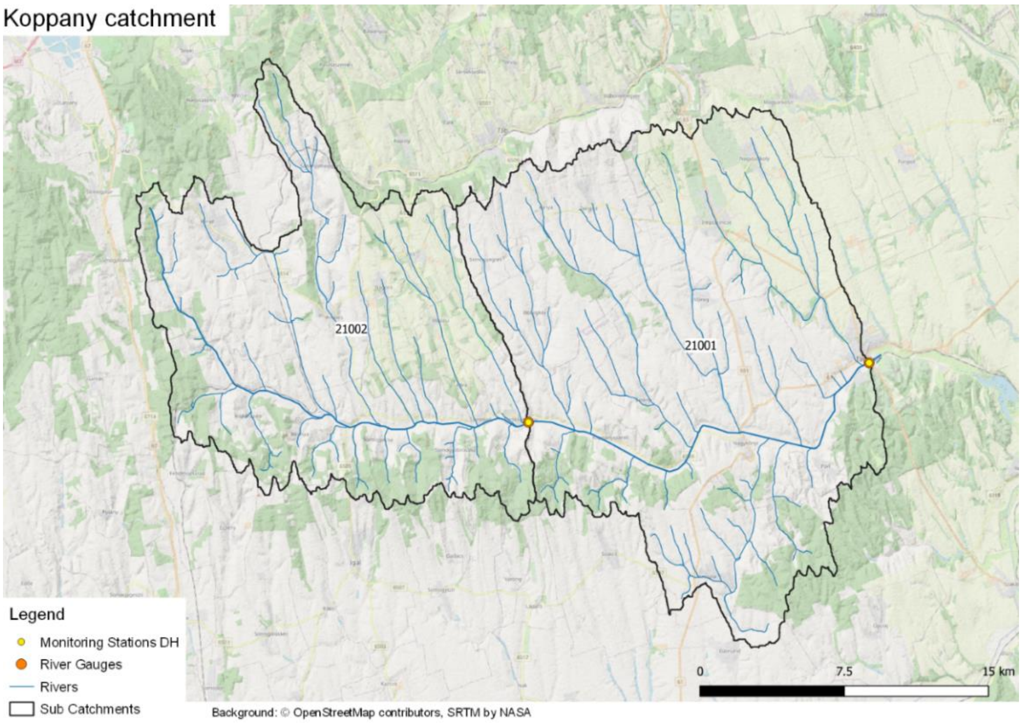

Figure 4-4: Koppany catchment, subdivided into two sub-catchments.

In both sub-catchments one municipal WWTP is located. In the downstream catchment additionally one industrial treatment plant discharges.
Arable land dominates the landuse, with a high share of practiced agriculture on slopes steeper than 4 %. The population density is low. The long-term runoff is low, too. With 60 mm it is comparable to other pilot regions with similar conditions (Wulka, AT; Zagyva, HU).

Table 4-4: Characteristic values in the Koppany pilot region.

Pilot region	Catchment Area [km^2]	Mean Elevation [m]	Population density [Inh/km^2]	Arable land [%]	Arable land > 4% slope [%]	Pasture [%]	Forest [%]	Urban Area [%]	Runoff [mm]
Koppany	658.4	181	27	60.6	38.9	3.5	24.9	2.8	60

4.2.4 Zagyva pilot region

For the Zagyva pilot, five sub-catchments were delineated. In four of five sub-catchments a model validation is possible, because of the construction of monitoring stations.
In all five sub-catchments municipal WWTPs are located. The highest share of WWTP effluent on the net runoff is documented for the upstream sub-catchment 22005 (around 35%). In the upstream catchments 22005 and 22004 the share of WWTP effluent is 13%. In the downstream catchment the share decreases to less than 2%. Discharges from industrial WWTPs are also located in almost all sub-catchments. Only in 22004 no industrial Waste Water Treatment Plant is reported in the cadaster.

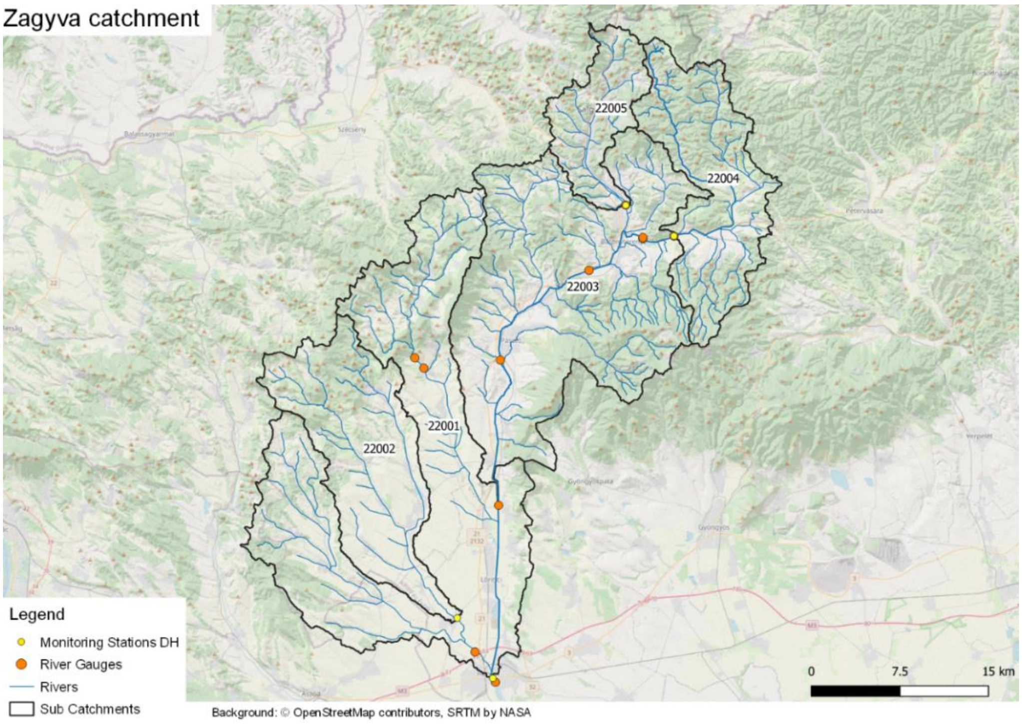

Figure 4-5: Koppany catchment, subdivided into two sub-catchments.

Forests dominate the landuse in the upstream catchments in the north, but even in the western parts of the catchment. The arable land, which also has high shares on landuse are situated in the southern parts in sub-catchment 22002 and 22001. The population density is moderate to high (also expressed in moderate to high values of urban area). The long-term runoff is the lowest in all pilot regions.

Table 4-5: Characteristic values in the Zagyva pilot region.

Pilot region	Catchment Area [km^2]	Mean Elevation [m]	Population density [Inh/km^2]	Arable land [%]	Arable land > 4% slope [%]	Pasture [%]	Forest [%]	Urban Area [%]	Runoff [mm]
Zagyva	1200.2	266.3	95	30.5	15.4	11.0	45.8	5.4	40

4.2.5 Somesul Mic pilot region

The modelled catchment consists of six analytical units. The outlet of the investigated area (analytical unit 31001) is situated downstream the town of Cluj-Napoca with more than 320,000 inhabitants. Monitoring sites are situated at the outlet (31001), the upstream area (31003) and the tributary Nadas. The extension of the formerly plant catchment of around 100 km^2 ensures to have industrial discharges from TETAROM INDUSTRIAL PARK - JUCU, Cluj included, which was the intention in the beginning of the project. However, the extension also causes a distinct discrepancy of the existing gauging station and the catchment outlet. In accordance with the Viseau catchment (Viseu pilot region), this lack of validation opportunity should be counteracted by combining quality and quantity measurements (with water level measurements) at the outlet and transfer them to the time series of the upstream gauge to generate a valid water level – discharge relationship at the outlet. Of course, this might cause higher uncertainties with respect to runoff accuracy.

Wastewater Treatment Plants are located in the outlet sub-catchment 31001. Here, the large municipal WWTP of Cluj Napoca (capacity of 414,000 PE and a load of 366,867 PE, equipped with nutrient removal stage (N and P)) is located and also the above mentioned industrial WWTP is discharging.

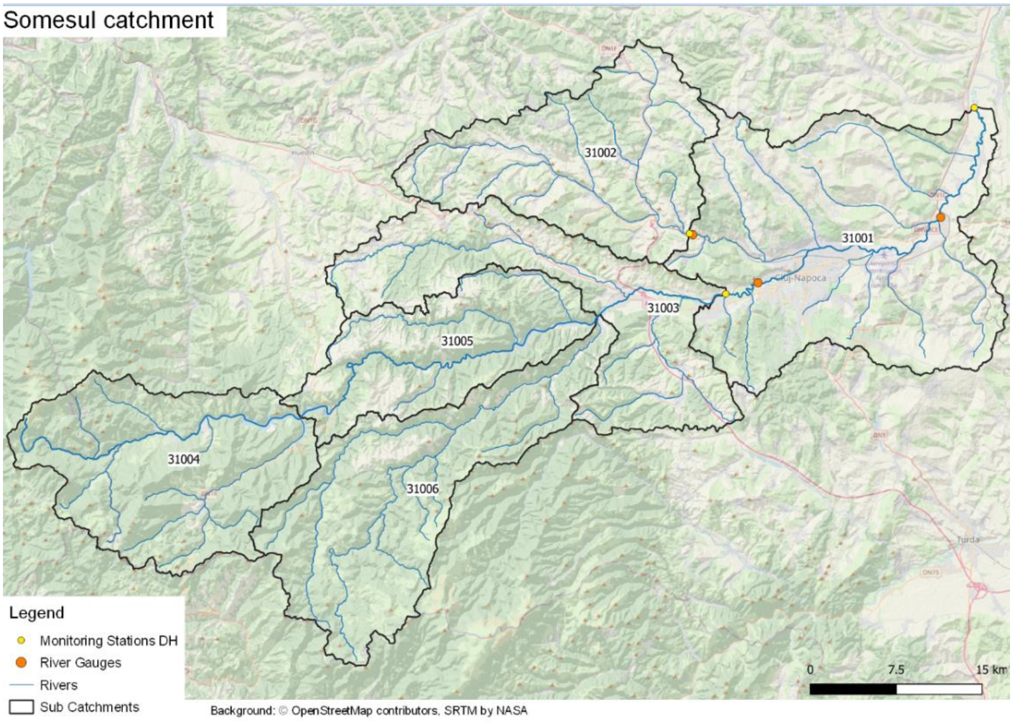

Figure 4-6: Somesul catchment, subdivided into six sub-catchments.

While the upstream area is dominated by forests and pastures in the downstream regions agriculture and urban areas become more important. The increased population density of around 200 inhabitants per km² is due to the high number of inhabitants in Cluj-Napoca. The same applies to the relatively high proportion of urban area. The pilot region has a moderate runoff.

Table 4-6: Characteristic values in the Somesul Mic pilot region.

Pilot region	Catchment Area [km²]	Mean Elevation [m]	Population density [Inh/km²]	Arable land [%]	Arable land > 4% slope [%]	Pasture [%]	Forest [%]	Urban Area [%]	Runoff [mm]
Somesul Mic	1959.7	787	197	10.5	6.7	17.2	48.6	5.6	246

4.2.6 Viseu pilot region

The Viseu pilot region was delineated into three sub-catchments with two monitoring stations at the catchment outlet (32001) and the Tisla tributary (32003), influenced by mining. The delineation of the sub catchments were prepared in such a way that each outlet coincides with either discharge measurements or a water quality monitoring station. Because monitoring station and runoff measurements are subject to a tolerable deviation and no relevant tributaries or sources of additional discharges are known between gauging station and quality monitoring station, it was decided to use the existing runoff measurements and adapt them in 32003 (area specific runoff correction). The outlet sub-catchment (AU 32001) is characterized by the second quality monitoring station in the Viseau catchment. Here no discharge measurement is available. To solve this problem the quality sampling at the outlet was combined with additional flow measurements. In a second step, the water level was adjusted to the Moisei hydrometric station (about ten kilometers upstream). For AU 32002 only runoff measurements are available.

In sub-catchment 32003 and 32002 municipal WWTP are operating. However, the share of WWTP effluent on the total net runoff is small (0.5% in 32002 and 0,1% in 32003).

In the central and northern parts of AU 32003, several abandoned mining sites are localized. Five well defined effluents of abandoned mining sites were monitored. Unfortunately, it was not possible to determine an average annual runoff because of inaccessibility during the winter half-year. Consequently, the runoff and load evaluation from abandoned mining effluents could only be estimated.

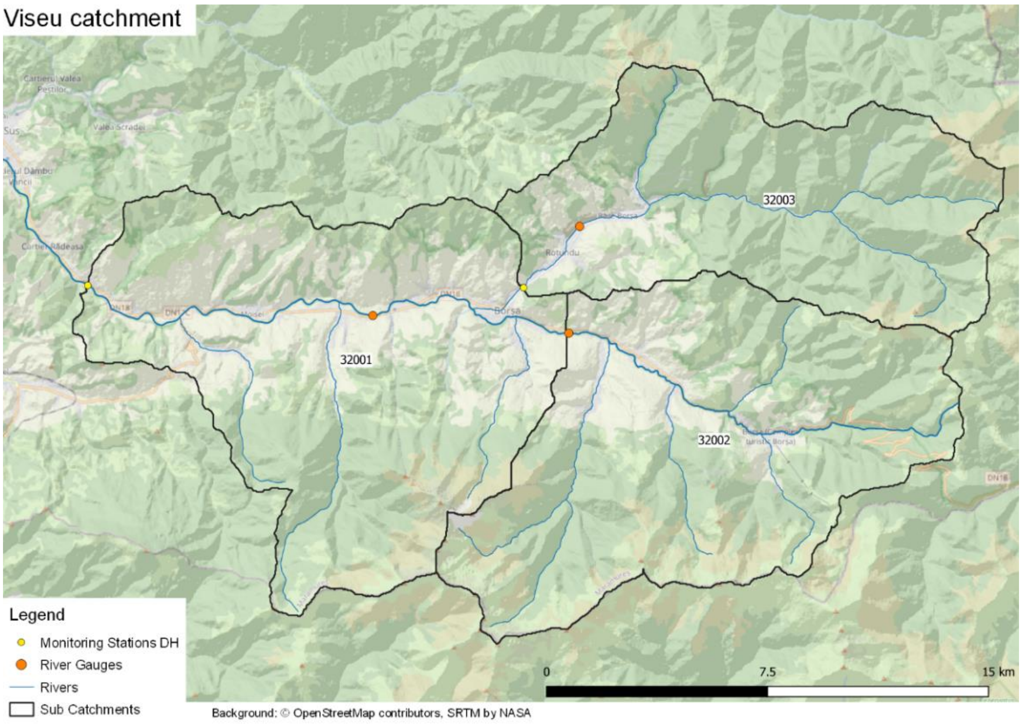

Figure 4-7: Viseu catchment subdivided into three sub-catchments.

Forests dominate the upstream regions of the Viseu catchments, which has a mean elevation of more than 1100 m. Pastures are even relevant landscape elements. The population density is above the Romanian average (around 79 inhabitants per km^2). The runoff is the highest of all seven pilot regions under evaluation.

Table 4-7: Characteristic values in the Viseu pilot region.

Pilot region	Catchment Area [km^2]	Mean Elevation [m]	Population density [Inh/km^2]	Arable land [%]	Arable land > 4% slope [%]	Pasture [%]	Forest [%]	Urban Area [%]	Runoff [mm]
Viseu	378	1148.3	137	0.2	0.2	20.0	64.8	3.2	959

4.2.7 Vit pilot region

The Vit pilot is delineated into five sub-catchments. At both upstream catchments (41004 and 41005) a monitoring station is installed, which is combined with a gauging station. The same situation can be found at the outlet of the Vit catchment.

Small WWTPs are located in sub-catchment 41002 and 41003 but have only very little affect (with share of effluent on the net runoff ranging wide below 0,1%). In Vit a high share of population is connected to sewer systems, which are not transported to WWTPs but is directly discharging into surface water.

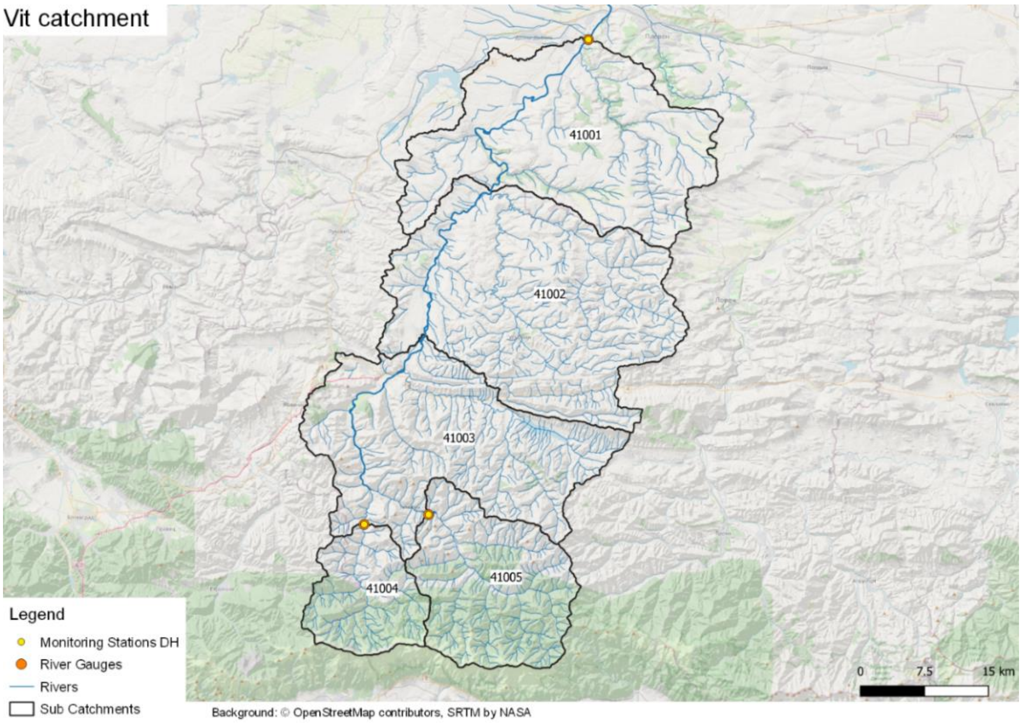

Figure 4-8: Vit catchment, subdivided into five sub-catchments.

The dominant landuse in the upper, mountainous region of the pilot region is forest. In the downstream parts the influence of agriculture increases, with a clear focus on arable land. Rather 30 % of the arable land is situated on fields with a slope of more than 4%. The area has the lowest population density of all pilot regions and the runoff is moderate.

Table 4-8: Characteristic values in the Viseu pilot region.

Pilot region	Catchment Area [km^2]	Mean Elevation [m]	Population density [Inh/km^2]	Arable land [%]	Arable land > 4% slope [%]	Pasture [%]	Forest [%]	Urban Area [%]	Runoff [mm]
Vit	2206.3	519.8	7	42.8	28.9	5.4	45.4	2.3	197

5. Water balance and sediment balance

5.1 Water balance

The water balance is a crucial model parameter, which contributes significantly to the weighting of the modelled pathways among each other. The approach of calculation os demonstrated in the water balance.

The net runoff for each sub-catchment is an annual input data for the model. Consequently, the single years reflect the possible variations in climatic conditions in the sub-catchments of the pilot regions.

In Figure 5-1 comparison of the six-year average (2016-2021) and the single year 2021 is presented for the entire region of the pilot catchments. This comparison to some extent points out possible fluctuations that occurred in 2021, the year in which measurements were taken to validate the model results, thus providing initial indications of the representativeness of the measurement period.

First, the big range of runoff conditions in the pilots under investigation becomes apparent. The lowest runoff can be found in the three Pannonian pilot regions Wulka, Koppany and Zagyva, which range between 50 and 70 mm. Vit and Somesul Mic show medium conditions, with discharges in a range of 230 to 270 mm, while in the Ybbs and Viseu pilot regions the largest mean runoff is documented with 800 - 810 mm.

In most pilot regions the match between the runoff in the modelled period (average) and in the monitored year 2021 is very good, with deviations that fluctuate only within a range of -2,5% to 4%. That makes the year 2021 generally spoken representative for the complete modelling period. In contrast, the deviations in the Viseu and Koppany pilots are much higher. While in Viseu the 2021 runoff is 19% higher (955 mm compared to 801 mm) than in the modelled period, the runoff in Koppany, which has the lowest value among all regions, decreases by 31 % (from 50 mm to 35 mm).

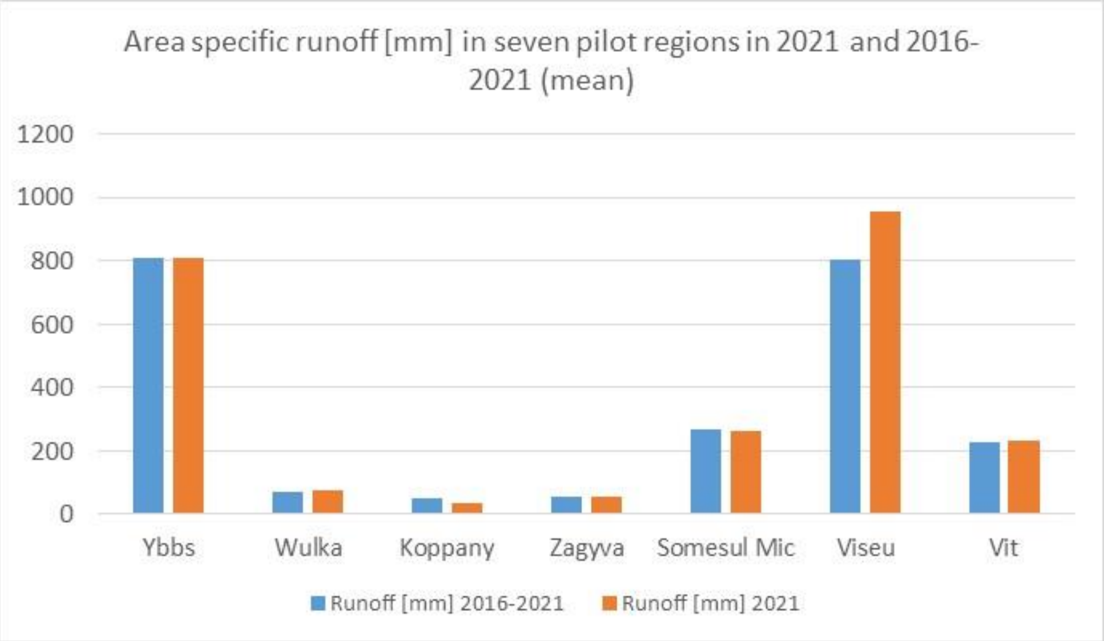

Figure 5-1: Comparison of mean runoff [mm] of 2021 and the mean annual runoff of the period 2016-2021 in seven pilot regions.

Beyond this comparison, it must be mentioned that the mean annual runoff, as is demonstrated in Figure 5-1 only gives a first hint of the repetitiveness of the years for which measurements were made. It does not provide any information on the temporal distribution of runoff or the occurrence of flood events. In the Ybbs pilot (e.g.) in 2021, an HQ5 event transported considerable amounts of suspended solids and associated substances within few days with mean daily discharges of more than 600 m^3/s (MQ = 31,5 m^3/s). This specific event, which had a huge impact on loads, is hidden in the mean annual 2021 runoff, with often rather dry periods, which makes the mean of 2021 comparable to the six-year average.

In Figure 5-2 the different components and shares of the water balance in all pilot regions is demonstrated. Furthermore, the model period 2016-2021 is compared to 2021, the year where measurements were made as a basis for model validation ( ).
It becomes clear, that the Ybbs, Viseu and Vit pilot regions have comparable conditions with respect to the water balance. Here, a clear dominance of groundwater (baseflow and intermediate flow) with a > 75% share is calculated.
Surface runoff is the second component with a high proportion around 25%. Other water balance components, like runoff from WWTPs or sewer systems in these pilot regions, characterized by a high share of forests and open, mountainous areas, is only of minor importance. In addition, the share of runoff from the inhabitants connected to sewer systems, which direct discharge into the surface water in the Vit pilot region is of low impact, due to the documented low number of inhabitants.
Of course, this can also vary greatly in the individual sub-catchments. Especially in the downstream sub-catchments the share of urban water balance components will significantly increase.
To a significant extent, this is also the case in Somesul Mic. Here the water balance in the upstream sub-catchments show similar shares like the above-mentioned pilots. Only the high share of treated wastewater from the large WWTP of Cluj Napoca in the outlet catchment of the pilot region (around 10% of the total runoff) leads to a different appearance.
A comparable appearance of the water balance can also be stated for the Hungarian pilot regions Koppany und Zagyva. Around 75% stem from the subsurface discharges baseflow, interflow and drainages and around 11% from surface runoff. Five to seven percent are related to treated municipal wastewater, with slightly higher shares in Koppany. While discharge from storm water effluents are of some importance in the Zagyva pilot region (around 2%) this is also the case for Koppany with 3% share on the total water balance from atmospheric deposition, caused by a high share of open surface water areas from a dense network of partly embanked ditches.
The Wulka catchment shows a unique appearance among the pilot region water balances . Here the strong anthropogenic impact becomes visible, with highest shares on the water balance from municipal wastewater (around 40%). Additionally, a high share of 15% stem from combined sewer overflows, which was also found in a former study (Amann et al., 2019). Only 30% of the runoff is addressed to exfiltration from the underground, characterized by baseflow, interflow and drainages.
As stated above, specific conditions increase when switching from pilot area scale to sub-catchment scale.
The examples below underline the influence on the water balance in the specific sub-catchment:

- Viseu (abandoned mining influenced upstream catchment 32003): 1% stems from direct discharges of untreated abandoned mining effluent,
- Somesul Mic: 50% of WWTP effluent from Treatment Plant Cluj Napoca (sub-catchment/outlet 31001),
- Zagyva (upstream catchment 22005) 40% of runoff from municipal and industrial wastewater treatment plants,

- Wulka (12001 outlet catchment) 70% of WWTP effluent (sub catchment 12003: 30% from combined sewer overflow).

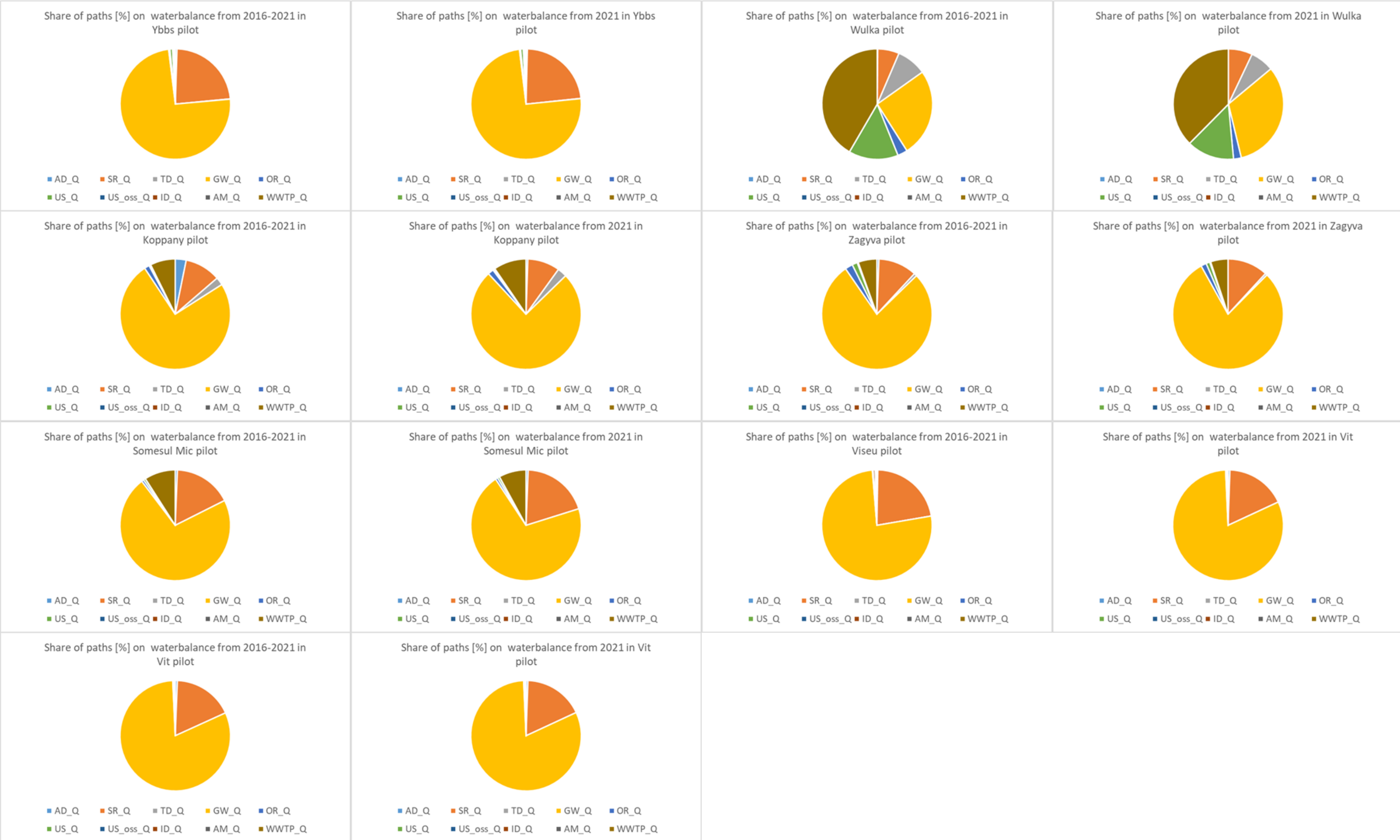

Figure 5-2: Comparison of the components of the water balance [%] in seven pilot regions (2016 to 2021 average and 2021). (AD_Q: atmospheric deposition; SR_Q: surface runoff; TD_Q: Drainages; GW_Q: subsurface flow (base flow interflow); OR_Q: extra-urban roads; US_Q: combined storm water overflow and storm system; US_oss_Q: ID_Q: industrial WWTPs; sewer systems without connection to WWTP; AM_Q: abandoned mining; WWTP_Q: municipal WWTPs).

5.2 Sediment balance

The balance of the sediments transported in the river systems is a crucial parameter for hazardous substances that have an increased tendency to adsorb. This is particularly important for a large number of the heavy metals investigated and modelled in the project, but may also be relevant for other substances, such as benzo(a)pyrene or fluroanthene.
If particle-bound transport plays a role in the pollutant, accurate quantification of the annual load is particularly dependent on valid recording of pollutant transport during flood events. Furthermore, the validation of suspended solids loads in the pilot regions is a helpful information for understanding the material flows and also provides indirect information into potential retention capacities, e.g. from reservoirs.
The MoRE model quantifies suspended solids emissions from a multitude of natural and technical systems and has been adapted to the specific conditions in the pilot regions also with respect to data certainty (chapter Fine solid balance The most relevant emission stem from agricultural and natural soils. Other components, which can significantly contribute to the suspended solid balance are glaciers (not relevant in the pilot regions) and matter load from open (mountainous) areas, which play only a subordinate role in the pilot regions.
Comparing loads calculated from the monitoring at 20 sites representing outlet points of sub-catchments with loads calculated by the model (year 2021) shows a sufficient match for most catchments. In the pilot regions Somesul Mic (RS), Viseu (RV) and Wulka (AW), modelled and calculated data show a good match. In other pilots, like Vit (BV), Koppany (HK), the outlet of Zagyva (HZ6) and Ybbs (AY) the match is much weaker (Figure 5-3)

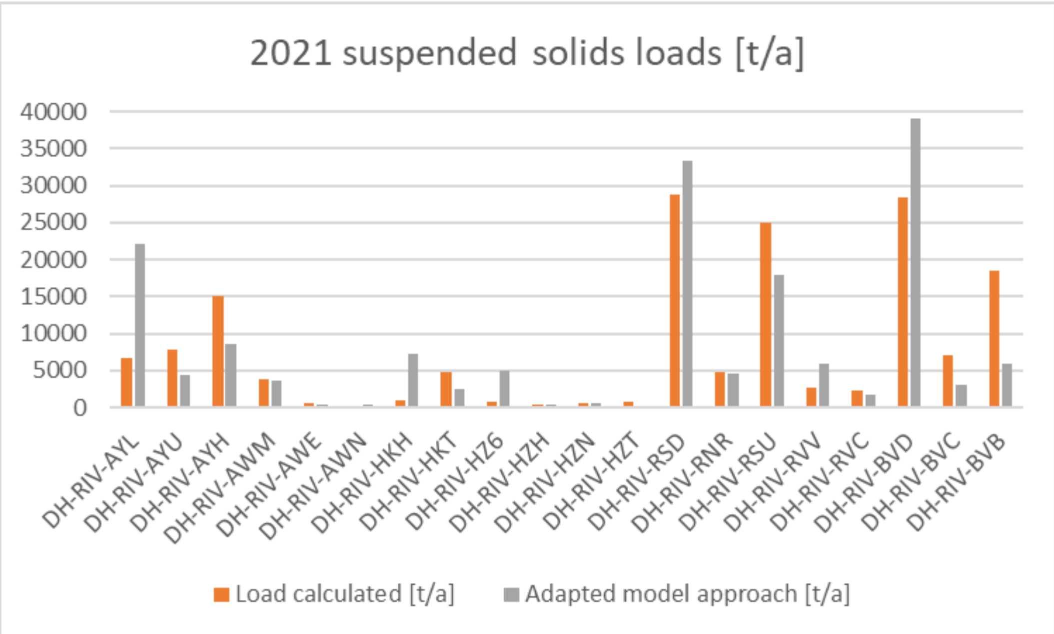

Figure 5-3: Calculated and modelled loads of suspended solids [t/a] in 2021 at all pilot region monitoring sites.

Reasons for the weaker match in the listed pilots are manifold. In the Vit catchment the sediment load form natural areas seems to be significantly underestimated, while the sediment input from agriculture, which stems from a Europe-wide soil loss investigation (already corrected) is still too high. In the Hungarian catchments, due to a very dry monitoring period, the calculated loads of suspended solids are extremely low, but can be reproduced in the sub-catchments of Zagyva (HZ). The outlet HZ6 is significantly overestimated, which results from an overestimation of agriculture suspended solids emission from the catchment above and HZ6 itself, which together account for 66% of the total catchment area. Another reason for the mismatch might be an underestimation of monitored suspended solids from load calculation.

A similar situation can be seen at the outlet of the Koppany pilot region, where the outlet catchment HKH seems to be underestimated by the monitoring load calculations, compared to its upstream sub-catchment HKT. Another explanation could be that large amounts of suspended solids are retained and the model approach overestimated the solid load from agricultural areas.
In the Ybbs catchment, the calculated load from monitoring is influenced by a flood event (Figure 5-4), which lead to transport of big amounts of suspended solids for three days. The calculated loads for the headwater (AYH) and the agriculturally influenced sub-catchment Url seems to be reasonable. The solid transport in the main river is heavily influenced by several reservoirs, which may lead to sedimentation. Nevertheless, a smaller load at the outlet (AVL) compared to that of the small tributary Url (AYU) - as was calculated - is unrealistic. Here a problem with the number of actual measured suspended solids concentrations might be the reason for a load calculation with high uncertainties. Estimates from continuous suspended solid measurements led to significantly higher loads of suspended solids.

The different components of the water balance in the pilot regions for the modelled period 2016-2021 and the monitored year 2021 are shown in Figure 5-4.

The total loads in all pilots range from around 100 kg/ha to 280 kg/ha. The latter is found in the Koppany pilot region, characterized by high shares of agricultural land, often on steep slopes, but it is also the region with the smallest runoff. The lowest total loads are modelled in Zagyva. All other pilots range between 150 and 200 kg/ha.
The dominating pathways from the model approach are erosion from natural areas (forests), with dominant suspended solid emission in Ybbs, Somesul Mic, Viseu and Vit pilots, and from agricultural areas. The latter dominates in the pilot region Koppany and even in the Wulka pilot. In Zagyva and Vit soil loads from agricultural areas are in the same magnitude as suspended solid loads from natural areas. In the Wulka pilot, loads from combined sewer overflows reach a remarkable share.
When the average suspended solids balance from the model period (2016-2021) is compared to the year of monitoring, significant differences can be determined. This is especially true in the Pannonian pilot regions Wulka, Koppany and Zagyva. Here, 2021 is a year with significantly lower emission of suspended solids, which reach only 1/3 of the model period. The high stability of suspended solids in all other pilots and the higher dynamic in the Pannonian pilots have two main reasons:

- Loads from natural areas: due to significant uncertainties and overestimation, the approach established in Austria, with a dynamic calculation of suspended solids from natural areas, open areas and glaciers (the latter two not relevant here) could only be applied in Wulka, Koppany and Zagyva pilots. As a consequence, the suspended solid loads from natural areas can vary also here, while in the other pilots a constant area specific rate is applied from earlier approaches.
- Loads form agricultural areas: they vary on an annual base by the R-factor, which is calculated from the intensity of the summer half-year precipitation. In Wulka, Koppany and Zagyva the low precipitation in 2021 leads to a considerably reduced erosion and input of suspended solids into surface waters compared to 2016-2021. Even in Somesul Mic, the loads from agriculture decrease in 2021, while the other pilots show average suspended solids emissions from agricultural areas.

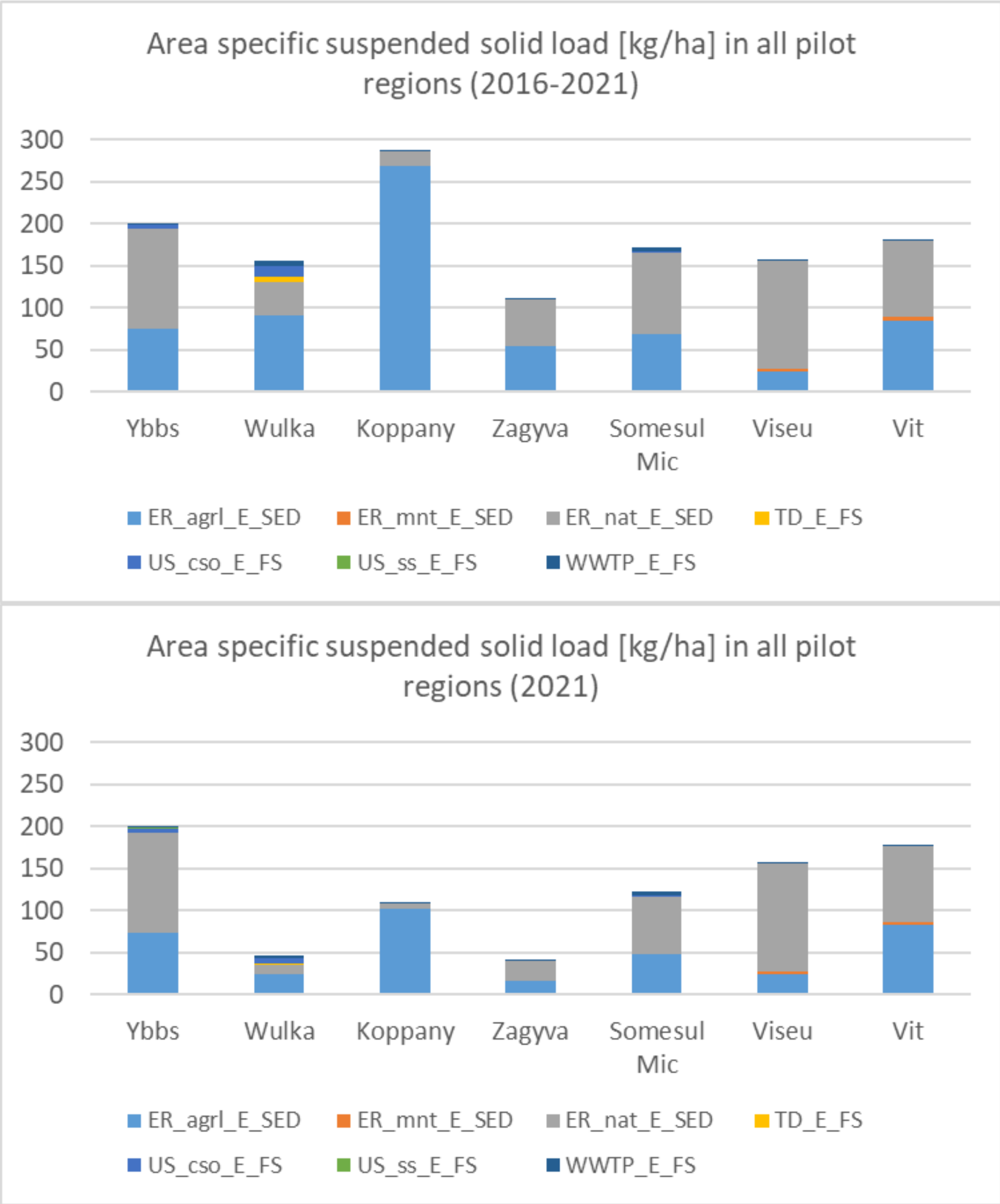

Figure 5-4: Water balance components: erosion (ER) from agriculture, mountainous areas, natural areas (forests), tile drainages (TD), combined sewer systems (US_cso), storm sewer systems (US_ss) and WWTP for all pilot region in 2016-2021 and 2021.

In general, the results underline the character of the modelling approach, which is adopted to reproduce mean conditions and on one hand has only a limited ability to capture the natural dynamics in its natural expression (e.g. area specific, static soil loss from natural area). On the other hand, specific, more dynamic approaches developed on the base of empiric data sets, cannot always be transferred to other regions, with other characteristics.

For relevant soil loss from natural areas, two different approaches were used. This is in contrast to the objectives of setting up a model that is as harmonized as possible, but was applied for reasons of realistic modeling and as a consequence of the availability of only one year of measurements of suspended solids.

It becomes clear that in case of extreme conditions (here extreme low discharges or serious flood events), which appeared in 2021 (the year of measurements), the sensitivity of the model approaches has deficiencies to reflect these extremes. In the case of the Vit pilot area,

also the relevance of input data quality (soil loss calculation from agricultural areas) becomes apparent.
Modeling of substances with enhanced transport in particulate form should be based on a reliable multi-year suspended sediment transport database, which represents mean and event-driven conditions.

6. Model validation

The comparison between modelled and monitored loads and concentrations (16 substances from four substance groups) is provided for 20 monitoring stations from seven pilot regions with different characteristics. In each pilot region, two to four monitoring stations are installed. For each pilot the outlet is monitored as well as upstream sub-catchments, headwaters and tributaries. The monitored loads and concentrations (PFOS) are compared to the aggregated in-stream loads and concentrations modelled along the discharge tree and considers retention by sedimentation, e.g. in case of heavy metals.
Two different kind of scatter plots are presented for different substance groups and substances.
The first one shows the best fit of the model. Here best and most reliable data sets were selected from the database queries and also variations of the statistical values (10, 25, 50, 75 and 90 percentiles) were applied. This approach was used to demonstrate the opportunities of model accuracy, but on the other hand also to outline possibilities of using the model results in the EU WFD policy cycle, e.g. for a risk analysis, with accuracies of model results playing a decisive role.
The second plot shows the possibility to use variants to approach the model fit to the calculated monitoring loads and express the uncertainties of modelling and input data. Here the best and most reliable data sets were selected from the database queries, with:

- the median (50 percentile) used for the base model variant,
- the 25 percentile used for the best case variant and
- the 75 percentile used for the worst case variant.

In this application, the uncertainties of load calculations are also implemented. Three variants are calculated by applying different conventions to concentrations < LOQ and by varying the calculation by “Regression on Order Statistics”. Uncertainties are presented as horizontal and vertical error bars. A detailed description can be found in (O.T.1.2).

6.1 Substance group PFAS

6.1.1 PFOS

The validation of PFOS model results was established based on a comparison between loads and concentration. The validation of concentrations was implemented to test a possible use of model results for risk analyses.
With the exception of the outlet sub-catchment of Somesul Mic pilot region the comparison of modelled and monitored PFOS loads is very good.

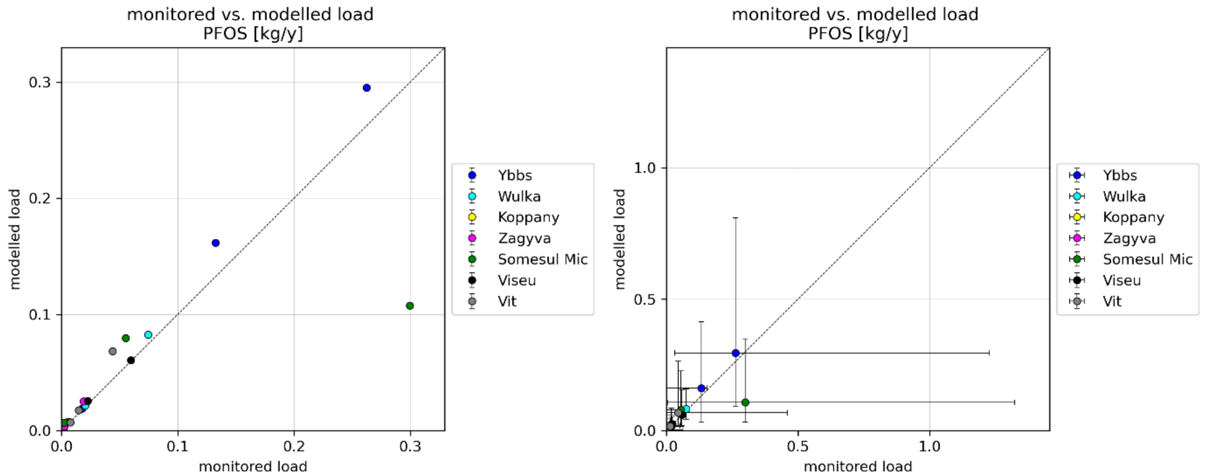

Figure 6-1: Modelled and monitored PFOS load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 20 monitoring sites.

Only a very slight tendency of overestimation can be determined. The assumption that the discrepancy of the loads originates from an underestimation of the PFOS flux from the large wastewater treatment plant Cluj Napoca is not confirmed by the monitoring results. Three wastewater treatment plants including Cluj Napoca were monitored in the pilot area of Somesul Mic and showed comparable or even slightly lower effluent concentrations than measurements from the other pilot regions. To avoid the low sample number of effluent measurements in the pilot region (n=9), the slightly higher mean concentrations of all municipal WWTP effluents from the Danube Hazard m3c sampling campaign (n=35) were used in the model.
In addition to a possible unrecorded increased influence of industrial facilities, the low groundwater concentrations (having a significant share on the total emission) are also likely to cause the underestimation. For both PFOS and PFOA (6.1.2 PFOA) parametrization of groundwater concentration were split into:

- Data set “landuse forests” for sub-catchments dominated by natural conditions (forests),
- Median concentrations from a large data set available for Austria for all other sub-catchments.

For PFOA the groundwater concentrations in the database are threefold higher, while concentrations in municipal and industrial WWTPs are comparable. The significantly higher groundwater concentration for PFOA leads to a good model fit with the monitored loads in the Somesul Mic pilot region (6.1.2 PFOA).
Model variants (Figure 6-1, right side) with a similar distribution of base variant compared to the optimized variant demonstrate only little adaptations for optimization.
Concentrations of PFOS calculated from the model results also show a good accordance with the monitored concentration (Figure 6-2).

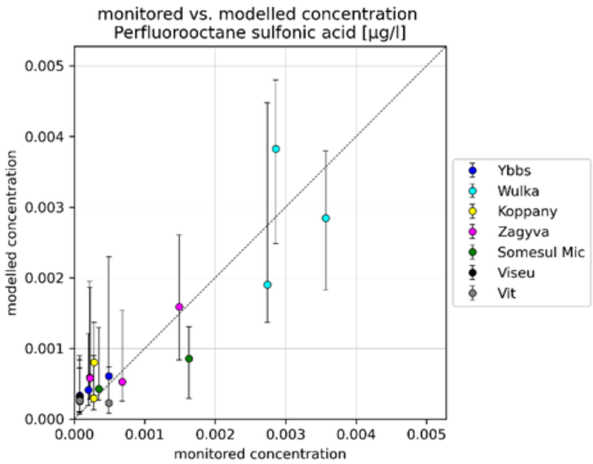

Figure 6-2: Modelled and monitored PFOS concentrations [µg/l] (base- minimum and maximum variant) - validation based on 20 monitoring sites.

6.1.2 PFOA

The validation of PFOA model results was established based on annual loads for 2021.

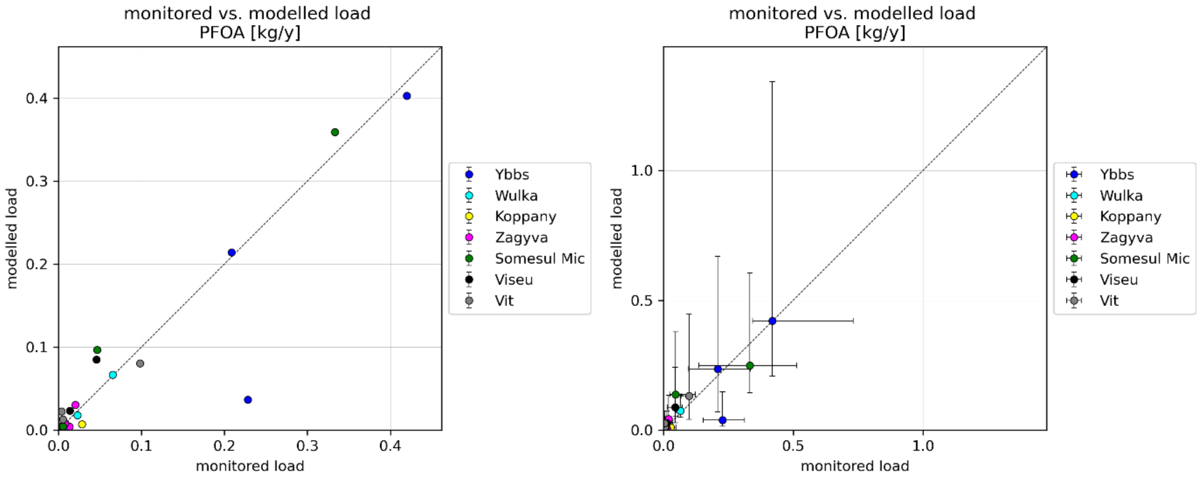

Figure 6-3: Modelled and monitored PFOA load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 20 monitoring sites.

The model fit shows a good agreement with the calculated loads from the monitoring results. For low monitored values < 0.01 kg/y the model results show a higher deviation. Significant underestimation of the model results is found in the Ybbs pilot in the tributary Url, characterized by intensive agriculture, but without municipal or industrial wastewater effluents. The load calculated from monitoring results including event flow is five times higher than those calculated at base flow conditions. In addition, the mean PFOA concentrations are six times higher than during base flow conditions. The model cannot reproduce the significant influence of floods on PFOA concentrations and loads in the Url sub-catchment. The sources, which lead to the increase in concentration and loads of PFOA at events, cannot be clearly addressed. A significantly increased influence from combined sewer overflow and storm sewer could be an explanation.
The base variant on the right side of Figure 6-2 also shows a rather good accordance compared to the monitoring results.
The large horizontal and vertical bars to some extent express the uncertainties of load calculation (bars end at the y-axis) and the range of model results, using statistical values from the database queries.

6.2 Substance group Heavy Metals

Modelling of heavy metals was prepared for Arsenic, Cadmium, Chrome, Copper, Lead, Mercury, Nickel and Zinc. For Arsenic and Lead no sufficient model performance was achieved. Reasons for that failure are unclear so far. Even the optimization of the model results by using different data base queries and by variation of the statistical options from the data base does not lead to adequate results.

6.2.1 Dissolved Cadmium

Cadmium loads calculated from monitoring results in the pilot regions range from 0.06 kg/y in Koppany and Zagyva to 8 kg/y at the outlet of the Ybbs pilot.
Extraordinarily high loads (not shown here) were calculated in Viseu, with 473 kg/y in the small tributary Tisla (32003) and 174 kg/y at the outlet of Viseu (32001). The model results show a good accordance with the monitored loads using the optimized validation approach. The similar appearance of the base variant on the right side of Figure 6-4 compared with the optimized model adaptation underlines that the median concentration values from the data sets are sufficient for a very good model fit, or in other words, no extended adaptation was necessary to achieve a very good model result.

The large horizontal and vertical bars express the range of load calculation (bars end at the y-axis) applying different conventions for concentrations < LOD and the range of model results using different statistical values from the database queries.

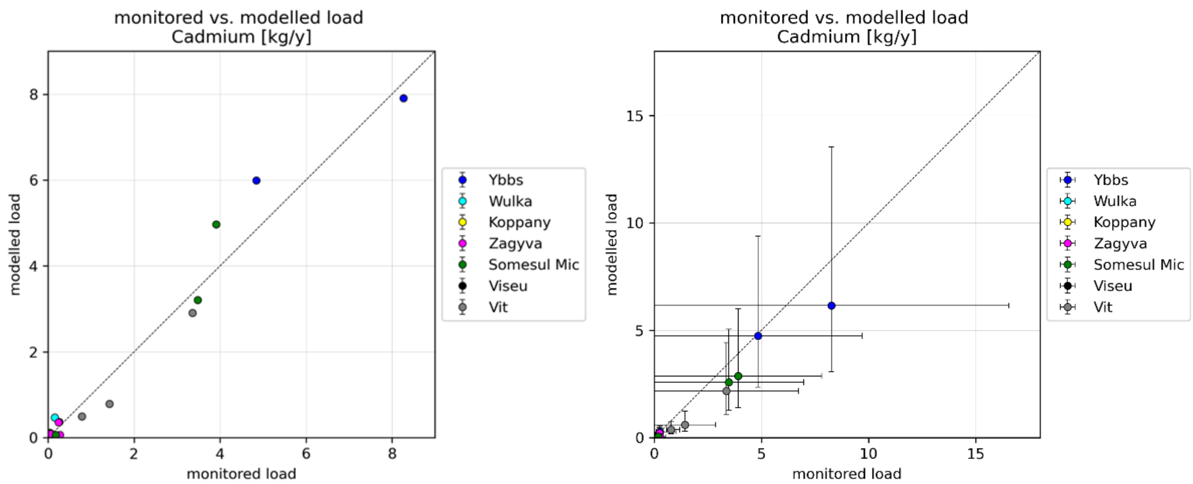

Figure 6-4: Modelled and monitored Cadmium load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 18 monitoring sites (Viseu excluded).

6.2.2 Dissolved Copper

Copper loads calculated from monitoring results in the pilot regions range from 4 kg/y in Wulka (tributary Nodbach) to 1122 kg/y at the outlet of the Ybbs pilot.
Extraordinarily high loads were calculated in Viseu, with 3520 kg/y in the small tributary Tisla (32003) and 4561 kg/y at the outlet of Viseu (32001).

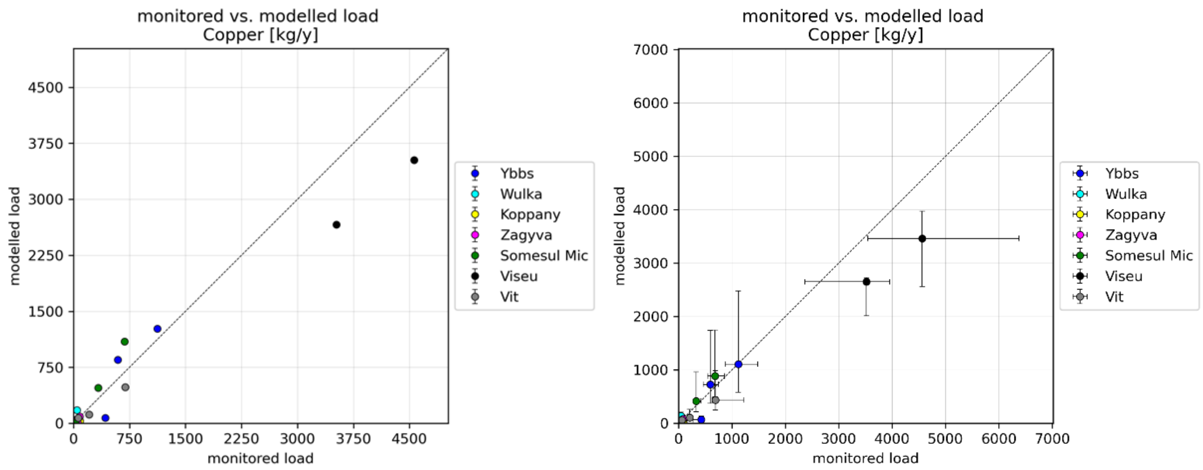

Figure 6-5: Modelled and monitored Copper load [kg/y] (optimal variant, left; base- minimum and maximum variant, right)) - validation based on 20 monitoring sites.

The model results show a good accordance with the monitored loads using the optimized validation approach. The high loads in Viseu caused by abandoned mining are underestimated by the model but are in the same magnitude. No special adjustments to the data sets were necessary in the case of copper either: the median values were sufficient for a good model adjustment.

6.2.3 Dissolved Chromium

Chromium was added to the MoRE approach. Chromium loads calculated from monitoring results in the pilot regions range from 0.2 kg/y in Wulka (tributary Nodbach) to 132 kg/y at the outlet of the Ybbs pilot region. Model results show an overestimation at higher loads, but in general, the model adaptation is sufficient. Sub-catchments with lower loads show higher deviations with over- and underestimations by the model results. The identical appearance of the base variant on the right side of Figure 6-6 compared with the optimized model adaptation underlines that the median concentration values from the data sets are sufficient for a good model fit. The large vertical bars express the large range of model results in the maximum and minimum variant.

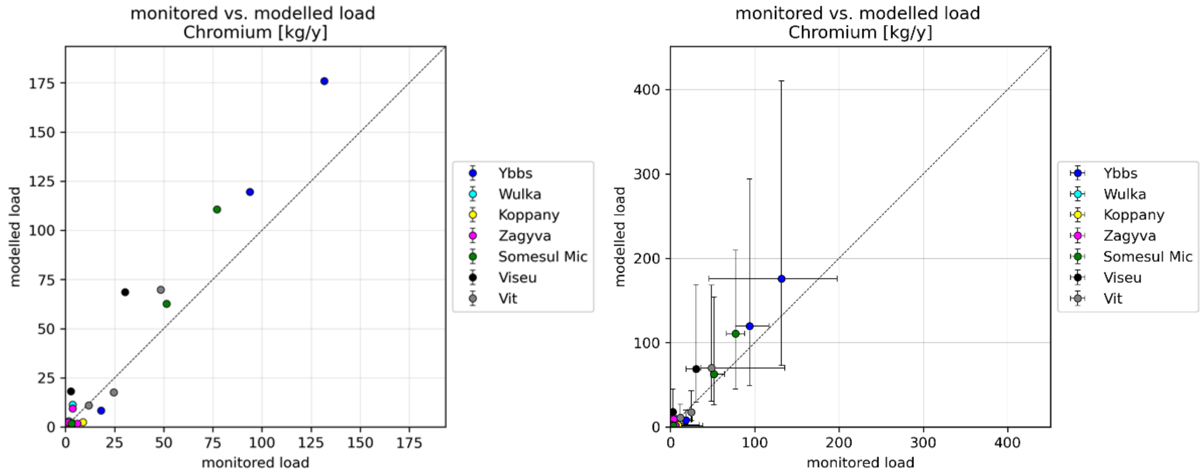

Figure 6-6: Modelled and monitored Chromium load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 20 monitoring sites.

6.2.4 Dissolved Mercury

Mercury loads calculated from monitoring results in the pilot regions range from 0.001 kg/y in Wulka (tributary Nodbach) to 1.4 kg/y at the outlet of the Ybbs pilot region. Calculated loads from monitoring < 0.1 kg/y show high deviations with an overestimation by the model approach. Higher loads are reproduced much better. A significant underestimation of the Ybbs outlet may be caused by the integration of a serious flood event (HQ5) in the load calculation, which cannot be mapped by the model approach.

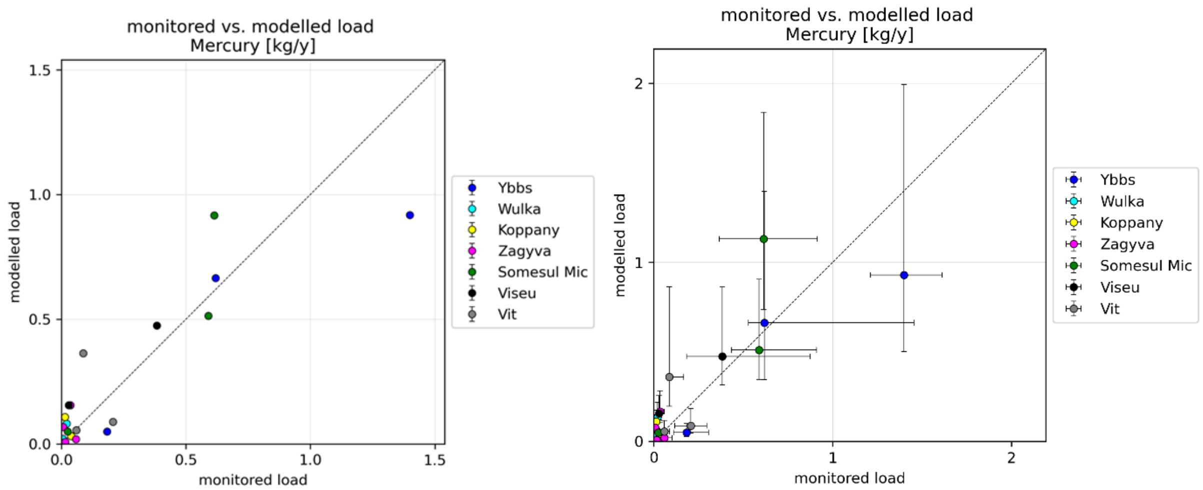

Figure 6-7: Modelled and monitored Mercury load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 20 monitoring sites.

6.2.5 Dissolved Nickel

Nickel loads calculated from monitoring results in the pilot regions range from 2.3 kg/y in Wulka (tributary Nodbach) to 551 kg/y at the outlet of the Somesul Mic pilot region. Model results show a large variance compared to the calculated loads from monitoring with a serious underestimation at loads smaller than 100 kg/y. This leads to a weak model performance.

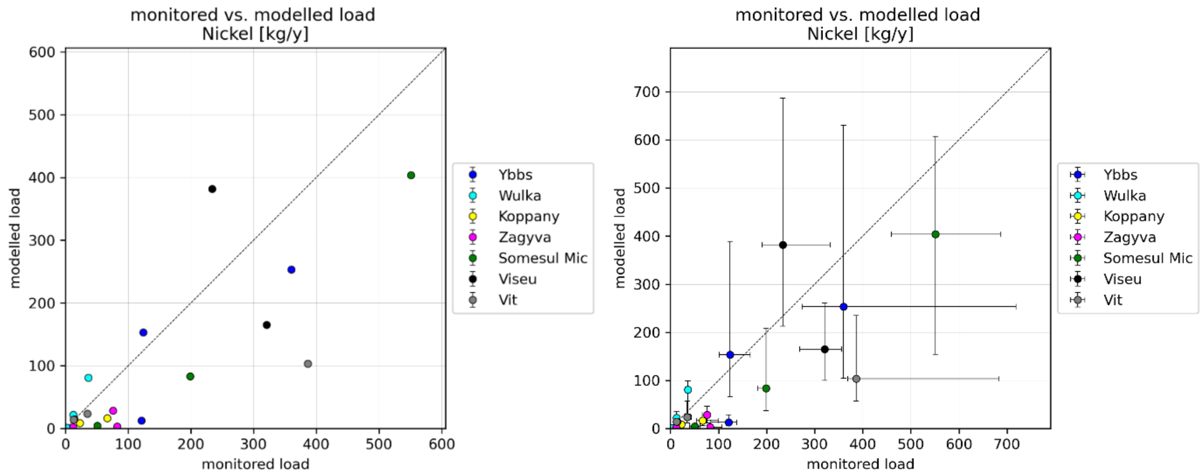

Figure 6-8: Modelled and monitored Nickel load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 20 monitoring sites.

The base variant on the right side of the figure is exactly the same as the optimized variant. In this case, further optimizations did not lead to a significant improvement of the model performance.

6.2.6 Dissolved Zinc

Zinc loads calculated from monitoring results in the pilot regions range from 5 kg/y in Wulka (tributary Nodbach) to 7383 kg/y at the outlet of the Vit pilot region. The extremely high Zinc loads at the outlet of the Vit pilot region are significantly underestimated by the model. Loads from the Viseu pilot (not shown) are extraordinarily high and are calculated with 117,606 kg/y at Tisla tributary (32003), influenced by abandoned mining and 34,489 kg/y at the outlet 32001. Modelled loads significantly overestimate the monitored loads by factor 2. In total the model fit is not sufficient.

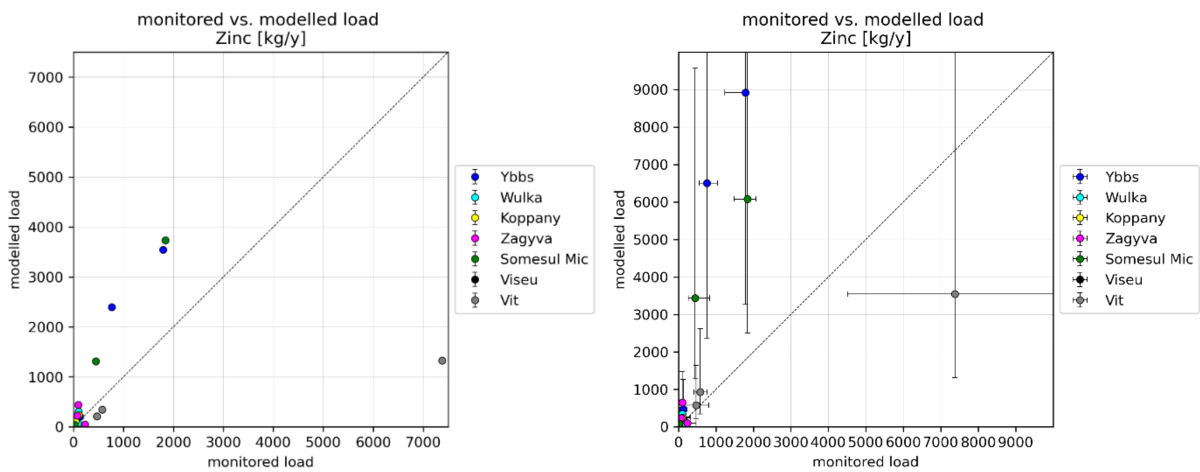

Figure 6-9: Modelled and monitored Zinc load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 18 monitoring sites (Viseu excluded).

The clear differences between optimized variant and base variant at the right side of Figure 6-9 illustrates the improvements that could be achieved through optimization.

6.2.7 Abandoned mining influence of Heavy metals

In the Viseu pilot region the tributary Tisla (32003) is affected by abandoned mining. The calculated loads and concentration significantly influence the downstream sub-catchment and outlet 32001. The substances Copper, Cadmium and Zinc are particularly affected. Because loads for Cadmium and Zinc in all other monitored sub-catchment were much lower, we refrained from displaying the results in the scatter plots above.
To reproduce the magnitude of loads monitored by the modelling approach for this sub-catchment, a specific data set was established, which represents the extraordinarily high concentrations in different technical (e.g. WWTP) and natural compartments (e.g. groundwater concentrations) influenced by abandoned mining (Abandoned mining).
A comparison of the calculated in-stream loads and the modelled loads of the most influenced substances is presented in Figure 6-10.
For Copper the annual loads in tributary Tisla and at the outlet of Viseu are underestimated by the model approach and the researched data set, but can be sufficiently reproduced. In case of Cadmium and Zinc a significant underestimation of the load in the tributary Tisla occur (Cadmium by factor 4 and Zinc by factor 6), while the outlet catchment of Viseu is slightly overestimated.
The extraordinarily high values of Cadmium and Zinc in Tisla River exceed the possible adjustments to the model by the new data set for abandoned mines. Unfortunately, the fluxes of the direct discharges from well-known and monitored abandoned mining effluents could only be estimated. Valid discharge measurements were impossible because of the inaccessibility of the sites in most parts of the year. The estimation of the discharge (from photos during summer time) were conservative and loads from mining effluent might be much higher. Furthermore, it is likely that several other diffuse (maybe temporary) discharges in this sub-catchment occur and will lead to a further impact, not represented by the model and only partially compensated by the assumption of high groundwater concentrations.
The satisfying reproduction of Cadmium and Zinc loads at the outlet of Viseu (32001) is partly realized by high groundwater emission from the upstream sub-catchment 32002, which has a similar geology as 32003. On the other hand, the large decrease of measured Cadmium and Zinc loads from the upstream to the downstream catchment points out significant retention processes, like biochemical precipitation, a process that might be relevant in environments influenced by abandoned mining but not yet implemented in the MoRE model.

Figure 6-10: Modelled and monitored Copper, Cadmium and Zinc loads [kg/y] in the pilot region Viseu.

6.3 Substance group Pharmaceuticals

6.3.1 Diclofenac and Carbamazepine

Loads of Diclofenac are overestimated in general but show a good fit with monitored loads. Obviously, for Zagyva (22002, HZN) monitored loads are extraordinarily high and show significant deviations compared to modelled loads. Less than 0.5 kg/y are calculated from WWTP effluent and only 0.1 kg/y from the other possible pathways (combined sewer systems, storm sewers and groundwater). It is possible that other sources are not yet implemented in the model, or are significantly underestimated.
Another possible explanation is a significant overestimation of the monitored loads. This assumption is supported by the Diclofenac load calculated at the outlet of the pilot (22001, HZ6), which is significantly lower as these from the tributary (22002, HZN), which should be a share of the outlet loads.

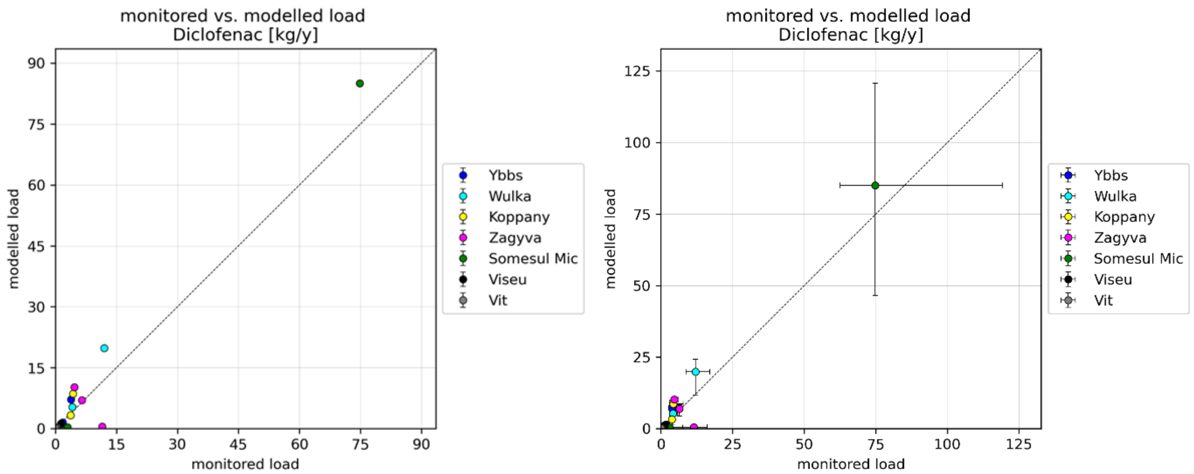

Figure 6-11: Modelled and monitored Diclofenac load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 20 monitoring sites.

For Pharmaceuticals, the substance specific data base is weaker than for heavy metals or PFAS. Often a specific adaptation is not possible. This is reflected in the same data points for the optimized and the base variant.

Model validation of Carbamazepine shows a medium model fit, with a tendency of underestimating the monitored loads. Significant deviations are found in the Zagyva pilot region (22002, HZN and 22001, HZ6). Again, a significant underestimation of the monitored loads occurs using the model approach in tributary 22002, which might have the same reason as stated for Diclofenac. Nevertheless, the model significantly underestimated the monitored load at the pilot outlet in Zagyva (factor > 2).
For Carbamazepine the optimized model version is equal to the base version. The reason for this is explained above.

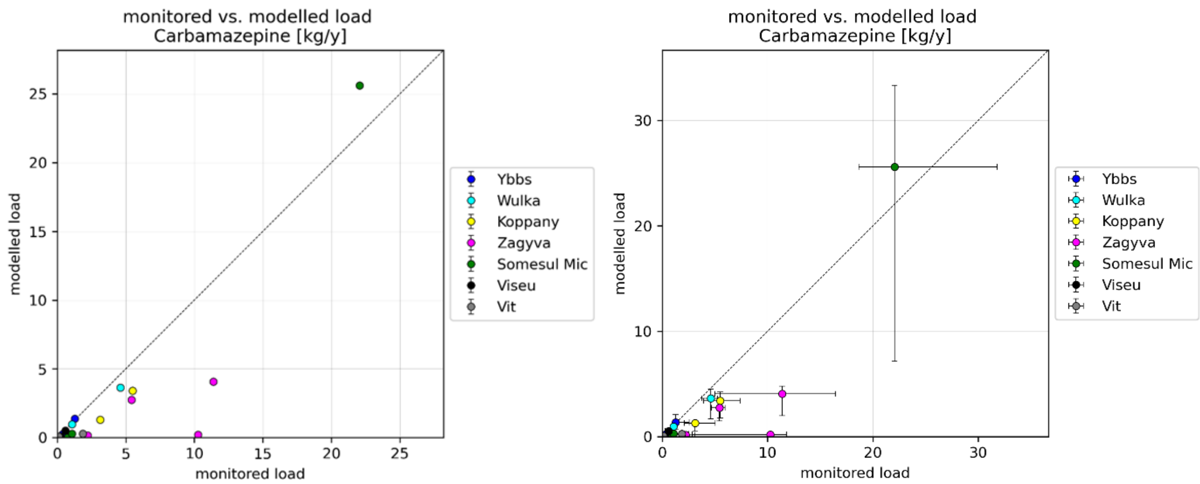

Figure 6-12: Modelled and monitored Carbamazepine load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 20 monitoring sites.

6.4 Substance group Pesticides

An approach to model pesticides with MoRe was established for the first time (see chapter Pesticides) In this model application two new substance groups were implemented: fungicides and herbizides. For both substances the standard model approach, was chosen. Due to the monitoring and the establishment of the database in the sope of the project, the data availability was sufficient to model all relevant pathways for pesticides. A second approach was set up and tested. This ons is based on culture specific applicatopn rates and empiric transfer functions. A detailed description is given in. O.T2.1 Appendix II.

Pesticides represent a substance group, which are characterized by dynamic concentration values with a high temporal resolution. Time and place of application, type of application and weather conditions during and after application significantly determine the input of these substances, leading to significant loads and concentration over short periods.

It was questionable, whether or to which extent such a substance behavior can be captured by the adapted stratified monitoring and whether this can be represented by a model application with MoRE.

Two different approached were established. The first one represents a typical MoRE approach, with all potential pathways parametrized by subctance-specifiy concentrations (which com almost exclusively from the Danube Harazrd m3c monitoring campaign, see Pesticides) In this model application two new substance groups were implemented: fungicides and herbizides. For both substances the standard model approach, was chosen. Due to the monitoring and the establishment of the database in the scope of the project, the data availability was sufficient to model all the relevant pathways for pesticides.

A second approach was setup and tested. This one is based on culture specific application rates and empiric transfer functions. A detailed description is given in O.T2.1, Appendix II.

The second one was established for Metolachlor and its metabolites based on annual culture-specific application rates from agricultural statistics and transfer functions, derived from an Austrian special measurement program for Pesticides. This simple approach, which was established when the quality of monitoring results were widely unknown, is applied to calculate concentrations and gives no information on pathways.

6.4.1 Metolachlor

The specific MoRE model approach falls back on a (up to now) limited number of substance specific input data. This leads to a twofold underestimation compared to the loads from the monitoring in general (Figure 6-13). Significantly higher deviations are found for the Vit outlet and especially at the outlet of Koppany. The latter one shows the highest concentrations of Metolachlor of all pilots (during twelve high flow events the concentration shows mean values of 17 µg/l), which leads to the highest annual loads of more than 8 kg/y. In this case, the significant underestimation of the model underlines the lack of substance-specific input data. Obviously, specific pathways relevant in Koppany, like surface runoff, or groundwater are completely underestimated in this first model version. In the Vit pilot region only in the outlet sub-catchment (41001), characterized by high shares of arable land, Metolachlor concentration above the LOD were analyzed (five from nine). Concentrations range from 0.1µg/l (LOD) to 1.0 µg/l and lead to high loads because of high discharges. This effect also produces the high loads at the Ybbs outlet. Here only one out of eight measurements in surface water was above LOD, which leads to a load of more than 6 kg/y because of high discharges.

The first results of Metolachlor modelling with MoRE stresses two aspects:

- On one hand, high uncertainties determine the load calculation from monitoring and the modelling approach, that up to now shows a serious lack of data for relevant pathways,
- On the other hand, the model approach seems to be a proper base for further investigation.

The discrepancy of the optimized and the base variant underlines that a first adaptation based on the results from the database was possible. Obviously, more substance specific input data are needed to achieve a more sufficient model adaptation.

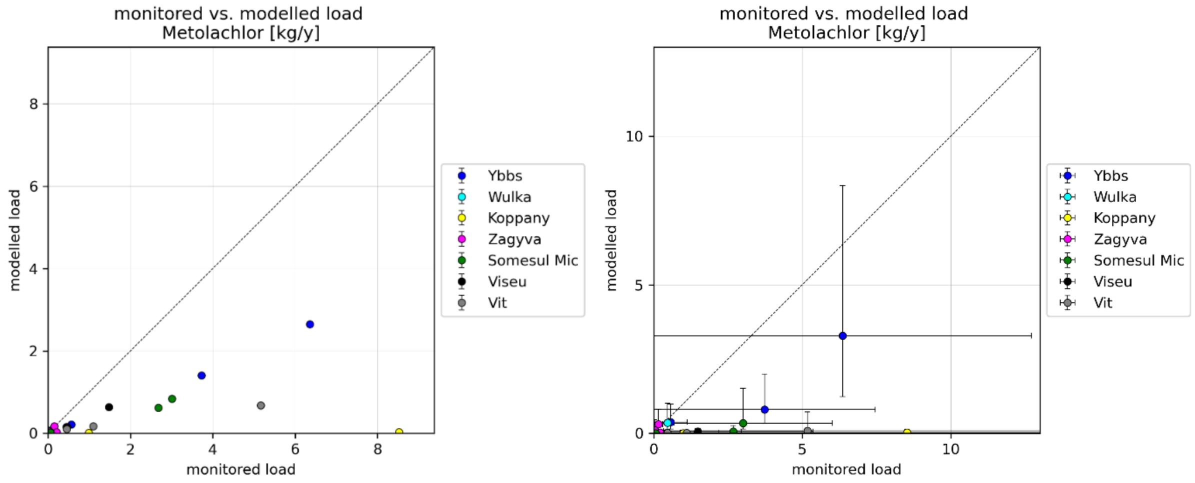

Figure 6-13: Modelled and monitored Metolachlor load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 20 monitoring sites.

For the metabolite Metolachlor-OA similar results could be achieved. Here in general a tendency of underestimation by the model results was found, while single sub-catchments in Ybbs, Koppany and Vit pilot were significantly underestimated.

For Metolachlor-ESA (another metabolite of Metolachlor) loads calculated from monitoring could not be reproduced by the model approach.

6.4.2 Approach from culture specific application rates

The second approach evaluated in the Danube Hazard m3c model based on the calculation of potential application rates of Metolachlor was applied only to the Austrian and the Hungarian pilot regions. In other catchments a crop specific evaluation of potential application rates was not possible on base of sub-catchments. The approach leads to an overestimation of the mean annual concentration calculated from monitoring results.

Exemplarily the model approach for metabolite Metolachlor - ESA is presented, which leads to a slight overestimation but also several sub-catchments with increased model results, where no or only very few concentrations above LOD were measured (Figure 6-14).

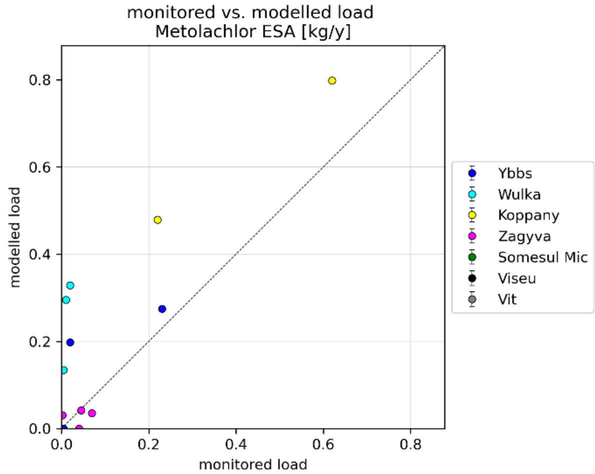

Figure 6-14: Modelled and monitored Metolachlor-ESA concentration [µg/l] - validation based on 12 monitoring sites in Austria and Hungary.

6.4.3 Tebuconazole

Tebuconazole was analyzed in concentrations above LOD mainly in Wulka and Koppany pilots. In other pilot regions only single concentrations above LOD were measured. The calculated loads range from 0.01 kg/y in the Wulka tributary Nodbach (12003) to 6.4 kg/y at the outlet of the Ybbs pilot. The modelled loads show a good fit with the calculated loads from monitoring, which underlie large uncertainties, with a majority of measurements range below the LOD. Nevertheless, the model approach seems to represent a base for further investigations.

The discrepancy of the optimized and the base variant (right side) underlines that a first adaptation based on the results from the database was possible and leads to rather sufficient first results.

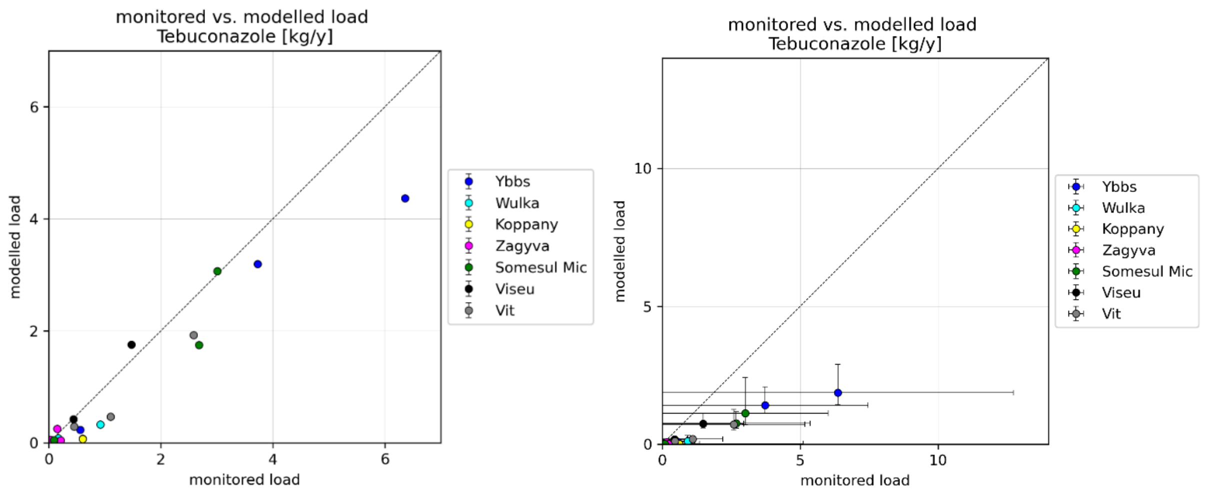

Figure 6-15: Modelled and monitored Tebuconazole load [kg/y] (optimal variant, left; base- minimum and maximum variant, right) - validation based on 20 monitoring sites.

6.5 Conclusions of model validations

Sixteen substances from four different substance groups (PFAS (industrial chemicals)), Heavy Metals, Pharmaceuticals and Pesticides) were modelled in seven pilot regions. Results from 20 monitoring stations (annual mean load and concentration for 2021) well distributed over the pilot regions were made available from the stratified monitoring approach (O.T.1.2). Arsenic and Chrome and Carbamazepine model approaches were implemented in the model, while the substance group of Pesticides was also implemented and tested for the first time. Substances, which represent the substance group of Pesticides, are Metolachlor and the metabolites Metolachlor-ESA and Metolachlor-OA and Terbuconazole.

For a multitude of substances, a good model fit could be achieved on base of annual loads. An optimized model version, using the opportunities of differentiated queries from the new inventory (O.T.1.1) shows the best accordance. An additional model evaluation underlining the uncertainties of input data and the model approach was established. This is based on the implementation of model variants using median concentration for the base version and 25 and 75 percentile for a best case and a worst case evaluation.

Not only the modelling underlies uncertainties but measurements and calculation of mean annual loads and concentrations, too. Consequently, even these uncertainties are considered in the comparison of modelling and monitoring results (using median loads, 25 and 75 percentiles).

Due to input data quality and availability and the state of the model approach (e.g. the newly implemented Pesticides) the model fit shows a wide range (Figure 6-1). Often only one or two sub-catchments out of 20 show significant discrepancies with the monitored results. The reasons for this can be manifold and range from specific conditions with insufficient coverage by the input data (e.g. abandoned mining), problems in the load and concentration calculations due to high proportions of measurements below the LOQ, or inadequate model approaches.

In total, a satisfactory model performance for most substances could be achieved.

Table 6-1: Nash Sutcliffe model efficiency coefficient for 16 modelled substances. At an estimation error variance equal to zero, the resulting Nash–Sutcliffe Efficiency equals 1 (NSE = 1). A model with an estimation error variance equal to the variance of the observed time series results in a Nash–Sutcliffe Efficiency of 0.0 (NSE = 0).

Nr.	Substance group	Substance	Optimal NSC
1	Pharmaceuticals	DCF	0.93
2	Pharmaceuticals	CAR	0.68

3	PFAS (industrial chemicals)	PFOS	0.71
4	PFAS (industrial chemicals)	PFOA	1.00
5	Heavy Metals	Cr	0.77
6	Heavy Metals	Ni	0.60
7	Heavy Metals	Cu	0.92
8	Heavy Metals	Zn	0.39
9	Heavy Metals	Ar	0.37
10	Heavy Metals	Cd	0.45/ 0.96*
11	Heavy Metals	Pb	-3.54
12	Heavy Metals	Hg	0.79
13	Pesticides	Met	0.18
14	Pesticides	Met-ESA	0.06
15	Pesticides	Met-OA	0.05
16	Pesticides	TCZ	0.87

*not including Viseu

7. Risk analyses

7.1 Limitations of model use in risk analysis

Supporting a risk analysis with model results is a useful complement to an assessment based solely on monitoring data. By using the model, statements can be made in catchments where no current monitoring is carried out. Thus, the increase in knowledge can be enormous, although the results naturally require conscientious interpretation and analysis.
However, the use of models as a complementary tool for risk analysis places also significantly higher demands on model performance, robustness of approaches, and accuracy in reproducing mean concentrations. This is complicated by sometimes extremely low EQS, as frequent and larger deviations in the nanogram range must be reduced as much as possible. The evaluation of PFOS is a striking example in this respect. Although a good fit of the model results could be achieved, a higher number of deviating modelling results occur in the EQS range (0.00065 µg/l), which increases uncertainties of information.
Figure 7-1 shows model results on y-axis and monitoring on x-axis, with an overestimation and an underestimation that would lead to an incorrect designation of the risk in two cases. The other 12 monitoring sites (although not reproduced exactly) with respect to a risk assessment would reflect the correct results.

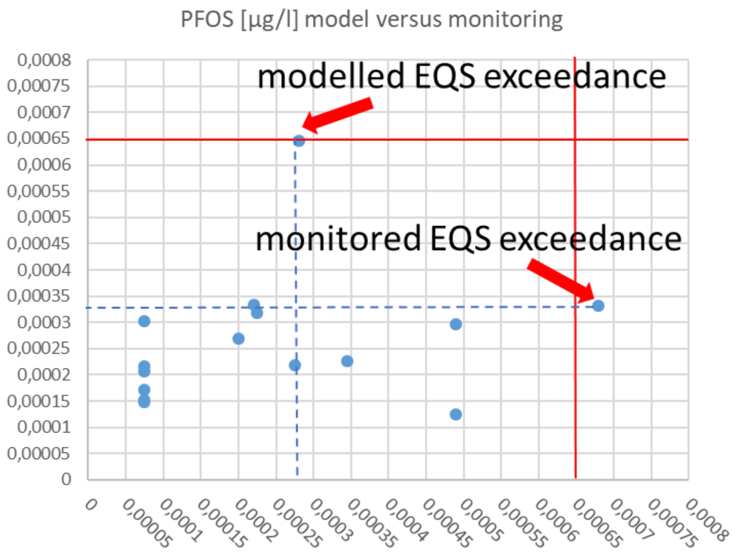

Figure 7-1: Modelled and monitored PFOS concentration [µg/l] in the range of the EQS of 0,00065µg/l.

Knowing the limitations of a model-based risk assessment and taking them into account makes modelling a valuable additional instrument supporting an assessment, which is based on monitoring results.

7.2 Procedure of risk analyses in Danube Hazard m3c

In the project, a sound stratified monitoring strategy was applied, combining analyses at low or medium water levels and event-related sampling at high water levels. Based on this database, an evaluation of the risk was possible for 20 monitoring sites in seven pilot regions (O.T.1.2).
A national hazardous substances monitoring is often done by taking 6-12 grab samples per year in equidistant time steps without consideration of the flow situation. Due to the more frequent occurrence of low- to mid-flow conditions, the chance that the low frequency grab samples are received during such situations is very high (O.T1.2). To reproduce this procedure as best as possible the mean concentration of the base flow samples is used (six

composite samples integrating weekly sampling over one year). Data below LOD are considered as LOD/2.
An exception to this approach was made for Pesticides. In accordance with their process behavior and limited application periods, Pesticides naturally show a significant dynamic with increased occurrence when application and rain or storm event occur simultaneously or shortly after each other. Although provoking an overestimation, when taking all monitoring data including specific event sampling into account, we believe that using only composite samples would lead to a underestimation, either, because event-driven concentration peaks will be masked by preparing two monthly composite samples based on eight-weekly grab samples.
Figure 7-2 underlines the effect of significant flushes from the catchment with increased impacts of surface runoff, erosion and subsurface flow on Pesticide concentration in surface waters.

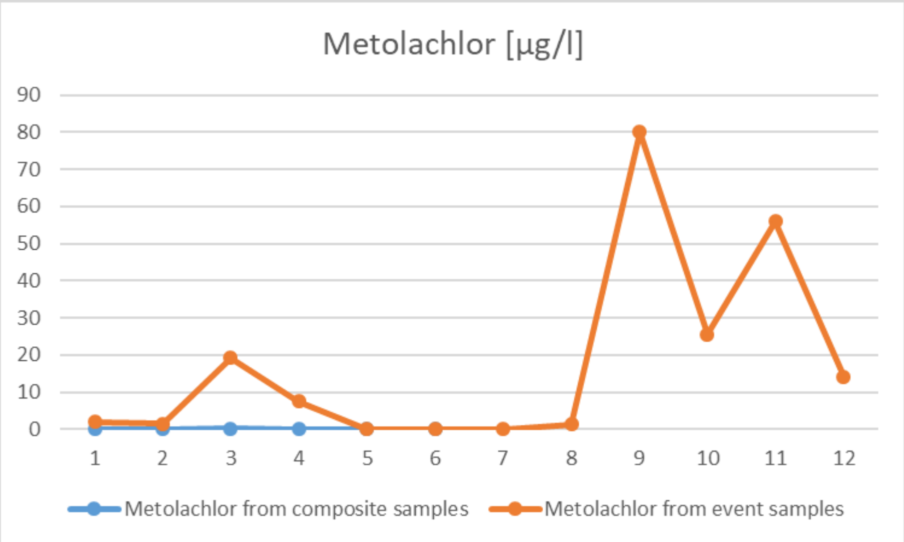

Figure 7-2: Monitored Metolachlor concentration [µg/l] in composite samples and event driven sampling.

For the risk analysis supported by the modelling approach, the emission were summed over the different input pathways at the area outlet of all sub-catchments and mean annual concentrations were calculated. These calculated mean water body concentrations were compared with the environmental quality standards (EQS) and a risk quotient (RQ) was determined.
The procedure is only exemplarily provided for substances preselected from the monitoring results (O.T.1.2). Substances of interest were PFOS, Cadmium, Copper, Zinc and Metolachlor (regulated in the National Substance List of Hungary).
The EQS of metals are related to dissolved concentrations, which were also addressed in the model validation (6 Model validation). The environmental quality standard of the metals Cadmium regulated in (Directive 2013/39/EU), Copper and Zinc (both regulated in the National Substance Lists) depend on the hardness and are available in different classes.
Additionally, some chemicals proposed for inclusion in the revised Priority Substances List are included in this first assessment. These are PFOA, Diclofenac and Bisphenol A, whereby for the latter only monitoring results are available.

7.3 Risk assessment from monitoring and modelling results

In a first step, the evaluation of the risk from monitoring results is presented for 20 sub-catchments. Table 7-1 gives an overview of the risk analyses prepared on the base of the monitoring results.

Table 7-1: Result of risk assessment considering all monitored substances and outlook to possible further risk in future (proposed new substances and proposed EQS).

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]	RC - Factor
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	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	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

Assessing the substances under investigation and with regulations already in place, PFOS is the substance that exceeds the EQS in the monitored sub-catchment most often and in all four countries, where pilot regions were established (Table 7-1). The exceedance is not restricted to pilot regions like Wulka, Zagyva or the outlet of Somesul Mic with the large WWTP of Cluj Napoca, but also monitored in largely natural pilot regions with a rather low anthropogenic use, like Ybbs and Vit. In the latter ones, the RQ is close to one, which underlines the only slight exceedance of the EQS. In the Wulka pilot, the most significant exceedances were found with RQs between 5.4 and 6.2.
The exceedance of Heavy metals (Copper, Cadmium and Zinc) is clearly associated with the Viseu pilot region, were the influence of abandoned mining was evaluated. Here, the mean dissolved concentrations in the tributary Tisla (32003) were significantly above the predicted EQS and also lead to exceedance in the downstream catchment (32001).
For Pesticides, remarkable concentrations of Metolachlor were evaluated during event flow in the Koppany pilot region (both sub-catchments: 21002 and 21001). The Koppany pilot region was originally selected as an example for intensive agricultural use.
For substances not yet regulated, several potential exceedances of the proposed EQS were monitored. Bisphenol A with a proposed EQS of 0.00034 µg/l would have been overshot at all monitored stations, whether in the unaffected headwater, or in the more heavily impacted downstream areas. In some cases, this is caused by the low EQS, which is many times lower than the LOD. Thus according to the existing calculation conventions of mean annual concentrations per se a mean value > EQS is calculated, even if no measured value is available.
Proposed Diclofenac EQS (0.04 µg/l) would have been overshot in all monitoring stations characterized by an increased anthropogenic use (Wulka, Koppany, Zagyva and also the downstream area of Somesul Mic).
PFOA, with an proposed EQS of 0.0044 µg/l would lead to an exceedance by the monitoring results only in one sub-catchment of the Wulka pilot region (12002).
Table 7-2 gives an overview of the investigated, regulated substances, which exceed the EQS, the number of exceedances, pilot regions and countries, as well as the regulation in force.

Table 7-2: Result of risk assessment considering all monitored substances, number of exceedance, number of pilot region and regulation in force.

Substance > EQS	Substance Group	No of monitoring sites	No of pilot regions	No of countries	Regulation
PFOS	Industry	9	5	4	Directive 2008/105/EU
Cu	Heavy Metals	2	1	1	National Substance List
Cd	Heavy Metals	2	1	1	Directive 2008/105/EU
Zn	Heavy Metals	2	1	1	National Substance List
s-Metolachlor	Pesticides	2	1	1	National Substance List

As was explained in 6.2, information from monitoring was extended to all 34 sub-catchments through the modeling results.
Of course, the ratio of modelled and monitored data from the project rarely corresponds to real-world conditions. In countries or water districts, the proportion of monitored values is often significantly lower than that derived solely from modeling, which makes this additional information more valuable. In a recent modeling exercise in Austria, for example, the ratio of modeled to measured catchments was about 7:1.
In the model approach, only four out of nine sub-catchments monitored with exceedance of PFOS could be reproduced. To express the sensitivity of the model approach, these were all sub-catchments with an RC-factor > 2 (Wulka and Zagyva). The other, often only slight exceedances of PFOS EQS (e.g. in the Ybbs pilot, the Vit and the outlet of Somesul Mic) were underestimated by the model. Additionally, the model calculates exceedances in sub-catchments not monitored in the Wulka pilot (12004 and 12005) and in Zagyva pilot (22003),

which seems to be realistic. The upstream sub-catchment in Koppany was overestimated by the model approach (Table 7-3).
For Cadmium, Copper and Zinc also a good reproduction of the monitored EQS exceedances in Viseu can be stated. For Copper the outlet of Viseu is calculated slightly below the Romanian EQS.
One monitored value in the Wulka pilot, which slightly exceeded the proposed PFOA EQS is exactly reproduced by the model approach.
The comparison of monitored and modelled exceedances of Diclofenac provides a good accordance. Only two sub-catchments in Somesul Mic were underestimated. One additional and not monitored sub-catchment in Zagyva pilot was recorded.

Table 7-3: Modelled versus monitored exceedances of EQS for different substances.

Pilot region	ID	Monitored	PFOS [µg/l]	Cadmium [µg/l]	Copper [µg/l]	Zinc [µg/l]	PFOA [µg/l]	Diclofenac [µg/l]
Ybbs	11001	x	0,00030	0,00878	1,40862	3,93866	0,00043	0,00789
Ybbs	11002	x	0,00036	0,00687	1,38713	3,91210	0,00066	0,00163
Ybbs	11003		0,00022	0,00919	1,33066	3,76291	0,00036	0,00227
Ybbs	11004		0,00026	0,00869	1,36802	3,90664	0,00038	0,00556
Ybbs	11005	x	0,00021	0,00946	1,34103	3,78221	0,00034	0,00183
Ybbs	11006		0,00021	0,00954	1,34795	3,80102	0,00034	0,00174
Ybbs	11007		0,00021	0,00959	1,35616	3,81394	0,00034	0,00237
Ybbs	11008		0,00021	0,00973	1,37404	3,89574	0,00035	0,00038
Wulka	12001	x	0,00287	0,01694	6,43965	11,09479	0,00290	0,64215
Wulka	12002	x	0,00471	0,02671	10,55986	17,72634	0,00442	1,11026
Wulka	12003	x	0,00138	0,00749	4,05408	10,48725	0,00273	0,06641
Wulka	12004		0,00089	0,00535	2,69460	6,93355	0,00173	0,03856
Wulka	12005		0,00090	0,00591	2,72153	7,11308	0,00178	0,03824
Koppany	21001	x	0,00022	0,00453	1,12360	4,99029	0,00029	0,08628
Koppany	21002	x	0,00069	0,01297	4,32283	31,60342	0,00085	0,95467
Zagyva	22001	x	0,00036	0,00537	1,37672	6,55101	0,00054	0,11952
Zagyva	22002	x	0,00030	0,00559	1,18654	4,32665	0,00055	0,04275
Zagyva	22003		0,00077	0,00811	2,89313	17,74660	0,00086	0,43526
Zagyva	22004	x	0,00046	0,00556	1,50048	6,13209	0,00067	0,09166
Zagyva	22005	x	0,00159	0,01732	6,24658	44,48322	0,00163	1,19177
Somesul Mic	31001	x	0,00019	0,00734	1,21095	3,30475	0,00034	0,00273
Somesul Mic	31002	x	0,00022	0,00382	1,13186	2,65278	0,00044	0,00064
Somesul Mic	31003	x	0,00018	0,00841	1,25136	3,45082	0,00030	0,00065
Somesul Mic	31004		0,00012	0,00450	0,87850	2,17795	0,00021	0,00021
Somesul Mic	31005		0,00020	0,01059	1,48220	4,05109	0,00033	0,00064
Somesul Mic	31006		0,00019	0,00792	1,24331	3,52022	0,00033	0,00063
Viseu	32001	x	0,00019	0,68015	9,77042	116,40053	0,00031	0,00362
Viseu	32002		0,00019	0,91418	5,31993	116,79648	0,00032	0,00834
Viseu	32003	x	0,00022	1,36768	30,07601	292,78631	0,00031	0,00086
Vit	41001	x	0,00013	0,00564	0,93898	2,57327	0,00022	0,00068
Vit	41002		0,00014	0,00600	0,97876	2,71638	0,00023	0,00078
Vit	41003		0,00014	0,00632	0,99078	2,78283	0,00023	0,00086
Vit	41004	x	0,00015	0,00757	1,12787	3,17943	0,00027	0,00061
Vit	41005	x	0,00018	0,00730	1,11307	3,22522	0,00027	0,00086

xxxx	monitored and modelled
xxxx	monitored and underestimated by model
	not monitored and modelled risk

For Metolachlor, which significantly exceeds the EQS from the National Substance List in Koppany, when taking event flow into account, the model approaches are not yet available in such quality that a risk analysis appears feasible. Further work is needed on the model approach, in particular on the input data. However, the model adaptations are promising, especially for Tebuconazole.

8. Analyses of regional pathways

8.1 PFAS

Highest area specific rates of PFOS are modelled in the Austrian pilot regions Ybbs and Wulka. Increased industrial production and consumption of products containing PFOS in the western region of the Danube Basin, support the values found and are in agreement with the calculations made in O.T.1.2. The values from Somesul Mic were found in the same range (O.T.1.2), but could not be reproduced by the model results (chapter 6.1). As was stated above, there is no clear evidence, that loads from WWTPs in Somesul Mic are underestimated and the missing source or underestimated pathway is not clear yet.
In the Austrian pilots, the pathways leading to increased rates differ significantly. In the Wulka pilot region, there is a clear dominance of emission from WWTPs and combined storm water overflows, which represents the classic picture of PFOS inputs. In the Ybbs pilot, there are high shares of loads from subsurface flow (groundwater baseflow, interflow and drainages) and from surface runoff. This pattern is repeated in Viseu, Vit and up to the downstream area in the Somesul Mic pilot region and represents PFOS emission from natural areas. However, the amount of the rate monitored and modelled in the Ybbs is surprising.
In Koppany and Zagyva the smallest area specific rates are found. For Koppany, with a clear dominance of agriculture, this result is not surprising. For the Zagyva pilot, the loads at the outlet are surprisingly low. In Zagyva upstream sub-catchments, even higher rates were monitored and modelled.

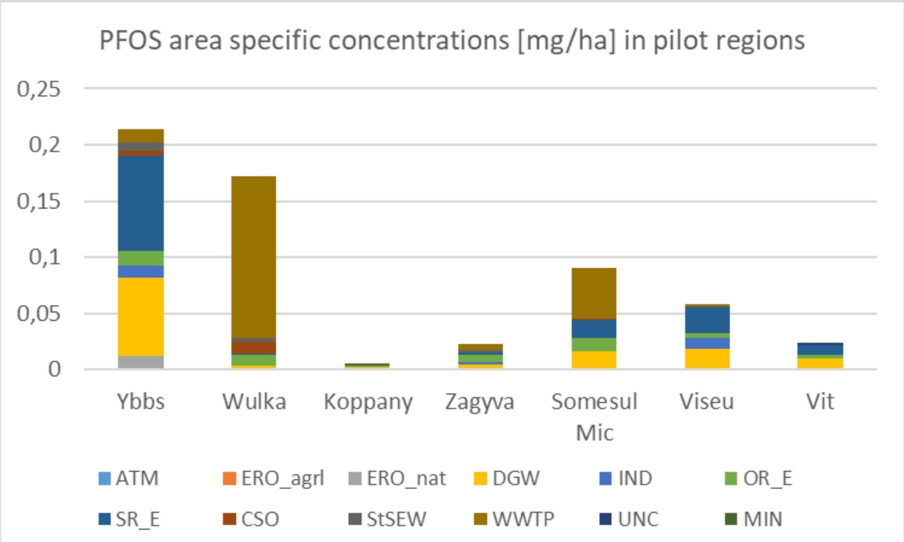

*Figure 8-1: Modelled area specific rates [mg/ha*a^{-1}] at the outlet of the pilot regions and relevance of pathways. (ATM: atmospheric deposition; ERO_agrl: erosion from agricultural land; ERO_nat: erosion from forests; DGW: groundwater baseflow+interflow+drainages; IND: industrial point sources; OR_E: extra-urban roads; SR_E: surface runoff; CSO: combined stormwater overflow; StSEW: strom sewer; WWTP: municipal WWTP; UNC: sewer systems not connected to WWTP; MIN: abandoned mining).*

For PFOA very similar results are modelled. In contrast to the PFOS modeling, the loads for the pilot region Somesul Mic are also well represented here.

8.1.1 Specific pathways

The relative share of pathways in percent for all pilot regions clarifies the statements from above (Figure 8-2). In Koppany and Zagyva, due to low total loads, the share of extra urban roads is very high. In addition, the influence of atmospheric deposition caused by a high share of open surface water areas (See chapter 4.2.3) in Koppany. In Somesul Mic, the share of

WWTPs, clearly dominated by the large WWTP of Cluj Napoca together with a minor influence from combined sewer overflow (representing the influence of the settlement area of Cluj Napoca for PFOS emission), accounts for almost 70%. In the Viseu and in the Ybbs pilot region, also a considerable share of emission stem from industrial WWTPs. In Wulka the share of groundwater is very low, which is a consequence of the water balance (Chapter 2.2.5.1).

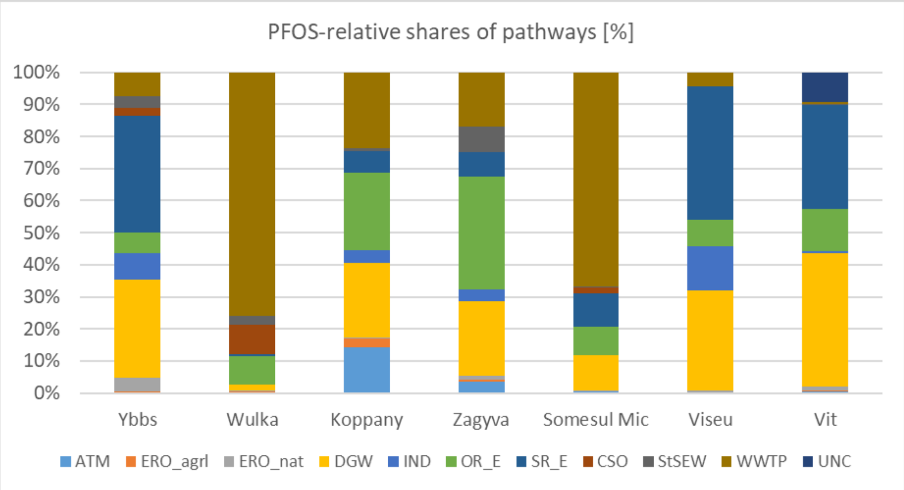

Figure 8-2: Shares [%] of modelled pathways at the outlet of the pilot regions. (ATM: atmospheric deposition; ERO_agrl: erosion from agricultural land; ERO_nat: erosion from forests; DGW: groundwater baseflow+interflow+drainages; IND: industrial point sources; OR_E: extra-urban roads; SR_E: surface runoff; CSO: combined stormwater overflow; StSEW: strom sewer; WWTP: municipal WWTP; UNC: sewer systems not connected to WWTP; MIN: abandoned mining).

8.2 Heavy metals

The area specific rates of dissolved Cadmium, Copper and Zinc, which are exemplarily presented for Heavy metals in all pilot regions, are dominated by the Viseu pilot region (up to 30 times higher rates). Consequently, the Viseu pilot region is presented separately (Figure 6-10).

With the exception of Viseu, especially Ybbs, Somesul Mic and Vit, characterized as the most "natural" pilot regions show the highest area specific rates of Cadmium.

In those pilot regions, the relevance of pathways show a similar pattern, with dominant shares of surface runoff and groundwater. In Somesul Mic the large WWTP of Cluj Napoca leads to a remarkable share on the total emission. Wulka, Koppany and Zagyva are dominated by WWTP emission and emission from sewer systems.

The pathways show comparable shares for Copper and Zinc. With the exception of the Wulka pilot, with high area specific loads of Copper (predominantly from WWTP effluents), the highest area specific rates again are found for the more natural pilot regions Ybbs, Somesul Mic and Vit. In general the effluents from WWTPs and from combined stormwater overflows and stormwater sewers show a higher relevance for Copper and Zinc compared to Cadmium. For all three parameters the Hungarian pilot regions Koppany and Zagyva show the lowest rates, distributed about several pathways: mainly WWTPs, surface runoff and extra-urban roads. For Copper even the erosion from agricultural areas has some influence on the total emission.

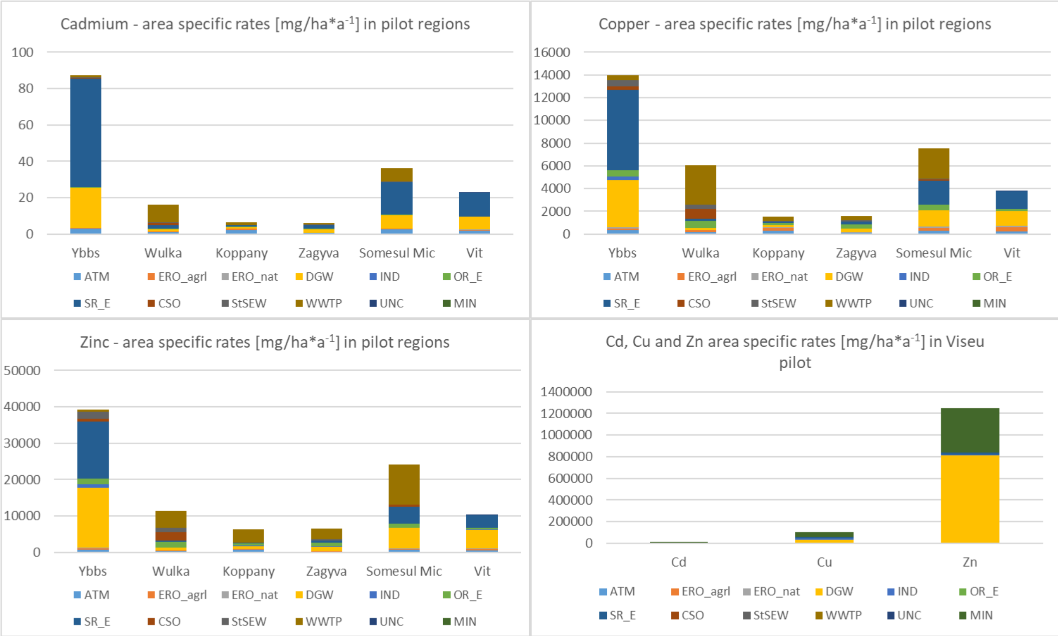

*Figure 8-3: Area specific rates [mg/ha*a^{-1}] of modelled pathways at the outlet of the pilot regions for Cadmium, Copper and Zinc (dissolved). (ATM: atmospheric deposition; ERO_agrl: erosion from agricultural land; ERO_nat: erosion from forests; DGW: groundwater baseflow+interflow+drainages; IND: industrial point sources; OR_E: extra-urban roads; SR_E: surface runoff; CSO: combined stormwater overflow; StSEW: strom sewer; WWTP: municipal WWTP; UNC: sewer systems not connected to WWTP; MIN: abandoned mining).*

The Viseu pilot region is characterized by significant influences from abandoned mining sites. Inactive mines are situated in Tisla sub-catchment (32003) and directly influences the downstream catchment and outlet of the Vit pilot (32001). The area specific rates of Cadmium, Copper and Zinc exceed the maximum values of the other pilots by factor 100, 10 and 30, illustrating the extreme strain of this pilot region.
The dominant share of the extreme high emission stem from direct discharges of abandoned mining effluents and from groundwater. Copper concentrations in the Vit are dominated by abandoned mining, while Cadmium and Zinc show even higher shares from the subsurface flow paths.

8.2.1 Specific pathways

The share of the modelled pathways on Copper emission in all pilot regions is expressed in Figure 8-4 and support the explanations given in the previous chapter.

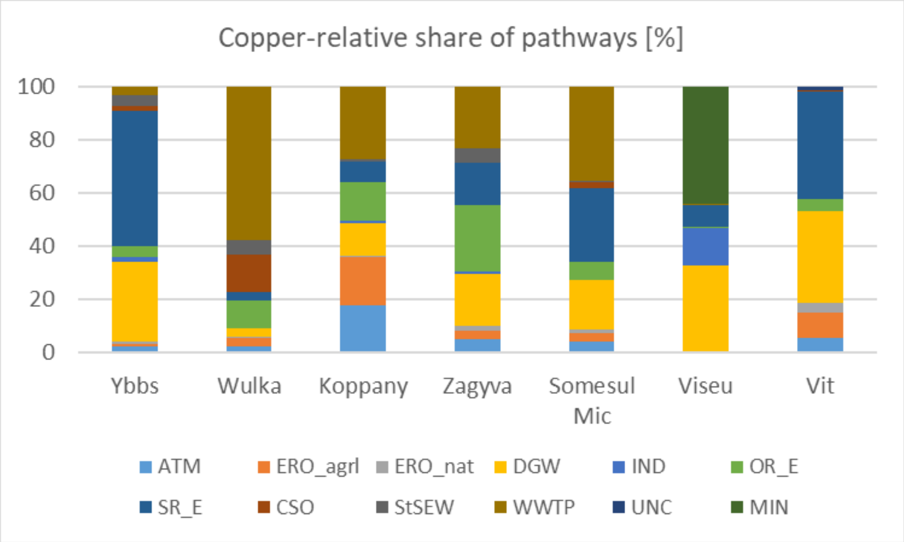

Figure 8-4: Shares [%] of modelled Copper pathways at the outlet of the pilot regions. (ATM: atmospheric deposition; ERO_agrl: erosion from agricultural land; ERO_nat: erosion from forests; DGW: groundwater baseflow+interflow+drainages; IND: industrial point sources; OR_E: extra-urban roads; SR_E: surface runoff; CSO: combined stormwater overflow; StSEW: strom sewer; WWTP: municipal WWTP; UNC: sewer systems not connected to WWTP; MIN: abandoned mining).

8.3 Pharmaceuticals

In Danube Hazard m³c Diclofenac and Carbamazepine represent the large group of Pharmaceuticals. These substances are mainly introduced into the public cycle and the environment through direct ingestion and excretion, or through improper disposal. Consequently, emission pathways to surface waters are WWTP effluents and fluxes from combined storm water overflows or direct emission from sewer systems not connected to WWTPs. Other pathways, which were found to be of some relevance, are emission from the subsurface flow. In the data base low concentrations of pharmaceuticals were documented in groundwater. This may stem from leaking sewer systems, which are most common in older systems, or in poorly maintained systems. The leaking leads to fluxes into the underground and to the groundwater. Consequently, complementing older model approaches for Pharmaceuticals, the groundwater pathway was additionally modelled.

Distribution of area specific rates in the pilot regions and even the share of the specific pathways are comparable for Diclofenac and Carbamazepine, thus Diclofenac is presented exemplarily (Figure 8-5).

Pilot regions with the highest share on urban areas and an increased population density (Wulka and Somesul Mic) show the highest area specific rates of Diclofenac emitted into surface waters. The lower the population density, the lower the area specific rates, with clear minimum in Vit but also in the Viseu pilot region.

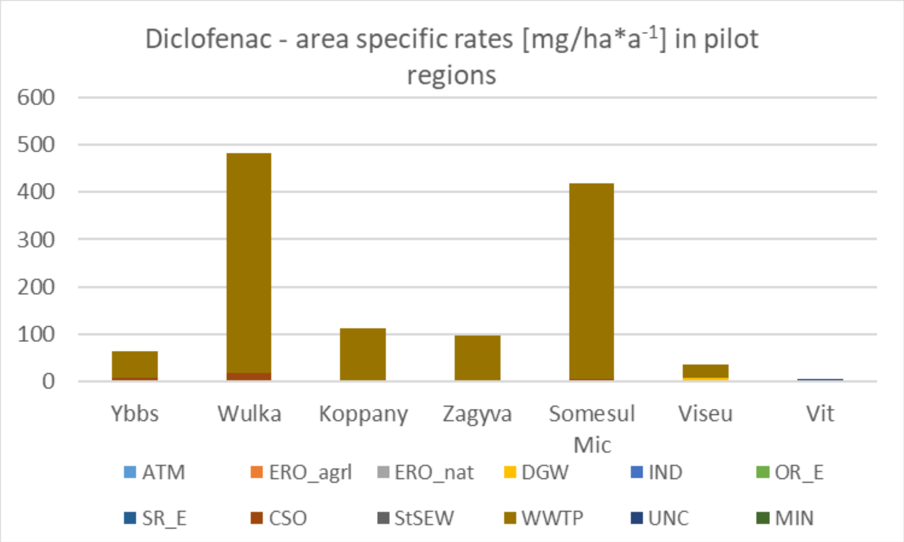

*Figure 8-5: Area specific rates [mg/ha*a^{-1}] of modelled pathways at the outlet of the pilot regions for Diclofenac. (ATM: atmospheric deposition; ERO_agrl: erosion from agricultural land; ERO_nat: erosion from forests; DGW: groundwater baseflow+interflow+drainages; IND: industrial point sources; OR_E: extra-urban roads; SR_E: surface runoff; CSO: combined stormwater overflow; StSEW: strom sewer; WWTP: municipal WWTP; UNC: sewer systems not connected to WWTP; MIN: abandoned mining).*

8.3.1 Specific pathways

The interpretation of the specific pathways, which emit Diclofenac to the surface water depends on additional information from the model validation. To prepare an optimized model fit, the groundwater concentration in Vit and Viseu pilot region had been increased. While for the other pilots the groundwater concentrations were set to 0.00017 µg/l from the overall data base, in Romania and Bulgaria a database (with a huge number of measurements) from Hungary were implemented with 0.00103 µg/l groundwater concentration. Another explanation for the increased proportions from groundwater is the extremely low overall emissions to the water bodies. Thus, even low fluxes lead to high percentages (Figure 8-6).

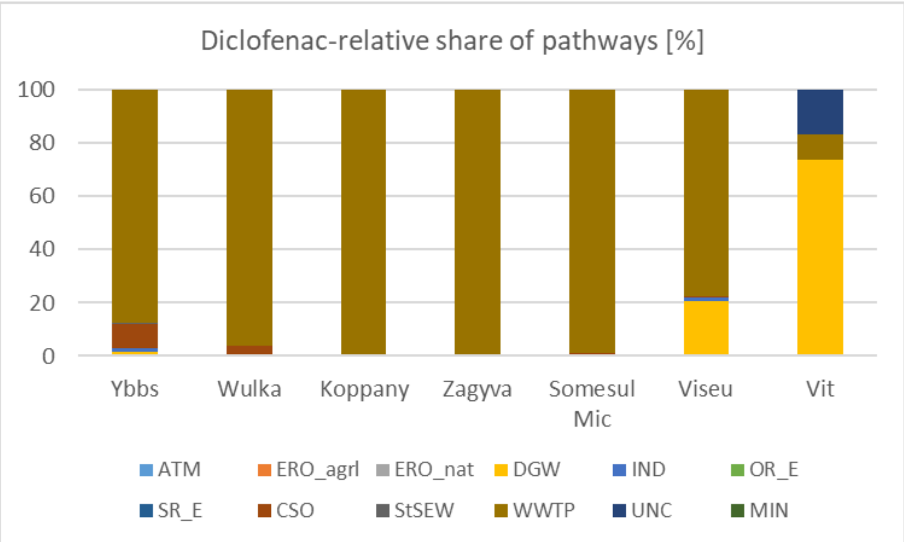

Figure 8-6: Shares [%] of modelled Diclofenac pathways at the outlet of the pilot regions. (ATM: atmospheric deposition; ERO_agrl: erosion from agricultural land; ERO_nat: erosion from forests; DGW: groundwater baseflow+interflow+drainages; IND: industrial point sources; OR_E: extra-urban roads; SR_E: surface runoff; CSO: combined stormwater overflow; StSEW: strom sewer; WWTP: municipal WWTP; UNC: sewer systems not connected to WWTP; MIN: abandoned mining).

8.4 Pesticides

The modelling of Pesticides in Danube Hazard m3c is to be seen as a starting point, which is still far from creating resilient information. Two approaches were investigated, both with current weaknesses.
The first one is based on culture specific application rates (Metolachlor and metabolites) traced by an empirical transfer function to in-stream concentrations. In this approach pathways can only be calculated retrospectively, for example via the proportions of the water balance. The transformation of the approach to Austrian and Hungarian pilot regions led to a significant overestimation of pesticide concentrations.
The second approach represents the "classical" MoRE approach with calculations of different pathways from a modelled water balance multiplied by substance-specific data.
Applying this approach could not reproduce monitoring data in a sufficient way for Metolachlor and its metabolites. An optimization of the model results to some extent was possible, but leads to unrealistic shares of pathways and therefore was canceled at this point. The fact that good and realistic model fits were obtained for Tebuconazole suggests that more data need to be collected to obtain a better model fit. However, at this point it has also to be addressed that Tebuconazole in the surface water monitoring in the pilot regions very often shows values below the LOD.
In Figure 8-7 area specific shares of Tebuconazole are presented.

As was stated above, the high area specific rates in Ybbs and Viseu, Somesul Mic and Vit derive from little varying concentrations due to a very high proportion of measured values < LOQ in all pilots and thus address more the runoff characteristic in the pilot regions. Consequently, to test the sensitivity and robustness of the new approach, more and other catchments are needed in which the varying use of the substance is evidenced by a large number of varying measured values. As long as this is not implemented, an interpretation of the pathways is rather in the realm of speculation, although they appear to be realistic.

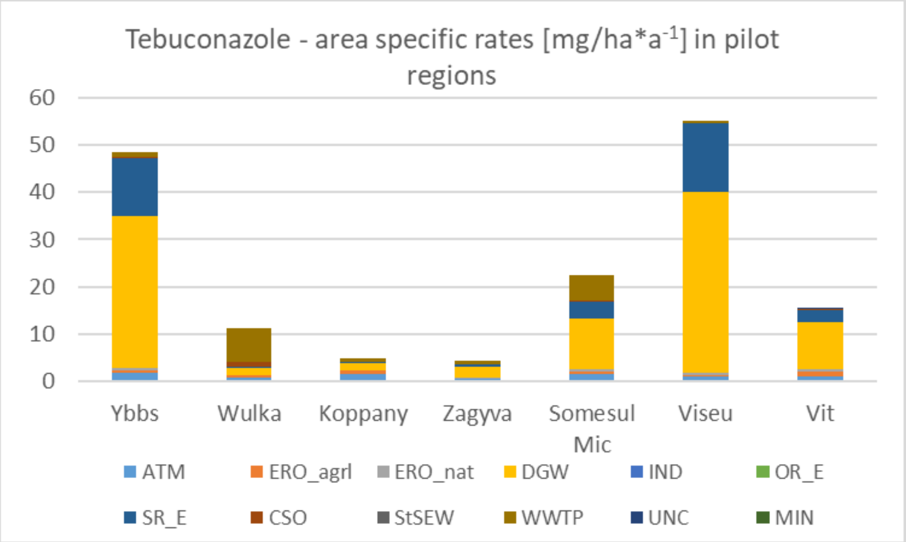

*Figure 8-7: Area specific rates [mg/ha*a^{-1}] of modelled pathways at the outlet of the pilot regions for Tebuconazole. (ATM: atmospheric deposition; ERO_agrl: erosion from agricultural land; ERO_nat: erosion from forests; DGW: groundwater baseflow+interflow+drainages; IND: industrial point sources; OR_E: extra-urban roads; SR_E: surface runoff; CSO: combined stormwater overflow; StSEW: strom sewer; WWTP: municipal WWTP; UNC: sewer systems not connected to WWTP; MIN: abandoned mining).*

9. Mitigation measures

The risk analyses from monitoring and modelling results (chapter 7) and the regional pathway analyses (Chapter 8), with a precise evaluation of sources and input pathways form the backbone for the designation of mitigation measures.
For each pilot region, realistic measures were formulated and a stakeholder participation started (O.T.2.3). The assessment culminates in the formulation of a catalog of measures, the most relevant of which have been quantified through model scenarios.

9.1.1 Specific situation in Wulka pilot region (PFOS)

In the Wulka pilot region the treatment plants under investigation have a capacity of 54,000 PE (12002) and 110,000 PE (12001) and are equipped with nutrient removal (N and P). In both sub-catchments emissions from WWTPs represent the dominant pathway for PFOS 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 current proposals from the revised UWWTD presented for discussion with the member states. Here, a fourth treatment stage on municipal wastewater treatment plants >100,000 PE to be implemented by 2035 is proposed. For municipal WWTPs >10,000 EW – 100,000 PE 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, Amann et al., 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). 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 these 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 PE (2030) as well as possible integrated management plans for municipal Wastewater for settlement areas > 10,000 – 100,000 PE (2035) in case of a risk.

Proposal for potential mitigation measures can be summarized as:

- Advanced wastewater treatment at treatment plant “Wulkatal” (100,000 PE) and “Eisenstadt” (54,000 PE); adsorption stage (activated carbon) for municipal wastewater treatment plants,
- Increased retention capacity of combined sewer overflow and treatment on the plant “Wulkatal”.

9.1.2 Specific situation in the Zagyva pilot region (PFOS)

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 result 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) points 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 (STOBIMO Spurenstoffe, Amann et al., 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).

Proposals for potential mitigation measures can be summarized as:

- Advanced wastewater treatment at the municipal treatment plant in sub-catchment 22005 > 10,000 PE; 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 PE (2040) in case of a risk.

9.1.3 Specific situation in the Ybbs pilot region (PFOS)

The catchment outlet of Ybbs (ID 11001) show slight exceedances of the PFOS EQS (factor 1,1).
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 PE), industrial direct dischargers and emission from rainwater discharges via separate sewer systems in this more urban area of the pilot region. 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, Amann et al., 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).

Proposals for potential mitigation measures can be summarized as:

- Advanced wastewater treatment at treatment plants in sub-catchment 11001 > 10,000 PE; adsorption stage (activated carbon) for municipal wastewater treatment plants,
- Advanced wastewater treatment for industrial direct dischargers.

9.1.4 Specific situation in Somesul Mic pilot region (PFOS)

At the catchment outlet in Somesul Mic (ID 32001) a moderate exceedance of the PFOS EQS (factor 1,5) is evaluated. While in the analytical 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 emissions do not result in an exceedance of PFOS EQS in the upstream catchments. This conclusion is also supported by the model results in the other sub-catchments, which calculate concentrations 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 of the assessment, it is proposed to lay the focus on the emission from the outlet catchment 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 PE, a load of 366,867 PE 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 4th treatment stage on municipal wastewater treatment plants >100,000 PE to be implemented by 2035 is proposed.

Proposals for potential mitigation measures can be summarized as:

- Advanced wastewater treatment for municipal wastewater treatment plants with a capacity of > 100,000 PE; 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.

9.1.5 Specific situation in Vit pilot region (PFOS)

In the Vit pilot 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 decreasing 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.

Proposals for potential mitigation measures can be summarized as:

- 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 reduction of PFOS concentrations in surface waters.

9.1.6 Specific situation in Viseu pilot region (Heavy metals)

In the Viseu pilot region, monitored concentrations of cadmium, copper and zinc show extremely high values. The highest emissions are related to the upstream sub-catchment ID 32003, where direct discharges from abandoned mining sites could be monitored.
In soil probes, partly high concentrations were found for Cadmium, Zinc and Copper, too. Concentrations in Waste Water Treatment Plant effluents are still high, when influenced by mining (32003), with Copper and Zinc in a range of 1 or 0.5 mg/l and Cadmium with 0.04 mg/l. Untreated mining water monitored in this project in five different well-known effluents shows the highest concentrations. Here mean Copper and Zinc concentrations range in a magnitude of 0.6 to 4 mg/l and 2 to 35 mg/l, while Cadmium concentrations 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).
The system description and the model results prepared so far underlie significant uncertainties. Using maximum literature data of groundwater concentrations from mining influenced areas still lead to a significant underestimation of dissolved concentrations of Cadmium, Copper and Zinc monitored in the surface water in sub-catchment 32003. Reasons for this can be manifold. Either the discharge of untreated mining water is significantly underestimated or serious amounts of Cadmium, Copper and Zinc are emitted from unknown, untreated diffuse discharges of abandoned mining sites, from pits or pump sumps, entering the surface water system by percolation, interflow and via small temporary trickles. Of course, a combination of all 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 Copper and Zinc and 40% of Cadmium stem from untreated, but well-known discharges of abandoned mining in sub-catchment 32003. For Copper even the discharge of the treated mining influenced wastewater still has 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 less relevant surface runoff.

Proposals for potential mitigation measures can be summarized as:

- Step 1: regular discharge measurements of well-known abandoned mining effluent to increase system knowledge,
- Step 2: treatment of abandoned mining effluent,
- Step 3: improvement of existing WWTP influenced by mining water, especially for Copper,
- Step 4: remediation of abandoned mining sites and reduction of diffuse emission from the subsurface pathway.

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 (Cadmium), 0.79 (Copper) and 0.66 (Zinc). After optimization, in actual treatment plants, an even better purification could be managed, with: 96% (Cadmium), 90% (Copper) and 86% (Zinc) (Diepold, 2020). Similar purification rates could be achieved in mining waters (e.g. Gallagher et al., 2012).
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.

9.1.7 Specific situation in Koppany pilot region (Pesticides)

In the Koppany pilot region Metolachlor significantly exceeded the EQS from the National Substance List of 0.2 µg/l.
Concentrations of 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 Metolachlor were increased. In atmospheric deposition Metolachlor concentrations were analyzed above the limit of detection in May and June.
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.

Proposals for potential mitigation measures can be summarized as:

- Source control - reduction of Metolachlor application by 50% on all relevant crops,
- Reduction of erosion from arable land by 50%.

9.1.8 Catalogue of measures

The detailed analyses led to the elaboration of a catalog of measures (Table 9-1). On one hand, the effectiveness of measures was taken into account, on the other hand even the practicability was considered.

Table 9-1: Catalogue of measures based on a detailed system analyses derived from monitoring and modelling results.

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 PE): Adsorption stage (activated carbon) for municipal wastewater treatment plants.
AT	Wulka	AWE	12002	PFOS	Advanced wastewater treatment at treatment plant "Eisenstadt" (54,000 PE): 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	Advanced wastewater treatment at treatment plant "Oberes Urltal" and "Waidhofen": Adsorption stage (activated carbon) for municipal wastewater treatment plants.
AT	Ybbs	AYU, AYH	11002-12008	PFOS	No specific further measures.
HU	Zagyva	HZ6	22001	PFOS	No specific further measures.
HU	Zagyva	HZH	22002	PFOS	No specific further measures.
HU	Zagyva	-	22003	PFOS	Advanced wastewater treatment at treatment plant (35,800 PE): Adsorption stage (activated carbon) for municipal wastewater treatment plants.
HU	Zagyva	HZN	22004	PFOS	No specific further measures.
HU	Zagyva	HZT	22005	PFOS	Advanced wastewater treatment at the municipal treatment plant 75,000 PE: 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 414,022 PE.: Adsorption stage (activated carbon) for municipal wastewater treatment plants.
RO	Somesul Mic	RSU, RNR	31002-31006	PFOS	No specific further measures.
BG	Vit	BVD	41001	PFOS	Repair of the sewerage system; Construction of well-operated small wastewater treatment plants; Optimization of existing wastewater treatment plants.
BG	Vit	BVB, BVC	41002-41005	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	No specific further measures.
RO	Viseu	-	32002	Cadmium	No specific further measures.
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	No specific further measures.
RO	Viseu	-	32002	Copper	No specific further measures.
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	No specific further measures.
RO	Viseu	-	32002	Zinc	No specific further measures.
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%.

9.2 Modelling the effect of selected mitigation measures by scenario calculation

Based on the catalogue of measures, two scenario calculations were implemented in the MoRE Scenario Manager:

- Scenario I: Reduction of PFOS effluent concentrations by 75% from municipal WWWTPs > 10,000 PE in all pilot sites with exceedance of PFOS EQS (Ybbs, Wulka, Zagyva, Somesul Mic and Vit),

- Scenario II: Treatment of abandoned mining effluent on constructed, new WWTPs with increased purification rates (Viseu):
  - Cadmium 96%,
  - Copper 90% and
  - Zinc 86%.

The scenarios represent the implementation of mitigation measures, which are most promising in a direct reduction of the pollution in pilot regions and on the other hand can be implemented most easily and fastest.

9.2.1 Results Scenario I

As described in chapter 8.1the share of WWTPs on total PFOS emissions and the resulting concentrations in surface waters (and with that, the extent to which the EQS has been exceeded) show a very different manifestation among the pilot regions. This will have a huge influence on the effectiveness of the calculated measures. Table 9-2 gives an overview on the extent of the exceedance (monitored and modelled results) and on the relevance of the wastewater treatment plants in the pilot regions (model results) as well as on the results achieved by implementing Scenario I. In the Ybbs and Somesul Mic pilot regions, only the situation at the outlet is considered. For Vit no results are available. In this pilot region no WWTP > 10,000 PE is in place. For the more affected pilots Wulka and Zagyva results are shown for each sub-catchment.

Table 9-2: Results of implementation of advanced treatment on WWTPs >10,000 PE for PFOS.

Pilot region	ID	Direct affected PE*	Concentration [µg/l]	RC-factor	Reduction of in-stream concentration [%]	Resulting in-stream concentration [µg/l]	Resulting R-factor
Ybbs	11001	49.000	0,00072	*1,1*	5,7	0,00067	1,0
Wulka	12001	110.000	0,00397	*6,1*	63,5	0,00145	2,2
Wulka	12002	42.000	0,00403	*6,2*	65,7	0,00138	2,1
Wulka	12003	0	*0,00351*	*5,4*	0	0,00351	5,4
Wulka	12004	0	*0,00091*	*1,4*	0	0,00091	1,4
Wulka	12005	0	*0,00091*	*1,4*	0	0,00091	1,4
Zagyva	22001	0	*0,00020*	*0,3*	11,9	0,00017	0,3
Zagyva	22002	0	0,00130	*2,0*	0	0,00130	2,0
Zagyva	22003	35.800	0,00078	*1,2*	28	0,00056	0,9
Zagyva	22004	0	0,00091	*1,4*	0	0,00091	1,4
Zagyva	22005	75.000	0,00143	*2,2*	40,8	0,00085	1,3
Somesul Mic	31001	414.022	0,00098	*1,5*	50,4	0,00048	0,7

* Capacity

The scenario analyses underline a significant effect of the implementation of an advanced treatment on WWTPs > 10,000 PE in reducing PFOS.
The highest effectiveness of this measure could be achieved in Somesul Mic pilot with its large WWTP. In total, an in-stream concentration reduction of PFOS of about 50% could be achieved. The slight exceedance of the PFOS EQS can be converted into a clear undershoot.

Even in the Ybbs pilot, the slight exceedance of the PFOS EQS can be avoided by implementing this measure. The effectiveness of the measure is significantly lower compared to Somesul Mic due to the much lower flux affected and is around 5%.
Highest reductions in sub-catchment directly affected can be found in the Wulka pilot with more than 60% reduction of in-stream concentrations. A WWTP capacity of 152,000 PE would be affected by the effect of the measure. Here the highest RC-factors of all pilots could be significantly reduced by this measure (from 6 to 2). In catchment 12003, a tributary without recent WWTP, the high exceedance of PFOS EQS is unaffected. Here the measures must be targeted at the reduction of emission from the sewerage system. The same applies to the other upstream sub-catchments in the Wulka pilot region.
In Zagyva, in total 110,800 PE are affected by the measure, with 75,000 PE in the upstream sub-catchment (22005) which leads to a reduction of in-stream concentrations by more than 40%. The big reduction potential would lead to concentrations close to the EQS. In sub-catchment 22003, in which the second WWTP is located, the resulting concentration could undershoot the PFOS EQS. Even in sub-catchments downstream (22001), without WWTPs, an effect of the implemented measures can be quantified. Sub-catchments 22004 and 22002 will not be affected by the measure.

9.2.2 Results Scenario II

In the Viseu pilot region, the concentrations of Cadmium, Copper and Zinc significantly exceed the EQS (Table 9-3) and lead to a serious pollution of the River. In a first step, the most significant and easy to handle source of pollution – the discharges from abandoned mining sites form the tributary Tisla (32003) should be addressed. The collection and purification of this extremely heavily polluted wastewater would have a significant influence on water quality. The extent of pollution can be understood by comparing monitored (32003 and 32001) and modelled (32002) concentrations to the prescribed EQS (Table 9-2).

Table 9-3: Mean annual concentrations in Viseu sub-catchments (green=below EQS; ochre= above EQS).

	River concentration in µg/l (32002 model results)		
ID of analytical unit	**dissolved CD**	**dissolved CU**	**dissolved ZN**
32001	0,780	15,970	174,384
32002	0,914	5,319	116,796
32003	5,524	36,977	1572,124
EQS	0,25	10	73

The reduction of the pollution would be significant (Table 9-4).

While the downstream sub-catchment 32001will be directly affected by the reduction of emission from abandoned mining and water quality would significantly improve, the situation in the Viseu upstream catchment 32002 will be unchanged.
Here, based on our knowledge, which in a first step could be largely improved by carefully determining discharges of abandoned mining sites in Tisla tributary, the highest share of pollution stems from groundwater.
The reduction of surface water Heavy metal concentrations in the directly affected tributary Tisla (32003) would be significant. Around 30% of Cadmium concentration and up to 50% of Zinc and 60% of Copper could be avoided by this measure.

Table 9-4: Potential reduction of River concentration [%].

	% reduction in River concentration		
ID of analytical unit	**dissolved CD**	**dissolved CU**	**dissolved ZN**
32001	15	43	30
32002	0	0	0
32003	31	57	51

The demonstration of the resulting in-stream concentrations is prepared in Table 9-5.
It becomes clear that the implemented measures would lead to a significant reduction of pollution by Heavy metals in the Viseu pilot. In case of Copper the resulting concentration would even fall below the EQS in 32001.
Although the reduction in concentrations is remarkable, it must be noted that due to the tremendously high initial concentration, high concentration must be expected to remain even after the implementation of this measure. This illustrates that the implementation of this measure can be only the first step in a series of measures that must be implemented (partly addressed in this report) in this heavily polluted pilot region in order to achieve good water quality and prevent humans and aquatic life from serious risk.

Table 9-5: Resulting concentration after implementation of Scenario II (green=below EQS; ochre= above EQS).

	River concentration in µg/l (32002 model results)		
ID of analytical unit	**dissolved CD**	**dissolved CU**	**dissolved ZN**
32001	0,663	9,1029	122,0688
32002	0,914	5,319	116,796
32003	3,81156	15,90011	770,34076
EQS	0,25	10	73

10. Conclusions

More model implementation

The More model was setup and applied in all seven pilot regions in four upstream to downstream countries of the Danube River Basin. Input data quality differs among the pilot regions but was sufficient to setup a first model to quantify hazardous substances emission from different pathways. Biggest data gaps especially in the more downstream Danube countries can be identified for substance specific data. The developed data base (O.T1.3) providing substance specific data in different technical and environmental compartments strongly supports the successful setup of a model approach for chemicals from different substance groups.

The establishment of the database shows that still not all substances and compartments are represented sufficiently. Especially data on industrial effluents are underrepresented. For specific substances even data sets for single compartments are underrepresented or not available. Among others, surface runoff concentrations are substituted by concentrations from atmospheric deposition, because they are not available and also data from drainages are also missing.

With respect to basic input data, improvements could be achieved by establishing national soil loss calculations for Somesul Mic, Viseu and Vit pilot region, which is now supplemented by a European approach from JRC. Input data on drained areas are not available are not available for the Romanian and the Bulgarian pilot regions.

Furthermore, calculating the area of non-urban roads from Chorine Landcover leads to overestimations, which must be corrected.

In the project, the MoRE model could be adapted to specific conditions:

- abandoned mining sites and
- collected but not connected sewer.

Both approaches were added. A complete first English version was established. For the first time two different approaches for calculating concentrations and pathways of Pesticide emission were implemented. Among the substances modelled in this project, the model already provides the complete setup for several other substances, like Benzo(a)pyrene, Fluoroanthene, Nonylphenole and Bispenol A and is ready to be applied.

The model is provided on https://www.interreg-danube.eu/approved-projects/danube-hazard-m3c as an SQLite version, including all necessary functionalities.

More model validation

Model validation was prepared on base of four variants. An optimal model variant with a best model fit (results used for risk analyses and system analyses) validated based on best dataset with varying statistical data queries, flanked by a base, a maximum and a minimum model variant. The base variant is produced from the best fit database but always related to the 50 Percentile from the database queries, while the minimum variant (best case evaluation) always uses the 25 percentile as input data and the maximum variant (worst case) always uses the 75 percentile from the database on substance specific data. The base, minimum and maximum variant was implemented to consider uncertainties from input data and model approaches and to test the suitability of the input data for a generalized model approach. Model results from this variants were compared to three variants of load calculations (base, maximum, minimum) using the same percentiles, to address also the uncertainties from the load calculation approach.

In many cases it was found that optimization of the model results could be successfully applied and becomes necessary, when model results are:

- Used for risk assessment,
- A detailed assessment of the regional relevance of pathways and
- The calculation of mitigation measures.

A good model fit could be established for PFAS (PFOS and PFOA), most dissolved heavy metals (Cd, Cu, Cr,), Pharmaceuticals Diclofenac and the Pesticide Terbuconazole. Sufficient model adaptations are found for Hg and Ni (all dissolved) as well as for Carbamazepine. Insufficient and unsuitable model adaptations were found for Pb, Zn and As (all dissolved) and for Metolachlor and its metabolites.

Regional system Analyses
The water balance is a decisive variable in the modelling of inorganic and organic pollutants with the MoRE approach. In general, the pilot regions represent three different runoff types:

- Very low runoff, significantly below 80 mm (Wulka, Koppany, Zagyva),
- Medium runoff, with more than 200 mm (Somesul Mic and Vit),
- High runoff, above 800mm (Ybbs and Viseu).

The water balance characterizes two kinds of catchments:

- Natural catchments, with low anthropogenic use (high shares of groundwater and surface water runoff (Ybbs, Viseu, Vit and Somesul Mic, with the exception of the downstream catchment),
- Catchment under significant anthropogenic use, with significant higher shares of WWTP and sewer systems (Wulka, Zagyva, Koppany, Somesul Mic downstream catchment).

The sediment balance, important when particle bound substances are addressed, in some catchments shows serious discrepancies and could be partly adapted. However, in Vit the calculation of sediment input from agricultural area, from a European dataset can be significantly improved, while in the Romanian pilot region the same database leads to a good reproduction of the sediment loads, which predominantly stems from forests and from agriculture.
Although partly unaffected by human activities, pilot regions with high runoff show the highest area specific rates and loads (mainly caused by groundwater and surface runoff with high shares on the water balance), but low concentrations due to the high dilution potential. Pilots with low runoff and often significantly lower loads and area specific rates showed increased concentrations based on the extreme low dilution.
With respect to PFAS high area specific loads could be investigated for the Ybbs catchment but significant increased concentrations were monitored and modelled in pilots under increased anthropogenic pressure and with low runoff (Wulka, Zagyva and the outlet of Somesul Mic). Exceedance of EQS for PFOS at the outlet of Vit and Ybbs also expresses the ubiquitous character of the substance and the low EQS of PFOS. In sub-catchments with exceedance of the EQS, the dominant pathways are WWTPs and sewer systems.
A similar situation is found for Heavy metals. Highest area specific loads are found in natural, often mountainous areas, but increased concentrations are monitored and modelled in the pilot region with increased human activities. While in natural areas emission a strongly related to the surface runoff and the groundwater pathway, in more anthropogenic catchments high shares from WWTP and also partly from sewer systems were modelled.
Loads and concentrations in Viseu, influenced by abandoned mining, represent a clear extreme situation, especially in the sub-catchment of Tisla. This upstream tributary leads to concentrations and area specific loads (Cd, Cu and Zn) 10 to 100 times higher than in all other pilot regions. Model results based on a specific dataset adapted to abandoned mining, evaluated in this project, shows a good fit with respect to Copper, but significantly underestimates the measured loads of Cadmium and Zinc. The underestimation might result

from significantly higher emissions from abandoned mining effluent, which is direct emitted to the main rivers. Here, a monitoring underlines extreme high concentration values of Cadmium, Copper and Zinc, but the discharge remains unclear and could be only estimated. Other sources, not addressed in the model approach might be further diffuse emission from smaller abandoned mining effluents, not addressed in this project and largely unknown. The extreme high emission lead to a significant exceedance of EQS regulated by EU (Cd) or on base of national regulation (Zn and Cu).
In Koppany pilot region, characterized by intensive agricultural use, Metolachlor concentration significantly increase during event monitoring with increasing runoffs. Taking these measurements in account, which in case of Pesticides would be meaningful, in Koppany a clear exceedance of the EQS from the National Substance List, is found.
Terbuconazole concentrations are not often detected above LOQ, which makes it difficult to assess the model validity. In the pilots the model shows a good accordance to the calculated loads. However, in case of very few monitored data and a high share of concentration < LOQ load calculations from monitoring data are extremely influenced by the runoff of the pilot regions and do not show huge catchment specific differences.
A second approach based on crop specific application rates was developed and tested – but could be only developed for Metolachlor and its metabolites (Metolachlor-OA and Metolachlor-ESA). While the calculated application rates for Metolachlor showed reasonable results, the calculation of concentrations for Metolachlor and both metabolites derived from transfer functions (applied in Hungarian and Austrian pilot regions with sufficient information on crops from agricultural statistics) were significantly overestimated.
With respect to Pesticides, more investigations and data are needed to further test and develop the model approach with sufficient reliability.
The Pharmaceuticals Diclofenac and Terbuconazole show increased area specific loads with increasing population density. The main pathways are WWTP and small shares of combined storm water overflows in Austria but larger shares of groundwater in Vit and Viseu pilot at very low area specific rates. The higher share is a consequence of higher groundwater concentrations from the database, which led to an optimized model fit. The higher shares of emission from groundwater is in line with findings from the Danube Hazardous Substances Model, which addressed a higher rate of leakage from sewer systems as a possible interpretation.
In the Vit pilot, additionally emission from sewer collected in sewer systems but without transport to WWTPs were quantified.

Risk assessment
A risk analysis was carried out on the basis of the monitoring results in 20 sub-catchments and the other 14 exclusively modelled sub-catchments. For PFOS, Cd, Cu and Zn and Metolachlor exceedances of EQS were evaluated (monitored and modelled). The most affected pilot regions are Wulka and Zagyva (PFOS and Diclofenac – not yet regulated). Other pilot outlets like Somesul Mic, influenced by the large WWTP of Somesul Mic, but also Ybbs and Vit also showed exceedances of PFOS. In addition to PFOS, cases of exceedances for Pesticides (Koppany) and Heavy metals (Cd, Cu, Zn) were monitored and modelled, which can be attributed to specific uses in the pilot areas.
Modelled results could reproduce concentrations, e.g. for PFOS, but there were discrepancies especially at very low concentration values. The higher modelled deviations at low concentration values lead to uncertainties in reproducing the status of a surface water, which also show the existing limits of emission modelling. However, valid reproduction of the risk for PFOS could be achieved when the RC-factor was > 2. A match of monitored and modelled results was also found for Heavy metals. Here the clear exceedance for Cd, Cu, Zn in Viseu could be partly reproduced, by clear underestimations of Cd and Zn, using a dataset

from a small literature research for areas affected by abandoned mining. In case of Viseu the led to the correct result.
Pesticides cannot yet be evaluated.
Even with respect to the proposed substances and EQS (from the revised List of Priority substances) the model approach showed a good accordance to monitored exceedances and gave additional information in sub catchments without monitoring. Here the possibility is provided to asses PFOA and Diclofenac in future.
However, the expectation that an emission model, such as MoRE, can map an exact representation of exceedances or shortfalls of possible substances for each sub-catchment would exceed the requirements for emission modelling. It is clear that modelling cannot replace but supplement monitoring. It can describe hot spots of pollution and can contribute to a risk assessment with a sensitivity, which must be considered.
As presented in Chapter 7, not all exceedances recorded from the monitoring could be represented with the model approach. Nevertheless, the model results provided further, plausible information on possible additional pollution hotspots that affect the areas not covered by monitoring.

Catalogue of measures and scenario analyses
Based on a risk assessment and regionalized pathway analyses a catalogue of measures was developed. Here Taylor-made mitigation measures were addressed, which range from:

- Advanced wastewater treatment at treatment plants >10,000 PE (PFOS),
- Increased retention capacity of combined sewer overflow and additional treatment on WWTPs (PFOS),
- Repair of the sewerage system (Vit pilot region),
- Construction of well-operated small wastewater treatment plants (Vit pilot region),
- Optimization of existing wastewater treatment plants (Vit pilot region),
- Reduction of s-Metolachlor application by 50% on all relevant crops (Koppany),
- Reduction of erosion from arable land by 50% (Koppany),
- Cleaning of abandoned mining effluent from well-known and diffuse runoff (Viseu),
- Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment) (Viseu).

For PFOS and heavy metals, the most effective and practicable measures were implemented as scenarios in the model.
Scenario I: describes the effects of advanced treatment on WWTPs > 10,000 PE for PFOS (relevant in Ybbs, Wulka, Zagyva, Somesul Mic pilot) but not practicable in Vit, because no WWTPs > 10,000PE are in place.
The scenario underlines, that significant reduction of PFOS are possible and in some cases even can change status from a risk exceedance to PFOS concentration below EQS.
Scenario II: collecting and treatment of abandoned mining effluent in Tisla tributary for Cd, Cu and Zn. The calculations show an enormous effect on water quality but in most cases the pollution reminds high even after a significant reduction of the concentrations of above 50%.
Based on the results obtained and the measures proposed, in each pilot region a first survey of national and regional stakeholders was initiated, which can be used for further discussion and intensified consultation.

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Appendix

The Appendix I consists of 20 flowcharts expressing the detailed calculation of pathways, balances, retention processes and load accumulation in the pilot regions.

It is presented as a Zip-File with 20 seperate pdf-files.