Interreg
EUROPEAN UNION
Danube Transnational Programme
Danube Hazard m^{3}c

Deliverable D.T2.1.2

Technical documentation of the model setup in the pilot regions

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Table of contents

1. Introduction

1.1 Background

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 can give information 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. However, reporting of the inventory under the second river basin management plans was patchy and largely incomparable between Member States.

Several projects related to emissions to water, carried out in recent years for the European Commission (EC) (Roovaart, J., et al., 2013) and the EEA (ETC/ICM 2017, EEA 2018a, EEA 2018b) show serious problems regarding 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)

In the current DRB District Management Plan (DRBMP) and national plans of the Danube region, this topic is 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.
At this moment, the considerations on possible measures are often related to punctual, continuous sources such as the discharge of municipal wastewater treatment plants. Emission from point sources are often well described due to a dense and standardized monitoring system, in addition often detailed process knowledge builds a sound fundament to assess the effect on potential measures. Another advantage is that once measures have been implemented at wastewater treatment plants, the effect is immediate and leads to verifiable reductions in pollution.

However, other, often diffuse, substance-specific input pathways are also of great relevance. This is particularly important for ubiquitous Persistent, Bioaccumulative and Toxic substances (uPBTs). Especially uPBTs are subject to bans or restrictions, but due to their properties (persistence and accumulation potential), they can be displaced over long distances, are not degradable and accumulate in certain environmental compartments. Knowledge on both distribution and concentration in these compartments often is marginal, while process knowledge describing the behavior of these substances in some cases is insufficient.
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 fluxes introduced into the 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.

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 m3c) in seven pilot regions all over the Danube emission modelling will be performed with MoRE (Modelling of Regionalized Emissions).

All pilot regions with specific but representative physical characteristics and a typical expression of different pressures of hazardous substances will be setup and can be used as “Role Model” for further application in the Danube region. With a total area of around 7.900 km^2 the pilots cover nearly one percent of the total Danube catchment area and 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).

Furthermore, they represent distinctive characteristics with respect to climate, hydrology, land-use and pollution pressure (Del. 1.2.1, 2020), which cover the aspects of “natural background”, “intensive agricultural use”, “high share of treated wastewater”, “high share of untreated wastewater”, “rural wastewater management” and “abandoned and active mining”. The scope of modelled substances includes substances that are relevant for the Danube River Basin (DRB), are mobile, and provide information on specific sources and emission pathways: industrial chemicals with wide dispersive use, pharmaceuticals, herbicides, fungicides, and metals. Specifically, the following substances will be analysed:

- Perfluorooctanesulfonic acid (PFOS), Perfluorooctanoic acid (PFOA) (industrial chemicals)
- 16 EPA Polycyclic aromatic hydrocarbons (PAHs, industrial chemicals, and combustion by-products)
- Mercury (Hg), Cadmium (Cd), Copper (Cu), Nickel (Ni), Lead (Pb), Zinc (Zn), and Arsenic (As) (metals)
- Diclofenac and Carbamazepine (pharmaceuticals)
- 4-tert-Octylphenol (industrial chemical)
- Nonylphenol (industrial chemical)
- Bisphenol A (industrial chemical)
- S-Metolachlor (herbicide) including Metolachlor-ESA and Metolachlor-OA (metabolites)
- Tebuconazole (fungicide) (Del. 1.2.2, 2020)

Modelling period will be 2016 – 2021 and modelling time steps will be annual. Because most data for 2020 and 2021 are not already available or ordering specific data sets will cause costs, once they are requested, and thus should be ordered only once, it is clear that the data set presented in this deliverable cannot represent a completed version at this stage, but has to be improved step by step. This is also true for some content and algorithm related

developments in the model during the project period, which will make adaption, changes and additions of data necessary throughout the whole model application.
The project partners Umweltbundesamt (Ybbs), TU Wien (Wulka), BME (Zagyva and Koppány), BWA (Vit) and NARW (Someșul Mic and Vișeu) are responsible to provide data and crucial information on specific conditions in the pilot regions. Coordination, technical support on data evaluation, as well as model setup is prepared by Umweltbundesamt. The model setup is supported by TU Wien.

1.2 Objectives

In this deliverable, a sound documentation of the technical setup of the MoRE model application in all seven pilot regions is prepared. One main task was to setup an English version of the model. This made it necessary to rebuild the model structure and create the model parameters, versions, formulas, calculation stacks for each modelled substance.
The Deliverable will concentrate on the documentation of four main topics:

- Documentation and specification of applied model algorithms in the form of technical files.
- Development, differentiation and improvement of model approaches to implement calculations of new pathways and/or substances, in particular:
    - Implement an approach to calculate emission from the pathway abandoned mining sites with ore deposits
    - Implement an approach to calculate pesticides (s-Metolachlor and Tebuconazole)
    - Implement different approaches reflecting the specific situation of urban wastewater management and data availability in different pilot regions

Together with Deliverable 2.1.1 Deliverable 2.1.2 presents a sound documentation of the technical setup of the MoRE model applied in seven pilot regions in the Danube catchment. Because of delays in the project schedule, especially in WP T1, which originally was planned to transfer the substance-specific input data to WP T2 at the end of period three, the Deliverable can only be presented as a draft at this stage. Consequently, the “Description of model input data with a clear focus on substance specific input data (as a supplement to the basic input data described in Deliverable 2.1.1)” can be not presented so far.
Even the development of new approaches, among others depending on the availability of input data (e.g. pesticide loads) or on measurements from the project specific monitoring campaign (mining sites) will be under evaluation even during the fourth project period. Nevertheless, a temporary approach will be presented already in this version.

1.3 Overview on MoRE Model

"Modeling of Regionalized Emissions" (MoRE) is a model for the regionalised pathway analysis of substance inputs into surface waters (Fuchs et al., 2017) based on sub-catchments with a seize of around 100 km^2. The emissions 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 pathways that can be assigned to different sources. In some cases the pathways are related to more than one source (see Figure 1).

In general the pathways under evaluation are:

- Point source emission, from Urban wastewater
    - connected to a sewer system and a treatment plant
    - connected to a sewer system but not connected to a treatment plant
    - connected to a leaking sewer system and not connected to a treatment plant (new diversification of pathway)
    - gathered in Individual Appropriate Systems (IAS, like septic tanks) transported to treatment plants
    - gathered in Individual Appropriate Systems (IAS, like septic tanks) leaking (new diversification of pathway)

- Point source emission from industrial direct dischargers
- Point source emission from abandoned mining sites (new diversification of pathway)
- Emission from storm water and combined water overflows
- Emission of atmospheric deposition (direct on water surfaces)
- Emission from Surface runoff
- Emission from Erosion (agricultural and natural)
- Emission from Tile Drainages
- Emission from Groundwater (including baseflow and interflow)
- Emission from country roads and highways (implemented during STOBIMO Spurenstoffe (Amann et al., 2019))

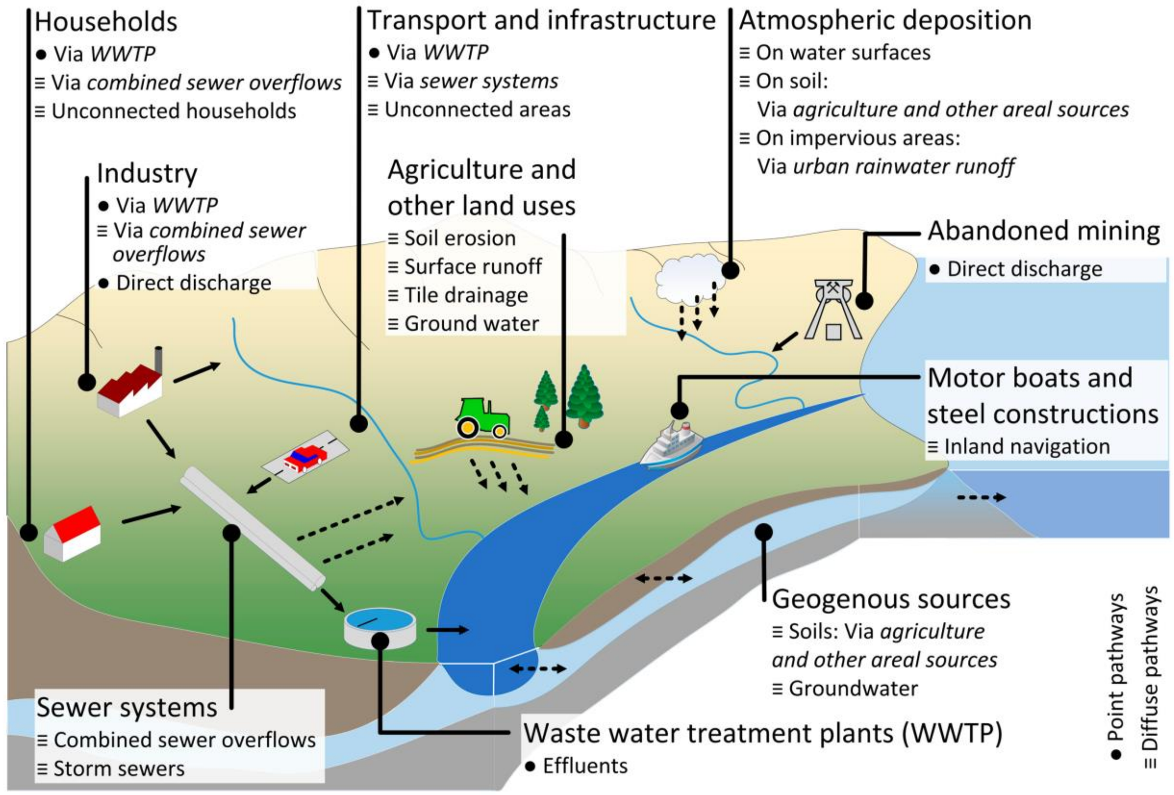


Figure 1: Substance emission pathways of current MoRE applications, arranged by source type (Fuchs et al., 2017)

It calculates emission to the surface water in annual time steps for hydrological sub-catchments and takes into account the retention (sedimentation or degradation/gassing) of substances. 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).

2. Description of input data

To run the model a huge number 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.

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 spot can build these database. 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 data, which is needed. 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 area height 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 derived from complex calculation methods.

The required 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 for monthly values and 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, modelled pathways even 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 the definition of these dataset cannot be understand as irrevocable. In the opposite, prescribed input data need to be evaluated with respect to the prevailing data situation, the input data set, and the model algorithms can be modified and balanced during an iterative determination.

All basic input data sets mainly prepared in the cooperation of the project partners responsible for the pilot regions and Umweltbundesamt are prepared in Deliverable 2.1.1. The documentation includes an exemplary description of the use of the basic input data in the model approaches for specific pathways, it gives a sound overview about the master data and a presentation of all model input files.

A description of the establishment of substance specific input data are presented in Deliverable 1.1.2 “Database of pre-existing data on HS concentrations“. Here, already identified gaps, which are critical for the implementation of WPs T2 and T3, will be filled with targeted measurements conducted in rivers and in emission pathways in seven pilot regions.

Furthermore, within WPT1 an inventory is setup with a focus of substances modelled in this project but also for many other substances, being of interest in further investigations. The inventory fulfills the provisions of the EU guidance document 28 (EC, 2012). It will contain data on hazardous substance concentration levels in surface water bodies and in major emission pathways into surface waters within the whole DRB. Namely atmospheric deposition, soil, groundwater, surface runoff, sediment in surface waters, runoff and wastewater from mining sites, raw municipal wastewater and wastewater treatment plant effluents as well as industrial wastewater effluents, and combined and rain sewer overflows are adressed. The inventory will contain single measurements as well as aggregated values, in addition to all available metadata. Data will be implemented in the MoRE model as substance specific data.

2.1 Substance specific input data

The concentration specific input data are not available yet, due to delays mainly in WP T1 described in chapter 1.2. Results and procedure of data evaluation will be supplemented later.

3. 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 flowchart 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

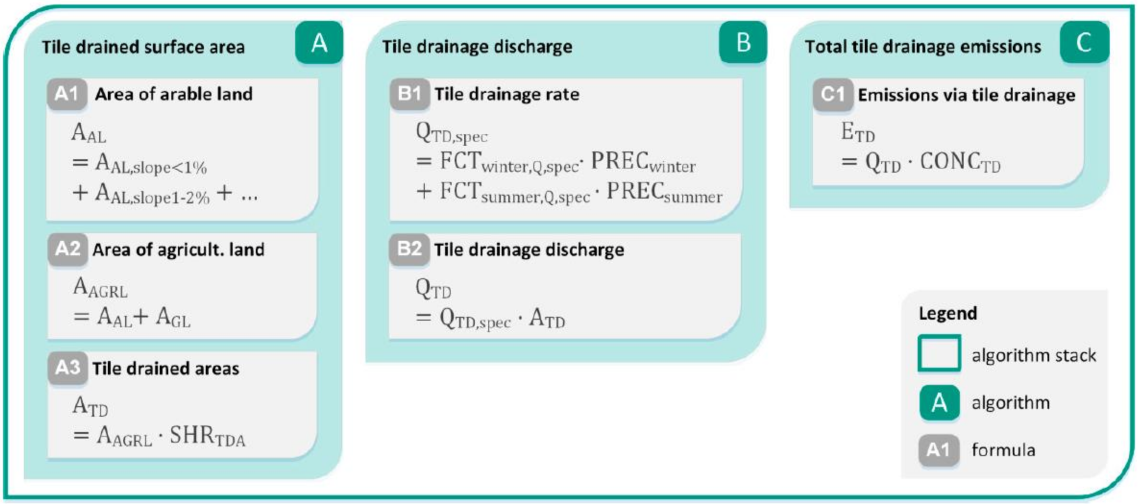


Figure 2: Example of the hierarchic implementation of the modelling approaches in MoRE (Fuchs et al., 2017) A: Area; SHR: share; Q: Discharge; FCT: factor; PREC: Precipitation; E: Emissions; CONC: concentration. Subscripts: TD: tile drainage; TDA: tile drained area; AGRL: agricultural area; AL: arable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

In **Fehler! Verweisquelle konnte nicht gefunden werden.**, 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 calculation for a specific pathway are the same for different substances, the flowcharts are (exemplarily) only given for one substance in this report.

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 1700 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.

Even the variables, formulas, algorithms and algorithm stacks for nutrients (nitrogen and phosphorus) are still present in the model as they can be used as an example for other substances in some cases, even though they are not modelled in this project.

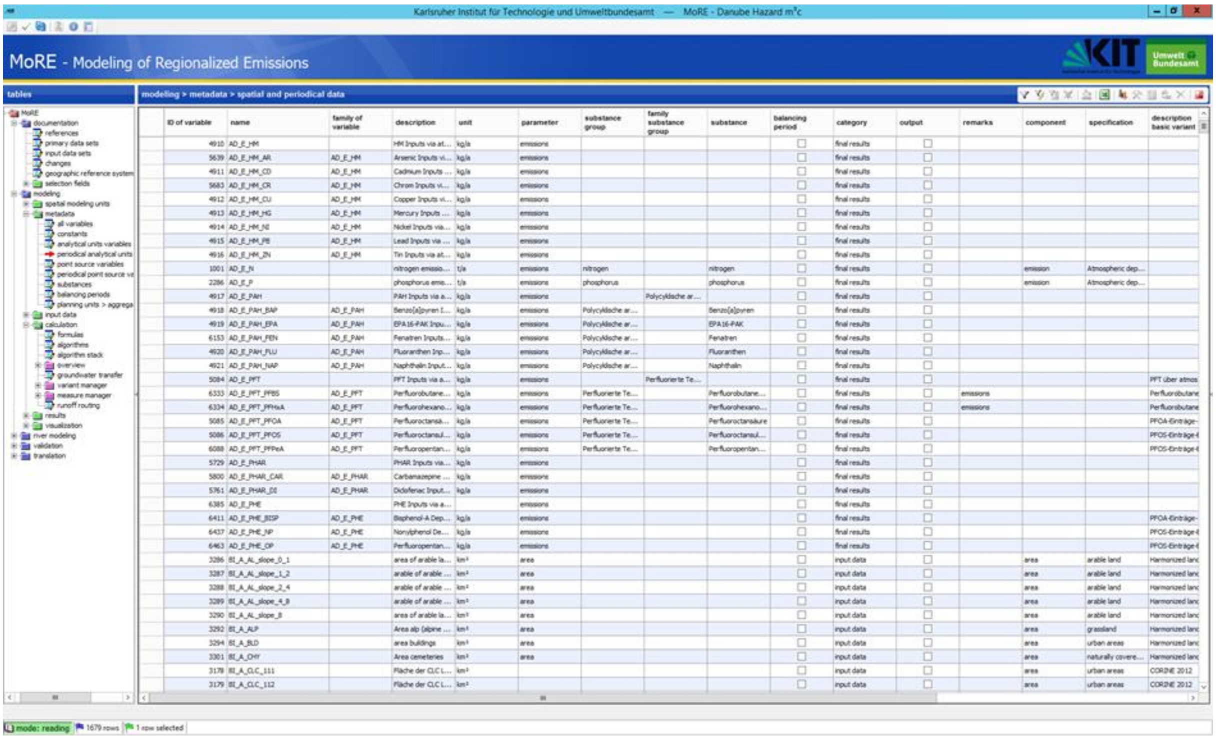
An overview of which algorithms/algorithm stacks are represented in which flowchart is given in Appendix I.

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

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

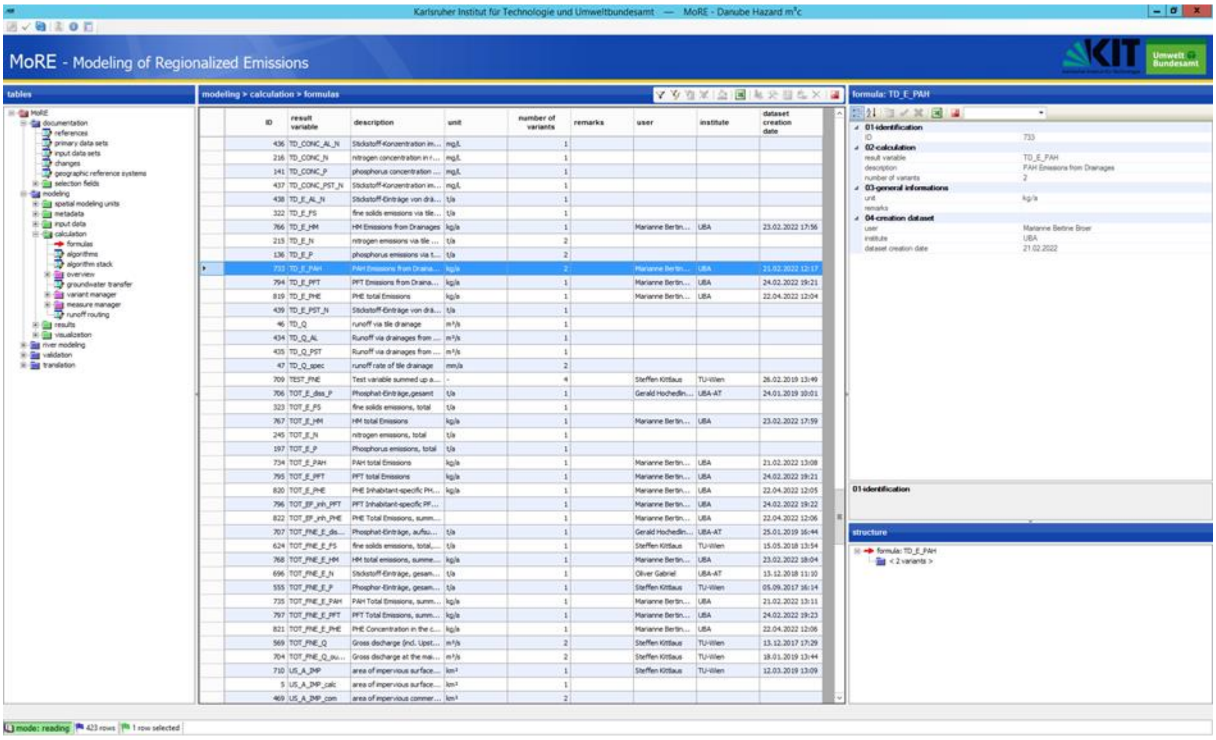
The MoRE model consist of around 500 formulas, which are always applied on an entire substance group. Each formula has a result variable. For each result variable it is possible the have more than one formula in the model, however only one formula can be active. In this model, if new formulas are constructed, 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.



ID of variable	name	family of variable	description	unit	parameter	substance group	family substance group	substance	balancing period	category	output	remarks	component	specification	description basic variant
4910	AD_E_HM		HM Inputs via at...	kg/a	emissions				☐	final results	☐				
5639	AD_E_HM_AR	AD_E_HM	Arsenic Inputs vi...	kg/a	emissions				☐	final results	☐				
4911	AD_E_HM_CD	AD_E_HM	Cadmium Inputs ...	kg/a	emissions				☐	final results	☐				
5683	AD_E_HM_CR	AD_E_HM	Chrom Inputs vi...	kg/a	emissions				☐	final results	☐				
4912	AD_E_HM_CU	AD_E_HM	Copper Inputs vi...	kg/a	emissions				☐	final results	☐				
4913	AD_E_HM_HG	AD_E_HM	Mercury Inputs ...	kg/a	emissions				☐	final results	☐				
4914	AD_E_HM_NI	AD_E_HM	Nickel Inputs via...	kg/a	emissions				☐	final results	☐				
4915	AD_E_HM_PB	AD_E_HM	Lead Inputs via ...	kg/a	emissions				☐	final results	☐				
4916	AD_E_HM_ZN	AD_E_HM	Tin Inputs via at...	kg/a	emissions				☐	final results	☐				
1001	AD_E_N		nitrogen emissio...	t/a	emissions	nitrogen		nitrogen	☐	final results	☐		emission	Atmospheric dep...	
2286	AD_E_P		phosphorus emis...	t/a	emissions	phosphorus		phosphorus	☐	final results	☐		emission	Atmospheric dep...	
4917	AD_E_PAH		PAH Inputs via a...	kg/a	emissions		Polycyklische ar...		☐	final results	☐				
4918	AD_E_PAH_BAP	AD_E_PAH	Benzo[a]pyren I...	kg/a	emissions	Polycyklische ar...		Benzo[a]pyren	☐	final results	☐				
4919	AD_E_PAH_EPA	AD_E_PAH	EPA16-PAK Inpu...	kg/a	emissions	Polycyklische ar...		EPA16-PAK	☐	final results	☐				
6153	AD_E_PAH_FEN	AD_E_PAH	Fenatren Inputs...	kg/a	emissions	Polycyklische ar...		Fenatren	☐	final results	☐				
4920	AD_E_PAH_FLU	AD_E_PAH	Fluoranthen Inp...	kg/a	emissions	Polycyklische ar...		Fluoranthen	☐	final results	☐				
4921	AD_E_PAH_NAP	AD_E_PAH	Naphthalin Input...	kg/a	emissions	Polycyklische ar...		Naphthalin	☐	final results	☐				
5084	AD_E_PFT		PFT Inputs via a...	kg/a	emissions		Perfluorierte Te...		☐	final results	☐				PFT über atmos
6333	AD_E_PFT_PFBS	AD_E_PFT	Perfluorobutane...	kg/a	emissions	Perfluorierte Te...		Perfluorobutane...	☐	final results	☐	emissions			Perfluorobutane
6334	AD_E_PFT_PFHxA	AD_E_PFT	Perfluorohexano...	kg/a	emissions	Perfluorierte Te...		Perfluorohexano...	☐	final results	☐	emissions			Perfluorobutane
5085	AD_E_PFT_PFOA	AD_E_PFT	Perfluoroctansä...	kg/a	emissions	Perfluorierte Te...		Perfluoroctansäure	☐	final results	☐				PFOA-Einträge-
5086	AD_E_PFT_PFOS	AD_E_PFT	Perfluoroctansul...	kg/a	emissions	Perfluorierte Te...		Perfluoroctansul...	☐	final results	☐				PFOS-Einträge-
6088	AD_E_PFT_PFPeA	AD_E_PFT	Perfluoropentan...	kg/a	emissions	Perfluorierte Te...		Perfluoropentan...	☐	final results	☐				PFOS-Einträge-
5729	AD_E_PHAR		PHAR Inputs via...	kg/a	emissions				☐	final results	☐				
5800	AD_E_PHAR_CAR	AD_E_PHAR	Carbamazepine ...	kg/a	emissions				☐	final results	☐				
5761	AD_E_PHAR_DI	AD_E_PHAR	Diclofenac Input...	kg/a	emissions				☐	final results	☐				
6385	AD_E_PHE		PHE Inputs via a...		emissions				☐	final results	☐				
6411	AD_E_PHE_BISP	AD_E_PHE	Bisphenol-A Dep...	kg/a	emissions				☐	final results	☐				PFOA-Einträge-
6437	AD_E_PHE_NP	AD_E_PHE	Nonylphenol De...	kg/a	emissions				☐	final results	☐				PFOS-Einträge-
6463	AD_E_PHE_OP	AD_E_PHE	Perfluoropentan...	kg/a	emissions				☐	final results	☐				PFOS-Einträge-
3286	BI_A_AL_slope_0_1		area of arable la...	km^2	area				☐	input data	☐		area	arable land	Harmonized lan
3287	BI_A_AL_slope_1_2		arable of arable ...	km^2	area				☐	input data	☐		area	arable land	Harmonized lan
3288	BI_A_AL_slope_2_4		arable of arable ...	km^2	area				☐	input data	☐		area	arable land	Harmonized lan
3289	BI_A_AL_slope_4_8		arable of arable ...	km^2	area				☐	input data	☐		area	arable land	Harmonized lan
3290	BI_A_AL_slope_8		area of arable la...	km^2	area				☐	input data	☐		area	arable land	Harmonized lan
3292	BI_A_ALP		Area alp (alpine ...	km^2	area				☐	input data	☐		area	grassland	Harmonized lan
3294	BI_A_BLD		area buildings	km^2	area				☐	input data	☐		area	urban areas	Harmonized lan
3301	BI_A_CMY		Area cemeteries	km^2	area				☐	input data	☐		area	naturally covere...	Harmonized lan
3178	BI_A_CLC_111		Fläche der CLC L...	km^2					☐	input data	☐		area	urban areas	CORINE 2012
3179	BI_A_CLC_112		Fläche der CLC L...	km^2					☐	input data	☐		area	urban areas	CORINE 2012

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



ID	result variable	description	unit	number of variants	remarks	user	institute	dataset creation date
436	TD_CONC_AL_N	Stickstoff-Konzentration im...	mg/L	1				
216	TD_CONC_N	nitrogen concentration in r...	mg/L	1				
141	TD_CONC_P	phosphorus concentration ...	mg/L	1				
437	TD_CONC_PST_N	Stickstoff-Konzentration im...	mg/L	1				
438	TD_E_AL_N	Stickstoff-Einträge von drä...	t/a	1				
322	TD_E_FS	fine solids emissions via tile...	t/a	1				
766	TD_E_HM	HM Emissions from Drainages	kg/a	1		Marianne Bertin...	UBA	23.02.2022 17:56
215	TD_E_N	nitrogen emissions via tile ...	t/a	2				
136	TD_E_P	phosphorus emissions via t...	t/a	2				
733	TD_E_PAH	PAH Emissions from Draina...	kg/a	2		Marianne Bertin...	UBA	21.02.2022 12:17
794	TD_E_PFT	PFT Emissions from Draina...	kg/a	1		Marianne Bertin...	UBA	24.02.2022 19:21
819	TD_E_PHE	PHE total Emissions	kg/a	1		Marianne Bertin...	UBA	22.04.2022 12:04
439	TD_E_PST_N	Stickstoff-Einträge von drä...	t/a	1				
46	TD_Q	runoff via tile drainage	m^3/s	1				
434	TD_Q_AL	Runoff via drainages from ...	m^3/s	1				
435	TD_Q_PST	Runoff via drainages from ...	m^3/s	1				
47	TD_Q_spec	runoff rate of tile drainage	mm/a	2				
709	TEST_FNE	Test variable summed up a...	-	4		Steffen Kittlaus	TU-Wien	26.02.2019 13:49
706	TOT_E_diss_P	Phosphat-Einträge,gesamt	t/a	1		Gerald Hochedlin...	UBA-AT	24.01.2019 10:01
323	TOT_E_FS	fine solids emissions, total	t/a	1				
767	TOT_E_HM	HM total Emissions	kg/a	1		Marianne Bertin...	UBA	23.02.2022 17:59
245	TOT_E_N	nitrogen emissions, total	t/a	1				
197	TOT_E_P	Phosphorus emissions, total	t/a	1				
734	TOT_E_PAH	PAH total Emissions	kg/a	1		Marianne Bertin...	UBA	21.02.2022 13:08
795	TOT_E_PFT	PFT total Emissions	kg/a	1		Marianne Bertin...	UBA	24.02.2022 19:21
820	TOT_E_PHE	PHE Inhabitant-specific PH...	kg/a	1		Marianne Bertin...	UBA	22.04.2022 12:05
796	TOT_EP_inh_PFT	PFT Inhabitant-specific PF...		1		Marianne Bertin...	UBA	24.02.2022 19:22
822	TOT_EP_inh_PHE	PHE Total Emissions, summ...		1		Marianne Bertin...	UBA	22.04.2022 12:06
707	TOT_FNE_E_dis...	Phosphat-Einträge, aufsu...	t/a	1		Gerald Hochedlin...	UBA-AT	25.01.2019 16:44
624	TOT_FNE_E_FS	fine solids emissions, total,...	t/a	1		Steffen Kittlaus	TU-Wien	15.05.2018 13:54
768	TOT_FNE_E_HM	HM total emissions, summe...	kg/a	1		Marianne Bertin...	UBA	23.02.2022 18:04
696	TOT_FNE_E_N	Stickstoff-Einträge, gesam...	t/a	1		Oliver Gabriel	UBA-AT	13.12.2018 11:10
555	TOT_FNE_E_P	Phosphor-Einträge, gesam...	t/a	1		Steffen Kittlaus	TU-Wien	05.09.2017 16:14
735	TOT_FNE_E_PAH	PAH Total Emissions, summ...	kg/a	1		Marianne Bertin...	UBA	21.02.2022 13:11
797	TOT_FNE_E_PFT	PFT Total Emissions, summ...	kg/a	1		Marianne Bertin...	UBA	24.02.2022 19:23
821	TOT_FNE_E_PHE	PHE Concentration in the c...	kg/a	1		Marianne Bertin...	UBA	22.04.2022 12:06
569	TOT_FNE_Q	Gross discharge (incl. Upst...	m^3/s	2		Steffen Kittlaus	TU-Wien	13.12.2017 17:29
704	TOT_FNE_Q_su...	Gross discharge at the mai...	m^3/s	2		Steffen Kittlaus	TU-Wien	18.01.2019 13:44
710	US_A_IMP	area of impervious surface...	km^2	1		Steffen Kittlaus	TU-Wien	12.03.2019 13:09
5	US_A_IMP_calc	area of impervious surface...	km^2	1				
469	US_A_IMP_com	area of impervious commer...	km^2	2				

formula: TD_E_PAH

- 01-identification
  - ID: 733
- 02-calculation
  - result variable: TD_E_PAH
  - description: PAH Emissions from Drainages
  - number of variants: 2
- 03-general informations
  - unit: kg/a
  - remarks:
- 04-creation dataset
  - user: Marianne Bettina Broer
  - institute: UBA
  - dataset creation date: 21.02.2022

01-identification

structure

formula: TD_E_PAH
< 2 variants >

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

3.1 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. In the second and third group point source- and diffuse pathways addressed and quantified in the model approach are presented. In the last group information on the calculation of total emission, retention in surface water and the calculation of loads and concentration in the surface waters are presented.

3.1.1 General calculations

3.1.1.1 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 argricultural 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 I named 01_Land_use.

3.1.1.2 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 waterbalance 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 I named 30_Water_balance.

3.1.1.3 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 (Amann et al., 2019). 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.

The long-term average soil erosion of agricultural land was calculated and imported into the model as input data (chapter 3.1.3.2).

In the model, the R-factor of the soil erosion equation is varied if possible 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):

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

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) 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 alpine 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. 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. A balance check of the fine solid balance will be applied when the load calculation on suspended solids on sub-catchment area are available.

The flowchart for this algorithm stack can be found in Appendix I named 90_Fine_solids_balance.

3.1.2 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.

3.1.2.1 Urban Wastewater Treatment plants

For plants with a capacity of 2,000 p.e. 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 for each plant. 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 p.e. are available, calculated loads (summed up wastewater discharge aggregated per sub-catchment x concentration) are added to the loads from plants > 2000 p.e. (see flowchart 09_WWTP_PAH in Appendix I).

Substance specific concentrations of discharges from WWTPs will be provided from the established database and the own monitoring results of the project.

3.1.2.2 Direct discharges from industrial Treatment Plants

Similar to the municipal treatment plants, the discharge from industrial treatment plants is aggregated to a sub-catchment and summed up and multiplied with a substance specific concentration and summed up (see flowchart 08_ID_PAH in Appendix I).
If it is possible to classify substance specific concentrations with respect to different sectors based on data from the database and project specific own measurements, substance specific loads from all industrial treatment plants will be preprocessed and accumulated to the sub-catchment.

3.1.2.3 Discharges from abandoned mining sites

The discharges from abandoned mining sites implemented in the model structure and representing the situation in the pilot region Viseau is described more in detail in chapter 3.2.2 but is briefly mentioned here as it is created and implemented as a special case of point source emission.
Discharges from abandoned mining sites will be handled in the model and calculated like industrial treatment plants (chapter 3.1.2.2)

3.1.2.4 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 source, while most of the others pathways included in this approach are more related to the diffuse 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 3.2.3 (see flowchart 11_US_PAH in Appendix I).

3.1.3 Diffuse sources

In this chapter, a short introduction on the calculated pathways from diffuse 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.

3.1.3.1 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. 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).

Information on basic input data (calculation of surface water area) is presented in Deliverable 2.1.1. An example (PAHs) of the flowchart for this algorithm can be found in Appendix I as 02_AD_PAH.

Distributed input data of several substances are available from the EMEP database. Additional substance specific concentration data should be made available by WP1 from the database and own measurements in atmospheric deposition of the pilot regions.

3.1.3.2 Emissions via erosion

As documented in Amann, 2019 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 discharges 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, PAHs and PBDEs, 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, PAHs and PBDEs 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.
For heavy metals, sediment inputs from alpine open areas (from the solids balance) are multiplied by the heavy metal contents of the rocks. For other trace substances, no inputs are modeled here.

Information on basic input data (calculation of erosion from arable land) is presented in Deliverable 2.1.1. An example (PAHs) of the flowchart for this algorithm can be found in Appendix I named 06_ER_PAH.

3.1.3.3 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 Deliverable 2.1.1. The flowchart for this algorithm can be found in Appendix I named 03_TD_PAH.

Concentration should be made available by WP T1 from the database. 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.

3.1.3.4 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 (from the runoff balance, chapter 3.1.1.2).The flowchart for this algorithm can be found in Appendix I named 10_SR_PAH.

3.1.3.5 Emissions via groundwater and interflow

This input pathway describes the input of trace substances by underground transport via groundwater 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).
The flowchart for this algorithm can be found in Appendix I named 07_GW_PAH.

3.1.3.6 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 discharge it 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). The concentrations are not yet prepared.
The flowchart for this algorithm can be found in Appendix I named 12_OR_PAH.

3.1.4 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.

3.1.4.1 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)

- MINING_E_PAH (point sources from mining, not yet implemented)
- 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 I named 13_TOT_PAH.

3.1.4.2 Retention in tributaries and main rivers

Not all of the 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, either by 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 (m^3/s)
A = area of the analysis area (km^2)

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 (km^2)

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 (km²)

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 I named 82_RM_Retention.

3.1.4.3 River loads and concentrations

While no retention by sedimentation is assumed for the polyfluorinated surfactants and for Carbamazepin due to their rather good solubility, the water loads for substances and substance classes are calculated including retention.

Assuming that point sources and combined sewer overflows are predominantly found on the mainstream in the downstream parts of an 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 (Amann et al., 2019):

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

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):

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

The flowchart for this algorithm can be found in Appendix I named

3.2 New and modified approaches

3.2.1 Plant Protection Products

3.2.1.1 Background

Plant Protection Products (PPPs) are used in agriculture and in households and are released into the environment after their application. They are defined as chemical substances, which protect plants or plant products from harmful organisms (killing) or are applicated to hinder the reduction of germination, growth and reproduction of plants by these harmful organisms. Depending on their effect, pesticides are divided into different groups (BfR, 2015) (herbicides – substances against weeds; insecticides – against insects; fungicides – against fungal diseases; molluscicides – against gastropods; acaricides - against mites; rodenticides against rodents and growth regulators to control biological processes.

Crop protection products are usually mixtures of one or more active ingredients and adjuvants, with the active ingredient as the active component controlling the pest. The additives often result in better handling, storage or application.

Pesticides are not yet implemented in the model calculation structure of MoRE. Therefore, it has to be tested, if sound approaches already exist or can be developed, which make an evaluation of pesticide emission possible on the spatial meso-scale and on base of annual or multiannual evaluation time steps.

This seems to be especial challenging, because pesticides:

- Are highly dynamic and large shares are often transported within small time periods short after the application
- Often metabolize, and not all metabolites are well known and/or can be detected

In this study, two different substances were chosen to evaluate the possibilities of an investigation:

- Metolachlor, a herbicide including the well-known metabolites Metolachlor-ESA and Metolachlor-OA and
- Tebuconazole, a fungicide.

In order to approach this topic, the first step was to review various literature sources, collect and evaluate data and information on pesticide application in the different pilot regions (if available) and evaluate measurement campaigns mainly from Austria to develop and test a first, simple approach to quantify pesticide emissions in river catchments. Outcomes are presented below.

The placing on the market and use of plant protection products is subject to different legal regulations in the European Union. The authorization and trade of plant protection products are regulated by the EU Regulation VO (EU) 1107/2009. Maximum levels of pesticide residues in or on feed and food are regulated in the EU Regulation No. 396/205 in the current version.

PPPs are applied to large areas of agricultural land to control harmful organisms to keep crop yields high. After application, (in most cases (especially herbicides) during distinct and relatively short seasonal periods. or even by application of stained seeds they are released to adjacent water bodies by different pathways.

One pathway is drift, which is directly related to spraying the pesticides in the vicinity of surface water areas and being transported by wind or via atmospheric deposition. Other important pathways from agricultural areas is surface runoff, because of rain events, but also transport by drainages and yard runoff. For soils and the transport of pesticides into groundwater (and into surface water caused by exfiltration), leakage plays the most important role (UBA, 2021). From large-scale studies that monitored herbicide losses to surface water it can be concluded that, on average, less than 2% of the total mass applied within large catchments is ultimately lost to surface waters and that losses occur primarily during and right after the application period (Capel et al., 2001). Other detailed field studies underline, that pesticide contamination in surface water mostly occurs during stormflow events (Boithias, et al., 2014). Consequently, high shares of annual loads are released and transported during a short time period.

In a mesoscale, annual or multiannual approach as applied with the MoRE model such highly dynamic processes cannot be reproduced. In addition, complex hydrological and biogeochemical processes, e.g. leading to metabolization must be highly simplified. Therefore, the focus of evaluation is laid on more common approaches for larger watersheds. In a review from Payraudeau & Gregoire (2012) it is stated that the most approaches to describe pesticides pollution at catchment scale are the use of indicators and conceptual models due to a trade-off between environmental relevance and adaptation to user’s needs. They further stated that at the catchment scale, the hydrological connectivity is perhaps the primary hydrological variable required to correctly assess rapid flow processes as surface runoff and associated pesticide transfer. In the review even the importance of taking into account the pesticide transport both in the dissolved and particulate phases and to integrate erosion processes in such an approach with the fate of pesticide adsorbed to these particles is stressed.

In different EU countries, mainly in the middle, western and northern parts different model approaches are applied to calculate emission from fields under pesticide application into surface waters. The models under the FOCUS group are EU-wide harmonized e-fate models that calculate the concentrations of pesticides in water bodies. The European Food Safety Authoriy (EFSA) prepared guidance on tiered risk assessment for plant protection products for aquatic organisms (EFSA Journal, 2013).

The tiered procedure consists of different steps, whereby the first step represents a very simple approach using simple kinetics, and assuming a loading equivalent to a maximum annual application. The second step is the estimation of concentrations taking into account a sequence of loadings, and the third step focuses on more detailed modelling taking into account realistic worst-case‘ amounts entering surface water via relevant routes (run-off, spray drift, drainage).

The aims of FOCUS (2001) for step 1 and 2 calculations were to represent worst-case loadings‘ and ‗loadings based on sequential application patterns‘ respectively, but should not be specific to any climate, crop, topography or soil type. FOCUS (2001) considered the assumptions at both steps 1 and 2 as very conservative. Spray drift values are essentially based around drift numbers calculated from BBA (2000) and an estimation of the potential loading of PPPs to surface water via run-off, erosion and/or drainage. This loading represents any entry of PPP from the treated field to the associated water body at the edge of the field.

Already at step 1 and 2, concentrations can be calculated, not only for the a.s., but also for metabolites formed in the soil before run-off/drainage occurs. The user must define the properties of the metabolite, including the maximum occurrence of the respective metabolite in soil studies and the ratio of the molecular masses of the parent and metabolite (EFSA Journal, 2013). One of the most important parameters is the ratio of area were pesticides are applicate and the area of surface waters. In the MoRE approach, this ratio can be calculated only in a simplified way. For all of the above mentioned pathways the FOCUS (2001) approach provides algorithms and specifications (based on different crops or application techniques) for some input parameters available at https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2013.3290.

Here only the more simple algorithms for step 1 is presented, which includes calculation of spray drift, surface runoff, erosion or drainage (EFSA Journal, 2013).

Calculation of concentrations resulting from spray drift

Spray drift deposition is the mass that enters the water per surface area of water, and assumed to be a certain fraction of the mass applied per surface area on the treated field:

$$C = \frac{Dsd\ x\ App}{h} \qquad \text{(Equation 16)}$$

Where:
C: concentration in surface water (g/m^3)
App: application dose (rate) (g/m^2)
Dsd: spray drift deposition as fraction of the application dose, that is, mass deposited per surface area of surface water divided by mass deposited per surface area of field (-)
h: surface water depth (m)

With respect to drift, it is assumed that transport appears within the day of application only. One day later, the compound is distributed between water and sediment.

Calculation of concentrations resulting from run-off, erosion or drainage

Run-off, erosion or drainage loadings are defined as the PPP mass that enters the water and is expressed as a fraction of the total mass applied on the contributing treated field multiplied by the surface area of the contributing field:

$$C = \frac{App\ x\ Afield\ x\ LRo}{h\ Asw} \qquad \text{(Equation 17)}$$

Where:
App: application dose (rate) (g/m^2)
LRO:run-off loss as fraction of the applied PPP mass (-)
Afield: area of the field contributing to run-off (m^2)
Asw: surface area of surface water (m^2)
C: concentration in surface water (g/m^3)

An explicit width or length of the water body for the initial step is not defined, because drift loadings are based upon a percentage of the application rate in the treated field. In the EFSA guidelines results from model scenario applications are prepared on the share of drift emitted to surface water based on different crop groups and application techniques.
For run-off, erosion or drainage entries, only a fixed ratio Afield/Asw of 10:1 is defined to reflect the proportion of a treated field from which PPPs are lost to surface water. Model runs of PRZM, MACRO and TOXSWA (FOCUS, 2001) calibrated this number.
In contrast to the drift approach, the run-off/erosion/drainage entry is distributed instantaneously between water and sediment at the time of loading according to the Koc of the compound in order to simulate the process of deposition of eroded soil particles containing

PPPs. In this way, compounds are distributed directly between sediment and water. The relationship between Koc and the distribution between water and sediment is calculated as follows:

$$Fraction\ of\ runoff\ in\ water = \frac{W}{(W+(Seff\ x\ bd\ x\ oc\ x\ Koc)} \qquad \text{(Equation 18)}$$

Where:
W: mass of water (30 g)
Seff:mass of sediment available for partition (0.8 g)
oc: mass fraction of organic carbon in sediment (0.05 g/g)
Koc: PPP organic carbon partition coefficient (cm3/g)
bd:bulk density of the sediment (g/cm3)

Other, even more simple approaches, which consider the often very poor data availability are summarized in draft papers of the ongoing activity of the EEA (together with the input of a subgroup of the Chemicals WG on emission) to prepare guidelines for the emission quantification to surface waters, which also considers pesticides (EEA, 2022, unpublished). Here two methods are described with the first one is based on the national sold volume of pesticides and the second one is based on the application rate per treatment per pesticide on treated area level.

While national sold volumes of pesticides are reported in the EUROSTAT database, the sale of individual pesticides are often known in the MS but is in most cases considered as confidential information. If the volume of a specific pesticide is known as well as the area of application (or can be estimated by crop statistics) the application rate per pollutant per treatment can be combined with the area where the pollutant has been applied and the percentage of the substance reaching the surface water, with:

$$Lsw = Emission\ factor\ x\ Activity\ Rate\ 2 + \%sw \qquad \text{(Equation 19)}$$

Where:
Lsw = load to surface water per pollutant
Emission factor = application rate per pollutant treatment is the maximal use of the pesticide per treatment (in kg active substance per hectare)
Activity Rate 2 = area where the pesticide has been applied in hectare
%sw = estimation of the percentage of pesticides reaching surface water

Obviously, the main goal is to define the factor %sw, which might differ extremely due to several varying factors, like substance behavior, method of application, slope, hydrology, surface water area.

The draft guideline presents different studies were, based on model application, the share of pesticides reaching surface waters, from these, which was applicate to the agricultural area in catchments was quantified (EEA, 2022, unpublished). They conclude, that percentage of pesticides used ending up in the surface water range from 0% (in case no surface water is present) to 5% as a maximum in areas (with abundant surface water like some areas in the Netherlands). In many cases they presented recovery rates well below 1%.

As was mentioned above a multitude of more complex model approaches is available and used in different catchments and areas. Specific models, with the need of numerous input parameters are applied, often on the river reach scale and smaller scales, addressing only one of the above-mentioned pathways. An overview of pesticide models used in the EU can be found on: https://www.pesticidemodels.eu/.

3.2.1.2 Data Availability

Data on sales and uses of Plant Protection Products (PPP) and biocides in Europe is rather limited and often only available on the national scale. This makes it difficult to draw conclusions on local hotspots or assessments of the environmental impact (Mohaupt et al., 2020).

Nevertheless, a large number of different pesticide active ingredients and, in some cases their metabolites, are regularly detected in surface water monitoring approaches of several EU member states to comply with specifications from the Water Framework Directive 2000/60/EC (WFD). In accordance with the requirements of the WFD, the main focus is on the larger surface waters and in most cases are lacking an integration of event-related monitoring approaches (UBA, 2022). The data availability leads to limited data on actual risks of pesticides to European waters (EEA, 2018).

In this project, we aim to merge information and data we could investigate in the pilot region countries with own monitoring data. In detail, this belongs to pesticide sales rates, information on crop-specific application practices, information on relevant crop types in the sub catchments and on pilot specific deposition-, soils, Waste Water- and surface water data from the own investigations (considering base flow and event flow conditions).
Unfortunately, data from own measurements are still not completely available, so that various applications and tests could not yet be carried out.

In the following, the data available in the different pilot regions is described, which mainly relies on data availability in the specific countries.

Romania (Somesul Mic and Viseau)

For the Romanian pilot regions, (Somesul Mic and Viseau) annual national sale rates for 2017 – 2020 could be made available. In this period, a mean of 545 t of s-Metolachlor and 385 t of Tebuconazole was sold in Romania. Furthermore, the agricultural land was calculated, where application seems to be reasonable. Calculating mean annual application rates to the agricultural land in Romania (with potential application) leads to mean application rate of 0,04 (s-Metolachlor) and 0,03 kg/ha*a^{-1} (Tebuconazole).

Information on landuse was derived from Corine Land Cover 2018 (CLC, 2018) – which is not or only very roughly applicable, when e.g. the investigation of crop-specific application is targeted. From this data base a regionalization of application rates is not possible. Consequently, alternative data on crop cultivation in the pilot regions were investigated. The EUROCROPMAP 2018 (Copernicus Sentinel data with 10m resolution) (d'Andrimont, Raphaël et al., 2021) seems to be a database, which could be used to investigate crop-specific information on pilot region scale in Somesul Mic and Viseau.

Bulgaria (Vit)

In Bulgaria product specific information on the application of Tebuconazole and – s-Metolachlor were investigated. For Tebuconazole 22 products containing the substance were found, for s-Metolachlor information on seven products were made available.
Information on minimum and maximum values of dosage, the frequency of application, the crop the product is generally applicate to and the amount of the specific substance

(Tebuconazole and s-Metolachlor) within the applicate dosage is provided. The EUROCROPMAP 2018 (Copernicus Sentinel data with 10m resolution) (d'Andrimont, Raphaël et al., 2021) seems to be a database, which could be used to investigate crop-specific information on pilot region scale in the Vit catchment.

Because, there is no information which product is used for which crop or to which extend, data are difficult to be transformed in a balance, expressing the application of the different substances.
From this data base a regionalization of application rates is not possible. Consequently, alternative data on crop cultivation in the pilot regions were investigated.

Hungary (Zagyva, Koppány)
Data availability on pesticides was best compared with all pilot regions in Zagyva and Koppány. Based on farmers diaries in the catchments very specific information could be provided here, reflecting the yearly rates of Tebuconazole and s-Metolachlor applicate on a multitude of different crops over a period of three years (2016).
Within the database, the number of data sets (probes) and the calculated mean annual- and mean three annual values are available (see Table 1 and Table 2).

Table 1: Number of farmer statistics under evaluation and mean application rates in three years (2016-2018) as well as three years average for Tebuconazole.

Tebuconazole	**No of samples**			**Mean application (kg/ha)**			
	2016	2017	2018	2016	2017	2018	Mean
alfalfa	21	31	15	0,422	0,017	0,028	0,156
water melone	14	13	-	0,040	0,033	-	0,036
coleseed	1258	1705	1493	2,225	0,553	0,021	0,933
poppy-seed	18	17	-	0,189	0,036	-	0,113
oil reddish	13	-	-	0,242	-	-	0,242
sunflower	740	817	301	0,170	0,020	0,014	0,068
winter wheat	6021	6053	5268	0,177	0,022	0,016	0,072
spring wheat	45	93	30	0,201	0,038	0,021	0,087
durum wheat	100	167	150	0,181	0,015	0,018	0,071
spring durum wheat	16	10	-	0,141	0,027	-	0,084
rye	47	38	43	0,147	0,021	0,008	0,059
winter barley	1625	1514	853	0,171	0,023	0,016	0,070
spring barley	226	254	109	0,180	0,026	0,015	0,074
spring oat	96	110	61	0,234	0,037	0,014	0,095
winter oat	15	-	-	0,186	-	-	0,186
maize	49	72	28	0,198	0,012	0,032	0,081
sweet corn	13	17	-	0,140	0,049	-	0,095
triticale	526	509	246	0,188	0,022	0,018	0,076
wild rice	30	-	-	0,200	-	-	0,200
common millet	46	-	-	0,014	-	-	0,014
fallow	11	14	-	0,533	0,085	-	0,309
feed pea	10	-	-	0,242	-	-	0,242
green fallow	13	-	-	0,274	-	-	0,274
apple	1768	1482	1516	1,539	0,040	0,040	0,540
peach	122	242	208	0,209	0,111	0,085	0,135

appricot	305	410	365	0,221	0,078	0,060	0,120
nectarine	11	32	13	0,203	0,158	0,111	0,157
plum	498	626	663	0,215	0,079	0,061	0,118
nut	32	46	53	0,218	0,021	0,019	0,086
mixed fruit	20	11	-	0,188	0,295	-	0,241
pear	100	58	65	0,139	0,055	0,043	0,079
sour cherry	1270	1540	1579	0,202	0,055	0,053	0,103
cherry	293	347	426	0,216	0,072	0,056	0,114
vineyard	3878	9128	9834	0,075	0,047	0,044	0,055
other vine	47	165	177	0,065	0,060	0,062	0,063

Table 2: Number of farmer statistics under evaluation and mean application rates in three years (2016-2018) as well as three years average for s-Metolachlor

s-Metolachlor	**No of samples**			**Mean application (kg/ha)**			
	2016	2017	2018	2016	2017	2018	Mean
potato	22	41	23	0,302	0,179	0,122	0,201
sugar beet	37	54	39	0,373	0,383	0,211	0,322
soybean	244	273	219	0,214	0,174	0,149	0,179
sunflower	1706	2420	1310	0,188	0,180	0,120	0,163
hybrid Sunflower	29	37	22	0,093	0,090	0,091	0,091
Rye	11	31	29	0,136	0,098	0,051	0,095
maize	1181	1600	901	0,316	0,264	0,163	0,248
sweet corn	128	133	95	0,284	0,147	0,115	0,182
silage maze	117	238	72	0,182	0,148	0,079	0,137
hybrid maze	57	86	59	0,086	0,092	0,035	0,071
sorghum	44	85	95	0,222	0,233	0,101	0,185
silage sorghum	87	125	76	0,135	0,138	0,087	0,120
yellow pea	20	-	-	0,316	-	-	0,316
feed pea	13	-	-	0,552	-	-	0,552
grean peas	44	75	26	0,164	0,201	0,098	0,154
apple	28	-	-	0,423	-	-	0,423
sour cherry	26	-	21	0,109	-	0,274	0,192
cherry	19	-	-	0,550	-	-	0,550
vineyard	186	466	134	0,403	0,578	0,275	0,419
oil pumpkin	61	16	-	0,220	0,351	-	0,286

The numbers express rather high annual and crop-specific variation, considering the number of samples but also the calculated crop-specific rates. Rates are highest in 2016 and decrease to 2018 in some cases (crops) by one order of magnitude, in other cases they show comparable results. Due to these partly high variations, it was decided to calculate a multiannual mean crop-specific rate.

Application rates for 35 different crops could be investigated for the Hungarian catchments. With respect to crops the application rates of Tebuconazole range from 0,014 kg/ha*a^{-1} (common millet) to 0,540 kg/ha*a^{-1} (apples). Extraordinary high rates were found in coleseed (0,933 kg/ha*a^{-1}). The mean application to all crops listed is 0,156 kg/ha*a^{-1}.

In case of s-Metolachlor 20 crop-specific application rates could be evaluated. The rates range from 0,091 (hybrid sunflowers) to 0,552 kg/ha*a^{-1} (feed peas). The mean of all crops is 0,244 kg/ha*a^{-1}.

The crop-specific landuse data aggregated by the Hungarian colleagues on base of sub-catchments stem from the national Invekos database and give a sound picture of the relevant crops under cultivation.

For 25 crops area-specific data were evaluated. In the Koppány catchment the reported crops represent 95% of the cultivated area, in the Zagyva pilot around 90%. In Koppány pilot the dominant culture is winter weed, with maize and sunflower are also important crops. In Zagyva also winter weed is the dominant crop cultivated. Here even pastures play a relevant role (not relevant for pesticide application). Beneath winter weed, especial large areas of sunflowers and coleseed are cultivated.

Austria (Ybbs, Wulka)

In Austria, a similar data record like in Hungary could be investigated. With support of the Österreichische Agentur für Gesundheit und Ernährungssicherheit GmbH (AGES) crop-specific application rates could be evaluated for s-Metolachlor and Tebuconazole.

As a precondition to evaluate pesticide and crop-specific application rates, farm records (from Austria) and seed certification data were extrapolated. From around 940 farms and a cultivated area of 28,200 ha evaluated in a AGES project founded by the Federal Ministry of Agriculture, Regions and Tourism, Austrian-wide data from 2017 were used to calculate mean application rates (AGES, 2022).

For 16 crops an evaluation of the use of pesticides was made. For winegrowing and apple production, an evaluation according to the farming method (organic/conventional) was performed. In the arable crops, the evaluation was only carried out for the conventional farming method.

Table 3: Mean cop-specific application rates (most common crops in Austria) of Tebuconazole based on farmer statistics from 2017

Tebuconazole	**kg/ha**
fruits (apples)	0,046
vine	0,037
oat	0,011
spring barly	0,059
spring wheat	0,067
winter barly	0,031
winter rape	0,180
winter rye	0,104
winter triticale	0,053
winter wheat	0,130
maize	0,000*

*0,000018

Table 4: Mean cop-specific application rates (most common crops in Austria) of s-Metolachlor based on farmer statistics from 2017

s-Metolachlor	**kg/ha**

oil pumpkin	0,666
soybean	0,091
sugar beet	0,014
maize	0,102

Application rates of Tebuconazole for eleven main crops calculated in Austria range from 0,011 kg/ha*a^{-1} (oat) to 0,180 kg/ha*a^{-1} (winter rape). Main application rates (excluding the extreme low values for maize) are 0,072 kg/ha*a^{-1}, which is rather half of the mean rate documented in Hungary.

For s-Metolachlor application rates calculated for four main crops range from 0,014 kg/ha*a^{-1} (sugar beet) to 0,666 kg/ha*a^{-1} (oil pumpkin). Mean values of s-Metolachlor are 0,218 kg/ha*a^{-1}, which is similar to that of Hungary, mainly caused by high rates of application to oil pumpkin in Austria.

Detailed information on crops cultivated in the sub-catchments were derived from Invekos data base. To be consistent with the application rates data from 2017 were taken into account. Intersection of data available on level of cadastral municipality with sub-catchments leads to a regionalization of crops, relevant for the application of Tebuconazole and s-Metolachlor.

In the Ybbs catchment eleven crops relevant for Tebuconazole application were cultivated, with fruit trees, vines, oats, spring barley, spring wheat, winter barley, winter rape, winter rye, winter triticale, winter wheat, maize in the downstream sub-catchments. Most common crops were maize and winter wheat. With respect to Metolachlor all relevant crops considered in the application rate assessment were found (Oil pumpkin, soybean, sugar beet and maize), with a clear dominance of maize.

3.2.1.3 Approach

Due to a brief literature review, investigating different modelling approaches on catchment scale and due to data availability (see chapter 3.2.1.1 and 3.2.1.2), it was decided to provide a two-step approach.

In the first step, a crop-specific application rate of the modelled substances is calculated. Such a crop specific approach has the advantage that the application of the pesticides under investigation is clearly related to the situation in the sub-catchment and to the agricultural practice. Consequently, this approach allows a distinct regionalization.

One problem, which might arise, is the inhomogeneous data availability. While in Hungary and Austria detailed information on crops are available from the Invekos database on a scale suitable to aggregate information to the sub-catchments, such data could not be investigated for the other catchments in Bulgaria and Romania, yet. A test, if other data sources, like the EUROCROPMAP 2018 is suitable to provide the missing information in the other catchments and in the Danube basin, can only be verified when the annual loads and concentrations have been calculated on the basis of the own measurements in the sub-catchments. This data set also takes into account the rain and flood events, which are especially important for pesticides and should guarantee a sound adjustment of the model results.

Another hurdle arise from the partly significant differences in the crop- and substance-specific application rates, available in Austria and Hungary. In Hungary, for Tebuconazole the data from 2016 are much higher for some crops, than for 2017 and 2018. While in Hungary many more crop specific mean annual application rates per hectare are quantified, some crop rates show huge difference within the countries, while others are very similar. Due to different agricultural practices, which might arise in the different countries, a mixture of the data set might not be reasonable. In case of pilot regions without this information, both data sets will be tested, to evaluate the best fit.

The second step is a comparison of the annual application rates in sub-catchments with the calculated mean annual loads or concentration. Based on this information a transfer coefficient or a simple algorithm can be calculated to assess the mean annual load or concentration on base of annual application rates.

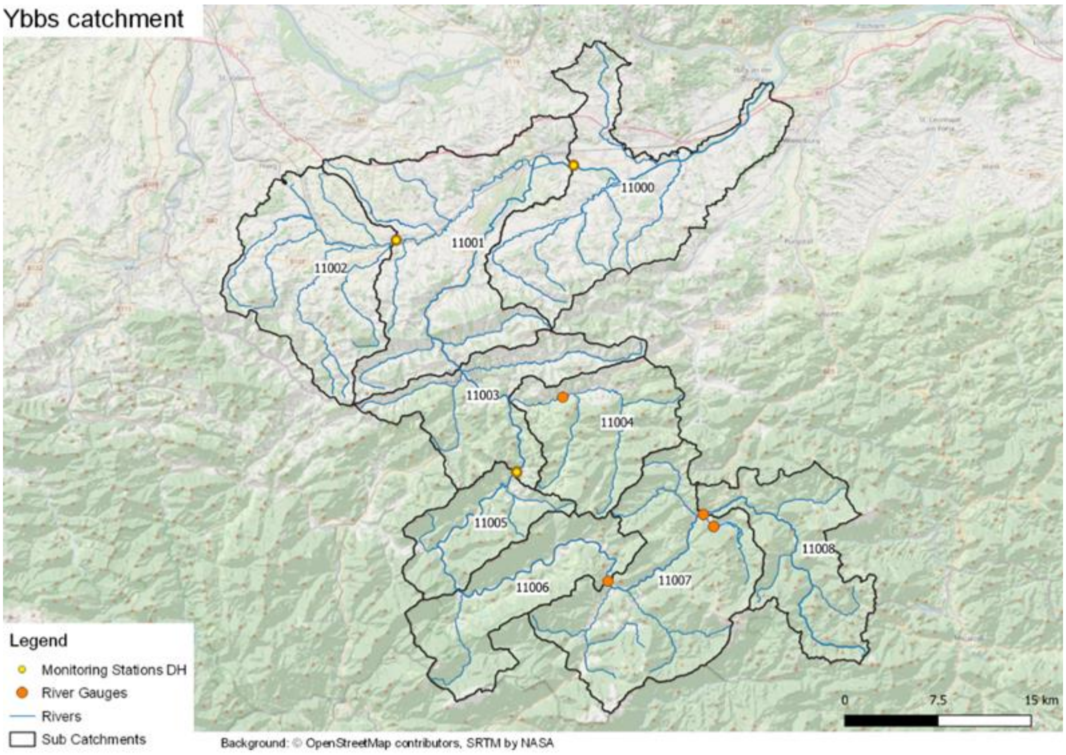
This could be even the starting point for a more detailed view, considering important pathways (like deposition, surface runoff, drainage and erosion), which relies on availability and quality of data.

To prove the concept described above, different evaluations have already been carried out, which are summarized below.

<u>Evaluation of crop-specific cultivation in sub-catchments</u>
In Austrian and Hungarian pilot regions, Invekos build a sound database for crop-specific information. In Austria (exemplarily shown here), data from 2017 were used (sample year for the evaluation of the application rates) related to the cadastral municipality. GIS intersected all crops reported in Invekos with the area of the sub-catchment and information aggregated to the area of the sub-catchment.

In a second step, different crop-types reported were selected and partly aggregated, representing the cultivation types for which application rates were available.

Due to the pre-alpine character of the Ybbs catchment (see Figure 5), only in the downstream sub-catchments 11000 to 11003 crops with potential pesticide application are cultivated, with 11003 only on some minor areas.



Background: © OpenStreetMap contributors, SRTM by NASA

Figure 5: The Ybbs catchment, nine sub-catchments, the DHm3c monitoring stations and additional river gauges.

The area to which Tebuconazole and s-Metolachlor is applicated is exclusively situated in the downstream catchments. In subcatchments 11000 to 11002 the share of crops to which Tebuconazole is applicated is around 20 % of the total sub-catchment area.

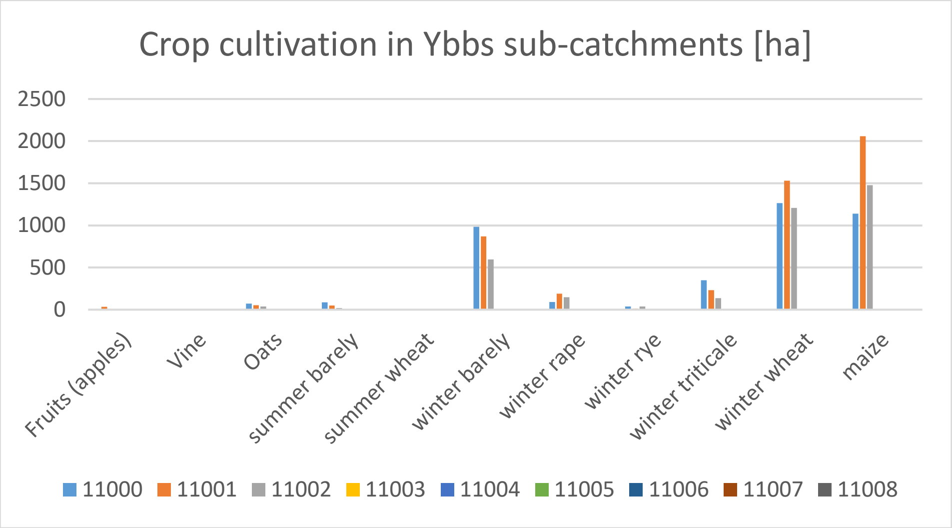


Figure 6: Crop cultivation area with Tebuconazole application in the Ybbs sub-catchments.

For Tebuconazole maize and winter wheat but also winter barely are the cultures of outstanding relevance.

In case of s-Metolachlor the share of the area where crops is applicate decreases compared to Tebuconazole significantly to around 10% in the downstream-catchment.

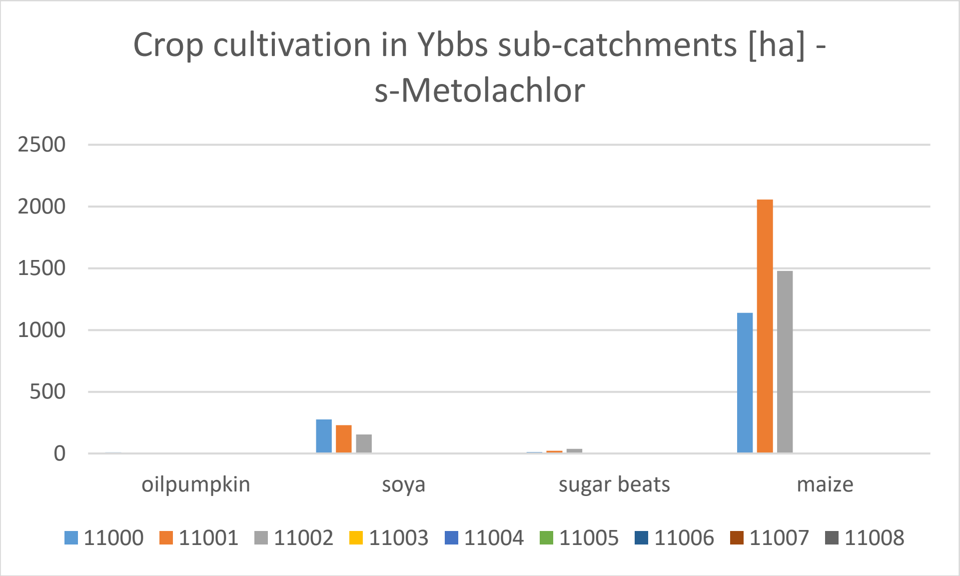


Figure 7: Crops cultivation area with s-Metolachlor application in the Ybbs sub-catchments.

In case of s-Metolachlor, maize is the most relevant crop, which will cause application. Even the cultivation of Soya is of some relevance in the downstream catchments.

The multiplication of the area of potential application with the reported pesticides application rates results in the load of pesticides, which was applied to the sub-catchment.

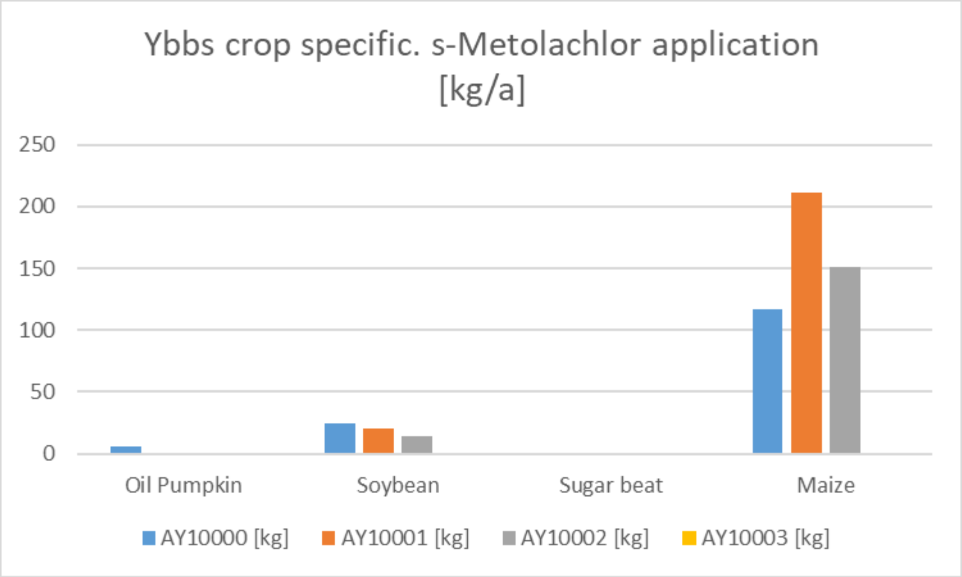


Figure 8: Crop-specific s-Metolachlor application in the Ybbs sub-catchments.

It is found, that 215 to 280 kg/a Tebuconazole (not shown here) and 150 to 230 kg/a s-Metolachlor was potentially applicated to the sub-catchments 11000 to 11002. In 11003 only 0,2 kg Tebuconazole and 0,01 kg/a s-Metolachlor was potentially applicate, while in all the other upstream catchments based on this approach no pesticide application is quantified. In the downstream catchments relating the applicated amount of Tebuconazole and s-Metolachlor to the total area (to provide a comparable annual rate) the rates range only slightly.

Table 5 provides an overview of potential annual application rates [kg/ha*a^{-1}] of Tebuconazole and s-Metolachlor in subcatchments of the pilot regions in Austria and Hungary.

Highest values of Tebuconazole were found in the catchments with an extensive agricultural landuse - Koppany, Zagyva and Wulka. Rates range from 0,126 kg/ha*a^{-1} to 0,030 kg/ha*a^{-1} with maximum values in Koppany and downstream catchments of Zagyva. Rates of s-Metolachlor show a similar picture, with highest values in Koppany but moderate values in Zagyva upstream catchments and in Wulka and Ybbs downstream-catchments. No, or very little rates were found in the Ybbs upstream catchments as well as in the Zagyva upstream catchment (22005).

Table 5: Potential, annual rates calculated from crop-specific Tebuconazole and s-Metolachlor application in Hungarian and Austrian pilot regions.

Pilot region	**sub-catchment ID**	**Tebuconazole [kg/ha*a^{-1}]**	**s-Metolachlor [kg/ha*a^{-1}]**
Koppany*	21001	0,074	0,087
Koppany*	21002	0,126	0,084
Zagyva*	22001	0,074	0,024
Zagyva*	22002	0,091	0,020
Zagyva*	22003	0,026	0,004

Zagyva*	22004	0,006	0,002
Zagyva*	22005	0,001	0,000
Wulka	12000	0,015	0,006
Wulka	12001	0,030	0,005
Wulka	12002	0,026	0,006
Wulka	12003	0,031	0,012
Wulka	12004	0,031	0,015
Wulka	12005	0,015	0,005
Ybbs	11000	0,013	0,008
Ybbs	11001	0,012	0,010
Ybbs	11002	0,014	0,011
Ybbs	11003	0,000	0,000
Ybbs	11004	0,000	0,000
Ybbs	11005	0,000	0,000
Ybbs	11006	0,000	0,000
Ybbs	11007	0,000	0,000
Ybbs	11008	0,000	0,000

* calculated with hungarian application rates

A first rough calculation of loads at the Ybbs outlet results in the following recovery rates (loads calculated with < Limit of Detection (LOD) = ½ LOD):

- 1% Tebuconazole
- 1% s-Metolachlor
- 7% s-Metolachlor-ESA + 4% s-Metolachlor-OA

While the recovery rate found is well in line with the rates addressed in literature, the rate of s-Metolachlor, especially of the metabolites is very high. An assessment of the other catchments should provide more detailed information. It is planned to proceed such an evaluation for all the monitoring sites in the Danube Hazard project.

As long as these data are not available, based on an Austrian data base a verification of plausibility was proceeded, calculating crop-specific application rates of Tebuconazole and s-Metolachlor and relate them to mean concentration from a special measurement program (BMNT, 2016).

44 surface waters and four lakes were selected for the 2015 surveys in cooperation with the federal states. Catchment area ranges from 4,5 to 2783,5 km^2, with 20 catchments below 100 km^2. Most catchments are under intensive agricultural- or moderate agricultural use (25). Further eight catchments show a mixture of agricultural use and are also covered by woods and open areas. The remaining 11 catchments are characterized by wood and aopen areas. Monitoring takes place from April to November on a monthly base (8 samples). Catchments of the monitoring stations were delineated and landuse calculated.
Specific crop types were evaluated based on Invekos data for all catchments. With these data the approach presented above was applied based on the Austrian crop-specific information and potential application rates calculated for Tebuconazole and s-Metolachlor. Figure 9 shows the results of the calculated potential catchment related application rates as box plots.

The calculated application rates (without outliers) range from 0,0 to 0,016 kg/ha*a^{-1} (Tebuconazole) and 0,0 to 0,015 kg/ha*a^{-1} (s-Metolachlor) and show a good accordance with the rates calculated in the Austrian pilot regions.

The data underline that in the subcatchments of the pilot region Wulka, maximum values are calculated for Tebuconazole and values in the area of the 95 Percentile of this bigger sample from the Austrian wide monitoring for s-Metolachlor.

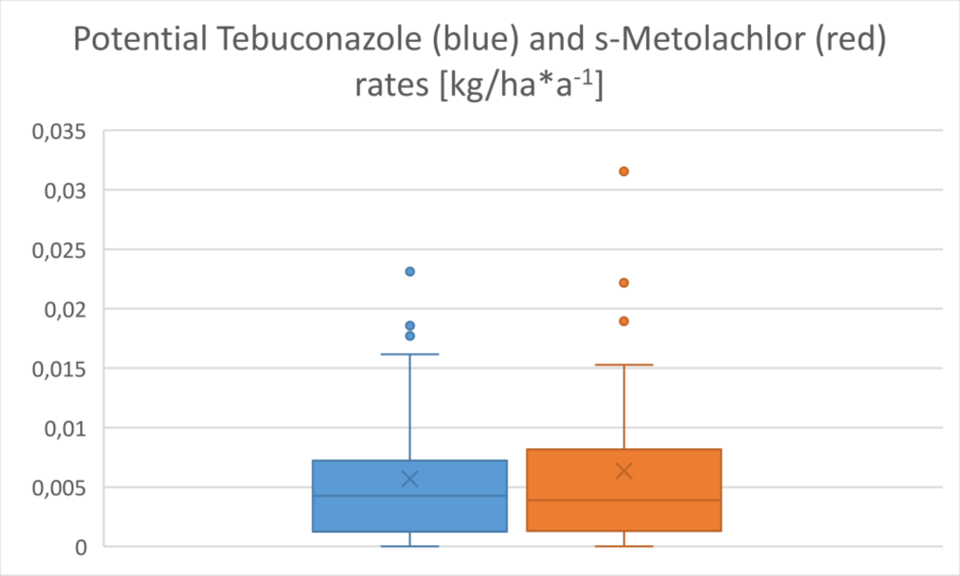


Figure 9: Potential, annual application rates for Tebuconazole and s-Metolachlor from 44 surface water-monitoring sites in Austria. Whisker plots represent the 25 and 75 Percentile, Mean (cross) and Median (crossbar in Whisker), crossbars outside Whisker represent the 95 and 5 Percentile.

It was found, that for s-Metolachlor and for the metabolite Metolachlor – OA there is a good relation between an increasing potential application and the number of values above LOD. For the metabolite Metolachlor – ESA and for Tebuconazole this relation could not be proved.

However for s-Metolachlor as well as for Metolachlor – OA and Metolachlor – ESA a good correspondence could be proved between increasing potential application rates and the mean measured concentration of these substances in surface waters within the survey (Figure 10).

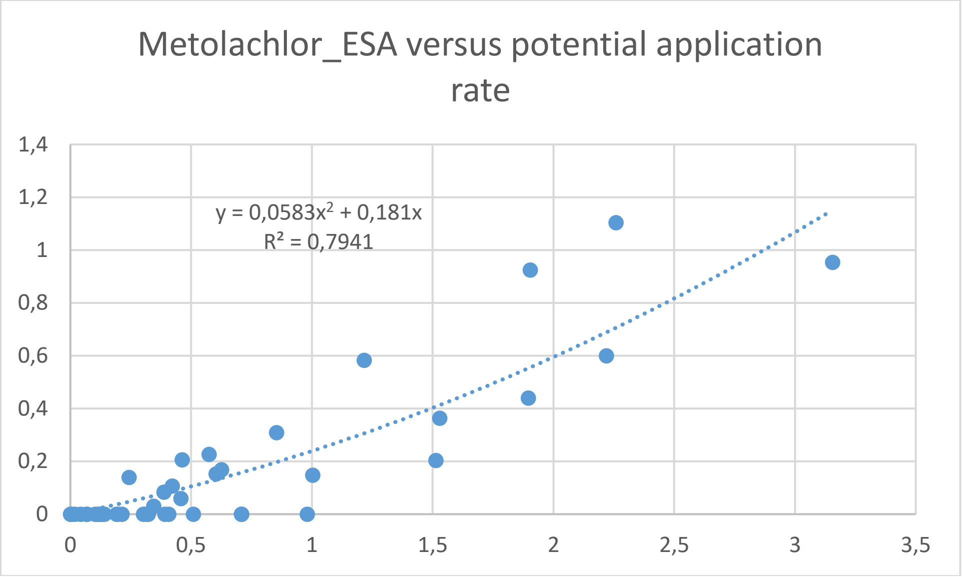


Figure 10: Potential, annual application rates for Metolachlor ESA [kg/km^2*a^{-1}- X-axis] and mean calculated concentration from eight monthly measurements [µg/L^{-1} - Y-axis] from 44 surface water-monitoring sites in Austria (2015).

On the one hand, the results are promising to establish a meso-scale approach to estimate pesticide loads or concentrations based on potential crop-specific application rates. On the other hand there are still open questions to be solved, like:

- Will event specific monitoring from own measurements confirm the results and increase reliability of this first approach?
- How can atmospheric deposition be addressed? - (in some catchments with open area and woods (potential application rate = 0) concentration in surface waters were measured
- Can other specific influences (e.g. catchment and hydrology) be identified? – (in some catchments we calculate potential application rates but have detected no pesticides in surface water)
- Will it be possible to calculate pathway specific emission of pesticides?

These questions will be further evaluated within this project.

3.2.2 Mining sites

3.2.2.1 Background

Mining being addressed concentrates on abandoned non-coal mines levels and adits, with a horizontal passage and less often on mineshafts. Discharges or losses of pollutants as a result of operational mining activities should be reported under the E-PRTR Regulation.

Distinct data from mining and information on approaches to estimate its impact on surface water are rather sparse. This is especially true with respect to diffuse emission. Diffuse pollution from abandoned mining is extremely complex and individually, dependent on a large number of input data and background information, which are usually not available, and which particularly include aspects such as sound information on geology, hydrogeology, biogeochemical processes and even technical information (Nordstrom, 2012) – often related to the small or to the river reach scale. If information are available on the local scale, such cases can be individually modelled following detailed field investigations, using groundwater flow models coupled to substance specific geochemical tools, but cannot be applied for an emission modelling approach on the meso-scale, as is practiced with the MoRE model.

Consequently, the focus on our evaluation is clearly related to the impact of mining from direct discharges, measurable as volume and concentrations and more specific, especially the impact of mining of metal-bearing minerals.

Water pollution problems due to the oxidation and dissolution of metal-bearing minerals, during and after mining, are (for example) widespread in the UK (Jarvis and Mayes, 2012), which leads to intensive investigations in this field. In the above cited, led by the British Environment Agency a method was developed to undertake a national impact assessment, which addresses such matters.

The approach, which can be described as a combination of an non coal mining site-inventory and an surface water monitoring based risk assessment (on EQS values), follows four broad stages, summarized as follows:

1) The identification and provisional prioritisation of water bodies (i.e. sub-basins defined by the European Commission’s Water Framework Directive: 2000/60/EC) impacted by pollution from abandoned non-coal mines.
2) The prioritisation of water bodies with respect to pollution from abandoned non-coal mines against a range of criteria including surface water quality impact, groundwater quality impact, ecological impact and other impacts on water resources (where such information exists).
3) The identification of polluting abandoned non-coal mine sites within priority water bodies.
4) The formulation of priority lists with technical summaries for (a) mine sites with risk of mine water outbreak, and (b) mine sites with surface waste issues with regard to the Mining Waste Directive.

In this project, the Romanian catchment Viseu was selected to address and evaluate the impact of abandoned mining sites on water quality in surface waters for pre-selected substances. To improve the database measurements were performed in discharges of abandoned mining sites and in the receiving surface water.

3.2.2.2 Data Availability

In total six different mining sites were monitored (three-times each) during the project in the region of Maramureș. In case of Emerik, the discharge is treated in all other cases the runoff is directly discharged to the surface waters.

- Gura Băii, 1 Mine
- Colbu, 2 Mine
- Burloaia, 3 Mine
- Emerik II (Toroioaga), 4 Mine (treated)
- Borsa, 5 Mine
- Colbu (Mine Gallery), 6 Mine

For most of the sides, there are additional background information available.

<u>Gura Băii mining perimeter</u>

At this side the mine waters stem from only one gallery. The abandoned mine consists of copper and complex (polymetallic) ore deposits. The gallery is closed with a concrete wall and mine waste backfilling provided with the water drainage pipe and the respective gas drainage pipe. The water flow from the gallery is continuous. The mine waters from the gallery are discharged without treatment into Secu river, a right tributary of the Cisla river. The elevation of the discharge point 1410.77 m.

Colbu mining perimeter

Mine waters are discharged from the Colbu gallery. The discharge point has an elevation of 1000 m and discharges directly into the Colbu river, a right tributary of the Cisla river. The gallery is closed with a concrete wall and a mine waste backfilling. It has an area of 12.000 m^2 and consists of copper and complex (polymetallic) ore deposits.

Burloaia mining perimeter

The mine waters are discharged from the gallery, with an elevation of 931.5 m, in the Cislişoara river, a left tributary of the Cisla river without treatment. The gallery was closed with two concrete walls and mine waste filling between the walls. The abandoned mine consists of copper and complex (polymetallic) ore deposits. The mine waters stem from drainage water of several galleries directed to the basic gallery. The water flow from the gallery is continuous.

Toroioaga mining perimeter (Emerik II)

The discharge coming from the Toroioaga mining perimeter are collected from 4 galleries and are directed to the Emerik II basic gallery from where through a pipe they are discharged in the treatment plant. The mine-water treatment plant has a mechanic and chemical treatment and has a capacity of 90 l / s – (Qmax.day = 7776 m^3/d). The water flow from the gallery is continuous. The abandoned mine consists of copper and complex (polymetallic) ore deposits.

For the two other sides are no specific information available.

3.2.2.3 Approach

The discharge from mining will be implemented into the model structure as a specific point source pathway. Similar to industrial direct discharger the point source will be characterized by metadata and discharge data and concentration data implemented. Annual loads to the surface water will be calculated by a simple multiplication of discharge and concentration and the allocation is assigned to the sub-catchment via coordinates of the discharge point.

3.2.3 Urban systems

3.2.3.1 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, we face conditions in wastewater management in some catchments and sub-catchments of the pilot regions, which are far 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 (tightness) of sewer systems).

For the modelling of the urban systems in the pilot regions first an inventory of situation and the available data in the pilot regions was done. 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 the MoRE model is very flexible with respect to how the calculations are done, both the structure of the urban systems as well as the data availability in the different pilot regions where the key criteria in adapting and constructing the algorithms.

The urban system can be divided into several pathways, which might not be all relevant in all pilot areas. *Table 6* shows a comprehensive 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 6: Overview of the pathways within the urban system 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.

3.2.3.2 Data Availability

Bulgaria (Vit)

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. Some additional data will be obtained in the scope of this project, for instance the concentrations of hazardous substances and discharge in the sewer system from Tetevan during wet and dry conditions.

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

3.2.3.3 Approach

Bulgaria (Vit)
A described in paragraph 3.2.2.2 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.

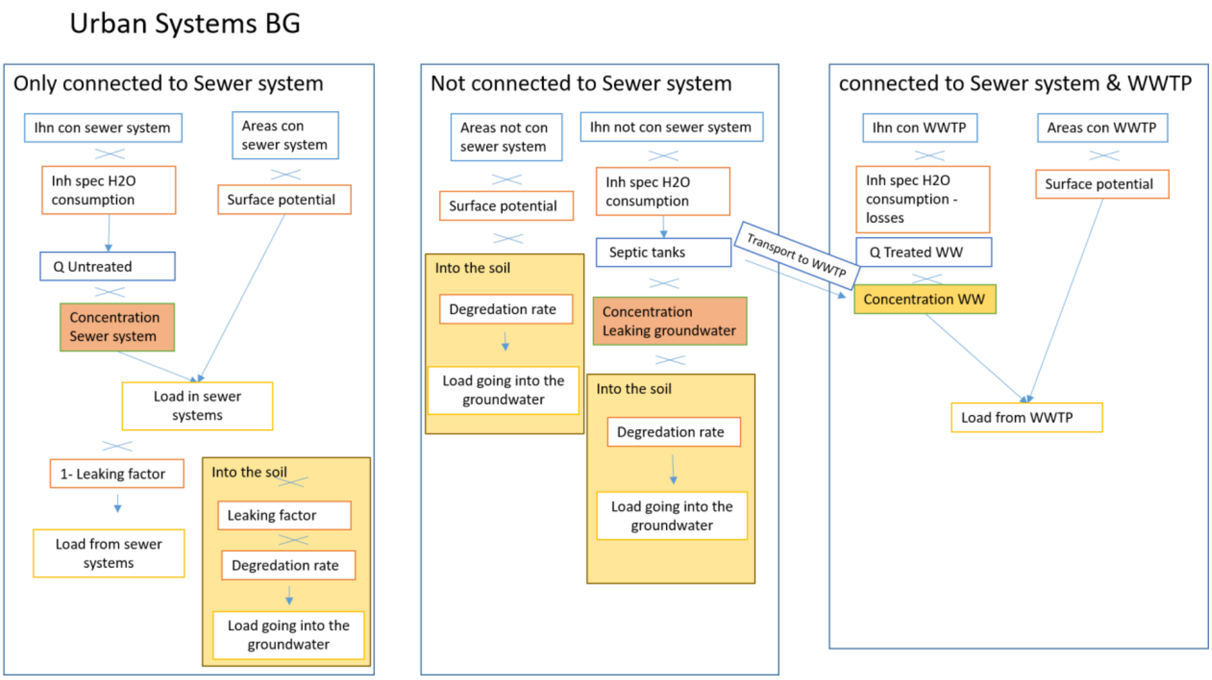


Figure 11: Schematic overview of the urban systems for Bulgaria

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.

Stormwater systems

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 strom water will be obtained from a previous Austrian Project SCHTURM or from measurements in the scope of this project.

Austria (Ybbs, Wulka)

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.

3.2.4 Newly implemented substances

In the following paragraph the modelling approaches for the newly implemented substances will be described. The modeling approach for pesticides are covered in chapter 3.2.1 P as the required an completely new approach, where the approaches for other new substances were leaned based on already existing algorithms.

3.2.4.1 Pharmaceuticals (Diclofenac and Carbamazepine)

For Pharmaceuticals, only the following pathways were deemed relevant: Urban systems & WWTP, these algorithms were copied from already existing algorithms from other substances.

3.2.4.2 Nonylphenol, Bisphenol A and 4-Tert-Octylphenol

For Nonylphenol, Bisphenol-A and 4-Tert-Octylphenol all modelled pathways where are relevant and the needed algorithms were copied from already existing algorithms from other substances.

4. Conclusions

The MoRE model is characterized by flexible model frame, which allows the consideration and representation of specific conditions in the pilot regions. While some variables, formulas and calculation stacks could be taken over from previous applications, with plausibility checks applied, corrections implemented (if necessary) and translation into an English version executed, even all new variables, formulas and calculation stacks were established.

For new substances under evaluation in this project, the new model structure was established and possibilities to implement new approaches to consider pesticide pollution on the meso-scale and specific impacts from mining sites are presented.

Furthermore, the model setup was tested by checking the landuse balances and the water balances. All balances add up and produce meaningful results in case of water balances.

Due to the model structure, approaches could be adapted to specific conditions and data availabilities in different pilot regions (e.g. adaptation of the calculation of urban areas).

All approaches used in the model are illustrated in flowcharts, which give a comprehensive overview of data, variables and formulas involved in the model calculation.

Beneath this progress, there are still open issues, especially related to substance-specific concentrations, which has to be prepared together with WPT1. Associated to this topic is the completion of the pesticide approach and its implementation into the model, but also the check of the balance of suspended solids, which for some substances, is a crucial parameter for a sound model adaptation and the evaluation of annual loads, which is a prerequisite to validate and some extend calibrate the model results.

5. Outlook

A sound model structure to calculate emission from several point and diffuse pathways was setup in a new English model version. To complete modelling, the next important steps are summarized here:

- Calculate substance-specific input data for all pathways in close cooperation with WPT1 (considering three variants: minimum, maximum and mean)
- Setup the substance specific data in the model and implement the variants
- Calculate annual substance-specific loads and suspended solids loads from the monitoring approach in close cooperation with WPT1 (considering three variants: minimum, maximum and mean)
- Test and complete the model approach for pesticides based on the load calculations
- Validate the model results by comparing them with load measurements and adapt the model (if necessary and meaningful)
- Start the system analyses and proceed a risk assessment based on the finalized model results
- Implement scenario analyses on mitigation measures to quantify the potential to reduce loads and concentrations of hazardous substances in surface waters.

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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.