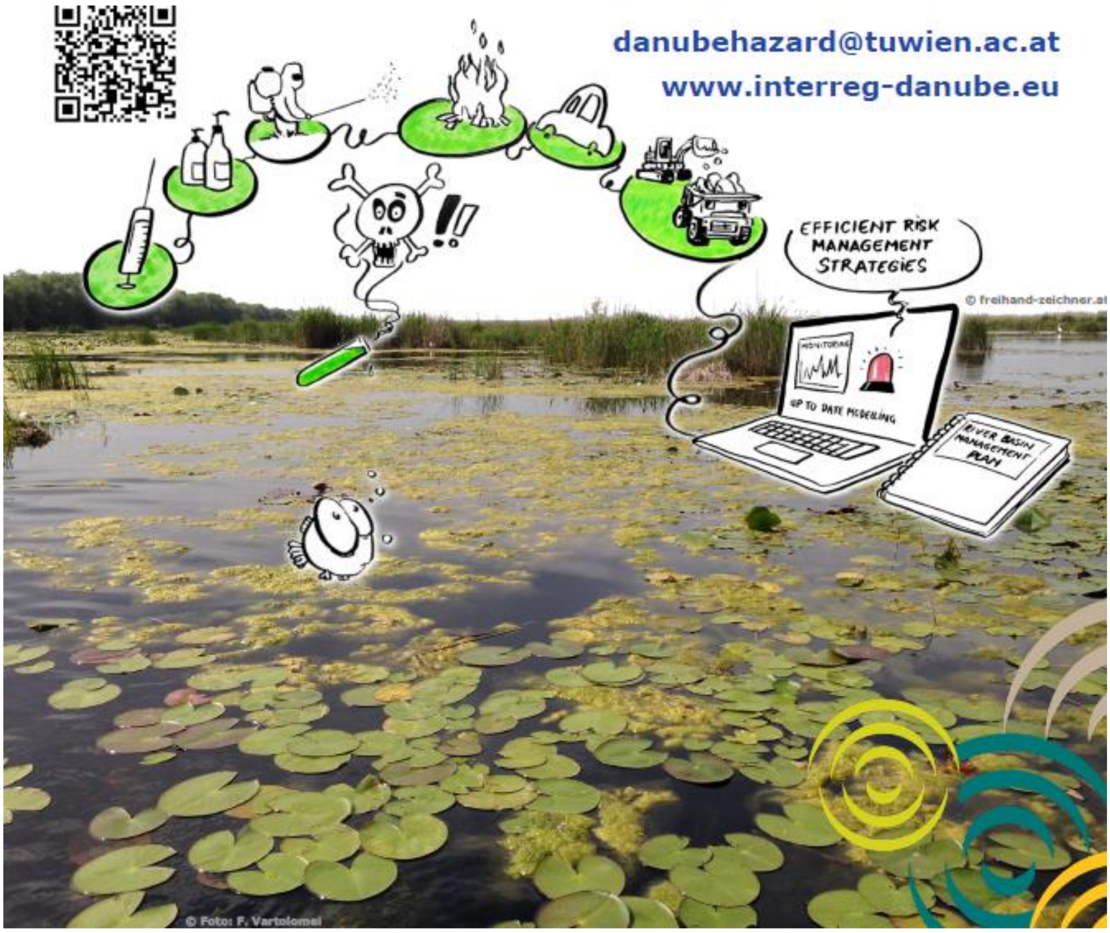

Output O.T3.2

Upgraded version of the Solutions model adapted to territorial needs for transnational modelling of HS emissions in the DRB

(Danube Hazardous Substances Model)

Interreg
EUROPEAN UNION
Danube Transnational Programme

March 2023

PROJECT TITLE: Tackling Hazardous Substances Pollution in the Danube River Basin by Measuring, Modelling-based Management and Capacity building

ACRONYM: Danube Hazard m^{3}c

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Responsible of the Output: International Commission for the Protection of the Danube River

Summary

This output constitutes the upgraded version of the Solutions model adapted to territorial needs for transnational modelling of Hazardous Substances emissions in the Danube River Basin. The model was implemented within the Danube Hazard m3c project and is denoted as Danube Hazardous Substances Model (DHSM).

The DHSM has been set up on the basis of the generic Delft3D open-source modelling framework, the central version of which is maintained by Deltares. The use of this framework is supported by a dedicated portal to download source code and manuals, to exchange experiences and to ask questions (https://oss.deltares.nl/web/delft3d).

This output consists of a file package and an annex, which can be downloaded from here: https://doi.org/10.48436/1yam1-e0y86.

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1 File package

The file package contains four folders:

- DHSM: the generic software plus all input files that together form the implementation of DHSM to the DRB.
- Scenarios: alternative sets of input data for the P25, best estimate (P50) and P75 emission estimates, and for the scenarios S01-S07.
- Supportive: some supportive files for presentation of the results.
- Documentation:
  - The general principles and operation of the DELWAQ framework used for the DHSM are documented in a User Manual (https://content.oss.deltares.nl/delft3d4/D-Water_Quality_User_Manual.pdf)
  - The input file format is documented in a separate manual: (https://content.oss.deltares.nl/delft3d4/D-Water_Quality_Input_File_Description.pdf)
  - The mass balances output is documented in a separate manual, included in the package[1].

The accompanying annex “Danube River Basin Scale Assessment Report” provides a full account of the model approach and implementation.

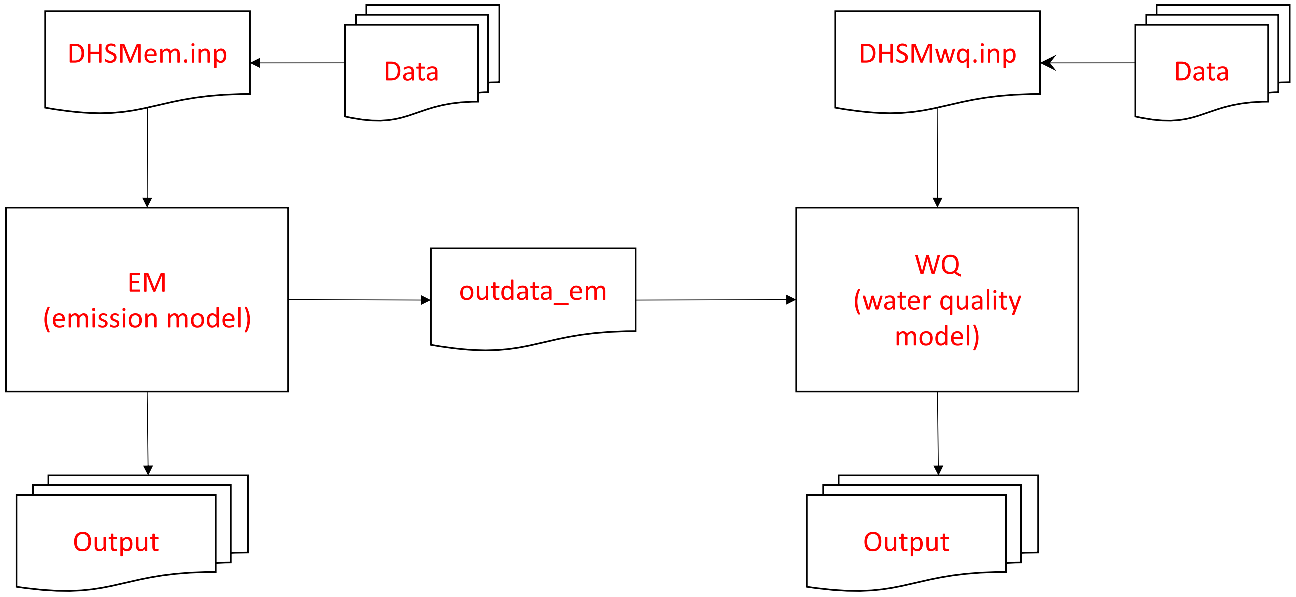
---

[1] Deltares (2018). Water Quality Modelling. Using the mass balances facilities. User Manual. Jos van Gils, Jan van Beek, Erwin Meijers, Version: 5.01. SVN Revision: 57623. August 30, 2018.

2 Guidance on the use of DHSM

2.1 General

The procedure to run DHSM is shown in the below figure:



This figure shows two modelling steps:

1. The emission model, starting from the input file DHSMem.inp
2. The water quality model, starting from the input file DHSMwq.inp

Both steps make use of the same software.

For both steps, the input file contains references to other files, indicated in the scheme as “Data”. The organisation of these files is completely free. This is further explained in the Input File Description Manual. The way this is organized in the current output is just one way to do it and was chosen by the modelling team that developed the DHSM.

The running of both EM and WQ again requires two separate steps. The first step entails the reading of the input file and included data files. The second step is the true simulation. This is explained in the User Manual of the DELWAQ framework.

These two steps are conducted from the command line:

```
delwaq1.exe DHSMem.inp -p<proc_def_em>
delwaq2.exe DHSMem.inp -openpb<em.dll>

delwaq1.exe DHSMwq.inp -p<proc_def_wq>
delwaq2.exe DHSMwq.inp -openpb<wq.dll>
```

where items enclosed in < > are references to system files. The above is a simplified representation. The true commands need to reflect the file locations of the executables, input files and system files.

The output is provided in different text and binary files, as described in the User Manual of the DELWAQ framework. Some supportive tools are available to convert this output to various tabulated text files.

2.2 Organization of the run process

As mentioned above, the organisation of the input file and the references to additional data files is completely free. The DHSM development team has chosen an approach that completely avoids duplication of input for different hazardous substances. Therefore, the primary input files DHSMem and DHSMwq are independent of the modelled substance. Different substances are modelled by copying different versions of the substance dependent data files from the data folder (\DHSM\Data\) to the run folder (\DHSM\Q_Danube\).

The output files inherit their name from the input files. As the same input files are used for all substances, the output files initially have a generic name. They are given a substance specific name and copied to a separate folder (\DHSM\Q_Danube\output\).

This whole process is arranged by a sequence of bat-fles, that starts from:

\DHSM\Q_Danube\runall-em.bat

\DHSM\Q_Danube\runall-wq.bat

We repeat that this is just one way of organizing the simulation process. This organization can be modified as desired, evidently satisfying constraints formulated in the manuals.

2.3 Input

Input files are stored in different folders:

- \DHSM\H_Danube\: data on the schematization and the hydrology;
- \DHSM\S_Danube\: data on the sediment delivery to streams and the in-stream concentrations of SPM;
- \DHSM\Data\: all input for the hazardous substances modelling, including general data and substance-specific data.

The \DHSM\Data\ folder is organized as follows:

Name	**description**
raintot.inc	File containing space dependent total rainfall
agrlu_km2.inc	File containing space dependent area with agricuoture land use
population.inc	File containing space dependent population
flows.inp	File containing flow data to extract output for pilot regions for high flows and low flows in the correct year
FrRainSew.inc	File containing space dependent connection rate to central stormwater collection
wwman_final.inc	File containing space dependent wastewater management data
AR_traffic.inc	File containing space dependent traffic activity rates
CSO_thres.inc	File containing space dependent rainfall threshold for CSOs
pcww.inc	File containing per capita generated waste water

Name	**description**
Built	Folder with files providing source data for built environment
Drydep	Folder with files providing source data for atmospheric deposition
dummy	Folder with files providing dummy data for undefined sources
farms	Folder with files providing source data for agriculture
Households	Folder with files providing source data for households
Industry	Folder with files providing source data for industry
Navigation	Folder with files providing source data for navigation
S1	Folder with files providing data for initial concentrations in soils and soil fate and transport parameters
SubsProps	Folder with files providing data for surface water fate and transport parameters
traffic	Folder with files providing source data for traffic
Treatment	Folder with files providing data for treatment

All input in the \DHSM\Data\ is in text format and contains in most cases either a constant value or a series of 3477 values for all schematization elements in the correct order. Constant values are specified as

```
CONSTANTS name DATA number
```

Space dependent input is specified as:

```
PARAMETERS name ALL DATA 3477 numbers
```

It is noted that a specific format to repeat a certain value is sometimes used (note the absence of spaces in this sequence):

```
3477*1.0
```

Input is recognized by prescribed names, which are listed in section 3.

2.4 Output

The procedure included in the file package collects 8 output files per substance (XX represents a substance abbreviation used in the running of DHSM):

Name	**Contents**
XX_DHSMem-bal.his	From EM: all mass balance terms for all simulated compartments, for “mass balance areas” for every time step
XX_DHSMem-stat.map	From EM: annual means of the emissions to water for 10 years and all schematization elements
XX_DHSMem.his	From EM: time series of masses in all simulated compartments plus additional output at request, for “mass balance areas” for every time step
XX_outdata_em.bin	From EM: emissions data for use in WQ
XX_outdata_em.txt	From EM: emissions description for use in WQ
XXwq-bal.his	From WQ: mass balances per day for the whole model domain

Name	Contents
XXwq-stat.map	From WQ: annual means of the total and dissolved concentrations for 10 years and all schematization elements
XXwq.his	From WQ: time series of concentrations at selected points for every time step

The “mass balance areas” can be defined in two ways:

1. Country-by-country (file: \DHSM\Q_Danube\zones\em-countries.inc)
2. For individual schematization elements (file: \DHSM\Q_Danube\zones\em-maps.inc)

This is arranged in two different versions of \DHSM\Q_Danube\runall-em.bat.

Each of the two versions allows different forms of output processing. The second version leads to long runtimes, big output files and long output processing times, and should only be used to produce output for maps.

As the output files are custom and binary, some tools are provided to extract information. These tools are operated by bat files in the run folder. Each one of these invokes a tool, reads a file with the extension “.def” that defines the information to extract and writes a text file in comma-separated-value format.

Bat file	Purpose	Remarks
balance-em-sources-pathways-emissions.bat	Extracts basin-wide EM mass balance terms for all compartments	For producing figures 2-3 to 2-8 of D.T3.4.1
balance-wq.bat	Extracts basin-wide WQ mass balance terms for surface waters	For producing figure 2-9 of D.T3.4.1
collect-concentrations-annual-averages-tot-dis.bat	Extracts annual concentration averages for total and dissolved concentrations respectively	For producing figures 8-1 to 8-17 of D.T3.4.1
collect-concentrations-pilots.bat	Extracts time series of concentration at pilot areas outlet points	For producing figures in section 9.4 of D.T3.4.1
collect-emissions-annual-totals.bat	Extracts annual total emissions for all segments	For producing figure 3-1 of D.T3.4.1
collect-emissions-countries.bat	Extracts total emissions per pathway for all countries	For producing lower part of figures 2-10 to 2-14 of D.T3.4.1, *will not work if EM is run with map balance areas*
collect-emissions-maps.bat	Extracts total emissions per pathway for all segments	For producing upper part of figures 2-10 to 2-14 of D.T3.4.1, *will only work if EM is run with map balance areas*
aggregate_emission_mapresults.bat	Further processes results from previous step	As above, converts to area-specific values and clusters pathways

Ìt is noted that the output files can also be read using tools like MatLab, Python and R. Reference is made to the User Manual.

Output is provided with prescribed names, which are listed in section 3.

2.5 Supportive files

The file package also provides some supportive files that are needed to prepare input or present output. This concerns:

- File DHSM_spatial_31012023.xlsx that provides spatial data including the order, ID and key properties of the schematization elements.
- File EHype-DBRD.shp that provides the shapes of the schematization elements.

- File DRBMP2021_River4000-DHSM.shp that provides the network of rivers, cut in sections with an attribute “subid-corr” that defines the equivalent schematization element. This file could be used to produce a map with river segments coloured according to their concentrations.
- File DRBMP2021_LWBody100-DHSM.shp that provides the larger lakes, with an attribute “subid” that defines the equivalent schematization element. This file could be used to produce a map with lakes coloured according to their concentrations.

3 Names of model input and output items

3.1 Definitions in EM

The EM part of DHSM distinguishes 6 compartments:

Compartment	Description
Sew	Mixed sewers and WWTPs
Pav	Impermeable surfaces
Unp	Permeable surfaces
Stw	Separated sewers
Sfw	Surface waters (what arrives in this compartment is passed to WQ as emissions)
Soi	Top soil (thickness from the hydrology model)

The sources are numbered as follows:

Source	Description
1	Agriculture
2	Road traffic
3	Built environment
4	Households
5	Industry
6	Navigation
7	Mining (not implemented)
8	Empty

3.2 Input for EM

Item	Description	Unit
ADTot	Total deposition	(g/km2/y)
RainTot	Mean annual rainfall	(mm/y)
FrWet	Fraction allocated to wet deposition	(-)
EV_Bii	Activity rate for source ii	(X)
EF_Bii	emission factor for source ii	(kg/d/X)
BiitoWW	released fraction of source ii to wastewater (further allocated to compartments depending on local infrastructure)	(-)
BiitoSew	released fraction of source ii to receptor Sew	(-)
BiitoPav	released fraction of source ii to receptor Pav	(-)
BiitoUnp	released fraction of source ii to receptor Unp	(-)
BiitoStw	released fraction of source ii to receptor Stw	(-)
BiitoSfw	released fraction of source ii to receptor Sfw	(-)

Item	**Description**	**Unit**
BiitoSoi	released fraction of source ii to receptor Soi	(-)
Pest2Unp	Fraction to soil (pesticides)	(-)
Pest2Air	Fraction to air (pesticides), used to estimate fraction to water	(-)
TotArea	total surface area	(m2)
fPaved	fraction paved	(-)
fUnpaved	fraction unpaved	(-)
fOpenWater	fraction open water	(-)
Rainfall	actual rainfall	(m3/s)
RunoffPav	runoff from paved surfaces	(m3/s)
RunoffUnp	runoff from unpaved surfaces	(m3/s)
Infiltr	infiltration	(m3/s)
Exfiltr	exfiltration	(m3/s)
FrRainSew	fraction of stormwater to sewer systems	(-)
Population	population	(cap)
PCWastWat	per capita production of wastewater	(L/cap/d)
FrSewered	fraction of wastewater to sewer systems	(-)
FrSldgRem	fraction of sludge removed (not reused)	(-)
FrSeptic	fraction of wastewater to septic tanks	(-)
FrTreat1	fraction primary treated of collected wastewater	(-)
FrTreat2	fraction secondary treated of collected wastewater	(-)
FrTreat3	fraction tertiary treated of collected wastewater	(-)
Eff_Septic	fraction to surface water from septic tanks	(-)
Eff_Treat1	fraction to effluent for primary treatment	(-)
Eff_Treat2	fraction to effluent for secondary treatment	(-)
Eff_Treat3	fraction to effluent for tertiary treatment	(-)
Sld_Septic	fraction to soils for septic tanks	(-)
Sld_Treat1	fraction to sludge for primary treatment	(-)
Sld_Treat2	fraction to sludge for secondary treatment	(-)
Sld_Treat3	fraction to sludge for tertiary treatment	(-)
Eff_RS	Fraction to effluent of rain sewers influent	(-)
Sld_RS	Fraction to sludge of rain sewers influent	(-)
fComSew	fraction of combined sewers	(-)
SewLeakage	sewer leakage / CSO definition	(- or mm)
SoilThick	soil thickness	(m)
SoilPoros	soil porosity	(-)
RhoDM	soil dry matter density	(kg/m3)
FacErod	scale factor on erosion terms	(-)
ErodIM1	erosion flux of 1st fraction	(g/d)
kBurial	burial rate of unpaved pool	(-)
DecPav	decay rate paved	(/d)
DecUnp	decay rate unpaved	(/d)

Item	Description	Unit
KdUnpa	mobile fraction in Unp	(-)
DecSoi	decay rate soils	(/d)
KdSoi	mobile fraction in Soi	(-)
ro_lothr	run-off from hard surfaces lower threshold	(mm/d)
ro_hithr	run-off from hard surfaces upper threshold	(mm/d)
disp_hithr	dissolved transport, threshold for runoff + infilt	(mm/d)

3.3 Output from EM

Fluxes in balances:

Item	Description	Unit
dInitSoi	release to receptor Soi at initialization	(g/d)
dRelAtmxxx	release from atmospheric deposition to receptor xxx	(g/d)
dRelBiixxx	release from source ii to receptor xxx	(g/d)
dpav2sew	paved areas to mixed sewers	(g/d)
dpav2stw	paved areas to separated sewers	(g/d)
dpav2sfw	paved areas to surface waters (direct)	(g/d)
dpav2soi	paved areas to soils	(g/d)
dpav2dec	degradation on paved areas	(g/d)
dunp2sfwro	surface runoff from permeable areas	(g/d)
dunp2soiin	infiltration from permeable areas into soils	(g/d)
dunp2soibu	burial from permeable areas to soils	(g/d)
dunp2dec	degradation on permeable areas	(g/d)
dsew2sfwl	combined sewer overflows or leakages	(g/d)
dsew2rem	removal in treatment plants	(g/d)
dsew2sfwe	effluents from treatment to surface waters	(g/d)
dsew2soi	distributed sludge from treatment	(g/d)
dsew2sfwu	discharges from unconnected sewers	(g/d)
dstw2rem	removal in stormwater collection systems	(g/d)
dstw2sfw	from separated sewers to surface waters	(g/d)
dstw2soi	from separated sewers to soils	(g/d)
dsoi2rem	removal in soils	(g/d)
dsoi2sfwer	from soils to surface waters (erosion)	(g/d)
dsos2sfw	from soils to surface waters (subsurface)	(g/d)
dsfw2exp	total emissions to surface waters from EM to WQ	(g/d)

Other output:

Item	**Description**	**Unit**
Emis_Sfw	emission to water	(g/s)
RO2ComSew	runoff from paved areas to mixed sewers	(m3/s)
WW2ComSew	wastewater to mixed sewers	(m3/s)
ConcROp	concentration in runoff from paved areas	(g/m3)
ConcROu	concentration in runoff from unpaved areas	(g/m3)
ConcWW	concentration in raw WWTP influents	(g/m3)
ConcDR	concentration in drainage from soils	(g/m3)
Sew	mass in compartment Sew	(g)
Pav	mass in compartment Pav	(g)
Unp	mass in compartment Unp	(g)
Stw	mass in compartment Stw	(g)
Sfw	mass in compartment Sfw	(g)
Soi	mass in compartment Soi	(g)

3.4 Definitions in WQ

The WQ part of DHSM has a single state variable:

Item	**Description**	**Unit**
HAZ	Hazardous Substance	(g/m3)

3.5 Input for WQ

Item	**Description**	**Unit**
ErodIM1	fine sediment delivered to streams	(g/d)
IM1	inorganic matter (IM1), represents SPM	(gDW/m3)
VSedIM1	net settling velocity IM1	(m/d)
KdHAZIM1	partition coefficient to IM1	(m3/kgDM)
RcHAZ	first-order rate const. loss HAZ	(1/d)
TcHAZ	temperature coefficient loss HAZ in water	(-)

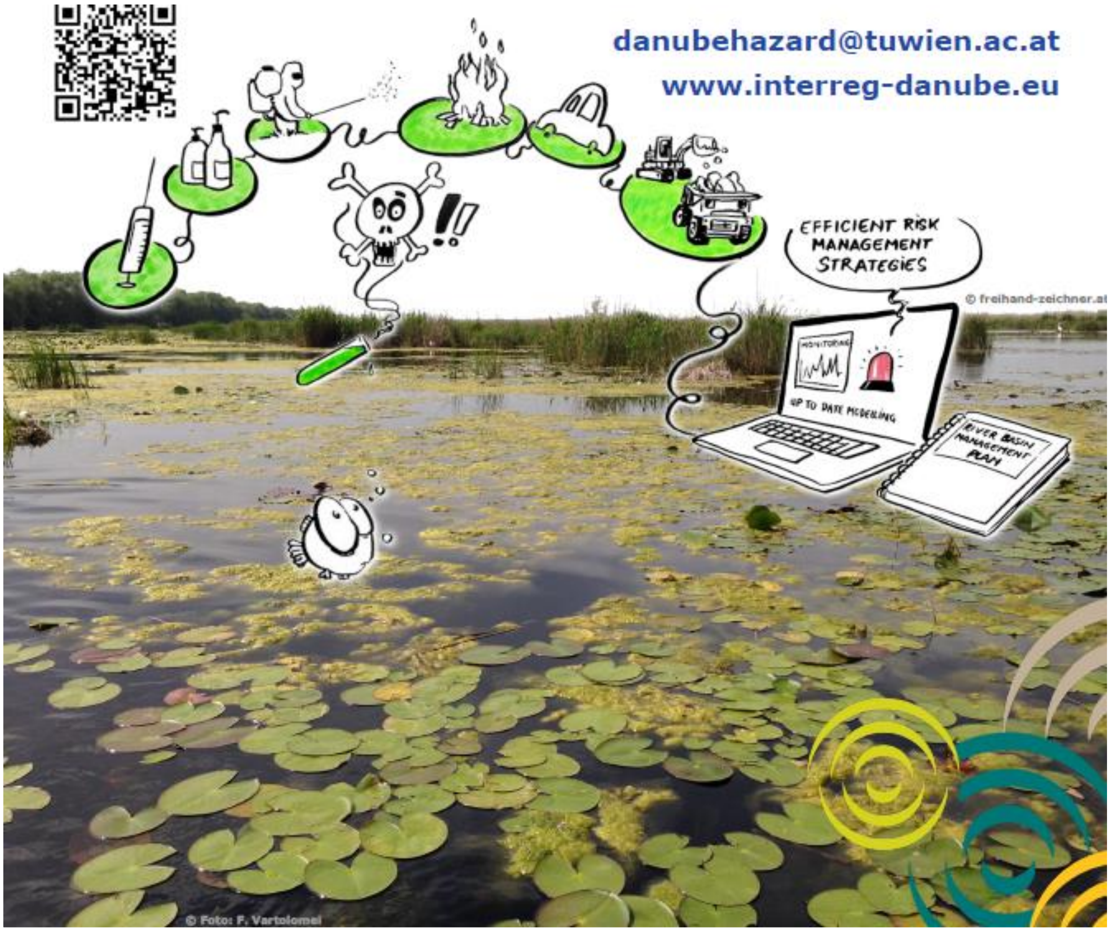
3.6 Output from WQ

Fluxes in balances:

Item	**Description**	**Unit**
dEmis	Emission flux received from EM part	(g/d)
dLossHAZ	overall loss flux HAZ in water	(g/d)
dSedHAZ	net settling flux HAZ towards sediment	(g/d)

Other output:

Item	Description	Unit
FrHAZDis	fraction free dissolved HAZ in water column	(-)
FrHAZIM1	fraction adsorbed to IM1	(-)
DisHAZ	free dissolved HAZ in water column	(g/m3)
QHAZSS	overall suspended solid quality HAZ	(mg/kgDW)
fSedHAZ	sedimentation flux HAZ towards S1	(gHAZ/m2/d)



Annex to Output O.T3.2

Danube River Basin Scale Assessment Report

Interreg
EUROPEAN UNION
Danube Transnational Programme

March 2023

PROJECT TITLE: Tackling Hazardous Substances Pollution in the Danube River Basin by Measuring, Modelling-based Management and Capacity building

ACRONYM: Danube Hazard m^{3}c

PROJECT CODE: DTP3-299-2.1

DATE OF PREPARATION: 31. March.2023

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Responsible of the Output: International Commission for the Protection of the Danube River

The DHSM schematization and hydrology data were derived from output from the E-Hype model by the Swedish Hydrological and Meteorological Institute SMHI.

Executive summary

The Danube Hazard m3c Project, funded by the Danube Transnational Program (DTP), aims to achieve a durable and effective transnational control and reduction of hazardous substances (HS) water pollution. It builds on the three elements of water governance (monitoring, modelling and management) complemented by capacity building. Among many other things, Danube Hazard m3c aims to develop pollution assessments and recommendations for management interventions at the scale of the Danube River Basin (DRB). To support such assessments and recommendations, the Danube Hazardous Substances Model (DHSM) was developed and implemented.

This report is divided into two parts. The first part provides a Danube River Basin Scale assessment of HS pollution, realized on the basis of DHSM model simulations. This is an updated version of the preliminary assessment reported in 2021. These earlier results already provided input to the 2021 3rd Danube River Basin District Management Plan (DRBMP). The present assessment is intended to support the development of the 2027 4th DRBMP and to contribute guidance to the related water management activities in the DRB until 2027 and beyond.

This report presents a basin-wide emission inventory for 17 HS. These substances were selected to represent relevant sources and pathways of HS, so that their emission inventories would provide valuable insights not just for these 17 substances, but for a wide spectrum of HS. The adopted methodology was directly derived from the relevant EU Guidance. The “source-oriented” approach was selected to offer the best possible insight in the origin of the emissions, as a basis for the definition of emission reduction measures.

The method relies on mass balances: it quantifies “sources” of HS to the environment and traces them via various pathways towards the surface waters. It makes use of spatial information (population, land use, wastewater management, etc.) to quantify these sources and pathways. Spatio-temporal information about the basin hydrology and about sediment transports is used to quantify temporal variability of emissions and surface water quality.

Emissions have been quantified as a function of time and space for the whole Danube River Basin, using 10 different hydrological years. The results therefore give insight in the inter-annual variability of the emissions as affected by climate variability. In addition, in-stream concentrations have been calculated for the same period. The simulated concentrations show a satisfactory agreement with measured concentrations. For HS where data from the existing Transnational Monitoring Network were not sufficient for the model validation, results from complementary monitoring conducted within Danube Hazard m3c were used. Targeted measurement campaigns carried out in pilot regions were available to fill critical data gaps and to support a critical evaluation of the modelling results in these regions.

Next to the overall emissions inventory, this report presents their subdivision over all pathways distinguished in the EU Guidance. Spatial gradients were mapped and country inventories were presented to further elucidate spatial gradients in the Danube River Basin. Basin-wide mass balances for various key compartments (e.g. impermeable surfaces, sewers and wastewater treatment, soils, surface waters) were presented for all 17 HS to provide further insight in HS mass flows.

To reflect the uncertainty of emission estimates, a low and a high estimate were developed, next to the middle (best) estimate. The inter-annual variability of emissions and water quality due to climate variability was quantified. Metals emissions typically vary by a factor of 2-4 between individual years, as a result of the variability of erosion. For other HS, the variability of emissions is a factor 2 at most, with very low variability for pharmaceuticals as their emissions are not affected by weather. For the concentrations along the river Danube, the inter-annual variability is again highest for the metals (typically a factor 1.5-2.5), again due to the variable erosion. There is also considerable inter-annual variability (almost a factor 2) for HS with by approximation constant emissions (e.g.

pharmaceuticals), due to the variable in-stream dilution. This inter-annual variability is however mostly smaller than the uncertainty of the calculated emission (typically a factor 2-4).

The uncertainty of the DHSM results increases with decreasing spatial scale. Many spatially variable input quantities could only be quantified on a country-by-country basis. This implies that the results for the main branch of the Danube and for the large international tributaries like Sava and Tisa are probably more robust than those for the smaller tributaries.

Based on the results presented in this report, climate change could possibly have two effects at the scale of the Danube Basin as a whole. First, an increasing occurrence of high erosion events would lead to increasing emissions of HS whose emissions are (partly) determined by erosion. Second, an increasing occurrence of low discharge events would lead to higher concentrations of a wide range of HS due to lower dilution. Whether or not such climatic changes can indeed be expected was not subject of study.

Exploratory scenarios were simulated to investigate the potential effect of pollution control measures. The success of measures targeting wastewater management was found to be dependent on the removal in treatment plants. Advanced treatment to remove pharmaceuticals (quaternary step) was found to be specially effective if all plants > 10,000 population equivalents would be upgraded.

Some scenarios targeted stormwater management. A scenario investigating collection and treatment of stormwater showed variable results. The concentrations of some HS would actually increase, dependent on the concentrations in stormwater and the removal in treatment plants. A scenario investigating storage and infiltration of stormwater showed a consistent reduction of emissions and improvement of water quality.

A final scenario investigating erosion reduction measures showed positive effects on all metals and, to a lesser extent on other HS with a more limited contribution of erosion to the total emissions.

The second part of this report provides a complete account of the modelling methodology, of the implementation and of the validation of the DHSM. It discusses the overall modelling approach, the target chemicals addressed, the overall model setup and the details about emission and fate and transport modelling. The report further details all aspects of the actual implementation of the DHSM, including the general data that are needed to perform the modelling, such as population and land-use, hydrology and wastewater management, as well as the quantification of individual sources of HS. The validation of the DHSM includes a comparison of simulated concentrations and regular monitoring data from the Transnational Monitoring Network, data from the Joint Danube Survey 4, supplemented by data collected in the Danube Hazard m3c project in 2021-2022 at 6 selected stations.

The Danube Hazard m3c project collected supplementary data in 7 pilot regions across the basin. These data have been used to evaluate the model performance in these smaller regions, and to identify the need for improvements of the basin-wide DHSM during the implementation stage. An interesting aspect of the pilot region sampling is the high resolution in time, which allows the separation of low flows and high flows. This allowed a comparison between DHSM simulated concentrations and pilot region observed concentrations for low flows and high flows separately. A good agreement between simulated and observed concentrations in the pilot regions was not an objective by itself. The comparison served to find inconsistencies and possible improvements of the full basin application. This implies that “generic” aspects were considered most relevant and local aspects were only considered if they offered a possible improvement at the basin scale.

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List of Abbreviations

AR	Activity rate, used in definition of sources
CSO	combined sewer overflow
DHm3c	Danube Hazard m3c project
DHSM	Danube Hazardous Substances Model
DRBD	Danube River Basin District
DRBMP	Danube River Basin Management Plan
EF	Emission factor, used in definition of sources
E-PRTR	European Pollution Release and Transfer Register
EQS	environmental quality standards
HS	Hazardous Substances
IAS	Individual and other Appropriate Systems

ICPDR	International Commission for the Protection of the Danube River
JDS	Joint Danube Survey
LS	local systems
PAH	Polycyclic Aromatic Hydrocarbon
PFAS	Per- and polyfluoroalkyl substances
SE	Schematization element
SPM	Suspended Particulate Matter
TNMN	Transnational Monitoring Network
WWTP	Wastewater treatment Plant
UWWTD	Urban Wastewater Treatment Directive
WFD	Water Framework Directive

Substance abbreviations used:

Cd	Cadmium
Pb	Lead
Cu	Copper
As	Arsenic
Ni	Nickel
Hg	Mercury
Zn	Zinc
BaP	Benzo[*a*]pyrene
PFOS	perfluorooctanesulfonic acid
PFOA	perfluorooctanoic acid
BpA	Bisphenol A
NP	Nonylphenol
OP	4-tert-octylphenol
Met	Metolachlor
Tcz	Tebuconazole
Cbz	Carbamezepine
Dcf	Diclofenac

Country abbreviations used:

AT	Austria
BA	Bosnia and Herzegovina
BG	Bulgaria
HR	Croatia
CZ	Czech Republic
DE	Germany
HU	Hungary
MD	Moldova
ME	Montenegro
RO	Romania
RS	Serbia
SK	Slovakia
SI	Slovenia
UA	Ukraine

Part A – Danube River Basin scale assessment

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1 Introduction

1.1 The Danube Hazard m3c project

The Danube Hazard m3c Project, funded by the Danube Transnational Program (DTP), aims to achieve a durable and effective transnational control and reduction of hazardous substances (HS) water pollution. It builds on the three elements of water governance (monitoring, modelling and management) complemented by capacity building. Specifically, the project aims to improve the knowledge and understanding of the status quo of HS water pollution in the Danube River Basin (DRB), by integrating and harmonizing available existing data of HS concentration levels and by modelling emissions at catchment scale and in pilot regions. Although not the main focus of the project, targeted measurement campaigns have been carried out to fill critical data gaps needed to provide a robust basis for modelling and management. A further goal is to enhance the transnational management of HS water pollution, through: (i) coordinated prioritization of transnational measures with consideration of territorial needs, pursued through basin-wide emission modelling, assessment of management scenarios and elaboration of policy recommendations and (ii) tailor-made training activities.

Danube Hazard m3c aims to develop pollution assessments and recommendations for management interventions at the scale of the DRB. To this end, the project builds on the project SOLUTIONS (https://www.solutions-project.eu/), funded by the EU 7th Framework Programme, that was completed in 2018. Within the SOLUTIONS project, a spatially and temporally explicit model to assess HS water pollution was developed that was set up, tested and validated for inter alia the DRB. An updated version of this model, the Danube Hazardous Substances Model (DHSM), was used to perform hazardous substances modelling within Danube Hazard m3c. The update involved the extension of the SOLUTIONS model to substances relevant for the DRB, and the adaptation of the SOLUTIONS model to specific territorial needs and deeper system understanding.

1.2 Scope and outline of this report

This report is divided into two parts. The first part provides a Danube River Basin Scale assessment of HS pollution, realized on the basis of DHSM model simulations. This is an updated version of the preliminary assessment reported in 2021 (Deltares, 2021, 2021a). These earlier results already provided input to the 2021 3rd Danube River Basin District Management Plan (DRBMP). The present assessment is intended to support the development of the 2027 4th DRBMP and to contribute guidance to the related water management activities in the DRB until 2027 and beyond.

Section 2 presents an inventory of current emissions and provides basin-wide mass balances of key compartments. The spatial variability is addressed in the form of maps and a country-by-country emission inventory. Section 3 discusses the uncertainty of the emission inventory, in the context of the variability of emissions and water quality caused by climate variability. The relation between HS pollution and climate change is of specific interest. Though the relation with climate change is out of the scope of Danube Hazard m3c, the effect of climate variability could be investigated and is discussed here. Section 4 explores the effects of pollution control measures on the emissions of HS and on the water quality. Section 5 presents the conclusions and recommendations from the first part of the report.

The second part of this report provides a complete account of the modelling methodology, of the implementation and of the validation of the DHSM. Section 6 discusses the overall modelling approach. It discusses the target chemicals addressed, the overall model setup and the details about emission and fate and transport modelling. Section 7 presents all aspects of the actual implementation of the DHSM, including the general data that are needed to perform the modelling, such as population and land-use, hydrology and wastewater management, as well as the quantification of individual sources of HS. Section 8 presents the validation of the DHSM.

2 Present emissions of hazardous substances in the DRB

2.1 Methodology

The emission inventory presented below relies on the Technical Guidance on the Preparation of an Inventory of Emissions, Discharges and Losses of Priority and Priority Hazardous Substances (European Commission, 2012). It further makes use of a recent report issued by the European Environment Agency (van de Roovaart et al., 2022), which provides supplementary advice and aims to provide practically applicable methods, and to contribute to the harmonisation of the methods used across Europe.

The Technical Guidance defines **sources** as “all processes and activities that are likely to contribute to the input of pollutants into the environment”. **Pathways** are “the means or routes by which specific substances can migrate or are transported from their various sources to the aquatic environment”. The Technical Guidance defines three approaches to compile an emission inventory for the aquatic environment: the “source oriented”, the “pathway oriented” and the “riverine load” approaches, see Figure 2.1.

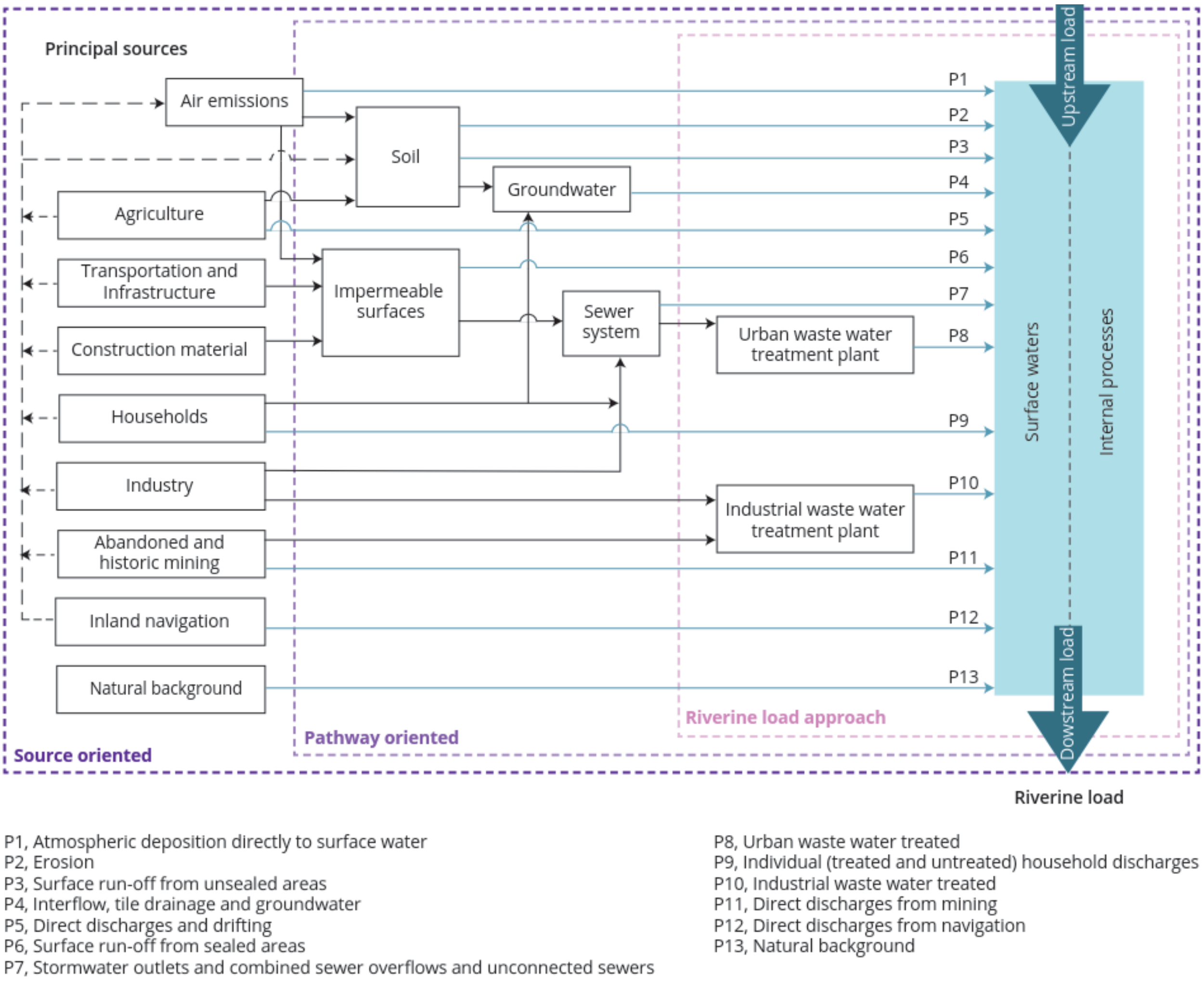
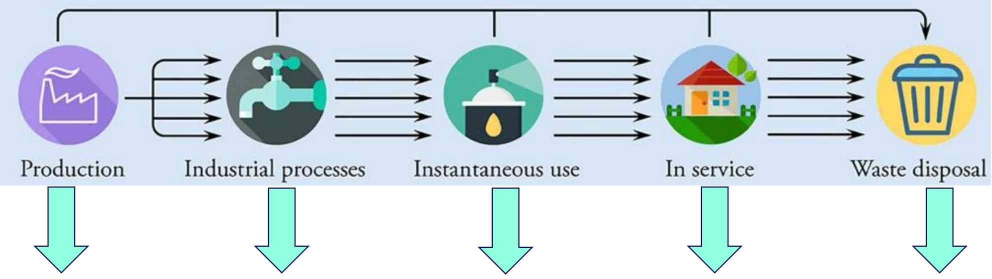


Figure 2.1: Schematic representation of source-oriented approach towards emission modelling and key pathways (source: Whalley et al., 2018, after an original from European Commission, 2012).

The present inventory is based on a source-oriented approach. As this approach provides the best possible insight in the origin of the emissions, it produces essential information for the definition of emission reduction measures. The source-oriented method in principle relies on a Material Flow Analysis. For man-made chemicals, this starts from the production of the chemical. Losses to the environment (sources) can be associated to various life-cycle stages, see Figure 2.2. This includes losses during production and industrial use, from consumptive use, from stocks in products, buildings, infrastructure, and from waste management. Consequently, the sources distinguished in the modelling can be from any of these life cycle stages.



(adapted from Li et al., 2021)

Figure 2.2: Symbolic representation of sources of HS generated during various life cycle stages.

The Technical Guidance considers atmospheric deposition as a source, though actually it is a pathway. It is the result of sources towards the atmosphere being transported to the aquatic and terrestrial environment. To consider atmospheric deposition a pathway is a practical solution, also because atmospheric transports often involve larger spatial scales that exceed river basin boundaries. As it is a pathway, the interpretation towards the underlying true sources needs to be provided by expert judgement.

The build-up of stocks in the techno-sphere may take a longer period after the start of the use of a chemical. Depending on the service-lifetime of the products or constructions involved, this could span a period of decades or more. To avoid such timescales in the simulation of emissions, the present stocks of HS are seen as the “activity” contributing to the input of HS into the environment. For natural HS (typically metals) a similar consideration holds for their natural presence and/or build-up of stocks in the soils.

The Danube Hazardous Substances Model has been implemented and validated using the methodology outlined above. A full account is provided in Part 2 of this report. Part 1 presents an emission inventory and various assessments based on the DHSM.

2.2 Basin-wide emissions to surface waters

Basin-wide emissions to surface waters have been estimated for current conditions. The emissions are subdivided according to the pathways listed in Table 2.1. Column 2 of this table links to the terminology in the Guidance (Figure 2.1). Column 3 lists the abbreviations used in tables and graphs of this report. Column 4 indicates the clusters used in some map presentations in this report. It is noted that the discharges to surface waters from (abandoned and historic) mining (P11 in Figure 2.1) could not be quantified on the basin scale and therefore had to be left out of the inventory.

Table 2.1: Overview of pathways included in the emission inventory

Description	Abbrev.	Pathway	Cluster
Atmospheric deposition directly to surface waters	Atm	P1	Direct releases
Erosion	Ero	P2	Erosion - subsurface flow
Surface runoff from permeable surfaces	SRO	P3	Surface runoff
Drainage + Groundwater (subsurface flow)	DGW	P4	Erosion - subsurface flow
Direct emissions to surface waters from agriculture (spray drift)	Agr	P5	Direct releases
Runoff from impermeable surfaces to surface waters (outside urban areas)	ROimp	P6	Stormwater and CSOs
Emissions from wastewater collected but not connected to a WWTP	Unc	P7	Wastewater
Combined sewer overflows	CSO	P7	Stormwater and CSOs
Emissions from separate storm water collection systems (in urban areas)	StSew	P7	Stormwater and CSOs
Emissions from treated domestic wastewater collected in sewers	WWTP	P8	Wastewater
Direct emissions to surface waters from unconnected households	HHo	P9	Direct releases
Discharges to surface waters from industry	Ind	P10	Direct releases
Direct emissions to surface waters from navigation	Nav	P12	Direct releases

The relative contribution of these pathways to the basin-wide emissions of the 17 simulated chemicals is graphically presented in Figure 2.3. The emission inventory results are listed in Table 2.2 and Table 2.3.

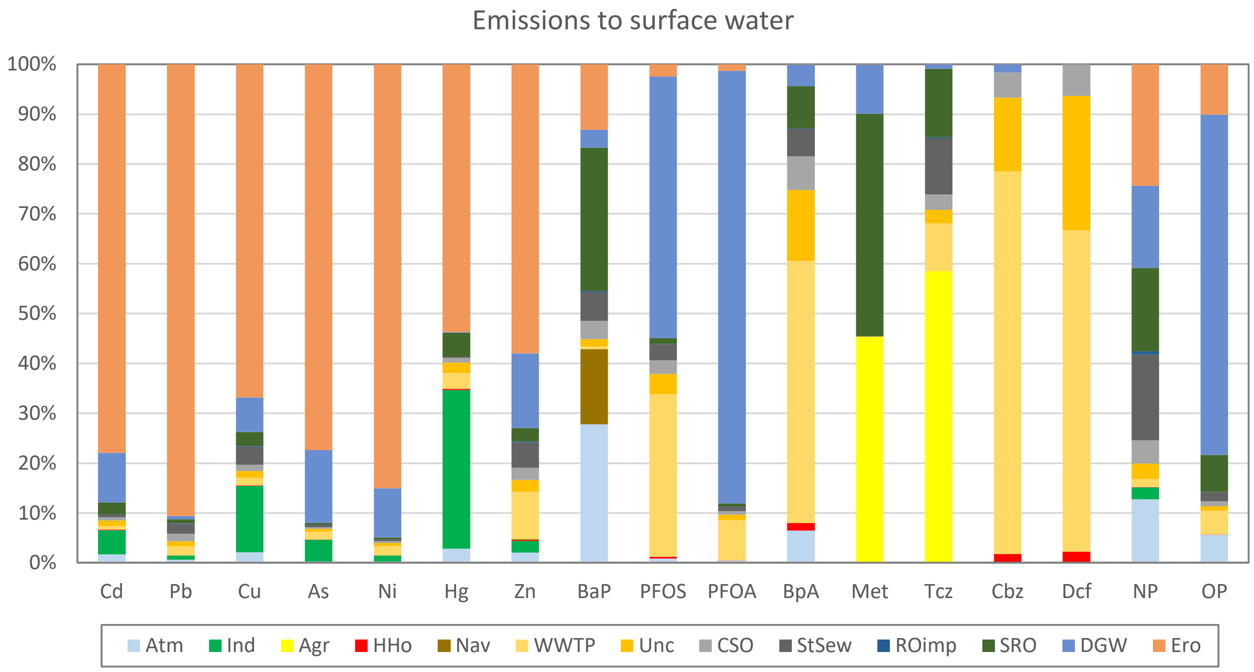


Figure 2.3: Relative distribution of emissions to surface waters over pathways for the simulated HS.

Table 2.2: DRB emissions to surface water in kg/y subdivided over pathways.

	Atm	Ind	Agr	HHo	Nav	WWTP	Unc
Cd	220	635	0	15	0	96	151
Pb	5354	7598	0	316	0	16537	8931
Cu	20449	128660	0	839	0	14808	13042
As	1168	20487	0	245	0	7251	2703
Ni	2594	12139	0	589	0	19140	6381
Hg	140	1592	0	12	0	158	104
Zn	86734	98639	0	7358	6877	401960	102730
BaP	339	0	0	1	183	6	19
PFOS	1	0	0	1	0	51	6
PFOA	3	0	0	1	0	56	8
BpA	163	0	0	37	0	1331	359
Met	0	0	4100	0	0	4	1
Tcz	0	0	108	0	0	18	5
Cbz	0	0	0	63	0	2762	534
Dcf	0	0	0	279	0	8135	3414
NP	83	16	0	1	0	11	20
OP	89	0	0	1	0	76	14

	CSO	StSew	ROimp	SRO	DGW	Ero	Total
Cd	88	76	3	300	1312	10218	13113
Pb	13598	18002	603	7765	5873	815290	899867
Cu	12149	35665	1149	26874	66861	644960	965456
As	1523	2173	54	1535	68715	361990	467844
Ni	3531	4604	122	3409	101420	876660	1030588
Hg	49	12	1	242	4	2684	4997
Zn	102450	214390	7498	113990	634020	2451800	4228447
BaP	44	70	3	352	43	160	1220
PFOS	4	5	0	2	82	4	156
PFOA	5	7	0	4	600	9	692
BpA	171	138	3	215	108	1	2528
Met	1	4	0	4037	890	4	9040
Tcz	6	21	0	25	2	0	185
Cbz	179	0	0	0	60	0	3598
Dcf	791	0	0	0	4	0	12623
NP	30	112	4	109	108	159	654
OP	15	30	1	117	1077	159	1577

Table 2.3: DRB emissions to surface water, relative share of pathways.

	Atm	Ind	Agr	HHo	Nav	WWTP	Unc
Cd	2%	5%	0%	0%	0%	1%	1%
Pb	1%	1%	0%	0%	0%	2%	1%
Cu	2%	13%	0%	0%	0%	2%	1%
As	0%	4%	0%	0%	0%	2%	1%
Ni	0%	1%	0%	0%	0%	2%	1%
Hg	3%	32%	0%	0%	0%	3%	2%
Zn	2%	2%	0%	0%	0%	10%	2%
BaP	28%	0%	0%	0%	15%	1%	2%
PFOS	1%	0%	0%	0%	0%	33%	4%
PFOA	0%	0%	0%	0%	0%	8%	1%
BpA	6%	0%	0%	1%	0%	53%	14%
Met	0%	0%	45%	0%	0%	0%	0%
Tcz	0%	0%	58%	0%	0%	10%	3%
Cbz	0%	0%	0%	2%	0%	77%	15%
Dcf	0%	0%	0%	2%	0%	64%	27%
NP	13%	2%	0%	0%	0%	2%	3%
OP	6%	0%	0%	0%	0%	5%	1%

	CSO	StSew	ROimp	SRO	DGW	Ero	Total
Cd	1%	1%	0%	2%	10%	78%	100%
Pb	2%	2%	0%	1%	1%	91%	100%
Cu	1%	4%	0%	3%	7%	67%	100%
As	0%	0%	0%	0%	15%	77%	100%
Ni	0%	0%	0%	0%	10%	85%	100%
Hg	1%	0%	0%	5%	0%	54%	100%
Zn	2%	5%	0%	3%	15%	58%	100%
BaP	4%	6%	0%	29%	4%	13%	100%
PFOS	3%	3%	0%	1%	53%	2%	100%
PFOA	1%	1%	0%	1%	87%	1%	100%
BpA	7%	5%	0%	9%	4%	0%	100%
Met	0%	0%	0%	45%	10%	0%	100%
Tcz	3%	11%	0%	14%	1%	0%	100%
Cbz	5%	0%	0%	0%	2%	0%	100%
Dcf	6%	0%	0%	0%	0%	0%	100%
NP	5%	17%	1%	17%	16%	24%	100%
OP	1%	2%	0%	7%	68%	10%	100%

2.3 Hazardous substances fluxes in key compartments and pathways

In this paragraph, some detailed results for parts of the conceptual model are presented. In all cases, basin-wide totals are presented, while the relevant part of the conceptual model is indicated in the modelling methodology scheme (for details, reference is made to Section 6).

2.3.1 Impermeable surfaces

Figure 2.4 shows the basin-wide balance terms for the impermeable surfaces compartment.

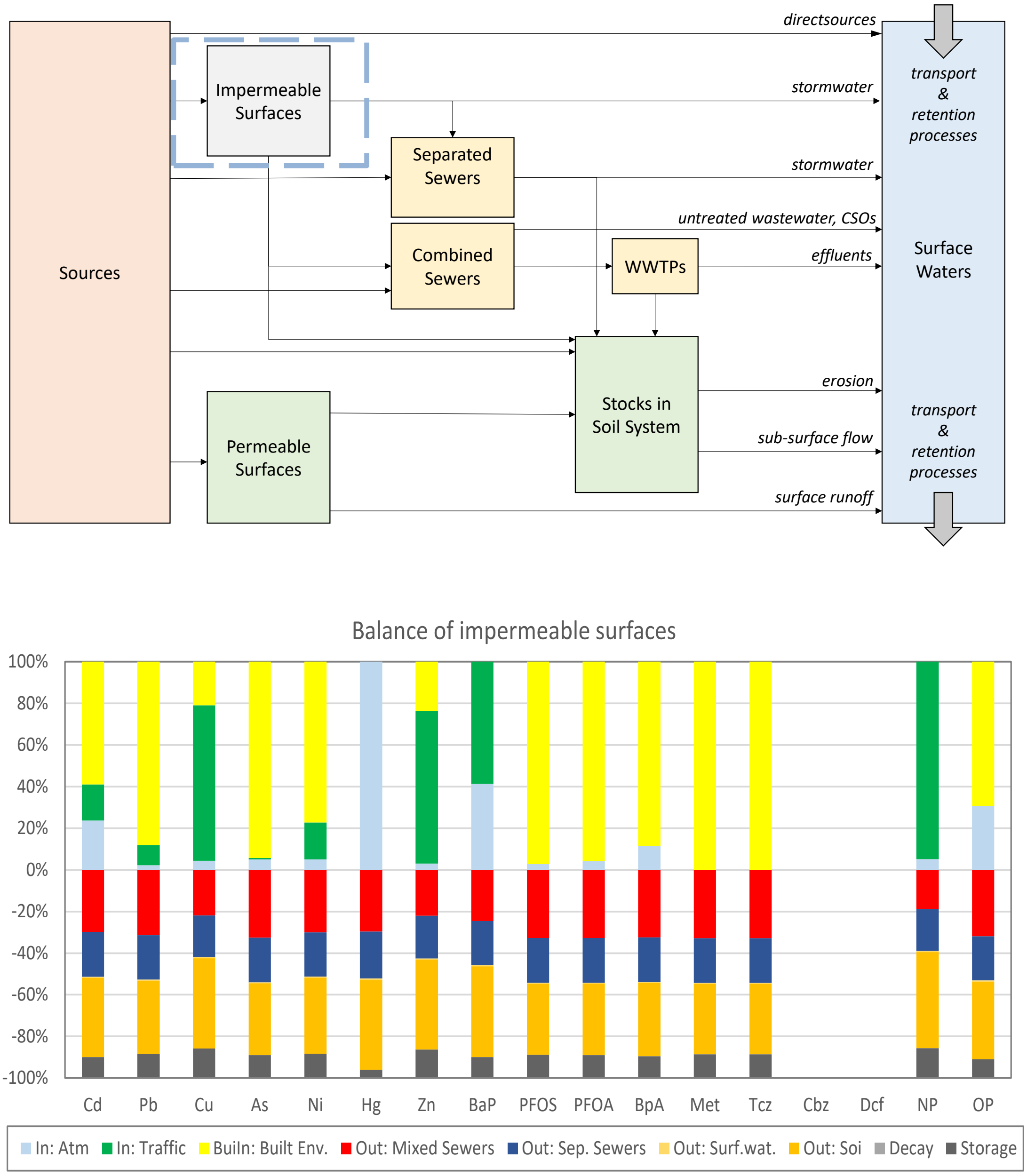


Figure 2.4: Basin-wide mass balance of the impermeable surfaces compartment.

Note that for the pharmaceuticals, there are no releases to impermeable surfaces. For these substances, the graph is empty.

2.3.2 Separated sewer systems

Figure 2.5 shows the basin-wide balance terms for the separate stormwater sewers compartment.

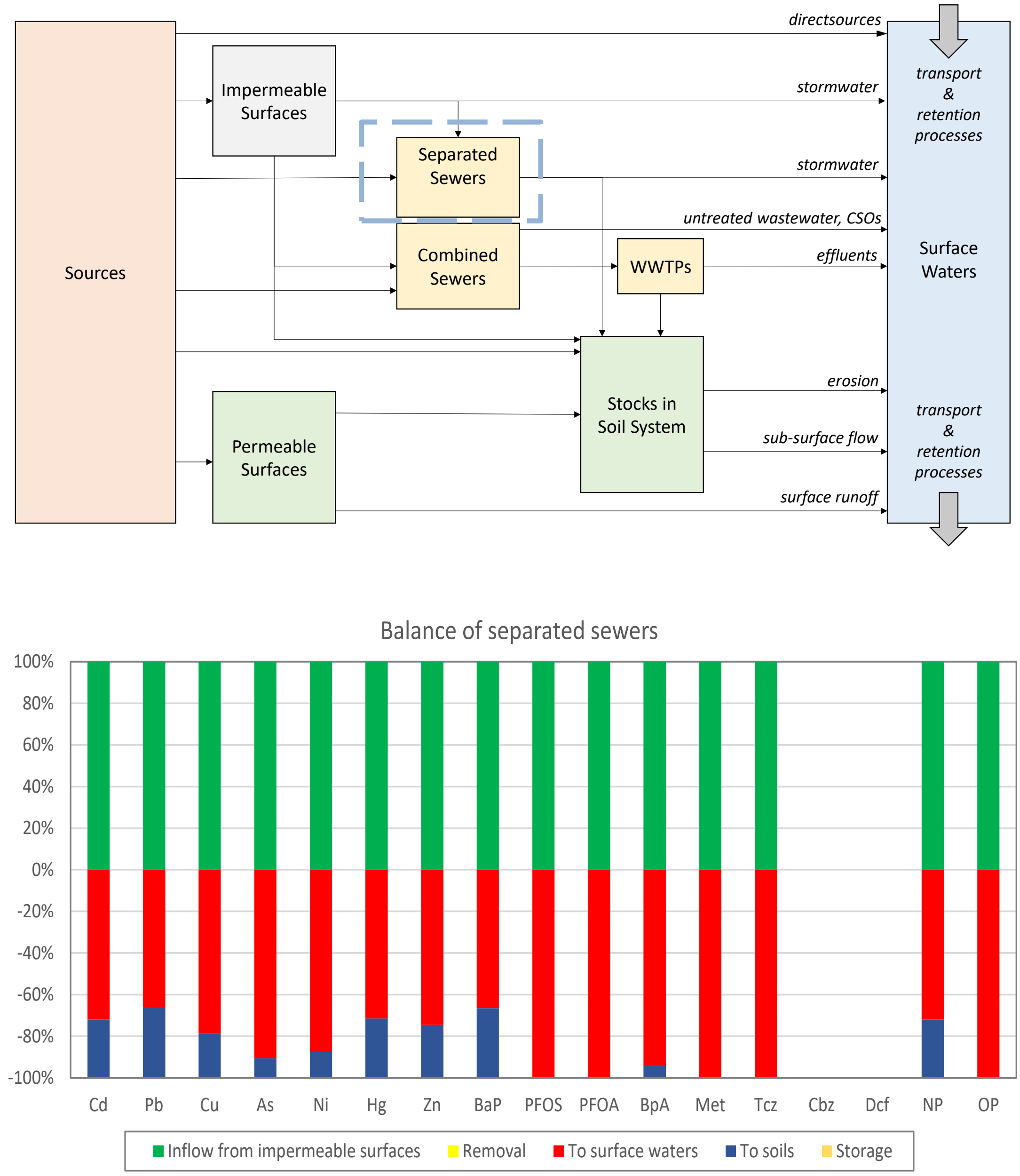


Figure 2.5: Basin-wide mass balance of the separated sewers compartment.

Note that for pharmaceuticals there are no releases to impermeable surfaces, and therefore there is no mass balance for separated sewers.

2.3.3 Combined sewers and WWTPs

Figure 2.6 shows the basin-wide balance terms for the combined sewers and WWTPs compartments.

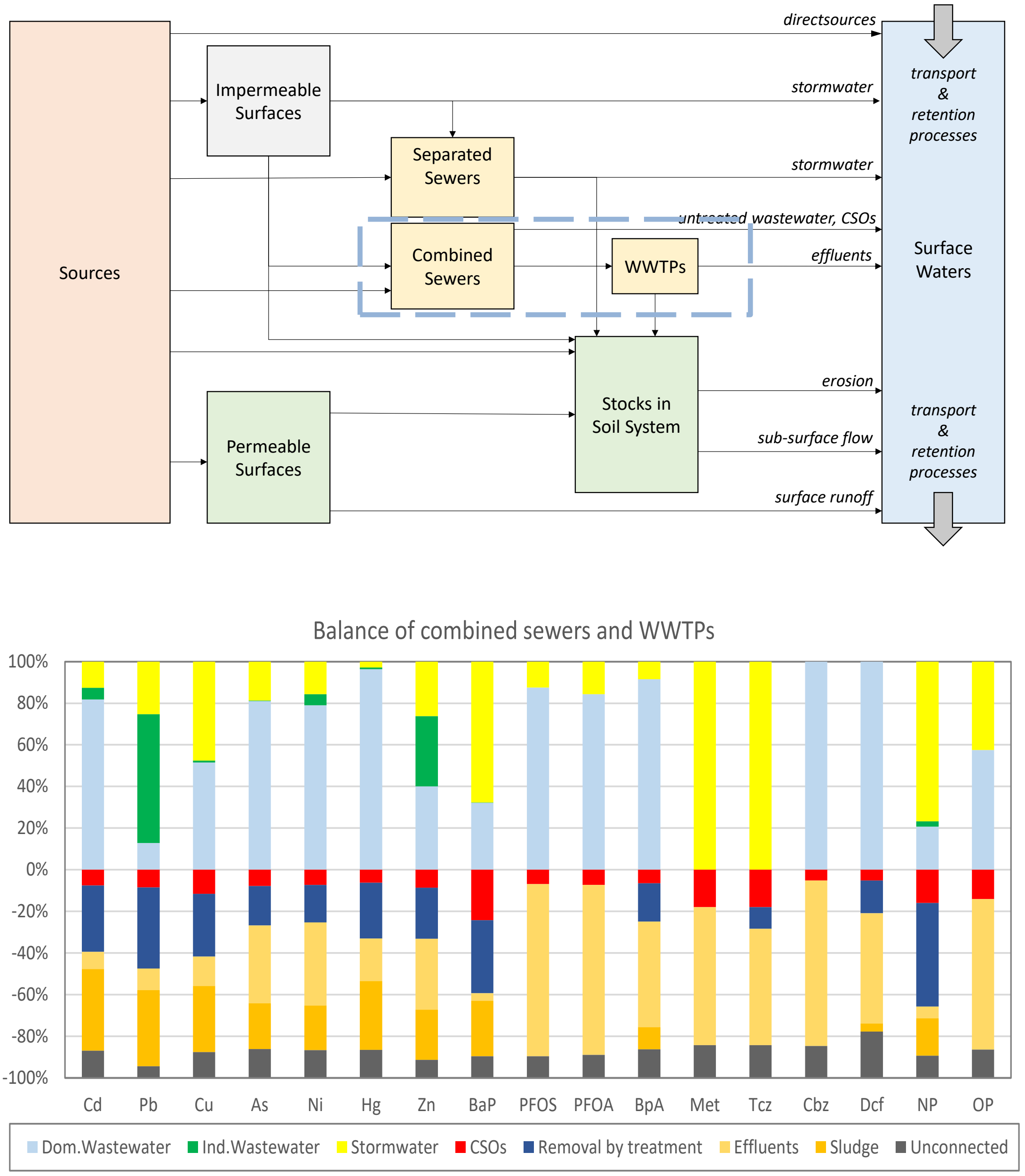


Figure 2.6: Basin-wide mass balance of the combined sewers and WWTPs compartments.

2.3.4 Permeable surfaces

Figure 2.7 shows the basin-wide balance terms for the permeable surfaces compartment.

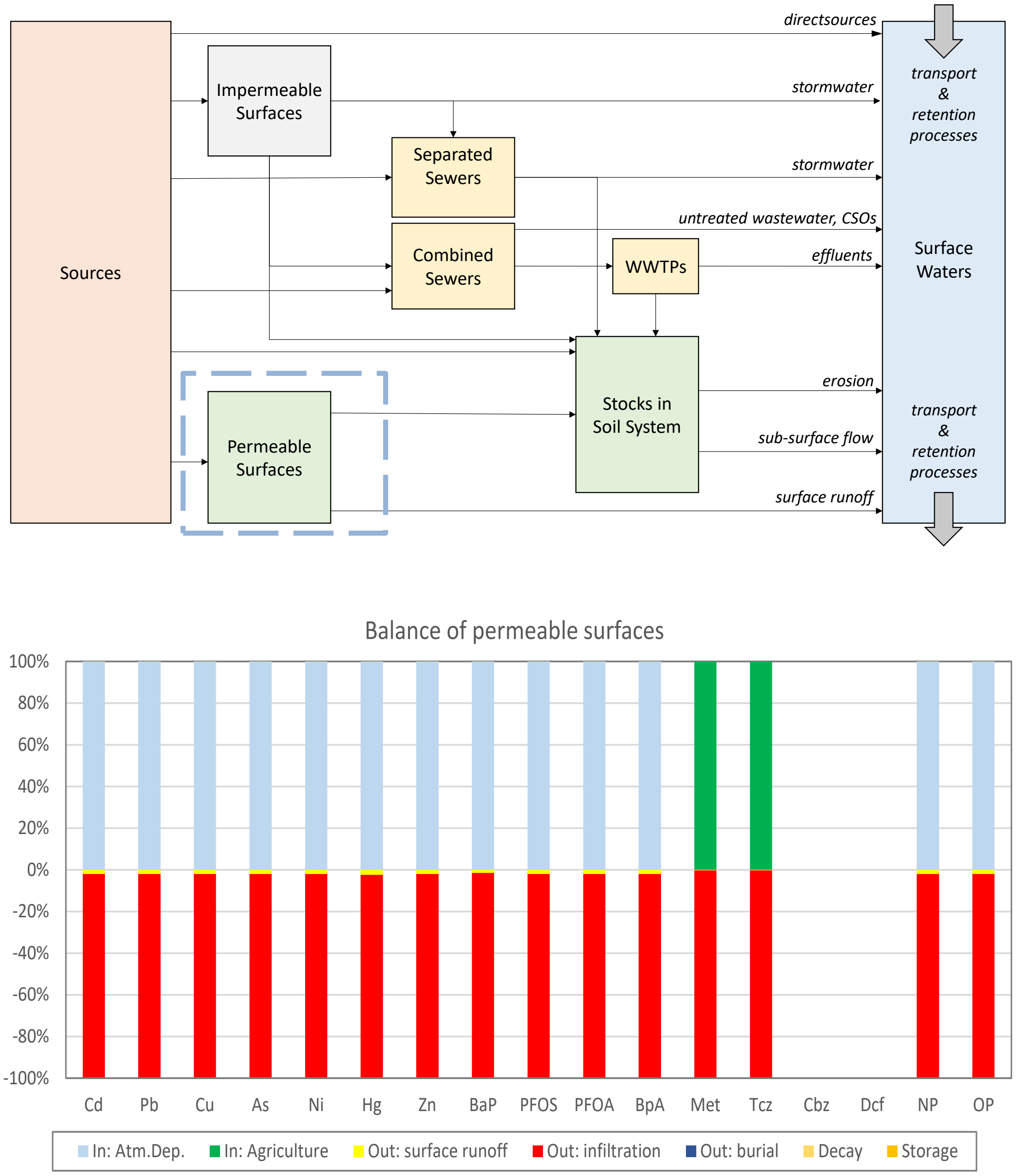


Figure 2.7: Basin-wide mass balance of the permeable surfaces compartment.

Note that for the pharmaceuticals, releases to permeable surfaces have not been quantified. For these substances, the graph is empty.

2.3.5 Soil system

Figure 2.8 shows the basin-wide mass balance for the soil compartment.

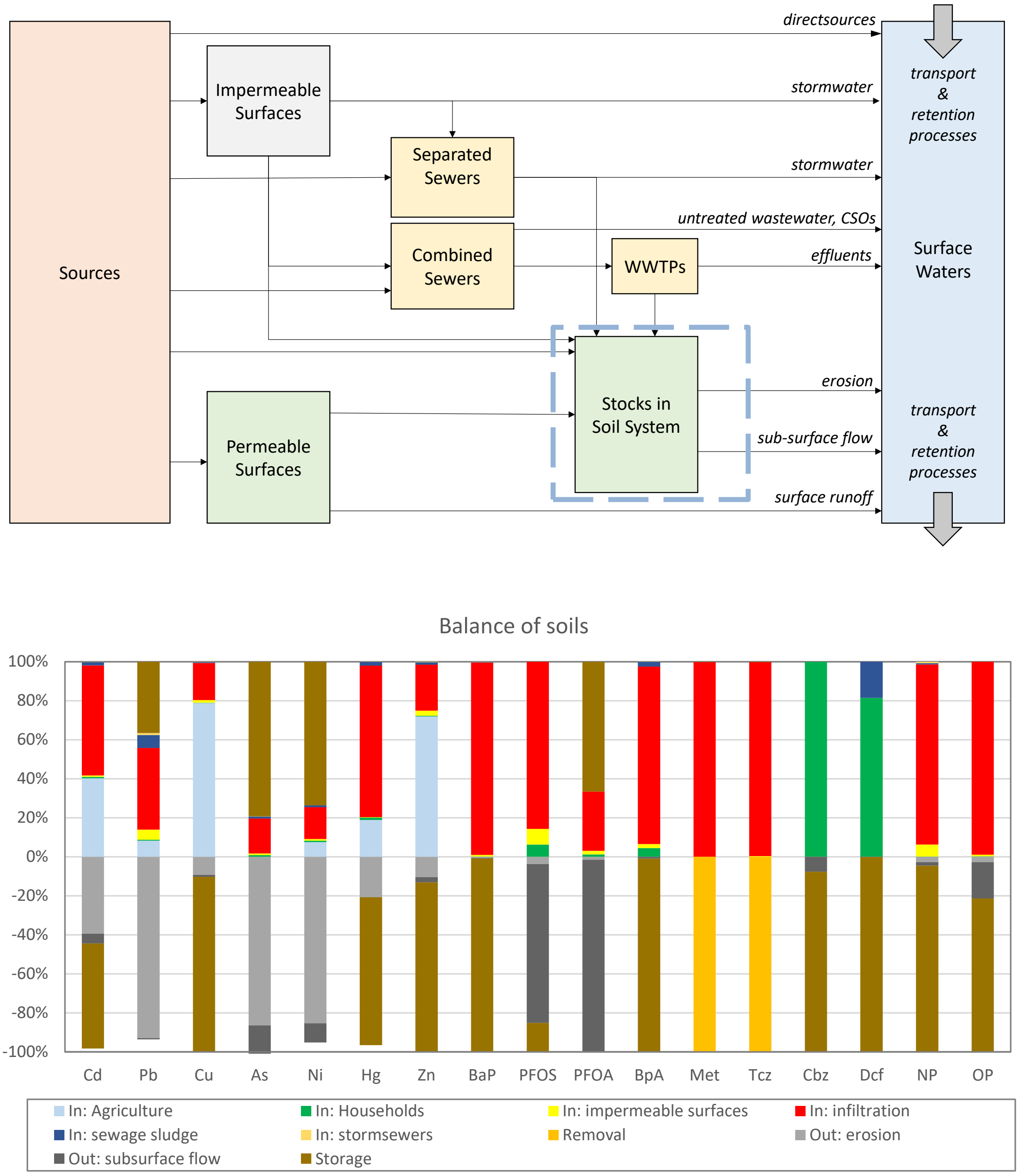


Figure 2.8: Basin-wide mass balance of the soil compartment.

2.3.6 Fate in surface waters

Figure 2.9 shows the basin-wide mass balance of the surface waters compartment. The positive side of this balance is the total of the emissions. The negative side shows the outflow to the Black Sea, the outflow via various abstractions, the net settling that leads to retention in aquatic sediments and (for diclofenac) the degradation.

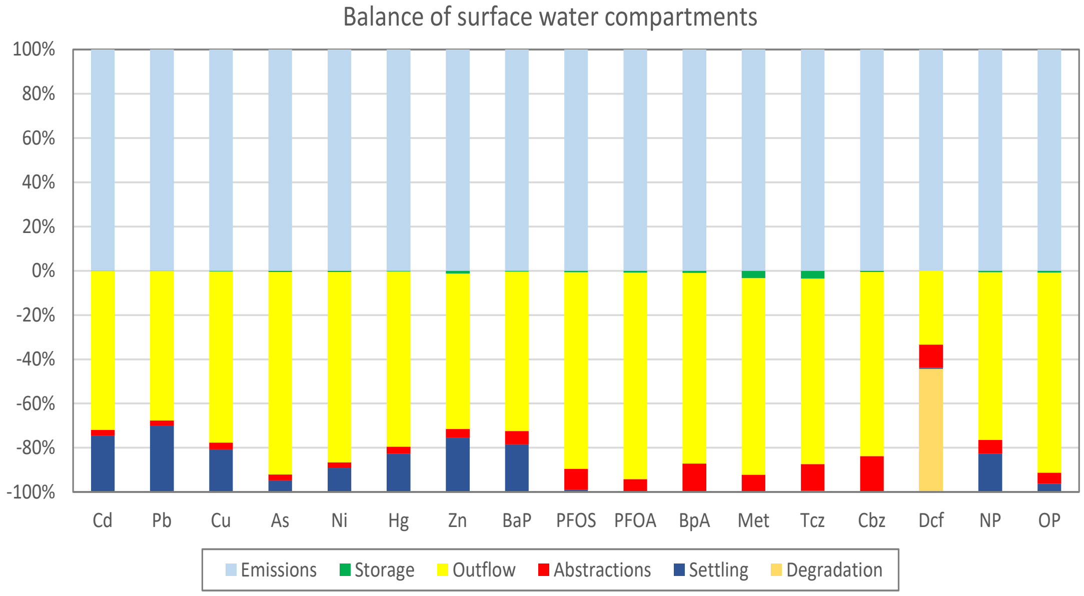


Figure 2.9: Basin-wide mass balance of the surface waters compartment.

2.4 Spatial variability of emissions to surface waters

The spatial variability of the emissions of HS in the Danube River Basin is illustrated by maps showing the total emissions to surface waters expressed in g km^{-2} y^{-1} by a division by the surface area of the schematization elements. The dominant pathway is indicated in a map as well, where the aggregated pathways as indicated in Table 2.1 are distinguished. In addition, the mean value per country is shown in a bar chart that also shows the subdivision over the pathways. Results are shown for selected substances with different characteristics in Figure 2.10 to Figure 2.14.

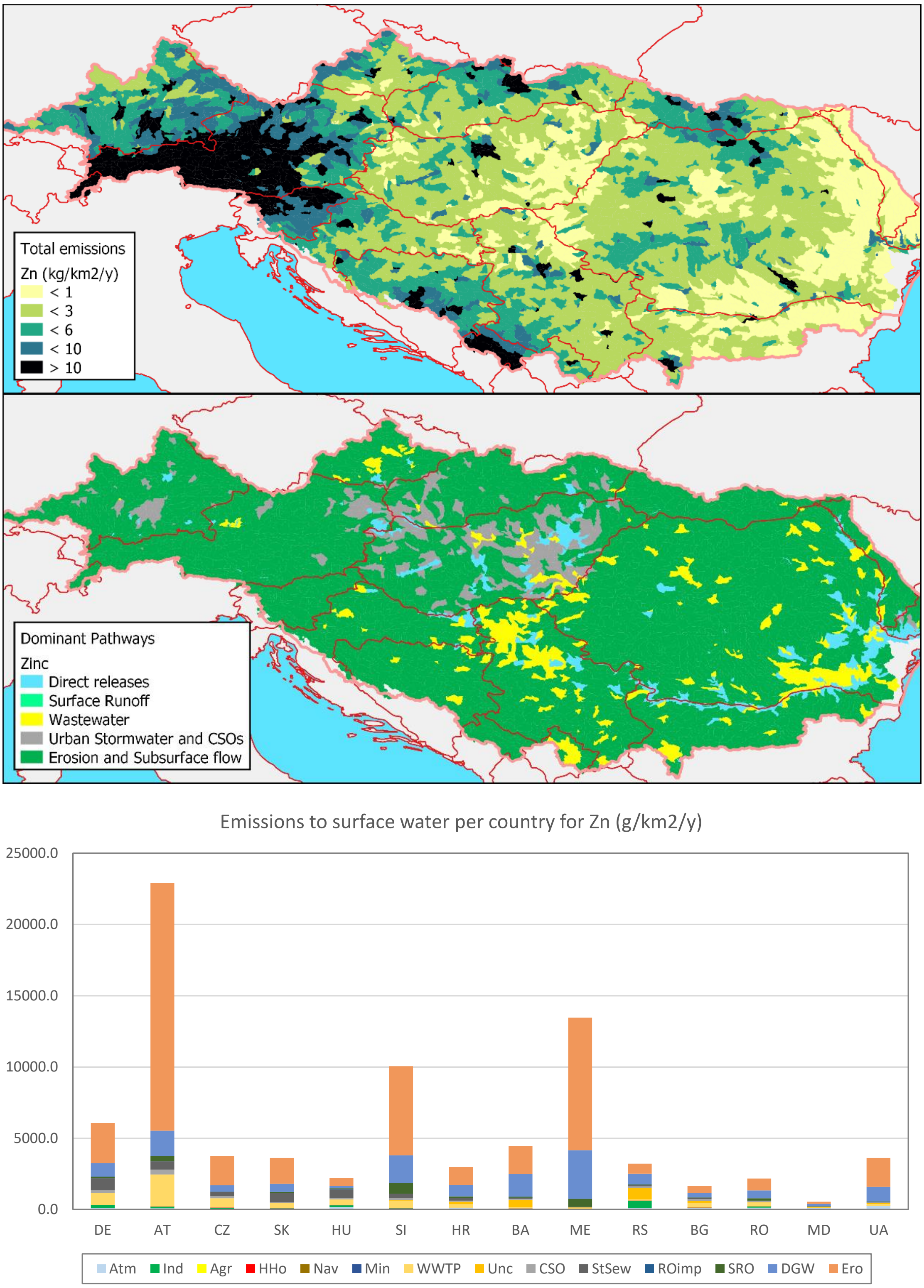


Figure 2.10: Spatial variability of emissions and dominant pathway: zinc.

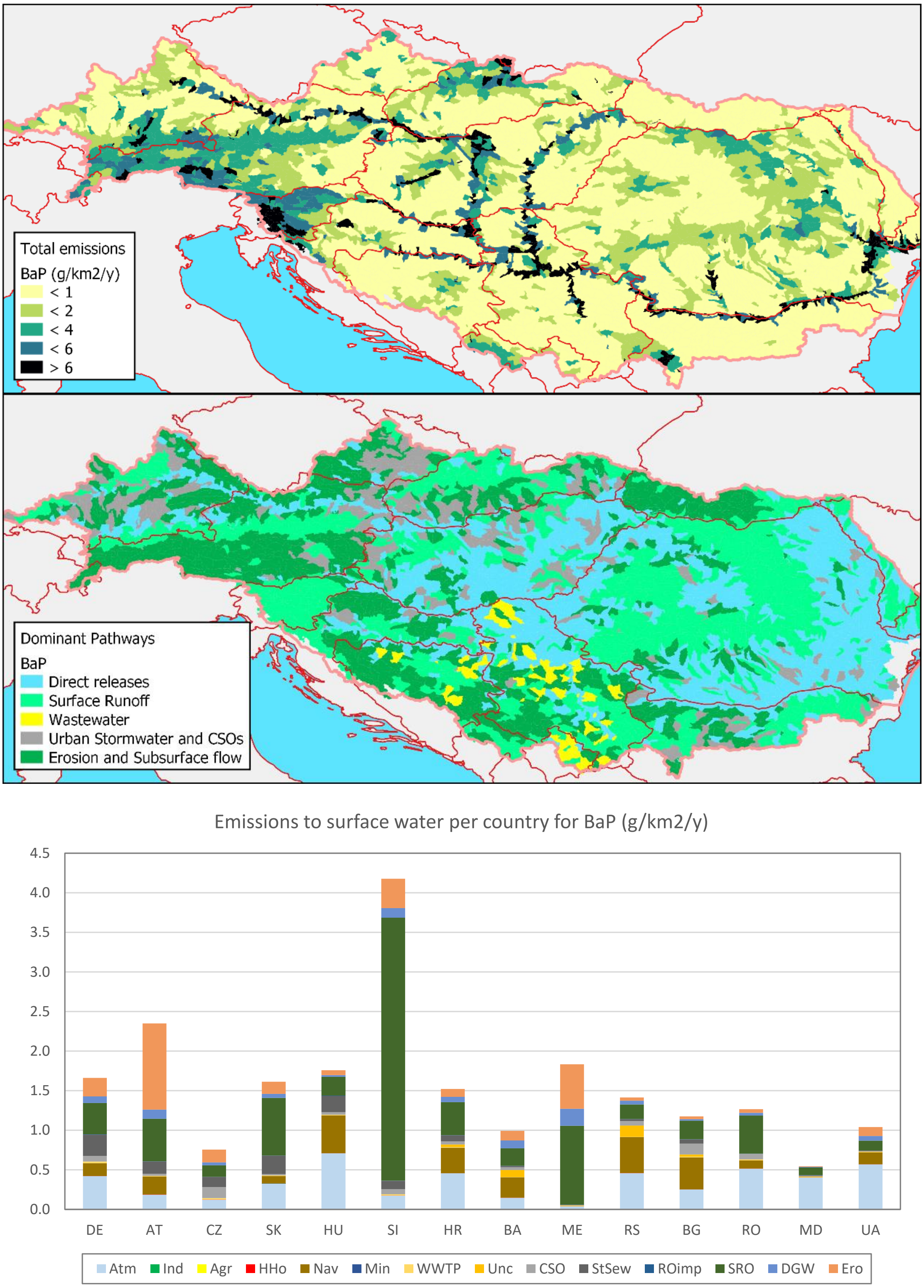


Figure 2.11: Spatial variability of emissions and dominant pathway: benzo[a]pyrene.

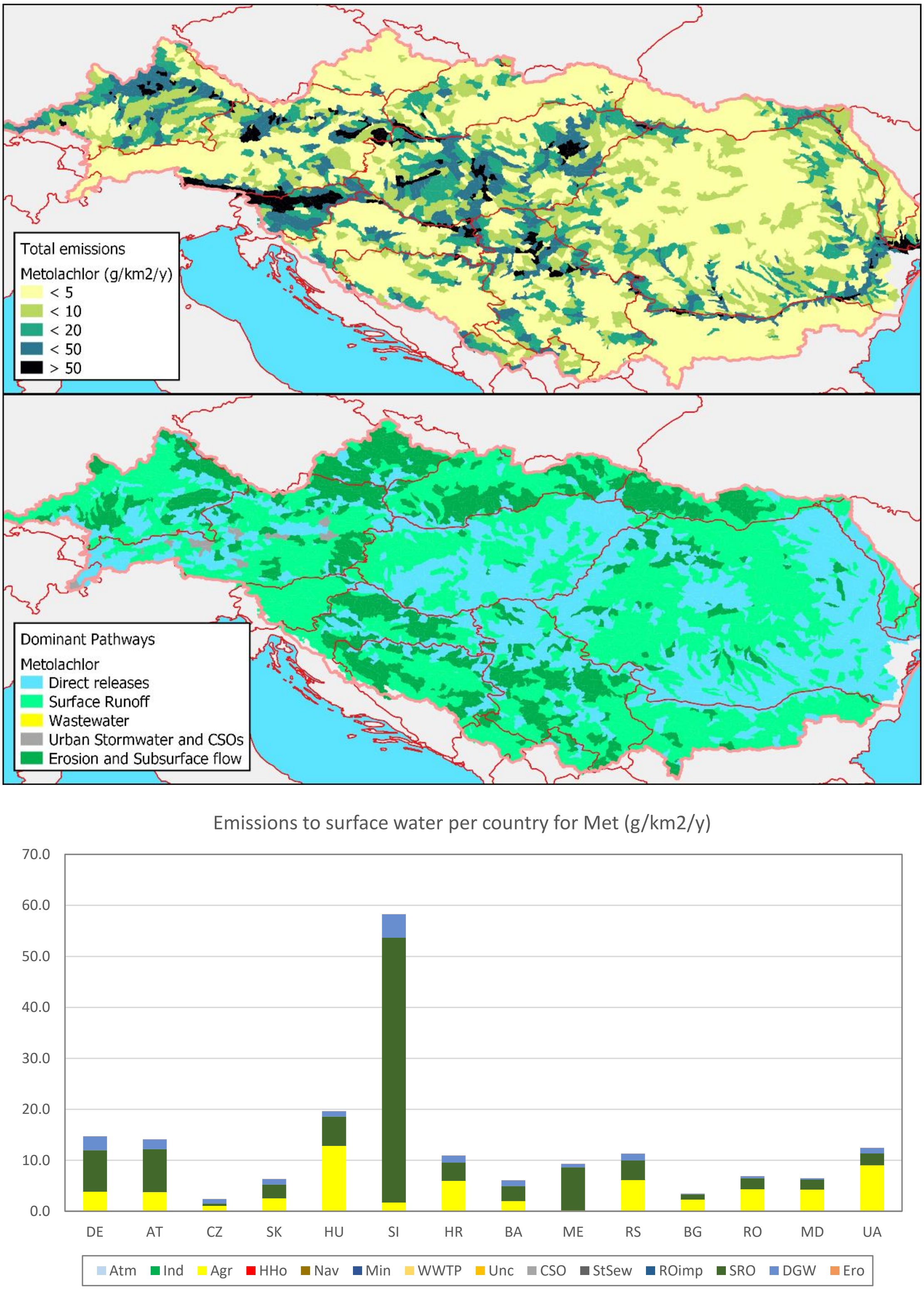


Figure 2.12: Spatial variability of emissions and dominant pathway: metolachlor.

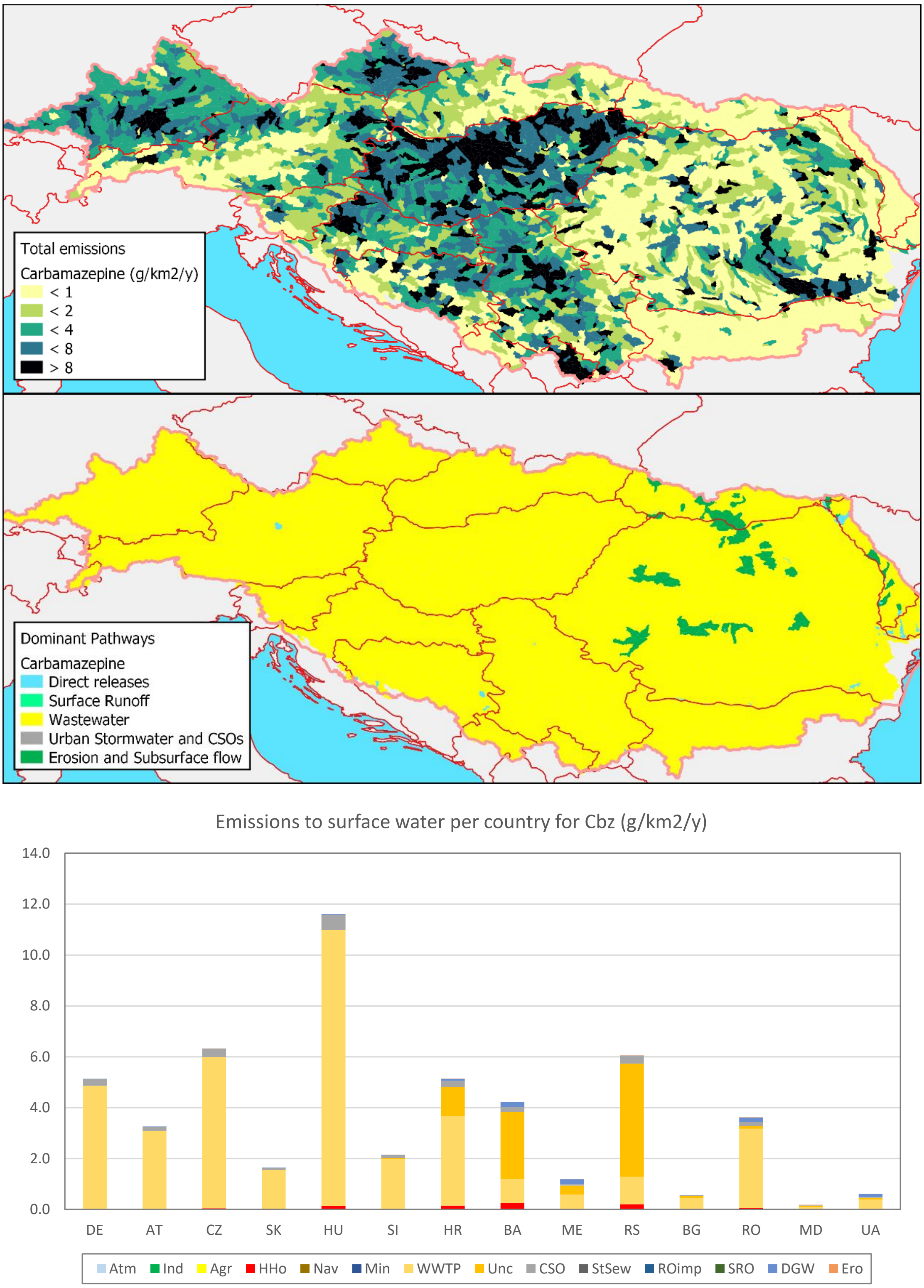


Figure 2.13: Spatial variability of emissions and dominant pathway: carbamazepine.

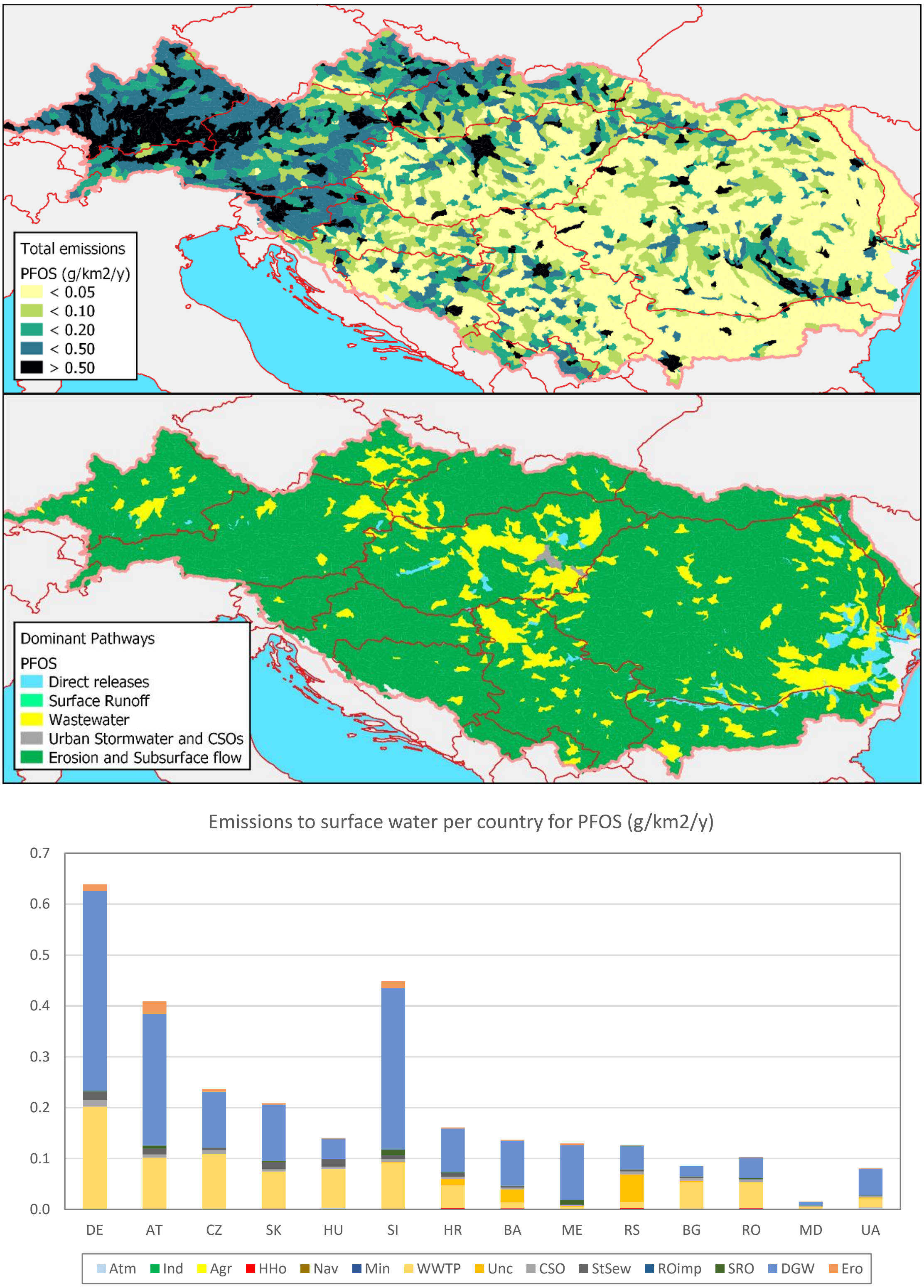


Figure 2.14: Spatial variability of emissions and dominant pathway: PFOS.

2.5 Discussion

The results presented above lead to the following observations.

2.5.1 Metals

The metals show a wide spectrum of sources and pathways. They are important today, but in the past they had been used in even larger quantities - partly uncontrolled. Metals were emitted by the flue gases of combustion plants (coal-fired power plants, waste incinerators), they are present in built-in materials (roads, roofs, buildings, structures, vehicles), and were widely used in gasoline (lead) and fertilizers (cadmium) whose impacts can be still observed. Consequently, pollution over several decades has accumulated in the environment, mainly in soils, from where metals were washed into the surface and underground waters over time.

For metals, the combined soils related pathways provide the largest contribution (typically 70% or more). Contributions > 10% occur for industry discharges (Cu, Hg) and UWWTPs (Zn). The spatial results for zinc show emission gradients probably controlled by terrain and hydrology gradients that drive the soil related pathways. A second important driver may be the spatially variable historical pollution in soils. In most places the soil related pathways are dominant. Locally, direct sources are dominant (atmospheric deposition on large lakes, industrial point sources). In other places, the contribution from wastewater is dominant (from mixed sewers collecting wastewater and urban stormwater) or from stormwater and CSOs.

2.5.2 PAHs

Benzo*[a]*pyrene is emitted by incineration (combustion plants, household heating), but it is usually transported over short distances in the atmosphere (in contrast to mercury, which can even cross a country or larger areas). Benzo*[a]*pyrene quickly settles and accumulates attached to particles. For benzo*[a]*pyrene the modelling results show large contributions from surface runoff (29%) and from direct atmospheric deposition (28%), with noticeable contributions from navigation and erosion (> 10%). The spatial results for benzo*[a]*pyrene show high emissions in large lakes and larger rivers, and in places with high local atmospheric deposition and high rainfall (e.g. in Slovenia). Locally high atmospheric deposition may be attributed to nearby industrial and domestic incineration or intensive combustion engine traffic. Often, surface runoff or erosion and sub-surface flow are dominant pathways. In many places direct sources are dominant (atmospheric deposition on large lakes, inland navigation in larger rivers). Occasionally, stormwater and CSOs or wastewater dominate.

2.5.3 Pharmaceuticals

For the investigated pharmaceuticals, only contributions from households could be quantified. Wastewater related pathways therefore contribute >90% to the emissions. The spatial results for carbamazepine show highest emissions to water in places with high population and a high connection rate to sewers. As country-specific emission factors have been applied, some differences between countries can be observed. UWWTPs are the dominant pathway, except for areas with low connection rates to sewers, where household releases to soil possibly supplemented by re-used sewage sludge find their way to the surface water via sub-surface flow. Such areas are visible in the middle panel of Figure 2.13 in some parts of Romania. The release of pharmaceuticals due to veterinary use could not be quantified.

2.5.4 Industrial chemicals

The use of PFOS in products has already been banned, but there are still many products currently in use in households and accumulated in the so-called stock of long-living goods, from which they will be still released over the coming years. For PFOS, households are an important source and wastewater is a relevant pathway (37%). Subsurface flow is an important pathway, too (53%). The modelling results show an east-west gradient in the emissions, caused by an assumed correlation of emission factors and soil concentrations to population density and Gross Domestic Product. Also, population centres show high emissions. In many places the erosion and subsurface flow pathway is dominant, as a result of accumulation in soils. In drier areas, the wastewater pathways dominate. Near larger water surfaces, direct atmospheric deposition dominates.

For the other investigated industrial chemicals, a diverse spectrum of pathways exists. For Bisphenol-A, households are an important source and wastewater is an important pathway (67%). Subsurface flow is an important pathway, especially for PFOA (87%). For nonylphenol, stormwater is an important pathway (17%). For both phenols erosion contributes significantly (>10%).

2.5.5 Pesticides

For the investigated pesticides, important pathways are direct losses to surface water during application in agriculture (45-58%) and surface runoff (14-45%). For metolachlor, subsurface flow is relevant (10%). For tebuconazole there are significant contributions (>10%) from stormwater and WWTPs, due to the use as a biocide. The spatial results for metolachlor reflect the use in agriculture. In most places, surface runoff or direct emission by spray drift are the dominant pathway. Locally, this is subsurface flow.

2.5.6 Partial balances for specific compartments

The partial balances for impermeable surfaces show a blend of inputs from atmosphere, traffic and the built environment (substance-dependent). The output is similar for all HS, as this is mostly infrastructure controlled.

For permeable surfaces there is a substance-specific blend of inputs from atmosphere and agriculture. In the output, there is a relatively small contribution from surface runoff, while most of the output is directed to the soil system.

For the soil system, the input from permeable surfaces is dominating, with some input from agriculture for metals. For all substances there are contributions from unconnected households and re-use of sewage sludge.

The combined sewers and WWTPs show variable input from domestic wastewater, industrial wastewater and urban runoff. The fate of the HS in this subsystem is strongly substance dependent, as the treatment efficiency differs per HS.

3 Uncertainty and climate variability

3.1 Basin-wide emissions to surface waters

The input data used for the emission inventory of HS are to some extent uncertain. To show the impact of this uncertainty, three different estimates are provided. The best (middle) estimate was presented in the previous chapter. In addition, a low (“P25”) and a high (“P75”) estimate were compiled[1]. Section 7.3.10 discusses how these estimates were realized.

In addition, climate variability also affects the emission inventory. The weather conditions affect for example the erosion and surface runoff pathway, but also the stormwater related pathways and the occurrence of combined sewer overflows. The modelling is fully time dependent and is driven by hydrology data for 10 different years. These differences are therefore resolved by the modelling. The average emissions over 10

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[1] “P25” and “P75” refer to the fact that where applicable, 25-percentiles and 75-percentiles of the available data were used instead of than 50-percentiles for the middle estimate.

years were presented in the pervious chapter. The year with the lowest emissions and the year with the highest emissions are determined to indicate the effect of climate variability on the emissions.

Both the uncertainty of the emissions and the effect of climate variability are shown in Figure 3.1.

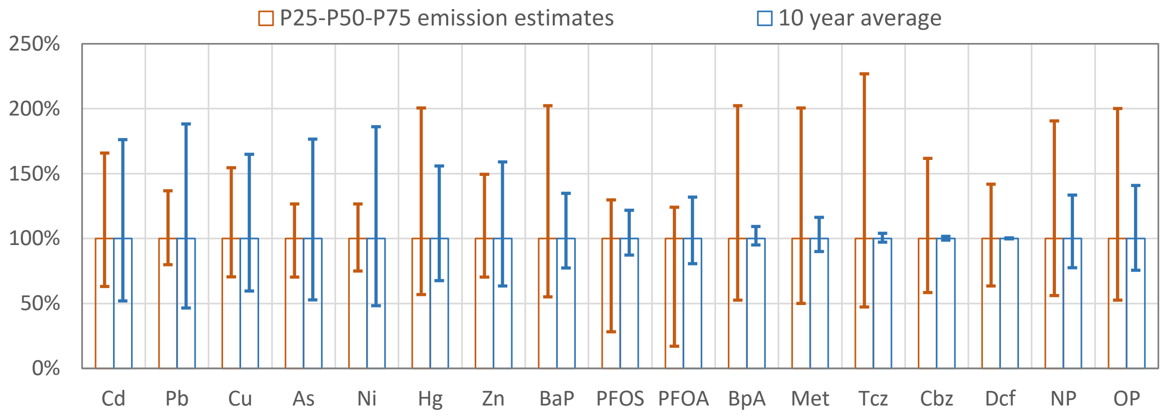


Figure 3.1: Range of estimated emissions in the P25 and P75 variants, relative to the best estimate (P50) for the 17 simulated HS, plotted with the variability of emissions between 10 simulated hydrological years, relative to the mean value of the whole period.

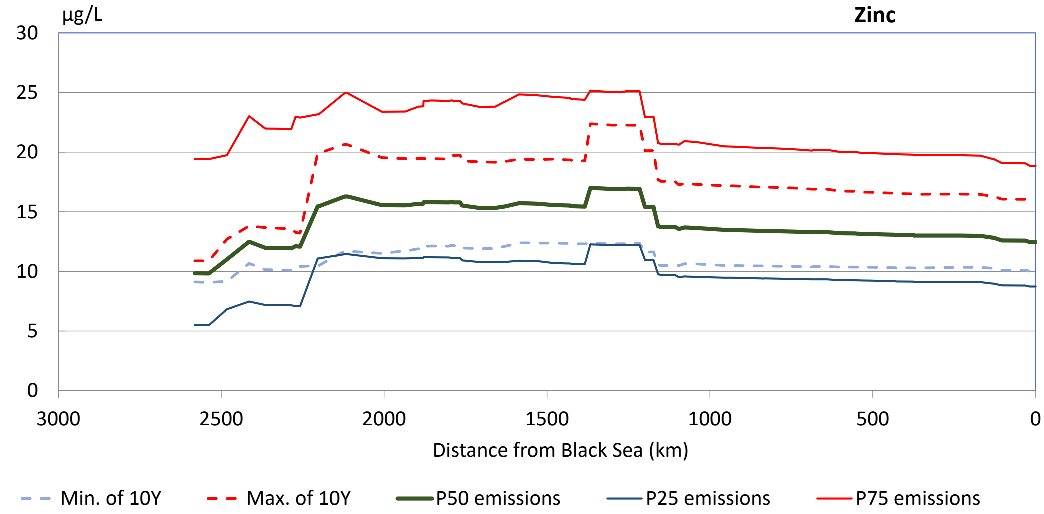
The uncertainty and the climate variability are for most substances in the same order. Low emission estimates can reach about 20% of the middle estimate. High emission estimates > 200%. Climate variability has the biggest impact on metals emissions (about 50-175%), because of their dependency on erosion and surface runoff. It has almost no impact on pharmaceuticals emissions. Maximum emissions were typically found for 2013 (high erosion) and 2010 (high sub-surface flow). Both were years with a high simulated discharge, but apparently 2013 had more strong runoff events. Minimum emissions were typically found for 2007 (low erosion) and 2011 (low sub-surface flow). Both were years with a relatively low simulated discharge. Depending on the relative share of these pathways in the emissions for specific substances, these years show the lowest and highest emissions respectively. The rainfall related pathways in wastewater and stormwater management also show variability between individual years. Quantitatively, this variability is not decisive for the variability of the total emissions. Section 9.5 list the years with the lowest and highest emissions per substance.

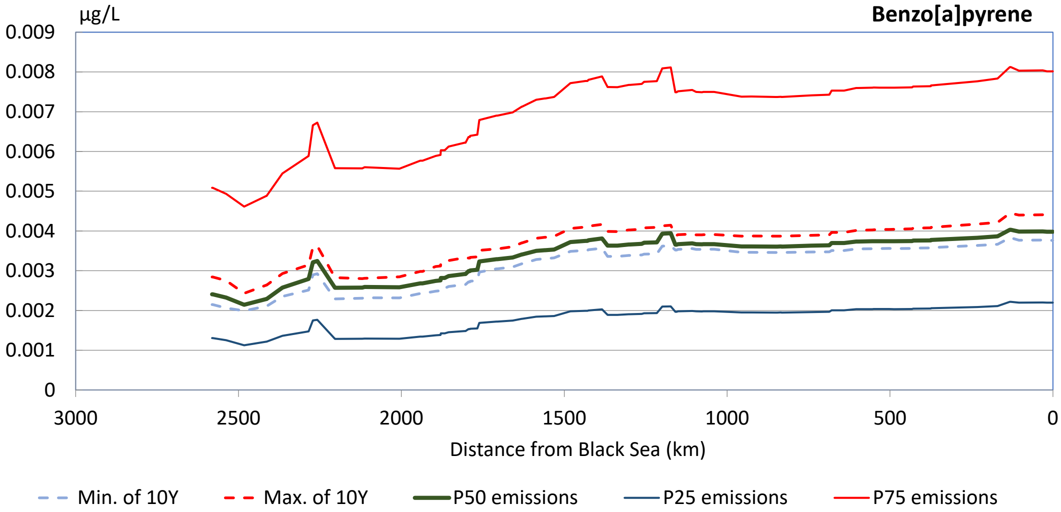
3.2 Concentrations in surface waters

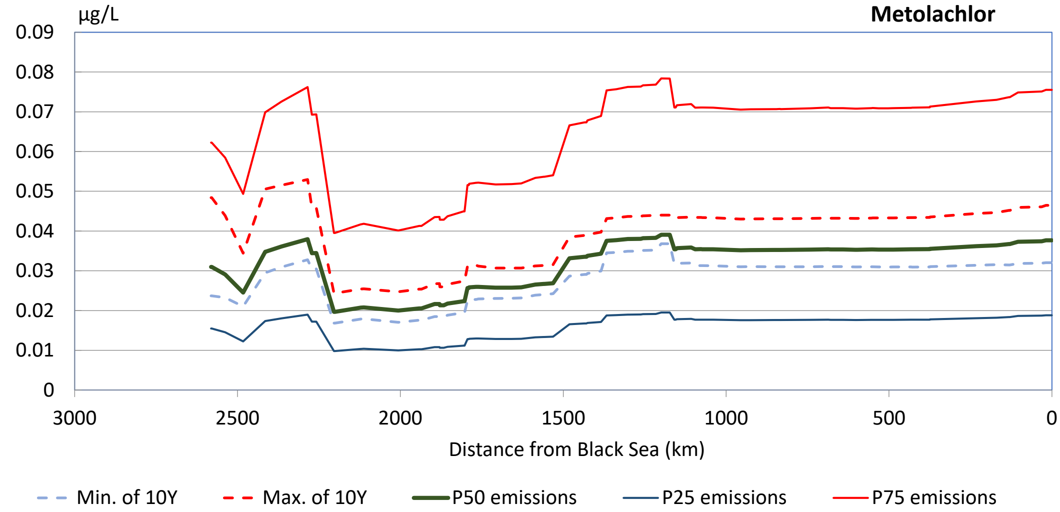
The uncertainty of emission estimates and the climate variability also affect the HS concentrations in surface waters. Regarding climate variability, an additional factor comes into play: the variable river discharge in relation to the variable emissions. This interplay is conceptually simple, but hard to quantify without using a model.

The uncertainty and variability of HS concentrations in surface waters are shown by longitudinal plots of the river concentrations along the main axis of the Danube. 10-year averages of the concentrations using the P25-, middle and P75 emission estimates are plotted together with the highest and lowest annual concentration from the 10-year sequence. Thus, the effect of emission uncertainty and climate variability is shown in one plot.

Figure 3.2 shows examples of the results for selected substances. For metals, the differences between the emission estimates are comparable to the differences between a favourable and an unfavourable year. For most of the other HS, the effect of climate variability is smaller than the effect of emission uncertainty, sometimes much smaller.


µg/L
Zinc
30
25
20
15
10
5
0
3000
2500
2000
1500
1000
500
0
Distance from Black Sea (km)
Min. of 10Y
Max. of 10Y
P50 emissions
P25 emissions
P75 emissions


µg/L
Benzo[a]pyrene
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
3000
2500
2000
1500
1000
500
0
Distance from Black Sea (km)
Min. of 10Y
Max. of 10Y
P50 emissions
P25 emissions
P75 emissions


µg/L
Metolachlor
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
3000
2500
2000
1500
1000
500
0
Distance from Black Sea (km)
Min. of 10Y
Max. of 10Y
P50 emissions
P25 emissions
P75 emissions

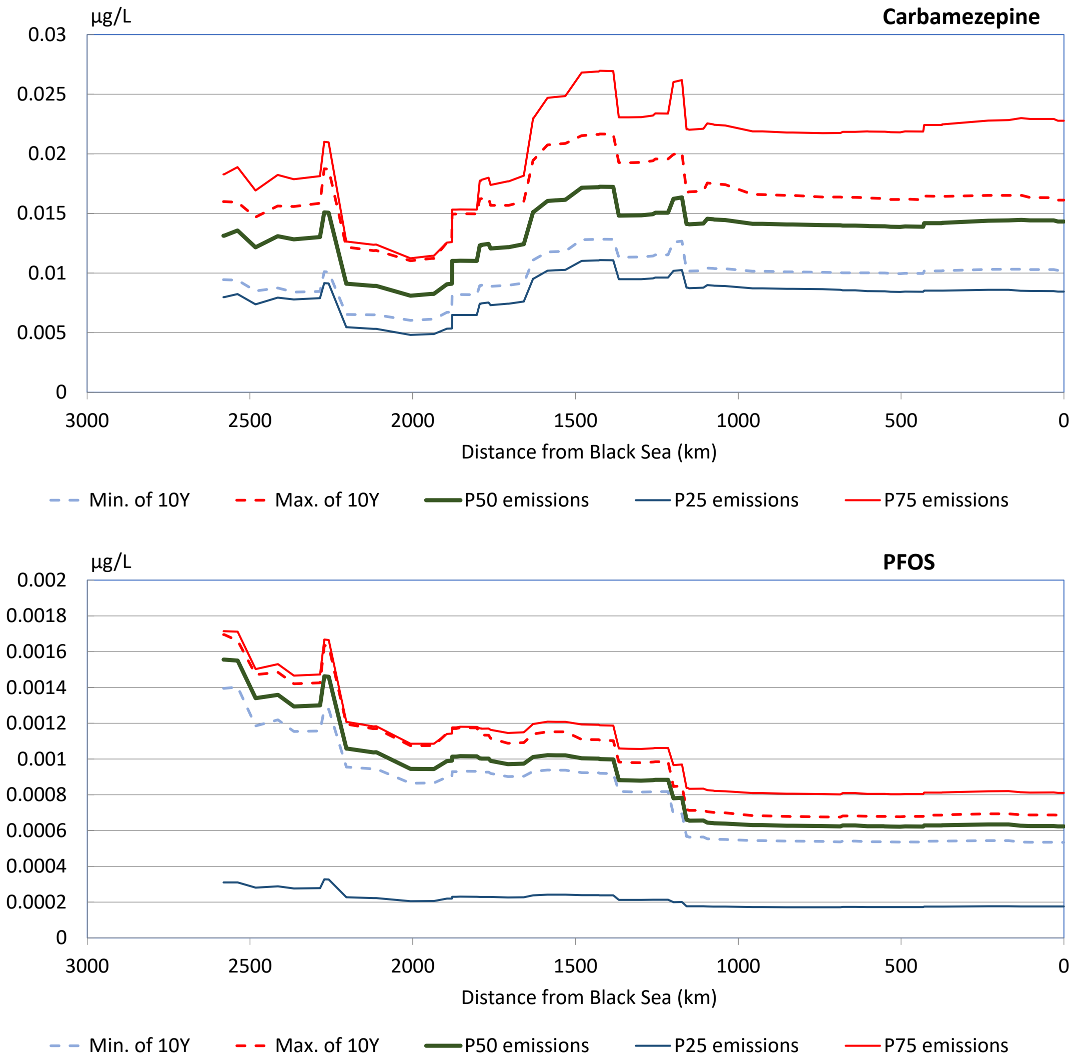


Figure 3.2: Simulated concentration profiles along the Danube River; 10 year means for different emission estimates plotted together with the highest and the lowest annual mean within the 10 year simulation period.

The year showing the minimum or maximum in-stream concentration can be variable along the river. For metals, 2007 is the year with lowest concentrations. This follows their emissions. The year with highest emissions 2013 often shows the highest concentrations as well. For the metals with a relatively low share of erosion in the emissions (Cu, Hg, Zn) there are river stretches where the low dilution year 2012 shows the highest concentration.

For pharmaceuticals, whose emissions are mostly independent of the weather, 2013 together with 2010 often shows the lowest concentrations. Both years have a high discharge on average, which causes high dilution. 2011 and 2012 tend to show highest concentrations. These are dry years with low dilution. Upstream of river km 1,200, the year 2006 shows highest concentrations of pharmaceuticals. Though an average year for the basin as a whole, this year showed low discharges in the upper and middle stretches.

For benzo[*a*]pyrene, the discharge dependency is not very pronounced. The year 2011 with the lowest emissions also shows the lowest concentrations in many places. The low discharge years 2007, 2012 and the year 2006 (upstream of km 1,200) show the highest concentrations.

For pesticides, lowest concentrations are in many locations encountered in the wet years 2010 and 2013, while highest concentrations are often found in dry years 2011 and (upstream of km 1,200) 2006.

For industrial chemicals including PFAS, the discharge dependency is again not very pronounced. The high discharge years 2010 and 2013 show the lowest concentrations, and low discharge years often show the highest concentrations.

The main outcomes of the above:

- There are two opposing climate related factors that affect instream concentrations: (1) the strong increase of erosion during high runoff events, and (2) the increase of dilution with increasing river discharge.
- The above implies that high discharge years typically show highest concentrations of metals (high erosion) and lowest concentrations of pharmaceuticals (high dilution). For other substance groups, the two effects more or less balance each other, and a relatively small climate induced variability is found.
- For the importance of erosion not just the mean discharge is relevant, but also the occurrence of events with very high runoff.
- All of the above is space-dependent. Especially when looking at smaller sub-basins and tributaries, the characterization of a certain hydrological year may differ from the characterization at the level of the Danube as a whole.

Some supportive information is compiled in Section 9.5.

4 Effects of measures

4.1 Types of measures

This section explores the effects on emissions and on surface water quality of three kinds of measures. First, the collection and treatment of wastewater is studied by a series of scenarios:

- S01: a scenario in which full connection to sewer systems is provided to all DRB inhabitants, without any changes to the wastewater treatment. So, all additionally collected wastewater is left untreated.
- S02: a scenario as S01, with tertiary treatment applied for agglomerations with more than 100,000 population equivalents, and secondary treatment applied for agglomerations with more than 10,000 population equivalents.
- S03: a scenario as S02, with advanced treatment applied for agglomerations with more than 100,000 population equivalents.
- S04: a scenario as S02, with advanced treatment applied for agglomerations with more than 10,000 population equivalents.

These scenarios are simulated for the two pharmaceuticals studied here (carbamazepine and diclofenac). The removal of these substances in secondary and tertiary treatment is assumed 0% for carbamazepine and 27% for diclofenac. In the advanced treatment, the removal of both HS is assumed 90%.

Next, the management of stormwater is studied by a series of scenarios:

- S05: a scenario as S02, with 100% collection of stormwater, 100% treatment of the collected stormwater and no combined sewer overflows.

- S06: a scenario as S02, with 100% local storage and infiltration of stormwater and no combined sewer overflows.

These scenarios are simulated for all 17 HS .

A final scenario is dedicated to the reduction of erosion:

- S07: starting from the present situation, all erosion is reduced by 50%.

This scenario is also simulated for all 17 HS.

4.2 Effects on emissions to surface waters

Table 4.1 lists the relative change of the basin wide emissions under the various scenarios. For the pharmaceuticals, scenarios S01-S04 are relevant. The results show an increase of the emissions as a result of the construction of sewers (S01: increase 20-22%), that is only partly (for diclofenac) or not at all (for carbamazepine) compensated by conventional treatment (S02: increase 13-20%). Advanced treatment in agglomerations > 100,000 PE compensates the increase (S03: decrease 6-8%), while advanced treatment in agglomerations > 10,000 PE leads to a very substantial reduction (S04: decrease 45-46%).

For the other simulated substances, the construction of sewers and implementation of conventional treatment leads to limited changes, with the exception of bisphenol-A and PFOS, both substances with a relatively high share of emissions from wastewater and no or very limited removal by conventional treatment.

Table 4.1: Relative change of basin-wide emissions under the various scenarios

	S01	S02	S03	S04	S05	S06	S07
Cd		0%			0%	-1%	-39%
Pb		0%			-1%	-4%	-45%
Cu		0%			0%	-6%	-33%
As		0%			0%	-1%	-39%
Ni		0%			1%	-1%	-42%
Hg		1%			1%	0%	-27%
Zn		1%			5%	-9%	-29%
BaP		0%			-4%	-10%	-7%
PFOS		4%			9%	-4%	-1%
PFOA		1%			3%	-1%	-1%
BPA		14%			17%	1%	0%
Met		0%			0%	0%	0%
Tcz		0%			13%	-26%	0%
Cbz	20%	20%	-6%	-46%	20%	20%	0%
Dcf	22%	13%	-8%	-45%	11%	11%	0%
NP		-1%			-8%	-24%	-12%
OP		1%			4%	-4%	-5%

The stormwater management scenario with collection and treatment of all stormwater (S05) shows a diverse response: for some substances the emissions increase, for others they decrease. Factors controlling this are the loads in stormwater and the removal by conventional treatment. For all substances the emissions to surface water are lower if all stormwater is stored and infiltrated rather than collected and treated (S06). This is quite obvious. For mobile substances, the loads towards the soil system may lead to increased groundwater pollution.

The reduced erosion scenario shows large decreases in the emissions of HS for which this pathway is relevant, notably the metals and to a lesser extent benzo[*a*]pyrene and the phenols.

The above is further illustrated in Figure 4.2Figure 4.1 and Figure 4.2 that show the breakdown of the emissions of carbamazepine and zinc under the different scenarios.

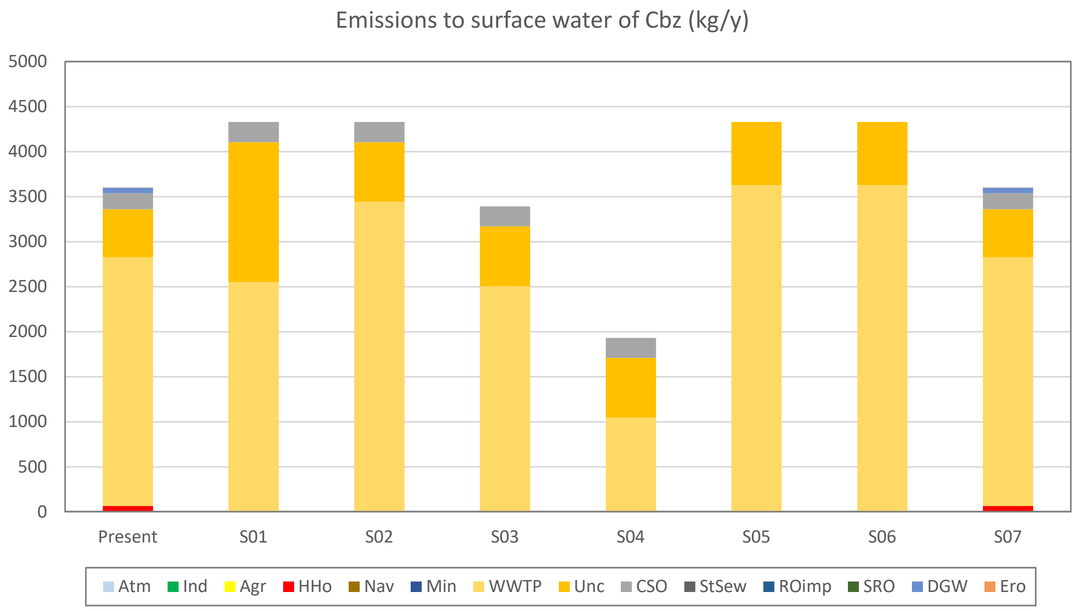


Figure 4.1: Breakdown of basin-wide emissions of carbamazepine in the various scenarios.

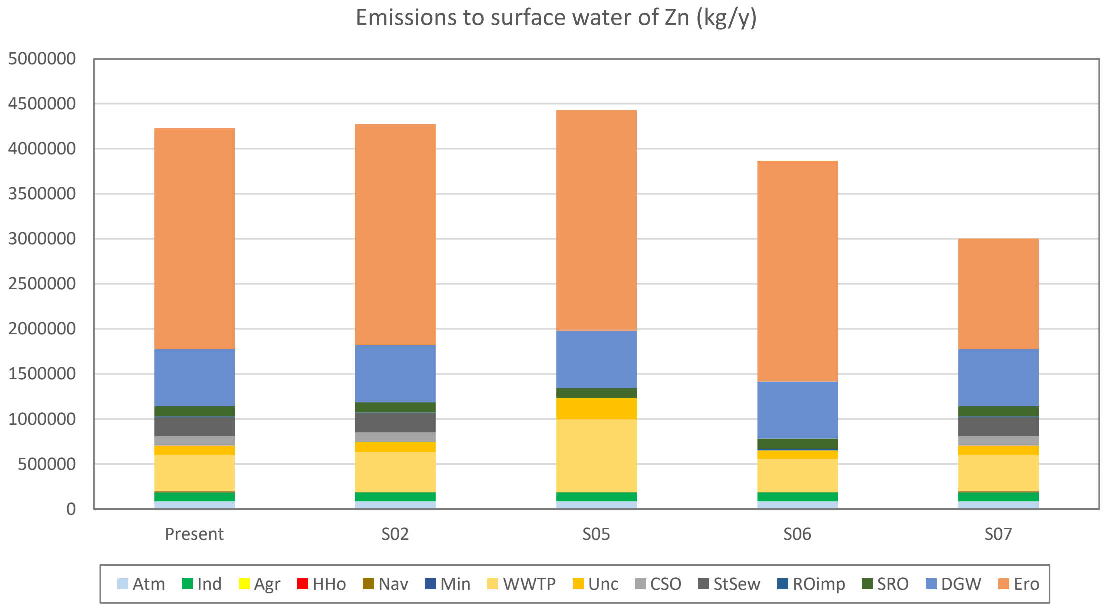


Figure 4.2: Breakdown of basin-wide emissions of zinc in the various scenarios.

4.3 Effects on concentrations in surface waters

The effects of the various scenarios on the concentrations along the Danube River are shown in longitudinal plots. For all scenarios, 10-year average concentrations are shown. In the plots also the range of the 10 annually averaged concentrations calculated for different hydrological years and present emissions is shown. This allows an interpretation whether the expected change is large or not compared to the normal inter-annual variability.

For zinc (Figure 4.3), the stormwater collection scenario S05 has a small negative effect, and the stormwater infiltration scenario S06 a positive effect. The reduced erosion scenario S07 has a strong positive effect that goes beyond normal inter-annual variability.

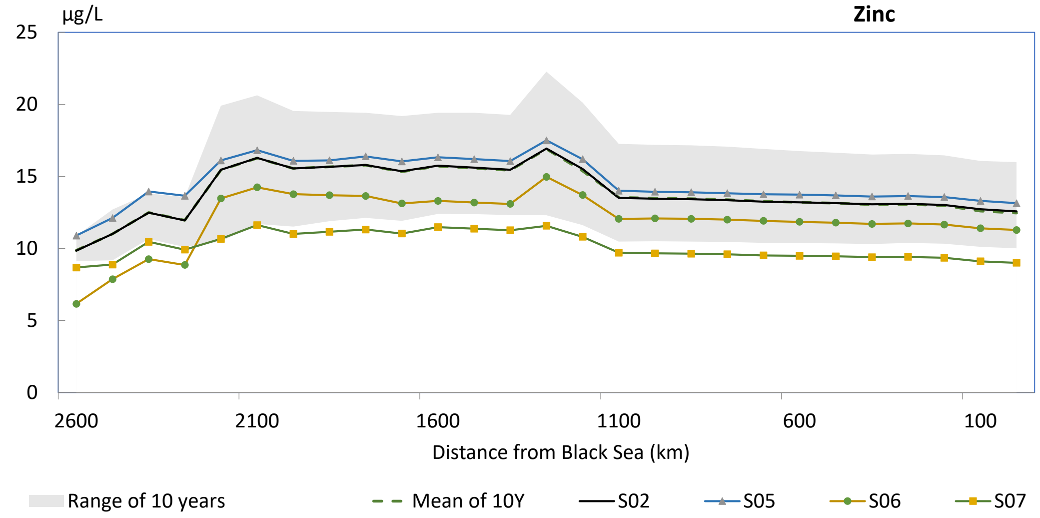


Figure 4.3: Concentrations along the Danube River of zinc in the various scenarios.

For benzo[*a*]pyrene (Figure 4.4), all stormwater and erosion scenarios have a small positive effect. The largest effect is from the stormwater infiltration scenario. The scenarios have small effects as they do not touch the most relevant pathways for this HS: atmospheric deposition, navigation and surface runoff.

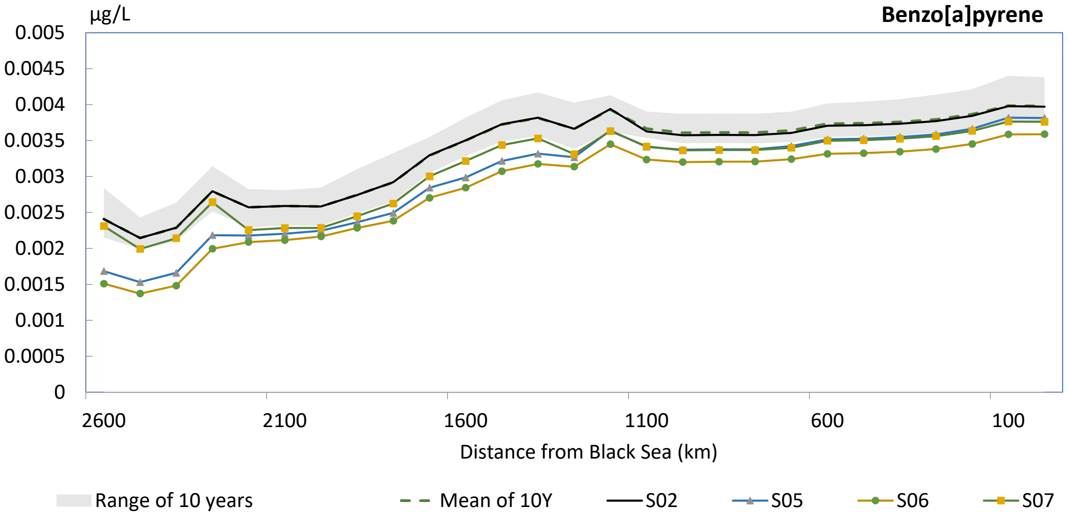


Figure 4.4: Concentrations along the Danube River of benzo[a]pyrene in the various scenarios.

As none of the scenarios showed any impact on the pesticide metolachlor, Figure 4.5 shows the results for tebuconazole. The stormwater collection scenario S05 has a significant negative effect, while the stormwater infiltration scenario S06 a strong positive effect. These results trace back to the fact that a substantial part of the simulated emissions stem from the use of this HS as a biocide in the built environment.

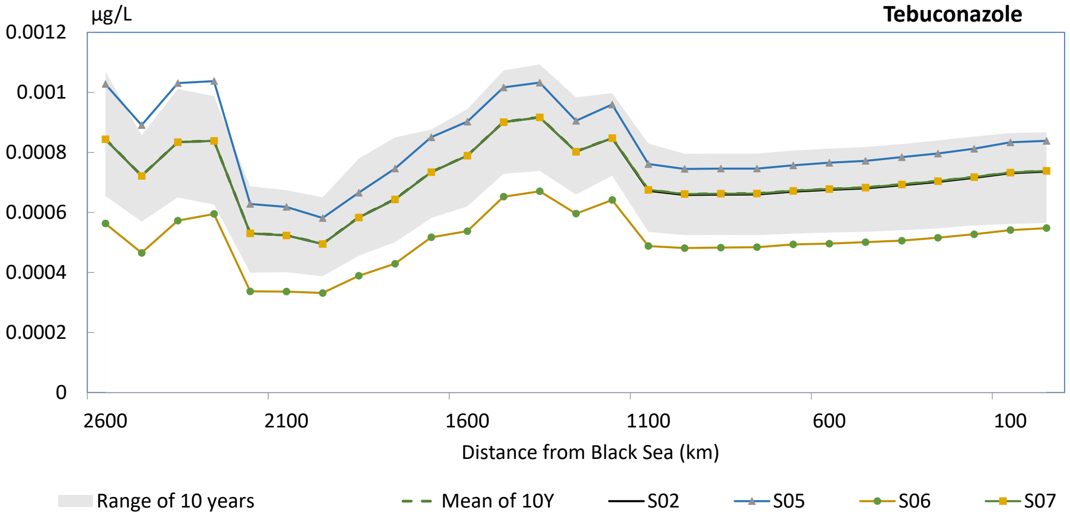


Figure 4.5: Concentrations along the Danube River of tebuconazole in the various scenarios.

The concentrations of carbamazepine show an increase in the downstream sections in the sewer construction scenario S1 and in the scenarios with conventional treatment S02 (Figure 4.6). Advanced treatment (S03) in larger agglomerations only (S03) has a small positive effect, while implementation also in middle size agglomerations (S04) leads to a strong decrease.

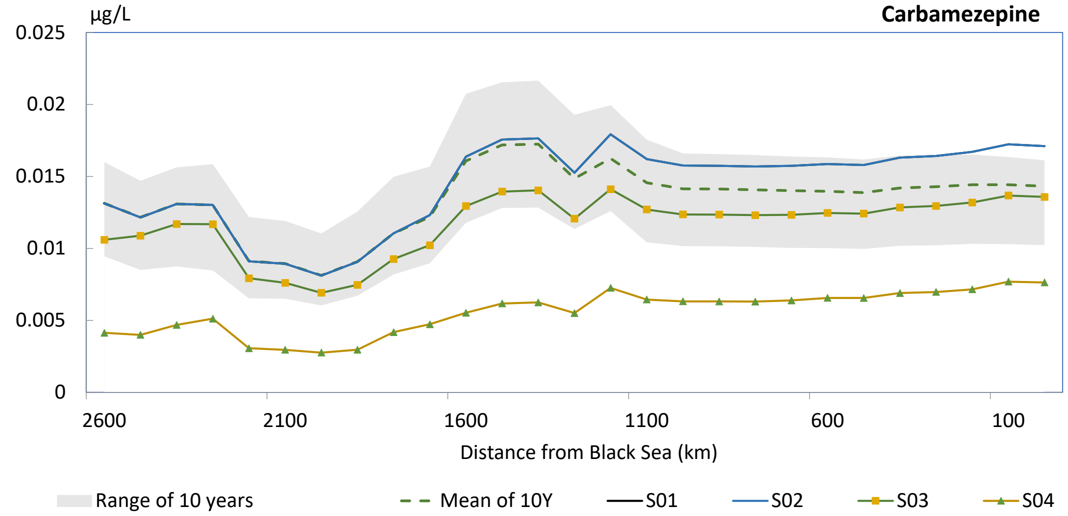


Figure 4.6: Concentrations along the Danube River of carbamazepine in the various scenarios.

Finally, Figure 4.7 shows the concentrations for PFOS. These are only marginally affected by any of the scenarios. This is the consequence of the lack of removal by treatment and the fact that the most significant (simulated) pathway of subsurface flow is not affected by any of the measures.

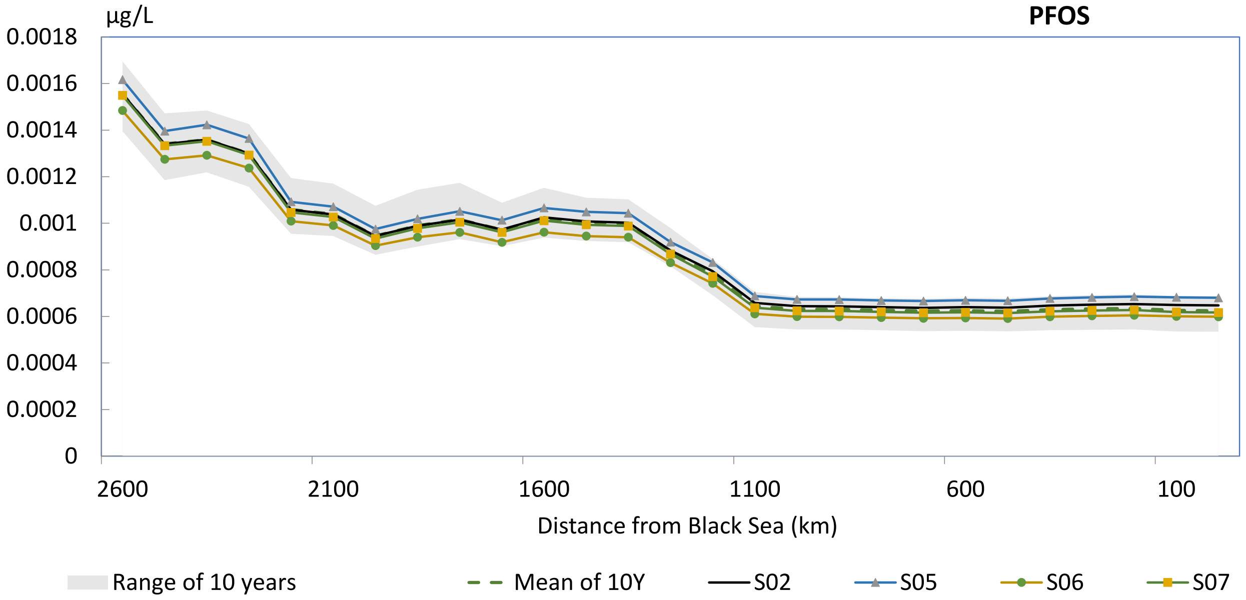


Figure 4.7: Concentrations along the Danube River of PFOS in the various scenarios.

4.4 Effects in smaller rivers

This section discussed basin-wide emissions and concentrations along the Danube. These results show the trends and tendencies very well, but typically in a moderate way. In tributaries draining smaller basins, the response of the water quality to interventions may be expected to be stronger and more diverse. If a measure addresses a pathway or source that is very relevant in a given subbasin, the response will be stronger than the "average" response shown above. Also the opposite holds: if a measure addresses a locally less relevant pathway. The maps shown in Section 2 illustrate this spatial variability.

5 Concluding remarks

The current assessment report presents a basin-wide emission inventory for 17 Hazardous Substances (HS). These substances were selected to represent relevant sources and pathways of HS, so that their emission inventories would provide valuable insights not just for these 17 substances, but for a wide spectrum of HS. The adopted methodology was directly derived from the relevant EU Guidance. The "source-oriented" approach was selected to offer the best possible insight in the origin of the emissions, as a basis for the definition of emission reduction measures. From the 12 emission pathways identified in the guidance, all except emissions from "abandoned and historic mining" could be quantified. This is expected to affect the accuracy of the emission inventory for certain metals.

The method relies on mass balances: it quantifies "sources" of HS to the environment and traces them via various pathways towards the surface waters. It makes use of spatial information (population, land use, wastewater management, etc.) to quantify these sources and pathways. Spatio-temporal information about the basin hydrology and about sediment transports is used to quantify temporal variability of emissions and surface water quality.

Emissions have been quantified as a function of time and space for the whole Danube River Basin, using 10 different hydrological years. The results therefore give insight in the inter-annual variability of the emissions as affected by climate variability. In addition, in-stream concentrations have been calculated for the same period. The simulated concentrations show a satisfactory agreement with measured concentrations. For HS where data from the existing Transnational Monitoring Network were not sufficient for the model validation, results from complementary monitoring conducted within Danube Hazard m3c were used. Targeted measurement campaigns carried out in pilot regions were available to fill critical data gaps and to support a critical evaluation of the modelling results in these regions.

Next to the overall emissions inventory, this report presents their subdivision over all pathways distinguished in the EU Guidance. Spatial gradients were mapped and country inventories were presented to further elucidate spatial gradients in the Danube River Basin. Basin-wide mass balances for various key compartments (e.g. impermeable surfaces, sewers and wastewater treatment, soils, surface waters) were presented for all 17 HS to provide further insight in HS mass flows.

The emission inventory can only be as good as its input data are. As the amount of input is significant, there is always a degree of uncertainty. The unquantified emissions from abandoned mining sites are part of this uncertainty. In this context also the reported incompleteness of E-PRTR can be mentioned (van de Roovaart et al., 2022, and references therein). To reflect the uncertainty of emission estimates, a low and a high estimate were developed, next to the middle (best) estimate.

The inter-annual variability of emissions and water quality due to climate variability was quantified. Metals emissions typically vary by a factor of 2-4 between individual years, as a result of the variability of erosion. For other HS, the variability of emissions is a factor 2 at most, with very low variability for pharmaceuticals as their emissions are not affected by weather. For the concentrations along the river Danube, the inter-annual variability is again highest for the metals (typically a factor 1.5-2.5), again due to the variable erosion. There is also considerable inter-annual variability (almost a factor 2) for HS with by approximation constant emissions (e.g. pharmaceuticals), due to the variable in-stream dilution. This inter-annual variability is however mostly smaller than the uncertainty of the calculated emission (typically a factor 2-4).

The uncertainty of the DHSM results increases with decreasing spatial scale. Many spatially variable input quantities could only be quantified on a country-by-country basis. This implies that the results for the main branch of the Danube and for the large international tributaries like Sava and Tisa are probably more robust than those for the smaller tributaries. Based on the results presented in this report, climate change could possibly have two effects at the scale of the Danube Basin as a whole:

1. an increasing occurrence of high erosion events would lead to increasing emissions of HS whose emissions are (partly) determined by erosion;
2. an increasing occurrence of low discharge events would lead to higher concentrations of a wide range of HS due to lower dilution.

Whether or not such climatic changes can indeed be expected was not subject of study.

Exploratory scenarios were simulated to investigate the potential effect of pollution control measures. The success of measures targeting wastewater management was found to be dependent on the removal in treatment plants. Advanced treatment to remove pharmaceuticals (quaternary step) was found to be specially effective if all plants > 10,000 population equivalents would be upgraded.

Some scenarios targeted stormwater management. A scenario investigating collection and treatment of stormwater showed variable results. The concentrations of some HS would actually increase, dependent on the concentrations in stormwater and the removal in treatment plants. A scenario investigating storage and infiltration of stormwater showed a consistent reduction of emissions and improvement of water quality.

A final scenario investigating erosion reduction measures showed positive effects on all metals and, to a lesser extent on other HS with a more limited contribution of erosion to the total emissions.

A final observation is that inter-annual variability and the responses to HS control measures would be stronger in smaller rivers than in the large rivers that have been the focus of this report.

Part B – Danube Hazardous Substances Model

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6 Approach

6.1 General

Following the considerations discussed in Section 2.1, the Danube Hazardous Substances Model uses the flow-chart shown in Figure 6.1 for its emission calculations. The pathways shown in this scheme will be discussed in detail below.

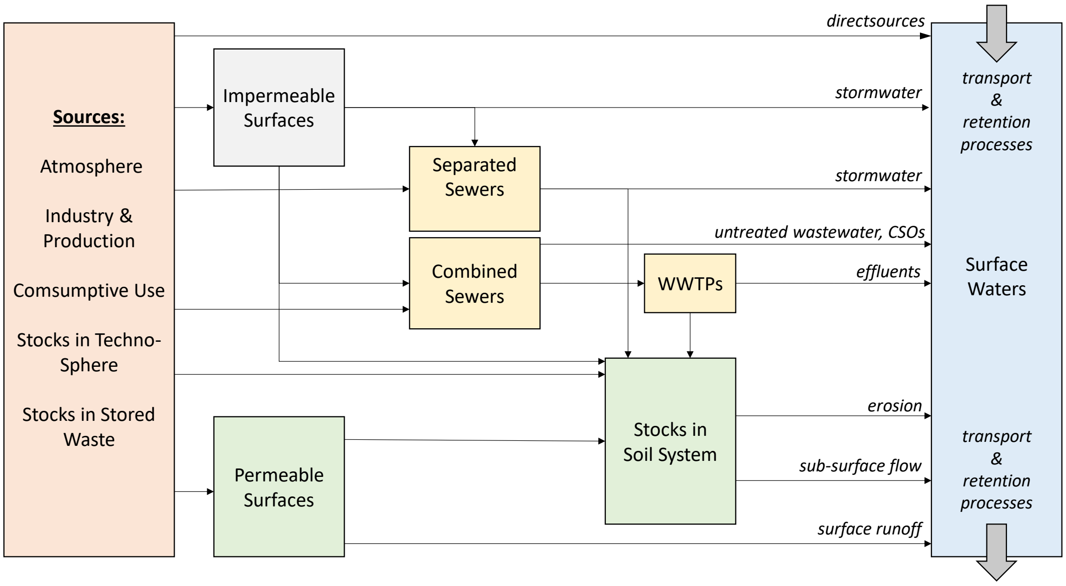

Figure 6.1: Set-up of the model system

6.2 Quantification of sources

The quantification of the losses of HS associated to the various sources proceeds by the emission factor method. A variable collection of sources can be considered. Losses (L) of a pollutant “p” for a certain socio-economic activity “a” are calculated by multiplying an activity rate (AR_a) by an emission factor for this activity and a certain pollutant ($EF_{p,a}$):

$$L_{p,a} = AR_a \text{ x } EF_{p,a}$$

Losses are distributed in space according to alternative methods. If the activity rate is known for a larger geographic area only (DRB, country), the losses are first calculated at this aggregated level and then distributed in space using an auxiliary spatial variable called a “locator”. It is also possible that the activity rate and/or the emission factors is already a spatially distributed variable and can be directly used to calculate spatially variable losses.

The quantified losses are allocated to various initial receptors and routed through connected compartments towards the surface waters (as shown in Figure 6.1). Initial receptors can be: (1) the surface waters (directly), (2) the soil system, (3) impermeable surfaces, (4) permeable surfaces, (5) the sewage collection system (combined or separated) and (6) the separate rainwater collection system.

The selection of sources included relies on the Technical Guidance (European Commission, 2012) and on data availability. This is further discussed in Section @@.

6.3 Pathways

Following the scheme in Figure 2.3, the DHSM uses a detailed representation of various pathways.

6.3.1 Wastewater

Wastewater management is divided in three categories: (1) centrally collected by sewer systems; (2) collected in “individual or appropriate systems” (IAS) as defined under the Urban Wastewater Treatment Directive (UWWTD), or the equivalent “local systems” (LS) as defined in the DRBMP; (3) uncollected wastewater. Wastewater collected in IAS or LS undergoes some losses to the environment (soils) while part of the HS load is transported to WWTPs. Uncollected wastewater is for a small part released to surface waters (equal to the local share of surface waters in the total area), while the remainder is released to soils.

Thus, the allocation of wastewater to the modelled compartments is:

$$\mathit{WWtoSew} = \mathit{FrSewered} + \mathit{FrSeptic}*(1-\mathit{Soi\_Septic})$$

$$\mathit{WWtoSfw} = (1-\mathit{FrSewered}-\mathit{FrSeptic})*\mathit{fOpenWater}$$

$$\mathit{WWtoSoi} = (1-\mathit{FrSewered}-\mathit{FrSeptic})*(1-\mathit{fOpenWater}) + \mathit{FrSeptic}*\mathit{Soi\_Septic}$$

where *WWtoSew*, *WWtoSfw* and *WWtoSoi* are the fractions of wastewater allocated to the sewer system, the surface water and the soils respectively, *FrSewered* and *FrSeptic* are the fractions collected by sewers and IAS/LS respectively, *Soi_Septic* is the fraction of HS collected in IAS/LS allocated to soils and *fOpenWater* is the local share of open water surfaces.

The fraction of wastewater allocated to the sewage system can remain untreated (*FrTreat0*) or undergo treatment at three different levels (*FrTreat1*, *FrTreat2*, *FrTreat3*). For each of the three treatment levels, the fraction of the influent reaching the effluent (*Eff_Treati*) and the sludge (*Sld_Treati*) respectively is specified. For the untreated fraction all influent reaches the effluent. So, the overall fractions reaching the effluent (*Eff_WWTP*) and the sludge (*Sld_WWTP*) equal:

$$\mathit{Eff\_WWTP} = \mathit{FrTreat0} + \mathit{FrTreat1}*\mathit{Eff\_Treat1} + \mathit{FrTreat2}*\mathit{Eff\_Treat2} + \mathit{FrTreat3}*\mathit{Eff\_Treat3}$$

$$\mathit{Sld\_WWTP} = \mathit{FrTreat1}*\mathit{Sld\_Treat1} + \mathit{FrTreat2}*\mathit{Sld\_Treat2} + \mathit{FrTreat3}*\mathit{Sld\_Treat3}$$

Note that removal during treatment is implicitly defined if $\mathit{EffTreat} + \mathit{Sld\_Treat} < 1$. In a final step, the fraction reaching sludge is corrected for “removal” of sludge by incineration and isolation (*fSldgRem*):

$$\mathit{Sld\_WWTP} = \mathit{Sld\_WWTP}*(1-\mathit{fSldgRem})$$

Loads allocated to the sewer system are subject to overflow events (CSOs), during which the treatment is bypassed; CSOs are assumed to occur if a rainfall threshold is exceeded.

6.3.2 Stormwater

The substances washed off from impermeable areas find their way to a separate rainwater collection system, a combined collection system for stormwater and wastewater or to surface waters and soils in places where there is no collection system. Separate collection systems discharge to surface waters, while a retention term can be defined that is allocated to soils. Combined collection systems undergo the pathway as indicated above for wastewater.

6.3.3 Soil related pathways

In the original SOLUTIONS approach, all soil-related pathways were simulated inside a multi-media fate and transport model (Lindim et al., 2016). This approach was reconsidered because of its complexity and its excessive computational burden. The selected approach is shown in Figure 6.2.

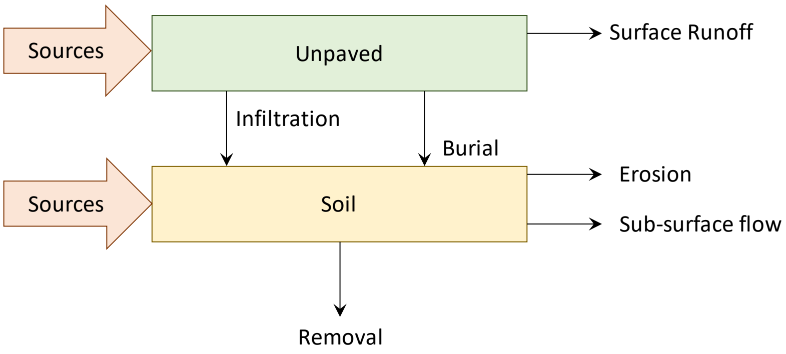

Figure 6.2: Schematic representation of soil-related pathways

DHSM uses a 2-layer system, where the "Unpaved" layer is very small and controls the surface runoff. The underlying soil layer controls erosion and subsurface flow. The surface runoff and infiltration are formulated as follows:

$$k_{mob} = \max\left(\min\left(\frac{RO + INF}{MOB_{thr}}, 1\right), 0\right)$$

$$F_{runoff} = \max\left(\min\left(\frac{RO}{RO + INF}, 1\right), 0\right) \times k_{mob} \times M$$

$$F_{infilt} = \max\left(\min\left(\frac{INF}{RO + INF}, 1\right), 0\right) \times k_{mob} \times M$$

where

k_{mob}	mobilization rate by runoff or infiltration (d^{-1})
RO	actual surface runoff intensity (mm/d, input)
INF	actual infiltration intensity (mm/d, input)
MOB_{thr}	threshold for mobilisation (mm/d, parameter)
M	HS mass (g)
F_{runoff}	HS runoff flux (g/d)
F_{infilt}	HS infiltration flux (g/d)

HS can move from the Unpaved layer to the soils by "burial":

$$F_{burial} = k_{burial} \times M$$

where

M	HS mass in the unpaved compartment (g)
k_{burial}	burial rate (1/d, parameter)
F_{burial}	HS burial flux (g/d)

The erosion is calculated as follows:

$$F_{erosion} = F_{part} \times Q_{soil} \times f_{enr}$$

where

f_{enr}	enrichment factor (-, parameter)
F_{part}	sediment delivery to streams (g/d, input)
Q_{soil}	quality of top soil (gHS/gDW)
$F_{erosion}$	erosion flux (gDW/d)

The HS flux related to subsurface flow is calculated as follows:

$$F_{sub} = \frac{EXF}{SoilThick \times SoilPor} \times f_{mob} \times M$$

where

f_{mob}	mobile fraction of HS (-)
EXF	exfiltration rate (m/d, input)
M	mass of HS (g)
$SoilThick$	layer thickness (m, input)
$SoilPor$	Soil Porosity (-, input)
F_{sub}	HS flux by subsurface flow (g/d)

Removal in soils is calculated as follows:

$$F_{removal} = k_{soil} \times M$$

where

M	HS mass in the soil compartment (g)
k_{soil}	HS removal rate (1/d, parameter)
$F_{removal}$	HS removal flux (g/d)

An initial concentration in the soil system needs to be defined for naturally occurring (metals) and persistent legacy substances. The mobile fraction is calculated using an equilibrium partitioning.

6.4 In-stream processes

In the surface waters, the simulated HS are subject to various processes that can be responsible for retention:

- Partitioning between the freely dissolved phase and the suspended particulate matter (SPM), using an equilibrium partitioning concept, using a K_d parameter (m^3/kg).
- Net settling of the fraction associated with SPM, represented by a first order process with a rate constant equal to the settling velocity of SPM (v_s, m/d) divided by the local water depth (H, m).
- Degradation by various processes (bio-degradation, hydrolysis, photolysis), represented by a first order process with a rate constant k (1/d) and a temperature dependency formulated as $\theta^{(T-20°C)}$.

6.5 Spatial scale

6.5.1 Schematization

The DHSM adopts the spatial schematization of the E-Hype model (Hundecha et al., 2016). For the DRB[2], this schematization exists of 3,523 elements with a total surface area of 807,336 km^2, which makes for an average area of 229 km^2 per cell. Figure 6.3 shows the schematization of the DHSM, together with the DRB delineation, the rivers with a catchment area exceeding 4,000 km^2 and the lakes with a surface exceeding 100 km^2, as identified by ICPDR[3]. For the presentation of model results, a mapping has been made of the E-Hype schematization elements on these rivers and lakes.

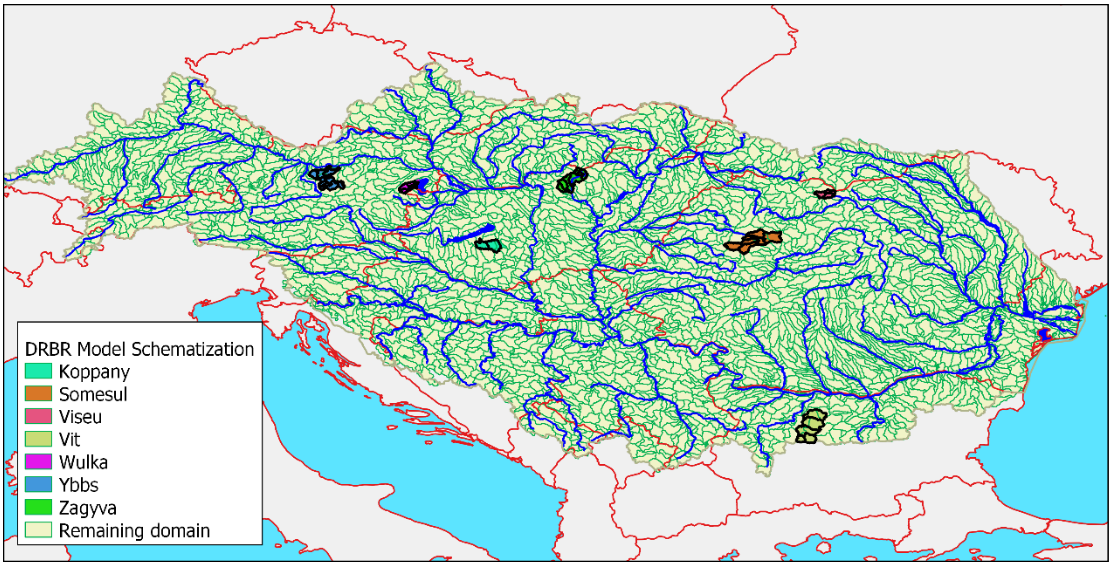

Figure 6.3: Overview of DHSM schematization, main rivers, lakes and pilot regions.

6.5.2 Pilot regions

The Danube Hazard m3c project distinguishes 7 pilot regions (indicated in Figure 6.3). In these pilot regions, targeted measurement campaigns have been carried out to fill critical data gaps needed to provide a robust basis for modelling and management. A detailed modelling of HS pathways using the MoRE model (Fuchs et al., 2017) has been carried out. The information derived from these pilot regions has been used to support the implementation of the DHSM (see Section 8).

6.6 Temporal resolution

Emission inventories as described in the Technical Guidance typically aim at quantifying annual emissions. To achieve this, the DHSM uses a time dependent representation of some sources (e.g. atmospheric deposition) and especially of the pathways affected by the hydrology. This supports the representation of certain pathways that respond to events. It also supports the representation of interannual variability as controlled by climate variability. The DHSM is therefore set up for a sequence of hydrological years, so that the impact of climate variability can be quantified.

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[2] It is noted that the schematization does not completely follow the official ICPDR delineation of the DRB. This cannot be resolved as the DHm3c team does not have access to the spatial schematization of the E-Hype model. This is not expected to have a noticeable impact on the results.

[3] It concerns the public version of these layers as downloaded on 22 March 2021.

6.7 Target substances

The DHSM was implemented for the following 17 chemicals:

- Metals: arsenic (As), cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn) and mercury (Hg).
- Benzo[*a*]pyrene (BaP), as a representative of the group of Polycyclic Aromatic Hydrocarbons or PAHs.
- Pharmaceuticals: diclofenac, an anti-inflammatory drug and painkiller (Dcf), and carbamazepine, an anticonvulsant used in the treatment of epilepsy and neuropathic pain (Cbz).
- Industrial chemicals with wide dispersive use: octylphenol, (OP), nonylphenol (NP), bisphenol-A (BpA).
- Per- and polyfluoroalkyl substances (PFAS): perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid)PFOA).
- Pesticides: tebuconazole (Tcz), a fungicide used for wood preservation, and metolachlor (Met), a herbicide in agriculture.

This selection reflects the target chemicals of the Danube Hazard m3c project, selected to fulfil various criteria: (1) substances representing relevant sources and pathways, (2) substances relevant for ICPDR, national and regional authorities in the basin, (3) substances that can be actually detected and measured, so that data can be expected to be available. During the initial model development (Deltares, 2021) it appeared that some of the target chemicals of the Danube Hazard m3c project could not be modelled due to data gaps.

PFOS and PFOA are the “legacy” PFAS, which have been widely studied, monitored and which are being increasingly banned from products and industrial processes. They are being replaced in the market by several short-chain PFAS (e.g. PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA, L-PFBS, L-PFHxS), for which much less is known.

The group of 16 so called “EPA PAHs” includes many well-known PAH substances, some of them priority substances under the Water Framework Directive. In the DHSM, Benzo[*a*]pyrene is included to represent the wider group of PAHs.

The term "octylphenol" represents a large number of isomeric compounds (compounds with the same molecular formula, but a different molecular structure). Of these potential isomers, 4-tertoctylphenol (CAS No. 140-66-9) is the most commercially important. Similarly, nonylphenols are a family of closely related organic compounds, of which 4-n-nonylphenol (CAS 104-40-5) and branched 4-nonylphenols (CAS 84852-15-3) are representatives.

7 DHSM implementation

7.1 General

7.1.1 Software used

Within every schematization element (SE), a calculation procedure as shown in Figure 6.1 is carried out. The model system consists of two building blocks: (1) an emission model, and (2) an in-stream water quality model. The emission model is formulated in terms of mass flows. The water quality model is based on the advection-diffusion equation. Both building blocks are implemented within the generic open source water quality modelling software Delft3D[4]. This generic framework takes care of input, output, numerical integration of the governing equations, in-stream processes and the compilation of mass balances. Dedicated plug-ins provide the emission modelling algorithms[5].

For the present project, some modifications were implemented in the emission modelling plug-in. This concerns the explicit separation of some pathways (erosion, surface runoff, subsurface flow, unconnected sewers) and the provision of extra output for validation (simulated concentrations in stormwater, WWTP influents, surface runoff and subsurface flow).

7.1.2 Input data

The input data to the model consists of general input data and sources information. General input is independent of specific HS and characterizes factors affecting the spatial distribution of sources of HS and the representation of various pathways. Sources information is used to quantify the different sources of HS. Both types of input will be discussed below.

7.1.3 Model output

The software used provides output in the form of text files and (system-dependent) binary data files[6]. To avoid the complexities of having to read these system dependent binary files, supportive tools are available to extract specific information in (comma-separated value) text files.

7.2 General data

7.2.1 Population

Population data have been derived from the Global Human Settlement Layer (Florczyk et al., 2019). Per country, the total population in the DRBD has been scaled to match the population in the DRBD reported in the 2021 RBMP (ICPDR, 2021). Per SE, the population has been aggregated as a total. Figure 7.1 shows the results.

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[4] https://oss.deltares.nl/

[5] The emission modelling functionality is expected to be included in the generic version of the Delft3D software in the course of the year 2023. Until that time, the plug-ins need to be used.

[6] These system specific formats are in the process of being replaced by NetCDF files.

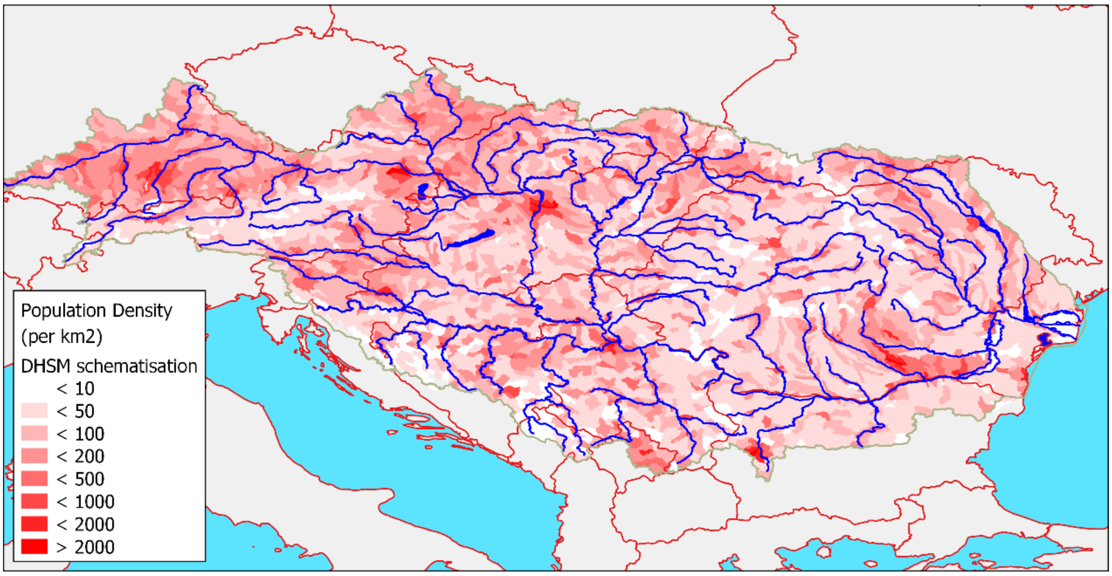

Figure 7.1: Population numbers used in the DHSM, expressed as population density per km^2.

The same source subdivides population in various urbanization classes. Per SE, the fraction of urban population[7] has been determined as input to the model, see Figure 7.2.

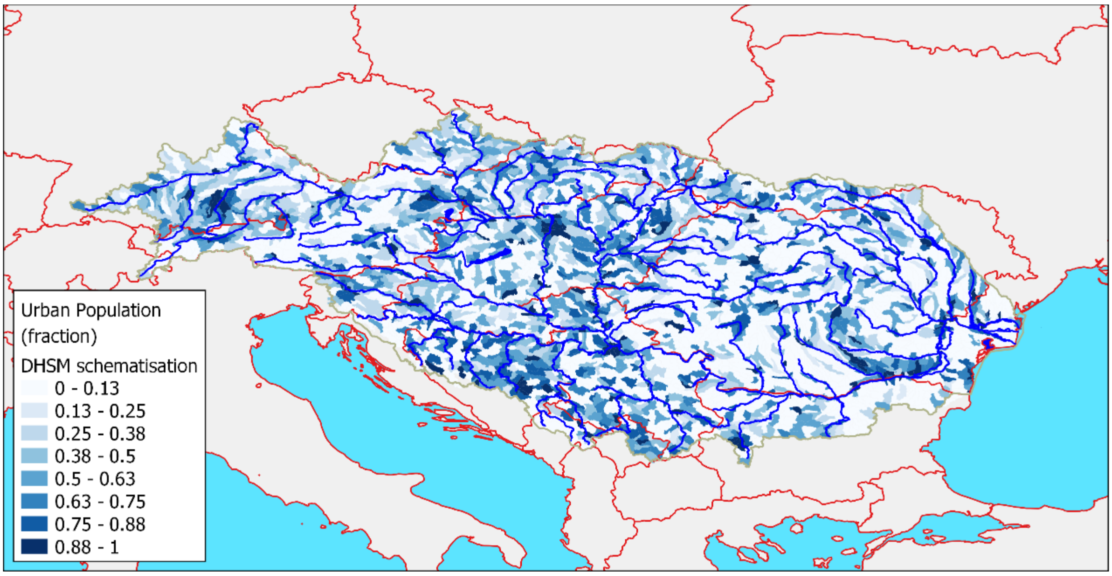

Figure 7.2: Fraction of urban population used in the DHSM.

7.2.2 Hydrology

Hydrology data were generated by E-Hype (Hundecha et al., 2016) and have been converted to a format suitable for use by the DHSM during the SOLUTIONS project. Hydrology data are available with a daily frequency, for a period stretching 11 years. This period is considered sufficient to provide an appropriate

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[7] "Urban" is defined here as the total of classes 21 ("Suburban"), 22 ("Semi-dense urban cluster"), 23 ("Dense urban cluster") and 30 ("Urban Centre").

representation of the spatial and temporal variability of the basin hydrology, and the impact thereof on the emissions, transport and fate of HS in the DRB. For all SEs, hydrology data comprise the surface water volumes and the longitudinal water fluxes connecting the river stretches in each SE. Specific hydrological process fluxes or combinations thereof have been extracted to support the emission calculations. This concerns rainfall, runoff from impermeable surfaces, surface runoff from permeable surfaces, infiltration and exfiltration.

The data are available for 2003-2011 with a daily interval (Figure 7.3). During this period, the simulated mean discharge is 7,205 m^3/s (Table 7.1). The year with the lowest discharge is 2003 (5,630 m^3/s, 22% lower than the average). The year with the highest discharge is 2010 (10,709 m^3/s, 49% higher than the average). Years with an annual discharge within 10% of the mean are 2004, 2005, 2006 and 2009. The sequence 2009-2011 represents a normal, an extremely wet and a dry year. Daily discharge values range from 1,615 m^3/s (September 2003) to 22,075 m^3/s (April 2013).

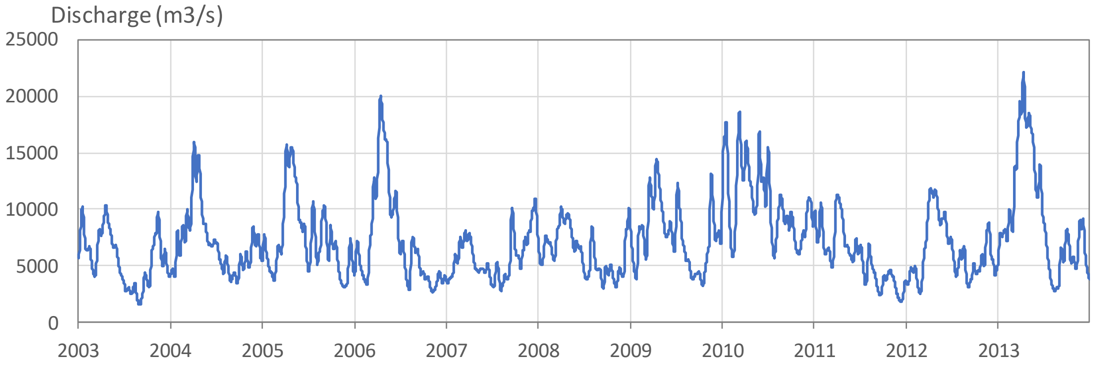

Figure 7.3: Simulated Danube River discharge just upstream of the Danube Delta during the period 2003-2013.

Table 7.1: Simulated mean annual discharges over the years 2003-2013

Year	Mean flow (m^3/s)	Anomaly	Year	Mean flow (m^3/s)	Anomaly
2003	5630	-22%	2009	7685	7%
2004	7061	-2%	2010	10709	49%
2005	7538	5%	2011	5729	-20%
2006	7255	1%	2012	6258	-13%
2007	5825	-19%	2013	9382	30%
2008	6192	-14%	2003-2013	7205	

The simulated time and space dependent rainfall has been used to derive spatial fields of simulated daily rainfall intensity with a given return time. The local P95 value is used as a threshold for the occurrence of combine sewer overflows, see Figure 7.4.

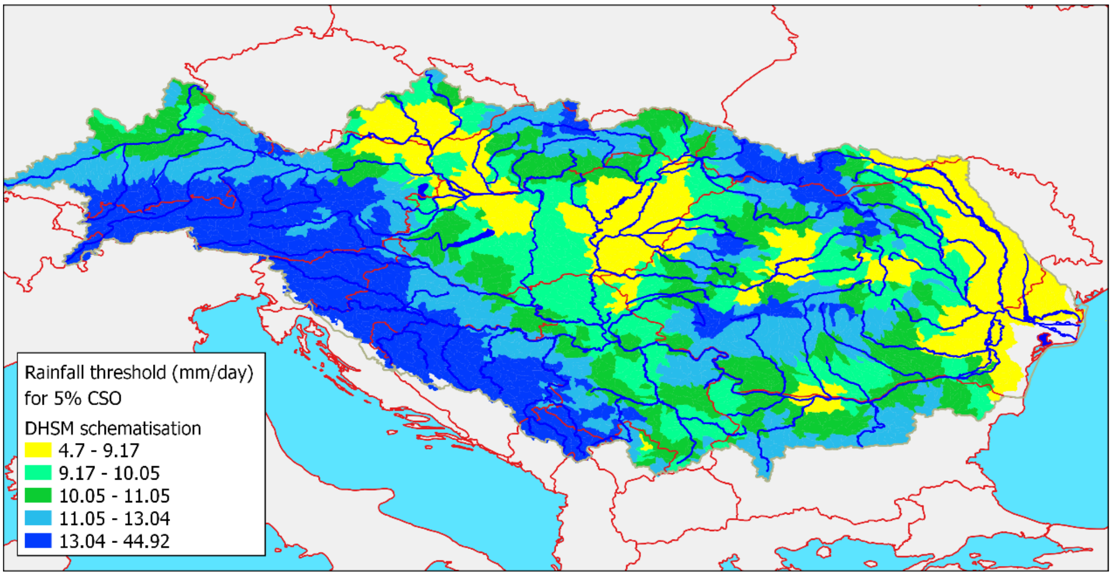

Figure 7.4: Local 95%tile of simulated daily rainfall over the period 2003-2013, used as a threshold for CSOs.

7.2.3 Land-use

Land use information was derived from the E-Hype hydrology model (Hundecha et al., 2016). The hydrology model distinguishes so-called "soil/land-use classes" of SLC. Each SLC consists of a combination of a defined soil type and a defined land use. Each schematization element (SE) is composed of a combination of SLCs, each defined by the fraction of its surface covered. The use of land-use information derived from the hydrology model guarantees consistency with the hydrology data. For the current implementation, the following aggregated land uses are compiled from the SLCs discussed above:

- water surface;
- impermeable surfaces;
- permeable surfaces;
- agriculture area.

7.2.4 Wastewater management

General information about wastewater management practices has been derived from the ICPDR UWWTD inventory (ICPDR, 2021; version provided on 8 September 2021). The following tables were used:

- The "agglo" table that defines agglomerations, the amount of wastewater produced and collected;
- The "tp" table that defines WWTPs and their treatment levels.
- The "tp-agglo" table that connects the two previous tables, where one agglomeration might have more WWTPs or one WWTP can be connected to more agglomerations.

Per country, the agglomerations were split in "urban" and "rural" by projecting their co-ordinates on the settlement type map discussed in Section 7.2.1. Using the inventory, the fate of the generated wastewater was aggregated per country and per settlement type into the classes used in the 2021 RBMP:

- Wastewater collected by sewers
  - not treated
  - undergoing primary treatment
  - undergoing secondary treatment
  - undergoing tertiary treatment
  - undergoing advanced treatment

- Wastewater collected by Individual Appropriate Systems (IAS; EU member states) or Local Systems (LS; non-member states)
- Wastewater not collected

The result is shown in Figure 7.5 (the data are included in Section 9.2).

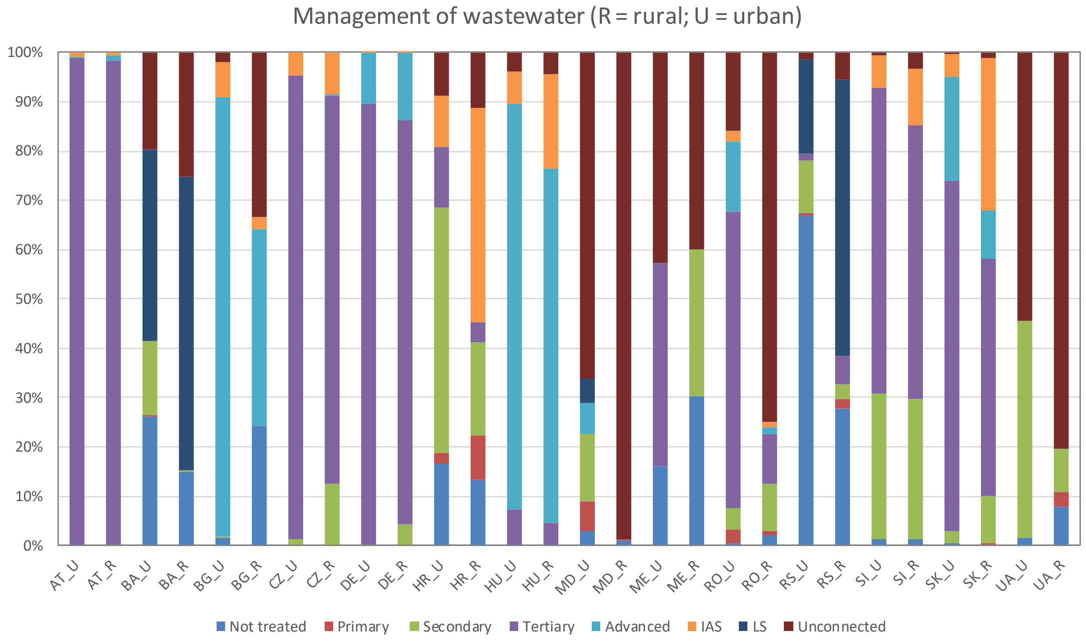

Figure 7.5: Classification of wastewater management per country and per settlement type.

Per SE, the population distribution over urban and rural (Section 7.2.1) was used to classify the fate of the locally generated wastewater. Example maps are shown in Figure 7.6 (fraction of collected wastewater by sewers) Figure 7.7 (fraction not treated).

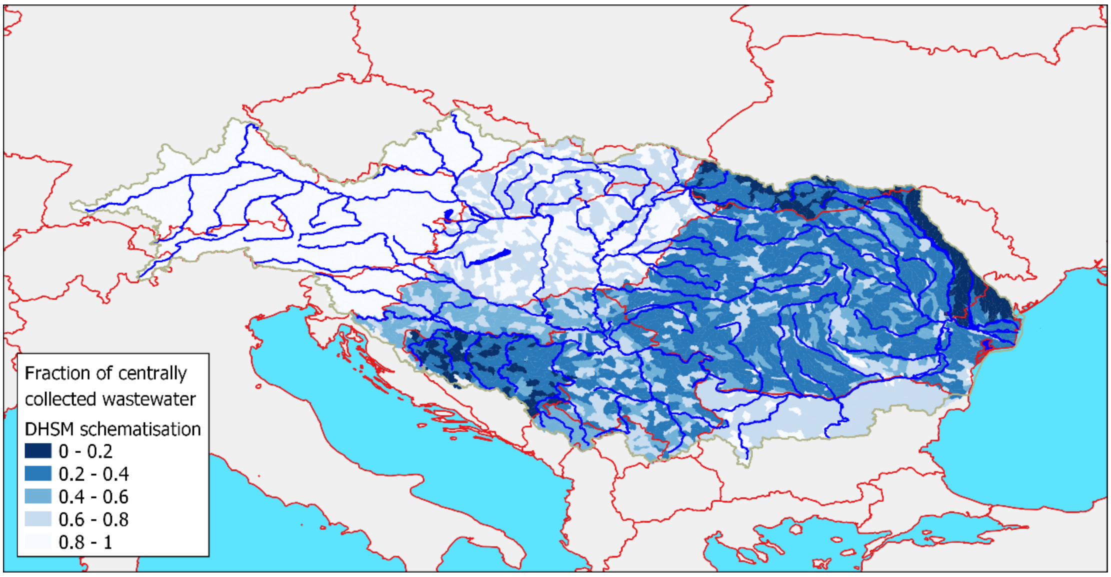

Figure 7.6: Fraction of wastewater collected, as derived from the ICPDR UWWTD inventory.

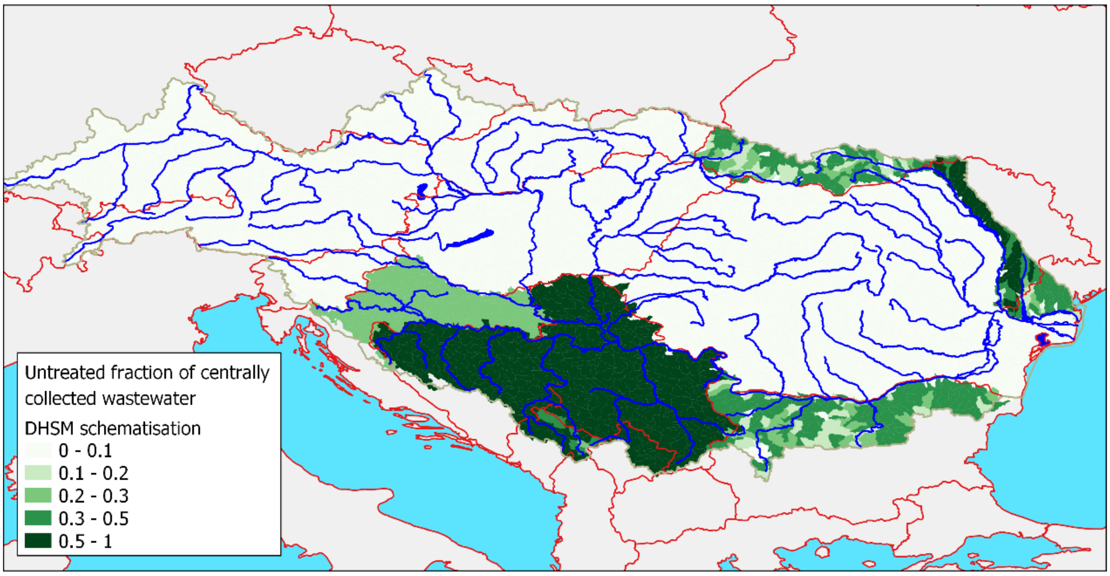

Figure 7.7: Fraction of collected wastewater not treated, as derived from the ICPDR UWWTD inventory.

7.2.5 Stormwater and sewage sludge

Data about the fraction of sewage sludge re-used in agriculture was available at the country level, as collected in the SOLUTIONS project (van Gils et al., 2020), supplemented by data for Germany from Roskosch et al. (2018). The share of combined sewer systems was taken from van de Roovaart et al. (2022), complemented with expert judgement. Results are compiled in Table 7.2.

Table 7.2: Additional waste water management data used at the country level

	Fraction of sewage sludge incinerated or isolated	Fraction of combined sewer systems
Austria	0.56	0.29
Bosnia_and_Herz.	0.20	*0.80*
Bulgaria	0.30	0.80
Croatia	0.20	0.50
Czech_Rep.	0.11	0.70
Germany	0.65	0.43
Hungary	0.18	0.03 (Budapest: 0.62)
Italy	0.52	0.80
Kosovo	0.20	*0.80*
Moldova	0.20	*0.80*
Montenegro	0.20	*0.80*
Poland	0.20	0.80
Romania	0.74	1.00
Serbia	0.20	*0.80*
Slovakia	0.10	0.10
Slovenia	0.82	0.59
Switzerland	0.90	*0.40*
Ukraine	0.20	*0.80*

The DHSM assumes that stormwater from impermeable surfaces is collected in centralized systems in the urban environment. It is further assumed that the impermeable surfaces in every SE are distributed over urban and rural areas in the same proportion as the population (Figure 7.2).

7.2.6 Per capita water volume delivered to WWTPs

For the benefit of calculating certain EFs in the remainder of this section, an estimate of the per capita inflow to WWTPs is derived in Table 7.3.

Table 7.3: Estimate of the per capita inflow to WWTPs.

Country	**Population in DRBD (millions)[1]**	**Wastewater to sewers (L/cap/d)[2]**	**Fraction of combined sewer systems[3]**	**Mean Rainfall (mm/y)[4]**	**Storm water to mixed sewers (L/cap/d)[5]**	**Total influent (L/cap/d)[6]**
AT	8.4	219	0.29	1231	99	318
BA	3.2	247	0.8	1092	241	488
BG	3.57	329	0.8	653	144	473
HR	2.9	301	0.5	944	130	432
CZ	2.7	164	0.7	689	133	298
DE	10.07	164	0.43	1017	121	285
HU	9.8	192	0.15	637	26	218
MD	0.96	192	0.8	544	120	312
ME	0.18	274	0.8	1807	399	673
RO	19.5	164	1	718	198	363
RS	7	247	0.8	753	167	413
SK	5.2	164	0.1	782	22	186
SI	1.82	219	0.59	1399	228	447
UA	3.03	192	0.8	860	190	382
DRBD Averages[7]					136	337

1. Source: ICPDR (2021) supplemented by data listed in Section 7.2.1.
2. Source: country data from Eurostat (2020), supplemented by expert judgement.
3. As discussed in Section 7.2.5.
4. Derived from hydrology model, averages for 2003-2013.
5. Product of an estimated 126 m2/cap of impermeable surfaces (Liefting and de Man, 2017), the average rainfall, the fraction of combined sewers and a runoff coefficient of 0.8.
6. Sum of previous columns.
7. Population weighed averages.

7.2.7 Erosion and sediment delivery

The sediment delivered to streams is relevant for the DHSM in two ways. First, it controls the emissions via erosion. Second, it controls the availability of suspended particulate matter (SPM) in the water column, the partitioning of HS in the surface waters and the trapping of HS in aquatic sediments. Such information was originally derived from the SOLUTIONS project (van Gils et al., 2020). During model validation, this information proved not very accurate. On top, the information turned out to be available only from 2006 onwards, which compromised the objective to provide insight in interannual climate-derived variability. For these reasons, newly available, unpublished[8] data were derived from the EU R&D project DOORS (https://www.doorsblacksea.eu/).

As the DOORS generated data cover another period (2011-2020), the cumulative sediment delivery to streams over this period was used as input and projected on the DHSM schematization. This quantity was then distributed over time in proportion to the locally generated total runoff to the power 3.

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[8] These results are expected to be published in the course of 2023.

7.3 Sources

7.3.1 General

Information to characterize the sources of HS has as much as possible been derived from the data collected in the Danube Hazard m3c project. This concerns partly external data collected by the project partners and partly the data derived from supplementary monitoring at 7 pilot areas. The data were compiled in a database. For the results presented in this report, an extract from 27 January 2023 was used. The data in the database were statistically processed by Steffen Kittlaus of project partner TU Vienna. For the results presented in this report, processing results generated on 7 March 2023 (PFAS and pharmaceuticals) and 19 January 2023 (other substances) were used.

7.3.2 Atmospheric deposition

7.3.2.1 EMEP simulated atmospheric deposition

Simulated atmospheric deposition fields covering the complete basin are available for three metals (Cd, Hg, Pb) and for BaP from the European Monitoring and Evaluation Programme (EMEP)[9] inventory. Data were generated by the Meteorological Synthesizing Centre - East (MSC-E), one of the international research Centres of the EMEP programme operating under the Convention on Long-range Transboundary Air Pollution (CLRTAP) of the United Nations Economic Commission for Europe (UNECE). The data are available at a 0.1-degree resolution rectangular grid. Data for the 4 most recent years (2017-2020) were downloaded from https://www.msceast.org/pollution-assessment/emep-domain-menu/data-hm-pop-menu, selecting the versions with emissions and climate from the same year. Every SE is attributed the mean value over 2017-2020 of the closest available data point (see Figure 7.8 and Figure 7.9 for examples).

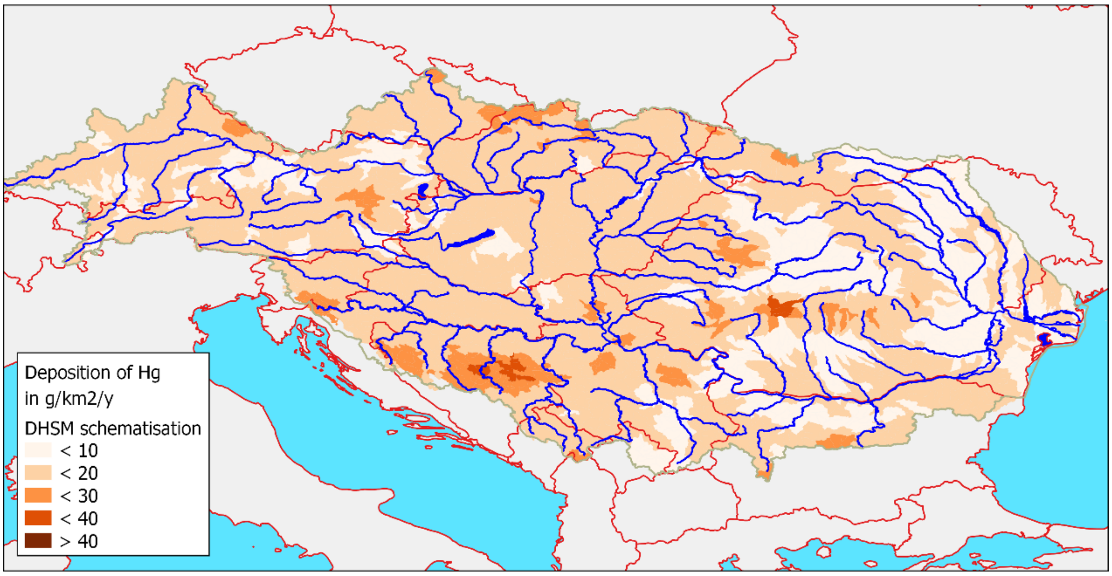

Figure 7.8: Annual atmospheric deposition of Hg for 2017-2020, as derived from EMEP simulation results.

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[9] A co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe.

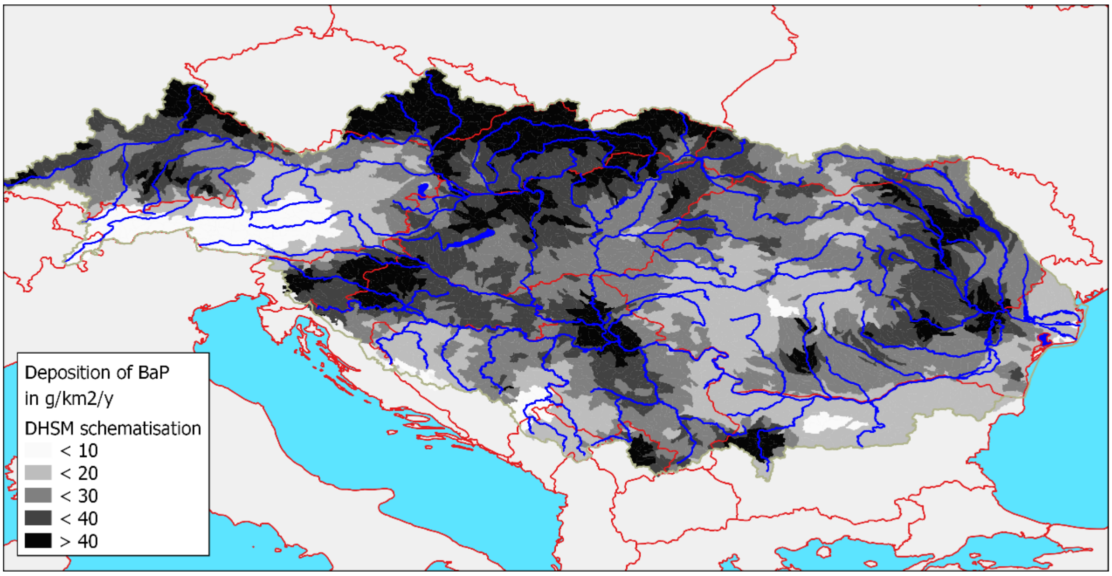

Figure 7.9: Annual atmospheric deposition of BaP for 2017-2020, as derived from EMEP simulation results.

7.3.2.2 Data for other substances

For the remaining substances, homogeneous values have been selected based on the available data from the 7 pilot areas, see Table 7.4. For the pharmaceuticals and pesticides, no atmospheric deposition was applied.

Table 7.4: Overview of selected values for atmospheric deposition (g km^{-2} y^{-1}).

Substances	**P25$^{(1)}$**	**P50$^{(1)}$**	**P75$^{(1)}$**
As	66.38985	95.83805	243.1667
Cu	1220.706	1677.431	2657.638
Ni	121.2786	212.7731	432.817
Zn	4144.575	7114.945	11582.18
OP	4.97422	7.284305	13.74298
NP	4.5479	6.827325	10.21161
PFOS	0.0763	0.110372	0.175846
PFOA	0.124151	0.236228	0.375147
BpA	6.932445	13.41156	30.63445

(1) Individual analysis results for the concentration were converted to a load using the precipitation in the sample or the precipitation during the sampling period. The indicated percentiles were derived from the results for the 7 pilot areas.

7.3.2.3 Spatial and temporal distribution

The EMEP data showed good spatial correlation between the metals Cd, Hg and Pb (correlation coefficient between 0.81-0.91), and limited correlation between BaP and the metals Cd, Hg and Pb (0.15-0.33). Relevant spatial correlations between the variables resolved by EMEP could not be observed in the 7 pilot areas. The same held for correlations between Cd, Hg, Pb or BaP and any of the other HS. Hence, the pilot area data did not offer a basis for using the spatial EMEP data to estimate the spatial variability of other HS. The project database only provides data for Austria and Hungary, so country-specific values could not be derived for any of the HS. Finally, neither population density (with or without weighing on GDP) nor rainfall was a good predictor for atmospheric deposition. Therefore, no spatial variability could be applied to the atmospheric deposition (other than for the variables derived from EMEP).

Atmospheric deposition can be separated in a dry and a wet component:

- Dry deposition: AR = surface area; EF = deposition rate (mass/area/time).
- Wet deposition: AR = rainfall volume; EF = concentration in rain.

The division over these components is controlled by a complex of factors including the total precipitation and the temporal distribution thereof. This dependency is however hard to quantify. Atmospheric deposition is hypothesized to be partly responsible for the increasing concentration of many chemicals during high river discharge periods (Zoboli et al., 2019). For this reason, the atmospheric deposition was applied as wet deposition only, using the mean simulated discharge over 2003-2013 to calculate the concentration in rainfall. As a consequence, atmospheric deposition in the model exhibits inter-annual variability as a result of rainfall variability.

The losses are allocated to surface water, permeable surfaces and impermeable surfaces, dependent on their respective surface area.

7.3.3 Agriculture

For emissions from agriculture, a load per unit area of agriculture land use is applied:

- Agriculture emissions: AR = agriculture area; EF = area-specific load (mass/area/time).

7.3.3.1 Metals

Area-specific loads for agriculture areas in a number of countries have been compiled from data by Comber (2021; 2023). These sources provide information for Cd, Cu, Ni and Pb. The area specific loads are significantly smaller than the older data reported for Germany in 2005 (Fuchs et al., 2010). As this latter source also reports loads for Hg and Zn, it has been used to obtain recent estimates for Hg and Zn as well. The results are compiled in Table 7.5.

Table 7.5: Area specific loads of metals to agricultural soils (kg km^{-2} y^{-1}) in various countries.

Country	Cd (1)	Cu (1)	Ni (1)	Pb (1)	Zn (2)	Hg (2)
AT	0.039	16.8	0.35	0.25	53	0.0076
BA	0.016	2.9	0.15	0.11	10	0.0014
BG	0.016	11.5	0.10	0.07	35	0.0051
HR	0.029	16.7	0.20	0.15	52	0.0075
CZ	0.026	14.1	0.21	0.14	44	0.0063
DE	0.045	11.2	0.41	0.29	36	0.0052
HU	0.047	32.4	0.36	0.26	100	0.0144
RO	0.021	11.2	0.14	0.13	35	0.0050
RS	0.028	12.8	0.15	0.42	40	0.0058
SK	0.021	7.0	0.15	0.11	22	0.0032
SI	0.067	29.9	0.58	0.41	94	0.0135

(2) Sum of sources from application of manure and inorganic fertilizers, as well as use in plant protection products (Cu). Atmospheric deposition and application of biosolids have been omitted to avoid double-counting.

(3) Estimated from the ratio to the sum of Cd, Cu, Ni and Pb (3.026 for Zn, 0.000437 for Hg) reported by Fuchs et al. (2010).

The losses are defined for most countries. For Montenegro, data from Bosnia and Herzegovina were used. For Moldova and Ukraine, data from Romania have been used. The losses were allocated to top soils.

7.3.3.2 Pesticides

From the target pesticides, metolachlor is mostly used as a plant protection product in agriculture, tebuconazole is also used as biocide. In the EU, tebuconazole has been approved for use as a wood preservative, while approval procedures for use as a film preservative and a construction material preservative were ongoing by mid 2022 (Antje Ulrich, pers. comm.).

Various sources exist that quantify the use volume of pesticides based on a method that multiplies areas with specific crops and crop- and product-specific application rates. Here, the 2020H estimates from the PEST-CHEMGRIDS global gridded maps were used (Maggi et al., 2019). It is noted that another data source was used for the preliminary DHSM (Sala et al. 2014). AS the model validation results were not very good, another data source was chosen.

For the use in agriculture, the direct losses to surface water by spray drift were assumed equal to the losses to air (15% for both HS; Sala et al. 2014) multiplied with the local fraction of surface water area. The losses to soils are assumed 20% for tebuconazole and 74% for metolachlor (Sala et al., 2014).

Ideally, pesticides use volumes are based on sales data, as these encompass all uses, not just the plant protection use. While the total volume of sold pesticides groups is known at the country level, the sale of individual pesticides is in most cases considered confidential. The use of pesticides in the built environment is further discussed in Section 7.3.5.

7.3.4 Road Traffic

Emissions from road traffic were quantified for tyre wear, road wear, brake wear and leakage of motor oils, following a methodology documented in the Netherlands PRTR (Deltares and TNO, 2016a-d). Emissions of individual substances are linked to the emissions of particles, expressed as a loss per vehicle kilometre (Table 7.6; modified after Deltares and TNO, 2016a-c) and to the loss of 10 mg motor oils per vkm (Deltares and TNO, 2016d).

Table 7.6: Emission factors for road traffic related particle emissions

	Cars	**Buses**	**Vans**	**Motorcycles**
Tire wear (mg/vkm)	100	300	600	50
Break wear (mg/vkm)	10	30	40	5
Road surface wear (mg/vkm)	150	700	700	60

Data on the presence of the target substances in these particle and oil emissions are listed in Table 7.7 (Deltares and TNO, 2016a-d; Comber, 23; Hjortenkrans, 2008).

Table 7.7: Concentrations of target substances in traffic related particle emissions (units: mg/kg)

Substance	Tire wear (light traffic)	Tire wear (heavy traffic)	Brake wear (light traffic)	Brake wear (heavy traffic)	Road wear	Motor oils
Cd	1	1	0	0	0.09	0.5
BaP	5.4	1.7	0	0	0.028 (1)	12
As	1	1	0	0	0	0.1
Cu	50	50	50000	2200	12.2	26
Pb	100	100	420	420	25.6	2
Zn	9500	17000	1500	1500	35.7	700
Ni	50	50	100	100	1.2	6
NP	10	10	0	0	0	0

(1) Based on the assumption that 40% of roads are asphalt (0.07 mg/kg) and the remainder is concrete or stone.

The traffic volume has been estimated on statistics from the International Road Federation World Road Statistics 2019 Report (IRF-WRS2019, 2019). These are proprietary data that cannot be duplicated here. This source provides data for the annual traffic volume for 2017, subdivided over passenger cars, buses, vans and motorcycles, for some countries in the DRB (Austria, Croatia, Germany, Hungary, Poland, Romania, Slovenia, Switzerland). For all countries in the DRB, the total vehicle fleet is known. The traffic volume data for the countries mentioned above were first converted to per capita numbers. The same was done for the vehicle fleet. For countries without data, the per capita traffic volume was copied from a neighbouring country, optionally scaled with a factor based on the per capita vehicle fleet (Table 7.8).

Table 7.8: Source of traffic volume data per country

Country	Data from	Scaled with ..	Country	Data from	Scaled with ..
Austria	Austria		Moldova	Romania	0.67
Bosnia Herz.	Romania	0.67	Montenegro	Romania	1
Bulgaria	Hungary	1	Poland	Poland	
Croatia	Croatia		Romania	Romania	
Czech Rep.	Germany		Serbia	Romania	1
Germany	Germany		Slovakia	Hungary	1
Hungary	Hungary		Slovenia	Slovenia	
Italy	Switzerland		Switzerland	Switzerland	
Kosovo	Romania	0.33	Ukraine	Romania	0.67

This resulted in the per capita traffic volumes as listed in Table 7.9.

Table 7.9: Per capita traffic volume (Mvkm/cap/y) in DRB countries

Country	Cars	Buses	Vans	Motorcycles
Austria	8.79E-03	6.88E-05	1.58E-03	2.77E-04
Bosnia and Herzegovina	1.27E-03	9.45E-05	2.77E-04	2.39E-05
Bulgaria	3.01E-03	7.15E-05	1.14E-03	4.54E-05
Croatia	4.43E-03	7.13E-05	5.10E-04	5.24E-05
Czech Republic	7.83E-03	5.61E-05	1.16E-03	1.68E-04
Germany	7.83E-03	5.61E-05	1.16E-03	1.68E-04
Hungary	3.01E-03	7.15E-05	1.14E-03	4.54E-05
Italy	8.31E-03	1.92E-05	9.39E-04	2.84E-04
Kosovo	6.25E-04	4.65E-05	1.37E-04	1.18E-05
Moldova	1.27E-03	9.45E-05	2.77E-04	2.39E-05
Montenegro	1.89E-03	1.41E-04	4.14E-04	3.56E-05
Poland	5.10E-03	4.53E-05	9.81E-04	1.07E-04
Romania	1.89E-03	1.41E-04	4.14E-04	3.56E-05
Serbia	1.89E-03	1.41E-04	4.14E-04	3.56E-05
Slovakia	3.01E-03	7.15E-05	1.14E-03	4.54E-05
Slovenia	5.70E-03	4.89E-05	1.19E-03	5.75E-05
Switzerland	8.31E-03	1.92E-05	9.39E-04	2.84E-04
Ukraine	1.27E-03	9.45E-05	2.77E-04	2.39E-05

By combination of Table 7.6, Table 7.7 and Table 7.9, the per capita emissions of target substances are determined in all countries.

For road traffic, the road length (Meijer et al., 2018) is used as the final AR. Road length is split into highways and other roads. Highways typically have a higher traffic density per km. Based on information by Unice et al. (2019), highways are assumed to have a 6 times higher traffic density. Per country, per capita emissions are scaled by the total population over the total of road length to obtain final country-dependent EFs.

- Road traffic emissions: AR = 6 x highway length + other roads length (km); EF = country-specific emission per unit AR (mass/km/time).

The losses are allocated to impermeable surfaces.

7.3.5 Built Environment

There is little information to quantify the source from the built environment in detail. Expected relevant contributions are the use of biocides in the built environment, the corrosion of various metals used in buildings, industrial installations, transport infrastructure, as well as the losses of industrial chemicals from any objects in the outdoor urban environment. For only a few substances, estimates could be made based on various fact sheets in the NL-PRTR (http://www.emissieregistratie.nl/erpubliek/bumper.en.aspx) and Comber (2023).

- Built environment : AR = population; EF = per capita emission (mass/cap/time).

Estimated EFs in mg/cap/y are 4.16 for Zn, 1.41 for Pb and 0.59 for Cu.

The project database offers measurement data of stormwater collected in separated sewer systems. The observed ratios of the concentrations in stormwater were used to estimate EFs for some other substances as well, see Table 7.10.

Table 7.10: Derived EFs for the built environment

	Conc. In storm-water[1] (µg/L)	EF Traffic[2] (mg/cap/y)	EF Built.Env. (mg/cap/y)	Ratio[3]	Target total EF[4] (mg/cap/y)	Estimated EF Built.Env.[5] (mg/cap/y)
Cu	19.3	2123	594	141		
Pb	3.655	155	1406	427		
Zn	78.5	12853	4158	217		
As	1.35	0.92	0		135	134
Cd	0.047	1.06	0		4.7	3.6
Ni	2.985	55.3	0		298.5	243
PFOA	0.00395	0	0		0.395	0.395
PFOS	0.0029	0	0		0.29	0.29
BpA	0.077	0	0		7.7	7.7
OP	0.0122	0	0		1.22	1.22

(1) Median value from DH m3c database for Hungary or Austria, or the mean of both median if available.
(2) Mean of model domain
(3) Sum of EFs divided by measured concentration
(4) Measured concentration multiplied by 100 (conservative estimate based on ratios obtained for Cu, Pb and Zn).
(5) Target minus EF for traffic, to obtain an estimate for the built environment.

There is a risk of partly double counting the sources from the built environment in the contribution by households. The per capita emissions for that source are often based on concentrations measured in WWTP influents. As also urban runoff finds its way to WWTPs via combined sewer systems, the households EF may include part of the built environment related sources. The estimates made here have been chosen conservatively, to avoid them to reach values comparable to the EFs form households derived below.

7.3.6 Households

Loads from domestic wastewater are quantified using per capita emission factors.

- Loads to domestic wastewater: AR = population; EF = per capita emission (mass/cap/time).

To quantify the EF, exclusive use has been made of the DHm3c database. For most of the HS, homogeneous EFs have been derived from the influent concentrations and the mean annual influent volume in the DRB of 337 L/cap/d (Section 7.2.6), see Table 7.11.

Table 7.11: Concentrations in WWTP influents/effluents (µg/L) for target substances

Substances	P25	P50	P75	Remark
NP		0.005		Estimate, only censored values available
As	0.674	2	3.78	
BaP	0.00354	0.0074	0.016	
BpA	0.162	0.305	0.577	
Cd	0.0415	0.12	0.979	
Cu	3	6.84	25	
Hg	0.029	0.095	0.423	
Met	0.000301	0.00177	0.0144	Effluent value was used as it was higher than the P50 for influents
Ni	1.4	4.8	10	
OP	0.00349	0.00761	0.0166	Effluent value was used as it was higher than the P50 for influents
Pb	0.897	2.58	6.71	
TCZ	0.00399	0.01	0.03	
Zn	19	60	176	

For pharmaceuticals, country-dependent values have been derived using also country-specific mean annual influent volumes, see Table 7.12. For Montenegro and Bosnia and Herzegovina, data from Serbia were used. For Moldova, data from Ukraine were used.

Table 7.12: Country specific concentrations (median values) in WWTP influents/effluents (µg/L) for pharmaceuticals.

Country	CBZ	DCF
AT	0.27	2.9
BG	0.052	0.23
CZ	0.466	1.22
DE	0.27	2.28
HR	0.415	0.879
HU	1.47	3.01
RO	0.54	1.4
RS	0.434	3.01
SI	0.118	0.852
SK	0.224	1.08
UA	0.103	0.68

For PFOS and PFOA, the range observed between the P10 and the P90 in the effluent concentrations was the basis for a basin-wide extrapolation using population density multiplied with the per capita GDP, see Table 7.13. By choosing effluent concentrations, also the generated load from precursors in the treatment process is included in the EF.

Table 7.13: Range of concentrations of FOS and PFOA in effluents (ng/L).

	P10	P90
PFOA	1.75	11
PFOS	0.65	11

7.3.7 Industry

Industry point sources have been derived from the E-PRTR database (EEA, 2023). For the present purpose, we selected the most recent 2017 reports by EU Member States and other participating countries. The facilities with a recorded location inside the DRBD were selected. Facilities with an activity type “urban wastewater treatment plant” were omitted from the selection. The emissions to water and soil (releases) and to wastewater (transfers) were included in the model and allocated to the respective SE and compartments. Loads are provided for 7 metals, nonylphenol and PAHs.

An additional diffuse source related to industry was added for PFOA at a site in Gendorf (Germany) with legacy pollution due to extensive past releases of PFOA (Kittlaus, 2022). A mass of 4 tons of PFOA was added to the soils, resulting in a top soil concentration of 25 µg/kg averaged over the local SE.

7.3.8 Navigation

Emissions from navigation were quantified for coatings, bilge water losses and zinc anodes, following a methodology documented in the Netherlands PRTR (Deltares and TNO, 2016e-g). For coatings, a tar-based coating was estimated to emit 4 kg/ship/y of 10 PAHs commonly assessed by the Ministry of the Environment (3.2% benzo[a]pyrene[10]). A bitumen-based coating was estimated to emit 0.02 kg/ship/y of the same 10 PAHs (Deltares and TNO, 2016e) (10.1% benzo[a]pyrene). The application rate of both types of coatings in the DRB has not been studied yet. Provisional homogeneous values of 30% for tar coatings and 70% for bitumen coatings have been applied. For bilge water, the losses of oil were estimated as 1 kg/ship/y (Deltares and TNO, 2016f) (containing 20 mg/kg of benzo[a]pyrene). For zinc anodes, the zinc emission was estimated as 1.5 kg/ship/y (Deltares and TNO, 2016g).

The allocation of these emissions per ship to the DRB waterways was done in steps:

- The transported tonnage in the DRB was estimated from data reported by van de Roovaart et al. (2013) as 26,116 Mtkm/y[11].
- The navigable river length was estimated as the sum of all river stretches in the DRB schematization with a cumulative upstream catchment area of 30,000 km^2 or more. This was motivated by a global comparison to a map of navigable waterways referenced by van de Roovaart et al. (2013). The resulting distance was 2142 km.
- The ratio of the above numbers provides a navigation intensity per unit river length of 12.2 Mtkm/km/y.
- The transport performance of a single ship was estimated as 8.64 Mtkm/ship/y, based on data available for the Netherlands (transport performance of 49,327 Mtkm/y by 5,707 ships, Deltares and TNO, 2016e, g).
- The number of ships per km of navigable waterway was calculated as the ratio between the tonnage transported per km river length and the tonnage transported per ship. This provided 1.41 ships/km.
- The emissions per ship per year were converted to emissions per km of navigable river length per year using the number from the previous step.

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[10] The sources used here also provide the concentrations of other PAHs.

[11] One tkm is the equivalent of 1 ton of cargo transported over a distance of 1 km.

Finally, for all SEs classified as navigable, the emissions were calculated:

- Emissions from inland navigation: AR = navigable river length (km), EF = emission per unit river length per year (mass/km/time).

7.3.9 Concentrations in top soil

Concentrations of HS in top soils were obtained from the DHm3c database, supplemented with the Foregs database (Salminen et al., 2005). The DMm3c data cover 7 countries, while Foregs provides 3 additional countries. The data are compiled in Table 7.14. Data form Montenegro were used also for Republic of Serbia and Bosnia and Herzegovina. Data from Romania were used for Moldova and Ukraine.

Table 7.14: Overview of data used for concentrations in top soils (µg kg^{-1}).

	AT(1)	BG(1)	DE(1)	HU(1)	ME(1)	RO(1)	SI(1)	CZ(2)	HR(2)	SK(2)
As	12500	12800	8600	6520	9400	12100	12000	9000	11000	9000
Cd	311	218	230	200	650	253	555	220	180	270
Cu	21300	23800	14000	11700	25000	23200	23000	13500	18000	14000
Hg(3)	75	93	100	93	139	93	105	68	39	78
Ni	28100	37200	20000	21100	29000	34900	29500	16500	32000	24000
Pb	25700	29000	25000	17400	27000	26300	30500	25500	17000	30000
Zn	80300	73800	61000	44600	83400	91000	86500	65500	64000	62000

(1) Median of country values in DHm3c data.
(2) Medan of data in Foregs database.
(3) No data for HU, BG and RO, median of remaining data was used.

For BaP, OP and NP an estimated value of 5 µg/kg was used. Foe BpA, a value of zero was found to lead to a reasonable validation result. For pharmaceuticals and pesticides, no stocks in soils were provided.

For PFOS and PFOA, the same approach as for households was used: a spatial variability controlled by population density weighed with per capita GDP, spanning the P10-P90 range, see Table 7.15.

Table 7.15: Range of concentrations of FOS and PFOA in top soils (µg/kg).

	P10	P90
PFOA	0.0169	1.2
PFOS	0.0186	0.49

7.3.10 Uncertainty of sources information

The present report provides three different emission estimates: a middle, best estimate as well as high and low estimates. Insofar as emissions are based on data extracted from the project database, the 25-, 50- and 75-%tiles are used. Table 7.16 list the assumptions for deriving the low and high emission estimates.

Table 7.16: Assumptions underlying the low (P25) and high (P75) emission estimates.

Source	P25	P75	Notes
Atmospheric deposition	EMEP: scale factor 0.63, other: P25 of data	EMEP: scale factor 1.85, other: P25 of data	Scale factors for EMEP are averages of P25/P50 and P75/P50 of other HS
Agriculture	Metals: scale factor 0.5, Metolachlor: scale factor 0.5, Tebuconazole: no change	Metals: scale factor 2.0, Metolachlor: no change, Tebuconazole: scale factor 2.0	for pesticides, the changes are connected to the mismatch between model and field data in the best estimate
Road Traffic	Scale factor 0.50	Scale factor 2.35	Median of the P25/P50 and P75/P50 ranges of concentrations in storm water
Built Environment	Scale factor 0.50	Scale factor 2.35	Median of the P25/P50 and P75/P50 ranges of concentrations in storm water
Households	P25 of data, range P10-P50 for PFOS and PFOA	P75 of data, range P50-P90 for PFOS and PFOA	
Industry	Scale factor 0.50	Scale factor 2.0	
Navigation	Scale factor 0.50	Scale factor 2.0	
Soil concentrations	P25 of data, range P10-P50 for PFOS and PFOA, Gendorf scaled 0.5	P75 of data, range P50-P90 for PFOS and PFOA, Gendorf scaled 2.0	

7.4 Model parameters

The parameters used in the DHSM are summarized in Table 7.17. The table refers to the related section in Chapter 6 and, where applicable, to data tables in Section 9.3.

Table 7.17: Summary of model parameters.

Parameter	Described in	Value	Remarks
Soi_Septic	Section 6.3.1	0.2	expert judgement
Removal by treatment	Section 6.3.1	Section 9.3.1	derived from literature
Enrichment ratio	Section 6.3.3	1.5	set to obtain realistic results, reflects also accuracy of input data
Threshold for mobilisation	Section 6.3.3	5 mm/d	set to obtain realistic results
Burial rate	Section 6.3.3	0 /d	set to obtain realistic results
Removal rate in soils	Section 6.3.3	0.01 d^{-1} 0.0 d^{-1}	for pesticides, to avoid build-up in soils for all other HS
Soil partition coefficients	Section 6.3.3	Section 9.3.2	partly calibrated to match ground water concentrations
Soil porosity	Section 6.3.3	0.4	not available from the hydrology model, expert judgement
Settling velocity	Section 6.4	0.2 m/d	calibrated on observed SPM
Water partition coefficients	Section 6.4	Section 9.3.2	partly calibrated to match surface water concentrations
Water degradation	Section 6.4	Section 9.3.2	

8 DHSM evaluation

8.1 Available data

Data considered for the evaluation of the model at the scale of the complete basin were:

- regular monitoring data (12-24 samples per year) from the Transnational Monitoring Network (TNMN), up to and including 2019;
- data from the Joint Danube Surveys JDS3 (in 2013) and JDS4 (2019);
- data collected in the DHm3c project in 2021-2022 at 6 selected TNMN stations (about 12 samples);
- data collected in the pilot regions in the DH m3c project.

The JDS3 data have not been used for model validation, partly because they are quite old and partly because they represent a single survey that does not necessarily project a representative image of the river concentrations for a model validation. JDS4 data, also from a single survey, have nevertheless been used, as they are recent and supplement the limited coverage of organic chemicals in the other datasets. The TNMN data (regular and additional DH m3c) cover longer periods and are therefore considered very valuable for the model validation. To avoid scatter related to time trends, older TNMN data from before 2015 have been omitted.

The data collected in the pilot regions are not immediately representative for the complete basin, as it concerns 7 relatively small sub-basins (425-2195 km^2 in DHSM). They have been used to evaluate the model performance, and to identify the need for improvements during the implementation stage.

8.2 Evaluation results

Simulations were performed for the 17 chemicals discussed above. The model has been run for a period of 11 years, based on the hydrology from 2003-2013. This period starts with a “clean” river, so a certain period is required to obtain realistic results. For this reason, only the results from the second year onwards are used. This is a period of 10 years. For every year, an annual mean concentration was determined.

TNMN analysis results below the Limit of Quantification or the Limit of Detection have been replaced by these respective limit values, and have been flagged as censored values. The values per station and parameter were averaged. Averages with more than 80% censored values were again flagged.

The simulation results were evaluated by plotting longitudinal profiles of:

- the minimum and maximum annually averaged simulated concentration (out of the hydrology years 2004-2013);
- the mean of the observed concentrations from regular TNMN monitoring (“TNMN”), from additional DH m3c monitoring (“DH m3c”) and from the JDS4 survey (“JDS4”), with means based on more than 80% of censored values[12] indicated by a different symbol;
- for the metals, separate plots for dissolved and total concentrations are included.

Figure 8.1 to Figure 8.17 show the results.

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[12] This also applies to JDS4 as there are up to three samples collected per sampling station, from the left and right banks and from the middle of the river.

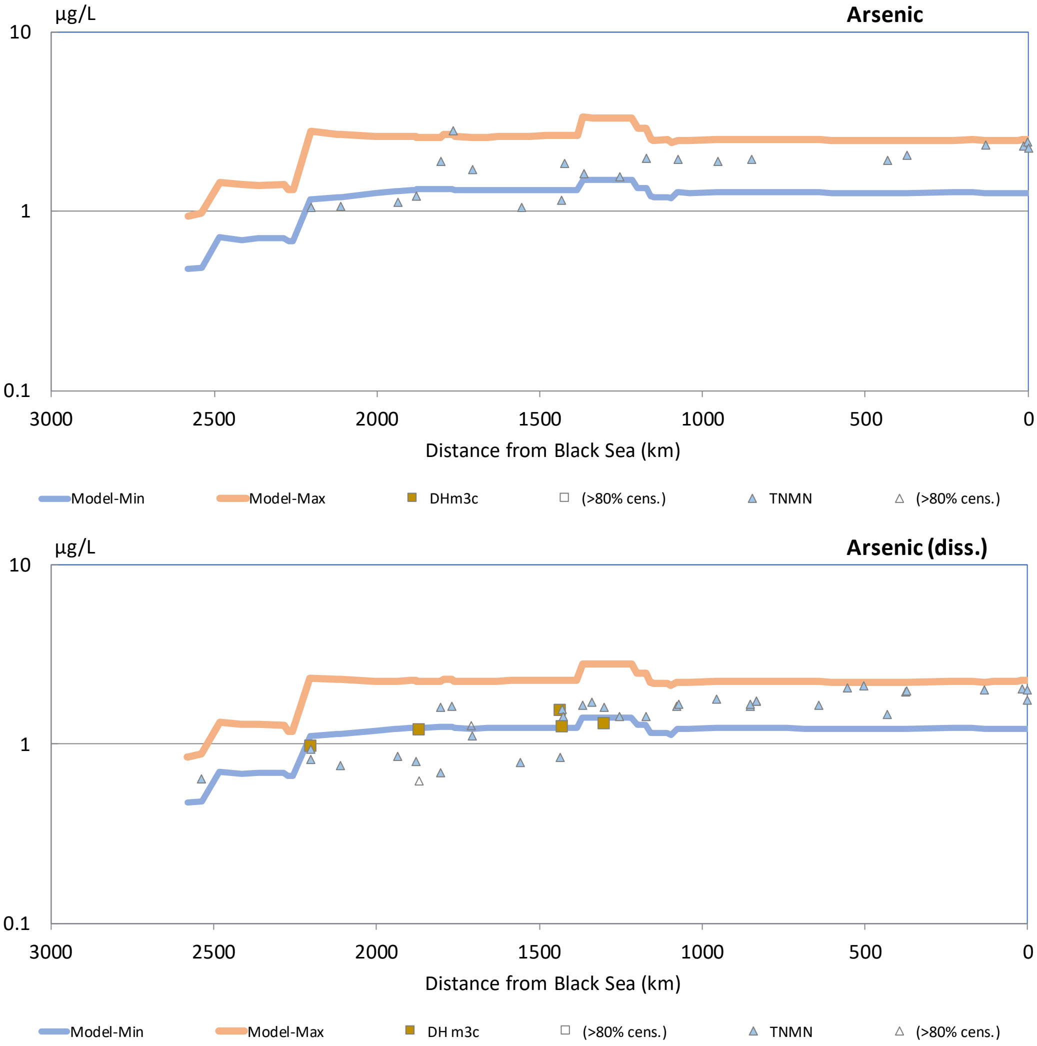


Figure 8.1: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for arsenic.

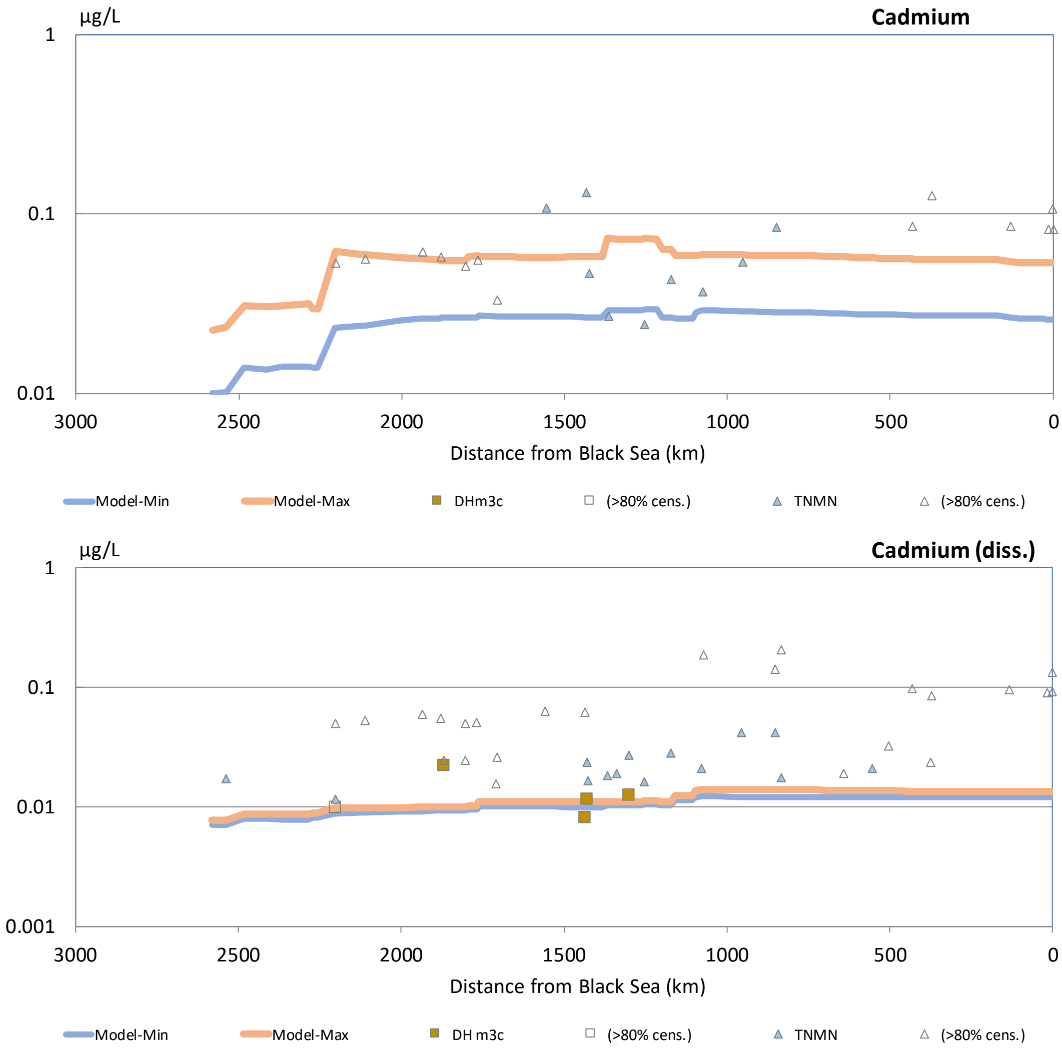
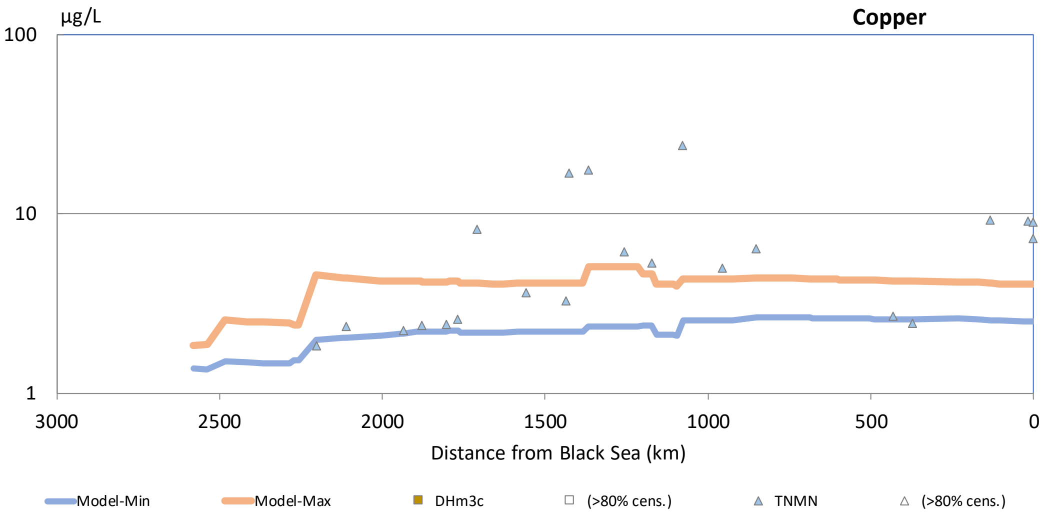


Figure 8.2: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for cadmium.



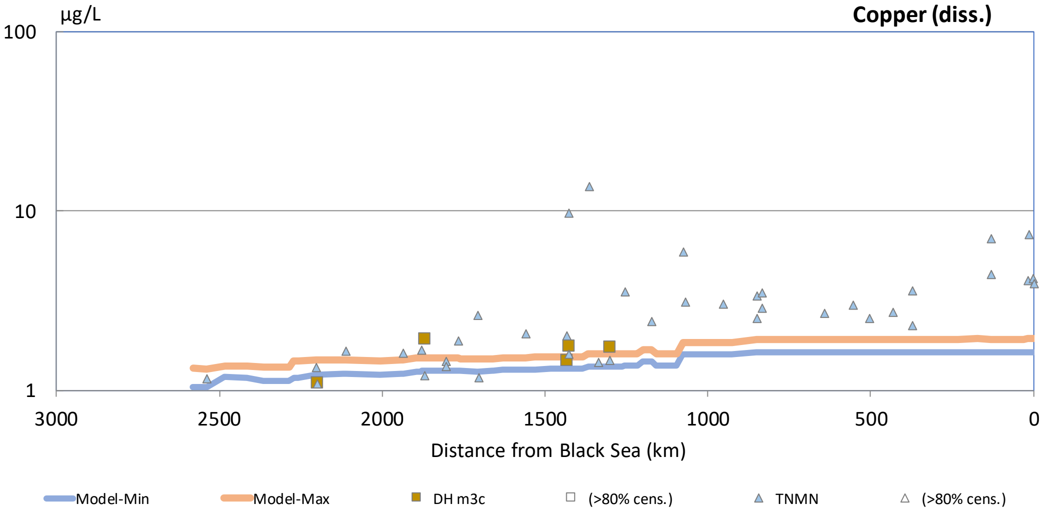
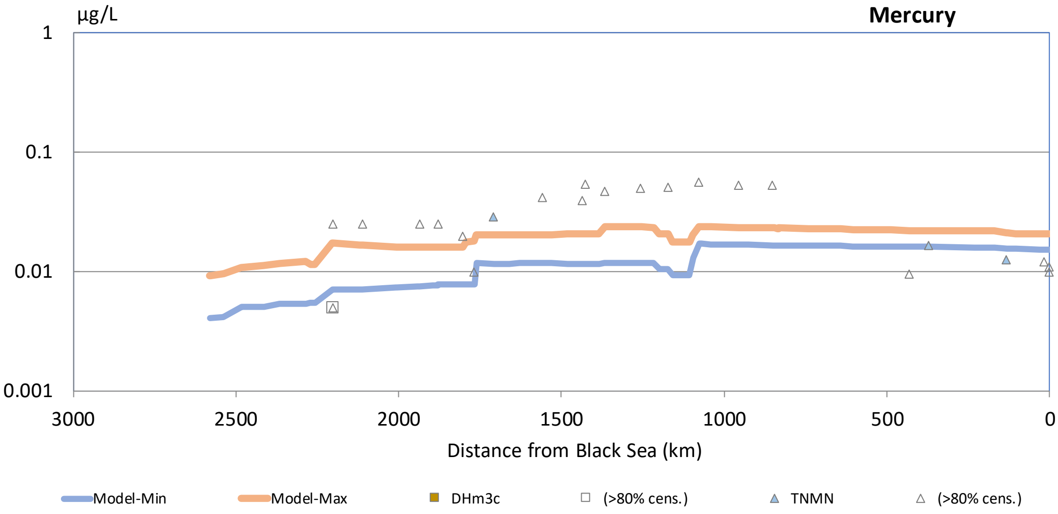


Figure 8.3: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for copper.



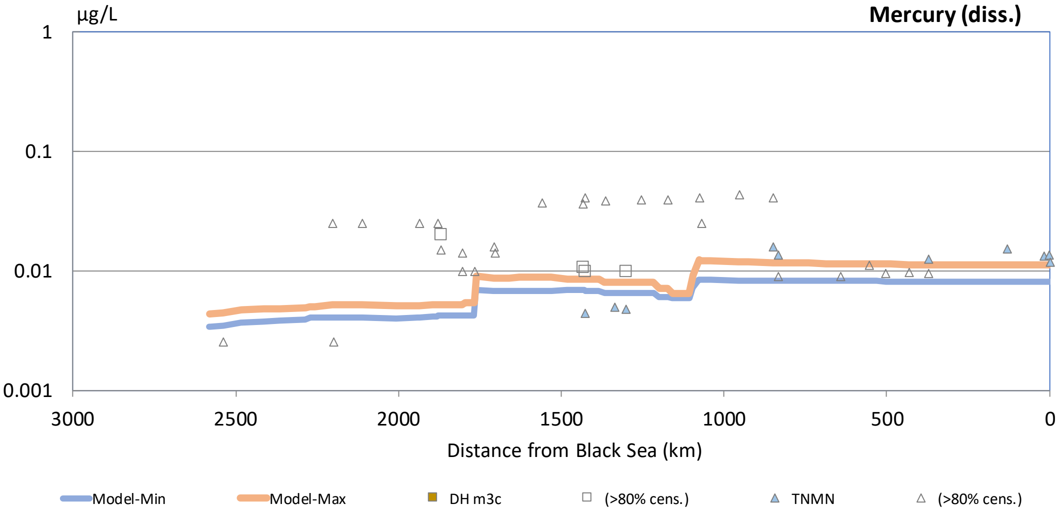


Figure 8.4: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for mercury.

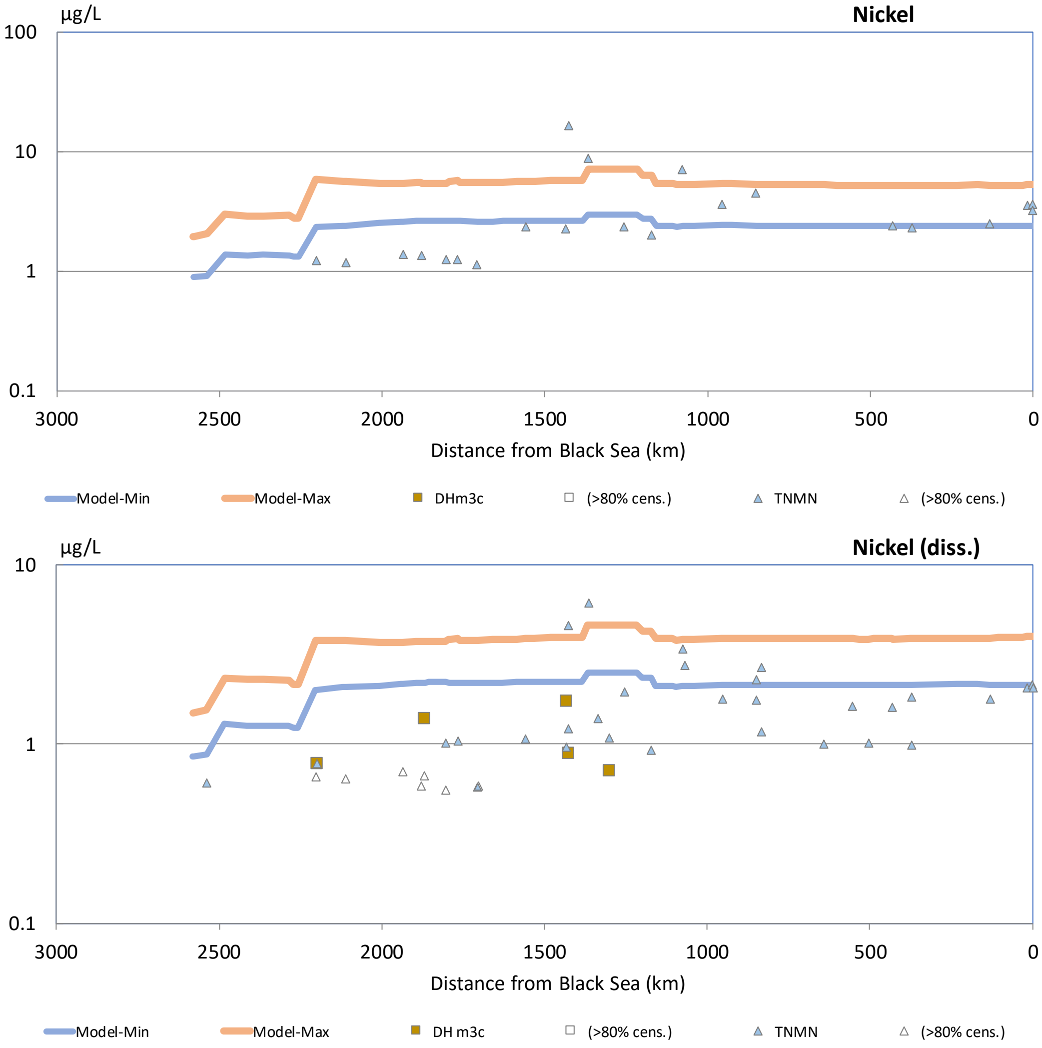


Figure 8.5: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for nickel.

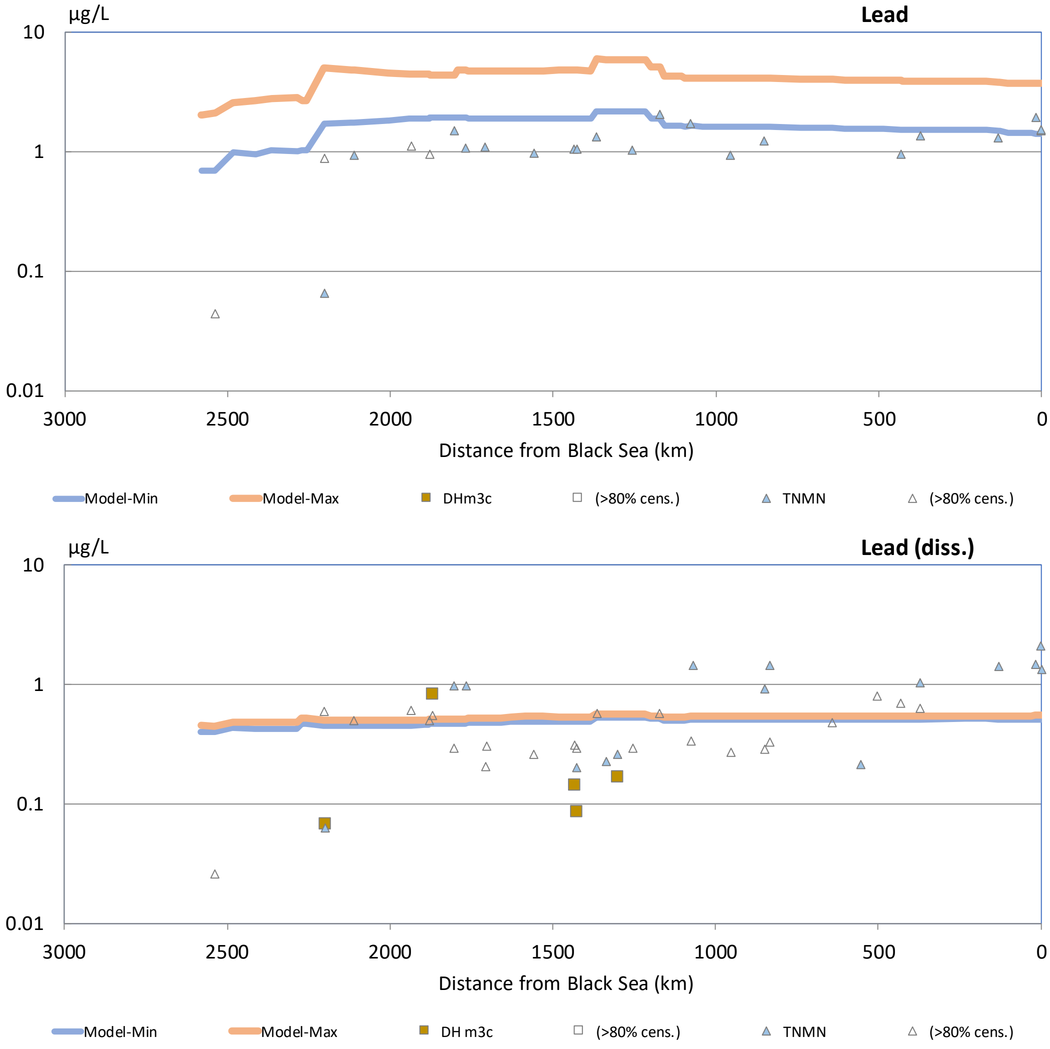
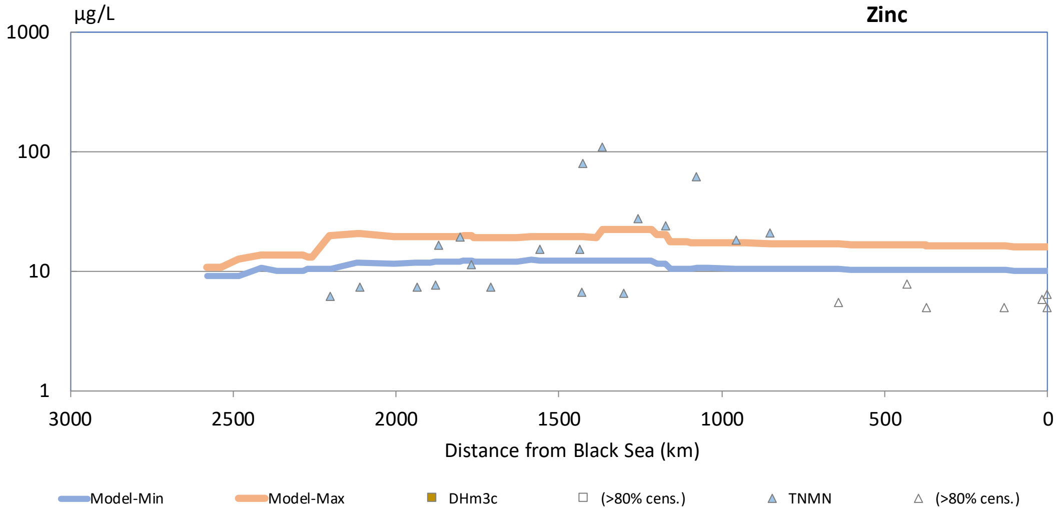


Figure 8.6: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for lead.



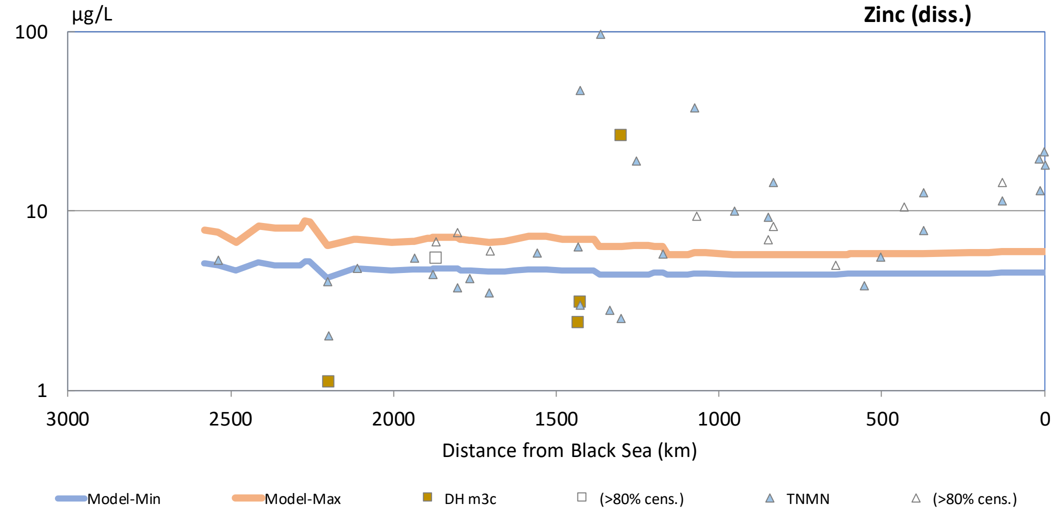


Figure 8.7: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for zinc.

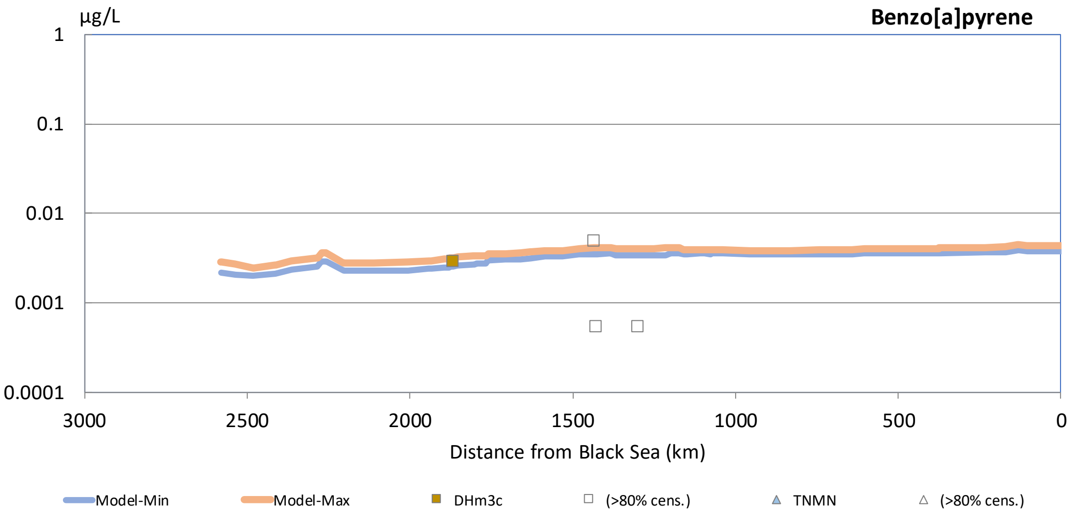


Figure 8.8: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for Benzo[a]pyrene.

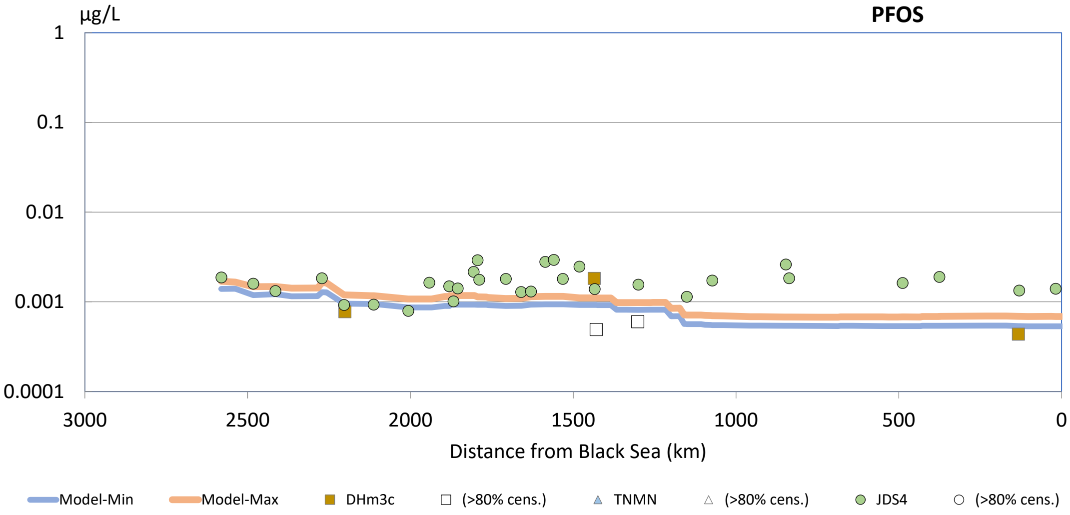


Figure 8.9: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for PFOS.

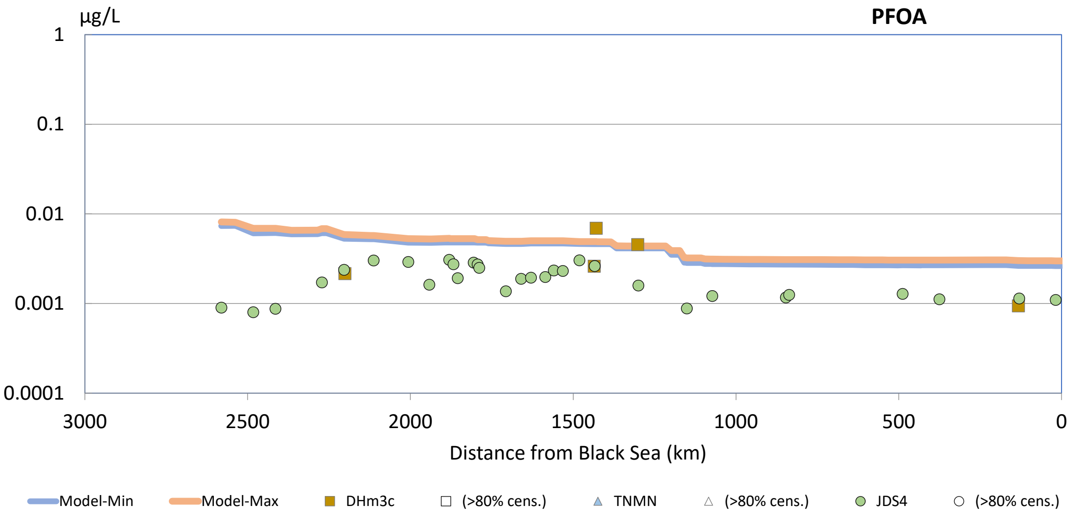


Figure 8.10: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for PFOA.

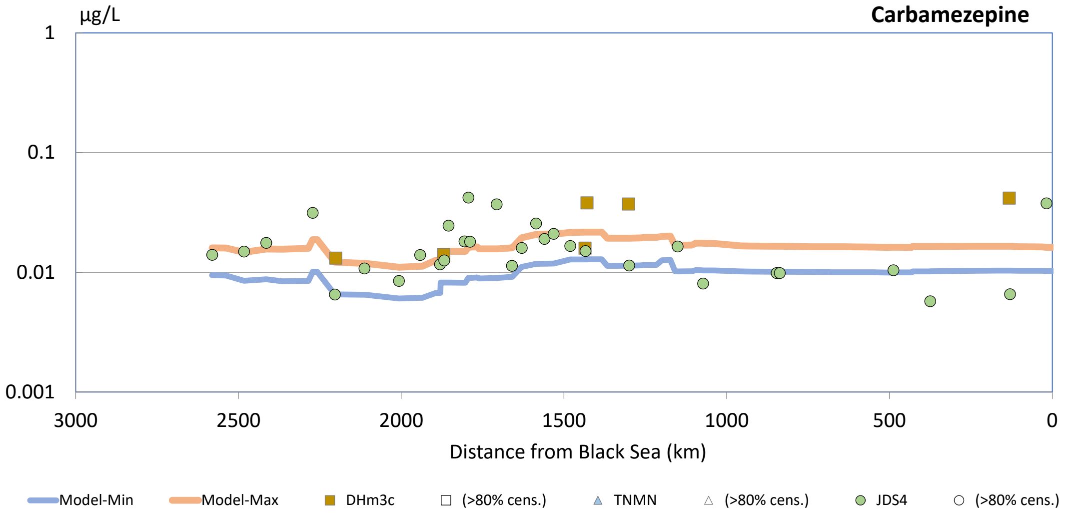


Figure 8.11: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for carbamazepine.

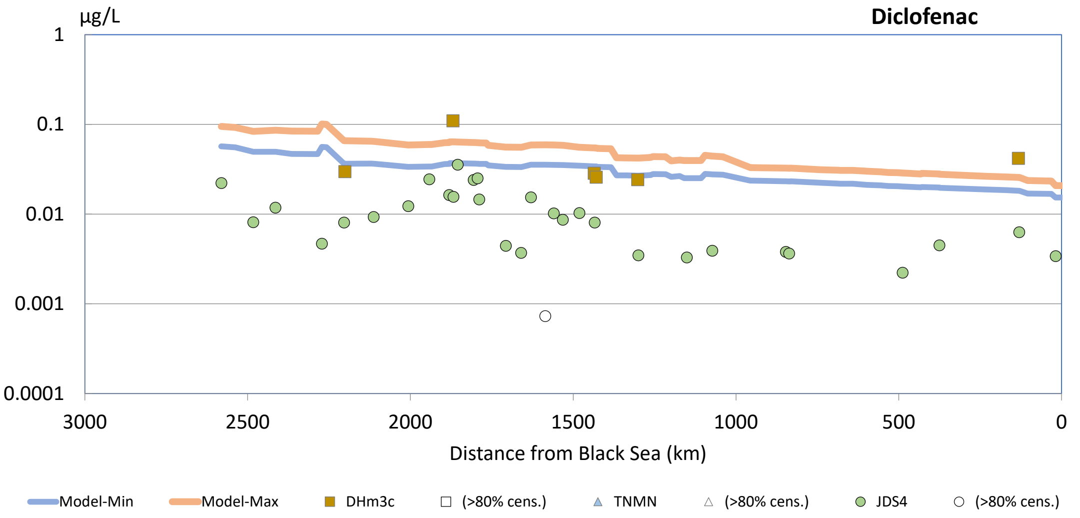


Figure 8.12: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for diclofenac.

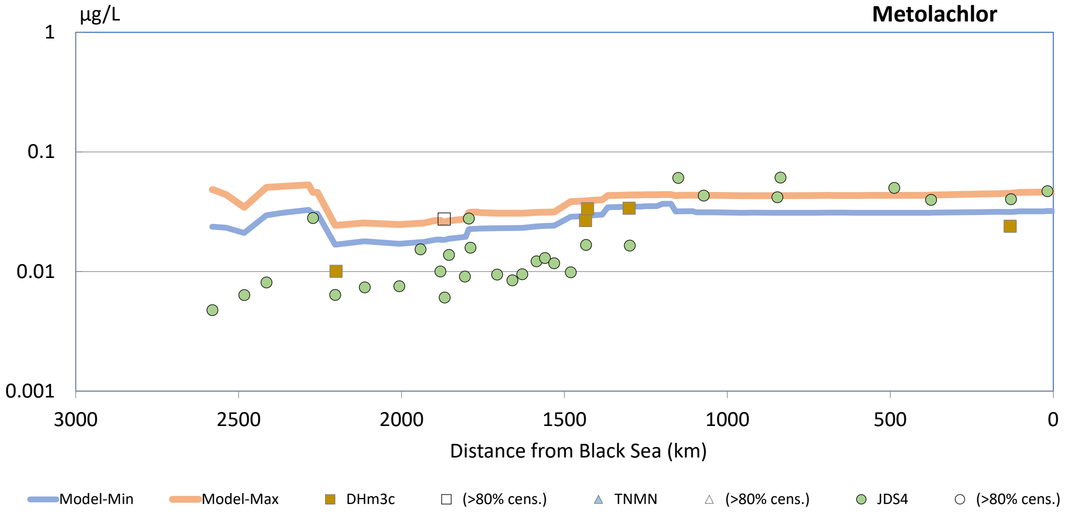


Figure 8.13: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for metolachlor.

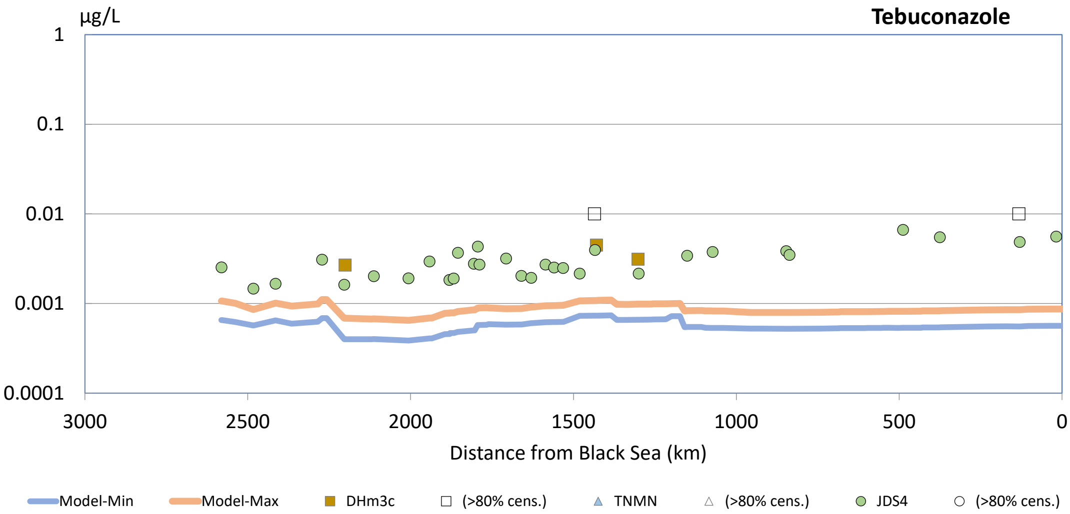


Figure 8.14: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for tebuconazole.

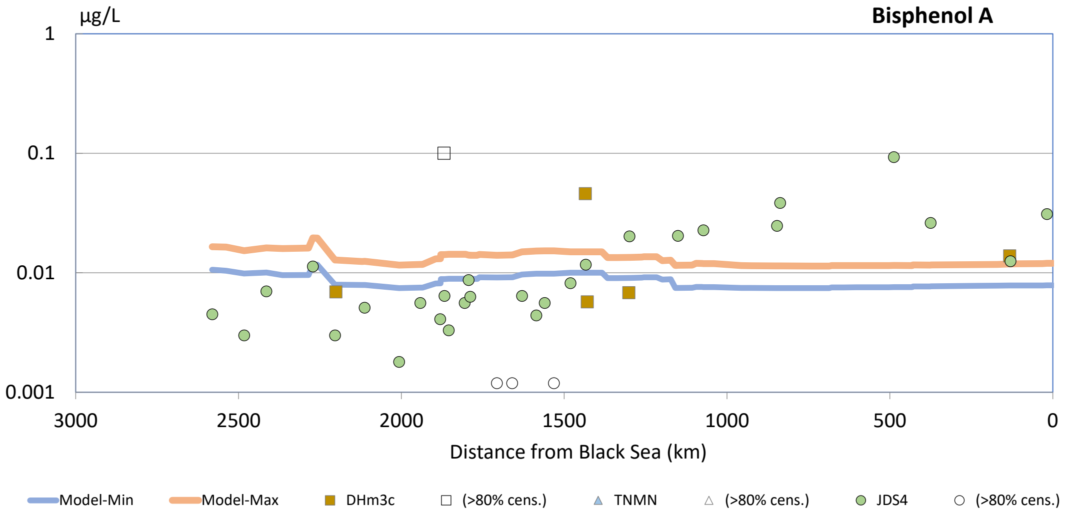


Figure 8.15: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for bisphenol-A.

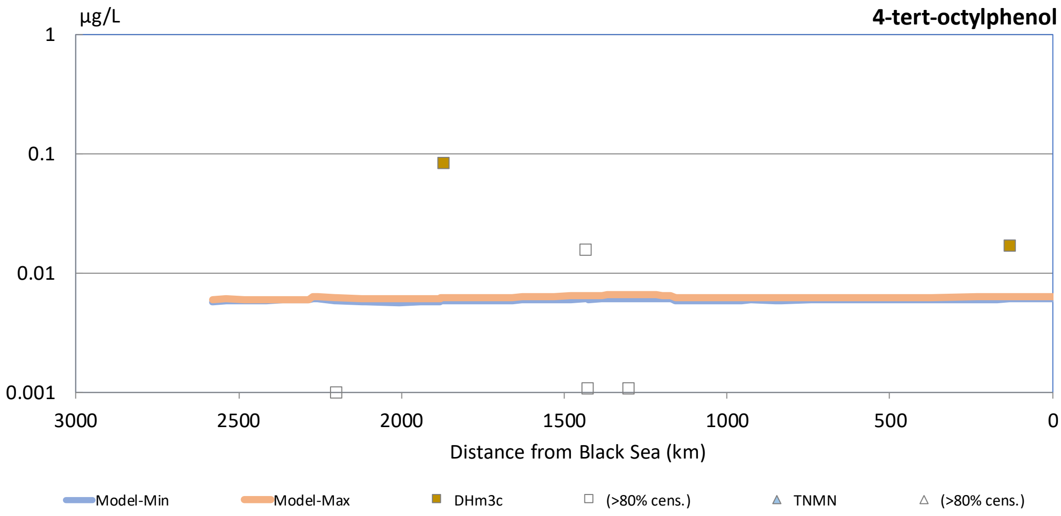


Figure 8.16: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for 4-tert-octylphenol.

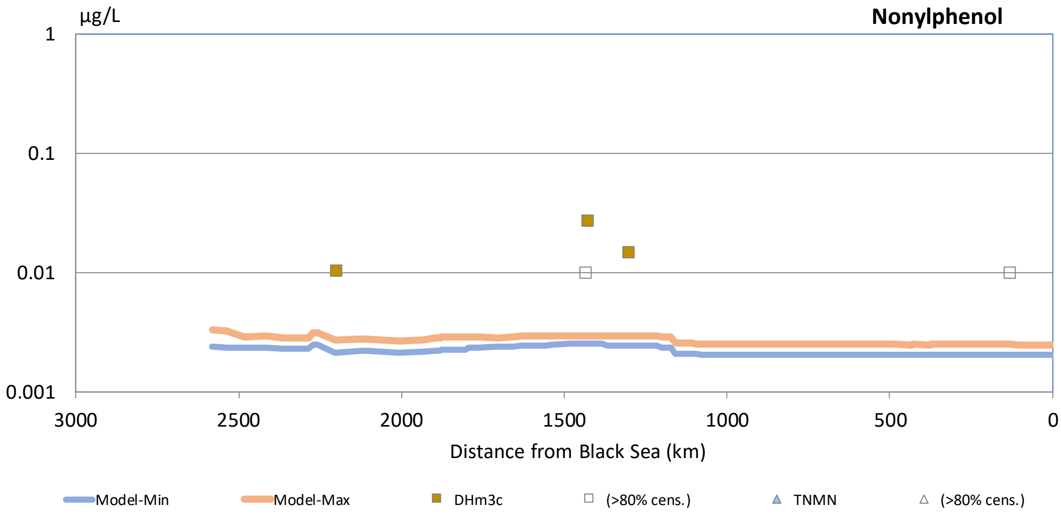


Figure 8.17: Comparison of simulated concentrations and observations from different datasets, plotted along the length of the Danube River for nonylphenol.

8.3 Model evaluation in pilot regions

The data collected in the pilot regions have been used to improve the model implementation. To this end, a specific approach was developed. The initial comparison of the preliminary DHSM simulated concentrations using 2013 hydrology (Deltares, 2021) and the measured concentrations in the pilot areas showed large differences. A key cause was the fact that simulated river flows in 2013 differed strongly from the actual flows during the pilot region sampling. So, for this evaluation, the most suitable year was selected from the available hydrological sequence for the model evaluation in the pilot regions, see Table 8.1.

Table 8.1: Matching of observed flows and simulated flows in the DH m3c pilot areas

	Koppany	**Somesul**	**Viseu**	**Vit**	**Wulka**	**Ybbs**	**Zagyva**
Observed (m^3/s)	1.29	18.22	8.39	13.60	0.87	40.30	0.88
Selected year	2008	2011	2011	2006	2012	2013	2007
Simulated(m^3/s)	1.09	18.95	12.46	8.77	2.05	36.72	0.61

Further, an interesting aspect of the pilot region sampling is the high resolution in time, which allows the separation of low flows and high flows. For this reason, the comparison between DHSM simulated concentrations and pilot region observed concentrations was made for low flows and high flows separately. Observed concentrations were separated based on the mean observed discharge included in the project database. Simulated concentrations were separated based on the mean simulated discharge during the selected year.

The results of the comparison are included in Section 9.4. It is noted that only the outflow points of the pilot region have been considered. In view of the size of the pilot region areas and the mean DHSM resolution, a comparison for other stations at sub-basin outlets of the pilot regions was not considered meaningful.

A good agreement between simulated and observed concentrations in the pilot regions was not an objective by itself. The comparison served to find inconsistencies and possible improvements of the full basin application. This implies that “generic” aspects were considered most relevant and local aspects were only considered if they offered a possible improvement at the basin scale.

8.4 Discussion

The basin-wide results presented above lead to the following observations.

- For the metals, the simulated concentrations are mostly in the correct order of magnitude. The simulated concentrations for lead and nickel are higher than observations. For this substance group, all pathways included in the WFD Guidance could be quantified, except emissions from abandoned mining sites. This may be the reason why the model does not represent some locally higher values in the middle stretches of the Danube River. In this context also the reported incompleteness of E-PRTR can be mentioned (van de Roovaart et al., 2022, and references therein).
- The results for Benzo[*a*]pyrene cannot be compared to field data very well, but seem to be reasonable.
- Compared to the preliminary results (Deltares, 2021), the results for PFOS and PFOA are in much better agreement with the measured concentrations. In the current version, better estimates for point sources were available and some diffuse sources were added. Especially relative to JDS4 observed concentrations, the simulated PFOA concentrations are somewhat overestimated. In view of the distribution of PFOA emissions over the different pathways, this could well be the result of uncertainty of concentrations in soil and/or the simulated fate of PFOA in soils.
- As in the preliminary model, the pesticide concentrations are still not well-predicted, though the source estimates were modified. As this concerns chemicals with a specific and known use type, a likely explanation is the lack of regionalized use data.
- For pharmaceuticals, concentrations of carbamazepine are a little underestimated, and of diclofenac about the correct level. The reason for the underestimation is not clear. It is noted that the JDS4 survey was conducted in summer when in-stream removal of diclofenac is assumed highest (Section 9.3.2). This could be the reason that JDS4 measured summer concentrations are lower than DH m3c measured average concentrations and the simulated annually averaged concentration in the downstream part.
- The results for the phenols are variable. For bisphenol-A, the agreement with field data seems reasonable. For octyl- and nonyl-phenols, the comparison to field data is difficult because of the

many censored values, but the modelled concentrations are probably too low. This mismatch may well be caused by the frequent occurrence of censored values also in the data used to estimate the sources.

The pilot region results presented in Appendix C lead to additional observations:

- Especially in the Ybbs area, high flow concentrations are often much higher than low flow concentrations. This is presumably the result of intensive erosion or surface runoff in this mountainous area. The model is underestimating this. To achieve a better performance, the sediment delivery forcing was already modified (Section 7.2.7). The remaining discrepancy may be connected to the limited spatial resolution of DHSM.
- Some discrepancies between DHSM results and pilot area sampling are unavoidable, as input data availability is limited at the basin scale. Examples are the point sources from mining (relevant in Viseu for some metals, not available at basin scale) and the transfer of wastewater across sub-basins (not resolved by DHSM, important for pilot regions, but much less at the basin scale).
- It is clear from the present results that the sources in Zagyva are overestimated in DHSM.
- The DHSM obtained for pilot regions suggest that soil related pathways can be relevant for pharmaceuticals in areas with high rainfall and a low connection rate. These pathways are not commonly considered for pharmaceuticals.

Concentrations calculated by DHSM are true time averages and as such they reflect the annual mean concentrations that are regulated by EQS under the WFD. True time averaged concentrations may differ from the quotient of the annual emissions and the mean river discharge. The difference is the result of the time variability of the emissions in the watershed and the river discharges. Present DHSM results in the Arges River (Romania) for example show that the true annual mean concentration is 10-20% higher than the quotient of the annual emissions and the mean river discharge. In the Iskar River (Bulgaria), this difference is 50-100%.

9 Appendices

9.1 References

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9.2 Management of wastewater

The management of urban wastewater for urban (_U) and rural (_R) agglomerations is compiled in the table below.

S0 = collected but not treated; S1 = primary treatment; S2 = secondary treatment; S3 = tertiary treatment; S4 = advanced treatment. UIAS = collected in IAS; ULS = collected in LS, UNC = uncollected. The 8 fractions add up to 1.

Cluster	S0	S1	S2	S3	S4	UIAS	ULS	UNC
AT_U	0.000	0.000	0.000	0.988	0.005	0.007	0.000	0.000
AT_R	0.000	0.000	0.001	0.982	0.012	0.005	0.000	0.000
BA_U	0.262	0.002	0.151	0.000	0.000	0.000	0.387	0.198
BA_R	0.150	0.000	0.002	0.000	0.000	0.000	0.597	0.251
BG_U	0.017	0.000	0.001	0.000	0.892	0.072	0.000	0.019
BG_R	0.243	0.000	0.000	0.000	0.400	0.024	0.000	0.333
CZ_U	0.000	0.000	0.012	0.941	0.000	0.048	0.000	0.000
CZ_R	0.000	0.000	0.124	0.788	0.003	0.085	0.000	0.000
DE_U	0.000	0.000	0.001	0.897	0.102	0.001	0.000	0.000
DE_R	0.000	0.000	0.043	0.821	0.135	0.001	0.000	0.000
HR_U	0.166	0.021	0.498	0.124	0.000	0.105	0.000	0.087
HR_R	0.133	0.090	0.189	0.041	0.000	0.435	0.000	0.112
HU_U	0.000	0.000	0.000	0.072	0.824	0.065	0.000	0.039
HU_R	0.000	0.000	0.000	0.045	0.719	0.193	0.000	0.043
MD_U	0.029	0.059	0.137	0.000	0.063	0.000	0.049	0.663
MD_R	0.011	0.000	0.000	0.000	0.000	0.000	0.000	0.988
ME_U	0.160	0.000	0.000	0.413	0.000	0.000	0.000	0.426
ME_R	0.303	0.000	0.296	0.000	0.000	0.000	0.000	0.400
RO_U	0.005	0.028	0.043	0.603	0.141	0.023	0.000	0.158
RO_R	0.021	0.007	0.097	0.101	0.012	0.011	0.000	0.750
RS_U	0.670	0.004	0.108	0.012	0.000	0.000	0.191	0.014
RS_R	0.279	0.018	0.031	0.057	0.000	0.000	0.561	0.054
SI_U	0.013	0.000	0.295	0.619	0.000	0.067	0.000	0.005
SI_R	0.013	0.000	0.286	0.555	0.000	0.115	0.000	0.032
SK_U	0.006	0.000	0.022	0.712	0.211	0.047	0.000	0.002
SK_R	0.001	0.004	0.095	0.482	0.097	0.309	0.000	0.012
UA_U	0.016	0.000	0.440	0.000	0.000	0.000	0.000	0.545
UA_R	0.077	0.031	0.088	0.000	0.000	0.000	0.000	0.804

9.3 Model parameters

9.3.1 Treatment in WWTPs

Information about the removal of target substances by treatment has been derived from WWTP sampling (ICPDR, 2021a,b) and from data reported in the NL-PRTR (Partners 4 Urban Water and Deltares, 2020).

Substance	**Fraction to effluent for secondary treatment**	**Fraction to effluent for primary treatment (1)**
Cd	0.1 (3)	0.44
BPA	0.63 (2)	0.88
BaP	0.05 (1)	0.33
As	0.47 (1)	0.81
Cu	0.18 (2)	0.57
Ni	0.5 (2)	0.75
Pb	0.12 (2)	0.32
Zn	0.41 (2)	0.49
Hg	0.25 (1)	0.43
PFOS	1 (2)	1
PFOA	1 (2)	1
Dcf	0.73 (2)	0.8
Cbz	1 (2)	1
NP	0.07 (1)	0.44
OP	1 (4)	1
Teb	0.84 (2)	1
Met	1 (2)	1

1. From Partners 4 Urban Water and Deltares (2020)
2. Based on sampling in JDS4
3. Estimate based on DH m3c sampling in pilot regions
4. No data available

9.3.2 Environmental fate

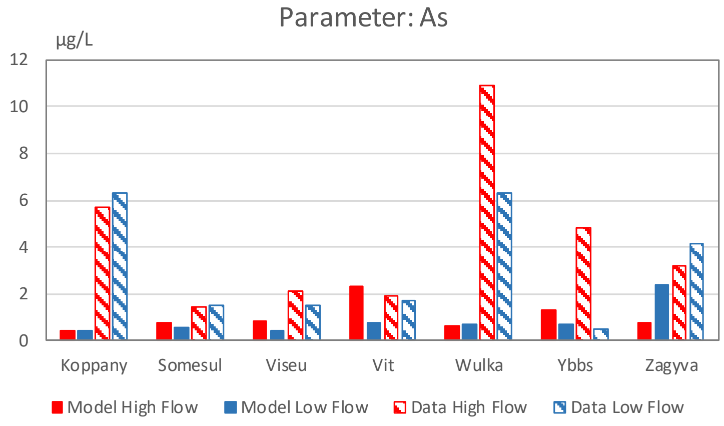
Partition coefficients for metals have been calibrated to obtain a match with field data: for surface waters by reproducing the difference between dissolved and total concentrations along the river Danube; for soils by reproducing observed concentrations in groundwater. Partition coefficients for organic chemicals were taken from van Gils et al. (2020) as a K_{OC}, and converted to a K_d, using 5% of organic carbon in soils and 3% of organic carbon in surface water.

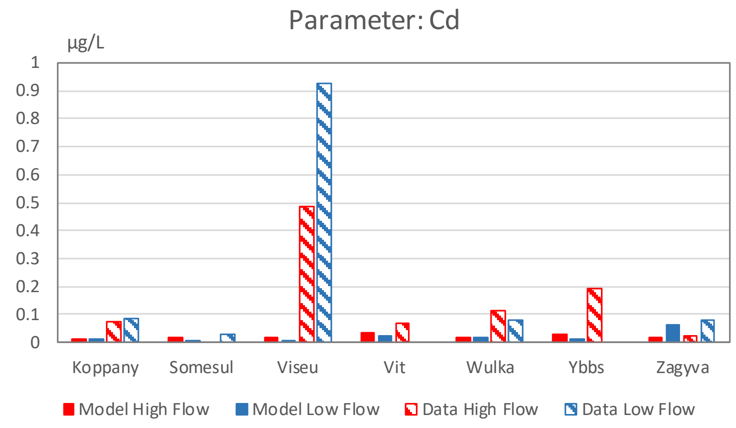
Substance	Partition coefficient in soils (m^3/kg)	Partition coefficient in surface water (m^3/kg)
As	84	1
Cd	146	40
Cu	167	15
Hg	14000	17
Ni	152	3
Pb	2360	70
Zn	66	30
OP	2.51	1.50
BaP	62.95	37.77
BPA	0.20	0.12
Cbz	0.01	0.01
Dcf	1.00	0.60
Met	0.08	0.05
NP	25.06	15.04
PFOA	0.25	0.15
PFOS	0.79	0.48
Teb	0.32	0.19

Only for diclofenac, in-stream removal was applied, presumably due to photolysis by UV radiation (Poirier-Larabie et al., 2016). The estimated rate was 0.1 d^{-1}, with a temperature coefficient of 1.1 to reflect the strong seasonal variability of UV radiation.

9.4 Evaluation in pilot areas

This Section compiles the comparison of DHSM results in the 7 pilot areas to DH m3c additional collected data. Both modelled and observed concentrations are shown as means for high and low flows respectively. Where more than 90% of observations were censored, no data are shown.

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0.2
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Koppany
Somesul
Viseu
Vit
Wulka
Ybbs
Zagyva
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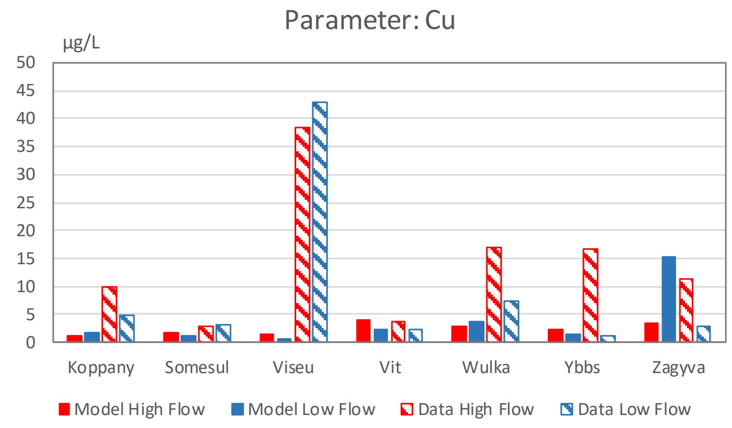
Model Low Flow
Data High Flow
Data Low Flow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µg/L
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30
25
20
15
10
5
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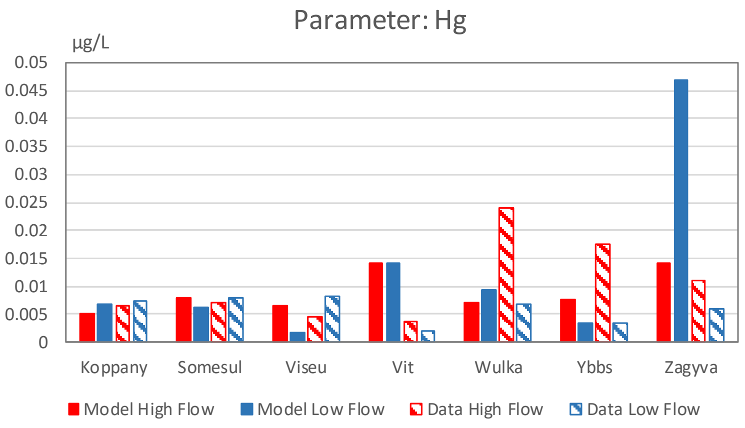
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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0.015
0.01
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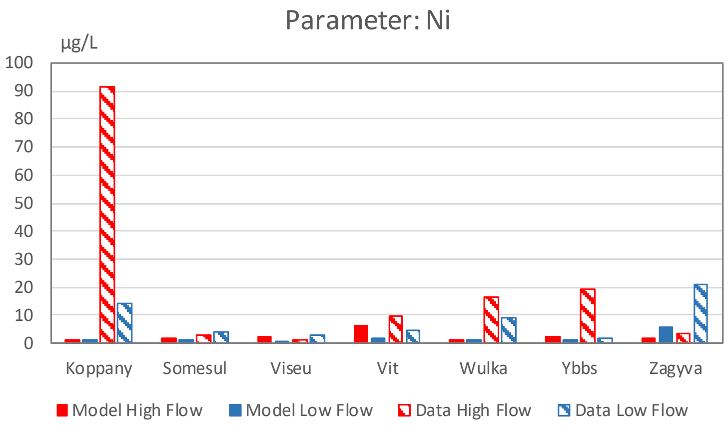
Somesul
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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µg/L
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90
80
70
60
50
40
30
20
10
0
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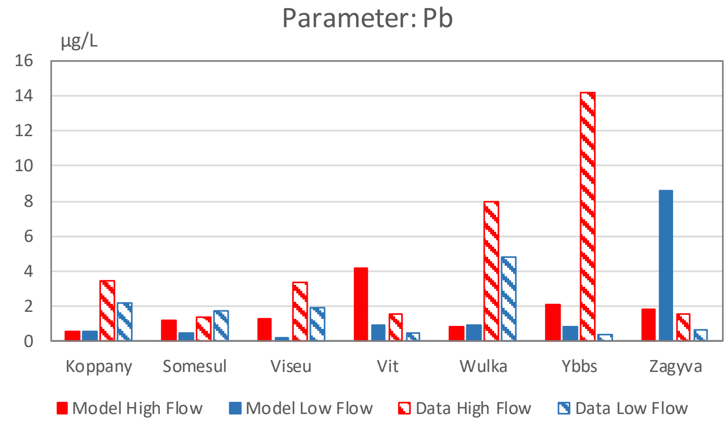
Somesul
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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µg/L
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14
12
10
8
6
4
2
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Viseu
Vit
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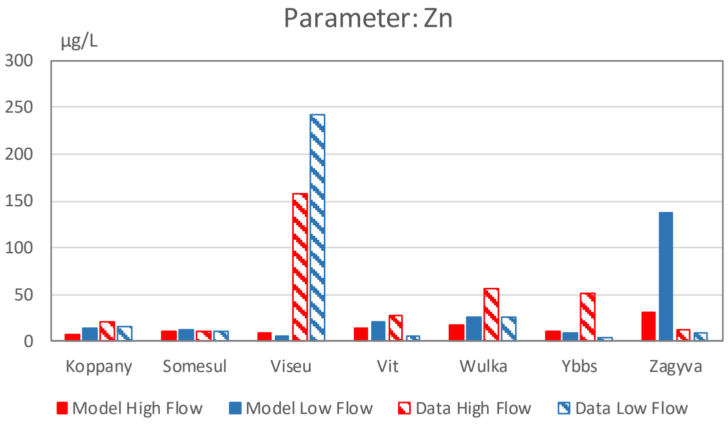
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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µg/L
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250
200
150
100
50
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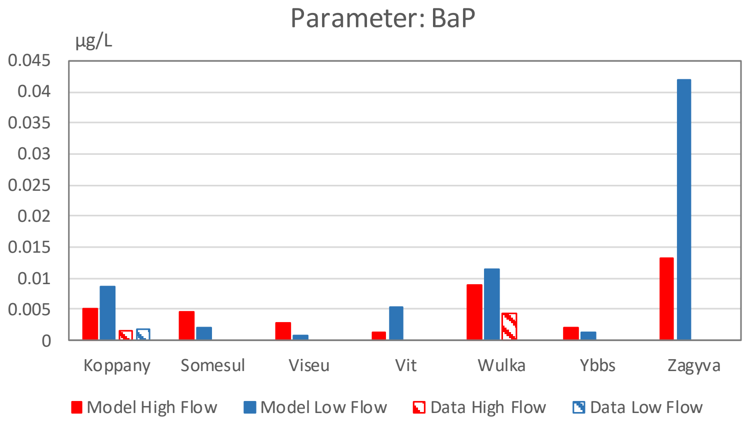
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
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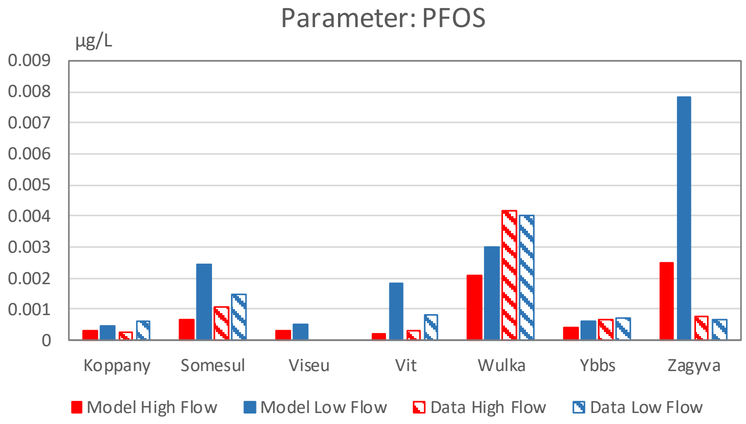
Somesul
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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µg/L
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0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
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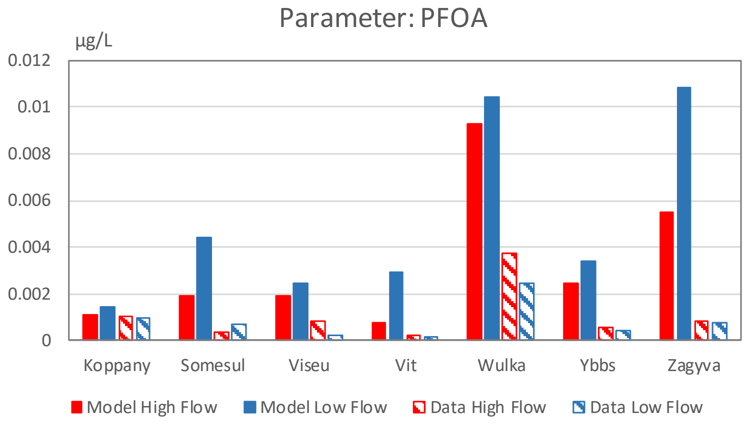
Somesul
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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0.006
0.004
0.002
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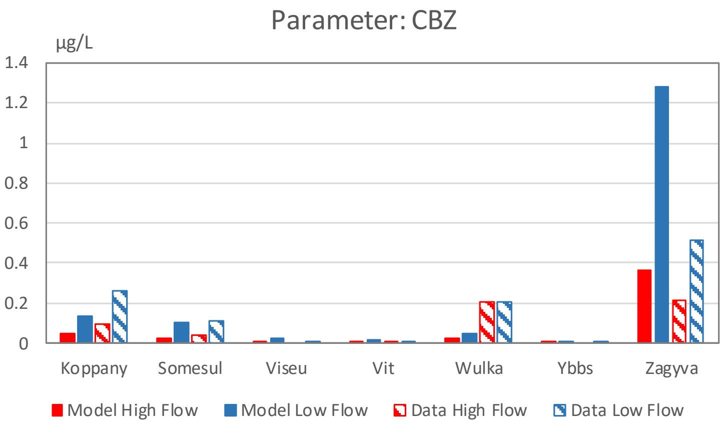
Somesul
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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µg/L
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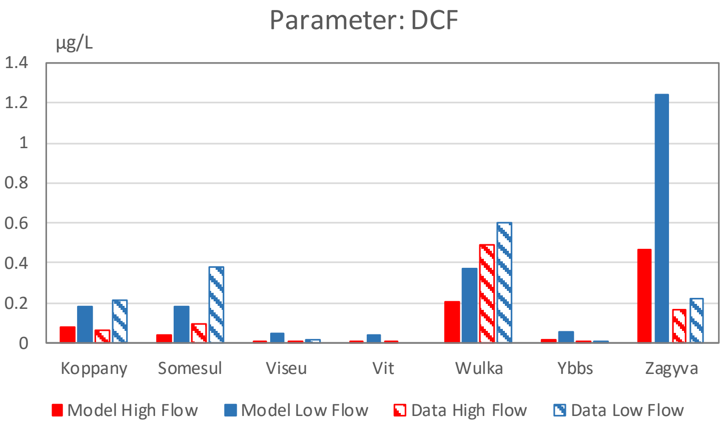
1.2
1
0.8
0.6
0.4
0.2
0
Koppany
Somesul
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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µg/L
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1.2
1
0.8
0.6
0.4
0.2
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Koppany
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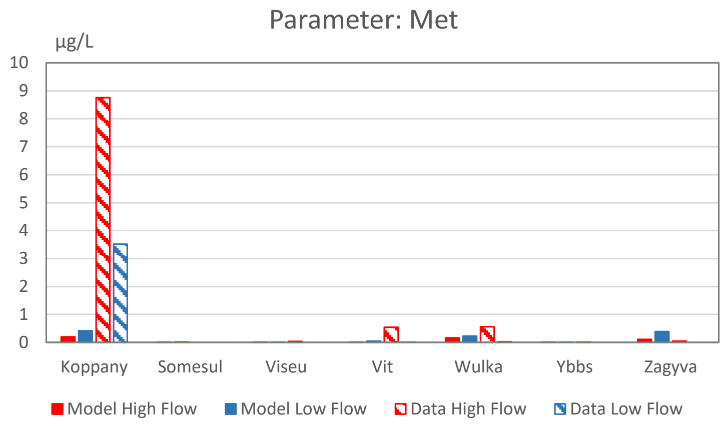
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow


Parameter: Met
µg/L
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9
8
7
6
5
4
3
2
1
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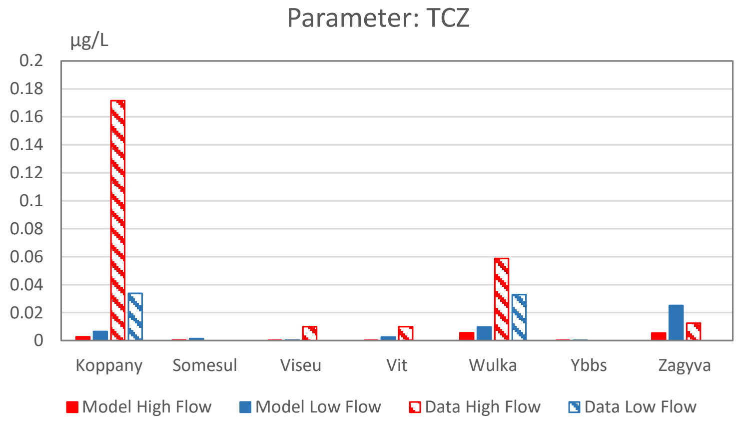
Somesul
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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0.14
0.12
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0.06
0.04
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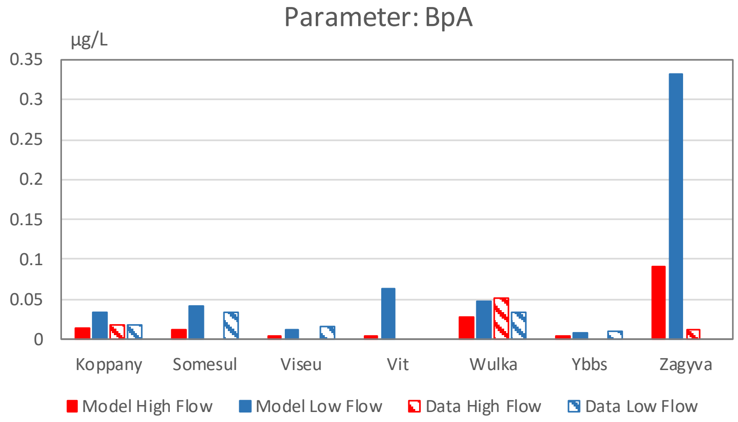
Koppany
Somesul
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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0.1
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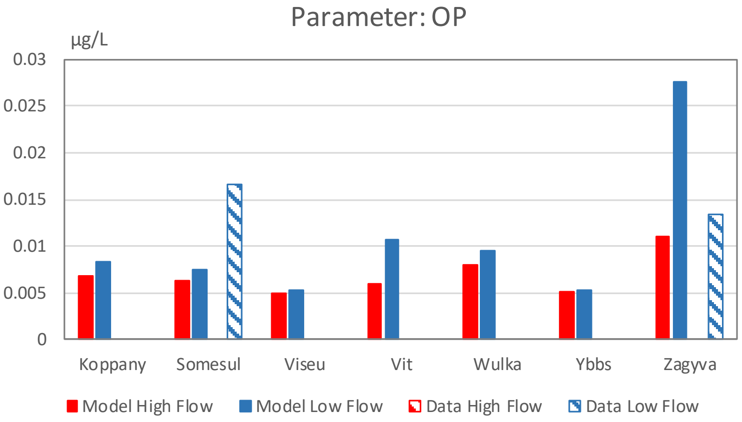
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow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µg/L
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0.015
0.01
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0
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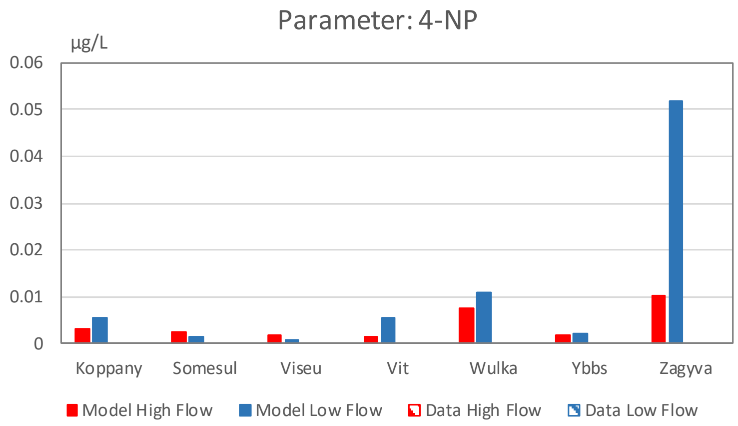
Somesul
Viseu
Vit
Wulka
Ybbs
Zagyva
Model High Flow
Model Low Flow
Data High Flow
Data Low Flow



9.5 Variability of emissions and concentrations

	Max/Min	**P75/P25**	**Year-MinEmis**	**Year-MaxEmis**	**MinYears**	**MaxYears**
Cadmium	2.2	2.4	2007	2013	2007	2013
Lead	2.6	1.7	2007	2013	2007	2013
Copper	1.8	2.3	2007	2013	2007	2012-2013
Arsenic	2.0	1.8	2007	2013	2007	2013
Nickel	2.2	1.8	2007	2013	2007	2013
Mercury	1.8	3.6	2007	2013	2007	2012-2013
Zinc	1.6	2.3	2007	2013	2007	2012-2013
Benzo[*a*]pyrene	1.2	3.9	2011	2010	2004-2011	2006-2007-2012
Metolachlor	1.4	4.0	2007	2010	2008-2010	2011
Tebuconazole	1.6	4.9	2008	2010	2010-2013	2006-2011
Carbamezepine	1.7	2.5	2004	2013	2010-2013	2006-2011
Diclofenac	1.6	2.1	2011	2010	2010-2013	2006-2012
PFOS	1.2	4.9	2011	2010	2010-2013	2006-2011-2012
PFOA	1.1	7.8	2011	2010	2010-2011-2012	2005-2006-2012
Bisphenol A	1.5	3.8	2004	2010	2010-2013	2006-2011
Nonylphenol	1.2	3.7	2011	2010	2004-2007	2006-2012
4-tert-octylphenol	1.1	3.9	2011	2010	2004	2012-2013

Max/Min: mean ratio of highest annually averaged concentration and lowest annually averaged concentration along the river.

P75/P25: mean ratio of 10-year averaged concentration using P75 and P25 emission estimates along the river.

YearMinEmis: year with lowest total emissions.

YearMaxEmis: year with highest total emissions.

MinYears: year(s) showing lowest average concentrations at different locations along the Danube.

MaxYears: year(s) showing highest average concentrations at different locations along the Danube.