# INTERACTION EFFECTS IN GLOBAL MULTI-POLLUTANT MODELLING OF RIVER EXPORT

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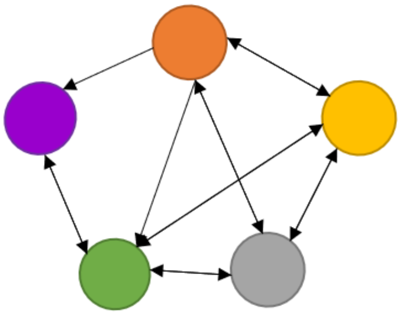

M.Sc. Thesis by Fiona van Schaik

August 2nd, 2019

Water Systems and Global Change Group

*Frontpage figure:  Chapter 2*

# INTERACTION EFFECTS IN GLOBAL MULTI-POLLUTANT MODELLING OF RIVER EXPORT

## *A study of interactions between groups of pollutants in rivers, and the possibilities for the incorporation of these interactions into global modelling of river export of multiple pollutants*

Master Thesis at the Water Systems and Global Change Group submitted in partial fulfillment of the degree of Master of Science in Environmental Sciences at Wageningen University & Research, the Netherlands

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# Summary

Water quality is compromised by the occurrence of multiple pollutants worldwide. Pollution of water can have a range of negative impacts, including the deterioration of coral reef health and human health. Good water quality is, therefore, important for both nature and society. Accordingly, Sustainable Development Goal 6 is about clean water and sanitation. However, data sparsity can challenge the monitoring and assessment of trends in water quality problems and trends. Global water quality models can compensate for this lack of data. Currently, most of these models do not explicitly consider how multiple pollutants can interact with each other. Pollutants may interact through common sources and their impacts. Moreover, in the river itself pollutants may have effects on each other during river transport. Considering these effects may improve the accuracy of water quality models and allow for effective management solutions for pollution issues.

The objective of this thesis is, therefore, to identify interactions between groups of pollutants in rivers, and explore possibilities for the incorporation of these interactions in a global model for river export of multiple pollutants. To meet this objective, this thesis strives to answer the following four research questions:

RQ1. What interactions exist between groups of pollutants in rivers?
RQ2. How can existing water quality models be integrated into a global model for river export of multiple pollutants?
RQ3. Which model parameters of a global model for river export of multiple pollutants are associated with interactions between groups of pollutants?
RQ4. How can interaction effects be incorporated in a global model for river export of multiple pollutants?

To answer these research questions, I used the following methods. I conducted an extensive literature review on potential interactions between groups of pollutants. Various experts were consulted through an interactive panel session and interviews (RQ1, Chapter 2). Several large scale water quality models were analysed to gain insight into the modelling of different types of pollutants in rivers. I used this knowledge to integrate modelling approaches for the river export of individual pollutants into a new global model for river export of multiple pollutants. The global model for point source inputs of multiple pollutants functioned as the starting point of this new model (RQ2, Chapter 3). Based on the identified interactions between groups of pollutants, I linked the model parameters of the global model for river export of multiple pollutants to the interactions that could theoretically affect these parameters (RQ3, Chapter 4). Two possibilities are developed for the incorporation of interaction effects in a global model for river export of multiple pollutants (RQ4, Chapter 4).

Four main outcomes of this thesis are presented below.

First, eleven types of potential interactions are identified between five selected groups of pollutants (RQ1, Chapter 2). I defined the following groups of pollutants: nutrients (such as nitrogen and phosphorous), hazardous solids (such as plastics), chemicals (such as triclosan), pathogens (such as *Cryptosporidium*) and toxins (such as mycrocystins). These groups of pollutants may interact with each other in the following ways, that are classified from A to K:

A. Biofouling-dependent: Nutrients → Hazardous solids (A1)
B. Sorption-dependent: Nutrients ↔ Hazardous solids (B1);
Chemicals ↔ Hazardous solids (B2);
Pathogens ↔ Hazardous solids (B3);
Chemicals ↔ Hazardous solids (B4)

C. Food-web dependent: Nutrients → Hazardous solids (C1)
D. Light-dependent: Hazardous solids → Nutrients (D1);
Hazardous solids → Pathogens (C2)
E. Carbon cycle-dependent: Nutrients → Chemicals (E1)
F. Toxic stress-dependent: Chemicals → Nutrients (F1);
Chemicals → Pathogens (F2);
Toxins → Pathogens (F3)
G. Supply-dependent: Nutrients → Pathogens (G1)
H. Organic matter-dependent: Nutrients → Pathogens (H1)
I. Cyanobacteria-dependent: Nutrients → Toxins (I1)
J. Leaching-dependent: Hazardous solids → Chemicals (J1)
K. Biomass dilution-dependent: Pathogens → Toxins (K)

Second, a design for a new, global model for river export of multiple pollutants integrates modelling approaches for individual pollutants (RQ2, Chapter 3). The basis for this new model is a global model for point source inputs of multiple pollutants. I extended the model by including retentions and losses of pollutants in rivers to quantify their river export. I synthesised existing modelling approaches for nutrients, microplastics, triclosan and *Cryptosporidium* and adjusted the modelling approaches to the level of sub-basins. The result is the design of an integrated, global model that quantifies the river export of these pollutants from point sources per sub-basin. This model opens up an opportunity to include interactions between these pollutants in rivers.

Third, a first attempt is made to link interactions between pollutants in rivers to model parameters in a global model for river export of multiple pollutants (RQ3, Chapter 4). The model parameters are associated with retentions and losses of the pollutants in rivers, lakes and reservoirs. These retentions and losses may be affected by the effects of potential interactions, i.e. increases or decreases. Therefore, the model parameters that reflect these retentions and losses may need to be adjusted to account for the effects of these interactions. Further research is needed to quantify the interaction effects. Several possibilities for the incorporation of these interaction effects into global modelling of river export of multiple pollutants exist.

Fourth, two possibilities to incorporate interaction effects in a global model of river export of multiple pollutants are further developed in this thesis (RQ4, Chapter 4). Possibility 1 is to adapt existing modelling approaches concerning retentions and losses of pollutants. These adaptations would be based on the interactions and associated processes. Possibility 2 is to add a new, statistically determined interaction factor to existing modelling approaches. This interaction factor would be approximated with a more lumped approach in quantifying interaction effects, for example by lumping relevant interactions into groups. These two possibilities provide insight into the methods that could potentially be developed to incorporate interaction effects in global modelling of river export of multiple pollutants. Possibility 1 is a more process-based approach in comparison to Possibility 2, which is a more statistical approach. In contrast to Possibility 1, Possibility 2 does not require the quantification of all relevant processes individually. However, a lack of data could challenge the derivation of the statistical methods of Possibility 2. Furthermore, Possibility 2 risks the double counting of interactions.

This thesis contributes to the scientific field of global surface water quality modelling with new insights into interactions in rivers. This thesis forms a starting point for the incorporation of interactions in global models for river export of multiple pollutants. It provides a basis for further research on these interactions, their effects and their incorporation into global water quality models. Global water quality models can likely be improved by incorporating interaction effects. Such models can be useful tools to more accurately identify hotspots of multiple pollutants, their sources and their impacts. These models can, therefore, contribute to exploring effective management solutions for multi-pollutant problems worldwide. This will help to achieve Sustainable Development Goal 6: clean water and sanitation for all.

# Acknowledgements

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Finally, I would like to express my gratitude for everyone who has supported me along the way. Thank you very much.

Thank you.

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# Chapter 1. Introduction

## 1.1 Pollution problems

Water quality has been declining in many rivers worldwide. According to the United Nations (2018), pollution levels have increased in nearly all Asian, African and Latin-American rivers during the previous decades. Various pollutants contribute to the deterioration of river water quality. In Africa, the Medjerda river is affected by, among others, nutrients. The nutrient levels in the Elbe, in Europe, too, still exceed target levels, though they have decreased as a result of efforts to do so (UNEP, 2016). Microplastic pollution, for example, has been detected on beaches of the Pearl estuary in China (Fok & Cheung, 2015), but also throughout the European river Rhine (Mani et al., 2015). Triclosan (TCS), based on a ranking of 500 pollutants, is the 6th most problematic pollutant in the Elbe (Von der Ohe et al., 2012). Though monitoring data are scarce, TCS is likely also causing river pollution issues elsewhere, because TCS is applied all around the world (Von der Ohe et al., 2012). The pathogen *Cryptosporidium* occurs in surface waters in, for example, Europe (Ongerth et al., 2018) and South-America (Bautista et al., 2018; Neto et al., 2010). Cyanotoxins, too, have been reported in surface waters at various continents (Merel et al., 2013). Pollution of rivers by nutrients, microplastics, TCS, *Cryptosporidium* and cyanotoxins thus occurs throughout the world.

These pollutants come from various sources. Human activities on land can lead to the emissions of pollutants to rivers. Agriculture, for example, may be a source of plastic from fertilizers and waste (van Wijnen et al., 2019), pathogens such as *Cryptosporidium* from manure (Hofstra et al., 2013; Vermeulen et al., 2017) and nutrients from synthetic fertilizers and manure (Mayorga et al., 2010; Seitzinger et al., 2010). Nutrient enrichment of surface waters, in turn, may lead to the emission of cyanotoxins (Pelaez et al., 2010). For example through sewage discharges, urban areas may be a source of TCS from personal care products (Zhao et al., 2013), pathogens (Hofstra et al., 2013), microplastics (Siegfried et al., 2017) and other pollutants.

River contamination by each of these pollutants can have severe consequences. Nutrient pollution is associated with eutrophication, harmful algal blooms and seasonal coral reef decline (Duprey et al., 2016; Zaneveld et al., 2016; Glibert, 2017). Microplastics may be consumed by and damage organisms of all trophic levels, and may also impact these organisms by e.g. facilitating transport of chemicals (Eerkes-Medrano et al., 2015). TCS, an endocrine disrupting chemical, may have detrimental consequences for female reproduction (Rattan et al., 2017). *Cryptosporidium* typically leads to diarrhoea in children. Cyanotoxins may, for example, damage liver and nerve tissue (Funari & Testai, 2008). Water quality is, in other words, threatened in many regions of the world by various pollutants. This could prove problematic as the demand for water increases (van Vliet et al., 2017).

Water of good quality is important to us all. One of the UN Sustainable Development Goals (SDGs) is, therefore, *Clean Water and Sanitation* (SDG 6). According to a snapshot report of UNEP (2016), river basins worldwide are faced by similar pollution issues, that often are related to other societal goals such as good health (UNEP, 2016; United Nations, 2018; Alcamo, 2019). In many parts of the world, however, water quality is not sufficiently monitored. Consequently, water quality data is sparse (United Nations, 2018). This is a challenge in tracking progress on SDG 6.

## 1.2 Interactions between pollutants

The multiple pollutants present in rivers may have links to each other (Kroeze et al., 2016). These links may consist of having the same source, having effects on each other and/or having various effects combinedly (Kataoka et al., 2019; Kroeze et al., 2016). As mentioned, both sewage discharges and agricultural runoff can be a source of multiple pollutants and each pollutant can have different consequences for both nature and society. Within the river, the pollutants may also interact with each other. Such interactions[1] occur within a pollutant group as nutrients, e.g. between nitrogen and phosphorous. Possibly, interactions exist between pollutant groups as well, e.g. between nutrients and chemicals that do not naturally occur in rivers (Kroeze et al., 2013). For example, chemicals may be bound to plastics prior to sedimentation or may be diluted in biomass due to higher nutrient levels (Kroeze et al., 2016). This could have consequences for the impacts that these chemicals have on their environment. Hence, considering the effects of pollutants from different pollutant groups on each other may be important in analysing water quality, also at a global scale. However, these interactions between groups of pollutants in rivers have received little attention in global water quality research in comparison with the interactions between individual nutrients (Kroeze et al., 2013).

## 1.3 Global multi-pollutant modelling

### Models for quantifying individual pollutants

A lack of data can partially be compensated for by the use of water quality models. These models can clarify the nature and development of pollution issues in data-sparse world regions (Kroeze et al., 2016). Many different surface water quality models exist, differing in their complexity, and spatial and temporal resolutions and extents. The models can range from being simple, empirically/statistically based models to highly complex models that incorporate underlying processes. The complexity of water quality models tends to increase as the area covered by and time steps included in the model become smaller (Bouwman et al., 2013; Tang et al., 2019). Global models are relatively simple compared to regional water quality models such as SWAT. For this reason, the global models are especially useful in pointing out areas where waters are polluted and to observe trends over longer time periods (Tang et al., 2019).

Global or continental water quality models have been developed for each of the aforementioned pollutants (Kroeze et al., 2016). Among others, Global NEWS 2 (Nutrient Export from WaterSheds 2) (Mayorga et al., 2010; Seitzinger et al., 2010), IMAGE-GNM (Global Nutrient Model) (Beusen et al., 2015) and WorldQual (UNEP, 2016) model nutrient pollution from land to sea. Models for river export of microplastic river transport and export models have European (Siegfried et al., 2017) and worldwide (van Wijnen et al., 2019) applications. TCS (van Wijnen et al., 2018) is modelled from emissions into rivers to the sea. A global model for the pharmaceutical diclofenac is also developed (Font et al., 2019). Concentrations of the pathogen *Cryptosporidium* in rivers over the whole world are computed per grid cell of 0.5° (Vermeulen et al., 2019). The models available to the Water Systems and Global Change group at which this thesis is fulfilled are displayed in Table 1.1. During the last three decades, more and more of such large scale water quality models have been developed (van Vliet et al., 2019). However, because these models tend to focus on one pollutant or one group of pollutant only, the links between these pollutants have been neglected (Kroeze et al., 2016).

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[1] See Chapter 2

### Models for quantifying multiple pollutants simultaneously

Several global water quality models have been developed, each for a distinct pollutant (group). On a continental scale, WorldQual quantifies pollutants from more than one group (for example nutrients, bacteria), but not simultaneously (Strokal et al., 2019). Therefore, WorldQual is not able to address interactions between pollutants in rivers. To address the interactions between multiple pollutants, Kroeze et al. (2016) argue for a more integrated approach: a global multi-pollutant model. According to Kroeze et al. (2016), a modelling approach that combines multiple pollutants and incorporates the sources that they originate from could contribute to finding out which measures are most effective in overcoming pollution issues simultaneously. Therefore, first attempts to combine different large scale water quality models are made. Strokal et al. (2019) combine approaches used in nutrient, microplastic, TCS and *Cryptosporidium* models (Table 1.1). Combining the different models is shown to allow for the identification of various hotspots of these pollutants. Strokal et al. (2019) identifies various challenges for the development and evaluation of such global multi-pollutant models. The lack of consistent worldwide datasets and the differences in the complexity of existing models are among these. Both Kroeze et al. (2016) and Strokal et al. (2019) distinguish the need for such multi-pollutant models to incorporate what pollutants have or do not have in common (e.g. origins, impacts) and the effects of pollutants on each other.

Interactions and their effects have not been incorporated into most global water quality models (Kroeze et al., 2016). However, an approach considering such effects may be useful in identifying and solving severe water quality issues in which multiple pollutants play a role (Kroeze et al., 2016). Strokal et al. (2019) introduce the first global multi-pollutant model for river water quality. This model quantifies point source inputs of nutrients, microplastics, TCS and *Cryptosporidium* into rivers. The model and framework by Strokal et al. (2019) open an opportunity for the inclusion of interactions between pollutants in rivers once river exports are quantified. However, including interactions in modelling is currently challenging, in part because of a knowledge gap on interactions between pollutants in rivers (Strokal et al., 2019). To ensure, therefore, that global multi-pollutant modelling efforts consider interactions and their effects in rivers, it is necessary to address this knowledge gap on interactions and to start thinking about the potential incorporation of interactions into global multi-pollutant models.

## 1.4 Research objective and questions

The research objective of this thesis is, therefore, as follows:

*To identify interactions between groups of pollutants in rivers, and explore possibilities for the incorporation of these interactions in a global model for river export of multiple pollutants.*

To meet the research objective, this thesis strives to provide an answer to four research questions (RQs). These are:

| | |
|---|---|
| ***RQ1*** | *What interactions exist between groups of pollutants in rivers?* |
| ***RQ2*** | *How can existing water quality models be integrated into a global model for river export of multiple pollutants?* |
| ***RQ3*** | *Which model parameters of a global model for river export of multiple pollutants are associated with interactions between groups of pollutants?* |
| ***RQ4*** | *How can interaction effects be incorporated in a global model for river export of multiple pollutants?* |

These research questions are addressed in Chapter 2, Chapter 3, Chapter 4 and Chapter 4 respectively.

*Table 1.1. Models available to, and partially developed by, the Water Systems and Global Change group of Wageningen University and Research, used for their assessments on water quality. *coupled to the VIC hydrology model (first publication: Liang, et al. (1994). Source: [https://www.wur.nl/en/Research-Results/Chair-groups/Environmental-Sciences/Water-Systems-and-Global-Change-Group/research/Water-pollution-assessments-1.htm](https://www.wur.nl/en/Research-Results/Chair-groups/Environmental-Sciences/Water-Systems-and-Global-Change-Group/research/Water-pollution-assessments-1.htm)*

| **Model name (abbreviation)** | **Water quality aspect** | **Literature** |
|---|---|---|
| Global Nutrient Export from WaterSheds (Global NEWS) | Nutrients | Mayorga et al. (2010); Seitzinger et al. (2010) |
| Model to Assess River Inputs of Nutrients to seAs (MARINA) | Nutrients | Strokal, Kroeze, et al. (2016) |
| NUtrient flows in Food chains, Environment and Resources use (NUFER) | Nutrients | Ma et al. (2010, 2012) |
| Microplastics model | Microplastics | Siegfried et al. (2017);<br>van Wijnen et al. (2019) |
| Global triclosan model (Global TCS) | Triclosan (TCS) | van Wijnen et al. (2018) |
| Global Waterborne Pathogen model (GloWPa)* | Pathogens (*Rotavirus*, *Cryptosporidium*) | Hofstra and Vermeulen (2016); Vermeulen et al. (2019) |
| Salinity model* | Salinity | van Vliet et al. (2017)[2] |
| River Basin Model (RBM)* | Water temperature | Yearsley (2009, 2012) |
| Oxygen model* | Oxygen | van Vliet et al. (2017)[3] |

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[2] Project *Quality matters: Including water quality in global water stress projections (https://www.wur.nl/en/Persons/Michelle-dr.-MTH-Michelle-van-Vliet.htm?subpage=projects)*

[3] Project *Quality matters: Including water quality in global water stress projections (https://www.wur.nl/en/Persons/Michelle-dr.-MTH-Michelle-van-Vliet.htm?subpage=projects)*

# Chapter 2. Pollutant interactions in river systems

## 2.1 Introduction

Chapter 2 provides an answer to Research Question 1:

*What interactions exist between groups of pollutants in rivers?*

Chapter 2 addresses the knowledge gap on the interactions between groups of pollutants in river systems. An overview of potential interactions between groups of pollutants in river systems is provided in this chapter. This overview can be useful to improve global water quality models.

In the next section, Section 2.2, the methods used to answer this research question are described. The explanation for the use of these methods to address Research Question 1 is also provided in Section 2.2. Section 2.3 gives a brief overview of interactions relating to the sources of pollutants in rivers and impacts of pollutants on society and nature. Section 2.4 is attributed to the potential interactions between groups of pollutants in rivers. Section 2.5 is attributed to environmental conditions that could play a role in the potential interactions and might affect the environment where the interactions may be dominant. The conclusions are drawn in Section 2.6.

## 2.2 Methodology

### 2.2.1 Literature review

To obtain more knowledge on interactions in river systems, a literature review was conducted. Experts were consulted to ensure that the most relevant interactions and associated literature were appropriately part of this review. An important aspect of this was an interactive seminar with an expert panel, conducted in February 2019 between experts of the Aquatic Ecology and Water Management group and the Water Systems and Global Change group of Wageningen University and Research. During this seminar, the possible interactions between each of the couples of pollutant groups were considered and potential interactions were identified. The occurrence and mechanisms of these interactions were then further supported and described using peer-reviewed literature. In addition, individual experts in global modelling of nutrients, plastics, chemicals (triclosan) and pathogens were consulted for their expert judgement in the definitions of the identified potential interactions between groups of pollutants in rivers. The experts also provided literature to support the overview on the identified interactions presented in this chapter.

The literature obtained for this review was retrieved via search engines as Scopus and Google Scholar. Identified articles were also used as a starting point for finding more literature by checking cited and citing literature for these articles ("snowball method"). Criteria for the inclusion of literature were:

- It concerns at least one of the pollutants groups;
- It covers direct or indirect interactions or effects of interactions between the selected pollutant groups;

- The interactions take place in the river.

In case literature on riverine interactions was lacking, however, literature on the potential interactions in the marine environment was included. Though environmental conditions are substantially different, this may nevertheless give an idea of what interactions could potentially occur in freshwater systems.

### 2.2.2 Definitions of the groups of pollutants

Five main groups of pollutants were identified: nutrients, hazardous solids, chemicals, pathogens and toxins. Nutrients are defined here as substances required by organisms for their growth and survival. Examples of nutrients are nitrogen (N) and phosphorous (P). Hazardous solids are defined here as solids of anthropogenic origin to which potentially harmful substances could bind. Examples of hazardous solids are plastics and synthetic nanoparticles. Chemicals are defined here as organic chemicals of anthropogenic origin. Nutrients and hazardous solids are excluded from this group. Examples of chemicals are triclosan (TCS), dioxins, PCBs, phthalate esters and PAHs. Pathogens are defined here as bacteria, viruses and protozoa that can cause diseases. In particular, attention is paid to faecal-oral pathogens. Examples of pathogens are *Cryptosporidium* and *Rotavirus*. Toxins are here defined as toxic substances emitted by cyanobacteria. Examples of toxins are microcystins.

## 2.3 Sources and impacts of pollutants in rivers

Various pollutants tend to enter rivers from common sources (Bloodworth et al., 2015; Kroeze et al., 2016; Strokal et al., 2019; Figure 2.1). These sources are often divided into point sources and diffuse sources. Point sources are, for example, sewage discharge, open defecation (particularly in Southern Asia and Sub-Saharan Africa (Vermeulen et al., 2015; WHO, 2014)), direct manure discharge (China (Strokal, Ma, et al., 2016)) and mining (e.g. lake Dianchi (Li et al., 2019)). Diffuse sources are agricultural runoff of synthetic fertilizers and manure, N deposition, P weathering (many rivers in the world (Mayorga et al., 2010; Seitzinger et al., 2010)) and mining (e.g. lake Dianchi (Li et al., 2019)). Some sources are specific for certain pollutants (e.g. P weathering and N deposition), regions (e.g. direct manure discharge in China, open defecation in developing countries) or locations (e.g. mining). However, both point and diffuse sources can release multiple pollutants into rivers and many of these common sources may occur globally. For example, water discharged from sewage systems may be a source of pollutants such as pathogens (Hofstra et al., 2013; Hofstra & Vermeulen, 2016; Malham et al., 2014; Vermeulen et al., 2015; Vermeulen et al., 2019), microplastics (Kooi et al., 2018; Lebreton et al., 2017; Schmidt et al., 2017; Siegfried et al., 2017), pharmaceuticals (Font et al., 2019; Kay et al., 2017) and many other pollutants. The quantity of pollutants discharged into rivers from sewage systems depends on the inputs of pollutants into these systems and the removal efficiency of the pollutants during treatment. Similarly, multiple pollutants originate from agricultural runoff, such as pathogens (Hofstra et al., 2013; Malham et al., 2014; Vermeulen et al., 2015; Vermeulen et al., 2017; Vermeulen et al., 2019), microplastics (van Wijnen et al., 2019) and nutrients (Beusen et al., 2015, 2016; Mayorga et al., 2010; Schoumans et al., 2014). Thus, linkages between multiple pollutants exist in relation to the sources of these pollutants in rivers. Therefore, considering the origin of these pollutants in rivers is relevant for effective solutions (Bloodworth et al., 2015).

Multiple pollutants can lead to diverse impacts on society and nature (Figure 2.1). Water pollution affects human health (e.g. Wang and Yang (2016) and Törnqvist et al. (2011)). For example, nitrate and nitrite pollution may, through limiting oxygen transport in the body, cause the “Blue Baby Syndrome” in infants (Majumdar, 2003; Törnqvist et al., 2011). Human physical health is significantly correlated to mercury, COD (chemical oxygen demand) and $NH_3$-N (ammonia-nitrogen) (Wang & Yang, 2016). Pathogens can lead to diarrhoea (Walker et al., 2013). Kidney damage can result from cadmium, copper, lead and mercury pollution (Törnqvist et al., 2011). Heavy metals also affect human mental health (Wang & Yang, 2016). Amphibians are negatively affected by pathogens, but also by pesticides and cyanotoxins (Milotic et al., 2018). Pathogens, nutrients, heavy metals and microplastics are among various pollutants that could negatively impact coral reef health (Reichert et al., 2018; Wear & Thurber, 2015). Despite various examples of the combined impacts of multiple pollutants and several voices advocating the study of the effects of multiple stressors (O'Brien et al., In Press; Ormerod et al., 2010), few studies consider these interactive effects of multiple stressors (Nõges et al., 2016; O'Brien et al., In Press). Thus, it is necessary to better understand the linkages between pollutants in relation to their sources and impacts.

Furthermore, pollutants may interact in the river (Figure 2.1). Details on the interactions of pollutants in rivers are given in the next section.

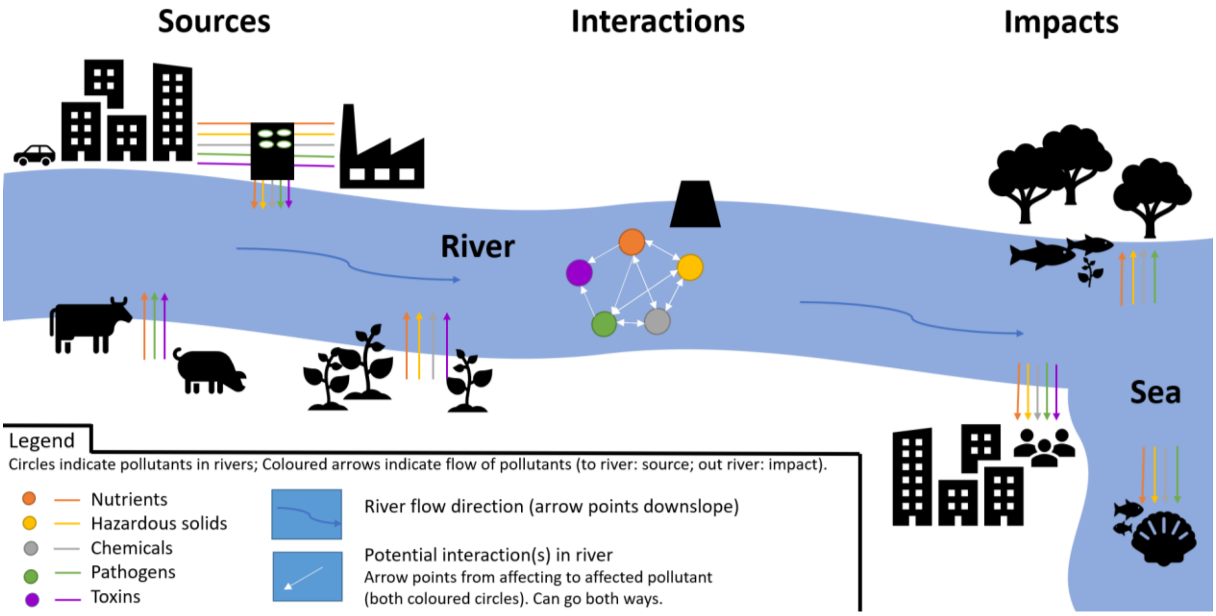

*Figure 2.1. A schematic overview of river export of multiple pollutants from land activities (sources as agricultural runoff and sewage systems) and potential interactions between groups of pollutants: nutrients (e.g. nitrogen (N) and phosphorous (P)), hazardous solids (e.g. microplastics), chemicals (e.g. triclosan (TCS)), pathogens (faecal-oral bacteria, viruses and protozoa) and toxins (cyanotoxins). Pollution of rivers and coastal seas by multiple pollutants can cause various impacts (e.g. decreased human health, declines in coral reef health). Based on literature review (see Section 2.2.1 and Section 2.3).*

## 2.4 Potential interactions of pollutants in rivers

The word *"interaction"* here refers to an influence that one pollutant or pollutant group (directly or indirectly) has on another pollutant. An interaction is here defined as: *"A particular way in which a (group of) pollutant(s) affects another"* (see Appendix A.1, Figure A.1.1 and Figure A.1.2). Interactions may have implications for the river export and the combined impacts of multiple pollutants (Figure 2.1 above). Potential interactions in the river are discussed in this section.

### 2.4.1 An overview of potential interactions between riverine pollutants

This section provides an overview of potential interactions between the five groups of pollutants in rivers (nutrients, hazardous solids, chemicals, pathogens and toxins). Many interactions between these groups may exist. Potential interactions are identified and described in this section (see Figure 2.2.). The overview should not be viewed as complete. Rather, the overview is meant to contribute to a better understanding of the potential interactions that could be relevant for improving global water quality models.

Based on literature review and expert knowledge, 11 types of potential interactions between five groups of pollutants in the river are identified in consultation with various water quality experts (Figure 2.2; A-K: letters for the type of interactions). Some types of potential interactions are relevant for more than two groups of pollutants (e.g. sorption-dependent interaction). Each of the interactions is classified as an interaction with direct effects or an interaction with indirect effects (Figure 2.2 and Table 2.1). Temperature, oxygen, UV/light, pH and salinity are indicated as important factors and may affect a number of the identified potential interactions (Figure 2.2; examples in Sections 2.4.2-2.4.12). The potential interactions that are identified are displayed in Figure 2.2 and classified into types A-K as:

A. Biofouling-dependent interaction
    - Between nutrients and hazardous solids (A1)
B. Sorption-dependent interaction
    - Between nutrients and hazardous solids (B1)
    - Between chemicals and hazardous solids (B2)
    - Between pathogens and hazardous solids (B3)
    - Between chemicals and pathogens (B4)
C. Food web-dependent interaction
    - Between nutrients and hazardous solids (C1)
D. Light-dependent interaction
    - Between hazardous solids and nutrients (D1)
    - Between hazardous solids and pathogens (D2)
E. Carbon cycle-dependent interaction
    - Between nutrients and chemicals (E1)
F. Toxic stress-dependent interaction
    - Between chemicals and nutrients (F1)
    - Between chemicals and pathogens (F2)
    - Between toxins and pathogens (F3)
G. Supply-dependent interaction
    - Between nutrients and pathogens (G1)
H. Organic matter-dependent interaction
    - Between nutrients and pathogens (H1)
I. Cyanobacteria-dependent interaction
    - Between nutrients and toxins (I1)
J. Leaching-dependent interaction
    - Between hazardous solids and chemicals (J1)
K. Biomass dilution-dependent interaction
    - Between pathogens and toxins (K1)

The following sections (Sections 2.4.2-2.4.12) elaborate on each of the types of interactions. These sections present definitions of the interactions, their descriptions and examples when available. Potential interactions between hazardous solids and toxins and between chemicals and toxins were not identified during the interactive seminar with experts. A summary is given in Table 2.1.

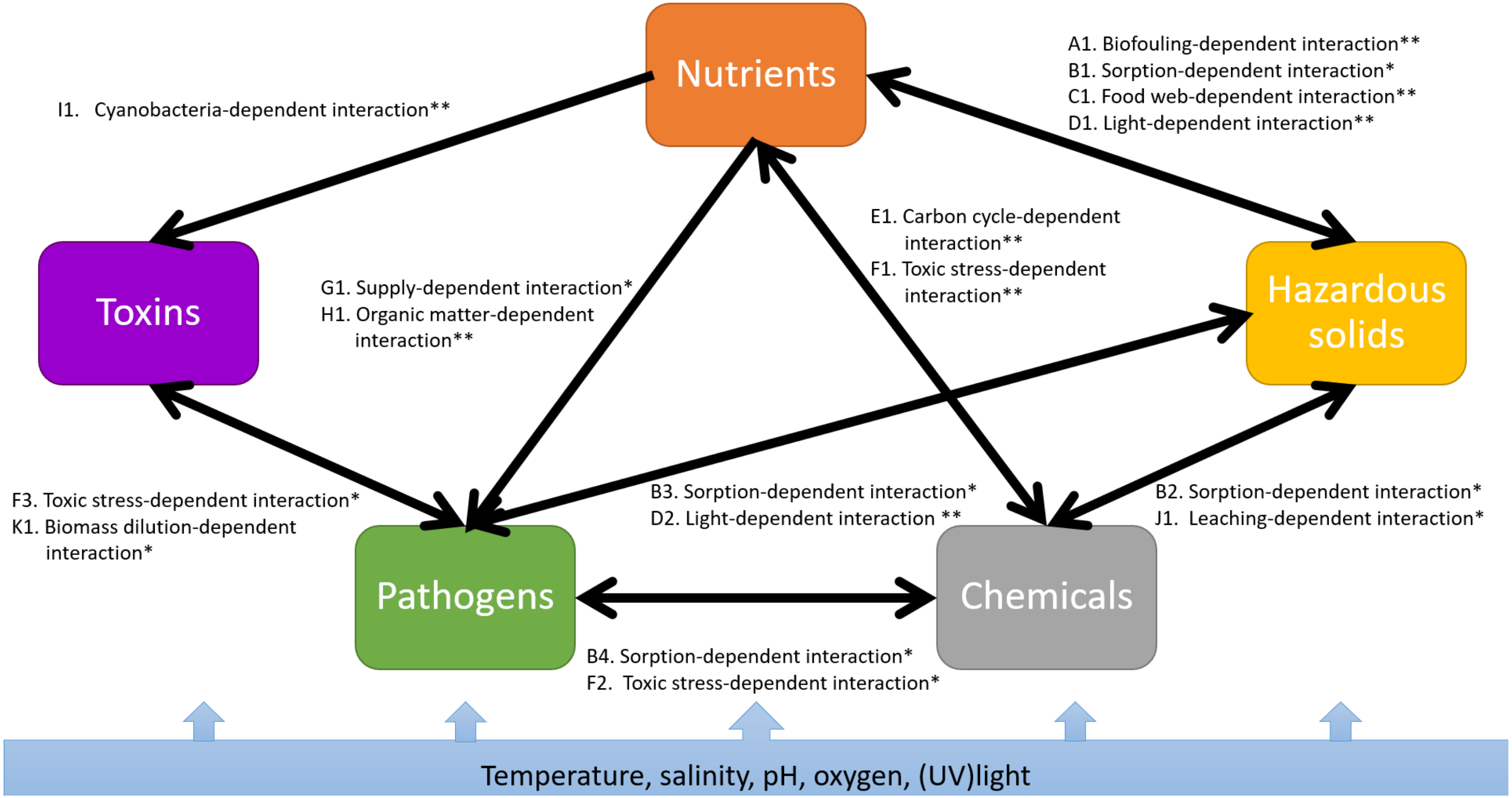

*Figure 2.2. Identified potential interactions between five groups of pollutants (nutrients, hazardous solids, chemicals, pathogens and toxins) in rivers and their directions. The letter refers to the type of interaction, the number distinguishes interactions of the same type between different pollutants. * indicates a direct interaction. ** indicates an indirect interaction (i.e. may occur via another pollutant group, the food web, etc.). The black arrow points from the affecting pollutant group towards the affected pollutant group. Double arrows (with two endings) indicate that the two pollutant groups affect each other. Temperature, salinity, pH, oxygen, (UV)light are important environmental factors that might affect the interactions. The identified potential interactions are described in Sections 2.4.2-2.4.12 and summarized in Table 2.1. Source: synthesis of literature and expert knowledge (see Section 2.2.1, Section 2.3 and Section 2.4).*

### 2.4.2 Interaction type A: Biofouling-dependent interaction

This interaction is identified once, between nutrients and hazardous solids.

#### A1: Nutrients → Hazardous solids

*Definition:* Nutrients affect hazardous solids by promoting growth of organisms on the surface of the hazardous solids, because these organisms can attach to the surface area through a process called biofouling. Biofouling is the formation of biofilm (by microorganisms) on solid surfaces in water.

*Description:* Biofilms could be seen as microbial covers. Biofilms consist of microorganisms irrevocably attached to a surface (Donlan, 2002), for example the surface of hazardous solids. The formation of biofilm can be supported particularly through the presence of nutrients (Flemming, 2002). Nutrients have a dual role in the formation of biofilms. Biofilms will form when nutrient concentrations are not too low and not too high. These biofilms seem to be constructed for optimal nutrient retrieval. When levels of nutrients are at the low or high extremes, it becomes less advantageous for microorganisms to obtain nutrients as part of the biofilm. Access to nutrients may then be higher for unattached microorganisms (Stanley & Lazazzera, 2004). Thus, depending on the already existing nutrient conditions in the river, increases in nutrient concentrations will make biofilm formation less or more likely. Similarly, decreases in nutrient concentrations are likely to affect biofilm formation, probably enhancing or decreasing their occurrence dependent on the initial concentrations of nutrients. Other factors that affect biofouling are the species present (Stanley & Lazazzera, 2004) and properties of the surface that the biofilm could potentially be formed on, such as the surface's texture (Donlan, 2002). The structure of the biofilm itself can depend on e.g. streamflow and nutrient conditions (Hall-Stoodley et al., 2004). After the formation of biofilms, organisms may aggregate upon the biofilm, depending on the type of solid (Lagarde et al., 2016) and the algae species present (Long et al., 2017).

*Example:* Biofilms have been reported to occur on plastics (Harrison et al., 2018; Lagarde et al., 2016). Plastics are hydrophobic and nonpolar. Therefore, plastics have particularly been suggested as favoured substrates for biofilm development (Donlan, 2002).

### 2.4.3 Interaction type B: Sorption-dependent interaction

The sorption-dependent interaction is the only identified interaction that is considered to affect both pollutant groups involved. This interaction involves sorption. Sorption is the adsorption or absorption (i.e. attachment) of a substance to another substance. As it is often difficult to determine whether adsorption or absorption takes place, sorption is used as a collective term for both processes (Endo & Koelmans, 2016). The sorption-dependent interaction (B) is identified for four sets of groups of pollutants: nutrients and hazardous solids (B1); chemicals and hazardous solids (B2); pathogens and hazardous solids (B3); and chemicals and pathogens (B4). Both sorption (attachment) and desorption (detachment) may occur (Figure 2.2).

#### B1: Nutrients ↔ Hazardous solids

*Definition:* Nutrients and hazardous solids affect each other through sorption (/desorption), where nutrients and hazardous solids attach to each other (/are detached from each other).

*Description:* (De)sorption is a direct interaction between nutrients and hazardous solids. The abundance of the substances and their physical properties (e.g. their charge, specific surface area) determine to what extent sorption takes place.

*Example:* Prata et al. (2019) state that nutrients (e.g. vitamin B12) can be adsorbed to microplastics. Microplastics can also reduce the absorption of nutrients (Prata et al., 2019).

### B2: Chemicals ↔ Hazardous solids

*Definition:* Chemicals and hazardous solids affect each other through sorption (/desorption), where chemicals and hazardous solids attach to each other (/are detached from each other).

*Description:* A potential interaction between chemicals to hazardous solids is through sorption. Factors that influence the extent to which sorption takes place are, among others, the types of solids and chemicals involved, their concentrations, temperature, weathering and the levels of organic matter and inorganic salts (Endo & Koelmans, 2016; Hartmann et al., 2017; Scherer et al., 2018). Therefore, a difference in the extent to which sorption occurs between freshwater and marine ecosystems likely exists (Scherer et al., 2018). Typically, media such as water and natural particulate matter tend to be a larger vector in transporting hydrophobic organic chemicals than microplastics (Hartmann et al., 2017; Koelmans et al., 2016), but with changing concentrations and the occurrence of hotspots of microplastics, this interaction may still be relevant to consider (Hartmann et al., 2017). Of the smaller chemicals (with a molecular weight of <1000), particularly hydrophobical chemicals can be adsorbed to and desorbed from plastics (Teuten et al., 2009). The term "Trojan Horse effect" is used to describe the hypothesis that consumption of nanomaterials can promote uptake of chemicals bound to these materials (Naasz et al., 2018). However, a review by Naasz et al. (2018) revealed that, even though the "Trojan Horse effect" was observed in many studies, mixtures of chemicals and nanomaterials may not always interact as the "Trojan Horse effect" hypothesis suggests: the nanomaterial and chemical may not interact, and when sorption does occur they may not be consumed by organisms, or desorption of the chemical from the nanomaterial may not occur within the organism. The latter of these interactions would actually decrease exposure to the chemicals (Naasz et al., 2018).

*Example:* Chemicals such as PCBs may attach to plastic particles. Sorption of PCBs to micro-polyethylene (10-180 μm) is reported to occur to a similar extent as sorption of PCBs to organic matter (Velzeboer et al., 2014). In comparison, the sorption of PCBs to several nanoparticles (e.g. 70 nm polystyrene) is relatively strong, in part due to the relatively greater surface area (Velzeboer et al., 2014). Sorption of TCS to polyethelene particles of 250 to 280 μm has also been reported, and has been found to be affected by organic matter (humic acid) and salinity (Wu et al., 2016).

### B3: Pathogens ↔ Hazardous solids

*Definition:* Pathogens and hazardous solids affect each other through sorption (/desorption), where pathogens and hazardous solids attach to each other (/are detached from each other).

*Description:* Next to chemicals, hazardous solids may also carry pathogens that, through sorption, bind to the solids as part of biofilms (see interaction A1). Whether the pathogens bind to microplastics varies spatially and depends on factors such as nutrients and salinity. Sorption of viruses onto surfaces is both directly and indirectly affected by pH and salinity (Sobsey & Meschke, 2008). In some environmental conditions, communities may develop specificity for the substrate (Oberbeckmann et al., 2018). This implies that the communities that use plastics as substrate are composed of different species than the communities that use, for example, wood as substrate.

*Example:* The pathogens *Vibro* spp. and *Aeromonas salmonicida* have been detected on microplastics in marine environments (Kirstein et al., 2016; Viršek et al., 2017). Various genera having pathogenic taxa have been detected in an urban river (McCormick et al., 2014), but this is the only evidence of pathogen binding to microplastics in unmanaged freshwaters so far according to Harrison et al. (2018).

**B4: Chemicals ↔ Pathogens**

*Definition:* Chemicals and pathogens affect each other through sorption (/desorption), where chemicals and pathogens attach to each other (/are detached from each other).

*Description:* Potentially, pathogens bind to chemicals. Such binding may occur through for example ionic attraction[4] and hydrophobic interactions[5] (Sobsey & Meschke, 2008). Adsorption may increase survival of pathogenic viruses (Sobsey & Meschke, 2008). Microbial particles may compete with organic matter for sorption sites (Schijven, 2015).

*Example: Rotavirus* may adsorb to hydrophobic sand particles to a moderate extent, as *Rotavirus* is quite hydrophilic (Farkas et al., 2015). Nevertheless, the limited extent of sorption to hydrophobic matter suggests that sorption of *Rotavirus* to, for example, (surfaces with) hydrophobic organic chemicals might occur.

### 2.4.4 Interaction type C: Food web-dependent interaction

This interaction is identified once, between nutrients and hazardous solids (C1 in Figure 2.2).

**C1: Nutrients → Hazardous solids**

*Definition:* Nutrients affect hazardous solids by regulating river community structure and, therefore, affecting the rate at which hazardous solids are ingested by organisms.

*Description:* Nutrients may affect hazardous solids through affecting the food web and thus the extent to which hazardous solids are possibly ingested by organisms. Nutrient levels can affect community structures. After disturbances, when dominant species in recolonizing the ecosystem tend to reproduce quickly, nutrient enrichment may, for example, induce shifts towards species that live longer and are larger (Kendrick et al., 2019). Such shifts may alter food web dynamics (Chase, 1999) and thus river community composition (i.e. which organisms that are present in the river). Ingestion of e.g. plastic microbeads differs between various taxa, influenced by animal behaviour and feeding methods (Setälä et al., 2016). Possibly, this might imply that (lasting) increases or decreases in nutrient levels affect the food web structure, and perhaps therefore, also the rates at which ingestion of hazardous solids by organisms takes place. Changes in the rate of ingestion of hazardous solids could potentially affect the levels of nutrients in the river itself. Additionally, when food is limited, ingestion of hazardous solids by organisms could be higher as a consequence (Scherer et al., 2017).

*Example:* Ingestion of plastics has been reported since the 1960s and can have detrimental consequences such as death, damage, release of additives and malnutrition (Besseling et al., 2014; Kühn et al., 2015; Scherer et al., 2018). Scherer et al. (2017) find that the extent to which microplastics are consumed by various invertebrates is reduced due to the presence of food. However, hardly any studies seem to explicitly link nutrient levels to ingestion of plastic.

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[4] Ionic or electrostatic attraction: the attraction between ions with opposite charge (negatively charged particles and positively charged particles).

[5] Hydrophobic particles do not interact with water. Hydrophobic particles in aqueous environments, therefore, tend to gather.

### 2.4.5 Interaction type D: Light-dependent interaction

This interaction is an pollutant interaction where one group of pollutants may have consequences for the transmission of light in the river. This may affect another group of pollutants. A light-dependent interaction (D) is identified between hazardous solids and nutrients (D1) and between hazardous solids and pathogens (D2) (see  Figure 2.2).

**D1: Hazardous solids → Nutrients**

*Definition:* Hazardous solids affect nutrients by physically restraining the transmission of light in the river, less light affects the food web that is nutrient driven, thus the levels of nutrients might be affected.

*Description:* This interaction is indirect and consists of several steps. Firstly, hazardous solids in rivers, being solid particles, limit the influx of light into rivers and the function of organisms in these rivers (Besseling et al., 2014). Secondly, less light may affect the abundance of, for example, algae and bacteria in these rivers. Thirdly, the changes in species abundance and thus food web structure presumably affect the rates at which nutrients are consumed, and thus the nutrient availability in the rivers. Light can be paramount in determining community structure (i.e. which organisms are present) of some algae and phytoplankton, reportedly having a greater influence than nutrients for some species (Lange et al., 2011; Whalen & Benson, 2007). If light transmission is significantly blocked, and there is less light in the river as a consequence, this may thus impact the community structure in rivers and reservoirs. Species composition may thus be affected by the presence of hazardous solids that block light. The extent of nutrient consumption is species-dependent. As species consume nutrients, an altered community structure could potentially affect nutrient ratios and availability.

*Example:* Adsorption of plastic particles onto algae, for example, could reduce photosynthesis by algae (Bhattacharya et al., 2010). Bhattacharya et al. (2010) suggest that the reduction in photosynthesis by algae could be attributed to the physically limited access of the algae to light due to the presence of the plastic nanoparticles. Light thus plays a major role in this interaction. Also a reduced air flow to the algae could lead to a lower photosynthesis due to the presence of the small plastic particles (Bhattacharya et al., 2010). Wright et al. (2013), however, remark that Bhattacharya et al. (2010) use very high concentrations of plastic particles (polystyrene beads with a size of 20 nm): 1.6-40mg/mL. The results of Bhattacharya et al. (2010) nevertheless indicate that plastics could attach to algae and consequently perhaps limit photosynthesis (Wright et al., 2013). Effects of non-contact shading on photosynthesis may be negligible in comparison to the effects of adsorption and aggregation (Zhang et al., 2017).

**D2: Hazardous solids → Pathogens**

*Definition:* Hazardous solids affect pathogens by physically restraining the transmission of (UV) light in the river. Limited transmission of light may decrease (UV) light-dependent decay of pathogens in rivers.

*Description:* Hazardous solids may block the transmission of solar radiation pathogens and as a result promote the persistence of these pathogens. Synthetic nanoparticles behave as natural colloids, affected by, for example, pH, particle size and surface charge[6] (Kaegi et al., 2008).

*Example:* The protozoa *Cryptosporidium* is, for example, known to decrease in infectivity by exposure to solar radiation, particularly to UV (Connelly et al., 2007; Vermeulen et al., 2019). Water transparency is, thus, probably an important factor in the inactivation of *Cryptosporidium* (Connelly et al., 2007). The

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[6] The differences in charge of the surface of a colloid and its surroundings

presence of (hazardous) solids in water presumably decreases the water's transparency and thus the transmission of solar radiation to pathogens such as *Cryptosporidium*. As a consequence, inactivation rates of these pathogens due to solar radiation may be reduced.

## 2.4.6 Interaction type E: Carbon cycle-dependent interaction

Nutrients may affect chemicals through a carbon cycle-dependent interaction (E1, Figure 2.2).

**E1: Nutrients → Chemicals**

*Definition:* Nutrients affect chemicals by affecting the carbon cycle through biomass production; biomass production may dilute chemicals (in more biomass), stimulate sedimentation of chemicals and the ingestion of chemicals.

*Description:* More eutrophic rivers/lakes will have more biomass. Increases in biomass effectively 'dilute' the chemicals within the biomass (biomass dilution) and may also increase the uptake of the chemicals into the food web (Larsson et al., 2000). In the food web, biomagnification[7] of the chemicals can occur. Food web length is shorter in more eutrophic systems. Particularly with increasing food web length, the extent to which the chemicals concentrate in organisms at higher trophic levels (higher in the food chain) would be increased (Larsson et al., 2000). Sedimentation is also affected by eutrophication. Relatively higher sedimentation rates for organic matter and lipids are found in eutrophic environments. Chemicals, however, may be sedimented with a lower rate than in more oligotrophic environments, since their concentrations in the matter that sediments are relatively low (Larsson et al., 2000). Contrastingly, Shi et al. (2017) detect higher concentrations of HCHs, DDTs and PAHs in surface sediments of water bodies with phytoplankton blooms than in waters without these blooms. This could perhaps be attributed to the existence of an optimum of nutrient levels for sedimentation of chemicals, or other factors, such as how hydrophobic the chemicals are. According to an experimental modelling study by Roessink et al. (2010), especially mobile hydrophobic organic chemicals (less aged/hydrophobic) are affected by alterations in the state that an ecosystem is in (e.g. a suspended solid – phytoplankton dominated state). Overall, the presence of more nutrients could imply that concentrations of chemicals in water bodies is decreased through biomass dilution especially in eutrophic systems. Sedimentation rates of chemicals could be affected as a consequence. At the same time, more nutrients in the river system could indirectly contribute to higher concentrations of chemicals in organisms. Next to nutrients, the presence of (planktonic) biomass is mainly affected by temperature. Temperature may be more a more dominant factor in biomass development than nutrients (Tao et al., 2017). Biomass dilution of chemicals may, therefore, be induced by temperature (Tao et al., 2017).

*Example:* Biomass dilution in phytoplankton has, for example, been noted for DDTs, PAHs and some HCHs and is relatively stronger for more hydrophobic chemicals (Shi et al., 2017). Another study has found a biomass dilution effect for endocrine disruptive compounds, as a result of high cyanobacteria biomass in periods with algal blooms in lake Taihu, China (Jia, 2018).

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[7] Concentrations increase with higher food chain levels (trophic levels)

### 2.4.7 Interaction type F: Toxic stress-dependent interaction

A pollutant may be toxic to organisms when exceeding a certain level. This interaction (F) may occur between chemicals and nutrients (F1), chemicals and pathogens (F2), and toxins and pathogens (F3, Figure 2.2).

**F1: Chemicals → Nutrients**

*Definition:* Chemicals affect nutrients when their levels exceed the tolerance levels of organisms and thus causes toxic stress in these organisms. These organisms may consequently die. As organisms consume nutrients, their death may affect the nutrient levels in the river.

*Description:* Chemicals can potentially alter the food web, through toxic stress and subsequent selection for surviving this stressor, and through that nutrient supplies. Pollution may impact freshwater communities through, for example, species elimination, changes in competition and food web structure and adaptation (Medina et al., 2007). Depending on the levels of chemicals present and the possible consequential biomass mortality, many organisms may die. Events leading to high mortality could potentially induce resource pulses, with a temporary rarely high increased availability of nutrients and energy (Sousa et al., 2012; Yang, 2004). Organisms could also be affected through bioaccumulation and -magnification of chemicals (Tao et al., 2017). Both bioaccumulation and -magnification may also be temperature-dependent (Tao et al., 2017). On the long term, the altered community structure and interactions could affect nutrient availability, through e.g. excretion, defecation and transport (Kitchell et al., 1979; Vanni, 1996).

*Examples:* Benthic organisms may release nutrients from sediments through bioturbation (Kitchell et al., 1979). These organisms might be eliminated or become more abundant as a result of the elimination of a competitor due to toxic stress by chemicals. In that case, the increased or decreased prevalence of these benthic organisms would have consequences for nutrient availability in lakes. Another example is the decrease in denitrification probably due to the detrimental effects that some antibiotics have on denitrifying bacteria (Costanzo et al., 2005). At higher temperatures, the biomagnification of PAHs from phytoplankton to other organisms increases (Tao et al., 2017). This increase in biomagnification of PAHs to other organisms suggests that chemicals and temperature together may lead to eventual damage/mortality to organisms at higher trophic levels.

**F2: Chemicals → Pathogens**

*Definition:* Chemicals affect pathogens when their levels exceed the tolerance levels of pathogens and thus cause toxic stress in pathogens, resulting in pathogen decay.

*Description:* Relatively high levels of chemicals can exceed the tolerance levels of some pathogens for these chemicals. When that happens, this causes toxic stress in these pathogens. The toxic stress could lead to the decay of pathogens. (Bacterial) pathogens may be killed by chemicals due to toxic stress. Viral pathogens may be inactivated due to the application of antiviral chemicals (Sobsey & Meschke, 2008). Thus, this is a direct effect that the presence of high levels of chemicals can have on the abundance of (some) pathogens. Light and the pH affect this interaction. Some antiviral chemicals are especially effective at a certain pH (Sobsey & Meschke, 2008). The interaction might also be affected by the presence of toxins: even though these might not be antibacterial, the indicator species *Escherichia coli* is more likely to be affected by hydrophobic chemicals (antibiotics) with a high molecular mass when cyanotoxins (in this case microcystin) are present (Dixon et al., 2004). This indicates that the co-occurrence of the chemicals and cyanotoxins may especially be harmful to bacteria (Dixon et al., 2004). These bacteria might be pathogenic.

*Example:* The use of TCS as an antimicrobial agent indicates that at least some of the chemicals included in the pollutant group are toxic to microbiota. Anionic and cationic detergents have been reported to decrease survival of bacteria (in combination with toxins) and viruses (Dixon et al., 2004; Sobsey & Meschke, 2008).

### F3: Toxins → Pathogens

*Definition:* Toxins affect pathogens when their levels exceed the tolerance levels of pathogens and thus cause toxic stress in pathogens, resulting in pathogen decay.

*Description:* Pathogens may be exposed to toxic stress due to cyanobacteria and -toxins through direct or indirect ingestion. As a consequence, some pathogens (e.g. pathogenic bacteria) might die. The extent to which cyanotoxins are harmful for pathogens may depend on the type of toxin and pathogens: Microcystin does not seem to affect indicator species *Escherichia coli* to a large extent (Dixon et al., 2004).

*Example:* This interaction has, for example, been shown for *A. castellanii*, a pathogenic protozoa, possibly through ingestion of toxic cells (Urrutia-Cordero et al., 2013). Though *A. castellanii* is not a fecal-oral pathogen, the effects of cyanotoxins on the species may be indicative of their effects on fecal-oral protozoa.

## 2.4.8 Interaction type G: Supply-dependent interaction

This interaction may occur between nutrients and pathogens (G1, Figure 2.2).

### G1: Nutrients → Pathogens

*Definition:* Nutrients affect pathogens, as the supply of nutrients contributes to the persistence of some pathogens. Persistence is the prolonging of fecal-oral bacteria/viruses/protozoa, which remain pathogenic, in the river. Nutrients are consumed by pathogenic bacteria and, therefore, essential for their survival. This interaction indicates that the supply of nutrients can sustain and/or promote the existence of these pathogens in the river directly through consumption.

*Description:* For pathogen persistence, the supply of nutrients in rivers is vital (Malham et al., 2014). Direct effects on the growth and survival of pathogens are most probable for bacteria, but unlikely to be found for protozoa and viruses. Pathogen persistence is also affected by light (with more light decreasing persistence), pH (having different effects on different species), temperature, water potential and salinity (Ferguson et al., 2003; Vermeulen et al., 2019).

*Example:* Addition of nutrients to water may result in nonlinear population increases of the bacteria *Escherichia coli*, an indicator species for potential pathogen contamination (Shelton et al., 2014). This demonstrates the need for linking models of riverine nutrients to models of riverine fate of such indicator species (Cho et al., 2016). The response of *Escherichia coli* to the addition of nutrients suggests that pathogenic bacteria populations could likewise grow as a consequence of nutrient inputs. The growth of the pathogen *Flavobacterium columnare* outside of hosts is supported by high nutrient levels, which are also reported to increase the ability of the bacterium to cause disease in rainbow trout and zebra fish (Kinnula et al., 2017).

## 2.4.9 Interaction type H: Organic matter-dependent interaction

Nutrients and pathogens may interact through an organic matter-dependent interaction (H1, Figure 2.2).

### H1: Nutrients → Pathogens

*Definition:* Nutrients affect pathogens by regulating the amount of organic matter and consequently the conditions that are favourable (e.g. certain levels of oxygen) for pathogens to be in rivers.

*Description:* Rich levels of nutrients in rivers contribute to the formation of biomass and thus organic matter. Microbes, such as pathogens, thrive when there is relatively a lot of organic matter (Brookes et al., 2004). Bacteria can use the organic compounds as substrate in order to grow (Marsollier et al., 2004; Unnithan et al., 2014). Viruses are supported by, for example, the formation of biofilms and flocculation. As discussed for interaction A1 (see Section 2.4.2), the formation of biofilms may be promoted by nutrient levels (Malham et al., 2014). Eutrophication, due to high nutrient levels, may through its consequences for the loads of organic matter in the water lead to hypoxia (oxygen deficiency) (see the example below). Oxygen deficiencies alter sediment chemistry, for example by limiting nitrification, but increasing denitrification (N losses to air). Oxygen deficient conditions might be a favourable conditions for pathogens to stay longer in river sediments (Unnithan et al., 2014). This might explain why pathogens may persist longer in sediments than in rivers (Garzio-Hadzick et al., 2010).

*Example:* High nutrient levels may lead to eutrophication. Algal blooms may occur as a consequence. These algal blooms generate high loads of organic matter. Due to high organic matter loads, oxygen levels may be severely decreased (Paerl et al., 1998). Therefore, eutrophication may induce oxygen deficiency. Anaerobic conditions (less oxygen) may be favourable to pathogen persistence (Unnithan et al., 2014). Organic matter may also limit the radiation of UV into rivers (Morris et al., 1995; Zepp et al., 2007). Reduced exposure to UV radiation increases pathogen persistence (King et al., 2008; Vermeulen et al., 2019).

## 2.4.10 Interaction type I: Cyanobacteria-dependent interaction

This interaction may occur between nutrients and toxins (I1, Figure 2.2).

### I1: Nutrients → Toxins

*Definition:* Nutrients affect release of toxins. An example is that nutrients sustain or promote cyanobacterial growth. The cyanobacteria, in turn, release toxins.

*Description:* Nutrients promote the growth of cyanobacteria, some of which can secrete toxins (Pelaez et al., 2010). These toxins are commonly called cyanotoxins (Cyano-HABs). In favourable, warm and eutrophic conditions, cyanobacteria can grow densely and form algal blooms (Pelaez et al., 2010). Such blooms have been documented globally (Breitburg et al., 2018; Pelaez et al., 2010). Increases of nutrients in surface waters tend to stimulate the relative abundance of cyanobacteria in phytoplankton communities (Davis et al., 2009). Especially higher P levels are associated with this effect. For toxic cyanobacteria blooms to take place, however, increases in N levels can also be important (Davis et al., 2009). This is confirmed by Dolman et al. (2012), who find that particularly when the ratio of N to P is high, lakes are subjected to more cyanobacteria. Being affected by for example nutrients, temperature and light, particularly the content of toxins in cyanobacteria cells control the concentrations of cyanotoxins in water (Dolman et al., 2012).

*Example:* Elevations in P concentrations could, particularly in combination with higher temperatures, stimulate the growth of *Microcystis* cells, which are toxic (Davis et al., 2009). P and N concentrations both increase the biomass of each *Microcystis* cyanobacteria species (Vaitomaa, 2006). In addition, relatively more toxin-producing *Microcystis* than cyanobacteria that do not produce microcystins are present at high nutrient levels (Vaitomaa, 2006; Vézie et al. 2002).

### 2.4.11 Interaction type J: Leaching-dependent interaction

Hazardous solids may in rivers function as a secondary source of chemicals through a leaching-dependent interaction (J1, Figure 2.2).

**J1: Hazardous solids → Chemicals**

*Definition:* Hazardous solids (e.g. microplastics) affect release of chemicals into rivers by releasing secondary chemicals through leaching. For example, microplastics may release additives into rivers.

*Description:* Solids such as plastics may be a direct source of chemicals. This may not be a typical interaction. Nevertheless, the abundance of one pollutant group may affect the abundance of another. Therefore, the release of secondary chemicals into the river is included in the review. These chemicals are part of for example plastics as additives, monomers and oligomers and may leach from plastics (Kwan & Takada, 2019; Teuten et al., 2009). The pH is seen as an important factor in releasing the chemicals from plastics in landfills. Lower pH of the surrounding waste leachates is associated with decreased release of chemicals (Teuten et al., 2009). This indicates that the pH may play a role in the release of additives from plastics in rivers too.

*Example:* Organic plastic additives can leach from plastic, as experiments with simulated marine environments have demonstrated (Suhrhoff & Scholz-Böttcher, 2016). In comparison to freshwaters, marine waters are relatively distant from the sources of microplastics. Therefore, microplastics in freshwaters are thought to have higher levels of additives than microplastics in marine waters (Scherer et al., 2018). Yet, relatively little research has been performed into the effects of plastics in the freshwater environment (Thompson et al., 2009).

### 2.4.12 Interaction type K: Biomass dilution-dependent interaction

This interaction may occur between pathogens and toxins (K1, Figure 2.2).

**K1: Pathogens → Toxins**

*Definition:* Pathogens affect toxins by being a part of the biomass and as such diluting toxins in biomass.

*Description:* Microorganisms such as bacteria constitute a part of the carbon pool, and effectively contribute biomass to the ecosystem. Hence, when there are more fecal-oral bacteria present, biomass dilution of toxins is expected to occur. Nutrients can promote biomass growth. More biomass in the rivers implies that there is more organic matter in the river. Therefore, the concentration of toxins per a certain amount of biomass is lower.

*Example:* Biodilution of microcystins has been found to dominate over biomagnification for most aquatic consumers (Kozlowsky-Suzuki et al., 2012).

*Table 2.1. Potential interactions between the groups of the pollutants in rivers that are involved in this study, the definition (with an example) and a short description of these potential interactions between groups of pollutants in rivers. The code refers to the code used for the interaction in Figure 2.2. Arrows indicate the direction of the interaction: from affecting to affected pollutant/substance/factor/organism). Double arrows indicate mutual effects. In this table, the retention of both pollutant groups is affected similarly as a consequence of the interaction.. The text above the arrow in the description indicates how the pollutants/substances/factors/organisms interact with each other: "+" indicates an increased presence in the river, "-"indicates a decreased presence in the river, "0" indicates that there is no effect, "?" indicates that the effect is unknown. In the description, one arrow between the two groups of pollutants indicates that the interaction between those groups is direct. A minimum of two arrows in between the two groups of pollutants indicates that the interaction between those groups is indirect. Source: synthesis of literature and expert knowledge (Section 2.2 and Section 2.4) and expert consultations.*

| **Type of interaction from Figure 2.2.** | **Groups of pollutants from Figure 2.2.** | **Sub-type of interaction from Figure 2.2.** | **Definition** | **Short description** |
|---|---|---|---|---|
| **A. Biofouling-dependent interaction** | 1. Nutrients → Hazardous solids | A1 | Nutrients affect hazardous solids by promoting growth of organisms on the surface of the hazardous solids, because these organisms can attach to the surface area of these hazardous solids through a process called biofouling. Biofouling is the formation of biofilm (by microorganisms) on surfaces in water. For example, plastics can be covered by biofilm. | Nutrients $\xrightarrow{growth\ (+)}$ Microorganisms $\xrightarrow{fouling\ (?)}$ Hazardous solids |
| **B. Sorption-dependent interaction** | 1. Nutrients ↔ Hazardous solids | B1 | Nutrients and hazardous solids affect each other through sorption (/desorption), where nutrients and hazardous solids attach to each other (/are detached from each other). For example, vitamin B12 may be adsorbed to microplastics. | Hazardous solids $\xleftrightarrow{sorption\ (-)}$ Nutrients |
|  | 2. Chemicals ↔ Hazardous solids | B2 | Chemicals and hazardous solids affect each other through sorption (/desorption), where chemicals and hazardous solids attach to each other | Hazardous solids $\xleftrightarrow{sorption\ (-)}$ Chemicals |

|  |  |  |  |  |
|---|---|---|---|---|
|  |  |  | (/are detached from each other). For example, PCBs may attach to microplastics. |  |
|  | 3. Pathogens ↔ Hazardous solids | B3 | Pathogens and hazardous solids affect each other through sorption (/desorption), where pathogens and hazardous solids attach to each other (/are detached from each other). For example, *Vibro* spp. may attach to microplastics. | $\text{Pathogens} \xleftrightarrow{sorption\ (-)} \text{Hazardous solids}$ |
|  | 4. Chemicals ↔ Pathogens | B4 | Chemicals and pathogens affect each other through sorption (/desorption), where chemicals and pathogens attach to each other (/are detached from each other). | $\text{Chemicals} \xleftrightarrow{sorption\ (-)} \text{Pathogens}$ |
| **C. Food web-dependent interaction** | 1. Nutrients → Hazardous solids | C1 | Nutrients affect hazardous solids by regulating river community structure and, therefore, affecting the rate at which hazardous solids are ingested by organisms. | $\text{Nutrients} \xrightarrow{growth\ (+)} \text{Organisms} \xrightarrow{ingestion\ (-)} \text{Hazardous solids}$ |
| **D. Light-dependent interaction** | 1. Hazardous solids → Nutrients | D1 | Hazardous solids affect nutrients by physically restraining the transmission of light in the river, less light affects the food web that is nutrient driven, thus the levels of nutrients might be affected. Plastics sorption to algae may reduce light availability to and thus photosynthesis by these algae. This might affect consumption of nutrients, for example by algae. | $\text{Hazardous solids} \xrightarrow{transmission\ (-)} \text{Light} \xrightarrow{growth\ (+\ or\ -\ or\ 0)} \text{Algae, bacteria, etc.} \xrightarrow{consumption\ (-)} \text{Nutrients}$ |
|  | 2. Hazardous solids → Pathogens | D2 | Hazardous solids affect pathogens by physically restraining the transmission of (UV) light in the river. Limited transmission of light | $\text{Hazardous solids} \xrightarrow{transmission\ (-)} \text{Light} \xrightarrow{persistence\ (-)} \text{Pathogens}$ |

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|---|---|---|---|---|
| | | | may decrease (UV) light-dependent decay of pathogens in rivers. | |
| **E. Carbon cycle-dependent interaction** | 1. Nutrients → Chemicals | E1 | Nutrients affect chemicals by affecting the carbon cycle through biomass production; biomass production may dilute chemicals (in more biomass), as reported for, for example, DDTs in phytoplankton biomass, stimulate sedimentation of chemicals and the ingestion of chemicals. | $\text{Nutrients} \xrightarrow{growth\ (+)} \text{Biomass} \xrightarrow{dilution\ (-)} \text{Chemicals}$<br>$\xrightarrow{food\ uptake\ (-)} \text{Chemicals}$<br>$\xrightarrow{sedimentation\ (-)} \text{Chemicals}$ |
| **F. Toxic stress-dependent interaction** | 1. Chemicals → Nutrients | F1 | Chemicals affect nutrients when their levels exceed the tolerance levels of organisms and thus causes toxic stress in these organisms. These organisms may consequently die. As organisms consume or otherwise affect nutrients (for example, benthic organisms may release nutrients from sediments), their death may affect the nutrient levels in the river. | $\text{Chemicals} \xrightarrow{toxic\ stress\ (-)} \text{Organisms} \xrightarrow{consumption\ \text{etc.}\ (?)} \text{Nutrients}$ |
| | 2. Chemicals → Pathogens | F2 | Chemicals affect pathogens when their levels exceed the tolerance levels of pathogens and thus cause toxic stress in pathogens, resulting in pathogen decay. For example, triclosan (TCS) is used as antimicrobial. | $\text{Chemicals} \xrightarrow{toxic\ stress\ (-)} \text{Pathogens}$ |
| | 3. Toxins → Pathogens | F3 | Toxins affect pathogens when their levels exceed the tolerance levels of pathogens and thus cause toxic stress in pathogens (for example, protozoa), resulting in pathogen decay. | $\text{Toxins} \xrightarrow{toxic\ stress\ (-)} \text{Pathogens}$ |

| | | | | |
|---|---|---|---|---|
| **G. Supply-dependent interaction** | 1. Nutrients → Pathogens | G1 | Nutrients affect pathogens, as the supply of nutrients contributes to the persistence of some pathogens Nutrients are consumed by pathogenic bacteria and, therefore, essential for their survival. Abundance of indicator species *E. coli*, for example, is affected by nutrient levels. | $\text{Nutrients} \xrightarrow{\text{supply } (+)} \text{Pathogens}$ |
| **H. Organic matter-dependent interaction** | 1. Nutrients → Pathogens | H1 | Nutrients affect pathogens by regulating the amount of organic matter and consequently the conditions that are favourable (for example, levels of oxygen) for pathogens to be in rivers. Anaerobic conditions would for example be favourable to pathogen persistence in rivers. | $\text{Nutrients} \xrightarrow{\text{growth } (+)} \text{Organic matter} \xrightarrow{affect\ (?)} \text{Pathogens}$ |
| **I. Cyanobacteria-dependent interaction** | 1. Nutrients → Toxins | I1 | Nutrients affect release of toxins. An example is that nutrients sustain or promote cyanobacterial growth. The cyanobacteria, in turn, release toxins. | $\text{Nutrients} \xrightarrow{growth\ (+)} \text{Cyanobacteria} \xrightarrow{excrete\ (+)} \text{Toxins}$ |
| **J. Leaching-dependent interaction** | 1. Hazardous solids → Chemicals | J1 | Hazardous solids (for example microplastics) affect release of chemicals into rivers by releasing secondary chemicals through leaching. For example, microplastics may release additives into rivers. | $\text{Hazardous solids} \xrightarrow{\text{leaching } (+)} \text{Chemicals}$ |
| **K. Biomass dilution-dependent interaction** | 1. Pathogens → Toxins | K1 | Pathogens affect toxins by being a part of the biomass and as such diluting toxins in biomass. | $\text{Pathogens} \xrightarrow{increase\ (+)} \text{Biomass} \xrightarrow{dilution\ (-)} \text{Toxins}$ |

## 2.5 Potential interactions of pollutants under certain conditions

The 11 types of potential interactions identified in Section 2.4 do not stand alone (see Appendix A.2, Figure A.2.1). The interactions may be affected by the environmental conditions of the rivers and reservoirs that they occur in. Such water systems can be characterised in different ways, depending on different factors. One of the classifications depends on nutrient levels. Here, water systems are generally classified as eutrophic or oligotrophic (‘clear’). Eutrophic rivers and reservoirs contain relatively high nutrient levels, whereas oligotrophic water bodies have relatively low nutrient levels. Enrichment of water bodies with nutrients could lead to eutrophication. Eutrophication may prompt various other water quality problems, such as oxygen deficiency and the presence of toxins (Kroeze et al., 2013). As such, the state of the water system as eutrophic or oligotrophic may affect (e.g. the prevalence of) the potential interactions discussed in Section 2.4 (see Table 2.2). This is discussed in the next paragraphs.

Interactions in which nutrients are the affecting pollutants might be more dominant in eutrophic water (Table 2.2). This is because eutrophic systems have high nutrient levels in comparison to oligotrophic systems. Examples of such interactions are cyanobacteria-dependent (I1), supply-dependent (G1) and organic matter-dependent (H1) (see Figure 2.2, Table 2.1). In contrast, interactions that are directed towards nutrients (as affected pollutant) might be assumed to be more important in oligotrophic systems. This is because the abundance of nutrients is lower in oligotrophic systems and any changes in the nutrient levels might thus have a larger impact. For example, cyanobacteria are relatively more abundant in eutrophic systems (Davis et al., 2009). This makes the excretion of cyanotoxins by these bacteria (interaction I1) likely to be a more dominant interaction in eutrophic systems than in systems that are comparably ‘clear’. Another example: the organic matter-dependent interaction (H1) seems more likely to occur in eutrophic conditions (Paerl et al., 1998; Urrutia-Cordero et al., 2013).

However, other interactions where nutrients are less dominant as affecting pollutant could also be affected by the state of a water body (eutrophic or oligotrophic) (Table 2.2). Regime shifts, potentially triggered by eutrophication, have for example been shown to be of importance to the distribution and bioaccumulation of hydrophobic organic chemicals (e.g. PAHs) in sediments, suspended solids and various organisms (Roessink et al., 2010). Relatively mobile chemicals are particularly likely to be affected by changes in levels of e.g. suspended solids and phytoplankton (Roessink et al., 2010). As regime shifts due to eutrophication might thus impact distribution and bioaccumulation of the chemicals. Therefore, interactions B2 and B4, both sorption-dependent may likely be affected. Such regime shifts might also have implications for the organisms that they are toxic to. Consequently, toxic-stress dependent interactions F1 and F2 may be affected. The abundance of pathogens is assumed to be higher in eutrophic systems. The higher abundance of pathogens would thus make interactions from pathogens to other pollutants more important in eutrophic systems. In clear systems, however, the interactions towards pathogens may be more important (excluding F3, G1 and G3, see Table 2.1 or Figure 2.2). Thus, some interactions might be dominant in eutrophic river systems and others in clear river systems (Table 2.2).

Next to the eutrophic and oligotrophic state of a water body, water flow may play a role in (some of) the identified interactions. Levels of cyanobacteria have, for example, been documented to be higher in reservoirs and lakes (low flow) in comparison to rivers (high flow) (Makarewicz et al., 2009). This would make interaction I1 more likely to take place in reservoirs and lakes. Reservoirs and lakes might be more susceptible to toxins due to this cyanobacteria-dependent interaction (I1). Interactions such as sorption-dependent interactions (B1-B4) may also be more dominant in reservoirs and lakes. The relatively low flow of water in reservoirs and lakes. In rivers, the water flow is higher, presumably resulting in less time for the sorption-dependent interaction to take place.

*Table 2.2. Indication in which water system potential interactions between groups of pollutants may especially be important (in eutrophic or clear waters). See Section 2.4, Figure 2.2 and Table 2.1. Source: Section 2.5.*

| Eutrophic and oligotrophic water systems | Interaction |
|---|---|
| Eutrophic | Biofouling-dependent interaction A1;<br>Sorption-dependent interactions B1, B2, B3, B4;<br>Food web-dependent interaction C1;<br>Carbon cycle-dependent interaction E1;<br>Toxic stress-dependent interaction F3;<br>Supply-dependent interaction G1;<br>Organic matter-dependent interaction H1;<br>Leaching-dependent interaction J1;<br>Biomass dilution-dependent interaction K1. |
| Oligotrophic | Light-dependent interaction D1, D2;<br>Sorption-dependent interaction B1, B2, B3, B4;<br>Toxic stress-dependent interaction F1, F2;<br>Leaching-dependent interaction J1. |

## 2.6 Conclusions

The aim of this chapter is to formulate an answer to Research Question 1: **What interactions exist between groups of pollutants in rivers?** To answer this research question, a literature review was conducted, with guidance of experts in the field. Five different groups of pollutants were distinguished: nutrients (e.g. nitrogen (N), phosphorous (P)), hazardous solids (e.g. microplastics), chemicals (e.g. triclosan (TCS)), pathogens (e.g. *Cryptosporidium*) and toxins (e.g. microcystins). In particular, attention was paid to potential interactions that could be relevant to improve global water quality models. The main findings are summarised below.

Multiple pollutants in rivers often come from common sources and generate various impacts on nature and society. There are point and diffuse sources of pollutants in rivers. Sewage systems are examples of point sources. Sewage systems discharge pharmaceuticals, plastics and pathogens. Diffuse sources can also release various pollutants. For example, agricultural runoff can pollute rivers with nutrients, plastics and pathogens. Some sources are, however, pollutant- and/or region-specific. Examples are direct manure discharges in China and open defecation in developing countries. These are point sources and add nutrients and pathogens to rivers. Impacts of multiple pollutants on nature are, for example, eutrophication caused by nutrients and a decline in coral reef health caused by pathogens, nutrients and other pollutants. Society could be impacted by, for example, diarrhoea as a consequence of pathogens, the "Blue Baby Syndrome" caused by high N concentrations and decreases in mental health caused by heavy metal pollution. As combinations of multiple pollutants can thus have a range of harmful consequences for nature and society, the linkages between pollutants need to be considered.

Among the five groups of pollutants, 11 types of potential interactions in rivers are identified. Interactions are defined as: *"A particular way in which a (group of) pollutant(s) affects another."* Some of these interactions are direct and others are indirect. A few of the interactions are relevant for more than two groups of pollutants. The interactions are classified into types A-K. Interaction type A is biofouling-dependent and occurs between nutrients and hazardous solids (A1). Interaction type B is sorption-dependent and is identified between nutrients and hazardous solids (B1), hazardous solids and chemicals (B2), hazardous solids and pathogens (B3), and chemicals and pathogens (B4). Interaction type C is food web-dependent and occurs between nutrients and hazardous solids (C1). Interaction type D is light-dependent and occurs between nutrients and hazardous solids (D1) and hazardous solids and pathogens (D2). Interaction type E is carbon cycle-dependent, with an interaction between nutrients and chemicals (E1). Interaction type F is toxic stress-dependent and is identified between nutrients and chemicals (F1), chemicals and pathogens (F2), and pathogens and toxins (F3). Interaction type G is supply-dependent, with an interaction between nutrients and pathogens (G1). Interaction type H is organic matter-dependent and is identified between nutrients and pathogens (H1). Interaction type I is cyanobacteria-dependent and occurs between nutrients and toxins. Interaction J is leaching-dependent and identified between hazardous solids and chemicals (J1). Interaction type K is biomass dilution-dependent and occurs between pathogens and toxins (K1). Each of these interactions is explained in Chapter 2. More interactions may exist. Nevertheless, this chapter gives a first overview of potential interactions between pollutant groups in rivers.

Some interactions may be more dominant in eutrophic and others in oligotrophic systems. For example, as more nutrients are present in eutrophic systems, more cyanobacteria can thrive there. In turn, then, more toxins would be emitted by these cyanobacteria. Thus, cyanobacteria-dependent interaction I1 seems more likely to occur in eutrophic systems. On the other hand, interactions such as light-dependent interaction D1 may have larger consequences on nutrient availability when the nutrient concentrations are low, thus in oligotrophic conditions. Some interactions are more dominant in standing waters (reservoirs, lakes) and others in flowing waters (rivers). Examples are sorption-dependent interactions (B1, B2, B3 and B4) and the leaching-dependent interaction (J1) that seem more likely to take place in water bodies with a low water flow (reservoirs, lakes) rather than in rivers. Thus, the dominance of certain potential interactions may depend on the state of a water body (e.g. eutrophic) and water flow of that water body (e.g. low flow typical for reservoirs). In addition, temperature, salinity, pH, oxygen and UV/light are also factors that likely affect the potential interactions and should, therefore, be considered in further studies.

The new insights into the interactions between groups of pollutants in rivers could be relevant to include in and improve global water quality models. A pollutant group in a river does not occur in isolation. Rather, groups of pollutants in rivers are affected by a range of biological, physical and chemical processes and environmental factors that link and affect the pollutants and their potential impacts on nature and society. Interactions between the groups of pollutants in rivers, therefore, need to be considered for a better understanding of their impacts on nature and society. This will aid to improve water quality assessments. Accounting for interaction effects is also relevant for analyses of future river pollution.

# Chapter 3: Global multi-pollutant modelling

## 3.1 Introduction

The aim of Chapter 3 is to provide an answer to Research Question 2:

*How can existing water quality models be integrated into a global model for river export of multiple pollutants?*

Chapter 3 builds on the global multi-pollutant model by Strokal et al. (2019). The global multi-pollutant model by Strokal et al. (2019) quantifies point source inputs of nitrogen (N), phosphorous (P) (nutrients), microplastics (hazardous solid), triclosan (TCS) (chemical) and *Cryptosporidium* (pathogen). In Chapter 3, it is explained how this model could be used as a starting point for further integration of existing water quality models. A further integration of these models could expand the global multi-pollutant model in such a way that it does not only model inputs from point sources into sub-basins as in Strokal et al. (2019), but also quantifies the retention and export of each of the pollutants included at the sub-basin outlet and the river outlet. This allows, for example, for analysis of multi-pollutant hotspots at river mouths. Due to the sub-basin approach, the model could also aid in tracking the pollution sources.

The methods used in Chapter 3 to address Research Question 2 are explained in Section 3.2. Subsequently, Section 3.3 discusses three existing multi-pollutant modelling approaches. Section 3.4 addresses and elaborates upon one of these approaches, the global model for point source inputs of multiple pollutants by Strokal et al. (2019). Section 3.5 gives illustrative examples of possible outputs generated by this approach, with a focus on the parameters for retention. The conclusions of Chapter 3 are drawn in Section 3.6.

## 3.2 Methodology

Chapter 3 is primarily based on literature review, used for a model analysis. The literature review consists of two components. The first component is a general review of existing multi-pollutant models. The selection of multi-pollutants models to include in this review was based on existing reviews of water quality models (Kroeze et al., 2016; Strokal et al., 2019; Tang et al., 2019). The multi-pollutant model by Strokal et al. (2019) was compared to models with respectively a continental and a river basin spatial extent: WorldQual and SWAT. The second component of the literature review consists of a more detailed analysis of the multi-pollutant model by Strokal et al. (2019), the framework that Strokal et al. (2019) provide for expanding the model and the different water quality models that the multi-pollutant model is based on. Special attention was paid to the parameters that describe pollutant retention. These parameters may offer opportunities to include effects of interactions discussed in Chapter 2 and thus be useful for Chapter 4.

The illustrative examples in this chapter are constructed using Model Builder in ArcMap of ArcGIS (Esri Inc., 2017), with data from HydroLAKES (Messager et al., 2016) for reservoirs and lakes and the global multi-pollutant model by Strokal et al. (2019) for sub-basin polygons.

## 3.3 Existing multi-pollutant modelling approaches

### 3.3.1 Model description

Many different water quality models exist (Strokal et al., 2019). However, few global models focus on more than one type of pollution. None of these models include interactions between groups of pollutants in rivers. Water quality models were selected for assessment based on several water quality model reviews (Kroeze et al., 2016; Strokal et al., 2019; Tang et al., 2019). The models are assessed on, for example, model purpose, modelled pollutants, spatial and temporal resolutions and extents, and modelling approaches.

In this study, three multi-pollutant models are selected for further analysis. These models are the global multi-pollutant model of Strokal et al. (2019), WorldQual (UNEP, 2016) and SWAT (Arnold et al., 1998) (Table 3.1). The multi-pollutant model of Strokal et al. (2019) and WorldQual are selected as these are global and continental water quality models, respectively. They focus on more than one pollutant. SWAT (Arnold et al., 1998) is included because of its worldwide application on river basin or watershed level and its process-based approach (Gassman et al., 2014).

The global multi-pollutant model by Strokal et al. (2019) is designed for water quality analysis for multiple pollutants simultaneously (Table 3.1). The models aims to identify point-source pollution hotspots, where multiple pollutants have high levels, and potentially, suitable management options. So far, the model includes TCS, microplastics, nutrients and *Cryptosporidium* for the year 2010. The global multi-pollutant model quantifies inputs of these pollutants from point sources (sewage and open defecations) into sub-basins of rivers based on existing modelling approaches for individual pollutants (as explained in Section 3.4). The model is an empirical, steady-state model at the sub-basin scale. The model runs on an annual basis. The global multi-pollutant model is further explained in Section 3.4.

The continental WorldQual model quantifies multiple pollutants in river streams (Voß et al., 2012). However, this is not performed simultaneously, in contrast to the model of Strokal et al. (2019). WorldQual aims to assess climate change effects on water quality and to incorporate management scenarios for water quality (Table 3.1). Input data include hydrological variables such as river discharge and flow velocity. These hydrological values are provided by the hydrological model WaterGAP (Water – Global Assessment and Prognosis). WaterGAP takes into account both hydrology and water use. In addition, WorldQual uses input data on pollutant loadings from both point and diffuse sources. The point source inputs include manufacturing, domestic and urban sources, whereas the diffuse source inputs come from, for example, agriculture and natural sources. The diverse input data are downscaled from country scale (Voß et al., 2012). WorldQual is an empirical model and considers multiple pollutants, but not their interactions. The model runs on a 5 arc minute grid cell with a monthly time step (UNEP, 2016). WorldQual quantifies concentrations of pollutants in river streams that are routed towards the outlet of the river. Various pollutants can be included, for example, faecal coliform bacteria, biological oxygen demand (BOD) and total P. Faecal coliform decays that are included are solar radiation, temperature and settling. BOD decay is based on river temperature. P retention is empirically obtained for the whole river basin and depends on the annual runoff and lake surface area (UNEP, 2016). A user can include scenarios into the model. For example, Voß et al. (2012) included two IPCC SRES A2 scenarios for climate change. The temporal extent, likewise, can be set by the user (UNEP, 2016; Voß et al., 2012).

The Soil and Water Assessment Tool (SWAT) is designed to analyse diffuse water pollution and the effectiveness of water management options (Arnold et al., 1998). The focus of the model therein is on the consequences of certain land uses and management on sediments, agricultural pollution and water resources (Arnold et al., 2012; Table 3.1). Therefore, it includes input data on, for example, hydrology, weather, soil and plants. The model uses a daily time step. Spatially, hydrologic response units are typically used. A hydrological response unit, part of a user-defined subwatershed, is seen as a spatial unit that is homogenous in its soil properties, topography, land use and management (Arnold et al., 2012; Douglas-Mankin et al., 2010). SWAT has been applied frequently, and the temporal and spatial extent of the model tend to differ per study. Douglas-Mankin et al. (2010) note for SWAT simulations of water flow and pollutants that the diverse application range from using a watershed scale of 0.004 $km^2$ to one of 491,665 $km^2$. SWAT is a process-based model and is based on the water balance (Arnold et al., 2012). The water balance affects the processes that are included in the model. In SWAT, different forms (including their transformation) of N, P, pesticides and sediments in rivers are modelled throughout the watershed. The SWAT model distinguishes two different phases: the land phase (inputs of pollutants, water etc. into the main channel of every sub-basin) and the in-stream phase (how pollutants, water etc. in the channels reach the outlet of the watershed) (Arnold et al., 2012). The inputs of pollutants (sediments, nutrients, pesticides, bacteria) are aggregated from the hydrologic response units to the subwatershed. These inputs from the subwatershed are then modelled throughout the watershed until they reach the outlet. Point sources are also included. The in-stream phase of the model is based on the QUAL2E model and includes, for example, processes as degradation and volatilization for pesticides and bacteria. Though heavy metals can also be simulated, the model does not consider changes in their form or decay for heavy metals (Gassman et al., 2007).

### 3.3.2 Interactions between pollutants in existing water quality models

The global multi-pollutant model by Strokal et al. (2019) considers interactions in the source attribution of pollutants. The model is currently being developed to include interactions in the management of the pollutants. For example, treatment of nutrients in wastewater may also result in treatment of plastics (for example through sedimentation and settling processes). Interactions between pollutants within rivers or the impacts of multiple pollutants may also be incorporated into the model. However, only point source inputs are modelled. River retention and export of pollutants is not modelled so far (Strokal et al., 2019).

In contrast, WorldQual does model the export of multiple pollutants simultaneously and does not consider interactions between these pollutants (Strokal et al., 2019). SWAT includes important factors such as temperature, oxygen and light (Neitsch et al., 2011). Despite the high level of detail, however, SWAT does not seem to incorporate interactions between pollutants as nutrients, hazardous solids, chemicals, pathogens and toxins in-stream. This could partly be attributed to the fact that the model does not consider the pollutant groups of hazardous solids and toxins. Nevertheless, SWAT does include, for example, nutrients adsorption to sediments. These are modelled to be deposited with the sediments. It also considers, for example, the stimulation of algal growth by nutrients and light (Neitsch et al., 2011). These processes may resemble sorption- and growth-related interactions that are identified in Chapter 2. The multi-pollutant model by Strokal et al. (2019) also includes such processes implicitly, lumped together into model parameters on pollutant retention. In WorldQual (UNEP, 2016), too, some process may have been incorporated implicitly, for example, in the settling rate of bacteria.

*Table 3.1. A selection of multi-pollutant models and their characteristics (see Section 3.3). Source: Kroeze et al. (2016), Strokal et al. (2019), and Tang et al., (2019).*

| ***Model*** | **Purpose** | **Pollutants** | **Spatial resolution and extent** | **Temporal resolution and extent** | **Scenarios** | **Modelling approach** | **Included sources** | **Interactions** | **Impacts** |
|---|---|---|---|---|---|---|---|---|---|
| *Global multi-pollutant model (Strokal et al., 2019)* | Quantify inputs of multiple pollutants to rivers by source simultaneously | Triclosan, plastics, nutrients (nitrogen and phosphorous), pathogens (*Cryptosporidium*) | Extent:<br>Global (10,226 sub-basins)<br>Resolution:<br>30 degree arc-minute grid cells (inputs), sub-basins (outputs) | Extent:<br>2010<br>(to be developed: 2010-2100)<br>Resolution:<br>Annual | (under development) | Empirical, steady-state | Point sources | At the source: source attribution, management options (in progress) and in rivers (this study) | Only an indicator for hotspots, with high river inputs of all five pollutants |
| *WorldQual (UNEP, 2016; Voß et al., 2012)* | Quantify pollutant loadings by source to river streams | Nutrients, faecal coliform bacteria, biochemical oxygen demand, dissolved solids | Extent: Continental<br>Resolution: 5 degree arc-minute grid cells and river streams | Extent: Varying per study<br>Resolution: Monthly | User-dependent; e.g. Voß et al. (2012) use IPCC SRES A2 climate scenarios[8] | Empirical, pollutants not calculated simultaneously | Point and diffuse sources | Not included | Not included |
| *SWAT (Arnold et al., 2012; Douglas-Mankin et al., 2010)* | Analyse diffuse pollution and effectiveness of management options on water quality | Sediment, nutrients, pesticides, biochemical oxygen demand, algae, (fecal) bacteria, heavy metals | Resolution:<br>Hydrologic response units (each with homogenous characteristics), as part of subwatersheds (%) or subwatersheds only (each having dominant characteristics)<br>Extent:<br>River basin; Continental applications exist e.g. for Europe, see Abbaspour et al. (2015). | Extent: Past; extent varying per study<br>Resolution: Daily (or monthly or annually; varying per study) | User-dependent; e.g. management and climate change scenarios. | Process-based, continuous, deterministic | Point and diffuse sources | Nutrients dynamically simulated; No interactions of Chapter 2 directly included. | User-dependent. E.g. impacts for bioenergy crops (Cibin et al., 2016) |

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[8] These are scenarios within the A2 group of scenarios in the Special Report on Emissions Scenarios (SRES) by the Intergovernmental Panel on Climate Change (IPCC). These scenarios are described by a storyline that has a focus on the regional identity (IPCC, 2000). See IPCC (2000) for more information.

## 3.4 Global model for river export of multiple pollutants

### 3.4.1 General description

Strokal et al. (2019) provide a first global multi-pollutant model that quantifies yearly inputs of multiple pollutants (N, P, TCS, microplastics, *Cryptosporidium*) from point sources to rivers (Figure 3.1). This multi-pollutant model by Strokal et al. (2019) integrates the approaches of existing models for nutrients, microplastics, TCS and *Cryptosporidium*. These models are the MARINA model (Strokal, Kroeze, et al., 2016), the Microplastics model (Siegfried et al., 2017), the Global TCS model (van Wijnen et al., 2018) and the GloWPa model (Hofstra et al., 2013; Vermeulen et al., 2019), respectively.

MARINA is an abbreviation of Model to Assess River Inputs of Nutrients to seAs. The model quantifies past and future annual export of dissolved inorganic and organic forms of N and P from rivers in China at the sub-basin scale (Strokal, Kroeze, et al., 2016). This is done as a function of human activities on land and sub-basin characteristics (e.g. hydrology, land use). The Microplastics model quantifies the inputs of various microplastic types from point sources and the export of these microplastics from source to seas for European rivers. The Microplastics model bases these inputs and exports on sewage management and retention of plastics in rivers (Siegfried et al., 2017). The Global TCS model (Global triclosan model) quantifies export of TCS by rivers worldwide as a function of sewage discharges of TCS and river export fractions (van Wijnen et al., 2018). GloWPa stands for Global Waterborne Pathogen model. For *Cryptosporidium*, it quantifies the inputs of oocysts from both point and diffuse sources of *Cryptosporidium* oocysts to rivers (Hofstra et al., 2013). GloWPa also quantifies concentrations of *Cryptosporidium* oocysts in rivers with a routing model (following water flow), taking into account decays of *Cryptosporidium* due to temperature, solar radiation and sedimentation (Vermeulen et al., 2019). GloWPa models *Cryptosporidium* inputs and transport globally, as its name suggests.

The work of Strokal et al. (2019) opens an opportunity to quantify river export of multiple pollutants. Strokal et al. (2019) show a framework on how the model could be expanded by including more sources (e.g. diffuse sources as agricultural runoff) and river retentions of multiple pollutants based on existing modelling approaches (Strokal et al., 2019; Figure 3.1). This study, therefore, builds on this multi-pollutant approach of Strokal et al. (2019).

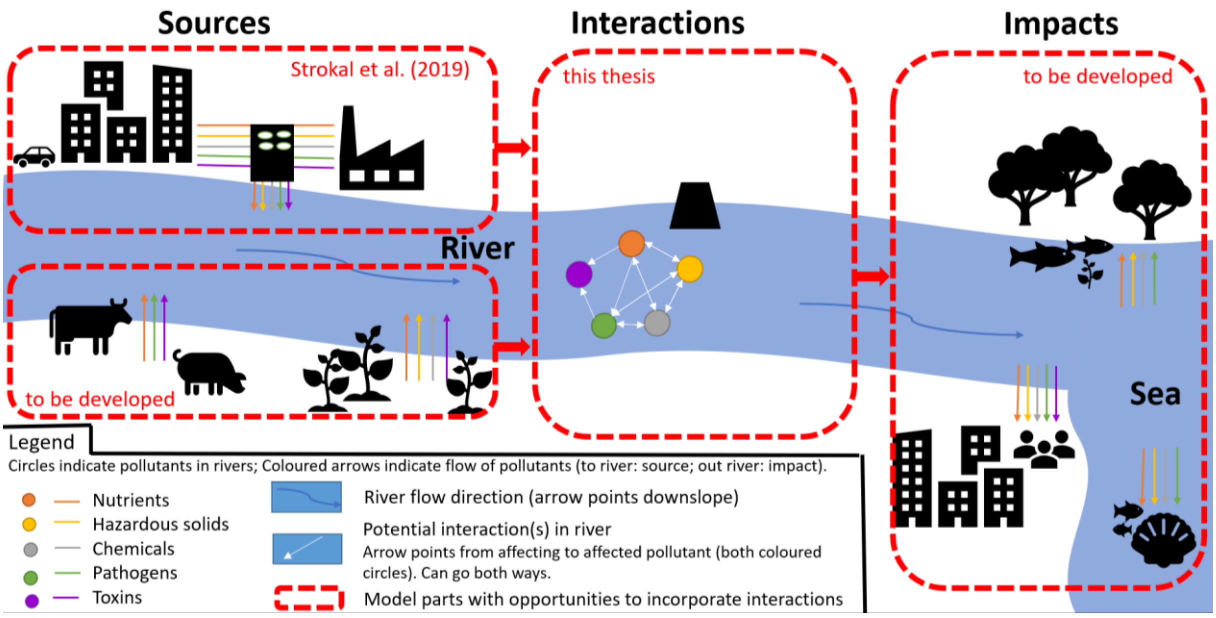

*Figure 3.1. A schematic overview of river export of multiple pollutants from land activities (sources as agricultural runoff and sewage systems) and potential interactions between groups of pollutants: nutrients (e.g. nitrogen and phosphorous), hazardous solids (e.g. microplastics), chemicals (e.g. triclosan), pathogens (faecal-oral bacteria, viruses and protozoa) and toxins (cyanotoxins). Pollution of rivers and coastal seas by multiple pollutants can have various impacts (e.g. decreased human health, declines in coral reef health). The red boxes show opportunities for the incorporation of interactions in the global multi-pollutant models. This thesis is mainly focussed on the interactions within the river itself. The model of Strokal et al. (2019) is the starting point, providing inputs of various pollutants to the river and considering some interactions (see section 3.4.1). Source: Chapter 2 and Section 3.4.1.*

This study focuses on the river export of pollutants from point sources at the sub-basin scale, accounting for river retention of pollutants (Figure 3.1). The global multi-pollutant model of Strokal et al. (2019) is combined with the sub-basin modelling approach initially developed for modelling nutrient export by Strokal, Kroeze, et al. (2016). In this study, this sub-basin approach of Strokal, Kroeze, et al. (2016), for which the main equation is given for point sources only in Equation 1, is also applied to microplastics, TCS and *Cryptosporidium*[9] based on existing approaches for each of these pollutants (Siegfried et al., 2017; van Wijnen et al., 2018; Vermeulen et al., 2019).

Equation 1 quantifies annual river export of multiple pollutants from point sources at the sub-basin scale according to Strokal, Kroeze, et al. (2016):

$$M_{pnt.p.s.j} = RS_{pnt.p.s.j} \cdot FE_{riv.p.outlet.j} \cdot FE_{riv.p.mouth.j} \quad \text{(Eq. 1)}$$

Where,

$M_{pnt.p.s.j}$ is the annual river export of pollutant $p$ by point source $s$ from sub-basin $j$ (kg/year);
$RS_{pnt.p.s.j}$ is the input of pollutant $p$ to rivers by point source $s$ in sub-basin $j$ (kg/year);
$FE_{riv.p.outlet.j}$ is the fraction of inputs of pollutant $p$ to rivers that is exported to the outlet of sub-basin $j$ (0-1);
$FE_{riv.p.mouth.j}$ is the fraction of pollutant $p$ at the outlet of sub-basin $j$ that is exported to the river mouth (coastal waters) from sub-basin $j$ (0-1).

$FE_{riv.p.outlet.j}$ is quantified with the sub-basin modelling approach of Strokal, Kroeze, et al. (2016), but adapted to existing modelling approaches in order to include multiple pollutants.

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[9] See Section 3.4.2

$FE_{riv.p.outlet.j}$ for nutrients, microplastics and TCS is computed by Equation 2 (Siegfried et al., 2017; Strokal, Kroeze, et al., 2016; van Wijnen et al., 2018):

$$FE_{riv.p.outlet.j} = (1 - L_{p.j}) \cdot (1 - D_{p.j}) \cdot (1 - FQrem_j) \qquad \text{(Eq. 2)}$$

Where,

$L_{p.j}$ is the fraction of pollutant *p* retained/lost in rivers of sub-basin *j* (0-1);
$D_{p.j}$ is the fraction of pollutant *p* retained/lost in reservoirs of sub-basin *j* (0-1);
$FQrem_j$ is the fraction of pollutant *p* lost from sub-basin *j* through consumption of water (0-1).

$FQrem_j$ is obtained with the original ('natural') water discharge at the outlet of sub-basin *j* by the actual ('after water withdrawal for consumption') water discharge at the outlet of sub-basin $j$. $FQrem_j$ is calculated according to Strokal, Kroeze, et al. (2016) as:

$$FQrem_j = 1 - Q_{act.j}/Q_{nat.j} \qquad \text{(Eq. 3)}$$

Where,

$Q_{act.j}$ is the actual water discharge at the outlet of sub-basin *j* (after water is obtained for consumption) (km$^3$/year);
$Q_{nat.j}$ is the original ('natural') water discharge at the outlet of sub-basin *j* (before water is obtained for consumption) (km$^3$/year).

$L_{p.j}$ and $D_{p.j}$ are quantified depending on which pollutant is modelled (Table 3.1). For example, in the MARINA model, $L_{DIN.j}$ is the fraction of dissolved inorganic nitrogen (DIN) retained/lost in rivers of sub-basin $j$ through denitrification, whereas $L_{DIP.j}$ is the fraction of dissolved inorganic phosphorous (DIP) retained/lost in rivers of sub-basin $j$ through sedimentation (Strokal, Kroeze, et al., 2016). $L_{TCS.j}$ describes retention/loss of TCS due to sorption, sedimentation and biodegradation (van Wijnen et al., 2018). The meaning of $L_{p.j}$ and $D_{p.j}$ for nutrients, microplastics and TCS is given in Table 3.1. Retention of *Cryptosporidium* is modelled distinctly (see Table 3.1). The next section (Section 3.4.2) gives details on these model parameters for N, P, microplastics, TCS and *Cryptosporidium*.

$FE_{riv.p.mouth.j}$ is quantified based on $FE_{riv.p.outlet.j}$, following the modelling approach of Strokal, Kroeze, et al. (2016), but for multiple pollutants. The equations are presented in Strokal, Kroeze, et al. (2016). In brief, $FE_{riv.p.mouth.j}$ is quantified per type of sub-basin, distinguishing between sub-basins with the main channel and sub-basins with only tributaries of the river. $FE_{riv.p.mouth.j}$ is calculated for upstream, middlestream and downstream sub-basins distinctly. For example, $FE_{riv.p.mouth.juT}$, the fraction exported from upstream tributaries (*juT*) is quantified as a function of the $FE_{riv.p.outlet.j}$ of the upstream, the middlestream and the downstream sub-basins of that tributary.

*Table 3.2. Summary of the model parameters to quantify retentions of the studied pollutants in rivers and the fraction of pollutants that is exported by rivers to the sub-basin outlets. Parameters modified from existing water quality models are included: the MARINA model (Model to Assess River Inputs of Nutrients to seAs) for nutrients (nitrogen and phosphorous), the Microplastics model for microplastics, the Global TCS (Global triclosan model) for triclosan (TCS) and the GloWPa model (Global Waterborne Pathogen model) for Cryptosporidium. These modelling approaches were modified to match the sub-basin approach of Strokal, Kroeze, et al. (2016), according to Section 3.4.* $L_{p.j}$ *is the fraction of pollutant p retained/lost in rivers of sub-basin j (0-1);* $D_{p.j}$ *is the fraction of pollutant p retained/lost in reservoirs of sub-basin j (0-1);* $FQrem_j$ *is the fraction of pollutant p lost from sub-basin j through consumption of water (0-1).* $FE_{riv.p.outlet.j}$ *is the fraction of inputs of pollutant p to rivers that is exported to the outlet of sub-basin j (0-1). Source: Section 3.4.*

| ***Model*** | ***Pollutants in this study*** | $\boldsymbol{L_{p.j}}$ ***(retention in rivers)*** | $\boldsymbol{D_{p.j}}$ ***(retention in reservoirs)*** | $\boldsymbol{FQrem_j}$ ***(losses from rivers)*** | $\boldsymbol{FE_{riv.p.outlet.j}}$ ***(export fraction)*** |
|---|---|---|---|---|---|
| *MARINA (Strokal, Kroeze, et al., 2016)* | Nutrients (DIN[10], DIP[11], DON[12], DOP[13]) | Retention/loss due to denitrification (DIN), sedimentation (DIP) | Retention due to river damming (DIN, DIP) | Consumptive water use | Eq. 2 |
| *Microplastics model (Siegfried, et al., 2017)* | Microplastics | Retention for each microplastic source (personal care products, household dust, laundry textiles and tyre and road wear particles) | 0 (not modelled) | Consumptive water use | Eq. 2 |
| *Global TCS (van Wijnen et al., 2018)* | TCS | Retention/loss due to sorption, sedimentation and biodegradation | Retention due to river damming (through reservoir trapping and sedimentation) | Consumptive water use | Eq. 2 |
| *GloWPa (Hofstra et al., 2013; Vermeulen et al., 2019)* | *Cryptosporidium* | Temperature- and solar radiation-dependent decays, sedimentation losses | 0 | 0 | Eq. 11 |

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[10] Dissolved inorganic nitrogen
[11] Dissolved inorganic phosphorous
[12] Dissolved organic nitrogen
[13] Dissolved organic phosphorous

## 3.4.2 Modelling retentions of individual pollutants in rivers

### Nitrogen (N)

N losses from/retentions in the river, $L_{DIN.j}$ (0-1) and $D_{DIN.j}$ (0-1) are described in this section. $L_{DON.j}$ and $D_{DON.j}$ for dissolved organic nitrogen (DON) are assumed to be zero (Strokal, Kroeze, et al., 2016).

River retention of DIN in sub-basin *j* ($L_{DIN,j}$) is according to Strokal, Kroeze, et al. (2016) quantified with Equation 4:

$$L_{DIN,j} = 0.0605 \times \ln(Area_j) - 0.0443 \quad \text{(Eq. 4)}$$

With $0 \leq L_{DIN} \leq 0.65$

Where,

$Area_j$ is the drainage area of sub-basin *j* (km$^2$).

The coefficients (0.0605 and -0.0443) are fitted based on Seitzinger et al. (2002) and Dumont et al. (2005) (Strokal, Kroeze, et al., 2016). The use of 0.65 as maximum of $L_{DIN}$ was set as such in order to avoid error due to extrapolation, as the 16 US rivers used to estimate the coefficients had $L_{DIN}$ values lower than 0.65 (Dumont et al., 2005; Strokal, Kroeze, et al., 2016).

Retention within reservoirs is obtained according to Strokal, Kroeze, et al. (2016) by Equation 5.

$$D_{DIN,j} = (\frac{1}{Q_{act,j}}) \sum_{i=1\ldots n}(Q_{act,i} \times D_{DIN,i}) \quad \text{(Eq. 5)}$$

With $0 \leq D_{DIN} \leq 0.965$

Where,

$Q_{act.j}$ is the actual water discharge at the outlet of sub-basin *j* (after water is obtained for consumption) (km$^3$/year);

$Q_{act.i}$ is the actual water discharge for reservoir *i* (km$^3$/year);

$D_{DIN,i}$ is the fraction of DIN retained in reservoir *i* of sub-basin *j* (0-1). It is given by Equation 6 (Strokal, Kroeze, et al., 2016):

$$D_{DIN,i} = 0.8845 \times (\frac{h_i}{\tau_{R,i}})^{-0.3677} \quad \text{(Eq. 6)}$$

Where,

$D_{DIN,i}$ is the fraction of DIN retained in reservoir *i* of sub-basin *j* (0-1);

$h_i$ is the depth of reservoir *i* (m); and

$\tau_{R,i}$ is the water residence time for reservoir *i* (years). It is quantified with Equation 9 (Strokal, Kroeze, et al., 2016):

$$\tau_{R,i} = V_i \times Q_{act,i} \quad \text{(Eq. 7)}$$

With $V_i \geq 0.5$ km$^3$

Where,

$Q_{act.i}$ is the actual water discharge for reservoir *i* of sub-basin *j* (km$^3$/year);

$V_i$ is the volume (storage capacity) of reservoir *i* of sub-basin *j* (km$^3$/year). Reservoirs with a storage capacity of at least 0.5 km$^3$ are included. The volume of the reservoirs given in HydroLAKES is multiplied by 0.67 to match reservoir operation (Strokal, Kroeze, et al., 2016; Vörösmarty et al., 2003).

This method to compute reservoir retention of $D_{DIN,i}$ is based Seitzinger et al. (2002) and Maryorga et al. (2010). For the estimation of the coefficients, 0.965 is the maximum value of $D_{DIN}$ for the basins used for determining this coefficients.

## Phosphorous (P)

This section treats $L_{DIP.j}$ (0-1) and $D_{DIP.j}$ (0-1) for dissolved inorganic phosphorous (DIP). $L_{DOP.j}$ and $D_{DOP.j}$ for dissolved organic phosphorous (DOP) are assumed to be zero (Strokal, Kroeze, et al., 2016).

$L_{DIP.j}$ represents the river retentions of DIP in rivers of sub-basin j due to, for example, sedimentation. $L_{DIP.j}$ is attributed a value of 0.5 or 0.9 (Strokal, Kroeze, et al., 2016). Usually $L_{DIP.j}$ is given a value of 0.5, with the exception of the sub-basins of dry rivers that have <0.1 m runoff per year (Strokal, Kroeze, et al., 2016). For these sub-basins, retention is set to 0.9.

$D_{DIP.j}$ represents the reservoir retention of DIP. $D_{DIP.j}$ is obtained according to Strokal, Kroeze, et al. (2016) by Equation 8:

$$D_{DIP.j} = \left(\frac{1}{Q_{act.j}}\right) \sum_{i=1 \ldots n} (Q_{act.i} \times D_{DIP,i}) \qquad \text{(Eq. 8)}$$

With $0 \leq D_{DIP,i} \leq 0.85$

Where,

$D_{DIP.j}$ is the fraction of DIP retained/lost in reservoirs of sub-basin *j* (0-1);

$Q_{act.j}$ is the actual water discharge at the outlet of sub-basin *j* (after water is obtained for consumption) (km$^3$/year);

$Q_{act.i}$ is the actual water discharge for reservoir *i* (km$^3$/year);

$D_{DIP,i}$ is the fraction of DIP retained in reservoir *i* of sub-basin *j* (0-1). The method used to calculate $D_{DIP,i}$ is based on the Global NEWS model (Mayorga et al., 2010; Seitzinger et al., 2002). It is given by Equation 8 (Strokal, Kroeze, et al., 2016):

$$D_{DIP,i} = 0.85 \times (1 - e^{-0.0807 \times 365 \times \tau_{R,i}}) \qquad \text{(Eq. 9)}$$

Where,

$\tau_{R,i}$ is the water residence time for reservoir *i* of sub-basin *j* (years) (Equation 7).

## Microplastics

Descriptions of $L_{MP.j}$ (0-1) and $D_{MP.j}$ (0-1) for microplastics (MP) are given in this section. Originally the fraction of microplastics retained in the whole basin (Siegfried et al., 2017), $L_{MP.j}$ is a fraction that contains the retentions of microplastics in rivers of sub-basin *j* of a river basin. Retention of microplastics in rivers occurs through settling. $L_{MP.j}$ is attributed a value based on the source of microplastics: 0.2 for personal care products, 0.75 for household dust, laundry textiles and tyre and road wear particles in small basins and 0.9 for household dust, laundry textiles and tyre and road wear particles in large basins (Siegfried et al., 2017). These values per source, based on Besseling et al. (2017), reflect the effects of particle size: the settling rate of microplastics is affected by the efficiency of aggregation of plastic particles to suspended solids, heteroaggregation, when particle sizes are relatively small, but not when they are large. Thus, the shape and density of the microplastics affects the settling process (Besseling et al., 2017). The larger microplastics tend to be retained to a higher extent.

Reservoir retention is not included in the Microplastics model (Siegfried et al., 2017). Therefore, the reservoir retention in a sub-basin $j$ ($D_{MP.j}$) is not yet included in the microplastics model.

## Triclosan (TCS)

This section provides a description of $L_{TCS.j}$ (0-1) and $D_{TCS.j}$ (0-1) for TCS. The methods to estimate these fractions originate from the Global TCS model (van Wijnen et al., 2018), but were applied on the scale of the sub-basin (Strokal, Kroeze, et al., 2016) instead of the basin.

$L_{TCS.j}$ represents retention of TCS in rivers of sub-basins $j$ due to sorption, sedimentation and biodegradation (0-1) (van Wijnen et al., 2018). It is quantified according to van Wijnen et al. (2018) as:

$$L_{TCS.j} = 1 - e^{-k \times t_{res,TCS.j}} \qquad \text{(Eq. 10)}$$

Where,

$L_{TCS.j}$ is the fraction of TCS retained/lost in rivers of sub-basin $j$ (0-1);

$k$ is the coefficient for loss rates of degradation and net-sedimentation ($\text{day}^{-1}$). The loss rate used by van Wijnen et al. (2018) amounts to 0.06 $h^{-1}$ ($2 \times 10^{-5}$ $s^{-1}$).

$t_{res,TCS.j}$ is the residence time of TCS in sub-basin $j$ (days). The equations to determine $t_{res,TCS.j}$ are presented in van Wijnen et al. (2018).

$D_{TCS.j}$ represents retentions of TCS in rivers due to river damming (0-1). $D_{TCS.j}$ is assumed to be 15% of the reservoir retention fraction for total suspended solids as provided by Mayorga et al. (2010) (van Wijnen et al., 2018).

## Cryptosporidium

As mentioned in Section 3.4.1, persistence of *Cryptosporidium* in rivers is originally modelled distinctly from the export fractions of TCS, microplastics and nutrients discussed in the previous sections. This section considers how retention of *Cryptosporidium* is modelled. Equations A and B of the GloWPa model are presented in Box 1. These equations are modified to quantify *Cryptosporidium (C)* losses for sub-basin $j$ per year. These are modified to match Equation 1 and its terms as follows:

$$M_{pnt.C.s.j} = RS_{pnt.C.s.j} \cdot FE_{riv.C.outlet.j} \cdot FE_{riv.C.mouth.j} \qquad \text{(Eq. 1, adjusted: \textit{Cryptosporidium})}$$

Where,

$M_{pnt.C..s.j}$ is the annual river export of *Cryptosporidium* by point source $s$ from sub-basin $j$ (oocysts/year);
$RS_{pnt.C.s.j}$ is the input of *Cryptosporidium* to rivers by point source $s$ in sub-basin $j$ (oocysts/year);
$FE_{riv.C.outlet.j}$ is the fraction of inputs of *Cryptosporidium* to rivers that is exported (persists) to the outlet of sub-basin $j$ (0-1);

$FE_{riv.C.mouth.j}$ is the fraction of *Cryptosporidium* at the outlet of sub-basin $j$ that is exported (persists) to the river mouth (coastal waters) from sub-basin $j$ (0-1). It is quantified based on $FE_{riv.C.outlet.j}$ with the equations presented in Strokal, Kroeze, et al. (2016). Salinity (e.g. at the river mouth) is not yet taken into account (thus freshwater river mouths are assumed), but might affect *Cryptosporidium* export (Chapter 2). However, Nasser et al. (2003) find that survival of *Cryptosporidium* is similar for stream, brackish and sea waters.

$RS_{pnt.C.s.j}$ is the point source input of *Cryptosporidium* in Equation 13, modelled per year and per sub-basin. As such, it replaces $SP_i$ in Equation A in Box 1, which is the point source input of *Cryptosporidium* per month and per grid cell. $RS_{pnt.C.s.j}$ is modelled by Strokal, Kroeze, et al. (2019). Diffuse sources ($SD_i$ in Equation A) are not yet taken into account in the multi-pollutant model by Strokal et al. (2019). Therefore, I do not include diffuse sources in the global model for river export of multiple pollutants presented this chapter. Pollution from upstream sub-basins (originally $L_{n-1}$ for grid cells in Equation A, Box 1) is accounted for with the sub-basin approach of Strokal, Kroeze, et al. (2016).

$FE_{riv.C.outlet.j}$ and $FE_{riv.C.mouth.j}$ are the export fractions of *Cryptosporidium*. Equation 11 for $FE_{riv.C.outlet.j}$ matches Equation 2 when $D_{C.j}$ and $FQrem_{C.j}$ are set to 0, and may in further modelling studies be modified to include $D_{C.j}$ and $FQrem_{C.j}$:

$$FE_{riv.C.outlet.j} = 1 - L_{C.j} \qquad \text{(Eq. 11)}$$

Where,

$FE_{riv.C.outlet.j}$ is the fraction of inputs of *Cryptosporidium* to rivers that is exported (persists) to the outlet of sub-basin $j$ (0-1);
$L_{C.j}$ is the fraction of *Cryptosporidium* retained/lost in rivers of sub-basin $j$ (0-1). It is determined with Equation 12 according to the retention part of Equation A and is in line with Equation 10 for TCS:

$$L_{C.j} = 1 - e^{-K_j \times t_j} \qquad \text{(Eq. 12)}$$

Where,

$L_{C.j}$ is the fraction of *Cryptosporidium* retained/lost in rivers of sub-basin $j$ (0-1);
$t_j$ is the water residence time in the sub-basin $j$ in a year (year$^{-1}$) in the grid cell of the outlet of sub-basin $j$;
$K_j$ is the loss rate coefficient in sub-basin $j$ in a year (year$^{-1}$). It is determined with Equation 13 based on Equation A in Box 1:

$$K_j = K_{T,j} + K_{R,j} + K_{S,j} \qquad \text{(Eq. 13)}$$

Where,

$K_{T,j}$ is the temperature-dependent decay rate in a year in sub-basin $j$ (year$^{-1}$).
$K_{R,j}$ is the solar radiation-dependent decay rate in a year in sub-basin $j$ (day$^{-1}$).
$K_{S,j}$ is the loss rate due to sedimentation in a year in sub-basin $j$ (day$^{-1}$).

$K_{T,j}$, $K_{R,j}$ and $K_{S,j}$ in Equation 16 are each summed up for 12 months ($i$ = 1, 2 … 12) for respectively $K_{T,i}$, $K_{R,i}$ and $K_{S,i}$ in Equation 12.

*Box 1. Original approach to model Cryptosporidium from the GloWPa model (Vermeulen et al., 2019). GloWPa is the Global Waterborne Pathogen model. The equations presented here are used in GloWPa to quantify the monthly loads of Cryptosporidium oocysts per grid cell of a river basin.*

## *Cryptosporidium* losses in GloWPa

Originally, *Cryptosporidium* is modelled with a monthly time-step and on a grid-cell basis. *Cryptosporidium* oocysts in month *i* in a grid cell with flow accumulation number $n$ (number of grid cells flowing into that grid cell) (oocysts/month) is determined according to Vermeulen et al. (2019) as:

$$L_{i,n} = (SD_i + SP_i + L_{i,n-1}) \times e^{-K_i \times t_i} \qquad \text{(Eq. A)}$$

Where,

$L_{i,n}$ is the load of *Cryptosporidium* oocysts in month *i* in a grid cell with flow accumulation number *n* (oocysts/month);

$SD_i$ is the stream inputs of oocysts from diffuse sources in month *i* (oocysts/month). These inputs are not included in Strokal et al. (2019);

$SP_i$ is the inputs of oocysts from point sources in month *i* (oocysts/months);

$L_{i,n-1}$ is the load of oocysts from other grid cells going into the current grid cell (*n-1*) in month *i* (oocysts/month) and is not incorporated in Equation 1;

$K_i$ is the loss rate coefficient in month *i* (day$^{-1}$) (see Section 3.4.6); and

$t_i$ is the water residence time in the grid cell in month *i* (days).

Whereas $(SD_i + SP_i + L_{i,n-1})$ in Equation 11 is more alike $RS_{\ pnt.p.s.j}$ in Equation 1, $e^{-K_i \times t_i}$ in Equation 11 is more alike $FE_{riv.p.outlet.j}$ in Equation 1 and 2, though consisting of different parameters than those given in Equation 2.

The persistence of *Cryptosporidium* in the river is thus modelled with a part of Equation A: $e^{-K_i \times t_i}$ (see Table 3.2), where $K_i$ is the loss rate coefficient per day in month *i*, (day$^{-1}$) and $t_i$ is the water residence time (days). The loss rate coefficient ($K_i$) is calculated according to Vermeulen et al. (2019) with Equation B.

$$K_i = K_{T,i} + K_{R,i} + K_{S,i} \qquad \text{(Eq. B)}$$

Where,

$K_i$ is the loss rate coefficient of *Cryptosporidium* oocysts in month *i* (day$^{-1}$);
$K_{T,i}$ is the temperature-dependent decay rate in month *i* (day$^{-1}$);
$K_{R,i}$ is the solar radiation-dependent decay rate in month *i* (day$^{-1}$); and
$K_{S,i}$ is the loss rate due to sedimentation in month *i* (day$^{-1}$).

The equations for determining the temperature-dependent decay, the solar radiation-dependent decay and the loss rate due to sedimentation are presented in Vermeulen et al. (2019).

A summary of the parameters that are necessary to obtain to quantify retention of N, P, microplastics, TCS and *Cryptosporidium* is displayed in Table 3.3.

*Table 3.3. Parameters required to calculate retention fractions of pollutants in rivers ($L_{p.j}$, 0-1) and reservoirs ($D_{p.j}$, 0-1) in sub-basin j according to the global model for river export of multiple pollutants presented in Section 3.4. Included pollutants are nitrogen (N), phosphorous (P), microplastics, triclosan (TCS), and Cryptosporidium. DIN is short for dissolved inorganic nitrogen. DIP is short for dissolved inorganic phosphorous.*

| **Parameters required to quantify retentions** | **Unit** | **Pollutant(s)** | **Potential data source** |
|---|---|---|---|
| Actual water discharge per sub-basin ($Q_{act.j}$) | $km^3$/year | N, P, microplastics, TCS | VIC (van Vliet et al., 2019) |
| Natural water discharge per sub-basin ($Q_{nat.j}$) | $km^3$/year | N, P, microplastics, TCS | VIC (van Vliet et al., 2019) |
| Sub-basin drainage area ($Area_j$) | $km^2$ | DIN, microplastics (household dust, laundry textiles, tyre and road wear particles) | Strokal et al. (2019) |
| Actual water discharge per reservoir ($Q_{act.i}$) | $km^3$/year | DIN, DIP | VIC (van Vliet et al., 2019) combined with Global NEWS (Mayorga et al., 2010), or sub-basin specific consumption data |
| Depth per reservoir ($h_i$) | m | DIN | HydroLAKES (Messager et al., 2016) |
| Volume (storage capacity) per reservoir ($V_i$) | $km^3$ | DIP | HydroLAKES (Messager et al., 2016) |
| Sub-basin areas, used to estimate residence time of TCS for sub-basins according to van Wijnen et al. (2018)[14] | $km^2$ | TCS | Strokal et al. (2019) |
| The coefficient for loss rates of degradation and net-sedimentation of TCS ($k$) | $day^{-1}$ | TCS | Global TCS (van Wijnen et al., 2018) |
| Reservoir retention fraction for TCS ($D_{TCS.j}$), assumed to be 15% of the reservoir retention fraction for total suspended solids | 0-1 | TCS | Global TCS (van Wijnen et al., 2018) |
| Water residence time ($t_j$) | days | *Cryptosporidium* | GloWPa (Vermeulen et al., 2019) |
| Various parameters used to calculate survivals $K_{T.j}$, $K_{R.j}$ and $K_{S.j}$ of *Cryptosporidium* and are dependent on temperature, solar-radiation and sedimentation, respectively | per year (possibly obtained from daily or monthly values) | *Cryptosporidium* | GloWPa (Vermeulen et al., 2019) |

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[14] Originally based on the land areas of Global NEWS river basins (van Wijnen et al., 2018). Now for sub-basins instead of basins, adapting the equations to the sub-basin approach of Strokal, Kroeze, et al. (2016).

## 3.5 Examples of pollutant retentions

This section offers two illustrative examples of pollutant retentions: retentions of nutrients in reservoirs and retentions of microplastics in rivers.

### Retentions of nutrients in reservoirs (example of $D_{p,j}$)

To demonstrate retention in reservoirs and lakes, Figures 3.2.a and 3.2.b show $D_{DIN,i}$ and $D_{DIP,i}$ for reservoirs and lakes with a total volume of at least 0.5 km$^3$ worldwide. In combination with reservoir and lake discharge and river discharge, these parameters can be used to obtain $D_{DIN,j}$ and $D_{DIP,j}$ respectively (Section 3.4.2). Relatively few lakes and reservoirs of 0.5 km$^3$ or larger are located in the Southern Hemisphere, North Asia and North Africa. Particularly North America, but also Scandinavia and South-East Asia have relatively high densities of reservoirs and lakes (Figure 3.12). A close-up of one of these areas, South-East Asia, is therefore provided.

$D_{DIN,i}$ tends to be low worldwide, whereas more variety can be observed in $D_{DIP,i}$ (Figure 3.2.a and Figure 3.2.b respectively). Therefore, $D_{DIN,i}$ tends to be lower than $D_{DIP,i}$. Figure 3.2.a shows that $D_{DIN,i}$ for a majority of the lakes and reservoirs is ranging 0.0-0.2. This is attributable to reservoir depth, volume and discharge (Section 3.4). A few reservoirs or lakes have a value of $D_{DIN,i}$ that is higher than 0.6. Most of these seem to be located in Asia. More variation is observed in the values for $D_{DIP,i}$. For example, in North America, many lakes and reservoirs have a value of $D_{DIP,i}$ that is in between 0.8 and 0.85, the upper limit. However, many other lakes and reservoirs in the continent have much lower values for $D_{DIP,i}$.

The same differences are reflected when zooming in on part of South-East Asia: $D_{DIN,i}$ is tends to be low whereas $D_{DIP,i}$ tends to be higher (Figure 3.2.c and Figure 3.2.d respectively). Relatively close to the coast, in India, Eastern China and Indonesia, for example, the $D_{DIN,i}$ tends to have a value of 0.0-0.2. More centrally in Asia, $D_{DIN,i}$ is calculated to be higher and occasionally have a value of 0.8-1.0. Even though $D_{DIP,i}$ is more variable, a similar trend may be observed: In India and Eastern China, $D_{DIP,i}$ is relatively low and $D_{DIP,i}$ is typically relatively high more centrally in Asia. Lakes and reservoirs in Indonesia have, in contrast to this trend, remarkably often a high $D_{DIP,i}$ of 0.8-0.85.

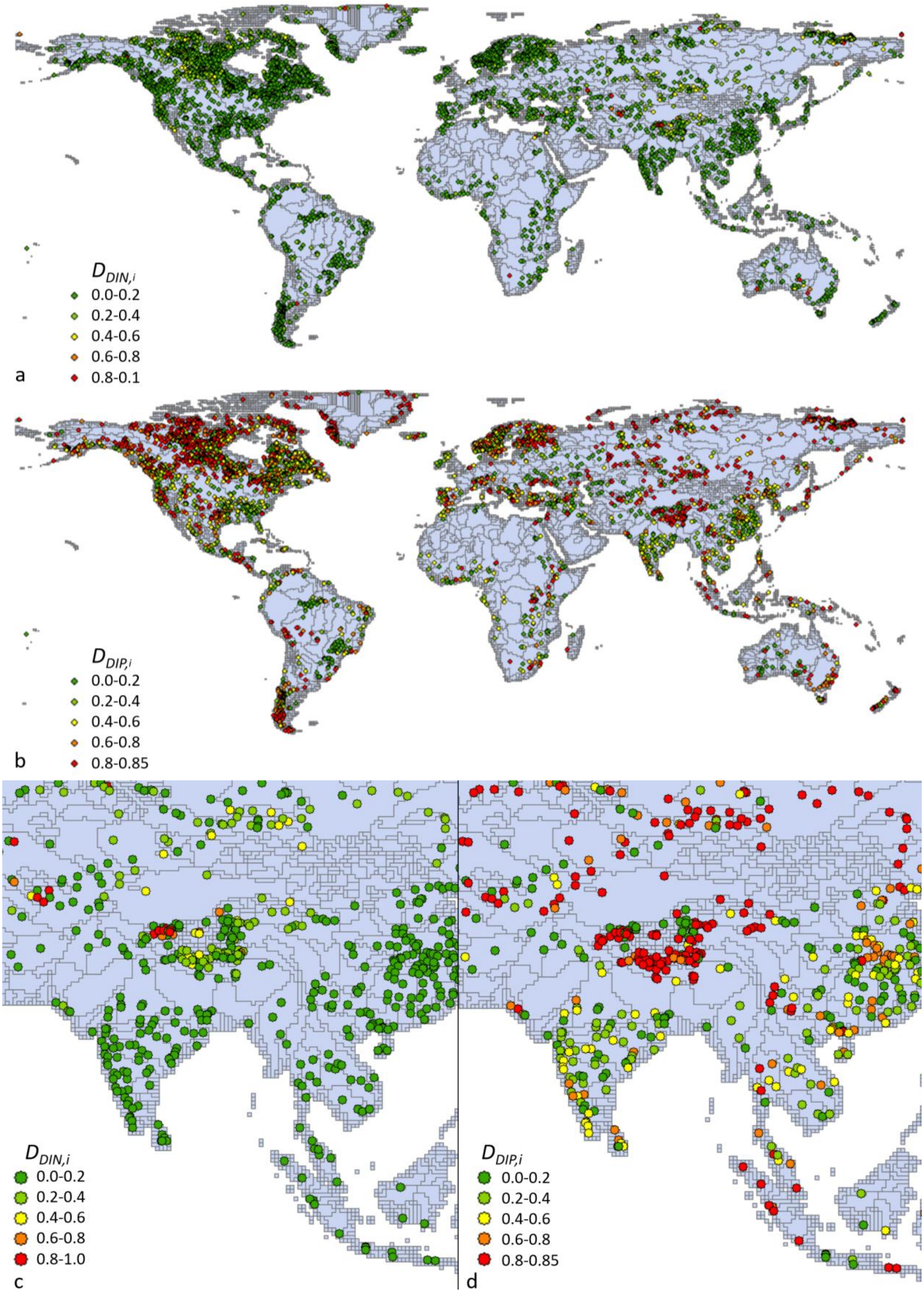

*Figure 3.2. Retention of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorous (DIP) in individual reservoirs and lakes i ($D_{DIN,i}$ and $D_{DIP,i}$) with a total volume ≥ 0.5 $km^3$ worldwide (0-1). (a) is for DIN. (b) is for DIP. (c) and (d) are for South-East Asia, for DIN and DIP respectively. The light-blue polygons show the locations of the sub-basins of Strokal et al. (2019). Source: HydroLAKES (Messager et al., 2016), MARINA (Strokal, Kroeze, et al., 2016)*

### Retentions of microplastics in rivers (example of $L_{p,j}$)

$L_{p.j}$ describes retention of pollutants in rivers (Equation 2; Section 3.4). In this paragraph, an example of this parameter is given for microplastics. In contrast to $D_{DIP.i}$ and $D_{DIP.j}$, $L_{MP.j}$ for each of the different sources included in the model is only dependent on one variable: sub-basin area (Section 3.4.2). Large basins are ≥ 3 grid cells (Siegfried et al., 2017). That is at least 7500 km$^2$. Small sub-basins are expected to retain smaller fractions of microplastics from household dust, laundry textiles and tyre and road wear particles in their rivers than the larger sub-basins.

Of the 10,226 sub-basins, 8448 of the sub-basins are classified as small sub-basins, whereas 1884 are classified as large sub-basins. Thus, about 82% of the sub-basins is attributed an $L_{MP.j}$ of 0.2 for microplastics from personal care products and 0.75 for microplastics from household dust, laundry textiles and tyre and road wear particles. The large sub-basins, about 18% of the sub-basins in the world, are attributed an $L_{MP.j}$ of 0.2 for microplastics from personal care products and 0.9 for microplastics from household dust, laundry textiles and tyre and road wear particles.

*Table 3.4. $L_{MP.j}$,the fraction of microplastics that is retained in rivers of sub-basin $j$ per microplastics source. These sub-basins are the 10,226 sub-basins from Strokal et al. (2019). This table shows that small sub-basins are attributed different values than large sub-basins. Source: Siegfried et al. (2017), Strokal et al. (2019) and Section 3.4.2.*

| **Microplastics source** | $L_{MP.j}$ | |
|---|---|---|
| | **Small sub-basin (count: 8448)** | **Large sub-basin (count: 1884)** |
| Personal care products | 0.2 | 0.2 |
| Household dust | 0.75 | 0.9 |
| Laundry textiles | 0.75 | 0.9 |
| Tyre and road wear particles | 0.75 | 0.9 |

## 3.6 Conclusions

The aim of Chapter 3 is to provide an answer to Research Question 2: **How can existing water quality models be integrated into a global model for river export of multiple pollutants?** To this end, a literature review is conducted. This review consists of two components. The first component is a review of three different multi-pollutant models, each with a different spatial extent. The second component builds on the global model for point source inputs of multiple pollutants by Strokal et al. (2019). Strokal et al. (2019) suggest a framework for further development of the model. Special attention is paid to the modelling of retentions of the included pollutants in rivers. Some modifications were made to design a global model for river export of multiple pollutants based on Strokal et al. (2019). The main findings are summarised below.

Multi-pollutant models have not yet explicitly incorporated the potential interactions between groups of pollutants in quantifying their river export. The global multi-pollutant by Strokal et al. (2019) only considers point sources and, therefore, only interactions at the source. The empirical, continental WorldQual model does not appear to model different pollutants simultaneously and does not model the interactions. SWAT, a process-based model for river basins, does not consider the interactions either, but does explicitly model the effects of environmental factors such as temperature and oxygen. In each of the models, processes such as sorption are more or less implicitly incorporated. These may resemble or be of importance to the potential interactions from Chapter 2.

Existing water quality models can be integrated into a global model for river export of multiple pollutants as follows. I combined the global multi-pollutant model for point source inputs with the sub-basin approach and existing modelling approaches for individual pollutants. This results in a global model for river export of multiple pollutants. The existing modelling approaches for individual pollutants are from four water quality models: MARINA for nitrogen (N) and phosphorous (P), the Microplastics model for microplastics from personal care products, household dust, laundry textiles and tyre and road wear particles, Global TCS for triclosan (TCS) and GloWPa for *Cryptosporidium*. Each of these approaches are applied to sub-basins worldwide for point sources. As such, the modelling approaches of MARINA, the Microplastics model, Global TCS and GloWPa are modified to match the sub-basin approach and to match the spatial extent. The export fractions are calculated based on the retentions and losses of N, P, microplastics, TCS and *Cryptosporidium* in rivers, reservoirs and lakes and due to water consumption.

Two examples are given to demonstrate how retentions of pollutants are quantified in the global model for river export of multiple pollutants. The first example is on the retentions of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorous (DIP) in individual reservoirs and lakes. Throughout the world, the fraction of DIN retained in individual reservoirs and lakes with a volume of at least 0.5 $km^3$ is calculated to be lower than for DIP. The range for DIN is 0.0-0.85 for the individual reservoirs an lakes. Typically, the retention fraction for DIN is 0.4 or lower. In contrast, the fraction of DIP retained in reservoirs and lakes ranges 0.0-1.0, with relatively many reservoirs and lakes having a retention fraction of DIP that is higher than 0.8. The second example is about the fraction of pollutants retained in rivers. The example is for microplastics (Table 3.4). The global multi-pollutant model has 10,226 sub-basins. Among them, 82% are small (area $< 7500$ $km^2$) and 18% are large (area $\geq 7500$ $km^2$). Whereas the river retention fraction of microplastics from household dust, laundry textiles and tyre and road wear particles is 0.75 in small sub-basins, it is 0.9 in large sub-basins.

This chapter presents the design of a global model for river export of multiple pollutants. The model could aid in identifying hotspots, sources and impacts of multiple pollutants. As the global model for river export of multiple pollutants can model multiple pollutants simultaneously, interactions between these pollutants could potentially be incorporated.

# Chapter 4: Possibilities for incorporating interaction effects into global multi-pollutant modelling

## 4.1 Introduction

The aim of Chapter 4 is to provide an answer to Research Question 3 and 4 (RQ3 and RQ4, respectively):

*RQ3: Which model parameters of a global model for river export of multiple pollutants are associated with interactions between groups of pollutants?*

*RQ4: How can interaction effects be incorporated in a global model of river export of multiple pollutants?*

In Chapter 2, 11 types of potential interactions between five groups of pollutants are discussed. These five groups of pollutants are nutrients, hazardous solids, chemicals, pathogens and toxins. Descriptions and examples of these groups can be found in Chapter 2. The 11 interactions (A-K) are: a biofouling-dependent interaction of nutrients with hazardous solids (A1); sorption-dependent interactions of nutrients with hazardous solids (B1), hazardous solids with chemicals (B2), hazardous solids with pathogens (B3), and chemicals with pathogens (B4); a food web-dependent interaction of nutrients with hazardous solids (C1); light-dependent interactions between nutrients and hazardous solids (D1) and hazardous solids and pathogens (D2); a carbon cycle-dependent interaction between nutrients and chemicals (E1); toxic stress-dependent interactions between nutrients and chemicals (F1), chemicals and pathogens (F2), and pathogens and toxins (F3); a supply-dependent interaction between nutrients and pathogens (G1); an organic matter-dependent interaction between nutrients and pathogens (H1); a cyanobacteria-dependent interaction between nutrients and toxins (I1); a leaching-dependent interaction (J1); and a biomass dilution-dependent interaction between pathogens and toxins (K1). These interactions are further described in Chapter 2. In Chapter 3, the design of a global multi-pollutant model for river export is provided. This model includes the following pollutants: nitrogen (N), phosphorous (P) (nutrients), microplastics (hazardous solids), triclosan (TCS) (chemicals) and *Cryptosporidium* (pathogens). Chapter 4, then, is an exploration of the possibilities to incorporate the effects of the interactions as identified in Chapter 2 into the global multi-pollutant model as described in Chapter 3.

Chapter 4 is structured as follows. Section 4.2 will outline and explain the methods used to answer Research Question 3. Section 4.3 discusses how model parameters of the global model for river export of multiple pollutants could be associated with potential interactions (RQ3). Section 4.4 outlines possibilities for the incorporation of interaction effects in modelling (RQ4). Section 4.5 gives an illustrative example of how effects of an interaction (B2) might be quantified for TCS. In Section 4.6, the conclusions of Chapter 4 are presented.

## 4.2 Methodology

Chapter 4 builds on Chapter 2 and Chapter 3, both of which are primarily based on literature review. Chapter 2 is used to retrieve insights on the interactions between pollutants, whereas Chapter 3 gives insight in global multi-pollutant modelling. In this chapter, the findings of these chapters are used as a starting point of an exploration of how to integrate the two chapters. Research Question 3 is addressed by an assessment of which model parameters of the global model for river export of multiple pollutants designed in Chapter 3 could be affected by which of the interactions as identified in Chapter 2. Research Question 4 is addressed by the development of two possibilities as a starting point for including the effects of these interactions in the global model for river export of multiple pollutants.

## 4.3 Potential interactions and model parameters

The multi-pollutant model of Chapter 3 is designed to quantify river export of multiple pollutants. River export is quantified based on point source inputs of pollutants and fractions reflecting the retentions and losses of pollutants in rivers. Several retentions and losses of pollutants are included in the model. These are retentions and losses of N, P, microplastics, TCS and *Cryptosporidium* as a consequence of different processes in rivers as reflected by model parameter $L_{p.j}$, in reservoirs and lakes due to damming as reflected by model parameter $D_{p.j}$ and water consumption as reflected by model parameter $FQrem_j$ (Chapter 3). Interactions between N, P, microplastics, TCS and *Cryptosporidium* and their effects are not explicitly incorporated[15]. However, the interactions identified in Chapter 2 might affect these retentions and losses of pollutants in rivers.

For example, the occurrence of biofouling-dependent interaction A1 likely has consequences for the retention of microplastics. Both in freshwater and marine environments, biofouling has been reported to affect the retention of microplastics through its effects on the density and buoyancy[16] of the microplastics (e.g. Besseling et al., 2017; Hoellein et al., 2019; Kaiser et al., 2017; Kooi et al., 2017; Rummel et al., 2017). Biofouling might especially affect the retention of microplastic particles smaller than 50 μm (Besseling et al., 2017; Hoellein et al., 2019). For some plastic particle sizes (in between 5 to 10 μm), biofilm formation enhances retention from about 40% to 70%. However, for particles that are ≤ 2 μm, the presence of a biofilm reduces retention from 60-50% to 50-40% (Besseling et al., 2017). Thus, the retention of microplastics might increase or decrease as a result of biofouling-dependent interaction A1.

Among the model parameters, particularly $L_{p.j}$ and $D_{p.j}$ might need to be adjusted to take interactions into account. These parameters reflect retention and losses of pollutants due to processes in rivers, reservoirs and lakes. The interactions identified in Chapter 2 are or consist of processes occurring in rivers, reservoirs and lakes. Therefore, the interactions might affect retention and losses in rivers, reservoirs and lakes. In contrast, the other model parameter, $FQrem_j$, reflects how processes outside the river affect pollutant losses through water consumption. Because the interactions occur in rivers, reservoirs and lakes, and $FQrem_j$ reflects an influence from outside these rivers, reservoirs and lakes, I

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[15] The effects might be implicitly modelled, as part of the lumped retention parameters $L_{p.j}$ and $D_{p.j}$. In that case, the retention parameters are, however, not made dependent on the pollutants that interact with pollutant $p$. For example, the effects of the biofouling-dependent interaction (A1) may be incorporated in the retention parameters for microplastics. However, as it is not explicitly modelled, the retention parameters would remain equal despite changes in the nutrient levels in the sub-basin that may, through biofouling, affect the retention of microplastics.

[16] Ability to float

assume that the losses due to consumption ($FQrem_j$) are not affected by interactions. Thus, this section discusses how parameters $L_{p.j}$ and $D_{p.j}$ might need to be adjusted to account for the effects of interactions (Table 3.3).

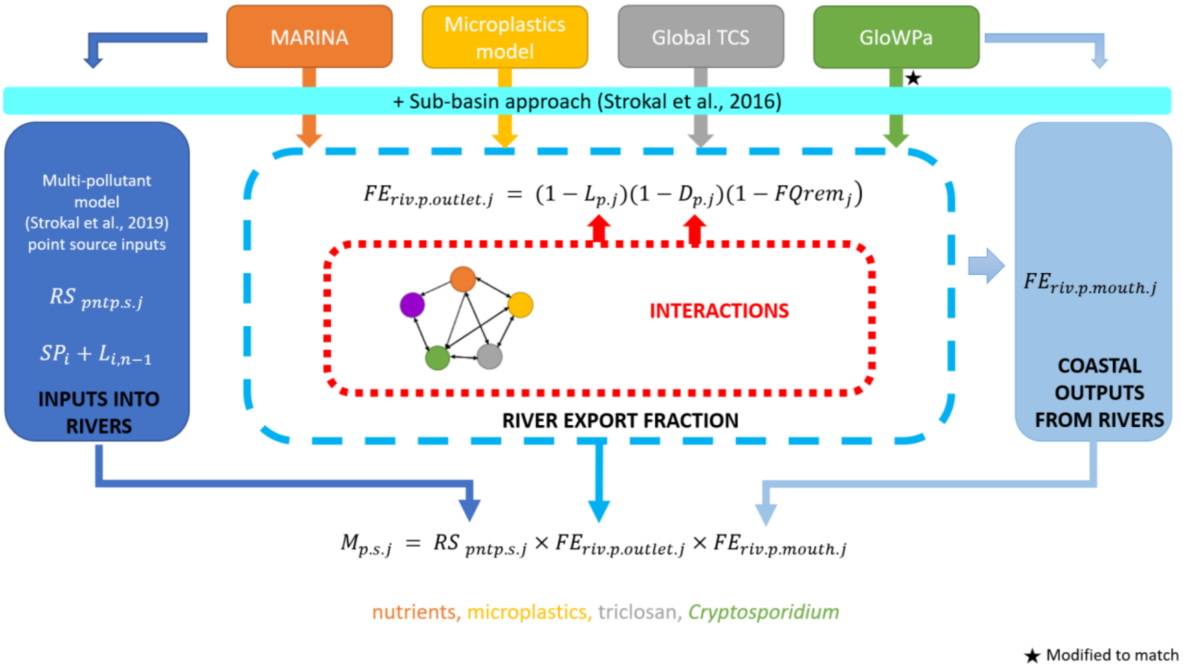

*Figure 4.1. The global multi-pollutant model of river export designed in Chapter 3 based on Strokal et al. (2019) with a focus on the model parameters might be affected by interactions between pollutants in rivers. The red arrows indicate which parameters might need to be modified to account for the effects of interactions between the pollutants (red box; as identified in Chapter 2). The multi-pollutant model is presented in Chapter 3 based on Strokal et al. (2019) and the sub-basin approach of Strokal, Kroeze, et al. (2016). It includes the approaches of the MARINA model (Model to Assess River Inputs of Nutrients to seAs) by Strokal et al. (2016) for nitrogen and phosphorous (nutrients), the Microplastics model by Siegfried et al. (2017) for microplastics (hazardous solid), the Global TCS (Global triclosan model) by van Wijnen et al. (2018) for triclosan (TCS) (chemical) and the GloWPa model (Global Waterborne Pathogen model) by Vermeulen et al. (2019) for Cryptosporidium (pathogen). The dark blue box represents pollutant inputs into rivers and is modelled by Strokal et al. (2019), whereas the light blue box represents the fraction of pollutants exported to the river mouth. The dotted-lined blue box represents (the computation of) river export fractions. The terms for the modelling of Cryptosporidium were altered from the original GloWPa model. The abbreviations and equations are explained in Chapter 3. Source: Chapter 3 and Section 4.3.*

Dissolved inorganic nitrogen (DIN) and phosphorous (DIP) are nutrients. Both retentions of DIN ($L_{DIN.j}$ and $D_{DIN.j}$) and DIP ($L_{DIP.j}$ and $D_{DIP.j}$) might, therefore, increase or decrease due to interactions that affect nutrients as a group. In Chapter 2, the following potential interactions are found to possibly affect nutrients: a sorption-dependent interaction with hazardous solids (B1), a light-dependent interaction with hazardous solids (D1) and a toxic stress-dependent interaction with chemicals (F1). These interactions might, therefore, have an effect on the retentions of N and P.

Microplastics are part of the pollutant group of hazardous solids. As such, $L_{MP.j}$ and $D_{MP.j}$ for microplastics might need to be adjusted for increases or decreases in retention of microplastics as a result of interactions identified in Chapter 2 that affect hazardous solids. The potential interactions that might affect hazardous solids are a biofouling-dependent interaction with nutrients (A1), three sorption-dependent interactions with nutrients (B1), with chemicals (B2) and with pathogens (B4), and a food web-dependent interaction with nutrients (C1).

TCS is part of the group of chemicals. Based on the interactions identified in Chapter 2, its retention, modelled as $L_{TCS.j}$ and $D_{TCS.j}$, might, therefore, be expected to increase or decrease due to interactions that affect chemicals. In Chapter 2, these interactions are two sorption-dependent interactions with hazardous solids (B2) and with pathogens (B4), a carbon cycle-dependent interaction with nutrients (E1) and a leaching-dependent interaction with hazardous solids (J1). The leaching-dependent interaction with hazardous solids, is, however, not expected to affect retention and associated model parameters $L_{TCS.j}$ and $D_{TCS.j}$. This is because this interaction concerns the secondary release of TCS in the river. It might thus be a potential source of TCS, rather than a retention factor.

*Cryptosporidium* is a pathogen. Retention of *Cryptosporidium* is represented by $L_{C.j}$, as described in Section 3.4.2 *Cryptosporidium* retention. Thus, $L_{C.j}$ could be increased or decreased to account for interactions affecting pathogens as identified in Chapter 2. These interactions include two sorption-dependent interactions with hazardous solids (B3) and with chemicals (B4), a light-dependent interaction with hazardous solids (D2), two toxic stress-dependent interactions with chemicals (F2) and toxins (F3), a supply-dependent interaction with nutrients (G1) and an organic matter-dependent interaction with nutrients (H1).

*Table 4.1. Model parameters in the global model for river export of multiple pollutants that quantify retentions and losses of pollutants in rivers and associated interactions between groups of pollutants.* $L_{p.j}$ *and* $D_{p.j}$ *are the fractions of pollutant p retained in or lost from rivers as a result of different processes (*$L_{p.j}$*, 0-1) and river damming (*$D_{p.j}$*, 0-1), which are, therefore, not exported to the river mouth. These retentions and losses are for the nutrient forms dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorous (DIP), microplastics (MP), triclosan (TCS) and Cryptosporidium (C). The potential interactions are identified in Chapter 2 (indicated by a code, as used in Chapter 2). The involved pollutant group is the group of pollutants that might have an interaction with the pollutant to which the model parameters belong. Based on Section 3.4 and Chapter 2.*

| **Model parameters for retentions and losses of pollutants** | **Potential interactions affecting retentions and losses of pollutants** | **Involved pollutant group** | **Code (Ch. 2)** |
|---|---|---|---|
| $\boldsymbol{L_{DIN.j}}$, $\boldsymbol{L_{DIP.j}}$, $\boldsymbol{D_{DIN.j}}$ and $\boldsymbol{D_{DIP.j}}$ | Sorption-dependent interaction | Hazardous solids | B1 |
| | Light-dependent interaction | Hazardous solids | D1 |
| | Toxic stress-dependent interaction | Chemicals | F1 |
| $\boldsymbol{L_{MP.j}}$ | Biofouling-dependent interaction | Nutrients | A1 |
| | Sorption-dependent interaction | Nutrients | B1 |
| | | Chemicals | B2 |
| | | Pathogens | B4 |
| | Food web-dependent interaction | Nutrients | C1 |
| $\boldsymbol{L_{TCS.j}}$ and $\boldsymbol{D_{TCS.j}}$ | Sorption-dependent interaction | Hazardous solids | B2 |
| | | Pathogens | B4 |
| | Carbon cycle-dependent interaction | Nutrients | E1 |
| $\boldsymbol{L_{C.j}}$ | Sorption-dependent interaction | Hazardous solids | B3 |
| | | Chemicals | B4 |
| | Light-dependent interaction | Hazardous solids | D2 |
| | Toxic stress-dependent interaction | Chemicals | F2 |
| | | Toxins | F3 |
| | Supply-dependent interaction | Nutrients | G1 |
| | Organic matter-dependent interaction | Nutrients | H1 |

## 4.4 Possibilities for incorporating interaction effects in global multi-pollutant modelling

Currently, the interactions between the different groups of pollutants in rivers have not been considered explicitly in the global model for point source inputs of multiple pollutants, SWAT, WorldQual and the design of the global model for river export of multiple pollutants (Chapter 3). This section considers the modifications that might be needed in order to take the potential effects of interactions on retentions and losses of pollutants in rivers to quantify their river export using a global multi-pollutant model (Chapter 3). Modelling approaches can range from very detailed, dynamic and process-based approaches that consider individual processes in rivers, to simple, lumped and statistical approaches that have a few model parameters to describe all processes combinedly (Kroeze et al., 2012). Interactions are, or consist of, various processes. As such, an approach that incorporates interactions into global models is at least partly process-based. However, more lumped modelling approaches may be convenient in data-sparse regions (Kroeze et al., 2012). Therefore, the possibilities for incorporating interactions into global multi-pollutant models may be partly process-based and partly statistical.

Two possibilities are identified to incorporate effects of interactions between groups of pollutants into models.

### 4.4.1 Possibility 1

Possibility 1 aims at modifying existing modelling approaches for retentions and losses of pollutants (Chapter 3) to include effects of interactions (Chapter 2). Different processes, such as sorption, sedimentation, and environmental factors as temperature and oxygen levels could serve as connecting bridges between groups of pollutants. As a result, the model parameters for retentions and losses of pollutants can be adjusted. For example, temperature could affect e.g. interactions that are sorption-dependent, carbon-cycle dependent and toxic stress-dependent (Interaction types B, E, and F, respectively. An advantage for global modelling of water quality is that this approach explicitly includes the processes and environmental factors that are relevant. Here, expert knowledge is highly needed to interpret the interactions and modify the model parameters accordingly. A disadvantage is that it involves bias in interpretations of the interactions for model parameters, requires the quantification of all, possibly complex, relevant processes and may require data to quantify the processes and include relevant environmental factors.

Possibility 1 is shown in a flow chart with examples of the processes and consequences of interactions for the retention of multiple pollutants (Figure 4.2). This flow chart displays the links between the interactions and certain processes or environmental factors. These processes or environmental factors, in turn, could be linked to the retention and losses of pollutants ($L_{p.j}$ and $D_{p.j}$). This could potentially include feedbacks. Figure 4.1 illustrates microplastics export in a river system in which N, P and TCS are present. Quantification and modelling of the interactions and their effects could be guided by such flow charts. A source for inspiration for incorporating interactions in this way may be the PCLake(+) model (Janse, 2005; Janssen et al., 2019). In the PCLake(+) model, nutrients and biota are connected through ecological processes as uptake, predation and mineralisation.

In Figure 4.2, I indicated some hypothetical consequences of processes in rivers, including those that are (part of) interactions. For example, I hypothesize that sorption of microplastics and nutrients and of microplastics and TCS decreases the river export of both microplastics and nutrients and of microplastics and TCS, respectively, as their density might increase due to sorption and retention might decrease as a consequence. Likewise, I hypothesize that increases in the consumption of nutrients by (micro)organisms decreases the river export of nutrients. Similarly, I hypothesize that the river export of microplastics will be reduced through the ingestion of plastics. In the example of Figure 4.2, the microplastics are of such a size that they are more likely to be retained in the river, because of the formation of biofilm on the microplastics (see Section 4.3). Sedimentation, too, decreases the export of microplastics (Siegfried et al., 2017). On the other hand, potential leaching of TCS from microplastics may increase the export of TCS from rivers (Figure 4.2). Further research and expert knowledge should be combined to confirm and quantify these effects.

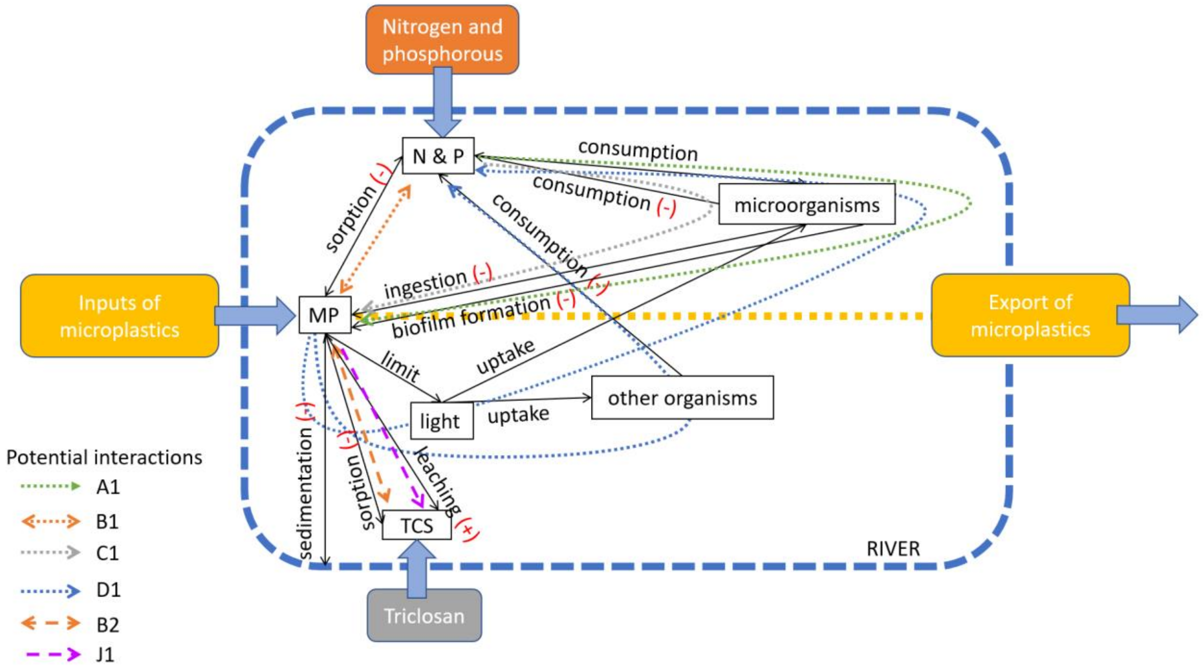

*Figure 4.2. Illustrative example of a flow chart of interactions (in the legend) between nutrients, microplastics and triclosan (TCS) and processes (here: sedimentation) in rivers that could affect the export of microplastics (MP). Interactions with nitrogen (N) and phosphorous (P) (nutrients) and TCS are displayed. (-) and (+) indicate examples of effects of the processes that are involved (black arrows) for the export of the pollutant (to which the arrow points) to the outlet of the river mouth. (-) indicates a potential decrease in the fraction of the pollutant (to which the arrow points) exported to the river mouth (retentions and losses in rivers are then increased). (+) indicates a potential increase in the fraction of the pollutant (to which the arrow points) exported to the river mouth (retentions and losses in rivers are then decreased). Potential interactions and their explanations are given in Chapter 2.*

## 4.4.2 Possibility 2

Possibility 2 aims at developing a new factor that reflects the effects of interactions. Such a factor could be developed using statistical methods for interactions between pollutants (see paragraphs below). This interaction factor could be added to existing modelling approaches. The interaction factor could be used to modify $L_{p.j}$ and $D_{p.j}$, depending on the levels of included pollutants. An advantage for global modelling of water quality is that it does not require quantification of all processes. Therefore, it is less detailed and less process-based than Possibility 1. A disadvantage for Possibility 2, however, is the lack of data for deriving these statistical methods. In addition, a risk for double counting in the retentions and losses of pollutants in rivers exists when using this factor together with already existing modelled retentions and losses. Double counting might occur, because this method presumes that $L_{p.j}$ and $D_{p.j}$ are quantified without containing part of the effects of the interactions already. Therefore, the values attributed to or equations used to estimate these retention and loss fraction might require re-evaluation. For example, sorption-dependent interactions (Interaction type B) may already be partially incorporated in $L_{MP.j}$ (Siegfried et al., 2017; Chapter 3). Likewise, the coefficients in Equation 4 for $L_{DIN,j}$ may need to be made dependent on the occurrence and effects of an interaction that affects DIN retention. The way in which interaction factors are incorporated in the model depends on the type of research available that could aid in quantifying effects of interactions between pollutants (e.g. statistical approaches or more process-based estimations).

I distinguish between Possibility 2a and 2b.

Possibility 2a combines individual types of interactions between two groups of pollutants e.g. microplastics and nutrients, microplastics and TCS (Figure 4.3). For Possibility 2a, "the statistical interaction approach" (p. 188) as used in multi-pollutant approaches in air quality research (Dominici et al., 2010) can be implemented. In air quality research, this approach is composed of statistical regression models that include both the general effects of the pollutant itself and an interaction factor for the effects of the interactions of each combination of the pollutant with another pollutant (Dominici et al., 2010). In air quality research, the effects mentioned are effects on human health. In the context of water quality modelling, I propose to adopt this approach as follows. Rather than effects on human health, I consider effects on pollutant retentions and losses in rivers, reservoirs and lakes, as reflected by model parameters $L_{p.j}$ and $D_{p.j}$. The existing modelling approaches for estimating $L_{p.j}$ and $D_{p.j}$ (Chapter 3) are adapted to also include the effects of each set of interactions that this pollutant has with another pollutant. That implies that, for example, the four different types of interactions between microplastics and nutrients (Chapter 2) are approached as one overall interaction between microplastics and nutrients. Likewise, the export of microplastics may be found to be affected by the levels of *Cryptosporidium* in the river without being able to address this to sorption-dependent interaction B3 or light-dependent interaction D2. Figure 4.3 displays how the export of microplastics may be considered to be affected by these and more interactions with this approach to quantify interactions. No distinction is made for the specific types of interactions involved. An alternative representation of Figure 4.3 is displayed in Appendix A.3 (Figure A.3.1).

Possibility 2b, in contrast, distinguishes individual types of interactions between two groups of pollutants. Thus, Possibility 2b looks at each of the four types of interactions between microplastics and nutrients (Figure 4.4). This might be a possibility if more research becomes available on the potential interactions identified in Chapter 2.

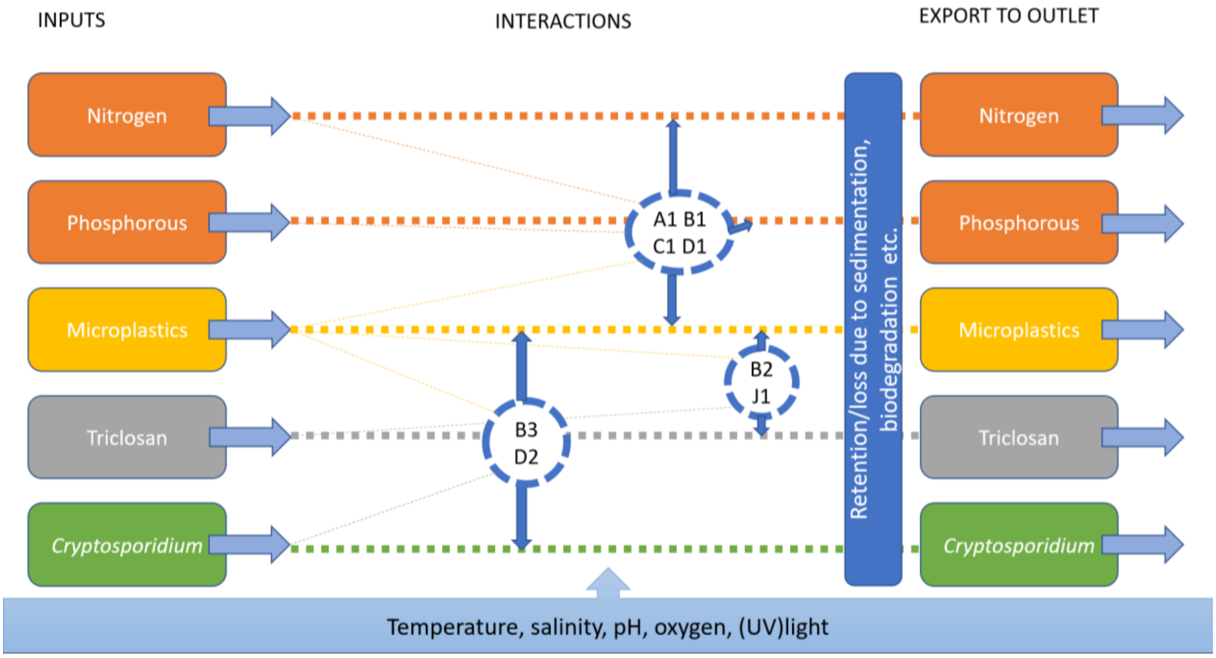

*Figure 4.3. Illustrative example of Possibility 2a to include interaction effects for river export of pollutants. For example, the export of microplastics to the outlet of a sub-basin j may be affected by interactions A1, B1, C1 and D1 with nutrients (nitrogen and phosphorous), interactions B2 and J1 with triclosan, and interactions B3 and D2 with Cryptosporidium. The interactions within a circle have indistinguishable effects. Each of the circles represents an interaction factor for microplastics. The inputs of the various pollutants might affect the extent to which the interactions affect the retention of microplastics. Additionally, the retention of microplastics is affected by sorption, sedimentation and biodegradation (van Wijnen et al., 2018). Source: Chapter 2, Chapter 3 and Section 4.3.*

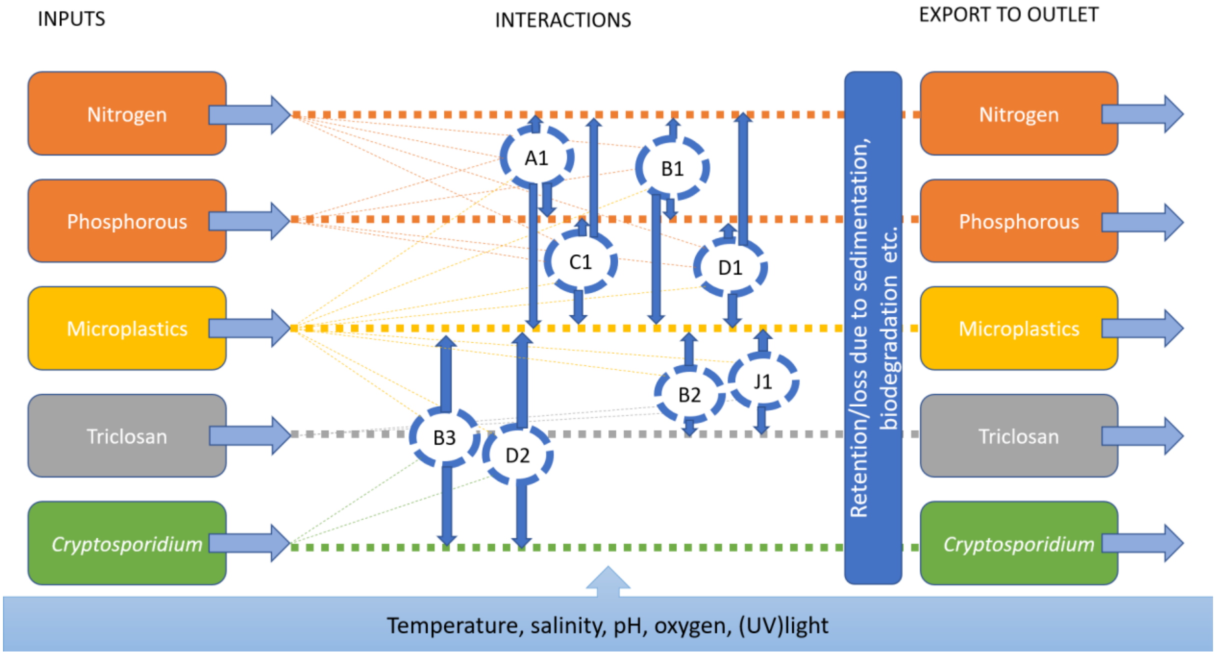

*Figure 4.4. Illustrative example of Possibility 2b to include interaction effects for river export of pollutants. For example, the export of microplastics to the outlet of a sub-basin j may be affected by interactions A1, B1, C1 and D1 with nutrients (nitrogen and phosphorous), interactions B2 and J1 with triclosan, and interactions B3 and D2 with Cryptosporidium. The interactions have distinguishable effects. Each of the circles represents an interaction factor for microplastics. The inputs of the various pollutants might affect the extent to which the interactions affect the retention of microplastics. Additionally, the retention of microplastics is affected by sorption, sedimentation and biodegradation (van Wijnen et al., 2018). Source: Chapter 2, Chapter 3 and Section 4.3.*

## 4.5 Illustrative example of interaction effects on river retention

This section provides an illustrative, hypothetical example of how interaction effects on river retention and losses could be quantified for TCS. TCS is part of the group of chemicals and its retention might, therefore, increase or decrease as a consequence of sorption-dependent interactions with hazardous solids and pathogens and a carbon cycle-dependent interaction with nutrients (Section 4.3). The sorption-dependent interaction of TCS with hazardous solids (B2) is calculated for a hypothetical basin to give an example of how interaction effects could potentially be calculated. No other interactions identified in Chapter 2 are considered in this example.

For this example, a hypothetical basin is used. In this basin of 4500 km$^2$, only sorption to polyethelene and organic matter occurs. The river basin has no dams or reservoirs (thus $D_{TCS}$ is not computed) and is not divided in smaller sub-basins, as it is relatively small. The water residence time is 1 day (maximum in Global TCS is 60 days for the largest rivers (van Wijnen et al., 2018)) and the salinity is 0.05%. First, it is explored what the effects of interaction B2 could be on retention of TCS ($L_{TCS}$). Subsequently, retention of TCS is calculated taking these effects into account.

Wu et al. (2016), conducting batch experiments, examine sorption of TCS to polyethylene (PE) particles with a size of 250 to 280 µm. They estimate the linear sorption coefficient to be 5140 L/kg at a salinity of 0.05% (Wu et al., 2016). In comparison, the sorption coefficient for dissolved organic carbon (75 mg/L in Aldrich humic acid) is estimated to be 776 L/kg. The sorption of TCS to PE is reduced when Aldrich humic acid is added, with TCS having a quite strong affiliation to Aldrich humic acid. However, the higher sorption coefficient for TCS to the plastic in comparison to the dissolved organic carbon might suggest that sorption to plastics dominates over sorption to dissolved organic matter.

For the purposes of this example, it is assumed that the different linear sorption coefficients represent the retention by sorption of TCS by polyethylene and organic matter. Sorption of TCS to other material does not occur in the hypothetical river. The loss rate of 0.06 h$^{-1}$ (this is 1.44 day$^{-1}$) as is used by van Wijnen et al. (2018) in Global TCS is assumed to cover diverse losses and retentions of TCS. However, of the sorption-related retentions, it is assumed that this loss rate only includes sorption by organic matter. About 19% of the loss rate is thought to be attributable to sorption and settling (Morrall et al., 2004). Thus a loss of about 0.01 h$^{-1}$ might be due to sorption of TCS to organic matter. A sorption coefficient of 776 L/kg would thus represent a loss rate of 0.01 h$^{-1}$, implying that a sorption coefficient of 5140 L/kg would represent a loss rate of 0.07 h$^{-1}$ due to sorption of TCS to polyethelene: 1.68 day$^{-1}$.

The residence time of TCS is estimated based on the river basin area and the water residence time (van Wijnen et al., 2018). Basins with an area smaller than 5000 km$^2$ are given a residence time of TCS that equalled the water residence time. The hypothetical basin is smaller. Thus, the residence time of TCS is set to 1 day. Now, the values of the parameters in Equation 5 for TCS retention are known (see Chapter 3 for equations).

$$L_{TCS} = 1 - e^{-k \times t_{res,TCS}} \qquad \text{(Eq. 10)}$$

Originally, this would be computed as:

$$L_{TCS} = 1 - e^{-1.44 \times 1.0} = 0.76$$

This includes sorption, but also other retentions and losses. Taking only sorption of TCS to hazardous solids (Interaction (*I*) B2) ($I_{TCS.B2}$) into account, it becomes:

$$I_{TCS.B2} = 1 - e^{-1.68 \times 1.0} = 0.81$$

Thus, $L_{TCS} = 0.76$ and $I_{TCS.B2} = 0.81$. Therefore, the total fraction retained and lost (including due to B2) in the river of this hypothetical basin becomes: $(L_{TCS} + I_{TCS.B2}) = 0.76 + 0.81 = 1.58$. However, as $(L_{TCS} + I_{TCS.B2})$ is constrained to a maximum of 1, it will be assigned this value. This suggests that TCS would not be exported from the basin and that interaction B2 contributes to the retention of TCS within the river. It should be emphasized that this illustrative example is hypothetical and that better ways to determine losses may exist.

## 4.6 Conclusions

The aim of chapter 4 is to provide an answer to Research Question 3 and 4: **Which model parameters of a global model for river export of multiple pollutants are associated with interactions between groups of pollutants (RQ3)?** and **How can interaction effects be incorporated in a global model for river export of multiple pollutants (RQ4)?** To formulate an answer to these research questions, findings from Chapter 2 and Chapter 3 are combined. Firstly, the model parameters might be affected by which potential interactions are identified. I considered the potential interactions between and the associated model parameters for nitrogen (N), phosphorous (P), microplastics, triclosan (TCS) and *Cryptosporidium.* Subsequently, two possibilities to account for interaction effects are suggested (RQ4).

Two model parameters in the design of the global model for river export of multiple pollutants might need to be adjusted to account for interactions between pollutants in rivers: $L_{p.j}$ and $D_{p.j}$ (RQ3). This is because these parameters reflect retentions and losses of pollutants in rivers ($L_{p.j}$), reservoirs and lakes ($D_{p.j}$). Such retentions and losses of pollutants in rivers, reservoirs and lakes might be affected by interactions between pollutants. Therefore, these model parameters, which are quantified to calculate river export of these pollutants, might need to be adjusted. Based on the interactions identified between pollutant groups (nutrients, hazardous solids, chemicals and pathogens) in Chapter 2, the parameters may need to be modified to account for these interactions. For example, parameters reflecting losses and retentions of TCS (chemical) might need to be adjusted to take into account sorption-dependent interactions with hazardous solids, pathogens and nutrients, and a carbon cycle-dependent interaction with nutrients. Parameters reflecting losses and retentions of microplastics (hazardous solid) might need to be adjusted to take into account a biofouling-dependent interaction with nutrients, sorption-dependent interactions with nutrients, chemicals and pathogens, and a food web-dependent interaction with nutrients. Parameters reflecting losses and retentions of N and P (nutrients) might need to be adjusted to take into account a sorption-dependent interaction and a light-dependent interaction with hazardous solids, and a toxic stress-dependent interaction with chemicals. The model parameter reflecting the decay of the pathogen *Cryptosporidium* might need to be adjusted to take into account sorption-dependent interactions with hazardous solids and chemicals, a light-dependent interaction with hazardous solids, toxic stress-dependent interactions with chemicals and toxins, and a supply-dependent and an organic matter-dependent interaction, both with nutrients.

Two possibilities are developed to incorporate the effects of interactions between pollutants in the design of a global model for river export of multiple pollutants (RQ4). Possibility 1 modifies existing approaches by quantifying retentions and losses in a more process-based way, in consideration of interactions between pollutants. As such, relevant interactions and associated processes are quantified in order to udate and replace existing model parameters. Possibility 2 builds on the existing modelling approaches, but adds a new, statistically determined interaction factor. Hence, Possibility 2 takes a more lumped approach. I distinguish Possibility 2a and 2b. Possibility 2a combines all the interactions between two pollutants, whereas Possibility 2b treats each of these as a separate interaction. Possibility 1 is challenging, because it requires the quantification of relevant processes, some of which are complex. Possibility 2 is less detailed than Possibly 1, because the relevant interactions do not need to be quantified individually. However, Possibility 2 risks the double counting of interactions and demands data to derive statistical methods. An hypothetical example to illustrate the quantification of interaction effects is given for sorption of TCS to polyethylene (PE), a plastic. Retention of TCS in a hypothetical river increased from 0.76 to 1.0 as a result of TCS sorption to PE (plastic). This increase in retention will thus lead to a decrease in river export of TCS to coastal waters.

This chapter presents the first step towards accounting for interaction effects in global modelling of river export of multiple pollutants by presenting a first attempt to link model parameters to interactions and by exploring possibilities for incorporating interaction effects in a global model for river export of multiple pollutants. This could aid in the further development of a method that integrates the modelling of multiple pollutants by considering the interactions between these pollutants. This could help to improve global modelling of water quality and thus facilitate the formulation of effective solutions.

# Chapter 5. Discussion, conclusion and future outlook

## 5.1 Introduction

The research objective of this thesis is:

*To identify interactions between groups of pollutants in rivers, and explore possibilities for the incorporation of these interactions in a global model for river export of multiple pollutants.*

Chapter 1 explains and justifies this research objective. Chapter 2 identifies interactions between groups of pollutants (RQ1). Chapter 3 looks into global modelling of river export of multiple pollutants (RQ2). Chapter 4 links Chapter 2 and Chapter 3 by exploring which model parameters of a global model for river export of pollutants could be affected by interactions (RQ3) and puts forward possibilities for incorporating interaction effects into global multi-pollutant modelling (RQ4). Figure 5.1 shows how Chapter 2, 3 and 4 are connected.

Chapter 5 reflects on whether and how this objective is achieved in this thesis. Therefore, Section 5.2 places this thesis in the context of other research and discusses the strengths and limitations of this thesis. Section 5.3 presents the conclusions of this thesis. Lastly, Section 5.4 describes the future outlook with recommendations for science and policy.

## 5.2 Discussion

### 5.2.1 Comparison with other studies

#### Potential interactions

In this thesis, an interaction is defined as: *"A particular way in which a (group of) pollutant(s) affects another"* (Appendix A.1, Figure A.1.1, Figure A.1.2). Other studies may define an interaction differently, in part depending on the scientific discipline that uses the term (Dominici et al., 2010). Whereas in the context of soil science, Ye et al. (2017) also imply the effects that pollutants biologically, physically and chemically have on each other, the term interaction in toxicology may refer to the combined effects of pollutants on the health of organisms (Cedergreen, 2014). The term interaction may be paired with the adjectives synergistic or antagonistic that describe the effect of this interaction (Piggott et al., 2015). I did not use this terminology, because I identified the interactions themselves rather than the effects of these interactions and the use of the terms synergistic and antagonistic may be confusing (Piggott et al., 2015). It may especially be confusing, because the implied effects could be effects on one or both pollutants and on pollutant retention or river export. I looked at both direct interactions (i.e. a pollutant has an effect on another pollutant without intermediate effects) and indirect interaction (i.e. a pollutant has an intermediate effect that, in turn, affects the other pollutant). Whereas Strokal et al. (2019) take interactions at the source into account, only the interactions in the river itself are considered in this thesis. The interactions in the various impacts of multiple pollutants could be assessed in further research. The Indicator of Coastal Eutrophication Potential (ICEP) is an example of an indicator of a combined effect of multiple nutrients (nitrogen (N), phosphorous (P), silica (Si)): coastal eutrophication (Billen & Garnier, 2007). The ICEP has been applied in models that quantify the river export of nutrients, such as the Global Nutrient Export from WaterSheds (Global NEWS) model (Seitzinger et al., 2010) and the MARINA model (Strokal, Kroeze, et al., 2016). Likewise, the combined effects of these and other pollutants could perhaps be indicated for, for example, coral reef health.

Nutrients, hazardous solids, chemicals, pathogens and toxins are the groups of pollutants between which interactions were identified in this thesis. I used these groups of pollutants and their names based on discussions with experts. However, these groups of pollutants may be named differently and/or may include other pollutants in other studies. Kroeze et al. (2016) and Strokal et al. (2019) use the same names as I did for nutrients, pathogens and chemicals. Plastics or plastic debris is the name for another group of pollutants that they both distinguish. Similarly, I attributed plastics to a different group than nutrients, pathogens and chemicals. However, I classified plastic as part of the hazardous solids group. I included nanoparticles as part of this group of pollutants. Strokal et al. (2019) treat nanoparticles as a distinct group. I discussed the wording for the groups of pollutants and the interactions with various experts. Nevertheless, some of the terms used in this thesis remain questionable. In particular, the use of ‘chemicals’ as group name might be subject to debate as it may refer to any substance. I defined chemicals as manmade organic chemicals that are not nutrients or hazardous solids. Possibly, one could instead distinguish e.g. industrials, pesticides and PPCPs (pharmaceuticals and personal care products) as groups of pollutants as Murray et al. (2010) do.

Likewise, the names used for the interactions could be up for further debate. I chose to reflect the dependency of an interaction on a certain factor, substance or process (e.g. biofouling) and assigned names accordingly (e.g. biofouling-dependent interaction). Another way in which the interactions could be classified is on the basis of whether they are primarily biological, chemical or physical (Kroeze et al., 2016). However, it might be difficult to establish this classification, because the interactions may depend on multiple processes and may be e.g. biological and chemical, or chemical and physical.

This thesis provides a comprehensive overview of interactions between each of the pollutant groups of nutrients, hazardous solids, chemicals, pathogens and toxins in rivers. Nevertheless, other reviews of interactions between pollutants in rivers exist. Koelmans et al. (2001), for example, list interactions between eutrophication and contaminants. These interactions are also included in the review presented in this thesis, grouped within the carbon cycle-dependent interaction between nutrients and chemicals (E1) and otherwise included through the toxic stress-dependent interaction between nutrients and chemicals (F1). The carbon cycle-dependent interaction between nutrients and chemicals is also indicated by Kroeze et al. (2016), who further mention the sorption-dependent interaction between hazardous solids and chemicals (B2). Interactions of the pollutant groups with environmental factors as temperature, oxygen, salinity and streamflow, for example indicated by Kroeze et al. (2016) and Strokal et al. (2019), and bedrock,[17] were not explicitly considered in this thesis. Additionally, interactions may have effects on other interactions. For example, the formation of biofilm onto hazardous solids such as microplastics (A1) could potentially increase or decrease the sorption of chemicals as hydrophobic organic chemicals and antibiotics on these hazardous solids (B2) (Rummel et al., 2017; Wunder et al., 2011). These factors and indirect effects could perhaps be considered more explicitly in further development of the overview. Some studies are completely dedicated to interactions between two substances or pollutant groups (e.g. Ravichandran (2004); Jia (2018)). Interactions within pollutants of the same group are also analysed (Kroeze et al., 2013). This hints at the complexity of the interactions that this thesis provides an overview of.

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[17] One expert mentioned that the type of bedrock (e.g. rock, sand, silt, clay) of the river may also be relevant to consider.

Interactions are also examined in other disciplines. In toxicology, for example, some studies assess the effects of mixtures of pollutants on the toxicity of these pollutants (Cedergreen, 2014). However, these studies focus on the interactive effects of pollutants on health, and at a different scale. For global surface water quality modelling, in contrast, interactions between pollutants in rivers are in this thesis primarily considered for their effects on retention and losses of pollutants in rivers (during river transport) for the improvement of global water quality models.

## Water quality models

This thesis reviews SWAT, WorldQual and the global model for point source inputs of multiple pollutants. Reviews of these and more water quality models exist (e.g. Tang et al. (2019); Kroeze et al. (2016)). The review in this thesis builds on Strokal et al. (2019), who compare their global multi-pollutant model for point source inputs to WorldQual. In this thesis, SWAT was also included to cover for one more multi-pollutant model and a different spatial scale.

This thesis continues with the model of Strokal et al. (2019) and their framework for further elaboration of the model. Therefore, the approaches of water quality models such as the MARINA (Strokal, Kroeze, et al., 2016), Microplastics (Siegfried et al., 2017), Global TCS (van Wijnen et al., 2018) and GloWPa (Vermeulen et al., 2019) models are combined in the design of a model that quantifies river export of representatives of four groups of pollutants: nitrogen (N), phosphorous (P) (nutrients), microplastics (hazardous solids), triclosan (TCS) (chemicals) and *Cryptosporidium* (pathogens). Another, global, version of the Microplastics model has recently been published (van Wijnen et al., 2019). This model is called the Global Riverine Export of Microplastics into Seas (GREMiS) (Van Wijnen et al., 2019). Some alterations to the approach of Siegfried et al. (2017) are made in GREMiS. For example, modifications are performed regarding the sources of microplastics. The fragmentation of macroplastics is included in GREMiS as a source of microplastics and found to be the source of most microplastics in rivers (van Wijnen et al., 2019). However, losses and retentions of microplastics are quantified with the same approach as Siegfried et al. (2017), albeit at a global scale. Therefore, the main model parameters considered in Chapter 3 and 4 remain unaltered.

Other global models quantifying the river export of multiple pollutants exist. Examples are the Global NEWS model (Mayorga et al., 2010; Seitzinger et al., 2010) and the Integrated Model to Assess the Global Environment - Global Nutrient Model (IMAGE-GNM) (Beusen et al., 2015). Both Global NEWS and IMAGE-GNM quantify river export of N and P. However, these are the only pollutants that are explicitly considered in IMAGE-GNM (Beusen et al., 2015; Beusen et al., 2016). Though Global NEWS considers some interactions, with carbon and silica, Global NEWS does not model pollutants from other groups of pollutants and does not explicitly incorporate interactions with pollutants from other groups (Mayorga et al., 2010; Seitzinger et al., 2010). Global NEWS uses a few parameters that reflect the effects of multiple processes on nutrient retention. In contrast to Global NEWS, IMAGE-GNM explicitly considers biogeochemical processes that affect nutrient retention and uses a nutrient spiralling approach (Beusen et al., 2015; Beusen et al., 2016; Kroeze et al., 2016). Such an approach considers nutrient cycles and takes into account that these do not occur at a certain place in the river, but that the nutrients are deposited downstream during these cycles (Newbold et al., 1981). Another water quality model that explicitly takes biogeochemical processes into account, is the food-web model PCLake+ (Janssen et al., 2019). This model, with potential for global application, is process-based and explicitly models the implications of biogeochemical processes and ecological interactions for lake water quality. For example, the model considers oxygen, (ratios of different) nutrients, water flow and diverse organisms in relation to processes such as predation, mineralisation, lake stratification and nutrient uptake (Janssen et al., 2019). PCLake+ may, therefore, provide some useful insights for further development of the global multi-pollutant model for river export described in Chapter 3. The global model for river export of multiple pollutants designed in this thesis offers an opportunity for the incorporation of effects of interactions between pollutants from different groups of pollutants (Chapter 3 and 4).

This thesis identifies the model parameters that might be affected by interactions between different pollutant groups and explores two possibilities for the incorporation of the effects of these interactions in global multi-pollutant modelling of river export. I consciously refer to the incorporation of interaction effects, rather than the incorporation of interactions, to acknowledge that models might not incorporate the full details of an interaction itself, but could quantify the effects of this interaction. Several studies indicate the need to consider interactions in global scale multi-pollutant modelling of river export (e.g. Kroeze et al. (2016, 2013); Strokal et al. (2019)), yet these studies do not seem to explicitly address model parameters that could be affected by interactions or the possibilities for the potential development of a method to incorporate interaction effects. This thesis presents a first tentative answer to the call of these studies.

### 5.2.2 Strengths of this thesis

The main strengths of this thesis are the novelties that this thesis presents (Figure 5.1). These novelties contribute to a better understanding of potential interactions between groups of pollutants and how these interactions could possibly be incorporated in global multi-pollutant modelling of river export. Improved understanding of interactions and of modelling interactions is a step towards a more intergrated modelling of multiple pollutants and gives a point of reference for further studies. There are four main achievements of this thesis.

Firstly, an overview of 11 types of potential interactions between groups of pollutants in rivers is provided in Chapter 2 (Figure 5.1). This overview of potential interactions between groups of pollutants contributes to a better understanding of these interactions and could function as a starting point for more research on these and other interactions. By clustering pollutants into groups, a greater array of interactions could be considered. Interactions were identified between specific pollutants that each are part of a group. By dealing with the pollutants as part of groups, suggestions are thus made for hypothetical interactions between other pollutants of the same groups that are not yet supported by literature. Therefore, the overview provided in Chapter 2 provides various hypothetical interactions that could be tested with further research. Both expert judgement and scientific literature were combined in developing this overview. As experts have experience in the field of research, their judgement was valuable in providing a starting point to review the potential interactions occurring between groups of pollutants in rivers. This starting point was vital and a source of credibility for the development of the overview of interactions between five groups of pollutants, because I have not encountered other overviews of interactions between all five groups in relation to global water quality modelling even though numersous scientific articles might relate to these interactions.

Secondly, a new design for a global model for river export of multiple pollutants is presented in Chapter 3. This model is based on the global model for point source inputs of multiple pollutants by Strokal et al. (2019) and existing modelling approaches for nutrients, microplastics, TCS and *Cryptosporidium*. The use of existing water quality models ensures that input data is fairly readily available and differences between the multi-pollutant approach with a single pollutant approach are relatively easily observable. The model could contribute to the identification of hotspots, sources and impacts of multiple pollutants globally. Moreover, this model could be used as a basis for a more integrated model that takes effects of interactions between multiple pollutants into account.

Thirdly, a first attempt is made to link interactions to model parameters reflecting retentions and losses of pollutants in rivers in global multi-pollutant modelling approaches in Chapter 4 (Figure 5.1). Linking interactions to these model parameters opens an opportunity to quantify the effects of interactions on river export of multiple pollutants. The model parameters considered here are derived from existing modelling approaches as implemented in the global model for river export of multiple pollutants (from Chapter 3). The links between the model parameters and the interactions identify what interaction effects could be relevant to consider for the modelling of N, P, microplastics, triclosan and *Cryptosporidium*.

Fourthly, two possibilities for incorporating interactions in global multi-pollutant modelling of river export are explored (Figure 5.1). The possibilities that are outlined in this thesis could form a beginning of the development of more elaborated methods to incorporate interaction effects in global multi-pollutant modelling of river export. Interaction effects could be incorporated in such models by adapting existing modelling approaches to explicilty reflect interactions and associated processes (Possibility 1). Alternatively, interaction effects could be incorporated by adding a statistically determined interaction factor that accounts for interactions between pollutants (Possibility 2). Depending on the amount of data available and knowledge on the interactions, one or both of these possibilities could be further developed.

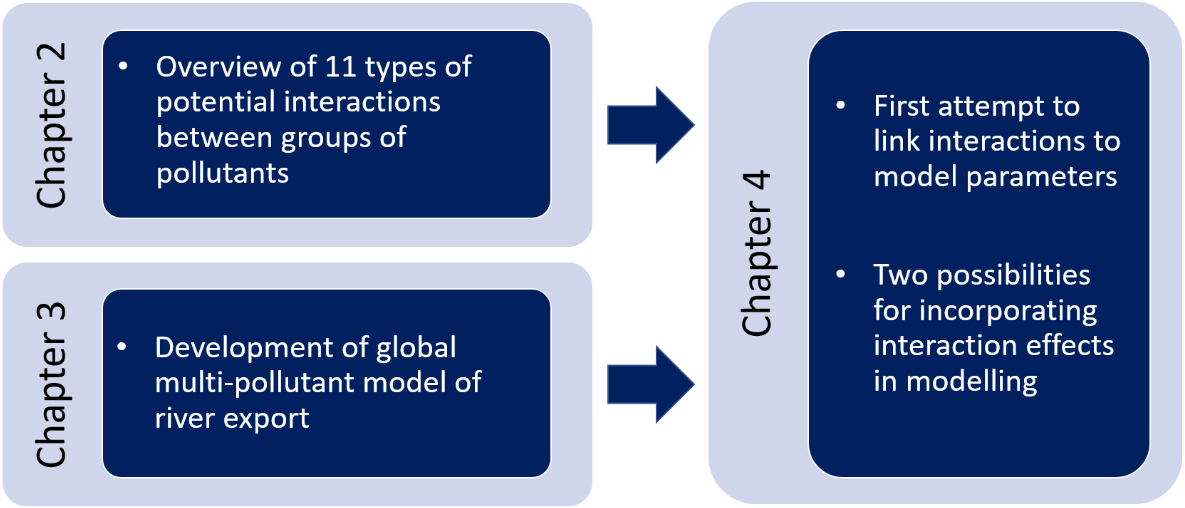

*Figure 5.1. The achievements of this thesis per chapter. The arrows indicate how the chapters are connected: Chapter 2 and Chapter 3 provide the basis for Chapter 4.*

### 5.2.3 Limitations of this thesis

Despite the achievements of this thesis, various limitations of this thesis can be distinguished in relation to the interactions and modelling.

#### Potential interactions

This thesis explores interactions between different groups of pollutants in rivers. That excludes the interactions between pollutants within the same group of pollutants (i.e. interactions among nutrients), and interactions of pollutants in their common sources and various impacts. The identification of interactions between groups of pollutants in Chapter 2 is first and foremost likely to have been affected by confirmation bias. That is, interactions that were previously identified by experts were more likely to be included in the literature review than interactions that were not mentioned. This occurred because discussions with experts formed a basis for further literature research to support the interactions that were identified. Similarly, once an interaction was identified, this interaction was more likely to be confirmed rather than to be refuted[18]. Nevertheless, even though an abundance of literature may relate to the interactions, I did not encounter other reviews on the interactions between all five groups of pollutants. Therefore, the overview of identified potential interaction between groups of pollutants as presented in Chapter 2 remains useful as a starting point for further research.

Several other limitations related to the identification of interactions can be identified. Firstly, no strict distinction is made that determines which interactions are 'interaction' enough to be included. Some interactions are indirect and pollutant retention may be more significantly affected by other factors. This questions when and whether pollutant groups can still be said to interact with each other. The relevance of the incorporation of indirect interactions in modelling could consequently be challenged. Another limitation follows: the lack of consideration of the actual effect of an interaction. Some of the potential interactions identified in Chapter 2 might be much more relevant to include than others. The lack of consideration stems from a focus on the identification of interactions and potential ways in which global models could consider these. Interactions may be site-specific. That is, interactions may occur in certain parts of the world or certain river basins, but not in others. Some interactions may also be more prevalent in lakes than in rivers (Section 2.5), for example. The prevalence and relevance of interactions between pollutants in a certain environment requires more attention in further studies. The discussion on whether some interactions are at all relevant to include is, therefore, left for further scientific debate. Likewise, the terms used in this thesis for the groups of pollutants, e.g. 'chemicals', and interactions, e.g. 'supply-dependent', may be subject to further scientific debate. In addition, not all potential interactions between the groups of pollutants may have been identified. Many factors and processes could affect the interactions. As such, many uncertainties exist regarding the nature of interactions and their effects on pollutant retention. Each of these limitations reinforce the need of an overview as provided in Chapter 2 as an hypothesis of potentially important interactions between groups of pollutants in rivers.

Another limitation concerns the reproducibility of the review. The review, expert panel session and interviews were conducted unstructuredly, because research on interactions does not seem to maintain a strict terminology and to maintain a more open approach. In addition, for both the interactive panel session and the expert interviews, the discussion itself was only noted and not recorded. This decision was in line with the preferences of the experts and allowed for more open discussions. Thus, the lack of transparency with which the review, panel session and interviews were conducted could temper with the reproducibility of identification of interactions between groups of pollutants. However, a more open-minded approach to potential interactions may have been achieved as a consequence. Perhaps, in contrast to a more structured approach, a wider range of potential interactions was identified as a consequence.

### Water quality models

In relation to the review of existing multi-pollutant models in Chapter 3, a limitation can be identified regarding the selection of models to be included. Only three models were included (SWAT, WorldQual, global model for point source inputs of multiple pollutants), in contrast to other reviews of water quality models (Section 5.2.1). Consequently, some multi-pollutant models that might consider interactions may have been excluded. The three models were selected, because this allowed for the analysis of multi-pollutant models at differing spatial extents (i.e. river basin, continental, global). The models each have a different spatial resolution and temporal extent and resolution.

Existing water quality modelling approaches were modified to model multiple pollutants simultaneously on a sub-basin scale with a yearly time-step. These modifications imply that the modelling approaches discussed in Section 3.4.2 should be re-evaluated for their use at sub-basin scales. Changes to the input

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[18] Perhaps in part because research that confirms a certain (part of an) interaction might also be more likely to be published (publication bias).

data may be required. For example, the modelling approach for *Cryptosporidium* is adapted from the approach of the GloWPa model (Section 3.4.2). To quantify yearly *Cryptosporidium* river exports, the monthly input data for GloWPa should first be converted into yearly data.

The model elaborated from Strokal et al. (2019) (see Chapter 3 for the design) has shortcomings regarding its potential for the incorporation of interaction effects. The temporal and spatial scale might namely not be sufficiently detailed to consider interactions appropriately. For example, the levels of one pollutant may be high in the river in spring, but not in autumn. If for another pollutant the reverse is true, these pollutants are rather unlikely to interact to the extent that yearly data might suggest. Similarly, the spatial output resolution of the sub-basin might be too coarse to estimate the effects of interactions between pollutants in the same sub-basin appropriately. These and other uncertainties regarding the interactions and the incorporation of their effects into models should be addressed. Thus, even when more research is available, incorporating interaction effects into global multi-pollutant modelling may be challenging. Additionally, I assume that the interactions are not affecting consumptive water use $(FQrem_j)$. Therefore, $FQrem_j$ would not need to be modified to account for interactions. However, one might imagine that the use of severely polluted surface water decreases if cleaner groundwater is available.

In relation to the incorporation of interactions into global multi-pollutant modelling, I briefly discussed different modelling approaches (i.e. process-based and statistical) in Chapter 4. I suggest that the modelling of interactions between pollutants in global models may be partly process-based and partly statistical. Of the two possibilities, Possiblity 1 is more process-based and therefore requires more explicit quantification of relevant processes. Possibility 2 is more statistical, thus, empirical data is needed for this possibility. For a more elaborate discussion of modelling approaches concerning the river export of pollutants (nutrients in particular), see Kroeze et al. (2012).

The major limitation regarding the exploration of possibilities to include interaction effects is the lack of research used to support the possibilities that were outlined. Hardly any research explicitly discusses how to incorporate effects of interactions between multiple pollutants in global water quality modelling. However, air quality studies (e.g. Dominici et al., 2010), as Kroeze et al. (2013) also suggested, and toxicological studies (e.g. Cedergreen, 2014) might offer some insight into multi-pollutant modelling. Further research could explore the applicability of multi-pollutant models from other disciplines for multi-pollutant modelling of river water quality.

## 5.3 Conclusion

**Eleven different types of potential interactions are identified between the following groups of pollutants in rivers: nutrients, hazardous solids, chemicals, pathogens and toxins (RQ1).** An interaction is defined as: *"A particular way in which a (group of) pollutant(s) affects another"*. Types of interactions are classified from A-K. Interaction A is biofouling-dependent, with an interaction between nutrients and hazardous solids (A1). Interaction B is sorption-dependent and occurs between nutrients and hazardous solids (B1), hazardous solids and chemicals (B2), hazardous solids and pathogens (B3), and chemicals and pathogens (B4). Interaction C is food web-dependent and is identified between nutrients and hazardous solids (C1). Interaction D is light-dependent and occurs between nutrients and hazardous solids (D1) and hazardous solids and pathogens (D2). Interaction E is carbon cycle-dependent and occurs between nutrients and chemicals (E1). Interaction F is toxic stress-dependent and is identified between nutrients and chemicals (F1), chemicals and pathogens (F2), and pathogens and toxins (F3). Interaction G is supply-dependent, with an interaction between nutrients and pathogens (G1). Interaction H is organic matter-dependent and identified between nutrients and pathogens (H1). Interaction I is cyanobacteria-dependent, occurring between nutrients and toxins. Interaction J is leaching-dependent, between hazardous solids and chemicals (J1). Interaction K is biomass dilution-dependent, occurring between pathogens and toxins (K1). These biological, physical and chemical interactions are influenced by environmental factors as temperature, oxygen and light.

**A design for a global model for river exports of multiple pollutants combines modelling approaches for individual pollutants (RQ2).** I synthesised modelling approaches for individual pollutants into a design for a global model for river export of multiple pollutants. I did this based on the first published global model for point source inputs of multiple pollutants. I included retentions of pollutants in rivers at the sub-basin scale. The resulting model is able to annually quantify river export of nitrogen (N), phosphorous (P), microplastics, triclosan (TCS) and *Cryptosporidium* from point sources. The model includes the fractions of pollutants that are exported to the outlet of sub-basins and to the river mouth. These factions reflect losses and retentions of pollutants in rivers, reservoirs and lakes and consumptive water use.

**A first attempt is made to link interaction effects to model parameters in a global model for river export of multiple pollutants (RQ3).** Interactions may affect (i.e. increase or decrease) retentions and losses of pollutants in rivers. The model parameters that describe these retentions and losses in rivers, lakes and reservoirs thus may need to be adjusted to reflect these changes. Based on the identified potential interactions between pollutant groups, model parameters on retention and losses of N, P (nutrients), microplastics (hazardous solids), TCS (chemicals) and/or *Cryptosporidium* (pathogens) may need to be adjusted to account for the following types of interactions between nutrients, hazardous solids, chemicals and pathogens: sorption-dependent interactions, light-dependent interactions, toxic stress dependent interactions, a biofouling-dependent interaction, a food web-dependent interaction, a carbon cycle-dependent interaction, a supply-dependent interaction and an organic matter-dependent interaction. The associated model parameters for each pollutant are linked to these interactions accordingly.

**Two possibilities are developed to incorporate interaction effects in a global model for river export of multiple pollutants (RQ4)**. Possibility 1 aims to modify existing modelling approaches for retentions of pollutants taking a more process-based approach. This implies that relevant interactions are quantified in such a way that existing model parameters for retentions and losses can be updated. These parameters are then included in global modelling for river export of multiple pollutants instead of the original model parameters. Possibility 2 aims to add a statistically determined interaction factor that accounts for interaction effects to existing modelling approaches and thus has a more lumped, statistical approach.

Possibility 2 is divided into option a and option b. Possibility 2a is to determine an interaction factor between pollutants without specifying the interactions between these pollutants. Possibility 2b is to determine an interaction factor between pollutants that distinguishes between different interactions that occur between these pollutants. Possibility 1 is challenging because it requires the quantification of relevant processes. Possibility 2 in contrast, does not demand for detailed knowledge and quantification of the interactions themselves, but risks double counting of interactions. In addition, Possibility 2 may be challenged by a lack of data for deriving statistical methods.

## 5.4 Future outlook

### Recommendations for science

This thesis contributes to the body of literature on global surface water quality modelling with new insights into interactions between pollutants in rivers. These interactions could be relevant to consider in modelling. This thesis presents an overview of interactions, a design for a global model for river export of multiple pollutants, attempts to link parameters of this model to interactions and two possibilities for incorporating interaction effects on retention in global modelling of river export of multiple pollutants (Section 5.2.2). Altogether, this forms a starting point for the incorporation of interaction effects into global models for river export of multiple pollutants. This thesis may, therefore, be used as a basis for further research on interactions between pollutants of different pollutant groups in rivers, the effects of these interactions and the incorporation of their effects into global water quality models. Global water quality models can presumably be improved by incorporating the effects of interactions between pollutants in rivers. Multiple pollutants are then linked to each other through their sources and their interactions in the river. As a result, such models may more accurately identify hotspots of multiple pollutants, their sources and their impacts.

To develop a global model for river export of multiple pollutants that takes interactions between these pollutants into account, I recommend the following. The first recommendation is to identify relevant interactions from the overview presented in this thesis and their interaction effects for the global modelling of river export of multiple pollutants. Preferably, these interactions have demonstrated effects on the retention of included pollutants. The second recommendation is to further develop a method for the incorporation of interaction effects on pollutant retentions in rivers in global modelling based on the two possibilities presented in this thesis. This method could then be used to incorporate effects of relevant interactions in a global model for river export of multiple pollutants. The method could first be developed and demonstrated for one relevant interaction. Other interactions could be modelled accordingly. The quantification of interactions should be kept relatively simple to be able to apply the model in data-sparse regions, but scientifically plausible. The third recommendation is to validate the model. The model outputs could be compared to case study data and output data from other models. Model outputs could be compared to output data of MARINA, the Microplastics model, Global TCS and GloWPa to reflect on whether the interactions are appropriately addressed. A sensitivity analysis could be conducted to address uncertainties. The model could be improved accordingly. The fourth recommendation is to conduct further research that assesses more interactions (e.g. with other pollutants, between interactions, in the drivers and impacts of pollutants), relevant factors (e.g. temperature, oxygen) and modelling approaches. Multi-pollutant modelling approaches as used in air quality and toxicological models could offer useful insights for the modelling of interactions between multiple pollutants.

## Recommendations for policy

Effective management solutions for pollution issues could be explored with the use of global models for river export of multiple pollutants that take effects of interactions between pollutants into account. Hotspots, sources and impacts of multiple pollutants can then be identified more accurately and might, therefore, be more appropriately addressed and managed. Reducing the inputs of one pollutant might increase or decrease the river export of pollutants that this pollutant interacts with at the source and in the river. A multi-pollutant approach that considers interactions could account for such effects. Knowledge of interactions and their effects could thus aid in identifying effective solutions for water quality problems. This will contribute to the achievement of Sustainable Development Goal 6 of the United Nations: *Clean Water and Sanitation*.

As the next step for policy regarding the management of pollution, I recommend to monitor more pollutants and to increase the frequency and extent of pollutant monitoring in rivers, if possible. Monitoring helps to identify and manage pollutant problems and their sources. The monitoring data could also give more insight into the interactions in rivers. Furthermore, the data could improve the modelling accuracy of water quality models, which, in turn, could aid in finding effective management solutions. This helps to achieve improvements in water quality.

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# Appendices

## Appendix A.1. Interaction terminology

In this thesis, the word *"interaction"*[19] refers to an influence that one pollutant or pollutant group (directly or indirectly) has on another pollutant. An interaction is here defined as: *"A particular way in which a (group of) pollutant(s) affects another."* This is explained in the following sections.

In the Oxford Online Dictionary[20], an interaction is defined as a: *"Reciprocal action or influence."* This definition is then further specified as *"Communication or direct involvement with someone or something"* or *"A particular way in which matter, fields, and atomic and subatomic particles affect one another, e.g. through gravitation or electromagnetism."* As this thesis is focused on interactions between (groups of) pollutants, the latter definition (from physics) seems most applicable. Based on these definitions, an interaction is in this thesis defined as: *"A particular way in which a (group of) pollutants affects another."*

Pollutant (groups) p1 and p2 may have an reciprocal influence on each other. Thus, pollutant p1 and p2 may interact. The interaction is then still a 'black box' and this is where the definition used for this thesis differs from the original definition. This reciprocal influence may namely occur through interaction *a*, but also through interaction *b* and *c* (see Figure A.1.1). As *a*, *b* and *c* together describe the interaction that pollutant p1 and p2 have with each other, *a*, *b* and *c* are – in this thesis – described as interactions (even though they may not affect both pollutants).

Thus, whereas an interaction is originally defined as an reciprocal action or influence, the use of the word *"interaction"* in this thesis refers to an influence that one pollutant (directly or indirectly) has on another pollutant. Taken together, these interactions (e.g. *a*, *b* and *c*) may (but need not) constitute a reciprocal effect of two pollutants on each other, though this may not occur through the same type of influence: Pollutant p1 may affect pollutant p2 through interaction *a* and *b*, whereas pollutant p2 may affect pollutant p1 through interaction *c*. An example is given in the next section.

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[19] The meaning of the word "interaction" differs between disciplines. For a short discussion on other interpretations, see Dominici et al. (2010).

[20] https://en.oxforddictionaries.com/definition/interaction

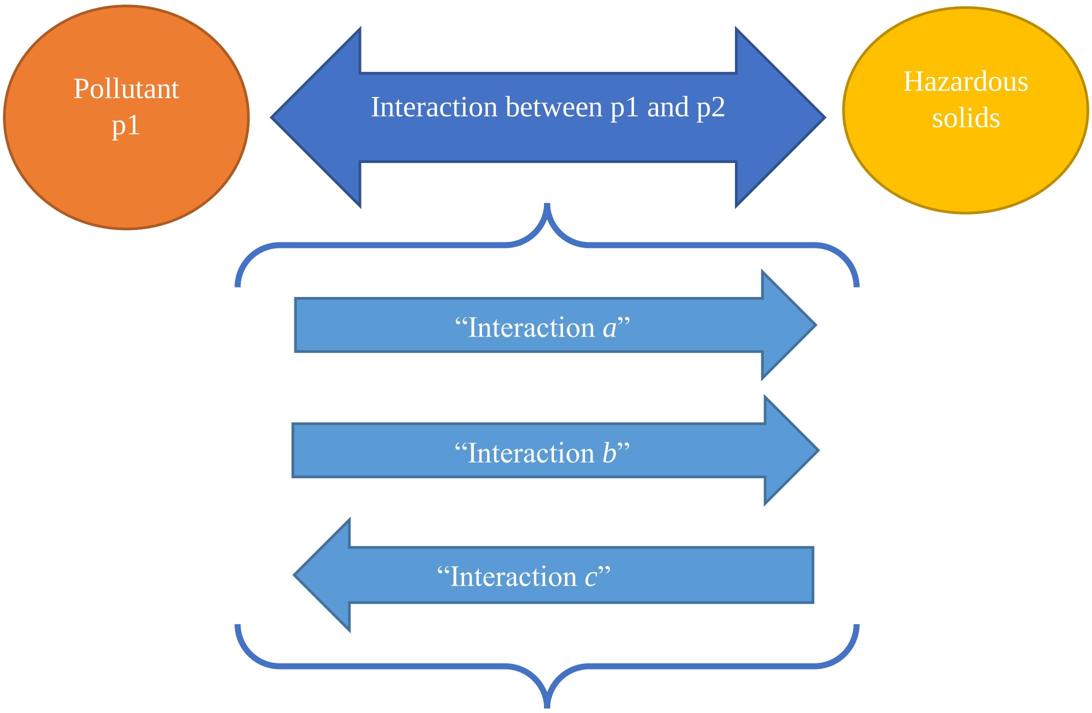

*Figure A.1.1. Interactions between (groups of) pollutants p1 and p2. A potentially mutual influence (Interaction between p1 and p2; double arrow) may be constituted of multiple ‘interactions’ (a, b and c; single arrows, but potentially also double arrows, e.g. for sorption), here defined as: “A particular way in which a (group of) pollutants affects another.” These are influences of one pollutant (group) that directly or indirectly affect another pollutant (group). The arrow points from the affected to the affecting pollutant (group).*

The following example serves to clarify what is meant with *“interaction.”* For this example, nutrients and hazardous solids are used as pollutant groups. In Chapter 2, four potential interactions between these groups of pollutants were identified: a biofouling-dependent interaction (A1), a sorption-dependent interaction (B1), a food web-dependent interaction (C1) and a light-dependent interaction (D1). With nutrients as pollutant p1 and hazardous solids as pollutant p2, the interactions between can be displayed as in Figure A.1.2. Interactions *a*, *b*, *c* (as in Figure A.1.1) can thus be replaced by interactions A1, B1, C1 and D1 (Figure A.1.2).

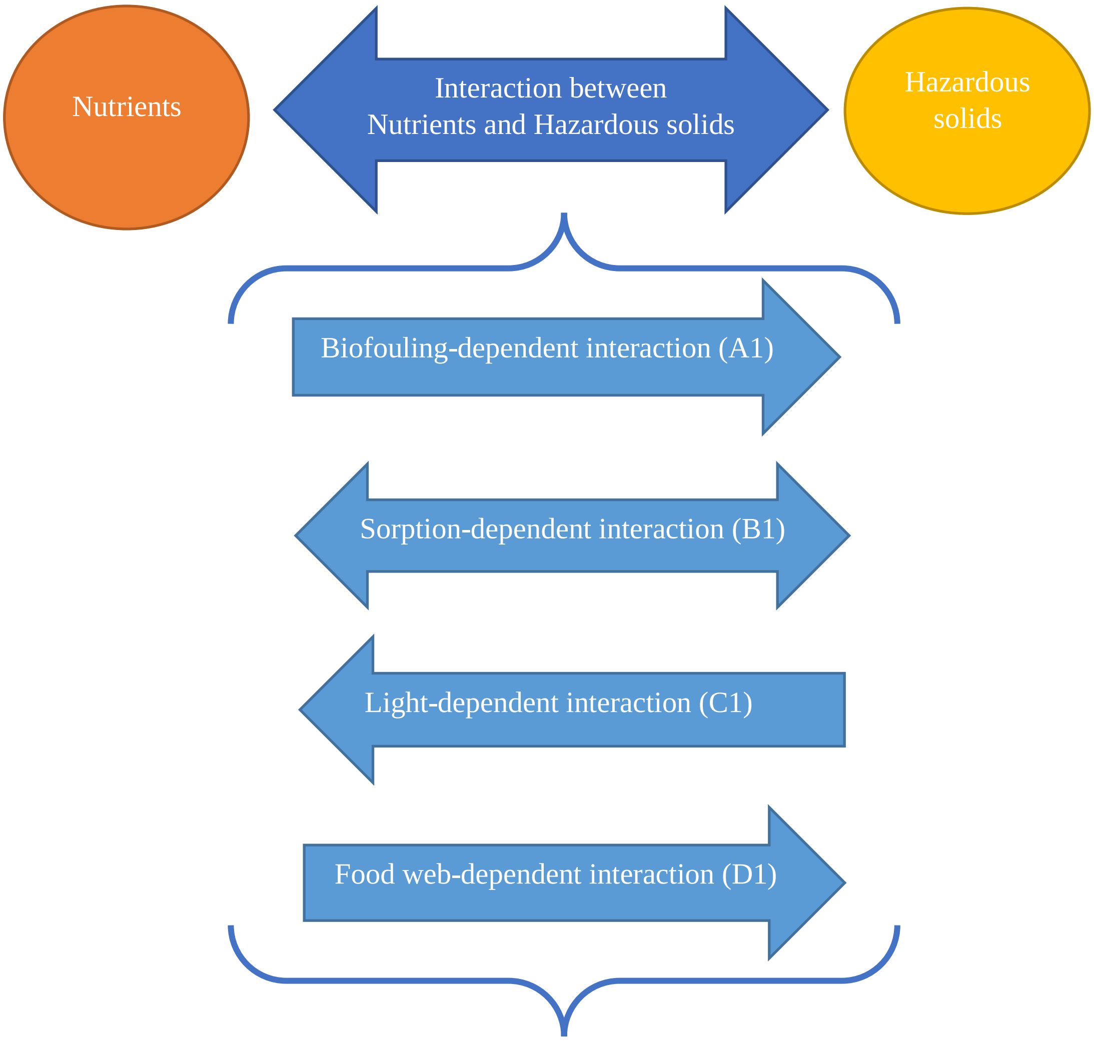

*Figure A.1.2. Interactions between nutrients and hazardous solids (Hazardous solids). The mutual influence that nutrients and hazardous solids have on each other is constituted of various interactions (as indicated by the accolades). These interactions are defined as: "A particular way in which a (group of) pollutants affects another." Biofouling-dependent interaction, light-dependent interaction, sorption-dependent interaction and food web-dependent interaction have been identified as potential interactions between nutrients and hazardous solids in Chapter 2. The arrow points from the affecting to the affected pollutant group.*

# Appendix A.2. Web of interactions

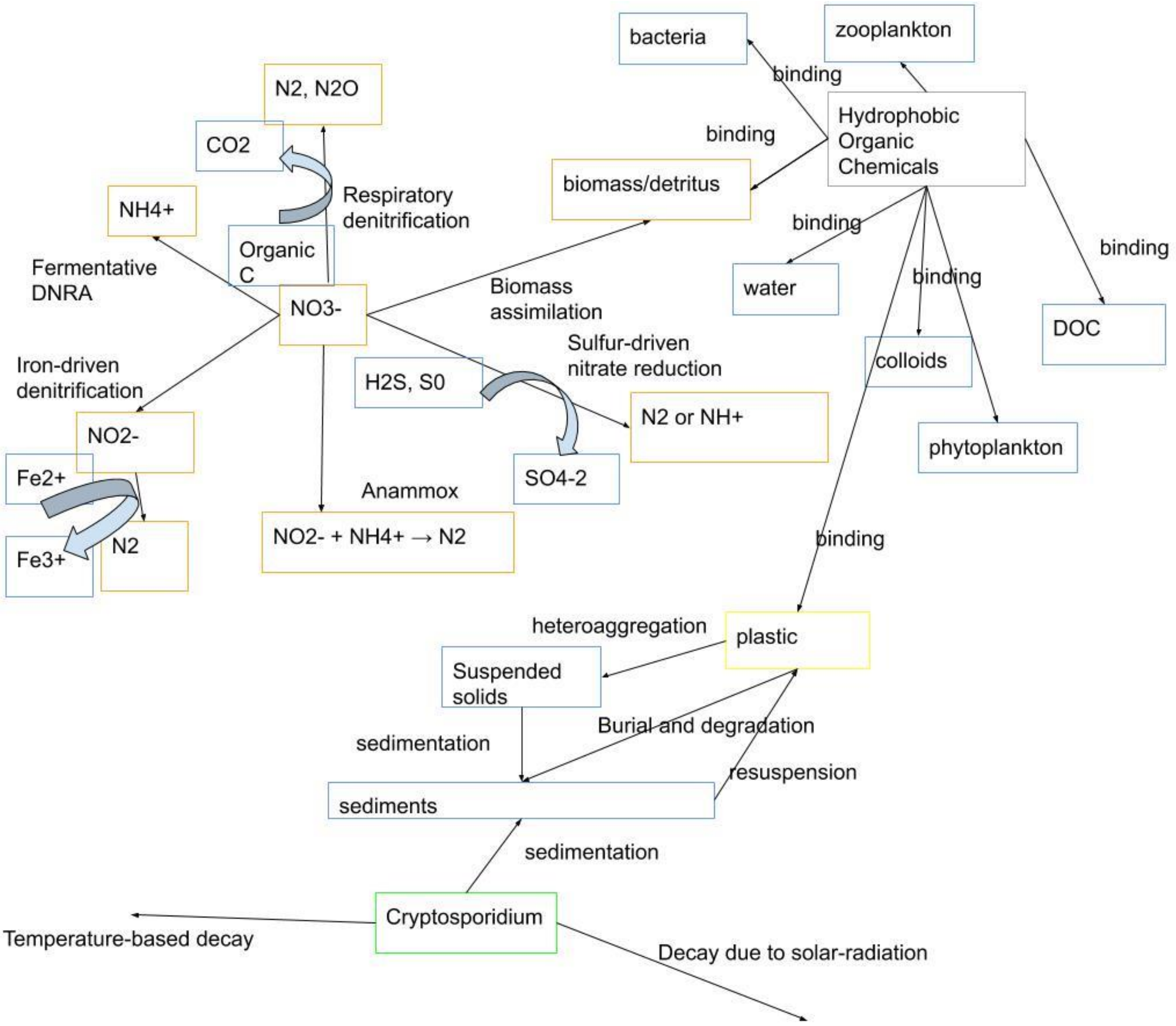

*Figure A.2.1. Web of interactions. This web includes examples of processes affecting the retention of nitrate (example for nutrients), hydrophobic organic chemicals (example for chemicals), plastic (example for hazardous solids) and Cryptosporidium (example for pathogens). The web shows some potential links between nitrate, hydrophobic organic chemicals, plastic and Cryptosporidium. Source: Burgin and Hamilton (2007) ($NO_3^-$ and links), Koelmans et al. (2016) (hydrophobic organic chemicals and links), Besseling et al. (2017) (plastic and links), and Vermeulen et al. (2019) (Cryptosporidium and links).*

# Appendix A.3. Alternative representation of Possibility 2

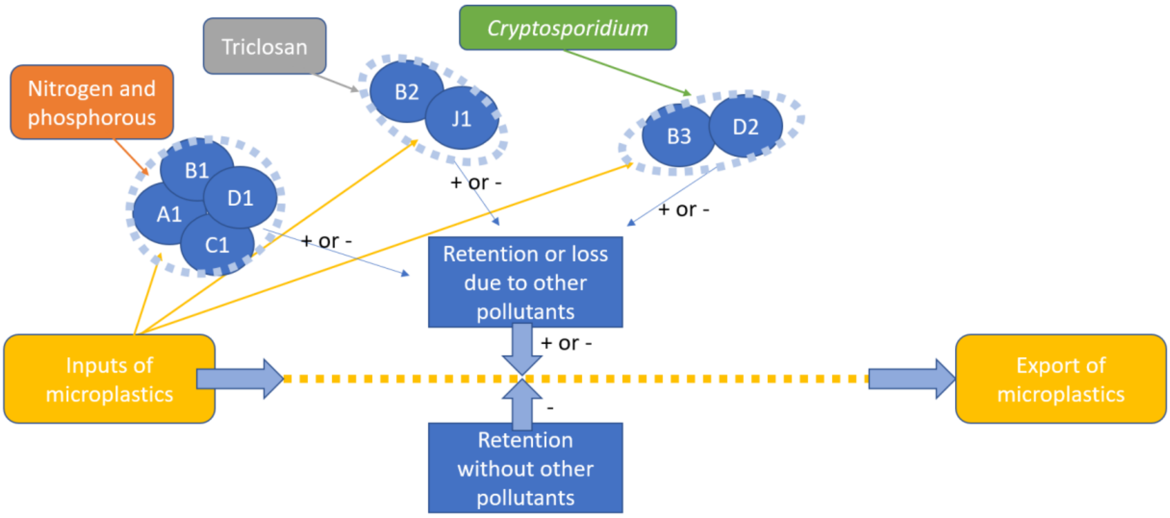

*Figure A.3.1. The export of microplastics to the outlet of a sub-basin j may be affected by interactions A1, B1, C1 and D1 with nutrients (nitrogen and phosphorous), interactions B2 and J1 with chemicals (triclosan), and interactions B3 and D2 with pathogens (Cryptosporidium). The interactions within a dotted-lined circle may have indistinguishable effects. Each of the circles represents an interaction factor for microplastics. The inputs of the various pollutants might affect the extent to which the interactions affect the retention of microplastics. Additionally, the retention of microplastics is affected by retention due to other factors ('Retention without other pollutants'), such as sorption, sedimentation and biodegradation (van Wijnen et al., 2018). Source: Chapter 2, Chapter 3 and Section 4.3.*