



Impact of industrial wastewater treatment plants on surface water quality

Industrial organic micro pollutants and their impact on Dutch surface water with drinking water functions

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“I want to learn more and more to see as beautiful what is necessary in things; then I shall be one of those who make things beautiful. Amor fati: let that be my love henceforth! I do not want to wage war against what is ugly. I do not want to accuse; I do not even want to accuse those who accuse. Looking away shall be my only negation. And all in all and on the whole: someday I wish to be only a Yes-sayer.”

—Friedrich Nietzsche, *The Joyous Wisdom*, 1882

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Abstract

Direct emissions of emerging and well known contaminants via industrial wastewater treatment plants (IWTPs) considerably impact Dutch surface water concentrations with vulnerable drinking water functions. In this nationwide impact study, the impact of 182 Dutch IWTPs was modelled, whilst taking geographic distribution, climatic variation, impact from abroad and variable types of industries into account. Modelled contaminants were 1,2-dichloroethane, DEHP, dichloromethane, benzene, toluene and vinyl chloride. Large amounts of contaminant groups (nonylphenols/nonylphenol ethoxyphtales, phenols, halogenated organic carbons and polycyclic aromatic hydrocarbons) follow the same emission path. Contaminant loads were estimated by normalizing emissions registered in the European Pollutant and Transfers Register (E-PRTR) over the Total Organic Carbon (TOC) emission per economic sector, and successively projecting these on actuals TOC emissions per IWTP. Only 13% of the IWTPs contribute to the impact regarding drinking water production. Between 65,6 and 80% of the average impact of all 6 modelled contaminants, on drinking water production volumes, originates from a single Dutch IWTP. Industrial sectors with the highest impact are the refined petroleum industry, paper industry and plastic industry.

Lexicon

Adverse	Unfavourable or antagonistic in purpose or effect.
Aetiology	The cause or origin of a disease.
Anthropogenic	Caused or produced by humans.
Appraise	To estimate the monetary value of; determine the worth of; assess.
Carcinogenicity	Any substance or agent that tends to produce a cancer.
Concentration	Amount of dissolved substance contained per unit of volume.
Conservative	disposed to preserve existing conditions.
Contaminant	Pollutant; something that contaminates.
Decayable	Gradually falling into an inferior condition; progressive decline; decompose; rot.
Discharge	Volume per time unit.
Endocrine	Hormonal.
Load	Mass per time unit.
Mitigation	Lessening the force or intensity of something unpleasant, as wrath, pain, grief, or extreme circumstances.
Normalization	To establish or resume (relations) in a normal manner; according to a normal distribution.
Plasticizers	Any of a group of substances that are used in plastics or other materials to impart viscosity, flexibility, softness, or other properties to the finished product.
Pollutant	Contaminant; something that pollutes.
Priori	Preceding in time or in order; earlier or former; previous.
Pristine	Having its original purity; uncorrupted or unsullied; of or relating to the earliest period or state; primitive.
Surfactants	Any substance that when dissolved in water or an aqueous solution reduces its surface tension or the interfacial tension between it and another liquid.
Susceptible	Capable of being influenced easily.
Ubiquitously	Existing or being everywhere, especially at the same time; omnipresent.
Utilization	To put to use; turn to profitable account.

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1. Introduction

1.1. Emerging contaminants and areas of potential risk

Amongst the large spectrum of pollutants, emerging contaminants are considered an important group contributing to diseases of uncertain aetiology (Halden, 2015). “Emerging contaminants” are according to Murray et al., (2010) and Matamoros & Salvadó, (2013) a large, relatively new group of unregulated compounds such as pharmaceuticals, personal care products, plasticizers, surfactants and pesticides about which there is relatively little toxicological information. Research has shown that many “new”, previously unknown compounds enter the environment, disperse, and persist to a great extent (Loos et al., 2009). For some of these chemicals, their sources, structures and effects on aquatic ecosystems are well known and described (Kidd et al., 2007), but the identity and effect of most of the compounds are still unknown (Ruff et al., 2015).

The release of emerging organic pollutants into the environment has increased with the growing population, urbanization and modernization (Mohapatra et al., 2010; Salgueiro-González et al., 2015). Currently over 345.000 chemicals are registered and regulated via national and international authorities globally and global chemical production is projected to continue growing—about 3% per year—with a doubling rate of 24 years, rapidly outpacing the rate of global population growth (Wilson & Schwarzman, 2009). Consequently a large body of primary literature and numerous reviews, document the extent and diversity of chemical pollution and attendant adverse health effects on humans and ecosystems (Diamond et al., 2015). E.g. Kolpin et al., (2002), Schwarzenbach et al., (2006), Richardson, (2014), Loos et al., (2009) and Kehrein et al., (2015) all state that chemical pollution of natural waters has become a major public concern in almost all parts of the world, whilst Pal et al., (2010) and Aldekoa et al., (2013) point out the interconnected impact of emerging contaminants, as they are used every day, in our homes, farms and industry.

It goes without saying that not all chemicals are toxic to the aquatic environment or human health. Although, for some of these chemicals, their sources, structures and effects on aquatic ecosystems are well known and described (Kidd et al., 2007), but the identity and effect of most of the compounds are still unknown (Ruff et al., 2015). Moreover, due to the

widespread utilization of emerging contaminants, their occurrence has been measured ubiquitously in European surface waters, ground waters, river sediments and living organisms (e.g. by Loos et al., (2009), Micić & Hofmann, (2009), Loos et al., (2010a), Loos et al., (2010b), Ruff et al., (2015) and Salgueiro-González et al., (2015)). Not only in industrialized areas but also in more remote and pristine environments (Loos et al., 2009).

It is very difficult to assess the effect on the aquatic environment of the thousands of synthetic and natural trace contaminants that may be present in water at low to very low concentrations (pg/L to ng/L) (Schwarzenbach et al., 2006; Loos et al., 2009). Although most of these compounds are present at low concentrations, many of them raise considerable toxicological and eco-toxicological concerns, particularly when present as components of complex mixtures (Loos et al., 2009). Emerging concerns, are mainly due to long-term effects of some substances, in particular through endocrine disruption, interference with reproduction and carcinogenicity, although the actual size of effects of real-life exposure is still an active and debated research topic (Mrema et al., 2013).

Together this implies that if emissions of increasing numbers and amounts of chemicals continue at current and anticipated increasing rates, concentrations of emerging contaminants in many parts of the world, alone or as mixtures, could push the global system beyond the safe operating space, which in turn could lead to erosion of vital ecosystems, ecosystem services, and human well-being (Diamond et al., 2015). Especially, since surface waters provide vital functions to humans, such as drinking water, nature, recreation and food production (Coppens et al., 2015). Therefore, it is fundamental to localize and control areas with potential environmental risk associated to emerging contaminants (Aldekoa et al., 2013), .

1.2. Impact and mitigation of emerging contaminants

Whilst some debate about the various possible toxicological effects of anthropogenic chemicals, others have started to look where, how and which mitigation measures could most efficiently be implemented to decrease their ubiquitous occurrence in the aquatic environment. Many use water quality modelling tools such as the GREAT-ER model (Kehrein et al., 2015; Aldekoa et al., 2013), the STREAM EU model (Lindim et al., 2015), the WFD Explorer 2.0 (Coppens et al., 2015), the SIAQUA-IPH model (Fan et al., 2015) or the GIS based water quality model LF2000-WQX (Price et al., 2010).

Ort et al., (2009) for instance gave a model-based evaluation of reduction strategies of organic micro pollutants from sewage treatment plants in the Swiss river network. Whilst, Coppens et al., (2015) revealed with a spatial and hydrological model, at which Dutch sewage treatment plants mitigation strategies would be most efficient to reduce the occurrence of pharmaceuticals in surface waters with susceptible functions. Another example of how spatial and hydrological water quality modelling can be used to find where and how mitigation strategies can most knowledgeable be implemented in order to minimize possible adverse effects, is given by Kehrein et al.,(2015), whom even implemented technical reduction measures in their model to evaluate the results (e.g. activated carbon and advanced oxidation).

Water quality modelling consists in the use of mathematical equations to simulate the fate and transport processes of pollutants spilled into water bodies (Fan et al., 2015), combined with the hydrological connections and processes between water bodies. There are several advantages of using water quality models for impact assessments and mitigation strategies of chemical substances in river basins. One of them is that assessing water quality only based on measurements is time consuming, expensive, not spatially detailed, and often neglects all the variables that affect the water quality of an entire catchment area (e.g. time related factors such as seasonal differences). Measured values are very much dependent on the time of sampling, sampling point, extraction efficiency prior to measurement and detection limit of the technique employed; hence they fail to give real spatial and temporal variation, which is a function of the hydrology of rivers and inflow variations (Johnson, 2010; Kugathas et al., 2012). According to Moschet et al., (2013), sufficient screening

measurements in large rivers and lakes are economically almost even impossible. To this end, watershed-scale mathematical modelling represents a useful tool to help supervising spatial and temporal distribution of emerging contaminants over large areas. Another important point in this context is the fact that even after real implementation of a measure, its effect can hardly be investigated by monitoring, because the improvement is often below the analytical uncertainty level and is additionally covered by the temporal variability of concentrations (Kehrein et al., 2015). Consequently Kehrein et al., (2015) appraise the possibility water quality models have for an “a priori evaluation” of mitigation strategies.

1.3. Aim and scope

The before mentioned mostly address contamination of surface waters with anthropogenic substances via sewage treatment plants (STPs). So far however, little attention has been given to water quality degradation with organic micro pollutants via industrial point sources. Even though in the work of Loos et al., (2009) the following is stated: “Increasing contamination of freshwater systems with industrial chemical compounds, which are released deliberately into the environment, is one of the key environmental problems we are facing today.”. Moreover, results from a sampling survey in the Danube river, conducted by Micić & Hofmann, (2009) shows that the occurrence of alkali phenolic compounds can be linked to industrial activity in that river basin and Ruff et al., (2015), concluded the same for the river Rhine, only then for six other organic micro pollutants. Additionally, the amount and total capacity of industrial wastewater treatment plants (IWTPs) in the Netherlands, are in the same order of magnitude as those of sewage treatment plants (CBS StatLine, 2015). Plus, as can be seen in Figure 1, Dutch drinking water companies that use surface water as a source for production, frequently stop their surface water intake as a result of anthropogenic contaminants present in Dutch surface waters annually, since (at least) 1983. Therefore the aim here is: ***to improve understanding of industrial effluent emissions and their impact on Dutch surface water quality, via a hydrological model, whilst taking potential mitigation strategies to minimize adverse impacts into account for stakeholders.***

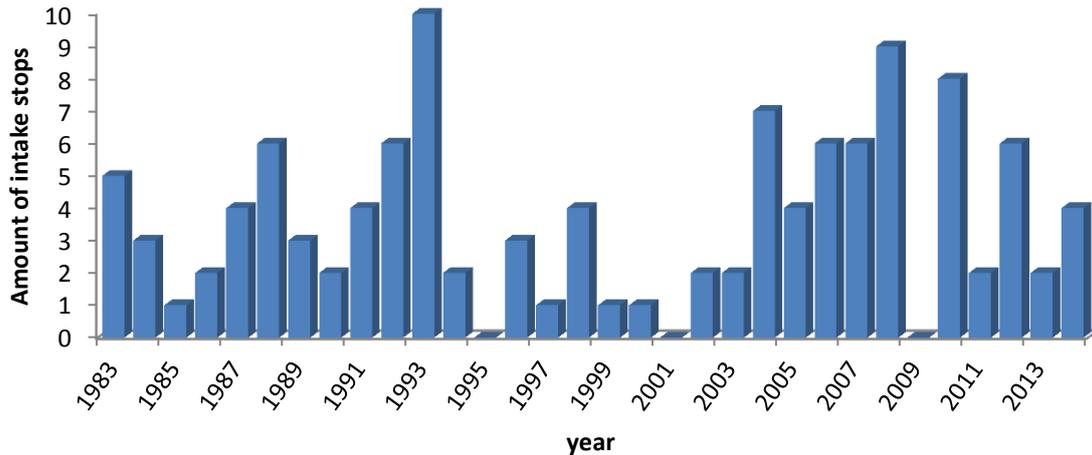


Figure 1 Intake stops of surface water from the river Meuse by drinking water company Evides. Intake stops all have an unnatural cause (e.g. discharges of pesticides, unknown sources of contamination or calamities with ships). Data used to compile the graph is retrieved from CBS, PBL, Wageningen UR, (2015).

1.4. The main question and its subsidiaries

The aim, as described in paragraph 2.4 leads to the following main research question: ***“Which impact do effluents of various types of industrial wastewater treatment plants have on the quality of Dutch surface waters with susceptible drinking water functions?”***. The research question is answered by carrying out and describing a spatial and tiered hydrological impact model. The model is combined with spatial analyses and mathematical equations (e.g. first order decay).

- In the first tier of the model, two ECs (one persistent and one degradable) that occur in drinking water and are known to be emitted by several types of industries are transferred from each IWTP through the Dutch surface water network, under two hydrological conditions (one dry and one wet).
- In the second tier, predicted contaminant concentrations are compared to measured concentrations of the same ECs, to establish a benchmark for the modelled results.
- In the third tier the predicted concentrations are used to calculate relative impact factors for all IWTPs. These impact factors are based on the contribution each IWTP has in the sum of concentrations at surface water locations with susceptible drinking water functions.

Each tier amounts in graphs or maps, which are used to describe the impact of IWTPs on the surface water quality in the Netherlands. To be more specific: on the surface water quality with susceptible drinking water functions. Consequently stakeholders will know at which IWTPs mitigation measures can most efficiently be implemented.

For the first tier of the model various types effluents of industries are analysed and ECs are selected out of the analyses. Thus the first subsidiary question arises: *Which contaminants occur in wastewater effluents of various types of industries?* Because predicted environmental concentrations of ECs in the second tier of the model are compared to measured concentrations, actual monitoring data are sought. Consequently the second subsidiary question: *“Which industrial contaminants occur in publicly available monitoring data?”*, is put forth. Based on the outcome of the first and second subsidiary questions compounds can be chosen for the model.

2. Methodology

2.1. Water quality modelling

To gain insight in the impact of variable industrial sectors on surface water quality with vulnerable drinking water functions, a hydrological and spatial water quality modelling is used, similar to the one described by Coppens et al., (2015). The water system in the Netherlands is complex due to flow patterns that change vary rapidly in time and show distinctive seasonal patterns, moreover because the water system is heavily managed as a large part of the Netherlands lies below sea level. The modelling program used in order to capture this complexity and answer the main question, is the water balance and pollutant transport model included in the Water Framework Directive (WFD) Explorer 2.0. According to Coppens et al., (2015) this model includes a network of approximately 8500 nodes of which 2575 nodes are Surface Water Units (SWUs). These SWUs represent the Dutch surface water bodies as designated by the WFD River Basin Management Plans. Two extreme hydrologic quarterly averaged water balance simulations were used for the model to gain insight in variable climatic circumstances. For dry conditions a low discharge simulation was

carried out with meteorological data from the 3rd quarter of 2003 and the 4th quarter of 1998 was used for an extreme wet simulation.

On the basis of the existing WFD-Explorer, a series of water quality (tracer) computations with D-WAQ (the pollutant transfer sub-model inside the WFD- Explore) were performed. The model assumes complete and instant mixing and for every active industrial wastewater treatment plant (IWTP) a separate simulation was carried out. By repeating this for all IWTP's, a "transfer-matrix" is created. 182 Dutch IWTPs were incorporated in the model as active. To begin with, four transfer matrices were made with the WFD explorer for all IWTPs (two for each discharge condition). Each of these matrices entailed a "pre-set" unit load emission of 1000 g/s, emitted from all 182 IWTPs for two tracers; one conservative and one undergoing first order decay, with a given decay rate. The resulting four matrices gave loads of contaminants (g/s) from each of the 183 IWTPs at each of the 2575 SWUs, which were scaled up with emission data and characteristics of 6 chosen contaminants, resulting in 12 matrices (one for each contaminant under the two climatic conditions). The formula needed to scale up the pre-set loads is the formula for first order environmental decay of organic substances in surface waters. For a detailed explanation of how the first order decay formula is used to scale up the four matrices, Coppens et al., (2015) can be taken as reference.

In addition to the 182 IWTPs, also cross-border 9 rivers were treated as if they were a IWTPs (point sources of emission). This allowed for the incorporation of "background" concentrations from IWTPs upstream of the presented model domain, or in other words: for calculating the relative contribution to Dutch surface water concentrations by incoming rivers from abroad.

Since constant emissions and instant mixing are assumed in the model, the sum of all loads from IWTPs and boundary points (incoming rivers from abroad) per SWU gives the total mass flux (g/s) at each SWU. Divided by the local discharge (Q in m^3/s), the concentration (C in g/m^3) in each water unit is obtained. This way, the hydrological distribution and transfer of chosen contaminants via IWTPs, was captured during a dry and wet season for the whole of the Netherlands.

2.2. Selecting compounds with high impact potential

The selection of compounds is partially based on a data driven prioritization work performed by Sjerps et al., (2016), whom prioritized 174 compounds through liquid chromatography high resolution mass spectrometry (LC-HRMS) suspect screening of 151 water samples (including effluent, surface, ground and drinking water). Included in the 174 prioritized compounds are chemicals applied in industry in volumes above 1000 and 100 tonnes per year in Europe, as registered under REACH legislation (Registration, Evaluation, Authorization and restriction of Chemicals, Regulation EC 1907/2006, (data obtained via the European Chemical Agency ECHA 2015; Sjerps et al., (2016)). Additionally substances of very high concern (SVHC) as defined under REACH for their carcinogenicity, mutagenicity, reproductive toxicity, persistency or bio accumulative properties (CMR and PBT) are amongst the prioritized substances. CMR compounds as defined under the CLP Regulation on classification, labelling and packaging of substances and mixtures (1272/2008) are included, completed by Dutch legislation on CMR compounds (Sjerps et al., 2016). Mixtures, inorganic chemicals, metalloids and non-ionisable chemicals were not included by Sjerps et al., (2016) to begin with, since they do not qualify for the (LC-HRMS) screening method.

To narrow down to chemicals mainly having industrial emissions as a source and rule out other emission pathways—as much as possible—chemicals befalling in one of the following data sources are removed from the list 174 prioritized compounds:

- 1) Human and veterinary pharmaceuticals as authorized under the EU Directives 2001/83/EC and 2001/82/EC (listed previously by Ter Laak, (2010) and also incorporated by Sjerps et al., (2016)).
- 2) Chemicals authorized on the Dutch market under the Plant Protection Product Regulation (528/2012/EC) and Biocide Product Regulation (528/2012/EC), obtained via the Dutch Board for the Authorization of Plant Products and Biocides (Sjerps et al., 2016).

Besides prioritized compounds from Sjerps et al., (2016) a selection of compounds was made from occurrence data in literature that can be linked to having industrial origins and compounds present in the Dutch E-PRTR database (Emissieregistratie, 2016).

Compounds from the literature survey are similarly selected on their occurrence in effluents, surface, ground and drinking water. In addition they are chosen based on appearance in recent and or well established literature. Moreover all selected compounds are checked for having a production number at least higher than 100 tonnes, according to REACH legislation.

The remaining compounds are filtered based on whether or not they occur on the monitoring list of the Dutch association of river water companies (RIWA/IAWR). This to ensure eventually modelled concentrations can be compared with actually measured concentrations, without having to conduct a monitoring expedition.

2.3. Normalization of E-PRTR emissions

To estimate emissions as model input the European Pollutant Release and Transfer Register was used, which was established as a data source for EU Member States. Reporting to the E-PRTR is governed by an EU regulation (Regulation (EC) No. 166/2006). This regulation requires that emission data from production are publically available, when emission of listed chemicals and chemical classes surpass given threshold values. Reported emissions to air and water from each site are published by each country at a mandatory web page of each country and are also available for the whole of Europe. In the Organisation of Economic Co-operation and Development (OECD), several countries report according to E-PRTR, for example Canada, Chile, Japan, Korea and USA. In total, emissions for 39 countries are available (Sörme et al., 2016).

The data to be reported annually (tonnes per year for any of the 91 E-PRTR pollutants) by each facility for which the applicable thresholds are exceeded are the following; 1) Releases to air, water and land and 2) Off-site transfers and pollutants in waste water destined for waste-water treatment outside the facilities, 3) Off-site transfers of waste for recovery or disposal. In this research the pollutant emissions to water (tonnes per year) from the year 2013 were taken as emission input for the model.

Consequently the 182 IWTPs in the Netherlands were divided into 19 and 43 industrial classes and sub-classes (respectively), according to their Statistical Classification of Economic Activity in the European Community, more commonly referred to as NACE-codes.

Six substances were chosen, based on having high annual emissions and or a high amount of emitting facilities (IWTPs). Furthermore the list of 91 E-PRTR pollutants was checked to see if any of the selected compounds with high impact potential also occurred in the E-PRTR database (E-PRTR, 2016).

In 2013 The E-PRTR covered 27 EU Member States as well as Iceland, Liechtenstein, Norway, Serbia and Switzerland and 2013 is the last year for which online public E-PRTR data could be found. The annual loads over 2013 of the six chosen substances—DEHP, benzene, dichloromethane, 1,2-dichloroethane, toluene and vinyl chloride—were then normalised on the emission of total organic carbon (TOC). This was done for each of the 43 industrial sub-classes, so as to obtain an annual emissions per chosen substance X per unit load of TOC per IWTP in that industrial sub-class (NACE-code) in Europe. These emissions (kg X/kg TOC/year/European IWTP) were then scaled up to the actual emission of TOC of each of the 182 Dutch IWTPs (in correspondence to their NACE-codes), so that each Dutch IWTP obtained a corresponding unit load emission in g/s, which is used in the model to scale up the pre-set loads of 1000 g/s.

2.3. Loads from boundary points

The nine incoming rivers from abroad, which had to be scaled up with genuine concentrations of modelled contaminants as well are the Rhine, Meuse, Scheldt, Sas van Gent (Canal), Roer, Swalm, Niers, Overijsselse Vecht, Mark / Weerijs and Dommel / Tongelreep. These rivers have already received a load of pollution in the country they originate from, and are taken into account in the model as normal point sources of pollution at their point of entry in the Netherlands.

Concentration of the 6 model contaminants at the locations of the largest incoming rivers (Rhine and Meuse) were obtained from Rijkswaterstaat, (2016). Monitored concentrations for these substances were presented by Rijkswaterstaat, (2016) in µg/L for each month and data was obtained for 10 consecutive years (2004-2014). From these 10 years the average quarterly concentrations were calculated of which the concentrations the 3rd and 4th quarter were taken as input for the model (in correlation to the high and low discharge conditions). Loads and concentrations from other incoming rivers were calculated

based on the concentrations and loads from the river Rhine at Lobith and the river Meuse at Eijsden combined, assuming similar incoming average loads (see Coppens et al., (2015) for the formulas used).

2.4. Evaluation of predicted surface water concentrations

The ratio between measured and predicted environmental concentrations (MEC/PEC) indicates the predictive performance of consumption-based hydrological modelling (Coppens et al., 2015). In this case this means the ratio between the MEC and PEC indicates the predictive performance of the hydrological model with normalised E-PRTR emissions over TOC emissions. Furthermore it means that PECs at several SWUs were compared with actually monitored concentrations, taking into account a hypothesized underestimation of predictive performance, since most direct industrial contaminants frequently have other emission pathways (e.g. in-direct emissions via STPs or emissions from diffuse sources and or globally stockpiled products containing these contaminants).

2.5. Relative contribution of IWTPs to the total concentration

The relative contribution R (-) to the concentration in water body j from Dutch IWTPs compared to the inflows from abroad is the concentration originating from Dutch IWTPs divided by the total concentration (Coppens et al., 2015):

$$R_j = \frac{C_{X,iNLj}}{C_{X,totj}}$$

2.6.. Spatial selection of vulnerable drinking water areas

The main point in this activity was to find out which SWUs have a location that is close to or in an area with susceptible drinking water functions (e.g. groundwater and surface water extraction areas from drinking water companies). For, when the SWUs having an impact on vulnerable drinking water sources are selected, the predicted concentrations in those SWUs are known and then successively the relatively contributed impact per IWTP can be

calculated in that SWU. Vulnerable drinking water extraction areas were already determined with ArcGIS mapping by Coppens et al., (2015). The general approach was to select SWUs with: 1) direct abstraction for drinking water production, 2) river bank filtrate abstractions nearby (if applicable in close proximity to their 25 year protection zone) and 3) permeable ground water areas nearby (Following a worst case approach, with no correction for dilution or mixing within the abstraction, and the assumption that the flow occurs from SWU to aquifers).

2.7. Impact assessment of IWTPs on vulnerable drinking water areas

To prioritize at which IWTPs at or in which service areas of IWTPs mitigation of contaminants is most efficient, IWTPs are ranked for their impact on SWUs hosting vulnerable drinking water functions. Per IWTP an impact factor (IF) is calculated by the following formula:

$$IF_{i,j} = \sum_j C_j \frac{F_{i,j}}{Q_j C_j} \frac{S_j}{S_{tot}}$$

The IF (g/m³) of IWTP *i* in SWU *j* is expressed by the local concentration *C_j* to represent the total impact on that SWU, multiplied by the load *F_{i,j}* to the to the total load of all IWTPs in that SWU (*Q_jC_j*), representing the share of IWTP_{*i*} within the total impact, and multiplied by a dimensionless weighing factor *S/S_{tot}* representing the relevance of the SWU for the function of interest. For the analysis of drinking water abstractions *S* is represented by the production volume (m³/y). When groundwater abstractions with multiple coupled SWUs are concerned, corresponding abstraction volumes were divided amongst the SWUs concerned (Coppens et al., 2015). In continuance the sum of *IF_i* over the SWUs gives *IF_i*, the impact factor of a certain IWTP *i*. IFs are calculated for both discharge conditions. All IWTPs having a *rIF_i* higher than a certain limit (%) are selected and ranked. The formula for the *rIF* goes as follows:

$$rIF = \frac{F_i}{\sum_i F_i}$$

3. Results

3.1. Selecting high impact compounds for industrial variation

The prioritized compounds with high industrial impact potential, resulting from the preliminary selection, can be found in Table 2. A corresponding list of references for Table 2 is shown in Table 1. Five of the selected compounds occur in drinking water, nine in effluent, seven in surface water and twelve in ground water. All except for five, have production volumes higher than 1000 tonnes per year according to REACH legislation, underlining the possibility these compounds have high emission loads. The five whom do not have production volumes above 1000 tonnes per year have production volumes between 100 and 1000 tonnes per year. All of the compounds that are selected are monitored by RIWA, ensuring the possibility of comparing predicted environmental concentrations with monitored concentrations.

Bis(2-ethylhexyl) phthalate (DEHP) was the only compound selected that could also be found in the E-PRTR database as having a high amount of emissions. Henceforth this compound is chosen as one of the primary compounds for the model. Though DEHP did not show up in the in the prioritization of Sjerps et al., (2016) it did occur in several different kinds of industrial wastewater as can be seen in the toxicology study of Roex et al., (2003).

Compounds that come out of the selection process mostly do not solitarily have industrial uses. The only one that does is most likely triphenylphosphine oxide (TPPO). For, TPPO according to Schlüsener et al., (2015) and according to R. Berbee (personal communication, march 29, 2016) is a known by product of the Wittig reaction, often applied in the chemical industry.

Other compounds have multiple uses and can arrive in surface waters via several routes. Three of the compounds for instances are phthalates, which are well known for being added to plastics such as PVC, in order to give it flexible properties. The same counts for the phenols that are selected. Phenols, additionally are also known to be added to paper for the creation of film layers (e.g. bisphenol A and bisphenol S). Further selected

compounds have multiple functions. An overview of these functions can be found in Appendix: B.

Since DEHP was the only compound that came out of the selection process and occurred in the E-PRTR database, five other substances were chosen as model compounds, for having high emission numbers according to the E-PRTR database. These contaminants are benzene, dichloromethane, toluene, 1,2-dichloroethane and vinyl chloride and were besides having high annual emissions chosen to create more variability between the different industrial sectors and because they were emitted by several industrial classes.

Table 1 Corresponding references for table 2

References
a Loos et al., (2009)
b Loos et al., (2010a)
c Loos et al., (2010b)
d Von der Ohe et al., (2011)
e Lapworth et al., (2012)
f Sjerps et al., (2016)
g Botolova et al., (2011)
h Velzeboer et al., (2014)
i Roex et al., (2003)
j Stepien & Püttmann, (2014)
k Kiss & Fries, (2009)
l Cristale et al., (2013)
m Cristale et al., (2013b)
n Ding et al., (2015)
o Rider et al., (2012)
p Tas & Pavlostathis, (2014)
q Baldwin et al., (2016)

Table 2 Selected compounds of high impact potential

Molecular formula	CAS-number	Industrial suspects	Effluent	Surface water	Ground-water	Drinking water	REACH >100 ton/year	REACH >1000 ton/year	RIMA monitoring	References
C8H18O4	112-49-2	1,2-bis(2-methoxyethoxy)-ethane (triglyme)			1			1	1	f, j
C6H12Cl3O4P	115-96-8	tris(2-chloroethyl) phosphate (TCEP)			1			1	1	b, c, e, f, l, m, n
C12H27O4P	126-73-8	tributyl phosphate (TBP)	1	1	1			1	1	b, c, f, l, m, n
C9H18Cl3O4P	13674-84-5	tris(2-chloro-1-methylethyl) phosphate (TCPP)		1	1			1	1	b, c, f, l, m, n
C7H7N3	29878-31-7	4-Methyl-1H-benzotriazole	1	1	1	1			1	f, k
C10H15NO2S	3622-84-2	N-butylbenzenesulphonamide			1			1	1	f, o
C19H30O5	51-03-6	2-(2-butoxyethoxy)ethyl 6-propylpiperonyl ether			1			1	1	f
C6H15O4P	78-40-0	triethyl phosphate	1	1	1	1		1	1	f, l, m, n
C18H15OP	791-28-6	triphenylphosphine oxide (TPPO)		1	1	1		1	1	f, l, m, n
C12H10O4S	80-09-1	4,4'-sulphonyldiphenol (bisphenol S)		1				1	1	f
C9H17NO	826-36-8	2,2,6,6-tetramethyl-4-piperidone			1	1		1	1	f
C13H15N3O2	83-15-8	N-Acetylaminoantipyrine			1		1		1	d, f
C16H22O4	84-69-5	diisobutyl phthalate	1			1		1	1	d, f, i
C16H22O4	84-74-2	dibutyl phthalate	1			1		1	1	d, f, i
C6H5N3	95-14-7	benzotriazole	1	1	1		1		1	a, b, c, f, k
C6H4Cl2	95-50-1	1,2-dichloorbenzeen						1	1	g
C6H7N	62-53-3	aniline						1	1	p
C6H5Cl2N	608-27-5	2,3-dichlooraniline						1	1	g, p
C6H5Cl2N	95-82-9	2,5-dichlooraniline						1	1	g, p
C12H27O4P	126-71-6	triisobutylfosfaat				1			1	b, c
C3H4N2	288-32-4	trifenyylimidazole-triglycine						1	1	h
C15H16O2	80-05-7	bisfenol A						1	1	e
C6H5Cl2N	554-00-7	2,4-dichlooraniline						1	1	g, p
C6H5Cl2N	95-76-1	3,4-dichlooraniline						1	1	g, p
C6H5Cl2N	626-43-7	3,5-dichlooraniline						1	1	g, p
C18H26O	1222-05-5	galaxolide (HHCB)						1	1	e
C24H38O4	117-81-7	bis(2-ethylhexyl) phthalate (DEHP)	1					1	1	i
C4H8O2	123-91-1	1,4-dioxane	1					1	1	i
C16H10	129-00-0	pyrene	1					1	1	i, q

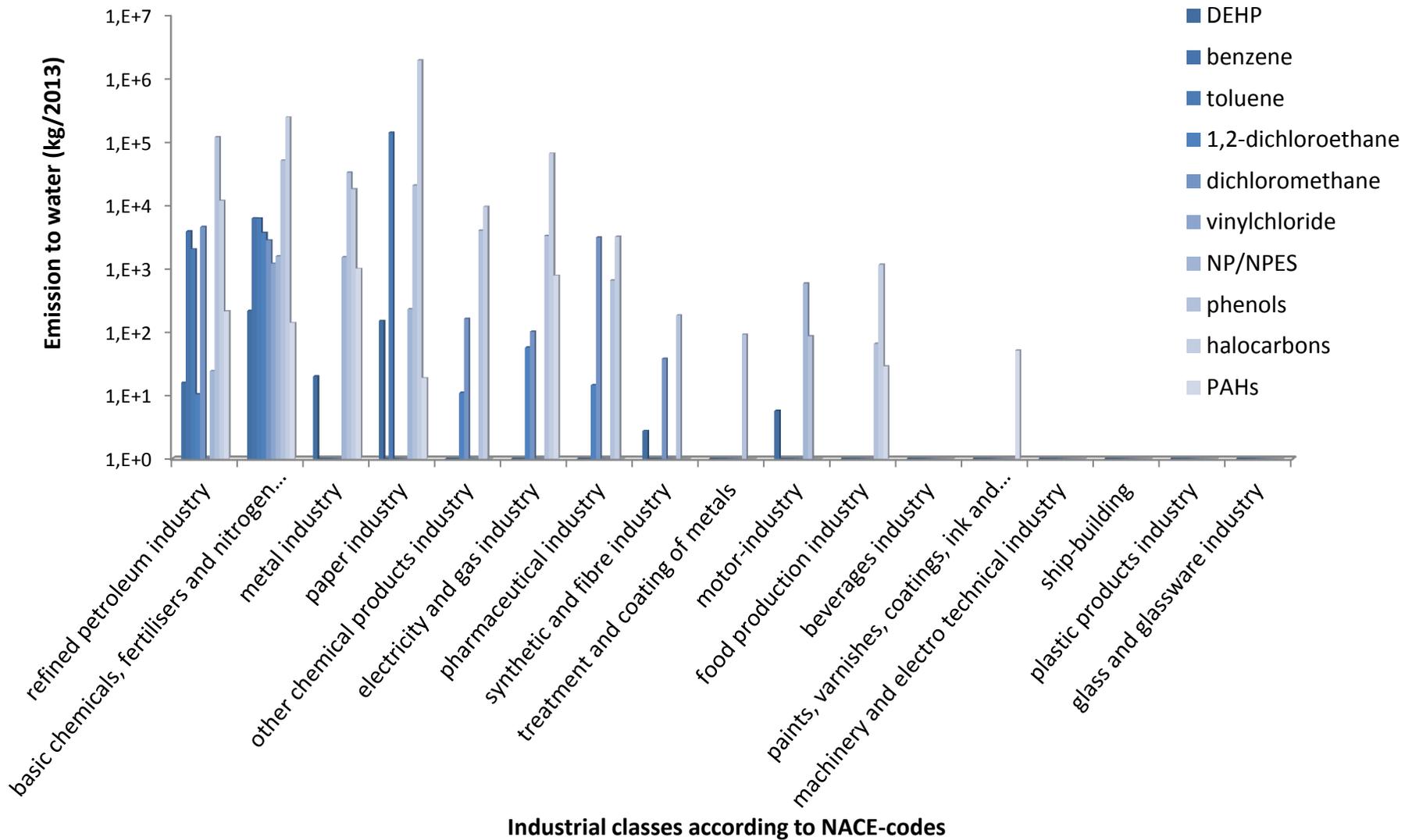


Figure 2 European industrial emissions to water in kg over the year 2013. Emission data of 6 substances and 4 substance groups was retrieved from the E-PRTR data base.

Figure 2 shows all six chosen model compounds and four compound groups. The compound groups are nonylphenols and nonylphenol ethoxylates (NP/NPES), phenols, halocarbons and polycyclic aromatic hydrocarbons (PAHs). As can be seen in Figure 2, all these compounds and compound groups have high emissions to water (note the log scale on the y-axis of the graph). Titanic differences in the amount of emissions can be seen between the various industrial classes. From left to right, the graph is ordered on the amount of phenol emissions from high to low correspondingly. For most of the selected chemicals, highest emissions, as can be seen, are reported for the refined petroleum and basic chemicals industry. The paper and metal industry come next in line. The food and beverages industry and all industries shown on the right of these in the graph of Figure 2, do not have mentionable individual contaminant emissions reported in the E-PRTR database. For the food industry and paint industry however emissions of contaminants groups are reported.

The overall amount of emitted contaminants groups is high. Nevertheless, these groups can consist of numerous contaminants, ruling out the possibility of detailed modelling with specific chemicals, as degradation constants between compounds within the group can vary too much. Under the heading phenols—according to the E-PRTR: “phenols as total C”—for instance both bisphenol A and S could be summed, though also numerous other kinds of phenols including the compound phenol itself.

Table 3 shows the environmental half-lives in surface water according to Howard, (1991). Corresponding decay constants (k_x) were calculated with the formula for first-order decay, taking into account half the concentration is reached at the given time.

Table 3 Environmental half-life values in surface water according to Howard, (1991) and correspondingly calculated decay constants.

substance or substance group	$t_{(1/2)}$ winter (days)	$t_{(1/2)}$ summer (days)	k_x winter	k_x summer
DEHP	23	5	-0,030	-0,139
benzene	16	5	-0,043	-0,139
toluene	22	4	-0,032	-0,173
1,2-dichloroethane	180	100	-0,004	-0,007
dichloromethane	28	7	-0,025	-0,099
vinyl chloride	180	28	-0,004	-0,025

3.2. TOC and normalized E-PRTR emissions of contaminants

By normalizing European emissions of contaminants onto emissions of total organic carbon, for each industrial sector with known emissions of total organic carbon (TOC) in the Netherlands, it was possible to capture the varying impact between industries. For, as can be seen in the comparison of Figure 2 and Figure 3, industrial sectors that emit large amounts of organic carbon, nitrogen or phosphorous do not necessarily emit contaminants of concern. E.g. the food and beverages industries emit large amounts of TOC (see Figure 3 and note the log scale on the y-axis), but none of the 6 modelled contaminants (see Figure 2).

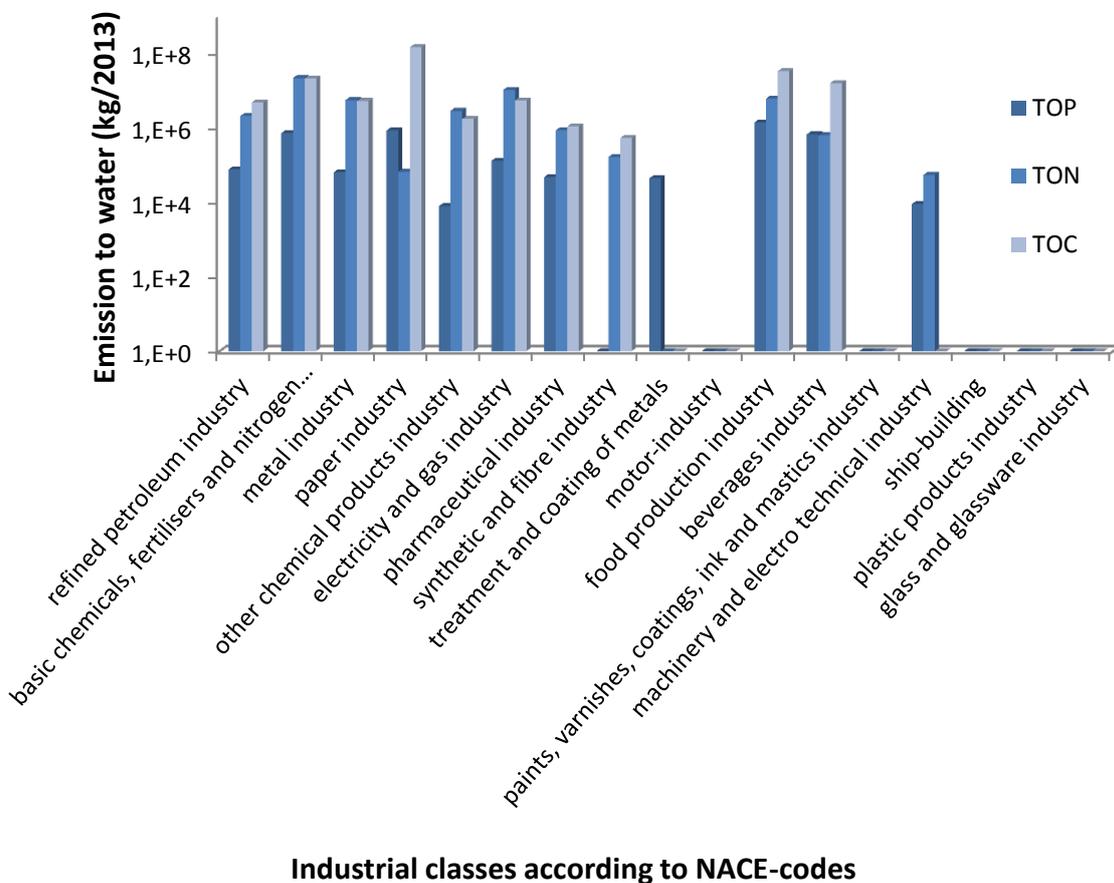


Figure 3 Emissions in kg per 2013 of Total Organic Carbon, Nitrogen and Phosphorous for the whole of Europe (data retrieved from E-PRTR).

To give an example: DEHP is emitted mainly by sub-classes of the basic chemicals and refined petroleum industry (Appendix: C, shows an example of the emitted loads of DEHP with corresponding NACE-codes). In the table of Appendix: C, Total Organic Carbon E-PRTR emissions to water (kg/2013) are shown for the whole of Europe and each NACE-code,

together with the total emission of DEHP. Besides emissions in kg, the number of industrial facilities is shown for which emissions are reported according to the E-PRTR register. Moreover the calculated emissions per facility per sector are shown for both DEHP and TOC). The normalized loads per NACE-code can be found in Appendix: D.

3.3. Industrial surface water concentrations

Predicted surface water concentrations can be found in Figure 5 till Figure 10. Concentrations are only shown for SWUs having higher concentrations than 0,0001 µg/L. During low discharge much more concentrations are present, because of seasonal differences in water management. Most likely more water is retained during low discharge whereas during high discharge water can flush through at more locations. For all contaminants the predicted environmental concentration (PEC) seems to be inaccurate as concentrations during high discharge are often higher than during low discharge, which is not to be expected as dilution during high discharge ought to cause the opposite. The error for this inaccuracy is caused by the modelled concentrations of the incoming rivers. For as can be seen in the example of DEHP (see Figure 4), concentrations of DEHP without background concentrations of incoming rivers do not portray this error.

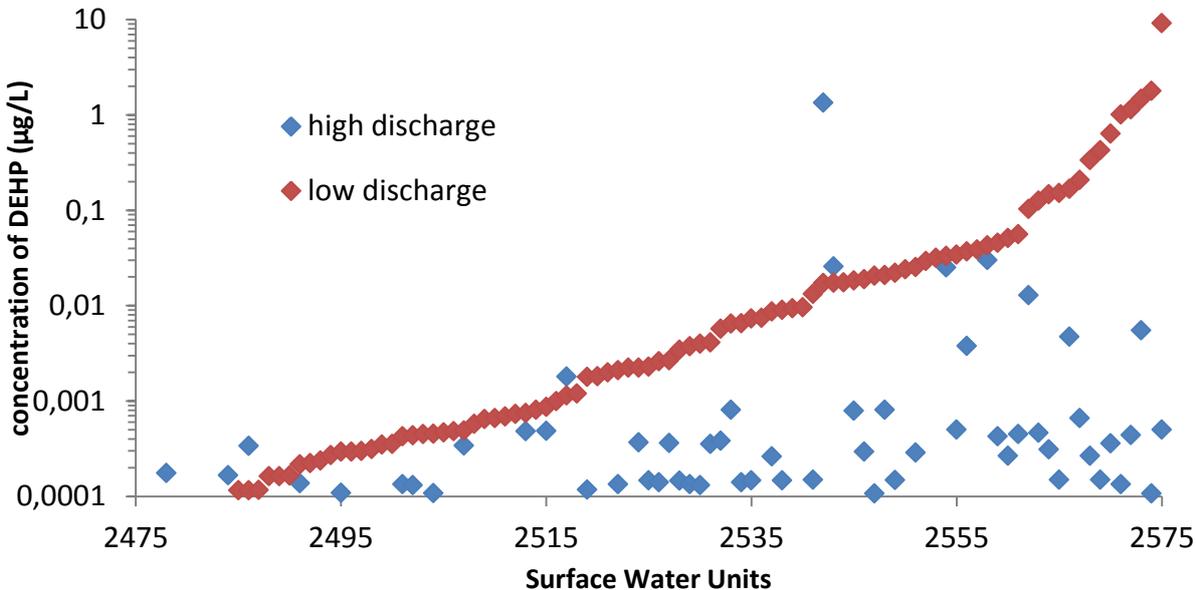


Figure 4 DEHP concentrations (without loads from incoming rivers) at SWUs during high and low discharge conditions (only concentrations of SWUs are shown with a concentration > 0,0001 µg/L during low discharge)

To be more exact the error seems only to occur for concentrations during high discharge and can be explained by the monitoring results used to calculate the loads of incoming rivers (see Appendix A). For, the concentrations used to calculate the incoming loads of the rivers at the boundaries of the model domain are almost similar in both discharge conditions. This resulted in much higher loads during high discharge conditions, as both concentrations (g/m^3) are multiplied with their corresponding discharge (m^3/s) in order to obtain a load (g/s), and the discharges under wet climatic conditions are much higher. Consequently one would have to remodel with more accurate monitored concentrations that portray the extremes of wet and dry conditions better in order to obtain more accurate results.

Something else that stands out are the extremely high concentrations of vinyl chloride. Also these are caused by the calculated load of incoming rivers during high discharge. Comparing these and other predicted concentrations with measured environmental concentrations (MEC) would provide validation of the modelled results. Within the given timeframe however this was not possible.

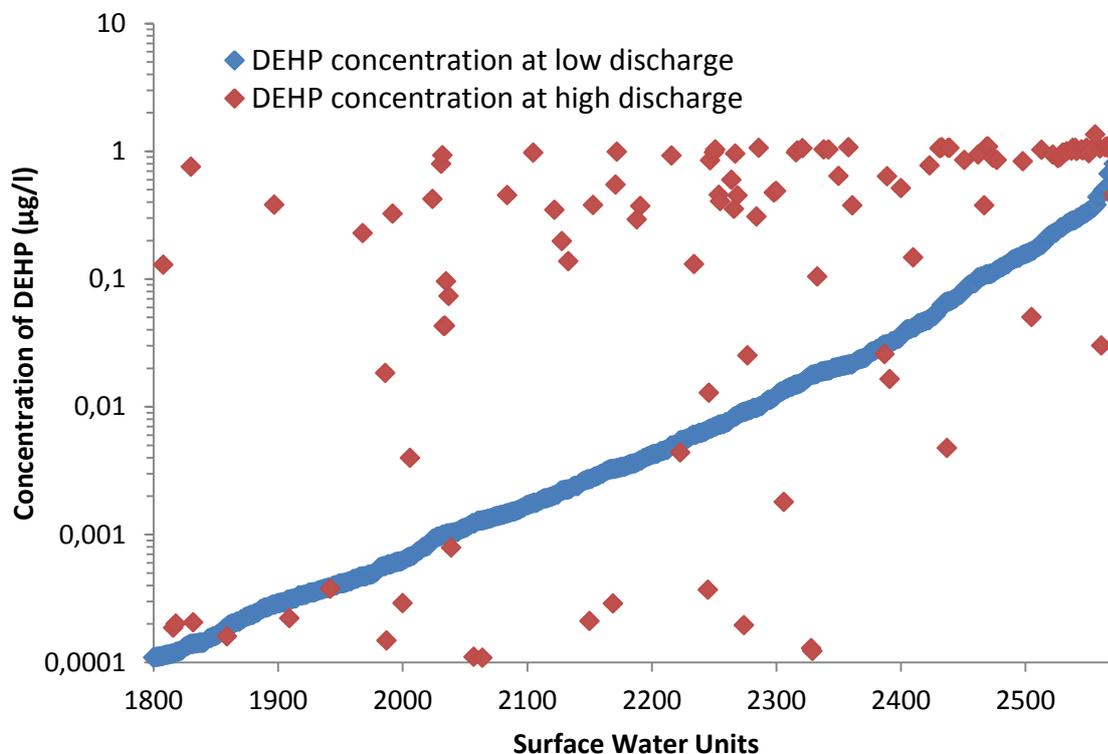


Figure 5 Predicted DEHP concentrations at SWUs during high and low discharge conditions (only concentrations of SWUs are shown with a concentration > 0,0001 $\mu\text{g}/\text{L}$ during low discharge)

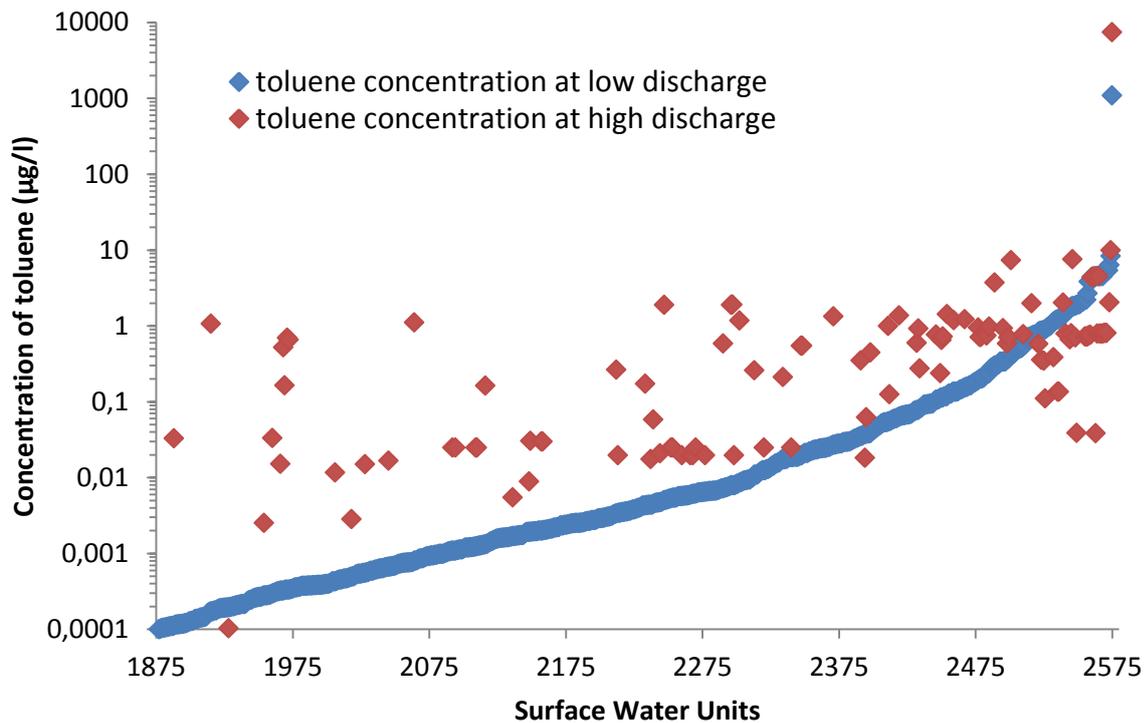


Figure 6 Predicted toluene concentrations at SWUs during high and low discharge conditions (only concentrations of SWUs are shown with a concentration > 0,0001 µg/L during low discharge)

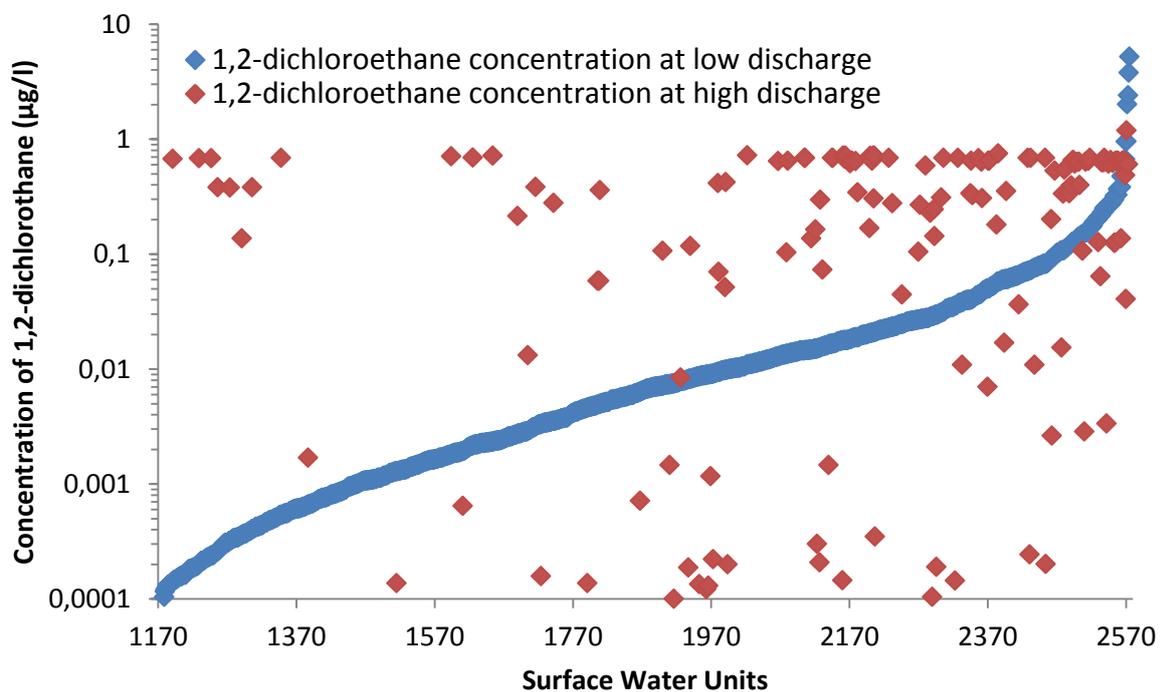


Figure 7 Predicted 1,2-dichloroethane concentrations at SWUs during high and low discharge conditions (only concentrations of SWUs are shown with a concentration > 0,0001 µg/L during low discharge)

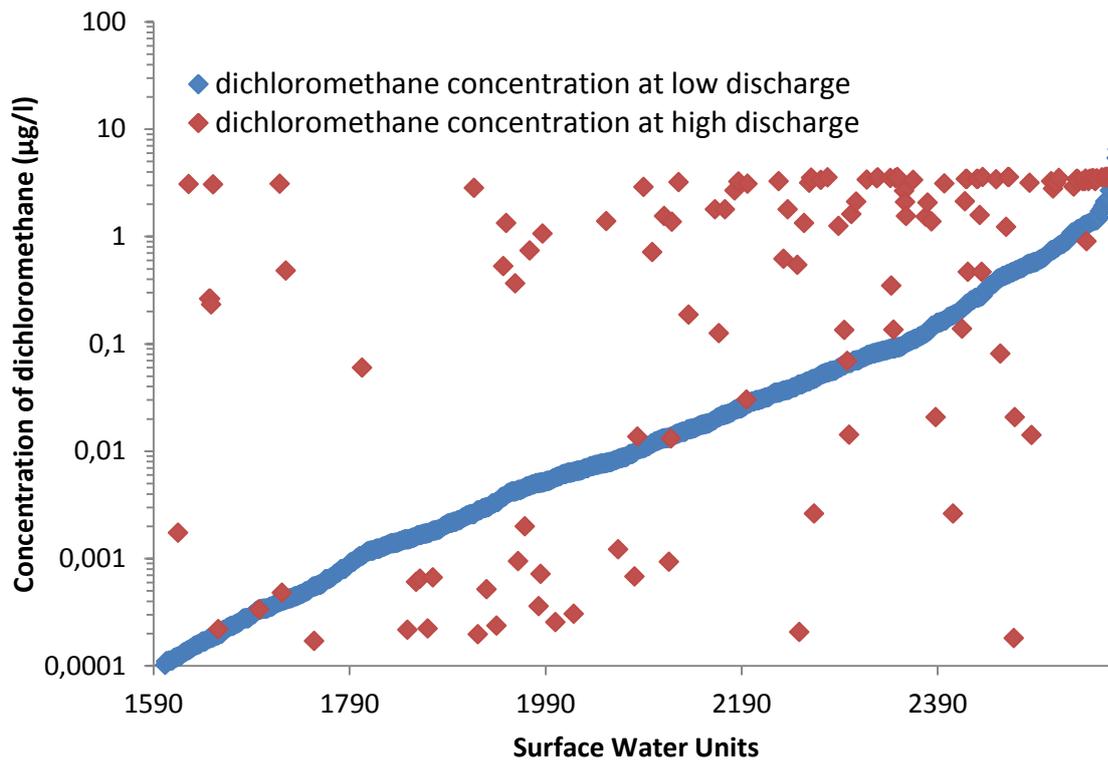


Figure 8 Predicted dichloromethane concentrations at SWUs during high and low discharge conditions (only concentrations of SWUs are shown with a concentration > 0,0001 µg/L during low discharge)

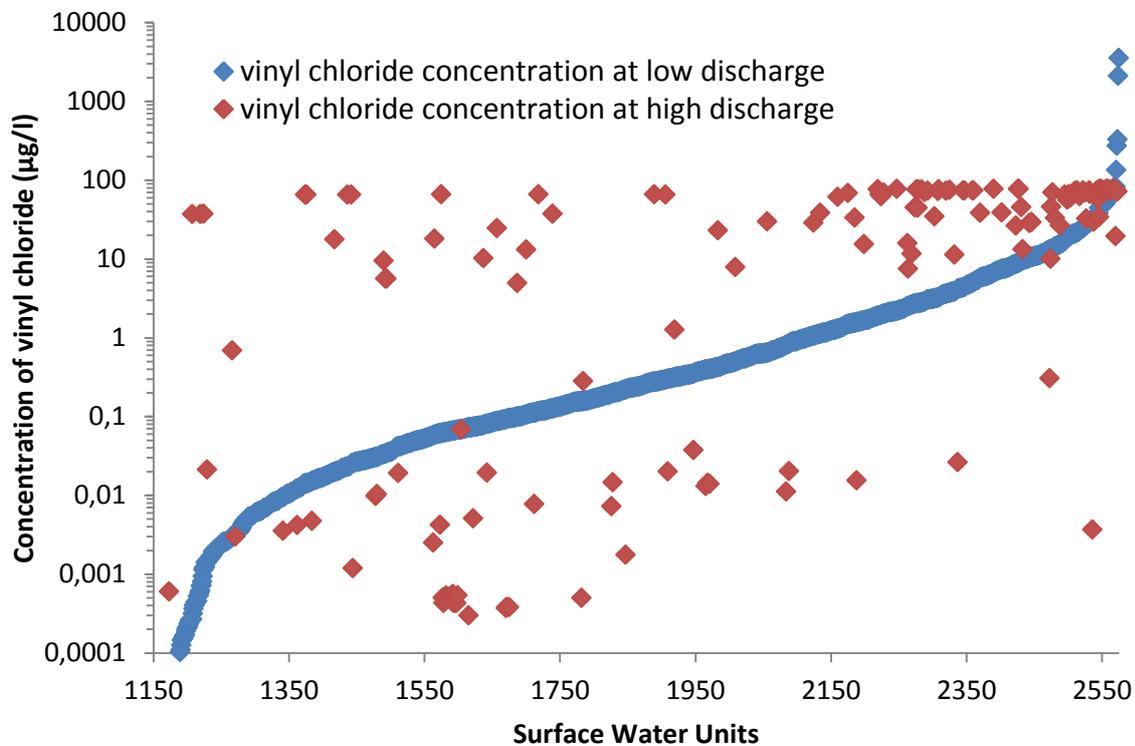


Figure 9 Predicted vinyl chloride concentrations at SWUs during high and low discharge conditions (only concentrations of SWUs are shown with a concentration > 0,0001 µg/L during low discharge)

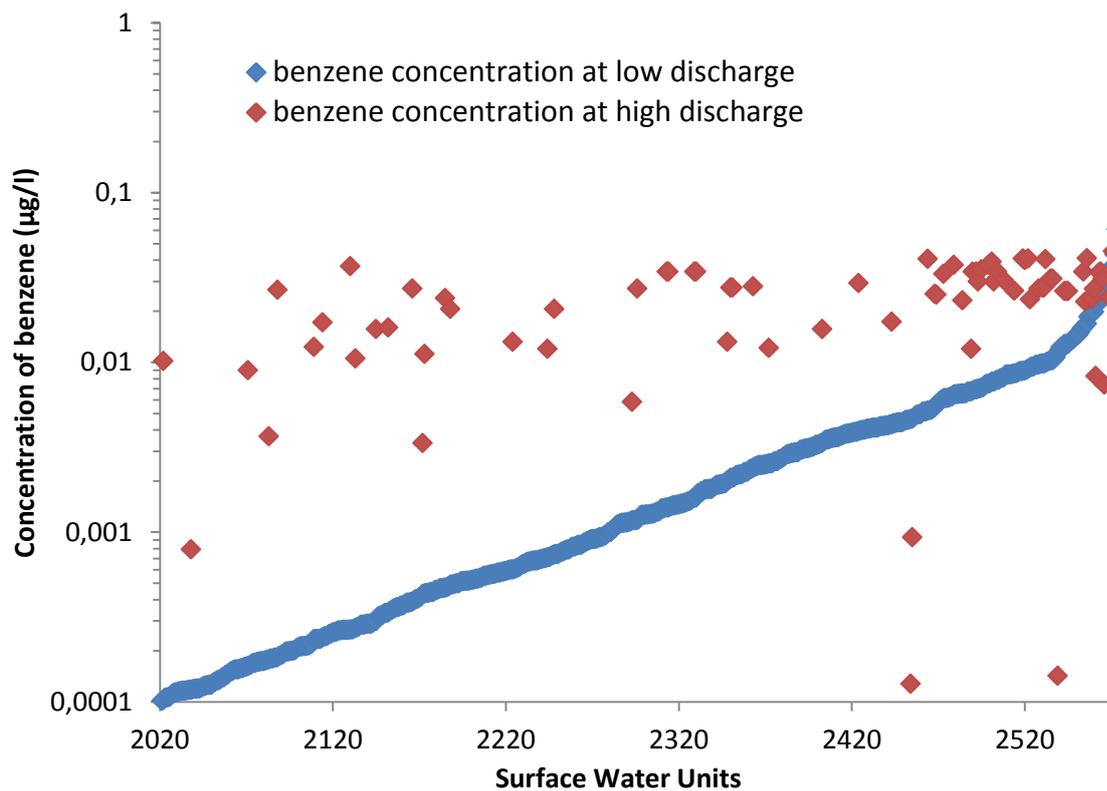


Figure 10 Predicted benzene concentrations at SWUs during high and low discharge conditions (only concentrations of SWUs are shown with a concentration > 0,0001 µg/L during low discharge)

3.4. Relative contribution Dutch IWTPs

The ratio between the contribution of Dutch IWTPs to the total surface waters concentrations provides insight in how much can be done in the Netherlands to mitigate negative impacts of concentrations of contaminants, and how much can be done abroad. Figure 11 shows this relative impact as a percentage of the total impacted SWUs. As can be seen the incoming impact from abroad (rIIF >0-20 %) is generally highest, except in the case of dichloromethane. For toluene and vinyl chloride the impact from abroad is highest, since between 77 and 100 % of the impacted SWUs for these contaminants are in the lower range of relative impact by Dutch IWTPs. In the case of DEHP, benzene and 1,2-dichloroethane the impact by Dutch IWTPs is lower than the impact from abroad, but the impact by Dutch IWTPs is still within a significant range of 15 to 44 %. The percentage of impacted SWUs during high and low discharge differs per substance and over the relative impact ranges. The likely over estimation of concentrations due to incoming rivers—as explained in the previous paragraph—should however be taken into account (especially during high discharge). For the result of this overestimation would also mean that the impact from Dutch IWTPs is higher than currently portrayed.

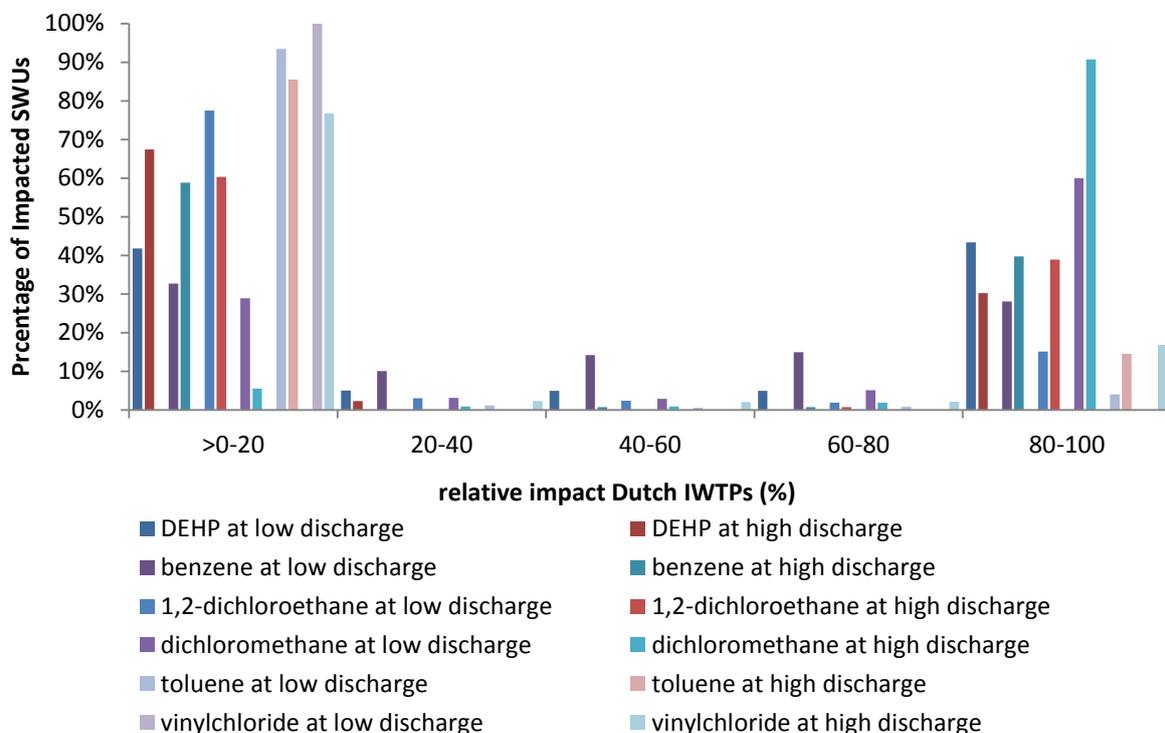


Figure 11 Relative contribution of Dutch IWTPs to the total surface water concentration

3.5. Impact of IWTPs on drinking water production

Table 4 and Table 5 show all assigned IWTP numbers with a calculated relative impact factor higher than 0,1 % for both high and low discharge conditions and for all 6 contaminants. Besides the relative impact factors also the economic sector to which the IWTPs belong, can be found in Table 4 and Table 5. Another thing that can be found in Table 4 and Table 5 is the average relative impact of all six contaminants combined. During low discharge 17 IWTPs have an impact on drinking water production higher than 0,1%, whereas during high discharge conditions only 12 IWTPs have an impact higher than 0,1%.

What stands out most is that for four of the contaminants during low discharge and for five of the contaminants during high discharge the most of the impact seems to come from only one IWTP (IWTP30, with manufacturing of plastics in primary form as economic sector). During high discharge this IWTP even has a relative impact factor of 100 % for four of the six contaminants. The two contaminants for which most variable impact per IWTP can be found are dichloromethane and toluene. Toluene seems to come mostly from the paper manufacturing industry and dichloromethane, besides coming from the plastics industry mostly originates from the refined petroleum products industry.

Figure 12 shows the average relative impact per IWTP during low discharge mapped out. Figure 12 until Figure 18 shows the same only than for each of the six contaminants. Most of the impact (for most of the contaminants) originates from the south east of the Netherlands. Mainly in the case of dichloromethane this does not seem to uphold. For as can be seen in Figure 16, the impact from dichloromethane on drinking water largely originates from the Rotterdam harbour. Most likely this is due to the fact that dichloromethane is mostly emitted by the refined petroleum industry, which is mostly located in the Rotterdam harbour. And also has large emissions of total organic carbon.

The reason IWTP30 has in numerous cases such a large impact on drinking water production locations, can be explained by its size of emission and its location. Emissions of IWTP30 simply reach more drinking water production locations, as IWTP30 (the only IWTP shown in Figure 18) is located almost as far upstream as possible and has a very large emission of TOC compared to other IWTPs.

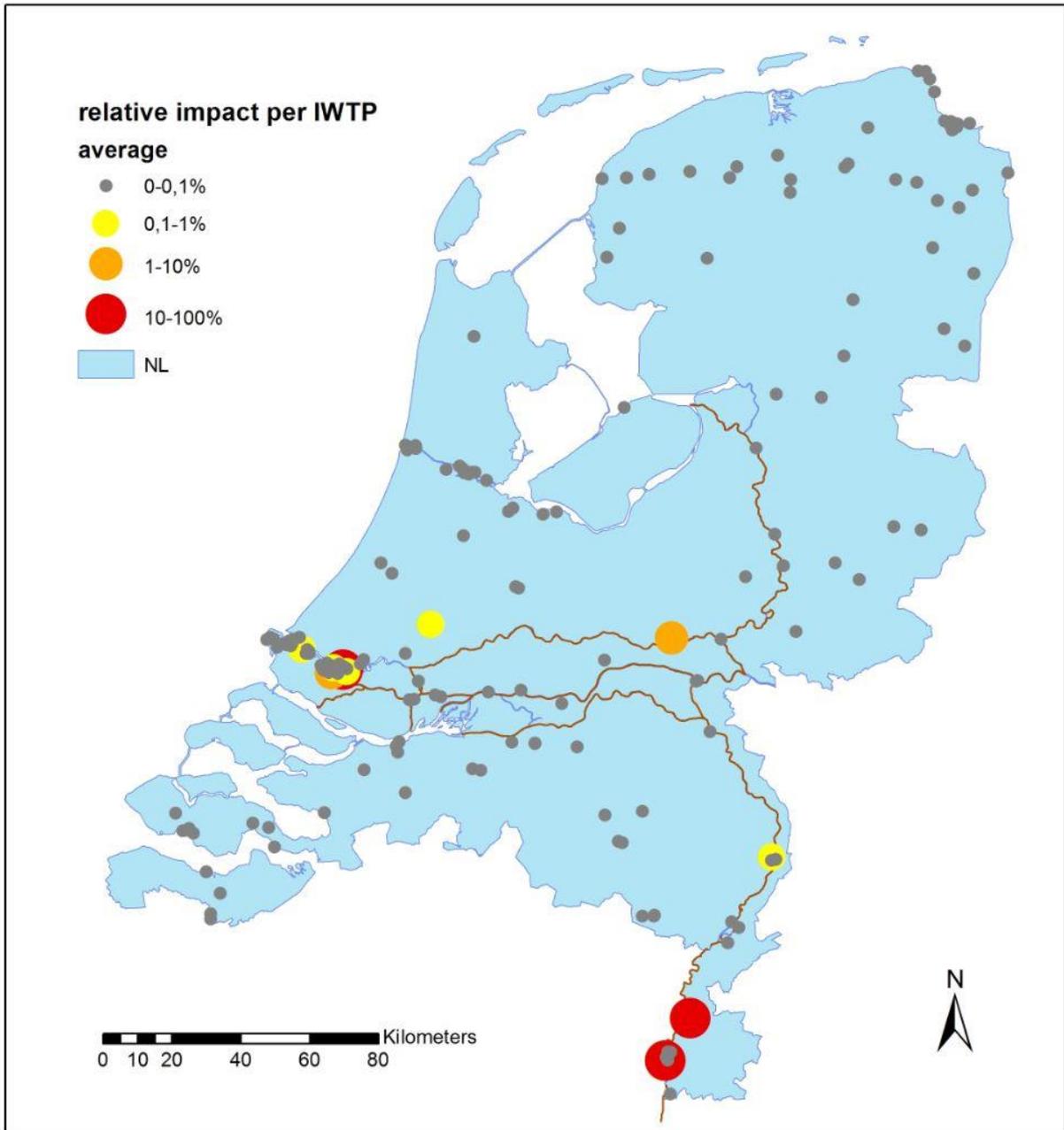


Figure 12 Average relative impact per IWTP on drinking water functions for all six modelled substances during low discharge

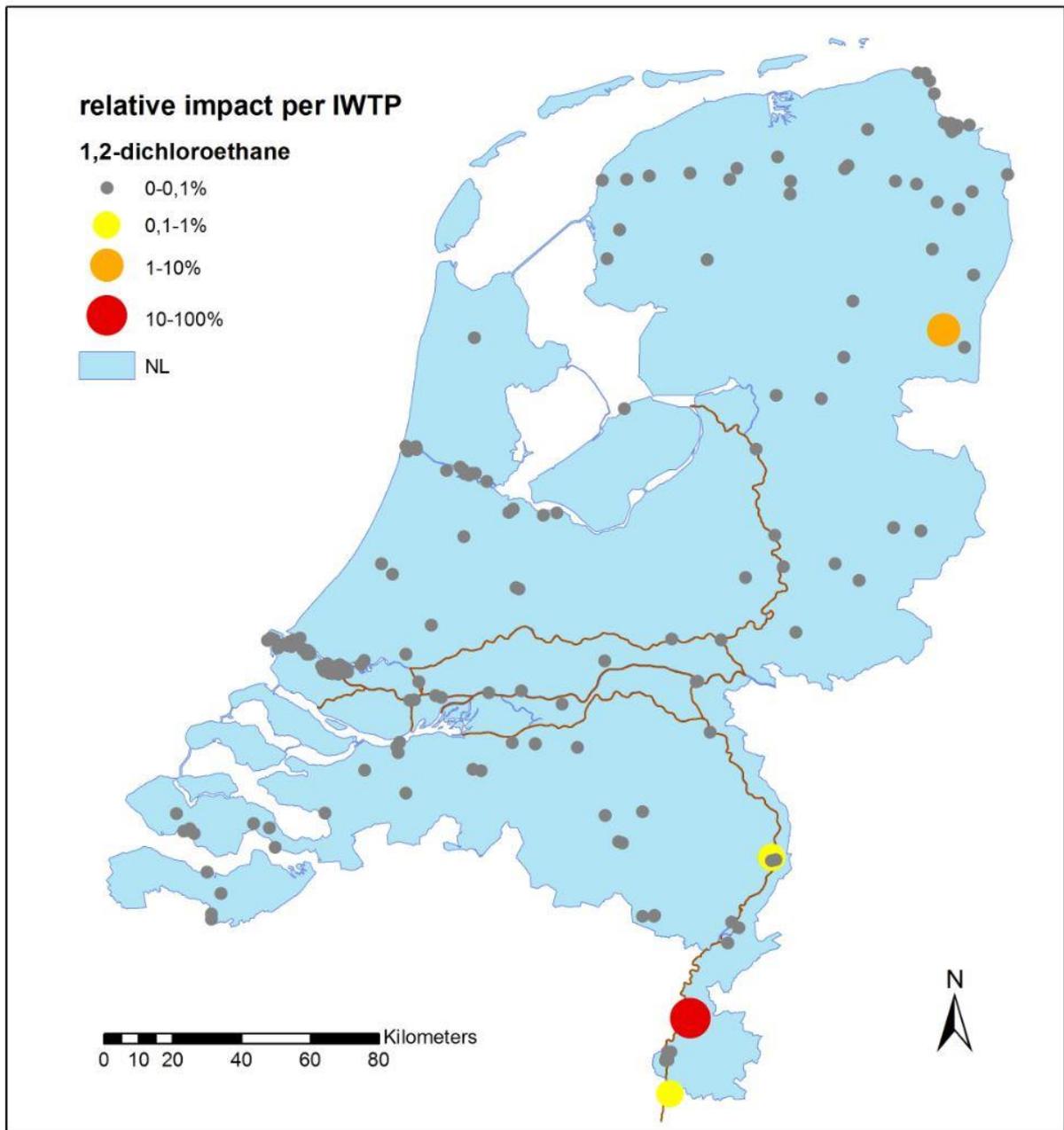


Figure 13 Relative impact per IWTP on drinking water functions for 1,2-dichloroethane during low discharge

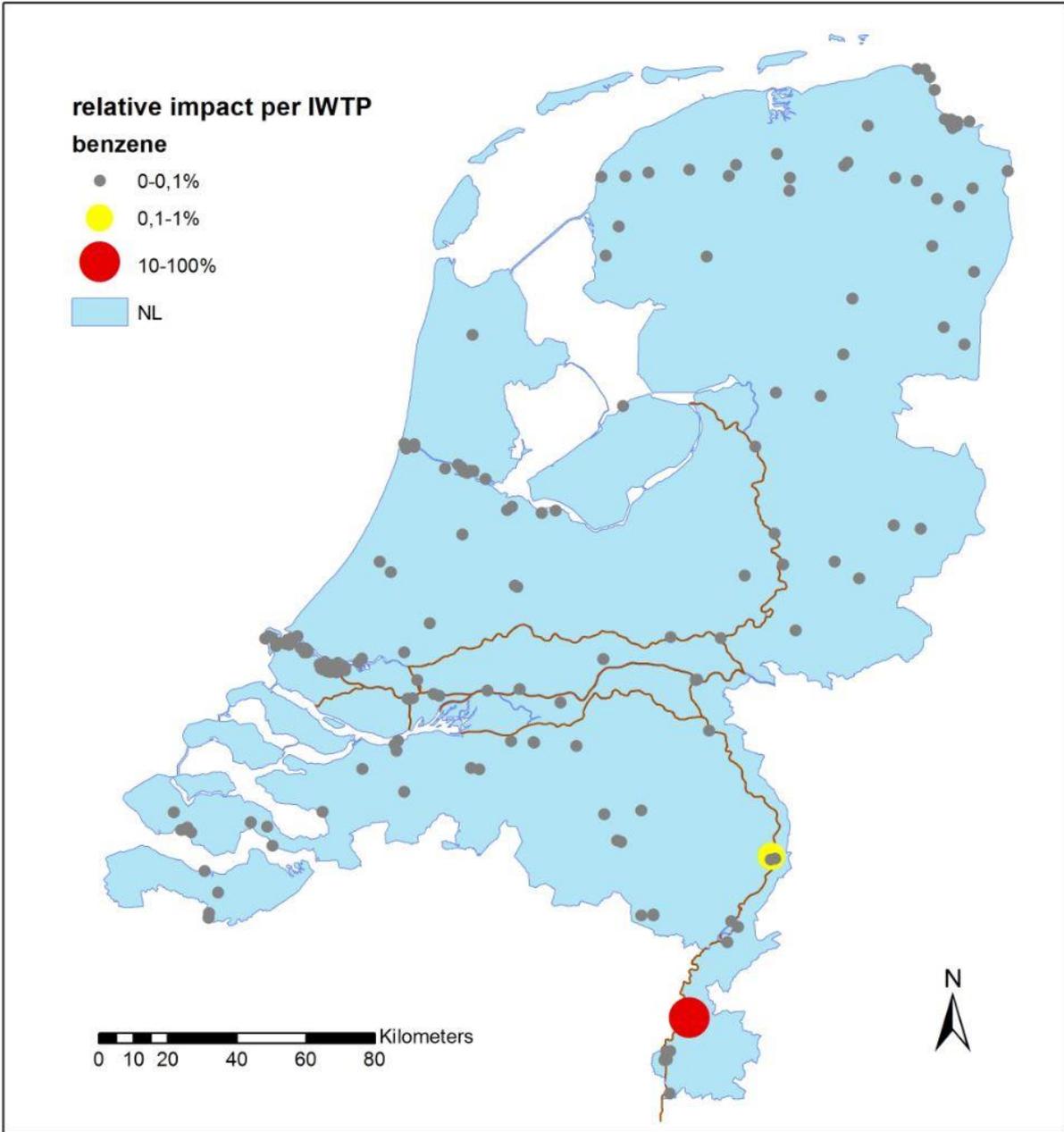


Figure 14 Relative impact per IWTP on drinking water functions for benzene during low discharge

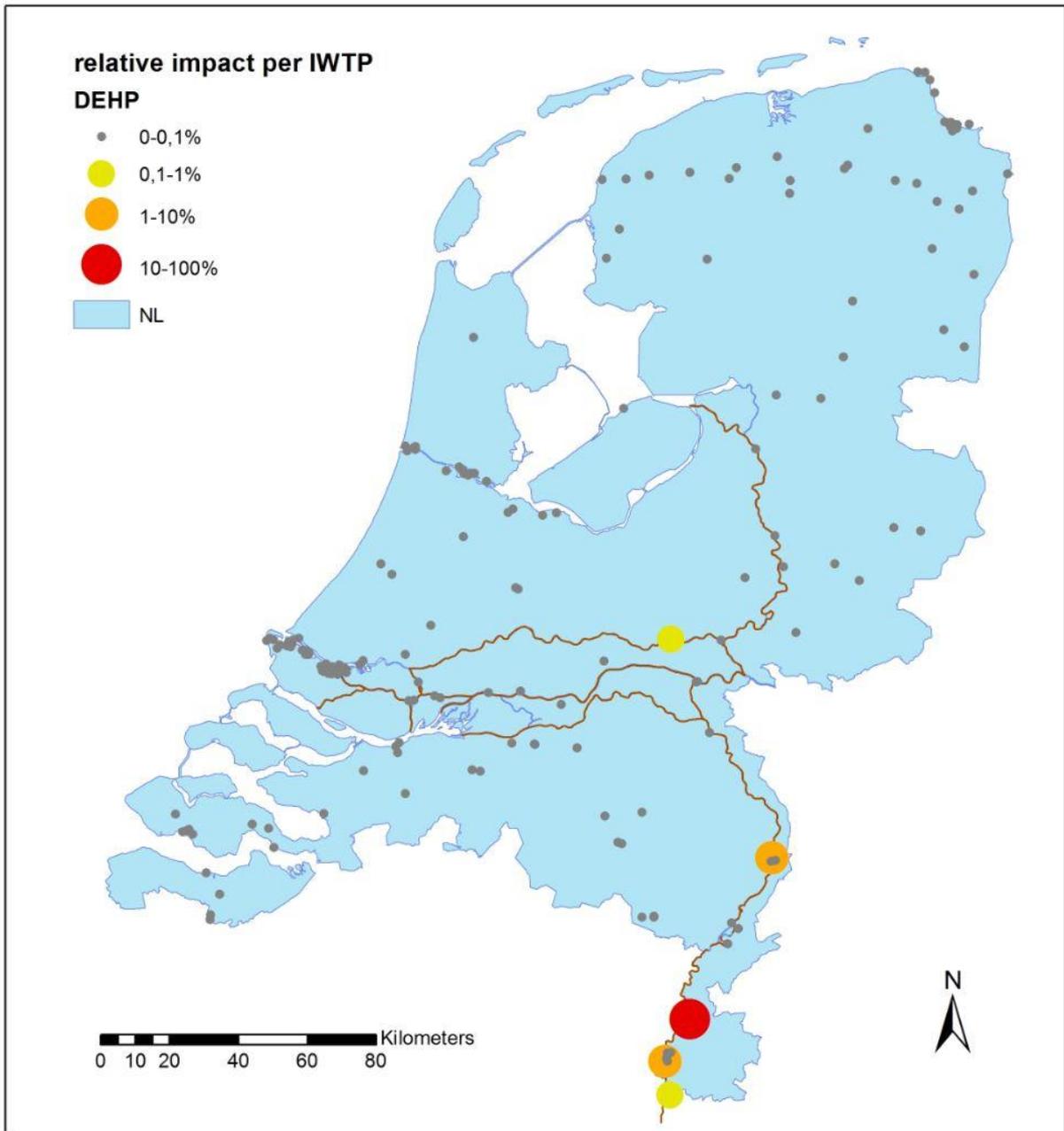


Figure 15 Relative impact per IWTP on drinking water functions for DEHP during low discharge

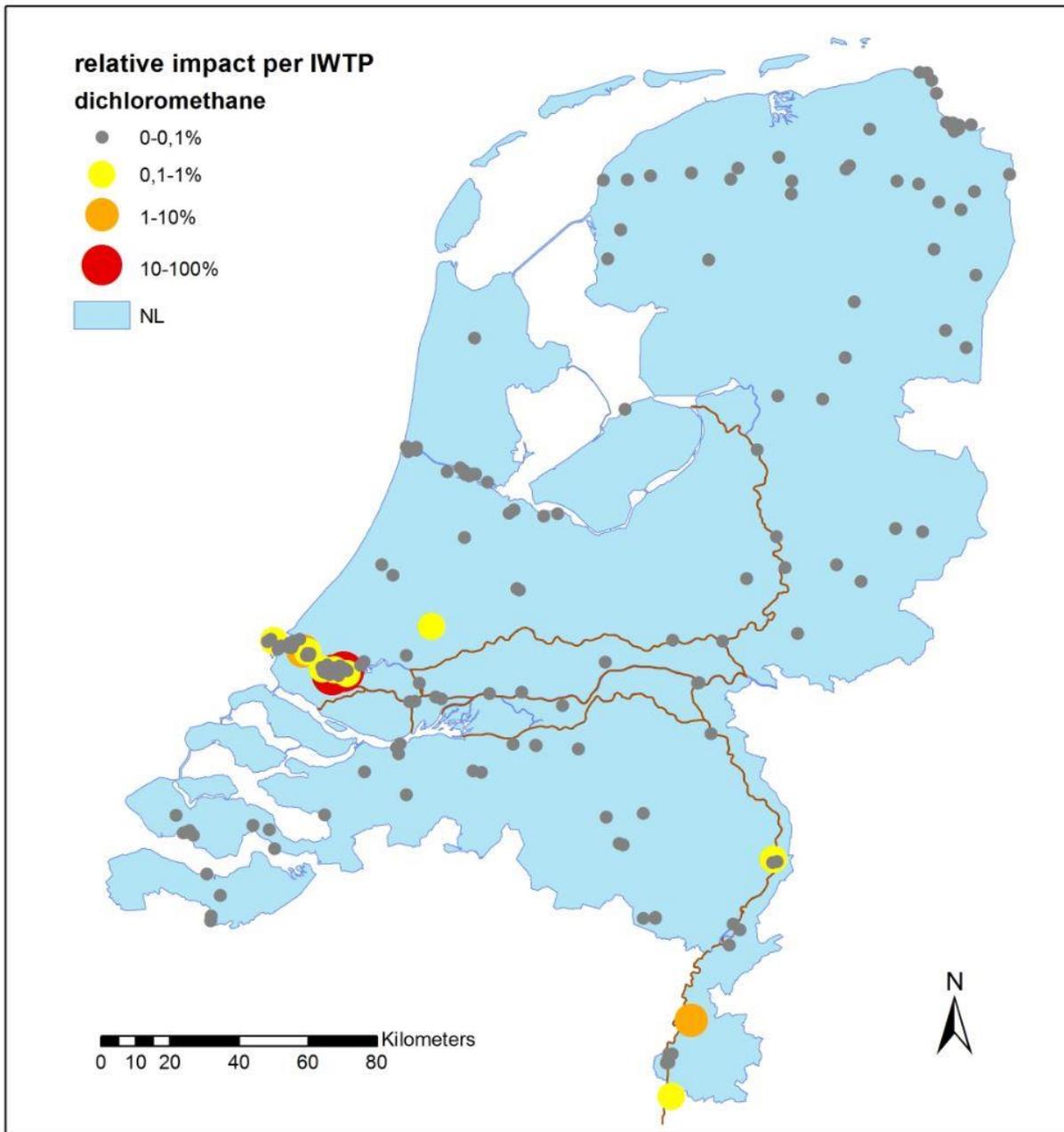


Figure 16 Relative impact per IWTP on drinking water functions for dichloromethane during low discharge

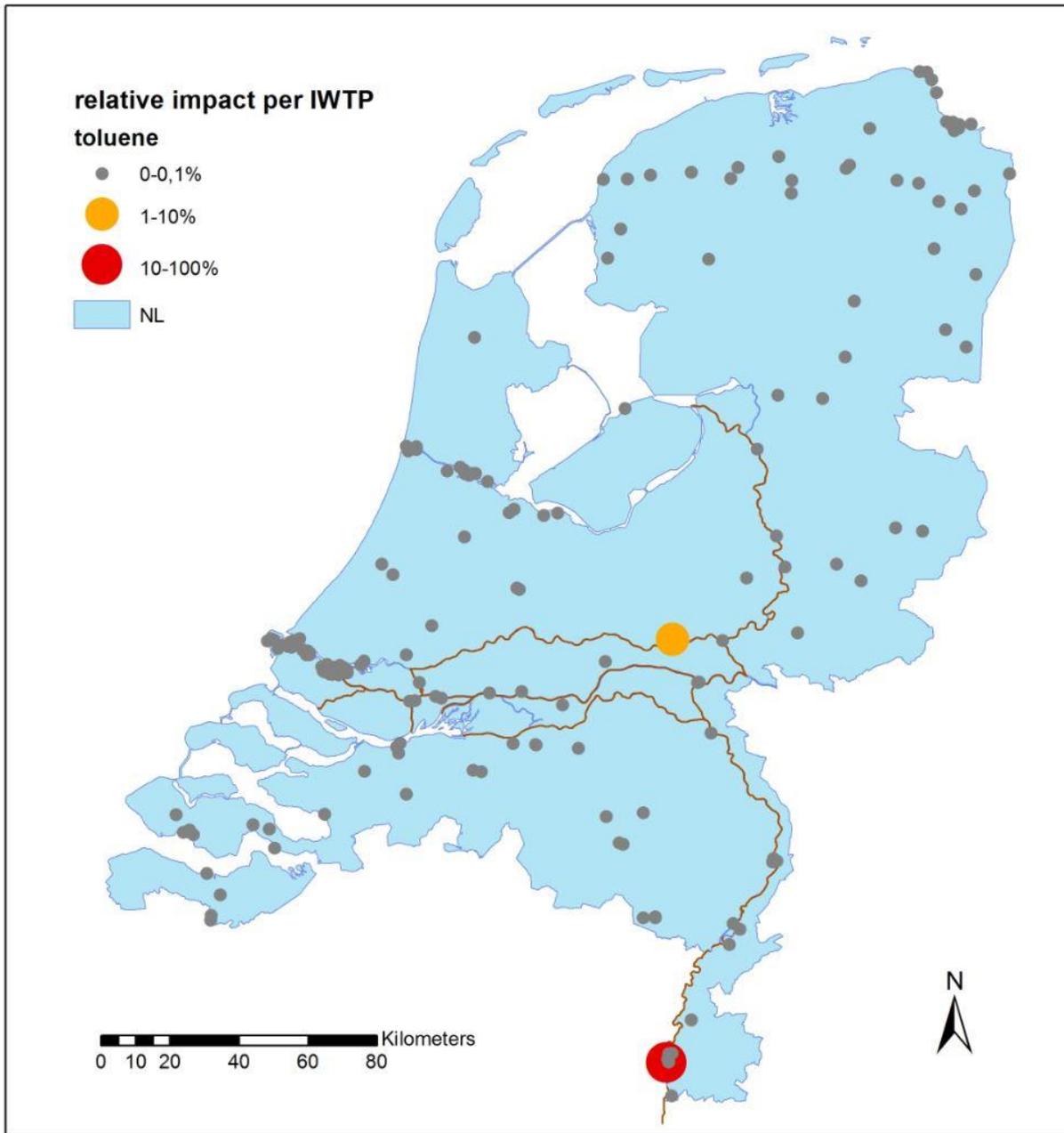


Figure 17 Relative impact per IWTP on drinking water functions for toluene during low discharge

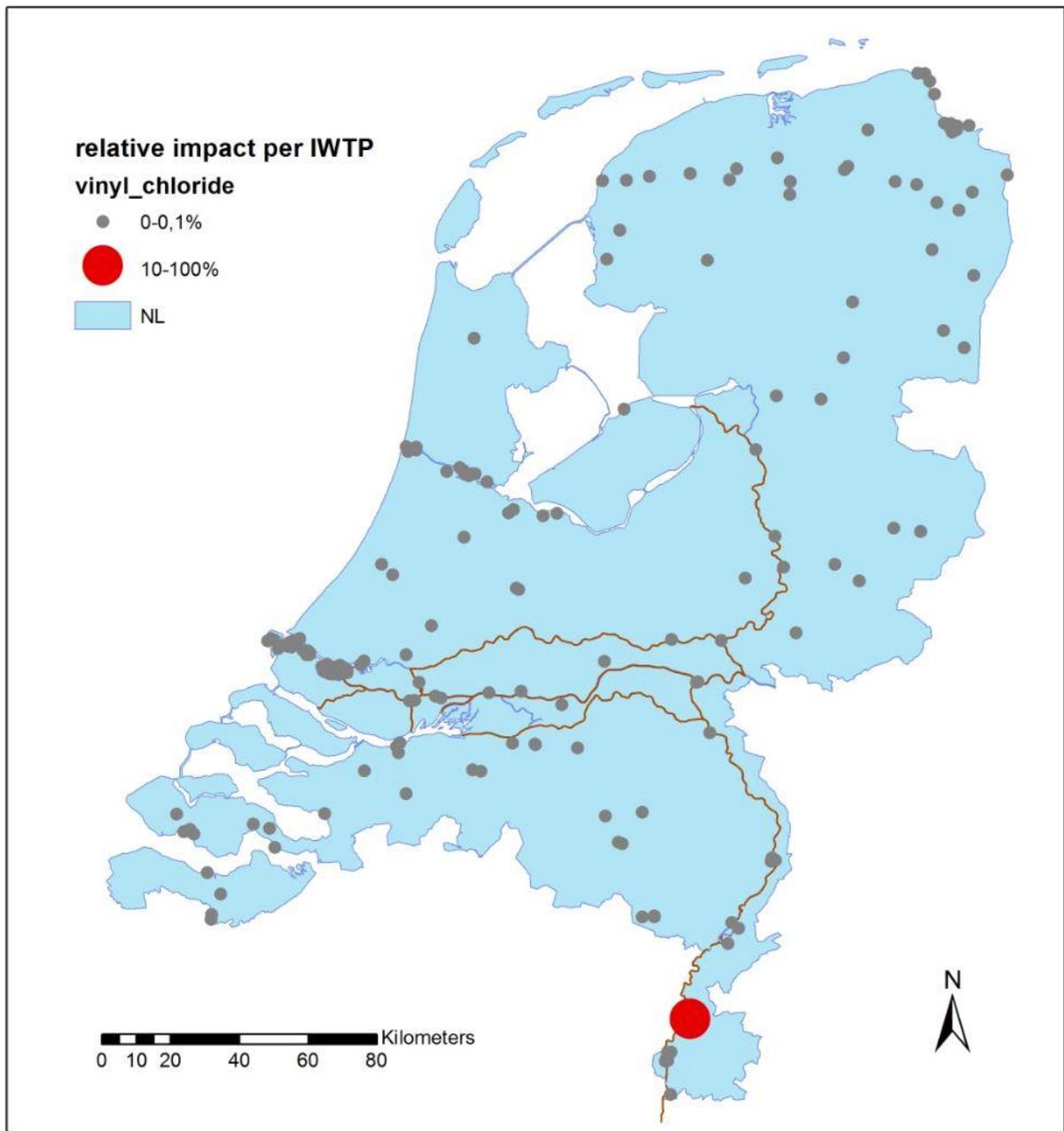


Figure 18 Relative impact per IWTP on drinking water functions for vinyl chloride during low discharge

Table 4 Average impact factors and impact factors per substance that have an impact factor above 0,1 % during low discharge

IWTP nr.	Average		DEHP		Benzene		1,2-dichloroethane		Dichloromethane		Toluene		Vinyl chloride		economic sector
	rIIF _i (%)	rIIF _{i,P} (%)													
IWTP30	65,6	67,7	89,3	92,1	99,9	99,8	95,4	99,6	9,1	14,8	0,0	0,0	99,9	100,0	manufacture of plastics in primary forms
IWTP130	17,0	16,6	8,9	6,6	0,0	0,0	0,0	0,0	0,0	0,0	93,3	93,2	0,0	0,0	manufacture of pulp, paper and paperboard
IWTP141	11,5	10,4	0,0	0,0	0,0	0,0	0,0	0,0	68,8	62,3	0,0	0,0	0,0	0,0	manufacture of refined petroleum products
IWTP138	2,8	2,5	0,0	0,0	0,0	0,0	0,0	0,0	16,7	15,1	0,0	0,0	0,0	0,0	manufacture of refined petroleum products
IWTP129	1,1	1,1	0,1	0,1	0,0	0,0	0,0	0,0	0,0	0,0	6,6	6,6	0,0	0,0	manufacture of pulp, paper and paperboard production and distribution of electricity and gas
IWTP105	0,6	0,0	0,0	0,0	0,0	0,0	3,8	0,1	0,0	0,0	0,0	0,0	0,0	0,0	manufacture of organic basic chemicals
IWTP37	0,4	0,6	1,0	1,0	0,1	0,2	0,5	0,3	0,8	1,9	0,0	0,0	0,1	0,0	manufacture of refined petroleum products
IWTP139	0,3	0,2	0,0	0,0	0,0	0,0	0,0	0,0	1,6	1,4	0,0	0,0	0,0	0,0	manufacture of inorganic basic chemicals
IWTP55	0,2	0,1	0,6	0,1	0,0	0,0	0,1	0,0	0,4	0,2	0,1	0,2	0,0	0,0	manufacture of refined petroleum products
IWTP136	0,1	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,8	0,8	0,0	0,0	0,0	0,0	manufacture of organic basic chemicals
IWTP32	0,1	0,2	0,0	0,0	0,0	0,0	0,0	0,0	0,5	1,2	0,0	0,0	0,0	0,0	manufacture of organic basic chemicals
IWTP61	0,1	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,4	0,9	0,0	0,0	0,0	0,0	manufacture of other chemical products n.e.c.
IWTP80	0,0	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,2	0,3	0,0	0,0	0,0	0,0	manufacture of refined petroleum products
IWTP140	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,2	0,2	0,0	0,0	0,0	0,0	manufacture of organic basic chemicals
IWTP17	0,0	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,2	0,5	0,0	0,0	0,0	0,0	manufacture of organic basic chemicals
IWTP24	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1	0,1	0,0	0,0	0,0	0,0	manufacture of other chemical products n.e.c.
IWTP78	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1	0,1	0,0	0,0	0,0	0,0	

Table 5 Average impact factors and impact factors per substance that have an impact factor above 0,1 % during high discharge

IWTP nr.	Average		DEHP		Benzene		1,2-dichloroethane		Dichloromethane		Toluene		Vinyl chloride		economic sector
	rIIF _i (%)	rIIF _{i,P} (%)													
IWTP30	80,0	81,0	100,0	100,0	100,0	100,0	100,0	100,0	79,8	86,2	0,0	0,0	100,0	100,0	manufacture of plastics in primary forms
IWTP129	7,6	7,5	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	45,4	45,3	0,0	0,0	manufacture of pulp, paper and paperboard
IWTP131	4,8	4,7	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	28,6	28,5	0,0	0,0	manufacture of pulp, paper and paperboard
IWTP130	4,0	4,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	24,0	23,9	0,0	0,0	manufacture of pulp, paper and paperboard
IWTP137	2,8	1,7	0,0	0,0	0,0	0,0	0,0	0,0	16,9	10,1	0,0	0,0	0,0	0,0	manufacture of refined petroleum products
IWTP132	0,3	0,3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	1,9	1,9	0,0	0,0	manufacture of pulp, paper and paperboard
IWTP37	0,3	0,5	0,0	0,0	0,0	0,0	0,0	0,0	1,5	2,3	0,1	0,4	0,0	0,0	manufacture of organic basic chemicals
IWTP55	0,2	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,9	0,4	0,0	0,0	0,0	0,0	manufacture of inorganic basic chemicals
IWTP89	0,1	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,5	0,4	0,0	0,0	0,0	0,0	manufacture of other chemical products n.e.c.
IWTP75	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,3	0,2	0,0	0,0	0,0	0,0	manufacture of other chemical products n.e.c.
IWTP116	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1	0,0	0,0	0,0	0,0	0,0	production and distribution of electricity and gas
IWTP51	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1	0,1	0,0	0,0	0,0	0,0	manufacture of organic basic chemicals

4. Discussion

4.1. Strengths, weaknesses, opportunities and threats

The variable impact per economic sector through normalised E-PRTR emissions, together with the fact that for several of the prioritised IWTPs the relative impact is extremely high in several cases, shows the major strength of the current model. For it shows the combined effect, which the capacity, geographic location and hydrologic distribution can have on surface water quality with vulnerable functions, whilst incorporating variability between industrial sectors.

One of the biggest weaknesses in the model seems to be the overestimation of impact from abroad (especially during high discharge). Consequently here also lays an opportunity for improvement of the model. A suggestion on this account would be to use concentrations from similar hydrological extremes for the estimation of incoming loads from abroad. The modelled impact per IWTP however, shows similar geographic distribution, as the prioritised STPs in the work of Coppens et al., (2015) and thus seems to be correct. Moreover, the error due to wrongly estimated concentrations from abroad results in an overestimated impact from abroad and does not affect the relative impact per IWTP, which means that in terms of mitigation, most likely a larger part could be mitigated than currently modelled.

Another weakness, is the fact that there was no time to compare modelled concentrations with actually monitored concentrations. This on the other hand might not be worthwhile, due to the fact that the modelled contaminants all have other emission pathways (e.g. indirect emissions via STPs or from stockpiled contaminants).

Besides that mapping out modelled surface water concentrations would improve understanding of the geographic distribution of contaminants. Especially in the case of dichloromethane this seems important, since for this contaminant a large part of the impact comes from an unexpected location (the Rotterdam harbour). Additionally, if the impact of several IWTPs in the Rotterdam harbour truly is as high as modelled, a possible

improvements of the model could be to model the impact of all IWTPS in the Rotterdam harbour as one point source. Namely because 43 of the 182 IWTPs that were taken into account in the model are located there within a radius of 10 km.

Continuingly Coppens et al., (2015) already mentioned several weaknesses of the KRW Explorer 2.0 itself (e.g. wrong mass fluxes in the Western Scheldt). These should also be taken into account in the current evaluation, as the same basis was used for this model. Hence an argument could be made to use a different programme to model with.

It can also be argued that none of the modelled contaminants are of concern to drinking water companies. For as Sjerps et al., (2016) and Schriks et al., (2010) explain: mainly very hydrophilic contaminants pose possible problems for frequently used drinking water technologies in the Netherlands (e.g. activated carbon). And, an evaluation of the modelled contaminants based on their corresponding logD value has yet to be conducted. Conversely the modelled contaminants are an example of how the contaminant groups (portrayed in Figure 2) could be emitted. And these groups most likely contain several of the by Sjerps et al., (2016) prioritised contaminants. In addition the relative impact results per IWTP most likely wouldn't differ much when other contaminants are concerned, especially because in the current model the variation between industries is incorporated by modelling a variety of six contaminants.

In this case the impact on vulnerable drinking water functions was investigated , but Coppens et al., (2015) likewise modelled the impact medicines from STPs have on Natera 2000 areas. This could be an interesting opportunity to take in to account in future scenarios.

5. Conclusion

To answer the research question: *“Which impact do effluents of various types of industrial wastewater treatment plants have on the quality of Dutch surface waters with susceptible drinking water functions?”* it can be said that out of the 182 investigated IWTPs, covering 43 industrial classes, almost all impact during high and low discharge conditions, is caused by only 24 IWTPs and the majority of impact even comes from fewer IWTPs. Industrial classes with most impact are the plastic industry, refined petroleum industry and paper industry. A considerable amount of impact is caused by IWTPs in the Netherlands, though according to the model (at current moment), the majority of impact comes from bordering countries. Besides the six modelled contaminants several compounds of high impact potential have been selected, which could have comparable impact results.

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Appendix: A Input data rivers from abroad

Data input for boundary points during high discharge conditions are shown below

segment	nodeid	NAME	discharge (m3/s)	concentration (µg/L)					
				DEHP	benzene	vinyl chloride	toluene	1,2-dichloroethane	dichloromethane
152	DM1001	Overijsselse Vecht	54,27	1,05818	0,03422	73,77300	0,02476	0,69087	3,42816
155	DM101	Roer	39,45	1,05818	0,03422	73,77300	0,02476	0,69087	3,42816
156	DM102	Swalm	1,99	1,05818	0,03422	73,77300	0,02476	0,69087	3,42816
157	DM103	Niers	14,92	1,05818	0,03422	73,77300	0,02476	0,69087	3,42816
158	DM104	Rijn bij Lobith	3439,39	1,03031	0,04086	70,01500	0,01974	0,72827	3,27167
173	DM111	Maas- Monsin	497,66	1,08605	0,02758	77,53100	0,02978	0,65347	3,58466
314	DM5098	Belgie	0,1	1,05818	0,03422	73,77300	0,02476	0,69087	3,42816
317	DM5101	Belgie (Mark & Weerij)	11,79	1,05818	0,03422	73,77300	0,02476	0,69087	3,42816
318	DM5102	Dommel & Tongelreep	4,63	1,05818	0,03422	73,77300	0,02476	0,69087	3,42816

segment	nodeid	NAME	discharge (m3/s)	concentration (g/m3)					
				DEHP	benzene	vinyl chloride	toluene	1,2-dichloroethane	dichloromethane
152	DM1001	Overijsselse Vecht	54,27	0,00106	0,00003	0,07377	0,00002	0,00069	0,00343
155	DM101	Roer	39,45	0,00106	0,00003	0,07377	0,00002	0,00069	0,00343
156	DM102	Swalm	1,99	0,00106	0,00003	0,07377	0,00002	0,00069	0,00343
157	DM103	Niers	14,92	0,00106	0,00003	0,07377	0,00002	0,00069	0,00343
158	DM104	Rijn bij Lobith	3439,39	0,00103	0,00004	0,07002	0,00002	0,00073	0,00327
173	DM111	Maas- Monsin	497,66	0,00109	0,00003	0,07753	0,00003	0,00065	0,00358
314	DM5098	Belgie	0,1	0,00106	0,00003	0,07377	0,00002	0,00069	0,00343
317	DM5101	Belgie (Mark & Weerij)	11,79	0,00106	0,00003	0,07377	0,00002	0,00069	0,00343
318	DM5102	Dommel & Tongelreep	4,63	0,00106	0,00003	0,07377	0,00002	0,00069	0,00343

segment	nodeid	NAME	discharge (m3/s)	load (g/s)					
				DEHP	benzene	vinyl chloride	toluene	1,2-dichloroethane	dichloromethane
152	DM1001	Overijsselse Vecht	54,27	0,05743	0,00186	4,00366	0,00134	0,03749	0,18605
155	DM101	Roer	39,45	0,04175	0,00135	2,91034	0,00098	0,02725	0,13524
156	DM102	Swalm	1,99	0,00211	0,00007	0,14681	0,00005	0,00137	0,00682
157	DM103	Niers	14,92	0,01579	0,00051	1,10069	0,00037	0,01031	0,05115
158	DM104	Rijn bij Lobith	3439,39	3,54365	0,14054	240,80889	0,06791	2,50481	11,25254
173	DM111	Maas- Monsin	497,66	0,54048	0,01373	38,58408	0,01482	0,32521	1,78394
314	DM5098	Belgie	0,1	0,00011	0,00000	0,00738	0,00000	0,00007	0,00034
317	DM5101	Belgie (Mark & Weerij)	11,79	0,01248	0,00040	0,86978	0,00029	0,00815	0,04042
318	DM5102	Dommel & Tongelreep	4,63	0,00490	0,00016	0,34157	0,00011	0,00320	0,01587

Data input for boundary points during low discharge are shown below

segment	nodeid	NAME	discharge (m3/s)	concentration (µg/L)					
				DEHP	benzene	vinyl chloride	toluene	1,2-dichloroethane	dichloromethane
152	DM1001	Overijsselse Vecht	3,18	0,99618	0,02380	74,36347	0,01857	0,24922	3,99138
155	DM101	Roer	11,29	0,99618	0,02380	74,36347	0,01857	0,24922	3,99138
156	DM102	Swalm	1,34	0,99618	0,02380	74,36347	0,01857	0,24922	3,99138
157	DM103	Niers	4,34	0,99618	0,02380	74,36347	0,01857	0,24922	3,99138
158	DM104	Rijn bij Lobith	1067,08	1,04324	0,02937	71,44286	0,01961	0,05754	4,08419
173	DM111	Maas- Monsin	56,95	0,94911	0,01823	77,28409	0,01753	0,44091	3,89857
314	DM5098	Belgie	0,1	0,99618	0,02380	74,36347	0,01857	0,24922	3,99138
317	DM5101	Belgie (Mark & Weerijis)	0,79	0,99618	0,02380	74,36347	0,01857	0,24922	3,99138
318	DM5102	Dommel & Tongelreep	1,53	0,99618	0,02380	74,36347	0,01857	0,24922	3,99138

segment	nodeid	NAME	discharge (m3/s)	concentration (g/m3)					
				DEHP	benzene	vinyl chloride	toluene	1,2-dichloroethane	dichloromethane
152	DM1001	Overijsselse Vecht	3,18	0,00100	0,00002	0,07436	0,00002	0,00025	0,00399
155	DM101	Roer	11,29	0,00100	0,00002	0,07436	0,00002	0,00025	0,00399
156	DM102	Swalm	1,34	0,00100	0,00002	0,07436	0,00002	0,00025	0,00399
157	DM103	Niers	4,34	0,00100	0,00002	0,07436	0,00002	0,00025	0,00399
158	DM104	Rijn bij Lobith	1067,08	0,00104	0,00003	0,07144	0,00002	0,00006	0,00408
173	DM111	Maas- Monsin	56,95	0,00095	0,00002	0,07728	0,00002	0,00044	0,00390
314	DM5098	Belgie	0,1	0,00100	0,00002	0,07436	0,00002	0,00025	0,00399
317	DM5101	Belgie (Mark & Weerijis)	0,79	0,00100	0,00002	0,07436	0,00002	0,00025	0,00399
318	DM5102	Dommel & Tongelreep	1,53	0,00100	0,00002	0,07436	0,00002	0,00025	0,00399

segment	nodeid	NAME	discharge (m3/s)	load (g/s)					
				DEHP	benzene	vinyl chloride	toluene	1,2-dichloroethane	dichloromethane
152	DM1001	Overijsselse Vecht	3,18	0,00002	0,00000	0,00138	0,00000	0,00000	0,00007
155	DM101	Roer	11,29	0,00002	0,00000	0,00138	0,00000	0,00000	0,00007
156	DM102	Swalm	1,34	0,00002	0,00000	0,00138	0,00000	0,00000	0,00007
157	DM103	Niers	4,34	0,00002	0,00000	0,00138	0,00000	0,00000	0,00007
158	DM104	Rijn bij Lobith	1067,08	0,00002	0,00000	0,00140	0,00000	0,00000	0,00008
173	DM111	Maas- Monsin	56,95	0,00002	0,00000	0,00135	0,00000	0,00001	0,00007
314	DM5098	Belgie	0,1	0,00002	0,00000	0,00138	0,00000	0,00000	0,00007
317	DM5101	Belgie (Mark & Weerijis)	0,79	0,00002	0,00000	0,00138	0,00000	0,00000	0,00007
318	DM5102	Dommel & Tongelreep	1,53	0,00002	0,00000	0,00138	0,00000	0,00000	0,00007

Appendix: B Overview of selected compounds and their applications

selected compounds and their functions according to Wikipedia.

Molecular formula	CAS-number	Suspect	Uses
C8H18O4	112-49-2	1,2-bis(2-methoxyethoxy)-ethane (triglyme)	solvent commonly used in ink, paints and cleaners
C6H12Cl3O4P	115-96-8	tris(2-chloroethyl) phosphate (TCEP)	frequently used reducing agent and flame retardent
C12H27O4P	126-73-8	tributyl phosphate (TBP)	solvent and plasticizer in inks, synthetic resins, gums, adhesives and extraction of rare earth metals (namely for veneer plywood) and herbicide and fungicide
C9H18Cl3O4P	13674-84-5	tris(2-chloro-1-methylethyl) phosphate (TCPP)	flame retardent and used in gums and platics
C7H7N3	29878-31-7	4-Methyl-1H-benzotriazole	corosion inhibitor, drug precursor, heating and cooling liquids
C10H15NO2S	3622-84-2	N-butylbenzenesulphonamide	frequently used plasticizer
C19H30O5	51-03-6	2-(2-butoxyethoxy)ethyl 6-propylpiperonyl ether	solvent commonly used in ink, paints and cleaners
C6H15O4P	78-40-0	triethyl phosphate	industrial catalyst, solvent, plasticizer, flame retardent an pesticide intermediate / precursor
C18H15OP	791-28-6	triphenylphosphine oxide (TPPO)	cristalizing agent
C12H10O4S	80-09-1	4,4'-sulphonyldiphenol (bisphenol S)	fast drying epoxy glues, corrosion inhibittor, paper, thermal paper etc..
C9H17NO	826-36-8	2,2,6,6-tetramethyl-4-piperidone	drug
C13H15N3O2	83-15-8	N-Acetylaminoantipyrine	drug
C16H22O4	84-69-5	diisobutyl phthalate	nail pollish, plastics, polish, plasticizer, inks
C16H22O4	84-74-2	dibutyl phthalate	nail pollish, plastics, polish, plasticizer, inks
C6H5N3	95-14-7	benzotriazole	corosion inhibitor, drug precursor, heating and cooling liquids
C6H4Cl2	95-50-1	1,2-dichloorbenzeen	solvent, insecticide
C6H7N	62-53-3	aniline	dyes, medicine, rocketfuels
C6H5Cl2N	608-27-5	2,3-dichlooraniline	dyes, medicine, rocketfuels
C6H5Cl2N	95-82-9	2,5-dichlooraniline	dyes, medicine, rocketfuels
C12H27O4P	126-71-6	triisobutylfosfaat	plasticizers, solvents, extraction rare earth metals, resins, paints, inks, pesticide precursor, antifoaming
C3H4N2	288-32-4	trifenyl-imidazole-triglycine	corosion inhibitor, flame retardent drugs and pesticed procursor

C15H16O2	80-05-7	bisfenol A	fast drying epoxy glues, corrosion inhibittor, paper, thermal paper etc..
C10H16N2O4	10543-57-4	tetra-acetyl-ethyleendiamine (TAED)	bleaching agent, household products and paperpulp
C6H12N4	100-97-0	methenamine	plastics, pharmaceuticals, rubber additives, explosives, fuel pellets
C6H5Cl2N	554-00-7	2,4-dichlooraniline	dyes, medicine, rocketfuels
C6H5Cl2N	608-31-1	2,6-dichlooraniline	dyes, medicine, rocketfuels
C6H5Cl2N	95-76-1	3,4-dichlooraniline	dyes, medicine, rocketfuels
C6H5Cl2N	626-43-7	3,5-dichlooraniline	dyes, medicine, rocketfuels
C18H26O	1222-05-5	galaxolide (HHCB)	personal care products and cleaning
C24H38O4	117-81-7	bis(2-ethylhexyl) phthalate (DEHP)	PVC, plasticizer, plastics
C4H8O2	123-91-1	1,4-dioxane	stabelizer aluminium packages, solvent in ink and adhesives
C16H10	129-00-0	pyrene	stabelizer aluminium packages, solvent in ink and adhesives

Appendix: C Example of TOC and DEHP emissions per sector

In the table below the Total Organic Carbon E-PRTR emissions to water (kg/2013) are shown for the whole of Europe , together with the total emission of DEHP. Next to the emission in kg, the number of industrial facilities is shown for which emissions are reported.

Industrial sectors (classes and sub-classes)	Total Organic Phosphorous (kg)	nr	Total Organic Phosphorous kg/nr	Total Organic Nitrogen (kg)	nr	Total Organic Nitrogen kg/nr	Total Organic Carbon (kg)	nr	Total Organic Carbon kg/nr	DEHP (kg)	nr	DEHP kg/nr
NACE 10: manufacture of food products	1358540	89	15264	5954400	57	104463	32303400	97	333025	0	0	0
NACE 10.1: processing and preserving of meat and poultry	85210	9	9468	404000		0	1467100	5	293420	0	0	0
NACE 10.3: processing and preserving of fruit and vegetables	83570	4	20893	90000		0	766200	5	153240	0	0	0
NACE 10.4: manufacture of oils and fats	10700	1	10700	0		0	75400	1	75400	0	0	0
NACE 10.5: dairy industry	115390	13	8876	128700		0	3298500	10	329850	0	0	0
NACE 10.6: manufacture of grain mill products, excl. starches and starch products	55940	3	18647	0		0	699300	6	116550	0	0	0
NACE 10.8 (excluding NACE 10.81 and 10.82): other manufacture of food products	138100	3	46033	220600		0	1270900	12	105908	0	0	0
NACE 10.81: manufacture of sugar	41700	1	41700	110600		0	738400	8	92300	0	0	0
NACE 10.9: manufacture of prepared animal feeds	0	2	0	0		0	10100	1	10100	0	0	0
NACE 11 manufacture of beverages	653770	3	217923	616000	1	616000	15670000	4	3917500	0	0	0
NACE 11.05: manufacture (brewing) of beer			0			0			0	0	0	0
NACE 11.07: manufacture of soft drinks and other beverages			0			0			0	0	0	0
NACE 17: manufacture of paper and paper products	824930	55	14999	64492	56	1152	#####	180	787594	150	6	25

NACE 17.1: manufacture of pulp, paper and paperboard	815790	54	15107	6369100	55	115802	1,4E+08	175	798973	150,4	6	25
NACE 17.2: manufacture of articles of paper and paperboard	9140	1	9140	80100	1	80100	1946700	5	389340	0	0	0
NACE 19.201: manufacture of refined petroleum products	74520	6	12420	2030100	19	106847	4765500	35	136157	16	4	4
NACE 20.1: manufacture of basic chemicals, fertilisers and nitrogen compounds, plastics and synthetic rubber in primary forms	704650	30	23488	21231500	78	272199	20593900	89	231392	215,68	12	18
NACE 20.11: manufacture of industrial gasses	0	0	0	0	0	0	0	0	0	0	0	0
NACE 20.12: manufacture of dyes and pigments	18110	2	9055	222200	2	111100	287100	3	95700	0	0	0
NACE 20.13: manufacture of inorganic basic chemicals	314700	7	44957	5287300	24	220304	5755300	16	359706	48,3	1	48
NACE 20.14: manufacture of organic basic chemicals	242120	13	18625	4416300	20	220815	10923600	42	260086	156,2	7	22
NACE 20.149: manufacture of organic basic chemicals (no petrochemicals)			0			0			0			0
NACE 20.15: manufacture of fertilizers and nitrogen compounds	111120	6	18520	10329000	26	397269	1206300	8	150788	7,47	1	7
NACE 20.16: manufacture of plastics in primary forms	18600	2	9300	915300	5	183060	2196600	18	122033	3,71	3	1
NACE 20.2: manufacture of pesticides	6950	1	6950	0	0	0	145200	1	145200	0	0	0
NACE 20.3: manufacture of paints, varnishes and similar coatings, printing ink and mastics	0	0	0	0	0	0	0	0	0	0	0	0
NACE 20.5 Manufacture of other chemical products	7740	1	7740	2820400	10	282040	1696600	10	169660	0	0	0
NACE 20.52: manufacture of glues and adhesives	0	0	0	0	0	0	0	0	0	0	0	0
NACE 20.53: manufacture of essential oils	0	0	0	0	0	0	0	0	0	0	0	0
NACE 20.59: manufacture of other chemical products n.e.c.	7740	1	7740	2461400	7	351629	1696600	10	169660	0	0	0

NACE 24 manufacture of basic metals	62910	5	12582	5445000	32	170156	5153500	21	245405	20	1	20
NACE 24 (excluding NACE 24.4/24.5): manufacture of metals in primary forms	62910	4	15728	4454200	27	164970	4925600	16	307850	20	1	20
NACE 24.45: manufacture of non-ferrous metals, aluminium	0	0	0	0	0	0	0	0	0	0	0	0
NACE 24.45: manufacture of other non- ferrous metals	0	0	0	155000	1	155000	0	0	0	0	0	0
NACE 24.5: casting of metals	0	0	0	0	0	0	54600	1	54600	0	0	0
NACE 25.61: treatment and coating of metals	43080	3	14360	0	0	0	0	0	0	0	0	0
NACE 26-28: manufacture of machinery and electro technical industry	8820	1	8820	53800	1	53800	0	0	0	0	0	0
NACE 29: motor-industry	0	0	0	0	0	0	0	0	0	6	2	3
NACE 30.1: ship-building	0	0	0	0	0	0	0	0	0	0	0	0
NACE 35: production and distribution of electricity and gas	127900	9	14211	10216100	21	486481	5320900	16	332556	0	0	0
NACE 20.6: manufacture of synthetic and artificial fibres	0	0	0	162000	2	81000	517000	3	172333	3	1	3
NACE 21.1: manufacture of pharmaceutical preparations	46670	4	11668	844800	3	281600	1083900	13	83377	0	0	0
NACE 22.2: manufacture of plastic products	0	0	0	0	0	0	0	0	0	0	0	0
NACE 23.1 (excluding NACE 23.12): manufacture of glass and glassware	0	0	0	0	0	0	0	0	0	0	0	0

Appendix: D Normalized loads of DEHP

	Nr. total reporting	nr	TOC kg/nr	nr	P (%)	DEHP Normalised	DEHP kg/nr
Facilities NACE 10.1: processing and preserving of meat and poultry	117	5	293420	0	0,000	0,0E+00	0
Facilities NACE 10.3: processing and preserving of fruit and vegetables	15	5	153240	0	0,000	0,0E+00	0
Facilities NACE 10.4: manufacture of oils and fats	47	1	75400	0	0,000	0,0E+00	0
Facilities NACE 10.5: dairy industry	71	10	329850	0	0,000	0,0E+00	0
Facilities NACE 10.6: manufacture of grain mill products, excl. starches and starch products	21	6	116550	0	0,000	0,0E+00	0
Facilities NACE 10.8 (excluding NACE 10.81 and 10.82): other manufacture of food products	96	12	105908	0	0,000	0,0E+00	0
Facilities NACE 10.81: manufacture of sugar	74	8	92300	0	0,000	0,0E+00	0
Facilities NACE 10.9: manufacture of prepared animal feeds	24	1	10100	0	0,000	0,0E+00	0
Facilities NACE 11.05: manufacture (brewing) of beer	8		0	0	0,000	0,0E+00	0
Facilities NACE 11.07: manufacture of soft drinks and other beverages	5		0	0	0,000	0,0E+00	0
Facilities NACE 17.1: manufacture of pulp, paper and paperboard	249	175	798973	6	0,017	3,1E-05	25
Facilities NACE 17.2: manufacture of articles of paper and paperboard	28	5	389340	0	0,000	0,0E+00	0
Facilities NACE 19.201: manufacture of refined petroleum products	116	35	136157	4	0,010	2,9E-05	4
Facilities NACE 20.11: manufacture of industrial gasses	23	0	0	0	0,000	0,0E+00	0
Facilities NACE 20.12: manufacture of dyes and pigments	34	3	95700	0	0,000	0,0E+00	0
Facilities NACE 20.13: manufacture of inorganic basic chemicals	138	16	359706	1	0,001	1,3E-04	48
Facilities NACE 20.14: manufacture of organic basic chemicals	224	42	260086	7	0,006	8,6E-05	22
Facilities NACE 20.15: manufacture of fertilizers and nitrogen compounds	58	8	150788	1	0,002	5,0E-05	7
Facilities NACE 20.16: manufacture of plastics in primary forms	90	18	122033	3	0,007	1,0E-05	1

Facilities NACE 20.2: manufacture of pesticides	18	1	145200	0	0,000	0,0E+00	0
Facilities NACE 20.3: manufacture of paints, varnishes and similar coatings, printing ink and mastics	18	0	0	0	0,000	0,0E+00	0
Facilities NACE 20.52: manufacture of glues and adhesives	4	0	0	0	0,000	0,0E+00	0
Facilities NACE 20.53: manufacture of essential oils	4	0	0	0	0,000	0,0E+00	0
Facilities NACE 20.59: manufacture of other chemical products n.e.c.	58	10	169660	0	0,000	0,0E+00	0
Facilities NACE 24 (excluding NACE 24.4/24.5): manufacture of metals in primary forms	346	16	307850	1	0,000	6,5E-05	20
Facilities NACE 24.45: manufacture of non-ferrous metals, aluminium	60	0	0	0	0,000	0,0E+00	0
Facilities NACE 24.45: manufacture of other non-ferrous metals	19	0	0	0	0,000	0,0E+00	0
Facilities NACE 24.5: casting of metals	111	1	54600	0	0,000	0,0E+00	0
Facilities NACE 25.61: treatment and coating of metals	97	0	0	0	0,000	0,0E+00	0
Facilities NACE 26-28: manufacture of machinery and electro technical industry	50	0	0	0	0,000	0,0E+00	0
Facilities NACE 29: motor-industry	115	0	0	2	0,000	0,0E+00	3
Facilities NACE 30.1: ship-building	11	0	0	0	0,000	0,0E+00	0
Facilities NACE 35: production and distribution of electricity and gas	1116	16	332556	0	0,000	0,0E+00	0
Facilities NACE 20.6: manufacture of synthetic and artificial fibres	17	3	172333	1	0,010	1,6E-05	3
Facilities NACE 21.1: manufacture of pharmaceutical preparations	95	13	83377	0	0,000	0,0E+00	0
Facilities NACE 22.2: manufacture of plastic products	85	0	0	0	0,000	0,0E+00	0
Facilities NACE 23.1 (excluding NACE 23.12): manufacture of glass and glassware	245	0	0	0	0,000	0,0E+00	0