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Impact of industrial waste water treatment plants on Dutch surface waters and drinking water sources

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Managementsamenvatting

Impact van industriële afvalwaterzuiveringsinstallaties op Nederlands oppervlaktewater en drinkwaterbronnen

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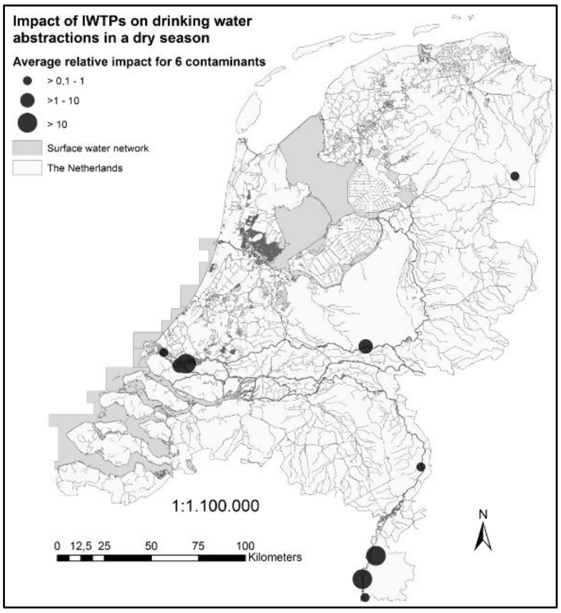
Nederland heeft ongeveer evenveel capaciteit aan rioolwaterzuiveringsinstallaties (RWZI's) als industriële afvalwaterzuiveringsinstallaties (IAZI's). Via beide komen opkomende, mogelijk schadelijke stoffen in het milieu terecht. Modellering van de oppervlaktewaterkwaliteit laat zien dat van alle 182 Nederlandse IAZI's slechts 15 een grote invloed hebben op de kwaliteit van het water voor drinkwaterproductie, waarvan één het grootste deel van de invloed verklaart. Bij de betreffende IAZI's kunnen kosteneffectief maatregelen worden genomen om emissies te beperken. Geschikte technologieën zijn daarvoor beschikbaar. Meer kennis en een betere beschikbaarheid van gegevens over industriële emissies en hun samenstelling is belangrijk voor alle watergebruikers in het stroomgebied.



IAZI's met een grote impact op de drinkwaterfunctie van het Nederlands watersysteem, gemiddeld over *zes gemodelleerde stoffen bij lage afvoer*

Belang: emissies opkomende stoffen vanuit industriële effluenten beïnvloeden waterkwaliteit

Opkomende stoffen – stoffen die pas sinds kort worden gebruikt of ontdekt in het milieu –beïnvloeden de oppervlaktewaterkwaliteit wanneer ze vanuit industriële afvalwaterzuiveringsinstallaties (IAZI's) worden geloosd. Emissies van opkomende stoffen uit IAZI's hebben tot nu toe veel minder aandacht gekregen dan emissies uit rioolwaterzuiverings-installaties (RWZI's), hoewel in Nederland het aantal en de totale capaciteit van IAZI's vergelijkbaar is met het aantal en de capaciteit van RWZI's.

Nederlandse drinkwaterbedrijven die drinkwater produceren uit oppervlaktewater moeten met enige regelmaat maatregelen nemen vanwege deze industriële emissies, van innamestops tot investeringen in aanvullende zuiveringstechnologieën. Er is behoefte aan kennis over risicovolle lozingen van opkomende stoffen uit IAZI's om handelingsopties te evalueren die de waterkwaliteit ten goede komen. Daarvoor is modellering van de waterkwaliteit bruikbaar.

Aanpak: impact directe emissies van IAZI's op waterkwaliteit modelleren met KRW-verkenner

In deze studie zijn directe industriële emissies via alle 182 Nederlandse IAZI's gemodelleerd om een beeld te krijgen van de invloed van die emissies op de Nederlandse oppervlaktewaterkwaliteit en de drinkwaterproductie. Op basis van meetgegevens op drinkwaterinnamepunten, eerder geprioriteerde stoffen en de literatuur is eerst een selectie gemaakt van relevante industriële chemicaliën. Vervolgens zijn gegevens van Nederlandse IAZI's en gegevens uit de Europese Emissieregistratie E-PRTR gekoppeld aan de KRW-verkenner, een gedetailleerd landelijk hydrologisch model dat ook rekening houdt met extreme afvoercondities. Omdat er onvoldoende gegevens beschikbaar zijn over stoffenemissies in Nederland, zijn de E-PRTR emissiegegevens van 39 landen gebruikt voor de gehaltes chemicaliën in industrieel effluent. Daarvoor zijn de E-PRTR-emissiegegevens per industriële sector genormaliseerd op basis van de emissies van totaal organisch koolstof, om ze te vertalen naar de Nederlandse situatie. Industriële emissies via RWZI's zijn niet meegenomen in de waterkwaliteits-modellering, omdat deze emissies niet centraal zijn geregistreerd.

Resultaten: vijftien IAZI's hebben meeste impact op drinkwaterbereiding

Voor de modellering zijn de industriële chemicaliën bis(2-ethylhexyl)ftalaat (DEHP), benzeen, dichloor-methaan, tolueen, 1,2-dichloorethaan en vinylchloride gebruikt. Over de emissies van deze stoffen, die relatief hoog zijn, is genoeg data beschikbaar in E-PRTR. De impact van een IAZI op de waterkwaliteit is een combinatie van de betreffende industriële sector, de capaciteit en de geografische locatie ten opzicht van innamepunten voor drinkwaterproductie. Van de 182 Nederlandse IAZI's hebben 15 plastic-, papier-, petroleum- of basischemicaliënindustrieën een grote invloed. Eén IAZI vertegenwoordigt het overgrote deel van de impact op de drinkwatervoorziening. In totaal wordt circa een derde van het water voor drinkwater-productie beïnvloed door IAZI's. Daaronder valt vrijwel alle direct onttrokken oppervlaktewater, ruim de helft van het oeverinfiltraat en minder dan een vijfde van het voor drinkwater gebruikte grondwater.

Implementatie: kennis en transparantie nodig van opkomende stoffen in industrieel effluent

Er is geen publiek register van alle chemicaliën en bijproducten die geproduceerd en gebruikt worden en via industrieel afvalwater in het milieu komen. Een dergelijk register met bandbreedtes van productievolumina sluit aan bij de Aarhus conventie, waarin de op toegang tot milieu-informatie vastgelegd is, en biedt zinvolle informatie voor alle watergebruikers in het stroomgebied en voor vergunningverleners voor industriële emissies.

Er zijn technieken om stoffen in het effluent te volgen, zoals hoge resolutie massaspectrometrie. In Nederland is de signaleringsparameter voor overige antropogene stoffen geïntroduceerd, met respectievelijk 1 en 0,1 μg/L voor drinkwater en bronnen voor drinkwater. Bij overschrijding van deze signaleringsparameter volgt onderzoek naar milieu- en gezondheidsrisico's, herkomst en verwijder-mogelijkheden van de betreffende stof. Doortrekken van deze systematiek van signaleringsparameters kan watergebruikers inzicht geven in de belasting van oppervlaktewater met opkomende stoffen.

Een klein aantal IAZI's heeft veel impact op drinkwaterbereiding. Bij die IAZI's kunnen kosteneffectief mitigerende maatregelen worden genomen. Geschikte conventionele en geavanceerde behandelingstechnologieën zijn beschikbaar. De keuze voor de beste verwijderingsmethode moet onder meer afhangen van de fysisch/chemische eigenschappen van de stoffen, de effluent matrix en operationele instellingen.

Rapport

De resultaten zijn beschreven in het KWR rapport 2018.006 *Impact of industrial waste water treatment plants on Dutch surface waters and drinking water sources* en het bijbehorende artikel (gesubmit in Science of the Total Environment).

Abstract

Direct industrial discharges of Chemicals of Emerging Concern (CEC) to surface water via industrial wastewater treatment plants (IWTP) gained relatively little attention compared to discharges via municipal sewage water treatment plants. IWTP effluents however may seriously affect surface water quality. Here we model direct industrial emissions of all182 Dutch IWTP (19 industrial classes) and their impact on Dutch surface water quality and drinking water production. After selecting industrial chemicals relevant for drinking water production, we use data from the European Pollutant Release and Transfer Register and data on Dutch IWTP. We couple these to a detailed hydrological model under two extreme river discharge conditions. The predicted concentrations are compared to measured concentrations. We further derive relative impact factors for the IWTP, based on their contribution to concentrations at surface water locations with a drinking water function. From all Dutch 182 IWTP a limited number of 15 has a high impact on surface water with a drinking water function. Mitigation measures can be taken cost-efficiently, and extra treatment technologies can be placed at the IWTP with high impact. These treatment technologies generally are available. In total 32% of the abstracted water for drinking water production is affected by the IWTP. Finally, we propose recommendations for licensing and controlling industrial aqueous emissions.

Keywords: industrial waste water, effluent, drinking water

Contents

1 Introduction

The production and use of chemicals continues to increase at a speed that outpaces other agents of global change. This holds for both the number of authorized chemicals and the volumes produced and used (Wilson and Schwarzman 2009, Bernhardt et al. 2017). Currently worldwide over 348.000 chemicals are registered and regulated (CHEMLIST 2017). Chemicals of emerging concern (CEC) are measured ubiquitously in low concentrations (mostly ng/L range) in European surface waters, effluents and groundwaters (Loos et al. 2009, 2010, 2013). CEC comprehend a large group of compounds that are not commonly monitored, for which there is scarce information on possible effects and for which no regulatory criteria or quality standards exist, while they potentially might pose risks (Halden, 2015). Example CEC are pharmaceuticals, personal care products, plasticizers, surfactants and pesticides, and industrial chemicals. After incidental releases, CEC concentrations in rivers can be orders of magnitude higher, up to µg/L levels (De Hoogh et al. 2006, Rebelo et al. 2014). Climate change and thus more frequent and severe low river discharges,leads to periods with increased surface water concentrations of synthetic chemicals (Van Vliet and Zwolsman 2008, Delpla et al. 2009, Petrovic et al. 2011, Sjerps et al. 2017). Chemical pollution of our waters is a global public concern (Schwarzenbach et al. 2006, Richardson et al. 2014, Malaj et al. 2014). Since surface waters provide vital functions, such as drinking water production, nature, recreation and food production, it is fundamental to localize and control areas with potential risk associated to CECs (Van Wezel et al. 2017).

Direct industrial discharges of CEC to surface water via industrial wastewater treatment plants (IWTP) gained relatively little attention compared to discharges via municipal sewage water treatment plants (STP). IWTP effluents however may seriously affect surface water quality (Ruff et al. 2015, Lindim et al. 2015, Salgueiro-González et al. 2015, Loos et al. 2007, Boiteux et al. 2017, Ahmad et al. 2008, Hu et al. 2016, Lee et al. 2011). For example, industrial effluents from textile, chemical or pharmaceutical manufacture industries with endocrine activity are found across Europe (Eggen et al. 2003; Vethaak et al. 2005; Schriks et al. 2010). In the Netherlands the number and total capacity of IWTP is comparable to that of STP (CBS Statline). Industrial plants may directly discharge via IWTP, or discharge indirectly via STP then with a mixed municipal and industrial effluent. The composition of industrial effluent is expected to vary more in time than that of municipal effluent, related to changes in the exact industrial production processes, batch-wise production, and maintenance. In Europe, IWTP emissions have to comply to the Industrial Emissions Directive (IED, 2010/75/EU). The IED establishes a procedure for authorising industrial activities, sets minimum requirements to be included in permits and prescribes the application of Best Available Techniques (BAT) (Evrard et al. 2016). BAT imply good industrial processes, such as storing waste or cleaning and rinsing baths (Derden and Huybrechts 2013, Ozturk et al. 2015), but also the application of effective waste water treatment technologies.

In the Netherlands 40% of the total drinking water production originates from surface water. Dutch drinking water companies that rely on surface water as a source frequently stop their surface water intake because of problems with industrial emissions (RIWA 2017). For example, during the summer of 2015, an IWTP emission of amongst others pyrazole resulted in a long-term stop of surface water intake for drinking water production (Baken et al. 2016). In 2017, the license for industrial emission of 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (FRD-903, ‘GenX’) is debated in the Dutch court because of expected future problems for drinking water production. Other examples of industrial emissions giving rise to water quality problems are described (Van Leerdam et al. 2014, Kosaka et al. 2014, Boiteux et al. 2017), portraying the relevance of industrial impact on surface water quality and drinking water production.

Next to water quality monitoring, modelling may also be used to localize areas with potential risks associated to CEC (Fan et al. 2015). Water quality modelling is fast and cheap compared to monitoring, and has a high spatial and temporal resolution. Various approaches have been developed to model concentrations of CEC (Aldekoa et al. 2013, Kehrein et al. 2015, Coppens et al. 2015, Lindim et al. 2016, Kapo et al. 2015, Ippolito et al. 2015, Kuroda et al. 2016), predominantly applied for specific down-the-drain consumer chemicals such as pharmaceuticals. Water quality models also can be used for an a priori evaluation of mitigation strategies (Coppens et al. 2015, Zijp et al. 2016).

Here we aim to model direct industrial emissions to surface water, their impact on Dutch surface water quality and drinking water production and the options to minimize adverse impacts. After selecting industrial chemicals which are relevant for drinking water production, we use data from the European Pollutant Release and Transfer Register and data on Dutch IWTP, and couple these to a detailed hydrological model under two extreme river discharge conditions. The predicted concentrations are compared to measured concentrations. We derive relative impact factors for the IWTP, based on their contribution to concentrations at surface water locations with a drinking water function. Finally, we propose recommendations for licensing and controlling industrial aqueous emissions.

2 Material and methods

2.1 Selection of industrial chemicals

To ensure that modelled concentrations can be compared to measured concentrations, chemicals for which monitoring data are available at surface water intake points of Dutch drinking water utilities are selected (total 955 chemicals, RIWA water quality database). These are combined with chemicals earlier prioritized based on their occurrence in Dutch surface waters and drinking water (Sjerps et al. 2016). In addition, literature data on occurrence and prioritization in effluents, surface-, ground- and drinking water are added.

Information on the industrial discharges of these chemicals in the Dutch and European Pollutant Release and Transfer Register (PRTR) is used for water quality modelling. Other pathways followed to retrieve information on industrial emissions and concentrations in industrial effluents for the selected chemicals are described in S.I. I, these include databases of permitting authorities, additional inventories amongst industries and case studies on permits for industrial discharges via IWTP.

2.2 Normalizing IWTP emissions based on PRTR

For specific industrial chemicals Dutch data on emissions are scarce, while for total organic carbon (TOC) data are abundant. Reporting to the European E-PRTR is governed by EC directive166/2006, requiring that annual emissions for 91 chemicals and chemical classes per industrial site are publicly reported if emission surpasses prescribed thresholds. In addition to the 28 EU member states several other countries report according to E-PRTR, so emission data for 39 countries are available (Sörme et al. 2016). E-PRTR data for compound groups are not used in this study for water quality modelling, as decay rates for chemicals within the group can vary highly.

The available E-PRTR data for 2013 for all EU-member states and Iceland, Liechtenstein, Norway, Serbia and Switzerland are used to estimate emissions per industrial class. The loads for emitted industrial chemical X are therefore based on all E-PRTR data normalised to the loads for emitted TOC per NACE-code for a specific industrial sector (Nomenclature statistique des Activités économiques dans la Communauté Européenne, from the Statistical Classification of Economic Activity in the European Community), according to:

$$\frac{X}{TOC} = \frac{\frac{X\ sum}{n_X}}{\frac{TOC\ sum}{n_{TOC}}}$$

The ratio of kg X per kg TOC is estimated by the ratio of the total E-PRTR summed emission of X (X_{sum}, kg/yr) by the number of IWTP reporting X (n_X) and the summed reported emission of TOC (TOC_{sum}, kg/yr) by the number of IWTP reporting TOC (n_{TOC}). The assumption is representation by the IWTP present in n_X for all IWTP present in n_{TOC}. Based on abundant actual yearly TOC emissions for the Dutch IWTP and their NACE-code, emissions of the selected industrial chemicals are then estimated per IWTP (g/s). These estimated industrial emissions per IWTP and the actual decay rates of the chemicals are used to scale the modelled hypothetical emissions of 1000 g/s (see below).

2.3 Water quality modelling

The Dutch water system is heavily managed, given that large parts of the Netherlands are below sea level. A spatially detailed hydrological water quality model, i.e. the Dutch Water Framework Directive (WFD) model version 2.0 in the WFD-Explorer software, is used to model concentrations from IWTP emissions in analogy to earlier work on pharmaceuticals and STP (Coppens et al. 2015). WFD Explorer 2.0 software uses a water balance and pollutant transport model. The Dutch WFD model is based on a network of approximately 17,500 nodes of which 2,575 are surface water units (SWU) and approximately 27,000 links representing the routing of the surface water. Quarterly averaged water balance data from an extreme dry and wet season are used to incorporate climate variability, i.e. the 3rd quarter of 2003 and the 4th quarter of 1998 respectively.

A series of water quality tracer computations is performed, assuming complete and instant mixing and first order decay. Data on Dutch IWTP and their NACE-code are retrieved from the Dutch Pollutant Release and Transfer Register (D-PRTR over 2013, www.emissieregistratie.nl). Indirect industrial discharges that take place via STP are not incorporated. IWTP/SWU transfer matrices are made for both a conservative and non-conservative tracer in two extreme discharge conditions, using a hypothetical emission of 1000 g/s per IWTP. The four resulting matrices list contaminant loads (g/s) from each of the 182 IWTP at each of the 2575 SWU. The 182 IWTP are classified in 19 industrial classes and 43 sub-classes, according to the NACE-codes from the Statistical Classification of Economic Activity in the European Community. These matrices are combined with emission data and decay rates of the emitted chemicals, as explained above.

In addition, loads entering the Dutch surface waters via 9 cross-border rivers, i.e. Rhine, Meuse, Scheldt, Sas van Gent (Canal), Roer, Swalm, Niers, Overijsselse Vecht, Mark or Weerijs and Dommel or Tongelreep, are incorporated in the model. RIWA monitoring data are used for Rhine at Lobith and Meuse at Eijsden (1987-2015). Concentrations reported as reporting limit are excluded, except for the lowest reporting limit reported. When the 10^{th} percentile of all RIWA data used equals the lowest reporting limit, half the lowest reporting limit is used. Concentrations in other cross-border rivers are estimated based on average yearly concentrations from Rhine and Meuse, and corrected for flow rates to obtain loads per cross-border river (see Coppens et al. 2015 for more details).

The sum of the loads from all IWTP and incoming rivers per SWU gives the total mass flux (g/s) at each SWU. When divided by the local discharge (Q in m^3/s), the predicted concentration (C in g/m^3) per SWU is obtained.

Predicted environmental concentrations (PEC) are compared with actually measured environmental concentrations (MEC) between 1989 to 2015 at surface water intake points for the production of drinking water.

2.4 Impact assessment of IWTP on vulnerable drinking water areas

SWU used as source for drinking water production are selected, including surface water intake points, abstraction for river bank filtration and infiltration in the 25-yr protection zone for groundwater abstraction (see Coppens et al. 2015 for further details).

IWTP are ranked for their impact on SWU hosting a drinking water function. Per IWTP an impact factor (IF) is calculated according to:

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

The $IF_{i,j}$ (g/m^3) of $IWTP_i$ in SWU_j is expressed by the local concentration C_j, multiplied by the load $F_{i,j}$ to the total load of all IWTP in that SWU_j ($Q_j C_j$), representing the share of $IWTP_i$ in the total impact, and multiplied by a dimensionless weighing factor S/S_{tot} representing the relevance of the SWU for drinking water as represented by the production volume at the production location (m^3/y). For groundwater abstractions with multiple coupled SWU, corresponding abstraction volumes are divided amongst these SWU (Coppens et al. 2015). The summed IF_i over all SWU gives the impact factor per $IWTP_i$. IFs are calculated for both discharge conditions.

The relative impact factor per IWTP rIF_i is calculated according to:

$$rIFi = \frac{IFi}{\Sigma \mathrm{IF}}$$

The relative contribution R_j (-) to the concentration in water body j from Dutch IWTP compared to the contribution from abroad is expressed by the concentration originating from Dutch IWTP (Cx,i_{NL},j) divided by the total concentration (Cx,i_{tot},j:

$$R_j = \frac{C_{X,i_{NL},j}}{C_{X,i_{tot},j}}$$

3 Results

3.1 Selection of industrial chemicals

The selected industrial chemicals of interest are given in Table 1. The majority of these 28 chemicals is produced in volumes above 1000 t/yr and is applied in consumer products, so next to industrial emission also household emissions are an important route. An exception might be triphenylphosphine oxide (Schlüsener et al. 2015) which is a unique by-product of the Wittig reaction applied in the chemical industry.

TABLE 1. SELECTED INDUSTRIAL CHEMICALS WITH OCCURRENCE IN THE WATER CYCLE AND AVAILABLE MONITORING DATA

CAS-number	Industrial chemical	Uses	REACH >100 ton/yr	REACH >1000	References*
112-49-2	1,2-bis(2-methoxyethoxy)-ethane (triglyme)	solvent used in ink, paints and cleaners		x	f,i
115-96-8	tris(2-chloroethyl) phosphate (TCEP)	reducing agent and flame retardant		x	b,c,e,f,l,m
126-73-8	tributyl phosphate (TBP)	solvent and plasticizer in inks, synthetic resins, gums, adhesives, herbicide and fungicide		x	b,c,f,k,l,m
13674-84-5	tris(2-chloro-1-methylethyl) phosphate (TCPP)	flame retardant and used in gums and plastics		x	b,c,f,k,l,m
29878-31-7	4-methyl-1H-benzotriazole	corrosion inhibitor, drug precursor, heating and cooling	x		f,j
3622-84-2	N-butylbenzenesulphonamide	plasticizer		x	f,n
51-03-6	2-(2-butoxyethoxy)ethyl 6-propylpiperonyl ether	solvent used in ink, paints and cleaners		x	f
78-40-0	triethyl phosphate	industrial catalyst, solvent, plasticizer, flame retardant		x	f,k,l,m
791-28-6	triphenylphosphine oxide (TPPO)	crystalizing agent		x	f,k,l,m
80-09-1	4,4'-sulphonyldiphenol (bisphenol S)	fast drying epoxy glues, corrosion inhibitor, paper		x	f

826-36-8	2,2,6,6-tetramethyl-4-piperidone	drug		x	f
83-15-8	N-acetylaminoantipyrine	drug	x	x	d,f
84-69-5	diisobutyl phthalate	plastics, nail polish, polish, inks		x	d,f,h
84-74-2	dibutyl phthalate	plastics, nail polish, polish, inks		x	d,f,h
95-14-7	benzotriazole	corrosion inhibitor, drug precursor, heating and cooling	x		a,b,c,f,k
62-53-3	Aniline	dyes, medicine, rocket fuel		x	o
608-27-5	2,3-dichlooraniline	dyes, medicine, rocket fuel		x	o
95-82-9	2,5-dichlooraniline	dyes, medicine, rocket fuel		x	o
126-71-6	triisobutylphosphate	plasticizers, solvent, resins, paints, inks, antifoaming	x		b,c
288-32-4	trifenyl-imidazole-triglycine	corrosion inhibitor, flame retardant		x	g
80-05-7	bisfenol A	fast drying epoxy glues, corrosion inhibitor, paper, thermal paper		x	e
554-00-7	2,4-dichlooraniline	dyes, medicine, rocket fuel		x	o
95-76-1	3,4-dichlooraniline	dyes, medicine, rocket fuel		x	o
626-43-7	3,5-dichlooraniline	dyes, medicine, rocket fuel		x	o
1222-05-5	galaxolide (HHCB)	personal care products, cleaning		x	e
117-81-7	bis(2-ethylhexyl) phthalate (DEHP)	PVC, plastics		x	h
123-91-1	1,4-dioxane	Stabilizer, aluminium packages, solvent in ink and adhesives		x	h
129-00-0	Pyrene	stabilizer aluminium packages, solvent in ink and adhesives		x	h,p

*: 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) Velzeboer et al. 2014, h) Roex et al. 2003, i) Stepien and Püttmann 2014, j) Kiss and Fries 2009, k) Cristale et al. 2013a, l) Cristale et al. 2013b, m) Ding et al. 2015, n) Rider et al. 2012, o) Tas and Pavlostathis 2014, p) Baldwin et al. 2016

3.2 Normalizing IWTP emissions based on E-PRTR

The Dutch PRTR database is scarce in emission data for specific chemicals, due to reporting thresholds. Figure 1 shows TOC normalized European emissions (formula 1) for industrial classes which are relevant for the Netherlands, for six chemicals and four compound groups with relatively high data abundance in E-PRTR. Highest TOC normalized emissions are reported for the refined petroleum and basic chemicals industry, and also for metal and paper industry.

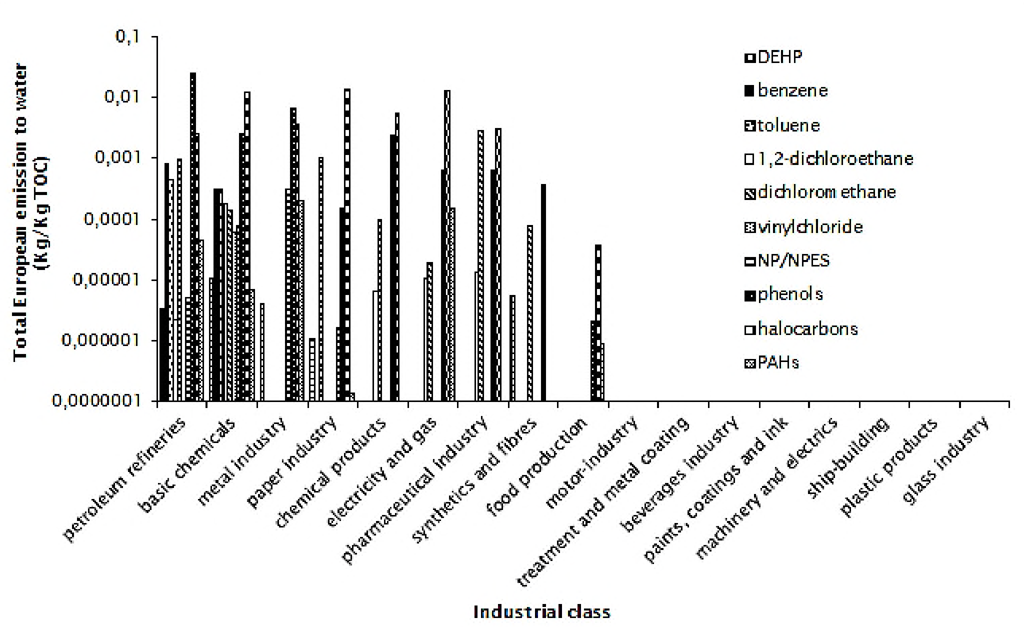


FIGURE 1. TOTAL EUROPEAN INDUSTRIAL EMISSIONS TO WATER IN KG PER KG TOC FOR THE YEAR 2013, FOR ALL EU-MEMBER STATES AND ICELAND, LICHTENSTEIN, NORWAY, SERVIA AND SWITZERLAND, PER INDUSTRIAL CLASS (SOURCE: E-PRTR)

Of the selected industrial chemicals of interest, only for bis(2-ethylhexyl)phthalate (DEHP) TOC normalized emissions based on the E-PRTR data can be derived. Next to DEHP, also benzene, dichloromethane, toluene, 1,2-dichloroethane and vinylchloride are used for further modelling, because of data availability and relative high aqueous emissions. Different industries dominate the emission of these model chemicals. Even when using E-PRTR data, sufficient sector-specific information on emissions is lacking. This also refers to relevant sectors as producers of dyes and pigments, pesticides or paints and coatings.

Environmental half-lives and corresponding decay rates for the selected chemicals are listed in Table 2, assuming first-order decay. The loads from cross-border rivers are given in Table 3. For DEHP and vinylchloride monitoring data from cross-border rivers are too scarce to further model surface water concentrations.

TABLE 2. ENVIRONMENTAL HALF-LIFE VALUES AND CORRESPONDING DECAY RATES (HOWARD 1991)

Chemical	t1/2 winter (d)	t1/2 summer (d)	kx winter	kx 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

TABLE 3. INPUT LOADS FROM CROSS-BORDER RIVERS

	Rhine at Lobith (µg/L)			Meuse at Eijsden (µg/L)		
Contaminant	90th percentile	10th percentile	n	90th percentile	10th percentile	n
1,2-dichloorethane	0,063	0,005	318	2,000	0,029	763
Benzene	0,040	0,005	290	0,100	0,005	460
Dichloromethane	0,116	0,005	65	4,480	0,020	565
Toluene	0,010	0,005	293	0,120	0,005	465

3.1 Predicted surface water concentrations and comparison to monitoring data

Predicted surface water concentrations for benzene, toluene, dichloromethane and 1,2-dichloroethane resulting from the combined industrial emissions and cross-border rivers under low discharge vary by over 3 orders of magnitude over the SWU (Figure 2). Maximum predicted concentrations are in the same range as predicted earlier for the pharmaceuticals carbamazepine and ibuprofen (Coppens et al. 2015). Using monitoring data at surface water intake points for comparison, the measured concentrations often exceed predicted concentrations (Figure 2). This underestimation was expected, since both indirect industrial emissions via STP and releases during the use and waste life cycle phase of industrial chemicals are not included in the modelling. The approach to use Rhine and Meuse monitoring data to estimate loads for small cross-border river could be further improved by correcting for the actual presence of IWTP and their NACE-codes in the cross-border river basins. As many large industries are located close to large rivers, our approach might overestimate cross-border inputs by smaller rivers. The Dutch WFD model is to be further improved especially on mass fluxes in large estuaries such as the Western Scheldt.

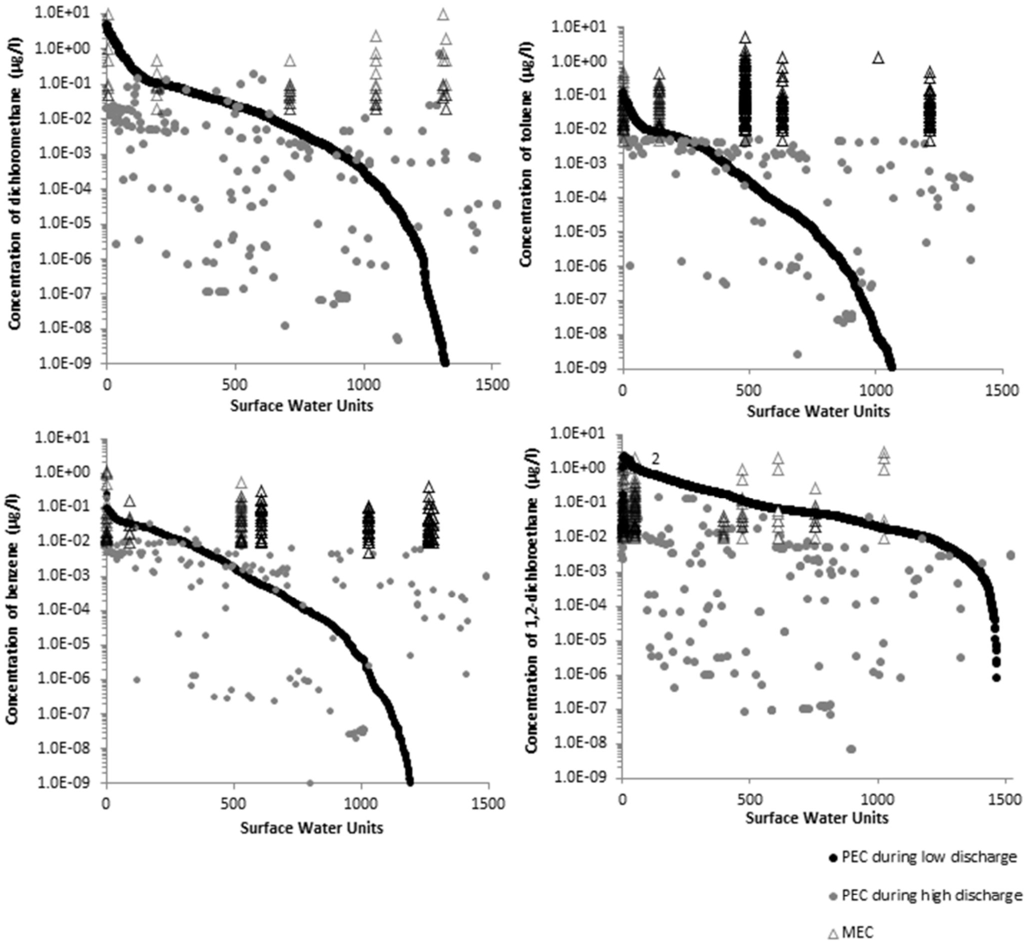


FIGURE 2. PREDICTED SURFACE WATER CONCENTRATIONS PER SURFACE WATER UNIT AT LOW AND HIGH DISCHARGE (PEC) COMPARED TO MEASURED CONCENTRATIONS IN DRINKING WATER INTAKE POINTS (MEC, DATA RIWA)

3.4 Impact assessment of IWTP on vulnerable drinking water areas

For only a limited share of the SWU with increased concentrations of the modelled industrial chemicals, the contribution of the Dutch IWTP is a dominant factor (Figure 3). Especially at high river discharges the modelled impact of the IWTP is limited.

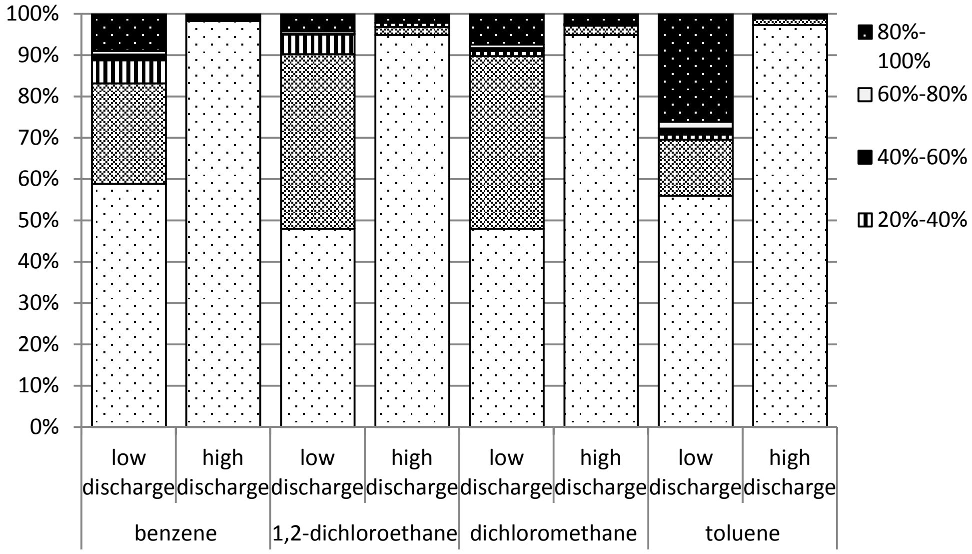
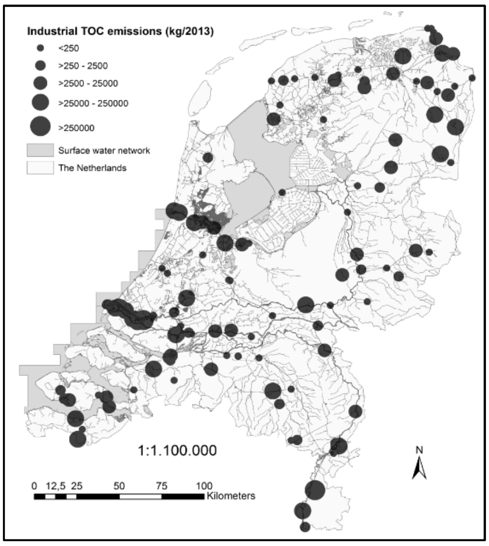
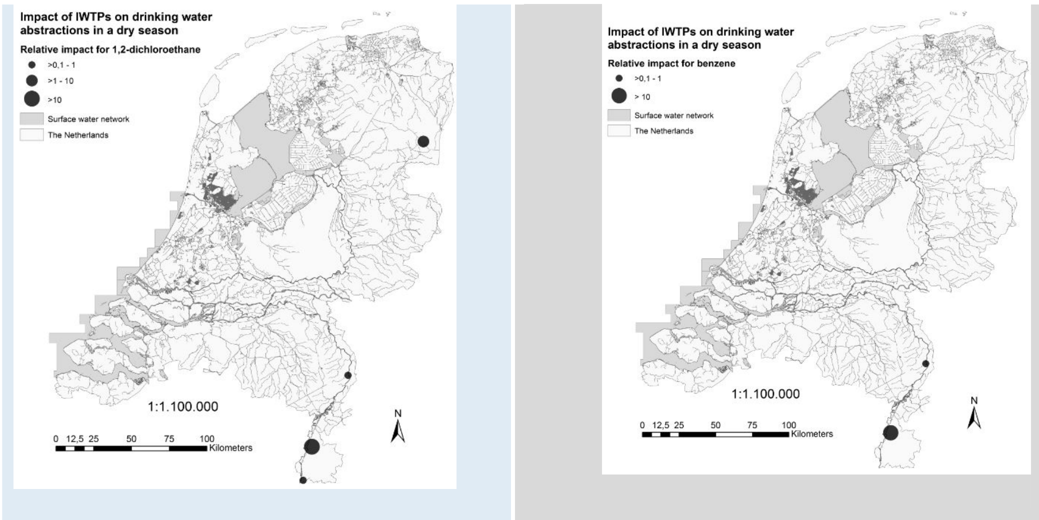


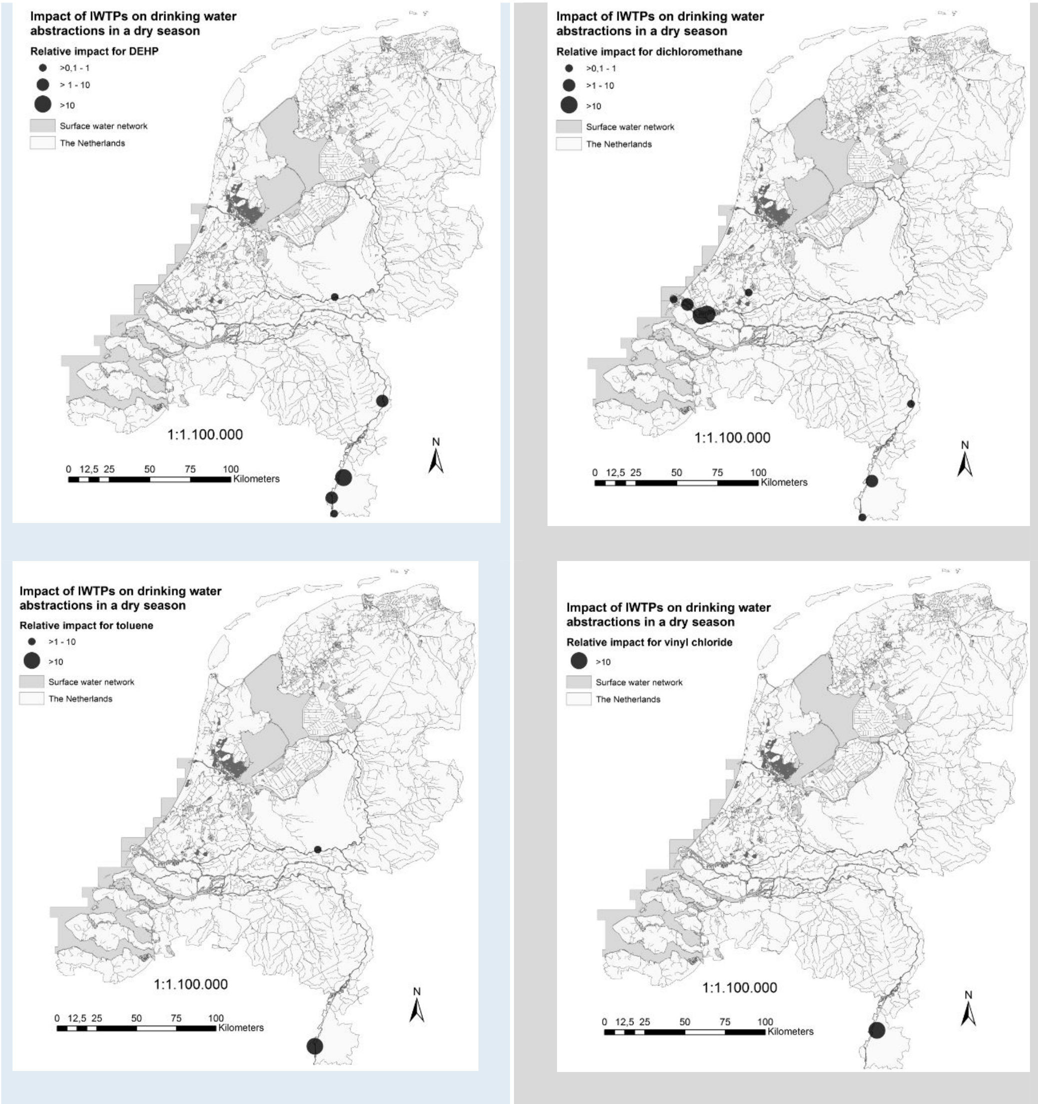
FIGURE 3. RELATIVE CONTRIBUTION FROM DUTCH IWTP TO THE CONCENTRATION IN SWU COMPARED TO THE CONTRIBUTION FROM ABROAD, SHADING INDICATES THE IMPACT EXPRESSED AS PERCENTAGE BY DUTCH IWTP

The impact of an IWTP on drinking water production is a combined effect of the industrial class concerned, the capacity or the IWTP, the geographic location and the hydrologic coupling to drinking water intake. From all Dutch 182 IWTP, that cover 43 different industrial (sub-)classes, a limited number of 15 IWTP at low discharge or 10 IWTP at high discharge have an impact factor higher than 0.1 % (Table 4a). These IWTP are typically related to the plastic, paper, petroleum or basic chemicals industry (Table 4b). One IWTP is responsible for a large share of the impact, which is related to its size and hydrological relation with drinking water intake. For most chemicals, IWTP in the south-east of the Netherlands show high impact. For dichloromethane which is emitted by the petroleum industry, also the Rotterdam harbour is important (Figure 4).

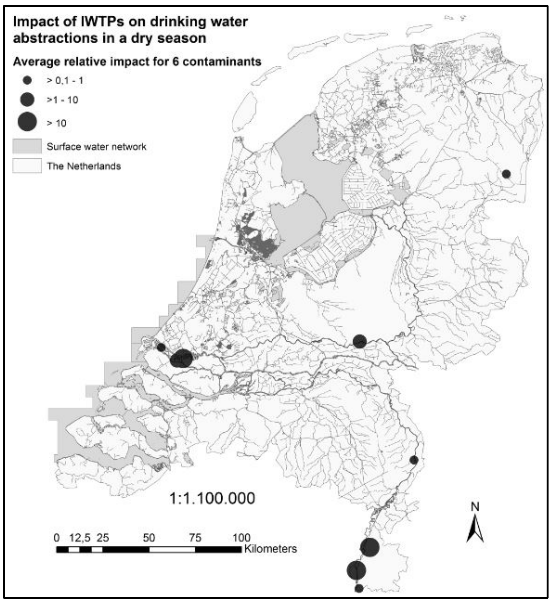

Industrial TOC emissions (kg/2013)
<250
>250 - 2500
>2500 - 25000
>25000 - 250000
>250000
Surface water network
The Netherlands
1:1.100.000
0 12,5 25 50 75 100
Kilometers
N

A.


Impact of IWTPs on drinking water abstractions in a dry season
Relative impact for 1,2-dichloroethane
>0,1 - 1
>1 - 10
>10
Surface water network
The Netherlands
1:1.100.000
0 12,5 25 50 75 100
Kilometers
N
Impact of IWTPs on drinking water abstractions in a dry season
Relative impact for benzene
>0,1 - 1
> 10
Surface water network
The Netherlands
1:1.100.000
0 12,5 25 50 75 100
Kilometers
N


Impact of IWTPs on drinking water abstractions in a dry season
Relative impact for DEHP
>0,1 - 1
> 1 - 10
>10
Surface water network
The Netherlands
1:1.100.000
0 12,5 25 50 75 100
Kilometers
N
Impact of IWTPs on drinking water abstractions in a dry season
Relative impact for dichloromethane
>0,1 - 1
>1 - 10
>10
Surface water network
The Netherlands
1:1.100.000
0 12,5 25 50 75 100
Kilometers
N
Impact of IWTPs on drinking water abstractions in a dry season
Relative impact for toluene
>1 - 10
>10
Surface water network
The Netherlands
1:1.100.000
0 12,5 25 50 75 100
Kilometers
N
Impact of IWTPs on drinking water abstractions in a dry season
Relative impact for vinyl chloride
>10
Surface water network
The Netherlands
1:1.100.000
0 12,5 25 50 75 100
Kilometers
N

B.



C.

FIGURE 4. OVERVIEW OF A) ALL 182 DUTCH IWTP WITH VARIABLE TOC EMISSIONS OVER THE YEAR 2013, AND IWTP HAVING A RELATIVE IMPACT HIGHER THAN 0,1 B) FOR THE SIX MODELLED INDUSTRIAL CHEMICALS AND C) FOR THE AVERAGED CHEMICALS AT LOW DISCHARGE

In total 32% of the abstracted water for drinking water production is affected by IWTP (Table 5), which is less than the 50% that is impacted by STP (Coppens et al. 2015).

TABLE 4A. NUMBER OF IMPACTFUL IWTP WITH RELATIVE IMPACT FACTOR (RIF) >0,1, BASED ON AVERAGED IMPACT OF THE MODELLED SIX CONTAMINANTS

Discharge condition	Number of impactful IWTP	% of total Dutch TOC emission	% cumulative impact Dutch IWTP by the impactful IWTP
Low	15 (8,2%)	44,7	99,9
High	10 (5,5%)	28,6	100

TABLE 4B. SELECTION IMPACTFUL IWTP PER SECTOR AT LOW AND HIGH RIVER DISCHARGE

Industry	Selected IWTP	% of total Dutch TOC emission	% cumulative impact Dutch IWTP
Low discharge			
manufacture of plastics in primary forms	1 (0,5%)	8,6	65,6
manufacture of pulp, paper and paperboard	2 (2%)	9,3	18,2
manufacture of refined petroleum products	5 (2,7)	18,6	11,5
production and distribution of electricity and gas	1 (0,5%)	0,8	0,6
manufacture of organic basic chemicals	4 (2,2%)	4,8	0,6
manufacture of inorganic basic chemicals	1 (0,5%)	0,0	0,2
manufacture of other chemical products n.e.c.	1 (0,5%)	2,5	0,0
Total	**15 (8,2%)**	**44,7**	**99,9**
High discharge			
manufacture of plastics in primary forms	1 (0,5%)	8,6	80,0
manufacture of pulp, paper and paperboard	4 (2,2%)	12,6	16,6
manufacture of refined petroleum products	1 (0,5%)	3,7	2,8
manufacture of organic basic chemicals	1 (0,5%)	0,5	0,3
manufacture of inorganic basic chemicals	1 (0,5%)	0,0	0,2
manufacture of other chemical products n.e.c.	2 (2%)	3,1	0,1
Total	**10 (5,5%)**	**28,6**	**100**

TABLE 5. NUMBER OF SWU WITH DRINKING WATER FUNCTION AND ABSTRACTION VOLUMES INFLUENCED BY AQUEOUS INDUSTRIAL EMISSIONS; BASED ON ALL 6 MODEL COMPOUNDS DURING LOW DISCHARGE

	Number of SWU with drinking water function	Influenced by IWTP	Total abstraction volume (million m^3/y)	Abstraction volume influenced by IWTP (million m^3/year)
Surface water	9	8	416	415 (99%)
Bank filtrate	20	13	108	62 (57%)
Groundwater	180	18	739	114 (15%)
Total	209	39	1262	415 (32%)

4 Discussion

4.1 Uncertainties of approach

Systematic information on concentrations or loads in IWTP effluents for many chemicals of interest is lacking (see also S.I. 1). This holds for a wide range of especially relatively hydrophilic chemicals, which are a concern for drinking water production because of their relatively low removal efficiencies by commonly used water treatment technologies.

For STP effluents more information on CEC is available then for IWTP effluents, both in scientific literature and in databases. In the Netherlands, as part of the PRTR, the Watson database on STP effluents contains over 900 chemicals. This includes 86 industrial chemicals with ≥10 measurements in the period 1990-2015 with concentrations in STP effluent above 0.01 µg/L (see S.I. 3), including flame retardants and endocrine disrupting chemicals. Most STP effluents result from mixed input by households and industrial waste water, e.g. 93% of Dutch STP treat mixed household and industrial waste water and the proportion of industrial influent is on average 24% with a maximum of 90% (personal communication Kees Baas Central Bureau for Statistics). A third of the total capacity of Dutch STP (24,2 million inhabitant equivalents) is used to treat industrial waste waters. The volume of industrial waste water treated via STP, equalling 7,9 million inhabitant equivalents, is in the same range as industrial waste water directly treated via Dutch IWTP with a total capacity of 13,8 million inhabitant equivalents (data by CBS Statline and personal communication Kees Baas). However, as the NACE-code of the industries of which the waste waters are treated by the STP is not registered, the STP effluent data in the Watson database cannot be generalized for modelling purposes.

We relied on EU-wide E-PRTR data, normalized per industrial sector on TOC, that was combined with data on Dutch industrial emissions for TOC per IWTP per NACE-code. Several uncertainties can be mentioned, e.g.:

- approach relies on the limited number of chemicals that are reported in the E-PRTR, which are not representative for the chemicals of interest.
- during normalization of chemical to TOC emissions, it is assumed that the selection of IWTP for which chemical emission data are available is an a-select part of the broader set of IWTP for which TOC emissions are available.
- an industrial area served by a IWTP may contain a mix of industrial sectors, in our approach we use available statistical data where the various activities are often combined to one NACE-code.
- incidental high industrial releases are not explicitly modelled, as the modelling approach is based on yearly averages for which emission data are reported. Aqueous concentrations as a result of incidental high IWTP emissions will be temporarily higher than modelled. Also short periods of extremely low river discharges are not covered

as 3 monthly averages periods are used in the modelling. These short periods of extremely low discharges also will temporarily result in higher concentrations than currently modelled.

4.2 European studies on industrial chemical emission to surface water

Currently 16.563 industrial substances are registered under REACH regulation (Registration, Evaluation and Authorization of CHemicals), 15% of which are produced in volumes over 1.000 tonnes per year. For the majority of registered compounds the tonnage is either confidential, or they are only registered as being for intermediate use. REACH focuses on the PBT criteria (persistent, bioaccumulation and toxic). From a drinking water perspective, the persistent, mobile and toxic organic compounds (PMOC) are more relevant (Reemtsma et al. 2016, Sjerps et al. 2016).

Although no systematic information on composition of industrial effluents is available, several cases based on analytical measurements of industrial effluents are described.

In Belgian and Italian textile industrial effluents octyl- and nonylphenol, their ethoxylates and carboxylates were measured (Loos et al. 2007). The use and production of nonylphenol ethoxylates have been banned in EU countries. Perfluorinated compounds (PFCs) are detected in numerous industrial waste water treatment plants during the last ten years (Loos et al. 2013; Arvaniti and Stasinakis, 2015; Castiglioni et al. 2015; Gebbink et al. 2017). In Italy, STP effluent with a large proportion of textile and furniture industry wastewater contained short and long chained perfluorinated carboxylic acids and perfluorooctanoic acid (PFOA) in concentrations varying from 37 to 786 ng/L (Castiglioni et al. 2015). In industrial waste water treatment plants, Loos et al. (2013) detected PFOA at the highest median concentration levels (12.9 ng/l), followed by other perfluorinated compounds (PFOS, PFHxA, PFHpA, PFHxS, PFDA, and PFNA). The PFOA replacer GenX was detected downstream from a chemical production plant in The Netherlands up to concentrations of 812 ng/L (Gebbink et al. 2017), the same pattern was followed by 11 emerging PFASs. The Dutch Watson database mentions STP effluent concentrations up to 0,74 µg/L for PFOS and 0,062 µg/L for PFOA. Estrogenic activity in industrial effluents is found widely across Europe, in particular in effluents from textile, chemical or pharmaceutical manufacture industries (Eggen et al. 2003), related to the presence of nonyphenol, nonylphenol ethoxylates, hydroxyphenyl hexanoic acid or bisphenol A. Also Van der Linden et al. (2008) found high activities of estrogen (ERα), progesterone (PR), glucocorticoid (GR) and androgen (AR) in the industrial effluent compared to STP effluents in the Netherlands, which were found to be partly explained by synthetic hormones up to a concentration of 247 ng/L for prednisolone (Schriks et al. 2010). In Croatian pharmaceutical industry effluents, veterinary antibiotics (fluoroquinolones, trimethoprim, sulfonamides and tetracyclines) ranged up to approx. 200 µg/L (Bielen et al. 2017). In a German study on paper industrial effluents photoinitiators, ink and thermal paper constituents were present such as Bisphenol A up to 6,1 µg/L (Dsikowitzky et al. 2015).

4.3 Suggestions for regulation regarding industrial aqueous emissions

A public register of all chemicals and by-products produced and thus possibly emitted via the industrial wastewaters by CAS numbers is currently not available in the Netherlands nor other European member states. Such a register, ideally including production volume ranges at the site, would be informative to other water users in the river basin, to focus their monitoring, modelling, risk assessment and risk management efforts. It would also be in line with the Aarhus convention as implemented in the EU in amongst others Directive 2003/4/EC on public access to environmental information.

Available information in the public REACH dossiers on all produced chemicals and by-products in an industrial process is to be implemented by the competent authorities in the licensing of industrial discharges. In the REACH dossiers restrictions can be prescribed, e.g. a product should not be allowed to enter water courses, or precautionary measures should be taken to prevent accidental spillages. Currently this implementation of REACH restrictions is not systematically taken into account during the licensing process (S.I.1.3). It would be helpful if in the public REACH dossiers information is provided on the NACE-codes of the industrial sectors where the chemical is produced or used, as currently only total European tonnage bands are given in the REACH dossiers.

When industry applies for a license to discharge their (treated) wastewater to the aqueous environment, they are obliged to provide specific information with regard to the relevant chemicals and by-products produced and the production processes to the competent authority. In the Netherlands, these are the national water authority Rijkswaterstaat or the regional water authorities for industrial discharges via privately owned IWTP, or the provinces for indirect industrial discharges via public STP. This specific information is then often translated in more general terms in the license, in accordance to the IED and associated 'Best available techniques reference documents' (BREFs).

In the Netherlands a limited general location-specific risk assessment is compulsory, this discharge test assesses the impact of the discharge upon the receiving surface water (http://www.immissietoets.nl/#version=nl-en). However, a refined location-specific risk assessment may be needed for the license, as the risks of the industrial discharge may influence specific downstream river basin water uses such as drinking water production, food production, nature or recreation. Location-specific risks of an industrial discharge further depend on the hydrological situation including climate variability, and contamination with other available sources. This location-specific risk assessment cannot be fulfilled by general legislation such as REACH, the Water Framework Directive (WFD, 2000/60/EC) or the Drinking Water Directive (DWD, 98/83/EC).

Currently, there is hardly any obligation for the industry or IWTP owner to report on CECs emitted, unless they are emitted in relevant concentrations. The term "relevant" has a subjective tone to it, and is also influenced by practical and financial constraints with respect to the monitoring of CECs. For example in the Netherlands the competent water authority, in cooperation with the licensee, is responsible for the compliance monitoring of the industrial effluent and thus has an interest to keep monitoring costs low. Therefore, compliance monitoring is often only targeted on a number of benchmark substances, which in the permitting phase are assessed to cover most of the substances emitted. Within this approach, relevant substances will be missed in the regular compliance monitoring. However, nowadays monitoring techniques like high-resolution screening techniques have evolved in such a way that emittance of a broad set of relevant chemicals can be followed (Hollender et al. 2017).

For drinking water and drinking water sources, in the Netherlands a signalling parameter for 'other anthropogenic substances' has been introduced of respectively 1 and 0,1 µg/L as a top-up on the EU Drinking Water Directive and EU Water Framework Directive. When a concentration of a synthetic chemical in drinking water or drinking water sources exceeds this signalling parameter, further research is carried out on the environmental and health risks, the sources and removal efficiencies during water treatment. This signalling value draws attention of water managers and drinking water utilities to the presence of the chemicals, also resulting in evaluation of their risks (Baken et al. submitted). Such a 'signalling value' for anthropogenic substances could also be implemented with regards to industrial effluents to further increase awareness of emitting industries.

4.4 Further mitigation of emissions by IWTP

In this modelling study, a limited number of IWTP, typically serving plastic, paper, petroleum or basic chemicals industry, drives the impact with regard to drinking water production. This might imply that mitigation measures can be taken cost-efficiently, so extra treatment technologies can be placed at the IWTP with high impact. However, also other susceptible functions of the water system such as nature, food production or recreation should be regarded, to decide where further emission reduction is most effective. Furthermore model uncertainties are to be considered, as well as treatment technologies already in place at the various IWTP.

Waste water treatment technologies generally are available (Van Wezel et al. 2017). Treatment technologies are well established for more general classical water quality parameters (Polders et al. 2012, Evrard et al. 2016), and are laid down in the BREF documents established for the different industrial sectors (available via http://eippcb.jrc.ec.europa.eu/reference/). Conventional biological treatment is most widely used, which is a good technique for removal of hydrophobic and well biodegradable substances. More advanced technologies are available for treatment of industrial effluents, examples are electrochemical methods for dyes (Brillas and Martínez-Huitle, 2015), membranes or electrocoagulation for textile industries (Dasgupta et al. 2015, Khandegar and Saroha, 2013), TiO_2 photocatalytic methods, advanced oxidation processes, membrane separation etc. for pharmaceutical industries (Kanakaraju et al. 2014, Caldwell et al. 2016) and electrochemical oxidation for chemical industry effluents containing perfluorinated compounds (Niu et al. 2016). It depends on the chemicals to be removed and their physical-chemical properties, the industrial effluent matrix involved and the particular operational settings, which treatment technology or combination of treatment techniques gives highest removal efficiencies (Van Wezel et al. 2017, Fisher et al. 2017).

5 Conclusions

- Systematic information on concentrations in IWTP effluents for many chemicals of interest for drinking water production is lacking, also for relevant chemical-intensive sectors. Of 28 selected industrial chemicals of interest, only for bis(2-ethylhexyl)phthalate (DEHP) TOC normalized emissions based on the E-PRTR data can be derived.
- A public register of all chemicals and by-products produced and used per industrial site is currently not available in European member states. Such a register would be in line with the Aarhus convention and informative to other water users in the river basin.
- Available information in the public REACH dossiers, such as restrictions for safe use or precautionary measures, is currently not systematically implemented by the competent authorities in the licensing of industrial discharges.
- Predicted surface water concentrations for benzene, toluene, dichloromethane and 1,2-dichloroethane vary by over 3 orders of magnitude over the surface water bodies. Maximum predicted concentrations are in the same range as predicted earlier for some pharmaceuticals.
- Measured concentrations often exceed predicted concentrations, explained since both indirect industrial emissions via STP and releases during the use and waste life cycle phase of industrial chemicals are not included in the model.
- From all Dutch 182 IWTP a limited number of 15 has a high impact on surface water with a drinking water function, these typically serve plastic, paper, petroleum or basic chemicals industry. In total 32% of the abstracted water for drinking water production is affected by the IWTP.

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Appendix I S.I. I. Other pathways followed to retrieve information on industrial emissions for selected chemicals, next to PRTR information

In order to retrieve information on the composition of industrial discharges several approaches were followed next to the use of the EU-PRTR information.

These are approaches are;

- Study of databases of permitting authorities
- Inventory amongst industries
- Case studies on permits for industrial discharges via IWTP

S.I.I.1. Study of databases of permitting authorities

Available industrial effluent monitoring data at the authority that is responsible for the water management of the Dutch large surface waters were requested. This authority, Rijkswaterstaat, provides most licenses for industrial aqueous discharges in the Netherlands. Rijkswaterstaat has a database, called Powerbrowser, in which they together with several regional water authorities collect data per emission point on industrial effluents which become available during compliance monitoring to check the emission licenses which are provided under the EU Industrial Emissions Directive (IED). The frequency of this compliance monitoring varies up to 20 times per year. The database mainly consists of data on parameters as mentioned in the Best available technique Reference Documents (BREF), on macroparameters, six metals, PAH, BTEX, fenols and incidently more complex organic substances such as amine or n-methylpyrrolidon.

Rijkswaterstaat was requested for information on relevant substances. However, it was concluded that for the substances of interest (Table 1) or the 174 suspect substances that were attributed in Sjerps et al. (2016), no monitoring data of concentration levels in industrial effluents are available. For none of these substances specific emission requirements are being given in the Dutch IED licences concerning industrial emissions to water (personal information, Rob Berbee Rijkswaterstaat), and thus also no compliance monitoring is requested. The assumption is that via means of the monitoring of aspecific parameters as Kjeldahl nitrogen and/or chemical oxygen demand, these more specific chemicals can be regulated. The authority stated that the available data in E-PRTR as generated by the industries are more extensive than the compliance monitoring data.

The same type of information was requested at the Flanders Environment Agency, they were able to provide information for the compounds (4-Chloro-2methylfenoxy) acetic acid, 2,3-Dichloroanilin, bisphenol A, chloridazon, dimethomorph, phenazon, irbesartan, mecoprop, metalochlor, metoprolol, pyrene, simazine and terbutylazin.

S.I.1.2. Inventory amongst industries

For the under S.I. I.1. mentioned industrial permits, further information was requested via the responsible authority, Rijkswaterstaat, regarding information on production processes, produced chemicals and by-products, waste water treatment technologies and data on influent and effluent quality. The same request for information was done via VEMW, a lobby and knowledge organization for professional water and energy users. However, this request did not yield a significant response.

During a discussion within the Dutch/Flemish network group on industry and water, the members (Air Liquide Benelux, BASF, Brabant Water, DOW, USG, Emmtec. Evides Industrywater, ISPT, Nuon, Oerlemans Foods, Pidpa, COSUN, Sabic, Shell, Sitech, Tata Steel, Peka Kroef, Yara) confirmed that in compliance with the monitoring requirements of their emission licences they do not have detailed information on concentrations of their produced chemicals or by-products in their industrial effluents.

S.I. I.3. Case studies on permits for industrial discharges via IWTP

A list of relevant IWTP was made, based on the expected relevance, a variety of industrial activities and a variety of receiving surface waters. These were Sappi Maastricht BV, Shell Nederland Raffinaderij BV, Norske Skog Parenco BV, Smurfit Kappa Roermond Papier BV, BP Rotterdam Refinery, Esso Nederland BV, Emmtec Services BV, DSM Pharma Chemicals Venlo BV, Smurfit Kappa Solid Board and Chemours. Two permits were studied in more depth, both of sites that appeared to be relevant to drinking water production in the recent years, i.e. Chemelot in Geleen and Chemours in Dordrecht. The information in the permits on produced chemicals and by-products, production processes and treatment technologies, and information and requirements on effluent quality was reviewed.

Chemelot is a large industrial complex, housing 50 chemical process installations owned by different companies among which DSM and SABIC. Examples are installations for the production of nafta, ammonia, nitric acid, fertiliser, melamine, caprolactam, acrylonitrile, plastics and resins. The industrial wastewaters are collectively treated by the IWTP in Stein, serviced by Sitech, that discharges on an artificial branch of a creek named Ur, that then after 100 m flows in the Meuse. The permit for the industrial discharge is provided by the regional water authority Limburg, and renewed in may 2016. The permit prescribes monitoring in effluent for general parameters as pH, T, total N and P. For chemicals, monitoring of PAHs, metals (As, Ni, Zn, Mo and Hg), monovinylchloride and pyrazole is obliged. Also the measurement regarding acute toxicity of the effluent to fish eggs, daphnia, bioluminescent bacteria, duck weed and algae is obliged. The parameter pyrazole is added in response to a long-term incident that influenced drinking water production (Baken et al. 2016). For this parameter and for AMPA a structural decline of emissions is obliged, with specific attention to the stability of the treatment efficiency. Furthermore, in response on the aforementioned incident a future screening on organic polar components is requested. Finally, the Dutch list of substances of very high concern has to be compared with the produced chemicals and by-products. The effluent is monitored by the water authority in order to check compliance.

Chemours Dordrecht is a prominent production location in Europe for fluoropolymers, chemicals for plastics and polymers such as teflon and nylon. The site discharges industrial wastewater indirectly via the STP, which is managed by the regional water authority Hollandse Delta. The province of Zuid-Holland provides the discharge licence. The april 2017 revised license of Chemours is currently debated in court, in relation to the height of the permitted aqueous emission of 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (FRD-903 or 'GenX') which originally was 6400 kg/yr and currently 2035 kg/yr. The industrial effluent is according to the current licence to be measured again on generic parameters, several metals (Cr, Cu, Pb, Ni, Zn) and specifically FRD-903. In accordance to a so-called 'general assessment methodology' Chemours can change the use of chemicals, except for substances of high concern, CMR chemicals or chemicals with high acute aquatic toxicity (LC50 > 0,01 mg/L) and chemicals mentioned in Annex I from Directive 2006/11/EG. In order to assess the effects of the industrial discharge for water quality, (eco)toxicological information is lacking to derive a (provisional) environmental quality standard which is needed for the water quality assessment, and therefore should be provided by Chemours. Furthermore research to prohibit in the long run emission and to improve the current waste water treatment efficiency of FRD-903 is prescribed by the license. Currently reverse osmose membrane treatment is used for the dispergent-rich part of the wastewater in order to recycle GenX. This technology is currently not applied for the remaining wastewater, which is treated with coagulation/flocculation and ion exchange. As a result of a now banned earlier production process for teflon by Chemours, surrounding groundwater was contaminated with PFOA up to concentrations of 25 μg/L (Mank 2017).

Appendix II S.I. 2. E-PRTR emission data per industrial class for DEHP, benzene, dichloromethane, toluene, 1,2-dichloroethane and vinyl chloride

Industrial class[a]	IWTP / NACE -code	kg TOC/ IWTP	kg DEHP / IWTP	mg DEHP/ kg TOC	kg benzene/ IWTP	mg benzene/ kg TOC	kg dichloro-methane / IWTP	g dichloro-methane/ kg TOC	kg toluene/ IWTP	g toluene/ kg TOC	kg 1,2-dichloro-ethane/ IWTP	mg 1,2-dichloro-ethane/ kg TOC	kg vinyl chloride/ IWTP	mg vinyl chloride / kg TOC
NACE 17.1: pulp, paper and paperboard	249	798.972	25,06	31,37	-	-	-	-	139000	174,0	-	-	-	-
NACE 19.201: refined petroleum products	116	136.157	3,98	29,25	72,72	534,1	903,8	6,638	506,25	3,718	3,5	25,71	-	-
NACE 20.13: inorganic basic chemicals	138	359.706	48,30	134,3	-	-	283,0	0,787	3790	10,54	221,8	616,7	28,50	79,23
NACE 20.14: organic basic chemicals	224	260.086	22,31	85,80	173,9	668,4	63,69	0,245	596,0	2,292	66,80	256,8	14,48	55,65
NACE 20.15: fertilizers and nitrogen compounds	58	150.788	7,470	49,54	-	-	-	-	-	-	328,0	2175	-	-
NACE 20.16: plastics in primary forms	90	122.033	1,237	10,13	45,43	372,3	1,457	0,012	-	-	120,5	987,4	42,67	349,6

NACE 20.59: other chemical products n.e.c.	58	169.660	-	-	-	-	22,13	0,130	-	-	11,00	64,84	-	-
NACE 24 (excluding NACE 24.4/24.5): metals in primary forms	346	307.850	20,00	64,97	-	-	-	-	-	-	-	-	-	-
NACE 29: motor-industry	115	0	2,870	-	-	-	-	-	-	-	-	-	-	-
NACE 35: electricity and gas	1116	332.556	--	-	-	-	50,60	0,152	-	-	28,40	85,40	-	-
NACE 20.6: synthetic and artificial fibres	17	172.333	2,770	16,07	-	-	18,90	0,110	-	-	-	-	-	-
NACE 21.1: pharmaceutical preparations	95	83.377	-	-	-	-	68,44	0,821	-	-	14,60	175,1	-	-

[a]For the following industrial classes no information on the specific industrial chemicals was available; NACE 10.1 meat and poultry; NACE 10.3 fruit and vegetables; NACE 10.4 oils and fats; NACE 10.5 dairy industry; NACE 10.6 grain mill products; NACE 10.8 (excluding NACE 10.81 and 10.82) other food products; NACE 10.81 sugar; NACE 10.9 prepared animal feeds; NACE 11.05 beer; NACE 11.07 soft drinks and other beverages; NACE 17.2 articles of paper and paperboard; NACE 20.11 industrial gasses; NACE 20.12 dyes and pigments; NACE 20.2 pesticides; NACE 20.3 paints, varnishes and similar coatings, printing ink and mastics; NACE 20.52 glues and adhesives; NACE 20.53 essential oils; NACE 24.45 non-ferrous metals, aluminium; NACE 24.45 other non-ferrous metals; NACE 24.5 casting of metals; NACE 25.61 treatment and coating of metals; NACE 26-28 manufacture of machinery and electro technical industry; NACE 30.1 ship-building; NACE 22.2 plastic products; NACE 23.1 (excluding NACE 23.12) glass and glassware

Appendix III S.I. 3. Industrial chemicals ≥10 measurements in the period 1990-2015 with concentrations in the STP effluent above 0.01 µg/L, all in µg/L (WATSON database)

Industrial chemicals	Average	90 percentile	# > LOQ	# totalL
Sum adsorbing organic halogen compounds	48.8	87.9	257	298
Mineral oil	13.22	59.2	23	145
Sum extractable organic halogen compounds	5.305	2.24	370	517
Methyl-tertiair-butylether	3.779	9.92	17	39
Sum dioctylphtalate and DEHP	2.917	4.86	10	29
9-Octadecenal	2.667	3.9	12	12
Camphorsulfonic acid	1.869	5.4	13	13
Tributylphosphate	1.726	5.6	23	23
Tris(2-butoxyethyl) phosphate	1.2	1.84	33	33
Nonylphenol	0.9688	2.02	84	94
Butylbenzenesulfonamid	0.8746	1	13	13
Benzoic acid	0.8214	1.1	86	86
Hexane acid	0.6815	1.3	87	87
Octane acid	0.6648	1.12	69	69
Dipentylphtalate	0.625	1	10	16
Triethylcitrate	0.6231	0.7	13	13
Versalid	0.6143	0.77	14	14
Benzothiazole	0.4873	0.849	102	102
Dipropylphtalate	0.3873	1	14	26
Dicyclohexylphtalate	0.3858	1	12	26
2-Fenoxyethanol	0.3701	0.758	85	85
Dibutylphtalate	0.3493	1	80	141
Diethylphtalate	0.3418	1	71	146

Dimethyldisulfid	0.3273	0.699	126	148
Dioctylphtalate	0.2556	0.128	15	83
Benzylbutylphtalate	0.2255	1	39	98
Diethyltoluamid	0.2076	0.4897	396	428
Dimethylphtalate	0.1773	1	24	93
Triisobutylphosphate	0.1552	0.24	11	11
Toluene	0.1353	0.17	77	448
Butylhydroxytoluene (BHT)	0.1346	0.108	63	63
Sum chlorophenols	0.102	0.151	20	20
Dimethylsulfid	0.07914	0.224	100	174
Benzene	0.0722	0	12	446
Perfluoroctaansulfonate	0.06217	0.126	27	27
Ethylbenzene	0.04804	0	10	448
Phenol	0.03701	0.1	21	117
Sum trichlorophenol-isomers	0.0332	0.06	15	15
Trifenylphosphate	0.02797	0.041	11	11
Perfluorohexane acid	0.02155	0.076	13	13
Perfluoro-1-butanesulfonate (linear)	0.02148	0.0558	17	17
Perfluoroctanic acid	0.02148	0.04022	27	27
Perfluoropentanic acid	0.01333	0.0422	12	13
Styrene	0.0122	0	10	125
Perfluoroheptanic acid	0.00851	0.01345	24	24
Perfluorodecanic acid	0.00494	0.01323	22	24
Perfluorononanic acid	0.003065	0.004715	21	23
Flame retardants				
Trichloropropylphosphate	1.227	2.1	11	11
Tris(2-chloro-1-(chloromethyl)ethyl)phosphate	0.2613	0.5	11	11
Tri(2-chloroethyl)phosphate	0.2056	0.449	14	14
Endocrine disrupting chemicals				
Bis(2-ethylhexyl)phtalate (DEHP)	1.202	3.82	98	319
Diisobutylphtalate	0.8678	2	85	116
Nonylphenolmonoethoxylate	0.2986	0.617	13	14
Bisphenol-A	0.2126	0.354	65	110
4-Tertiair-octylphenol	0.02832	0	27	337
PAHs				
Sum 6 PAH (Borneff)	0.09891	0.114	43	43
PAK total	0.05023	0.34	64	333
Sum 16 PAH (EPA)	0.0433	0.112	59	67

Sum benzo(b)fluoranthene and benzo(k)fluoranthene	0.03625	0.06	11	16
Phenantrene	0.01831	0.031	509	908
Pyrene	0.0124	0.026	225	770
Naftalene	0.01161	0.017	249	1430
Fluoranthene	0.01064	0.022	384	1357
Chrysene	0.007264	0.0166	187	748
Acenaftylene	0.006026	0	29	618
Benzo(a)antracene	0.00508	0.01	113	777
Benzo(b)fluoranthene	0.004482	0.00743	160	1370
Benzo(ghi)perylene	0.003984	0.0028	140	1375
Benzo(a)pyrene	0.003927	0	113	1353
Acenaftene	0.003243	0	63	755
Benzo(k)fluoranthene	0.002145	0	85	1375
Antracene	0.000708	0	72	1368
Remaining chemicals				
Methanal (formaldehyde)	54.01	85.5	36	36
Tetradecanic acid	6.726	16.5	136	136
Farnesol	4.125	10	102	102
Hexadecanic acid	4.096	7.07	110	110
Dihydrocholesterol	3.111	7.31	88	88
Dodecanic acid	2.694	7	137	137
Octadecanic acid	2.197	3.5	109	109
Decanic acid	1.487	2.2	111	111
5-Cholestene	0.159	0.172	29	29
Estron	0.01214	0.0204	24	83

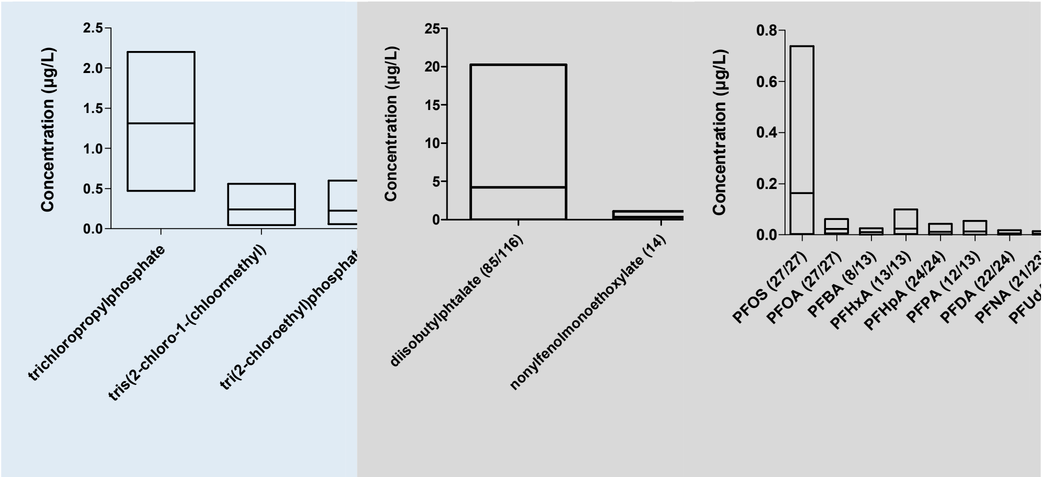

FIGURE S.I.3. BOX PLOTS OF CONCENTRATIONS AS REPORTED IN STP EFFLUENTS FOR FLAME RETARDANTS (A), SOME ENDOCRINE DISRUPTING CHEMICALS (B) AND PERFLUORONATED CHEMICALS (C) (WATSON DATABASE, 2016).