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Fate of Organic Micropollutants in Activated Sludge Systems

Work package 1 report TKI Belissima

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Report

Fate of Organic Micropollutants in Activated Sludge Systems

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Summary

Nowadays organic micropollutants (OMP) concentrations have been reported in all environmental components namely water, soil an air. Existing wastewater treatment plants WWTPs were not designed to remove OMPs, nevertheless they do achieve a partial removal. As a point source of contamination, as opposed to a diffuse source, WWTPs offer an unique opportunity to retain these contaminants before reaching the aquatic environment. Overall, the removal of OMPs in WWTPs is not fully understood. It known that it is time, substance and location dependent. A fraction of the OMPs is already being removed in existing WWTPs and removal can be enhanced by installing advanced treatment, also designated in this context as post-treatment. However, the design and operation of the advanced treatment is relying on the effluent being produced by the previous WWTP treatment levels. The operation and performance of existing WWTP treatment levels has an effect on the OMP removal, which is often overlooked.

In this TKI project we focus on 11 OMPs indicators proposed by the *Ministerie van Infrastructuur en Waterstaat* (I&W), namely 4-5 methylbenzotriazole, benzotriazole, carbamazepine, clarithromycin, diclofenac, hydrochlorothiazide, metoprolol, propranolol, sotalol, sulfamethoxazole and trimethoprim. Currently, in the Netherlands, the municipal wastewater discharge limits do not include OMP discharge restrictions. However, there is the ambition to obtain a minimal removal of 70% of the I&W indicators, from influent to effluent.
In the TKI project Belissima we aim to improve the OMP removal in conventional activated sludge systems (CAS) and advanced treatment, by model development and experimental validation. The project will perform lab tests, WWTP monitoring and post-treatment pilot tests, to support the modelling exercise. The obtained combined model enables optimization studies, aiming for improvement of the effluent quality and savings on operational costs. In this report, we focus on the OMP removal taking place at the conventional activated sludge (CAS) system. The research questions addressed in this report are the following: which OMPs are being removed/transformed in CAS systems and to which degree?; what are the relevant removal mechanisms for OMP removal in CAS?; what are relevant parameters in CAS systems to improve OMP removal?. Furthermore, the report deals with the WWTP selection for this TKI project, which be object of research and modeling exercises. Additionally, the models to apply in the CAS are also addressed. The report is a literature review of consolidated knowledge, with data provided by the water authorities taking part in this TKI project. A second review of TKI Belissima deals with removal of OMPs in post-treatment technologies.

The water authorities participating in this TKI project provided information concerning the CAS configurations of their WWTPs, main operational parameters in place and availability to perform applied research. They were previously supported by a clarification of definitions on CAS configurations. From the overview obtained, it is possible to verify that there are several CAS configurations in use, with PhoRedox and UCT being the most commonly applied. Both are characterized by the ability to remove carbonaceous materials and nutrients; both have several tanks with various redox conditions, namely anaerobic, anoxic and aerobic, aiming for nitrification, denitrification and biological phosphorus removal processes. The WWTP research location will be the WWTP Walcheren, from Waterboard Scheldestromen. The WWTP has a PhoRedox CAS configuration, and applies an Sludge Retention Time (SRT) of 25 days, which might benefit OMP removal. As possible downside, there is a 20% industrial component in the influent, possibly bringing influent variability or/and specific acclimation of the biomass to the influent characteristics. Results and modelling exercises obtained at WWTP Walcheren should not be directly extrapolated to other WWTPs.

The removal mechanisms of OMPs from wastewater are sorption, biotransformation and stripping. Stripping accounts for less than 10% of the compound removal, even for rather volatile musk substances not addressed in

this report. Therefore, stripping is considered negligible for the 11 I&W OPMs. Sorption and biotransformation can be assessed by measuring compound rate removal constants, by applying simplified batch test methodologies found in literature (Ternes et al. 2004, Joss et al. 2006). In this project, most rates constants of the 11 OMPs were found in literature, the remaining ones will be measured by batch tests, with samples collected at WWTP Walcheren. For modeling purposes, in simplified terms, OMP removal can be described by sorption and biotransformation. The required information is: values of rate removal constants, OMP concentrations in influent and effluent, CAS parameters, such as flows and solids concentrations.

Biotransformation seems to be the main removal mechanism for most of the 11 I&W OMPs, with the exception of propranolol, which has a likely removal pathway through sorption. The results of OMPs removal obtained in full-scale CAS systems are scarce, and vary between locations and compounds. Results of biotransformation, obtained with sludge of full-scale CAS systems, vary between a maximum of 95% for diclofenac (obtained in sludge with an extended SRT of 60 days) and a minimum of about 10% for hydrochlorothiazide (in sludge with an SRT of 13 d). The results of sorption, with the likely exception of propranolol, are accounting for less than 10 % OMP removal.

The CAS parameters influencing OMP removal are: SRT; redox conditions (aerobic, anoxic or anaerobic conditions); Hydraulic Retention Time (HRT); temperature; pH and sludge concentration. Additionally, availability of substrate, also linked to SRT and HRT, can influence biotransformation. Temperature and pH are not changed during CAS treatment, apart from local pH variations due to eventual addition of coagulants. The parameters SRT, HRT, redox conditions and sludge concentration are set by design, usually within pre-defined ranges. A limited set of improvement might be available by working within these ranges. The focus should be given to SRT and redox conditions. The TKI Belissima modelling approach is ideal to preliminary access possible improvements through steering of CAS parameters, without interfering with the WWTP performance.

In TKI Belissima, BioWin software will be used to model the CAS system of WWTP Walcheren. The CAS system will be modeled by the ASM models, which are integrated in BioWin. The OMP removal models will vary according to the compound. For sulfamethoxazole, diclofenac and carbamazepine, the ASM-X models will be applied. The Peterson matrixes and corresponding rates and coefficients are available in literature. For the remaining compounds, for which the ASM- X models are not yet developed, conventional modelling describing sorption and biotransformation removal mechanisms will be used. The equations are described in this report.

Further steps for the modeling of the CAS system with OMP removal include: lab work for determination of OMP removal rate constants (not found in literature); campaign monitoring of the WWTP Walcheren, to obtain remaining modeling parameters; and modeling activities of the CAS system and OMP removal.

Contents

1 Introduction

The presence of organic micropollutants (OMPs) has been detected in all environmental compartments, air, water and soil, with multiple consequences so far not completely understood. Eco-toxicological consequences with genetic effects for fish and animals, associated to the emissions of particular OMPs, have been measured (Muckter 2006). OMPs include a very wide variety of compounds such as pharmaceuticals, pesticides and herbicides, personal-care-products, industrial chemicals, that enter the aquatic environment by point and diffuse sources. Municipal wastewater collects mainly pharmaceuticals and personal-care-products, concentrating these pollutants into a single stream, and therefore providing a unique opportunity for removal in the Wastewater Treatment Plants (WWTP), preventing OMP release into the aquatic environment. Currently, the municipal WWTPs discharge limits do not include OMP discharge restrictions. At present, in the terms of surface water, there are no standards for single pharmaceutical compounds and only limited standards of other OMPs.

The OMPs concentrations in the WWTPs influent and effluent varies due to multiple factors. Concentrations of pharmaceuticals, for instance, are influenced by production, sales and practices associated with each compound, human metabolism of pharmaceuticals, water consumption per person and per day, design and operation of the WWTP, environmental persistency and removal rates of the WWTP operations and processes. Existing WWTPs, mainly based on biological treatment processes, were not designed for OMP removal. Nevertheless, removal of OMPs in WWTP does occur (Joss et al. 2006, Pieters et al. 2011, Bourgin et al. 2018), even if the extent of the removal, and reasons behind it are not fully understood. It is overall accepted that existing WWTPs are not able to remove all OMPs to acceptable discharge levels, therefore new technology has to be introduced in order to achieve it. Usually, these new technologies are placed after the biological treatment, therefore usually designated as advanced treatment or, as commonly designated, post-treatment. There are exceptions such as the addition of Powder Activated Carbon to the activated sludge, for OMP removal. Nevertheless, the lack of knowledge regarding the existing CAS systems, also hinders the post-treatment technologies, which currently have to be installed and operated at higher costs, to compensate for possible non-existing removal.

Currently, most WWTPs rely on Conventional Activated Sludge (CAS) systems for carbonaceous and nutrient removal. The design and operational settings are usually set within pre-defined ranges, aiming to address the variating quantity and quality of municipal wastewater, and always comply with the discharge limits. OMPs have specific pathways of removal, which when known, can be associated to a particular process and setting of the CAS. Parameters such as sludge retention time (SRT); existence or absence of dissolved oxygen and nitrate; substrate loading rates, have shown to influence certain OMPs removal (Joss et al. 2004, Falas et al. 2016, Gusmaroli et al. 2020). Therefore, it is possible that a window of opportunity is available to increase removal of OMPs in existing CAS systems. Nevertheless, an optimization towards the removal of a determined OMP, might compromise the removal of another, with a different removal pathway. Moreover, since variations of dissolved oxygen or substrate loads will influence removal of carbonaceous materials and nutrients, the operators of the WWTPs are reluctant to apply them. Models can test the borders of the existing design and operational ranges, and go beyond them, without compromising current operation. An integral model of the WWTP, combining the removal mechanisms of the different OMPs, allows testing the limits of OMP removal in existing WWTPs.

In this TKI project we focus on the 11 OMPs indicators proposed by *the Ministerie van Infrastructuur en Waterstaat* (I&W), namely 4-5 methylbenzotriazole, benzotriazole, carbamazepine, clarithromycin, diclofenac,

hydrochlorothiazide, metoprolol, propranolol, sotalol, sulfamethoxazole and trimethoprim. The selection provided from the *Rijksinstituut voor Volksgezondheid en Milieu* (RIVM), executing the task at the request of the Ministry I&W (RIVM 2019). So far the knowledge about these 11 compounds is scattered through different sources. A systematic approach about these OMPs, gathering information about the removal rates, removal mechanisms, connection to operational parameters, is necessary to understand if and which OMP removal can be optimized and what is the most likely route to succeed. The overall goal of this project is to find methods to improve the removal efficiencies of OMPs in WWTPs by combined modelling of CAS and post-treatment technologies. We want to explore the synergy of removal between CAS and post-treatment, in order to fully use the potential of CAS for OMP removal, and contribute to the optimization of design and operation of post-treatment technologies. This review will focus on OMP fate in CAS systems, and a second review of this TKI project will deal with removal of OMPs in post-treatment technologies. The approach of this TKI project consists of a combination of literature review, experimental tests and modelling.

According to the project plan of this TKI project, the present review aims to answer the following questions:

- Which OMPs are being removed/transformed in CAS systems and to which degree?
- What are the relevant removal mechanisms for OMP removal in CAS?
- What are relevant parameters in CAS systems to improve OMP removal?

In order to gain a better understanding of OMP removal in CAS systems, aiming to improve removal by tweaking CAS operation, this report will go through literature sources on the following themes: removal mechanisms, OMP removal per mechanism, removal rates at full-scale municipal WWTP and possible parameters to tweak the removal. The report will also address the models to apply, when modelling removal of OMPs in CAS systems. The report aims to be a review of the existing knowledge on OMP removal in CAS systems, to be used as support of project decisions, namely the choice of the WWTP to be submitted to modelling within this TKI project, and the experimental tests required to generate data to implement the model. The review focused on published literature with consolidated knowledge. Additionally, this report aims to describe the design and operational values of the WWTPs of the TKI partners, with relevance for the current project.

2 Conventional activated sludge for municipal wastewater treatment

2.1 Definitions

In this report we will use the definitions of treatment methods in wastewater as applied by Metcalf & Eddy (2003) and Metcalf & Eddy (2014). In a WWTP units of operations and processes are grouped together to provide different levels of treatment, namely: preliminary, primary, secondary, tertiary and advanced. The description of each treatment level is the following:

- Preliminary - removal of contaminants such as sticks, rags, grit and grease, able to cause maintenance and operational problems to following operations and processes.
- Primary- partial removal of suspended solids and organic matter; can be combined with an advanced primary level, comprising filtration or chemical addition.
- Secondary – chemical and/or biological processes for the removal of dissolved or suspended organic matter and suspended solids; a secondary treatment level with nutrient removal (nitrogen, phosphorus or both) is an option.
- Tertiary- removal of residual suspended solids, after secondary treatment; nutrient removal is often included in this definition; usually comprised of granular medium filters; disinfection is also typically designated as tertiary treatment level.
- Advanced- removal of dissolved and suspended materials, remaining after biological treatment, particularly when required for water reuse purposes.

The secondary treatment level with nutrient removal is particularly relevant for this report. The secondary level of treatment, with or without nutrient removal, is achieved by applying activated sludge processes. Due to intensive research since the last decades of the 20th century, the technologies applied for the secondary level of treatment with nutrient removal are currently considered as conventional technologies. Therefore, in this report all the activated sludge processes achieving nutrient removal, will be further designated as Conventional Activated Sludge (CAS).

The activated sludge process is used routinely for biological removal of contaminants in municipal and industrial wastewater. The process started to be developed in the early 1880's, and was named as activated sludge by Ardern and Lockett in 1914, because it involved the production of an activated mass of microorganisms with the ability to aerobically stabilize organic material in wastewater (Metcalf & Eddy 2014). In the Netherlands, after the Second World War, Dr. Ir. Aale Pasveer, while developing the oxidation ditch (the predecessor of the currently designated carrousel) supplied oxygen to the wastewater to speed up the conversion of organic matter. The impulse given by the use of artificial aeration enabled further developments of the activated sludge system. Presently, the activated sludge basic design system, i.e. a combination of operation and process units, consists of, as follows: a reactor, where the microorganisms are kept in suspension and aerated; a solid-liquid separation unit (settling tank or clarifier); and a recycle system for returning part of the solids removed from the liquid-solid separation unit to the reactor. An activated sludge process has the ability to produce flocculent settable solids that are usually removed by gravity in the settling tanks, also designated as clarifiers.

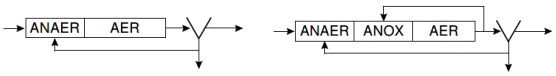
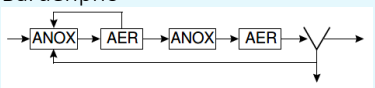
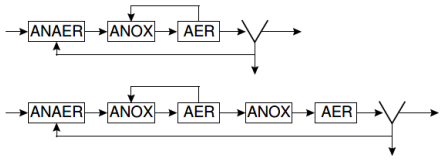
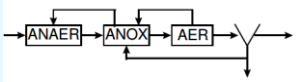
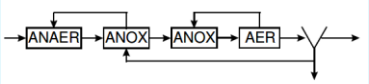
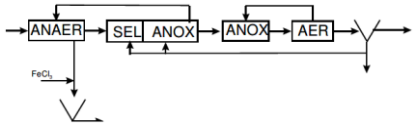
Multiple activated sludge configurations have evolved employing the basic design components, i.e. reactor, solid-liquid separation unit and recycle system. Presently, activated sludge processes frequently include nitrification,

denitrification /or biological phosphorus removal. The following sections discuss the most applied activated sludge configurations worldwide and in the Netherlands.

2.2 Conventional activated sludge configurations

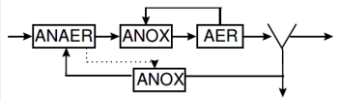
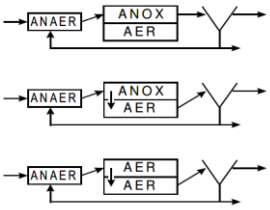
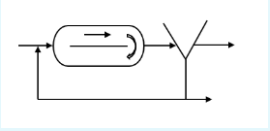
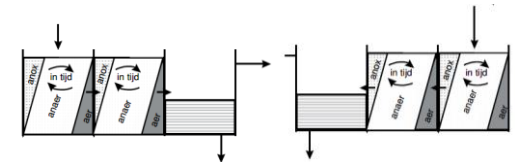
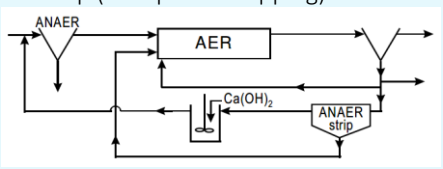
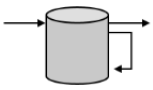
The Metcalf manuals propose a classification of the CAS configurations based on the hydrodynamic regimes applied in the biological reactors, such as completely mixed or plug-flow regimes (Metcalf & Eddy 2003, Metcalf & Eddy 2014). However, the Stowa report 2017-36 (Nieuwenhuijzen et al. 2007) provides a description of the most applied activated sludge configurations with nutrient removal, based on the historical developments and most frequent current applications. We will adopt the approach applied by Stowa, since it is more directed to the currently applied CAS systems. Table 1 shows the most significant activated sludge configurations worldwide.

Table 1- Most significant activated sludge configurations worldwide, identified by name, scheme and most significant features. All the configurations included allow the removal of carbonaceous material (Source: mostly adapted from Nieuwenhuijzen et al. (2007), otherwise reference included).

Name/Scheme	Description-main features
A/O and A^2/O (Anaerobic/Oxic) 	Designed for biological removal of phosphorus. A/O suited for high loaded plants, with no nitrification A^2/O suited for low loaded plants, with nitrification
Bardenpho 	Designed to achieve very high removal of nitrogen by nitrification and denitrification. High recirculation ration from the 1st aerobic tank to 1st anoxic tank. A 5-stage Bardenpho system (scheme showing 4-stage Bardenpho system) is also common.
PhoRedox 	One extra anaerobic tank, compared to Bardenpho, to avoid nitrate inhibition in the anoxic tanks.
UCT (University of Cape Town)  (M)UCT 	Design of the recycle sludge line: the recycle sludge line returns to the anoxic tank, and from there to the anaerobic tank, avoiding the nitrate inhibition in the anaerobic tank. In (M)UCT, the long sludge retention in the anoxic tank, leading to low settle-ability, is avoided by placing 2 anoxic tanks in series.
BCFS (*Biologisch-Chemische Fosfaat en Stikstofverwijdering*) 	Based on (M)UCT, including a selector, and the addition of chemicals for phosphate removal, where the obtained chemical sludge does not return to the biological tanks.

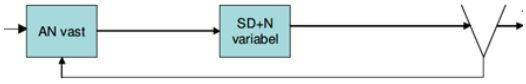
(continued in the next page)

(Continuation Table 1)

Name/Scheme	Description-main features
JHB (Johannesburg) ISAH (*Institut für Siedlungswasserwirtschaft und Abfalltechnik der Universitat Hannover*) 	Based on A^2/O the JHB and ISAH processes reduce further the nitrate by placing an anoxic tank in the sludge return line. The ISAH process has an extra connection from the anaerobic to the anoxic tank placed in the sludge return line (represented by the stripped line).
Biodenitro and Biodenipho 	Biodenitro (biological (de)nitrification) relies on pared nitrification and denitrification tanks, operated alternatively. Both tanks are provided with air, propulsion and mixing to allow both aerobic and anoxic conditions. In the Biodenipho (biological (de) nitrification and phosphorus removal) process an anaerobic tank is included.
Carrousel (oxidation ditch) 	Carrousel (or oxidation ditch) relies on a ring or oval channel with a unidirectional flow promoted by aeration and mixing devices, which also assure denitrification and aeration zones along the carrousel.(Metcalf & Eddy 2003). The predecessor of the carrousel was the oxidation ditch developed by Dr. Ir. Aale Pasveer after the Second World War.
Unitank 	Similar to an SBR (Sequential Batch Reactor) with 3 compartments than can alternate between aerobic, anoxic, anaerobic, or settler functions. Unlike SBRs it can be operated continuously. To allow removal of nitrogen and phosphorus the number of compartments can be extended, or operated with intermittent aeration.
Phostrip (Phosphate stripping) 	Combination of biological and chemical phosphorus removal, where the phosphorus removal takes place in side-stream from the recycle line. Biological removal of phosphorus takes place in a stripper operated as settler, and lime is added to the supernatant. The chemical sludge is removed by sedimentation in the primary settler.
Nereda 	Relies on aerobic granular sludge (AGS) technology, i.e. compact aerobic granules able to settle at high velocity with a low sludge volume index. Based on repeated feed batch process, allowing combined removal of carbon, nitrogen and phosphorous. Simultaneous feeding and effluent withdrawal period, reaction period, and a settling/sludge withdrawal/idle period. Biological phosphate removal can be supplemented with metal salt addition directly in the sludge bulk. (Pronk et al. 2015).

The configurations described in Table 1 were applied and adapted in/to the Netherlands, usually leading to designs with increased number of tanks in series, each one with its specific function. Some of the main reasons for this development, were a preference for biological removal of phosphorus, allowing savings on chemicals additions, and an increased control of the settle-ability of the sludge, operationally controlled by the obtained SVI (Sludge Volume Index) in the settler unit (Nieuwenhuijzen et al. 2007). According to Nieuwenhuijzen et al. (2007) the activated sludge configurations most applied in the Netherlands were the PhoRedox, the M(UCT) or similar, and PhoSim. The PhoSim can be described as follows:

- PhoSim- removal of carbon; removal of nitrogen through simultaneous denitrification and nitrification, with removal of phosphorus through PhoRedox, which can be completed by chemical removal



Key: Abbreviations in Dutch translated as follows: AN- anaerobic; SD-Simultaneous denitrification; N-Nitrification; variabel- variable.

2.2.1 Overview of partners CAS systems

Table 2 shows the number of WWTPs, the total installed capacity, and total removal percentages of Chemical Oxygen Demand (COD), Nitrogen (N) and Phosphorus (P) of the Dutch waterboards within this TKI project. Aquafin, the Belgium waterboard, also a partner of this TKI project, has a total of 323 WWTPs.

Table 2- Total number of WWTP per Dutch partner, installed capacity as population equivalents, and COD, N and P total removal rates (source WAVES database, *Unie van Waterschappen* (UvW 2018)).

	Number of WWTP	Total capacity [p.e.]	COD removal rate [%]	N removal rate [%]	P removal rate [%]
Amstel, Gooi en Vecht (waternet)	12	2023500	90	86,4	92,9
De Stichtse Rijnlanden	16	1388342	91,4	87,6	95
Brabantse Delta	17	1308900	84	80,3	92,2
Scheldestromen	16	794000	82,5	79	89,1

The TKI Belissima will include experimental tests at a selected WWTP (section 2.3). With that in mind, the TKI waterboard partners were asked to select WWTPs, where research activities could take place or be considered representative of/to their own WWTPs. A selection of 3 WWTPs per TKI waterboard partner is presented in Table 3. Some of the TKI waterboard partners also provided information about other WWTPs.The remaining collected information is shown in Annex I.

Table 3- WWTPs of the waterboards TKI partners Aquafin, Brabantse Delta, De Stichtse Rijnlanden, Scheldestromen and Amstel, Gooi en Vecht (Waternet).

Location	Design load [p.e.]	Max flow [m^3h^{-1}]	HRT [1] [h]	Influent-Industrial [%]	Configuration CAS [2]	Primary clarifier	Complementary information CAS configuration				SRT [3] [d]
							Anaerobic tank	Denitrification tank	Nitrification tank	Hydraulic regime	
Aquafin											
Aartselaar *	54.000	3.956	6	4	PhoRedox	No	Yes	Yes	Yes		10,5
Brugge	238.500	14.148	8	5	PhoRedox [4]	No	Yes	Yes	Yes	Carrousel	23,5
Gent	207.000	13.955	7	3	Bardenpho [4]	No	No	Yes	Yes	Carrousel	
Brabantse Delta											
Bath	471.000	20.000	13	40	NA	Yes	No	Yes	Yes	Carrousel	15
Nieuwver (Breda)	363.000	16.500	10	NA[5]	NA	No	No	Yes	Yes	AB (two-stage)	14
Dongemond (Oosterhout)	146.000	6.000	8	NA	NA	Yes	No	Yes	Yes	Carrousel	22
De Stichtse Rijnlanden											
Utrecht	432.000	6.600	12	10	Nereda	No	No	No	No	Mixed	12
Leidsche Rijn	165.255	5.000	12	10	UCT	No	Yes	Yes	Yes	Carrousel	16
Nieuwegein	144.000	3.500	12	10	UCT	yes	yes	yes	yes	Carrousel	18

(Table continues in the next page)

(Continuation of Table 3)

Location	Design load [p.e.]	Max flow [m^3h^{-1}]	HRT [1] [h]	Influent-industrial %	Configuration CAS [2]	Primary clarifier	Complementary information CAS configuration				SRT [3] [d]
							Anaerobic tank	Denitrification tank	Nitrification tank	Hydraulic regime	
Scheldestromen											
Walcheren *	178.700	8.015	6,3	20	PhoRedox	Yes	Yes	Yes	Yes	Mixed	25
Willem Annapolder *	90.000	4.600		30	Phoredox	Yes	Yes	Yes	Yes	Mixed	20
Terneuzen	86.400	3.100			PhoRedox	Yes	Yes	No	Yes	Mixed	
Amstel, Gooi en Vecht (Waternet)											
Hilversum	82.500	1.650	70 (at dw[6])	10	mUCT	Yes	Yes	Yes	Yes		31
Horstermeer *	150.000	5.000	52 (at dw)	10	mUCT	Yes	yes	Yes	Yes	Plug flow	22
Blaricum	30.000	1.430	57(at dw)	<1	carrousel	No	No	yes	Yes	carrousel	14

Key: (*) WWTP research location; [1] HRT- Hydraulic Retention Time; [2] Configurations in table 1; [3] SRT-Sludge Retention Time; [4] Similar to; [5] NA- Not available; [6] dw- dry weather flow conditions.

2.3 WWTP selection- representability in a modelling exercise

Table 3 and Table I-1 show the information received from the TKI Belissima waterboard partners. Table 3 shows the WWTPs selected by the waterboard partners as possible research locations or representative to their own WWTPs. From Table 3 is possible to verify that there are several CAS configurations in use, with PhoRedox and UCT being the most frequently applied. Both configurations allow removal of carbonaceous materials. The CAS tanks present various redox conditions, namely anaerobic, anoxic and aerobic, aiming for nitrification, denitrification and organic phosphorus removal processes. Sludge retention times of about 20 days benefit the biological conversion of nutrients, and might also favorably impact removal of OMPs.

Table 3 shows the WWTPs indicated as research locations. The WWTP chosen as experimental location for TKI Belissima is the WWTP Walcheren, from the waterboard Scheldestromen. WWTP Horstermeer is the main research location for Waternet and used as reference WWTP by Stowa. WWTP Horstemeer was not available as pilot location for TKI Belissima. The same occurred with WWTP Aartselaar used as main research location for Aquafin.

The WWTP Walcheren has a PhoRedox CAS configuration and applies a SRT of 25 days, complying with the preferences previously established. The influent of the plant has a 20% contribution of industrial influent, which might bring increased variability in the influent quality, particularly if the industry is discontinuously discharging effluent into the sewage network. If the industry, has a continuous discharge into the sewage network supplying influent to the WWTP, it is possible that the biomass is acclimated to the industrial effluent quality. Independently of the discharge regime and amount of industrial fraction to the WWTP influent, there is also variability in the domestic influent characteristics between different WWTPs locations. Therefore, results and modelling exercises obtained at WWTP Walcheren should not be directly extrapolated to other WWTPs, without further analysis.

3 OMP removal in CAS

3.1 Classification of OMPs

Organic micropollutants (OMPs) are a vast group of substances comprising pharmaceuticals, chemicals and other micropollutants of emerging concern. To facilitate research and promote the application of knowledge, a group of 12 substances were selected as indicators by the Swiss Federal Office for the Environment (FEON) (Annex II), after the publication of a new water protection law in 2016, aiming to improve the surface water quality by reducing the load of micropollutants at the WWTPs (Bourgin et al. 2018). The aim of the Swiss water law is to remove 80% on average of micropollutants, over the whole WWTP from influent to effluent, within the next 20 years. One of the reasons to select the 12 indicator substances was because they are non-easily biodegradable substances, normally not well removed by conventional wastewater treatment (Bourgin, Beck et al. 2018).

In the Netherlands, the *Ministerie van Infrastructuur en Waterstaat* (I&W) proposed a selection of 11 OMPs indicators, published by the *Rijksinstituut voor Volksgezondheid en Milieu* (RIVM)(RIVM 2019). The selected compounds are shown in Table 4. Table 4 also shows also the choice made by FEON. In the Netherlands, the OMPs indicators were selected because they were hardly removed at the WWTPs, but possibly removed by applying advanced treatment; could be measured accurately; and if their loads would be reduced at the WWTPs before discharge it would likely lead to the simultaneous removal of other OMPs (RIVM 2019). Furthermore, the goal, in the Netherlands, is to obtain a minimal removal of 70% of the I&W indicators, from influent to effluent, including additional technology. The OMPs indicators were also adopted by Stowa, even if Stowa extended the list to a total of 19 OMPs (Annex II). This TKI project is focusing on the OMPs proposed by the *Ministerie I&W*.

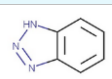
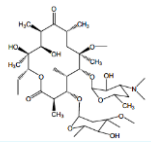
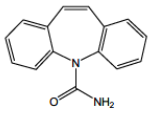
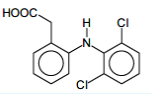
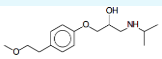
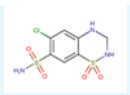
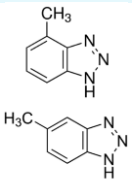
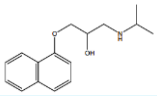
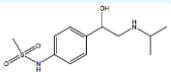
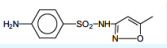
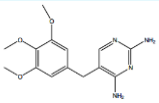
Table 4- Identification of the Organic Micropollutants (OMP) selected as indicators by the *Ministerie van Infrastructuur en Waterstaat* (RIVM 2019).

OMPs	Group/application	CAS number[2]	Molecule
Benzotriazole *	Industrial chemical- corrosion inhibitor [1]	95-14-7	$C_6H_5N_3$
Clarithromycin *	Pharmaceutical- antibiotic	81103-11-9	$C_{38}H_{69}NO_{13}$
Carbamazepine *	Pharmaceutical- antiepileptic	298-46-4	$C_{15}H_{12}N_2O_2$
Diclofenac *	Pharmaceutical-Anti-inflammatory	15307-86-5	$C_{14}H_{11}Cl_2NO_2$
Metoprolol *	Pharmaceutical- Beta-blocker	37350-58-6	$C_{15}H_{25}NO_3$
Hydrochlorothiazide *	Pharmaceutical-diuretic	58-93-5	$C_7H_8ClN_3O_4S_2$
4-, 5-methylbenzotriazole *	Industrial chemical - corrosion inhibitor[1]	29878-31-7 136-85-6	$C_7H_7N_3$
propranolol	Pharmaceutical Beta-blocker	525-66-6	$C_{16}H_{21}NO_2$
sotalol	Pharmaceutical Beta-blocker	3930-20-9	$C_{12}H_{20}N_2O_3S$
sulfamethoxazole	Pharmaceutical-antibiotic	723-46-6	$C_{10}H_{11}N_3O_3S$
trimethoprim	Pharmaceutical - antibiotic	738-70-5	$C_{14}H_{18}N_4O_3$

Key: * Also shortlisted as an indicator substance by the Swiss Federal Office for the Environment; [1] ECHA (2020); [2] CAS number- numerical designation of compounds provided by the American Chemical Society.

The main characteristics of the 11 OMPs indicators are shown in Table 5.

Table 5- Characteristics of the 11 OMPs I&W indicators, where pK_a is the acidity dissociation constant (pK_a= -log K_a) and Log K_{ow} is the logarithm of the K_{ow} octanol-water partition coefficient (sources: DrugBank (2020), ECHA (2020))

OMP	Chemical group	Structure	Molar weight [g.mol^{-1}]	pK_a	Log K_{OW}
benzotriazole			119.1	8.37	1.34
clarithromycin	Macrolide		747.9	8.99	2.69 3.16
carbamazepine	Tricycle dibenzazepine derivative		254.3	15.96(*)	2.45
diclofenac	Aromatic hydroxylamine		296.2	4.2	4.6
metoprolol	Propanolamine		267.4	9.7	1.9
Hydrochlorothiazide			297.7	7.9	-0.07
4-, 5-methylbenzotriazole			133.1		
propranolol	Propranolamine		2593	9.42	1.2 (pH 7.4)
sotalol			272.4	10.07(*)	0.2
sulfamethoxazole	sulphonamide		253.3	5.7	0.89
trimethoprim	Aminopyrimidine		290.3	17.33(*)	0.91

(*) with strongest acid

The amount of information found on each of the 11 OMPs is very variable. Very little was found about the chemicals benzotriazole, and 4-, 5-methylbenzotriazole. Both are anti-corrosion/anti-fouling compounds of industrial origin, contrary to the remaining compounds of pharmaceutical origin, as indicated in Table 4. ECHA (2020) refers that benzotriazole is mono-constituent substance, and that due to chemical structure the substance is not expected to be surface-active. Information about the pharmaceutical hydrochlorothiazide is also very scarce.

On the contrary, there is abundant information about carbamazepine, diclofenac and sulfamethoxazole. Literature sources on the beta-blockers metoprolol, propranolol and sotalol are also available, and about the antibiotics

clarithromycin and trimethoprim as well, even if it is less abundant than for carbamazepine, diclofenac and sulfamethoxazole. The available information comes from very different areas of knowledge, namely pharmaceuticals consumption; toxicology research; water treatment and wastewater treatment; and environmental risk assessments. The following paragraphs summarize relevant information found about the 11 OMPs I&W indicators.

Carbamazapine

Carbamazepine is an antiepileptic pharmaceutical, prescribed almost everywhere in Europe and USA in the treatment of epilepsy and neuropathic pain (Joss et al. 2006). The consumption trends vary per country, over time and sometimes per season. In the US the subscriptions of carbamazepine showed a decreasing trend from 1995-2001, while in the same period in Germany there was an increase (Joss et al. 2006). Carbamazepine is a compound of neutral charge, moderate hydrophobicity, with low affinity for adsorption to activated carbon, and a well-defined pattern of metabolites in human and animal degradation pathways (Muckter 2006). Carbamazepine metabolites and transformation products are particularly important, because as explained in section 3.3., carbamazepine is likely to retransform to the parent compound during WWTP operations and processes. The most important carbamazepine metabolites are the 10,11-epoxide and DHDC (10,11-dihydro-10-hydroxy-5H-dibenzazepine-5-carboxamide) found in humans and animals (Muckter 2006). A fraction of carbamazepine is directly hydroxylated and excreted as glucuronide (Muckter 2006, Polesel et al. 2016).

Carbamazepine and its metabolites have been detected in the whole water cycle, namely treated wastewater effluents, surface water and groundwater. Concentration values measured in wastewater effluents and surface water are shown in Table 6. However, the extent of carbamazepine contamination and consequently the concentrations measured in various river catchments and individual rivers can vary significantly, according to geographic and demographic factors (Knacker et al. 2006). Carbamazepine was also reported in groundwater in concentrations up to 1.1 $ng.L^{-1}$, and the compound was not removed during groundwater recharge, in anoxic saturated or aerobic unsaturated flow conditions, during travel times up to 8 years (multiple references compiled in Alder, Bruchet et al. (2006)). Due to its persistence, carbamazepine is considered a good indicator of municipal wastewater contamination, or transport of contamination to aquifers (Knacker et al. 2006). Furthermore, according to Knacker et al. (2006), who conducted risk assessments on selected OMPs, carbamazepine does not pose a risk for the aquatic environment, however it does pose a risk for benthic organisms, i.e. organism living near, on or in the bottom of aquatic environments.

Diclofenac

Diclofenac is an anti-inflammatory pharmaceutical. Annual prescriptions of diclofenac vary per country. Total prescriptions in a selection of European countries vary between a maximum of 49,000 $kg.a^{-1}$ in Germany and a minimum of 800 $kg.a^{-1}$ in France (Joss et al. 2006). As referred by Plosz et al. (2012), diclofenac is excreted in urine by about 6% unchanged; 16% as 4'-OH-Diclofenac; and 18% as other hydroxy metabolites (3'-OH-Diclofenac, 5'-OH-Diclofenac and 4'-5'-OH-Diclofenac) and glucuronide conjugate. The term conjugate, in chemistry, refers to a part of the original molecule. Diclofenac was found in treated wastewater effluents and surface waters in Europe and North America (Joss et al. 2006). Values of measured concentrations are shown in Table 6. Diclofenac has also been detected in groundwater of Germany. Besides musk fragrances only diclofenac was quantified above the detection limit in activated sludge samples from 3 German WWTPs with values of 0.2 to 0.45 $mg.kg^{-1}$, and in the digested sludge diclofenac was present with 0.22 $mg.kg^{-1}$ (Ternes et al, 2003 referred by Siegrist et al. (2012)). At environmental concentration ranges, diclofenac was identified as being responsible for renal alterations (Joss et al. 2006). Diclofenac is known to accumulate in bile or liver of rainbow trout's up to a concentration factor of about 2700 (Chewaiger et al 2004 referred by Joss et al. (2006)). Photo-transformation was identified as the main elimination process of diclofenac (Gunten et al. 2006) in drinking water. However, in wastewater, particularly in the CAS, this mechanism of removal is not significant.

Table 6- OMPs concentrations detected in treated wastewater and surface water in different countries, indicated as median/maximum in ng.L^{-1} (Source: adapted from Alder et al. (2006) referring to multiple sources).

Compound	France, Greece, Italy, Sweden	Germany	UK	Canada	USA
In treated wastewater					
Carbamazepine	870/1.200	920/22.000		110/2,300	
Diclofenac	680/5.500	1.500/10.000	420/2,400	360/28,400	60/80
Sulfamethoxazole	50/90	120/4.700	-/130	240/870	1,400/2,000
Metoprolol	80/390	620/9.120			60/160
Propranolol	10/90	40/650	80/280		20/50
Sotalol		0,63/6,5			
Clarithromycin		20/1.800		90/540	
Trimethoprim	: 40/130	40/1.500	70/1,300	70/190	550/1,900
In surface water					
Carbamazepine		70/1.810		20/650	74/270
Diclofenac		30/470		26/194	
Sulfamethoxazole		13/377		8/99	15/1,900
Metoprolol		17/1.800			
Propranolol			29/215		
Sotalol		49/950			
Clarithromycin					9/79
Trimethoprim		-/170	-/42	43/134	150/710

Sulfamethoxazole

Sulfamethoxazole is overall prescribed for the treatment of bacterial infections, and in Europe at a more or less constant rate (Alder et al. 2006). The metabolized percentage of sulfamethoxazole by the human body is variable, and is subsequently extracted via urine (Muckter 2006). About 50% of the dosage is excreted as an inactive metabolite N^4-acetylsulfamethoxazole, and about 10% as the unchanged compound (Muckter 2006). The human metabolism of sulfamethoxazole leads to the formation and release of hydroxylated, acetylated (N^4-acetylsulfamethoxazole) and glucuronide metabolites (Polesel et al. 2016). The N^4-acetylsulfamethoxazole metabolite can retransform to the active parent compound during wastewater treatment (Joss et al. 2006). However, during anaerobic digestion sulfamethoxazole is degraded by more than 80% (Joss et al. 2006).

Sulfamethoxazole has been detected in wastewater and surface water of Europe and North America (Table 6). Sulfamethoxazole was also found in groundwater of Germany and US, and in drinking water of Germany (Alder et al. 2006). Predictions of sulfamethoxazole concentrations in the aquatic environment, based on emission data, removal in WWTP and dilution factors produce satisfactory results, i.e. validated by measurements. The same occurs for predictions of carbamazepine (Knacker et al. 2006). Sulfamethoxazole is classified as presenting risk for the aquatic environment (Knacker et al. 2006).

Metoprolol, propranolol and sotalol

Metoprolol, propranolol and sotalol are beta-blockers, usually prescribed for hart arrhythmias and hypertension. While metoprolol and propranolol can be of human and veterinary use, sotalol is only for human use (Muckter

2006). Propranolol and metoprolol, with very similar chemical structure (Table 5), are more lipophilic molecules, which are largely metabolized, with less than 1% of oral propranolol being recovered unchanged in urine, while metoprolol is less than 5% (Muckter 2006). On the contrary, more than 85% of sotalol is excreted without being metabolized (Muckter 2006). An increased trend in the consumption of metoprolol was found in countries such as Germany and USA, at least between 1995 and 2001 (Alder et al. 2006).

The beta-blockers metoprolol, propranolol and sotalol have been found in wastewater at various concentrations in European countries and the US (Table 6). Regarding surface waters (Table 6) metoprolol was also detected in Germany; while propranolol was below the detection limit in Germany but measurable in the UK. Sotalol was present in German surface water and groundwater. Propranolol has the particularity of being used as a tracer of raw and treated wastewater in the environment (Joss et al. 2006).

Clarithromycin

Clarithromycin is a prescribed antibiotic (Table 4), excreted at hospitals and households. Both in Switzerland and Canada clarithromycin was classified as one of the most abundant antibiotics in treated wastewater and surface water, and the most abundant macrolide in Switzerland (McArdell et al 2003 referred by Alder et al. (2006)). The molecular structure consists of large macrocyclic lactone rings to which sugar molecules attach (Table 3). Macrolide antibiotics are named after the macrocyclic lactone structure of the parent compound erythromycin, and were introduced in the market in the 80's and 90's with success (Muckter 2006). Values of clarithromycin in treated wastewater and surface water are shown in Table 6.

Trimethoprim

Trimethoprim is an antibiotic (Table 4) that, such as sulfamethoxazole, is used to treat bacterial infections (Alder et al. 2006). Antimicrobial pharmaceuticals, such as trimethoprim, are usually discussed because of their potential role in the spread and maintenance of multi-resistant bacteria (Muckter 2006). Trimethoprim can be administrated both for human and veterinarian use (Muckter 2006). There have been reported cases of combined resistance of sulfadiazine/trimethoprim in animal and fish farming environments (Muckter 2006). Trimethoprim has been detected in treated wastewater of Europe and North America (Table 6). At WWTPs trimethoprim was reported as being removed at sludge age (θ) above 15 d, and as having a very high removal rate with θ above 50 d (Joss et al. 2006).

3.2 Removal mechanisms

The most important OMP removal mechanisms in CAS are:
(1) sorption to activated sludge and subsequent removal by sedimentation as secondary sludge;
(2) biological transformation that might lead to mineralization of substances by bacteria;
(3) stripping by aeration.

Regarding stripping the mechanism is negligible due to the low OMP volatility (Ternes et al. 2010). According to the conclusions obtained by the EU project NEPTUNE (Ternes et al. 2010), even for rather volatile musk fragrances, not addressed in this report, stripping will account for less than 10% of the compound removal. Therefore, stripping will only described as a mechanism and not taken into account when identifying removal rates/coefficients in literature.

The OMP removal mechanisms can interfere with, the so-called retransformation processes (Polesel et al. 2016). According to Polesel et al. (2016), the retransformation processes are responsible for the negative removal rates observed in some parent OMP compounds in full-scale WWTPs. Examples of retransformation processes are as follows (Polesel et al. 2016):

- De-conjugation of metabolites: when conjugated metabolites of parent compounds retransform back to the parent compound.
- Formation of analogues and structurally related chemicals: it might occur during human metabolism or as products of biological transformation in wastewater treatment, which might then retransform back to a certain OMP.
- Release from fecal matter: OMPs excreted as fecal matter might be released into the liquid phase only in a later stage of the wastewater treatment.
- Hydrolysis of particulate and colloidal matter: hydrolysable and colloidal organics undergo hydrolysis by extracellular enzymes, with potential release of sorbed chemicals into the liquid phase.

Desorption, as the inverse reaction to sorption is also considered as a retransformation process, however sorption is often considered as in equilibrium with desorption, and does not seem to be responsible for negative removal rates. The knowledge on retransformation processes is relevant for an integrated approach on the fate assessment of OMPs. Regarding the 11 I&W OMPs, the following influences of retransformation processes were reported (Polesel et al. 2016):

- de-conjugation of metabolites has been found relevant/ hypothesized for carbamazepine and its metabolites, and diclofenac;
- release from fecal matter is a possibility at least for clarithromycin.

Presently, the available information on retransformation processes regarding most of the 11 I&W OMPs is still limited, therefore sections 3.2.2 and 3.2.3 will focus on consolidated knowledge, and mention the retransformation processes only whenever relevant and known.

The OMP removal mechanisms might involve phase-changes from liquid to solid, solid to liquid, and liquid to gas, depending on the mechanism addressed. However, considering the complex nature of activated sludge, being a three phase component with particulate, colloidal and dissolved materials or molecules, a strict separation between phases is not easily defined, particularly addressing the biological transformation of OMPs. Sections 3.2.1 to 3.2.3 will describe the relevant mechanisms for OMP removal in WWTPs, and address the phase-changes associated with, when they are presented as consolidated knowledge. Sections 3.2.1 to 3.2.3 will also address the simplest methods to quantify the OMP removal associated to each mechanism.

3.2.1 Sorption

OMP sorption onto particulate matter can be an important removal mechanism in CAS systems, depending on the tendency of the OMP to attach to secondary sludge (Joss et al. 2006). Plosz et al. (2012) considers that sorption might occur either in aerobic or in anoxic conditions. OMPs can absorb onto bacteria lipid structure and fat fraction of the primary sludge or activated sludge through hydrophobic interactions, such as aliphatic and aromatic groups; onto negatively charged polysaccharide structures on the outside of bacterial cells through electrostatic interactions, such as amino groups; and/or they can bind chemically to bacterial proteins and nucleic acids (Meakins et al (1994) referred by Radjenovic et al. (2009)). Mechanisms such as hydrogen bonding, ion exchange, surface complexation may interfere in the sorption process (Tolls (2001) referred by Radjenovic et al. (2009)). Adsorption can also be influenced by intermolecular forces such as Van der Waals forces, since it was suggested that hydrophobic interactions with the sludge matrix can occur despite the presence of ionic charges and/or a low octanol-water partition coefficient (log K_{ow}) of trace organic pollutants (Radjenovic et al. 2009).

In the context of OMP removal in wastewater, sorption refers specifically to: sorption (as adsorption from liquid to solid), and desorption from the solids to the liquid (Metcalf & Eddy 2003). An equilibrium is reached when the rate of both reactions is equal. In real practice, reaction rates for sorption and desorption are difficult to obtain.

Nevertheless, considering that in wastewater treatment diffusion occurs fast, when compared to the Hydraulic Retention Time (HRT) or biological removal of most compounds, an equilibrium between sorption and desorption can be assumed (Joss et al. 2006). The sorption reaction rate is characterized by the sorption coefficient K_d, also designated as solid-water distribution coefficient.

At a certain time and/or place in the reactor, the total OMP concentration (C) can be described as:

$$C = X + S \text{ (Equation 1)}$$

Where:
C - Total OMP concentration
X – OMP concentration sorbed onto sludge per unit reactor volume [µg.L^{-1}]
S - Dissolved OMP concentration [µg.L^{-1}]

Under equilibrium conditions, i.e. when the rate of sorption and desorption are equal, the total OMP concentration in the reactor can be obtained as follows:

$$C = S \times (1 + X_{SS} \times K_d) \text{(Equation 2)}$$

Where:
X_{SS} - Suspended solids concentration in the secondary treatment per L of wastewater [gSS.L^{-1}].
K_d - Solid-water distribution coefficient, also designated sorption coefficient [L.gSS^{-1}].

The concentration of a compound sorbed onto sludge (X) can also be described by a simplified Freundlich isotherm, i.e. a linear Equation, as follows:

$$X = K_d \times X_{SS} \times S \text{(Equation 3)}$$

The simplest way to quantify the removal by sorption of a particular OMP in a WWTP, is through a mass balance concentration, focusing on obtaining the load of OMP in the excess sludge withdrawn. By comparing the load of the OMP in the excess sludge withdrawn, to the total influent load, as proposed by Joss et al. (2006), the unknown load can be obtained, as follows:

$$\frac{M_{SP}}{M_{in}} = \frac{S_{out} \times SP \times K_d}{S_{in} \times (1 + X_{WW} \times K_{d,prim})} \text{ (Equation 4)}$$

Where:
M_{SP} - OMP load withdrawn with the excess sludge expressed per unit of treated wastewater [µg.L^{-1}].
M_{in} - Influent OMP load expressed per unit of treated wastewater [µg.L^{-1}].
S_{out} - Soluble OMP concentration in the effluent [µg.L^{-1}].
S_{in} - Soluble OMP concentration in the influent to the biological unit [µg.L^{-1}].
SP - Sludge production expressed per unit of treated wastewater [gSS.L^{-1}].
X_{ww} - Solids content in the influent to the biological unit (primary effluent) [gSS.L^{-1}].
$K_{d,prim}$- Solid-water distribution coefficient (sorption coefficient) of the influent to the biological unit [L.gSS^{-1}].

Equation 4 can be simplified, if the OMP is not being degraded significantly and not being stripped. In that case, the OMP removal through the excess sludge withdrawn, can be obtained as follows (Joss et al. 2006):

$$\frac{M_{SP}}{M_{in}} = \frac{SP \times K_d}{1 + SP \times K_d} \text{ (Equation 5)}$$

The sludge production (SP) is a common calculation in wastewater treatment, and it is defined as the amount of sludge produced per volume of wastewater treated. SP depends on flow rates of treated wastewater and excess sludge, and concentrations of suspended solids in the effluent and excess sludge.

When sorption is a relevant mechanism of removal for a certain OMP, and sorption and desorption reactions are known to take place without (yet) reaching an equilibrium, the reactions can be considered independent. Joss et al. (2006), proposed the following dynamic model for batch tests, assuming that biotransformation and stripping were not taking place:

$$\begin{cases} \frac{dS}{dt} = -k_{sor} \times X_{SS} \times S + k_{des} \times X \\ \frac{dX}{dt} = k_{sor} \times X_{SS} \times S - k_{des} \times X \end{cases}$$ (Equations 6 and 7, respectively)

Where:
t -time [d].
k_{sor} -rate constant for sorption [$m^3.gSS^{-1}.d^{-1}$].
k_{des} -rate constant for desorption [d^{-1}].

The equilibrium constant K_d is defined as:

$$K_d = \frac{k_{sor}}{k_{des}}$$ (Equation 8)

The equilibrium constant K_d has also been addressed as solid-water distribution coefficient in Equation 4, where the assumption of equilibrium between sorption and desorption is embedded. K_d can also be addressed as sorption constant, always assuming that sorption and desorption are in equilibrium; in this case k_{sor} in equation 8 represents specifically adsorption (Joss et al. 2006).

The differential Equations 6 and 7 lead to the following solutions, respectively:

$$S_t = S_0 - \left(S_0 - \frac{C_0}{1+K_d \times X_{SS}}\right) \times \left(1 - e^{-k_{des} \times (1+K_d \times X_{SS}) \times t}\right)$$ Equation 9

$$X_t = X_0 - \left(X_0 - \frac{C_0 \times K_d \times X_{SS}}{1+K_d \times X_{SS}}\right) \times \left(1 - e^{-k_{des} \times (1+K_d \times X_{SS}) \times t}\right)$$ Equation 10

Where:
S_t -Soluble compound concentration as a function of time [µg.L^{-1}].
S_0- Initial soluble compound concentration [µg.L^{-1}].
C_0- Initial total compound concentration; $C_0 = S_0 + X_0$ [µg.L^{-1}].
X_t- Sorbed compound concentration as a function of time [µg.L^{-1}].
X_0- Initial sorbed compound concentration [µg.L^{-1}].

According to Ternes et al. (2004), the sorption equilibrium was reached in batch experiments with a sludge concentration of 4 g.L^{-1} after 0.5 h after spike addition. Consequently, Joss et al. (2006) explain that the term $\left(1 - e^{-k_{des} \times (1+K_d \times X_{SS}) \times t}\right)$ becomes ≥ 0.9 , with an accuracy of about 20%. Therefore, for compounds with a known K_d, a range of k_{des} values can be obtained, based on the result of the latter mathematical term.

3.2.2 Biological transformation

Biological transformation is the removal or conversion of OMPs based on microorganism's activity. The biological transformation can be total or partial. OMPs can be degraded directly by microorganisms, or by becoming a part of the microorganism's metabolic route. OMPs might also be indirectly degraded, through enzymes produced for other primary purposes, which is designated as co-metabolism. Furthermore, a primary transformation of a compound can lead to total mineralization, but it does not necessarily occur (Ternes et al. 2010). Instead of mineralization, stable transformation products are formed, with similar chemical structure to the parent compound, which should be considered in addition to the target compound (Ternes et al. 2010). For instance, N^4-acetylsulfamethoxazole concentrations should be considered in addition to sulfamethoxazole concentrations.

The biological conversion of OMPs is characterized by the reaction rate constant k_{biol}, which depends on the biodegradability of each OMP and on the sludge composition. In particular, sludge characteristics such as biodiversity of the active biomass, fraction of active biomass in the total suspended solids and even morphological characteristics such as size, are considered important for biological transformation (Joss et al. 2006). In the calculations of biological OMP removal or conversion, it is usually assumed that due to their low concentrations, namely in the range of µg as opposed to COD loads 100 x above, OMPs are not contributing to microorganism's growth (Joss, Carballa et al. 2006).

An exponential decrease of the OMP concentrations over time due to biological activity was observed in previous research, therefore pseudo-first-order kinetics were selected to describe the removal or conversion of OMPs, as follows (Joss et al. 2006):

$$\frac{dC}{dt} = -k_{biol} \times X_{SS} \times S \text{ (Equation 11)}$$

Where:
C- Total OMP concentration [µg.L^{-1}]
T- Time [d]
k_{biol}- Reaction rate constant [L.gSS^{-1}.d^{-1}]
X_{SS} - Suspended solids concentration in the reactor [gSS.L^{-1}]
S - Soluble OMP concentration [µg.L^{-1}]

By combining Equation 11 with Equation 2, once more assuming that sorption and desorption are in equilibrium, the following Equation is obtained:

$$\frac{dS}{dt} = \frac{-k_{biol}}{1+K_{d,sec} \times X_{SS}} \times X_{SS} \times S \text{ (Equation 12)}$$

Where:
$K_{d,\,sec}$- solid-water distribution coefficient/ equilibrium sorption constant/ sorption constant for secondary sludge [L.gSS^{-1}].

Equation 12 describes the variation of soluble OMP with time, when the OMP is being removed by sorption and biological transformation.

3.2.3 Stripping

Stripping is the OMP phase-change from the liquid to the gas phase, i.e. from water to air. The amount of stripping for a particular OMP depends on the amount of air getting in contact with the wastewater, which varies according to the amount and bubble size (diffuse vs coarse bubble aeration) and on the air-water partitioning coefficient, designated as Henry coefficient (K_H) (Joss et al. 2006).

The OMP amount being transferred into the air, can be calculated as follows (Joss et al. 2006):

$$F_{gas} = S \times K_H \times q_{air}$$

(Equation 13)

Where:
F_{gas} - OMP load stripped into the air [$\mu g.L^{-1}_{wastewater}$].
S - Soluble concentration of OMP [$\mu g.L^{-1}$]
K_H - Henry or air water partitioning coefficient [-].
q_{air} - Air required [$L_{air}.L^{-1}_{wastewater}$].

In CAS systems an approximate amount of 5 to 15 [$L_{air}.L^{-1}_{wastewater}$] as q_{air} is applied.

The total OMP amount, assuming no degradation is taking place, can be obtained as follows (Joss et al. 2006):

$$F_t = S + X + F_{gas} = S \times (1 + K_d \times X_{ss} + K_H \times q_{air})$$

(Equation 14)

Where F_t represents the total amount of OMP [$mg.m^{-3}_{wastewater}$].

For batch systems, and assuming no elimination by sorption and biological degradation takes place, stripping can be described as (Joss et al. 2006):

$$\frac{dS}{dt} = -K_H \times \frac{Q_{air}}{V} \times S$$

(Equation 15)

Where:
Q_{air} -air applied per volume of reactor and time [$L_{air}.d^{-1}$].
V -volume of reactor [$L_{reactor}$].

According to Joss et al. (2006) for fine bubble aeration systems, a K_H value below 0.1 means that an equilibrium between the gas bubble and the dissolved concentration is achieved after 0.5 m rising height in the water column, while a K_H above 3.10^{-3} is needed to observe air stripping. However, mechanical surface aerators, with a higher air to water exchange, are expected to have significantly higher stripping efficiency. Since pharmaceuticals are usually intended to take effect in the blood stream, and have a rather hydrophilic nature, most have K_H values below 10^{-5} (Joss et al. 2006). Therefore, at least for most pharmaceuticals, a soluble OMP concentration is assumed constant and in equilibrium with the gas phase(Joss et al. 2006).

3.3 OMPs removal per mechanism

3.3.1 Quantification of OMP removal per mechanism

As shown in Section 3.2 the quantification of OMP removal mechanisms by applying the simplest methods, requires the following knowledge:

- OMP concentrations in influent and effluent.
- CAS parameters such as excess sludge flows, solids concentrations (MLSS) and supplied air (bubble size and DO).
- Specific reaction rates and coefficients associated to sorption, biological transformation and stripping.

The OMP concentrations are derived from monitoring campaigns, and CAS parameters are defined and applied per WWTP. Table 7 shows the definitions of the specific reaction rates and coefficients associated to the different OMP removal mechanisms.

Table 7- Reaction rates and coefficient definitions per OMP removal mechanisms in CAS, namely sorption, biological transformation and stripping (adapted from Joss et al. (2006)).

Mechanism	Rate/Coefficient	Equation
Sorption	K_d - Sorption Coefficient (= Solid-water distribution coefficient) [$L.gSS^{-1}$]	$K_d = \frac{X_{part}}{S} = \frac{X}{X_{SS} \times S}$ X - Concentration sorbed onto sludge per unit reactor volume [$\mu g.L^{-1}$] X_{part} - Concentration sorbed per amount of sludge dry matter [$\mu g.gSS^{-1}$] X_{SS} - Suspended solids concentration [$gSS.L^{-1}$] S- Soluble OMP concentration [$\mu g.L^{-1}$]
Biological transformation	k_{biol} Reaction rate constant [$L.gSS^{-1}.d^{-1}$]	$\frac{dC}{dt} == -k_{biol} \times X_{SS} \times S$ C - Total OMP concentration [$\mu g.L^{-1}$] T- Time [d] k_{biol}- Reaction rate constant [$L.gSS^{-1}.d^{-1}$] X_{SS}- Suspended solids concentration in the reactor [$gSS.L^{-1}$] S- Soluble OMP concentration [$\mu g.L^{-1}$]
Stripping	K_H- Henry Coefficient (= Air-water partitioning coefficient) [-]	$K_H = \frac{C_{air}}{S} = \frac{MWG \times p_p}{S \times R \times T}$ C_{air} – OMP concentration in air [$\mu g.L^{-1}.m^{-3}air$] S - Soluble OMP concentration [$\mu g.L^{-1}.m^{-3}$] MWG - Molar weight [$\mu g.Mol^{-1}$] P_p - Partial pressure of OMP in the gas phase [Pa] R - Universal gas constant; 8.314 [$J.Mol^{-1}.K^{-1}$] T- temperature [K]

Experimental methods to quantify K_d and K_{biol} in activated sludge were defined by Ternes et al. (2004) and Joss et al. (2006), respectively. Both experimental methods rely on batch tests, performed with full-scale activated sludge.

Ternes et al. (2004) established the experimental method to determine Kd (sorption coefficient), which basically consists on the use of argon to remove oxygen when collecting the samples, followed by measurements of OMP concentrations in the liquid and solid phase. Joss et al. (2006) described spiked batch tests allowing the calculation of K_{biol}.

3.3.2 Reaction rates and coefficients per OMP

Table 8 shows the sorption coefficient (K_d) and reaction rate constant (k_{biol}) values, for the 11 I&W OMPs, found in literature.

Table 8 - Sorption Coefficient (K_d) and reaction rate constant (k_{biol}) for secondary sludge per OMP. Sources: (1) multiple sources referred by Joss et al. (2006), with accuracy indicated as 95% confidence interval for K_d; (2) Stasinakis et al. (2013); (3) Martinez-Alcala et al. (2017); (4) Göbel et al (2005) referred by Berthod et al. (2017); (5) 7 references referred by Berthod et al. (2017); (6) 6 references referred by Berthod et al. (2017); (7) (Radjenovic et al. 2009, Berthod et al. 2017); (8) Radjenovic et al. (2009); (9) AstraZeneca referred by Berthod et al. (2017); (10) Wick et al (2009) referred by Berthod et al. (2017); (11) Hyland et al. (2012) referred by Berthod et al. (2017); (12) 5 references referred by Berthod et al. (2017).

OMP	K_d secondary sludge [$L.gSS^{-1}$]	k_{biol} [$L.gSS^{-1}.d^{-1}$]
benzotriazole	0.133±0.104 (2)	
clarithromycin	0.26±0.01 (1) 0.26 (4)	≤0.4 (1)
carbamazepine	0.0012±0.0005 (1) 0.135 to 0.001 (5) 0.135 (8)	<0.01 (1) -0.87 [$L.gSS^{-1}.h^{-1}$] (3)
diclofenac	0.016±0.003 (1) 0.151 to 0.016 (6) 0.118 (8)	≤0.1 (1) 1.31 [$L.gSS^{-1}.h^{-1}$] (3)
metoprolol	0.006 (10)	
Hydrochlorothiazide	0.020 (7)	
4- and 5-methylbenzotriazole		
propranolol	0.363 (8) 0.417 (9)	
sotalol	0.018 (10)	
sulfamethoxazole	0.26±0.17 (1) 0.078 (8) 0.257 (4) 0.269 (11)	<0.1 (1)
N^4-acetylsulfamethoxazole		5.9-6.7 (1)
trimethoprim	0.076 to 0.251 (12)	

The values of K_d shown in Table 6, obtained from various sources, present some variability. A possible explanation can be that the results were obtained from different WWTPs, therefore with different activated sludge quality. Figure 1 shows a comparison between K_d values obtained at different WWTPs.

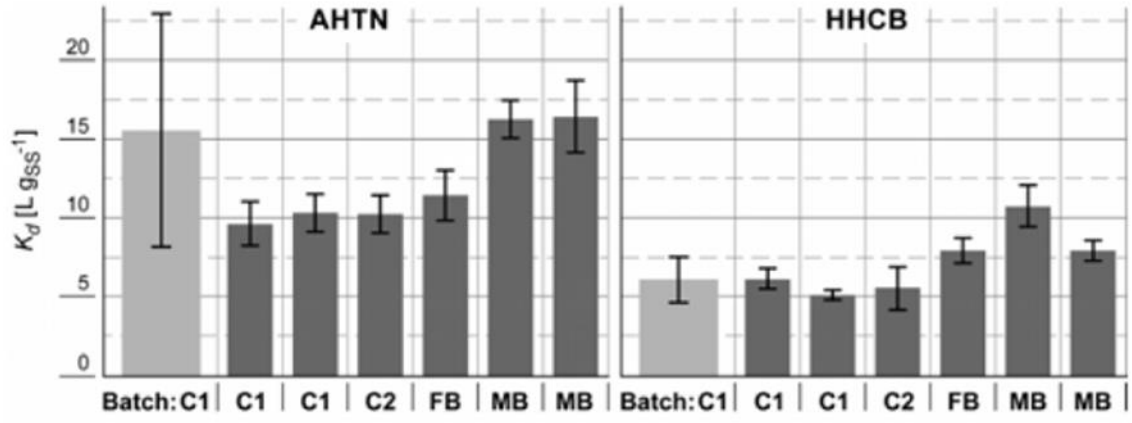


Figure 1- K_d values of musk fragrances AHTN and HHCB, obtained at different WWTPs with the following systems: C1 and C2- CAS; FB- fixed bed biofilm reactor; MB- MBR. Errors bars indicate standard deviation in 3 measured samples. Batch refers to measurements done in batch experiments, with all remaining ones being taken directly from WWTP plants. Source: Joss et al. (2006) referring to McArdell et al. (2005).

Figure 1 shows that the K_d values obtained with samples from CAS systems, show a relatively good reproducibility. The authors suggest that when sorption is quantitatively relevant for a certain OMP, the K_d should be assessed on site (Joss et al. 2006). The EU project NEPTUNE concluded (Ternes et al. 2010) that for a sorption removal above 50%, K_d values above 3-5 L.gSS^{-1} are required. In Table 6, none of the available results are above this value, which is not surprising considering the overall non-charged nature of activated sludge. Furthermore, Joss et al. (2006) showed that the removal in a municipal WWTP is negligible, i.e. below 10%, for compounds with a K_d equal or below to 0,3 L.gSS^{-1}. From the values found in literature shown in Table 6, only propranolol is expected to have a sorbed fraction above 10%.

Biodegradation of OMPs is influenced by desorption of compounds from the sludge matrix and by microbial activity, and the final outcome will depend on a balance from the two processes/removal mechanisms. Similarly, sorption/desorption processes will depend on the different biodegradation rates in solid and aqueous phase (Radjenovic, Petrovic et al. 2009). According to Radjenovic et al. (2009), sorption is a minor removal pathway for most OMPs (i.e. lower than 10%), and measured concentrations in the solid phase do indicate that sewage sludge will have trace concentrations of not only hydrophobic compounds, but also negatively charged drugs and positively charged beta-blockers.

The k_{biol} values presented in Table 6 origin from 2 different sources, however they were obtained applying the methodology, as defined by Joss et al. (2006). The variation in results is most likely the result of differences in influent wastewater quality and/or process parameters of the sampled WWTP, combined with the properties of each OMP. For instance, OMPs with a more polar character, such as carbamazepine, are not susceptible or less susceptible to sorption. Regarding neutral components with lipophilic character, Joss et al. (2006) refer to a removal of 20 to 70% with physical-chemical treatment in primary treatment, and if a lower pH achieved, removals can be achieved for even some acidic substances. The authors indicate that the referred removals with coagulation-flocculation are expected to occur to a large extent also in the activated sludge system.

Joss et al. (2006) classified micropollutants according to their biodegradation constant k_{biol} as follows:

- k_{biol}< 0.1 L.gSS^{-1}.d^{-1} micropollutants not removed to a significant extent (<20%);
- k_{biol}> 10 L.gSS^{-1}.d^{-1} – micropollutants transformed by more than 90%;
- 0.1< k_{biol}< 10 L.gSS^{-1}.d^{-1} moderate removal is expected.

According to the classification proposed by Joss et al. (2006), and comparing with the values shown in Table 6, a moderate biological removal is expected for clarithromycin and the metabolite N^4-acetylsulfamethoxazole, while no significant removal should be expected for carbamazepine, sulfamethoxazole and probably diclofenac. It is also assumed that some OMPs are being degraded by enzymes produced for other purposes (co-metabolism). Currently, the information about microorganism's biochemical pathways and products formed is starting to be available. Nevertheless, information concerning the OMPs referred to in this report, which included the biochemical microorganisms was not found.

4 OMP removal in full-scale CAS

4.1 Available data in Europa: removal rates and prevailing mechanisms

Table 9 shows the removal rates of OMPs, per removal mechanisms, obtained at full-scale CAS systems of domestic WWTPs. In January 2016, a new water protection law came into force in Switzerland, aiming to improve the surface water quality by reducing the load of micropollutants at the WWTPs. The Swiss law aims to remove 80% OMPs on average, over the whole WWTP from influent to effluent, within the next 20 years, in about 100 of the 700 Swiss WWTPs. Bourgin et al. (2018) describe the results obtained at the first WWTP of Switzerland applying a full-scale ozonation step as post-treatment of a CAS system. The CAS system is operated with a sludge age of 13 d, which is a normal setting to achieve nitrification, and a Hydraulic Retention Time (HRT) of 18h (excluding the HRT of the secondary settler). The Neugut WWTP treats 105. 000 population equivalents, which corresponds to 50.000 persons and the remaining load providing from industrial sources, in particular food industries, responsible for about 50% of the COD load. The authors present the removal rates of 550 compounds, including the 12 indicator substances proposed by the Swiss government, in the CAS systems and further post-treatment steps. The relevant results for this TKI project are included in Table 9.

Radjenovic et al. (2009) describe the removal rates of 31 pharmaceuticals in a full-scale WWTP in the proximity of Barcelona, applying a CAS system consisting of pre-denitrification and nitrification tanks, followed by secondary clarifiers. The CAS HRT was of about 11,5h and the WWTP was being operated with a sludge age of 10 d. The WWTP Terrassa treats 277. 000 population equivalents, of domestic and industrial source, particularly from pharmaceutical and textile industry. The relevant results for this TKI project are included in Table 9.

The knowledge on which removal route takes place per OMP is important to understand in order to tweak removal, and to support experimental and modelling choices. SRT, also designated as sludge age, is one of the most significant CAS parameters, linked to redox conditions, MLSS concentrations, volume and flow of reactors. Table 9 shows the removal rates of the 11 I&W OMPs per mechanism, obtained in full-scale sampling campaigns in municipal WWTP, including the results obtained at the WWTPs researched by Bourgin et al. (2018) and Radjenovic et al. (2009). Therefore, Table 9 also indicates the SRT of the analyzed sludge.

Table 9- Removal rates of OMPs per mechanism and as total removal, obtained in full scale WWTP campaigns. Key: (*) includes N_4-acetylsulfamethoxazole. Sources: [(1)] multiple sources compiled by Joss et al. (2006); [(2)] Radjenovic et al. (2009); [(3)] Bourgin et al. (2018).

OMP	Sludge age (θ) [d]	Biotransformation [%]	Sorption [%]	Effluent- total removal [%]
benzotriazole	13			66±3; 62±7; 63±6; 64±3 [(3)]
clarithromycin	< 20 > 50 13	< 10 [(1)] ≈ 90 [(1)]	< 10 [(1)] < 5 [(1)]	≈10 [(1)] > 90 [(1)] 51±2; 28±19; 45±6; 52±8 [(3)]
carbamazepine	4-60 10 13	< 40 [(1)]	< 5 [(1)]	> 60 [(1)] < 10 [(1)] -16±12; -14±19; -33±23; -24±8 [(3)]
diclofenac	4-60 10 13	5 to 45 [(1)]	< 5 [(1)]	55 to 95 [(1)] 21.8±28.5 [(2)] 22±8; 23±8;11±10 13±18 [(3)]
metoprolol	10 13	Likely pathway[(2)]		24.7% ± 31.5 [(2)] 41±7; 38±5; 37±8; 38±4 [(3)]
hydrochlorothiazide	13			9±13; 13±9; -2±17 1±10 [(3)]
4- and 5-methylbenzotriazole	13			45±22; 61±4; 2±22; 28±12 [(3)]
propranolol	10		Likely pathway [(2)]	58.8 ± 24.5 [(2)]
sotalol	10	Likely pathway l[(2)]		21.4 ± 31.5 [(2)]
sulfamethoxazole	4-12 10 13	50-90 *[(1)]	<5 * [(1)]	10 to 50 [(1)] 73.8 ± 12.7 [(1)] 55±3; 46±6;31±6 34±2 [(2)]
trimethoprim	< 20 > 50 13	<10 [(1)] ≈90 [(1)]	≤5 [(1)] ≤5 [(1)]	> 10 [(1)] > 90 [(1)] 89±4; 85±6;75±6 83±3 [(2)]

Sludge age is indicated as a particularly important parameter for biological transformation mechanisms, namely for clarithromycin and trimethoprim. Joss et al. (2006) report measurements where an approximate removal of 90% for both aforementioned OMPs was obtained, when the sludge reached 50 d of retention time. Nevertheless, SRTs above 25 d are not usually applied, particularly in municipal WWTPs treating large volumes of wastewater. In biological systems with attached biomass, higher SRTs are possible.

Regarding diclofenac, no sorption removal pathways have been identified. Apparently diclofenac has a slow biodegradation path (Radjenovic et al. 2009), with increasing removal rates at longer sludge ages. The assumption is confirmed by research described by Joss et al. (2006), where a biotransformation of 45% was achieved at sludge ages of 60 d. The latter authors also describe results where diclofenac reaches a removal rate up to a maximum of 75%, in anaerobic digestion after sludge adaptation. Furthermore, as previously mentioned, diclofenac can be removed 20 to 70% by coagulation with ferric and aluminum salts, as long as a lower pH is achieved, enabling reactions with more acidic compounds.

The beta-blockers OMPs have different removal pathways. The authors Radjenovic et al. (2009) reported a removal of propranolol until about 60% in the CAS system, while sotatol and metoprolol are removed to a lower extent. According to the authors only for propranolol is sorption a possible removal pathway, due to lipophilic interactions with sludge particles, while stereo-selective biological degradation is the most likely path for sotalol and metoprolol.

Sulfamethoxazole is mostly removed through biological transformation (between 50-90%), and sorption around 5% (Table 9) is expected to the negatively charged sewage sludge, which is confirmed by low concentrations values (ng/g) found in the solid sludge phase (Radjenovic et al. 2009). The full-scale CAS sulfamethoxazole removal rates are very variable, from about 75% (Radjenovic et al. 2009) to 45% removal (Bourgin et al. 2018). Contributing to this fact might be a retransformation to the parent compound, which is known to take place in the WWTP, and result in decreasing removal rates. During human or animal assimilation only a variable percentage of the sulfamethoxazole is metabolized. About 50% of the dosage is excreted as the inactive metabolite N^4-acetylsulfamethoxazole and about 10% as the unchanged compound. Is it known that the N^4-acetylsulfamethoxazole metabolite retransforms to the active parent compound during wastewater treatment (Ternes et al. 2006). Complete removal of sulfamethoxazole (99 ± 1%) is achieved at mesophilic conditions in anaerobic digestion, without requiring sludge adaptation (Joss et al. 2006). The higher temperatures (20-45°C) and/or the anaerobic environment with their own specific microorganisms seem to be ideal for the removal of sulfamethoxazole.

Similar behavior to sulfamethoxazole, with patterns of retransformation to the parent compound, can be expected from carbamazepine, which would explain the negative removals obtained by Bourgin et al. (2018).

4.1.1 Available data in the Netherlands

The Stowa report 2020-06 mentions two data-sets, with OMP removal results, from full-scale WWTP in the Netherlands (Nieuwenhuis et al. 2021). One data-set provided by a *Royal Haskoning-DHV* (RH-DHV) report dating to 2019, where the WWTPs of the region east of the Rijn were analyzed for OMP removal. The results of RH-DHV referred in the Stowa report are limited, showing only the total average removal of the 11 I&W OMPs per WWTP, measured in a total of 5 samples per WWTP, collected during the whole year. The aforementioned results, report the total removal for the 11 I&W OMPs, with a minimal average removal of 10% and a maximum removal of 50%, and an average removal of 30% (Nieuwenhuis et al. 2021).

The second set of data mentioned in the Stowa 2020-06 report (Nieuwenhuis et al. 2021), shows results from the monitoring of the 11 I&W OMPs at the WWTP of Aarle- Rixtel (Figure 2).

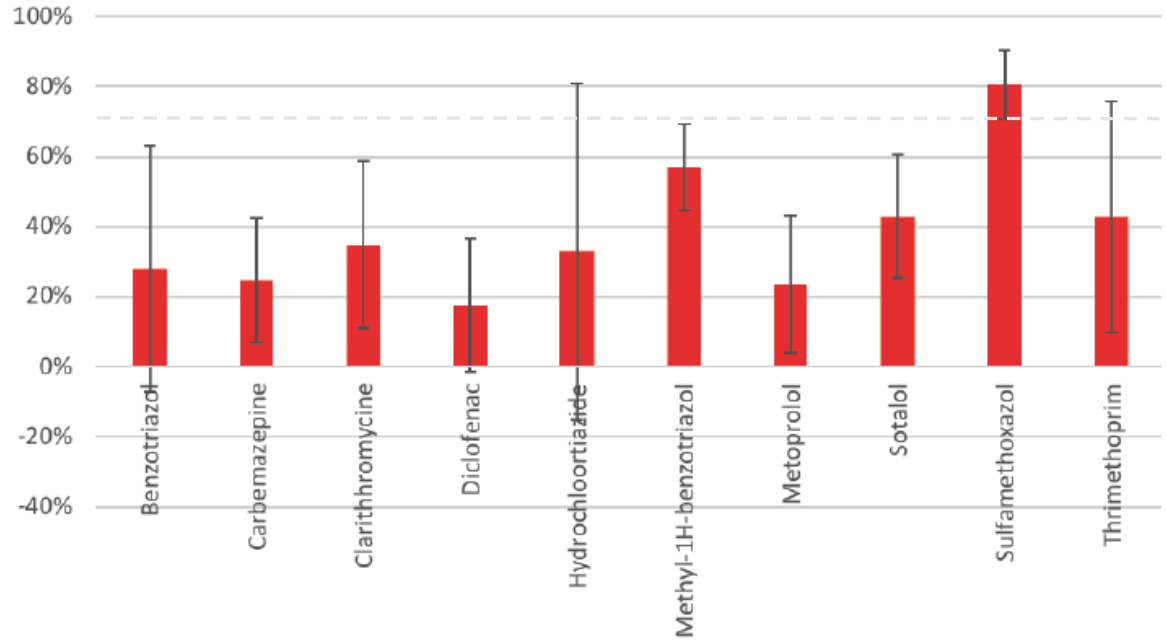


Figure 2- Removal rate of OMPs at the WWTP of Aarle- Rixtel, in a total of 10 composite samples, collected during a 24h period. The monitoring period was from 10 May to 27 June, 2019. Propranolol was monitored, but the concentrations were below detection level (Source: Nieuwenhuis et al. (2021)). The added dotted line indicates the target of 70% OMP removal, proposed by the *Ministerie* I&W.

The results shown in Figure 2, seem to indicate removal rates above the reported in the RH-DHV report, even if comparisons are impossible without the raw data. According to Stowa (Nieuwenhuis et al. 2021), no reasons were found in any of the data-sets, for the variations in OMP removal and per WWTP. For the purposes of post-treatment design, such as the addition of Powder Activated Carbon (PAC) to the activated sludge, the overall removal rate of OMPs at existing WWTP in the Netherlands is currently set at 10%. To the best of the authors' knowledge, the removal of OMPs from WWTP in the Netherlands has given priority to the deployment of pilots, as post-treatment to CAS or as addition of adsorbents to CAS. It is overall accepted that, even if the CAS systems contribute to the removal of OMPs, extra technology will always be necessary to reduce the load of OMPs at WWTPs.

Furthermore, some information is available about OMPs removal in the Watson database (Rijksoverheid 2018), i.e. the registration database for the discharge emissions of the Dutch WWTPs. This database contains data about compliance with discharge limits, which currently do not include OMP concentrations. Nevertheless, single measurements of one or other OMP have occurred during the years at some WWTPs, however with no regular pattern of measurements was found. Moreover, the data-base does not seem to have been updated since 2018. Nevertheless, there are reports applying the data available on the database, as follows.

Pieters et al. (2011) evaluated the efficiency of the Watson database registration for calculations of effluent loads, and reported the removal efficiency of OMPs in the Dutch WWTPs. Table 10 presents the average removal rate of OMPs, included in the I&W OMP group, obtained by the latter authors.

Table 10- Average removal rate of different OMPs at the Dutch WWTPs, calculated based on data from 2000-2009 obtained at the Watson database (Source: Pieters et al. (2011).

Compound	Average removal Watson database (2000-2009) [%]
carbamazepine	27
diclofenac	40
metoprolol	41
sotalol	50
sulfamethoxazole	58

Table 10 shows that a considerable removal is taking place at the existing WWTPs. The data of Table 10 is helpful to have a general idea, but different scenarios are likely to occur when analyzing a single WWTP.

The Watson database influent and effluent data were also applied to develop quantitative structure-biodegradation relationships models (QSBR), to obtain k_{bio} values of various OMPs (Nolte et al. 2020), namely pharmaceuticals, aromatics, herbicides, insecticides, among others. The global QSBR had a reasonable validation with a R^2 of 0.5, however the class-specific QSBRs were more accurate with R^2 between 0.7 and 0.8. The author's suggested using the obtained results particularly to the field of risk assessments.

4.2 Relevant CAS parameters to steer OMP removal

The fate of a certain OMP in a WWTP, and more particularly in the CAS system, will depend on the applied SRT, also designated as sludge age (θ); HRT; temperature; pH and sludge concentration (Radjenovic et al. 2009). Some of these parameters can be adjusted during the operation of a CAS systems, contrary to parameters such as temperature and pH, considered as inherent characteristics of the wastewater and not changed during the CAS treatment. Controlling the temperature in the CAS will lead to an unacceptable high operational costs. Nevertheless, higher temperatures almost always lead to increased OMP removals, as shown in Table 11, at least for biotransformation removal mechanisms. Within the optimal ranges for microorganism's growth, the reaction kinetics for OMP biodegradation are temperature dependent, with increasing rates at increased temperatures. The pH corrections are not implemented in a CAS system because of the high sludge buffer capacity. On the other hand, pH corrections would certainly affect the biological activity. Microorganisms do have an optimal pH range, as well as an optimal temperature range. However, local variations in pH may occur if coagulants or substrates are being added, with no known negative effects to the overall microorganism's activity. Removal of diclofenac has been associated to coagulant dosing in primary sludge, which can occur if there is a pH decrease (Joss et al. 2006); and pH decrease in activated sludge has been observed by the authors of this report, after substrate addition.

Group	Compound	Temperature 20°C vs. 10°C	Sludge age 20d vs. 10d
Antibiotics	Sulfamethoxazole	comparable	comparable
Drugs	Bezafibrate	20°C > 10°C	comparable
	Diclofenac	comparable	comparable
	Ibuprofen	20°C > 10°C	20d > 10d
	Ibuprofen-OH	20°C > 10°C	comparable
	Ketoprofen	20°C > 10°C	20d > 10d
	Naproxen	20°C > 10°C	20d > 10d
	Pentoxifyllin	20°C > 10°C	comparable

Table 11 - Influence of temperature and sludge age in OMP removal of a batch reactor. Source: reproduction of Joss et al. (2006) referring to the work of Zabczynski et al.

Parameters such as HRT, sludge concentration and SRT are usually set at the CAS design phase, aiming for an optimal operation of the CAS system. HRT is flow dependent, while SRT and sludge concentrations are set within a pre-defined range, aiming to obtain a certain carbonaceous and nutrient removal. Nevertheless, there might be a certain range for OMP removal improvement in existing CAS systems, which can potentially lead to improved design of future CAS systems.

The SRT or sludge age is considered very relevant to increase removal of determined OMPs. It was shown that at a sludge age of 10-15 d, suitable for nutrient removal, most OMPs are at least partially transformed or degraded, while at a sludge age shorter than or equal to 4 d, suitable to carbonaceous removal, almost no biological degradation has taken place (Clara et at, 2005, referred by Joss et al. (2006)). At sludge ages above 50 d, almost 90% of clarithromycin removal was observed (Gobel et al, 2005 referred by Joss et al. (2006)). According to Ternes et al. (2010), there are several possible explanations for the OMPs biotransformation increase with sludge age, as follows: the bacterial population may become more diversified, with slow-growing bacteria also reaching significant numbers; the lower substrate availability associated with longer sludge ages, may result in an increased diversification of microbial activity expressed by a broader enzyme spectrum. Polesel et al. (2016) suggests a third possible explanation, based on enhanced adaptation to trace chemicals. Regarding the hypothesis of a lower substrate availability leading to a broader enzyme spectrum, the latter authors suggest that the threshold of

substrate requirement might be OMP specific, since the presence of growth substrate also seems to be beneficial for the degradation of trace chemicals. Overall, Polesel et al. (2016) concludes that, so far, enhanced removal of pharmaceuticals by extended SRT remains substance-dependent, which can be concluded by several comparative studies. A similar conclusion can be retrieved from the results presented in Table 11, which does not invalidate the fact that extended sludge age systems, seem to be more thorough on the removal of at least part of the OMPs.

Another relevant factor is the redox potential of the reactors, i.e. the availability of electron receptors such as molecular oxygen or nitrate. Biological transformation can occur under aerobic (molecular oxygen available), anoxic (nitrate available and no molecular oxygen) or anaerobic (neither nitrate nor molecular oxygen available) conditions (Ternes et al. 2010). For OMPs, such as sulfamethoxazole, the removal rate k_{biol} is much higher if molecular oxygen is available, as compared to nitrate or electron receptors of lower redox potential (Siegrist et al. 2012). Good nitrifying activity increased the biodegradation rates of several OMPs, which was related to the presence of the ammonium monooxygenase enzyme (Fernandez-Fontaina et al. 2012, Fernandez-Fontaina et al. 2016). Nevertheless, there are contradictory studies, where no significant transformation was achieved in the presence of the ammonium monooxygenase enzyme, as referred by Polesel et al. (2016). The latter authors conclude, that enhanced elimination in the presence of active nitrifying bacteria or their enzymes, was not demonstrated for all the reported OMPs.

5 Modelling of CAS with OMP removal

5.1 Models and simulators

The development of activated sludge models (ASM) started before the 1980's with several research groups developing their own models, each with their own approach and notation, first in steady-state models and later on in dynamic models (van Loosdrecht et al. 2015). By each notation, we mean that each group was applying their own system of written symbols to represent the model parameters, and taking into consideration different parameters. At the time, the International Water Association (IWA) designated by International Association of Water Pollution, Research and Control, organized an international task group on mathematical modelling for design and operation of biological wastewater treatment, aiming to combine the most relevant and applied methods into a common unified model. The effort resulted in various models, starting by Activated Sludge Model 1 (ASM1)(Henze et al. 1987), and followed by the ASM2 (Henze et al. 1995), ASM2d (Henze et al. 1999) and finally ASM3 (Gujer et al. 1999).

The ASM models were developed to describe the oxygen uptake rate, sludge production coupled to the chemical oxygen demand (COD) balance and N and P conversions in domestic WWTP. They are designated for practical purposes, and are not sanitation models describing the removal of pathogens. As van Loosdrecht et al. (2015) explains, the ASM1 model is based on the Monod kinetics, which describe the rate of the biological reactions. In terms of input required, the wastewater is characterized by seven dissolved and six particulate components, used to describe two biomass groups; seven fractions of COD and four fractions of N. Furthermore, the dissolved oxygen concentration and alkalinity are also required. The ASM1 describes eight biological processes, three related to the growth of heterotrophic and autotrophic microorganisms, two related to biomass decay or death-regeneration theory, and the remaining three related to hydrolysis. The major limitation of ASM1 is that it does not include enhanced biological phosphorus removal (EBPR), therefore the ASM2 was developed. The ASM2 model includes phosphate accumulating organisms (PAO), which grow exclusively in aerobic conditions. The ASM2d describes the dynamic changes of the activated sludge community, but is does not describe completely the dynamics in terms of hydrolyses and EBPR processes. The ASM3, due to the introduction of the storage of organics role, has the ability to correctly describe the uptake of readily biodegradable COD, contrary to ASM1. ASM3 is particularly indicated for simulations of, as follows: high loaded nitrification-denitrification systems with short anoxic retention times; selectors design; aeration demands in step-feed operations or when high amounts of soluble industrial components are present in the influent; easing of automatic calibration. Nevertheless, ASM1 is a satisfactory model to describe nitrogen removal systems because nitrification is a slow process, therefore there is enough time available for the degradation of slowly biodegradable COD.

Currently, the ASM models are considered reliable and capable of describing complex WWTPs. The development of computer capacity, facilitated the work with mathematical models with large numbers of processes and variables, which is now current practice in North America, Australia and many countries of Europe (van Loosdrecht et al. 2015). The widespread use is also due to the integration of the ASM models in commercial software packages developed to simulate the design, optimization and operation of WWTPs. Examples of the commercial packages are BioWin, GPS-X, SIMBA, STOAT, WEST, among others. The commercial modelling simulators allow users to view the response of the treatment systems to changes in a number of variables.

The BioWin software, from Envirosim, Canada, has built-in the IWA models, namely the ASM1 (Henze et al. 1987), ASM 2 (Henze et al. 1995), ASM2d (Henze et al. 1999) and ASM3 (Gujer et al. 1999). The company developed its own activated sludge-digested model (ASDM), to allow the simulation of the water and sludge line of the WWTP,

without the need to couple more than one model (Elawwad et al. 2019). The CAS systems are described by the ASM IWA models. BioWin is being used successfully to optimize municipal and industrial WWTPs (Elawwad et al. 2019). The BioWin software will be used in this TKI project to simulate the CAS system, and integrate it with OMP removal modeling.

The acknowledgement of the potential adverse effects caused by micropollutants to the aquatic environment, and the awareness that centralized emissions of OMPs to the aquatic environment were associated to WWTP discharge points, brought the need to extend the activated sludge models to describe OMPs. Furthermore, the high costs associated with OMP measurements also stimulated the use of models. The proposed models, with the first ones dating back to 1998, describe the fate of OMPs based on volatilization, sorption/desorption and biotransformation (Snip et al. 2016).

Joss et al. (2006) propose the following model to simulate the biological degradation, sorption and desorption of OMPs, in each tank (compartment) of a cascade CAS system:

$$\frac{dS_i}{dt} = \frac{1+R}{\theta_h}(S_{i-1} - S_i) - k_{sor}X_{SS,i}S_i + k_{des}X_i - k_{biol}X_{SS,i}S_i$$

$$\frac{dX_i}{dt} = \frac{1+R}{\theta_h}(X_{i-1} - X_i) + k_{sor}X_{SS,i}S_i - k_{des}X_i$$

(Equation 16 and Equation 17, respectively)

Where:
i- Tank (compartment) number (1 to *n*) and i-1 the preceding tank, in a total of n tanks;
R- flow rate of the sludge recycle, relative to the flow rate of the treated wastewater [-];
k_{sor}- rate constant for sorption [L $g_{SS}^{-1}d^{-1}$];
k_{des}- rate constant for desorption [d^{-1}];
θ_h- hydraulic retention time [d].

By assuming sorption equilibrium and comparable biological activity in all tanks (anoxic and aerobic), the relative reduction in soluble compound concentration can be calculated for a cascade of mixed reactors as follows:

$$\frac{S_{out}}{S_{WW}} = \frac{1+K_{d,prim}X_{SS,WW}}{1+K_dX_{SS}} \times \frac{1}{(1+R)\left[\left(1+\frac{k_{biol}X_{SS}\ \ \theta_h}{(1+R)(1+K_dX_{SS})\ n}\right)^n - 1\right] + \frac{1+K_dSP}{1+K_dX_{SS}}}$$

(Equation 18)

Where:
S_{WW}- soluble OMP concentration the wastewater before mixing with the return sludge [µg L^{-1}];
$K_{d,prim}$ the sorption coefficient of the primary sludge [L g_{SS}^{-1}];
$X_{ss,WW}$- the primary sludge content of wastewater before mixing with the return sludge [g_{SS} $m^{3,-1}$]

Furthermore, the authors Joss et al. (2006) propose a similar equation to Equation 18 for plug-flow and batch reactors, to account for the different types of CAS configurations. The model proposed by these authors derives the k_{biol} rate constants from aerobic batch experiments obtained with sludge samples collected at a CAS WWTP, with nitrification, partial denitrification and chemical phosphorus removal, and a sludge retention time of about 11 d. Furthermore, the K_d coefficients applied in the model are, either obtained from batch experiments described by Ternes et al. (2004), or from literature sources.

Models such as the described by Joss et al. (2006) provide a simplified approach to the fate of OMPs in WWTPs, where the missing rates and coefficients can be obtained by performing batch tests at lab scale, as described in the

literature. Nevertheless, the model described by Joss et al. (2006), and similar models relying on the pseudo-first-order kinetics and sorption/desorption equations, have limitations. Snip et al. (2014) summarized these limitations as follows: not taking into account the presence of substances that facilitate or inhibit biotransformation; not considering the influence of redox conditions in the removal of OMPs; not taking into account the retransformation processes, such as the production of a parent compound, from its conjugated metabolites, during WWTP; and not explicitly representing the total concentration of microorganisms with the metabolic activity to bio-transform OMPs. Nevertheless, to completely overcome the aforementioned limitations, knowledge of the microorganisms' metabolic pathways for each OMP needs to be available.

The authors Plosz et al. (2010), describe the framework of the Activated Sludge Models for Xenobiotics (ASM-X) for the removal of three pharmaceuticals in CAS systems, including sulfamethoxazole. Plosz et al. (2012) apply the ASM-X to diclofenac and carbamazepine. In the ASM-X models the concentrations of the different fractions are described by three states, namely, dissolved parent fraction; sorbed parent fraction and re-transformable fraction. The processes describe (1) biotransformation of the parent fraction, (2) retransformation of the re-transformable fraction to dissolved parent fraction; (3) sorption onto sludge and (4) desorption from sludge (Polesel et al. 2016). To characterize the processes, the following rate constants are required: biotransformation rate constant (k_{bio}), retransformation rate constant(q_C), the solid-liquid partition coefficient or sorption rate (K_d) and the desorption rate (k_{des}). Plosz et al. (2012) explain that the model simulations were done applying the software WEST (DHI, Hørsholm, Denmark), with the ASM1 model being applied to simulate aerobic and anoxic conditions. The parameter values used by the authors in the ASM-X and ASM1 models are shown in Table 12, demonstrating the size of the data-base required to implement the ASM-X models to single compounds. Plosz et al. (2010) provide the corresponding information, regarding the application of the ASM1 and ASM-X to sulfamethoxazole. The ASM-X models were also applied to diclofenac and carbamazepine (Plosz et al. 2012), but not to the remaining OMPs of the 11 I&W OMP group. As aforementioned, to apply the ASM-X models the removal pathway of the OMP has to be known or at least proposed. Developing the ASM-X models for single compounds requires a very strong effort, relying on multiple sources of published data, specific lab tests, and full-scale data, particularly representing the daily and seasonal quality variations of the wastewater influent.

As the CAS OMPs models developed in complexity to fully represent the processes of removal and retransformation of the several OMPs in WWTPs, so did the needs in terms of influent time-series. Campaign measurements of OMPs are intensive and costly, therefore models have also been used to generate influent time-series, able to represent the natural variability of OMPs dynamics as accurately as possible. Snip, Flores-Alsina et al. (2016) describe the use of the BSM2 influent generator model, to mimic the influent dynamics of 3 OMPs previously modeled by the ASM-X. The combination of BSM2 models and ASM-X modelled successfully carbamazepine removal in WWTPs, and was less successful for sulfamethoxazole and N^4-acetylsulfamethoxazole.

Symbol	Definition	Unit	Compound	
			Diclofenac	Carbamazepine
	CAS registry #		105307-86-5	298-46-4 85756-57-6
	Annual consumption (Norway)	kg year^{-1}	1588[a]	3619
	Average daily influent C_{LI} load measured	mg day^{-1} 1,000 PE^{-1}	58 ± 14	192 ± 48
	Average daily influent C_{CJ} load calculated	mg day^{-1} 1,000 PE^{-1}	65 ± 15	77 ± 18
Kinetic model parameters				
k_{Des}	De-sorption rate coefficient for C_{SL}	day^{-1}	100[c]	100[c]
K_S	Half-saturation coefficient for S_S	mg L^{-1}	10[f]	10[f]
K_O	Half-saturation coefficient for dissolved oxygen	mg L^{-1}	0.2[f]	0.2[f]
Aerobic process parameters				
$K_{D,Ox}$	Aerobic solids-liquid sorption coefficient	L g X_{SS}^{-1}	0.019[c], 0.09[e]	0.0012[c]
$k_{Dec,Ox}$	Aerobic biotransformation rate coefficient for C_{CJ}	L g^{-1} day^{-1}	5[e]	5[e]
$q_{C,Ox}$	Aerobic maximum specific cometabolic substrate biotransformation rate in the presence of growth substrates for C_{LI}	L g^{-1} day^{-1}	1.6[d]	2[d]
$k_{Bio,Ox,SRT=16\ days}$	Aerobic biotransformation rate coefficient under growth substrate limiting conditions for C_{LI}	L g^{-1} day^{-1}	0.14[d]	0.01[d]
Anoxic process parameters				
$K_{D,Ax}$	Anoxic solids-liquid sorption coefficient	L g X_{SS}^{-1}	0.019[c]	0.0012[c]
$k_{Dec,Ax}$	Anoxic biotransformation rate coefficient for C_{CJ}	L g^{-1} day^{-1}	5[e]	5[e]
$q_{C,Ax}$	Anoxic maximum specific cometabolic substrate biotransformation rate in the presence of growth substrates for C_{LI}	L g^{-1} day^{-1}	0.96[d]	1.2[d]
$k_{Bio,Ax,SRT=16\ days}$	Anoxic biotransformation rate coefficient under growth substrate limiting conditions for C_{LI}	L g^{-1} day^{-1}	0.1[d]	0.01[d]
$k_{Bio,SRT>20\ days}$	Aerobic/anoxic biotransformation rate coefficients at SRT > 20 days	L g^{-1} day^{-1}	1.04[g]	—
Parameters for the dynamic input time-series				
$C_{LI,Inf}/C_{CJ,Inf}$	Ratio of the pre-clarified influent C_{LI} and C_{CJ} concentration values for the three daily inflow regimes[b]			
10:00–18:00 h	Parameter value for the morning increased inflow	—	0.85[e]	2.5[e]
18:00–02:00 h	Parameter value for the daily peak inflow	—	0.85[e]	2.5[e]
02:00–10:00 h	Parameter value for the midnight low inflow	—	0.85[e]	2.5[e]
$C_{SL,I,Inf}/C_{LI,Inf}$	Ratio of the pre-clarified influent C_{LI} and $C_{SL,I}$ concentration values	%	2.2[e]	1
$C_{LI,0,ss}$	Steady-state concentration value used in the dynamic WWTP simulations as initial condition for influent xenobiotic concentration	ng L^{-1}	100[e]	375[e]

[a]Diclofenac consumption data is presented by Grung et al. (2008).
[b]More information on the flow boundary conditions are shown by (Plósz et al., 2010c).
[c]Parameter value derived from literature (Ternes and Joss, 2006; Plósz et al., 2010a).
[d]Parameter values estimated using the measured batch experimental data.
[e]Parameter values estimated using the full-scale experimental data.
[f]ASM1 parameter values according to Spanjers et al. (1998).
[g]Estimated model parameter values used in approximating literature data with the full-scale input and WWTP data of this study (Fig. 3a).

Table 12- Reproduction of Table II, as published by Plosz et al. (2012), presenting the information on diclofenac and carbamazepine, and model parameter values, applied to simulate the ASM-X and ASM1 models.

A model can be represented as a structural matrix, whom in biochemical fields are designated as Peterson matrixes and in sanitary engineering as Gujer matrixes. The matrix contains stoichiometric coefficients and a kinetic vector. The state variables involved in a process are displayed in columns, and all the processes where the state variable is involved are presented in the rows. They are used for deriving a system of equations, representing biochemical reactions and employed in the development of a mathematical model of activated sludge systems. The IWA ASM models were represented in Petersen or Gujer matrixes. The Petersen matrixes are particularly useful for complex models where several processes and variables are taken into consideration. The matrixes of IWA ASM models are in current use, and included in available commercial software. The Petersen matrix of the ASM-X models, referring to sulfamethoxazole, diclofenac, and carbamazepine are shown in Annex III.

6 Conclusions

6.1 Selected CAS configuration and representability in the modelling exercise

The WWTP Walcheren, from waterboard Scheldestromen, will be the WWTP were further research from TKI Belissima will take place. The WWTP has a PhoRedox CAS configuration. According to the information supplied the TKI waterboard partners PhoRedox and UCT are frequently applied. A PhoRedox CAS configuration assures the removal of carbonaceous material, nitrification and denitrification processes. The WWTP Walcheren applies an SRT of 25 days, which is favorable for the biological conversion of nutrients and might benefit OMP removal. The WWTP has a 20% industrial component in the influent, which might bring added influent variability or/and acclimation of the biomass to specific industrial wastewater characteristics. In any case, domestic wastewater also varies in quantity and quality between locations. Therefore, results and modelling exercises obtained at WWTP Walcheren should not be directly extrapolated to other WWTPs.

6.2 Knowledge gaps on OMP removal mechanisms

The present TKI project is focusing on the removal of the 11 indicator OMPs, proposed by I&W and also adopted in the selection of Stowa. There is abundant information about carbamazepine, diclofenac and sulfamethoxazole. There are literature sources on the antibiotics clarithromycin and trimethoprim, and the beta-blockers metoprolol, propranolol and sotalol. As opposed, there is few information on the chemicals benzotriazole, and 4-, 5-methylbenzotriazole, used as anti-corrosion and anti-fouling substances, and the pharmaceutical hydrochlorothiazide.

As removal mechanisms of OMPs from wastewater, sorption, biotransformation and stripping were identified and described. Stripping will account for less than 10% of the compound removal, even for rather volatile musk fragrances not addressed in this report, according to the conclusions obtained in the EU project NEPTUNE (Ternes et al. 2010). Therefore, stripping is considered negligible for the 11 I&M OMPs. The OMP removal mechanisms, and in particular sorption and biotransformation, can be assessed by measuring the respective rate constants or coefficients through batch tests described from literature.

According to the information found in literature, biotransformation seems to be the main removal mechanism for most of the 11 I&W OMPs, with the exception of propranolol, with a likely removal pathway through sorption. Removal rates obtained with activated sludge of full-scale WWTP are scarce. The results vary between locations and OMPs. The removal rate results for biotransformation vary between a maximum of 95% for diclofenac, obtained with an extended sludge age of 60 days, and a minimum of 10% removal for hydrochlorothiazide.

In simplified terms, OMP removal can be described by mechanisms of sorption and biotransformation. Besides the knowledge of the specific reaction rates and coefficients, knowledge of OMP concentrations in influent and effluent, and CAS parameters, such as flows and solids concentrations, are required.

6.3 Steering OMP removal in existing CAS systems

The following parameters of existing CAS systems were listed as having an influence on the fate of OMPs, as follows: (1) Sludge Retention Time (SRT) (also designated as sludge age (θ)); (2) redox conditions (aerobic, anoxic or

anaerobic conditions); (3) Hydraulic Retention Time (HRT); (4) temperature; (5) pH and (6) sludge concentration. SRT and HRT are linked to the availability of substrate, which might influence the biotransformation removal. The CAS parameters and availability of substrate impact the extent of biomass adaptation to a specific OMP.

Parameters such as HRT, sludge concentration and SRT are set by design. HRT is flow dependent, while SRT and sludge concentrations are set within a pre-defined range, to obtain the desired carbonaceous and nutrient removal. A limited range of OMP removal improvement is available in existing CAS systems, by working within these ranges. An extended SRT leading to increased removal seems to be OMP dependent. However, it's clear that extended SRTs do allow increased removal of at least some of the OMPs.

The information on the influence of redox conditions on the removal of OMPs is not consensual. There are literature sources reporting an increased removal by nitrifying microorganisms and/or their enzymes, while others attribute it to increased heterotrophic activity. However, it seems clear that the effect of redox conditions is also substance specific, therefore an increased knowledge on the microbiological pathways of removal of each OMPs, will clarify, in time, which OMPs are being removed in aerobic, anoxic and anaerobic conditions.

Temperature and pH are inherent characteristics of the wastewater, which are almost not changed during the CAS treatment. However, local variations in pH may occur if coagulants or additional substrates are being applied. Regarding temperature, a temperature control in the CAS has a too high operational cost, therefore is not a practice in municipal CAS systems. Nevertheless, higher temperatures do seem to lead to increased OMP removals, likely due to an increased microbiological activity.

Overall, it can be concluded that the possibilities to steer OMP removal in existing CAS systems, is certainly a subject requiring further research. The focus should be given to SRT and redox conditions. The modelling approach adopted in this TKI project is the ideal approach to quantify how much, in terms of removal, is there to gain.

6.4 Modelling of CAS with OMP removal

In this TKI project we will apply the BioWin software, from Envirosim, Canada, for modelling of the selected CAS system at WWTP Walcheren. BioWin has the ASM1, ASM2d and ASM3 models built-in, allowing the modelling of the CAS system according to the IWA models.

The model of the OMP removal, will vary with the OMP considered. Peterson matrixes of the ASM-X models, and the corresponding rates and coefficients to be used for each process, are available for sulfamethoxazole, diclofenac and carbamazepine. The knowledge and effort required in the ASM-X models, to obtain the rates and coefficients for each OMP, aside from the full-scale monitoring data, are considerable. Therefore, for the remaining OMPs of this TKI project, conventional modelling describing sorption and biotransformation removal mechanisms will be applied.

I Annex –TKI partners WWTPs

Table I-1- WWTP characteristics of TKI Belissima partners (complementing table 3)

Location	Design load [p.e.]	Maximum flow [$m^3 h^{-1}$]	HRT (1) [h]	Influent-% industrial	Configuration CAS (2)	Primary clarifier	Complementary information CAS configuration				SRT [d]
							Anaerobic tank	Denitrification tank	Nitrification tank	Hydraulic regime (3)	
Aquafin											
Oostende	198.000	6840	11	4		No	Yes	Yes	Yes	Carrousel	14,5
Deurne	193.500	13968	9	1		No	Yes	Yes	Yes	Carrousel	22
Antwerpen-Zuid	171.000	12103	8	3		No	Yes	Yes	Yes	Carrousel	23
Leuven	135.000	4821	9	6		No	Yes	Yes	Yes	Carrousel	
Harelbeke	116.100	8294	7	3		No	Yes	Yes	Yes	Carrousel	
De Stichtse Rijnlanden											
Breukelen	31.200	885	12	10	UCT	yes	yes	yes	yes	carrousel	21
Bunnik	38.400	1.030	12	40	A/O	no	no	yes	yes	mixed	16
De Bilt	73.920	2.850	12	20	Carrousel (step feed)	no	yes	yes	yes	carrousel	20
De Meern	38.640	1850	12	10	UCT	no	yes	yes	yes	carrousel	12
Driebergen	44.400	1800	12	10	Phoredox	no	yes	yes	Yes	carrousel	26
Houten	72.000	2850	12	10	phoredox	no	yes	yes	yes	carrousel	27
Lopik	33.333	780	12	10	UCT	no	yes	yes	yes	carrousel	21
Montfoort	18.529	900	12	10	A/O	no	no	yes	yes	mixed	15

(continuation of table I-1)

Location	Design load [p.e.]	Maximum flow [$m^3 h^{-1}$]	HRT [1] [h]	Influent-% industrial	Configuration CAS [2]	Primary clarifier	Complementary information CAS configuration				SRT [3] [d]
							Anaerobic tank	Denitrification tank	Nitrification tank	Hydraulic regime	
De Stichtse Rijnlanden											
Oudewater	24.400	550	12	10	UCT	no	yes	yes	yes	carrousel	27
Rhenen	46.800	2000	12	10	UCT	no	yes	yes	yes	carrousel	22
Wijk bij Duurstede	31.800	1360	12	10 %	UCT	no	yes	yes	yes	mixed	16
Scheldestromen											
Camperlandpolder	34.000	694			PhoRedox	No	Yes	Yes	Yes	mixed	
Mastgat	24.500	734			PhoSim	No	Yes	No	No	carrousel	
Sint Maartensdijk	37.200	1,006			PhoRedox	No	Yes	No	Yes	mixed	
Tholen	18.200	823			PhoSim	No	No	No	No	carrousel	
De Verseput	31.500	1,128			PhoRedox	No	Yes	Yes	Yes	mixed	
Waarde	78.900	1,408			PhoSim	No	Yes	No	Yes	mixed	
Westerschouwen	73.500	1,138			PhoRedox	No	Yes	Yes	Yes	Plug-flow	
Terneuzen	86.400	3,100			PhoRedox	Yes	Yes	No	Yes	mixed	
Hulst	36.800	1,675			PhoSim	No	No	No	Yes	mixed	
Kloosterzande	9.000	436			PhoRedox	No	No	Yes	Yes	mixed	
Breskens	36.150	1,040			Nereda	No	No	No	Yes	mixed	
Oostburg	14.000	686			PhoRedox	No	Yes	No	Yes	mixed	
Retranchement	50.200	972				No	No	No	Yes	mixed	

Key: [1] HRT- Hydraulic Retention Time; [2] Configurations definitions in table 1; [3] SRT-Sludge Retention Time

II Annex – Organic Micropollutants (OMPs) Indicators Lists

OMPs indicators list- Swiss Federal Office for the Environment (FEON)- 2016 (Bourgin et al. 2018)

1. Amisulpride
2. Carbamazepine
3. Citalopram
4. Clarithromycin
5. Diclofenac
6. Hydrochlorothiazide
7. Metoprolol
8. Venlafaxine
9. Benzotriazole
10. Methylbenzotriazole
11. Candesartan
12. Irbesartan

OMPs indicators list- Stowa- 2021 (Nieuwenhuis et al. 2021)

1. 4-5 methylbenzotriazole (addition of the 2 compounds)
2. Amisulpride
3. Azithromycin
4. Benzotriazole
5. Candesartan
6. Carbamazepine
7. Citalopram
8. Clarithromycin
9. Diclofenac
10. Furosemide
11. Gabapentine
12. Hydrochlorothiazide
13. Irbesartan
14. Metoprolol
15. Propanolol
16. Sotalol
17. Sulfamethoxazole
18. Trimethoprim
19. Venlafaxine

III Annex –Peterson matrixes

component → i j process ↓	1 C_{LI}	2 C_{CJ}	3 C_{SL}	process rate
desorption	1		−1	$k_{Des} \cdot C_{SL}$
		aerobic processes		
sorption	−1		1	$k_{Des} \cdot K_{D,Ox} \cdot C_{LI} \frac{S_O}{K_O + S_O} X_{SS}$
parent compound formation	1	−1		$k_{Dec,Ox} \cdot C_{CJ} \frac{K_S \cdot \eta_{Dec}}{K_S \cdot \eta_{Dec} + S_S} \frac{S_O}{K_O + S_O} X_{SS}$
biodegradation	−1			$k_{Bio,Ox} \cdot C_{LI} \frac{K_S \cdot \eta_{Bio}}{K_S \cdot \eta_{Bio} + S_S} \frac{S_O}{K_O + S_O} X_{SS}$
		anoxic processes		
sorption	−1		1	$k_{Des} \cdot K_{D,Ax} \cdot C_{LI} \frac{K_O}{K_O + S_O} X_{SS}$
parent compound formation	1	−1		$k_{Dec,Ax} \cdot C_{CJ} \frac{K_S \cdot \eta_{Dec}}{K_S \cdot \eta_{Dec} + S_S} \frac{K_O}{K_O + S_O} X_{SS}$
biodegradation	−1			$k_{Bio,Ax} \cdot C_{LI} \frac{K_S \cdot \eta_{Bio}}{K_S \cdot \eta_{Bio} + S_S} \frac{K_O}{K_O + S_O} X_{SS}$

Table III-1 - Reproduction of Table 1, as published by Plosz et al. (2010), presenting the Gujer matrix of the ASM-X model for xenobiotics, in particular for sulfamethoxazole.

Component → i	1	2	3	4	
j Process ↓	C_{LI}	C_{CJ}	C_{SL}	$C_{SL,I}$	Process rate
De-sorption	1		−1		$k_{Des} C_{SL}$
Aerobic processes					
Sorption	−1		1		$k_{Des} K_{D,Ox} C_{LI} \frac{S_O}{K_O + S_O} X_{SS}$
Parent compound retransformation	1	−1			$k_{Dec,Ox} f(S_S) \times C_{CJ} \frac{S_O}{K_O + S_O} X_{SS}$
Biotransformation	−1				$[q_{C,Ox} f(S_S) + k_{Bio,Ox}] C_{LI} \frac{S_O}{K_O + S_O} X_{SS}$
Anoxic processes					
Sorption	−1		1		$k_{Des} K_{D,Ax} C_{LI} \frac{K_O}{K_O + S_O} X_{SS}$
Parent compound retransformation	1	−1			$k_{Dec,Ax} f(S_S) C_{CJ} \frac{K_O}{K_O + S_O} X_{SS}$
Biotransformation	−1				$[q_{C,Ax} f(S_S) + k_{Bio,Ax}] C_{LI} \frac{K_O}{K_O + S_O} X_{SS}$

		Impact of SRT on biotransformation			
	Impact of growth substrate, $f(S_S)$, on	Diclofenac			Carbamaz.
Parent compound re-transformation	No observed impact	SRT (day)			No observed impact
Biotransformation	$\frac{S_S}{K_S + S_S}$	0–6	6–20	>20	
		—	$k_{Bio,SRT<20}$	$k_{Bio,SRT>20}$	

Table III-2- Reproduction of Table I, as published by Plosz et al. (2012), presenting the Gujer matrix of the ASM-X model for OMPs, namely Diclofenac and Carbamazepine.

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