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Additional UV/H_2O_2 treatment for removal of polar organic micropollutants at Drinking water production site Heel

KWR Watercycle Research Institute

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Project manager
Luc Palmen

Client
WML

Quality Assurance
Emile Cornelissen

Author
Roberta Hofman-Caris, Danny Harmsen, Bas Wols

Sent to
Willen van Pol (WML), Peter van Diepenbeek (WML), Ton van Remmen (van Remmen UV Techniek), Kaspar Groot Kormelink (van Remmen UV Techniek)

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More information
Roberta Hofman-Caris
T 0031 30 6069674
E roberta.hofman-caris@kwrwater.nl

PO Box 1072
3430 BB Nieuwegein
The Netherlands

T +31 (0)30 60 69 511
F +31 (0)30 60 61 165
E
I www.kwrwater.nl

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Management Summary

Based on previous research it is to be expected that concentrations of organic micropollutants, like pharmaceuticals, pesticides, sweeteners etc., in surface water will increase during the next few decades. As WTP Heel uses surface water as a source for drinking water production, it was studied whether an additional treatment process can prevent these micropollutants to be present in drinking water.

Several processes can be applied for the removal of organic micropollutants:

- Membrane processes can be efficient for the removal of organic micropollutants, but their main disadvantage is the concentrate formed, which will have to be dealt with. In case of WTP Heel this will be a problem, as the concentrate cannot be discharged.
- Ozone based processes are widely applied for the removal of organic micropollutants, as they can degrade a broad range of electron rich compounds. However, it is known that bromide is easily converted into bromate by ozone. Due to a local bromide contamination of the groundwater in the area of WTP Heel ozone processes cannot be applied, as the ozone would immediately convert bromide into the suspected carcinogen bromate.
- UV/H_2O_2 processes are very effective for the degradation of a very wide range of organic micropollutants (the processes are less selective than e.g. ozone processes). These UV/H_2O_2 advanced oxidation processes are applicable at Heel, but their main disadvantage is the relatively high energy use.

It was decided to carry out pilot experiments with a UV/H_2O_2 process, based on a low pressure UV lamp.

It was found that a broad variety of organic micropollutants (a wide range of pharmaceuticals, sweeteners, NDMA and EDTA) can effectively and efficiently be removed from the water using the UV/H_2O_2 process. DMS, a compound of special interest to WML as it occurs in its sources for drinking water, can be removed too. However, this compound requires a relatively high UV dose of about 800 mJ/cm^2, whereas for the majority of other compounds about 350 mJ/cm^2 would be sufficient. Another parameter that can be optimized is the hydrogen peroxide (H_2O_2) content. However, it still has to be decided by WML which target compound or set of target compounds should be taken into account to calculate the UV dose and hydrogen peroxide content required. Besides, incomplete conversion, resulting in the possible formation of transformation products and metabolites at lower UV doses and/or hydrogen peroxide concentrations, will have to be taken into account, although the pilot showed that such compounds probably are effectively removed by activated carbon filtration after the UV/H_2O_2 process. Such a filtration step is required not only for removal of such compounds, but also to remove the excess of hydrogen peroxide.

Experiments showed that application of the UV/H_2O_2 process does not result in the formation of mutagenic compounds, and that the biostability of the water after the process would remain sufficient .

As the water at Heel has a very high UV transmission (UV-T) value of 94%, the UV process at Heel is very efficient. Reflection of UV radiation at the outer reactor wall increases the energy

efficiency of the process by about 20%, whereas an additional improvement is obtained by a further increase of UV-T to 96% during the process. Besides, in this pilot project a reactor was used of which the geometry had been optimized for advanced oxidation, based on a model that describes the conversion inside the reactor. This reactor had been shown to require 30-40% less energy than a common disinfection UV reactor, which in general is applied in advanced oxidation processes. Taking all this into account, it is estimated that application of the UV/H_2O_2 process at WTP Heel would cost about 0.11 €/m^3.

Summary

Previous research had shown that the water of the river Meuse and its tributaries may contain relatively high concentrations of pharmaceuticals and metabolites, up to some dozens of micrograms per liter. Also other (polar) organic micropollutants were observed in the Meuse water, like DMS, glyphosate, AMPA etc. It is expected that factors like demographic developments ("aging": elder people use more pharmaceuticals) and climate change (resulting in e.g. periods with a low river discharge) will result in higher concentrations of organic micropollutants. Therefore, it was decided to investigate whether a UV/H_2O_2 process may be applied at the WML drinking water production site Heel to remove micropollutants.

At KWR a model has been developed which describes the conversion of organic micropollutants in a UV/H_2O_2 reactor. This model was used to optimize the geometry of the UV reactor. Several types of optimized reactors (for different water quality and flows) were built by Van Remmen UV Techniek, and tested both at Van Remmen and at Dunea. One type of reactor, D200 equipped with two flowplates and low pressure (LP) UV lamps, was tested in a pilot set-up at site Heel during this project.

Three sets of experiments were carried out, in which a mixture of pharmaceuticals was added to the pre-treated water at Heel. Reaction conditions were adapted based upon results obtained in previous experiments.

During the first set of experiments, three different flows were applied, corresponding to three different UV doses. It was found that the conversion of the micropollutants was significantly higher than the model had predicted (average conversion 92%, whereas about 80% had been predicted). This mainly was explained by the fact that the UV-transmission in the reactor was very high (94%), as a result of which reflection at the outer reactor wall also had to be taken into account. Thus, it was decided to reduce the lamp power and increase the flow, as less energy would be required to obtain sufficient conversion.

During the second set of experiments the average conversion still appeared to be a little higher than the predicted values (81-90% for flows ranging from 1 to 2 m^3/hour, whereas 68-84% had been predicted). This probably results from the UV-T increase from 94% to 96% during the process.

As in this reactor the flow couldn't be increased any further, in order to find further optimization possibilities, the H_2O_2 content during the experiments was decreased from 10 to 3 mg/L. Indeed it was found that a decrease in H_2O_2 content results in a significant decrease in conversion for most micropollutants.

Reaction conditions can be optimized taking one compound or a set of compounds as a model. The conversion required to reduce the concentration to an acceptable level (e.g. below the reporting limit) then can be taken as a target, where the UV dose and H_2O_2 content should be adjusted to.

However, it was shown that the water contains higher metabolite and/or transformation product concentration when less H_2O_2 was applied, or when the UV dose was decreased

significantly. This effect should be taken into account when optimizing reaction conditions, as this means that not only the conversion of parent compounds, but also the formation and conversion of transformation products may be important for the water quality.

During the first and third series of experiments, Ames Fluctuation Assays were applied to determine the possible formation of mutagenicity. From these tests it was concluded that the UV/H_2O_2 reactor, which had been equipped with a Low Pressure UV lamp, did not add any mutagenicity to the water. None of the samples tested (before or after UV) was found to be mutagenic.

After the UV/H_2O_2 reactor activated carbon filtration (ACF) was applied. This was done for two reasons:

1. To remove the excess of H_2O_2 from the water
2. To guarantee that no dosed micropollutants or transformation products would enter the water cycle.

It was found that complete removal of the micropollutants was obtained during the experiments.

Furthermore, determination of the content of assimilable organic carbon (AOC) and the biofilm production potential (BFP) showed that, indeed these values increase due to the UV/H_2O_2 process (as had been expected), but that still the biostability of the water produced is high enough.

After these dosing experiments some additional experiments were carried out with compounds which are of special interest to WML: DMS, NDMA, AMPA, EDTA, Acesulfame-K, Aspartame, Cyclamate, Saccharine and Sucralose. All sweeteners, NDMA and EDTA were effectively removed by the advanced oxidation. For AMPA no clear results were obtained during this experiment. For DMS it was found that removal is possible by applying a UV/H_2O_2 process, but that this will require a relatively high UV dose (about 800 mJ/cm^2) to remove the DMS to a level below the reporting limit).

Finally, a cost estimation was made, showing that applying UV/H_2O_2 as an additional treatment process at WTP Heel would result in extra costs of about 0.11 €/m^3.

Contents

1 Introduction

1.1 Prior research into pharmaceuticals in the water system of the Southern part of the province of Limburg

In 2011 and 2012 the presence of pharmaceuticals in the water system of the Southern part of the province of Limburg was investigated, upstream of the intake of the drinking water production site at Heel (WPH) (ter Laak et al., 2013 en 2014; Hofman et al., 2013). It was shown that the water of the river Meuse and its tributaries may contain relative high concentrations of pharmaceuticals and metabolites, up to some dozens of micrograms per liter. Also other (polar) organic micropollutants were observed in the Meuse water, like DMS, glyphosate, AMPA etc. It is expected that because of REACH the use of polar compounds, and as a result their concentrations in surface water, will increase over time (Schriks et al., 2010; Schoep and Schriks et al., 2010). Furthermore, improving analytical techniques will enable us to detect more and more compounds in surface water.

1.2 Future developments

A factor which may affect organic micropollutants concentrations is climate change. It is expected that periods with a low river discharge will occur more often, and will take longer. This will result in higher concentrations of organic micropollutants in the surface water.

Pharmaceuticals and their metabolites mainly enter the surface water via wastewater treatment plants (WWTPs). Research by the RIVM (v.d. Aa et al., 2011) shows that in the Netherlands demographic developments (like an aging population) will lead to an increase in the use of pharmaceuticals with almost 40% within the next 35 years. Besides, industrial discharges and diffuse sources (like diffusion of manure to the ground water) contribute to the load of organic micropollutants. About six million people live in the Meuse basin, 5.3 million of them outside the Netherlands. Only a large scale and transnational approach of the water sources and the removal of pharmaceuticals and their metabolites at WWTPs will result in improvement of water quality and protection of the drinking water sources. Realization of such an approach will require much time and energy.

1.3 Protection of drinking water

In order to be able to produce drinking water of a good quality, in the short and mid-long term additional treatment at drinking water production sites may be required. During the pilot research described in this report a UV/H_2O_2 process was studied, to determine the possibilities of this technique at site Heel. The effect on the removal of organic micropollutants from water, pretreated by rapid sand filtration, was investigated at various UV doses and H_2O_2 concentrations. For this purpose a mixture of a broad range of pharmaceuticals was dosed to the water. Furthermore, the degradation of compounds which are of special interest to WML (DMS, NDMA, AMPA, EDTA, Acesulfame-K, Aspartame, Cyclamate, Saccharine and Sucralose) were studied. Besides, is was determined how UV/H_2O_2 technology can be incorporated into the present treatment process, at what costs, environmental impact and energy demands. Furthermore, is was established what the effect of this additional treatment will be on other water quality aspects, like biological stability.

1.4 The UV/H_2O_2 process

1.4.1 Advanced oxidation processes

Advanced oxidation processes are characterized by the presence of hydroxyl radicals, which are very effective oxidants. There are several processes in which these radicals are involved, like e.g. O_3/H_2O_2, UV/O_3, UV/H_2O_2, $O_3/H_2O_2/UV$, UV/TiO_2 processes. Internationally, ozone based processes are very often used, as they are relatively cheap easy to perform. However, their main disadvantage is the formation of bromate in bromide containing water. In such a case application of a UV/H_2O_2 process may be advantageous. In this project the UV/H_2O_2 process was applied, as in near Heel a local groundwater contamination with bromide has been established. Bromide is not turned into bromate by means of photolysis or oxidation by hydroxyl ions.

2 UV/H_2O_2 process and reactor

2.1 UV/H_2O_2 processes

During a UV/H_2O_2 process two types of reaction take place simultaneously: photolysis and oxidation. Depending on their molecular structure and the wavelength applied, molecules may absorb (UV) irradiation, resulting in a chemical reaction of the molecule, often leading to its degradation. In general two types of mercury containing UV lamps are used for this purpose:

- Medium pressure (MP) UV-lamps, emitting over a wavelength range of 200 to 300 nm.
- Low pressure (LP) UV-lamps, emitting irradiation with a wavelength of 253,7 nm.

As the MP lamps emit over a broad range of wavelengths more compounds will be able to absorb irradiation, resulting in reactions. Thus, MP lamps are more effective in photolysis. This, however, has the disadvantage that more byproducts may be formed, which in some cases even may be toxic or mutagenic (Hofman-Caris et al., 2013). For LP lamps this disadvantage will occur to a much lesser extent, but as a result photolysis also will be less effective.

Both types of lamps can be applied to decompose H_2O_2 by means of photolysis, resulting in the formation of hydroxyl radicals. These, in turn, can oxidize a wide variety of organic compounds. By combining UV irradiation with the presence of H_2O_2 a very effective advanced oxidation process is obtained, which can efficiently be applied to convert organic micropollutants (Hofman-Caris en Beerendonk, 2011; Hofman-Caris et al., 2012).

2.2 Models describing the UV/H_2O_2 process

During the UV/H_2O_2 process both photolysis and oxidation of organic micropollutants and natural organic matter (NOM) take place simultaneously. KWR developed a kinetic model, which describes and predicts the conversion of micropollutants as a function of the UV dose applied (Wols et al. 2013 en 2014). These models take into account other reactions like of carbonate, hydrogen carbonate, nitrate and dissolved organic carbon (DOC), which may occur and will affect the conversion of organic micropollutants.

By means of Computational Fluid Dynamics (CFD) the UV dose distribution in a UV reactor can be calculated for various flows. By combining this model with the kinetic model, which calculates the conversion as a function of the UV dose, the conversion of organic micropollutants in the UV/H_2O_2 reactor can accurately be predicted.

2.3 Optimization of UV-reactors.

The model referred to in section 2.2, which predicts the conversion of organic micropollutants in UV/H_2O_2 reactors, can also be applied to optimize the reactor geometry. So far UV/H_2O_2 processes have always been carried out in reactors that were designed and built for disinfection purposes. By decreasing the flow the UV dose is increased, as for advanced oxidation a higher dose is required. However, the model can also be used to calculate the effect of another reactor geometry on the reactor performance. Thus, a new geometry was designed, specially optimized for UV/H_2O_2 processes on a relatively small scale (1-2.5 m^3/hour). This reactor was called “D200”, and two types were built by van Remmen UV Technology: one equipped with one baffle and one with two baffles. The reactor vessel with

one baffle was totally modelled by CFD. For the version with two baffles, calculations appeared to become too difficult, as a result of which a full CFD modeling of this reactor was not possible. Thus, for both versions of D200 the same mathematical models were applied. However, experiments at Van Remmen UV Technology in Wijhe showed that the difference in conversion of micropollutants by both reactor types is small. Both reactors were tested at van Remmen UV Technology, showing that the energy demand at equal degradation level was about 30% less compared with the regular disinfection reactors. The reactor equipped with two baffles gave a little higher conversion (about 1-2%) at a similar energy use. This reactor was applied in the present pilot investigation at site Heel.

3 Pilot experiments at site Heel

3.1 Pilot set-up

The pilot research described in this report was conducted with a pilot set-up which was especially designed for this research. The PI&D of the pilot set-up at site Heel is shown in Figure 3-1.

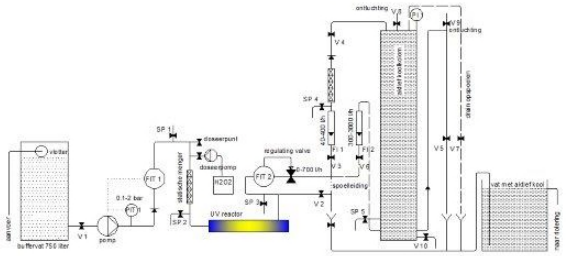


Figure 3-1: PI&D of the pilot set-up at site Heel

Van Remmen UV Techniek (Wijhe, Nederland) built a reactor according to specifications calculated by Bas Wols (KWR), based on kinetic and CFD modeling. This should result in a ca. 30% lower energy demand compared to regular UV disinfection reactors.

Specifications of the reactor (D200, equipped with two flow plates):
UV reactor: D8 200mm
UV lamps: 1 low pressure UV lamp; Van Remmen 120W Long Life; art. nr.:121202/ nr. 08/130984

The activated carbon filter (ACF) (positioned directly after the UV reactor) was built by KWR. The column was filled with 100 L activated carbon (AC) from the production process at site Heel.
Activated carbon specifications: ROW 0.8 Supra van Norit. Age about 14 years, regenerated 1,3 years ago (at the start of the present UV/H_2O_2 experiments).
Besides, an additional activated carbon filter is present for treatment of the total effluent before discharge into the sewage system. This filter had been filled with 1000 L of activated carbon from the production process at site Heel (idem: ROW 0.8 Supra).

Directly after the feed pump (dp pumps; DPVSF 4111B, 2,2KW(1,57KW), 50 Hz) two quick connections are available for dosing additional solutions. One connection was used for constant H_2O_2 dosing (dosing pump: smart Digital- DDA; Grundfos). The other connection was used to dose organic micropollutant compounds during so-called dosing tests (dosing pump: Promint Veder; Gamma/L, GALA0413PPE2000A000000). After the quick connectors a static mixer was installed to ensure a homogeneous mixture at the entrance of the UV reactor. The feed flow (Endress & Hauser; Promag 50) and inlet pressure (Endress & Hauser; Ceraphant T, PTC31) were measured before the UV reactor. The maximum pressure before the UV reactor was set at 2 bar. If the pressure exceeds this maximum value the installation

will be shut down automatically. The flow (Endress & Hauser; Promag 50) through the active carbon filter was regulated by an regulation valve (Samson 3767-000112001.05 + Samson 3510) which also recorded the flow through the active carbon filter.

3.2 Chemicals

Unless stated otherwise an aqueous 10% H_2O_2 solution (Breustedt Chemie Apeldoorn) was used as dosing solution throughout the entire experimental period.

3.2.1 Dosing experiments

During the dosing experiments a mixture of organic micropollutants was dosed at the entrance of the pilot set-up. For these experiments some reference compounds (like atrazine, caffeine and p-CBA) and a broad range of pharmaceuticals were used. This compounds was selected as it concerns pharmaceuticals often observed in sources for drinking water, that represent a wide range of molecular properties and can relatively easy be analyzed. Furthermore, this set of compounds has been used in previous research too (Wols et al., 2013, 2014). The list of used compounds and their chemical structures is shown in Appendix I. In **Error! Reference source not found.** more detailed information about the mixture of organic micropollutants is given.

Table 3-1: Composition mixture of organic micropollutants solution during dosing experiments

Compound	CAS number	Detection limit	Concentration inline	stock
		µg/L	µg/L	mg/L
Atenolol	29122-68-7	0,01	1	1
Bezafibrate	41859-67-0	0,01	1	1
Carbamazepine	298-46-4	0,01	1	1
Clenbuterol	37148-27-9	0,01	1	1
Clofibric acid	882-09-7	0,01	1	1
Cortisol	50-23-7	0,03	3	3
Cortisone	53-06-5	0,03	3	3
Cyclophosphamide	50-18-0	0,01	1	1
Diatrizoic acid	737-31-5	0,01	1	1
Diclofenac	15307-86-5	0,01	1	1
Erythromycin A	114-07-8	0,03	3	3
Fluoxetine	54910-89-3	0,01	1	1
Furosemide	54-31-9	0,01	1	1
Gemfibrozil	25812-30-0	0,01	1	1
Ifosfamide	3778-73-2	0,01	1	1
Ketoprofen	22071-15-4	0,01	1	1
Lincomycin	154-21-2	0,01	1	1
Metformin	657-24-9	0,05	5	5
Metoprolol	51384-51-1	0,01	1	1
Metronidazole	443-48-1	0,01	1	1
Naproxen	22204-53-1	0,01	1	1
Niacin	59-67-6	0,01	1	1
Paracetamol	103-90-2	0,01	1	1
Paroxetine	61869-08-7	0,05	5	5
Pentoxyfylline	6493-05-6	0,01	1	1
Phenazone	60-80-0	0,01	1	1
Pindolol	13523-86-9	0,01	1	1
Prednisolone	50-24-8	0,05	5	5
Propranolol	525-66-6	0,01	1	1
Sotalol	3930-20-9	0,01	1	1
Sulfachloropyridazine	102-65-8	0,01	1	1
Sulfadiazine	68-35-9	0,01	1	1
Sulfamethoxazole	723-46-6	0,01	1	1
Sulfaquinoxalin	59-40-5	0,01	1	1
Terbutaline	23031-25-6	0,01	1	1
Tramadol	27203-92-5	0,01	1	1
Trimethoprim	738-70-5	0,01	1	1
Venlafaxin	93413-69-5	0,01	1	1
para-chlorobenzoic acid (pCBA)	74-11-3	0,1	10	10
Atrazine	1912-24-9	0,01	1	1
Guanylurea	141-83-3	0,05	5	5
Caffeine	58-08-2	0,05	5	5
Bisoprolol	66722-44-9	0,01	1	1
Oxacilline[1]	66-79-5	?		

[1] Not analyzed only added to the stock solution

Furthermore some known metabolites of pharmaceuticals were analyzed. It was checked whether these can be forme during oxidation with UV/H_2O_2 too. These had not been added, as they are very expensive. At the KWR laboratory standards are known, which are used to quantify the amounts of these metabolites. The analyses of the compounds were conducted by the KWR laboratories according to standard procedures, and the detection limits are shown in Table 3-2.

Table 3-2 List of metabolites analyzed by the KWR laboratories, and their detection limits

Compound	CAS number	Detection limit µg/L
Salicylic acid	69-72-7	5,0
2-hydroxy carbamazepine	68011-66-5	0,01
3-hydroxy carbamazepine	68011-67-6	0,01
10,11-trans-diol-carbamazepine	35079-97-1	0,01
Carbamazepine-10,11-epoxide	36507-30-9	0,01
Oxcarbazepine	28721-07-5	0,01
clofibric acid	882-09-7	0,01
Anhydro-erythromycin A	23893-13-2	0,05
Norfluoxetine	83891-03-6	0,50
Hydroxy ibuprofen	51146-55-5	0,50
AMPH	38604-70-5	0,01
Dimethylaminophenazone	58-15-1	0,01
α-Hydroxy metoprolol	56392-16-6	0,01
O-Desmethyl metoprolol	62572-94-5	0,01
O-Desmethyl Naproxen	123050-98-6	0,05
4-Acetaminophen sulfate	32113-41-0	0,03
4-Formylaminoantipyrine	1672-58-8	0,01
Acetyl sulfadiazine	127-74-2	0,01
N4-acetyl sulfamethoxazole	21312-10-7	0,01
O-Desmethyltramadol	73986-53-5	0,01

3.2.2 Additional experiments

After the standard dosing experiments additional experiments were carried out with other types of micropollutants, which are of special interest to WML, as they sometimes are found in their sources for drinking water. During these additional experiments three mixtures of organic micropollutants were dosed at the entrance of the pilot set-up during various experiments. The list of compounds and their chemical structures is shown in Appendix I. In Table 3-3 till Table 3-5 more detailed information about the mixture of organic micropollutants is given. The analyses of the compounds were conducted by the KWR laboratories according to standard procedures.

Table 3-3 Composition mixture of organic micropollutants solution during additional experiments (mix 1)

Compound	CAS number	Detection limit	Concentration inline	stock
		µg/L	µg/L	mg/L
DMS	3984-14-3	0.03	0.5	0.5
NDMA	62-75-9	0.001	0.1	1.0
AMPA	74341-63-2	0.02	2	2.0
Reference compounds				
atrazine	1912-24-9	0.01	1	1.0
Cyclophosphamide	50-18-0	0.01	1	1.0
Diatrizoic acid	737-31-5	0.01	1	1.0
Ifosfamide	3778-73-2	0.01	1	1.0
Metronidazole	443-48-1	0.01	1	1.0
sweeteners				
Acesulfame K	55589-62-3	0.33	33	33.0
Aspartame	22839-47-0	0.07	7	7.0
Cyclamate	139-05-9	0.03	3	3.0
Saccharine	81-07-2	0.20	20	20.0
Sucralose	56038-13-2	0.23	23	23.0

Table 3-4 Composition mixture of organic micropollutants solution during additional experiments (mix 2)

Compound	CAS number	Detection limit	Concentration inline	stock
		µg/L	µg/L	mg/L
DMS	3984-14-3	0.03	1.0	1.0
NDMA	62-75-9	0.001	0.1	1.0
AMPA	74341-63-2	0.02	2	2.0
Reference compounds				
atrazine	1912-24-9	0.01	1	1.0
Cyclophosphamide	50-18-0	0.01	1	1.0
Diatrizoic acid	737-31-5	0.01	1	1.0
Ifosfamide	3778-73-2	0.01	1	1.0
Metronidazole	443-48-1	0.01	1	1.0
sweeteners				
Acesulfame K	55589-62-3	0.33	33	33.0
Aspartame	22839-47-0	0.07	7	7.0
Cyclamate	139-05-9	0.03	3	3.0
Saccharine	81-07-2	0.20	20	20.0
Sucralose	56038-13-2	0.23	23	23.0

Table 3-5 Composition mixture of organic micropollutants solution during additional experiments (mix 3)

Compound	CAS number	Detection limit	Concentration inline	stock
		µg/L	µg/L	mg/L
EDTA	6381-92-6	5.00	500	50.0

3.3 General operation

The process was started on 11-09-2014, and has been operating continuously from 22-09-2014 until 10-04-2015. During the operating period the conditions for dosing experiments were changed several times. Until March 2015 the same activated carbon was applied. Afterwards, this was exchanged by carbon from filter 4, which was used for the remaining experiments.

Applying the model described in paragraph 2.2, the average UV dose was determined taking into account the actual UV-transmission, (UV-T) and the reactor geometry. For modeling purposes a D200 reactor with only one flow plate was used, whereas the reactor used in this project had been equipped with two flow plates. This may have caused a small difference in the average UV dose calculated. The results obtained during the first series, 11-09-2014, indicated that, as a result of the high UV-T value, reflection of irradiation at the reactor wall could not be neglected. This has a strong effect on the average UV dose calculated, as is shown in Table 3-6: on average the UV dose is increased by 21% as a result of this reflection. In this report the values corrected for the reflection effect will be shown.

Table 3-6: Effect of reflection of irradiation at the reactor wall on the calculated average UV dose at different lamp power settings, and a UV-T of 94%. 100% lamp power corresponds to 120 W.

Flow	**Without reflection**			**With reflection**		
(m^3/hour)	Lamp power 100%	Lamp power 80%	Lamp power 75%	Lamp power 100%	Lamp power 80%	Lamp power 75%
1.0	752	602	564	912	730	684
1.5	502	401	376	608	487	456
2.0	376	301	282	456	365	342
2.5	301	241	226	365	292	274

The process conditions during the total experimental period are shown in Table 3-7. Reflection was taken into account for the calculation of the average UV dose, as was mentioned before.

Table 3-7: Operating conditions of pilot plant at site Heel, since 11-09-2014

period	Flow	H_2O_2 Conc.	UV installation		ACF		
			Lamp intensity	UV dose	Volume	Flow	Contact time (EBCT)
	m^3/h	mg/L	%	mJ/cm^2	L	L/h	min
Period A: 11-9-2014 till 22-9-2014	1	10	100	912	100	200	30
Period B: 22-9-2014 till 18-11-2014	1	10	100	912	100	300	20
Period C: 18-11-2014 till 10-4-2015	1	10	80	730	100	300	20

In this way an understanding was gained about the energy consumption and other operational conditions of the process during a period of 6 months. The UV intensity of the lamp, the flow through the UV reactor and ACF and the pressure before the UV reactor were recorded a few times per week by a WML operator

The pilot was fed with pretreated (surface) water from drinking water production site Heel, after rapid sand filtration. A scheme of the water treatment process at Heel is shown in Figure 3-2.

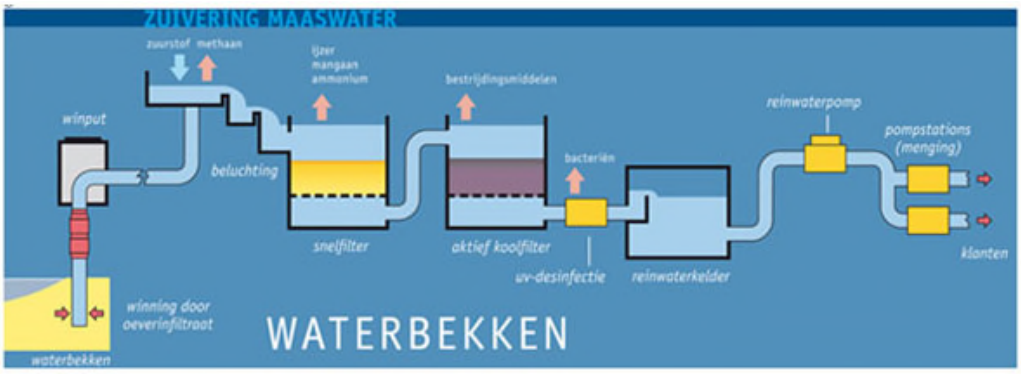


Figure 3-2: Drinking water production process at site Heel (http://www.wml.nl/nl-nl/158/5905/waterproductie.aspx).

The values of several parameters of the pretreated water, measured at 30-09-2014, are shown in Table 3-8.

Table 3-8: Values of several parameters determined in the pretreated water at site Heel before the first pilot experiments (30-09-2014).

meting	Parameter	Value
1	Temperature during experiment	18 °C
	Nitrate	2 mg/l NO_3
	N,N-dimethylaminosulfanilide (DMSA)	<0.05 µg/l (0,0250 µg/l)
	N,N-dimethylsulfamide (DMS)	0,1 µg/l
	N,N-dimethylaminosulfotoluidide (DMST)	<0.05 µg/l (0,0250 µg/l)
	pH	7,52
	Degree of turbidity	<0.1 FTE (0,0500 FTE)
	Hydrogen carbonate	167 mg/l HCO_3
	Totaal organic carbon(TOC)	1,4 mg/l C
2	Nitrate (calculated)	0,5 mg/l N
	N,N-dimethylaminosulfanilide (DMSA)	<0.05 µg/l (0,0250µg/l)
	N,N-dimethylsulfamide (DMS)	<0.05 µg/l (0,0250 µg/l)
	N,N-dimethylaminosulfotoluidide (DMST)	<0.05 µg/l (0,0250 µg/l)
	Total organic carbon (TOC)	1,5 mg/l C
3	N,N-dimethylaminosulfanilide (DMSA)	<0.05 µg/l (0,0250 µg/l)
	N,N-dimethylsulfamide (DMS)	<0.05 µg/l (0,0250 µg/l)
	N,N-dimethylaminosulfotoluidide (DMST)	<0.05 µg/l (0,0250 µg/l)
	Total organic carbon (TOC)	1,1 mg/l C

3.4 Residence time distribution measurements

In order to determine the residence time in the reactor at several points in the set-up a residence time distribution experiment was conducted using sodium chloride as a tracer. During several hours 2 g/L sodium chloride (NaCl, Baker analyzed, cas number 7647-14-5) was dosed before the UV unit. During the dosing period the conductivity was measured with a conductivity meter (Radiometer CDM83 labmeter). Samples were taken before the UV reactor, after the UV-reactor and after the two AC Filters. Samples were taken after 0, 1, 2, 3, 4, 5, 6, 8, 10 and 15 minutes. After 15 minutes samples were taken once every 5 minutes untill the breakthrough of sodium chloride through the AC Filter. From these measurements it was concluded that the first sample can be taken after 60 min. of operating time, as then it can be assumed that the reactor is running stably. During the first dosing experiments 90 min. was applied, which is sufficient.

3.5 Dosing experiments

Three series of dosing experiments were carried out, the first one on 30-09-2014, the second one on 18-11-2014, and the third one on 11-03-2015.

3.5.1 First dosing series (30-09-2014): determination of mutagenicity, AOC and BBP formation and conversion of micropollutants at one UV dose.

The first series of dosing experiments was conducted on 30-09-2014. All experiments were conducted at a fixed feed flow of 1 m^3/h over the UV reactor and a 10 mg/L H_2O_2 concentration. The UV lamp power was set at 100%, The flow over the ACF was 300 L/h, which corresponds to a contact time of 20 minutes. During the test period the temperature (Testo 925, UAN090045), the UV transmission (Real tech UVT p200 BP) and H_2O_2 concentration (Prominent Dulcotest DT3B) were measured regularly using hand meters. Furthermore the UV intensity of the lamp, the flow through the UV reactor and ACF, and the pressure before the UV reactor were noted.

Samples were taken at different points in the set-up and of the drinking water at the end of the treatment process at plant Heel. All sampling points are shown in Table 3-9. Sampling points SP2, SP3 and SP5 are depicted in the PI&D of the set-up (Figure 3-1).

Table 3-9 Sampling points during dosing experiments 30-09-2014

Sampling points	PI&D
Pretreated water (“snelfiltraat” SF (FK01MK03; Voorfiltraatbuffer (voor LD pomp)	-
Before UV	SP2
After UV	SP3
After ACF	SP5
After ACF (additional)	-
Drinking water at Heel (RWL01/00; Levering 1 Helden)	-

First, samples were taken for the analyses of AMES, AOC and BPP. These samples were analyzed by the KWR laboratories according to standard procedures (LMW-058) unless stated otherwise. Furthermore, pH, HCO_3^-, turbidity and nitrate samples were taken from the pretreated water and analyzed by Aqualab Zuid according to standard procedures unless stated otherwise, DMS, DMST, DMSA and TOC samples were taken from the pretreated water, after UV and after ACF, and analyzed by Aqualab Zuid according to standard procedures unless stated otherwise.

After sampling the dosing of the mixture of organic micropollutants was started. It was decided to take the first series of samples after a contact time of at least 5 bed volumes (100 minutes)[1]. A second sampling took place 10 minutes later. The organic micropollutant samples were analyzed by KWR according to standard procedures.

In

[1] Because at this stage of the experiments the breakthrough of the ACF had not yet been determined

Table 3-10 an overview is given of the operational conditions, sampling points and analyses of the first series of the dosing experiments.

Table 3-10 Overview operational conditions, sampling points and analyses of the first series of the dosing experiments (30-09-2014). Lamp power 100%, reflection taken into account in dose calculation.

Experiment	dosage		UV		ACF		Analyses	Sampling points					
	mixture of organic micropollutants	H_2O_2	Flow	Dose	Flow	Contact time		Pretreated water (SF)	before UV	After UV	After ACF	After ACF (additional)	Drinking water
		mg/L	m^3/h	mJ/cm^2	m^3/h	min							
A1	no	10	1	912	0,3	20	AMES	2	2	2	2		2
A2	no	10	1	912	0,3	20	AOC	1		1	1		1
A3	no	10	1	912	0,3	20	BBP				1		1
A4	yes	10	1	912	0,3	20	Org. micropollutants + metabolites	2	2	2	2	2	

3.5.2 Second series (18-11-2014): experiments at three different UV doses.

The second series of dosing experiments was conducted on 18-11-2014. The first series of dosing experiments had shown a very high conversion, which was attributed to the UV dose applied, which was much higher than calculated before. This was supposed to be due to reflection of UV radiation at the outer reactor wall. Calculations, taking into account this reflection, showed that the actual UV dose had been significantly higher than calculated before. Based on the results of this first series of experiments (paragraph 4.2), it was decided to lower the UV dose. In order to do that the lamp power was set at 80%. Tests were conducted with three different flows through the UV reactor, 1.0, 1.5 and 2.0 m^3/h respectively. In all cases the H_2O_2 concentration was 10 mg/L. The flow over the ACF was 300 L/h which corresponds to a contact time of 20 minutes. During the test period the temperature (Testo 925), the UV transmission (Real tech UVT p200 BP) and H_2O_2 concentration (Prominent Dulcotest DT3B) were measured regularly using hand meters. Furthermore the UV intensity of the lamp, the flow through the UV reactor and ACF, and the pressure before the UV reactor were noted. The sampling points were identical to the sampling points during the first series of experiments (Table 3-9).

The first experiment was conducted at a flow of 1.0 m^3/h through the UV reactor. First, samples were taken for the analyses of pH/HCO_3, turbidity and nitrate. Samples were taken from the pretreated water and analyzed. DMS, DMST, DMSA and TOC samples were taken from the pretreated water, after UV and after ACF, and were analyzed.

After the samples had been taken the dosing of the mixture of organic micropollutants was started. Because at this stage of the experiments the breakthrough of the ACF was known (see paragraph 4.1.2) it was decided to take the first series of samples after 60 minutes. A second series of sampling took place 10 minutes later. After sampling the flow through the UV reactor was increased to 1.5 m^3/h and the dosage of the mixture of organic micropollutants was adjusted. After 60 and 70 minutes samples were taken for organic micropollutants analysis. The procedure was repeated at a flow through the UV reactor of 2.0 m^3/h. In Table 3-11 an overview is given of the operational conditions, sampling points and (micropollutants) analyses of the second series of the dosing experiments.

Table 3-11 Overview operational conditions, sampling points and (micropollutants) analyses of the second series of the dosing experiments (18-11-2014). Lamp power 80%.

Experiment	Dosage	UV		AKF		Sampling points				
	H_2O_2	Flow	Dose	Flow	Contact time	Pretreated water (SF)	before UV	After UV	After ACF	After ACF (additional)
	mg/L	m^3/h	mJ/cm^2	m^3/L	min					
B1	10	1	730	0,3	20	1	2	2	2	
B2	10	1.5	487	0,3	20		2	2	2	
B3	10	2	365	0,3	20		2	2	2	1

3.5.3 Third series (11-03-2015): varying H_2O_2 concentrations

The third series of dosing experiments was conducted on 11-03-2015. Based on the results of the first and second series of experiments (paragraph 4.2 and 4.5) it was decided to conduct experiments at the lowest UV dose tested during the first two series. For this, the lamp power was set at 80% and the feed flow (through the UV reactor) was 2.0 m^3/h. The flow over the ACF was 300 L/h, which corresponds to a contact time of 20 minutes. Furthermore the H_2O_2 concentration was decreased during the test period to investigate the influence of the H_2O_2 concentration on the degradation of the organic micropollutants. Instead of the standard 10% H_2O_2 solution a 1% H_2O_2 solution (Breustedt Chemie Apeldoorn) was used during the experiments in the third series.

During the test period the temperature (Testo 925), the UV transmission (Real tech UVT p200 BP) and H_2O_2 concentration (Prominent Dulcotest DT3B) were measured regularly using hand meters. Furthermore the UV intensity of the lamp, the flow through the UV reactor and ACF, and the pressure before the UV reactor were noted. The sampling points were identical to the sampling points during the first series (Table 3-9).

The first experiment was conducted at a H_2O_2 concentration of 10 mg/L. First, after 1 hour of operation, samples were taken for the analyses of pH/HCO_3, turbidity and nitrate. Samples were taken from the pretreated water and analyzed. Furthermore samples were taken for the analyses of BPP, AOC, DMS, DMST, DMSA and TOC. BPP and AOC samples were taken during this stage of the experiments, because this experiment was conducted under 'worst-case' conditions during this series of dosing experiments. After the samples had been taken the dosing of the mixture of organic micropollutants was started. After 60 minutes the first series of samples was taken. A second series of sampling took place 10 minutes later.

After sampling the dosing of the mixture was stopped and the H_2O_2 concentration was decreased to 5 mg/L. After 1 hour DMS, DMST, DMSA and TOC samples were taken followed by the start of the dosing of the mixture of organic micropollutants (N.B. DMS, DMST, DMSA and TOC were not dosed to the system). After 60 and 70 minutes the sampling took place for analysis of micropollutants.

Then, the H_2O_2 concentration was further decreased to 3 mg/L. After 1 hour samples were taken for the analyses of AMES, DMS, DMST, DMSA and TOC. AMES samples were taken during this stage of the experiments because these conditions correspond to probably 'worst-case' conditions during this series of dosing experiments. Previous experiments (Hofman-Caris et al., 2013) had shown that the chance of mutagenic byproducts formation increases with increasing UV dose and decreasing H_2O_2 concentrations (although for LP UV lamps chances are very small), so it was decided to carry out Ames Fluctuation Tests at the highest UV dose and lowest H_2O_2 concentration applied. After sampling the dosing of the mixture of organic micropollutants was started. As before samples were taken after 60 and 70 minutes.

In Table 3-12 an overview is given of the operational conditions, sampling points and (micropollutants) analyses of the third series of the dosing experiments.

Table 3-12 Overview operational conditions, sampling points and analyses of the third series of the dosing experiments (March 11th 2015). Lamp power 80%.

Experiment	dosage		UV		ACF			Sampling points					
	mixture of organic micropollutants	H_2O_2	Flow	Dose	Flow	Contact time	Analyses carried out in this experiment	Pretreated water (SF)	before UV	After UV	After ACF	After ACF (additional)	Drinking water
		mg/L	m^3/h	mJ/cm^2	m^3/h	min							
C1	no	10	2	365	0,3	20	BPP				1		1
C2	no	10	2	365	0,3	20	AOC	1		1	1		1
C3	no	10	2	365	0,3	20	DMS + TOC	1		1	1		
C4	yes	10	2	365	0,3	20	Org. micropollutants + metabolites	1	2	2	2		
C5	no	5	2	365	0,3	20	DMS + TOC	1		1	1		
C6	yes	5	2	365	0,3	20	Org. micropollutants + metabolites		2	2	2		
C7	no	3	2	365	0,3	20	AMES	2	2	2	2		2
C8	no	3	2	365	0,3	20	DMS + TOC	1		1	1		
C9	yes	3	2	365	0,3	20	Org. micropollutants + metabolites		2	2	2	1	

3.5.4 Additional DMS experiments

As the presence of DMS in the water source is a potential problem for WML, WML is very interested in the removal capacity of the UV/H_2O_2 process for DMS. During the third series of measurements at 11-03-2015 and 12-03-2015 also the presence of DMS in the influent before addition of H_2O_2, in the water after UV treatment, and after ACF was determined. The results are shown in Table 3-13.

Table 3-13: DMS measurements during the third series of experiments (11-03-2015 and 12-03-2015). DMS had not been dosed to the influent.

Experiment	Dosage	UV		AKF		Sampling points		
	H_2O_2	Flow	Dose	Flow	Contact time	Pretreated water (SF)	After UV	After ACF
	mg/L	m^3/h	mJ/cm^2	m^3/L	min			
D1	10	1	730	0,3	20	2	6	6

Additional DMS experiments, without dosing extra DMS, were conducted on 20-03-2015. The lamp power was set at 80%. Tests were conducted with two different flows through the UV reactor, respectively 1.0 and 2.0 m^3/h. The H_2O_2 concentration was also varied, respectively 10 and 5 mg/L. The flow over the ACF column was 300 L/h which corresponds to a contact time of 20 minutes. During the test period the temperature (Testo 925), was regularly measured with a hand meter, and appeared to vary between 12.0 and 12.2 °C. Furthermore the UV intensity of the lamp, the flow through the UV reactor and ACF, and the pressure before the UV reactor were noted. The sampling points were equal to the sampling points during the first series (Table 3-9).

The first experiment was conducted at a flow of 1.0 m^3/h through the UV reactor and a H_2O_2 concentration of 10 mg/L. First, samples were taken from the pretreated water for the analyses of pH/HCO_3, turbidity and nitrate. After one hour samples were taken for DMS, DMST, DMSA and TOC analyses.

After the experiment the flow was adjusted to 2.0 m^3/h through the UV reactor and the H_2O_2 concentration was still 10 mg/L. After one hour samples were taken for DMS, DMST, DMSA and TOC analyses. After this experiment the H_2O_2 concentration was decreased to 5 mg/L. Again samples were taken after 1 hour. In Table 3-14 an overview is given of the operational conditions, sampling points and analyses of the additional DMS experiments.

Table 3-14 Overview operational conditions, sampling points and analyses of the additional DMS experiments (March 20th 2015). Lamp power was set at 80%.

Experiment	Dosage	UV		AKF		Sampling points		
	H_2O_2	Flow	Dose	Flow	Contact time	Pretreated water (SF)	After UV	After ACF
	mg/L	m^3/h	mJ/cm^2	m^3/L	min			
E1	10	1	730	0,3	20	1	1	1
E2	10	2	365	0,3	20		1	1
E3	5	2	365	0,3	20		1	1

3.6 Collimated Beam experiments

To study the possibility to degrade DMS by means of a UV/H_2O_2 process experiments had to be carried out under well defined conditions, as the previous experiments did not give clear answers. For this purpose a collimated beam set-up was applied.

3.6.1 Collimated Beam installation

The UV dose is defined as the energy (or the amount of photons) absorbed by an irradiated object during a certain period per area or volume. In UV installations for water treatment, water flows along the lamps (or quartz sleeves). The UV dose then is determined by the lamp intensity and the residence time of a particle or microorganism in the reactor. This residence time in turn depends on the flow profile and the reactor geometry, which is difficult to characterize. Because of this reason often a collimated beam set up is used in laboratories, as it can be operated under standard, well defined, conditions.

A collimated beam set up offers the possibility to determine the effect of the UV dose on the inactivation of microorganisms and the conversion of chemical compounds under controlled and ideal conditions at laboratory scale. In the KWR installation dose-effect relations can be measured. The set up can be equipped with various types of UV lamps, like low pressure (LP) and medium pressure (MP) mercury lamps. In this way the dose-effect relation of a specific lamp can be determined (Harmsen, 2004). The collimated beam set up is schematically shown in Figure 3-3.

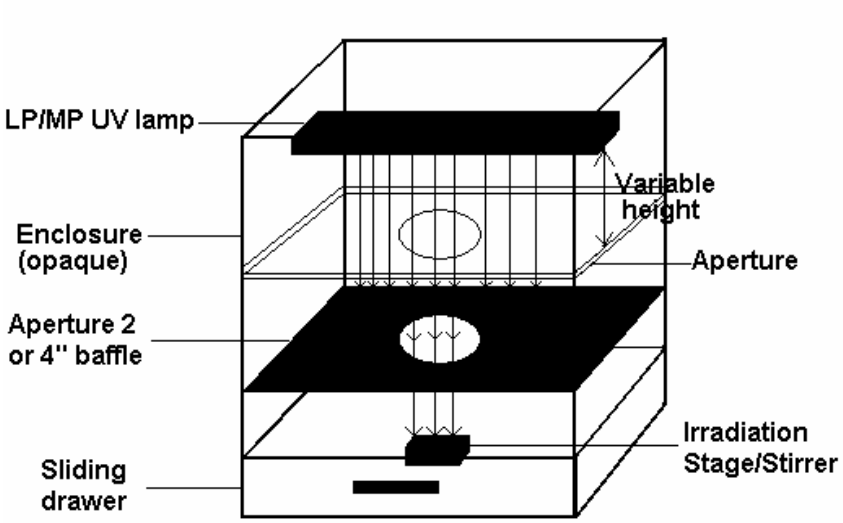


Figure 3-3: Schematic picture of a collimated beam installation

The lamp ('beamer' in Figure 3-3) is placed in a box made of stainless steel. The irradiation enters a wooden box through a hole. By means of a collimator, formed by adjustable plates, a parallel UV bundle hits the water sample. As the plates are removed or adjusted, the bundle can be adjusted, obtaining an optimal uniform irradiation of the sample surface. Furthermore, the sample is stirred during the irradiation.

By means of an automatic shutter, the UV irradiation is interrupted after a certain irradiation time. The required irradiation time is calculated based on specific conditions (for example UV_{254nm} (LP-lamp) or $UV_{200-300\,nm}$ (DBD- or MP-lamp), the UV-intensity of the lamp, sample volume, petri factor) using published calculation sheets (Bolton and Linden, 2003). If disinfection tests are carried out, a correction is made for the (DNA) absorption curve in the calculation of the irradiation time. During UV/H_2O_2 tests, such a correction is not made.

The UV dose (mJ/cm^2) has been defined as the product of the irradiation time (t in seconds) and the irradiation intensity (wavelength dependent UV output of the lamp) in mW/cm^2. A detailed description of the calculation of UV doses can be found in report BTO 04.014 "Protocol Collimated Beam UV" [Harmsen, 2004] and in the article "Standardization of Methods for Fluence (UV Dose) Determination in Bench-scale UV Experiments" (Bolton and Linden, 2003).

The lamp intensity (= irradiation intensity) is measured using an IL 1700 Research Radiometer and a SED sensor. This sensor detects UV-light between 185 and 310 nm. This equals the wavelength range that is applied for disinfection of microorganisms and conversion of organic micropollutants. Besides, the sensor has been equipped with a filter (the "wide-eye diffuser" (W)). This diffuser ensures that the light, entering the sensor under various corners, attributes equally to the total intensity measured.

3.6.2 Experimental method

Collimated Beam experiments were conducted with the pretreated water from site Heel. Different concentrations DMS (Dr. Ehrensdorfer; 99%; casnr. 3984-14-3) of 0.15, 0.50 and 1.0 µg/L and 10 mg/L H_2O_2 (JT Baker; Baker analyzed; casnr. 7722-84-1) respectively were added to the pretreated water. The three solutions were treated with a low pressure UV lamp. The distance between the lamp and the irradiated surface was 30 cm. The solutions were

treated using different UV-doses of 0, 100, 300, 500 and 700 mJ/cm^2 respectively. Each time 100 ml solution was irradiated. All samples were treated in an order chosen at random. In Table 3-15 an overview of the operational conditions and analyses is shown.

Table 3-15 Overview operational conditions and analyses during the Collimated Beam experiments

Experiment	Dosage		UV-dose	Analyses	
	DMS	H_2O_2		H_2O_2	DMS
	µg/L	mg/L	mJ/cm^2		
			0	X	X
			100		X
F1	0.15	10	300		X
			500		X
			700	X	X
			0	X	X
			100		X
F2	0.50	10	300		X
			500		X
			700	X	X
			0	X	X
			100		X
F3	1.0	10	300		X
			500		X
			700	X	X

All samples were analyzed for DMS by KWR according to standard procedures. As mentioned in Table 3-15 some samples were analyzed for H_2O_2 by KWR according to standard procedures. Furthermore blank H_2O_2, pH/HCO_3, turbidity, TOC and nitrate samples were taken from the tested solution (before addition of H_2O_2) from experiment 1 and analyzed by KWR according to standard procedures. pH and HCO_3, samples were also taken from the tested solutions 2 and 3 (without H_2O_2) from experiment 2 and 3.

3.7 Additional experiments with UV pilot reactor

Additional tests in the pilot reactor were conducted on July 8th 2015, based on the results of the dosing and the collimated beam experiments (Chapter 4 and 7) with DMS. Furthermore, in consultation with WML, additional compounds were tested. The lamp power was set at 80% and flow through the UV reactor was 1.0 m^3/h. The flow over the ACF was 300 L/h which corresponds to a contact time of 20 minutes. Furthermore the H_2O_2 concentration was 10 mg/L.

During the test period the temperature (Testo 925), the UV transmission (Real tech UVT p200 BP) and H_2O_2 concentration (Prominent Dulcotest DT3B) were measured regularly using hand meters. Furthermore the UV intensity of the lamp, the flow through the UV reactor and ACF, and the pressure before the UV reactor were noted. The sampling points were identical to the sampling points during the first series (Table 3-9).

Before the start of the dosing of several organic micropollutants, samples were taken for the analyses of pH/HCO_3, turbidity and nitrate. Samples were taken from the pretreated water and analyzed. Furthermore samples were taken from the pretreated water, after UV and after AKF for the analyses of TOC. After the samples had been taken the dosing of a first mixture of organic micropollutants, which contained among others 0.5 mg/L DMS, was started. Details of the composition of mixture 1 can be found in Table 3-3. After 60 minutes the samples were taken. After sampling the dosing of the mixture was stopped.

The dosing of a second mixture of organic micropollutants, which contained among others 1.0 mg/L DMS, was started. Details of the composition of mixture 2 can be found in Table 3-4. After 60 minutes the samples were taken and the dosing was stopped.

The dosing of a third mixture, which contained EDTA, was started. Details of the composition of mixture 3 can be found in Table 3-5. After 60 minutes the samples were taken. A second series of sampling took place 10 minutes later.

In Table 3-16 an overview is given of the operational conditions, sampling points and (micropollutants) analyses of the third series of the dosing experiments.

Table 3-16 Overview operational conditions, sampling points and analyses of the additional experiments (July 8th 2015). Lamp power 80%.

Experiment	dosage		UV		ACF			Sampling points			
	DMS	H_2O_2	Flow	Dose	Flow	Contact time	Analyses carried out per experiment	Pretreated water (SF)	before UV	After UV	After ACF
	µg/L	mg/L	m³/h	mJ/cm²	m³/h	min					
G1	0.5	10	1	730	0,3	20	DMS + NDMA +AMPA+ reference compounds+ sweeteners	1	1	1	1
G2	1.0	10	1	730	0,3	20			1	1	1
G3	0	10	1	730	0,3	20	EDTA	1	2	2	2

4 Results of pilot experiments in Heel

4.1 Modeling of the situation at site Heel

For the experiments the D200 reactor, equipped with two flow plates, was applied at a flow of 1 m^3/hour. The UV-transmission of the water is about 94%, as a result of which a relatively low amount of energy is required to obtain a certain UV-dose. To obtain information about the circumstances in the UV-reactor, CFD modeling was applied. An existing CFD model was used to approximate the average UV-dose in the reactor, and to determine how this will depend on the flow rate. In this model a reactor equipped with only one flow plate was used, but otherwise the reactor geometry was identical to the applied reactor at site Heel (which has two flow plates). Therefore, a difference might be expected between the modelled and applied reactors, but this difference will probably be small. Both reactors, with one and two flow plates were tested at Van Remmen UV Techniek in Wijhe, where it was found that the differences in actual conversion between both reactors are very small (difference in electrical energy per order < 10 % measured using water of the town of Wijhe, depending on the type of compound; also see section 5.1).

With the present modeling equipment it appeared not to be possible to calculate the exact flow through a reactor with two flow plates.In fact it would be necessary to perform a new CFD calculation when the flow through the reactor changes. However, in this case of changing flow rate the UV dose distribution was adjusted by a factor 1/Q (Q being the flow in m^3/hour). This assumption will be valid as long as the flow will be turbulent, which is expected as in these experiments only the flow was increased.

The distribution of the irradiation and UV-dose was calculated at a UV-T of 94%. The electric lamp power was assumed to be 120 W, with a UV-C power of 38 W. In order to decrease the lamp output, the power was decreased to e.g. 80%. For calculations the power was adjusted by multiplying the UV dose distribution by a factor P/120 (P being the electric lamp power in W). It is assumed that the UV-C power will change by the same factor.

At a UV-T of 94% reflection of irradiation by the reactor wall cannot be neglected, as is common practice for water with a lower UV-T value (like e.g. ± 75%, as was the case for Dunea, where the reactor also was tested). Taking into account this reflection, the UV-dose applied appeared to be significantly higher than estimated at the start of the project. This explains the relatively high UV doses applied in the first series of experiments.

A factor which at the moment cannotyet be accounted for in the model is the improvement of UV-T during the process. It was found that because of the treatment UV-T is increased from 94 to 96%. At such a high UV-T value a small increase in UV-T may cause a significant effect in degree of conversion. To obtain an idea on the magnitude of this effect modelling therefore was carried out at both 94 and 96% UV-T. The actual conversion probably will be between both predicted values.

The water matrix parameters are shown in Table 4-1.

Table 4-1: water matrix parameters, used in CFD modeling

pH	**7.5**
TOC	1.4 mg C/L
HCO_3^-	167 mg/L
NO_3^-	0.5 mg/L
H_2O_2	10 mg/L

In Table 3-6 an overview of the average UV-dose is provided at a certain lamp power at different flows through the reactor.

4.1.1 First dosing series (30-09-2014): determination of mutagenicity, AOC and BBP formation and conversion of micropollutants at one UV dose.

The experiments carried out on 30-09-2014 took place at a flow of 1 m^3/hour and a lamp power of 120 W, which results in a UV-dose of about 750 mJ/cm^2 (see Table 3-6).

4.1.2 Residence time distributions

By means of a dosed NaCl solution the residence time distribution was determined in the UV-reactor, in the first and in the second Activated Carbon (AC) filter. The results are shown in Figure 4-1.

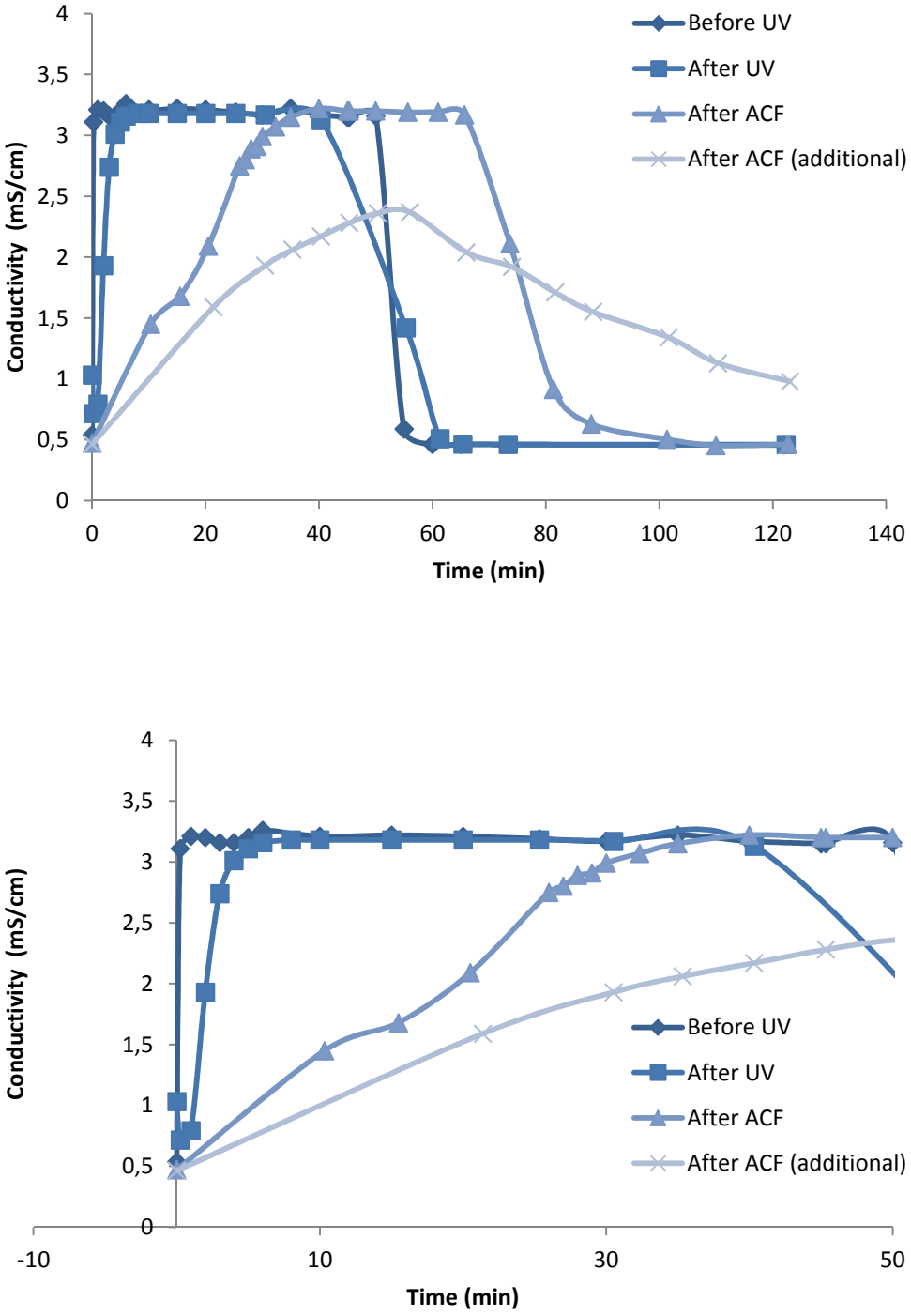


Figure 4-1: Residence time distribution in the UV-reactor and in both AC filters. Upper figure: residence time distribution curve over a period of two hours; lower figure: residence time distribution curve during the first 50 minutes.

From these data it was concluded that the UV-reactor shows a quick breakthrough with a small distribution. It seems to take a little longer before the salt passes through the reactor vessel, but this probably is caused by the fact that some conductivity data are missing at about t= 50 minutes. It takes about 10 minutes before the effluent of the UV-reactor reaches the first AC filter. However, as the conductivity increases rather rapidly, it can be concluded that there probably is a short-circuit current. As there are no data on activated carbon before t = 10 min., it is unknown what happened in the AC filter during this period. The breakthrough of the AC is faster, but during that period the conductivity decreases gradually. By comparing the breakthrough in the UV reactor and in the AC filter based on an average residence time (being circa 2 min. for the UV-reactor and circa 20 min. for the AC filter) it is shown that both are comparable, with regard to the number of bed volumes.

Based on these results it was decided to take the first AC sample after at least 60 min to be sure that the reactor was running stably. In fact, sampling for the UV reactor took place after 90 and 100 min., and for the AC filter after 110 and 120 min.

4.1.3 Dosing of organic micropollutants

A mixture of organic micropollutants (containing mainly pharmaceuticals and some reference compounds) was added to the pretreated feed water. Figure 4-2 shows the relation between the amounts added and the resulting initial concentrations of the various micropollutants.

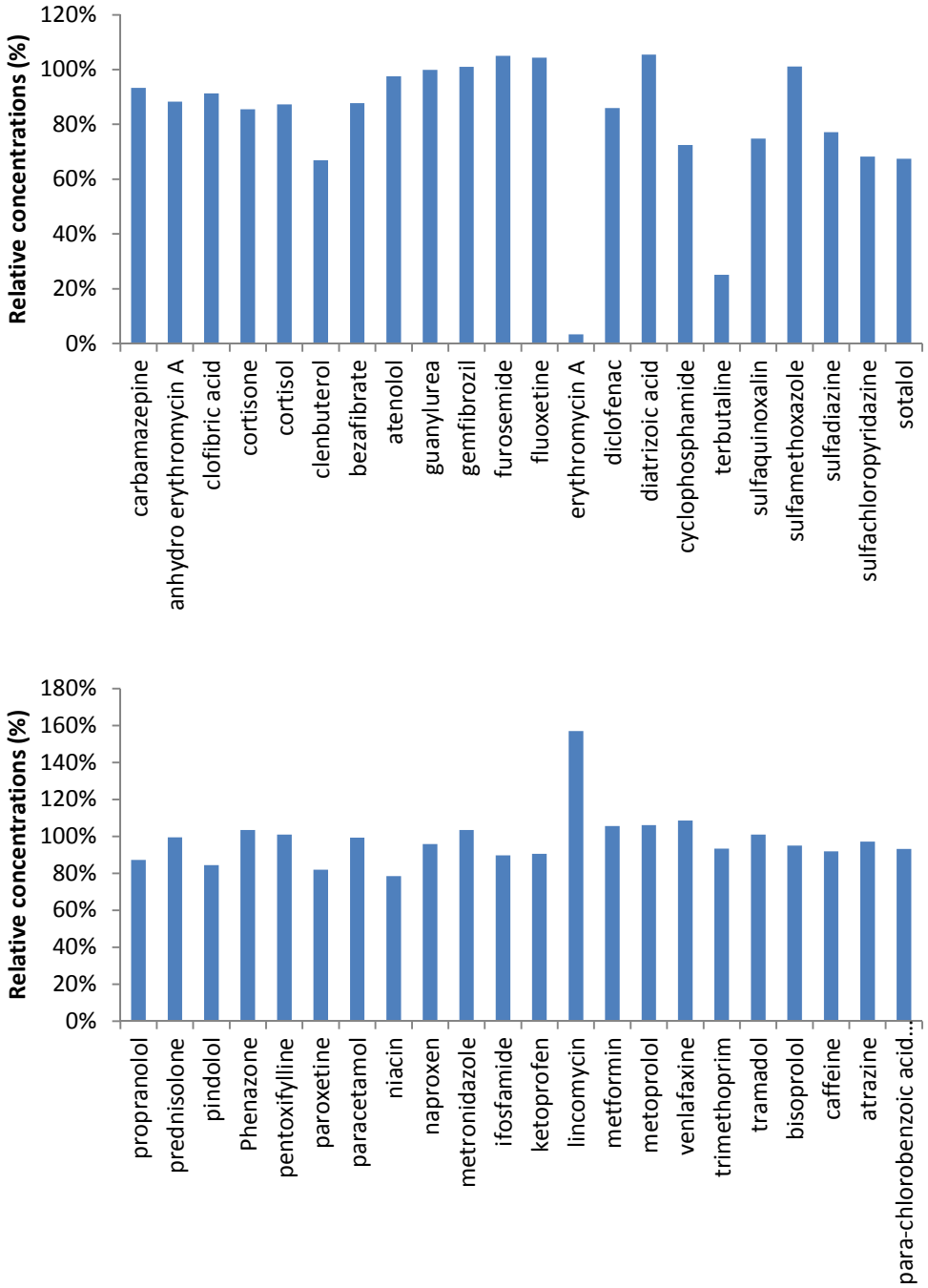


Figure 4-2: concentrations of organic micropollutants relative to the concentrations aimed at.

The measured erythromycin A concentration is very low, because this compound is rapidly converted into its metabolite anhydro-erythromycin A, which is observed in a relatively high concentration and was not dosed. The combined concentrations of both erythromycin A and anhydro-erythromycin A correspond with the added amount of erythromycin A.

Previous experiments already showed that some compounds are more difficult to analyze than others. This is mainly the case for terbutaline and niacin, which in this case too seem to be present in a lower concentration than was expected. It is not clear what caused the higher

concentration of lincomycin; previous analysis of the pretreated water (July 2014) did not show elevated concentrations in the water.

4.2 Removal of organic micropollutants

4.2.1 Water quality measurements

The water quality during the first series of dosing experiments is shown in Table 4-2. TOC is not changed by the UV process. This doesn't mean that the organic matter did not change due to the UV process, only that the total amount of organic matter didn't change. After ACF the TOC had been partly removed. It is known that the pesticide DMS can be observed in the influent of WTP Heel. Analysis of this compound also gives information on the possible presence of two other pesticides, DMST and DMSA. However, only DMS could be observed in the influent of the reactor. This compound was removed by the UV treatment.

Table 4-2: Water quality data for the first series of dosing experiments, 30-09-2014

	pH	HCO_3	nitrate		TOC	Turbidity	DMSA	DMS	DMST
		mg/l	mg/L NO_3	mg/L N	mg/L C	FTE	µg/L	µg/L	µg/L
Rapid sand filtrate	7.52	167	2	0.5	1.4	<0.1	< 0,05	0,1	< 0,05
After UV (912 mJ/cm²)					1.5		< 0,05	< 0,05	< 0,05
After ACF (CT 20 min.)					1.1		< 0,05	< 0,05	< 0,05

4.2.2 Conversion of organic micropollutants

The conversion or removal of organic micropollutants was measured after treatment with UV/H_2O_2. The results are shown in Figure 4-3.

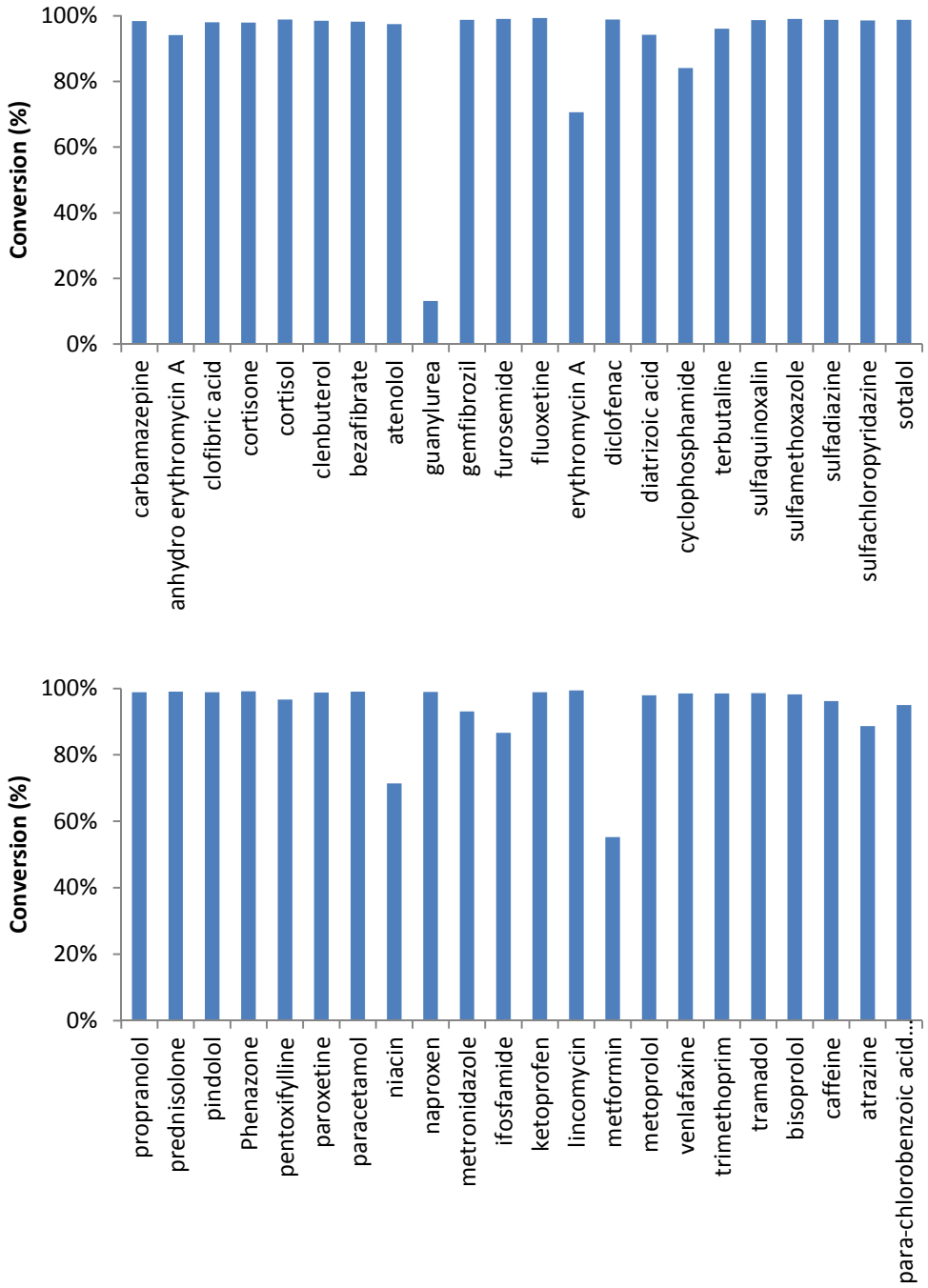


Figure 4-3: conversion of organic micropollutants during the UV/H_2O_2 process (30-09-2014). UV dose circa. 912 mJ/cm², 11 mg H_2O_2 /L.

It is known that metfomin (and its metabolite guanylurea) are difficult to convert by means of a UV/H_2O_2 process (Wols et al., 2014), as is confirmed by the results obtained. In case the effluent concentration was decreased below the reporting limit, the reporting limit was used as the effluent concentration in conversion calculations. As a result the conversions shown

represent minimum conversions: the real conversion may have been higher. Although Erythromycin A was converted to a concentration below the reporting limit, the conversion calculated is relatively low, which can be explained from the low initial concentration. Thus, it cannot be concluded that it is difficult to convert Erythromycin A by means of UV/H_2O_2. As its metabolite Anhydro-erythromycin A was degraded to a high extent, it can be assumed that the conversion of Erythromycin A also will be high.

A similar situation can be observed for niacin, which also was converted to a concentration below the reporting limit.

4.2.3 Activated carbon filtration

A UV/H_2O_2 process in general is followed by a filtration step over activated carbon (or in some cases dune filtration). This filtration step has a dual purpose:

1. To remove the excess of H_2O_2
2. To remove possibly formed byproducts

In the pilot experiments at site Heel two AC filters are applied: the second one to make sure that no organic micropollutants are introduced into the environment. The results of these filtration steps are shown in Figure 4-4 and Figure 4-5.

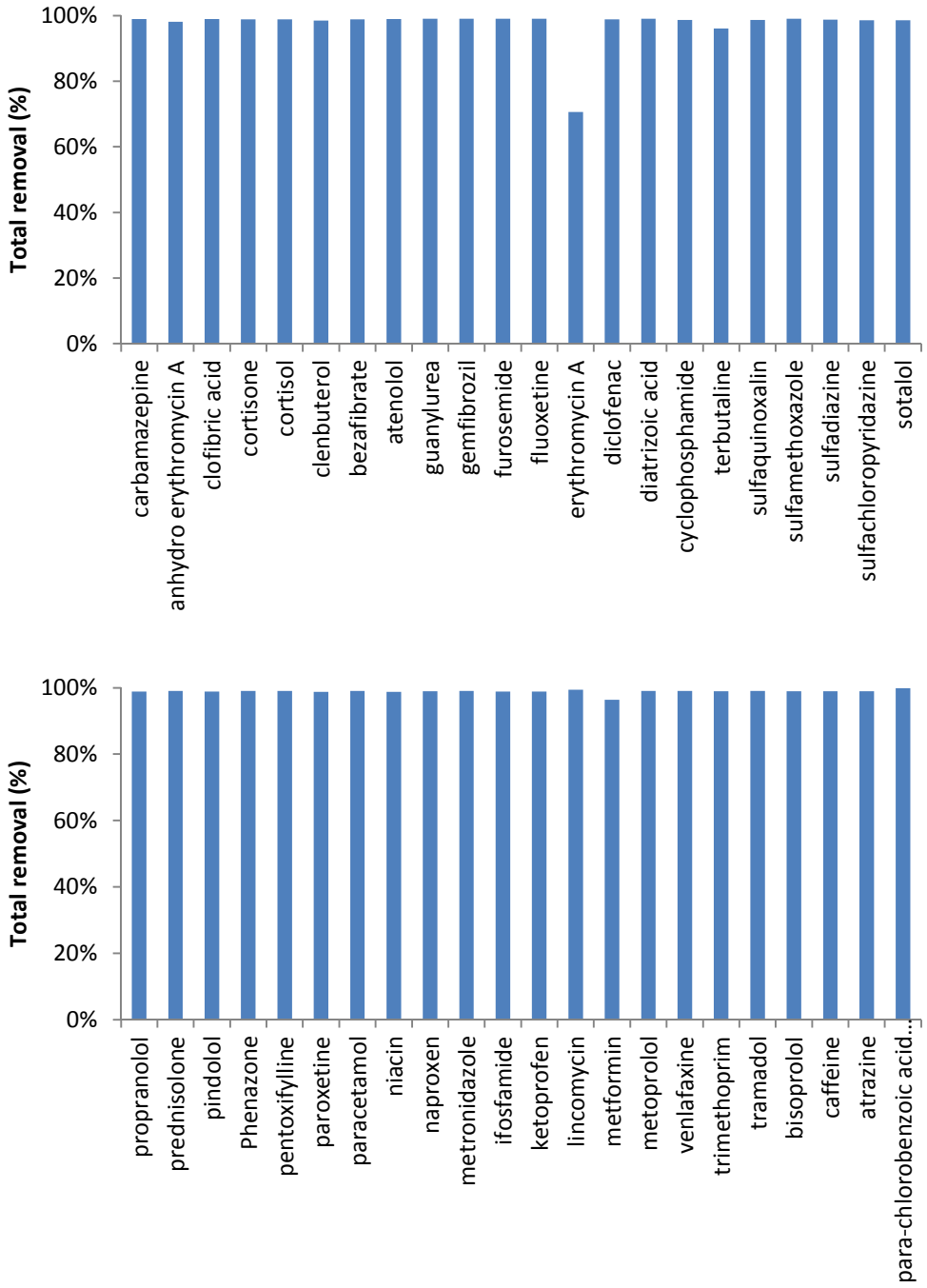


Figure 4-4: Total removal, based on influent concentrations, after the first filtration over activated carbon (contact time 20 min.).

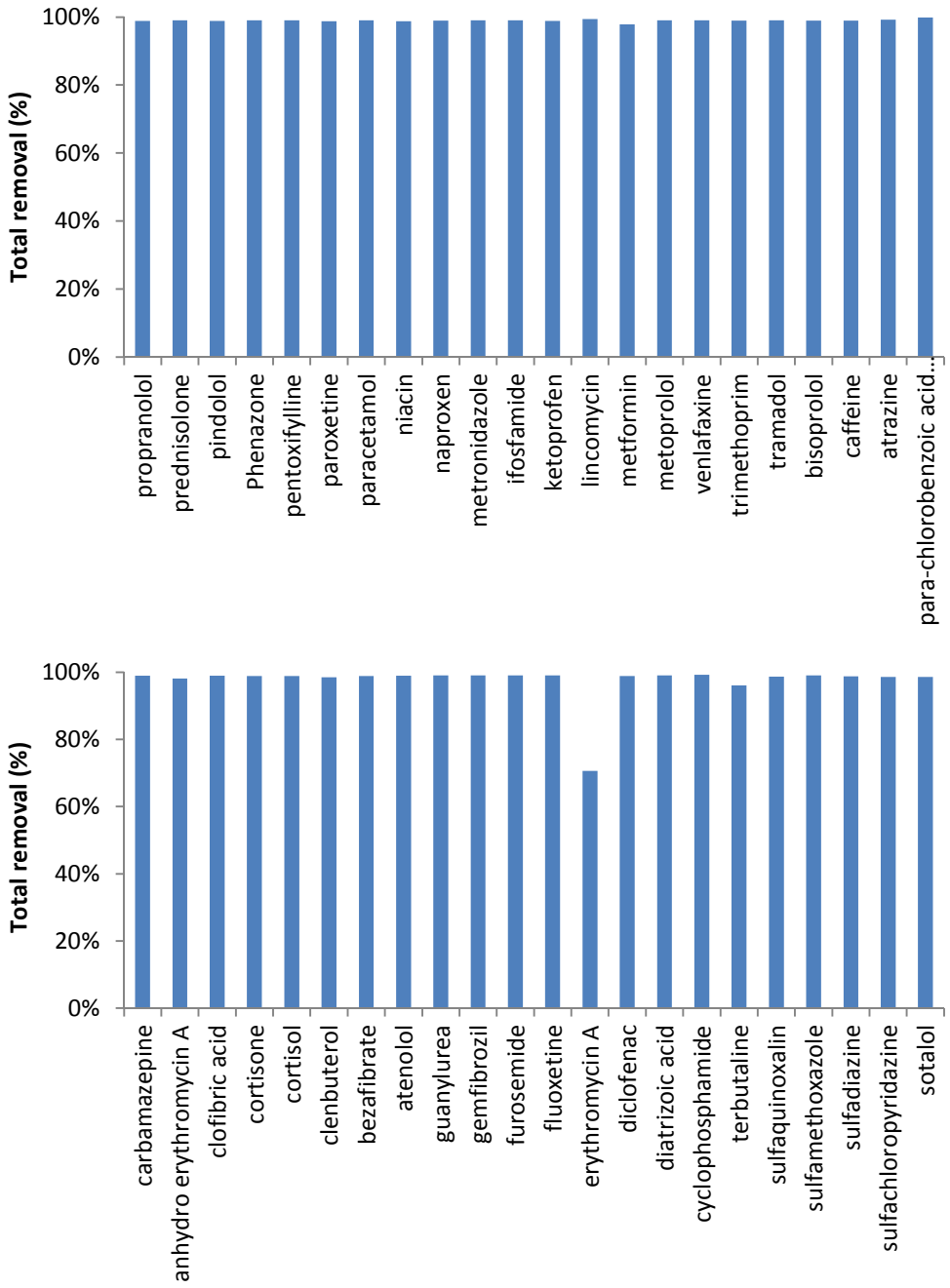


Figure 4-5: Total removal, based on influent concentrations, after filtration of the waste stream over activated carbon.

The results of the ACF step show that nearly all compounds are removed to a high extent (figure 4.4). The relatively low removal of erythromycin A again probably is caused by the calculation based on a low initial concentration, as the removal of its metabolite anhydro-erythromycin A is very high (there is no reason why this should be significantly different for erythromycin A itself).

From Figure 4-4 (and Figure 4-5) it can be concluded that the contact time is long enough to remove possible traces of organic micropollutants, and to prevent micropollutants from being present in the effluent of the process.

4.2.4 Fate of metabolites and transformation products

Special attention was paid to the fate of metabolites of (polar) organic micropollutants during the UV/H_2O_2 process. Although in literature much attention is being paid to the conversion of pharmaceuticals from (waste)water, hardly any research has been done on their metabolites. Besides, as not all compounds are mineralized during the process, it cannot be excluded that metabolites are formed during the process. Figure 4-6 shows the fate of known metabolites that can be analyzed. As the anhydro-erythromycin A concentration was relatively high, the fate of the other metabolites is shown in a separate graph.

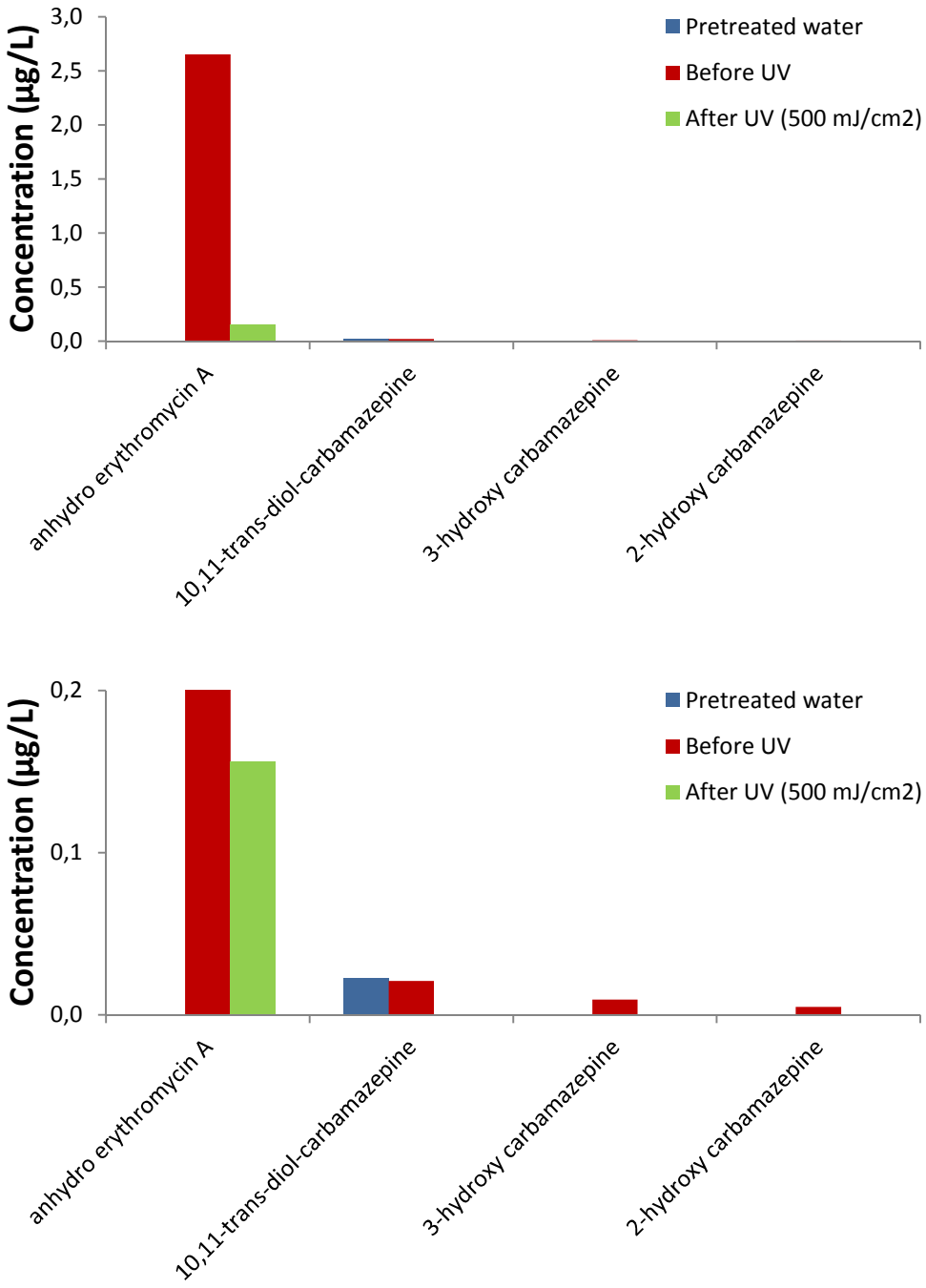


Figure 4-6: Conversion of some known metabolites during the UV/H_2O_2 process. Upper graph: total overview. Lower graph: overview of metabolites at lower concentrations (the concentration of anhydro erythromycin A is about 2.6 µg/L, see upper graph).

From these results it can be concluded that anhydro-erythromycin A is present from the start: it was formed almost instantaneously after addition of erythromycin A from the stock solution. The pretreated water from Heel appeared to contain a small amount of 10,11-trans-diol-carbamazepine, which decreased a little after addition of H_2O_2. It seems that addition of H_2O_2 results in the formation of two other metabolites of carbamazepine, 3-hydroxy- en 2-hydroxy-carbamazepine. However, these metabolites were found to be effectively degraded during the UV/H_2O_2 process, as they cannot be observed anymore afterwards.

In ozone processes the conversion of bromide into bromate can be a problem. This was the reason why ozone was not applied in this pilot investigation. However, it is well known that UV/H_2O_2 processes cannot convert bromide into bromate. Therefore, the bromate concentration in the treated water has not been measured.

4.2.5 Biological stability

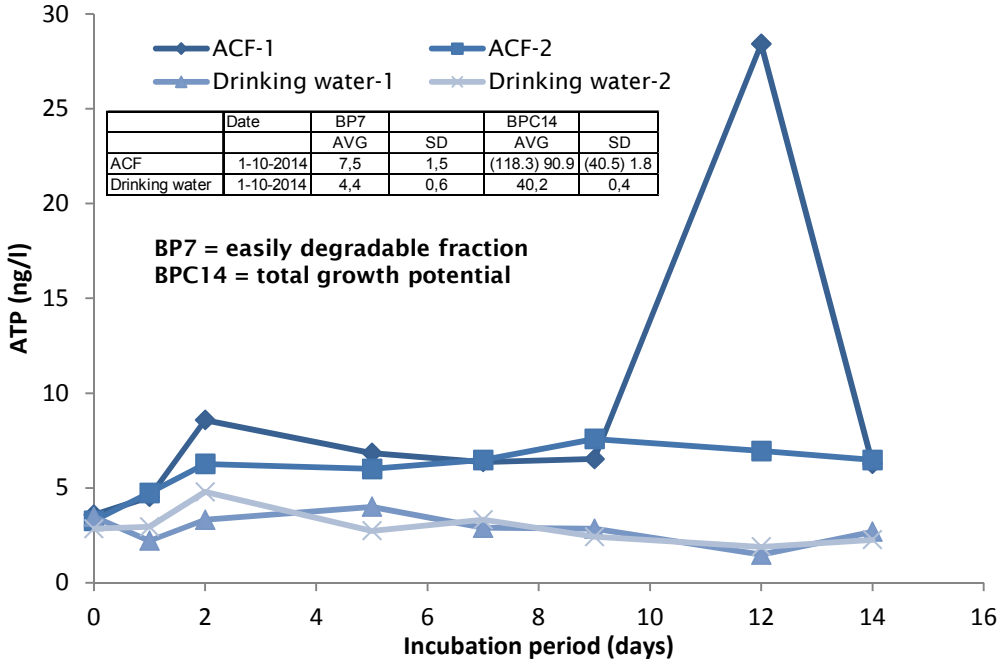
As advanced oxidation processes may also degrade natural organic matter, it is possible that the concentration of Assimilable Organic Carbon (AOC) may increase, resulting in a lower biological stability of the produced water . This was tested by measuring the amounts of AOC and the biomass production potential (BPP) in the water at different moments during the process. The BPP is measured as the total concentration of ATP (v.d. Kooij en Veenendaal, 2014)

. The results are shown in Table 4-3 and Figure 4-7

Table 4-3:biological stability: AOC and BPP

	AOC (µg/L)	BPP (ng/L.day)
Pretreated water	1.8 ± 0.1	
After UV/H_2O_2	0.1*) ± 0.0	
After ACF	9.8 ± 0.9	118.3 ± 40.5
Drinking water	3.5 ± 0.8	40.2 ± 0.4

*) no growth



	Date	BP7		BPC14	
		AVG	SD	AVG	SD
ACF	1-10-2014	7,5	1,5	(118.3) 90.9	(40.5) 1.8
Drinking water	1-10-2014	4,4	0,6	40,2	0,4

Figure 4-7: BPP of the treated water at several moments, measured in duplo (drinkingwater 1 and 2).

From Figure 4-7 it can be observed that:

- The BPP value of 118.3 measured after ACF probably is not realistic. A value of 90.9 seems to more probable.
- The BPP values of both water types (drinking water and after ACF) are low;
- The BPP after ACF is higher than in the finished water;
- BP7 after ACF > finished water: water after ACF contains more easily biodegradable compounds;
- Finished water contains no biopolymers, which are difficult to degrade. After a small maximum the amount decreases.
- ACF: the water contains more biopolymer (from the filter) but the BPP still is low.

Therefore, it can be concluded that the BPP of the water increases by the advanced oxidation process, but that, at least during this experiment, it still is low, and would not be a problem for drinking water production. In general it is assumed that at BPC14<100 no problems will arise with the biostability of drinking water (Wim Hijnen, KWR, 02-11-2015).

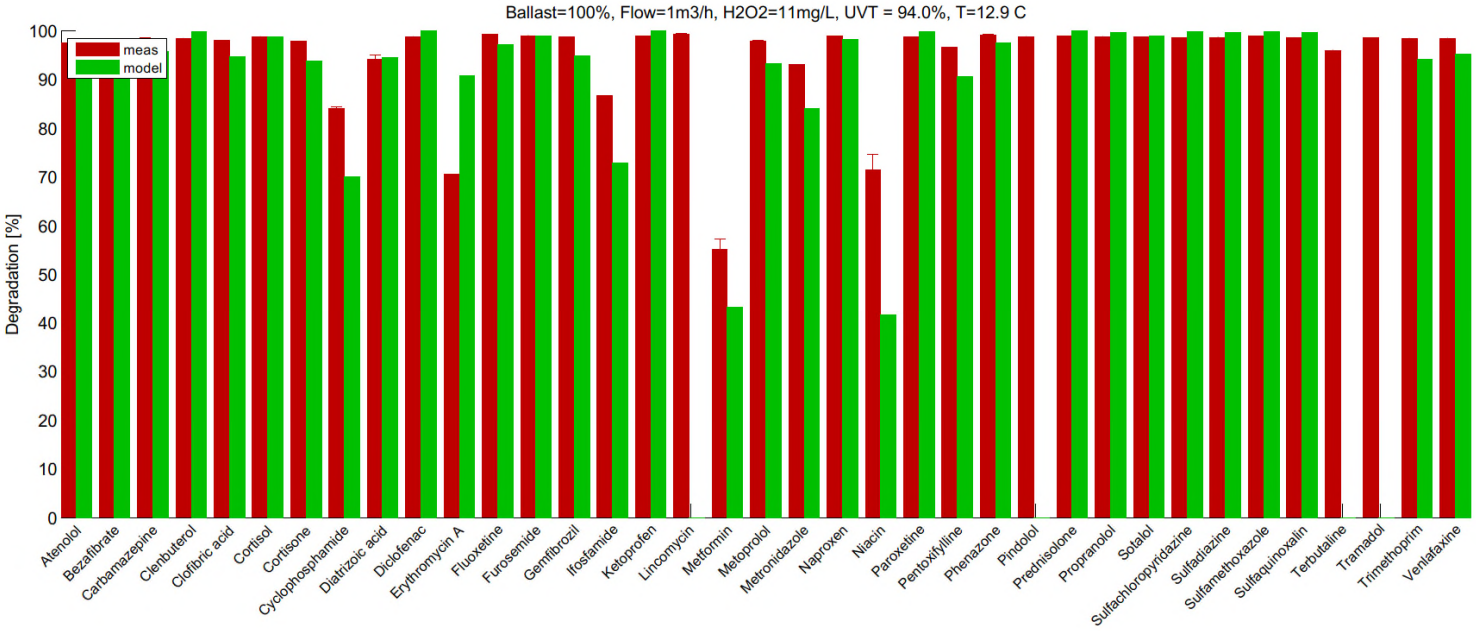
4.3 Comparison of pilot results and model calculations for experiments of 30-09-2014

OMP conversion results are presented as percentage conversion. It should be noticed that in this way the distinctiveness at conversions above 90% is limited (increasing the conversion from 90 to 99% requires at least twice as much energy). Figure 4-8 shows a comparison of the experimental conversions and the calculated conversions. For some compounds (lincomycin, pindolol, terbutaline and tramadol) no model calculations could be performed, as the reaction parameters required (quantum yield, reaction rate constants for the reaction with hydroxyl radicals, and the specific molar absorption coefficient) were not available.

From the comparison it can be concluded that there is a rather good agreement between the experimental and the predicted conversion: an average value of 92% versus 88%. The fact that the experimental conversion often appears to be a little higher than the predicted value can be explained from assumptions in the calculations (like the correction of the UV dose

distribution with a factor 1/Q), and the fact that the CFD calculation was made for a reactor equipped with one flow plate, whereas the reactor applied had two flow plates. Besides, in the calculations it was assumed that the composition of the DOC in this water was identical to the DOC in the water used for modeling. This probably will not have been exactly the case, as the UV-T of the water at site Heel is about 94%, whereas the water on which the model was based had a UV-T of about 75%. This may have affected the reactions that occurred, but, as explained in paragraph 4.1, this cannot be directly accounted for in the model.

In general conversions of most compounds are very high. Only for metformin and niacin lower conversions can be obtained. It is known that metformin is a compound which is very difficult to oxidize in a UV/H_2O_2 process, and also niacin requires a lot of energy for degradation (Wols et al., 2013). For lincomycin, pindolol, terbutaline and tramadol no information on reaction constants and quantum yield/ molar absorbance is available, as a result of which the conversion could not be predicted.


Ballast=100%, Flow=1m3/h, H2O2=11mg/L, UVT = 94.0%, T=12.9 C
meas
model
Degradation [%]
0
10
20
30
40
50
60
70
80
90
100
Atenolol
Bezafibrate
Carbamazepine
Clenbuterol
Clofibric acid
Cortisol
Cortisone
Cyclophosphamide
Diatrizoic acid
Diclofenac
Erythromycin A
Fluoxetine
Furosemide
Gemfibrozil
Ifosfamide
Ketoprofen
Lincomycin
Metformin
Metoprolol
Metronidazole
Naproxen
Niacin
Paroxetine
Pentoxifylline
Phenazone
Pindolol
Prednisolone
Propranolol
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Terbutaline
Tramadol
Trimethoprim
Venlafaxine

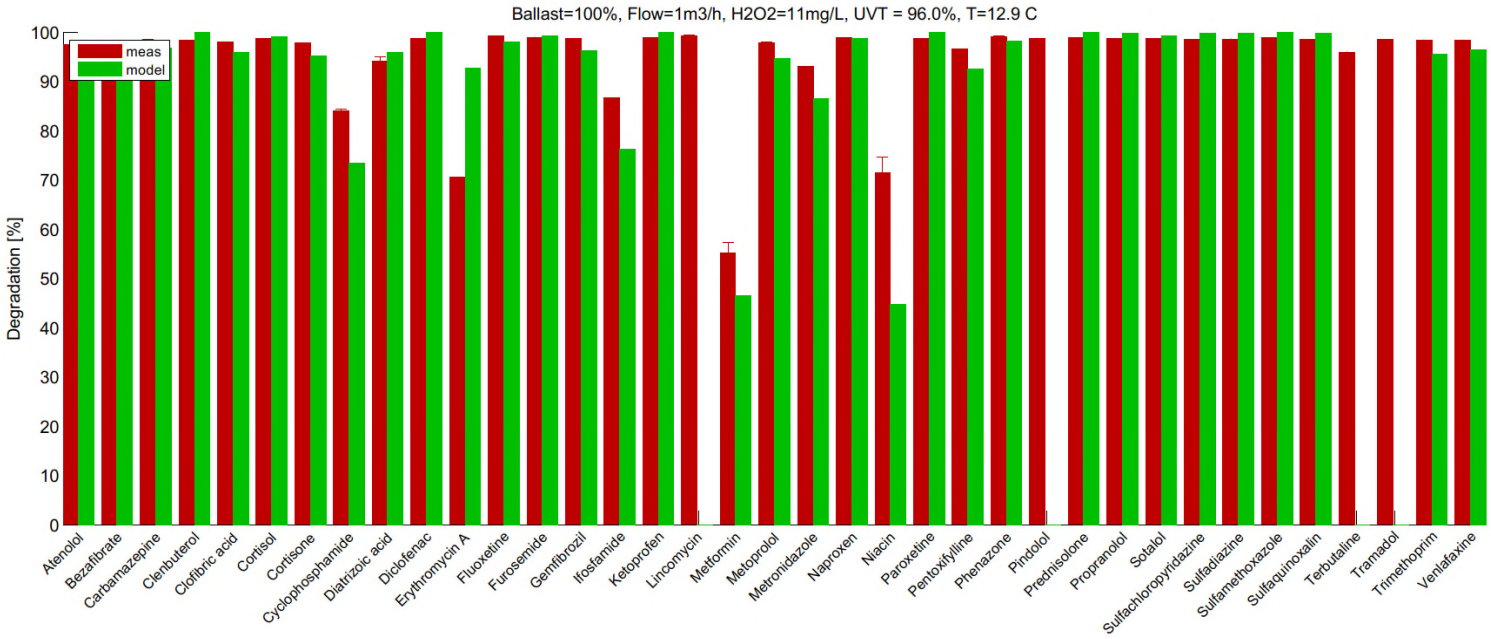


Figure 4-8: Measured and predicted conversions in the UV/H_2O_2 reactor at site Heel at 11 mg H_2O_2/L and P=120W. Upper graph predictions calculated with UV-T = 94%, lower graph predictions calculated with UV-T=96%. During the experiment UV-T increased from 94 to 96%

4.4 Predicted effects of reactor parameter settings, based on model calculations

The first series of experiments was carried out at a high UV dose of about 912 mJ/cm^2. As a result the average conversion of all organic micropollutants in the test was 92%. This is very high, and probably for full scale applications such a high conversion of all compounds will not be necessary. Therefore, a lower UV dose probably will result in sufficient conversion, decreasing the energy demand of the process. This will have a large effect on the operating conditions, as the increase in energy demand required to increase the conversion from high to very high is relatively large: increasing the conversion from 90 to 99% will require at least twice as much energy. Another factor that can be optimized, apart from the UV-dose, is the H_2O_2 dose.

To determine the required UV dose and H_2O_2 concentration, process settings can be based on the desired conversion of a certain (model or standard) component or a set of components. Process parameters of previous experiments with a UV/H_2O_2 pilot reactor at Dunea (Hofman-Caris en Beerendonk, 2011) were based on the conversion of atrazine as a model compound. The highest atrazine concentration in the pre-treated water was determined, and parameters were accordingly set to decrease the atrazine concentration below the reporting limit, in this case meaning 80% conversion. As atrazine is a relatively difficult compound to oxidize, a high conversion of atrazine will be accompanied by a high conversion of other micropollutants too. Such a target value has not yet been set for site Heel, but probably 100% conversion for all compounds will not be required.

By means of modeling it was investigated what will be the effect of decreasing UV doses or adjusting the H_2O_2 concentration on the conversion of organic micropollutants. During the experiments carried out on 30-09-2014 the average conversion was 92%, whereas 88% had been predicted. So, it was decided that a further decrease in conversion would be acceptable, and that the operating conditions could be further optimized.

There are two ways to decrease the UV dose in the reactor:

1. Increasing the flow (thus decreasing the residence time in the reactor)
2. Decreasing the lamp output. This, however, is limited to a certain value, as otherwise the stability of het output cannot be guaranteed.

The results of the modeling were already shown in Table 3-6. Table 4-4 shows the predicted effect of decreasing the UV dose (by decreasing the flow and/or adjusting the lamp power) on the conversion. Table 4-5 shows the effect of decreasing the H_2O_2 concentration at various lamp powers. These calculations were based on the average predicted conversion of the mixture of organic micropollutants (pharmaceuticals).

Table 4-4: Overview of the predicted average conversion of all pharmaceuticals at various flows through the UV/H_2O_2 pilot reactor at site Heel.

Flow [m^3/h]	Average conversion of pharmaceuticals at P=120 W [%]	Average conversion of pharmaceuticals at P=90 W [%]
1,0	88	84
1,5	81	75
2,0	75	68
2,5	70	62

Table 4-5: Overview of the predicted average conversion of all pharmaceuticals at various H_2O_2 concentrations in the UV/H_2O_2 pilot reactor at site Heel, at a flow of 1m³/uur and UV-T = 94%.

H_2O_2 [mg/L]	Average conversion of pharmaceuticals at P=120 W [%]	Average conversion of pharmaceuticals at P=90 W [%]
10	88	84
6	82	77
3	72	66
1	56	50
0	38	34

The results shown in the previous tables are shown in more detail in Figure 4-9-Figure 4-12.

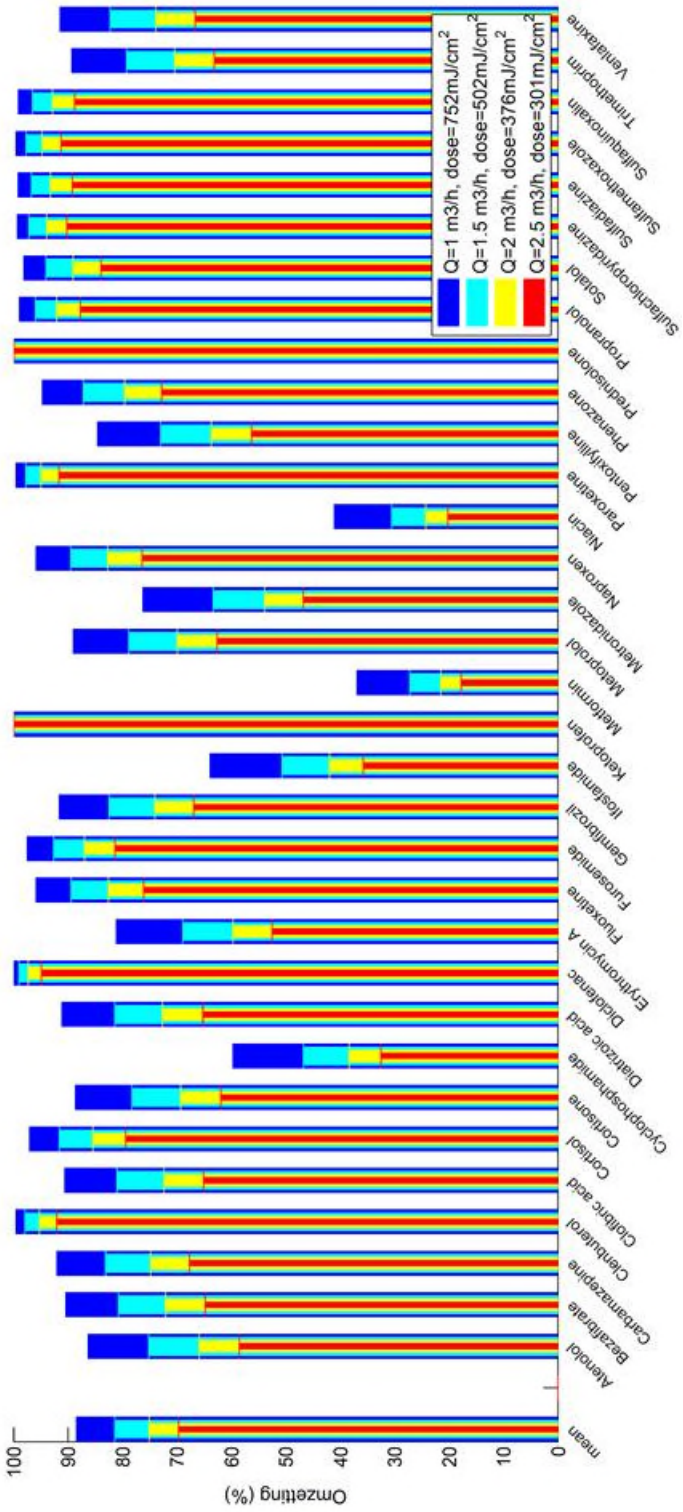


Figure 4-9: Effect of variation of flow: modeled conversion in the UV/H_2O_2 reactor at site Heel at 10 mg H_2O_2/L and P = 120 W.

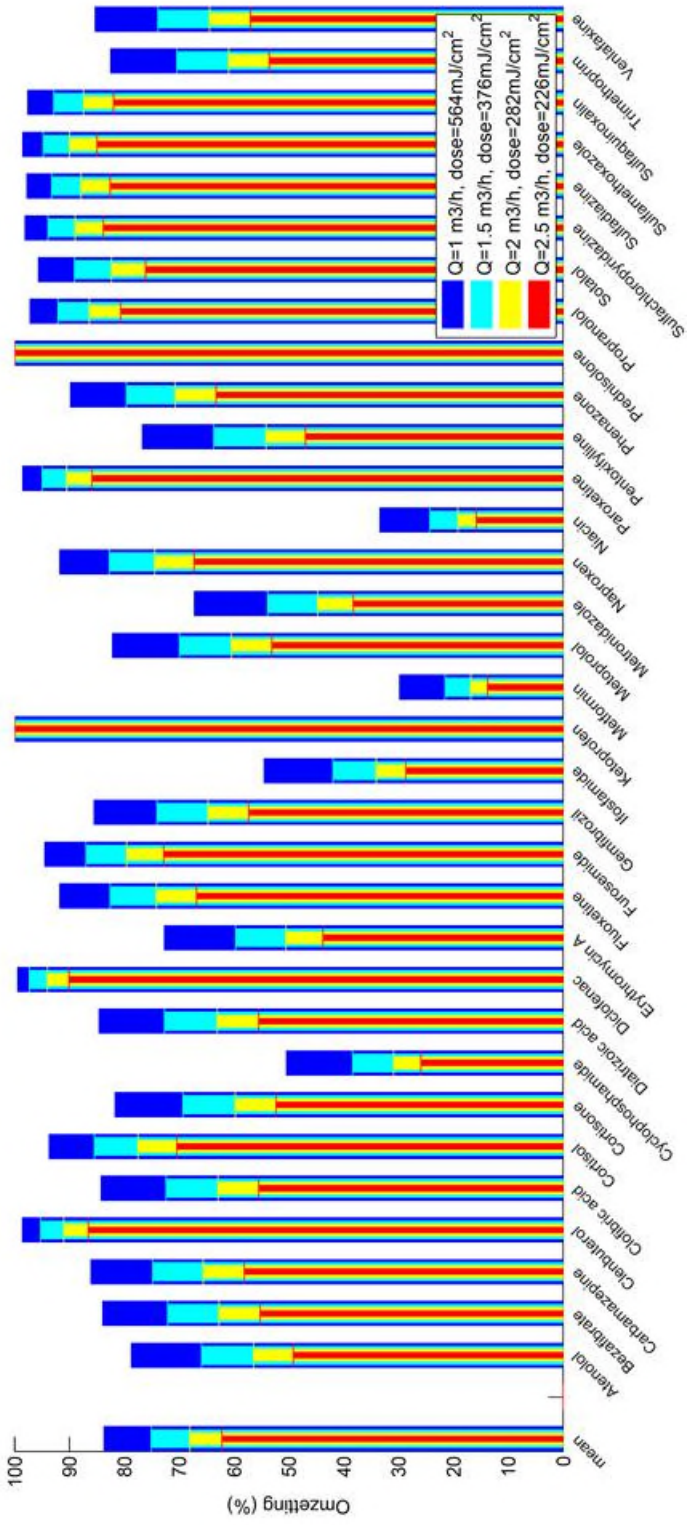


Figure 4-10: Effect of variation of flow: modeled conversion in the UV/H_2O_2 reactor at site Heel at 10 mg H_2O_2/L and P = 90 W.

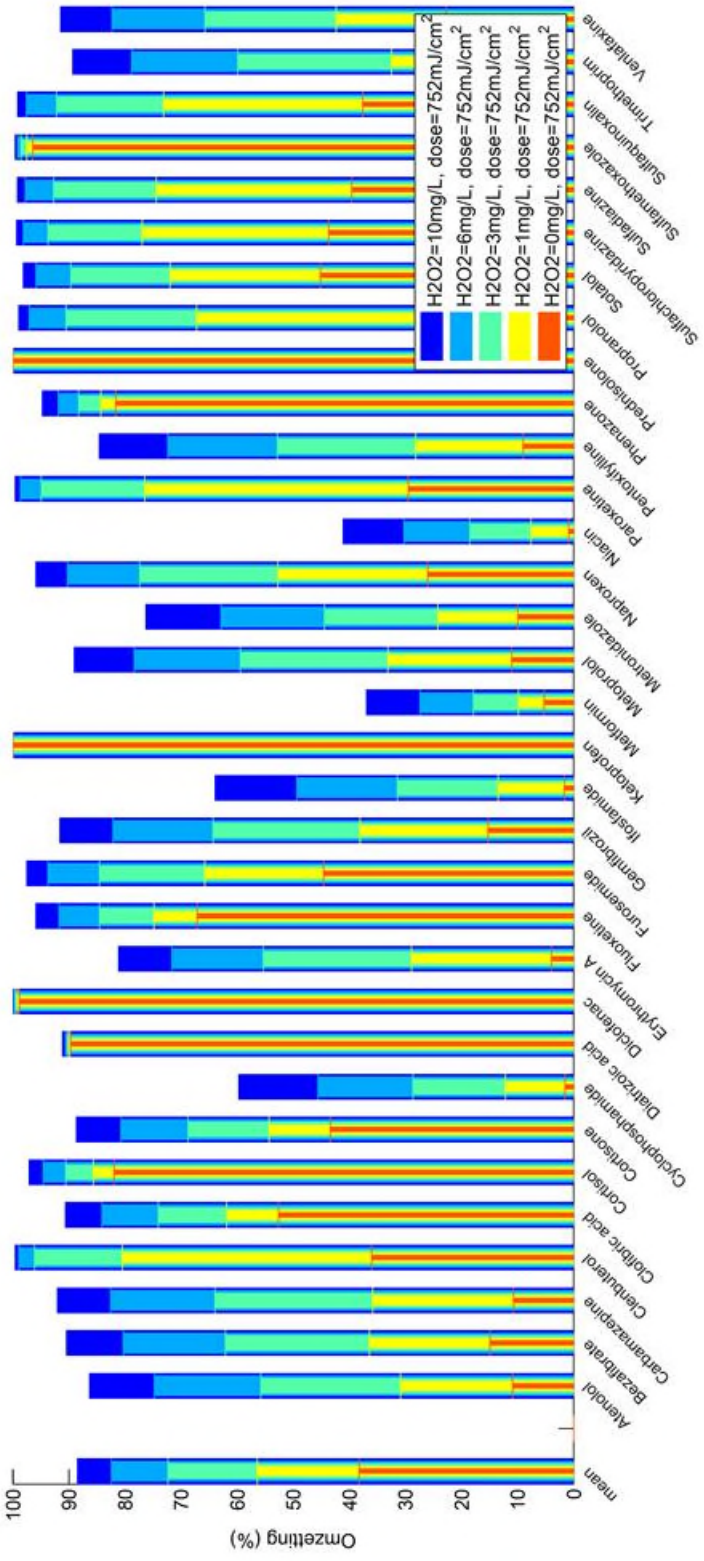


Figure 4-11: Effect of variation of H_2O_2 concentration: modeled conversion in the UV/H_2O_2 reactor at site Heel at 1 m^3/h and P = 120 W.

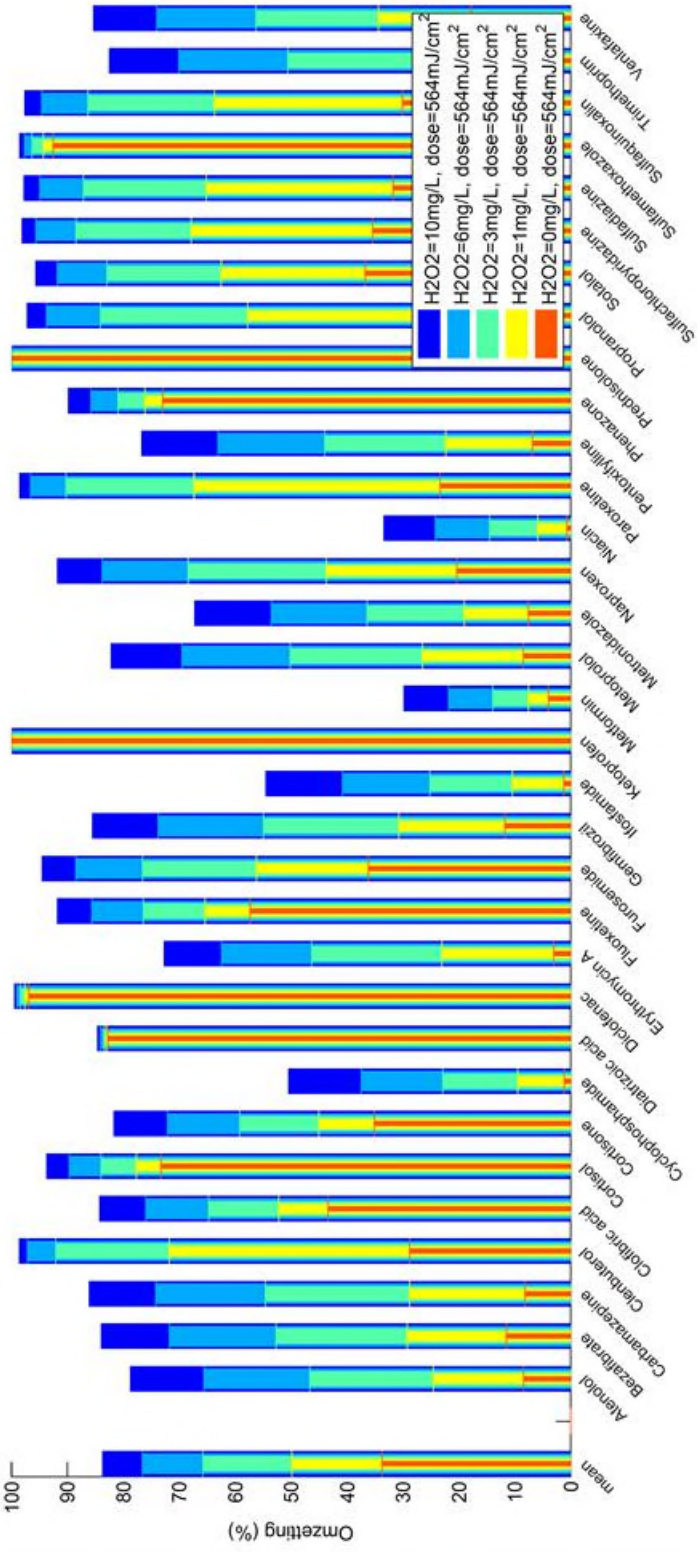


Figure 4-12: Effect of Variation of H_2O_2 concentration: modelled conversion in the UV/H_2O_2 reactor at site Heel at 1 m³/uur and P = 90 W.

4.5 Second series of experiments (18-11-2014); experiments at three different UV doses

Based on the predictions made in section 4.4 for the second series of experiments the flows and doses shown in Table 4-6 were chosen. For practical reasons the flow was not increased any further. It was decided to decrease the lamp power to 80% (96 W). H_2O_2 concentrations were kept constant at about 10 mg/L.

Table 4-6: Process conditions for the second series of experiments (18-11-2014). Calculations based on a lamp power of 80% (96W)

Flow (m^3/uur)	Calculated UV-dose (mJ/cm^2)
1	730
1.5	487
2	365

The experiments were carried out as was described before.

4.5.1 Preparation of influent

First the influent OMPs concentrations were compared to the expected concentrations. Figure 4-13 shows the organic micropollultant concentrations after dosing in the solution at the start of these experiments. During the second series of experiments it seems that some concentrations were significantly lower than was expected. Some compounds (anhydro-erythromycin A, furosemide, fluoxetine, terbutaline, sulfamethoxazole, sulfadiazine, pindolol, phenazone, lincomycin) displayed a strong decrease. At the moment it is not yet known what caused this decrease. The samples had been frozen prior to analysis, but there are no indications that this may have caused the decrease.

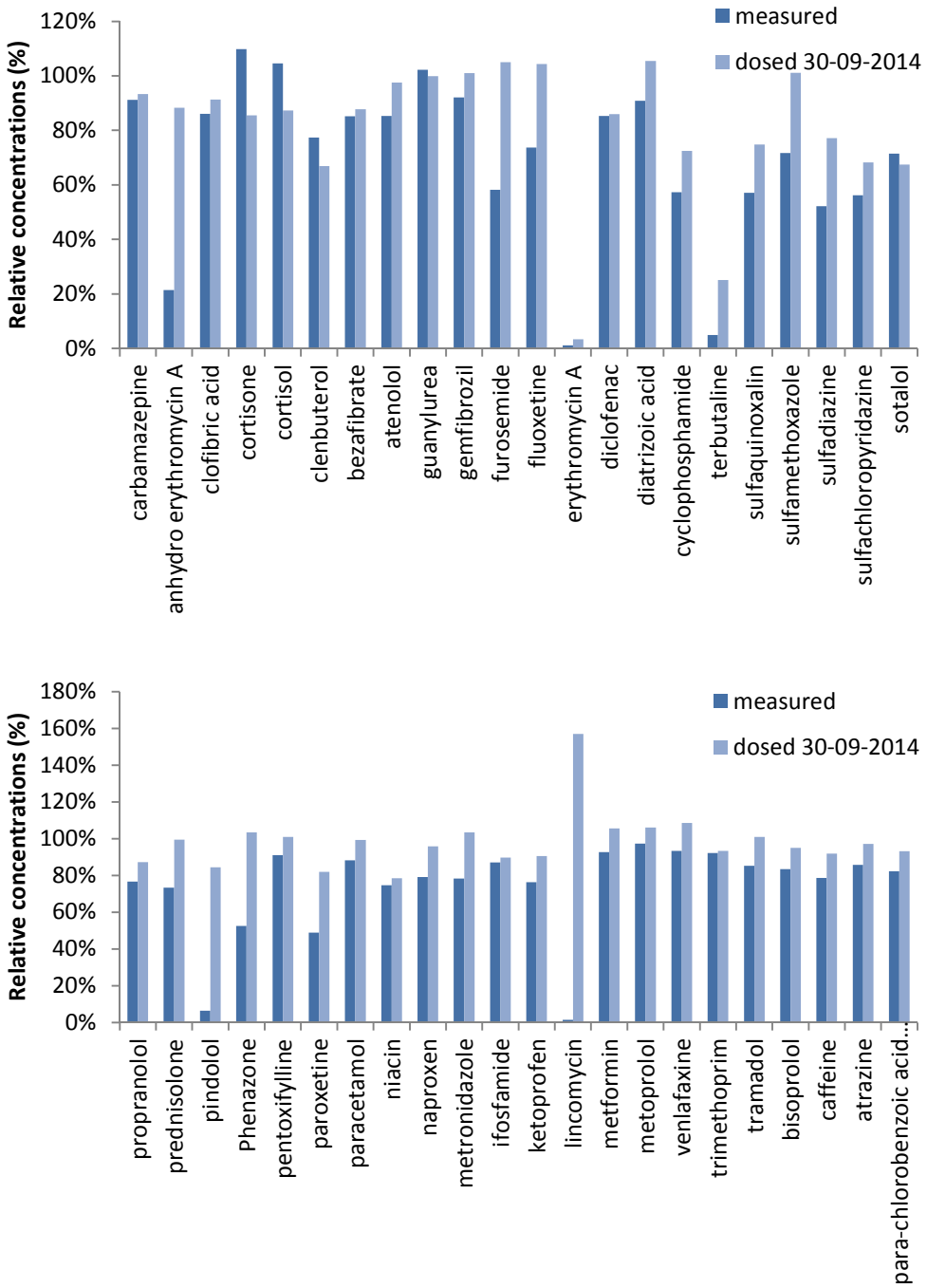


Figure 4-13: Relative concentrations of pharmaceuticals (based on theoretical concentrations) in solution used.

4.5.2 Conversion of pharmaceuticals

The conversion of the compounds was measured at different flow rates as described before. The results are shown in Figure 4-14. These measurements were carried out at a lamp power of 80%. It can be seen that the conversions in general decrease with increasing flow (related to a decreasing UV-dose). However, the decrease in conversion was less than was expected based on modeling, as shown in Table 4-7. Again the performance of the reactor was better than had been predicted.

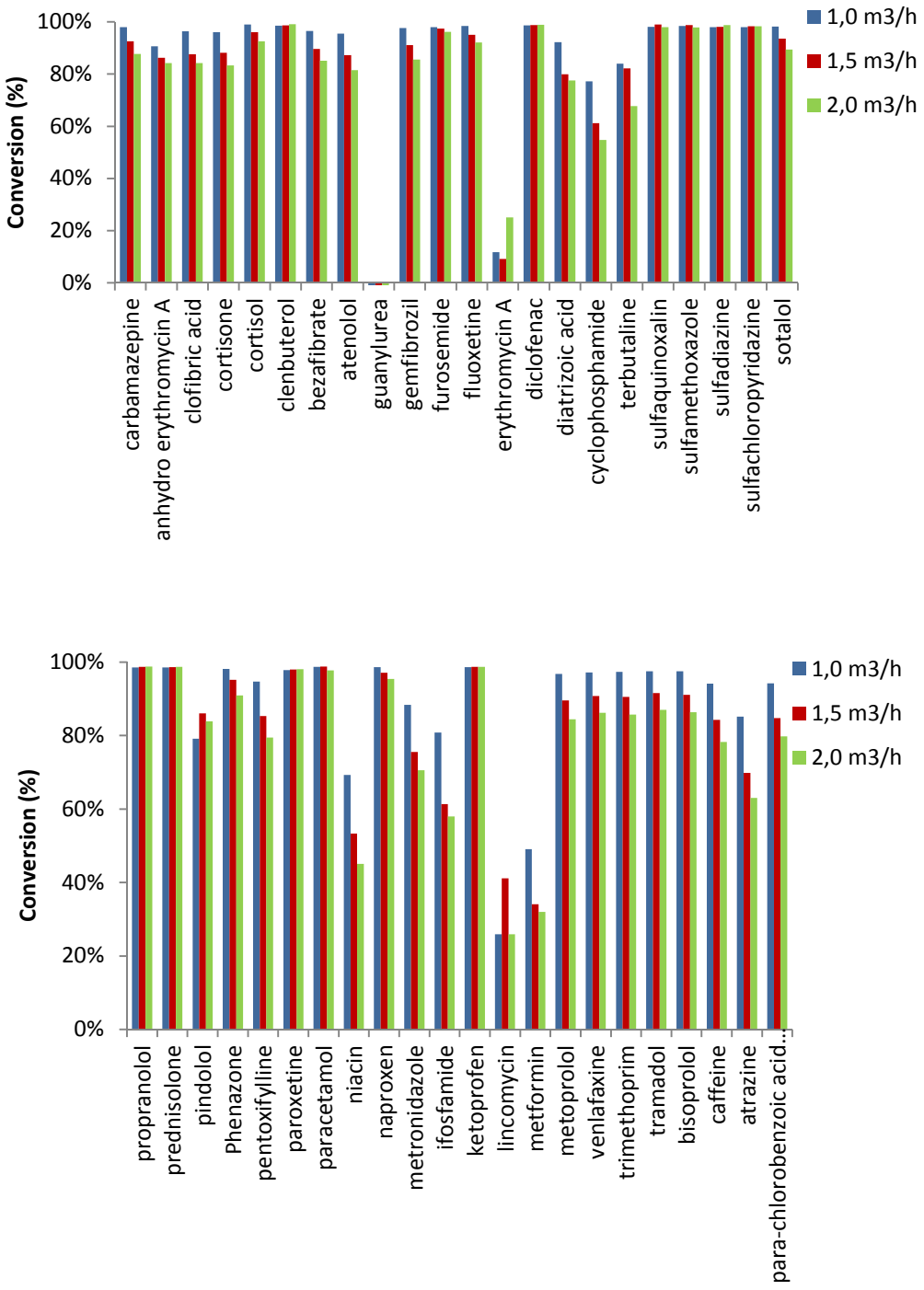


Figure 4-14: Conversion of pharmaceuticals during series 2. Influence of flow.

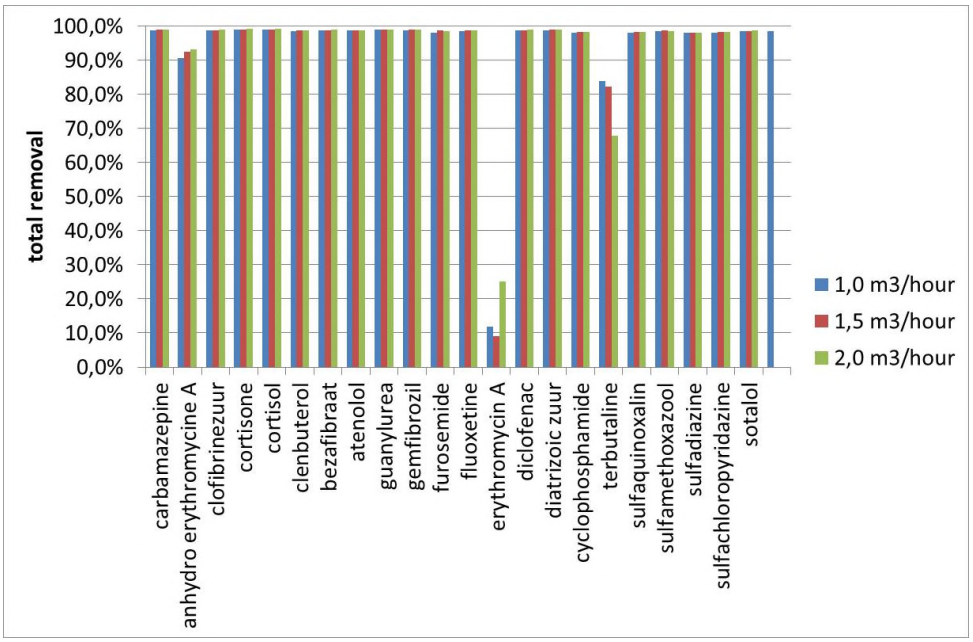
Table 4-7: Average conversion as a function of flow during series 2 (lamp power 80%).

Flow [m^3/h]	Average conversion of pharmaceuticals measured [%]	Average conversion of pharmaceuticals predicted [%]
1,0	90	84
1,5	85	75
2,0	81	68

4.5.3 OMP removal by activated carbon filtration

The removal of the residues of pharmaceuticals by ACF is shown in Figure 4-15 and Figure 4-16 for respectively the first and second column.

In both figures the total removal of the pharmaceuticals, including the effect of the UV/H_2O_2 reactor, is given. It can be concluded that after ACF hardly any pharmaceuticals can be observed in the water, and that after the second filtration the presence of pharmaceuticals in the effluent is negligible. Only for lincomycin it may seem that ACF removal is not very efficient. However, this is caused by the almost complete disappearance of the compound from the stock solution, as a result of which the influent concentration was very low, and thus also the removal calculated was low (the reporting limit was chosen as the effluent concentration, as the actual concentration measured was below this value). There is no reason to assume that lincomycin cannot be removed to a large extent.



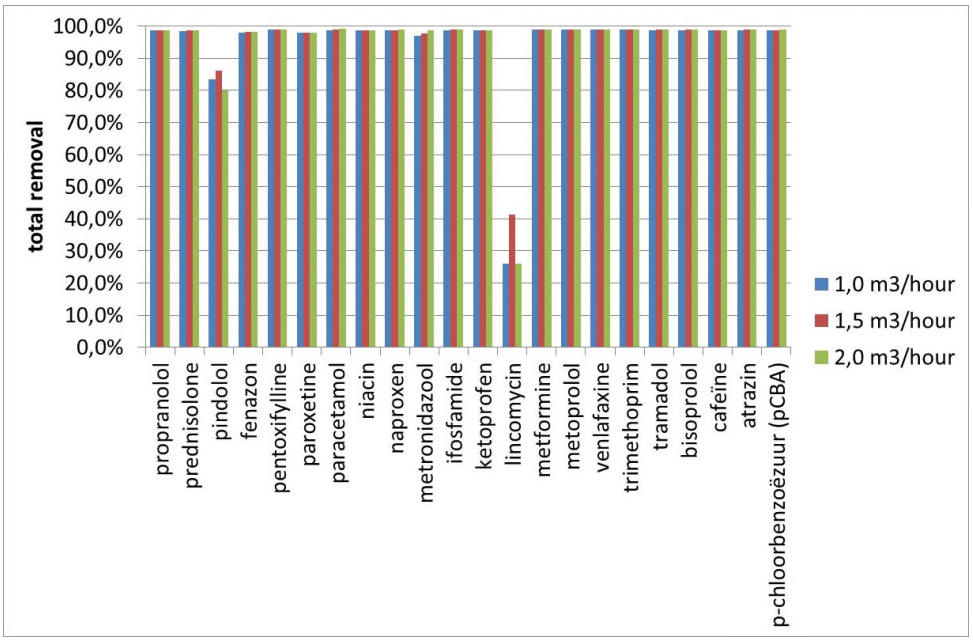


Figure 4-15: Total removal, based on influent concentrations, after the first filtration over activated carbon (contact time 20 min.).

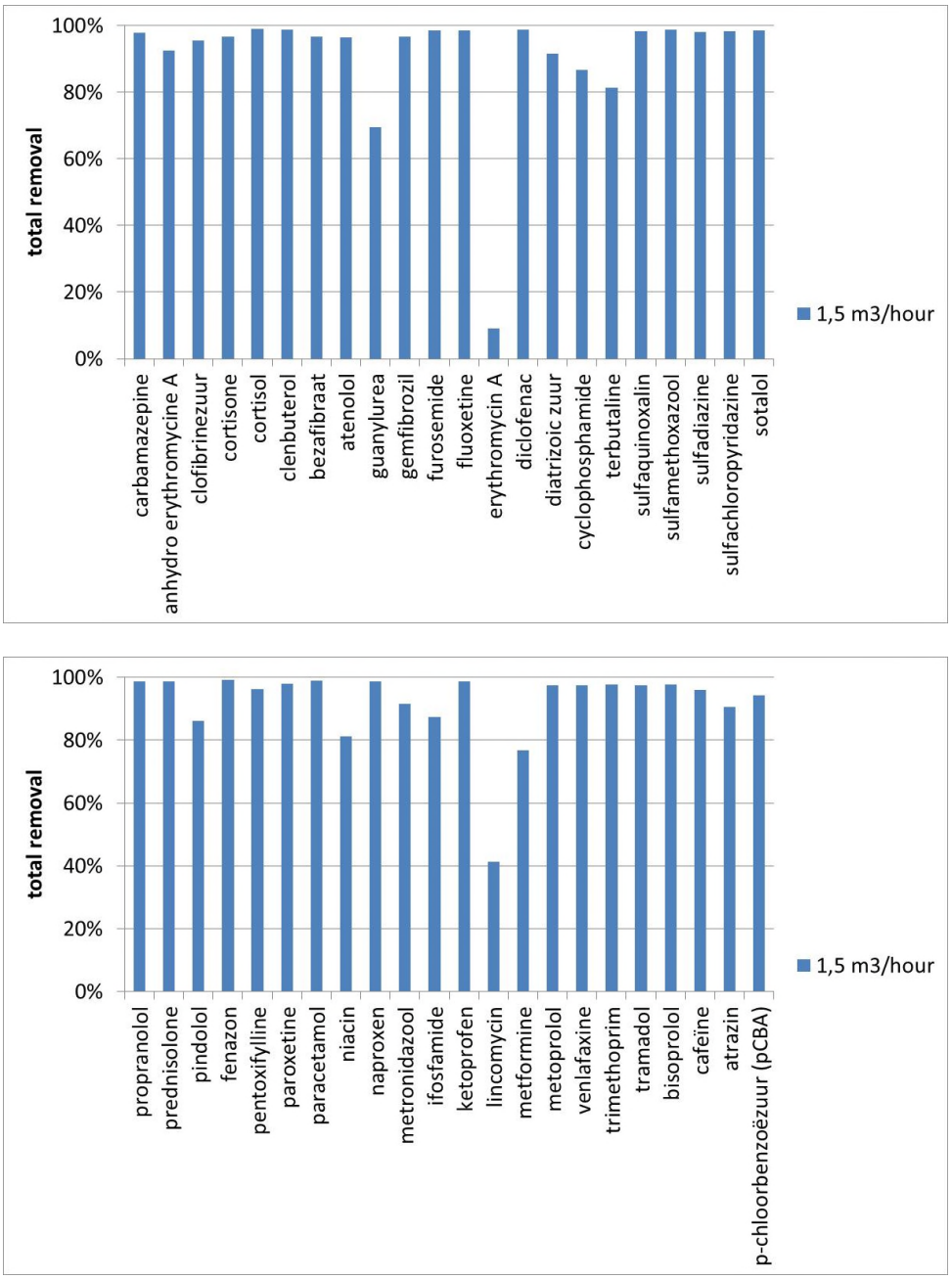


Figure 4-16: Total removal, based on influent concentrations, after filtration of the waste stream over the second activated carbon.

4.5.4 Formation and conversion of metabolites

In this series of dosing experiments special attention was paid to the fate of some known metabolites, as is shown in Figure 4-17.

The only metabolite detected in the pre-treated water of site Heel is 10,11-trans-diol-carbamazepine. Addition of H_2O_2 may increase this amount slightly, but this is not really significant. After UV, however, the concentration, appears to have decreased significantly. At the lowest UV-dose 3-hydroxy-carbamazepine and, to a lesser extent, 2-hydroxy-carbamazepine, are formed by the UV-process. With an increasing UV-dose the concentrations of these two compounds decrease and eventually, at the highest dose, disappear completely, indicating that the metabolites are formed but subsequently converted. After ACF these metabolites cannot be observed anymore. A similar behavior can be observed for O-desmethyl-metoprolol, which seems to be formed to a small extent by UV irradiation, but disappears at a higher UV dose and after AC filtration.

As expected, anhydro-erythromycin A is present in the water before UV irradiation. However, its concentration decreases upon irradiation (it is not yet clear why the concentrations at 2 and 1 m^3/hour were lower than at 1.5 m^3/hour: possibly this difference is within the experimental uncertainty).

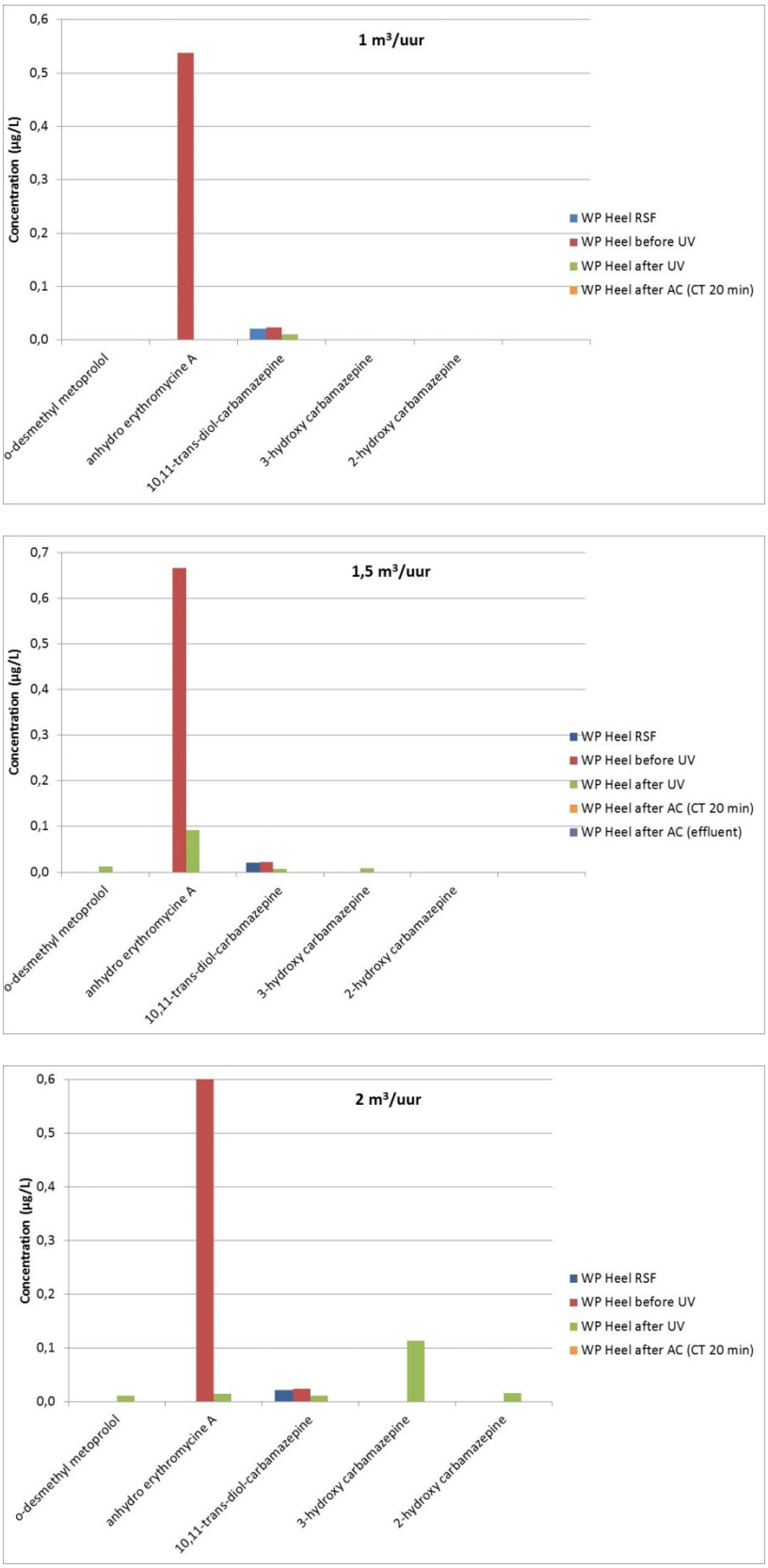


Figure 4-17: Formation and conversion of some known metabolites during the second series of dosing experiments

4.6 Modeling of second series of experiments (18-11-2014); varying H_2O_2 concentrations

The conversions obtained during the second series of experiments, in which the UV-doses were decreased, appeared to be unexpectedly high. It was suggested that this may be due to the very high UV-T value of the water. In this case the UV-T was about 94%, and will increase during the UV/H_2O_2 process, due to DOC conversion. As a result the UV irradiation may be able to reach the reactor wall, resulting in reflection by this wall contributing to the UV-dose. This was not accounted for in the model used at Dunea and in Wijhe, as this had been developed for water with a UV-T of about 75%, in which case reflection by the reactor wall does not play an important role. Reflection by the reactor wall now was incorporated into the CFD-model. It was found that indeed reflection contributes significantly to the actual UV-dose under these circumstances. The results, an increased UV-dose and the corresponding conversions, are shown in Figure 4-18. The conversions predicted in the adapted model correspond better to the results obtained. It also was found that a small difference in UV-T may significantly affect the results, as shown in Figure 4-19. As the UV-T will increase during the process, this may also contribute to the conversions observed.

A comparison of the measured and calculated conversions during series 2 is shown in Figure 4-19 (a full comparison of experimental and predicted results at UV-T = 94% and at 96% is given in Appendix IV).

It can be observed that again the conversion for most compounds is very high, but that for some compounds the process is less effective, like for metformin and niacin. For some compounds, like cyclophosphamide and metronidazole, the UV dose decrease has a relatively large effect on the degradation obtained: a decreasing dose results in a decreasing conversion. However, for other compounds, like paroxetine and prednisolone, hardly any effect can be observed. This is related to the contribution of the UV photolysis to the total conversion. Compounds for which this photolysis plays an important role will be more sensitive towards changes in UV dose than compounds which mainly are degraded by oxidation by hydroxyl radicals.

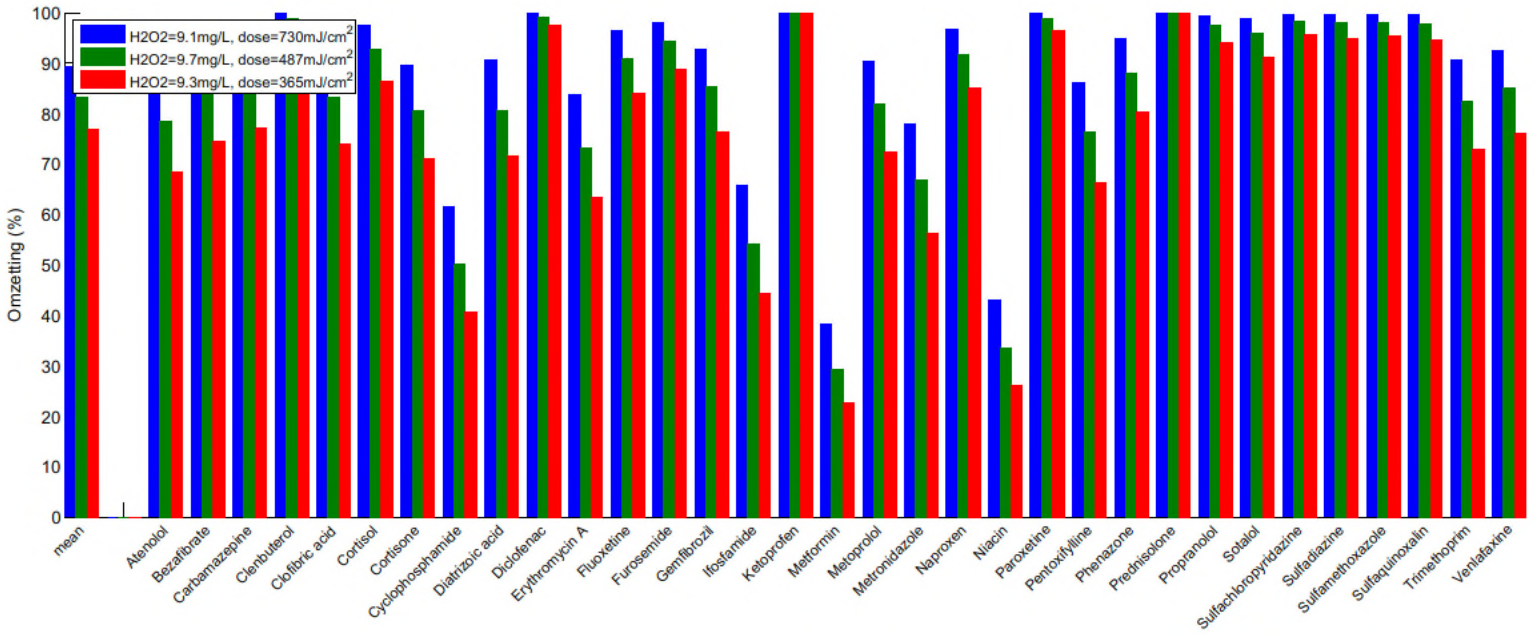


Figure 4-18: Predicted conversions at calculated UV-doses during the second series of experiments, taking into account the effect of reflection by the reactor wall (calculations based on UV-T = 94%).

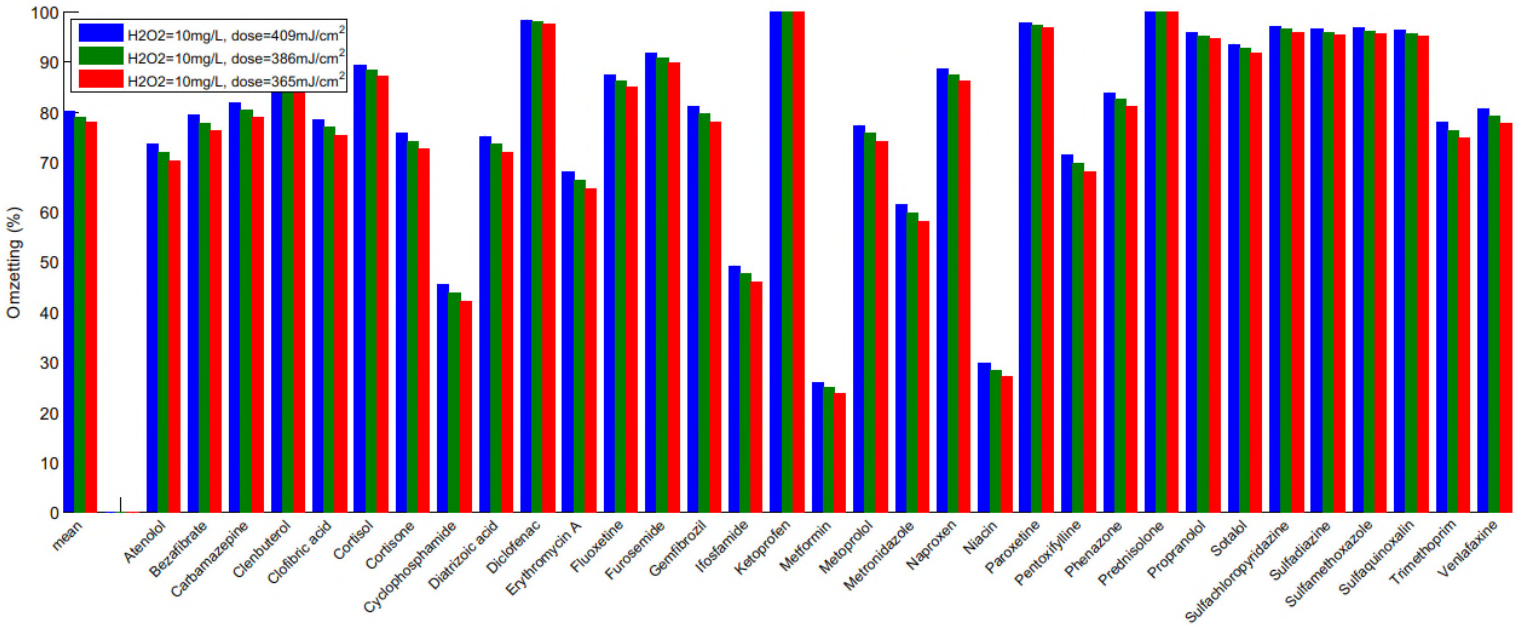


Figure 4-19: Effect of UV-T on UV-dose and predicted conversion of pharmaceuticals (according to the model applied). Blue bar UV-T=94%, green bar UV-T=95%, red bar UV-T=96%

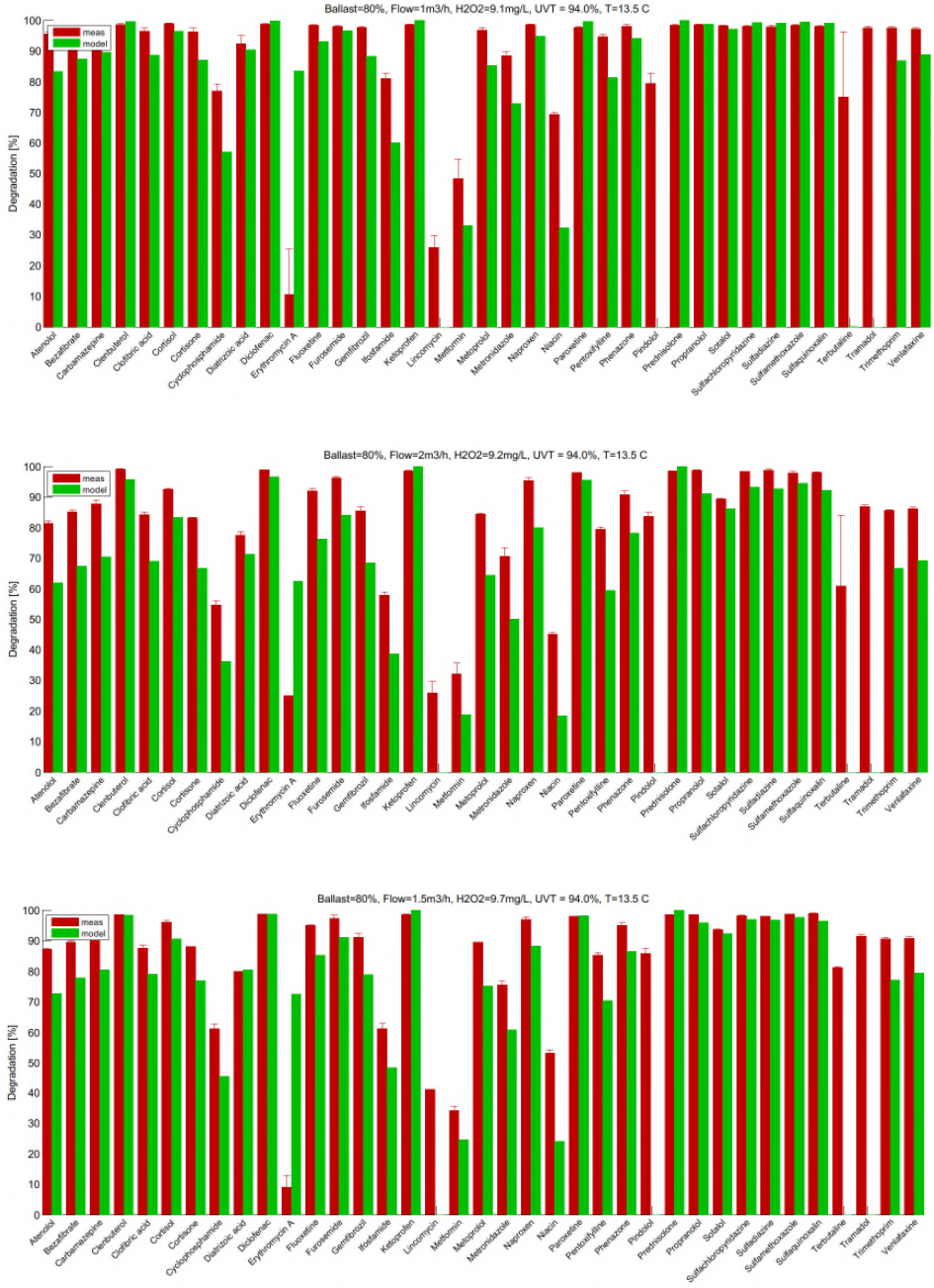


Figure 4-20: Predicted (green bars) and measured (red bars) conversions at three different flows during series 2. Calculations at UV-T = 94%

These results show that the energy requirement of a UV/H_2O_2 process at site Heel will be low, compared with common UV/H_2O_2 processes, that already are applied at full scale drinking water utilities. A lower UV dose probably will be sufficient for full scale applications. For practical reasons it appeared not to be possible to increase the flow or decrease lamp power any further (thus decreasing the UV dose in the reactor), although it can be expected that in a full scale installation a lower dose than 365 mJ/cm^2 will be sufficient., Another process parameter, however, that can be optimized is the H_2O_2 concentration. Although its influence is smaller than that of energy demand, it contributes to the environmental impact of the process, safety requirements, and the ACF step. Therefore, it was decided to calculate the effect of decreasing the H_2O_2 concentration in the process, which is shown in Figure 4-21.

The conversion in a UV/H_2O_2 process takes place via direct photolysis of the micropollutants by UV radiation, and by oxidation by formed hydroxyl radicals. In case the photolysis is the most important mechanism, a decrease in H_2O_2 concentration will have a small effect on the total conversion. This is the case for compounds like ketoprofen and prednisolone. However, in case oxidation is the main degradation process, a decrease in H_2O_2 concentration can have a large effect (e.g. for gemfibrozil and metoprolol).

From these results it can be concluded that a full scale process still can be effective for the degradation of a broad range of micropollutants at a relatively low UV-dose and a low H_2O_2 concentration.

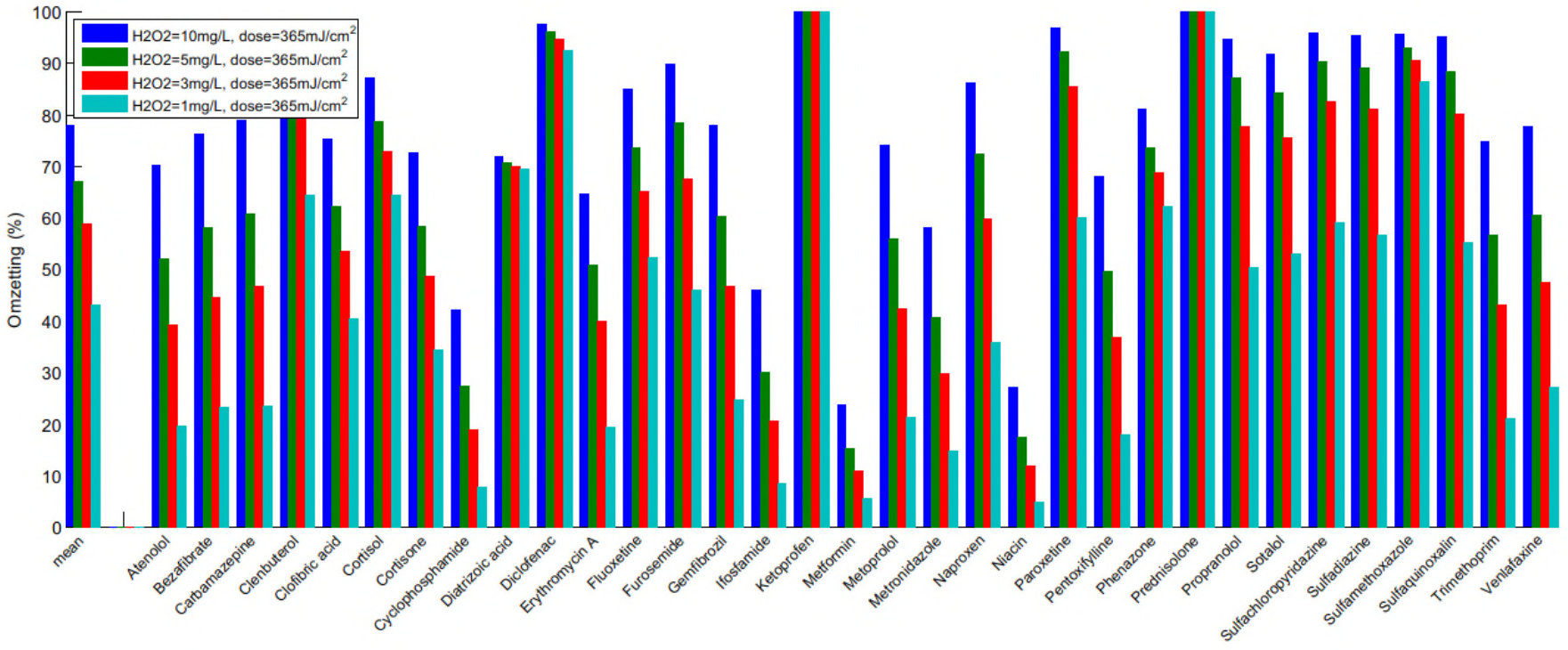


Figure 4-21: Predicted effect of lowering the H_2O_2 concentration on conversion of pharmaceuticals

4.7 Removal of pesticides

WML is also interested in the effects of UV/H_2O_2 and ACF on the removal of pesticide DMS. This was measured in the pilot set-up, and the results are shown in Table 4-8.

Table 4-8: Presence of pesticides in pretreated water from site Heel, and effect of UV/H_2O_2 and ACF treatment. Flow 1 m^3/hour, UV dose 730 mJ/cm^2

	Pretreated water	After UV/H_2O_2 (730 mJ/cm^2)	After ACF (contact time 20 min.)
pH	7.56		
HCO_3^- (mg/L)	175		
NO_3^- (mg NO_3^-/L)	2.1		
NO_3^- (mg N/L)	0.5		
TOC (mg C/L)	1.4	1.4	1.4
DMSA (µg/L)	<0.05	<0.05	<0.05
DMS (µg/L)	0.13	<0.05	0.05
DMST (µg/L)	<0.05	<0.05	<0.05

DMSA and DMST could not be measured in the pretreated water, but a low concentration of DMS was observed. After the UV process no DMS was observed anymore (<0.05 µg/L), indicating a conversion of at least 62%. TOC values did not change after UV/H_2O_2 and ACF treatment.

4.8 Third series of experiments (11-03-2015); varying H_2O_2 concentrations

4.8.1 Preparation of influent

As in the previous series the concentrations were slightly different from what had been expected (see paragraph 4.5.1), it was decided to prepare a new stock solution. As shown in Figure 4-22, now calculated and measured influent concentrations were in good accordance, similar to the observations made during the first series of experiments (section 3.5.1).

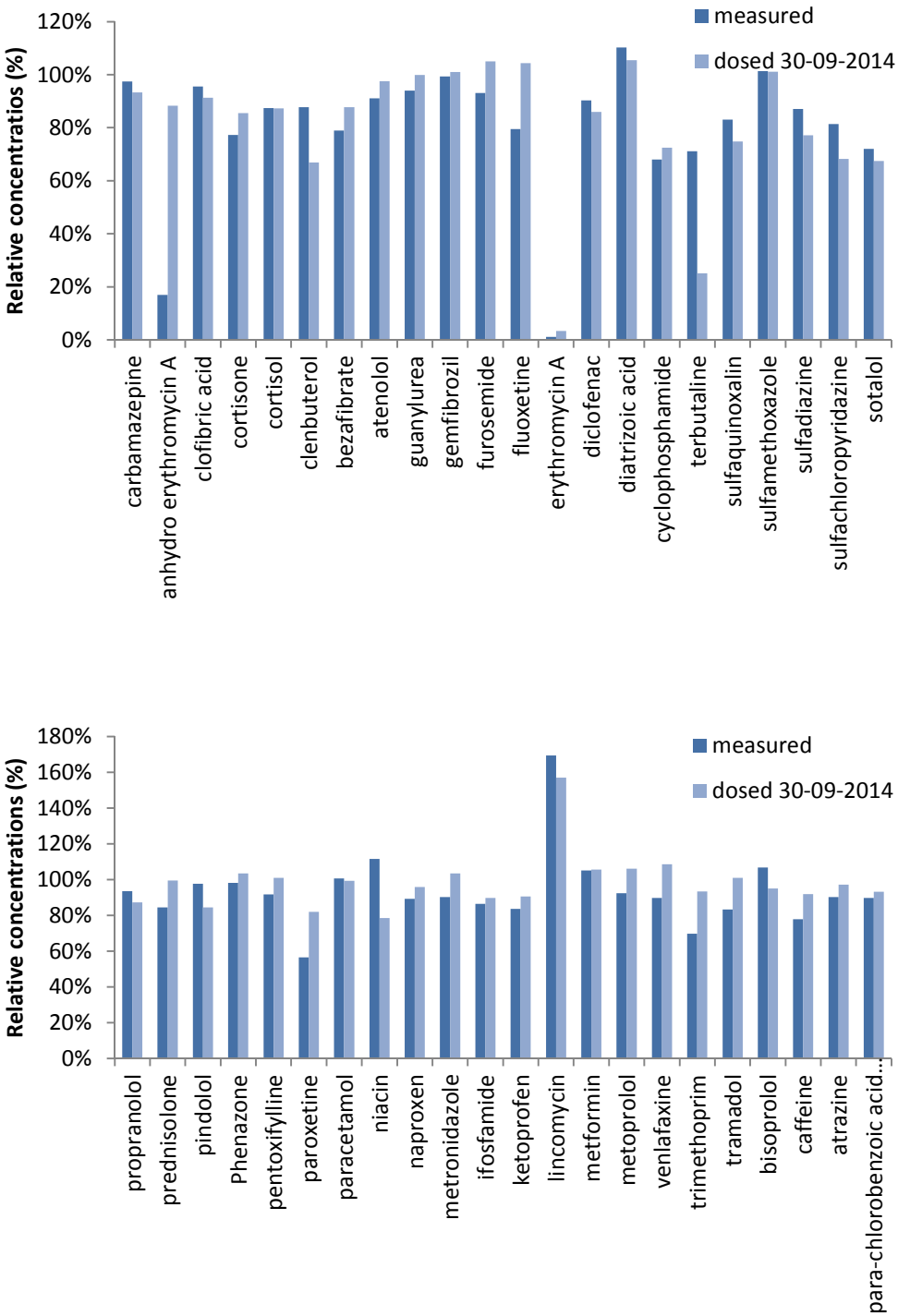


Figure 4-22: Relative concentrations of pharmaceuticals (based on theoretical concentrations) in solution used.

4.8.2 Conversion of pharmaceuticals by UV/H_2O_2

In Figure 4-23 both the predicted and measured conversions are shown for one flow (2 m^3/hour) and three different H_2O_2 concentrations (ca. 10, 5 and 3 mg/L). It can be observed that in this case too there is a fairly good accordance between modelled and measured data,

although, again, the measured conversions in general are a little higher. Furthermore, it can be concluded that a decrease in H_2O_2 concentration has a large effect on the conversions obtained.

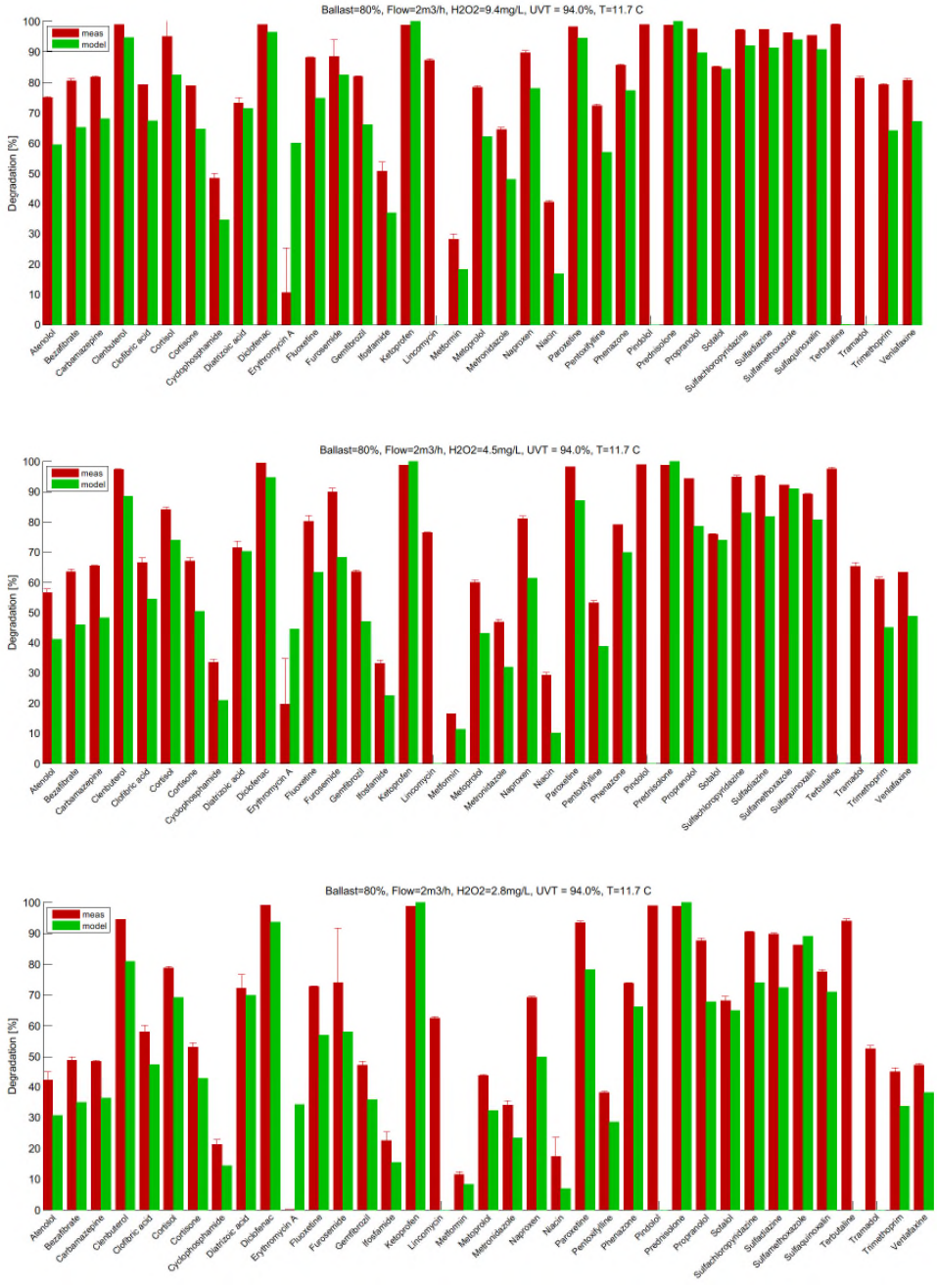


Figure 4-23: Predicted (green bars) and measured (red bars) conversions of pharmaceuticals at 365 mJ/cm² (2m³/hour) and three different H_2O_2 concentrations (left 9.4 mg/L, 4.5 mg/L and 2.8 mg/L) (UV-T = 94%)

The low conversion of erythromycin measured is explained from the fact that most of the erythromycin already was changed into anhydro-erythromycin at the start of the experiment.

As a result the influent concentration of this compound was very low. Conversions were calculated based on influent and effluent concentrations, taking the reporting limit as the effluent concentrations in case the concentrations appeared to be below that value (thus calculating a “worst case” degradation level). For erythromycin this results in a low conversion, but still it was removed to a concentration below the reporting limit of the compound. For some compounds, for which photolysis is relatively more important than oxidation like clenbuterol, ketoprofen and diclofenac), a decrease in H_2O_2 concentration does not have a large impact, whereas for others (like atenolol, bezafibrate trimethoprim and venlafaxine), for which oxidation plays the most important role, a significantly lower conversion is obtained.

4.8.3 OMPs removal using activated carbon filtration

After the first ACF column no micropollutants can be observed anymore (as was observed in the previous dosing experiments). As the second ACF also receives untreated material, effluent concentrations may be slightly higher. These measurements were carried out under “worst conditions”, i.e. the lowest H_2O_2 concentration (3 mg/L). However, it can be concluded that after UV/H_2O_2 followed by ACF in the water no OMPs will be found anymore.

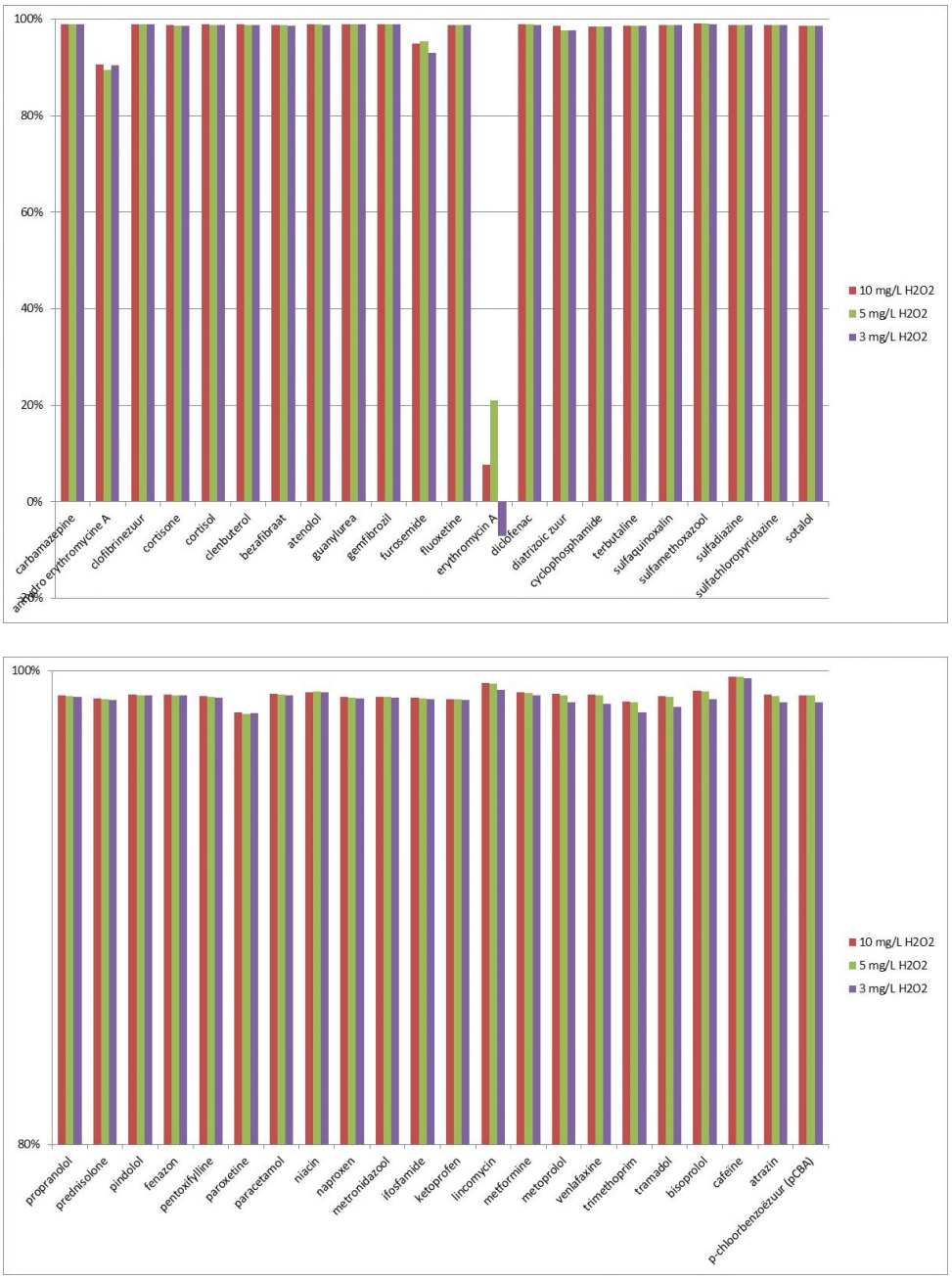


Figure 4-24: Total removal of pharmaceuticals after UV/H_2O_2 and AC filtration.

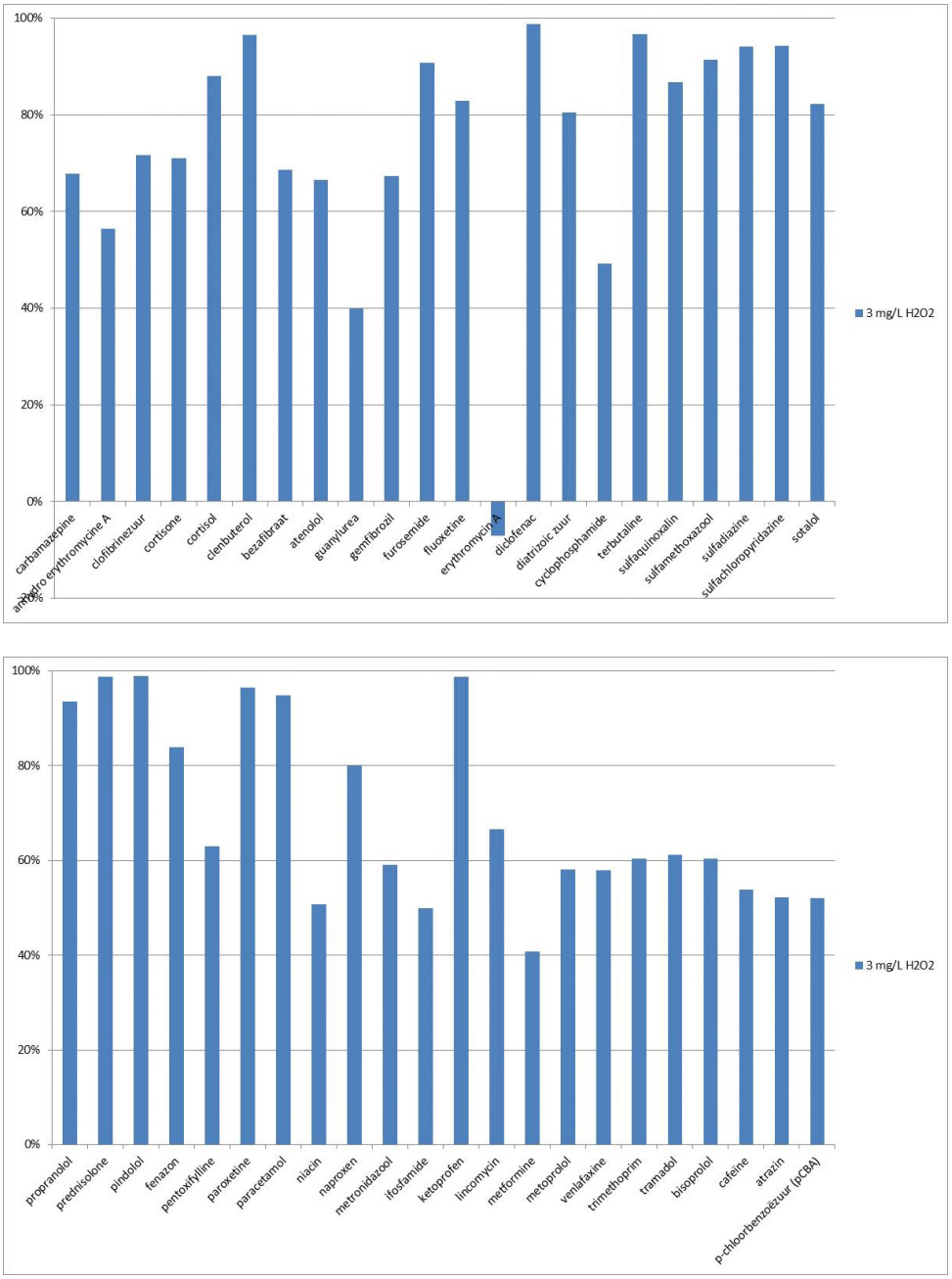


Figure 4-25: total removal of pharmaceuticals in effluent

4.8.4 Formation and conversion of metabolites

In Figure 4-26 an overview is given of the formation and conversion of some known metabolites during series 3, in which the H_2O_2 concentration was varied.

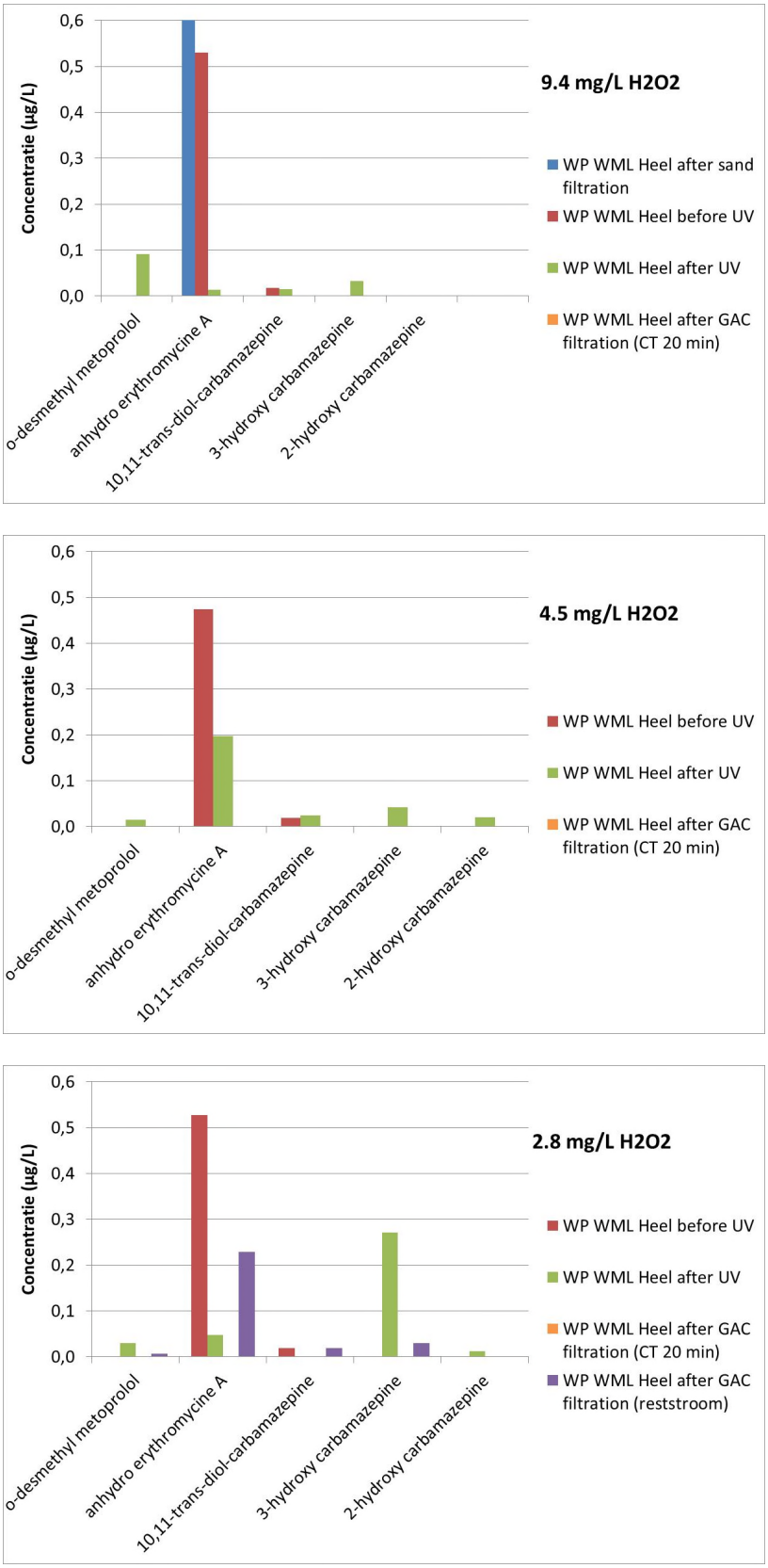


Figure 4-26: Formation and conversion of some known metabolites during series 3. UV dose 365 mJ/cm², varying H_2O_2 concentrations.

It can be seen that at lower H_2O_2 concentrations more metabolites can be observed in the water, probably due to incomplete conversion of compounds. Thus, when optimizing process conditions not only costs and environmental footprint should be taken into account, but also incomplete conversion, which may result in the formation of transformation products. Within this project only a limited number of known metabolites was analyzed, but certainly other (still unknown) transformation products will be formed as well. It cannot on forehand be excluded that such transformation products may be harmful.

4.8.5 Biological stability

The AOC levels and BPP again were measured (also see section 4.2.5), and the results are shown in Table 4-9 and Figure 4-27.

Table 4-9: Effect of water treatment on AOC formation

Sample	Per strain		Total
	AOC P17	AOC NOX	
Pretreated water	0,57 ± 0,20	2,04 ± 0,59	2,60 ± 0,78
After UV/H_2O_2	2,89 ± 0,78	29,00 ± 0,16	31,89 ± 0,62
After ACF	0,33 ± 0,03	10,22 ± 1,02	10,55 ± 0,99
Drinking water	0,23 ± 0.06	3,14 ± 0,12	3,37 ± 0,06

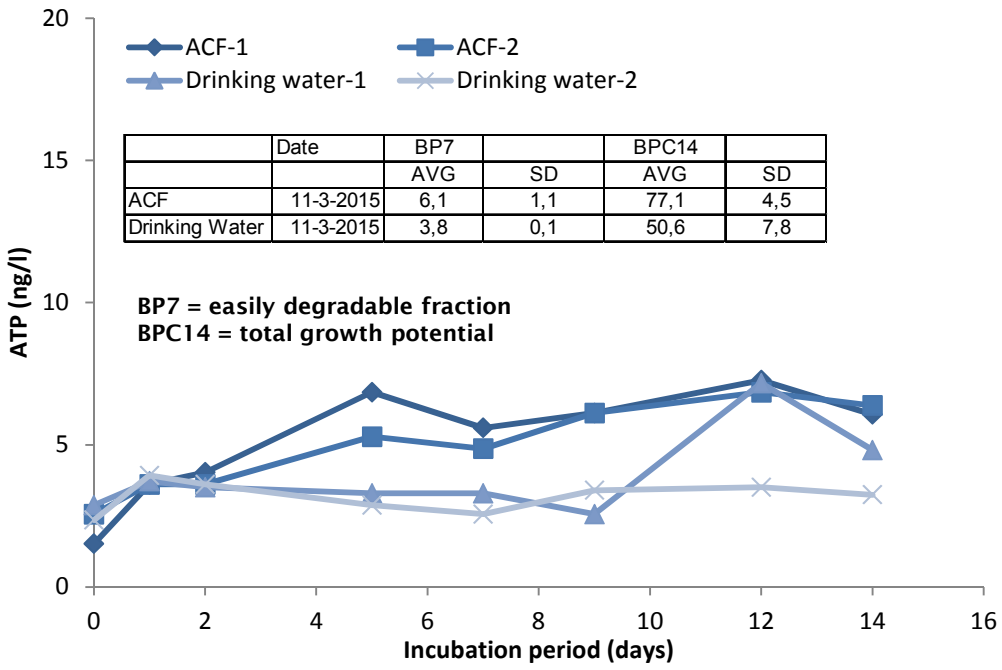


Figure 4-27: BPP of the treated water at several moments during the third series of measurements.

The data of the treated water, taken at different stage of the process during series 3, shown in Figure 4-27, are in good accordance with the data previously obtained (section 4.2.5). Again the BPP after ACF is a little higher than that of the finished water, but the values still a relatively low. For drinking water no problems are expected at BPC14 values < 100 (information Wim Hijnen, KWR). Advanced oxidation indeed increases the values, but not to an unacceptable level for drinking water.

4.8.6 Removal of pesticides

During this series the UV/H_2O_2 conversion of some pesticides, can be observed in the water sources of WML. The results are shown in Table 4-10.

Table 4-10: Presence of pesticides in pretreated water from site Heel, and effect of H_2O_2 and ACF treatment during third series of experiments (11-03-2015)

	Pretreated water	After UV	After ACF (contact time 20 min.)
pH	7.46		
HCO_3^- (mg/L)	179		
NO_3^- (mg NO_3^-/L)	0.4		
NO_3^- (mg N/L)	1.6		
10 mg/L H_2O_2			
TOC (mg C/L)	1.6	1.6	1.2
DMSA (µg/L)	<0.05	<0.05	<0.05
DMS (µg/L)	0.13	0.08	0.06
DMST (µg/L)	<0.05	<0.05	<0.05
5 mg/L H_2O_2			
TOC (mg C/L)		1.6	1.2
DMSA (µg/L)	<0.05	<0.05	<0.05
DMS (µg/L)		0.11	0.06
DMST (µg/L)	<0.05	<0.05	<0.05
3 mg/L H_2O_2			
TOC (mg C/L)		1.6	1.2
DMSA (µg/L)	<0.05	<0.05	<0.05
DMS (µg/L)		0.12	0.07
DMST (µg/L)	<0.05	<0.05	<0.05

It was found that DMST and DMSA were not present in concentrations above the detection limit, but DMS could be observed (see also sections 4.2.1 and 4.7). The conversion of DMS as a function of the H_2O_2 concentration is shown in Figure 4-28. In this figure also the conversion measured during the second series of dosing experiments (UV dose 730 mJ/cm^2, 10 mg H_2O_2/L) are shown (see section 4.7).

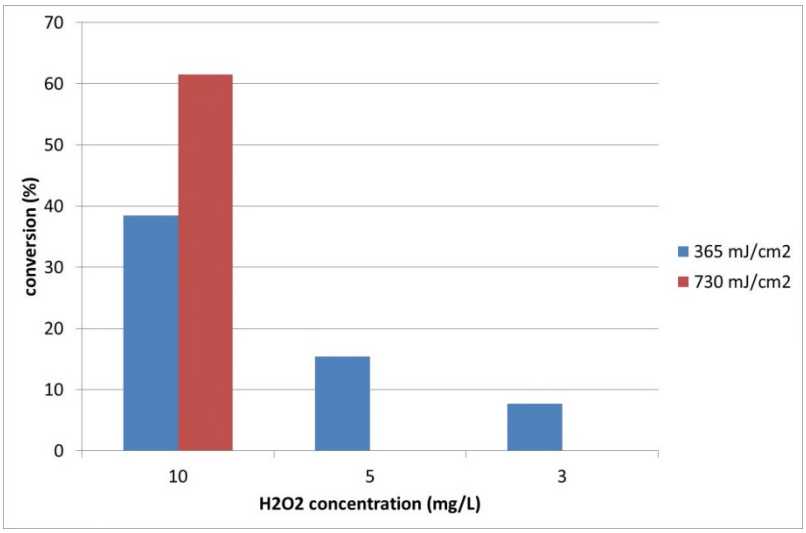


Figure 4-28: Conversion of DMS as a function of H_2O_2 concentration at a UV dose of 365 mJ/cm² (flow 2 m³/hour).

A clear relation was observed between the H_2O_2 concentration and the conversion of DMS: the DMS degradation decreases with decreasing H_2O_2 concentrations. Furthermore, it can be concluded that the conversion of DMS is significantly lower at a UV dose of 365 mJ/cm² than at a UV dose of 730 mJ/cm². After ACF most of the DMS appears to have been removed. It is not to be expected that activated carbon will be a very efficient adsorber for DMS, but at low influent concentrations, depending on conditions (like pH, surface charge of the carbon, electrical charge of the DMS and loading of the carbon) adsorption may be sufficient to reach concentrations below the reporting limit.

To obtain more information on the possibilities to convert DMS by means of a UV/H_2O_2 process, measurements were repeated under different conditions on 20-03-2015. The results are shown in Table 4-11.

Table 4-11: Presence of pesticides in pretreated water from site Heel, and effect of H_2O_2 and ACF treatment during additional DMS experiments, 20-03-2015.

	Pretreated water	After UV	After ACF (contact time 20 min.)
pH	7.44		
HCO_3^- (mg/L)	175		
NO_3^- (mg NO_3^-/L)	2.4		
NO_3^- (mg N/L)	0.5		
Flow: 1 m³/h 10 mg/L H_2O_2			
TOC (mg C/L)	1.5	1.6	1.2
DMSA (µg/L)	<0.05	<0.05	<0.05
DMS (µg/L)	0.15	0.16	0.06
DMST (µg/L)	<0.05	<0.05	<0.05
Flow: 2 m³/h 10 mg/L H_2O_2			
TOC (mg C/L)		1.5	1.2
DMSA (µg/L)	<0.05	<0.05	<0.05
DMS (µg/L)		0.16	0.07
DMST (µg/L)	<0.05	<0.05	<0.05
Flow: 2 m³/h 5 mg/L H_2O_2			
TOC (mg C/L)		1.6	1.2
DMSA (µg/L)	<0.05	<0.05	<0.05
DMS (µg/L)		0.16	0.07
DMST (µg/L)	<0.05	<0.05	<0.05

Contrary to previous results (during series 2), in this case no degradation of DMS seemed to occur, although after ACF most of the DMS was removed. It is not clear what caused these results, but it should be noted that concentrations involved are very low and near the detection limit, which may result in less reliable data. Therefore it was decided to carry out some CB experiments under well-defined UV-conditions and at higher DMS concentrations. Based on these results additional experiments were carried out in the pilot set-up. The results of these experiments have been described in chapters 7 and 8.

5 Effect of reactor geometry and water matrix

5.1 Electrical energy per order (E_{EO}) values

It is known that the relatively high energy use of a UV/H_2O_2 process is its main disadvantage. This energy use depends on several parameters:

- Type of component
- Water matrix
- Reactor geometry

As a result, it is very difficult to compare different reactors and/or processes. For this purpose in literature the E_{EO} value is applied, i.e. electrical energy per order, defined as:

$$E_{EO} = \frac{P}{F * \lg \frac{c_i}{c_e}}$$

In which P is the electrical power (kW), F is the flow (m^3/hour), c_i is the concentration in the influent and c_e is the concentration of the effluent. The unit of E_{EO} = kWh/m^3order.

This value shows the energy required to degrade 90% of a certain compound in a certain water type and in a certain UV reactor. It can be applied to compare the effectiveness of the UV/H_2O_2 process for different organic micropollutants, for different water matrices, or for various reactor types/geometries. In this chapter the effect of different water matrices (resulting in various UV-T values) and of the H_2O_2 concentration is shown.

5.2 Effect of reactor geometry and water matrix on E_{EO}

Figure 5-1shows the E_{EO} values for the D200 type reactor at different water matrices. For this purpose experiments were carried out at Dunea (after different pretreatment processes (O_3/H_2O_2 or ACF), resulting in various UV-T values), at Wijhe (were the reactors have been built and tested the first time) and at Heel. Previous research at Dunea in Bergambacht and at Van Remmen UV Techniek in Wijhe had already shown that the D200 is about 30% more efficient than a regular disinfection UV reactor. This means that about 30% less energy is required to obtain the same degree of micropollutant removal. In Figure 5-1 the influence of the water composition on the E_{EO}, is illustrated and thus on the energy demand. When compared to both other test locations, Bergambacht and Wijhe, the E_{EO} is about half as large, which means that the electrical energy requirement to obtain the same degree of degradation of micropollutants at WML is about half the energy demand at the other locations. Thus, it can be concluded that the UV/H_2O_2 process will be very efficient at PS Heel.

In Figure 5-2 it can be observed that the decrease in H_2O_2 concentration has a large effect on the E_{EO} values (to obtain the same degree of micropollutant degradation). For optimization of the process several parameters should be taken into account:

- Required degree of micropollutant removal
- Economic considerations on the expenses for energy and H_2O_2, including transport and storage of H_2O_2. For this purpose the E_{EO} value will be very useful.
- Footprint of the process (energy demand versus H_2O_2 use)
- Possible formation of (toxic?) transformation products.

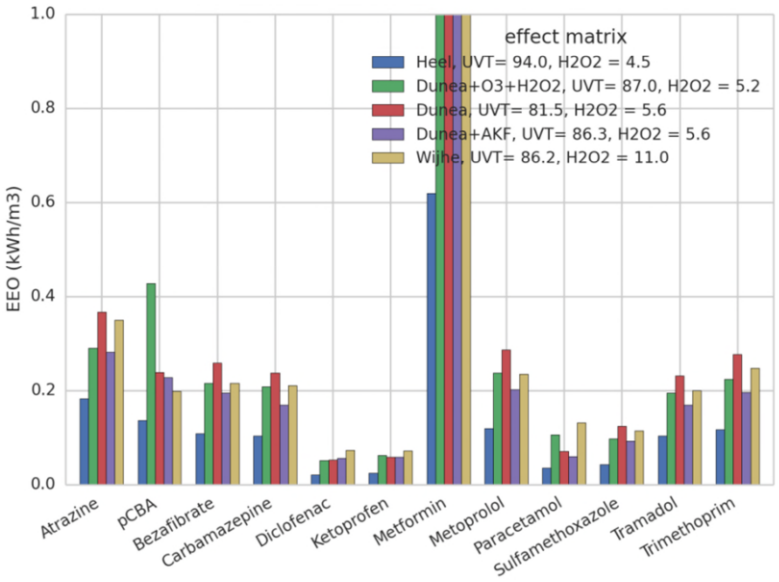


Figure 5-1: Effect of different matrices on the E_{EO} value for the D200 type reactor.

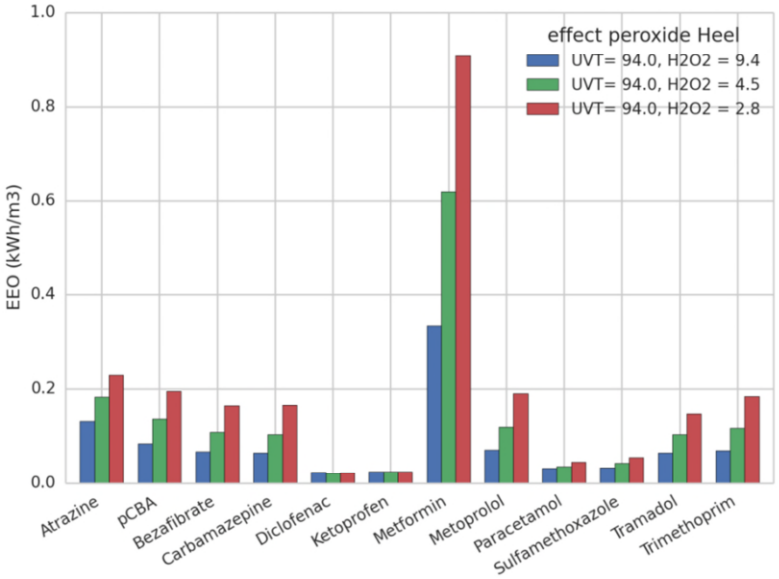


Figure 5-2: Effect of decreasing the H_2O_2 concentration on the E_{EO} value.

As was mentioned before (section 4.3), for some compounds much energy is required to obtain a high conversion (Wols et al, 2013). This is reflected in a high E_{EO} value for these compounds, as is shown for metformin.

6 Formation of possibly mutagenic byproducts

6.1 Formation of possibly mutagenic byproducts during UV-processes

Previous research showed that under certain circumstances mutagenic byproducts may be formed during UV-processes (Hofman-Caris et al., 2013). In general this mainly happens when medium pressure UV lamps are used. From previous research it is known that the chances that mutagenic byproducts are formed increase with increasing UV-dose, nitrate concentration and NOM content. It is supposed that mutagenic byproducts are formed by reactions of photolysis products of nitrate with (photolysis products of) NOM. Photolysis of nitrate mainly occurs at wavelengths <240 nm. As in the present pilot project a low pressure UV lamp was used and the nitrate content of the pretreated water is very low (0,5 mg/L), it is expected that the risk of mutagenic byproducts being formed during the UV/H_2O_2 process at site Heel is very small. However, the mutagenicity after UV/H_2O_2 was verified using an Ames fluctuation assay.

6.2 Ames flucutation assays

In some cases it is very difficult to determine the exact composition of a sample, as it is unknown which compounds may be present and should be analyzed. Furthermore, such an analysis will not answer the question whether or not this specific composition may be toxic: since there probably is no information on toxicity of mixtures of this composition. In such a case bio assays may offer the solution. These provide information whether a certain water composition may be toxic or not. An example of such a bio assay is the Ames fluctuation assay. This is used to determine whether a sample shows mutagenic activity, based on the reactions of two different bacterial strains. At KWR TA98 and TA100 are applied. TA98 is used to detect mainly frame shift mutations in the bacterial DNS, whereas TA100 gives information on base-pair substitutions in the DNA. As the structure of compounds may be changed by the metabolism (in the liver), the tests are conducted both with and without liver extract S9.

At KWR an SPE-extraction method is used to concentrate the sample for the Ames fluctuation assay. Previous research showed that this type of pretreatment is most suitable (Heringa, 2012). Therefore, this method also was applied in the present research.

Several control experiments are carried out to determine whether a sample gives reliable results, and moreover which response a sample should be characterized as mutagenic. This involves a negative control (NC), a positive control (PC), and a procedure control (PrC) experiment. All samples are measured three times in duplicate.

If a sample shows a significant positive response it contains compounds which have possibly mutagenic properties. This doesn't automatically imply that it will be toxic for humans, it only indicates that it may be important to do some more research.

6.3 Results of Ames tests

For this project samples were taken from the pretreated water ("snelfiltraat" (water after rapid sand filtration), SF) used as influent, and from the water after addition of H_2O_2 before the UV-reactor, after the UV-reactor, after ACF, and of the finished water at site Heel. The

results obtained during the first series of experiments are shown in Figure 6-1 and Figure 6-2 Samples were only taken at the highest UV-dose applied, as such conditions represent a "worst case" scenario, with relatively the highest risk that mutagenic byproducts may be formed.

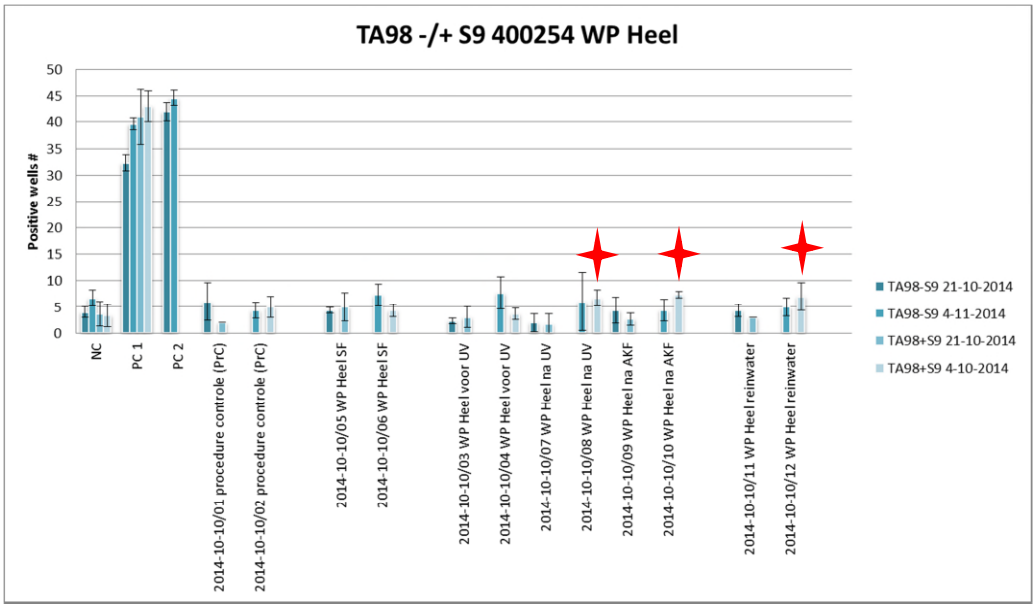


Figure 6-1: Results of the Ames fluctuation assay, obtained with TA98, with and without S9 (30-09-2014; 730 mJ/cm², 10 mg H_2O_2/L).

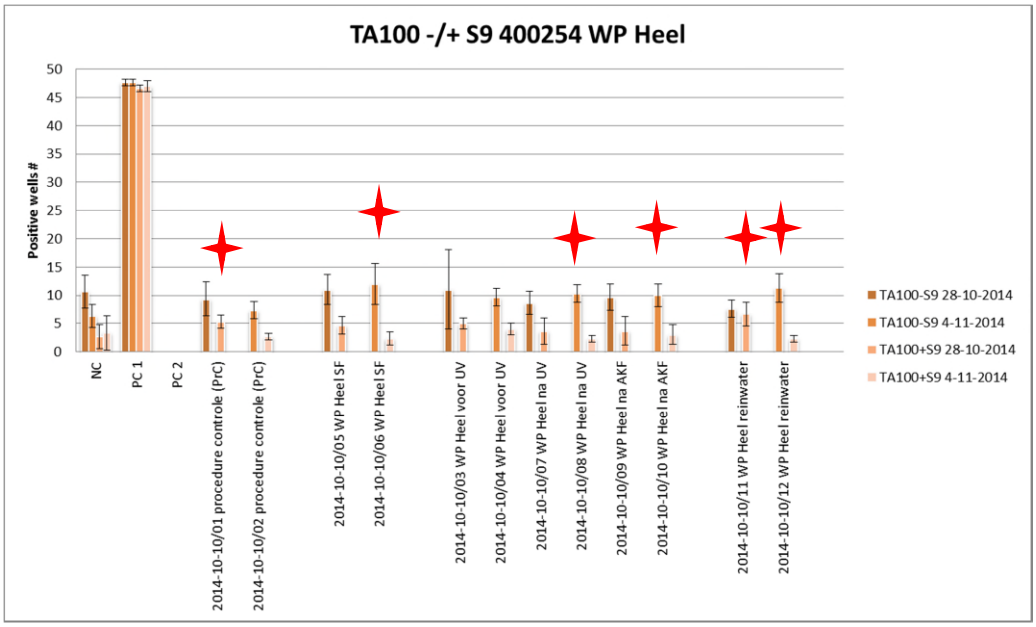


Figure 6-2: Results of het Ames fluctuation assay, obtained with TA100, with and without S9 (30-09-2014; 730 mJ/cm², 10 mg H_2O_2/L).

In general it can be concluded that responses are low. Some samples show a significant positive response (although just above the limit which is regarded as significant), but in

those cases only one of two duplicate samples gives this result. Therefore, the sample as such cannot be characterized as mutagenic.

For TA98 + S9 one of two samples after UV treatment seems to give a significant positive response. This implies that under influence of the UV irradiation a compound (or compounds) which causes this may have been formed. In general such a result is not to be expected with LP UV lamps, but in this case the UV dose applied (ca. 750 mJ/cm^2) was very high. It is remarkable that this significant response also is observed after ACF, although in all other cases (Heringa et al., 2011) it was found that ACF effectively removes such compounds. The duplicate sample, however, does not show this result. Furthermore, also the finished water of site Heel showed a positive response at that day. Therefore, it is possible that the intake water happened to contain such a compound during that day. Anyhow, as the duplicate sample did not shown a positive response, the sample itself cannot be characterized as mutagenic.

TA100 shows a little higher response than TA98, in general in combination with S9 (only once without S9). It is remarkable that this response can be observed both in the pretreated water and in the finished water.

In general it can be observed that no relation can be found between the type of bacterial strain (TA 98 or TA 100) and the occurrence of a positive response.

The experiment was repeated during the third series of experiments in March 2015. In this case the UV-dose applied was significantly lower (300 mJ/cm^2), but in order to create a kind of "worst case conditions" the samples were taken at the lowest H_2O_2 concentration applied (3 mg/L), as it is known that the presence of H_2O_2 hinders the formation of mutagenic byproducts, which arise from photolysis processes. The results are shown in Figure 6-3 and Figure 6-4.

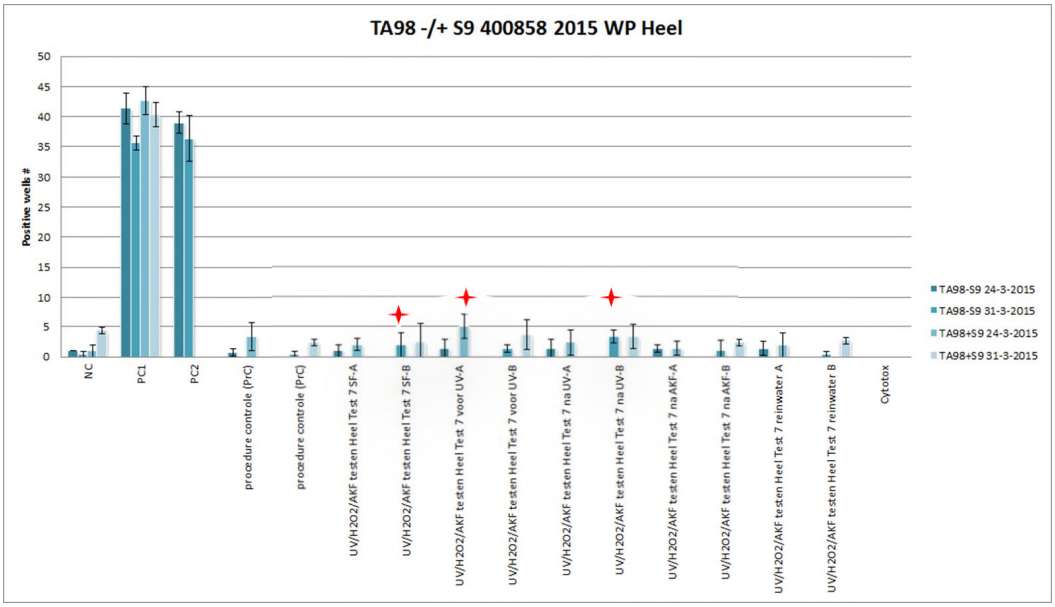


Figure 6-3: Results of het Ames fluctuation assay, obtained with TA98, with and without S9, during the third series of experiments (11-03-2015; 365 mJ/cm^2, 3 mg H_2O_2/L).

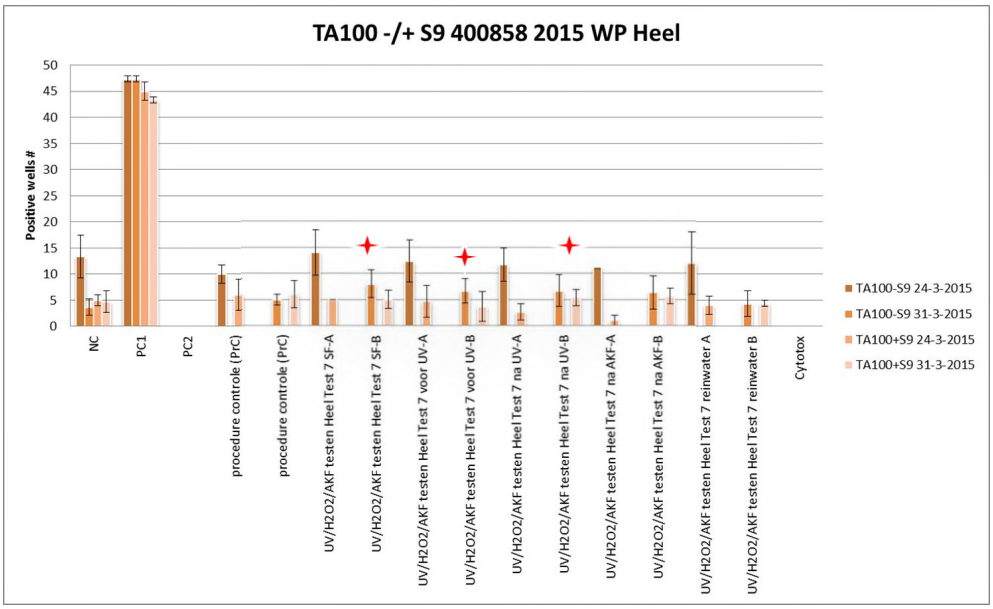


Figure 6-4: Results of het Ames fluctuation assay, obtained with TA100, with and without S9, during the third series of experiments (11-03-2015; 365 mJ/cm², 3 mg H_2O_2/L).

The SF sample seems to give a positive response in both TA98 and TA100-S9, but the same strains also show a positive response after UV. Thus, this does not seem to be caused by UV. In no case the duplicate showed a positive response, and therefore the samples cannot be considered as mutagenic.

In summary, during the first series finished water showed a non-reproducible positive response. It was concluded that this may have been caused by compounds that were already present the SF water itself, before the UV treatment. In the second series neither the finished water nor the water after activated carbon filtration showed a positive response. However, considering all results of Ames tests in finished water, it can be concluded that there is no reason for concern: a possibly positive response just may be a coincidence.

Although in some cases a very low significant response was observed, there is no reason to believe that this was specifically caused by UV/H_2O_2 process: similar observations can be made in all other types of water tested. The responses observed are not reproducible, very low, and after the UV process certainly not higher than in some cases in the pretreated or even finished water (which was not treated by this process). Furthermore, it cannot be seen that there is a relation with the type of bacterial strain (with or without S9).

Thus, it can be concluded that the UV/H_2O_2 process at site Heel does not result in the formation of mutagenic byproducts, and there is no concern for public health, applying this technique.

7 Results of Collimated Beam Experiments with DMS

7.1 Water quality

As the previous DMS experiments did not result in an unambiguous conclusion, it was decided to carry out some experiments with higher DMS concentrations and under well-defined UV conditions (see also section 4.8.6).

Before the start of the CB experiments water quality parameters were determined. These are shown in Table 7-1.

Table 7-1: Water quality data for the collimated beam experiments with DMS

Experiment	DMS	HCO_3^-	pH	NO_3^-	NO_3^-	TOC	Turbidity
	µg/L	(mg/L)		(mg N/L)	(mg NO_3/L)	(mg/L)	FTE
1	0.250	171	7,66	0,36	1,59	1,48	0,72
2	0.598	170,0	7,66				0,18
3	1.100	169	7,63				0,15

Before the start of the experiments the exact H_2O_2 concentration of the water was determined (see Table 7-2).

Table 7-2: H_2O_2 results for the collimated beam experiments

Experiment	UV-dose	H_2O_2
	mJ/cm²	(mg/L)
Pretreated water	0	< 0.6
1	0	10.9
	700	11.3
2	0	11.4
	700	10.8
3	0	11.2
	700	11.5

7.2 Collimated Beam experiments with DMS

Experiments were carried out at three different starting concentrations. Experimental conditions can be found in section 3.6.2. The conversions obtained during CB experiments are shown Figure 7-1.

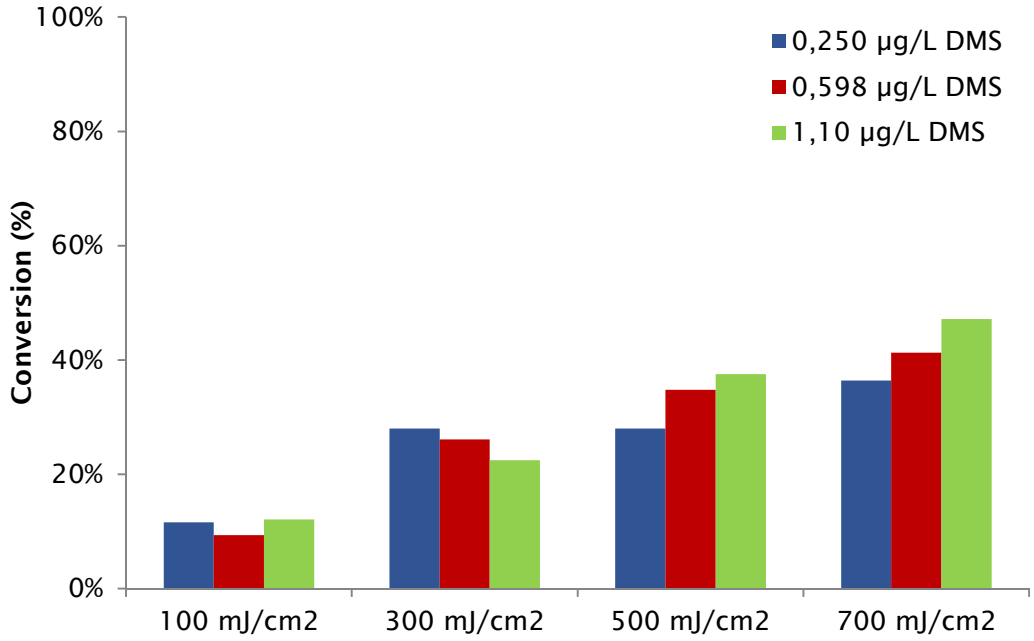


Figure 7-1: conversion of DMS at different UV dose during collimated beam tests with different amounts of DMS

In literature no data on the photolysis and/or oxidation of DMS can be found. An increasing UV dose clearly result in a higher DMS conversion, although the conversions obtained are relatively low. The conversion results obtained were applied to estimate a pseudo first order reaction rate constant.

An approximation for the reaction rate is given in equation 1:

$$ln\left(\frac{C}{C_0}\right) = -k_0' E \qquad \text{eq. 1}$$

In which C = concentration of DMS, C_0 = starting concentration of DMS, E = wavelength dependent fluence, and k_0' is the pseudo first order reaction constant. From above results it can be calculated that $k_0' = 9*10^{-4}$ cm²/mJ under these circumstances (LP UV lamp, 10 mg H_2O_2/L, pre-treated water from PS Heel).

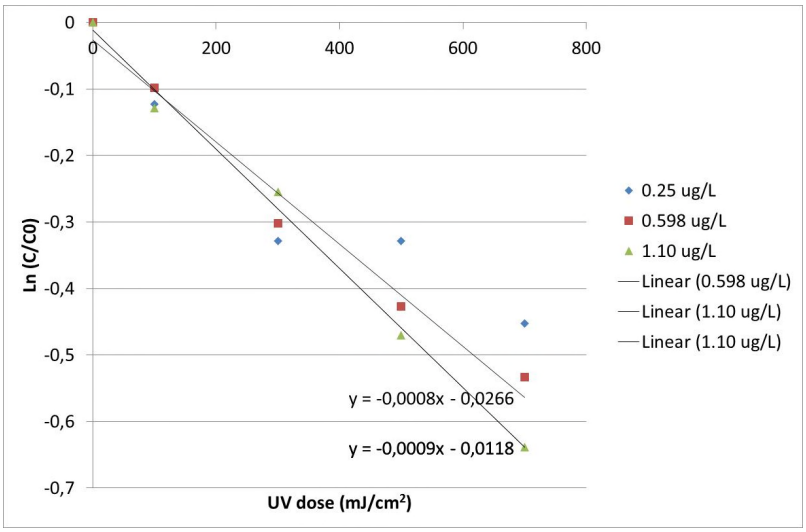


Figure 7-2: Conversion of DMS as a function of UV dose.

Obviously, the conversion kinetics of DMS can be considered a pseudo first order reaction. The pseudo first order rate constant is $9*10^{-4}$ cm^2/mJ, which indicates that the UV/H_2O_2 process may be applied for the removal of this pesticide. Although conversions are not extremely high, it depends on the influent DMS concentration whether such a conversion will be sufficient to decrease the DMS concentration to an acceptable level.

Based on these results it was decided to check the conversion of DMS, and some other micropollutants, by means of carrying out dosing experiments in the pilot UV reactor. The results have been described in the next chapter (chapter 8).

8 Results of additional experiments with some compounds, present in influent.

8.1 Conversion of DMS in influent

On 11-03-2015 and 12-03-2015 the concentration of DMS in the influent, before H_2O_2 addition, after the UV treatment and after ACF was determined. The results are shown in Table 8-1.

Table 8-1: Presence of DMS in influent, after UV treatment and after ACF on 11-03-2015 and 12-03-2015.

	Influent	After UV treatment	After ACF
Concentration	0.13	0,08	0,06
(µg/L)		0,11	0,06
		0,2	0,06
	0.15	0,16	0,06
		0,16	0,07
		0,15	0,07

Obviously, the results obtained do not give a clear answer to the question whether DMS can effectively be removed by means of a UV/H_2O_2 process. Possibly this is caused by the low DMS concentration in the influent, as a result of which the uncertainty in the data is relatively high. Therefore it was decided to do some additional experiments, in which DMS (and some other interesting compounds) were dosed to a level that gives more reliable results. These experiments and the results obtained are described in the following paragraphs.

8.2 Dosing of additional compounds

In the pilot set-up additional dosing experiments (series F; see Table 3-15) were carried out with compounds which may be found in the influent water of PS Heel. These include, apart from DMS, diatrizoic acid, cyclophosphamide,metronidazole, ifosfamide, atrazine (as reference compounds), acesulfame K, aspartame, cyclamate, saccharine, sucralose, NDMA, AMPA and EDTA.

The DMS concentrations for test 1 (0.5 µg/L) and test 2 (1.0 µg/L) were respectively 108.2 and 107.0% relative to the concentrations aimed at, probably caused by the presence of some of this compound in the pretreated water. The concentrations of the other compounds are shown in Figure 8-1- Figure 8-3.

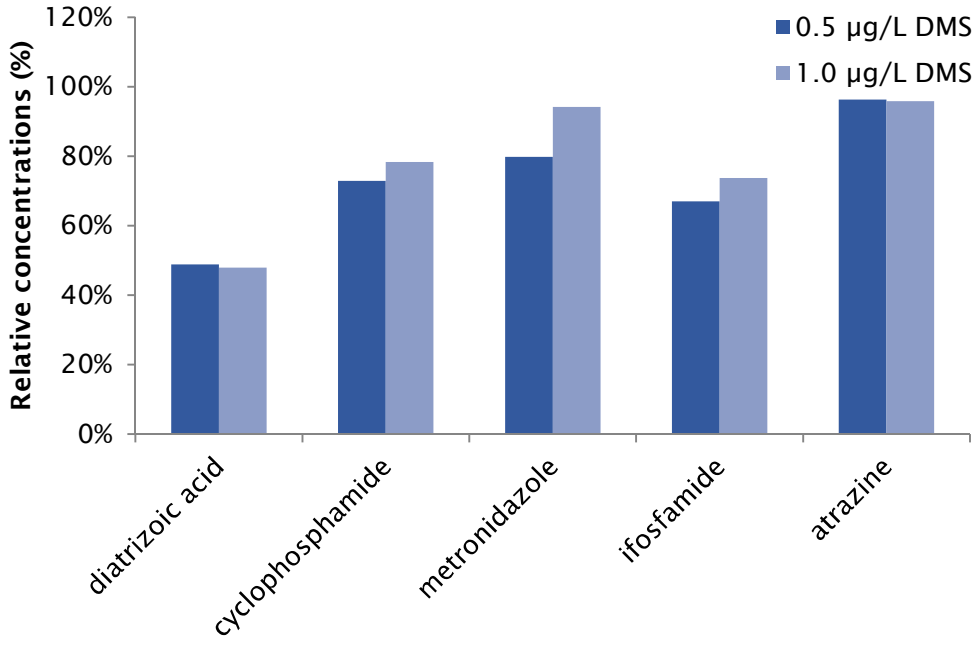


Figure 8-1: concentrations of reference compounds relative to the concentrations aimed at.

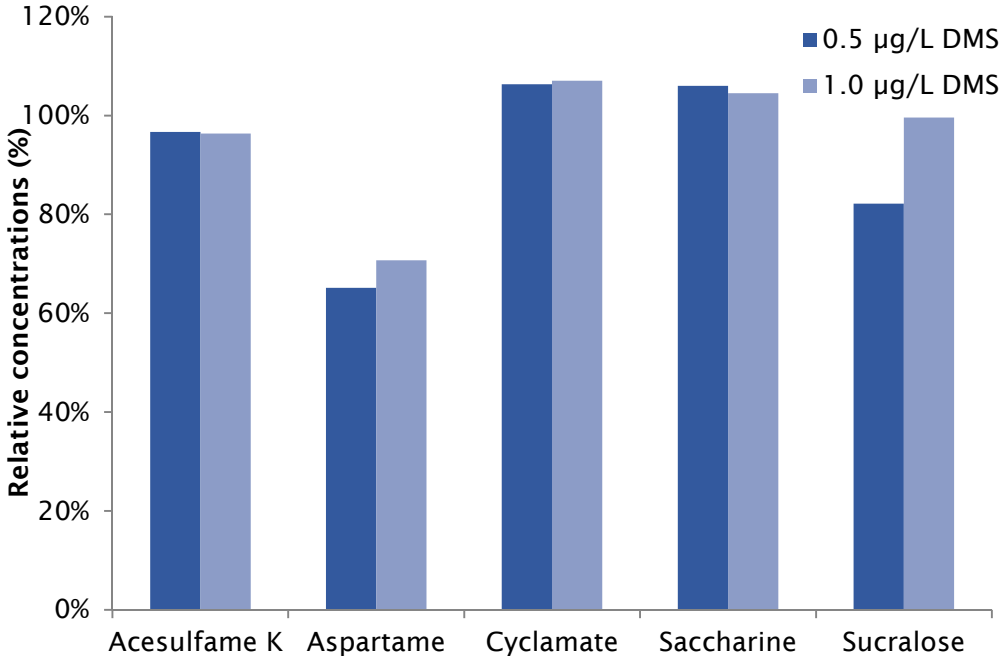


Figure 8-2: concentrations of sweeteners relative to the concentrations aimed at.

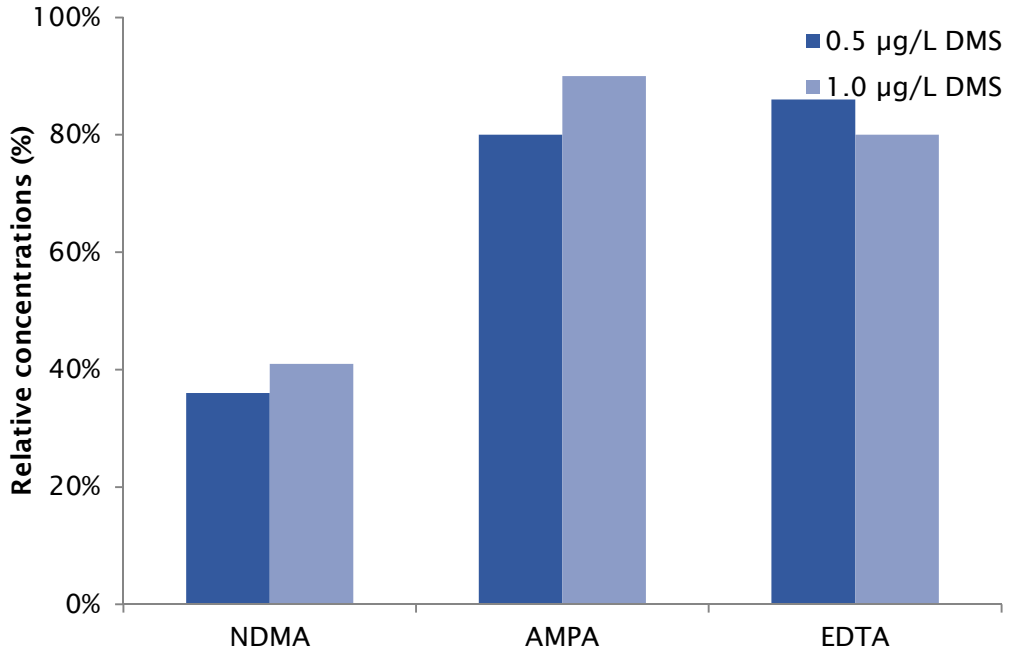


Figure 8-3: concentrations of NDMA, AMPA and EDTA relative to the concentrations aimed at.

For some compounds (diatrizoic acid, aspartame and NDMA) the influent concentrations appeared to be significantly lower than had been expected. It is not clear what caused this difference (whether e.g. already part of the material had been degraded before measurement). For further calculations the measured influent concentrations were used.

8.3 Water quality

Water quality data for the additional pilot experiments are shown in Table 8-2 and Table 8-3.

Table 8-2: Water quality data for the additional experiments, 08-07-2015

	pH	HCO_3	nitrate		TOC	Turbidity
		mg/L	mg/L NO_3	mg/L N	mg/L C	FTE
Rapid sand filtrate	7.46	179	1.6	0.4	1.6	<0.1
After UV (730 mJ/cm²)					1.6	
After ACF (CT 20 min.)					1.2	

Some of the compounds dosed during these experiments may also be found in the influent water before dosing, as can be concluded from Table 8-3. This is the case for DMS, Acesulfame K and Sucralose.

Table 8-3: Presence of additional compounds in pretreated water from site Heel

Compound	Concentration
	µg/L
DMS	0.077
NDMA	<0.001
AMPA	< 0.02
EDTA	< 5
Reference compounds	
atrazine	< 0.01
Cyclophosphamide	< 0.01
Diatrizoic acid	< 0.01
Ifosfamide	< 0.01
Metronidazole	< 0.01
sweeteners	
Acesulfame K	0.347
Aspartame	< 0.03
Cyclamate	< 0.03
Saccharine	< 0.10
Sucralose	0.224

Obviously, only DMS, acesulfame K and sucralose are present in the pretreated water, at concentrations above the reporting limit.

8.4 Conversion of additional compounds

The conversion or removal of the additional compounds was measured after treatment with UV/H_2O_2. The DMS conversions for test 1 (0.5 µg/L) and test 2 (1.0 µg/L) were respectively 57.3 and 61.4%. Based on the pseudo first order rate constant calculated in section 7.2, a conversion of about 48% would have been expected. However, the conditions within the CB set-up cannot directly be compared with the conditions within a UV reactor, as here the reactor geometry, the flow through the reactor and the specific output of the lamp used will also play an important role. Taking this difference into account, it can be concluded that there is a fairly good accordance between the laboratory experiments in the CB set-up and the real UV reactor applied, and that the DMS concentrations can be decreased in the pilot reactor by about 60% at a flow of 1 m^3/hour (ca. 730 mJ/cm^2) and a H_2O_2 concentration of 10 mg/L.

The conversions of the other compounds are shown in Figure 8-4- Figure 8-6.

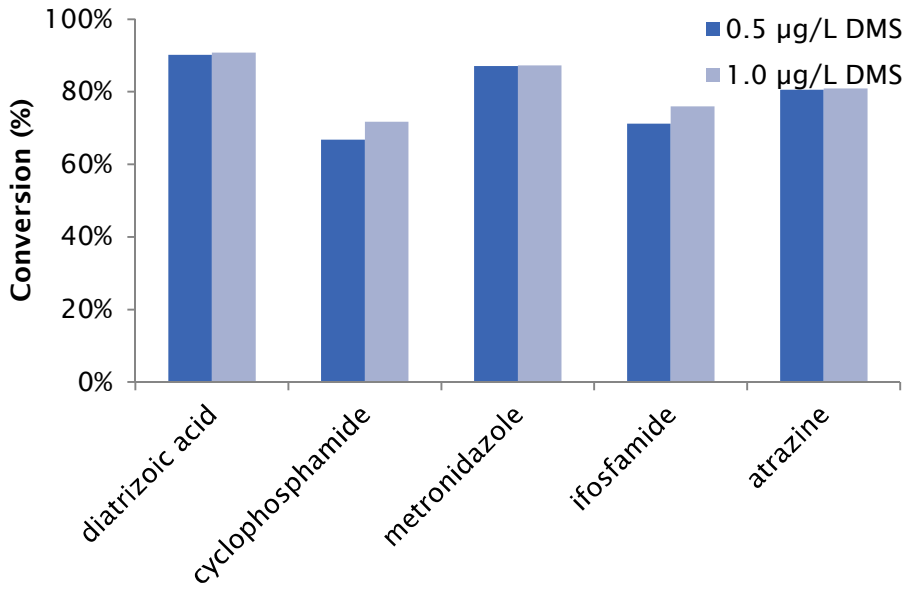


Figure 8-4: conversion of reference compounds during the UV/H_2O_2 process (08-07-2015). UV dose circa. 730 mJ/cm^2, 10 mg H_2O_2 /L.

For all reference compounds a good conversion was obtained under the circumstances applied. For cyclophosphamide and ifosfamide a degradation > 70% was obtained, for atrazine about 80%, and for diatrizoic acid and metronidazole of about 90%. At another drinking water utility, Dunea, the UV dose applied in a UV/H_2O_2 pilot reactor was based on 80% atrazine conversion, as this in general resulted in sufficient atrazine reduction to obtain concentrations below the detection limit, and would also give sufficient degradation of other micropollutants observed. Obviously, these criteria can be met at WML PS Heel too.

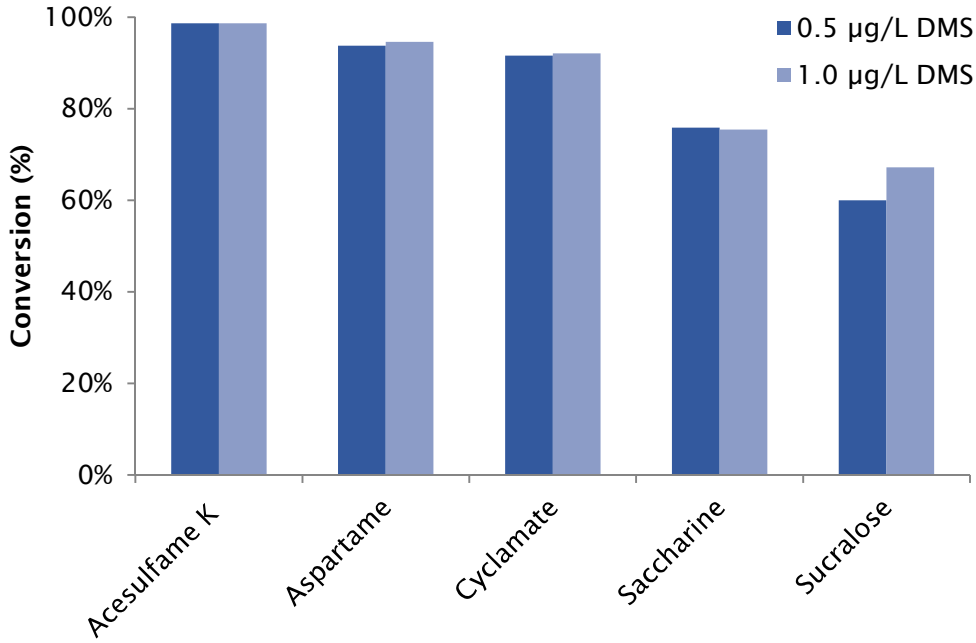


Figure 8-5: conversion of sweeteners during the UV/H_2O_2 process (08-07-2015). UV dose circa. 730 mJ/cm², 10 mg H_2O_2 /L.

Sweeteners can be found wherever traces of (treated) human wastewater are present As the influent of PS Heel is located at a short distance downstream of the local WWTP, it can be expected that sweeteners will be present in the influent. This is confirmed by Table 8-3, which shows that the influent water contains acesulfame K. Figure 8-5 shows the removal of sweeteners from the water by means of the UV/H_2O_2 process. According to the experimental results sucralose appears to be the most difficult compound to remove within this set of compounds, with an degradation level of about 65%. For Saccharine the conversion is about 75%, and for acesulfame K, aspartame and cyclamate the removal appears to be > 90%. This shows that the UV/H_2O_2 process is very effective for the removal of sweeteners.

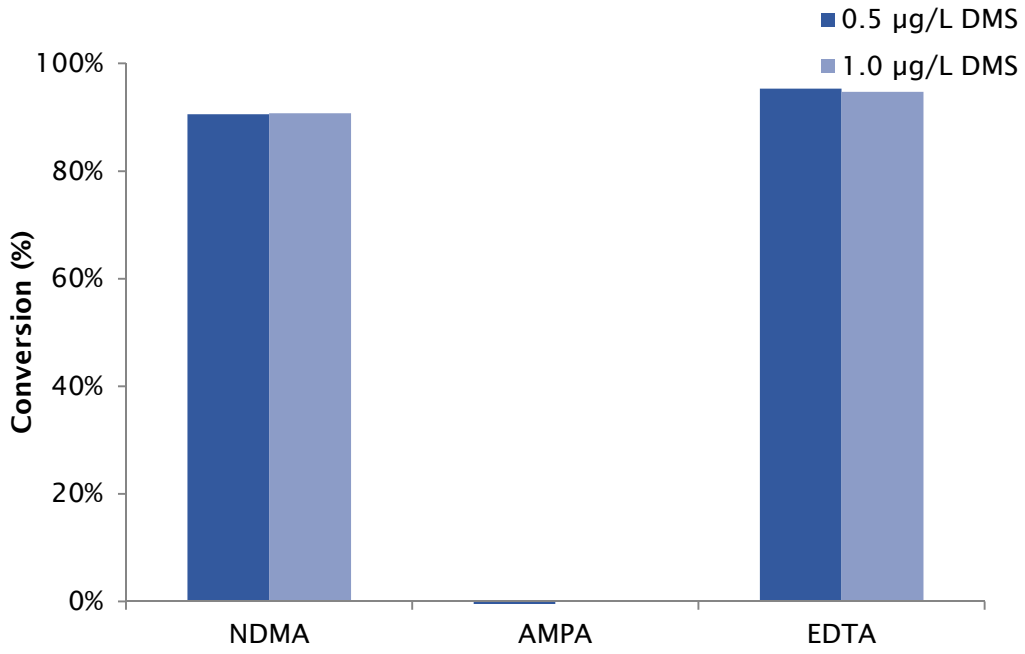


Figure 8-6: conversion of NDMA, AMPA and EDTA during the UV/H_2O_2 process (08-07-2015). UV dose circa. 730 mJ/cm², 10 mg H_2O_2 /L

Under the conditions applied, the UV/H_2O_2 process appeared to be able to remove both NDMA and EDTA to a level >90%. For NDMA this had been expected, as the compound is very liable to photolysis by means of UV-C irradiation, but also for EDTA the process appears to be very suitable too.

For AMPA the results appeared not to be reliable, possibly due to analytical uncertainties. In the experiment with 0,5 µg DMS/L a conversion of -19% was calculated, whereas in the second experiment (1,0 µg DMS/L) no conversion could be determined. It is not clear what caused these unexpected results: possibly the analysis of AMPA is less reliable, but there are no data to support this. Therefore, these results are not shown in Figure 8-6. It is not clear whether AMPA can be removed by means of the UV/H_2O_2 process; more research would be required to establish this.

8.5 Filtration over activated carbon

The total removal, based on influent concentrations, after the filtration over activated carbon (contact time 20 min.) of the additional compounds was measured. The total DMS removal for test 1 (0.5 µg/L) and test 2 (1.0 µg/L) was 87.2 and 82.7% respectively. The total removal of the other compounds is shown in Figure 8-7 - Figure 8-9.

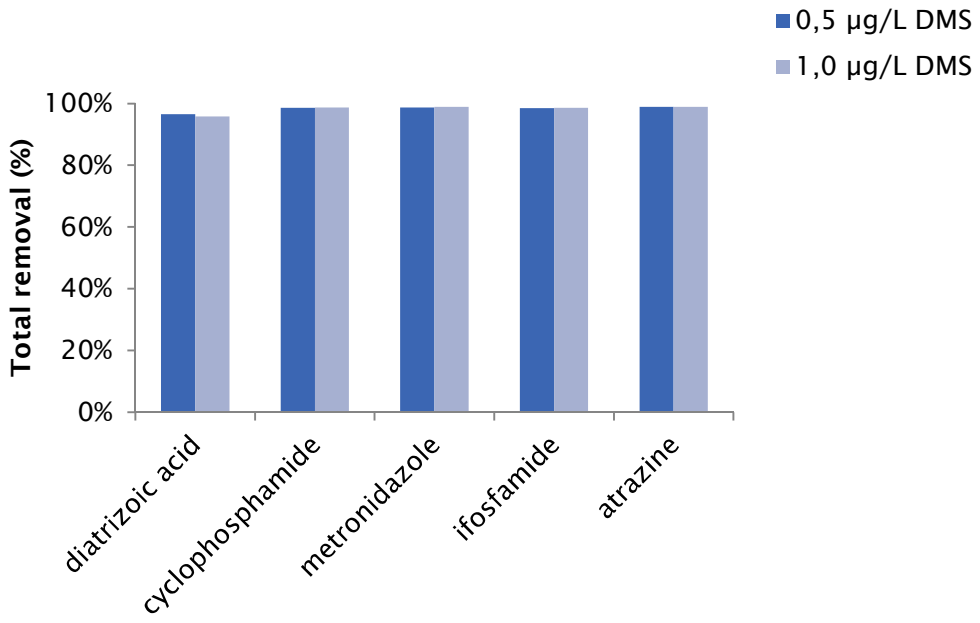


Figure 8-7: Total removal of reference compounds during the UV/H_2O_2 process (08-07-2015).

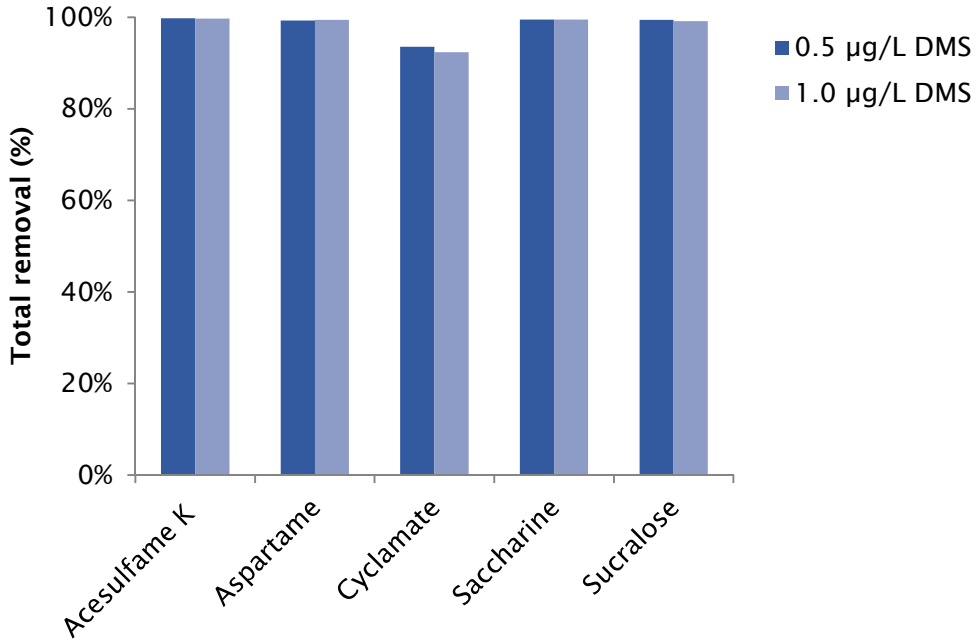


Figure 8-8: Total removal of sweeteners during the UV/H_2O_2 process (08-07-2015).

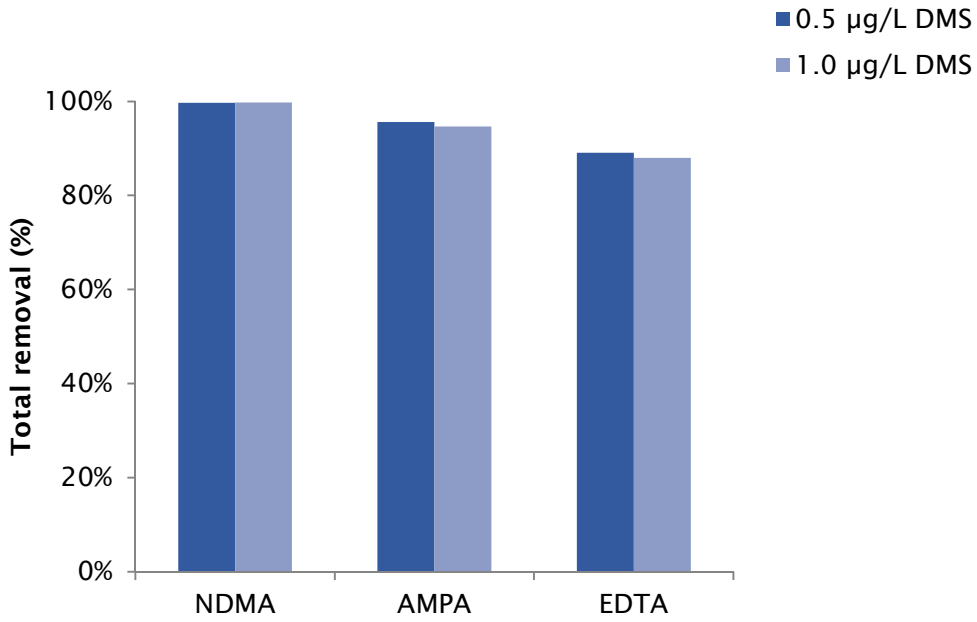


Figure 8-9: Total removal of NDMA, AMPA and EDTA during the UV/H_2O_2 process (08-07-2015).

The total removal for most compounds, under the circumstances applied, is > 95% . For cyclamate the total removal is > 90%, and for EDTA, for which the UV/H_2O_2 process did not give clear results, a removal of about 88% was obtained after activated carbon filtration.

9 Cost estimation of UV/H_2O_2 process

For the cost estimation it is important to define the goal of the process. It will not be necessary to degrade all organic micropollutant for 100%. In this case DMS was taken as a reference compound. According to measurements by WML during 2012-2014 DMS is present in concentrations of 0.08-0.15 μg/L, with an average of about 0.1 μg/L. A UV dose of about 800 mJ/cm^2 would be required to remove DMS to a concentration below the reporting limit of 0.03 μg/L.

The "Kostencalculator" model of RoyalHaskoningDHV was used to estimate the costs of the UV/H_2O_2 process, followed by activated carbon filtration (ACF). Initially, an energy demand of 260 Wh/m^3 was applied. The uncertainty in this model is ±30%. Besides, it does not take into account a specific UV dose or the water quality (UV-T), which in the case of Heel are very favorable for the process, as a result of which the process at Heel would require significantly less energy than an average UV/H_2O_2 process. An overview of the cost estimation is shown in Table 11-24. In this table the design capacity (20*10^6 m^3/year) of WTP Heel is taken as a starting point, but the actual production capacity at Heel is about 15*10^6 m^3/year instead of 20*10^6 m^3/year, which results in lower operational costs. Besides, during the pilot investigation it was found that the present residence time in the AC filter (ca. 30 minutes) should be sufficient to remove both the excess of H_2O_2 and possibly formed transformation products or metabolites. Therefore, it will not be necessary to extend the ACF capacity, as was assumed in the original cost estimation (Hofman et al., 2013). This results in the cost estimation shown in Table 11-25, which gives the additional costs involved with extension of the present treatment process with a UV/H_2O_2 process at a production capacity of 15*10^6 m^3/year. However, as the treatment plant at Heel was developed for a peak capacity of 20 *10^6 m^3/year, this capacity should be taken into account for estimation of investment costs. Combining Table 11-24 and Table 11-25 results in the data shown in Table 9-1.

*Table 9-1: Cost estimation for an additional UV/H_2O_2 treatment at WTP Heel, using the present ACF, assuming a peak capacity of 20*10^6 m^3/year and a production of 15*10^6 m^3/year*

costs	M€/year	remarks
Total investment (M€)	7.61	Peak capacity 20*10^6 m^3/year
Fixed costs (M€/year)	0.749	Peak capacity 20*10^6 m^3/year
Operational costs (M€/year)	0. 979	Production 15*10^6 m^3/year
Additional costs (administration and operation) (M€/year)	0.012	Production 15*10^6 m^3/year
Total costs (M€/year)	1.740	Production 15*10^6 m^3/year
Total costs (€/m^3)	0.116	Production 15*10^6 m^3/year

For the process at Heel two important parameters will help to reduce the energy requirement and thus energy costs:

1. The UV-T of the water is high, therefore the reflection at the outer wall has to be taken into account. According to Table 3-6 about 20% less energy is required to obtain the desired UV-dose.
2. The reactor geometry had been optimized, resulting in a decrease in energy demand of 30-40%.

Taking these parameters into account, the additional costs for the implementation of a UV/H_2O_2 process at WTP Heel will decrease as shown in Table 9-2.

Table 9-2: Effect of water quality and reactor design on additional cost estimation of the UV process.

	Total operational costs (M€/year)	Total costs (M€/year)	Total costs €/m³
Original estimation (260 Wh/m³)	0. 979	1.740	0.116
Taking into account 20% reflection (208 Wh/m³)	0.755	1.639	0.109
Taking into account optimized reactor design (30% energy savings) (145 Wh/m³)	0.878	1.516	0.101

Is seems that a decrease in energy demand of 44% in total only makes about 13% difference in operational costs, which is negligible taking into account 30% uncertainty in the total estimation. Therefore, it can be concluded that the total additional costs will be about 0.11 €/m³.

N.B. As in the present situation, an additional low dose UV disinfection step after the ACF might be necessary to reduce heterotrophic plate counts (HPCs) after the carbon filters.

10 Conclusions and recommendations

10.1 Conclusions

- The reactor applied, with a geometry optimized based on the model which describes the UV/H_2O_2 process, gives good results: high conversions can be obtained at a relatively low energy demand.
- As the UV-T of the water at PS Heel is very high (94%), the UV/H_2O_2 process is very effective here. This means that a low amount of energy is required to obtain a high conversion of a broad range of micropollutants (very low E_{EO} values).
- Some micropollutants that may be found in the source water of PS Heel, like DMS, NDMA, EDTA, the reference compounds diatrizoic acid, cyclophosphamide, metronidazole, ifosfamide, atrazine, and the sweeteners acesulfame K, aspartame, cyclamate, saccharine and sucralose also can be degraded to a high extent (>80%) applying the UV/H_2O_2 process. For AMPA no reliable analyses could be obtained, so it cannot be concluded whether this compound can be removed by means of UV/H_2O_2.
- Further optimization of the process is possible, as the conversion of most compounds under the test conditions probably was much higher than necessary. However, it should be decided to which level degradation should be obtained, and which compounds can be used as reference compounds for this purpose.
- Optimization of the process can be obtained by decreasing the UV dose (and thus the energy demand), or by decreasing the H_2O_2 concentration applied. However, the possible formation of transformation products should be taken into account as well.
- The additional costs for application of a UV/H_2O_2 process at WTP Heel will be about 0.11 €/m^3. For this estimation it is assumed that the present ACF will be sufficient for this process too, as was indicated by the pilot experiments.

10.2 Recommendations

- The UV/H_2O_2 process is very suitable for the removal of organic micropollutants at PS Heel.
- It is important to decide which reference compound, or set of reference compounds, should be used to base the degradation criteria on. Then it can be calculated which UV dose and H_2O_2 concentration are required, to obtain sufficient water treatment and the lowest possible energy use and smallest footprint.
- However, it also should be noted that by optimizing the reaction conditions based on the removal of some parent compounds, this may result in the formation of not fully degraded transformation products. The formation of transformation products and byproducts should further be studied. This can be done using a pilot set-up, but for such “fundamental” studies a collimated beam study probably would be more efficient, as in that case small amounts of water are required, and the experiments can be carried out under very well defined circumstances.
- It should be studied whether an additional UV disinfection after the ACF has to be recommended.

11 Literature

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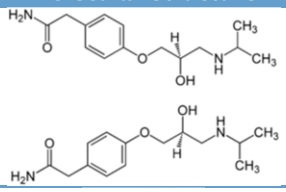
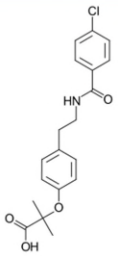
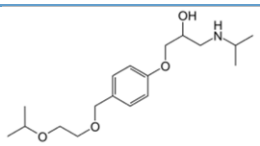
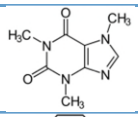
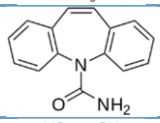
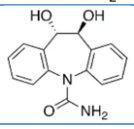
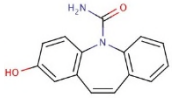
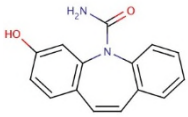
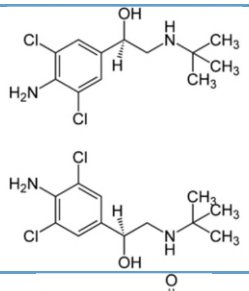
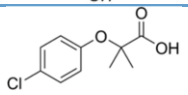
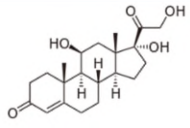
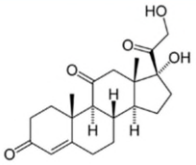
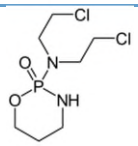
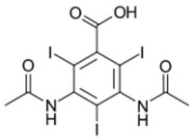
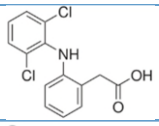
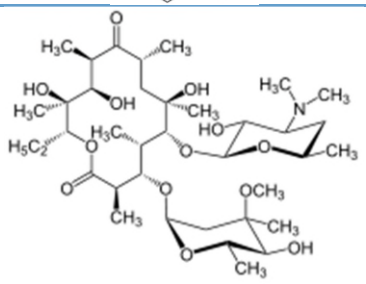
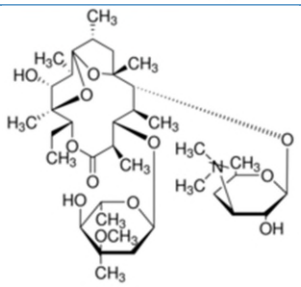
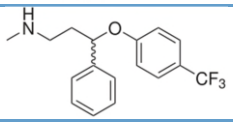
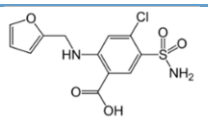
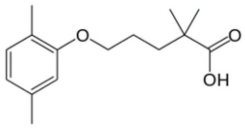
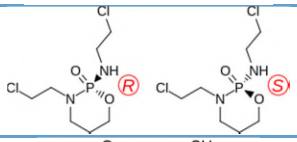
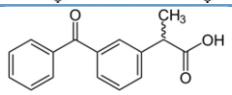
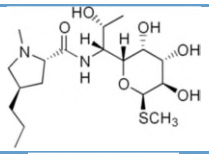
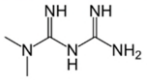
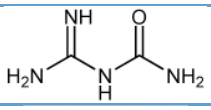
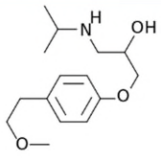
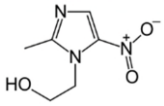
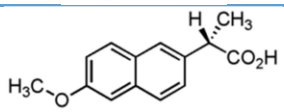
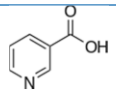
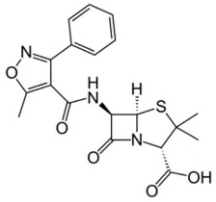
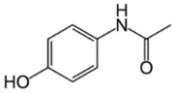
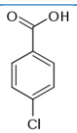
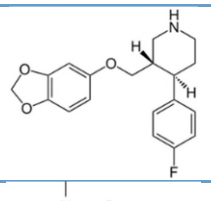
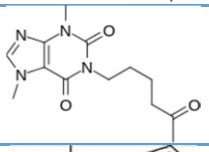
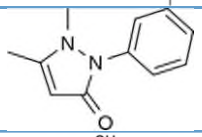
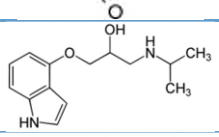
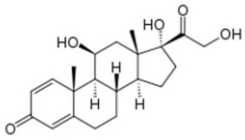
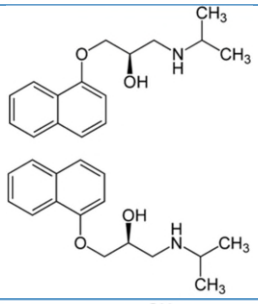
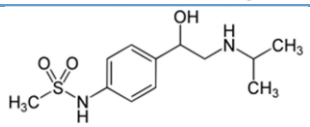
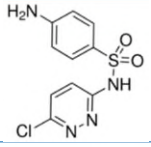
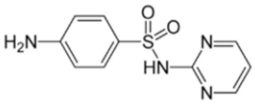
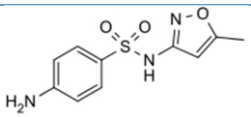
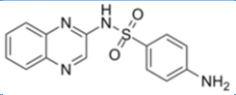
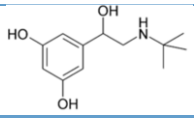
Appendix I Molecular structure of pharmaceuticals and some reference compounds applied

Table 11-1: Compounds applied in the first three series of dosing experiments (see section 3.5).

Pharmaceutical	Molecular structure
Atenolol **29122-68-7**	
Bezafibrate **41859-67-0**	
Bisoprolol **66722-44-9**	
caffeine	
Carbamazepine **298-46-4**	
10,11-trans-diol-carbamazepine	
2-hydroxy-carbamazepine	
3-hydroxy-carbamazepine	

Clenbuterol **37148-27-9**	
Clofibric acid **882-09-7**	
Cortisol **50-23-7**	
Cortisone **53-06-5**	
Cyclophosphamide **50-18-0**	
Diatrizoic acid **737-31-5**	
Diclofenac **15307-86-5**	
Erythromycin A **114-07-8**	
anhydro erythromycin A	
Fluoxetine **54910-89-3**	

Furosemide 54-31-9	
Gemfibrozil 25812-30-0	
Ifosfamide 3778-73-2	
Ketoprofen 22071-15-4	
Lincomycin 154-21-2	
Metformin 657-24-9	
Guanylurea 141-83-3	
Metoprolol 51384-51-1	
Metronidazole 443-48-1	
Naproxen 22204-53-1	
Niacin (vitamin B3, nicotinic acid) 59-67-6	
Oxacillin 66-79-5	
Paracetamol 103-90-2	
para-chlorobenzoic acid (pCBA) 74-11-3	

Paroxetine **61869-08-7**	
Pentoxifylline **6493-05-6**	
Phenazone **60-80-0**	
Pindolol **13523-86-9**	
Prednisolone **50-24-8**	
Propranolol **525-66-6**	
Sotalol **3930-20-9**	
Sulfachloropyridazine **102-65-8**	
Sulfadiazine **68-35-9**	
Sulfamethoxazole **723-46-6**	
Sulfaquinoxaline **59-40-5**	
Terbutaline **23031-25-6**	

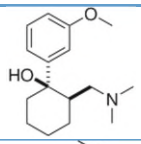
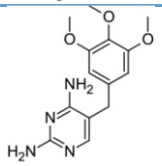
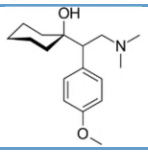
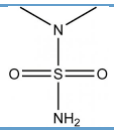
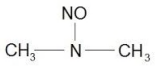
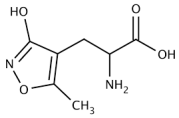
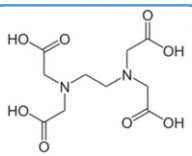
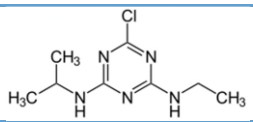
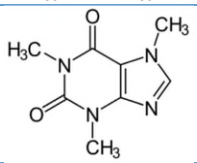
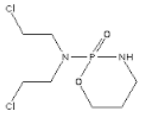
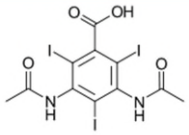
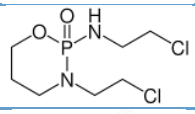
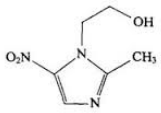
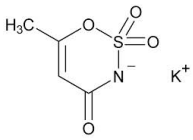
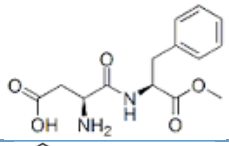
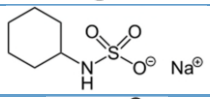
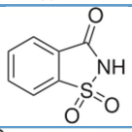
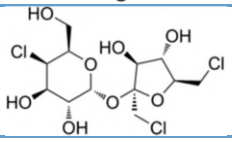
Tramadol **27203-92-5**	
Trimethoprim **738-70-5**	
Venlafaxine **93413-69-5**	

Table 11-2: Compounds applied in the additional experiments (see section 3.7).

Compound	Molecular structure
DMS Dimethylsulfamide 3984-14-3	
NDMA N-nitrosodimethylamine 62-75-9	
AMPA α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid 74341-63-2	
EDTA Ethylenediaminetetraacetic acid 6381-92-6	
Reference compounds	
Atrazine **1912-24-9**	
Caffeine **58-08-2**	
Cyclophosphamide **50-18-0**	

Diatrizoic acid **737-31-5**	
Ifosfamide **3778-73-2**	
Metronidazole **443-48-1**	
sweeteners	
Acesulfame K **55589-62-3**	
Aspartame **22839-47-0**	
Cyclamate **139-05-9**	
Saccharine **81-07-2**	
Sucralose **56038-13-2**	

Appendix II Experimental data dosing experiments

Table 11-3 Data first, second and third experiment first series dosing experiments (30-09-2014)

Code	Unit	Time				Before UV		After UV	
		11:21		11:36					
		Before UV	After UV	Before UV	After UV	avg	SD	avg	SD
UV sensor signal	W/m²	37.5		37.3		37.40	0.14		
UV-T_{254nm} (sp2)	%	94.6	96.5	94.6	96.7	94.60	0.00	96.60	0.14
Temperature Feed (SF)	°C	13.7		14.5		14.10	0.57		
Pressure (before UV/H_2O_2) (PIT1)	Bar	0.962		1.025		0.99	0.04		
Feed flow UV (FIT1)	L/h	993		996		995	2		
Feed flow ACF (FIT2)	L/h	299.8		301.5		301	1		
H_2O_2 concentration	mg/L	10.7	9.1	13.1	9.4	11.90	1.70	9.25	0.21

Table 11-4 Data fourth experiment first series dosing experiments (30-09-2014)

Code	Unit	Time						Before UV		After UV	
		13:25		13:55		14:35	14:55				
		Before UV	After UV	Before UV	After UV	Before UV	Before UV	avg	SD	avg	SD
UV sensor signal	W/m²	36.2		35.8		35.7	36.7	36.10	0.45		
UV-T_{254nm} (sp2)	%	93.5	96.2	93.9	96.1	93.8	93.4	93.72	0.21	95.37	0.07
Temperature Feed (SF)	°C	13.6		13.5		12.9	12.9	13.23	0.38		
Pressure (before UV/H_2O_2) (PIT1)	Bar	1.028		1.061		1.044	1.028	1.04	0.02		
Feed flow UV (FIT1)	L/h	984		999		989	1022	999	17		
Feed flow ACF (FIT2)	L/h	298.9		299.5		299.8	297.7	299	1		
H_2O_2 concentration	mg/L	13.7	9.1	10.4	8.9	11	11	11.53	1.48	9.00	0.14

Table 11-5 Data before start second series dosing experiments (18-11-2014)

Code	Unit	Time
		10:27
		Before UV
UV sensor signal	W/m^2	31.5
UV-T_{254nm} (sp2)	%	93.9
Temperature Feed (SF)	^0C	13.3
Temperature after UV	^0C	13.6
Temperature after ACF	^0C	13.6
Pressure (before UV/H_2O_2) (PIT1)	Bar	0.996
Feed flow UV (FIT1)	L/h	992
Feed flow ACF (FIT2)	L/h	299
H_2O_2 concentration	mg/L	9.1[1]

[1]flow H_2O_2 dosing pump adjusted to 90 mL/h

Table 11-6 Data first experiment second series dosing experiments (18-11-2014)

Code	Unit	Time						Before UV		After UV	
		10:50	11:15		11:35	11:45					
		Before UV	Before UV	After UV	Before UV	Before UV	After UV	avg	SD	avg	SD
UV sensor signal	W/m^2	30.4	30.8		30.3	30.5		30.50	0.22		
UV-T_{254nm} (sp2)	%	93.4	92.7	95.5	93.5	93.6	96.1	93.30	0.41	95.80	0.42
Temperature Feed (SF)	^0C				13.5	13.6		13.55	0.07		
Pressure (before UV/H_2O_2) (PIT1)	Bar				0.990	1.000		1.00	0.01		
Feed flow UV (FIT1)	L/h				1036	1006		1021	21		
Feed flow ACF (FIT2)	L/h				297	296		297	1		
H_2O_2 concentration[1]	mg/L	8.4	8.7	8.6	9.7	9.7	8.6	9.13	0.68	8.60	0.00

[1]flow H_2O_2 dosing pump adjusted to 100 mL/h

Table 11-7 Data second experiment second series dosing experiments (18-11-2014)

Code	Unit	Time						Before UV		After UV	
		13:10		13:30	13:53	14:03					
		Before UV	After UV	Before UV	Before UV	Before UV	After UV	avg	SD	avg	SD
UV sensor signal	W/m^2	27.9		27.7	28.0	28.3		27.98	0.25		
UV-T_{254nm} (sp2)	%	93.4	95.0	93.6	93.5	93.8	95.2	93.58	0.17	95.10	0.14
Temperature Feed (SF)	^0C				13.1	13.2		13.15	0.07		
Pressure (before UV/H_2O_2) (PIT1)	Bar				0.909	0.912		0.911	0.002		
Feed flow UV (FIT1)	L/h				2040	1997		2019	30		
Feed flow ACF (FIT2)	L/h				296	299		298	2		
H_2O_2 concentration[1]	mg/L	10.8	10.1	9.2	8.0	9.0	9.2	9.25	1.16	9.65	0.64

[1]flow H_2O_2 dosing pump adjusted to 220 mL/h

Table 11-8 Data third experiment second series dosing experiments (18-11-2014)

Code	Unit	Time	
		14:35	
		Before UV	after UV
UV sensor signal	W/m^2	27.3	
UV-T_{254nm} (sp2)	%	93.7	94.7
Temperature Feed (SF)	^0C		
Pressure (before UV/H_2O_2) (PIT1)	Bar		
Feed flow UV (FIT1)	L/h		
Feed flow ACF (FIT2)	L/h		
H_2O_2 concentration[1]	mg/L	10.4	9.1

[1]flow H_2O_2 dosing pump adjusted to 320 mL/h

At 14:45 there was emergency stop (low level feed tank). Experiment stopped and started again at a lower feed flow.

Table 11-9: Data third experiment second series dosing experiments (18-11-2014) after emergency stop.

Code	Unit	Time						Before UV		After UV	
		15:40	16:00		16:20	16:30					
		Before UV	Before UV	after UV	Before UV	Before UV	after UV	avg	SD	avg	SD
UV sensor signal	W/m^2	26.3	26		26.1	26		26.10	0.14		
UV-T_{254nm} (sp2)	%	93.8	93.3	95.6	93.7	93.9	95.5	93.68	0.26	95.55	0.07
Temperature Feed (SF)	^0C				13.3	13.3		13.3	0.0		
Pressure (before UV/H_2O_2) (PIT1)	Bar				1.25	1.25		1.25	0.00		
Feed flow UV (FIT1)	L/h				1466	1499		1483	23		
Feed flow ACF (FIT2)	L/h				294	300		297	4		
H_2O_2 concentration[1]	mg/L	8.4	10.9	9.2	9.8	9.5	9.4	9.65	1.03	9.30	0.14

[1]flow H_2O_2 dosing pump adjusted to 150 mL/h. 15:40: flow H_2O_2 dosing pump adjusted to 155 mL/h

Table 11-10 Data first, second and third experiment third series dosing experiments (11-03-2015)

Code	Unit	Time				Before UV	
		8:45	9:25	9:30			
		Before UV	Before UV	Before UV	After UV	avg	SD
UV sensor signal	W/m^2	24.7		24.7		24.70	0.00
UV-T_{254nm} (sp2)	%		93	92.9	94.5	92.95	0.07
Temperature Feed (SF)	^0C			11.7		11.70	
Pressure (before UV/H_2O_2) (PIT1)	Bar	0.729		0.727		0.728	0.001
Feed flow UV (FIT1)	L/h	2000		2002		2001	1
Feed flow ACF (FIT2)	L/h	300		299.7		299.85	0.21
H_2O_2 concentration[1]	mg/L	9.1	8.8	9.8	9.1	9.2	0.5

[1] Concentration stock solution H_2O_2 1%. Flow H_2O_2 dosing pump adjusted to 2 L/h

Table 11-11 Data fourth experiment third series dosing experiments (11-03-2015)

Code	Unit	Time			Before UV	
		10:25	10:40	10:50		
		Before UV	Before UV	Before UV	avg	SD
UV sensor signal	W/m^2	25	24.7	24.7	24.80	0.17
UV-T_{254nm} (sp2)	%	93.3	93.2	93.2	93.23	0.06
Temperature Feed (SF)	^0C	11.9	11.9	11.8	11.87	0.06
Pressure (before UV/H_2O_2) (PIT1)	Bar	0.733	0.733	0.720	0.729	0.008
Feed flow UV (FIT1)	L/h	2000	2000	1999	2000	1
Feed flow ACF (FIT2)	L/h	299	299	300.3	299.43	0.75
H_2O_2 concentration	mg/L	9.3	9.4	9.5	9.4	0.1

Table 11-12 Data fifth experiment third series dosing experiments (11-03-2015)

Code	Unit	Time				Before UV	
		11:00	11:05	11:45	11:55		
		Before UV	Before UV	Before UV	Before UV	avg	SD
UV sensor signal	W/m^2			26	26	26.00	0.00
UV-T_{254nm} (sp2)	%			93.9	93.9	93.90	0.00
Temperature Feed (SF)	^0C			11.8	11.7	11.75	0.07
Pressure (before UV/H_2O_2) (PIT1)	Bar			0.724	0.722	0.723	0.001
Feed flow UV (FIT1)	L/h			1998	1997	1998	1
Feed flow ACF (FIT2)	L/h			300	300.5	300.25	0.35
H_2O_2 concentration[1]	mg/L	4.6	4.8	4.8	4.4	4.7	0.2

[1] Concentration stock solution H_2O_2 1%. Flow H_2O_2 dosing pump adjusted to 1 L/h

Table 11-13 Data sixth experiment third series dosing experiments (11-03-2015)

Code	Unit	Time			Before UV	
		12:47	12:57	13:07		
		Before UV	Before UV	Before UV	avg	SD
UV sensor signal	W/m^2	25.8	26	26.1	25.97	0.15
UV-T_{254nm} (sp2)	%	94	94	94.1	94.03	0.06
Temperature Feed (SF)	^0C	11.8	11.7	11.7	11.73	0.06
Pressure (before UV/H_2O_2) (PIT1)	Bar	0.724	0.72	0.725	0.723	0.003
Feed flow UV (FIT1)	L/h	1980	1980	1980	1980	0
Feed flow ACF (FIT2)	L/h	300	300	300	300.00	0.00
H_2O_2 concentration	mg/L	4.3	4.8	4.4	4.5	0.3

Table 11-14 Data seventh and eighth experiment third series dosing experiments (11-03-2015)

Code	Unit	Time				Before UV	
		13:11	14:11		14:20		
		Before UV	Before UV	After UV	Before UV	avg	SD
UV sensor signal	W/m^2		26.4			26.40	
UV-T_{254nm} (sp2)	%		94.4	95.1		94.40	
Temperature Feed (SF)	^0C		11.7			11.70	
Pressure (before UV/H_2O_2) (PIT1)	Bar		0.716			0.716	
Feed flow UV (FIT1)	L/h		1990			1990	
Feed flow ACF (FIT2)	L/h		300.8			300.80	
H_2O_2 concentration[1]	mg/L	2.8	2.5	2.6	3.0	2.8	0.3

[1] Concentration stock solution H_2O_2 1%. Flow H_2O_2 dosing pump adjusted to 0.63 L/h

Table 11-15 Data ninth experiment third series dosing experiments (11-03-2015)

Code	Unit	Time			Before UV	
		15:05	15:20	15:30		
		Before UV	Before UV	Before UV	avg	SD
UV sensor signal	W/m^2		25.1	25.3	25.20	0.14
UV-T_{254nm} (sp2)	%		93.8	94.8	94.30	0.71
Temperature Feed (SF)	^0C		11.8	11.8	11.80	0.00
Pressure (before UV/H_2O_2) (PIT1)	Bar		0.719	0.715	0.717	0.003
Feed flow UV (FIT1)	L/h		1980	2000	1990	14
Feed flow ACF (FIT2)	L/h		300	299	299.50	0.71
H_2O_2 concentration	mg/L	2.9	2.8	2.9	2.9	0.1

Table 11-16 Data after third series dosing experiments (11-03-2015)

Code	Unit	Time
		16:00
		Before UV
UV sensor signal	W/m^2	27.0
UV-T_{254nm} (sp2)	%	
Temperature Feed (SF)	^0C	
Pressure (before UV/H_2O_2) (PIT1)	Bar	0.967
Feed flow UV (FIT1)	L/h	1000
Feed flow ACF (FIT2)	L/h	300
H_2O_2 concentration[1]	mg/L	10.9

[1]Concentration stock solution H_2O_2 10%. Flow H_2O_2 dosing pump adjusted to 0.1 L/h

Table 11-17 Data test 1 additional DMS experiments

Code	Unit	Time
		10:05
		Before UV
UV sensor signal	W/m^2	26.3
UV-T_{254nm} (sp2)	%	
Temperature Feed (SF)	^0C	12
Pressure (before UV/H_2O_2) (PIT1)	Bar	0.961
Feed flow UV (FIT1)	L/h	997.1
Feed flow ACF (FIT2)	L/h	299.5
H_2O_2 concentration	mg/L	100

Table 11-18 Data test 2 additional DMS experiments

Code	Unit	Time
		11:17
		Before UV
UV sensor signal	W/m^2	24.5
UV-T_{254nm} (sp2)	%	
Temperature Feed (SF)	^0C	12.2
Pressure (before UV/H_2O_2) (PIT1)	Bar	1.259
Feed flow UV (FIT1)	L/h	1997
Feed flow ACF (FIT2)	L/h	302.2
H_2O_2 concentration	mg/L	200

Table 11-19 Data test 3 additional DMS experiments

Code	Unit	Time
		13:45
		Before UV
UV sensor signal	W/m^2	28.1
UV-T_{254nm} (sp2)	%	
Temperature Feed (SF)	^0C	12.2
Pressure (before UV/H_2O_2) (PIT1)	Bar	0.883
Feed flow UV (FIT1)	L/h	2008.9
Feed flow ACF (FIT2)	L/h	299.7
H_2O_2 concentration	mg/L	100

Appendix III Experimental data additional experiments

Table 11-20 Data at the start of the additional experiments (08-07-2015)

Code	Unit	Time							
		10:10 Before UV	10:30 Before UV	10:35 Before UV	10:40 Before UV	10:50 Before UV	11:00 After UV	Before UV avg	Before UV SD
UV sensor signal	W/m^2						27.5		
UV-T_{254nm} (sp2)	%	92.3				93.7	93	93.0	0.7
Temperature Feed (SF)	^0C						12.1		
Pressure (before UV/H_2O_2) (PIT1)	Bar						1.043		
Feed flow UV (FIT1)	L/h						968		
Feed flow ACF (FIT2)	L/h						297		
H_2O_2 concentration[1]	mg/L	15.9	14.7	13.2	8.6	9.0	12.8	12.4	3.0

[1] 10:11: flow H_2O_2 dosing pump adjusted to 70 mL/h. 10:51: flow H_2O_2 dosing pump adjusted to 72 mL/h

Table 11-21 Data first experiment of the additional experiments (08-07-2015)

Code	Unit	Time				Before UV	
		10:10 Before UV	10:30 Before UV	10:35 Before UV	11:00 After UV	avg	SD
UV sensor signal	W/m²			26,7			
UV-T_{254nm} (sp2)	%			93	95,1		
Temperature Feed (SF)	°C			11,7			
Pressure (before UV/H_2O_2) (PIT1)	Bar			1,145			
Feed flow UV (FIT1)	L/h			995			
Feed flow ACF (FIT2)	L/h			299			
H_2O_2 concentration	mg/L	11,2	9,7	10,9	10,7	10,6	0,7

Table 11-22 Data second experiment of the additional experiments (08-07-2015)

Code	Unit	Time	
		13:35 Before UV	13:35 After UV
UV sensor signal	W/m²	27	
UV-T_{254nm} (sp2)	%	93,7	95,5
Temperature Feed (SF)	°C	11,7	
Pressure (before UV/H_2O_2) (PIT1)	Bar	1,050	
Feed flow UV (FIT1)	L/h	956	
Feed flow ACF (FIT2)	L/h	299	
H_2O_2 concentration	mg/L	8,9	10,6

Table 11-23 Data third experiment of the additional experiments (08-07-2015)

Code	Unit	Time						Before UV	
		14:15 Before UV	14:30 Before UV	14:45 Before UV	14:55 Before UV	After UV	15:05 Before UV	avg	SD
UV sensor signal	W/m^2				27,2		26,4	26,80	0,57
UV-T_{254nm} (sp2)	%				93,6	95,4			
Temperature Feed (SF)	^0C				11,7		11,7	11,70	0,00
Pressure (before UV/H_2O_2) (PIT1)	Bar				1,099		1,132	1,12	0,02
Feed flow UV (FIT1)	L/h				974		992	983	12,73
Feed flow ACF (FIT2)	L/h				298		298	298	0,00
H_2O_2 concentration	mg/L	11,7	9,9	9,6	9,5	10,3		10,18	1,03

Appendix IV Model calculations at UV-T = 94% and at UV-T = 96% versus actual conversion data

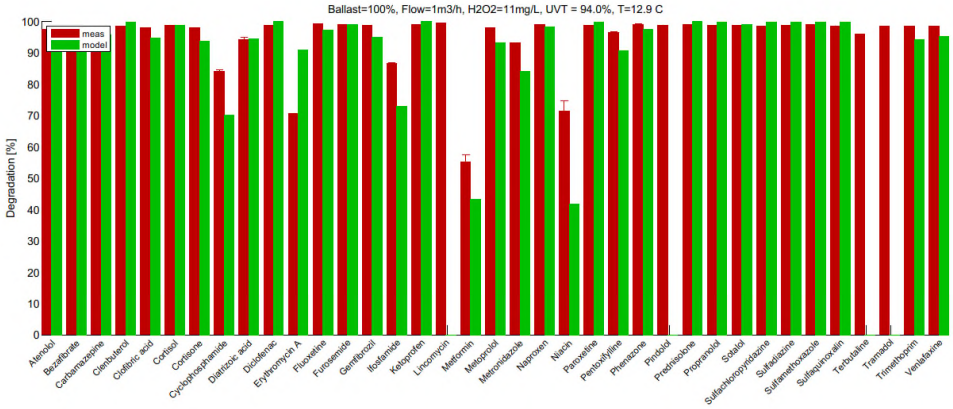


Figure 11-1 Calculations and actual conversion data during the first series of experiments; Ballast 100%, 1 m3/hour, 11 mg H_2O_2/L; UV-T = 94%

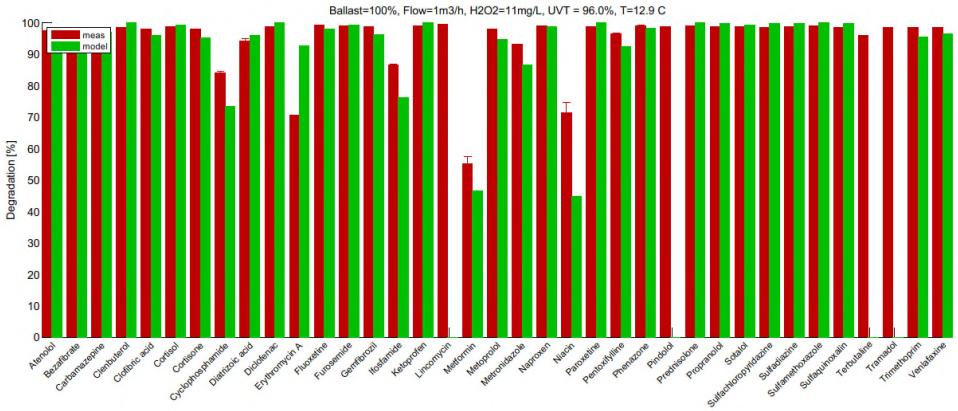


Figure 11-2 Calculations and actual conversion data during the first series of experiments; Ballast 100%, 1 m^3/hour, 11 mg H_2O_2/L; UV-T = 96%

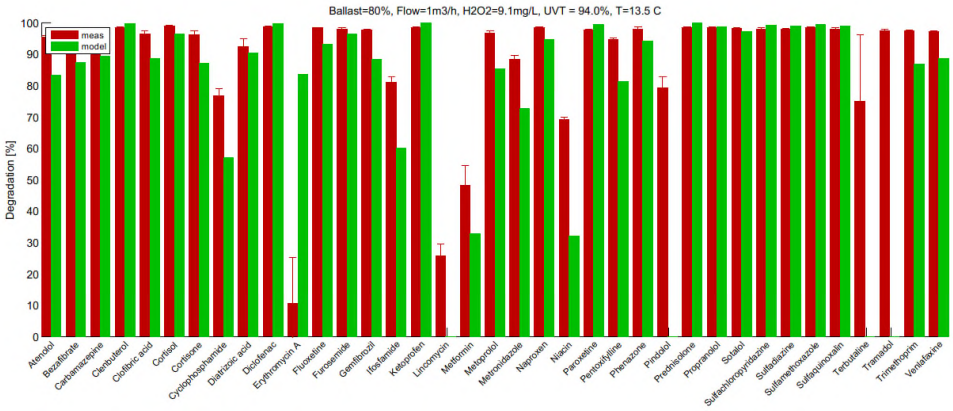


Figure 11-3: Calculations and actual conversion data during the second series of experiments; Ballast 80%, flow 1 m3/hour, 9.1 mg H_2O_2/L UV-T = 94%

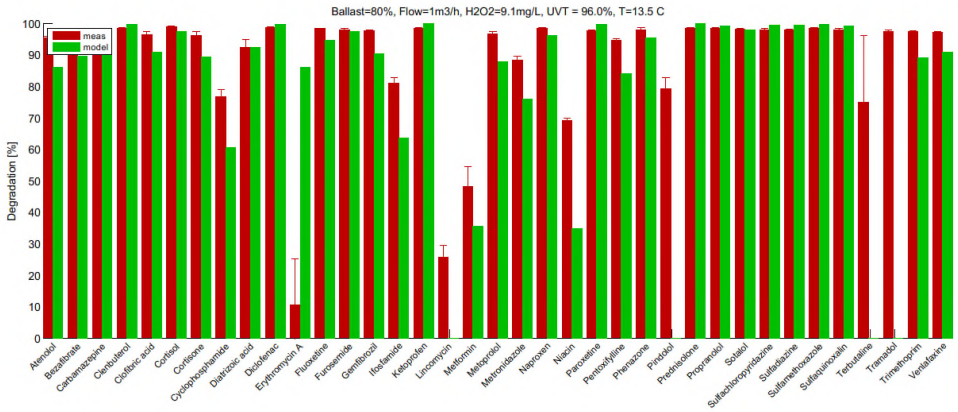


Figure 11-4: Calculations and actual conversion data during the second series of experiments; Ballast 80%, flow 1 m^3/hour, 9.1 mg H_2O_2/L UV-T = 96%

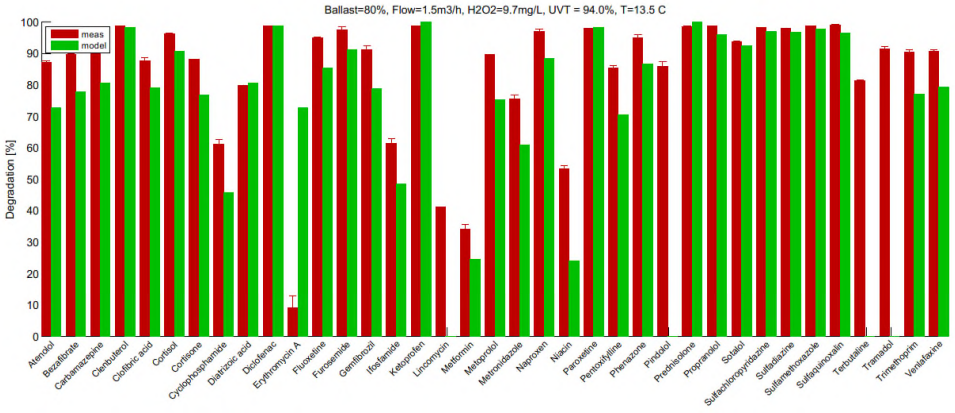


Figure 11-5: Calculations and actual conversion data during the second series of experiments; Ballast 80%, flow 1,5 m^3/hour, 9.7 mg H_2O_2/L ; UV-T = 94%

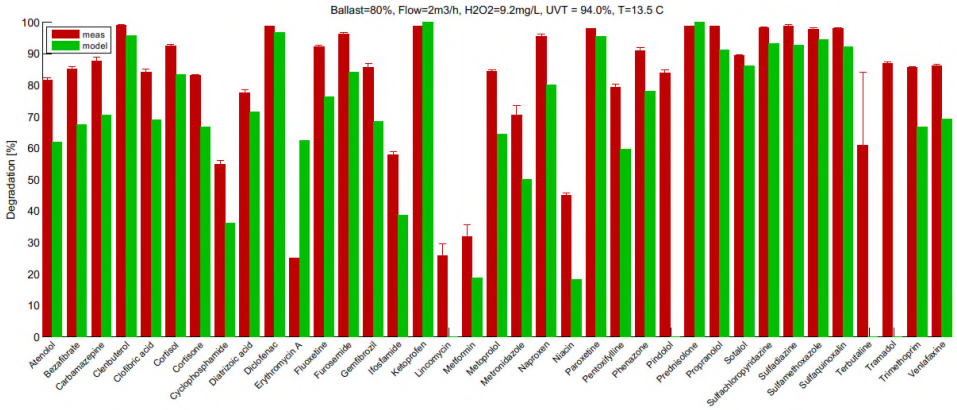


Figure 11-6: Calculations and actual conversion data during the second series of experiments; Ballast 80%, flow 2 m^3/hour, 9.2 mg H_2O_2/L ; UV-T = 94%

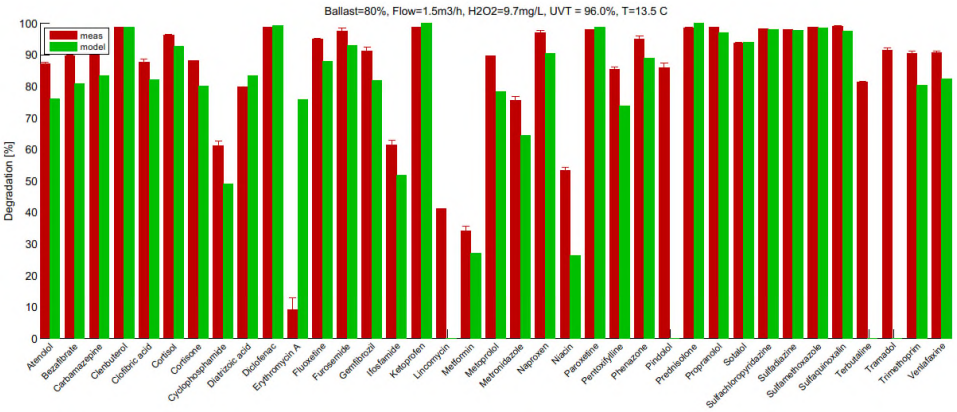


Figure 11-7: Calculations and actual conversion data during the second series of experiments; Ballast 80%, flow 2 m^3/hour, 9.2 mg H_2O_2/L ; UV-T = 96%

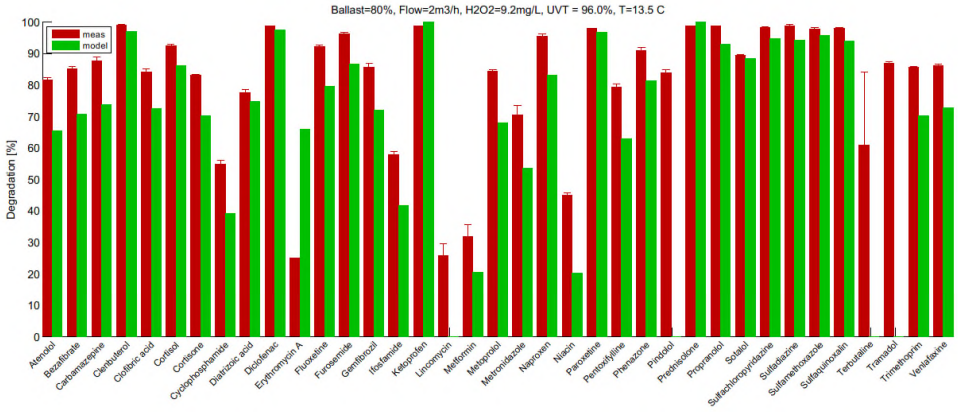


Figure 11-8: Calculations and actual conversion data during the second series of experiments; Ballast 80%, flow 2 m^3/hour, 9.2 mg H_2O_2/L ; UV-T = 96%

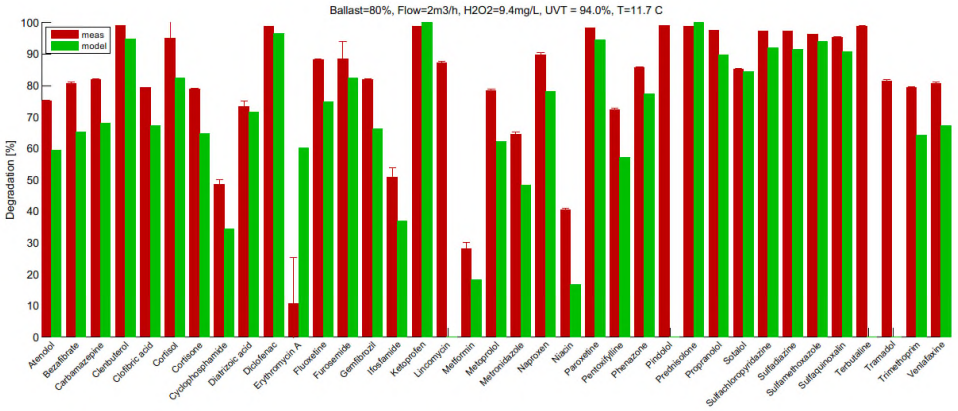


Figure 11-9: Calculations and actual conversion data during the third series of experiments; Ballast 80%, flow 2 m^3/hour, 9.4 mg H_2O_2/L ; UV-T = 94%

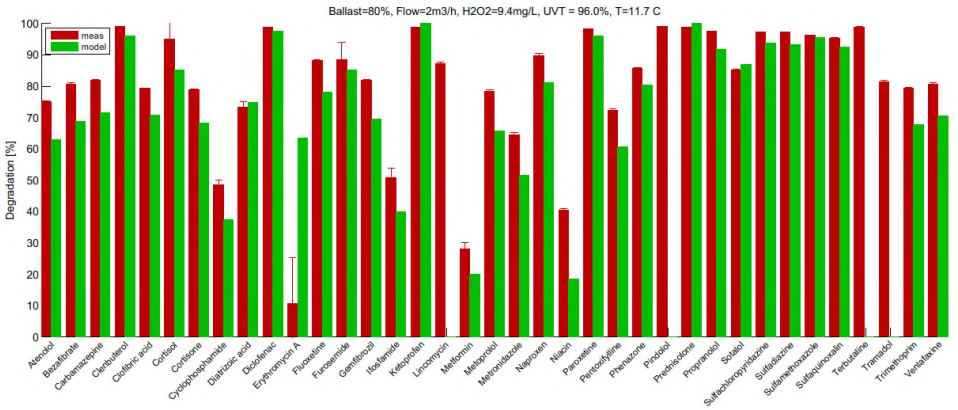


Figure 11-10: Calculations and actual conversion data during the third series of experiments; Ballast 80%, flow 2 m^3/hour, 9.4 mg H_2O_2/L ; UV-T = 96%

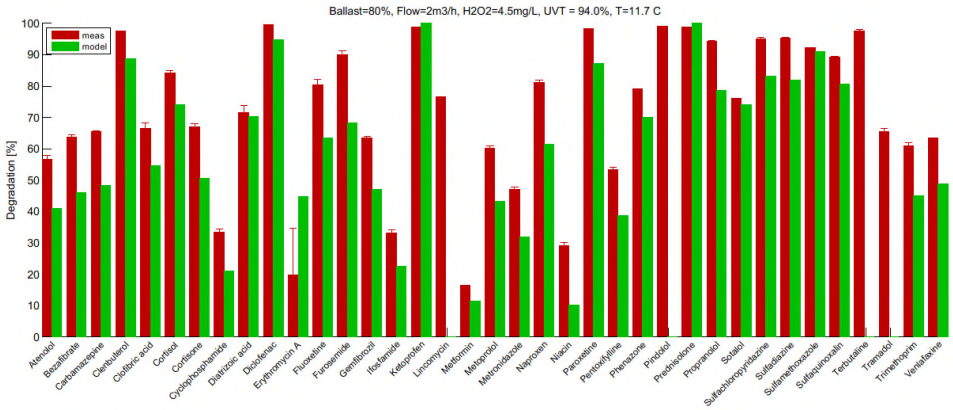


Figure 11-11: Calculations and actual conversion data during the third series of experiments; Ballast 80%, flow 2 m³/hour, 4.5 mg H_2O_2/L ; UV-T = 94%

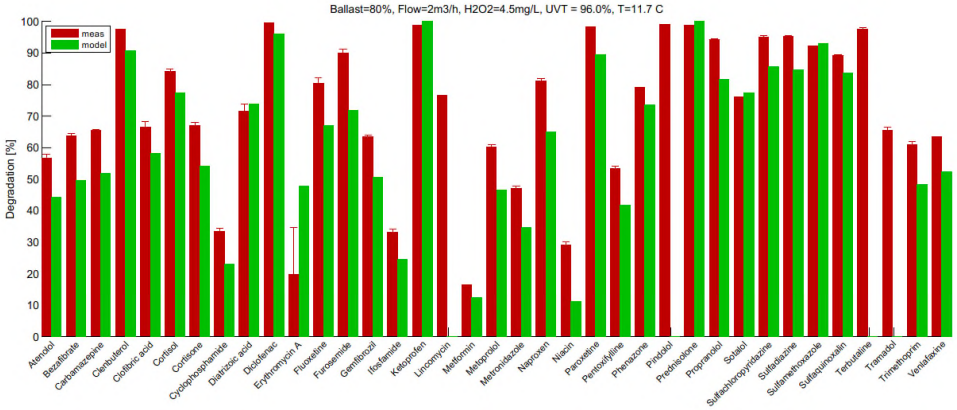


Figure 11-12: Calculations and actual conversion data during the third series of experiments; Ballast 80%, flow 2 m³/hour, 4.5 mg H_2O_2/L ; UV-T = 94%

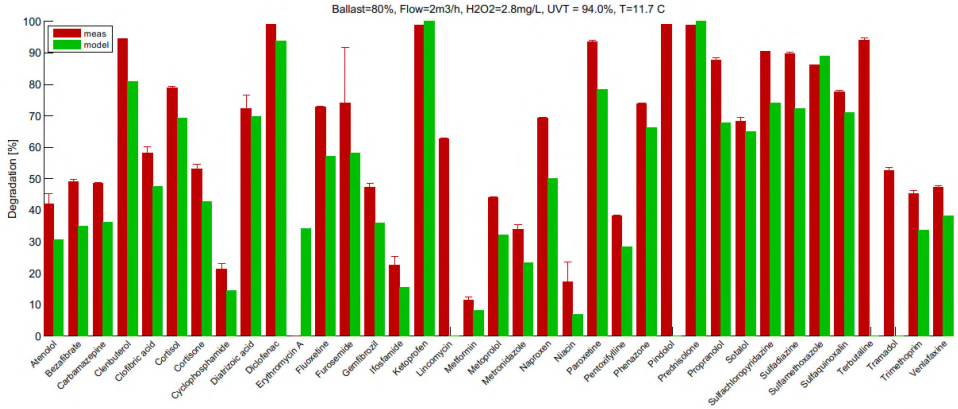


Figure 11-13: Calculations and actual conversion data during the third series of experiments; Ballast 80%, flow 2 m^3/hour, 2.8 mg H_2O_2/L; ; UV-T = 94%

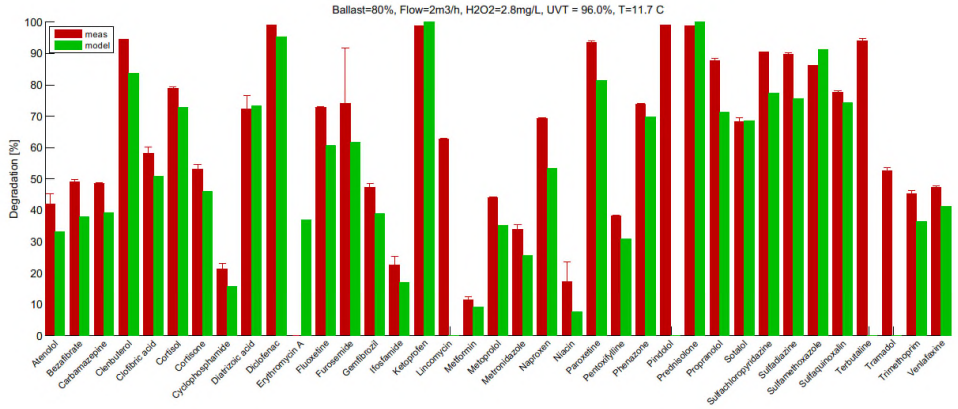


Figure 11-14: Calculations and actual conversion data during the third series of experiments; Ballast 80%, flow 2 m^3/hour, 2.8 mg H_2O_2/L; ; UV-T = 96%

Appendix V

Cost estimation of AOP processes

*Table 11-24: parameters for cost estimation of UV/H_2O_2 combined with ACF by means of RHDHV model, at a production of 20*10^6 m^3/year*

WPB Heel		20	Mm3/j		**EBCT Bestaande AKF**		20	min																							
		3200	m3/h																												
									BK	Inv	Totaal	Afschrijving			M€ / j			Variable kosten			M€ / j			Totale kosten							
Proces		Spoel	Jaarcap	Uurcap	Procesparameters				M€	M€	M€	Civ	Wtb	Elec	Overig	Totaal		Energie		Overige				M€ / j	€ / m3		Civiel	Wtb	Elek	Leidin	Totaal
			20,101																												
Pompkelder			20,101	3216,1	Verblijftijd	15	minuten		0,32	0,51	0,51	0,015	0,021	0,011				Wh/m3				Onderhoud					40%	40%	20%		100%
																		20				4,00%									
																0,047			0,052				0,013	0,112	0,006						
LD pomp zuivering			20,101	3216,1	opvoerhoogte	150	kPa		1,96	3,13	3,13	0,046	0,161	0,097				Wh/m3				Onderhoud					20%	50%	30%		100%
					efficiency	70%												60				4,00%									
																0,303			0,156				0,079	0,538	0,027						
Dosering	H2O2		20,101	3216,1	dosering	10	mg/l		0,05	0,08	0,08	0,001	0,006	0,001							Chemicaliën	Onderhoud					10%	75%	15%		100%
																						4,00%									
																0,008					0,201		0,002	0,211	0,011						
UV-desinfectie			20,101	3216,1					2,46	3,92	3,92	0,021	0,292	0,081				Wh/m3			Lampen	Onderhoud					7,5%	72,5%	20%		100%
																		260				4,00%									
																0,394			0,679		0,0201		0,098	1,192	0,060						
Actieve-koolfiltratie		0,5%	20,101	3216,1	Contacttijd	20	minuten		6,94	11,07	12,03	0,362	0,427	0,199	0,084			Wh/m3			Reactivatie	Onderhoud					45%	37,5%	#####		100%
extra					Reactivaties	24	maanden		Kool						Kool			0				4,00%									
					nieuw na	10	react.		0,965							1,073			0		0,1876		0,278	1,538	0,077						
			20,000	3200																											
							Totaal Investeringen				19,67							Subtotaal processen						3,590							
Bediening				0,20	mensjaar à €	50000												Bediening						0,01							
Adm. Beheerskosten				20%	van bediening													Adm. Beheerskosten						0,002							
Kwal. Bewaking																		Kwal. Bewaking						pm							
																		Totaal					M€/j	3,602							
Zuiveringsrendement			99,50%															Exploitatiekosten					€/m3	0,180							

*Table 11-25: parameters for additional cost estimation by means of RHDHV model, based on a production of 15*10⁶ m³/year, not taking into account the activated carbon filtration process.*

WPB Heel	15	Mm3/j		**EBCT Bestaande AKF**		30	min																								
	2400	m3/h																													
								BK	Inv	Totaal	Afschrijving		M€ / j			Variable kosten			M€ / j			Totale kosten								
Proces		Spoel	Jaarcap	Uurcap	Procesparameters			M€	M€	M€	Civ	Wtb	Elec	Overig	Totaal	Energie		Overige				M€ / j	€ / m3		Civiel	Wtb	Elek	Leiding	Totaal		
			15,000																												
Pompkelder			15,000	2400,0	Verblijftijd	15	minuten	0,24	0,38	0,38	0,011	0,016	0,008			Wh/m3				Onderhoud				40%	40%	20%		100%		
																20				4,00%										
															0,035		0,039				0,010	0,083	0,006							
LD pomp zuivering			15,000	2400,0	opvoerhoogte	150	kPa	1,51	2,41	2,41	0,035	0,124	0,075			Wh/m3				Onderhoud				20%	50%	30%		100%		
					efficiency	70%										60				4,00%										
															0,234		0,116				0,061	0,411	0,027							
Dosering	H2O2		15,000	2400,0	dosering	10	mg/l	0,05	0,08	0,08	0,001	0,006	0,001					Chemicaliën		Onderhoud				10%	75%	15%		100%		
																				4,00%										
															0,008				0,15		0,002	0,160	0,011							
UV-desinfectie			15,000	2400,0				1,97	3,14	3,14	0,017	0,235	0,065			Wh/m3		Lampen		Onderhoud				7,5%	72,5%	20%		100%		
																260				4,00%										
															0,317		0,507		0,015		0,079	0,918	0,061							
Actieve-koolfiltratie		0,0%	15,000	2400,0	Contacttijd	10	minuten	0,00	0,00	0,00	0,000	0,000	0,000	0,000		Wh/m3		Reactivatie		Onderhoud				45%	37,5%	#####		100%		
extra					Reactivaties	24	maanden	Kool						Kool		0				4,00%										
					nieuw na	10	react.	0,000							0,000		0		0		0,000	0,000	0,000							
			15,000	2400																											
							Totaal Investeringen			6,02						Subtotaal processen						1,571								
Bediening				0,20	mensjaar à €	50000										Bediening						0,01								
Adm. Beheerskosten				20%	van bediening											Adm. Beheerskosten						0,002								
Kwal. Bewaking																Kwal. Bewaking						pm								
																Totaal					M€/j	1,583								
Zuiveringsrendement			100,00%													Exploitatiekosten					€/m3	0,106								