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IGF-Forschungsvorhaben 202 EN

Elimination von Mikroschadstoffen und Transformationsprodukten mit einem Kombinationsprozess aus Ozonung, Photokatalyse und biologisch-adsorptiver Nachbehandlung (AOPTi)

Deutsches Teilprojekt des europäischen Cornet-Forschungsprojektes ”Assessment of Advanced Photocatalytic Oxidation process for Micropollutant Elimination in Municipal and Industrial Waste Water Treatment Plants”

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Dieser Cornet-Gesamtschlussbericht soll auch als IGF-Schlussbericht angesehen werden.

This Cornet final report should also be regarded as IGF final report.

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List of abbreviations

Abbreviation	Meaning
A-YES	Arxula yeast-based estrogenic screen
AES	atomic emission spectroscopy
BAC	Biologicaly activated carbon
BET	Brunauer-Emmett-Teller
BOD_5	Biological oxygen carbon
BV	Bed volumes
DAPI	4′,6-diamidine-2-phenylindole
DDT	Dichlorodiphenyltrichloroethane
DEHP	Bis(2-ethylhexyl) phthalate
DNA	Deoxyribonucleic acid
DMSO	Dimethyl sulfoxide
DOC	Dissolved organic carbon
EU	European Union
EEQ	Estradiol-equivalents
EC	Evaluation criteria
EC_{50}	Half maximal effective concentration
ESI	Electrospray ionization
GAC	Granulated activated carbon
GC	Gas chromatography
HRMS	High-resolution mass spectrometry
ICP	Inductively coupled plasma
IUPAC	International Union of pure and applied chemistry
IUTA	Institut für Energie- und Umwelttechnik e. V.
KOM-M.NRW	Kompetenzzentrum Mikroschadstoffe NRW
LC	Liquid chormatography
LP	Low pressure
NTS	Non-target screening
MetOH	Methanol
MP	Medium pressure
MS	Mass spectometry
MS/MS	Tandem mass spectrometry
MTT	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium-bromide
µLC	Microflow liquid chormatography

Abbreviation	**Meaning**
Non-target-classifiaction: C	Constant
Non-target-classifiaction: H	Higher
Non-target-classifiaction: L	Lower
Non-target-classifiaction: N	New
Non-target-classifiaction: R	Removed
NRW	Northrhine-Westphalia
OECD	Organization for economic co-operation and development
PAC	Powdered activated carbon
PBDE	Polybrominated diphenyl ethers
PE	Population equivalents
PFOS	Perfluorooctanesulfonic acid
R	programming language and free software environment for statistical computing and graphics
SAK	spectral adsorption coefficient
SEM	Sacinning electron microscopy
SME	Small or medium-sized enterprises
TiO_2	Titanium dioxide
TOC	Total organic carbon
TU	Toxic unit
ULG-NCE	University of Liege, Department of Chemical Engineering – Catalysis, Nanomaterials, Electrochemistry
UV	Ultraviolett
WP	Work packages1
WWTPs	Wastewater treatment plants
WFD	Water Framework Directive

1. Presentation of the research program and objectives

The continuous discharge of micropollutants resulted in an accumulation of these micropollutants in surface and ground water reservoirs. The EU Water Framework Directive (WFD), whose aim is the preservation of water resources, considered this problematic. In fact, the European legislation in the field of water quality and water and wastewater treatment is evolving constantly. The WFD (2000/60/EC) regulation adopted in 2000 has been amended in 2013, 2015 and 2018 with new micropollutants. A watch list of selected micropollutants is currently at the state of survey in the different European countries. After this period of surveillance, further regulations will probably be designed and enforced. Therefore, solutions for the reduction of the amount of micropollutants at the point source wastewater treatment plant (WWTP) effluent will be required to ensure a good chemical status of the receiving surface waters.

Other local legislations are considering the micropollutant content of wastewater. An indirect measure of the content of micropollutant is the evaluation of water toxicity. The analyses of resulting toxicity of water on *Daphnia magna* microorganisms is now mandatory in Wallonia since March 2016. This toxicity parameter is now included in the taxation calculation and is correlated to the global content of pollutants. The taxation value for companies will increase soon due to this parameter and reach high costs in a near future. Again, efficient solutions for wastewater treatment are needed.

The objective of this project was to mitigate the occurrence of hazardous micropollutants in effluents from municipal and industrial WWTPs. For decades, numerous micropollutants reached WWTPs as a result of urban and industrial usages of pharmaceuticals, cosmetic and hygiene products, as well as a result of the intensive application of pesticides and biocides (e.g. KOM-M.NRW 2016, UBA 2018). Historically, the objectives of traditional wastewater treatment were mainly on removal of organic carbon, nitrogen and phosphorus, named macropollutants and nutrients. As a result, pesticides, pharmaceuticals and other chemicals are partially or not degraded. These micropollutants are mostly stable chemical molecules. Depending on the chemical nature, these micropollutants may be adsorbed onto the activated sludge, volatilised or partially/totally biodegraded. Yet, certain micropollutants are soluble and not biodegradable, ending up in the effluent of the WWTP. For an effective reduction of micropollutants, traditional WWTPs need additional barriers, such as advanced treatment technologies (tertiary wastewater treatment).

Innovative treatment technologies for elimination of persistent, mobile and/or toxic micropollutants in wastewater are therefore needed [Joss, 2008; Jones, 2007]. The combination of ozonation with photocatalysis is a promising solution for almost complete elimination of micropollutants, considering previous lab scale results. Scale-up, improvement and demonstration of this novel technology is performed in this project. The assembling and design of the combined ozone-ultraviolet (UV) (photocatalytic) treatment is crucial to facilitate future implementation by small or medium-sized enterprises (SMEs) performed. The treatment plant using ozone-UV photocatalytic has to be designed, built and operated. Process parameters have to be determined depending on water composition to help SMEs. The process dimensioning, efficiency and cost assessments are then expected results from this project.

The project is divided in the following phases:

- Identification of the most efficient titanium dioxide (TiO_2) coating
- Evaluation of advanced oxidation processes combining ozonation and photocatalysis.
- Scale-up of a photocatalytic TiO_2 adherent and persistent coating.
- Development of a robust tertiary treatment process for companies active in wastewater treatment.
- Validation of the process at the WWTP scale.
- Characterization of resulting toxicity

The partners of the project are:

- CELABOR (Herve, Wallonia, Belgium) - Coordinator
- ULG-NCE (University of Liege, Department of Chemical Engineering – Catalysis, Nanomaterials, Electrochemistry, Liege, Wallonia, Belgium)
- IUTA (Institut für Energie- und Umwelttechnik e. V, Duisburg (Institute of Energy- and Environmental Technology e. V.), North Rhine-Westphalia, Germany)

The AOPTi research program is divided into 10 work packages (WP):

- WP1: Coordination
- WP2: Identification of relevant micropollutants depending on Regional and European legislation (chapter 3.1)
- WP3: Enhancement and optimization of the quantification methods using gas chromatography (GC) or liquid chromatography (LC) combined with tandem mass spectrometry (MS/MS) and the toxicity-based approach for the identification of transformation products (chapter 0).
- WP4: Assessment of the degradation properties TiO_2 photocatalyst UV-ozone technology on model water at lab-scale (chapter 5).
- WP5: Scale-up of the sol gel TiO_2 coating (chapter 5.1.10).
- WP6: Addition of a biological activated carbon for the adsorption of emerging TP and remaining micropollutants (chapter 6.1.2).
- WP7: Assessment of the process on municipal and industrial wastewaters with a demonstration scale plant (300 L/h) (chapter 0).
- WP8: Degradation experiments in a Municipal WWTP in demonstration-scale (1 up to 5 m^3/h) (chapter 8).
- WP9: Cost evaluation of the ozone-UV photocatalytic adsorption treatment and of the TiO_2 sol-gel coating0).
- WP10: Dissemination (chapter 12 and 0)

The structure of the project and the sequence of work packages is of the work packages is shown in Figure 1.

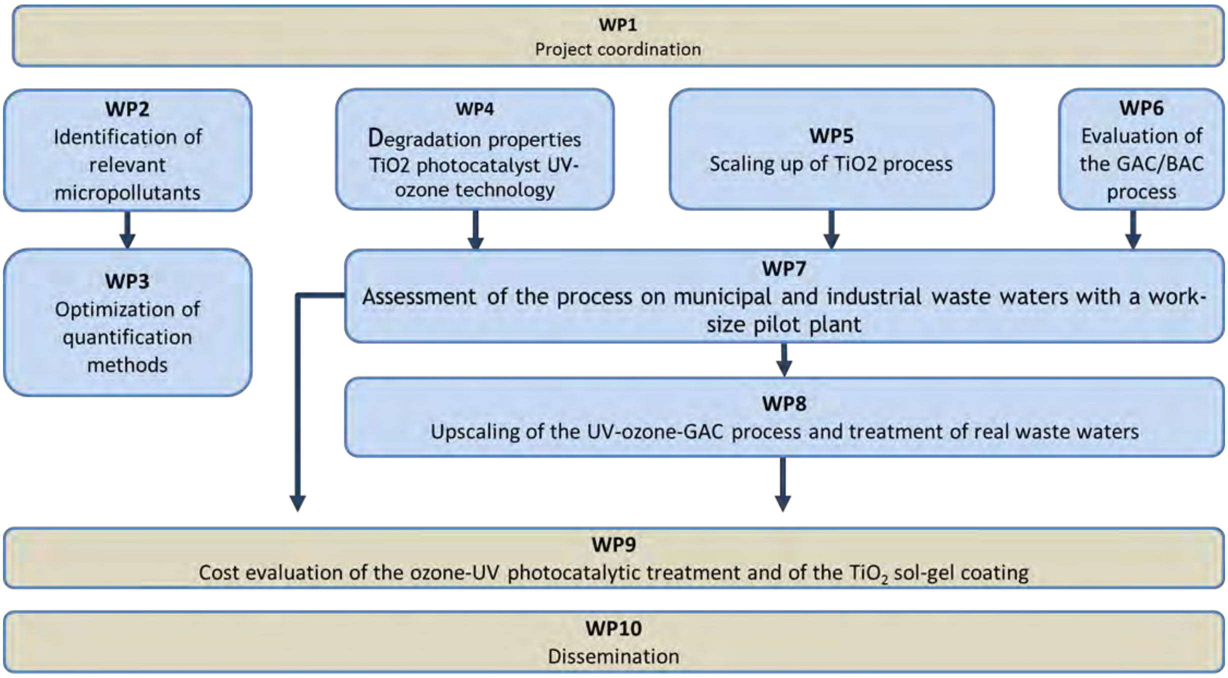


Figure 1: Overview of the AOPTi work packages.

2. State of the art and technological alternatives

Due to the increasing use of pharmaceuticals, industrial and household chemicals, biocides, pesticides, etc. in everyday life, these substances reach sewage treatment plants to a large extent via municipal wastewater (Rodriguez-Mozaz 2015). Some of these compounds can have a negative effect on aquatic ecosystems or the quality of drinking water resources. E.g. feminization of fish can be caused by the discharge of estrogenically active substances into a river (Jobling 1998, Kidd 2007) or antibiotic resistance can be increased by antibiotics in the environment (Pruden 2014).

However, conventional municipal wastewater treatment plants are designed to reduce nutrients (nitrogen and phosphorus compounds) and the organic load of the wastewater - BOD_5 (biological oxygen demand) or TOC (total organic carbon). Even though some substances can be successfully eliminated from the wastewater by a conventional wastewater treatment process (e.g. Ibuprofen) (Kim 2008), municipal wastewater treatment plants are one of the most important pathways of micropollutants entering near-surface waters (Gavrilescu 2015). The removal of micropollutants appears as one of the greatest challenges facing water management in the coming years (Schwarzenbach 2006, von Sonntag 2012). For this reason, a stakeholder dialogue has been conducted in Germany since 2015 in which measures to reduce micropollutants in water have been developed (BMU/UBA 2017, BMU/UBA 2019). These substances includes organic compounds from the fields of active pharmaceutical ingredients, personal care products, household chemicals, pesticides, etc. Although wastewater treatment in Germany has reached a very high level, more than 80% of surface waters have so far failed to meet the environmental objectives of Article 4 of the European Water Framework Directive.

This project will focus on an advanced elimination of micropollutants in the context of the WFD (2000/60/EC, 2008/105/EC, 2013/39/EU, EU 2015/495, EU 2018/840) like biocides, pesticides, chemicals and pharmaceutical active ingredients. Metals are not considered in this project because they cannot be degraded by AOP processes. The WFD contains a list of 45 priority substances (2013/39/EU). Two hormones (17α-ethinylestradiol, EE2, 17β-estradiol, E2) and a painkiller Diclofenac have been added in 2013 to the watch list (EU 39/2013). In 2015 another hormone (Estrone, E1), an anti-oxidant (2,6-Ditert-butyl-4-methylphenol, E321), an UV-filter (4-Methoxycinnamate), a carbamate pesticide (methiocarbe) and three macrolide antibiotics (Erythromycine, Clarithromycine and Azithromycine), 5 neonicotinoids (Imidacloprid, Thiacloprid, Thiamethoxam, Clothianidin and Acetamiprid) and two herbicides (Oxadiazon and Triallat) were added to the watch list (EU 2015/495) and have to be monitored in European surface waters and point sources like WWTPs.

During 2017, the Commission analysed the data from the first year of monitoring. On the basis of this, the Commission concluded that sufficient monitoring data are available for the substances Triallate, Oxadiazone, 2,6-Ditert-butyl-4-methylphenol and Diclofenac and that these substances should therefore be removed from the monitoring list. (EU 2018/840). The mentioned environmental quality standards for the priority substances have to be reached for the surface waters until 2027.

The industry and the civil society are also becoming interested in this topic. In the opinion of German industry, the avoidable wastewater pollution caused by micropollutants should be addressed in particular. The German industry therefore supports the strategy laid down in the Federal Government's policy paper to reduce the input of trace substances through measures at source, during application and through downstream measures (BDI 2018). The idea of this policy paper is a joint stakeholder dialogue between countries, municipalities, water management, producers, users and civil society in Germany. The aim of the stakeholder dialogue is to develop practicable and implementable solutions in dialogue. The results of the dialogue process are intended to propose a contribution to a common, technical understanding and a set of suitable strategies and measures for dealing with trace substances at federal level (BMU/UBA 2017).

Besides relevant micropollutants of the involved catchments and regions (Wallonia and Germany) the AOPTi project will focus on the priority substances of the Water Framework Directive. Main task will be the demonstration of the potential of photocatalytic advanced oxidation processes for elimination of these trace organic compounds from the water cycle.

Currently, there are several technologies available for micropollutant elimination. In a short summary, there are mainly two principal ways: the biological and the chemical-physical methods. In the biological way, biological reactors are composed of bacterial strains selected for their abilities to degrade some micropollutants but not all (Gillard 2014). By combining different aerobic and anaerobic treatments in the biological reactor, certain micropollutants may be degraded but these improvements are restricted to a limited number of compounds (Falås 2016). The second major way of micropollutant elimination is the physical chemical treatment. It may be integrated in the WWTP after the classical biological treatment. It can be ozone, UV, adsorption on activated carbon, membrane filtration, reverse osmose or a combination of some of these processes. The effectiveness of these hybrid technologies depends on the chemical nature of the molecules to be removed. Moreover, few data are available in the literature on the combination of ozone followed by UV-TiO_2 treatment (Tanaka 1996, Tanaka 2011).

Concerning the patents published in the field of ozone-UV photocatalytic, a patent study had been conducted with the help of the Association Picarré in Liège in September 2016. Some of the identified patents are related to the AOPTi project. Most of them are Chinese or Japanese and some are older than 20 years. By consequence, there is no trouble for exploitation in Europe, USA or Australia. Only one Chilean patent EP1686095 needs to be controlled for future exploitation. However, it has no validity in Europe and it is still in phase A. Additionally, the patent claims are for aquaculture and not industrial wastewater.

Concerning the situation in the surrounding countries, it needs to be mentioned hast to be known that Switzerland is one of the leader in that field. Indeed, Switzerland is very concerned about the problematic of micropollutants in their water (river, groundwater). Recently, the Swiss government has ordered a large study on micropollutant elimination processes (Rik 2014). These large scale studies preceded the Swiss decision to equip 100 of their 700 WWTPs with a tertiary treatment step. This survey suggests that ozonation and powdered activated carbon (PAC) are currently the technically most feasible methods for micropollutant elimination in Switzerland. Both methods, according to the above article, reduce the load of broad range micropollutants with 80% in average from influent to effluent of WWTP (Bourgin 2018). However, the ozone and powdered activated carbon techniques must be followed by a polishing step such as sand filtration to eliminate any bioavailable oxidation products and particles. These conclusions have been validated at the WWTP of Lausanne in Switzerland (Margot 2013). This study also concludes that, in addition to adsorption on activated carbon and ozonation, other processes are also suitable for removing micropollutants. Among others, this paper includes adsorption on granulated activated carbon, retention by selective membranes (nanofiltration, reverse osmosis), substance oxidation with OH radicals (Advanced Oxidation Processes, AOP) and use of ferrate. These processes are working properly but are not yet suitable for large scale use in WWTPs, because of lack of industrial scale experience and the Swiss government wanted to start implementing their WWTPs in 2016.

In Germany there were several WWTP equipped with an enhanced treatment step to remove micropollutants. Most of them were located in North Rhine-Westphalia or Baden-Württemberg (e.g. ARGE Spurenstoffe NRW 2014, MKULNV 2014, Ministerium für Umwelt, Klima und Energiewirtschaft Ba-Wü 2017). The treatment steps were divided into adsorption using granulated activated carbon (GAC), powdered activated carbon (PAC) or ozonation. In terms of energy, installation of an additional treatment stage increases the energy consumption of about by 30% (rapport office de l’environnement, Bern, 2012).

In conclusion, the AOPTi project, compared to all previous and current projects in the field of micropollutant elimination aims at the total destruction of micropollutants leading to no toxic by-products by a subsequent combination of ozone and UV photocatalytic treatment followed by an adsorption step as a post treatment.

3. Detailed presentation of the results achieved by the funding, taking the defined objectives into account

3.1 Identification of relevant micropollutants depending on Regional and European legislation (WP2; IUTA, Celabor)

The aim of the bibliographic study was to identify the most problematic micropollutants in European, German and Walloon Waters (in the frame of the project, the focus was effluents of wastewater treatment plants).

In Wallonia, the bibliographic study was based on sources described below.

- The Water Framework Directive (Directive 2000/60/EC)
- The book ‘Etat de l’Environnement Wallon 2017’
- The results of Walloon R&D projects like BIODIEN - IMHOTEP and SEMTEP. These projects were coordinated by the Walloon Region to highlight the most problematic substances in groundwater, surface water, WWTP effluents and potable water in Wallonia. The BIODIEN project was focus on endocrine disruptors, IMHOTEP on pharmaceuticals and SEMTEP on perchlorate
- The list of the most sold medicines in Belgium
- The list of the most sold pesticides in Belgium
- The Directive 2008/105/CE from European Parliament, application in 2014 to identify major priority substances rejected in industrial effluents.

Based on data of the bibliographic study on concentration and toxicity of the main micropollutants, a first model water with 5 micropollutants at 10 µg/L (Table 1) was prepared. These persistent pollutants were characterized in terms of degradation efficiency after AOPTi treatment.

Two model waters were prepared during the project.

- A first model water containing 5 micropollutants analysed by GC-MS/MS and 5 micropollutants analysed by LC-MS/MS. The first model water was used for the determination of the most efficient and durable coating.
- A second extended model water containing more than twenty micropollutants. This water was used to emphasize the effectiveness of the coating on a wide range of micropollutants.

In practice, Celabor analysed all molecules by GC-MS/MS and IUTA by LC-MS/MS.

Table 1: Model water used for the identification of the most efficient coating. Substances are analysed by GC-MS/MS.

Molecules	Classes	Properties	Problematic in Wallonia	WFD: priority list	Quantification
Bis(2-ethylhexyl) phthalate (DEHP)	phtalate	UV improved sensibility to ozone	X	X	GC-MS/MS
Tributyl phosphate	plastifiant	not sensible to ozone	X	X	GC-MS/MS
Atrazine	pesticide	sensible to ozone	X	X	GC-MS/MS
Lindane	pesticide	not sensible to ozone	X	X	GC-MS/MS
Polybrominated diphenyl ethers (PBDE)	flame retardant	sensible to ozone	X	X	GC-MS/MS

The micropollutants below (Table 2) at a concentration of 10 µg/L were added to the first model water. The TiO_2-based coating was validated on the whole list of micropollutants.

Table 2: Additional micropollutants of the model water (extended GC-MS/MS list).

Compound	compound type
Desethylatrazine	pesticide
2,6-dichlorobenzamide	pesticide
Bromacile	pesticide
Simazine	pesticide
Chlortoluron	pesticide
Isoproturon	pesticide
Dichlorodiphenyltrichloroethane (DDT)	pesticide

In Germany, the following sources for the literature research were used:

- Water Framework Directive (Directive 2000/60/EC)
- Statistic data of the most sold medicines in Germany and Belgium (IMS Health GmbH)
- Data of “Kompetenzzentrum Spurenstoffe Baden-Württemberg“ and „Kompentenzzentrum Mikroschadstoffe NRW“ (https://www.masterplan-wasser.nrw.de/other/index.html (currently not available), https://koms-bw.de/)
- Legislation in Switzerland for micropollutants monitoring in wastewater treatment plants (summary of informations at https://www.micropoll.ch/de/dokumente/gesetzliche-grundlagen/)
- Watch list (EU 2015, EU 2018)
- Directive 2008/105/EC from European Parliament, application in 2014 to identify major priority substances rejected in industrial effluents

At the beginning of the research of relevant micropollutants, the current legal regulations were reviewed. National and international guidelines, the watch list of the EU Water Framework Directive and the list of priority substances were considered. The selection of relevant micropollutants from both countries was restricted by including and statistically evaluating collected measurement data from Germany. Due to the lack of limit values for effluents of wastewater treatment plants for most micropollutants, an evaluation of the concentrations can be carried out analogous to the evaluation for surface waters according to the Water Framework Directive. As a "worst case" consideration the dilution by discharge into the aquatic environment was not considered. The evaluation serves only to assess the emissions of municipal wastewater treatment plants. The evaluation scheme is given in Table 3. A list of the evaluation criteria (EC) for NRW can be found in the so-called D4 list (https://www.flussgebiete.nrw.de/node/7724).

Table 3: Evaluation schemes for concentrations of micropollutants in surface waters.

excellent	good	satisfactorily	unsatisfyingly	bad
< ½ EC	½ EC – EC	EC – 2 EC	2 EC – 4 EC	> 4 EC

The following Table 4 shows a statistic evaluation of collected concentrations of micropollutants in the effluent of German wastewater treatment plants with an assessment of the potential risks for water organisms according to Table 3 .

The selected micropollutants were chosen for an emission-based approach of the evaluation of the emission of micropollutants into surface waters. For the emission-based approach, the achievement of the cleaning performance by ensuring an elimination of 80% in relation to the complete wastewater treatment plant for the selected indicator substances. The indicator substances are substances that can be easily or moderately degraded by additional wastewater treatment steps.

Table 4: Statistical evaluation of data of wastewater treatment plants.

	1*H*-Benzotriazole c [µg/L]	**Carbamazepine c [µg/L]**	**Diclofenac c [µg/L]**	**Metoprolol c [µg/L]**	**Sulfamethoxazole c [µg/L]**	**Clarithromycin c [µg/L]**
LQ	1	16	7	5	33	58
Number of measurements	594	885	835	866	811	280
Min	0.013	0.012	0.011	0.020	0.018	0
Max	34	6.3	9.1	6.0	2.7	3
Median	4.3	0.80	2.3	1.6	0.44	0.23
Average	4.9	1.0	2.5	1.9	0.55	0.36
25. Quartile	2.7	0.51	1.5	1.0	0.25	0
75. Quartile	6.5	1.3	3.2	2.6	0.76	0
Recommended EC	10	0.5	0.05	7.3	0.6	0.1

Without dilution, for three of the six substances concentrations above the EC were observed. Taking the dilution into consideration, surface waters with an amount of 50% treated wastewater will show similar exceeding EC. For Diclofenac, even a dilution of 50% will not lead to a compliance of the proposed EC.

The collected measurement results were compared with statistic results of the IMS Healths AG institute. The statistics show the consumer results for the most important prescription pharmaceuticals in Germany and Belgium. Consumer data for pharmaceuticals most sold in 2015 and 2016 are presented in Table 5 below.

Table 5: Statistic sales data IMS Health AG.

Micropollutants	**Germany 2015 t/year**	**Germany 2016 t/year**	**Belgium 2015 t/year**	**Belgium 2016 t/year**
Metoprolol	149	146	2.3	2.2
Diclofenac	44	40	3.0	3.1
Carbamzepine	43	40.2	5.3	5.3
Sulfamethoxazole	19	19	1.4	1.5
Clarithromycin	9.6	8.8	3.3	3.2

For the first preliminary tests of the research project, a "short-list" of selected relevant substances was drawn up on the basis of the research work in Germany and Belgium. The selected micropollutants are summarized in Table 6.

Table 6: Model water used for the identification of the most efficient coating. Substances are analysed by LC-MS/MS.

Compound	**Classes**	**Problematic in Germany**	**WFD: Watch list**
Metoprolol	Pharmaceutical	X	
Carbamazepine	Pharmaceutical	X	
Diclofenac	Pharmaceutical	X	X
Sulfamethoxazole	Pharmaceutical	X	
1*H*-Benzotriazole	Industrial chemical	X	

In the later course of the project, the "short list" was extended by 6 micropollutants. In the following Table 7 are shown the substances of the "extended list".

Table 7: Additional micropollutants of the model water (extended LC-MS/MS list).

Compound	**compound type**
Acetyl-4-Sulfamethoxazole	
Iohexole	Radio-opaque substance
Iopromide	Radio-opaque substance
Clarithromycin	Pharmaceutical
Terbutryn	Pesticide
Perfluorooctanesulfonic acid (PFOS)	Industrial chemical

4. Material und methods - Enhancement and optimization of the quantification methods using GC-MS/MS and LC-MS/MS. Toxicity based approach for the identification of transformation products (WP 3; CELABOR, IUTA).

CELABOR was responsible for the development of quantification methods for micropollutants using gas chromatography tandem mass spectrometry (GC-MS/MS).

Methods were first developed for the quantification of the model water composed of 5 micropollutants. Afterwards, the quantification method was adapted for the extended model water containing the additional micropollutants.

4.1 Description of the GC-MS/MS quantification methods (CELABOR).

A micropollutants stock solution was prepared at 1000 mg/L in methanol and stored at -20 °C. Ultra-sonication was used to solve the standards. A calibration curve was performed from 0.01 mg/L to 5 mg/L. To quantify phthalates and prevent contamination, all glass containers should be rinsed with acetone and then with n-hexane pestican grade. Plastic containers cannot be used. Nitrile gloves have to be used.

The decantation took place in a separator funnel of 100 mL under agitation during 1 h. About 50 mL of sample was mixed with 5 g $MgSO_4$ and 20 mL of a 90/10 mix n-hexane/ethyl acetate. The aqueous phase was collected and a second extraction was performed for 1 h with 20 mL of a mixture 50/50 n-hexane ethyl acetate. The organic phase was filtered on anhydric Na_2SO_4 and evaporated to 0.5 mL, n-hexane was added to 2 mL and samples were separated in 2 vials for GC-MS/MS injection.

The retention times of the different micropollutants are described in the table below (Table 8). The chromatogram below (Figure 2) highlights that the different compounds are well separated in term of retention time. The compounds simazine and atrazine were co-eluted but had different fragment ions to differentiate them.

Table 8: Retention times and mass spectrometric parameters of the GC-MS/MS method.

	RT [min]	Precursor *m/z*	Width	Energy [eV]	fragments *m/z*
Chlortoluron	9.57	167	5	4	132
Tributyl phosphate	13.12	99	2	3	81
Atrazine-desethyl	13.78	Full scan	-	-	172 +174
2,6-dichlorobenzamide	14.18	173	5	3	145 + 147
Simazine	15.05	Full scan	-	-	186 + 188
Atrazine	15.08	Full scan	-	-	215 + 217
Lindane	15.86	182	3	3	145 + 146 + 147
Isoproturon	18.48	146	2	2,5	128
Bromacile	19.32	205	5	3	188 + 190
DDT	24.53	235	5	3	199 + 200 +201
DEHP	25.66	149	3	3	121
BDE 100	27.91	404	5	4	295 + 297 +299

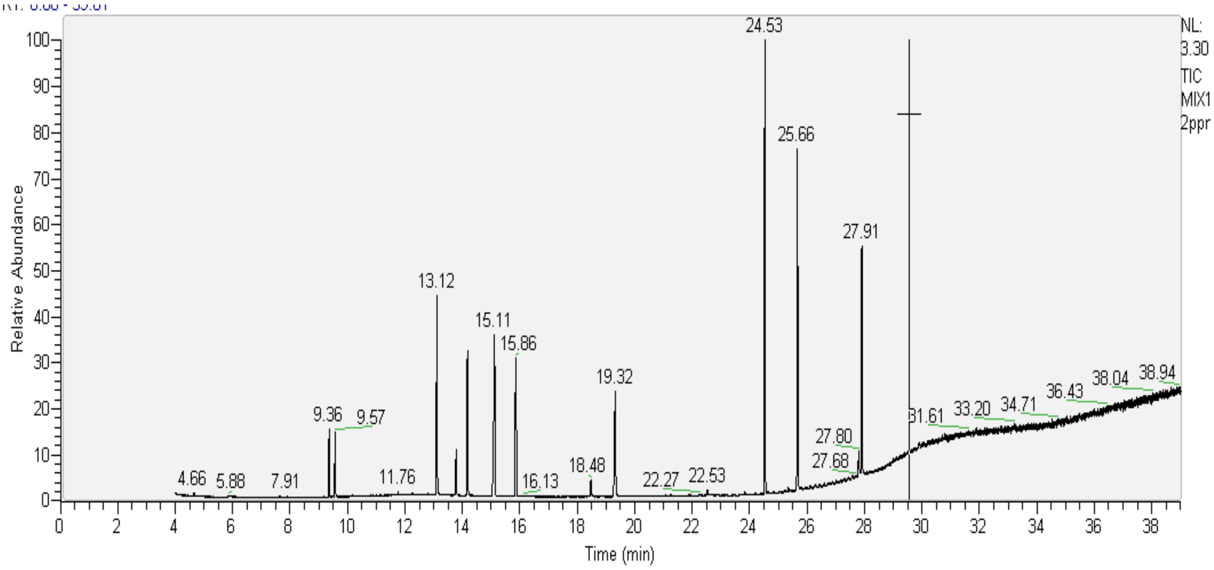


Figure 2: Full-scan GC-Chromatogram of the model water with relative abundance compared to the standards.

4.2 Characterization of toxicity tests with the micro-crustacea *Daphnia magma* (CELABOR).

One objective of the AOPTi project was also to characterize the toxicity of the model waters and the real water samples. The results of the model water and real water samples are shown in section 6.1.1. The toxicity was characterized on the microcrustacea *Daphnia magma* according to the ISO 6341 standard.

During this experiment, *Daphnia magma* micro-crustaceas were incubated during 24 h with different concentrations of model water. After 24 h of contact, the number of dead micro-crustaceas was counted. The graph of the number of dead microorganisms depending on the effluent concentration gives the EC_{50} (half maximal effective concentration) i.e. the concentration at which half of the microorganisms are dead. From the EC_{50}, the toxicity unit (TU) = $100/EC_{50}$ of the water is deduced.

4.3 Measurement parameters of the LC-MS/MS analysis (IUTA).

IUTA was responsible for the development of quantification methods for micropollutants by liquid chromatography tandem mass spectrometry (LC-MS/MS). Additionally to the classical quantification method using LC-MS/MS a µLC (Microflow LC)-MS/MS method for all substances except PFOS was evaluated. The advantages of µLC are a low consumption of solvents, a high linear flow velocity, short cycle times and a very small gradient residence volume. Therefore the sample throughput is increased.

Methods were first developed for the quantification of the model water composed of 5 micropollutants. Afterwards, the quantification methods were adapted for the extended model water containing more micropollutants. More information about the LC-MS/MS measurement method are shown in Table 9.

Table 9: Retention times and mass transitions of the LC-MS/MS and the µLC-MS/MS method.

	RT LC-MS/MS [min]	**RT µLC-MS/MS [min]**	**MRM 1 (Quantification) *m/z***	**MRM 2 (Verification) *m/z***
Short list				
Metoprolol	2.95	0.70	268 → 133	268 → 103
Carbamazepine	4.36	1.18	237 → 194	237 → 193
Diclofenac	6.43	1.79	296 → 214	296 → 215
Sulfamethoxazole	2.98	0.83	254 → 156	254 → 92
1*H*-Benzotriazole	2.20	0.60	120 → 65	120 → 92
Extended list				
Acetyl-4-Sulfamethoxazole	3.34	0.91	295 → 134	295 → 65
Iohexole	1.53	0.35	822 → 804	822 → 375
Iopromide	1.81	0.37	792 → 573	792 → 300
Clarithromycin	5.00	1.33	748 → 158	748 → 83
Terbutryn	4,50	1.31	242 → 186	242 → 68
PFOS	7.00	-	499 → 80	499 → 99

The chromatograms in Figure 3 show the detection peaks of all substances of the extended list except PFOS (a: conventional LC-MS/MS measurement and b: µLC-MS/MS measurement. PFOS has to be measured with a special method therefore it isn't included in the chromatograms in Figure 3 and no separate µLC-MS/MS method was developed. For all other substances it can be seen that the substance peaks are well separated.

The substances described are measured with a Sciex QTRAP 6500 mass spectrometer. For classical LC-MS/MS an Agilent 1100 LC system and for µLC-MS/MS a Sciex M3 µLC-System was used for the chromatographic separation. A Restek Raptor ARC-18 2.7 µm, 50*2.1 mm column with a Restek Raptor ARC-18 pre column 2.7 µm, 5*2.1 mm is used for the classical LC. For the µLC a YMC-Triart C18 S-3 µm, 50*0.3 mm with a YMC Triart pre column S-3µm, 5*2.1 mm is used. As solvents Acetonitrile (B) and LC-MS (A) water are used. The gradient for solvent B was 1 – 99% in 10 minutes for the classical LC and 10 – 99% in 2.1 minutes for µLC.

For calibration, an intermediate dilution is prepared from the stock solution. The stock solution is prepared at 1 g/L in 50% Acetonitrile and 50% LC-MS water and stored at 8°C for 12 month. Each calibration has to be prepared daily for each sample series. It is calibrated in the range of 0.001 -100 ng/mL.

For most pharmaceuticals (except X-ray contrast media), µLC achieved detection limits comparable or better than those of classical LC. This shows that with µLC a fast, environmental friendly and robust method with very good applicability for the evaluation of samples could be developed.

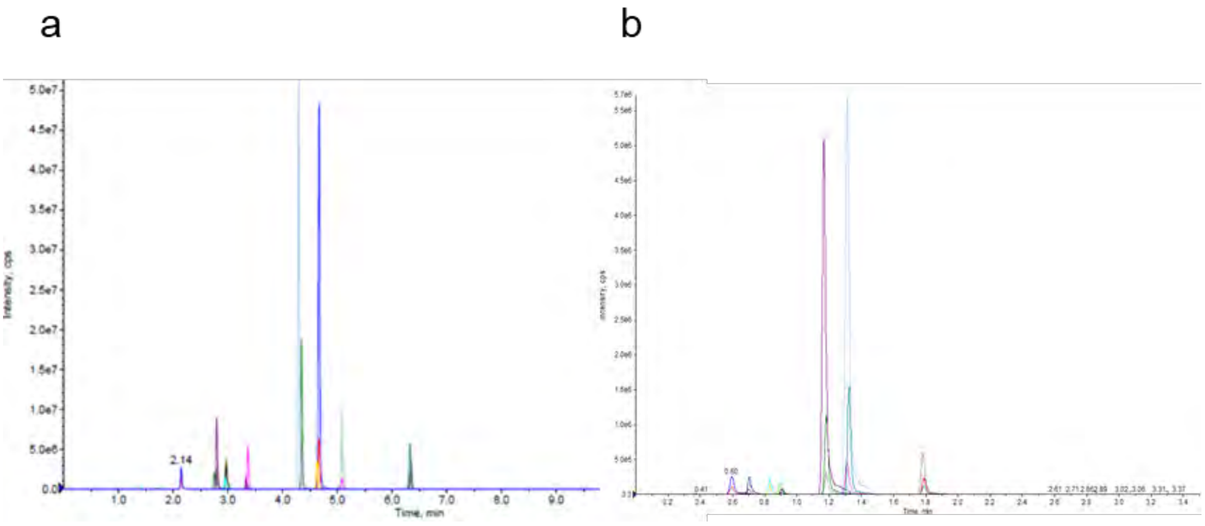


Figure 3: Chromatogram of 5 ng/mL-Standard of the conventional LC-MS/MS measurement (a) and the µLC-MS/MS measurement (b).

4.4 Analysis of estrogenic effects using A-YES assay (IUTA)

For estrogenic activity analysis, the samples were enriched by solid phase extraction within 48 h after sampling. The cartridges (150 mg, Oasis HLB 6 cc, Waters GmbH, Eschborn, Germany) were conditioned with Methanol (2 x 5 mL) and equilibrated with water (2 x 5 mL) before loaded with 1000 mL sample. After drying the cartridges under vacuum they were eluted with methyl-Tert-butylether (5 x 5 mL), which was evaporated afterwards at 50 °C under a nitrogen gas stream.

To determine endocrine effects, Arxula adeninivorans yeast-based estrogenic (A-YES) screenings (new_diagnostics, Berlin, Germany) were performed as described in the committee draft of ISO/CD 19040-2 (2016). The samples were re-dissolved in 2 mL water, resulting in an enrichment factor of 500. 17β-Estradiol (E2) served as calibration standard. Quantitative values are expressed as Estradiol equivalent quotients (EEQ).

4.5 Analysis of genotoxicity (IUTA)

4.5.1 UmuC-test

The umuC test detects primary Deoxyribonucleic acid (DNA) damage caused by the activation of the umuC gene, as part of the SOS repair system in bacteria. The test thus indicates the genotoxic potential of a sample, which does not necessarily lead to irreversible DNA damage, as this can still be repaired by the repair system. The umuC test thus provides indications whether the sample contains potential genotoxins, which in the worst case can lead to irreversible DNA damage. It is therefore to be understood as an indicator test to get a first assessment whether genotoxins are contained in the sample.

The umuC test was carried out with the genetically modified bacterium *Salmonella typhimurium* TA1535/pSK1002 (Moltox, USA) and was performed according to ISO 13829. The umuC test was conducted by an external laboratory (IWW Rheinisch-Westfälisches Institut für Wasser Beratungs- und Entwicklungsgesellschaft mbH).

4.5.2 In vitro micronucleus test

To exclude a cytotoxic effect of the samples on the CHO-9 cells used in the micronucleus test (cell line from ovaries of the Chinese hamster, ECACC, UK), the MTT test was used as a precursor. The method is based on the reduction of the soluble yellow tetrazolium salt 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium-bromide (MTT) to a blue-violet, insoluble formazan. Only in living cells can the dehydrogenases located in the mitochondrion reduce tetrazolium salts. In this form it can no longer leave the cell. During cell lysis, the formazan is released and photometrically quantified at a wavelength of 595 nm, the amount of formazan being proportional to the number of metabolically active eukaryotic cells. Since the reduction of MTT only takes place in living cells, this metabolic activity is a measure of the general cell damage (cytotoxicity). The activity of cells treated with a sample is compared with the activity of cells used in parallel without the test object (negative control). If the number of living cells is reduced to < 70% compared to the negative control, the test object has a cytotoxic potential (ISO 10993). In parallel, Dimethyl sulfoxide (DMSO) is tested as a positive control.

The micronucleus test was carried out in accordance with OECD Guideline No. 487 with ovarian cells of the Chinese hamster (CHO-9). With the in vitro micronucleus test, DNA damage such as chromosomal damage (clastogenic effect) and damage to the spindle apparatus (eye-eyelid effect) can be detected in dividing mammalian cells through the influence of genotoxic or mutagenic substances (Kirkland 2011). Micronuclei are chromosomal fragments or whole chromosomes enclosed by their own nuclear membrane, which were not integrated into the actual cell nucleus during cell division. A distinction is made between micronuclei which consist of chromosomal fragments (clastogenic effect) and micronuclei which consist of whole chromosomes as a result of chromosomal misalignment (ocular effect). In order to ensure that cell division takes place after exposure and thus the possibility of micronucleus formation exists, Cytochalasin B is added during exposure. It inhibits cell division so that double-nucleated cells with possibly micronuclei are available for evaluation. The micronuclei can be detected by DNA staining. If the micronucleus frequency in the treated cells is significantly increased compared to the negative control, a genotoxic effect of the sample can be assumed.

Before use in the micronucleus test, cell vitality was determined by means of the MTT test. The highest enrichment factor of the samples at which no cell damage occurred (cell vitality > 70%) was used in the micronucleus test. For all samples it was 10 times the original sample. After seeding the cells on slides, they were exposed to the samples for 24 hours. At the same time Cytochalasin B was added to prevent cell division. Mitomycin C was used as positive control. The cells were then washed and treated again with Cytochalasin B for 20 hours. After a hypotonic treatment and a fixation step of the cells on the slide, DNA staining was performed with the fluorescent dye 4′,6-diamidine-2-phenylindole (DAPI). The number of micronuclei in > 1000 binuclear cells was then determined under a fluorescence microscope using the Metafer 4 software. From this, the micronucleus rate (micronuclei/1000 cells) was calculated for all samples and controls.

In order to analyse whether a sample had genotoxic potential, the averaged micronucleus rates of each sample were compared with those of the negative control tested in parallel for significant differences. For this purpose, the results were examined with Chi2-Test (non-parametric, two-sided, α = 0.05). The null hypothesis that was tested is: The samples show no difference in micronuclei rate compared to the negative control. Statistical analysis was performed using GraphPad Prism 7.01.

The in-vitro micronucleus test is used to detect chromosomal damage and damage to the spindle apparatus of dividing mammalian cells caused by exposure to genotoxic or mutagenic substances.
The in-vitro micronucleus test was conducted by a external laboratory (IWW Rheinisch-Westfälisches Institut für Wasser Beratungs- und Entwicklungsgesellschaft mbH).

4.6 Non-target screening (IUTA)

The workflow for non-target screening (NTS) was implemented according to the recently published guideline for use of non-target screening by means of LC-ESI-HRMS in water analysis organized by the German Water Chemistry Society (Schulz 2019). For the analyses, an Agilent 6560 IM-QTOF coupled with an Agilent LC 1290 was used. The analytical method was based on the aforementioned guideline. The chromatographic separation was performed at 29°C with acetonitrile and water as mobile phases. In both solutions 0.1% formic acid was added. A Waters XSelect HSS T3 (C18) column (3.5 µm and 2.1x 75 mm) with a precolumn with the same composition was used. The chromatographic run started with 2 min of isocratic flow with 5% acetonitrile and 95% water. Then, the acetonitrile was increased to 95% in 22 min, decreased in 30 seconds to 5% and stayed at 5% for 6.5 min for re-equilibration. The HRMS was set to fragment two *m/z* higher than 5000 counts per cycle, acquiring automatically MS/MS data of peaks.

After the MS detection, the workflow was as presented in Figure 4. The categorization was adopted from the concept of Bader et al. (Bader 2017). The raw data from the HRMS instrument is converted to mzXML format to be further processed in the open source R environment (R Core Team, 2014). The R script for extraction and grouping of peaks across samples, categorization of peaks, and identification of peaks of interest is developed using as basis the XCMS package from the Bioconductor project (Smith et al., 2006). The parameters for peak picking and grouping are optimized according to the Isotopologue Parameter Optimization developed by Libiseller et al. (2015). Peak picking is preformed through the centWave method described in Smith et al. (2006), which is based on peak density to create regions of interest. Then, a gaussian fit is used for peak assignment. Grouping and alignment of peaks across samples is obtained by the obiwarp method described in Prince and Marcotte (2006). The alignment is based on retention time differences between samples.

For each sample triplicate, the filtering process includes the removal of peaks with intensity not higher than five times the intensity of the same peak in a triplicate black sample. Additionally, peaks with intensity lower than 5000 counts are removed. This fraction of peaks is then considered as the noise level. Adducts and isotopologues are identified and excluded from the peak list through the CAMERA package, which was build and implemented also in R environment by Kuhl et al. (2012). Identification of peaks is firstly done by suspect screening using a database with known *m/z* and retention time. Compound identification is preformed via the For-Ident platform (https://water.for-ident.org/#!home).

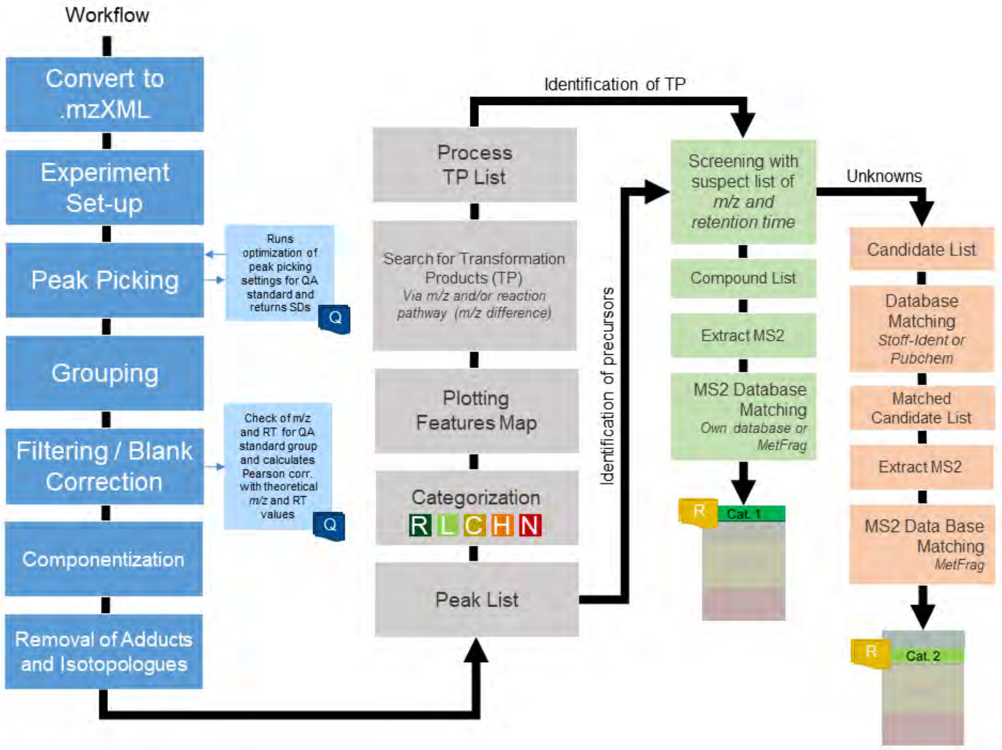


Figure 4: Non-target screening workflow. The categorization key consists of Removed (R), Lower (L), Constant (C), Higher (H), and New (N) peaks was adapted from Bader et al 2017.

4.7 Analytical method and workflow for effect directed identification of transformation products (Deliverable D3.2; IUTA)

As in previous projects, it was found that the estrogenic activities are reduced by ozonation. These activities are usually measured using genetically modified cell-based tests (e.g. the A-YES assay). As these bioassays are representing a sum parameter, also inhibitory effects such as antagonistic effects need to be further investigated as they are potentially reducing the detected activities. An example showing the relevance of such antagonistic activities is shown in Figure 5.

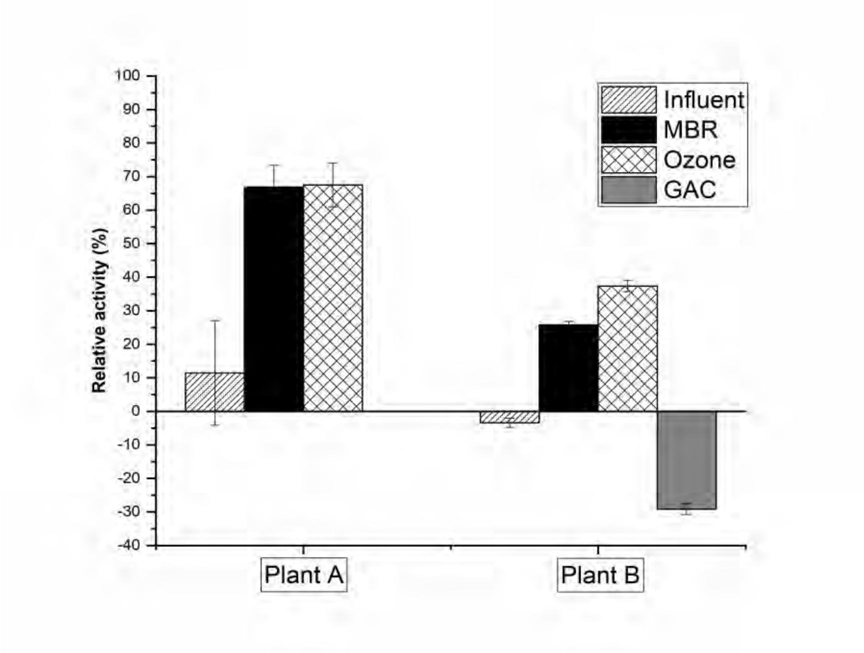


Figure 5 : Results of the bioassay monitoring using the anti-A-YES assay (Itzel et al. 2018).

Due to this resulting activity profile from the anti-A-YES analysis, a difference of the samples can be observed, which was not directly possible without fractionation. Fractionation was carried out using a HPLC-pump. The sample was dived into 25 fractions. Each fraction was used for the analysis of the anti-A-YES. To identify relevant compounds, active fractions can be further analysed using LC-ESI-HRMS non-target analysis. A scheme of the workflow for the effect directed analysis is given in Figure 6.

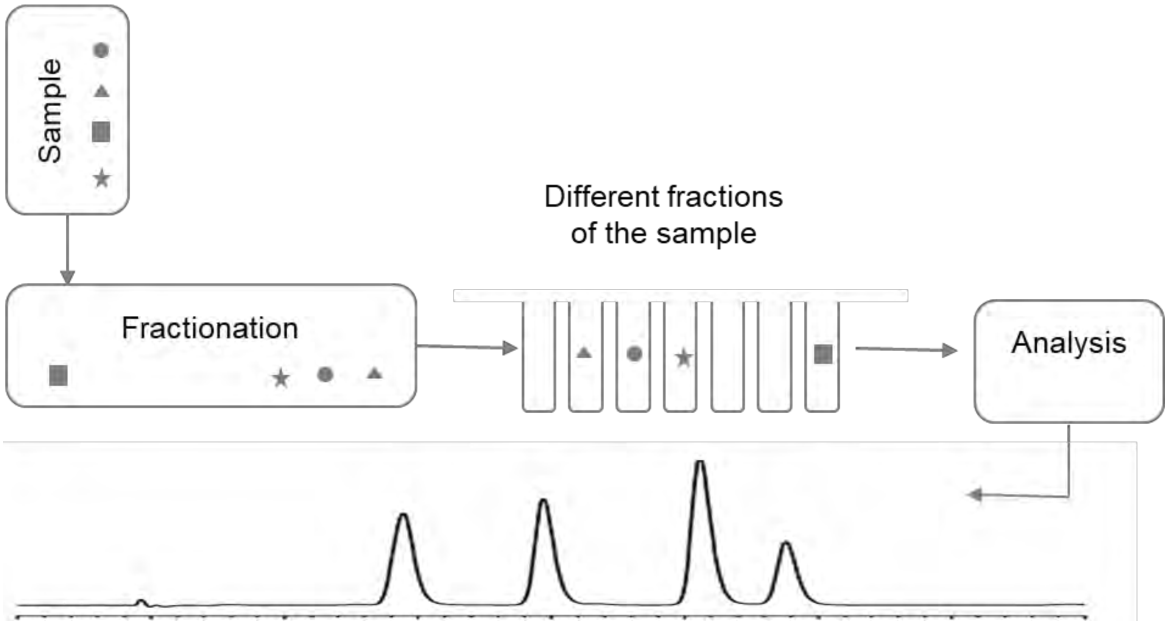


Figure 6: Scheme of the workflow of the effect directed analysis (Deliverable D3.2).

The main goal of this effect directed analysis approach is to reduce the number of unknown signals (features) to a minimum by the use of meta data such as the bioactivity. By using this approach, it was possible to filter more than 95% of potential candidates and end up with about 30 features of interest. As the last identification step has always to be done manually with high personal effort and costs, a prioritization of relevant features is one of the most important steps. In the framework of the AOPTi project, however, no toxicities were observed after treatment, so fractionation was not performed.

5. Assessment of the degradation properties TiO$_2$ photocatalyst UV-ozone technology on model water at lab-scale (WP4; ULg-NCE).

5.1.1 Description of the different photocatalytic coatings

Different coatings were synthesized and tested. The coatings are made from Ag/P25 doped TiO$_2$ sol-gel synthesis. The synthesis is as follow: (i) a mass, m_{AgAc}, of silver acetate (Merck, purity ≥ 99%, $(CH_3(O)O)Ag$, called AgAc) is weighed with a precision of at least 1%. The AgAc powder is then given into a 250 mL Erlenmeyer flask, where it is dissolved in 32 mL 2-methoxyethanol (Accros organics, purity ≥ 99.5%, $CH_3{-}O{-}CH_3{-}CH_2OH$, called MetOH). This solution is then agitated by an electromagnetic stirrer at 180 rpm for the rest of the synthesis. (ii) after 30 min, a volume, $VEDAS$, of *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (Sigma-Aldrich, purity 97%, $(CH_3O)_3Si(CH_2)_3NHCH_2NH_2$, called EDAS) is added to the above-mentioned solution. (iii) after 30 min, a first volume, $V_{H2O,1}$, of ultrapure water (18.2 MΩ·cm) is dissolved in 32 mL MetOH and then, this solution is added to the content of the Erlenmeyer flask. Between all of these 3 steps, the Erlenmeyer flask is closed by a parafilm; (iv) after 30 min, a volume, V_{TTIP}, of titanium tetraisopropoxide (Sigma-Aldrich, purity ≥ 97%, Ti-$(O{-}CH(CH_3)_2)_4$, called TTIP), dissolved in 96 mL MetOH, is added to the solution. After that, the parafilm is quickly exchanged by a rubber plug and then, the reagent mixture is put under nitrogen atmosphere; (v) after 45 min, a second volume, $V_{H2O,2}$, of ultrapure water is dissolved in 32 mL MetOH and then, this solution is added to the content of the Erlenmeyer flask. Once again, the mixture is put under nitrogen atmosphere. After another 45 min, the sol is ready for further use.

Some of the syntheses will use the commercial catalyst Evonik P25, which must be in a well-dispersed state for being usable in the preparation of the sol. The concerned syntheses are started with dissolving the volume of TTIP, $VTTIP$, in 96 ml MetOH. The mass of P25, $mP25$, is added to this solution. In the following, the flask that contains this solution is put into a thermostatic bath at 80 °C. At least 12 h later, the execution of the standard protocol above is started. Before arriving at step (iv), the prepared solution that contains the P25 is sonicated by ultrasound (Branson 2510 ultrasonicator) for 15 min. In step (iv), the solution with the well-dispersed P25 and TTIP is added to the content of the Erlenmeyer flask. Finally, 6 sols are produced and are denote in Table 10.

Table 10: List of sol-gel coating syntheses.

Test	Doping Agent 1	Doping agent 2
1,2	Ag 2%	
3	Ag 1%	P25 10%
	Ag 2%	P25 10%
	Ag 2%	P25 5%
	Ag 2%	P25 20%
4	Ag 4%	P25 10%

For film formation, glass microscope slides and stainless-steel slides, which have the same dimensions (2.5 cm x 7.5 cm x 0.7 cm), are used as substrates for dip-coating. For having good adherence of the films, the slides must be washed before the first dip-coating operation. The glass slides are cleaned with RBS soap, rinsed with deionized water, and finally washed with ethanol (denatured ethanol, purity 99%) in order to remove potential organic residues. The stainless-steel slides are put into a degreasing solution (ArcelorMittal, S 5183, 15 g/L), placed inside an ultrasonic bath for 15 min, and finally washed with ethanol.

The speed-up used on the dip-coating is 60 mm/min. To obtain crystalline anatase-TiO_2, the coating must be calcined. For glass samples, the calcination is performed at 500 °C for 1 h with a ramp of 10°C/min. Two dip-coating operations are conducted for each slide with a calcination step after each dip-coating (2 calcinations with the same parameters).

5.1.2 Description of the experimental test

All degradation tests were performed at lab scale according to the protocol described in Figure 7. The model water (10 µg/L of each micropollutant) is submitted during 30 min to ozonation. After the ozonation step, a subsequent photocatalytic step of 6 h is performed under UVC light (254 nm). The degradation efficiency of the coatings was tested on the different micropollutants of model water. Each pollutant was quantified before and after treatment by GC-MS/MS and LC-MS/MS according to the method described in the deliverable D3.1.

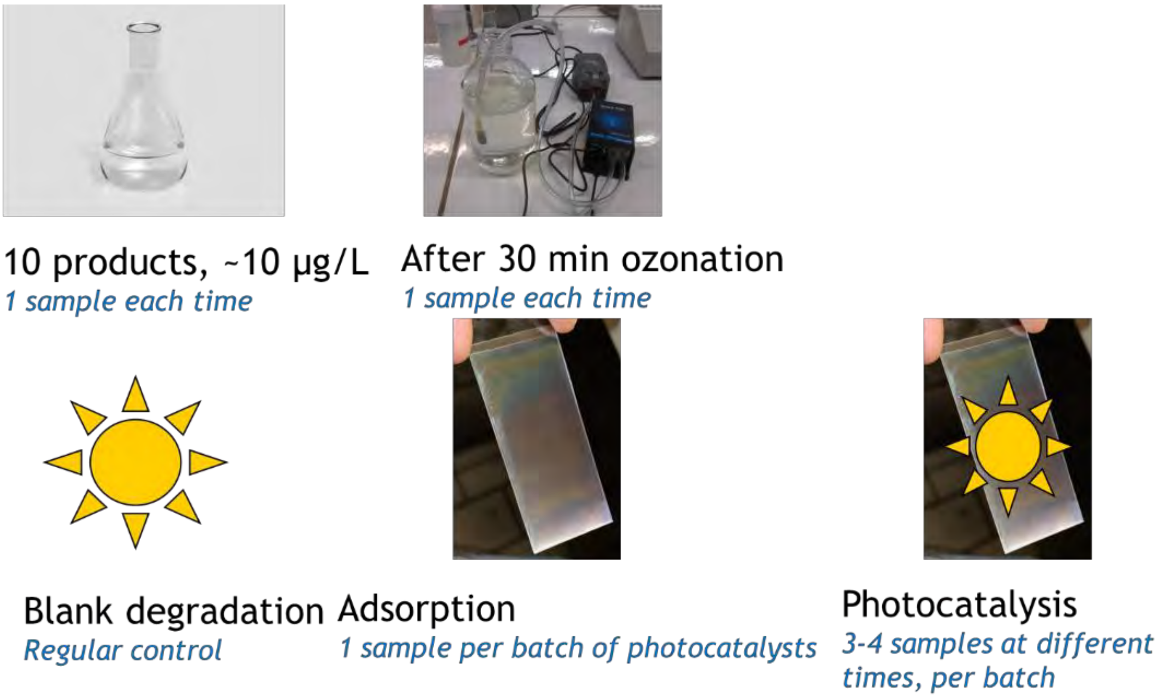


Figure 7: Degradation test protocol.

5.1.3 Effect of coating composition

The composition of the coating has been optimized in terms of silver composition (varying from 1 to 4%) and P25 composition (varying from 5 to 20%). The objective was to achieve the higher degradation potential of persistent micropollutants. The influence of the chemical composition of the coating on the degradation efficiency was evaluated using model water (Figure 8). First, the impact of the silver composition varying from 1 to 4% was evaluated (Figure 8A). It could be shown that the degradation efficiency increases when the Ag concentration increases. Anyway, the 4% Ag coating showed some leaching of the silver after 24 h incubation in water so it was eliminated. The best silver composition was equal to 2%. Secondly, the impact of the P25 composition varying from 5 to 20% was evaluated (Figure 8B). It could be shown that the degradation efficiency increases when P25 concentration increases. In any case, the 20% P25 composition is too viscous, so it was eliminated. The best P25 composition was 10%. The global impact of silver and P25 concentration in the sol-gel coating was highlighted in Figure 8C. It could be shown that the coating Ag2N-10P25 (2% Ag and 10% P25) ensures the higher degradation percentage of the 5 pollutants.

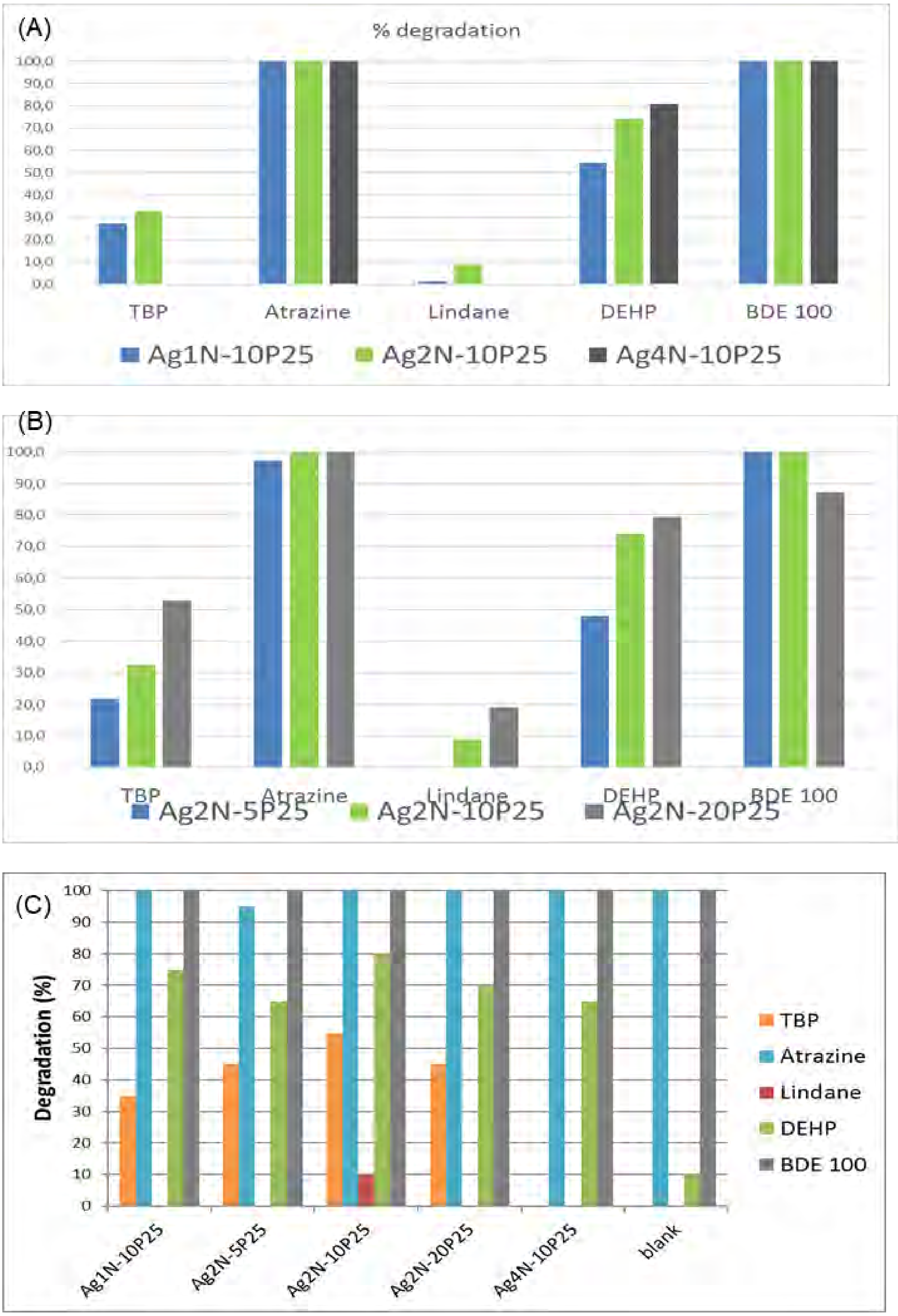


Figure 8: Degradation efficiency (%) of the 5 micropollutants (TBP, atrazine, lindane, DEHP, BDE) of the model water after ozonation 30’ and photocatalytic treatment during 6 h. (A) Influence of silver composition. (B) Influence of P25 composition. (C) Influence of Ag and P25 compositions (Ag 1 to 4%, P25 5 to 20%).

The same experiment was performed on model water but characterized by LC-MS. The degradation percentage of 1*H*-Benzotriazole, Carbamazepine, Diclofenac, Metoprolol, Sulfamethoxazole was quantified (Figure 9). The degradation percentages of micropollutants are the highest for the Ag1N-10P25 coating.

Nevertheless, as Carbamazepine, Diclofenac, and Sulfamethoxazole were already degraded by ozonation, the effect of photocatalysis on these compounds cannot be evaluated for the coatings that were treated with ozone before. However, as there was a problem with the ozonation during the test of Ag1N-10P25, one set of values is available for these three pollutants. It can be seen that Diclofenac and Sulfamethoxazole are completely degraded by photocatalysis, while almost half of the Carbamazepine remains in the solution after photocatalysis. In summary, these results clearly show the potential of the ozonation treatment.

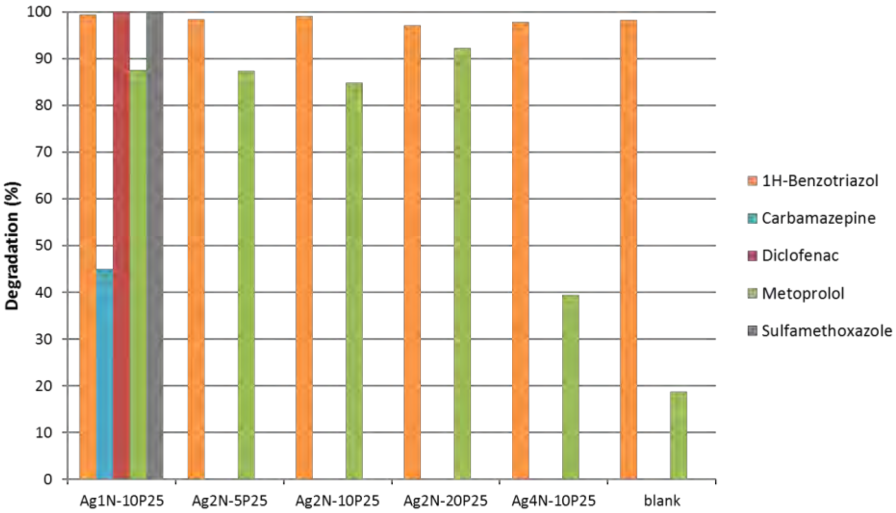
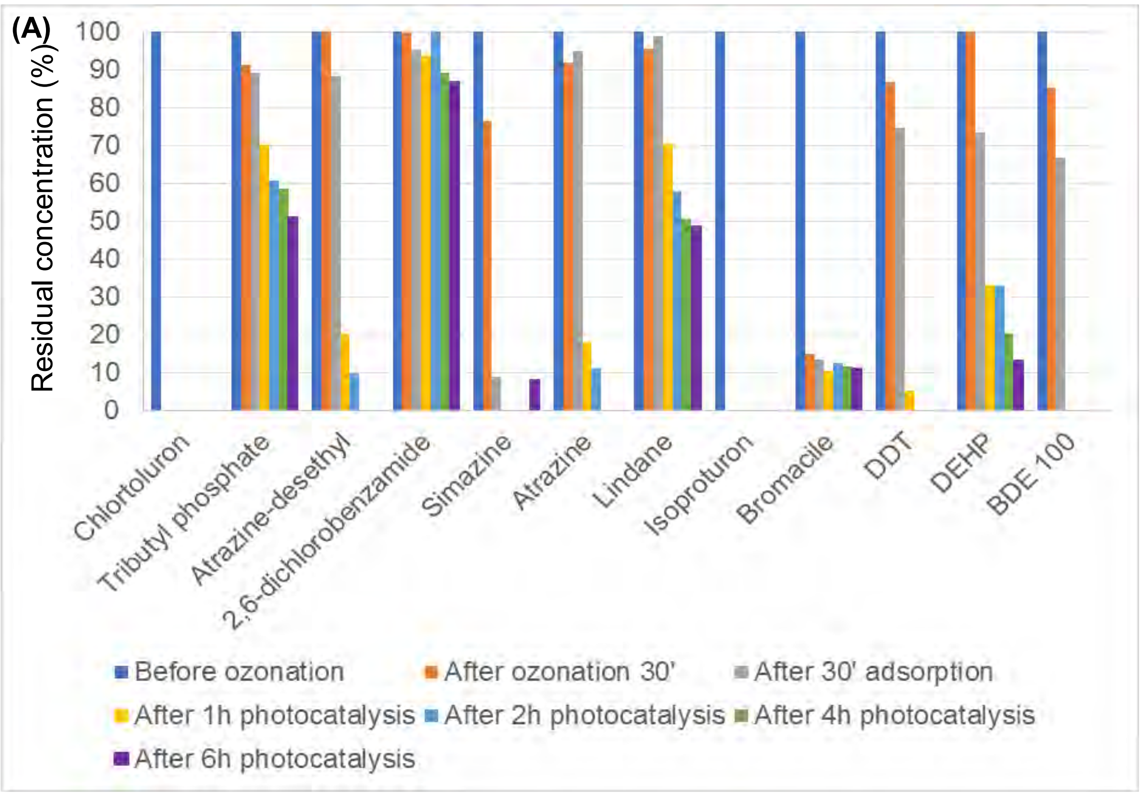


Figure 9: Degradation efficiency (%) of the 5 micropollutants (1*H*-Benzotriazole, Carbamazepine, Diclofenac, Metoprolol, Sulfamethoxazole) of the model water after ozonation 30' and photocatalytic treatment during 6 h. The different coatings compositions (Ag 1 to 4%, P25 5 to 20%) were tested (X axe).

The degradation of the micropollutants of the extended model water was characterized. Micropollutants were quantified before and after a 30 min treatment with ozone and 6 h photocatalytic treatment under UVC in the presence of a sol-gel coating Ag 2%P25 10%/TiO_2. Samples were collected after each treatment step to evaluate the contribution of each treatment.

The results were described in Figure 10 A and B by their residual concentrations after each treatment step. Figure 10 A shows that 2 micropollutants i.e. Chlortoluron and Isoproturon were totally degraded by ozonation during 30 min. The other micropollutants were resistant to ozone and need an additional treatment step. Tributylphosphate, 2,6-Dichlorobenzamide Lindane, Bromacile and DEHP were partially degraded after ozonation and photocatalytic treatment during 6 h. Atrazine, Atrazine-desethyl, Simazine, DDT and BDE 100 were totally disrupted during to the 6 h – photocatalytic treatment with TiO_2 sol-gel coating. The adsorption of micropollutants on the coating surface was performed as control (grey bar). Figure 10 B shows that 5 micropollutants i.e. Carbamazepin, Diclofenac, Sulfamethoxazole, Clarithromicyn and Terbutryn were totally degraded by ozonation after 30 min. The others micropollutants were resistant to ozone and need an additional treatment step. Metoprolol was partially degraded after ozonation and photocatalytic treatment during 6 h (about 12% remains).

The other pollutants were totally disrupted thanks to photocatalytic treatment on TiO_2 sol-gel coating.



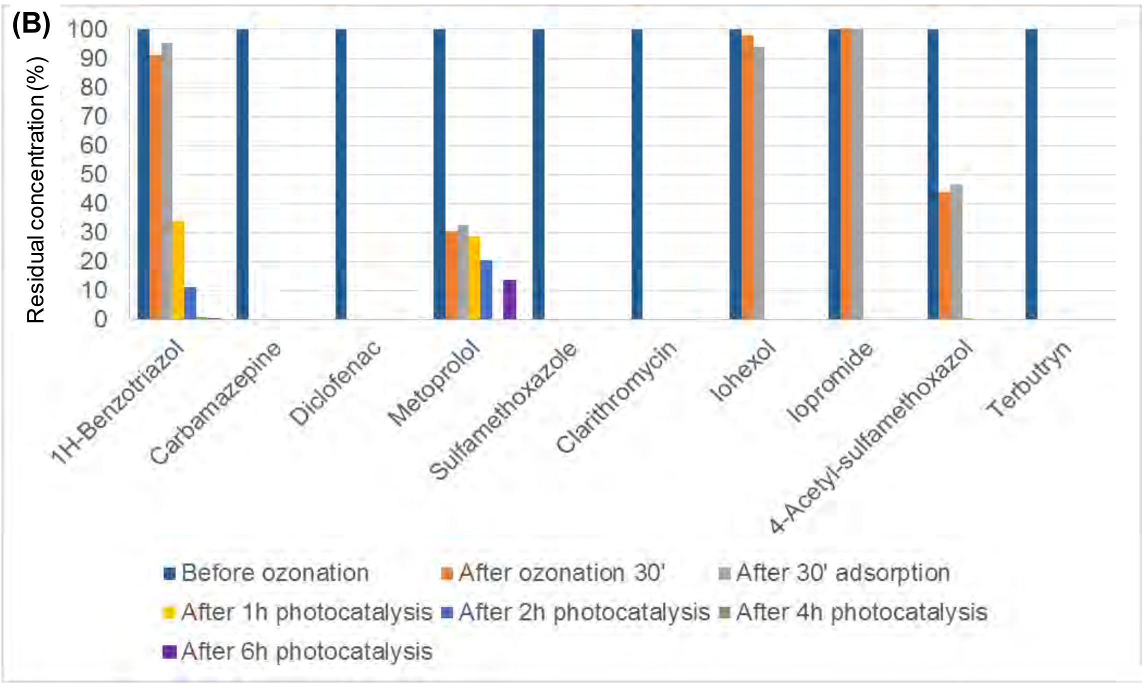


Figure 10: Residual concentration (%) of the different micropollutants before ozone treatment (blue), after ozonation during 30 min (orange), after adsorption step on the coating during 30 min = control (grey), after photocatalytic treatment during 1 h (yellow), after photocatalytic treatment during 2 h (light blue), after photocatalytic treatment during 4 h (green), and after photocatalytic treatment during 6 h (purple). (A) Micropollutants analysed by GC-MS/MS and (B) micropollutants analysed by LC-MS/MS.

Finally, Table 11 summarizes the degradation efficiency of the individual treatment steps used in the AOPTi project. Micropollutants were quantified after ozonation (30 min), after ozonation (30 min) and UVC treatment (6 h) and after ozonation (30 min) and photocatalytic UVC treatment (6 h with Ag2N-P2510/TiO_2 coating). Carbamazepine, Diclofenac and Sulfamethoxazole were totally degraded by ozone only. Atrazine, BDE 100 and 1*H*-Benzotriazole were totally degraded by UVC without the use of photocatalytic coating. TBP, Lindane, DEHP and Metoprolol need a photocatalytic UVC treatment in presence of the sol-gel coating Ag2NP2510/TiO_2 to be partially degraded.

Table 11: Degradation efficiency of each treatment step used in the AOPTi project. Micropollutants quantification after ozonation during 30 min (left column), after ozonation 30 min + UVC 6 h (middle column) and after ozonation 30 min and photocatalytic UVC treatment (6 h with Ag2N-P2510/TiO_2 sol-gel coating) (right column). Total degradation (> 99%) appears in grey.

Pollutant	Ozone	UVC	Photocatalysis
TBP			**53%**
Atrazine		▨	▨
Lindane			**10%**
DEHP			**80%**
BDE 100		▨	▨
1*H*-Benzotriazole		▨	▨
Carbamazepine	▨	▨	▨
Diclofenac	▨	▨	▨
Metoprolol			**96%**
Sulfamethoxazole	▨	▨	▨

From all the results, the best TiO_2-based sol-gel coating is Ag 2% NEW + 10% P25. And this is the coating that was scaled up to the 2 pilot reactors in WP5. The TiO_2 coating doped with Ag 2% and P25 10% was selected for the next steps of the project.

5.1.4 Stability of micropollutants degradation efficiency on Ag2N-P2510/TiO_2 sol-gel coating

The durability of the photocatalytic activity of Ag2N-P2510/TiO_2 sol-gel coating was tested in lab scale on a model water (12 micropollutants with 5 µg/L) with 3 consecutive tests (ozonation during 30 min + photocatalytic treatment during 6 h). For each new test, a new model water with 12 micropollutants (5 µg/L) was used. These were the same photocatalytic sol-gel coatings that were used in all tests. Between each degradation test, Ag2N-P2510/TiO_2 sol-gel coatings were washed with deionized water then dried with compressed air. The degradation percentage of each pollutant are presented in Figure 11.

In Figure 11, it is observed that chlorotoluron, isoproturon, atrazine, atrazine-desethyl, DDT and BDE 100 are completely degraded by the ozonation step. For the 6 other micropollutants, the presence of Ag2N-P2510/TiO_2 sol-gel coating increases each time their degradation percentage. Furthermore, it seems that the photocatalytic activity remains stable because similar degradation values are obtained and even after 3 cycles of photocatalytic tests with the same coating.

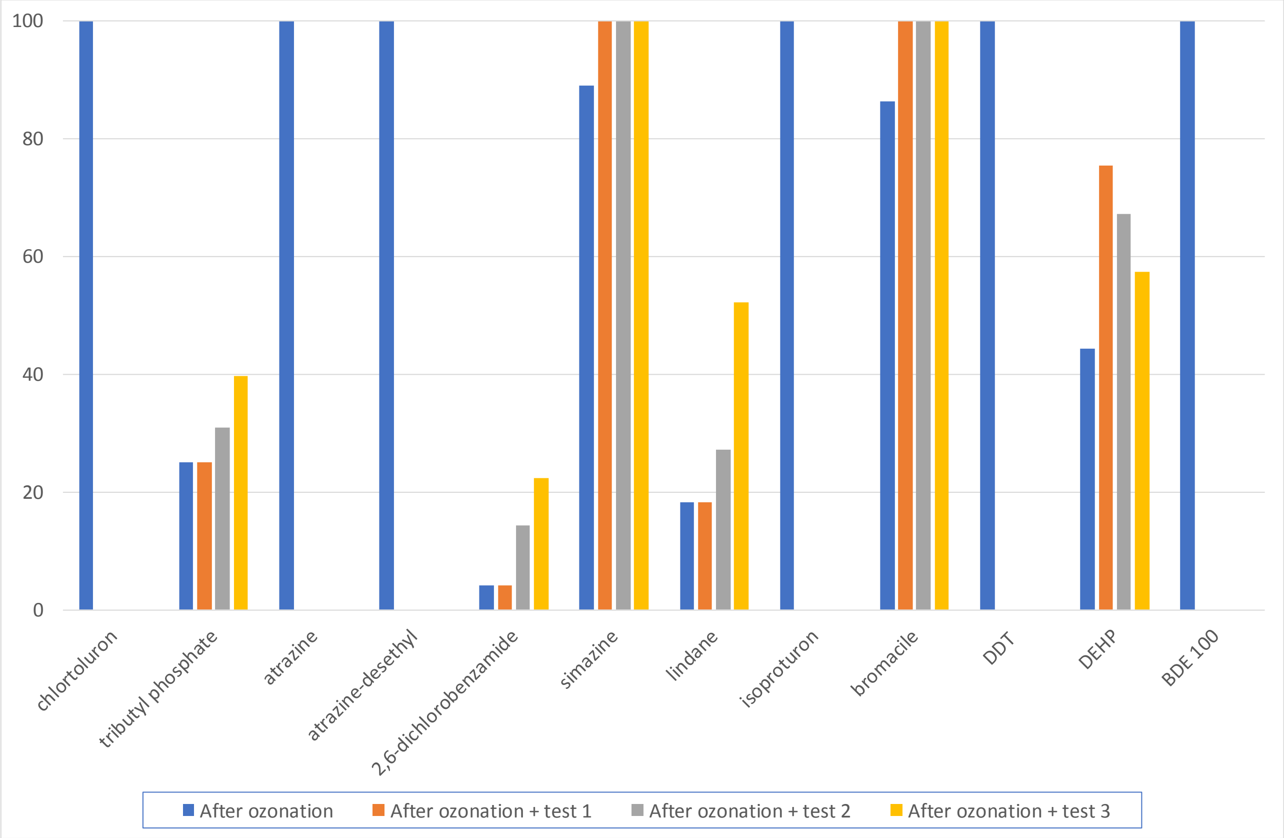


Figure 11: Degradation percentage of 12 micropollutants (i) after ozonation (30 min); (ii) after ozonation (30 min) + first photocatalytic test (6 h); (iii) after ozonation (30 min) + second photocatalytic test (6 h) with the same coatings used in the first photocatalytic test; (iv) after ozonation (30 min) + third photocatalytic test (6 h) with the same coatings used in the first two photocatalytic tests.

5.1.6 Longer photocatalytic tests on recalcitrant molecules

After the various tests carried out in this WP4, it appears that after ozonation (30 min) + photocatalytic test (6 h) 4 micropollutants are still present: tributylphosphate, 2,6-dichlorobenzamide, lindane and DEHP. In this way, longer photocatalytic tests (8 h, 24 h and 48 h) were performed on a lab scale with these 4 micropollutants (initial concentration = 5 µg/L). In parallel to the photocatalytic tests, the degradation of these 4 micropollutants was also monitored under UVC alone (without the presence of a photocatalyst). The results of these tests are shown in Table 12.

Table 12: Degradation percentages of recalcitrant micropollutants.

Compound	**After 8 h**		**After 24 h**		**After 48 h**	
	UVC only	**Coating**	**UVC only**	**Coating**	**UVC only**	**Coating**
Tributylphosphate	0	5	0	90	0	> 99
Dichlorobenzamide	0	30	0	80	0	> 99
Lindane	0	50	0	> 99	0	> 99
DEHP	0	90	0	> 99	0	> 99

Table 12 shows that these 4 recalcitrant molecules are not degraded by the use of UVC only. A photocatalyst is needed for their degradation. They are completely degraded after 24 h or 48 h of photocatalytic tests. Unfortunately, these treatment times are too long for a real application on Wastewater Treatments Plants. For this reason, activated carbons (WP6) for the adsorption of residual micropollutants are also being developed in this project.

5.1.7 Calcination parameters study

In parallel to degradation photocatalytic tests, the deposition of sol-gel coating on steel was investigated as the demonstration scale reactor is in steel.

One main challenge is the calcination temperature (500 °C), which is quite high for steel, but this process is necessary to obtain crystallized anatase-TiO_2 (photoactive form). For this reason, calcination below 500 °C would be beneficial to reduce the corrosion effects on the steel. To optimize the calcination temperature, especially for the steel, different times and calcination temperatures were tested. The findings are reported in Table 13: 3 temperatures (500 °C, 390 °C, 280 °C) and 3 calcination times (1 h, 6 h, 12 h) are chosen, leading to 7 conditions.

Table 13: Operating parameters chosen for the calcination study.

	t = 1 h	**t = 6 h**	**t = 12 h**
T = 280 °C		X	X
T = 390°C	X	X	X
T = 500 °C	X	X	

These calcination conditions are applied on both glass and steel and only one composition of photocatalyst is used for dip-coating: TiO2 doped with 2% of Ag and P25 10%. Crystallizations are obtained on glass for 500 °C/1 h, 500 °C/6 h, 390 °C/6 h and 390 °C/12 h; and on steel for 500 °C/1 h, 500 °C/6 h and 390 °C/12 h.

The degradation photocatalytic test has been made with these samples to ensure that the change in calcination parameters does not change the photoactivity of the coating. The results are presented in Figure 12.

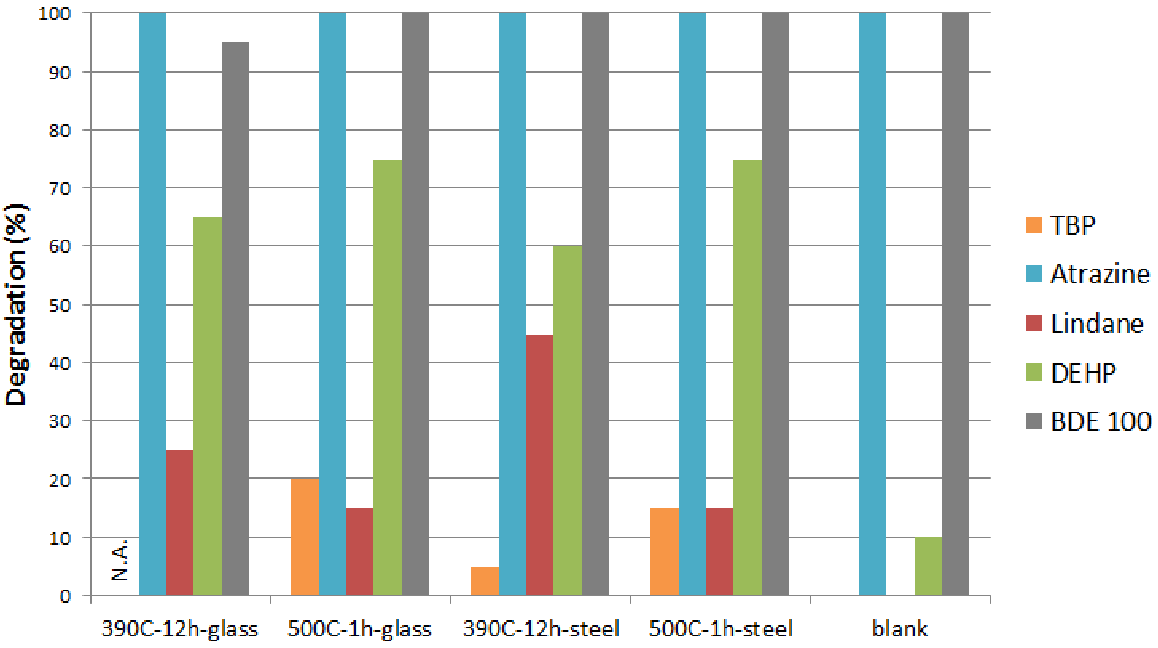


Figure 12: Degradation percentage of 5 micropollutants (alalysed using GC-MS/MS) after six hours of photocatalysis (N.A. = not available).

The efficiency of the Ag2/TiO_2 sol-gel coating is not affected if the calcination parameters and the substrate (glass or steel) are changed. Therfore, the calcination conditions at 390 °C for 12 h were chosen for steel deposition in demonstration scale (WP5).

5.1.8 Kinetics study

In this section, the degradation kinetics of the two IUTA pollutants that remain after ozonation, namely 1*H*-Benzotriazole and Metoprolol, will be studied more in details. The evolution of the pollutant concentrations is plotted as a function of time (Figure 13).

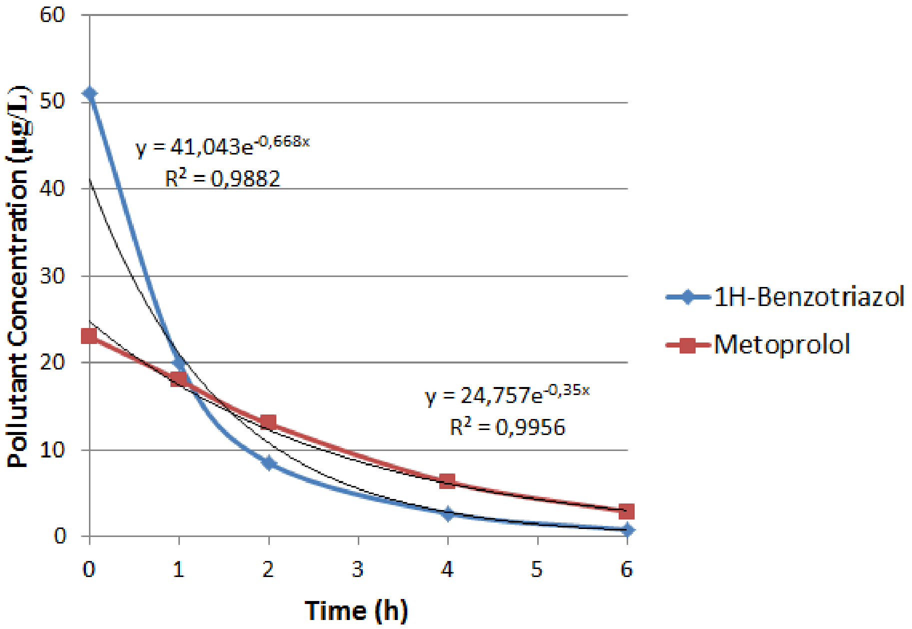


Figure 13: Degradation kinetics of the micropollutants 1*H*-Benzotriazole and Metoprolol on the sol-gel coating Ag2N-5P25/TiO_2.

It can be seen that the data can be fitted well by an exponential law, so the degradation reactions follow a first order kinetics. This is in good agreement with the literature and to the concentration C of a reactant in a first order kinetics applies:

$r = dC/dt = -kC$

where r is the reaction speed ($mol/m^3 \cdot L$) and k is the kinetic constant (h^{-1})

By solving the differential equation, the following expression is obtained:

$C = A \exp(-k\ t)$

where A is a constant (mol/L)

The values of the constants A and k can be determined by performing an exponential fit of the data from Figure 13. By taking a closer look to these fittings, several observations are made:

- The points that fit the worst are generally those, which were made after 6 h of photocatalysis, i.e. the smallest concentrations.
- The correlation coefficient, R^2, is systematically smaller for 1*H*-Benzotriazol than for Metoprolol.
- 1*H*-Benzotriazole reaches smaller concentrations after 6 h of photocatalysis than Metoprolol.

From these observations, it can be concluded that, at very low concentrations, the degradation kinetics move away from the first order. This can be due to two reasons:

- As the concentration of reactant decreases, diffusion becomes more and more the limiting phenomenon.
- Since the smallest concentrations are the most difficult to measure, the error in measurements for these concentrations is the highest.

In the following, a study is done for evaluating the effect of the silver and P25 fractions on the kinetic constants. Since for this study, exponential fittings with a high correlation coefficient are needed, the measurements after 6 h of photocatalysis for 1*H*-Benzotriazole are not taken into account. In addition, the measurements after 4 h are not taken into account either for the coatings that have the lowest correlation coefficient, *i.e.* Ag2N-5P25 and Ag2N-20P25. The results of these fittings are summarized in Table 14.

Table 14: Results of the exponential fittings for the micropollutants 1*H*-Benzotriazol and Metoprolol on different coatings.

	1*H*-Benzotriazole			**Metoprolol**		
	A (mol/L)	k (h^{-1})	R^2	A (mol/L)	k (h^{-1})	R^2
Ag1N-10P25	52	1.0	0.9975	52	0.35	0.9974
Ag2N-5P25	50	0.90	0.9993	25	0.35	0.9956
Ag2N-10P25	40	0.92	0.9940	3.0	0.31	0.9959
Ag2N-20P25	42	1.0	0.9990	2.3	0.44	0.9956
Ag4N-10P25	50	0.76	0.9956	37	0.081	0.9830

The kinetic constants are then plotted as a function of silver and P25 content of the coatings in Figure 14. It can be seen that the tendencies are the same for both pollutants: the kinetic constants decrease with increasing silver content and they increase with increasing P25 content.

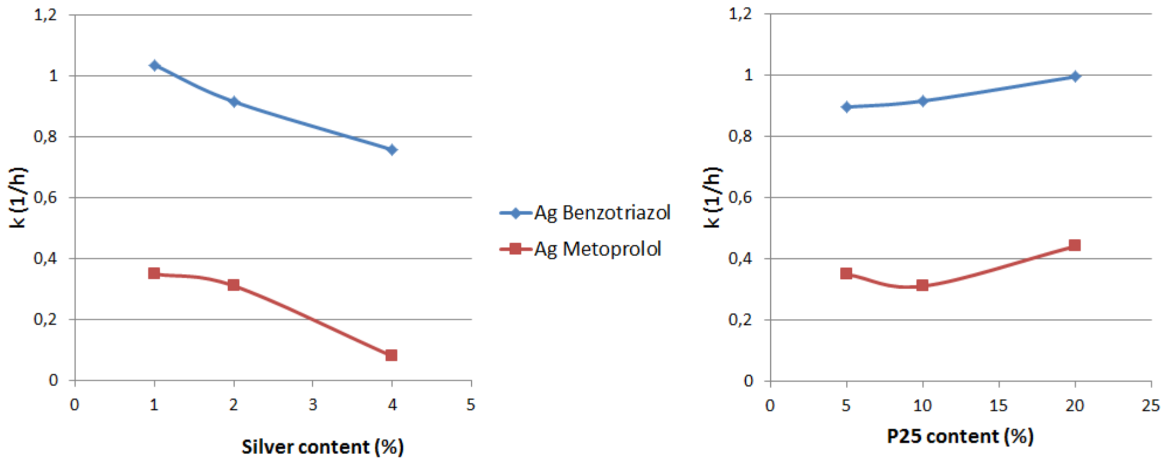


Figure 14: Evolution of the kinetic constants as a function of a) silver content, b) P25 content.

5.1.9 TiO_2-based photocatalyst coating with good adhesion and no leaching (Deliverable D4.2).

In order to test how coatings resist to their environment in the long term, leaching tests were performed. The tested coatings were Ag2N-20P25 and Ag4N-10P25, which should be representative for all the different compositions, taking into account that these are the coatings that have the highest fractions of P25 and silver, respectively.

The testing protocol was the following: For each of the mentioned compositions, a slide was put into a Petri dish and approximately 30 mL of water were added. Then, the upper shells were put onto the two Petri dishes and they were introduced into the thermostatic cabinet, fixed at the same conditions as for the other tests. The Petri dishes are agitated by the orbital shaker and the UVC lamp is turned on. After 96 h, the Petri dishes are taken out of the cabinet and the liquid is sent to Inductively Coupled Plasma (ICP-AES) for analysis. Using ICP, the quantity of silver and titanium, present in the solution due to leaching of the slides, can be measured. The results are given in Table 15. They indicate that there is no significant leaching of the coatings. Even if there are no limit values for silver and titanium in drinking water, having low leaching values is advantageous since this increases the lifetime of the photocatalyst. In addition to that, it can be considered that in practice the water will not be in contact with the photocatalyst for 96 h. Therefore, the actual concentrations of silver and titanium in wastewater, induced by a photocatalyst, should be even lower than the values given in Table 15.

Table 15: Results of the leaching tests.

Film	Ag (mg/L)	Ti (mg/L)
Ag2N-20P25	0.0027	0.03
Ag4N-10P25	0.0037	0.03

From all the results, the best TiO_2-based sol-gel coating is **Ag 2% NEW + 10% P25.** And this is this coating that has been scaled up in WP5 to cover the 2 demonstration scale reactors.

5.1.10 Scale-up of the sol-gel TiO_2 coating (WP5).

In order to scale up the based-TiO_2 coating method, spray coating at laboratory scale has been tested on steel substrate. Stainless steel 316 slides were washed by scrubbing them with paper soaked in RBS T105, rinsed with distilled water, then ethanol, and finally dried with a flux of compressed air. Some slides were used as such; the rest of them were dipped in a 2 mol/L solution of HNO_3 for 5 s, then dried with a flux of compressed air.

Each slide was manually spray-coated using an airbrush (Harder & Steenbeck). The nozzle was held about 5 cm above the slide and 3-bar compressed air was used to pulverize the sol onto the slide, as homogeneously as possible. Some tape prevented sol deposition at the edge of every slide to allow comparing the aspect of the uncoated and coated parts of the slides and to perform thickness measurements. In every case, 2 mL of 2Ag-10P25-TiO_2 were sprayed.

Afterwards, the slides were calcined at 390 °C for 12 h. All slides were subsequently analysed by profilometry, by X-ray diffraction and underwent the scotch test and the water flow test. In either test, if the aspect of the layer visibly changes, the test is considered a failure and the operating parameters are rejected.

The characteristics of TiO_2 layers spray coated onto steel 316 slides are shown in Table 16. It appears that a very slow deposition speed is necessary to obtain a layer that is resistant to the mechanical stress caused by the tape (or scotch). Furthermore, the nitric acid pretreatment is favorable to the layer's adherence, even though the corresponding non-treated layer is barely damaged by the tape. The main crystallo-graphic phase is Anatase. No damage after water flow test could be observed for each sample.

Table 16: Operating parameters for the spray coating of steel 316 slides (Anatase = main crystallo-graphic phase; no damage after water flow test).

Sample name	Pre-treatment	Flow rate (mL/min)	Quantity sprayed (mL)	Damage after tape test
Spray 2-very slow	-	0.125	2	Light
Spray H-2-fast	HNO_3	2	2	Severe
Spray H-2-medium	HNO_3	1	2	Severe
Spray H-2-slow	HNO_3	0.5	2	Light
Spray H-2-very slow	HNO_3	0.125	2	None
Spray H-0.5-very slow	HNO_3	0.5	0.5	None
Spray H-1-very slow	HNO_3	0.5	1	None
Spray H-3-very slow	HNO_3	0.5	3	Light
Spray H-4-very slow	HNO_3	0.5	4	Severe

Increasing the thickness of the layer by spraying more sol, is related to a lower adherence of the TiO_2 at the surface of the layer, as expected. As can be seen from Table 16, it is clear that this adhesion problem is related to thicknesses well above this value. The water flow test proved to be ineffective in damaging the calcined layers. XRD spectra are very similar in all samples, only anatase-TiO_2 (active photocatalytic crystallographic phase of TiO_2) is detected. The sol can be deposited with an industrial spray coating technic to realize the deposition on demonstration scale reactors of Celabor and IUTA.

5.1.11 TiO_2 sol-gel surface characterization (Deliverable D5.2).

When coatings on steel 316 presented a very homogeneous aspect and a good adhesion (Figure 15), they were observed by scanning electron microscopy (SEM) (Figure 16).

Figure 15: TiO2-based coatings on steel 316 slides.

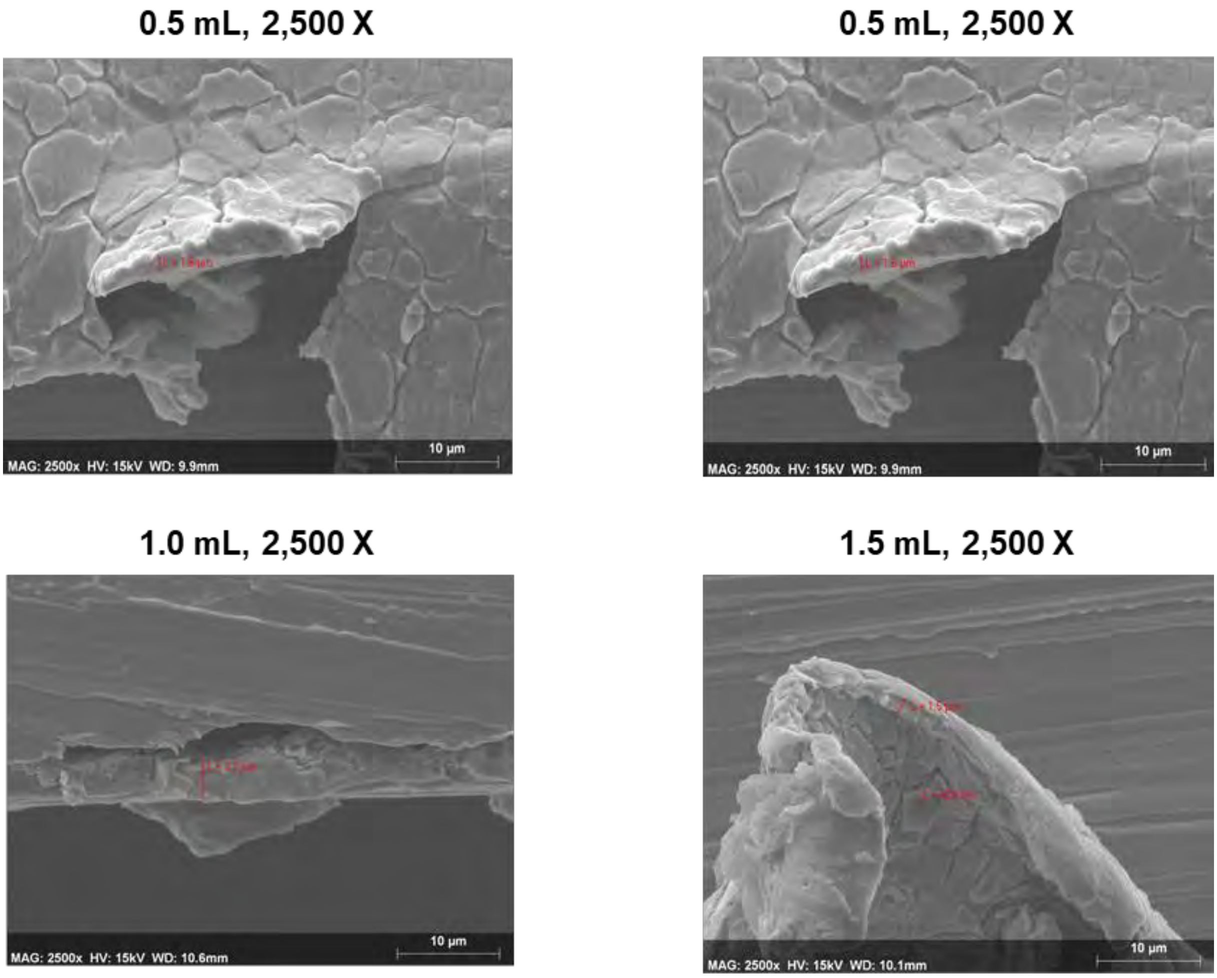


Figure 16: SEM micrographs on Ag2N10P25/TiO_2 coatings (magnification: 2500 X).

In Figure 16, it is observed that the thickness of the film increases with the amount of sol deposited on the steel slide. And the thickness of films evolves from around 1 µm to around 3 µm. The films are also composed of small anatase-TiO_2 crystallites with sizes from 10 nm to 50 nm.

5.1.12 Two industrial demonstration scale plants coated with TiO_2-based photocatalyst (Deliverable D5.3).

A demonstration scale cylindrical reactor (Figure 17) made of stainless steel was spray coated on its inside surface according to findings of section D.5.1. A nozzle was mounted on a motor-powered bar moving vertically along the central axis of the reactor from the top (Figure 18). At first, a nitric acid solution (weight concentration 50%) was abundantly sprayed inside the reactor, which was then heated at 120 °C to evaporate the water. The pipes and the nozzle were rinsed with 2-methoxyethanol before spraying 7 mL of a freshly prepared Ag2-10 P25-doped TiO_2 sol. Then, the reactor was dried at 120 °C again, and calcined at 390 °C for 12 h. A picture of reactor is presented in Figure 19 after calcination.

As the reactor is closed and the spray direction is horizontal, no loss of sol occurs. This allows us to compute the average thickness of the layer, which is equal to 104 nm after calcination.

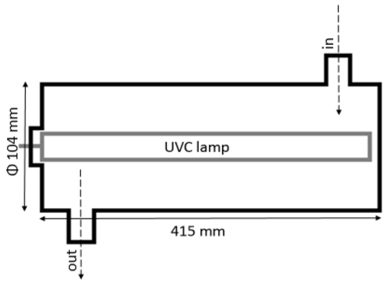


Figure 17: Scheme of an UV reactor for coating.

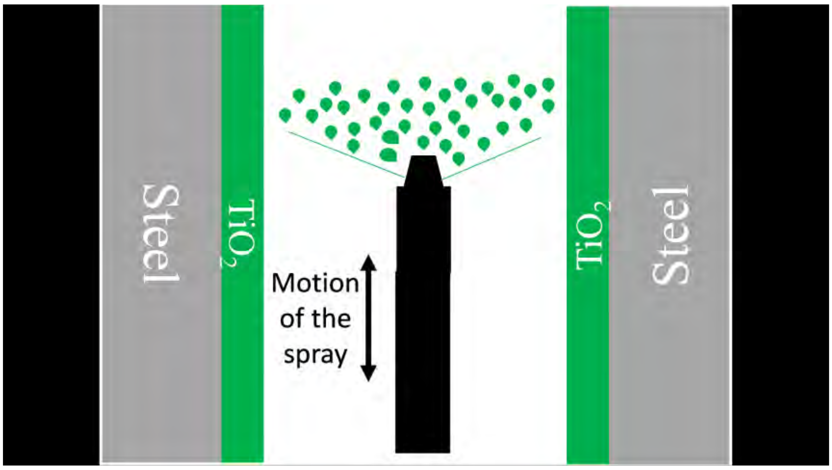


Figure 18: Vertical spray-coating used to coat inside steel reactors.

Figure 19: Reactor coated after calcination step.

The coated reactors were tested on a continuous demonstration scale plant with a flow rate of 300 L/h and at demonstration scale with flow rates of 1 m^3/h to 5 m^3/h.

6. Results of the lab-scale experiments

6.1.1 Results of the toxicity via Daphnia *magma* of the model waters

The 2 model waters with the 5 main micropollutants of the short lists of the GC-MS/MS and LC-MS/MS compounds with a concentration of each micropollutant of 10 µg/L were tested concerning their toxicity. In Table 17 are shown the evaluation parameters of the toxicity test. From a toxic unit (TU) of > 1 the water is already slightly toxic. The TU was calculated using lethal concentration (EC_{50}) values.

Table 17: Evaluation parameters of the *Daphnia magma* test.

non toxic	**TU = 0**
slightly toxic	0 < TU < 1
toxic	1 < TU < 10
highly toxic	10 < TU

In the following Figures are shown the results of the both model waters (Figure 20 and 21).

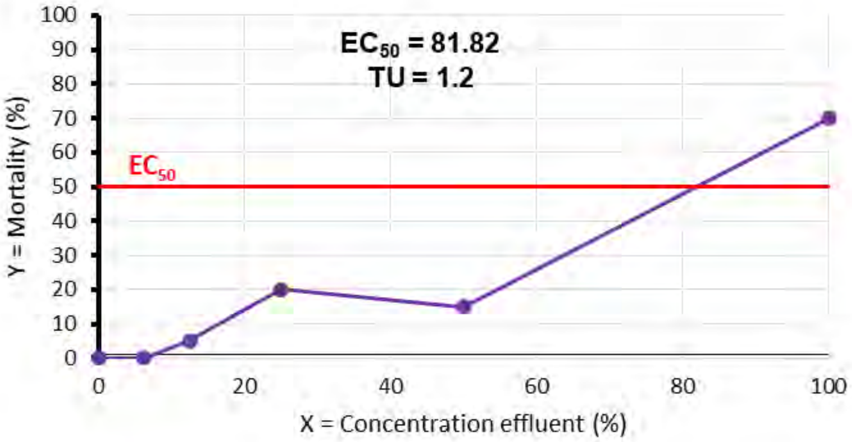


Figure 20: *Daphnia magma* Test on 1*H*-Benzotriazole, Diclofenac, Sulfamethoxazole, Metoprolol and Carbamazepine model water (c = 10 µg/L for each compound).

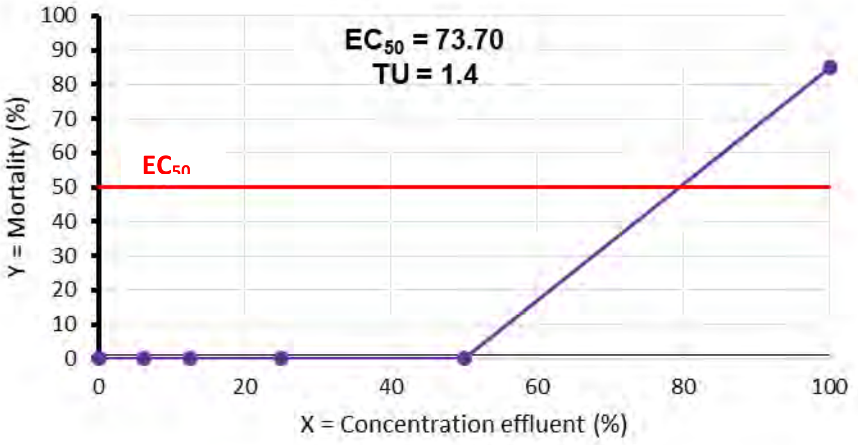


Figure 21: *Daphnia magma* Test on DEHP, Lindane, Tributylphosphate, Atrazine, PBDE model water (c = 10 µg/L of each compound).

Both waters are toxic and presents a toxicity around 1.2-1.4. The same experiment was performed on the extended list of the model water containing 12 micropollutants. The first treatment considered was ozone only and the second treatment was ozone plus photocatalyse. The results are described in the table below. The starting model water showed a toxicity TU = 8. After the two treatment steps, the toxicity decreased to 1.6 and to 1.2.

Table 18: *Daphnia magma* Test on the extended model water containing 12 micropollutants before and after ozone and UV photocatalytic treatment.

	Before ozone	**After ozone 30'**	**After ozone 30'-photocatalyse 6h**
EC50	12.5	61.5	83
TU	8	1.6	1.2

In conclusion, the ozone and UV treatment allows a decrease of toxicity of the water.

6.1.2 Addition of a biological activated carbon for adsorption of emerging TP and remaining micropollutants (WP6; IUTA)

PFOS, a regulated substance within the WFD, cannot be eliminated by ozonation. The elimination using photocatalytic approaches is not well described in literature. Adsorption processes have the potential for the elimination of PFOS. Therefore, a granulated activated carbon (GAC) process will be integrated after the oxidative treatment. A further opportunity for the GAC reactor is the elimination of formed transformation products and remaining micropollutants. Beside adsorption columns will be also investigated whether a stable biofilm for biological substance removal grows and therefore a biological activated carbon (BAC) filtration process is responsible for the compound removal. In the investigations, a distinction between adsorption and biodegradation should be done.

- Lab-scale experiments for the identification of a suitable adsorption material
- Lab scale experiments for the evaluation of the effect of biologically activation
- Scale-up of the GAC/BAC process for the demonstration-scale experiment

Seven different activated carbons and one activated coke were tested. The use of granulated activated carbon should then be tested with the focus to eliminate PFOS and in addition to eliminate the remaining micropollutants.

First a shaking test was performed. The shaking experiment helps to get a general information if a carbon is able to adsorb the selected compounds or not. The shaking experiment does not take into account physical influences which later play an additional role in a large column. For the shaking experiment, the carbons and the coke were grinded and sieved. The sieving machine and the grinded carbons are shown in the Figure 22 A and B.

Figure 22: A) sieving machine B) grinded and sieved carbons.

PAC with a particle size smaller than 50 µm were used to produce a carbon suspension. The carbon suspension had a concentration of 10 mg/L. The samples were doped with the PAC suspension and the mixture of substances (short LC and GC lists). These samples were shaked for 24 h on the shaker with 200 revolutions per minute. At the end of the experiment, the samples were filtered with a syringe filter of 0.45 µm and analysed via LC-MS/MS and GC-MS/MS. The results are shown in Figure 23 and 24.

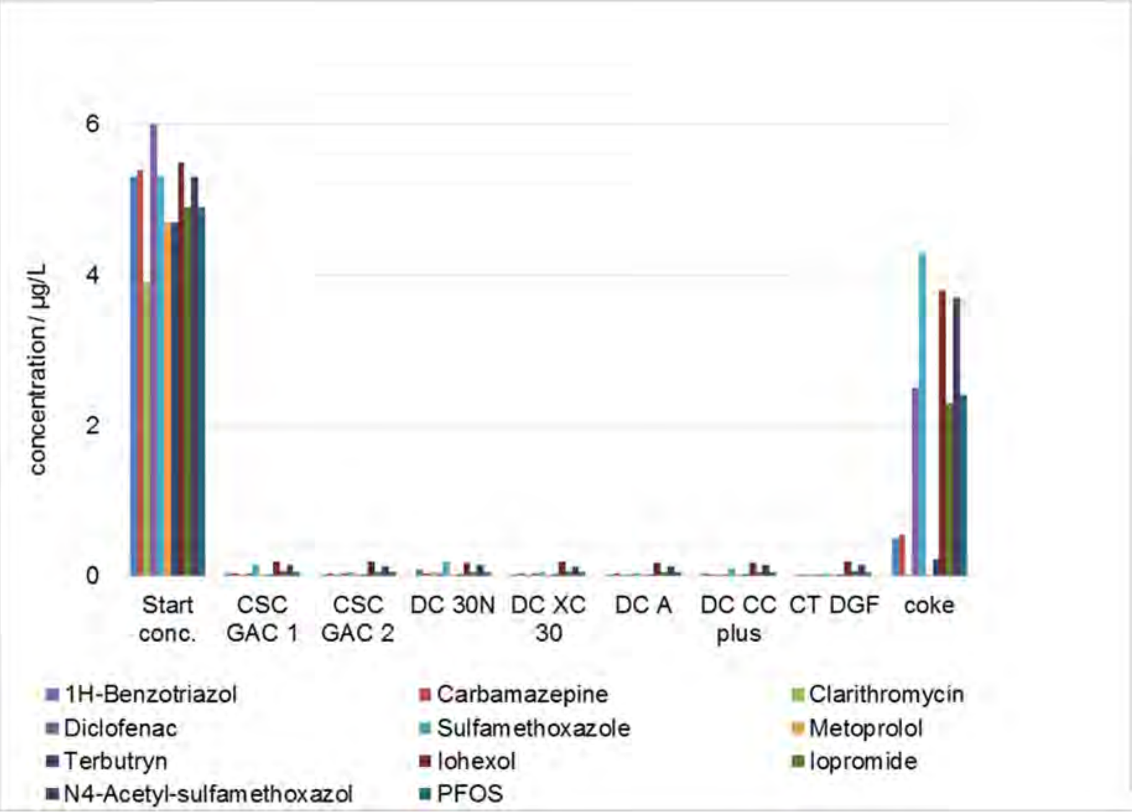


Figure 23: Results of the shaking experiment with LC-MS/MS substance mixture after 24 h shaking with the selected carbons.

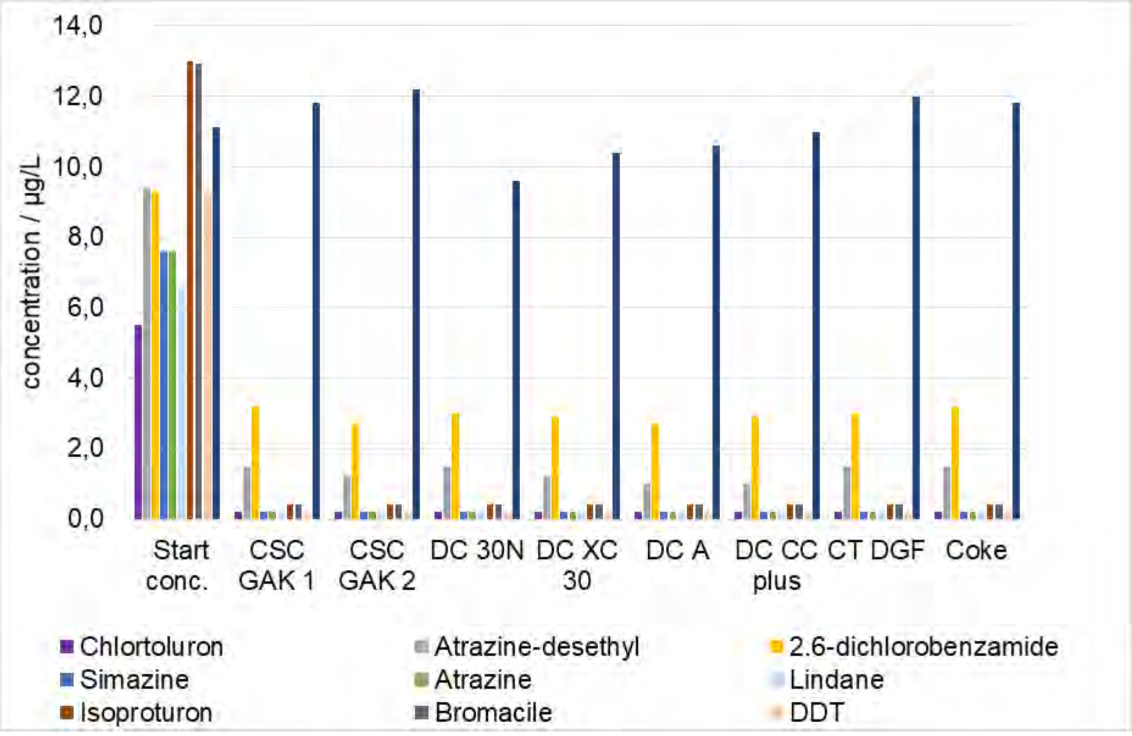


Figure 24: Results of the shaking experiment with GC-MS/MS substance mixture after 24 h shaking with the selected carbons.

The results in Figure 23 showed that **all carbons are general suitable for adsorbing substances analysed by LC-MS/MS.** Additionally, it can be seen that there are no significant differences in elimination between the different granulated activated carbons. The use of coke shows that significantly lower elimination can be achieved. The results in Figure 24 showed that the **GC-MS/MS substances were adsorbed excepted DEHP, Atrazin-desethyl and 2,6-Dichlorobenzamide**. For these three substances a significantly lower elimination was observed for all selected carbons and the coke. Since all substances are considered, especially PFOS the coke is rather not suitable for the process. Due to the poor biodegradability of PFOS (UBA 2020), tests on biologically activated adsorption were not carried out.

In order to be able to make further statement a further shaking test was carried out. In this test, different contact times were considered, because in real case the contact time is normally shorter than 24 h (Figure 25).

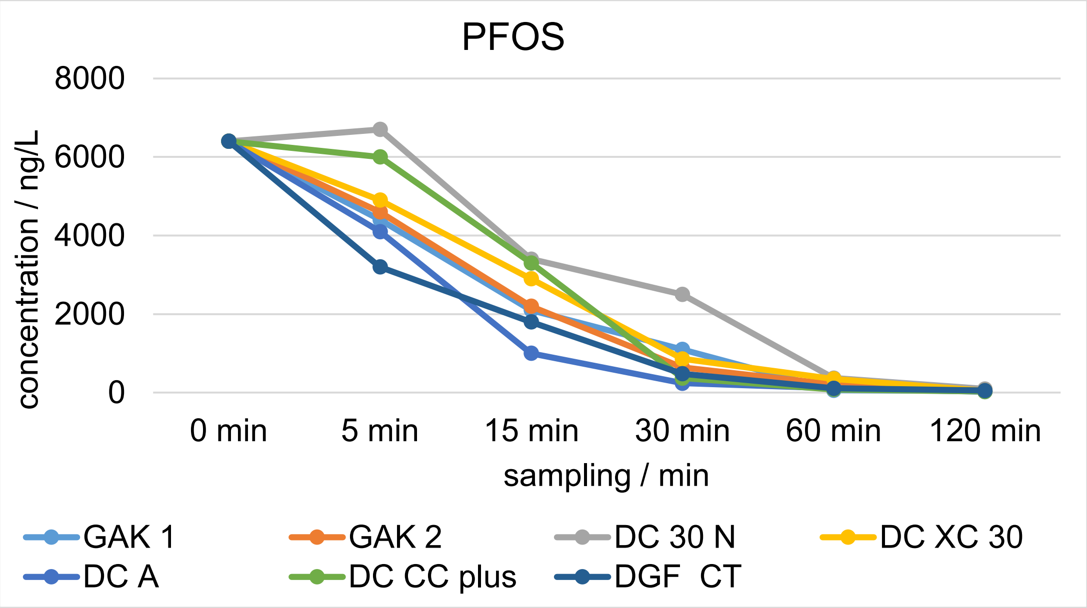


Figure 25: Elimination of PFOS with different activated carbons.

The results for PFOS showed first differences between the different carbons in the first 5 minutes. After 15 minutes, more than half of the sample was already adsorbed. After 30 minutes, a nearly complete adsorption of PFOS was achieved. Therefore, it should be tested at the later demonstration scale plant whether PFOS is almost completely removed in real case with contact times over 30 minutes. The results of the other substances looked similar (Annex 1). As shorter contact times are usually applied in WWTPs, it is important to select a carbon that achieves a high elimination already with a short contact time.

Additionally the specific surface area of the carbon was considered - using the Brunauer – Emmett – Teller (BET) method. An important point for adsorption capacity is that the specific surface area of the coal is as large as possible. The nitrogen adsorption-desorption isotherms are shown in Annex 2. In general the carbons showed no significant differences between their specific surface areas.

Since economic efficiency also plays an important role in the demonstration scale plant, the price of the used activated coal is relevant economic evaluation of the process. The corresponding activated coal prices are shown in Table 19. Even if the adsorber is not used as the main treatment step in this project, the coal has to be replaced after a certain period of time. This cost should not be underestimated.

Table 19: Specific surface area of coals and coal costs.

Carbon	Volume	Costs	Area
Donau Carbon Hydraffin 30N	500 Kg	938.80 €	1,035 m²/g
Donau Carbon Hydraffin CX 30	500 Kg	1,351.00 €	915 m²/g
Donau Carbon Hydraffin A 8x30	500 Kg	1,151.50 €	1160 m²/g
Donau Carbon Hydraffin CC 8x30 plus	500 Kg	1,947.90 €	1240 m²/g
CSC GAK 1	500 Kg	1,132.00 €	945 m²/g
CSC GAK 2	500 Kg	1,082.00 €	980 m²/g
CarboTech DGF 8x30	500 Kg	705.00 €	

The results of the shaking tests and the coal costs were used to make a preliminary selection for the column tests because not each carbon was tested on a column test. Finally of WP 6 the column tests were carried out. With column tests, statements can be made about the breakthrough behaviour or the adsorption capacity.

The small columns (diameter 2 cm) were filled with GAC (filter height 5 cm) and tested over one week. The columns were flowed through from top to bottom with a flow rate of 7 m/h. The results of the three carbons showed no significant differences. The decisive point that led to the selection of the coal, was ultimately the price. Therefore, the carbon manufacted by **CarboTech DGF** was selected. The technical data of the carbon is presented in Table 20.

Table 20: Technical data CarboTech DGF

CarboTech DGF 8x30 GL	
Specification	
water content	5%
Iodine value	Min. 800 mg/ g
particle size distribution	
> 8 mesh (2,36 mm)	max. 10%
< 30 mesh (0,6 mm)	max. 5%
Typical characteristics	
Vibration density	350 ± 30 g/L
Ash content	10%
MB-value	20 g / 100g
Abrasion hardness	90%
Costs per ton	1,410 €
Inner surface	ca. 1,000 m²/g

In addition to the tests for breakthrough behaviour, tests with biologically activated carbon were carried out. For this purpose, an aliquot of GAC was stored for one week in the water of the biological stage of a WWTP. After one week, a part of the carbon (for the GAC) was autoclaved, thus killing the existing biology. The subsequent column tests were carried out over a period of one week. During this test a throughput of 16,800 bed volumes was achieved. After one week the process had to be stopped because of the formation of a biofilm in the reference column. No significant difference was observed between the two columns (activated and non-activated) either.

In general, it can be said that ozonation creates more polar and more bioavailable substances. Due to the increasing polarity, the absorbability on the activated carbon is reduced. In contrast, the is the effect of biodegradability, which in theory can significantly increase the service life of GAC filters in wastewater to 50,000 – 60,000 bed volumes (Rattier 2012, Austermann-Haun 2018).

6.1.3 Scale-up of the GAC process for demonstration-scale experiments

Important parameters for the construction of the filter are the contact time, the flow rate and the filter velocity. One problem to be solved is the height of the filter and the operating weight. The **flow rate of the demonstration scale plant** should be designed between **1 – 5 m³/h** with a **contact time between 10 – 40 minutes**. The filter velocity should be between 1 - 10 m/h. This results in a wide area and it is very difficult to comply with all conditions.

To construct an adsorber with a flow rate between 1 - 5 m³/h and a filter velocity of 1 - 10 m/h, a **diameter of 80 cm** would be necessary. This is already a problem because this diameter has to be custom made which means an enormous cost increased.

Another point is the contact time will then be too short. Therefore, minimum **two adsorber columns** would be necessary to fulfill the desired conditions and requires a lot of space in the container. If you have two adsorber columns, there could be a problem with operating weight. The container floor has a load limit of 700 kg/m². This creates the danger that the floor will not be able to withstand this load and is no longer suitable for transport.

Therefore, an adsorber column was placed outside of the container. The chosen adsorber column was made of stainless steel as it is required to withstand external weather conditions. There are various activated carbon producers that produce and rent these adsorber columns. The smallest adsorber column is suitable for flows from 0.5 to 7 m³/h and has an activated carbon volume of 2 m³. For the demonstration scale plant with a flow rate between 1-5 m³/h, it signifies a contact time between 24 - 120 min. Filter speeds lie in the usually used range between 1 - 5 m/h. In an emergency or during maintenance of the ozonation and UV system components, the adsorber can also be used as main treatment step.

7. Assessment of the process on municipal and industrial wastewaters with a demonstration scale plant (300 L/h) (WP7; CELABOR)

The process efficiency will be validated on model water, municipal and industrial Wastewaters at demonstration scale. The different tasks are:

- Optimum ozone and UV Process Parameters determination with Model water spiked with micropollutants.
- Verification of the performance of UV-ozone process parameters on water going out from WWTPs (municipal AND industrial).
- Characterisation of water toxicity via *Daphnia magna* tests and A-YES assay before and after the combined process of industrial wastewaters.

7.1.1 Description of the 0.3 m^3/h demonstration scale plant.

To perform this work package, the demonstration scale plant described in Figure 26 been used. This is composed of a 180 L tank volume, a pump with a flow of 500 L/h and an ozone generator producing 8 to 60 g/h of O_3. The plant has been improved through the collaboration with Aquatic Sciences. Piping has been upgraded with additional ball valves to allow use of optional UVC-Reactors each 60W UV Lamp at max flow of 10,000 L/h. Currently, three lamps may be used in parallel:

- UVC synergy without coating
- UVC synergy with TiO_2 aqueous coating
- UVC synergy with AOPTi coating i.e. TiO_2 2% Ag 10%P25

Figure 26: (Left) oxidation pilot plant with O3 and/or UVC reactor. (Right) Three types of UVC lamps

7.1.2 Degradation Test at demonstration scale on model water.

First, a degradation test with 100 L of **model water** containing 11 PP at 10 µg/L was performed. Ozonation during 30 min and then UVC degradation during 60 min were used. The experiment was performed subsequently with the 2 UVC lamps *i.e.* with and without coating. Micropollutants were quantified by GC-MS/MS before and after treatment. Results are shown in Figure 27. Five out of eleven pollutants are fully degraded by the treatment. The other six micropollutants are not completely disrupted and would need a further adsorption step on activated carbon. Moreover, this experiment showed that lab scale results (WP4) were transposed at demonstration scale.

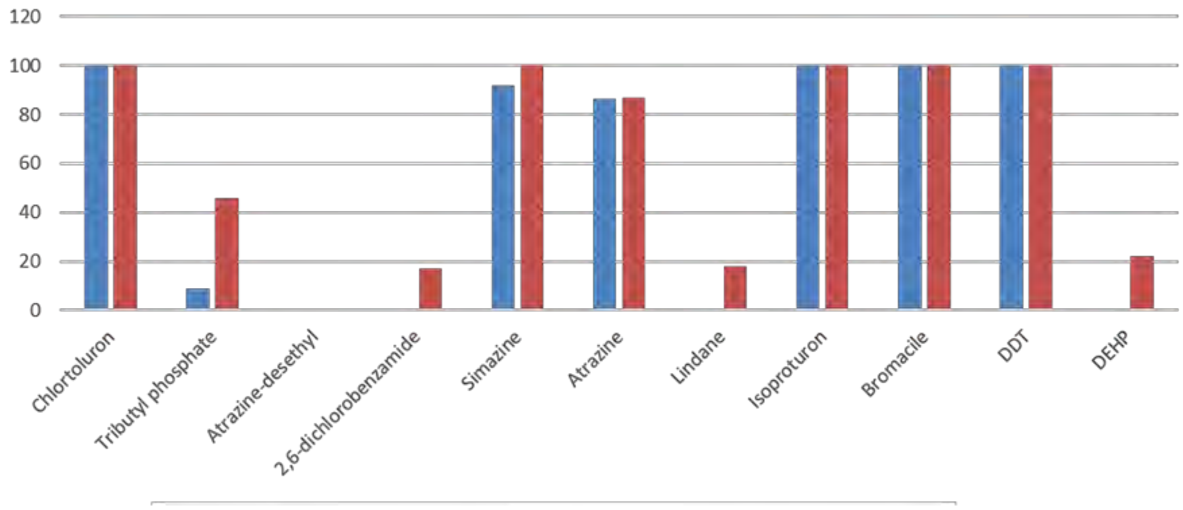


Figure 27: Degradation percentage of micropollutants on 0.3 m³/h demonstration scale (i) without coating (blue) and (ii) with photocatalytic coating (red).

Second, the second model water (analysed using LC-MS/MS) was treated as described above. 100 L of water containing 12 PP at 10 µg/L were treated with ozone and photocatalytic UV. Micropollutants were quantified by LC-MS/MS before and after treatment. Results are shown in Table 21. All micropollutants are fully degraded by the combined treatment ozone and UV photocatalytic with and without coating. Lab scale results are also comparable to the 0.3 m³/h demonstration scale.

Table 21: Micropollutants LC-MS/MS quantification before and after ozonation and UVC treatment.

	with coating			**without coating**		
	Start	**T= 60 UV Kat**	**Degrada-tion %**	**Start**	**T= 60 UV C**	**Degrada-tion %**
	ng/L	ng/L	%	ng/L	ng/L	97.0
1*H*-Benzotriazole	7,800	550	92.9	8,400	250	> 99
Carbamazepine	9,000	< 22.5	> 99	9,000	< 22. 5	> 99
Clarithromycin	7,300	23	> 99	6,800	< 22.5	> 99
Diclofenac	9,800	< 9	> 99	9,900	< 9	> 99
Sulfamethoxazole	11,000	< 9	> 99	11,000	< 9	> 99
Metoprolol	6,600	9.3	> 99	6,800	< 9	> 99
Terbutryn	8,400	< 22.5	> 99	8,200	< 22.5	> 99
Iohexol	7,500	< 20	> 99	7,400	< 20	> 99
Iopromide	9,000	< 9	> 99	8,900	10	> 99
N4-Acetylsulfamethoxazole	9,300	55	> 99	9,400	< 9	> 99
PFOS	8,200	260	96.8	7,500	340	95.5

Toxicity measurements with *Daphnia magma* (Table 22) showed that this model water is not toxic before and after treatment

Table 22: Toxicity of model water (LC-MS/MS) before (ozone T0) and after 30’ ozone (ozone T30) and after 30’ ozone + 60’ UVC photocatalyse (Photocatalyse T60).

	EC_{50} (%)	**TU**
Without coating		
Ozone T0	> 100	0
Ozone T30	80	1.3
Photocatalyse T60	70	1.4
With coating		
Ozone T0	> 100	0
OzoneT30	75	1.3
Photocatalyse T60	69	1.5

7.1.3 Degradation Test at 0.3 m³/h demonstration scale on Industrial wastewaters (CELABOR).

The objective of this experiment was to measure the degradation efficiency of advanced oxidation processes on industrial toxic waste-waters. Two toxic industrial wastewaters were tested.

First, the industrial Wastewater chosen was a **cleaning textile wastewater** of a local company. The experiment was performed with 100 L of wastewater submitted to 30 minutes ozone and then to 60’ UVC photocatalysis.

The *Daphnia magma* toxicity test was performed on cleaning textile water before and after treatment. Results are shown in Table 23. The starting water is highly toxic with a median effective concentration EC_{50} of 0,25% before treatment. It means that half of the daphnia crustacea are immobilized after 24h contact with the wastewater at a concentration of 0.25%. The toxicity TU of starting water is thus 100/EC50 = 400. After treatment, only a slightly decrease of toxicity was observed with or without coating.

Table 23: Toxicity of cleaning industrial wastewater before (ozone T0) and after 30' ozone (ozone T30) and after 30 minutes ozone + 60' UVC photocatalyse (Photocatalyse T60).

	EC_{50} (%)	**TU**
Without coating		
Ozone T0	0.25	400
Ozone T30	2.8	35
Photocatalyse T60	0.9	110
With coating		
Ozone T0	0.25	400
OzoneT30	0.58	171
Photocatalyse T60	0.5	200

The conclusion of this test is that efficiency of degradation by advanced oxidation processes depends on the water composition. Therefore, the whole AOPTi process should include an adsorption step such as adsorption onto activated carbon (see WP6) after or in replacement of advanced oxidation.

Adsorption tests were performed on granular activated carbon and it was shown that the toxicity decrease to TU 40 equitox/m^3 after adsorption. The financial impact of this adsorption treatment for textile **cleaning water industry** was calculated. The annual taxes was calculated before and after adsorption. The characteristics of the wastewater of this industry are:

- V = 45,697 m^3/year
- MES = 114 mg/L
- DCO = 1,416 mg/L
- N = 14.5 mg/L
- P = 2.1 mg/L

Without treatment, the toxicity TU is equal to 400 and the annual tax to 99,000 euros. After adsorption, the toxicity TU decreases to 40 and the tax to 82,000 euros. The cost decreased of the tax for this industry thanks to the adsorption step is equal to 0.37 €/m^3

Second, wastewaters of a company preparing **culture media** were characterized. 100 L of wastewater were treated by 30’ ozone and then by 30’ UVC-photocatalyse. Toxicity before and after treatment was characterized thanks to *Daphnia magma* test. The decrease of toxicity after ozone and UV treatment is highlighted in Table 24. With that type of pollutant, advanced photocatalytic process is efficient for the degradation of micropollutants and the decrease the water toxicty.

Table 24: Toxicity of culture media wastewater before treatment and after 30’ ozone (ozone T30) and after 30’ ozone + 30’ UVC photocatalyse.

	EC_{50} (%)	**TU**
Before treatment	2.5	40
After ozone 30’	28.75	3.5
After ozone 30’ and UV AOPTi 30’	29.29	3.4

To quantify the financial impact of this type of treatment for this **Culture Media industry**, the **annual tax** was calculated before and after AOPTi treatment. The characteristics of the wastewater of this industry are:

- V = 12,500 m^3/year
- MES = 26 mg/L
- DCO = 500 mg/L
- N = 20 mg/L
- P = 2 mg/L

Without any polishing treatment, the toxicity TU is equal to 40 and the annual tax to 8,694 euros. After advanced oxidation treatment, the toxicity TU decreases to 4 and the tax to 2,719 euros. The cost decrease of the tax for this industry with the AOPTi treatment is really interesting and equal to 0.478 €/m^3

In conclusion of these tests and depending on the wastewater nature and composition. Therefore, pilot tests are always necessary for industrial wastewater. Beside the whole AOPTi treatment process also each single step have to be evaluated in terms of compound and toxicity removal. Depending on the results also the combinations of 2 treatment procedures may be the solution for the final treatment process.

7.1.4 Degradation Test at 0.3 m³/h demonstration scale on municipal water (CELABOR).

Finally, the demonstration scale plant was tested with municipal wastewater. Water at the exit of the **WWTP in Esneux** was collected because this WWTP is closed to the CHU hospital. 100 L of wastewater were treated by 30’ ozone and then by 30’ UVC photocatalysis.

Toxicity before and after treatment was characterized thanks to *Daphnia magma* test. According to this test with that type of microorganism, the water is not toxic (Table 25).

Table 25: Toxicity of municipal wastewater before treatment, after 30’ ozone and after 30’ ozone + 30’ UVC with and without coating.

Sample	EC_{50} (%)	TU
Starting water	> 100	0
After ozone	> 100	0
After ozone – 30’ UV uncoated	> 100	0
After ozone – 30’ UV coated	> 100	0

Further toxicity assessment was performed using the A-YES test and LC-MS/MS quantification of the molecules of the model water. Interesting results are highlighted in Table 26. Most of the targeted molecules are present in the municipal water at the exit of the WWTP at concentration from a few ng/L (PFOS, Terbutryn) to hundred µg/L (Iohexol). Eight out of 11 molecules are fully degraded by ozone only. Iopromide is degraded by ozone and UVC. Degradation of PFOS and Iohexol are improved with the photocatalytic coating. The starting water highlights some estrogenic activity which decreases after each treatment step.

Table 26: A-YES test and LC-MS/MS quantification municipal wastewater before treatment, after 30’ ozone and after 30’ ozone + 30’ UVC with and without coating.

Sample description		T 0	30’ ozone	30’ ozone + 90’ UVC	30’ ozone + 90’ UVC with coating
1*H*-Benzotriazole	ng/L	970	49	89	160
Carbamazepine	ng/L	400	< 10	< 10	< 10
Clarithromycin	ng/L	210	< 10	< 10	< 10
Diclofenac	ng/L	840	< 10	< 10	< 10
Metoprolol	ng/L	98	< 10	< 10	< 10
Sulfamethoxazole	ng/L	2,900	< 10	< 10	< 10
Terbutryn	ng/L	52	< 10	< 10	< 10
N4-Acetylsulfamethoxazole	ng/L	< 10	< 10	< 10	< 10
Iohexol	ng/L	110,000	30,000	95	< 50
Iopromide	ng/L	12,000	3,300	< 90	< 90
PFOS	ng/L	26	3,0	41	6,5
Estrogenic activity	ng_{EEQ}/L	0.21	0.17	0.29	0.023

After, the demonstration scale plant was tested with Municipal Wastewater at the exit of the WWTP in Henry-Chapelle. This WWTP was chosen because it is closed to the Psychiatric Clinic of the Frère Alexiens. 100 L of wastewater were treated by 30’ ozone and then by 30’ UVC photocatalysis.

Toxicity before and after treatment was characterized thanks to D*aphnia magma* test. According to this test with that type of microorganism, the water is not toxic (Table 27).

Table 27: Toxicity of municipal wastewater before treatment, after 30’ ozone and after 30’ ozone + 30’ UVC with and without coating.

Sample	**EC_{50} (%)**	**TU**
Starting water	> 100	0
After ozone	> 100	0
After ozone – 30’ UV uncoated	> 100	0
After ozone – 30’ UV coated	> 100	0

Characterizations were performed on the same bases as previously described. The most relevant results are summarized in Table 28. Five out of ten model molecules were quantified at the exit of the WWTP. PFOS was not investigated during this investigation. They are all degraded by ozonation. The starting water shows some estrogenic activity which decreases after ozonation.

Table 28: A-YES test and LC-MS/MS quantification municipal wastewater before treatment, after 30’ ozone and after 30’ ozone + 30’ UVC with and without coating.

Sample description		**T 0**	**30’ ozone**	**30’ ozone + 90’ UVC**	**30’ ozone + 90’ UVC with coating**
1*H*-Benzotriazole	ng/L	750	120	200	200
Carbamazepine	ng/L	1,500	5	5	5
Clarithromycin	ng/L	82	13	13	13
Diclofenac	ng/L	460	5	5	5
Metoprolol	ng/L	< 9	< 10	< 10	< 10
Sulfamethoxazole	ng/L	< 9	< 10	< 10	< 10
Terbutryn	ng/L	11	5	5	5
N4-Acetylsulfamethoxazole	ng/L	< 10	< 10	< 10	< 10
Iohexol	ng/L	< 90	< 90	< 90	< 90
Iopromide	ng/L	< 50	< 50	< 50	< 50
Estrogenic activity	ng_{EEG}/L	0.15	0.007	0.038	0.04

Various 0.3 m³/h demonstration scale tests were performed on three types of water:

- Model waters (model waters with GC or LC substances)
- Industrial wastewaters (cleaning textile wastewater and culture media wastewater).
- Municipal wastewaters of WWTP closed to hospitals (Esneux closed to CHU hospital and Henry Chapelle closed to psychiatric hospital).

For model waters containing GC substances, it was shown that five out of eleven pollutants are fully degraded by the treatment. Six others micropollutants are not completely disrupted and would need a further adsorption step.

For model waters analysed using LC-MS/MS, it was shown that all micropollutants are degraded by the treatment ozone and UV photocatalysis with and without coating. Both experiments showed that lab scale results were transposed at demonstration scale. Toxicity measurements with *Daphnia magma* microorganisms showed that model water is not toxic before and after treatment.

For industrial wastewaters, results mainly depend on the wastewater nature and composition, photocatalysis and ozone are not active on all type of pollutants. By consequence, it is recommend to choice one or several degradations steps of the AOPTi process to achieve the most efficient and economical feasible treatment process. The steps are

- Ozone
- UV photocatalytic
- Adsorption on activated Carbon

For industrial wastewater, the financial impact of the additional final treatment was also calculated for 2 practical cases.

For the 2 municipal wastewaters, *Daphnia magma* test showed that the water is not toxic whereas A-YES analysis showed low estrogenic activity which decreases after each treatment step. LC-MS/MS quantification showed that most of the targeted molecules are present in the municipal wastewater at the exit of the WWTP at concentration from a few ng/L (PFOS, Terbutryn) to hundred µg/L (Iohexol). Majority of molecules are fully degraded by ozone only but improvement occurs with photocatalytic coating for some recalcitrant molecules.

8. Degradation experiments in a Municipal WWTP in demonstration-scale (WP8; IUTA)

A scale-up from demonstration-scale 1 (300 L/h) to demonstration scale 2 (5 m^3/h) was performed. The trials were conducted at the municipal wastewater treatment plant WWTP in Duisburg-Vierlinden, which is a 25,000 PE WWTP (Figure 28). At the WWTP, a full stream ozonation was installed for the removal of micropollutants.

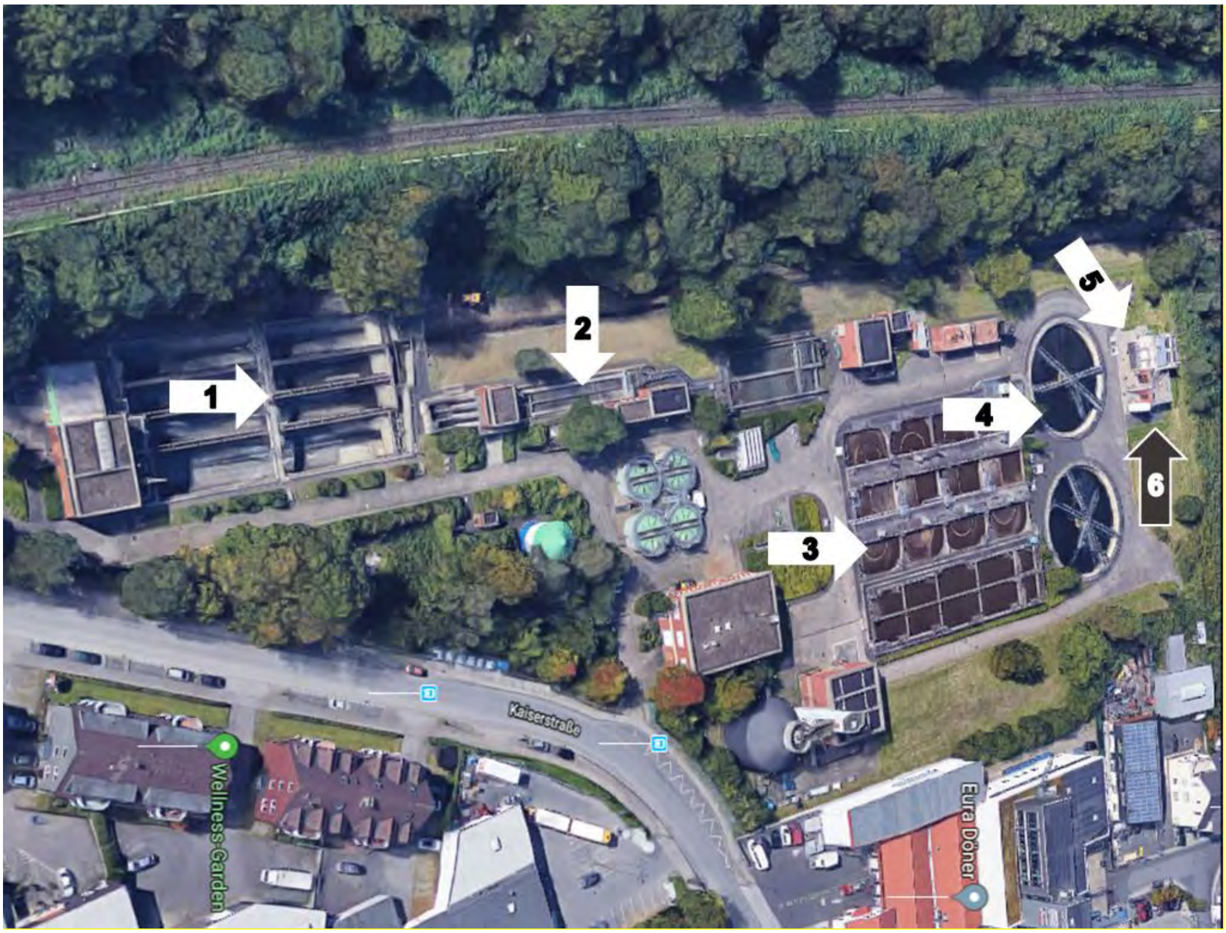


Figure 28: WWTP Duisburg-Vierlinden with 1) preclarification, 2) sand trap, 3) aeration basins, 4) final clarification, 5) ozonation and 6) location of the 1 – 5 m^3/h demonstration scale plant (Source: Google maps).

As inflow to the plant, the effluent of the WWTP without further ozonation was used. During the experiments in demonstration-scale, the elimination rates of the different micropollutants are observed for each treatment step. The validation of the process parameters of the combined treatment process (ozone, UV-TiO_2, GAC/BAC) will be achieved.

8.1.1 Process parameters for 5 m³/h demonstration-scale experiments in WWTP effluents

During implementation, the 1 up to 5 m³/h demonstration scale plant was installed in a container for mobile use. The plant consists of an ozonation and UV plants (Figure 29). The adsorber is located outside the container. The different treatment steps were connected in series via a piping system. With a bypass piping system, the treatment steps can also be used individually. The flow rate of the plant pump is between 1.6 – 5 m³/h. The technical data of ozone plant and UV-plant are listed in Table 29 and Table 30. The technical data of the adsorber were already described in WP6.

Table 29: Technical data of the ozonation part.

Technical Data Ozonation	
Production of O_3 [g/h]	4
Ozone concentration with flow 1.6 m³/h [mg/L]	5
Contact time [s]	18
$z_{specific}$ [mg O_3/ mg DOC]	0.4-0.5
DOC $_{effluent}$ [mg/L]	6-8

Table 30: Technical data of the UV part.

Technical Data UV plant		
Reactor	Small	Big
Diameter [mm]	100	200
Length [mm]	898	898
Volume [L]	5.6	26.8
Layer thickness between radiator and tube wall	27.5	77.5
Contact time with 2,5 m³/h [s]	8.1	38.6
Low pressure (LP) 200W		
Medium pressure (MP) 7000W		

Figure 29: UV plant with small reactor.

Different arrangements of **single treatment steps like ozone, UV** and adsorber were investigated. In addition, the uncoated (Table 31) and TiO_2 coated reactor (Table 32), the low-pressure lamp and medium pressure lamp were examined. An extract of the results obtained is presented in Table 31 and Table 32. Tests were selected with the coated and uncoated reactor with the two lamps (LP and MP). The contact time in the UV plant is 13 s with a flow of 1.6 m³/h. The ozone concentration is equal to 5 mg/L with a contact time of 18 s. In addition, cumulative parameters like DOC, pH, conductivity and COD were analysed.

Table 31: Combination of ozonation and UV-treatment (low pressure lamp 47.8 W/m², uncoated reactor).

Flow: 1,6 m³/h	**Unit**	**Before O_3**	**After O_3**	**After UV LP, uncoated**	**Elimination via O_3 (%)**	**Elimination via UV-**
Micropollutants						
1*H*-Benzotriazole	ng/L	7,900	6,100	3,200	23	48
Carbamazepine	ng/L	1,400	41	< 10	97	88
Clarithromycin	ng/L	170	61	41	64	33
4N-Acethylsulfamethoxazole	ng/L	42	34	26	19	24
Diclofenac	ng/L	4,600	44	< 10	99	89
Gabapentin	ng/L	2,300	1,900	1,600	17	16
Metoprolol	ng/L	1,800	1,100	990	39	10
Sulfamethoxazole	ng/L	440	110	63	75	43
Terbutryn	ng/L	27	20	17	26	15
Iohexole	ng/L	930	810	550	13	32
Iopromide	ng/L	460	420	220	9	48
PFOS	ng/L	2.7	2.7	2.4	0	11
DOC	mg/L	6.4	6.6	6.3	-	-
pH		6.8	6.88	6.91	-	-
Turbidity $_{254}$	1/m	16.5	13.5	11.9	-	-
COD	mg O_2/L	16.9	15.5	229	-	-
Conductivity	µS/cm	770	767	768	-	-

Using a coated reactor, results are comparable.

Table 32: Combination of ozonation and UV-photocatalytic treatment (low pressure lamp 57.8 W/m², coated reactor).

Flow: 1,6 m³/h	**Unit**	**Before O_3**	**After O_3**	**After UV LP, coated**	**Elimination via O_3 (%)**	**Elimination via UV + photo-catalyst (%)**
Micropollutants						
1*H*-Benzotriazole	ng/L	7,400	5,700	3,300	23	42
Carbamazepine	ng/L	1,300	28	< 10	98	82
Clarithromycin	ng/L	160	51	32	68	37
4N-Acethylsulfamethoxazole	ng/L	41	31	24	24	23
Diclofenac	ng/L	4,500	< 10	< 10	100	0
Gabapentin	ng/L	2,100	1,700	1,500	19	12
Metoprolol	ng/L	1,600	1,100	960	31	13
Sulfamethoxazole	ng/L	440	97	61	78	37
Terbutryn	ng/L	31	22	16	29	27
Iohexole	ng/L	740	690	480	7	30
Iopromide	ng/L	450	420	220	7	48
PFOS	ng/L	2.6	2.8	2.4	0	14
DOC	mg/L	6.9	6.4	6.3	-	-
pH		6.92	6.89	6.87	-	-
Turbidity$_{254}$	1/m	16.3	12	10.9	-	-
COD	mg O_2/L	14.8	14.8	14.7	-	-
Conductivity	µS/cm	768	770	769	-	-

The **total elimination** for the substances is calculated from influent ozonation to effluent UV-treatment. It is given in Table 33. In relation to the total influent concentrations, UV-treatment using UV-LP lamps is more efficient for the corrosion inhibitor 1*H*-Benzotriazole, the contrast agents Iohexole and Iopromide and the perfluorinated compound PFOS. Nevertheless, it is very important to highlight that the concentration of each micropollutant decreased strongly after the ozonation treatment, and that a very low concentration of micropollutant strongly influences the kinetics of degradation reactions during the UV-treatment. To conclude really if ozonation or UV-treatment is better for each micropollutant, further tests are necessary. These further tests will consider the by-pass of ozonation treatment and the introduction of effluent directly in the UV reactor.

In Table 31 and Table 32, it is observed that there are no significant differences with and without a TiO_2 coated reactor with the low-pressure lamp. No effect of the coating is noticeable using UV-LP lamps. The results show that not all substances are completely degraded after ozonation. With the UV-treatment, a further degradation of the selected substances can be achieved.

Table 33: Combination of elimination using ozonation and UV-treatment. (low pressure lamp, uncoated reactor).

Flow: 1.6 m³/h	**Total elimination %**	**Part of ozonation, %**	**Part of UV treatment %**
Micropollutants			
1*H*-Benzotriazole	59	23	**37**
Carbamazepine	> 99	97	3
Clarithromycin	76	64	12
4N-Acethylsulfamethoxazole	38	19	19
Diclofenac	> 99	99	1
Gabapentin	30	17	13
Metoprolol	45	39	6
Sulfamethoxazole	86	75	11
Terbutryn	37	26	11
Iohexole	41	13	28
Iopromide	52	9	43
PFOS	11	0	11

The evaluation concept proposed in North Rhine-Westphalia for the cleaning performance of micropollutant removal systems recommends a concentration reduction of micropollutants equal to 80% in WWTP. For this purpose, six indicator parameters (Figure 30) are considered. In order to achieve the elimination goal, a reduction of the indicator parameters by 80% as an average value is to be achieved during the complete wastewater treatment process, including the extended wastewater treatment. Taking these six micropollutants into account, the ozonation leads to an elimination rate of 60%. Taking the inlet of the UV-treatment and the outlet of the UV-treatment in consideration, the UV-treatment leads to an elimination rate of 52%. These calculated elimination rates were related to the respective feed concentration of the respective treatment step. If the degradation rates are related to the total concentration, a different picture emerges (Figure 30). The **total elimination** is shown for the six indicator parameters. At the next bar, the specific parts for ozone- and UV-treatment were given. In relation to the total degradation, the part of the ozonation was 85%. The UV-treatment leads to a further degradation of 15% in average, using the mentioned parameters.

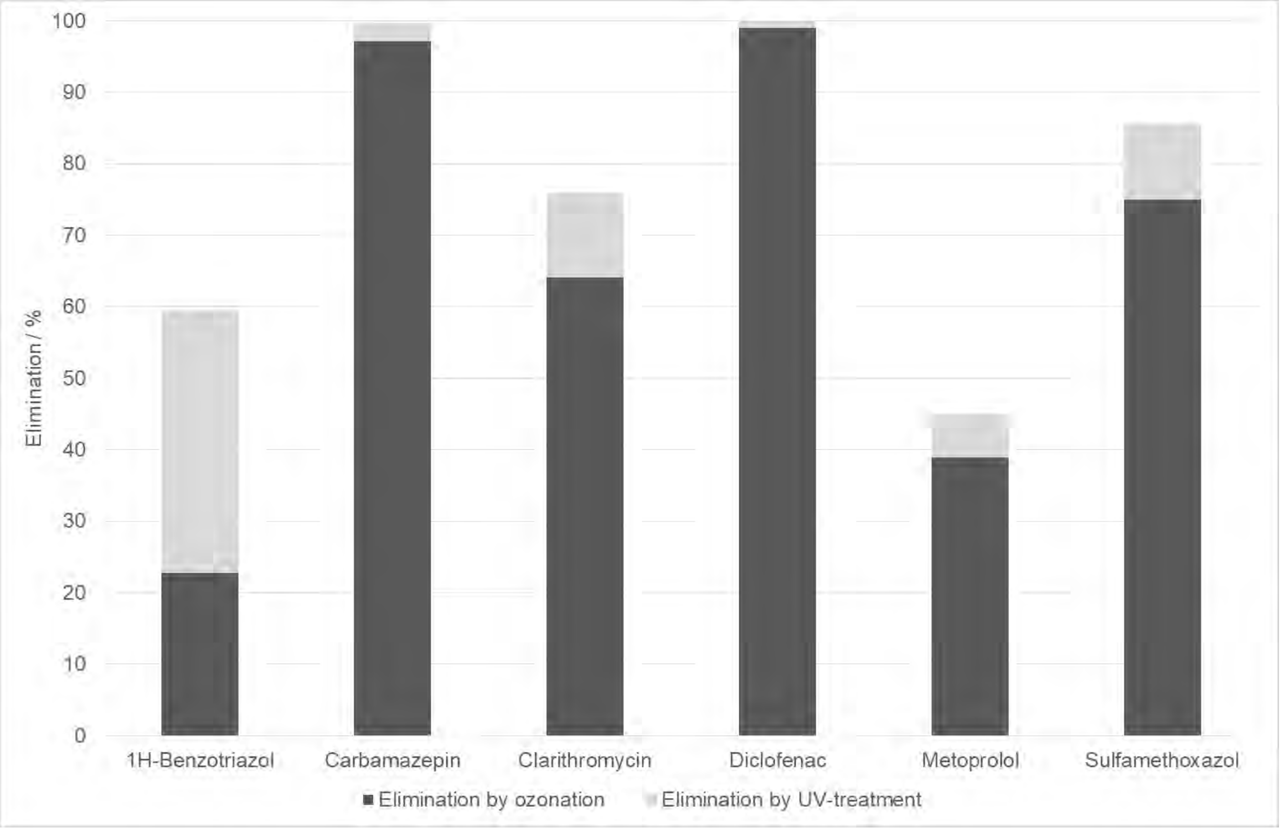


Figure 30: Elimination of the indicator parameters of the oxidative treatment using ozonation (5 mg/L) and UV-treatment (LP, uncoated reactor, 47.8 W/m²) and a flow rate of 1.6 m³/h.

The results using the **medium pressure (MP)** lamp are given in Table 34 and Table 35.

Table 34: Combination of ozonation and UV-treatment (medium pressure lamp 1,280 W/m², uncoated reactor).

Flow: 1.6 m³/h	**Unit**	**Before O_3**	**After O_3**	**After UV MP, uncoated**
Micropollutants				
1*H*-Benzotriazole	ng/L	6,100	3,200	25
Carbamazepine	ng/L	1,000	< 10	< 10
Clarithromycin	ng/L	58	13	78
4N-Acethylsulfamethoxazole	ng/L	86	67	< 10
Diclofenac	ng/L	2,600	< 10	< 10
Gabapentin	ng/L	2,100	1,500	750
Metoprolol	ng/L	1,200	580	190
Sulfamethoxazole	ng/L	570	50	< 10
Terbutryn	ng/L	35	21	< 10
Iohexole	ng/L	< 90	< 90	< 90
Iopromide	ng/L	1,100	980	< 10
PFOS	ng/L	10	2.6	4.8
DOC	mg/L	5.1	4.9	4.7
pH		6.89	7.01	6.96
Turbidity $_{254}$	1/m	13.3	10	8.4
COD	mg O_2/ L	2,380	1,766	1,750
Conductivity	µS/cm	532	541	539

Table 35: Combination of ozonation and UV-treatment (medium pressure lamp 1,055 W/m², coated reactor).

Flow: 1.6 m³/h	**Unit**	**Before O_3**	**After O_3**	**After UV MP, coated**
Micropollutants				
1*H*-Benzotriazole	ng/L	7,500	5,000	110
Carbamazepine	ng/L	1,300	< 10	< 10
Clarithromycin	ng/L	150	39	19
4N-Acethylsulfamethoxazole	ng/L	42	28	< 10
Diclofenac	ng/L	3,800	< 10	< 10
Gabapentin	ng/L	2,000	1,500	760
Metoprolol	ng/L	1,600	940	320
Sulfamethoxazole	ng/L	450	83	< 10
Terbutryn	ng/L	31	19	< 10
Iohexole	ng/L	790	870	45
Iopromide	ng/L	520	480	5
PFOS	ng/L	2.4	2.8	3.3
DOC	mg/L	6.0	6.4	6.4
pH		6.8	6.84	6.88
Turbidity $_{254}$	1/m	15.2	10.1	9.5
COD	mg O_2/L	14.7	14.9	13.8
Conductivity	µS/cm	769	766	767

In Table 34 and Table 35, if results are presented in percentage of degradation of each micropollutant, no differences between the uncoated UV-reactor and coated UV-reactor are observed. Furthermore, degradation results obtained with the medium pressure lamp showed higher elimination results than using low pressure lamp. This was expected because of the higher radiation capacity and the wider range of wavelengths that are covered. Nevertheless, operating a medium pressure lamp means a higher energy consumption. So the ratio between the "energy consumption/degradation percentage of micropollutants" should be absolutely estimated with a low pressure UV lamp and a medium pressure UV lamp.

In addition to ozonation and UV-treatment, the adsorber has been investigated. In Table 36, an example for an UV-treatment followed by an adsorption step is shown.

Table 36: Combination of UV-treatment with adsorber (low pressure lamp, uncoated reactor).

Flow: 1.6 m^3/h	**Unit**	**Before UV, LP, uncoated 21.9 W/m^2**	**After UV LP, uncoated 21.9 W/m^2**	**After UV and adsorber, contact time: 80 min**	**Elimination via UV (%)**	**Elimination via UV and absorber (%)**
Micropollutant	ng/L					
1*H*-Benzotriazole	ng/L	6.300	4.900	< 250	22	98
Carbamazepine	ng/L	2.100	2.100	< 10	0	100
Clarithromycin	ng/L	120	110	< 25	8	91
4N-Acethylsulfa-methoxazol	ng/L	26	23	< 10	12	83
Diclofenac	ng/L	4.100	920	< 50	78	99
Metoprolol	ng/L	670	630	< 10	6	99
Sulfamethoxazole	ng/L	890	550	< 10	38	99
Terbutryn	ng/L	< 9	< 9	< 10	-	-
Iohexol	ng/L	160	10	< 20	94	94
Iopromide	ng/L	950	530	< 10	44	100
PFOS	mg/L	26	30	2.6	-15	90
DOC	1/m	7.4	7.4	0.4	-	-
pH	mg/LO_2	6.87	6.73	6.41	-	-
Conductivity	µS/cm	20.4	20.3	30.9	-	-

All remaining substances could be removed by the adsorber used. Since the long-term tests will only investigated in the next few weeks, the coal in the adsorber is still very fresh. During the long-term tests, it should be verified that the absorption capacity of the adsorber remains the same.

8.1.2 Performance of various toxicity tests with the best obtained process parameters and assessment of the quality of the tertiary treated wastewater

The long-term experiments were all carried out at the wastewater treatment plant Duisburg-Vierlinden. The best obtained process parameters (highest elimination results) are the combination of ozone-, UV- and GAC-treatment. As a biofilm is formed on the carbon over time during GAC filtration, this is known as a biologically activated filter (BAC). For the long-term experiments the ozonation setting was a production of 5 mg/L In average the specific ozone dosage was 0.5 mg_{O3}/mg_{DOC}.. For the UV step was selected the small, coated reactor with medium pressure lamp. Due to changing water turbidity the setting of the UV-MD lamp was 100%. The average intensity during the nine experiments of the lamp was 765 W/m². The average total elimination of the indicator parameters was over 85%. As expected, Diclofenac was directly degraded by ozonation. 1*H*-Benzotriazole was mainly degraded after UV step. And Metoprolol was only fully degraded after adsorption step. After adsorption step nearly each substance was removed. Due to short test period the bed volume treated m³/m³ (BV) at the end was still under 1,000. For further experiments (BV 1,000 – 15,000) the treatment step after adsorber should be observed at which BV a worser removement comes noticeable. In previous investigations (only GAC treatment step) the elimination rates were between 31% and 82% after 4,600 BV and between 0% and 21% after 32,000 BV (Stowa, 2009). In the following table are shown the average results of the long-term experiments with the elimination rates.

Table 37: Results of long term experiments.

Flow 1.6 m³/h	Unit	before Ozone	after Ozone	after UV	after adsorber	Elimination %
1*H*-Benzotriazole	ng/L	6,175	4,692	791	125	98.0
4N-Acetylsulfamethoxazole	ng/L	< 30	< 30	< 30	< 10	-
Carbamazepine	ng/L	1,363	252	140	<10	99.3
Clarithromycin	ng/L	112	79	19	<10	91.1
Diclofenac	ng/L	3,883	233	41	14	99.6
Gabapentin	ng/L	992	861	564	<10	99.0
Metoprolol	ng/L	2,550	1,875	931	<10	99.6
Sulfamethoxazole	ng/L	245	83	35	<10	95.9
Terbutryn	ng/L	<10	<10	<10	<10	-
Iohexol	ng/L	710	643	< 90	<90	87.3
Iopromide	ng/L	1,158	1,099	< 90	<90	92.2
PFOS	ng/L	< 10	< 10	<10	< 10	-

A part of this samples were examined for endocrine disrupting compounds and genotoxic effects. The results of the yeast cell assay (A-YES) are shown in the following graph. The effect based trigger value of 0.4 ng/EEQ/L was used to evaluate the results (Kase 2018, Escher

2018). This orientation value describes the effect based limit. The results were all below the effect based limit (Figure 31).

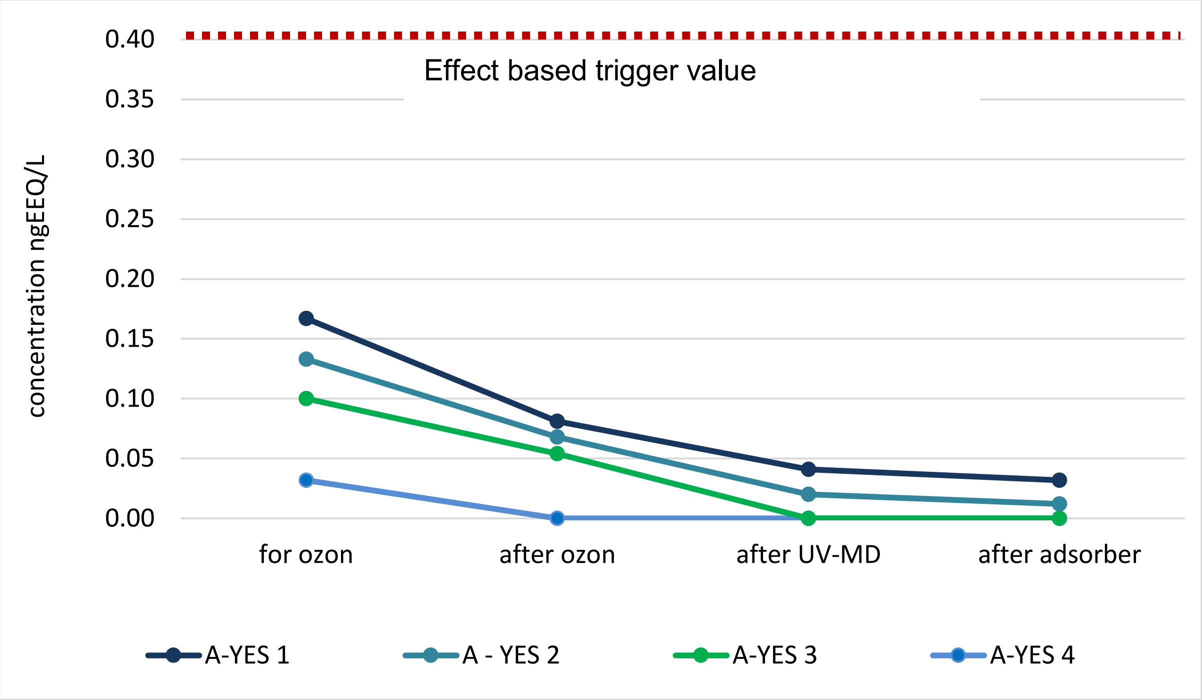


Figure 31: Estrogenic activity of the long term experiments measured by A-YES.

Only when the effect based trigger value is exceeded, substance-specific analysis have to be carried out to identify the causative substance more precisely. By this combination of screening analysis using effect based analysis and instrumental analysis for further target and non-target analysis it is possible to save costs for the complex instrumental analysis. For followed genotoxic investigations were tested some samples with two different genotoxicity tests: the umuC and the micronucleus test.

The umuC test and the micronucleus test show if in the sample are substances which stands for any damage to genetic apparatus, the genome. The results of the umuC test showed for some samples a low genotoxicity. This is shown in Table 38.

Table 38: Results of the genotoxicity of the long term experiments measured by umuC.

Sample number	Sample	Enrichment factor	Indication of toxicity
M 200416/103	for O_3	50	No
M 200416/104	after O_3	50	No
M 200416/105	after UV	50	No
M 200416/106	after adsorber	50	No
M 200416/107	for O_3	50	No
M 200416/108	after O_3	50	No
M 200416/109	after UV	50	No
M 200416/110	after adsorber	50	No
M200414/001	for O_3	50	No
M200414/002	after O_3	50	No
M200414/003	after UV	50	No
M200414/004	after adsorber	50	No
M200414/005	for O_3	50	No
M200414/006	after O_3	50	yes (IR = 1.78)
M200414/007	after UV	50	yes (IR = 1.55)
M200414/008	after adsorber	50	No
M200408/025	for O_3	50	yes (IR = 1.60)
M200408/026	after O_3	50	no
M200408/027	after UV	50	no
M200408/028	after adsorber	50	no
M 200408/029	for O_3	50	yes (IR = 1.81) [AF 100, IR = 2.37]
M 200408/030	after O_3	50	no
M 200408/031	after UV	50	no
M 200408/032	after adsorber	50	no

The measured genotoxicity is in a lower range. In order to be able to make an exact statement whether a sample is to be classified as genotoxic with a relevant effect, at least 2 different genotoxicity tests should be carried out. Based on the results of umuC test were selected six samples for the micronucleus test. The selected samples are marked grey in the Table 38. Sample M 200414/001 was selected to confirm the negative result of the umuC test. The sequence M 200408/25-28 was selected to consider each treatment step and the sample M 200414/008 was to confirm whether, if applicable, after a positive umuC test in the influent, there is also a positive result with the micronucleus test in the effluent (Figure 32).

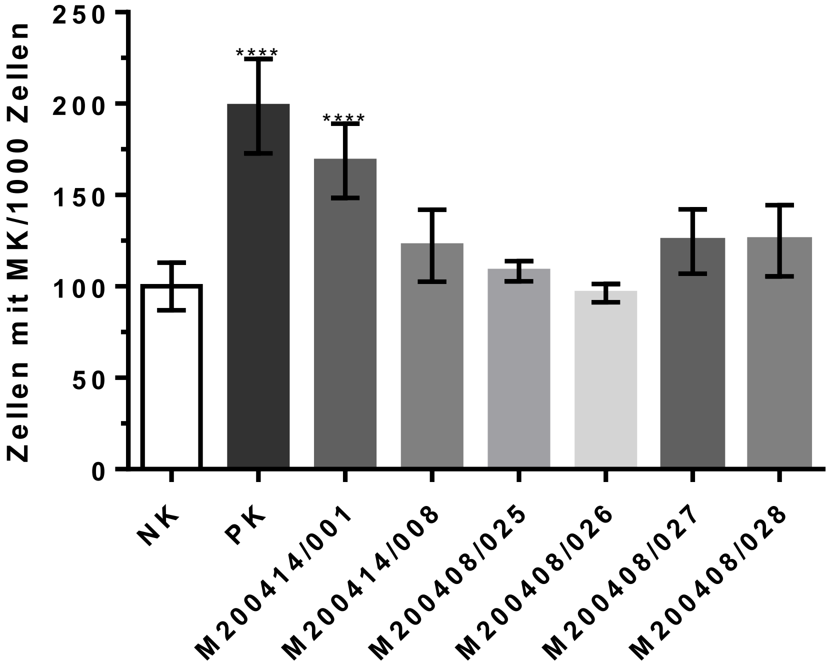


Figure 32: Results of the genotoxicity of the long term experiments measured by micronucleus test.

The results of the micronucleus test showed a positive genotoxic result for only one sample. The Sample M 200414/001 showed low genotoxicity. The result for this sample with umuC was negative. The results that none of the tested samples can be classified as genotoxic, since none of the samples was positive in both tested investigations.

Of the 24 samples investigated, a genotoxic potential was determined for seven samples by activating the repair system of the bacteria without metabolism. For all samples which showed a genotoxic potential in the preparation without S9, no evidence of genotoxins could be determined in the preparation with sample metabolism. This allows the conclusion that the potential genotoxins contained in the samples can be converted to non-genotoxic substances by mammalian metabolism.

The situation is different for sample M200416/107, which only showed a genotoxic potential when mixed with S9. From this it can be concluded that substances contained in the sample were converted to potentially genotoxic substances by the metabolism.

The in-vitro micronucleus test was carried out with six samples. In three of these samples, genotoxic substances were suspected by the preceding umuC test. However, only in the beginning without metabolism. None of these findings could be confirmed by the micronucleus test. This leads to the conclusion that the substances which lead to the induction of the bacterial DNA repair system are not relevant for mammalian cells.

The situation was different for sample M200414/001, where no genotoxic potential could be detected by the umuC test. However, the sample showed a genotoxic effect in the micronucleus. The result could be confirmed in three independent tests. In each experiment the sample was identified as genotoxic with a high statistical certainty ($p < 0.0001$) and thus showed a significantly higher number of micronuclei compared to the control. The different findings in both test systems can be explained by the fact that different organisms and endpoints were investigated. No test system is able to map all potential toxic effects, so a combination of several test systems is always recommended.

On the basis of these results, a more precise identification of the causative substances by HPTLC was waived, as no increased toxicity was observed after treatment.

8.1.3 Results of the Non-target screening (NTS) of the long term experiments.

The AOPTi process is composed of three sequential steps: ozonation, UV disinfection, and lastly adsorption via activated carbon. In a static approach (i.e. a sequence of samples before and after each step taken on the same day), a categorization of features can be performed over the treatment process, as shown in Figure 33. However, the prioritization of features is limited using this approach. Thus, NTS was performed over a period of 43 days.

In Figure 34, the deviation in the number of filtered features over the monitoring period is presented. The experiment is divided in four sampling points: IN, OZ, UV, and AC, consisting of influent, after ozonation, after UV disinfection, and after adsorption with activated carbon, respectively. Between each sampling point, a treatment process occurs. For instance, between IN and OZ, the ozonation takes place. Thus, features produced during ozonation, will have category N in the OZ feature list, as shown in Figure 33.

The NTS filtering process was explained in the previous report. Briefly, the filtering step consists of removal of features from the system and sample preparation, as well as removal of features with intensity lower than 3000 counts (i.e. 3 x the average noise level). Further optimisation of peak detection and filtering is necessary to improve the relevance of the features in the set. Despite the possible presence of irrelevant features, a clear reduction in the total number of features is observed after adsorption with activated carbon. A high number of features after UV disinfection is observed for some of the sampling dates, but still, the average is lower than after ozonation. The influent samples contained clearly more features than after ozonation, which had the second highest average number of features. These results are consistent with the targeted screening analysis as well as with the results from the NTS suspect screening, as shown in Figure 35. An in-house built and curated database was used for identification. In Figure 35, a list of relevant compounds for AOPTi is presented. The identification was based on the guideline from the German Water Chemistry Society, which requires for an identified compound the following criteria: retention time (± 0.15 min), exact mass (± 5 ppm), and a minimum of two expected MS2 fragments (Schulz and Lucke, 2019). When all criteria are fulfilled, category 1 is reached and the substance is identified. A total of 22 substances were identified over the monitoring period. All the identified compounds had a similar profile throughout the treatment scheme as the ones presented in Figure 35. In summary, after adsorption with activated carbon, the signal for all compounds could not be detected with the selected peak picking parameters and filtering criteria.

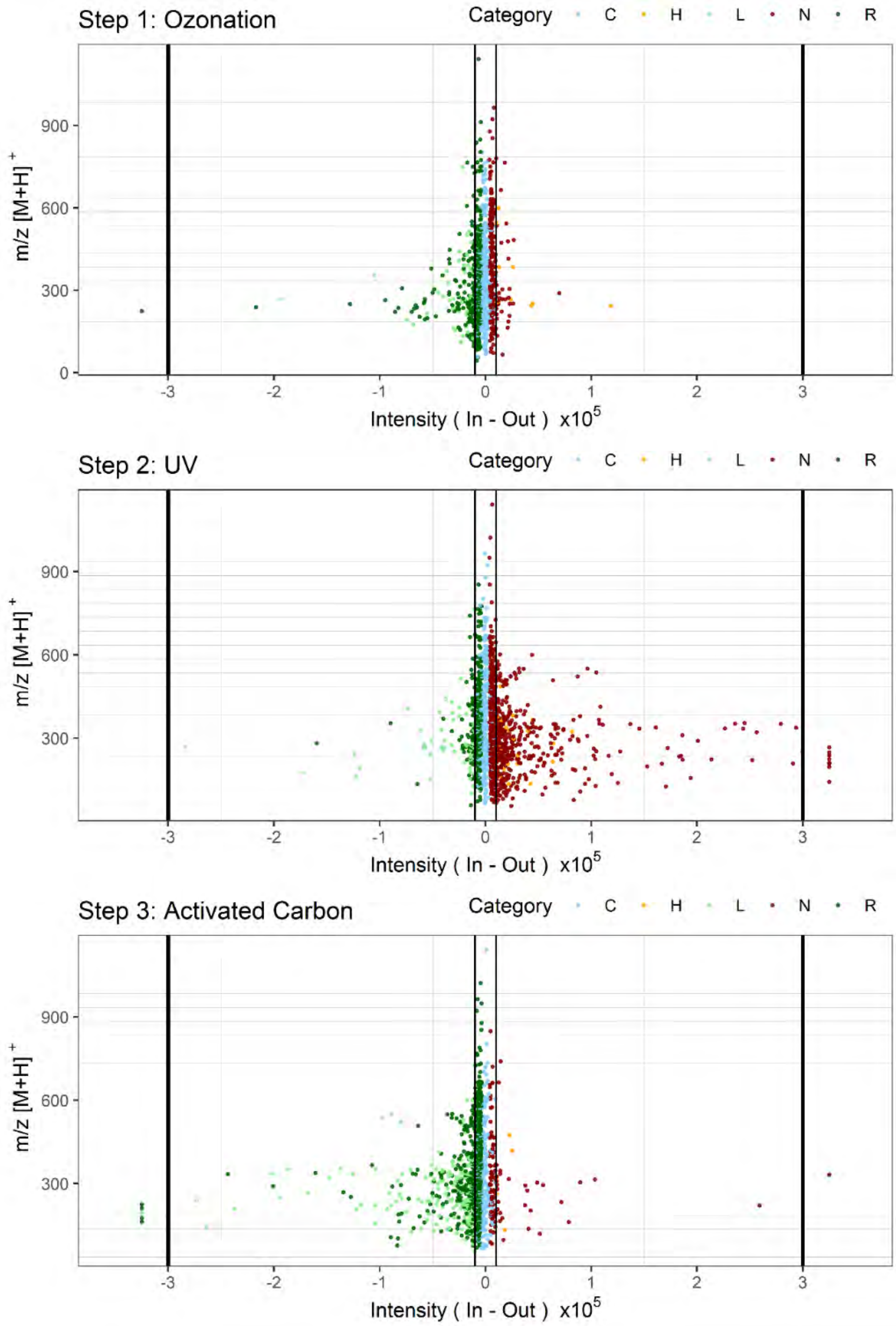


Figure 33: NTS results over the three treatment steps from a sample set taken from the 5 m³/h demonstration scale.(Week 3) The represented features (i.e. each data point) are divided in categories as Constant (C) in blue, Higher (H) in orange, Lower (L) in light green, New (N) in red, and Removed (R) in dark green. The categories describe the fate of each feature over the treatment scheme as the name indicates. New features (N) are then likely a product of removed (R) or lower (L) features. The other sampling dates are presented in the Annex.

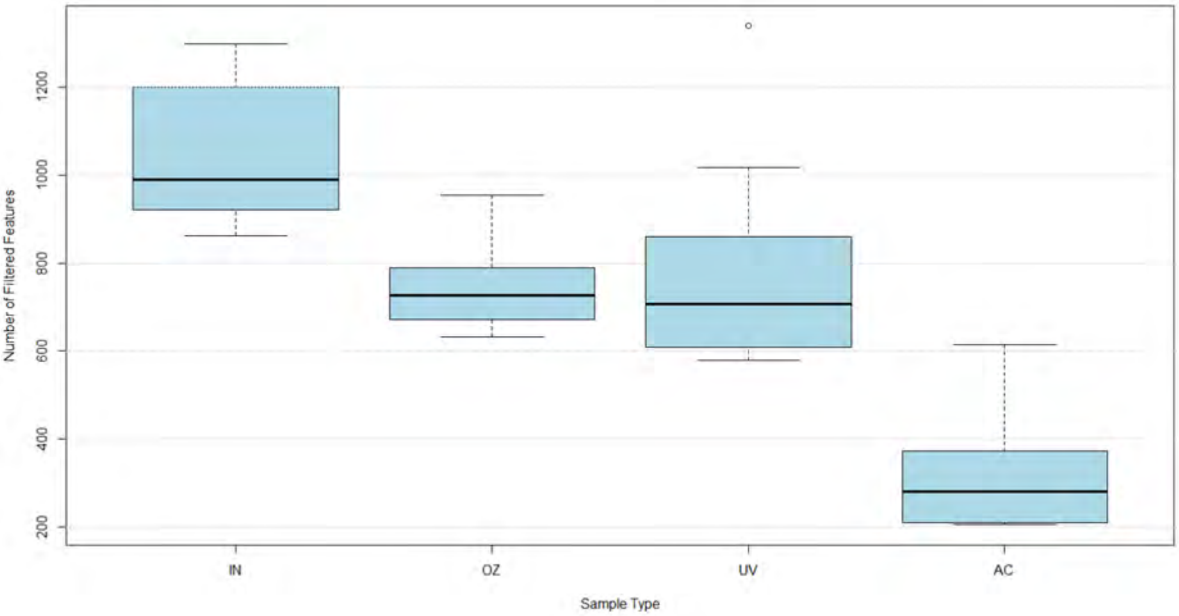


Figure 34: Variation in the number of features over the treatment scheme for all the sampling dates after the NTS filtering workflow, which consists of removal of features from the system and sample preparation as well as removal of features with intensity lower than 3000 counts (i.e. 3 x the noise level). IN, OZ, UV, and AC consist of influent, after ozonation, after UV disinfection, and after adsorption with activated carbon, respectively.

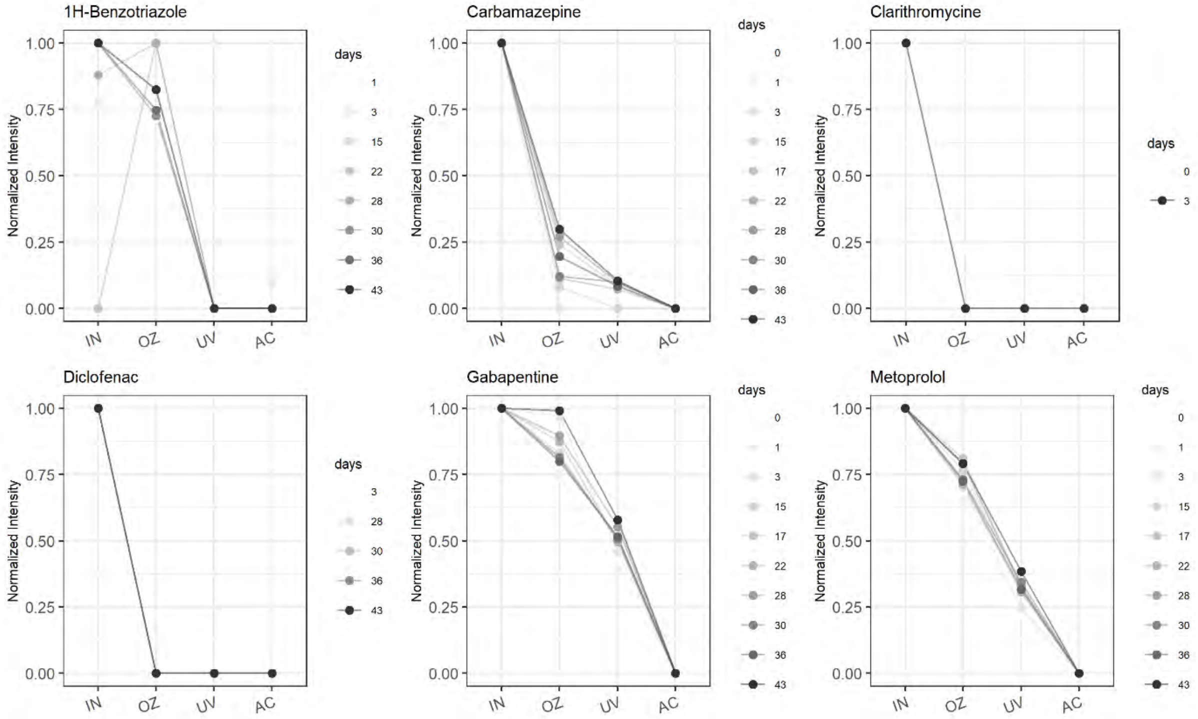


Figure 35: Selection of compounds found via suspect screening of the NTS workflow, using an in-house database. Identification was based on retention time (± 0.5 min), exact mass (± 5 ppm), and a minimum of two expected MS2 fragments. Intensity values were normalized and lines correspond to the monitoring days after the beginning of the sampling campaign. IN, OZ, UV, and AC consist of influent, after ozonation, after UV disinfection, and after adsorption with activated carbon, respectively.

8.1.3.1 Frequency Analysis

By combining the feature lists from all sampling dates for each sampling point (IN, OZ, UV, and AC), a frequency analysis can be performed using the criteria from the guideline as above described. Features are matched firstly by *m/z* (± 5 ppm), then retention time (± 0.15 min), and lastly, if available, a correlation between the MS2 fragment lists is performed.

The frequency analysis for each sampling point resulted in a large data set which is summarized in Table 39. The larger number of features appear only once. These features could be (1) background *m/z* bins (± 5 ppm) with shifting retention time and thus, leading to repeated entries in the data set, or (2) actual compounds that appeared only once in the experiment. In either case, the relevance is in principle not high. Therefore, for prioritization, we will focus on features that appear at least 3 times during the monitoring period.

Table 39: Number of features for each sampling point and the respective frequency from 1 to 10, which corresponds to the number of sampling dates. IN, OZ, UV, and AC consist of influent, after ozonation, after UV disinfection, and after adsorption with activated carbon, respectively. In red, are the features selected for further NTS processing

Frequency	*IN*	*OZ*	*UV*	*AC*
1	2306	1371	1956	916
2	483	318	511	334
3	242	171	198	**67**
4	154	117	115	**55**
5	131	100	83	**41**
6	73	59	71	**17**
7	99	90	71	**29**
8	99	81	64	**27**
9	94	85	78	**19**
10	237	158	120	**37**

To have a general elucidation about the properties of the produced and removed features during the treatment train, we analyse their distribution over the retention time. Note that the retention time of the features was obtained by reverse phase chromatography. In Figure 36, we examine the number of features with frequency higher than 3 (Table 39) across the retention time window. As expected, a reduction in the number features with higher retention is observed after activated carbon, whereas the number of features in the first 50 seconds slot of the retention time is the highest after activated carbon. A possibly explanation is the lower affinity of the activated carbon for certain substances (e.g. polar and small compounds). Note that reverse phase chromatography is limited for polar compounds, indicating that actual number of substances not adsorbed to the activated carbon is likely much higher than the number presented in Table 39.

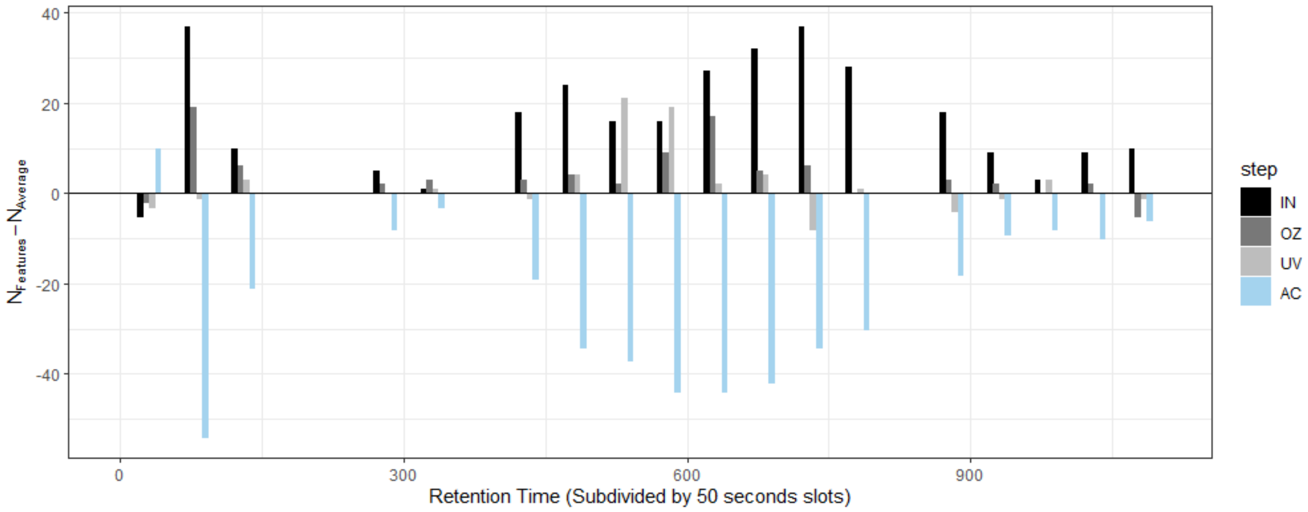


Figure 36: Evaluation of the number of features with frequency higher than 3 for each sampling point across the retention time, which was obtained by reverse phase chromatography. The retention time is divided in 50s slots. Then, the number of features in each slot is averaged among all sampling points and for each sampling point, the difference from the average number of features is return in the y-axis.

Following the prioritization as above described (i.e. features that at least appeared in 3 sampling dates), we further process the features that actually leave the treatment process (feature presented in red in Table 39). The relevance of these selected features is based on their potential impact due to the discharged into the natural aquatic environment.

Filtering the data set, we obtained 292 features that fulfil the criteria. As previously described, it is unlikely that identified compounds are in this group since all were removed during the AC step (Figure 37). However, transformation products are likely to be present. Thus, the next step is an evaluation of the fate of these 292 features over the treatment scheme in order to understand their origin and to find potential precursors upstream in the treatment line.

8.1.3.2 Trend Analysis

Firstly, the 292 features are divided into clusters according to their intensity profile across the treatment train. The optimum number of clusters or the optimum tree height of the hierarchical cluster analysis was 7, according to the silhouette analysis which evaluates the consistency between clusters (Figure 37). The intensity profile of the features for each sampling point was averaged and a standard deviation analysis showed a maximum deviation at 57%, meaning that the intensity deviations were relatively stable over the sampling monitoring. The average was performed for simplification during clustering. The 7 clusters are presented in Figure 38. Cluster 1 represent features already present in the influent and remain stable during the treatment process. Background *m/z* may be included in this cluster. Clusters 3, 4 and 7 include features that appear or increase after the ozonation treatment and UV disinfection. Finally, clusters 2, 5 and 6 represent features with higher intensity after the AC step.

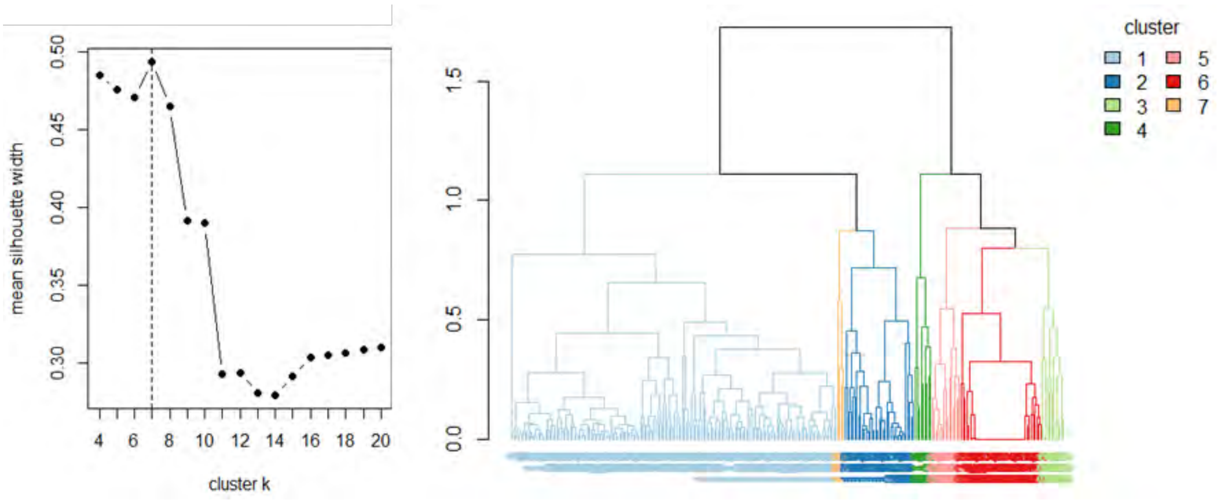


Figure 37: Silhouette average distribution of the hierarchical clustering for the features with frequency of at least 3 found after AC (left). Optimal number of clusters is 7. Dendrogram of the hierarchical clustering with the optimum tree cut (7) coloured (right).

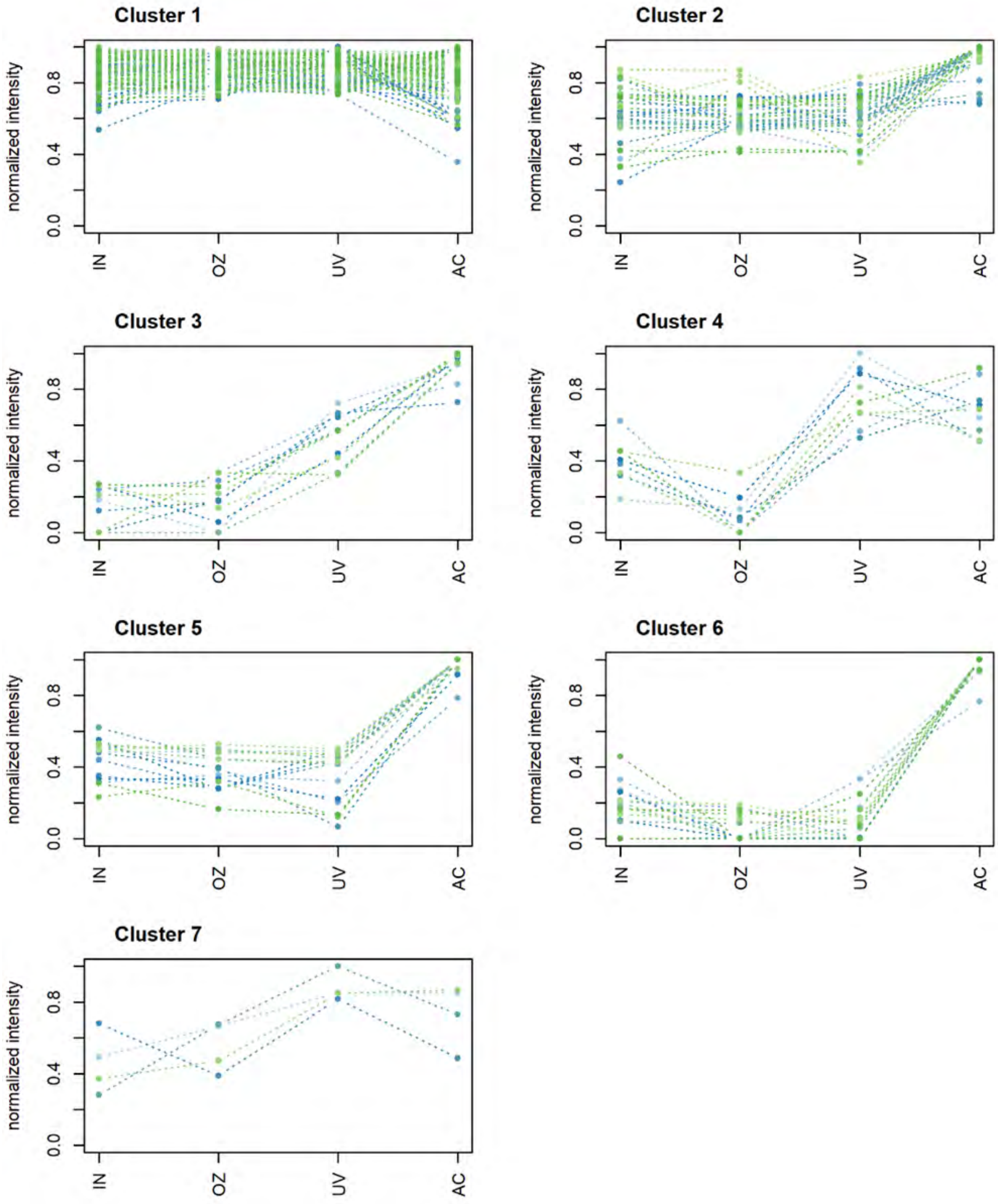


Figure 38: Profile clusters containing the averaged normalized intensity from the 292 features over the treatment train.

8.1.3.3 Transformation pathways

Features from clusters 3, 4 and 7 and clusters 2, 5 and 6 are possibly transformation products with low affinity to adsorb onto the activated carbon. Thus, a search for potential precursors of the features in the aforementioned clusters was performed for the OZ and UV steps, using a list of possible pathways (Table 40). In Figure 39, we have plotted the *m/z* of the transformation products found in the aforementioned clusters against their retention time. As expected the majority and most frequent transformation products have low retention time, indicating a possible low affinity to activated carbon.

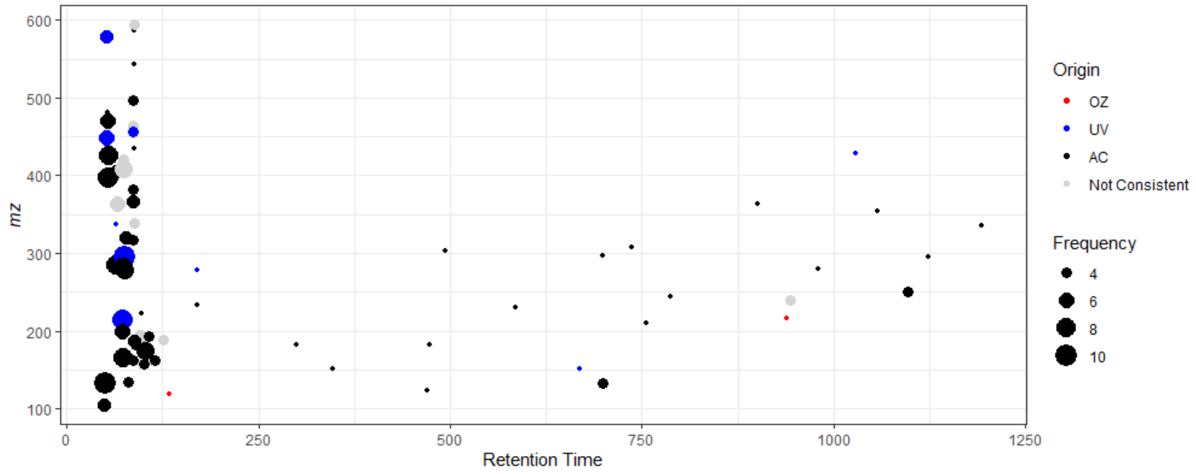


Figure 39: Transformation products found in the clusters 2,3,4,5,6, and 7 from each treatment step (colours). The frequency of appearance is represented by the dot size from 3 to 10. Not Consistent (grey) corresponds to transformation products without a consistent precursor feature within the monitoring period.

8.1.3.4 Identification

The platform FOR-IDENT was used to attempt the identification of the transformation products found after activated carbon (Figure 39). The retention time index (Figure 3940), acquired using the same chromatographic conditions as the samples, was implemented in the FOR-IDENT workflow to support the identification (Letzel 2018). The *m/z*, retention time, and, when available, MS2 data of each transformation product were use as search parameters. The transformation products were order by the average intensity before the identification for prioritization. Searching with 5 mg/L tolerance for the mass accuracy, 14 of the 74 transformation products returned with candidate matches. Prioritising the features with average intensity above 30000 counts, one match for the *m/z* 134.1177 return positive. This feature is from cluster 5 (Figure 38) and appears 4 times during the monitoring period. The possible transformation pathways matched to this feature are listed in Table 40. Note that transformation during the AC indicates that the precursor was present before the AC and it does not necessarily mean that it takes place during AC. The low number of results for identification of the transformation products listed in Table 41 may be explained by their low retention in reversed phase chromatography. Reversed phase is the most applied chromatographic methodology, resulting is lack of information for compounds with low affinity. Also, the first 30 seconds of the chromatographic separation in this study were not injected to the mass spectrometer, indicating that transformation products with lower affinity to the reverse phase were not detected. Further research should therefore focus on increasing the peak capacity for the features illustrated in Figure 36 39 and others with lower retention in the C18 column.

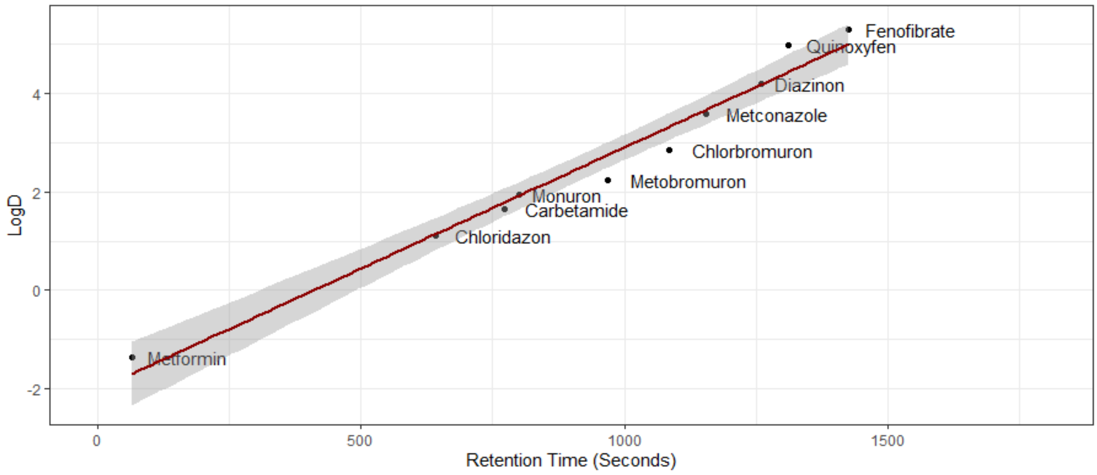


Figure 40: Retention time index calibration using the respective reference standards. The y-axis represents the LogD which is the partition of a chemical compound between the lipid and aqueous phases.

Table 40: List of possible transformations associated with the *m/z* 134.1177 for each treatment step.

m/z	RT (seconds)	Frequency	OZ	UV	AC
134.1177	79	4	$-C_2H_2O$ -F +H	$-C_2H_2O$ $-C_2H_4$	$+C_8H_6O$ $-C_2H_2O$ $-CH_2O$ $-C_2H_4$ -F +H $-CH_2$

Table 41: Candidates for feature with *m/z* 134.1177, based on mass accuracy and retention time index.

Candidate name (IUPAC)	Formula	SMILES
4,4-Dimethoxybutan-1-amine	C6H15NO2	COC(CCCN)OC
1-[(2-Hydroxypropyl)amino]propan-2-ol	C6H15NO2	CC(O)CNCC(C)O
2-[2-(Dimethylamino)ethoxy]ethan-1-ol	C6H15NO2	CN(C)CCOCCO

For an identification of the transformation products further investigations with orthogonal analytical techniques like NMR or Raman spectroscopy and/or reference standards would be needed. This huge effort would be only meaningful in the case of a relevant toxicity of the samples. This was not the case and therefore no compound identification was necessary.

8.2 Investigation of industrial process wastewater

In addition to municipal wastewater an industrial process wastewater was investigated in laboratory and demonstration scale. The process wastewater was heavily contaminated with inorganic compounds and a high concentration of an organic industrial compound (mg/L range). The focus of the elimination was on the degradation of the organic compound.

First laboratory experiments showed no removal using activated carbon, neglected reactivity of the target molecule with ozone.

Already at the beginning of the tests it was suspected that due to the strong coloration of the process water only a low transmission could be achieved with the UV-step. The results are shown in Table 42.

Table 42: Investigation of industrial process wastewater (uncoated reactor).

	Elimination after ozone	Elimination after UV
industrial compound	0%	20%

In contrast to municipal wastewater, where during the ozonation also hydroxyl radicals as reactive species are formed, for this specific industrial wastewater no hydroxyl radical formation could be observed and therefore nearly no reduction of the organic compound was measured. Only with the UV-part could be reached a reduction of 20%. With the coated reactor an elimination of 15% could be observed. The coating was not sufficient for an enhanced removal of the industrial compound.

The combination of ozone and UV had no significant improvement for the elimination of the industrial compound. Better results were obtained by the addition of H_2O_2. UV/H_2O_2 processes to form more hydroxyl radicals were not in focus of the AOPTi project. Therefore, the further process optimisation was not shown at this report. In conclusion this specific, very complex wastewater could not be sufficient treated by the AOPTi procedures.

9. Cost evaluation of the ozone-UV photocatalytic adsorption treatment and of the TiO_2 sol-gel coating (WP9; IUTA, ULg-NCE)

Depending on the operational conditions, demonstration scale plants will be optimized with the aim to reduce operating costs and to achieve required effluent quality in terms of selected priority substance removal. Electricity consumption and other necessary inputs (oxygen consumption, chemicals) will be monitored and measured.

- Evaluation of the cost of 1 m^2 of TiO_2 coating
- Estimation of the cost for treatment of 1 m^3 of wastewater in a 100,000 PE WWTP

9.1.1 Evaluation of the cost of 1 m^2 of TiO_2 coating (ULg-NCE)

The different prices of all reagents used for the synthesis of TiO_2 sol-gel coatings doped with 2 wt.% of silver and 10 wt.% of Evonik P25 are listed in Table 43. These prices are calculated to synthesize 1 L of this solution.

Table 43: Prices of all reagents used for the synthesis of TiO2 sol-gel coatings

Reagent	Purity	Amount	Price/unity	Total price (euros)
Silver acetate	Reagent grade	0.667 g	4.94 €/g	3.29
Silver chelatant	Industrial grade	0.004 L	2.87 €/L	0.01
Evonik P25	Industrial grade	2.04 g	1.05 €/g	2.14
Titanium isopropoxyde	Industrial grade	0.07 L	0.754 €/L	0.05
2-methoxyethanol	Industrial grade	0.92 L	0.1975 €/L	0.18
Distilled Water	-	0.009 L	0.17 €/L	Negligible
Total	-	-	-	**5.67**

In this project, the dimensions of the industrial UVC reactors are equal to 10.4 cm for the diameter, and 41.5 cm for the height. Being that it is only the inner wall of the reactor which is coated, it represents a surface equal to 0.135 m^2. In WP5, it is shown that only 7 mL of Ag2N10P25/TiO_2 sol are used to coat this industrial reactor. So it represents 52 mL of Ag2N10P25/TiO_2 sol to coat 1 m^2 of reactor.

The cost of Ag2N10P25/TiO_2 coating to coat 1 m^2 is equal to (0.052*5.67 €) = 0.29 €. This cost is negligible compared to the total treatment costs of 1 m^3 wastewater as will be shown at chapter 9.1.2.

9.1.2 Cost for treatment 1 m³ of wastewater in the demonstration scale (1.6 m³/h) plant (IUTA)

The calculation of the costs was done according to the recommendations of the KOM-M.NRW (2016). At the 1 - 5 m³/h demonstration scale plant a total volume of 1.6 m³/h wastewater is possible using all treatment steps. The investment and the operating costs for each step of these plant were given in Table 44. The energy demand is measured using each treatment step. The energy costs are calculated with a price of 0.19 €/kWh. The costs for pumping were calculated within the first treatment step – the ozonation. Using the 1 - 5 m³/h demonstration scale plant without ozonation, the costs for pumping have to be calculated separately. The costs for the change of the UV-lamps and the activated carbon were mentioned as consumption. Using UV-LP lamp, one lamp per year has to be changed. Using UV-MP lamps, 2.2 lamps per year have to be changed. Once a year the dip tube has to be replaced. The lifetime of the GAC/BAC step is estimated with 50,000 bed volumes. Using the demonstration scale plant, ozone is produced from dry air and not from oxygen. So consumption costs for the ozonation are not available.

The costs for the coating of the UV-rectors were included. But these costs were so low that they were completely negligible. The costs for the coating amount to 0.29 €/m² coating. Using typical reactors, the size of the shell surface lies between 0.3 (small reactor) and 0.6 m² (big reactor). Therefore the costs are 0.08 € to 0.16 €/reactor.

In some cases depending on the composition of the wastewater (e.g. very little suspended matter or very high transmission in the wastewater), it might be feasible if the UV treatment using MP-lamps is successful using only 10% of the energy. For this reason, a range of using 10% and 100% energy is given in Table 44 and Table 45.

Table 44: Invest and operating costs for the 1 - 5 m³/h demonstration scale plant.

Costs		**O_3**	**UV-LP**	**UV-MP 10%**	**UV-MP 100%**	**GAC/BAC**
Invest	€	*42,353*	*5,629*	*14,580*	*14,580*	*13,000*
Operating costs						
Energy	*€/year*	*8,799*	*333*	*1,165*	*11,651*	
Maintenance/ repair	*€/year*	*3,075*	*4,222*	*10,935*	*10,935*	*683*
Consumption	*€/year*		*600*	*2,116*	*2,116*	*353*

The calculation of the specific costs per m³ treated wastewater per year leads to the following costs (Table 45).

Table 45: Specific costs per m³ treated Wastewater using the 1 - 5 m³/h demonstration scale plant.

Costs for the treatment of 14,016 m³/a wastewater		**O_3**	**UV-LP**	**UV-MP 10%**	**UV-MP 100%**	**GAC/BAC**
Costs per year (total)	€/year	17,045	5,598	15,127	25,613	2,559
Specific costs per m³ treated wastewater	€/m³	1.22	0.40	1.14	1.88	0.18

The treatment costs for these plant were high compared to literature dates for the treatment of the wastewater of 100,000 population equivalents (PE) WWTP and other pilot studies.

9.1.3 Cost for treatment 1 m^3 of wastewater in 100,000 PE WWTP (IUTA)

The estimation for the specific costs for the treatment of 1 m³ wastewater in a 100,000 population equivalents WWTP were done using informations of the manufacturer of the UV-treatment system. For a disinfection step using classical UV-ND systems, 15 x 6 x 0.4 kW lamps were needed. An AOP process in this treatment plant with a flow of 10,300,000 m³/a would need 92 x 11 kW lamps. Invest costs were given by the manufacturer. Energy is calculated by consumption of the UV lamps. Using UV-LP lamps, each lamp per has to be changed in one year. Using UV-MP lamps, 2.2 x 92 lamps have to be changed. In addition, the dip tubes should be replaced once a year. The planned construction of the UV-treatment plant is a classical reactor design. For the addition of the coating, the coasts amount to approximately 8 € for all reactors. The investment and the operating costs were given in Table 46. Costs for the installation of a pumping station or similar site-specific costs were not included in the estimates.

Table 46: Investment and operating costs for the 100,000 PE WWTP.

Costs		**UV-LP**	**UV-MP**
Invest	*€*	*256,500*	*2,060,800*
Operating costs			
Energy	*€/year*	*59.918*	*1.684.373*
Maintenance/ repair	*€/year*	*27,500*	*55,000*
Consumption	*€/year*	*67,194*	*227,056*

The calculation of the specific costs per m³ treated wastewater per year leads to the following costs (Table 47).

Table 47: Specific costs per m^3 treated wastewater in a 100,000 PE WWTP.

Costs for the treatment of 10.3 Mio m^3/a wastewater		**UV-LP**	**UV-MP**
Costs per year (total)	€/year	182,398	2,156,960
Specific costs per m^3 treated wastewater	€/m^3	0.02	0.21

The use of UV-LED lamps to produce the UV radiation also promises a significant reduction in treatment costs.

For an enhanced wastewater treatment in general, it can be said that the larger the WWTP, the lower the specific costs. This is mainly due to the lower investment costs related to the higher PE. Examples for calculated values (with different PE) are given in Table 48.

Table 48: Literature values for an advanced treatment in WWTP for the removal of micropollutants.

Source	**Specific costs [€/m^3]**	
Kabasci, S., et al. 2007 Costs for the treatment of hospital wastewater (95% of elimination of the pharmaceuticals) – pilot scale (1 - 3,5 m^3/d)	UV-LP UV-MP O_3	15.49 7.12 5.60
Pinnekamp, J., et al. 2014 Specific costs for a treatment of a wastewater for a 100,000 PE WWTP (90% elimination of diclofenac)	O_3/H_2O_2 UV-MP/H_2O_2 UV/O_3	0.05 0.18 0.16 – 0.20
Pinnekamp, J., et al. 2011 Range of specific costs of each treatment process for the elimination of micropollutants at WWTPs (full scale).	O_3 PAC GAC AOP	0.02 – 0.26 0.03 – 0.35 0.10 – 0.32 0.025 – 0.46
Mikrolight (2014) Specific costs of different AOP processes for the treatment of a m^3 wastewater in a 100,000 PE WWTP	O_3/H_2O_2 UV/H_2O_2 UV/O_3	0,05 0.18 0.16 – 0.20
Metzger, S., et al. (2015) Costs of the PAC treatment in WWTP (full scale)	PAK	0.06 – 0.19
KOM-M.NRW 2016 Specific annual costs per m^3 of treated wastewater. Preferred variants from feasibility studies and realised full scale plants in North Rhine-Westphalia, Baden-Württemberg and Switzerland	PAC GAC O_3	0.04 – 0.30 0.07 – 0.21 0.06 – 0.33

The costs for “conventional” enhanced wastewater treatment for build systems were collected and graphically compiled by “Kompetenzzentrum Mikroschadstoffe NRW” (Figure 41). In the Figure the specific annual costs for the treatment of one m^3 treated wastewater for the different technologies (ozone, powdered activated carbon (PAC) and granular activated carbon (GAC)) for the constructed and the (theoretical) calculated systems of North Rhine-Westphalia, Baden-Württemberg and Switzerland were given.

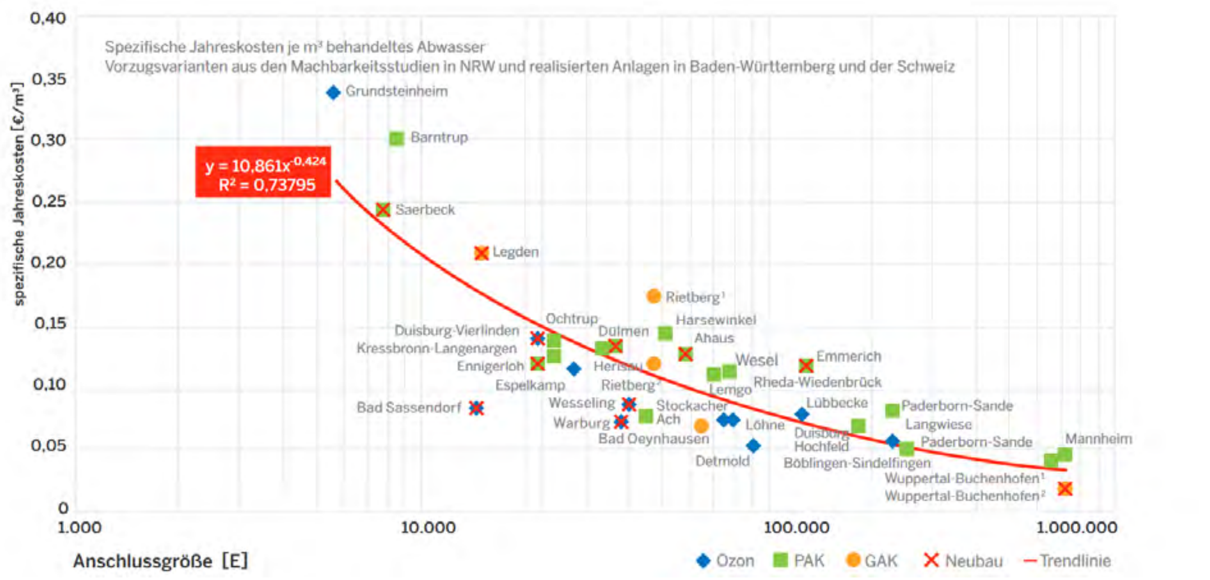


Figure 41: Specific annual costs for the treatment of one m³ treated wastewater for the different technologies (ozone, PAC, GAC) (Source: KOM-M.NRW 2016).

The costs of the combined process were higher than the single treatment steps. In Germany there are advanced treatment plants for micropollutant removal under construction, where oxidation using ozone and adsorption were combined.

The costs for the combination of ozone, UV-treatment and adsorption will be estimated as follows: The calculated costs for ozonation according to KOM-M.NRW are about 0.06 - 0.33 €/m³ wastewater. These costs are significantly influenced by the energy costs of ozone production. Therefore, a low ozone dosage can be achieved using further treatment steps. The UV treatment is calculated according to supplier informations. Using a GAC/BAC as last treatment step, leads to costs about 0.07 – 0.21 €/m³ wastewater. The costs of treatment with activated carbon are significantly influenced by the replacement of the carbon. Therefore, a BAC process will lead to lower specific costs because of the higher BV achieved. In summary, the specific costs for the treatment of 1 m³ wastewater in a 100,000 PE WWTP of a combined enhanced treatment consisting of ozonation (z_{spec} = 0.2 mgO_3/mg_{DOC}), UV-MD treatment (see Table 47) and BAC (60,000 BV) are estimated as follows:

Ozonation:	0.06 €/m³ wastewater (lower cost range of KOM-M calculations for ozonation)
UV-MD:	0.21 €/m³ wastewater (estimated according to treatment suppliers)
BAC:	0.07 €/m³ wastewater (lower cost range of KOM-M calculations for ozonation)

Estimated total specific costs: 0.34 €/m³ wastewater

10. Conclusion

Occurrence of hazardous micropollutants in municipal and industrial effluents is a serious threat. As a result of urban and industrial usages of pharmaceuticals, cosmetic and hygiene products as well as a result of the intensive application of biocides, industrial compounds, pesticides etc. micropollutants ends up in WWTPs. They are mostly stable chemical molecules that are not fully degraded by the conventional biological treatment step in the WWTP so that are still present in the effluent of the WWTP and receiving waters. Increasing amount and accumulation of micropollutants in surface and ground waters could be observed.

By consequence, innovative treatment for elimination of hydrophilic and non-biodegradable substances in wastewater are needed. This project focus on ozone-UV photocatalytic treatment in combination with GAC/BAC filtration for complete elimination of micropollutants. Scale-up and demonstration of this technology were highlighted in this project on industrial and municipal wastewaters.

The project was divided into several phases:

First, in WP2, a list of model compounds were determined based on current literature, a survey of the actual consumption of pharmaceuticals and legislation.

In the meantime, during the WP3, relevant micropollutants identified in WP2 were introduced into existing analytical methods. Enhancement and optimization of the quantification method by GC- and LC-MS/MS were performed. Toxicity using *Daphnia magma* and A-YES Assay were determined before and after treatment. It was shown that ozone and UV treatment allows a decrease of toxicity of the water and of estrogenic activity. The measured concentrations of the estrogenic activity of the wastewaters were in the effluents of the WWTPs and after the following treatment steps lower than the proposed effect-based trigger value of 0.4 ng EEQ/L (Jarosova 2014, Kase 2018).

In the WP4, the degradation performances of different photocatalytic coatings were characterized at lab scale on the model water containing various micropollutants. The aim was to identify the most efficient TiO_2 coating for advanced oxidation processes combining ozonation and photocatalysis in term of composition and calcination parameters. The TiO_2 sol-gel coating adhesion was also characterized. From all the results, the best coating is Ag2N10P25/TiO_2. At lab scale, all the micropollutants, which are not degraded by the ozonation step only, are either completely degraded or strongly impacted by the photocatalytic treatment. Furthermore, the photocatalytic activity remains stable over time because similar degradation values are obtained and even after 3 cycles of photocatalytic tests with the same coating.

In the WP5, the scale-up of the **Ag 2wt.%+10wt.% P25/TiO_2** adherent and persistent coating was performed on the UV-lamps reactors of and demonstration scale. To do this, a new shaping method to coat the steel inner wall of the reactors was developed: the motor-powered spray-coater. After spraying and calcination steps, photocatalytic coatings on steel 316 presented a very homogeneous aspect and a good adhesion. These reactors coated with photocatalytic film are tested in WP7.

In the WP6, adsorption processes on granulated (biological) activated carbon (GAC/BAC) was integrated into the treatment concept. GAC/BAC filtration offers the opportunity of the elimination of the emerging transformation products and the remaining micropollutants. Laboratory scale experiments were performed for the identification of a suitable adsorption material. Seven different activated carbons and one coke were tested to identify the most suitable material for the issued project objectives. The results of the first tests showed that there is no full degradation with ozone and UV +TiO_2 for some micropollutants of the short lists. These substances are for example 1*H*-Benzotriazole, Metoprolol, TBT. The use of granulated activated carbon were tested with the focus to eliminate the remaining micropollutants and PFOS. The results showed that all investigated activated carbons are suitable for adsorbing the more polar LC-MS/MS substances and that there are no significant differences in elimination between the different granulated activated carbons. Since economic efficiency also plays an important role in the demonstration scale plant, the material price is relevant. Even the GAC/BAC filtration is not used as the main treatment step in this project, the coal has to be replaced after a certain period of time. These costs were included for bed volumina of 18.000 (GAC) and 60.000 (BAC) at **WP 9**. For the further tests, three carbons with the lowest prices were selected for small columns tests with a flow rate of 10 m/h. The results of the three carbons showed no significant differences. The decisive point that led to the selection of the coal, was ultimately the price. Therefore, the selection of the carbon for the adsorber is the carbon **CarboTech DGF.**

During the WP7, **various** 0.3 m^3/h demonstration scale **tests were performed** on 3 types of wastewater:

- **Model waters** (spiked with GC-MS/MS and LC-MS/MS substances)
- **Industrial wastewaters** (cleaning textile wastewater and culture media wastewater).
- **Municipal wastewaters** of WWTP closed to hospitals (Esneux closed to CHU hospital and Henry Chapelle closed to psychiatric hospital).

For the **model water** with the non-polar GC-MS/MS compounds, it was shown that five out of eleven micropollutants were fully degraded. Six micropollutants are not completely reduced and would need a further adsorption step.

For the model water with the more polar LC-MS/MS compounds, it was shown that all micropollutants are fully degraded by ozone and UV with TiO_2 (Ag 2% NEW + 10% P25) coating (photocatalysis) and without coating (photolysis). Both experiments showed that laboratory scale results were successfully transferred to demonstration scale. Toxicity measurements with *Daphnia magma* showed that the model water was not toxic before and after treatment.

For **industrial wastewaters**, results mainly depend on the wastewater nature and composition, photocatalysis and ozone are not effective on all type of pollutants. By consequence, it is recommended to select one or several degradations steps of the AOPTi process for the specific wastewaters. Preliminary investigations could be done in laboratory scale. The single treatment steps are

- Ozonation
- UV (photolysis), UV or UV/TiO_2 (photocatalysis)
- Adsorption on activated carbon (GAC) or adsorption and biological elimination at BAC filtration

The different treatment steps (as single treatment step or in combination) can be used for the decrease of the toxicity. For industrial wastewater, the financial impact of the additional final treatment was also calculated for 2 practical cases.

For the **2 municipal wastewaters**, *Daphnia magma* test showed that the water is not toxic whereas the A-YES assay highlights some estrogenic activity which decreases after each treatment step. LC-MS/MS quantification showed that most of the target compounds are present in the municipal water at the exit of the WWTP at concentration from a few ng/L (PFOS, Terbutryn) up to hundred µg/L (Iohexol). Majority of micropollutants are fully degraded by ozone only but improvement occurs with photocatalytic coating for some recalcitrant compounds.

Finally, during the WP8, a scale-up from demonstration scale 1 (300L/h) to demonstration scale 2 (up to 5m^3/h) was performed. Trials were conducted at the **municipal WWTP Duisburg-Vierlinden**. The elimination rates of the different micropollutants were quantified after each treatment step. The validation of the process parameters of the combined treatment process (ozone, UV photocatalytic, GAC/BAC) was achieved with and without coating of the reactor. Low-pressure lamp and medium pressure lamps were examined. The contact time in the UV plant is 13 seconds with a flow of 1.6 m³/h. The ozone concentration is 5 mg/L with a contact time of 18 s. In addition, cumulative parameters like DOC, pH, conductivity, COD were analysed. The comparison of the results showed no significant differences with and without a TiO_2 coated reactor. No effect of the coating is noticeable using UV-LP or MP lamps in the framework of this project. Enhanced degradation of other substances cannot be excluded. The results show that not all substances are completely degraded after ozonation. With the UV-treatment, a further degradation of some of the selected substances can be achieved. After the adsorption step a further degradation could be observed.

The evaluation concept in Germany for the cleaning performance of micropollutant removal systems recommends an 80% reduction in WWTP of micropollutants. For this purpose, six indicator parameters are considered. In order to achieve the elimination goal, a reduction of the indicator parameters by 80% as an average value is to be achieved during the complete wastewater treatment process, including the advanced wastewater treatment for micropollutant removal. Taking these six micropollutants into account, the ozonation leads to an elimination rate of 60%. Taking the inlet of the UV-treatment and the outlet of the UV-treatment in consideration, the UV-treatment leads to an elimination rate of 52%. These calculated elimination rates were related to the respective feed concentration of the respective treatment step. In relation to the total degradation, the part of the ozonation was 85%. The UV-treatment leads to a further degradation of 15% in average, using the mentioned parameters. All remaining substances could be removed by the GAC/BAC filtration.

In WP9, the demonstration scale plant was optimized with the aim to reduce operating costs and to achieve required effluent quality in terms of selected priority substance removal. Electricity consumption and other necessary inputs (oxygen consumption, chemicals) were monitored and measured. The cost of Ag2N10P25/TiO_2 coating to cover up 1 m^2 of steel UVC reactor is equal to 0.29 € so it is negligible.

In the demonstration scale plant the treatment of 1.6 m³ wastewater per hour is possible using all of the treatment steps. The investment and the operating costs for each step of these plant were calculated. The specific costs for the treatment of 1 m³ wastewater were 1.22 € for ozonation, 1.88 € for UV MD treatment and 0.18 for GAC/BAC treatment using the demonstration scale plant.

The upscaling of the UV treatment for a 100,000 PE WWTP leads to specific costs for the treatment of 1 m³ wastewater of 0.21 €. For ozonation and GAC/BAC literature costs were estimated as follows: Ozonation: 0.06 €/m³, GAC/BAC: 0.07 €/m³. The combined treatment process is therefore considerably more expensive than the individual steps. One advantage, however, are the high elimination rates achieved. The use of UV-LED lamps to produce the UV radiation also promises a significant reduction in treatment costs.

11. Presentation of the scientific-technical and economic benefits of the results obtained, in particular for SMEs, as well as their innovative contribution and industrial application possibilities

Within the framework of the research project, a combination module for the oxidative and adsorptive treatment of wastewater was successfully developed. The development of a stable coating based on TiO2 to increase the effectiveness of UV treatment for individual substances could also be demonstrated on a laboratory scale. By combining oxidative and adsorptive processes, a wider range of substances can be eliminated from wastewater. Each process can be selected individually or, for particularly heavily polluted wastewater, a combination of processes can be selected. This is especially for different industrial wastewaters important.

The costs for the combined treatment of a wastewater are significantly higher than the costs for a single treatment step, but significantly lower than the costs for thermal disposal of liquid waste. The re-use idea and thus the resource-saving handling of the foodstuff water is also supported by the use of the wastewater treatment methods. Furthermore, pre-treatments for a more extensive biological degradation by means of oxidative technologies are conceivable.

As SMEs, both plant manufacturers and distributors of coatings or plant components can benefit from this type of wastewater treatment. The further developed technologies can be applied to both municipal and industrial wastewater treatment.

12. Updated plan for the transfer of results to the economy

12.1 Information of the companies of the Project Monitoring Committee

The majority of the members represented in the project-supporting committee come from plant manufacturers and plant constructors. During the project term, two meetings of the project-supporting committee (projektbegleitender Ausschuss PA) were held in Duisburg with the German SME participants. The final SME meeting took place as a joint SME meeting with the Belgian partners in Belgium.

12.2 Targeted addressing of potentially interested companies also outside the SME meetings

Both during the course of the project and after its completion, important conferences and trade fairs were or are used to inform other potentially interested companies about the project content and results. This measure was also implemented by means of numerous advisory meetings at the research institution or at the WWTP during the project period. Some SME partners visited the constructed demonstration plant at the WWTP.

12.3 List of all transfer measures carried out and those planned beyond the project duration

The presentation of the results during the project period was mainly in the form of publications, lectures and posters at conferences, trade fairs, seminars and regional sector-specific events. Information on the chronological sequence of these transfer measures can be found in Table 49.

Table 49: Transfer measures of the AOPTi project.

Date	Measure	Description
13.07.2017	Presentation	16ème Congrès de la Société Française de Génie des Procédés – SFGP 2017, “Advanced oxidative treatment for wastewater contamined by pharmaceutical products”, talk of Cédric Wolfs, Nancy, France
17.07.2017	Result presentation and workflow discussion	Meeting of the technical committee non-target analysis of the German Water Chemistry Society, Frankfurt, Germany
03.-08.09.2017	Poster presentation	19th International Sol-Gel Conference, Liege, Belgium

Date	Measure	Description
25.09.2017	Project meeting	Presentation and discussion of the project results and further coordination, Herve, Belgium.
17.01.2018	Project meeting	Presentation and discussion of the project results and further coordination, Duisburg, Germany
01.02.2018	SME meeting	The project and previous work in the field of AOPTi was presented, Duisburg, Germany
01.03.2018	SME meeting	The project and previous work in the field of AOPTi was presented, Herve, Belgium
27.03.2018	Presentation	LIEU, Gembloux, Belgium
17.04.2018	Project meeting	Presentation and discussion of the project results and further coordination, Liege, Belgium
08.-12.06.2018	Poster presentation	PREPA12 - 12th International Symposium on the Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain-la-Neuve, Belgium
03.07.2018	Project meeting	Presentation and discussion of the project results and further coordination, Herve, Belgium
17.-21.07.2018	Poster presentation	International Symposium on Inorganic and Environmental Materials 2018 – ISIEM 2018, Gand, Belgium
18.10.2018	Result presentation and workflow discussion	Meeting of the technical committee non-target analysis of the German Water Chemistry Society, Frankfurt, Germany
19.10.2018	Project meeting	Presentation and discussion of the project results and further coordination, Duisburg, Germany
23.-24.10.2018	Poster presentation	DECHEMA conference, Frankfurt, Germany
24.01.2019	SME meeting	The project and previous work in the field of AOPTi was presented, Duisburg, Germany
13.03.2019	SME meeting	The project and previous work in the field of AOPTi was presented, Herve, Belgium
28.01.2019	Project meeting	Presentation and discussion of the project results and further coordination, Liege, Belgium
26.02.2018	Presentation	LIEGE CREATIVE, “Elimination des micropolluants dans les eaux usées : deux traitements avancés pour demain”, talk of Stephanie Lambert, Liege, Belgium
22.03.2019	Presentation	LEUVEN ICESE: Assessment of Advanced Photocatalytic Oxidation process for Micropollutant Elimination in Municipal and Industrial WasteWater Treatment Plants, talk of Stephanie Lambert and Christelle Vreuls, Leuven, Belgium

Date	Measure	Description
25.-28.03.2019	Presentation	Anakon 2019, Instrumentelle und wirkungsbezogene Analytik bei der erweiterten Abwasserreinigung zur Spurenstoffelimination, talk of Jochen Tuerk, Münster, Germany
01.04.2019	Presentation	8. Berliner LC-MS/MS Symposium, Workshop, Schnelle Analytik mittels Mikro-LC-MS/MS – Vorteile und Vorurteile, talk of Jochen Tuerk Berlin, Germany
22.04.2019	Presentation	9th Edition of International Conference on Chemical Sciences, Advanced oxidative treatment for wastewater contaminated by micropollutants, talk of Stéphanie Lambert, Dublin, Ireland
20.05.2019	Project meeting	Presentation and discussion of the project results and further coordination, Herve, Belgium
06.06.2019	Presentation	4th International Conference “Nanomaterials & Applications - NANOAPP 2019, Advanced oxidative treatment for wastewater contaminated by micropollutants, talk of Stéphanie Lambert, Ljubljana, Slowenia
14.06.2019	Workshop	Phenomenex Workshop, Einführung in die LC-MS – LC-MS Einführung und Anwendung”, refenert Jochen Tuerk, Aschaffenburg, Germany
21.06.2019	Presentation	10th IWA International Symposium on Waste Management Problems in Agro-Industries, Assessment of Advanced Photocatalytic Oxidation process for Micropollutant Elimination in Municipal and Industrial WasteWater Treatment Plants, talk of Julien Mahy, Rhodes, Greece
17.07.2019	Result presentation and workflow discussion	Meeting of the technical committee non-target analysis of the German Water Chemistry Society, Frankfurt, Germany
17.09.2019	Presentation	ECCE 12 - 12th European Congress of Chemical Engineering, Assessment of Advanced Photocatalytic Oxidation process for Micropollutant Elimination in Municipal and Industrial WasteWater Treatment Plants, talk of Stéphanie Lambert, Firenze, Italy
18.-19.09.2019	Workshop	Dr. Klinkner & Partner Workshop, LC-MS Kopplung, referent Jochen Tuerk, Essen, Germany
26.09.2019	Project meeting	Presentation and discussion of the project results and further coordination, Duisburg, Germany

Date	Measure	Description
22.-24.10.2019	Conference	11th Micropol & Ecohazard Conference, participation Jochen Tuerk, Seoul, South Korea Discussion of AOPTi results with international scientists and representatives of public authorities after a talk on full scale ozonation as well at an IWA working group meeting on micropollutant removal.
11.-12.11.2019	Presentation	13. Langenauer Wasserforum, Bestimmung von Spurenstoffen in behandelten Abwässern und Oberflächengewässern mittels Mikro-LC-MS/MS, talk of Jochen Tuerk, Langenau, Germany
09.12.2019	Project meeting	Presentation and discussion of the project results and further coordination, Herve, Belgium
27.01.2020	Project meeting	Presentation and discussion of the project results and further coordination, Herve, Belgium
13.02.2020	Final SME meeting	The project and previous work in the field of AOPTi was presented, Herve, Belgium
13.02.2020	Poster presentation	Final SME meeting, Herve, Belgium

In light of current events, it should be pointed out that some of the transfer measures planned for 2020 will not be implemented as planned. Due to the corona crisis, many trade fairs, conferences and congresses were initially postponed or completely cancelled for the current year.

12.4 Assessment of the feasibility of the proposed and updated transfer concept

In the previous sub-chapter the individual transfer measures were identified. This shows that numerous measures have been taken by the research institution to reach a broad public. IUTA has a large interdisciplinary scientific network and collaborates intensively with small and medium-sized enterprises within the framework of innovation programmes and standardisation activities at DIN.

Due to its many years of experience and work in cooperation with SMEs, there is an excellent network, especially for the results achieved in the project, which enables an optimal transfer of knowledge to the economy. It is intended to advance the technical development of the demonstrator to the prototype stage within the framework of a further R&D measure via the central innovation programme for SMEs of the German Ministry of Energy and Economics.

In conclusion, it should be noted that the original transfer concept has been largely implemented in accordance with the strategy set out in the original research proposal.

13. Publications

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- Cunha, R., et al.: Assessment of transformation products from advanced oxidation of wastewater found after adsorption with activated carbon, in preparation

14. Use of the grant

14.1 Scientific and technical staff (Subsection A.1 of the financing plan)

In detail, the work of the employees was done as follows:

- 22 month of scientific-technical personnel

The additional months has already been communicated.

14.2 Equipment (Section B of the financing plan)

The following expenses were incurred for the successful implementation of the project as applied:

- Special unit for UV irradiation with different radiation sources
- Rent of adsorption unit
- Purchase of a container to set up the mobile plant

The purchase of a stationary cylinder was waived, since meanwhile tests using the bubble column could be carried out on a laboratory scale with a 1 m high column. For industrial wastewater, the flow rates are generally much lower, so that the purchase of a stand cylinder on a pilot scale is not necessary. The funds applied for are to be redirected to personnel resources, since a much larger proportion of the laboratory tests and the supervision of the pilot plant will have to be carried out by scientific staff.

14.3 Services provided by third parties (Section C of the financing plan)

The following expenses were incurred for the successful implementation of the project as applied:

Expenditure for services provided by third parties genotoxicity tests using micronucleus test and umuC test conducted by an external laboratory (IWW Rheinisch-Westfälisches Institut für Wasser Beratungs- und Entwicklungsgesellschaft mbH).

15. Necessity and appropriateness of the work done

The work carried out corresponded in large parts to the reviewed and approved application. Only the adjustment of expenditure and the transfer of these funds to staff (see Chapter 14) had to be adjusted in the course of the project. The work carried out was necessary and appropriate.

16. References

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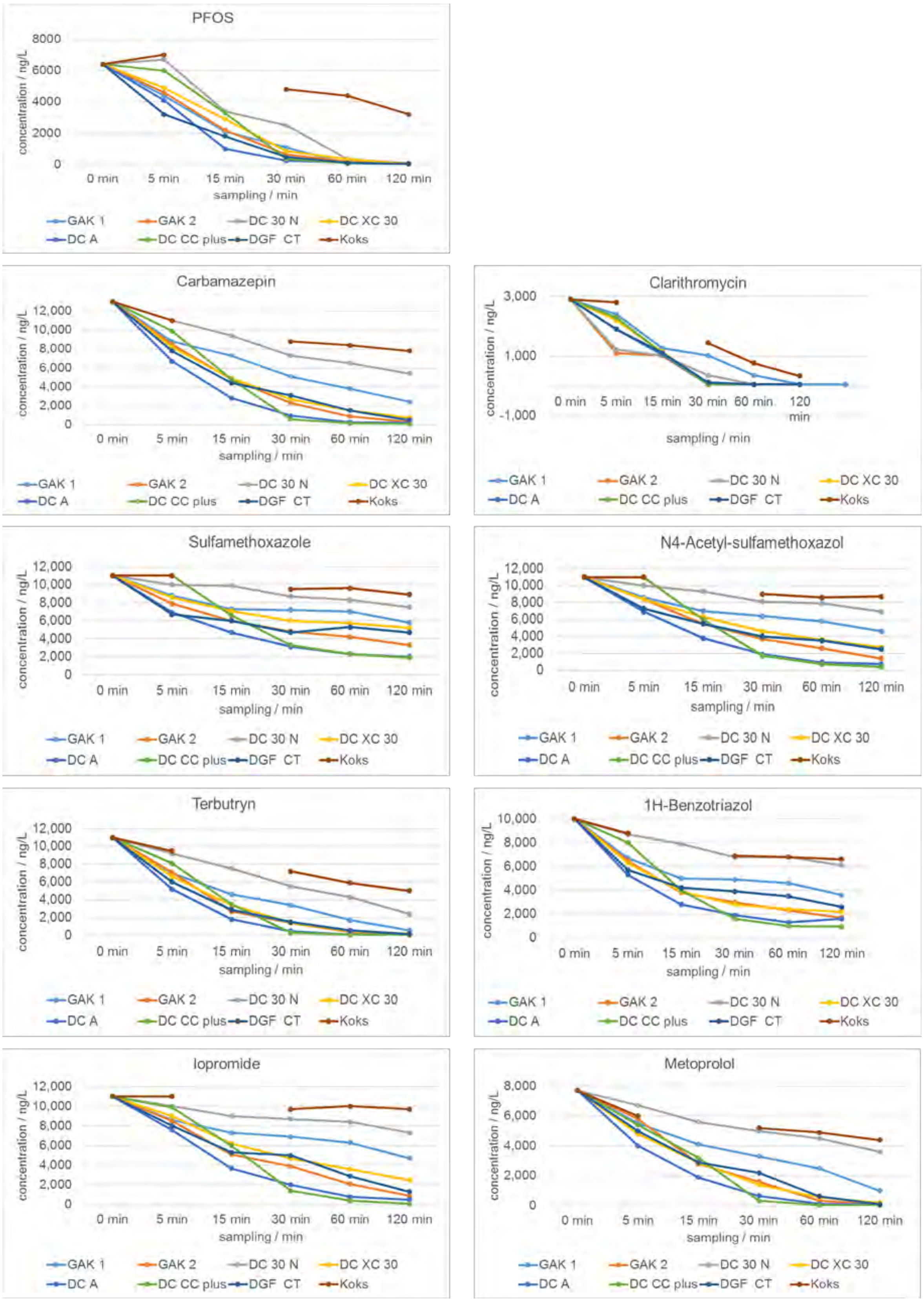
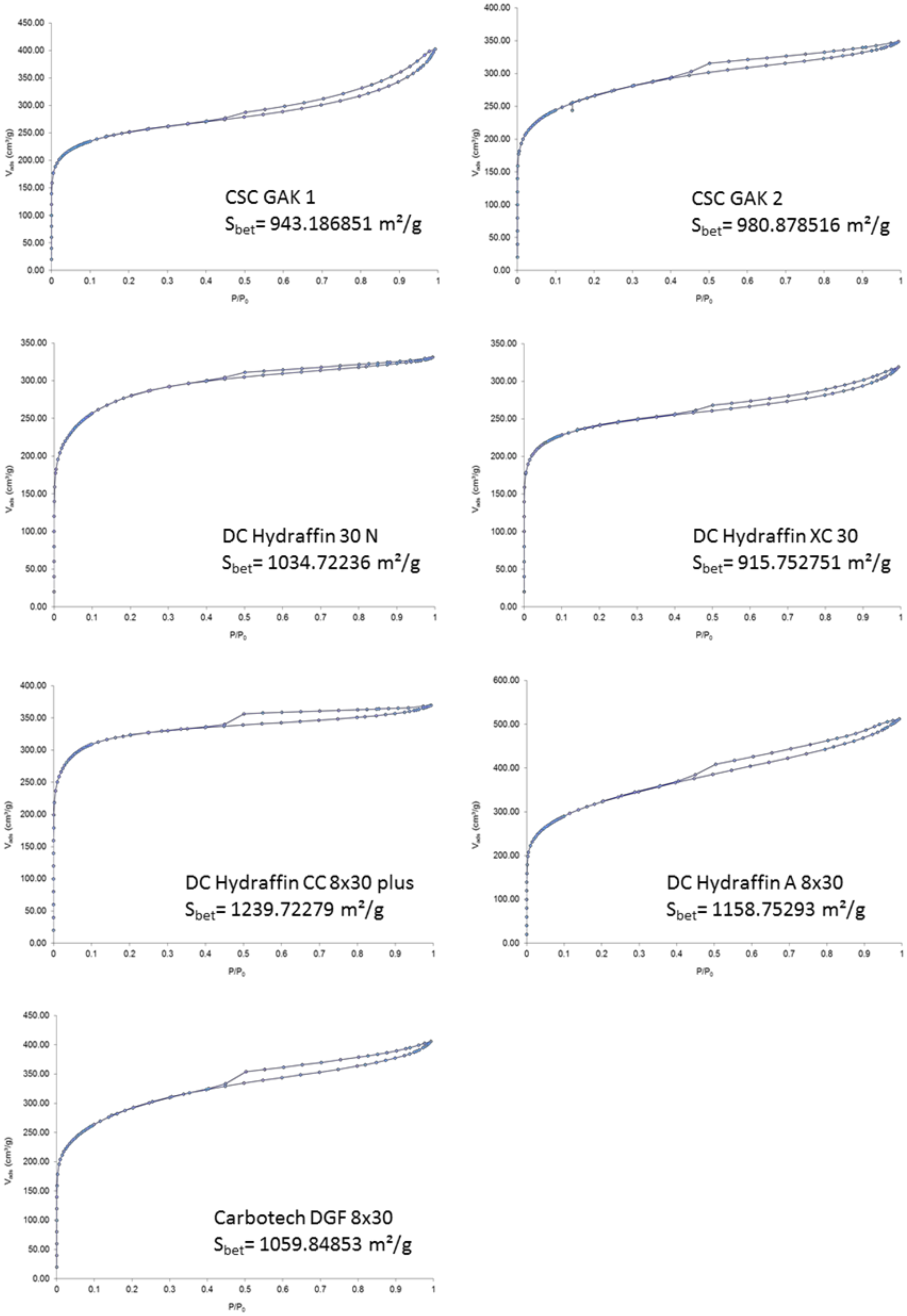
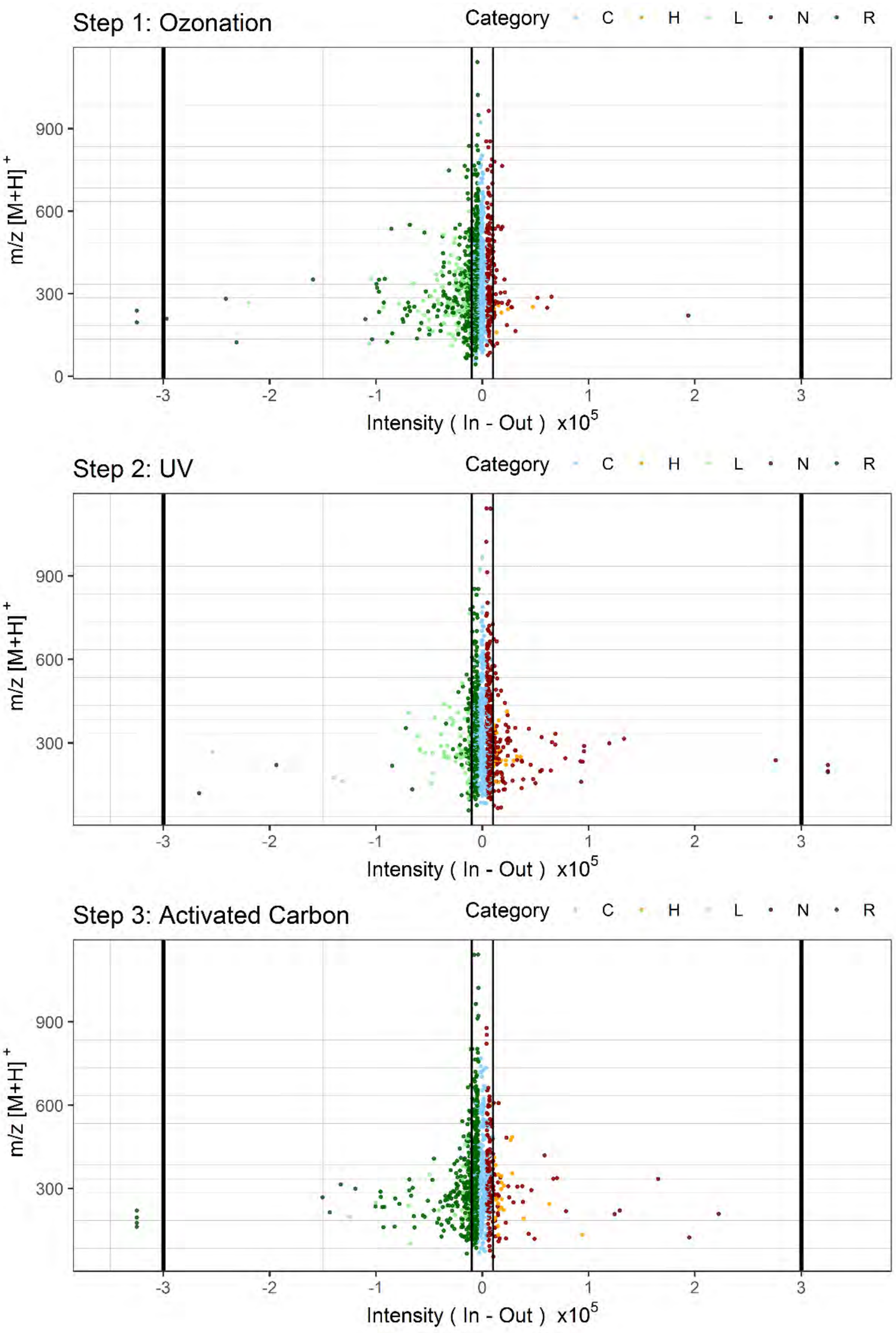
17. Annex



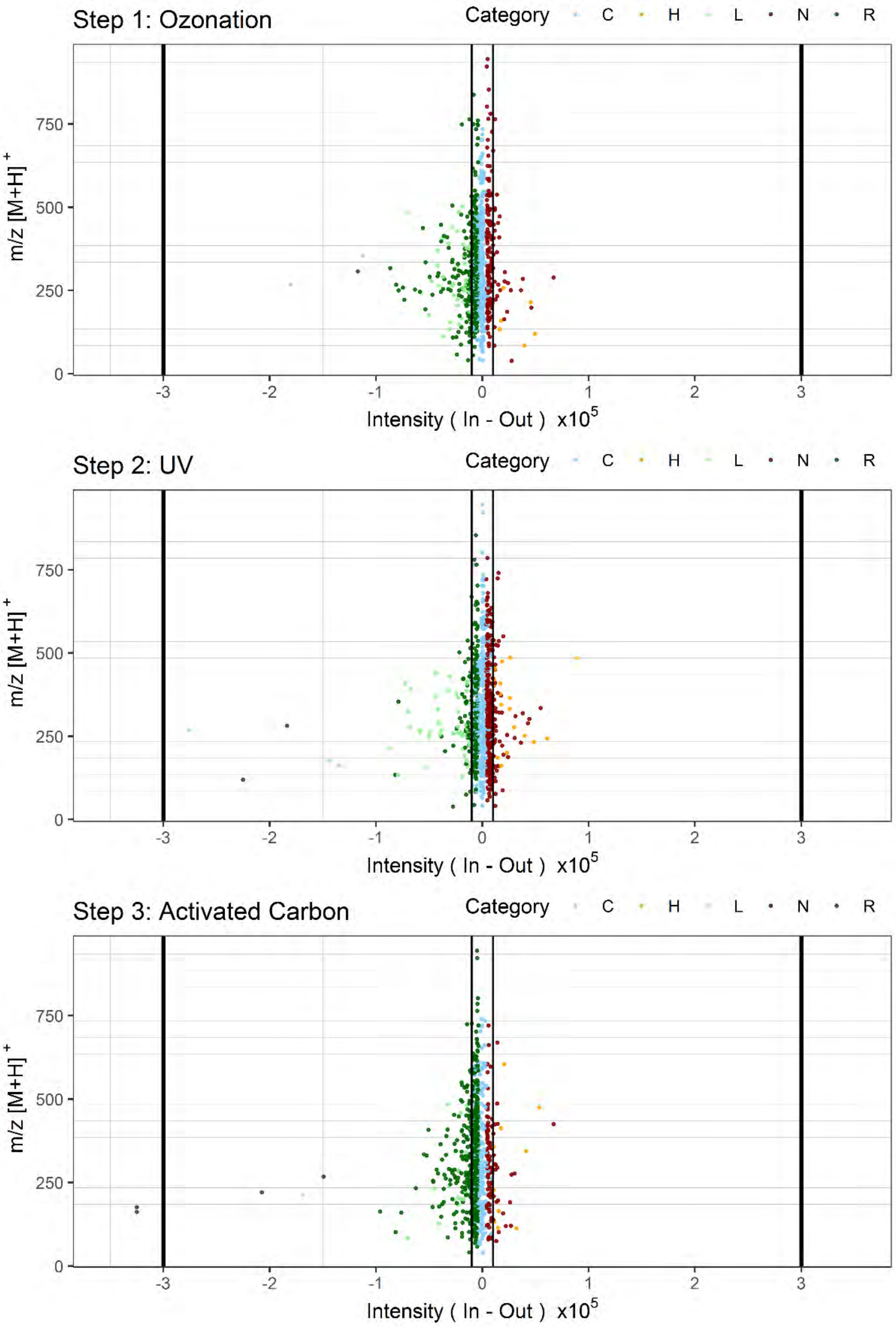
Annex 1: Elimination of the selected substances with different activated coals.



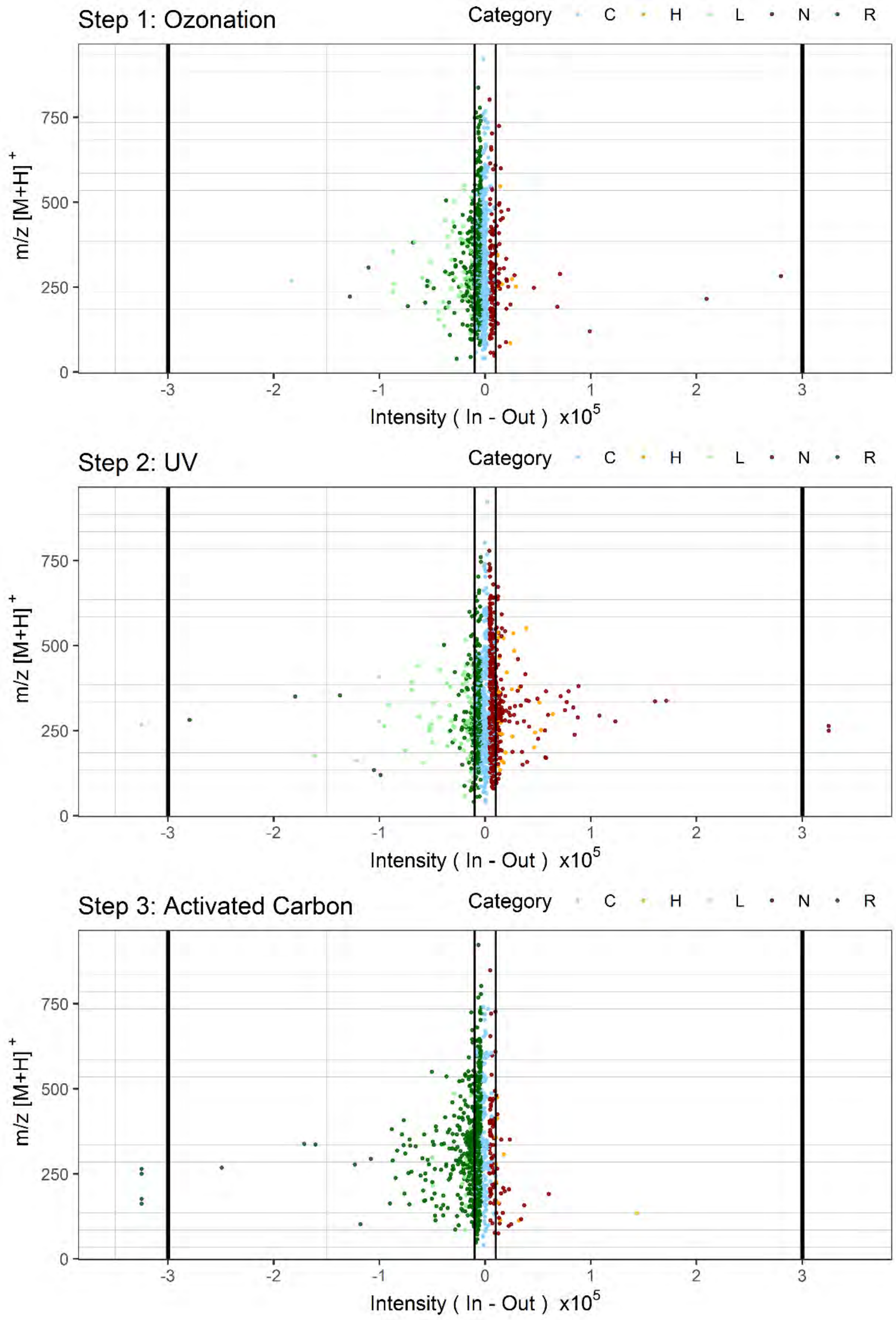
Annex 2: Nitrogen adsorption-desorption isotherms and specific surface area values determined by BET method (ULG).



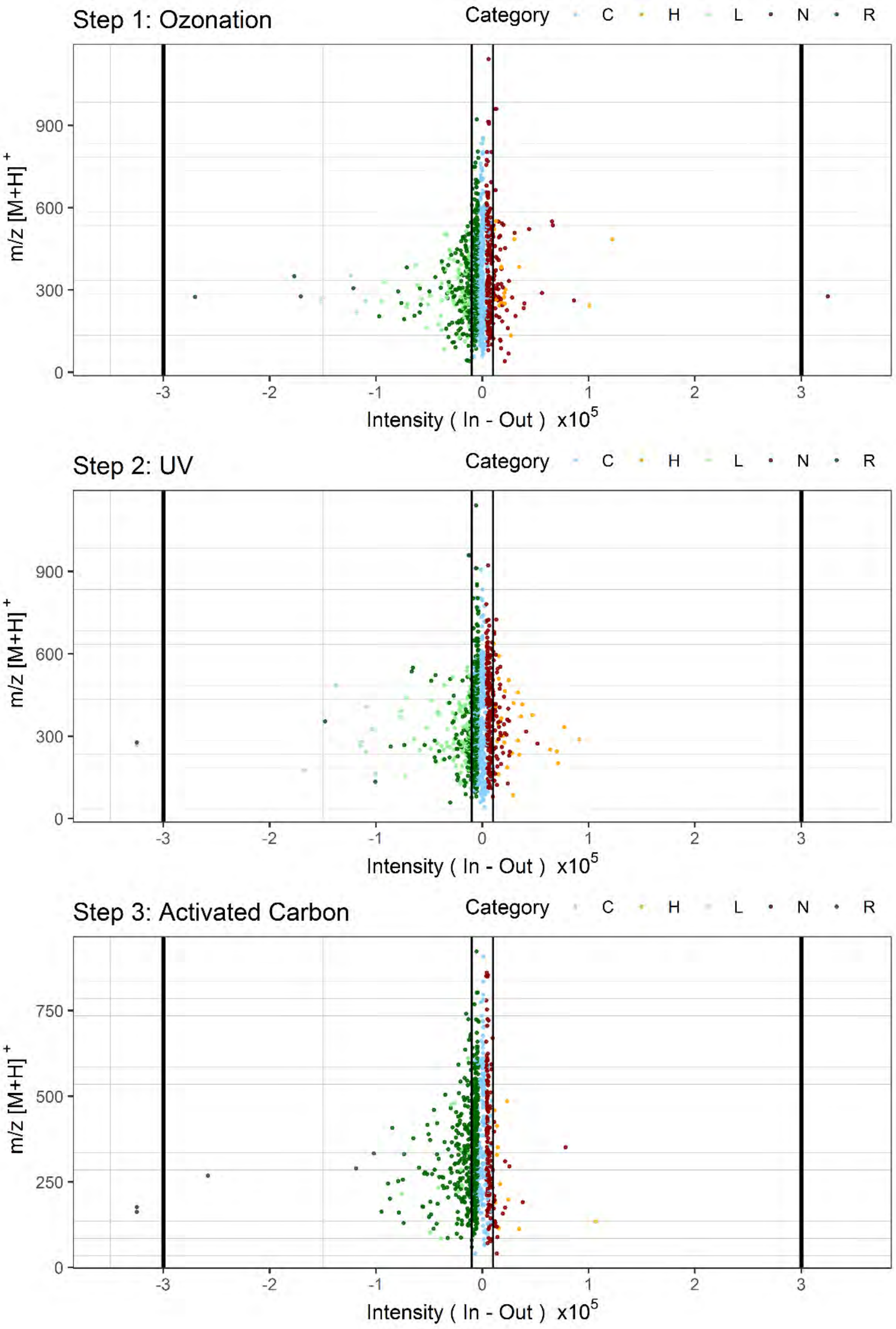
Annex 3: NTS results over the three treatment steps from a sample set taken from the pilot plant in week 1. The represented features (i.e. each data point) are divided in categories as Constant (C) in blue, Higher (H) in orange, Lower (L) in light green, New (N) in red, and Removed (R) in dark green. The categories describe the fate of each feature over the treatment scheme as the name indicates. New features (N) are then likely a product of removed (R) or lower (L) features.



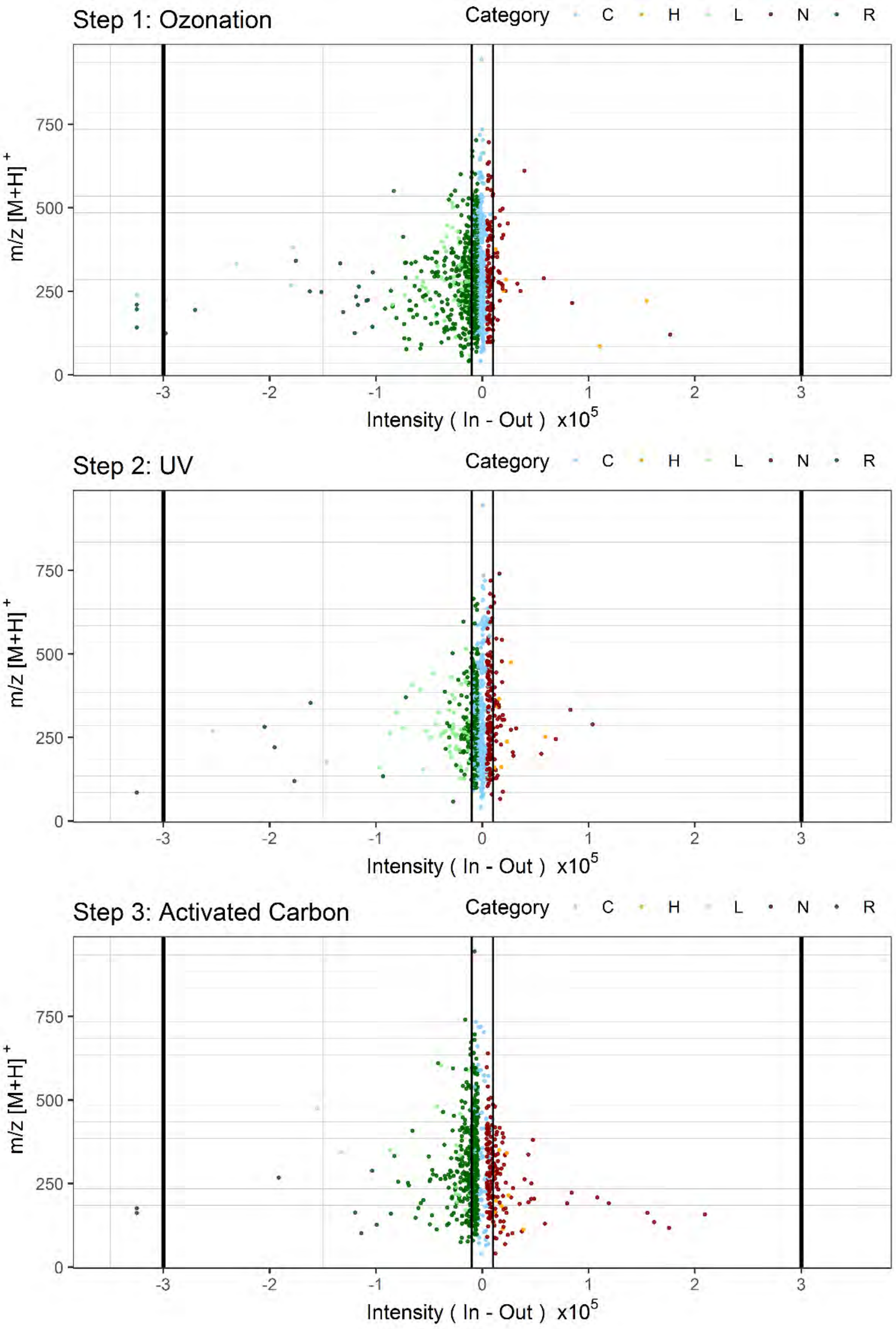
Annex 4: NTS results over the three treatment steps from a sample set taken from the pilot plant in week 2. The represented features (i.e. each data point) are divided in categories as Constant (C) in blue, Higher (H) in orange, Lower (L) in light green, New (N) in red, and Removed (R) in dark green. The categories describe the fate of each feature over the treatment scheme as the name indicates. New features (N) are then likely a product of removed (R) or lower (L) features.



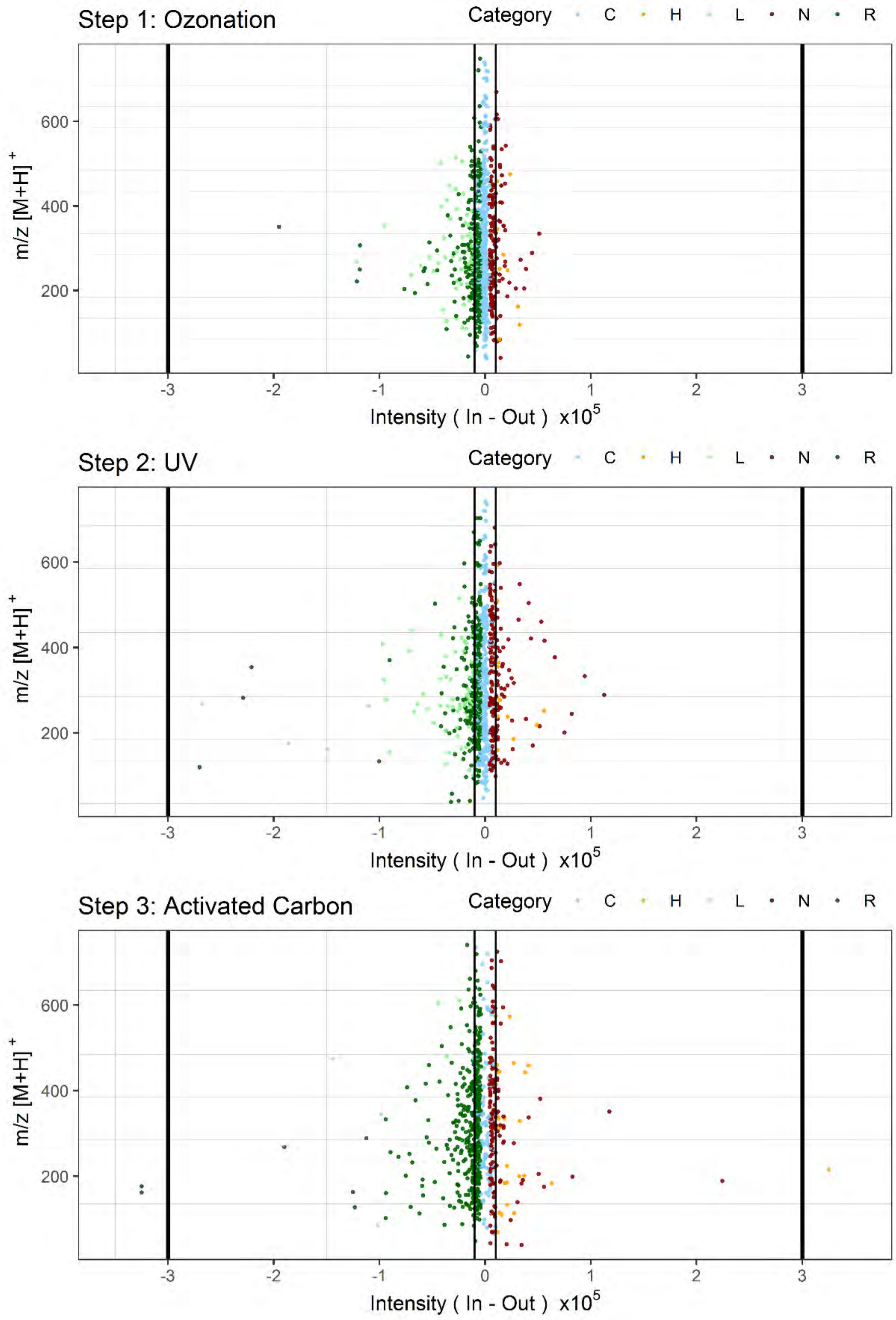
Annex 5: NTS results over the three treatment steps from a sample set taken from the pilot plant in week 4. The represented features (i.e. each data point) are divided in categories as Constant (C) in blue, Higher (H) in orange, Lower (L) in light green, New (N) in red, and Removed (R) in dark green. The categories describe the fate of each feature over the treatment scheme as the name indicates. New features (N) are then likely a product of removed (R) or lower (L) features.



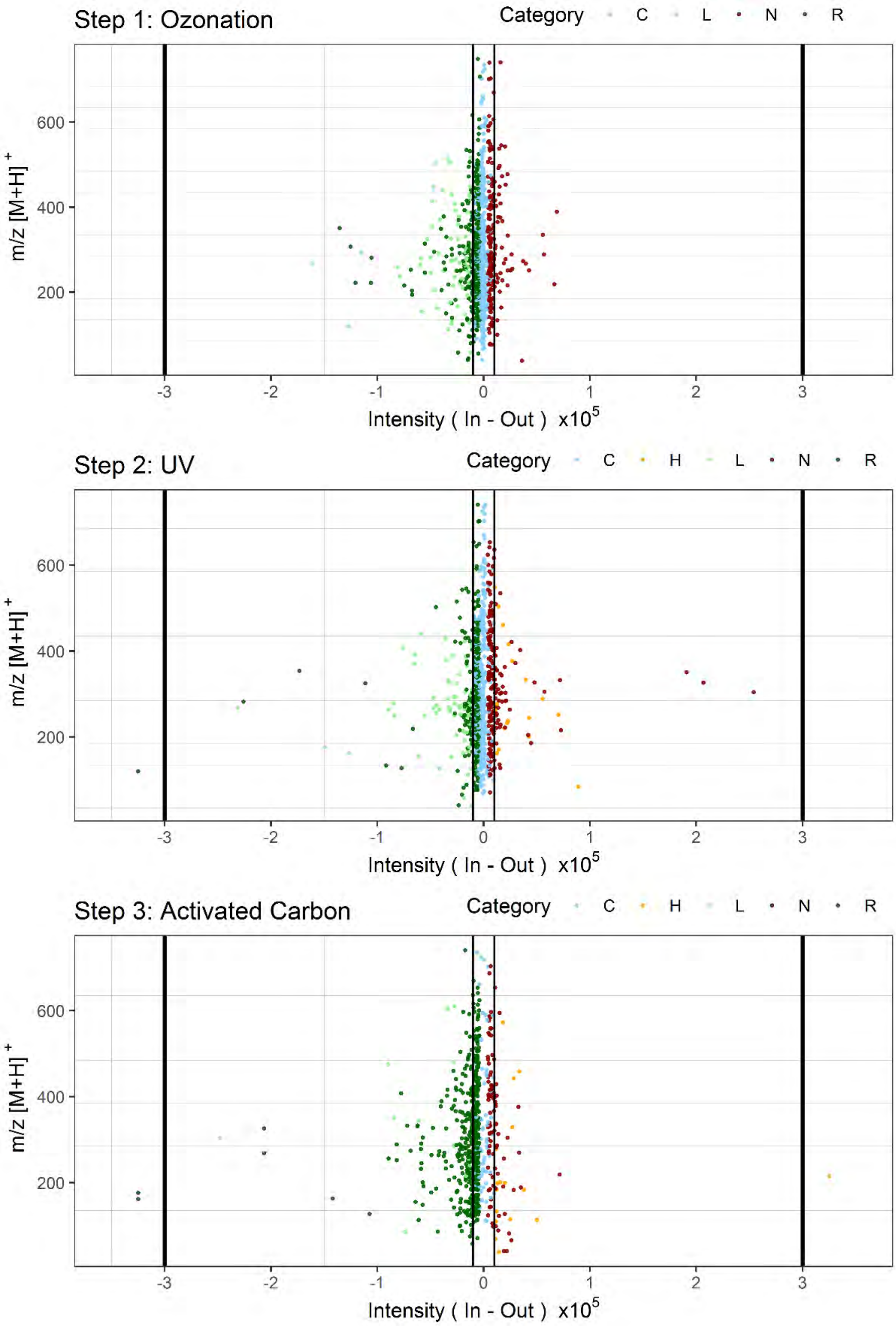
Annex 6: NTS results over the three treatment steps from a sample set taken from the pilot plant in week 5. The represented features (i.e. each data point) are divided in categories as Constant (C) in blue, Higher (H) in orange, Lower (L) in light green, New (N) in red, and Removed (R) in dark green. The categories describe the fate of each feature over the treatment scheme as the name indicates. New features (N) are then likely a product of removed (R) or lower (L) features.



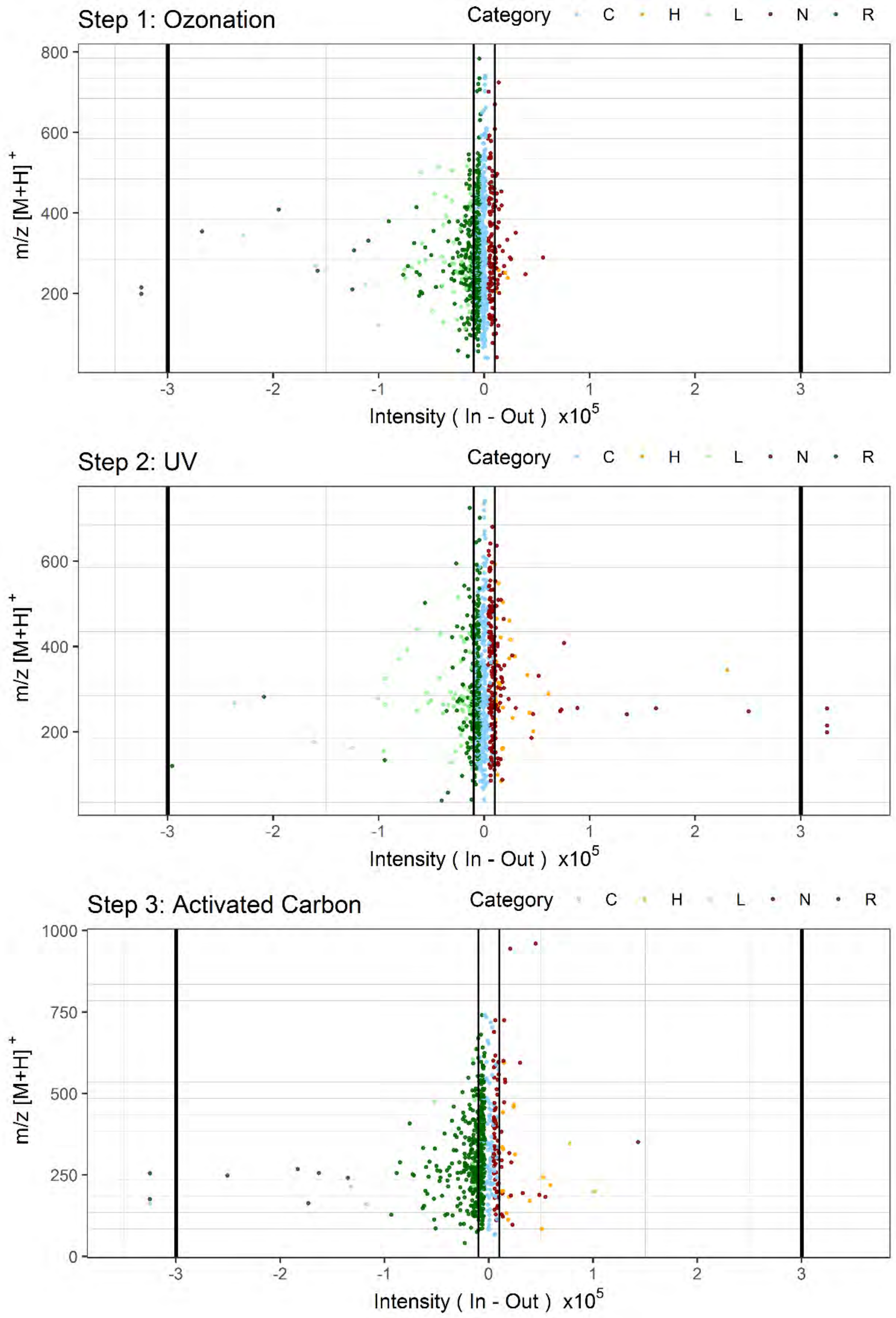
Annex 7: NTS results over the three treatment steps from a sample set taken from the pilot plant in week 6. The represented features (i.e. each data point) are divided in categories as Constant (C) in blue, Higher (H) in orange, Lower (L) in light green, New (N) in red, and Removed (R) in dark green. The categories describe the fate of each feature over the treatment scheme as the name indicates. New features (N) are then likely a product of removed (R) or lower (L) features.



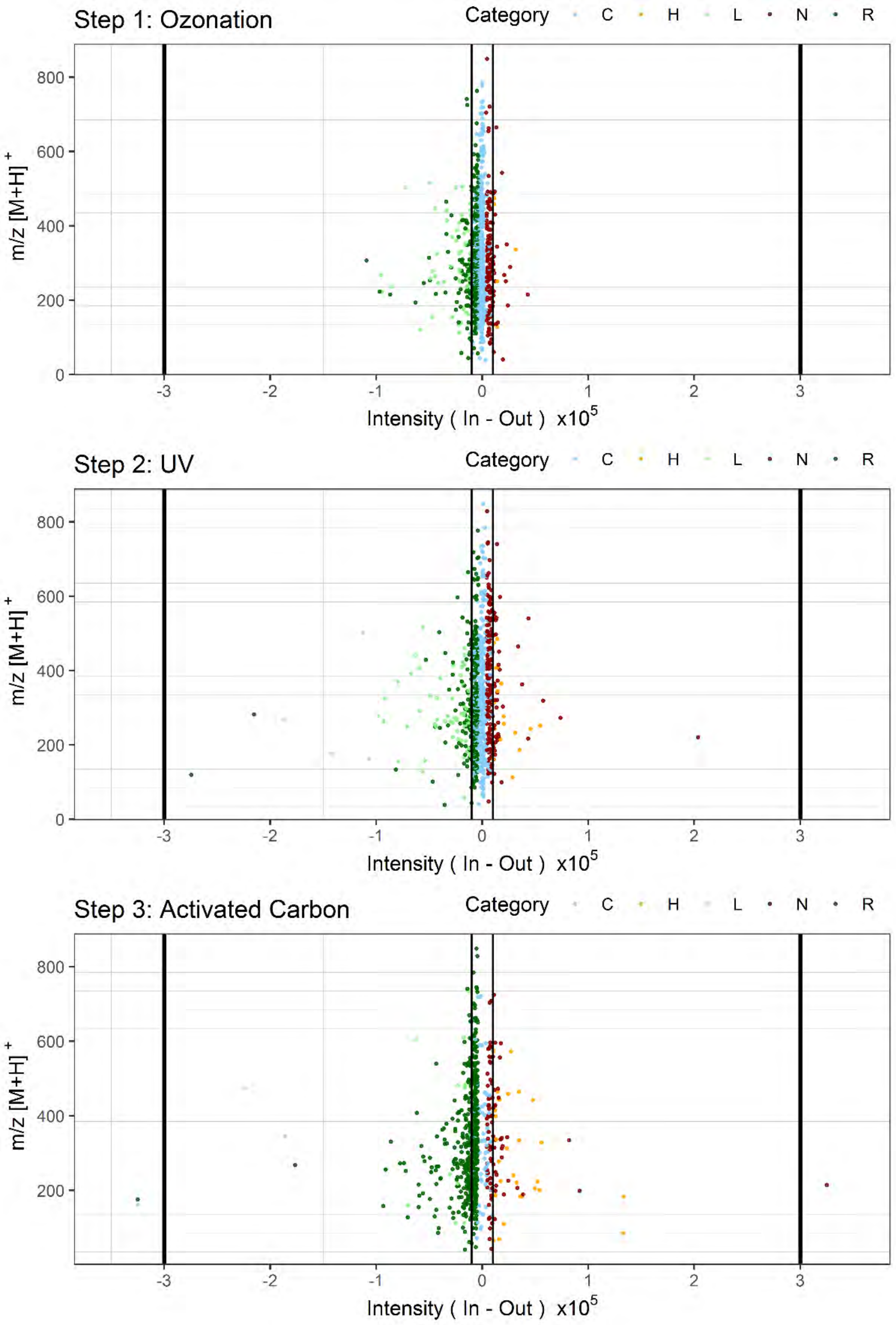
Annex 8: NTS results over the three treatment steps from a sample set taken from the pilot in week 7. The represented features (i.e. each data point) are divided in categories as Constant (C) in blue, Higher (H) in orange, Lower (L) in light green, New (N) in red, and Removed (R) in dark green. The categories describe the fate of each feature over the treatment scheme as the name indicates. New features (N) are then likely a product of removed (R) or lower (L) features.



Annex 9: NTS results over the three treatment steps from a sample set taken from the pilot plant in week 8. The represented features (i.e. each data point) are divided in categories as Constant (C) in blue, Higher (H) in orange, Lower (L) in light green, New (N) in red, and Removed (R) in dark green. The categories describe the fate of each feature over the treatment scheme as the name indicates. New features (N) are then likely a product of removed (R) or lower (L) features.



Annex 10: NTS results over the three treatment steps from a sample set taken from the pilot plant in week 9. The represented features (i.e. each data point) are divided in categories as Constant (C) in blue, Higher (H) in orange, Lower (L) in light green, New (N) in red, and Removed (R) in dark green. The categories describe the fate of each feature over the treatment scheme as the name indicates. New features (N) are then likely a product of removed (R) or lower (L) features.



Annex 11: NTS results over the three treatment steps from a sample set taken from the pilot plant in week 10. The represented features (i.e. each data point) are divided in categories as Constant (C) in blue, Higher (H) in orange, Lower (L) in light green, New (N) in red, and Removed (R) in dark green. The categories describe the fate of each feature over the treatment scheme as the name indicates. New features (N) are then likely a product of removed (R) or lower (L) features.