





NEPTUNE

New sustainable concepts and processes for optimization and upgrading municipal wastewater and sludge treatment

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Final activity report

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<u>CO</u> nfidential only for members of the consortium)		

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Executive summary

The scope of sewage treatment is changing: more and more seen as an interface between sanitation and environment, WWTP are delivering resources to the environment and for human activities (e.g. recharge drinking water reservoirs, recycling of nutrient, efficient energy use). This focus shift has implications on the quality goals for WWTP products:

Existing focus:

- New focus:
- nutrient removal
- nutrient recycling
- pathogens removal
- micropollutants and ecotoxicity removal
- energy optimization
- sludge disposal
- energy production
- reuse of sludge and of its resources

From November 1 2006 to March 31 2010, NEPTUNE joined 18 partner from Europe, Australia and Canada to focus on optimizing wastewater treatment (WorkPackage 1), developing new technologies (WP2), developing methods for assessing micropollutants and toxicity (WP3), improving life cycle analysis of wastewater treatment as a decision support tool (WP4). This report gives a summary of the project outcome. More details are found either in the Deliverables (see section 1.4) or in publications (reference list in section 2.5.4).



Figure 1: Separate sludge liquid treatment, SBR in WWTP Zurich

Full scale demonstrations

The **addition of Zeolite** (7 to 17 g m⁻³_{wastewater treated}) was shown to improve sludge settling allowing to increase the sludge age in overloaded plants to achieve nitrification as shown on several Bulgarian plants. With total costs of 0.014 to 0.033 \in m⁻³_{wastewater} this is a feasible option for seasonal plants or as transient measure prior to refurbishing.

Combined nitritation/anammox with the single sequencing batch reactor (SBR; Figure 1) was set into operation in five full scale reactors and proven robust. The process resulted in considerable cost savings (2% of the total WWTP costs) compared to the conventional SBR with methanol for heterotrophic denitrification; several follow-up projects are in planning phase. The chemicals added for sludge dewatering do not cause inhibition of the nitritation/anammox SBR, observed during the full scale operation.

Ozonation of WWTP effluent for micropollutant removal was demonstrated for over one year on a mid sized WWPT. In conjunction with the subsequent rapid sand filter confirmed the efficient elimination of a broad palette of micropollutants and disinfection as required by the EU bathing water regulation at total costs of 0.08 to $0.2 \notin m_{wastewater}^3$ depending on plant size. The costs are about half if the filtration already exists. Post-filtration is recommended to substantially reduce eco-toxicity of the formed by-products. The micropollutants and pathogen removal by ozonation was modelled.

Hospital wastewater is proved to be a significant point source for the pharmaceuticals; nevertheless current cost estimation ($2 \notin m^3$ for treatment in the hospital with membrane bioreactor and ozonation) indicate discharge into the sewer and treatment in the centralized municipal WWTP as the most cost effective solution in case micropollutant removal is done.

Thermal hydrolysis of sludge (20 min at 170°C and 8.5 bar) prior to digestion was shown economically advantageous, since it allows increasing biogas yields while keeping a low detention time in the digester of 10 to 12 d.

Combining **dynamic modelling** (ASM2d) and with **life cycle assessment** (LCA) was shown a worthy effort on several case studies in Flanders, where it allowed a well-founded optimization of the control strategy based on quality and cost targets. The optimization focused on improving instrumentation, control and automation, including the use of online sensors.

Advances in instrumentation, control and automation (ICA)

Standardized test for sensor comparison needs improvement to match field conditions. Long term study confirms UV-Vis spectral sensor as suitable for monitoring NO_3^- and NO_2^- . Benchmarking of control strategies for WWTP proved useful only if results are rated with a life cycle assessment approach. Fault detection algorithms for automatic supervision of online sensors proved not sufficiently reliable for regular operation.

In-situ monitoring device was developed to identify industrial polluters; the unit combines a variety of online sensors and may be used for monitoring WWTP influent as well as further upstream in the sewer.

Options for sludge handling

Segregating primary from secondary sludge allows for better reuse since the digestability of primary sludge is significantly better while secondary sludge is better suited for agricultural reuse, containing about double concentration in nutrients but significantly less organic contaminants (mainly non-polar compounds).

Ultrasound pre-treatment is estimated to be economic only in case of overloaded digester or if helpful in solving foaming problems.

The best **option for sludge inertisation** has not yet been identified. The following processes have been studied: incineration at 850°C, wet oxidation at ca. 300°C and 80 bar, supercritical wet oxidation at 374°C and 220 bar, pyrolysis at 1000°C and sludge gasification at 850°C.

Micropollutant removal requires advanced treatment

Biological wastewater treatment achieves only partial removal of micropollutants. For many compounds, degradation results in only slight transformation of the molecular structure, leaving a transformation product behind with probably comparable biological activity. Accordingly in terms of micropollutant removal the primary scope of biological treatment is to condition the wastewater to allow for an efficient post treatment (e.g. removing competing dissolved organic carbon).

Iodinated contrast media are best removed by source control, i.e. direct urine collection for 24h after application (e.g. via roadbag disposed into incineration) since a) the persistent tri-iodo-benzene structure is found at $\mu g \cdot L^{-1}$ concentrations in drinking, is persistent to chemical oxidation and too polar for efficient removal by sorption with activated carbon.

The **analytical methods for micropollutants** have been broadened significantly within Neptune, by a) describing methods for new compounds, b) describing an approach for identification of transformation products and c) by proposing a mobile unit to assist micropollutant and toxicity studies.

Assessing effluent toxicity requires combining *in vitro*, *in vivo* and *in situ* methods. *In vitro* methods detect specific toxicity and are the preferred test for routine monitoring, due to its lower costs. *In-vivo* methods expose organisms directly to the effluent, as opposed to *in vitro* tests that may miss out on polar compounds not extracted during sample pre-treatment.

Finally only *in situ* observation allows assessing the impact on the local fauna as opposed to specific organisms selected for *in vitro* test.

Sorption onto activated carbon sorption was shown to be concentration dependent for many compounds (i.e. requiring Freundlich isotherms rather than the constant sorption factor Kd mostly used for sorption on activated sludge). A post-treatment with 10 to 20 g powdered activated carbon (PAC) per $m^{-3}_{wastewater}$ has been confirmed to remove most micropollutant by >80% (hydraulic retention time of 0.5 to 1 h and 2 to 4 d PAC retention time). The recycling of the spent PAC from the post-treatment to the biological unit significantly increases the removal efficiency. If dosed directly into the biological step (no post-treatment) three to five time more PAC is required.

The combination of the **biological activated carbon with ultrafiltration (BioMac)** in the lab scale set-up was able to remove antibiotics and acid pharmaceuticals to a high extent and pathogens almost completely; the estimated life time of the GAC laboratory filter is maximally 20'000 empty bed volumes.

Ozonation as post-treatment was shown to efficiently remove specific toxicity but to increase unspecific toxicity, by forming reactive by-products. These are degraded to a significant extent in rapid sand filtration. The required dose strongly depends on the organic content in the effluent, but typically 0.6 to 1 $gO^3 gDOC^{-1}$ removes most compounds to >80%.

Wetland treatment with a surface of 1 to 2 m² person⁻¹ for effluent polishing resulted in only minor micropollutant removal.

New technologies tested at lab and pilot scale

The test with **microbial fuel cells** (MFC) put forward, that upscaling is a major issue for the process and that by producing chemicals (e.g. NaOH or H_2O_2 at the cathode) instead of energy with a similar set up much better economics are achieved. Accordingly the system ought to termed bioelectrical system (BES).

Ferrate (Fe^{VI}) has a comparable efficiency to oxidize organic compounds as ozone: while the reaction rates are smaller, the stability of Fe^{VI} is much higher. Besides oxidizing micropollutants the added iron also precipitates phosphorus. Ferrate cannot be dosed directly into the biological unit, since losses to non-target compounds would be too high; it must therefore be dosed in a post treatment step. Large-volume production of ferrate is not carried out yet but it would be interesting to test the handling an applicability of ferrate addition in a pilot-scale plant. A retention of particluates e.g. by sedimentation or sand filtration would be necessary but since a biologically active treatment step is also recommended after ozonation, ferrate might still be competitive to ozonation.

A biologically mediated micropollutant oxidation process based on **manganese oxide** (BioMnOx) was developed and showed good reactivity for several compounds. Similarly a

biologically mediate palladium (bioPd) redox cycle has been tested. The development is still at a too early stage for assessing the economic feasibility.

Pyrolysis was confirmed as suitable method for sludge inertization giving the possibility to recycle volatilized heavy metals (e.g. Zn) as well as produce syngas (CO and H₂). Pyrolysis of dried sludge takes place at 1000 to 1400°C during 5 to 15 min.

The process for **biopolymer production using thermally hydrolysed waste activated sludge as raw material** was demonstrated to be technically feasible, but further optimization of the process was identified. Thermal hydrolysis showed to increase the productivity of biopolymer due to the high organic loading rates possible.

Life cycle assessment (LCA): an important tool for decision making

Well-considered decision making in comparing alternative processes as well as considering the overall benefit of an additional treatment step (e.g. advanced treatment for micropollutant removal) requires considering all avoided and all induced impacts. To complement existing LCA, Neptune in cooperation with Innowatech proposes a method for **evaluating the impact of specific toxicity** induced by emitted micropollutants.

In case studies LCA was shown to be very helpful and feasible in decision support, e.g. for choosing the process control option allowing for best cost-efficiency.

Generally LCA rating of wastewater technologies are dominated by the (avoided) emissions, while the energy consumption plays a minor role: this is understandable in view of the fact that LCA accounts for global impacts and water treatment contributes to a minor extent to global energy demand.

Use of the results and expected impact

Results of Neptune will be used to reduce environmental impact while at the same time reducing overall costs of the environmental protection. New analytical tools for micropollutants detection will enable better management of the whole effluent toxicity. By comparing existing as well as new technologies developed within Neptune, using LCA, it will be achievable to find best combination of technologies for each specific demand in WW sector.

The impact NEPTUNE is going to have can therefore be summarized in two main focuses:

- environmental impact: improving the quality of European water and the efficiency of its management (aquatic environment and drinking water resources)
- economic development: strengthening the competitive position in exporting wastewater technology

Project outline 1

1.1 Objective

The scope of sewage treatment is changing: Up to date municipal wastewater treatment plants (WWTP) were seen as an end-of-pipe treatment just before discharge, having the aim to avoid eutrophication and hygienic health hazard in surface water. Due to the global demographic trends as well as new legislations (e.g. the Water Framework Directive, WFD) increased focus is put on quantity and quality of effluents: more and more seen as interface between sanitation and environment, WWTP are delivering resources to the environment and for human activities (recharge drinking water reservoirs, recycling of nutrient, efficient energy use). This focus shift has implications on the quality goals for WWTP products:

Existing focus:

New focus:

•

- nutrient removal •
- nutrient recycling • micropollutants and ecotoxicity removal
- pathogens removal
- energy optimization
- sludge disposal •
- energy production •
- reuse of sludge and of its resources •

NEPTUNE will approach these tasks by focusing on technology solutions allowing to meet present and future standards via upgrading of existing municipal infrastructure (new control strategies with online sensors; effluent upgrading with chemical oxidation, activated carbon or wetland treatment; safe sludge processing and reuse) as well as via new techniques (fuel cell applications; new oxidation processes; production of polymer and phosphate from sludge). By including pathogens and ecotoxicity aspects into life cycle assessment studies (LCA), the project is helping to improve the comparability of various technical options and propose a suitability ranking.

WWTP are the major pollutant point source for surface water, and consequently impact on the new focus legislated by the WFD. The emerging interest on organic (eco-)toxic compounds requires characterizing treated effluent and treatment technologies concerning ecotoxicologic aspects and micropollutants. NEPTUNE is contributing to this discussion by ecotoxicity assessment and micropollutant fate studies.

By directly involving European players of the water management sector, the generated know-how is expected to contribute to the export oriented knowledge based EU eco-industry. Further NEPTUNE will contribute to **sustainable growth** in the EU by helping to remove the barriers faced by new environmentally friendly integrated solutions, a) by covering knowledge gaps of new solutions and b) by evidencing pros and cons of technologic alternatives through direct comparison.

1.2 Project structure

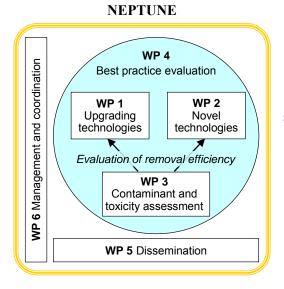


Figure 2: General project structure as subdivision into workpackages (WP).

The project is structured into two technical workpackages (WP1 and WP2; Figure 2) focusing on optimizing of existing technologies and forward-looking processes. Some key technologies studied in WP1 and WP2 are looked at for their micropollutant and pathogen removal capability (WP3) and compared for holistic impact with Life Cycle Assessment tools (WP4). Workpackages 5 and 6 support the project scope by disseminating the work done respectively by taking care of management and coordination. A summary of the detailed topics approached is given in Figure 3.

	WP 6 Management and Coordination				
Work Packages	WP 1 Upgrading of munic. WWTP	WP 2 Novel Technologies	WP 3 Contaminant / toxicity assess.	WP 4 Best practice evaluation	WP 5 Dissemination
Tasks	ICA, new sensors Effluent upgrade: AO, AC, Wetland Sludge triage, reduction, inertisation waste design (e.g. hospital WW, sludge liquid treatment)	 Fuel cells applications for N-removal Micropollutant oxid. with Fe⁶⁺ and MnO₂ High temp. Pyrolysis Polymer production Concepts/visions for sustainable UWM 	 Fate of micropollut., metabolites and pathogens in WWT Effluent ecotoxicity assessment Mobile analytical unit: setup and suggestion for required tests 	LCA as decision support tool for evaluation of best practice (comparison studies) Incorporation of micro pollutants, pathogens and eco- toxicological effects	workshops, confer. publications newspaper articles recommendations webpage contact to EU (WFD) End users



1.3 Partners

The project is coordinated by the Process Engineering Department of the Swiss Federal Institute of Aquatic Science and Technology. The coordinators contact details are:

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Partic. no.	Participant name	Participant short name	Country
1	Eidgenössische Anstalt für Wasserversorgung, Abwasserreinigung und Gewässerschutz	Eawag	Switzerland
2	Bundesanstalt für Gewässerkunde	BfG	Germany
3	Laboratory of Microbial Ecology and Technolgy, University of Gent	LabMET	Belgium
4	Consiglio Nazionale delle Richerche (CNR)	IRSA	Italy
5	University of Frankfurt	UniFra	Germany
6	Technical University of Denmark	DTU	Denmark
7	National Institute of Research and Development for Isotopic and Molecular Technology	INCDTIM	Romania
8	Aquafin NV	Aquafin	Belgium
9	Deutsche Projekt Union	DPU	Germany
10	Institute for Product Development	IPU	Denmark
11	SILUET B	SILUET B	Bulgaria
12	Pyromex PLC	Pyromex	Great Britain
13	Gebrüder Hunziker AG	Hunziker	Switzerland
14	SCAN Messtechnik GmbH	S::can	Austria
15	CAMBI A/S	CAMBI	Norway
16	AnoxKaldnes	Anox	Sweden
17	Université Laval	model <i>EAU</i>	Canada
18	Advanced Wastewater Management Center, The University of Queensland	AWMC	Australia

Table 1: List of partner institutions

1.3.1 Contributing persons

AnoxKaldnes: Fernando Morgan-Sagastume, Alan Werker, Anton Karlsson

Aquafin:	Marjoleine Weemaes
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AWMC: Damien Batstone, Jurg Keller, Paul Lant, Steven Pratt, Korneel Rabaey, Zhiguo Yuang

- BfG: Guido Fink, Christine Lachmund, Michael Schluesener, Thomas Ternes, Arne Wick
- Cambi: Thomas Seyffarth
- DPU: Sandra Ante, Stephan Ellerhorst

- DTU: Henrik Fred Larsen, Peter Augusto Hansen, Alexis Laurent, Stig Irving Olsen, Michael Hauschild
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- SDU: Henrik Wenzel

1.4 Project deliverables

Table 2: Neptune's deliverables list

No	Deliverable title	Responsible partner	Dissemi- nation
D1.1 D3.3	Fate and occurrence of micropollutants, microorganisms and viruses and strategies to minimize their release in plant effluent	Eawag, BfG	Public
D1.2	Strategies to improve nutrient removal	model <i>EAU</i>	Public
D1.3	Strategies for a sustainable and safe sludge management.	IRSA	Restricted
D2.1	Novel technologies for wastewater and sludge treatment	LabMET	Public
D2.2	New approaches for a sustainable WWTP design	LabMET	Public
D3.1	Ecotoxicity and microbiological testing methods (OECD and DIN/ISO guidelines) optimised for whole effluent testing	BfG, UniFra	Public
D3.2	Data set of ecotoxicity testing in relevant treatment processes and additionally of two emerging contaminants	BfG	Public
D3.4	Concept for mobile analytical unit	BfG	Public
D4.1	Homogeneous LCA methodology agreed by NEPTUNE and INNOWATECH	DPU, IPU	Public
D4.2	Methodology for including specific biological effects and pathogen aspects into LCA of wastewater treatment	DPU, IPU	Public
D4.3	Decision support guideline based on LCA and cost- efficiency assessment	DPU, IPU	Public
D5.1	Website construction with link to INNOWATECH	Eawag	Public
D5.2	Conclusions of the workshop about the revision of the WFD priority substances	BfG	Restricted
D5.3	End user conferences	LabMET, Aquafin	Public
D5.4	Catalogue with criteria for evaluating technologies	Aquafin +all partners	Public
D6.1	Consortium Agreement	Eawag +all partners	Restricted
D6.2	Annual report of the project	Eawag +all partners	Public
D6.3	Final report of the project	Eawag +all partners	Public

2 **Project summary by workpackage**

2.1 WP 1: Technologies for WWTP upgrading

To help improving the sustainability of wastewater treatment Neptune focused on the following aspects:

- Improving control strategies for nutrient elimination with robust control strategies and online sensors (section 2.1.1)
- Testing the use of zeolite as additive for wastewater treatment (section 2.1.1)
- Discussing separate disposal of primary sludge to improve the agricultural reuse of the nutrient contained in secondary sludge (section 2.1.2)
- Testing and comparing sludge disintegration and inertisation methods (section 2.1.2)
- Testing feasibility and cost effectiveness of separate treatment of hospital and nursery wastewater (section 2.1.3)
- Demonstrating combined nitritation/anammox at full scale: a new process to efficiently remove nitrogen from digester supernatant (section 2.1.3)
- Testing and modelling ozonation at full scale as WWTP effluent treatment step for micropollutant removal (section 2.1.4)
- Comparing alternative reactor schemes for applying powdered activated carbon for micropollutant removal (section 2.1.4)
- Testing the micropollutant removal capability of polishing wetlands (section 2.1.4)

Only a short summary of the results is given here since further details are found in the Neptune's Deliverable D1.1&D3.3, Deliverable D1.2 and Deliverable D1.3.

2.1.1 Improvement and optimization of nutrient removal in biological treatment

Sensor characterization protocol does not match field conditions

To date the most complete protocol regarding sensor characterisation in water quality is the ISO 15839:2003 "Water quality – On-line sensors/analysing equipment for water – Specifications and performance tests". Within Neptune it was tested for different nitrate sensors; the following improvements to the protocol are suggested:

 A comparison of sensor accuracy performed on the same measuring range for each sensor (i.e. the range of interest for each specific application) is more appropriate for product comparison targeted on a specific application. ISO 15839:2003 proposes to test each sensor in its measuring range The protocol does not specify any methods for field testing (e.g. signal interference by turbidity or air bubbles). A standardized procedure representative for field conditions has to be developed. A proposal for a protocol to test sensors subject to bubbles and turbidity is presented in <u>Deliverable D1.2</u>.

Spectral online sensor suitable for monitoring NO₃⁻ and NO₂⁻

The accuracy of a spectral in-situ sensor for nitrite and nitrate was tested in situ for a period of 1.5 years. It was able to accurately monitor the nitrite and nitrate concentration in the effluent with a precision of $\pm 0.32 \text{ mg NO}_2^-\text{-N/I}$ (95 % prediction interval at mean lab value of 1.15 mg NO₂⁻-N/I) and $\pm 1.08 \text{ mg NO}_3^-\text{-N/I}$ (at 5.55 mg NO₃⁻-N/I). This allows using the sensor for alarm systems as well as for control concepts at WWTPs (Rieger et al., 2008): the spectral sensor with automated cleaning with pressurized air has proven an excellent long-term stability without time-consuming calibration effort and only minimal maintenance. A second on-line unit for chemical analysis with a filtration unit was tested but removed due to significantly inferior results in terms of accuracy, consumption of chemicals and maintenance.

Benchmarking control strategies: LCA allows interpreting multidimensional results

A "*Neptune Simulation Benchmark*" is proposed for simulating different control schemes under the same conditions to allow unbiased comparisons of control strategies. It is based on the "*Benchmark Simulation Model No 1*" but bears a series of advantages: a) the plant configuration is designed according to accepted guidelines; b) the simulated influent has a low biodegradable fraction and a high nutrient load in order to test performance in critical situations; c) the control strategies are evaluated on a long term basis to analyse daily, monthly and seasonal variation; d) the biological model includes (bio)chemical nitrogen and phosphorus removal.

For interpreting the multidimensional results cluster analysis, principal component analysis, factor analysis and discriminant analysis have been applied. Nevertheless, the multidimensionality of the results still represents a challenge for its interpretation.

On the contrary, normalizing the different impact factors with a life cycle analysis type of approach (LCA), allows simplifying the multidimensionality of the analysis and drawing generalized conclusions:

- The nutrient elimination is the most relevant impact parameter, weighting significantly more than the induced impacts: energy consumption and other resources are quantitatively of minor importance
- Accordingly the best rating is achieved by the more advanced control strategies allowing better nutrient removal

• Chemicals and sludge are the most relevant induced impacts (N₂O emission, acute toxicity and local impacts like micropollutants have not been considered)

Full scale confirmation: dynamic modelling allows identifying the best control strategy

The dynamic model Asm2d was calibrated for three full scale WWTP's in Flanders. The calibration was done using only routine sampling data required for regular plant supervision. Nevertheless, energy consumption, sludge production, chemical demand, effluent nitrogen could be nicely modeled while phosphate showed some systematic deviation. Extra attention for a correct prediction of effluent phosphate concentration is necessary since phosphate in the effluent represents a large environmental impact (up to 50%).

The three plants were already equipped with sensors and an online control system. The goal of this exercise was to see to what extent extra sensors, different settings or different rulebased control algorithms could lead to better plant performance. Two optimisation strategies were compared: meeting the effluent consent and reducing costs versus reducing the environmental impact. The 'classic' optimisation strategy, meeting the consent at lowest costs, led to a cost reduction of 2 - 15 % and an impact reduction of 3 - 13 %. The optimisation strategy for the lowest environmental impact resulted in a cost reduction of 0 - 10 % and an impact reduction of 7 - 22 %.

The optimisation exercise for lowest environmental impact led in all cases to a significantly better effluent quality compared to the legal requirements. It also favours biological over chemical phosphorus removal and reduces effluent ammonia concentrations. The optimized control strategies are very compatible with the way operators tend to manually control the plants.

Applying the LCA approach with normalized impacts on a lowest cost and lowest impact scenario is a powerful approach to discuss prioritisation of investment. It is advisable to standardize the impacts of inputs and outputs of a WWTP in a European context. General agreement on which impact categories to include and how to weigh these impact categories ought to be achieved. A standardisation of the database to be used to determine the environmental impact of inputs and outputs is required.

Online control reduces operational costs and increases treatment efficiency. The case studies described in <u>Deliverable D1.2</u> demonstrate that significant improvement can be achieved on WWTPs already (partly) controlled by online sensors, if the controller settings are optimized with dynamic modeling. These optimal settings vary from plant to plant even when process layouts are similar, since every plant has its own characteristic influent composition.

Fault detection algorithms not sufficiently reliable to detect faulty online sensors

Robust control strategies based on online sensors include algorithms for automated detection of faulty sensors. Typical sensor faults include drift, offset shift, scaling shift, fixed value, complete failure, and calibration mistake. With dynamic modelling based on the simulation platform BSM1_LT different fault detection strategies were compared by simulating the following scenarios: a) no faults, b) faulty DO sensor, c) faulty DO and ammonia sensors. Different fault-detection methods were tested and compared: univariate control charts, principal component analysis (PCA) and unfolded PCA.

Low performance was observed for all fault-detection methods tested. The reason is that these methods cannot cope with non-linear process behaviour, changing process behaviour and the multivariate nature of the data. Accordingly these ought to be used to trigger an alarm for manual inspection of the on-line sensor, rather than for automated and direct interaction with the process control algorithm. Further research is encouraged to investigate the effect of variable selection and redundancy on the methods performance and the assessment of costs and benefits of positive alarm detection, false alarms, speed and accuracy. Awaiting for more robust fault detection methods, the main responsibility of supervising on-line sensor accuracy still resides in operator-based supervision and automatic adjustment of plant operation (i.e. fault tolerant control).

Zeolite addition improves performance of overloaded WWTPs

Zeolite addition was tested at full-scale in the period 2007 to 2009: a polymer-modified zeolite (SZEDIMENTIN-MW) was added into the biological step of seasonally loaded wastewater treatment plants in Bulgaria. A parallel process without addition of zeolite was run to allow monitoring of the process improvements.

Zeolite significantly improved settleability of sludge, prevented sludge bulking and thereby reduced sludge loss to the effluent and improved nitrification. At lab scale the maximal effect on settling velocity and sludge volume was achieved by adding 30 mg zeolite per litre of untreated activated sludge; at full scale doses of 7, 10 and 17 g Zeolite per $m^3_{wastewater treated}$ achieved increasing effluent quality. The total costs are estimated in the range of 0.014 to $0.033 \in per m^3_{wastewater treated}$.

The trials confirmed zeolite as a cost effective options for temporary overloaded WWTPs, increasing the plant capacity without construction of additional structures.

In-situ monitoring unit developed to identify industrial polluters

An in-situ sensor setup, permanently fed with sewage and equipped with spectrometer probe with delta-spectroscopy as well as sensors for ammonium, pH, redox and conductivity, was successful tested in the sewer system and inlet of a plant with 120'000 population equivalents as early warning system for the detection of industrial wastewater inhibiting or overloading biological treatment. Together with the industrial register of the community, specific industrial polluters could be identified and measures suggested for improving WWTP operation, e.g. temporary storage of highly loaded wastewater and implementation of an ammonium and COD pollution fee based on average and peak loads to reduce overloading of the WWTP.

2.1.2 Sustainable sludge handling, treatment and inertisation with resource recovery

Sludge segregation: primary for biogas and disposal, secondary for agricultural reuse Only for part of the micropollutants, a significantly lower concentration was found in secondary sludge compared to primary sludge. For the rather polar micropollutant comparable concentrations were found in primary or in secondary sludge originating from two German WWTPs. Significantly higher concentrations in primary sludge were found for the following compounds: organophosphate contaminants (TCPP and TBEP), and non-polar compounds like phthalates (DBP and BBzP), bisphenol A, hydrocarbons, extractable organic halogens (EOX) and methyl blue active substances (MBAS). Heavy metals were detected at very low concentration, comparable in primary and secondary sludge.

Nitrogen and phosphorus concentrations were 1.8 - 2.0 times higher in secondary than in primary sludge. This means that agricultural use of secondary sludge, according to nutrient requirement by crops, would take lower amount of contaminants to land with respect to mixed sludge.

In terms of gaseous emission during incineration primary and secondary sludge are comparable. At 130% of the theoretical stoichiometric oxygen consumption much higher combustion temperature (over 1100°C) is required to avoid increased gaseous emissions (e.g. dioxins, furans and PAH) than at strongly over stoichiometric O_2 supply (i.e. 260% O_2 and 850°C).

Thermal disintegration improves digester performance

Extensive trials with the Cambi process confirmed that exposing mixed sludge for 20 min to 170°C at 8.5 bar is a cost-effective option to improve sludge processing performance. Compared to digestion without pre-treatment it allows improving:

- Volatile solids destruction and biogas production by 40% to 60%
- sludge dewaterability, achieving 30% to 50% dry matter after dewatering
- increased digester performance allows reducing the digester volume by 50%, operating at reduced retention times of 10 to 12 days

- the process has been certified by the Norwegian authorities to fulfill the requirements for sludge pasteurization for subsequent agricultural use.
- the high dry solids concentration may require controlling ammonia in the digester to avoid inhibitions at concentrations >2.5 gNH₄⁺-N/L

Ultrasound pays off only in case of overloaded digester or foaming problems

The electricity input required for mechanical sludge disintegration with ultrasound is mostly in a similar or lower range as the extra yield gained by the improvement of the biogas production in the digester. In specific cases ultrasound treatment nevertheless has shown to be cost-effective: it was shown to mitigate foam formation in the digester or to allow regular operation for overloaded digesters.

Sludge inertisation: best-practice not yet identified

The data collected does not allow for a definitive identification of the best treatment option for sludge inertisation. The options being discussed are:

- Incineration at 850°C after drying is the most used process; it allows heat recovery but no direct recovery of nutrients (in all other processes better P recovery is expected due to better solubility of the ashes).
- Wet oxidation occurs at 250 to 300°C and 60 to 100 bar within 0.5 to 1 h. No drying of the sludge is required. The organic content of the product is ca. 3%. The process consumes 350 kWh and 875 kg pure O₂ per t dry solid.
- Supercritical wet oxidation occurs at 374°C and 220 bar within 1min. No drying of the sludge is required. Complete inertisation of constituents without any emissions.
 350kWh and 875kgO₂ are consumed per 1t TS treated.
- The pyrolysis of dry sludge at 1000°C produces syngas (CO and H₂) that may be used for energy generation or as raw material for chemical production. 320 kWh of electricity per 1t of TS treated are consumed by the process.
- Sludge gasification is an O₂ limited combustion at 850°C producing syngas. Electricity consumption amounts to 350 kWh/t dry solids.

2.1.3 Waste design methods to reduce nutrients and micropollutants in wastewater

Separate wastewater treatment in hospital and nursery homes

The cost-efficiency evaluation of onsite treatment for hospitals and nursery homes requires a case-by-case evaluation, since the costs are strongly dependent on the local conditions (e.g. availability of suitable housing). For the cases studied within Neptune, the onsite treatment

did not result in a cost-effective solution. In terms of technology choice, the processes applied to achieve onsite treatment are technically comparable to the most promising techniques applied in centralized municipal wastewater treatment: biological wastewater treatment (the only difference is that onsite membrane bioreactor are often preferred to conventional activated sludge systems with secondary sludge settling) followed by ozonation or powdered activated carbon treatment. The feasibility could be demonstrated.

The amount of pharmaceuticals present in hospital wastewater strongly differs for different compounds. Due to an increasing trend towards non-stationary patients, for most compounds the load excreted within the hospital is significantly below the amount of pharmaceuticals distributed by the hospital.

Iodinated contrast media: source control is the best option

The removal of iodinated contrast media (ICM) is most efficiently done by source control, i.e. direct urine collection for 24h after application (e.g. via roadbag disposed into incineration). This because the entire load is excreted within a very low number of events (i.e. ca. one person out of 10'000 is being treated with ICM per day and the excretion occurs mainly within only 24h). The acceptance of this solution requires involving practitioners, patients as well as the public: iodinated contrast media per se are not toxic but the μ g·L⁻¹ concentrations found in drinking water are perceived as an aesthetic problem. The rather high concentration found in drinking water is due to their persistence to biological degradation, oxidative chemicals as well as their very low partitioning to activated carbon.

Nitrogen removal with combined nitritation/anammox is proven at full scale

The application of partial nitritation and anammox in a single suspended-growth sequencing batch (SBR) reactor has been demonstrated at full scale on several installations (i.e. at three municipal WWTPs; five reactors in total). The process has been confirmed as suitable for removing nitrogen from digester supernatant, an ammonium-rich wastewater with low concentrations of BOD and suspended solids: the details of a simple and robust process control based on online ammonium or conductivity signals and the full-scale startup procedure have been published (Joss et al., 2009). Ammonium oxidation rates of up to 500 gN m⁻³d⁻¹ with conversion to N₂ of over 90% are achieved in a full-scale plant, but pilot results indicate that significantly higher rates are feasible. With continuous aeration at dissolved oxygen concentrations <0.5mgO₂·L⁻¹, the nitrite oxidation and the anammox reaction occur simultaneously, allowing increased overall performance and simplified process control compared to separate aerobic and anaerobic phases (segregated either temporally or in different reactors). Sedimentation of the sludge requires special attention only during startup. Although the observed N₂O emissions were slightly higher than in conventional nitrogen removal, the overall greenhouse gas emissions were lower, mainly due to energy-saving.

The first three years of full scale operation confirmed generally good process stability; nevertheless detailed analysis of the process data indicates that further improvement of process performance requires a better understanding of microbial population dynamics, biomass structure (i.e. floc structure) and toxic effects. This understanding is crucial for a sound discussion of different process schemes currently being proposed and tested at full scale (e.g. suspended biomass, granular sludge and attached biofilm reactors).

The principal drivers for applying nitritation/anammox based processes in practice are the cost savings and the lower environmental impact (energy) compared to processes based on denitrification. Therefore currently the interest in anammox based process is continuously growing.

2.1.4 Effluent treatment for removal of micropollutants and pathogens

Sorption on activated carbon

The efficiency of powdered activated carbon (PAC) treatment is significantly increased, if the spent carbon from the post-treatment unit is recycled to the preceding biological unit. This effect may be due to additional loading of the carbon with target micropollutants present at higher concentration in the biological unit as well as to better scavenging of non-target DOC competing with micropollutants adsorption on activated carbon, prior to the post-treatment unit.

Pilot scale tests showed that the sand filter needs not necessarily being preceded by a sedimentation unit for retaining the PAC. Full scale confirmation of this result is currently missing.

If the PAC is added directly into the biological unit without any post-treatment around three to five times more PAC is required for achieving a comparable micropollutant removal. This option may be interesting for decentralized solutions, where a simplified infrastructure may be more relevant than the minimization of the operating costs.

The BioMAC concept combining granular activated carbon (GAC) with a membrane postfiltration was shown to achieve good removal as post-treatment. For comparing the cost efficiency with PAC treatments further full scale testing with appropriate experimental periods is required (i.e. at a packing density of 460 kgGAC·m⁻³ treating of maximum 20'000 bed volumes (corresponding to about 25 gGAC·m⁻³) a comparable micropollutant elimination is reached as for the addition 10-15 gPAC·m⁻³).

Post treatment by chemical oxidation

Micropollutants with electron-rich moieties such as amine groups or conjugated double bonds are effectively transformed by ozone. Ferrate has similar though slightly lowered activity spectrum (especially concerning aromatic structures). The two oxidants form different products. Based on their chemical structures, some can be expected to have a high toxicological potential.

Full scale demonstration confirmed that fast reacting compounds are removed completely in the ozonation bubble column (i.e. the first section of a cascaded reactor). The removal of the slow reacting compounds can be modeled by coupling reactor hydraulics with chemical kinetics assessed in lab scale experiments within a factor of 2.5. E. coli was efficiently inactivated in a full scale ozonation reactor operated for a year for demonstration purposes. Aquatic colloids and particulates not considered in the model are assumed to explain the observed difference of model and measurement for micropollutants and pathogen removal. Sand filter following ozonation was shown to remove mainly the reactive organics (e.g.

aldehydes) without removing much of the residual micropollutants. The toxicity removal within the sand filter after ozonation is ascribed principally to the same reactive compounds formed during ozonation.

Post treatment with wetlands: no significant micropollutant removal

Wetland treatment as polishing step after biological nutrient elimination does not comply as significant barrier for most micropollutants that haven't been readily removed by the preceding biological nutrient removal WWTP. This result is based on sampling campaigns done on a full scale facility (3.85 ha wetland surface; 4 d of hydraulic retention time in the wetland; WWTP Land van Cuijk, The Netherlands) and the analysis of 36 compounds.

2.2 WP 2: Novel technologies for wastewater and sludge

The objectives of work package 2 were the development of technologies, which produce energy from the organic pollution of wastewater, reduce sludge production, reclaim the valuable constituents of sewage sludge (nutrients, heavy metals and organics) and reduce micropollutant load of plant effluent. A complete description on the novel technologies is given in <u>Deliverable 2.1</u>, "Novel technologies for wastewater and sludge treatment". The application in the wastewater treatment plant of the future is given in <u>Deliverables 2.2</u>, "New approaches for sustainable WWTP design". An overview that positions these technologies and their objectives is given in Figure 4. At time of the project termination the impact on the wastewater industry is rather limited because the technologies studied within WP2 are in their developing phase. However, in <u>Deliverable 2.2</u> it is discussed how and where these technologies can be applied and in the <u>Deliverable 5.4</u> "Catalogue with criteria for evaluating technologies" more technical information is give for potential end-users.

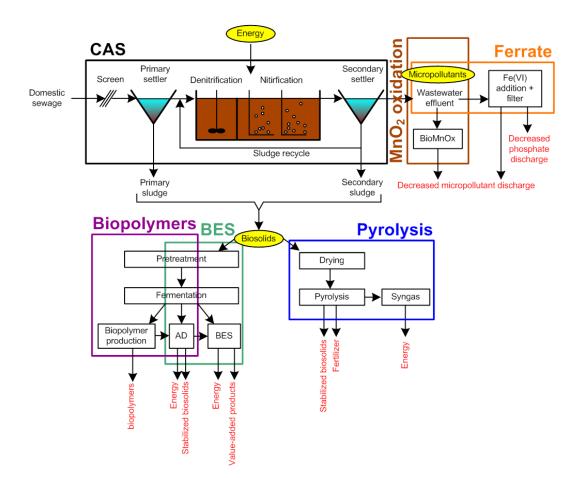


Figure 4: Overview of the technologies investigated within Neptune for improving the sustainability of conventional activated sludge systems (CAS): biopolymer production, bioelectrical systems (BES), ferrate, MnO₂ oxidation with biogenic manganese oxides (BioMnOx) and pyrolysis. AD: anaerobic digestion.

2.2.1 Microbial fuel cells (MFC)

Task 1: Select a performing electricity producing microbial consortium suited for the mix of soluble COD present in primary effluent. Until project termination, no typical consortium or monoculture had been found in the anodic compartment of MFCs. An overview of the different taxonomic classes in MFCs is published in Aelterman et al. (2008; Microbial Fuel Cells as an engineered ecosystem, In: Bioenergy, Wall J.D, Harwood C.S, Demain A.L., Eds., ASM). In the Neptune project, phenazine addition to stimulate certain micro-organisms to increase current production in MFC was investigated (Pham et al., 2008).

Task 2: Maximize energy recovery and COD removal by optimizing the anode potential. In the second year, the influence of an increase of the unit volume of the anodic compartment on the power density and the limiting factors for energy recovery were identified during an intermediate upscaling step (details are found in the second periodic report). The use of digestate as an energy source was investigated at AWMC (<u>Deliverable 2.2</u>)

Task 3: Investigate the influence of operational parameters on the removal of xenobiotics. During the first year, the fate of 17α -ethinylestradiol (EE2) in the anodic compartment was investigated (<u>Fist periodic report</u>). Peroxide production at the cathode was explored to be used as situ H₂O₂ production to combine with UV for micropollutant removal.

Task 4: Build a technical scale MFC for energy recovery and treatment of the primary effluent. In the first year, a pilot scale MFC was built in Brisbane by AWMC, University of Queensland. Results are given in the factsheet (<u>Catalogue D5.4</u>).

Task 5: Optimizing the cathodic compartment: from an MFC to a BES. A new chemical cathode was developed to increase the sustainability of MFCs (Second periodic report). In the Neptune project, we also explored the production of added-value products at the cathode. An added-value product has a higher economical value compared to the initial waste stream (details in the factsheet and the <u>Catalogue D5.4</u>). Accordingly the scope is more than just energy recuperation and the microbial fuel cell (MFC) is more appropriately termed bioelectrical systems (BES).

Task 6: Develop a cathodic denitrification process. A biocathode for denitrification was previously developed at AWMC's lab (Clauwaert et al. 2007) and was optimized during the Neptune project (Clauwaert et al. 2009).

2.2.2 Ferrate for micropollutant and P removal

Task 1: Develop a kinetic database for the oxidation of phenol-, amine-, and double-bondcontaining micropollutants of concern in wastewater. Second order reaction rate constants were determined for selected model compounds containing phenol-, amine- and double bond moieties at different pH values. These show that ferrate reacts readily with micropollutants (1 - 10⁴ M⁻¹ s⁻¹) containing these moieties at wastewater-relevant pH values (pH 6-8; <u>First</u> <u>periodic report, Lee et al. 2009</u>). In addition, the pH-dependant variations of the reaction constant could be explained by considering species-specific reactions between Fe(VI) species and acid-base species of an ionizable substrate (<u>Second periodic report, Lee et al.</u> <u>2009</u>).

Task 2: Investigate and model the oxidation of selected micropollutants by ferrate(VI) in wastewater matrices. Ferrate was shown to oxidize a broad range of micropollutants. Fast reacting compounds containing reactive moieties, such as sulfamethoxazole, carbamazepine and diclofenac, were completely oxidized for ferrate doses $\leq 5 \text{ mg Fe/L}$ (First periodic report, Deliverable 2.1, Lee et al. 2009). The oxidative elimination of these micropollutants in real biologically treated wastewater samples could successfully be modeled at pH 7 and 8 by using the determined second-order rate constants and the Fe(VI) exposure measured in the tested wastewaters (Second periodic report, Lee et al. 2009).

Task 3: Compare phosphate removal with ferrate(VI) to conventional P-removal with Fe(III) salts. For phosphate removal, Fe(VI) was similar to Fe(II) and superior to Fe(III) due to the relative homogeneous introduction in the final form of Fe(III) (reduction of Fe(VI) to Fe(III)) into the water (<u>First periodic report, Deliverable 2.1, Lee et al. 2009</u>).

Task 4: Investigate the potential application of ferrate(VI) for simultaneous oxidation of selected micropollutants and phosphate removal. Ferrate dose needed to achieve the Swiss regulatory limit of 0.8 mg PO₄-P in wastewater effluent was 7.5 mg Fe/L. This is higher than the dose needed for complete oxidation of fast-reacting micropollutants (<u>First periodic report</u>, <u>Deliverable 2.1, Lee et al. 2009</u>).

Task 5: Compare the oxidation of selected micropollutants by ferrate to the oxidation by ozone. For similar oxidant dose, ferrate was as or slightly less efficient than ozone even though second-order reaction-rate constants of ferrate with micropollutants were several orders of magnitude lower than those with ozone. This can be explained by a higher stability of ferrate (minutes) in wastewater compared to ozone (seconds; <u>First periodic report, Deliverable 2.1, Lee et al. 2009</u>).

Task 6: Compare the results for the oxidation of micropollutants at high concentrations (>> $20 \mu g/L$) to environmentally relevant concentrations (1 $\mu g/L$). The experiments gave the same results: in both concentration ranges, a significant elimination could be found for micropollutants containing reactive moieties such as phenols, amines and double bonds (Second periodic report).

Task 7: Summarize the knowledge about the current state of application, limitations and costs. This information can be taken from <u>Deliverable 2.2</u> and the <u>Factsheet on Ferrate oxidation</u>.

Task 8: Identify transformation products of tramadol as a model compound for tertiary amines during treatment with ferrate and compare them to those formed by ozone. (<u>Third</u> periodic report, Deliverable 3.3, Zimmermann et al., *in prep.*).

[CONFIDENTIAL INFORMATION]

For more information please see Annex I of this document.

2.2.3 Manganese oxide upflow bioreactor technology (MO-UBR)

From the first lab-scale MO-UBR, it was observed that the oxidation action by chemical MnO₂ was very slow and could not compete with other removal techniques such as co-metabolism during nitrification (Forrez et al. 2009; <u>First periodic report</u>). Further investigation with manganese-oxidizing bacteria and biogenic manganese oxides let to the development of BioMnOx comprising living Mn-oxidizing bacteria and MnO₂ precipitates on their cell wall. These BioMnOx were 10 times more active than chemical MnO₂ for the oxidation of diclofenac (Forrez et al. 2010a; <u>Second periodic report</u>).

Task 1: Develop a database on the removal of micropollutants out of treated wastewater by the MO-UBR technology and establish its removal kinetics. BioMnOx was applied in a labscale membrane bioreactor (MBR) operated on real secondary wastewater effluent. 14 out of 29 micropollutants were removed in this MBR (Forrez et al. 2010b) (<u>Third periodic report</u>). The removal kinetics were mainly investigated in the second year with diclofenac as model compound (Forrez et al. 2010a) (<u>Second periodic report</u>).

Task 2: Elucidate the role of manganese oxidizing bacteria in the regeneration of the manganese oxide and/or the removal of trace pollutants. During the second year it was found that a major role of manganese-oxidizing bacteria is to keep the aqueous and sorbed Mn^{2+} concentration very low. Because Mn^{2+} competes for the active surface sites on the

manganese oxide, Mn^{2+} decreases the oxidation reaction of the manganese oxides towards the pollutant. Because of the reoxidation action of Mn-oxidizing bacteria, BioMnOx is 10 times more reactive than chemical MnO_2 at pH 6.8. (Forrez et al. 2010a; Factsheet, <u>Catalogue D5.4</u>)

Task 3: Develop a pilot scale MO-UBR to provide effluent polishing for reuse. The lab-scale MO-UBR with chemical MnO_2 was not successful and therefore it was not recommended to build a pilot scale MO-UBR. However, several lab-scale BioMnOx-MBR were operated to investigate a broader range of micropollutants. To further explore the use of biometals, novel technology using palladium was explored for the removal of the highly recalcitrant iodinated contrast media (Third periodic report).

2.2.4 High temperature pyrolysis

Task 1: Operation of a pilot plant reactor to investigate the mass flux of heavy metals and phosphorus and the potential for their recovery from the product gas. The plant was operated with 70-90% TS, at 1100-1400°C and t 5-15 minutes detention time. The work in this area was postponed for one year due to the difficulties in the pilot plant construction. Major obstacles were higher prices than originally calculated due to the high requirements imposed by the German government as well as the shortage on the market of the rare metals, which were essential for the reactor tube.

The experiments proved that the concentration of heavy metals in the inert solid residue found in the reactor was significantly lower than in the solid residue or ash found in the gas system, indicating a partial volatilization of certain heavy metals. In addition, the main solid product proved to have the P concentration similar to conventional agricultural fertilizers. This fact indicated that the solid residue from the reactor could be used for P recycling, while the solids collected in the gas cleaning system may allow recycling metals, especially Zn (<u>Deliverable 2.1</u>). The energy balance gives a surplus of electrical energy but additional heat energy for drying is required (e.g. solar or biogas energy or heat from wastewater).

2.2.5 Polymer production out of sewage sludge

Task 1: Develop and demonstrate bio-solids, pre-treated to generate volatile fatty acids (VFAs), represent a suitable raw material for biomass enrichment and polymer (PHA) production. In the first year, the potential to produce VFAs from waste activated sludge (WAS) pretreated with high-pressure thermal hydrolysis (Cambi process) was assessed. This WAS pretreatment was demonstrated to solubilise suspended matter and render soluble

organic matter readily available for fermentation (<u>First periodic report</u>). A first optimisation of operating conditions of acidogenic fermenters was performed, demonstrating that pre-treated WAS fermentation can proceed at an HRT = 2 d with high VFA production rates, 3-5 fold higher than conventional primary and secondary WAS acidogenesis, despite the relatively lower VFA yields (0.5 gCOD_{VFA} per gSCOD; Morgan-Sagastume et al., 2010a, <u>First periodic report</u>).

Task 2: Understand the benefits and define the optimized implementation of high-pressure thermal hydrolysis for VFA release and subsequent PHA production. Fermentation work continued into the second and early third years. The maximum potential for VFA production from the fermentation of WAS, with and without pre-treatment via high-pressure thermal hydrolysis (Cambi process), was quantified (Second and third periodic reports). Our research showed that the fermenter can be operated down to a residence time of 1-2 days, conditions under which the VFA production rates are high due to high throughput in comparison to fermenting untreated WAS, which would require a larger reactor volume (Deliverable 2.1). In addition, the improved conditions for biopolymer production were evaluated based on selective growth of microorganisms the able to store polyhydroxyalkanoates (PHAs) using fermented sludge pretreated with high-pressure thermal hydrolysis (Cambi process; Second and third periodic reports).

Task 3: Demonstrate the potential in converting the fermented biosolids into a biopolymer with consistent properties, and define the level of controllable and uncontrollable variability in VFA yield and composition and its relevance to PHA quality control (copolymer composition and other important material attributes). Besides assessing process performance stability of reactors operating under previously Improved feast-famine conditions for the selection of PHA-storing microorganisms, the chemical and thermo-physical properties of biopolymer produced in batch accumulations were characterised (Second and third periodic reports). The production of PHA, composed of 3-hydroxybutyrate and 3-hydroxyvalerate, was demonstrated to be feasible in a reproducible fashion and yielding consistent polymer properties. However, the performance of the reactors was challenged by continuous foaming, the presence of non-VFA biodegradable compounds and high nutrient levels. (Morgan-Sagastume et al., 2010b, <u>Deliverables 2.1 and 2.2</u>). In order to address these process caveats, a preliminary study was conducted looking at nitrogen and phosphorus removal and recovery from WAS pretreated via high-pressure thermal hydrolysis (<u>Third periodic report</u>).

2.3 WP 3: Quantification and fate of contaminants and toxicity

The sum of all chemical, ecotoxicological and microbiological parameters determined in WP3 is the basis for the evaluation of the appropriateness of the different wastewater treatment processes investigated. Additionally, the outline a mobile analytical unit was summarized by UniFra and BfG for the on-site assessment of whole effluents in <u>Deliverable 3.4</u>.

Table 3 provides an overview of the main analytical objectives within WP3, the approaches and the partners involved.

Main objectives	Approach	Partner
	Method development and general analysis of	IRSA, INCDTIM,
Determination of organic	organic micropollutants	BfG
pollutants and	Biological degradation	BfG
metabolites	Chemical transformation	BfG, Eawag
(Section 5.3.2)	Sorption	INCDTIM, BfG,
	Chemical transformation Sorption	IRSA
	Tier 1 screening assays (YES, YAES, YAS,	
	YAAS, Mutagenicity Screen, Cytotoxicity	
	Screen)	
	Tier 2 tests (chronic and life-cycle exposure)	
Ecotoxicological	with Lemna minor (plant), Lumbriculus	
assessment of effluents	variegatus (worm), Potampyrgus	UniFra
(Section 5.3.3)	antipodarum (snail), Chironomus riparius	
	(insect) and Oncorrhynchus mykiss (fish)	
	Ecotoxicological characterization of two	
	emerging compounds (Tramadol, Primidon)	
	with tier 1 and tier 2 tests	
Identification of bacterial	E. coli and coliforms	
and viral indicators	Enterococci	BfG
(Section 5.3.4)	Somatic coliphages	

Table 3: Overview of WP3 objectives, approaches and partners involved

2.3.1 Approach for assessing water quality

The term "emerging micropollutants" comprises a huge number of several 10 thousand chemicals. A high percentage is likely to enter municipal WWTPs. Due to limited analytical capacities and available funding only a relative small subset of emerging pollutants can be analyzed today. However, for an overall evaluation of treatment processes the removal of a high number of organic pollutants is crucial. It would be a major drawback if chemicals of toxicological concerns or pathogens are passing favoured treatment processes. In order to minimize this risk, three parallel approaches have been applied in Neptune:

- i) determining the individual removal of a very broad range of emerging pollutants in aqueous and solid matrices
- ii) measuring the removal of specific effects covered by in-vitro assays
- iii) assessing the alteration of the overall toxicity by in-vivo tests using a set of different organisms.

Furthermore, for two selected contaminants (tramadol, primidone) an ecotoxicological characterization was performed. The benefit of this approach can be seen in the overall evaluation of treatment processes. Additionally, the determination of selected pathogen indicators was integrated into the monitoring campaigns, in order to complete the toxicological assessment.

2.3.2 New methods for analyzing organic micropollutants and their metabolites

Determination of emerging organic micropollutants in aqueous and solid matrices

In Neptune, analytical methods have been developed to determine target emerging contaminants in aqueous matrices (psycho-active drugs, biocides, UV-filters, benzothiazoles, antiviral drugs, phosphor organic flame retardants, perfluorinated compounds) as well as in solid matrices (biocides, UV-filters, benzothiazoles, polybrominated flame retardants, alkyl phenols, alkylphenolethoxylates; Wick et al., 2010; Prasse et al., 2010; Mascolo et al., 2010). Furthermore, a multitude of emerging pollutants (antibiotics, acidic pharmaceuticals such as antiphlogistics, lipid regulators, X-ray contrast media, triazines) was monitored in aqueous samples using analytical methods already established at BfG and INCDTIM. In solid samples IRSA monitored further environmental relevant organic pollutants such as PCBs, DDTs, PAHs. Tin organics were measured by BfG.

In addition, a new analytical method (alternative to the widely used GC-MS one) has been developed for target brominated flame retardants, namely polybrominated diphenyl ethers and tetrabromobisphenol A bis 2,3-dibromopropylether employing LC tandem MS (Mascolo et al., 2010). The advantages of the method include low detection limits, congener specificity and the potential benefit of also detecting metabolites of flame retardants, namely the

hydroxylated and the glucuronic acid or glutathione conjugates that are usually encountered as xenobiotic metabolites. These compounds, in fact, cannot be determined by GC-MS due to their high polarity.

2.3.3 Sorption of micropollutants to activated sludge

Sorption to activated sludge is a relevant process for the evaluation of removal and fate of micropollutants in biological wastewater treatment. In general, sorption to secondary sludge is of minor importance for the removal of polar to mid-polar micropollutants ($K_{OW} < 4$) and at ambient pH non-charged micropollutants such as triazines, phenylurea herbicides or benzophenone UV-filters. It has to be noted that positively charged compounds (e.g. imazalil and fenpropimorph) might significantly increase the sorption affinity of micropollutants to activated sludge (Wick et al., in prep.).

Sorption equilibrium of the selected micropollutants in secondary sludge was reached already within less than 1.5 h. For easily biodegradable contaminants a microbial deactivation might be useful for determining their sorption properties. Nevertheless, a significant influence of the inactivation process on the mass balance has to be excluded. For instance, it was observed that the biotransformation of the selected micropollutants was not always sufficiently inhibited when adding the biocide NaN₃. In any case, it is absolutely mandatory to quantify the analytes in both, the sludge and the aqueous phase: Analyzing only the dissolved concentration might lead to excessively high distribution coefficients in case of biodegradation (Wick et al., in prep.).

In general, the Freundlich model was appropriate to describe the sorption behavior of micropollutants in contact with secondary activated sludge. Since for many micropollutants the Freundlich exponents were close to 1, and thus $K_f \approx K_d$, the linear model $C_S=K_d*C_W$ can also be used for a rapid determination of sludge-water distribution coefficients (C_s : sorbed concentration; K_d : sorption coefficient; C_W : soluble concentration). However, 13 of 34 micro pollutants exhibited Freundlich exponents n significantly smaller than 1 indicating concentration dependent sorption to secondary sludge, i.e. a decreased sorption affinity to the sludge flocs with increasing aqueous concentrations. Therefore, K_d values from the linear model determined at relatively high spiking concentrations may underestimate the sorption affinity at lower environmental concentrations. Further details about the sorption studies can be found in <u>Deliverable 3.3</u>.

2.3.4 Biological degradation of micropollutants with activated sludge

It was observed that state-of-the-art WWTPs with multiple biological treatment units and high sludge retention times (SRTs) are insufficient barriers to prevent the emission into the receiving waters of beta blockers, psycho-active drugs and many other emerging pollutants (Wick et al., 2008). Nevertheless, transformations observed for codeine and morphine, which were transformed to more than 80%, are occurring only in biological units with elevated SRT (>10 days). Results of lab scale batch experiments with activated sludge taken from full-scale WWTPs can be used to describe and model primary biotransformation of micropollutants in full-scale WWTPs. In order to adjust stable pH and oxygen concentrations a definite rate of air and carbon dioxide was bubbled through the activated sludge. The primary biotransformation of beta blockers and psycho-active drugs could be described with sufficient accuracy by a pseudo-first order kinetic, while the removal by sorption was negligible.

Degraded compounds undergo only slight chemical transformation

To study the formation of biological transformation products (TPs), secondary sludge was diluted in batch experiments 1:10 or 1:20 with pristine groundwater to avoid separation problems between matrix components and evolving TPs (sludge concentration: 0.04 or 0.02 $g_{SS} L^{-1}$; Wick et al., in prep.). Different concentrations (200, 20 and 0.2 mg L^{-1}) of target compounds (e.g. codeine, dihydrocodeine and morphine) were incubated under aerobic conditions at neutral pH (continuously flushing with a mixture of air and CO₂). In order to determine the transformation pathways of organic micropollutants an overall approach was developed using HPLC fractionation in combination with fragmentation patterns of innovative detection techniques of mass spectrometry such as MS², MS³ scans, precursor scans using LC tandem MS with linear ion trap (LC/Qq-LIT-MS) and in combination with 1D- (1H, 13C-NMR) and 2D- (e.g. COSY, NOSY) NMR experiments. LC Fourier transform (FT)-MS/linear ion trap mass spectrometry was used for determinations of exact masses, i.e. their molecular formula, of TPs as well as their major fragments (Schulz et al., 2008; Kormos et al., 2009; Wick et al., in prep).

Using this approach, it was elucidated that the transformation pathway of codeine in contact with activated sludge is characterized by a combination of biological and chemical reactions. About 30 to 60% of codeine is transformed in biological wastewater treatment only to structural slightly modified transformation products (TPs). Since most of these TPs still have the basic analgesic structure of opium alkaloids, it is already known or it can be predicted that the identified TPs are still biologically active. Thus, it can be concluded, that frequently micropollutants are either not biotransformed in biological WWTPs or transformed only into biological active TPs with similar chemical structures as shown for codeine.

Some transformation reactions may be predictable

Most of the transformation reactions observed for codeine were also found with other opium alkaloids such as dihydrocodeine and morphine. Hydrocodone, the main TP of dihydrocodeine, has even a higher analgesic potential than the parent compound. Hence, it seems to be possible for chemically related compounds to predict at least some biotransformation reactions occurring in biological wastewater treatment.

lodinated contrast media are degraded only at their side chains

For the X-ray contrast media iopromide, iopamidol, iohexol and iomeprol in total 46 TPs were identified in the batch experiments (Schulz et al., 2008; Kormos et al., 2009, Kormos et al, 2010a). The degradation pathways were elucidated under aerobic conditions typical for nitrification. In biological wastewater treatment a transformation from about 30% (iopamidol) up to more than 80% (iopromide) were observed. However, in all cases the chemical structure of the identified TPs exhibited only a change at the side chains of the molecule. The tri-iodo benzene ring was never altered. Similar to codeine the X-ray contrast media are not degraded in wastewater treatment. They have been only slightly changed in their chemical structure, and the TPs are discharged by WWTPs into the receiving waters. It could be shown that X-ray contrast media are further biodegraded during bank filtration and soil passage and that those TPs which have been formed in the batch experiments at the end of the transformations pathways are even present in drinking water (Kormos et al, 2010b). Thus, under aerobic conditions extremely polar TPs are formed with a high likelihood to contaminate drinking water. Further details of the biodegradation results can be found in <u>Deliverable 3.3</u>.

2.3.5 Chemical degradation of micropollutants with ozone and ferrate

[CONFIDENTIAL INFORMATION]

For more information please see Annex I of this document

2.3.6 Sorption of micropollutants to powdered activated carbon (PAC)

Batch experiments similar to OECD guideline 106 have been performed to determine the sorption kinetic and sorption isotherms of selected micropollutants in filtered WWTP effluent (Fink et al., in prep.). The remaining dissolved concentrations were measured after solid phase extraction (SPE) with LC-tandem mass spectrometry. The total equilibrium time for the kinetic experiments was 14 d for all selected micropollutants. Obviously a rapid sorption is followed by a much slower one due to the increasing loading of the PAC. Without exception the sorption isotherms led to "log Kf" values (LⁿkgPAC⁻¹µg¹⁻ⁿ) ranging from 4.8 – 5.6. Thus, based on the lab-scale results PAC addition to treated wastewater should be appropriate for

the removal of polar to medium polar micropollutants. Nevertheless, mainly the first rapid sorption phase is of practical interest, since the PAC is normally retained for 2 to 4 days in the sorption reactor.

2.3.7 Ecotoxicological assessment of effluent

In vivo and in vitro tests are complementary

A selection of *in vivo* tests using species which represent different trophic and taxonomic levels was applied in combination with an *in vitro* test battery to compare the capability of different tertiary wastewater treatment methods for ecotoxicity removal. The combination of both *in vivo* and *in vitro* methods proved to be appropriate, since these yield complementary results. In particular the direct application of the tested water by the use of onsite *in vivo* testing in flow through conditions was essential for detecting non-specific toxicity caused by non-extractable substances (e.g. very polar compounds not extracted by the solid phase extraction used in the *in vitro* test). The fish early life stage toxicity test with rainbow trout, the *Lumbriculus variegatus* toxicity test and the comet assay with haemolymph of the zebra mussel (*Dreissena polymorpha*) were reliable in detecting adverse effects caused by ozonation byproducts (presumably degradable oxidation products) and their removal by a post-treatment like sand filtration.

PAC and ozonation reduce in vitro effects, but ozone increases in vivo toxicity

A comparative ecotoxicological evaluation provides indispensable information about the impact of treatment processes on the toxicity of treated wastewater to organisms (*in vivo*) and sub-organism levels (*in vitro*; Stalter et al. 2010c). The results of the recombinant yeast screens on endocrine activity indicated an effective removal or transformation of toxicants with receptor mediated mode of actions (e.g. estrogens, anti-androgens and dioxin-like pollutants) using ozonation or activated carbon treatment (Stalter et al. 2010d). While the genotoxicity determined with the umu assay was significantly reduced with both advanced treatment processes, the Ames test revealed a consistently increasing mutagenicity as a result of wastewater ozonation (Magdeburg et al., 2010). Furthermore, the *in-vivo* bioassays with several test organisms (annelid, zebra mussel, rainbow trout) revealed adverse effects after ozonation (Stalter et al. 2010a, b). The increased toxicity observed is very likely caused by oxidation byproducts and emphasizes the importance of a post treatment to remove or biodegrade the oxidation products (e.g. rapid sand filtration).

These results indicate that in addition to *in vitro* assays (performed after solid phase extraction) also *in vivo* test systems are crucial for a comprehensive evaluation.

In vivo tests are done directly in the effluent, while *in vitro* tests miss out on polar compounds

Due to the limited extractability of polar compounds, *in vivo* assays performed with treated wastewater in a flow-through test designs (without SPE enrichment) are indispensable to evaluate oxidative treatment processes such as ozonation, since these increase the polarity of most compounds transformed. Furthermore, the *in vivo* assays are appropriate to assess the efficiency of post treatment processes subsequent to ozonation such as sand filtration for detoxification (Stalter et al. 2010c).

In vitro alternatives for in vivo approaches are desirable

An appropriate selection of *in vitro* bioassays, which enable a fast and reliable toxicity screening, is desirable, because it could help to verify the byproduct removal with post treatments like sand filtration and could promote an effect directed identification of toxic oxidation byproducts. Reliable *in vitro* screening methods are preferable compared to chronic *in vivo* approaches due to logistical, cost and time constraints as well as ethical considerations. The applied Ames fluctuation assay (Magdeburg et al., 2010) and the cytotoxicity assay with GH3 cells (Stalter et al., 2010d) are suitable candidates for further research. Further research is also needed on the choice of extraction method to increase the portion of extractable oxidation products.

Assessing treatment benefit requires long term in situ observation

As seen by the results of the *in vitro* bioassays, ozonation and activated carbon filtration significantly diminished receptor mediated toxicity and genotoxicity, but on the other hand ozonation caused an increased non-specific toxicity and mutagenicity due to oxidation products formed. Sand filtration applied after ozonation significantly reduced the adverse effects of ozonation, but still the toxic levels present before ozonation were not entirely reached. Consequently, for a conclusive evaluation of the risks and benefits of advanced treatment steps long term on-site observations before and after establishing advanced treatment steps are indispensable, especially for streams receiving high wastewater loads. In particular, the monitoring of sensitive aquatic species might be promising to draw environmentally relevant conclusions (Stalter et al. 2010c).

2.3.8 Identification of bacterial and viral indicators

Microbiological analyses are mostly based on culture-dependent methodologies. Therefore sampling itself and processing the samples requires sterile techniques to avoid secondary

contaminations. The determination of bacterial and viral indicators in effluents included: total/fecal coliforms, streptococci, and bacteriophages. Samples before and after advanced wastewater treatment steps were analyzed to identify process variables that influence the removal of bacterial and viral indicators. For identification and enumeration of indicators and pathogens, test procedures according to EN ISO standards were adapted to whole effluent of WWTPs. The detection of *E. coli* and coliform bacteria was performed according to EN ISO 9308-1:2000 and of intestinal enterococci according to EN ISO 7899-2:2000. In both methods, water samples were filtered through a membrane which retains the bacteria. After filtration, the membranes were placed on selective and differential media and the cultures were incubated. For enumeration of viral indicators, a test procedure according to EN ISO standards has been adapted to whole WWTP effluents. The detection of somatic coliphages was performed according to EN ISO 10705-2:2001. Bacteriophages are bacterial viruses that infect prokaryotic cells and serve as indicators of viral removal in wastewater treatment plants.

Options for micropollutant removal are effective also for pathogens and viruses

Ozonation in combination with membrane filtration proved to be a very effective advanced treatment process for the reduction of bacterial and viral indicators. Both were reduced to zero or at least by 4 orders of magnitude at an ozone dose of 1 mg/mg DOC. At the WWTP Neuss coliform indicators and *E. coli* were reduced by about 1.5 orders of magnitude compared to conventional treated wastewater via effluent treatment with powdered activated carbon (20 mg/L) and subsequent sand filtration. Ozonation (0.7 mg/mg DOC) was more effective and achieved reduction rates of about 3 orders of magnitude, whereas the sand filter contributes a removal of approximately 1 order of magnitude. For enterococci and bacteriophages the removal effectiveness is in a similar range compared to the aforementioned.

2.4 WP 4: Life Cycle Assessment

Work package 4 "Assessment of environmental sustainability and best practices" aimed at fulfilling the following main objectives:

- 1. Developing a common LCA framework for INNOWATECH and NEPTUNE
- Developing new life cycle impact assessment (LCIA) methodology related to (waste) water and focusing on substances with specific toxic mode of action (e.g. endocrine disrupters), pathogens and whole effluent toxicity (WET)
- 3. Provide and compile inventory data and perform life cycle assessments on a variety of wastewater treatment technologies including sludge handling
- 4. Formulate decision support guidelines based on LCA and cost/efficiency assessment

2.4.1 Method development

In order to do a life cycle assessment (LCA) of a wastewater treatment technique (WWTT), a fitted system to handle the mapped inventory data and a life cycle impact assessment (LCIA) method/model is needed (objective 1). As both NEPTUNE and INNOWATECH (contract No. 036882), which is another EU-funded project running in parallel with NEPTUNE but focusing on industrial wastewater, was in need of such methodology it was decided to make a common deliverable (Deliverable 4.1) . So, also with the aim of facilitating cooperation between the two projects a common LCA methodology framework has been worked out and is described in Deliverable 4.1 "Homogeneous LCA methodology agreed by NEPTUNE and INNOWATECH". This methodology work has been done as a joint effort between NEPTUNE WP4 and INNOWATECH WP4. The work has been focused on fitting especially the EDIP97 LCIA methodology to be used for WWTTs and introducing the concept of "avoided-against-induced impacts" (Figure 5). Deliverable 4.1 also includes a review of existing LCAs on WWTTs. The LCA groups (WP4 groups) of NEPTUNE and INNOWATECH have had currently data exchange during the project period and 4 meetings.

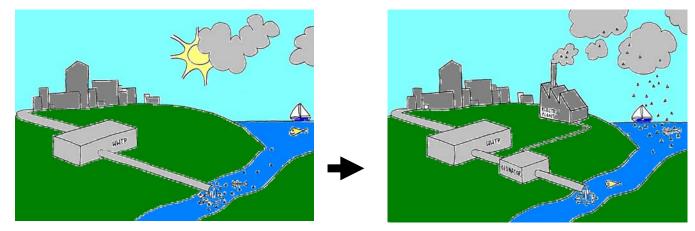


Figure 5: Do we induce more environmental impact than we avoid by introducing a new wastewater treatment technology (sub-optimisation)?

New general methodology developed on how to include ecotoxicity in LCA

The research regarding objective 2 on new methodology is reported in <u>Deliverable 4.2</u> "Methodology for including specific biological effects and pathogen aspects into LCA of wastewater treatment". In order to include the newest development on best available practice as regards ecotoxicity a new revised and updated EDIP 200X LCIA methodology has been developed and a first draft reported in <u>Deliverable 4.2</u>. One of the most significant features of this new method is that it is based on current fate and effect modelling but still key property based (i.e. only most important parameters included) and not multi-media based as most of the other recent developed life cycle impact models on toxicity. The existing LCA method used in NEPTUNE, i.e. EDIP97, also includes a key property LCIA model for toxicity

although far from being as comprehensive as the developed EDIP 200X model. Ecotoxicity characterization factors for more than 2000 chemicals have been calculated according to the new developed EDIP200X methodology and normalisation references have been estimated.

Methodology developed for including specific toxicity, whole effluent toxicity and pathogens

Preliminary methods descriptions on (discussions about) how to deal with whole effluent toxicity, pathogens, site-dependent assessment (eutrophication), land use, land filling, and normalization and weighting, as related to wastewater, are also reported in <u>Deliverable 4.2</u>. Drafts on characterisation factors for the methodology developed on pathogens and whole effluent toxicity (WET) are shown. For pathogens the characterization factors are based on bacterial counts (*E. coli* and enterococci) and for WET it regards estrogenicity (YES test equivalents). Furthermore, the effect of including the potential impact from water emissions of pharmaceuticals on the size of the normalization reference (aquatic ecotoxicity) used in LCA have also been investigated and reported in <u>Deliverable 4.2</u>. Finally, about 35 ecotoxicity characterization factors, according to the EDIP97 methodology, for "new" micropollutants (pharmaceuticals, endocrine disrupters and more) have been calculated and reported in <u>Deliverable 4.3</u> on "Decision support guideline based on LCA and cost/efficiency assessment".

2.4.2 Analysis of key wastewater technologies

Regarding objective 3, full LCA inventory data sets for about 15 WWTTs have been provided and compiled, especially for sludge handling techniques this has been done towards the end of the project period. These data sets are for most WWTTs dominated by measured data and mass balances done within NEPTUNE but also include literature data. On this basis it has been possible to do LCAs on these WWTTs, and divide them into clusters as shown below:

CLUSTER 1: (Post-)treatment technologies for micropollutant and pathogen removal (standard WWTP effluent composition)

- Reference: Direct emission of effluent (secondary) from a conventional WWTP
- PAC addition
 - PAC addition in the biological step
 - PAC addition to the effluent followed by tertiary sedimentation and sand filtration
- Ozonation and sand filtration
 - Ozonation of the effluent

- Sand filtration of the effluent
- Ozonation of the effluent followed by sand filtration

CLUSTER 2: In-line sensor control for nutrients removal (standard WWTP influent from Ecolnvent)

- Reference: Conventional WWT; mechanical, de/nitrification, activated sludge, P removal (Ecolnvent)
- Supernatant deammonification with combined nitrification/anammox process
- Instrumentation control and automation strategies based on online ammonia and nitrate control

CLUSTER 3: Options for sludge inertisation of digested sludge for decreasing the effect of final product disposal

- Reference: On-site incineration
- Wet oxidation
- Middle temperature pyrolysis (gasification)
- High temperature pyrolysis

CLUSTER 4: Sludge triage strategies for improving sludge quality for agricultural use by increasing nutrients content, as well as reducing micropollutants and pathogens (standard WWTP mixed, primary and secondary sludge composition). Combined with sludge disintegration for increasing available COD in sludge for digestion (sludge composition before digestion)

- Reference 1: mixed sludge digested with biogas use, dewatered, incinerated
- Reference 2: mixed sludge pasteurized, digested with biogas use, to agriculture
- Primary sludge incinerated, secondary sludge treated by short aerobic thermophilic treatment (no biogas), to agriculture
- Primary sludge incinerated, secondary sludge with thermal pre-treatment, mesophilic anaerobic digestion (MAD) with biogas use, to agriculture
- Primary sludge incinerated, secondary sludge treated by ultrasonic pre-treatment, mesophilic anaerobic digestion (MAD) with biogas use, to agriculture

Except for "Instrumentation, Control and Automation" (ICA, cluster 2) all compiled inventory data and all LCAs performed are reported in <u>Deliverable 4.3</u> on "Decision support guideline based on LCA and cost/efficiency assessment". This report also includes sensitivity analysis of the LCAs and a description of the systematic modifications of the modelling tool GaBi done within NEPTUNE.

By use of LCAs and the principle of "avoided-against-induced" environmental impacts all the included WWTTs have been assessed for environmental sustainability as part of objective 4:

- A. Is the WWTT an improvement in terms of environmental sustainability compared to conventional WWT, i.e. do we avoid more environmental impact than we induce by introducing the WWTT?
- B. How does the WWT technology compare to the others in the cluster?

For ozonation the results indicate that this treatment technology probably is environmental sustainable (i.e. avoided impacts higher than induced impacts). However, it has not been possible to include the appearance of whole effluent toxicity quantitatively in the LCA. Solving this problem by combining ozonation with sand filtration and including the additive effect of the filter on removal of phosphorus and metals significantly improves the environmental sustainability profile of ozonation combined with sand filtration. For PAC addition the environmental sustainability is less convincing – mainly due to high consumption of fossil fuel during the production of PAC leading to higher induced impacts than avoided in the resulting environmental sustainability profiles. Optimization of the PAC consumption (and micropollutant removal rates) due to recycling during the waste water treatment process, however, improves the sustainability profile for this process. The comparison of the four sludge inertisation methods, i.e. on-site incineration, wet oxidation, middle temperature pyrolysis and high temperature pyrolysis, indicate that wet oxidation has the best environmental sustainability profile.

The results of the assessments are reported in <u>Deliverable 4.3</u> except for ICA reported in <u>Deliverable 1.2</u> "Strategies to improve nutrient removal".

For a few of the assessed technologies (ozonation and PAC addition) costs have been provided and for those a simple cost/efficiency analysis is performed and reported in <u>Deliverable 4.3</u>.

The "avoided-against-induced impacts" concept and the LCIA methodology work done within NEPTUNE have contributed to the improvement and further comprehensiveness of the environmental sustainability tools available for assessing especially wastewater treatment technologies. The drafted tools on WET and pathogens are novel developments. The preliminary tools on WET and the discussions on site specific effects of nutrients (eutrophication) addressed in NEPTUNE will be further elaborated in the recently started EU FP7 project "LC-Impact".

The LCA models for each of the WWTTs included are parameterized meaning that changes in certain parameters (e.g. incoming micropollutant concentration and removal rates) can be relatively easily implemented in the model and a new impact profile created. These models may therefore be used for assessing the environmental sustainability of (new) improved WWTTs.

The environmental sustainability assessments reported in <u>Deliverable 4.3</u> (or new ones based on the developed LCA models) may be used as a decisions supporting guideline when prioritizing among different wastewater treatment technologies. The results of WP4 may therefore be used as a significant contribution to the political and strategic decisions within the water management sector. The developed models may also be used by industries or consultancies dealing with optimisation of environmental sustainability of wastewater treatment technologies or systems.

2.5 WP 5: Dissemination activities

The success of a project depends on the broad dissemination of the outcome of the project and the continuous exchange with the stakeholders. Dissemination of the project results was done by different dissemination channels:

2.5.1 Website (Deliverable 5.1)

Neptune's website was constructed and hosted by Eawag with a public section and one accessible only to the project partners. This website will remain active after the project is finished. The general public is served with the following information:

project overview

work package description

description of the partner institutions and their contacts

- a download section for publications, presentations (with links) and public deliverables links to related projects, incl. Innowatech
- newsletters

presentations from the workshops and conferences organized by Neptune The internal part served as information exchange platform for:

personal contact details

presentations and minutes of the meetings

- data exchange (ftp server for large documents)
- shared documents,

2.5.2 Newsletter

Two newsletters were composed with information on the progress of the project, directed towards end-users (after year 1 and year 2). The newsletters were sent to the Project Interest Group + distributed at relevant events and on the website.

The second newsletter was sent together with the Innowatech newsletter.

The Australian partner has made his own newsletter, parallel to Neptune's.

2.5.3 Workshops and end-user conference

Within totally eight workshops organized by Neptune's, the projects progress was presented and discussed to an audience of ca. 500 persons (Table 4).

Table 4: List of events organized by Neptune

Date	Event	Target public	<pre># of parti- cipants</pre>	Organizer
Oct 2007	Neptune workshop on 6 th conference on WasteWater Reclamation and Reuse	Specialized conference		EAWAG
May 2008	End user workshop joined with Innowatech (Zürich, Switzerland)	End users	64	EAWAG
Jun 2008	Workshop on Mixed Cultrure Polyhydroxyalkanoate Production (Lund, Sweden)	Research groups	31	Anox Kaldness
Nov 2008	End user workshop (Varna, Bulgaria)	Romanian - Bulgarian end-users	42	Siluet B
Apr 2009	Water Framework Directive and Emerging pollutants, (Koblenz, Germany)	Policy makers	94	BfG
Jun 2009	Neptune workshop on Micropol and Ecohazard conference (San Fransisco, USA)	Specialized conference		EAWAG
Jan 2010	End user conference joined Innowatech (Ghent, Belgium)	Specialized conference	155	Aquafin & LabMET
Mar 2010	Dissemination workshop (Quebec, Canada)	End users, International	42	modelEAU

The presentations of the workshops in Koblenz, Ghent and Quebec are available online on the Neptune website (www.eu-neptune.org)

The Koblenz workshop on the Water Framework directive an Emerging pollutants resulted in <u>Deliverable 5.2</u> on the revision of the WFD priority substances *based on the Neptune outcome.*

The end-user conference (Deliverable 5.3) attracted local press (magazines, newspapers, television), Water 21 attributed an article in their April 2010 edition.

2.5.4 Peer reviewed publications

Totally 49 publications have been accepted or submitted to peer reviewed journals (listed in alphabetic order below).

- Batstone, DJ, Balthes, C., and Barr, K. (2010) Model Assisted Startup of Anaerobic Digesters Fed with Thermally Hydrolysed Activated Sludge. Submitted *Wat. Sci. Tech* Feb 2010.
- Escher B.I., Baumgartner R., Koller M., Treyer K., Lienert J., McArdell C.S. (2010) Environmental toxicology and risk assessment of pharmaceuticals from hospital wastewater. Submitted Feb 13 2010.
- Forrez I, Carballa M, Verbeken K, Vanhaecke L., Schlüsener M, Ternes T, Boon N and Verstraete W (2010) **Diclofenac removal by biogenic manganese oxides**. *Environmental Science and Technology*, 44: 3449-3454.
- Freguia, S., E. H. Teh, N. Boon, K. M. Leung, J. Keller, and K. Rabaey. (2010) Microbial fuel cells operating on mixed fatty acids. *Bioresource Technology* 101:1233-1238
- Hennebel T, De Corte S, Vanherck K, Vanhaecke L, Forrez I, De Gusseme B, Verhagen P, Verbeken K, Van der Bruggen B, Vankelecom I, Boon N and Verstraete W. (2010)
 Removal of diatrizoate with catalytically active membranes including microbially produced palladium nanoparticles. *Water Research* 44(5): 1458-1506.
- Magdeburg A., Stalter D., Oehlmann J. (2010) Impact of ozonation and activated carbon treatment on genotoxicity and mutagenicity of sewage effluents. Chemosphere, in preparation.
- Magdeburg A., Stalter D., Oehlmann J. (2010) **Toxicity of two emerging contaminants in wastewater: tramadol and primidone.** CLEAN – Soil, Air, Water, in preparation.
- Mascolo G., Locaputo V., Mininni G. (2010) New perspective on the determination of flame retardants in sewage sludge by using ultra high pressure liquid chromatography-tandem mass spectrometry with different ion sources. J. Chromatogr. A, 1217, 27, 4601-4611.
- Moldovan Z., Marincas O., Avram V. Ternes T. (2010) **Determination of linear** alkylbenzenesulfonates (LASs) in water samples using characteristic ion profiles. To be submitted to *Journal of Mass Spectrometry*.
- Morgan-Sagastume F, Pratt A., Karlsson A, Cirne D, Lant P, Werker A (2010) **Production of** volatile fatty acids by fermentation of waste activated sludge pre-treated in full scale thermal hydrolysis plants. *Paper in preparation*.
- Morgan-Sagastume F, Karlsson A, Johansson P., Pratt S, Boon N., Lant P, Werker A (2010) **Production of polyhydroxyalkanoates (PHAs) in open, mixed cultures from a waste sludge stream containing high levels of soluble organics, nitrogen and phosphorus**. *Paper accepted for Water Research*.
- Prasse, C., Schlüsener M. P., Schulz, R., Ternes, T.A. (2010) Antiviral Drugs in Wastewater and Surface Waters: A new Pharmaceutical Class of Environmental Relevance? Environ. Sci. Technol. 44 (5), 1728-1735.
- Stalter D., Magdeburg A., Oehlmann J. (2010) Comparative toxicity assessment of ozone and activated carbon treated sewage effluents using an in vivo test battery. *Water Research*, 44(8), 2610-2620.

- Stalter D., Magdeburg A., Oehlmann J. (2010) **Oekotoxikologische Studien zu erweiterten Abwasseraufbereitungsmethoden - ein Ueberblick.** *Korrespondenz Abwasser und Abfall*, 57(2), 128-137.
- Stalter, D., Magdeburg, A., Wagner, M. and Oehlmann, J. (2010) **Impact of ozonation and** activated carbon filtration on endocrine activity and cytotoxicity of sewage effluents, Submitted (May 2010).
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- Zimmermann S. G., Wittenwiler M., Hollender J., Krauss M., Ort C., Siegrist H., von Gunten U.,(2010) Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: micropollutant oxidation, by-product formation and disinfection in preparation. to be submitted in February 2010 to *Water Research*.
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- Miladinovic N.D., Siegrist H. and Jeney P. (2010) Sewage sludge Pyrolysis an option for energy and phosphorus reuse. submitted to *Waste mangement* in May 2010.
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- Weissbrodt D., Kovalova L., Ort C., Pazhepurackel V., Moser R., Hollender J., Siegrist H., McArdell C.S. (2009) Mass flows of X-rax contrast media and cytostatics in hospital wastewater. Environ. Sci. Technol. 43, 4810-4817.
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- Joss A., Siegrist H. and Ternes T. A. (2008) Are we about to upgrade wastewater treatment for removing organic micropollutants? *Wat. Sci.* & *Tech.*, **57**(2), 251-255.
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- Tomei M.C., Braguglia C.M., Mininni G. (2008) Anaerobic degradation kinetics of particulate organic matter in untreated and sonicated sewage sludge: Role of the inoculum. *Bioresource Technology*, 99 (14), 6119-6126.
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- Schwätter F., Hannich C. B., Noethe C. B., Oehlmann J., Fahlenkamp H. (2007) Risk assessment for organic trace compounds in wastewater: Comparison of conventional and advanced treatment. *Wat. Sci. and Tech.*, 56, 9-13.

2.5.5 Presentations at workshops, conferences, exhibitions

Totally 68 presentations explicitly on Neptune's scope have been made (listed in descending chronologic order below).

- Boyer-Souchet F., Larsen H.F. (2010) Environmental sustainability of wastewater sludge treatments. Poster presentation at the 20th annual meeting of SETAC-Europe, 23 May 27 May 2010 in Seville, Spain. Abstract No.: 225.
- Corominas L, Flores X, Vanrolleghem PA, Larsen HF, Joss A, Siegrist H (2010). NEPTUNE

 Assessment of environmental sustainability of technologies using Life Cycle Analysis.
 Platform presentation at the 2nd IWA/WEF Wastewater Treatment Modelling Seminar, March 28-30, Mont-Sainte-Anne, Quebec, Canada.
- De Gussem K., Wambecq T., Roels J., Fenu A., De Gueldre G. and Van De Steene B. (2010)
- Cost Optimisation and Minimisation of The Environmental Impact Through Life Cycle Analysis of The Waste Water Treatment Plant of Bree (Belgium). Presentation at the IWA World Water Congress & Exhibition, September 19 - 24, Montréal, Québec, 2010.
- Larsen H.F. (2010) Putting micropollutants, energy, nutrients and GHG emissions on an equal basis: An LCA approach. Platform presentation at the WWTmod2010 Workshop, 28 March 2010, Quebec, Canada.
- Larsen H.F., Hansen P.A. (2010) Environmental sustainability of waste water ozonation. Poster presentation at the 20th annual meeting of SETAC-Europe, 23 May – 27 May 2010 in Seville, Spain. Abstract No.: 192.
- Morgan-Sagastume F, Karlsson A, Bengtsson S, Werker A, Pratt S., Lant P., Magnusson P, Johansson P (2010). **Production of bioplastics as by-products of waste treatment**. Neptune and Innowatech End User Conference, January 27, Ghent, Belgium.
- Moldovan Z., Marincas O., Avram V., Petrov P., Giurgiu M., Ternes T. (2010)
 Determination of linear alkylbenzene sulfonates in WWTP using GC/MS system.
 "Innovative and sustainable technologies for urban and industrial wastewater treatment", Neptune and Innovatech End User Conference, 27 of January, Genth.
- Mininni G., Braguglia, Gianico A. & Gallipoli A. (2010) Energy balance in a novel approach to sludge processing. Residuals and Biosolids 2010, Water Environment Federation, Savannah International Trade and Convention Center Savannah, Georgia, 23-26 May, 2010, 17 p.

- Siegrist H. (2010) Micropollutant removal from municipal wastewater dosing PAC promising flow schemes. Platform presentation at Workshop, WWTMod, 2nd IWA/WEF Wastewater Treatment Modelling Seminar, Quebec, Canada, 28 March.
- Siegrist H. (2010) Indicator compounds to monitor advanced processes for micropollutant removal. Platform presentation at Workshop, WWTMod, 2nd IWA/WEF Wastewater Treatment Modelling Seminar, Quebec, Canada, 28 March.
- Siegrist H. (2010) Fate and behavior of pharmaceuticals and EDCs in municipal wastewater treatment. Conference "20 Years of Research in the Field of Endocrine, Disruptors & Pharmaceutical Compounds - Challenges and Solutions for the Water Sector", Kompetenzzentrum Wasser Berlin, 10 February.
- Siegrist H. (2010) Micropollutants in the urban water cycle and removal options in advanced wastewater treatment key results from the EU projects Poseidon and Neptune. Advances in technology for safe drinking water under water scarcity conditions, 8th Regional Technology Platform, Tel Aviv, 9 June.
- Weemaes M., Fink G., Lachmund C., Magdeburg A., Stalter D., Thoeye* C., De Gueldre G., Van De Steene B. (2010) Removal of Micropollutants in WWTP Effluent by Biological Assisted Membrane Carbon Filtration (BioMAC). Presentation at the IWA World Water Congress & Exhibition, September 19 - 24, Montréal, Québec.
- Corominas Ll., Villez K., Aguado D., Rieger L., Rosén C., Vanrolleghem P.A. (2009) Evaluation of fault-detection strategies performance in wastewater treatment processes. Proceedings at the Conference Instrumentation, Control and Automation, June, Cairns, Australia.
- De Gusseme B, Hennebel T, Marcoen, A, Pycke B, Forrez I., Vlaeminck S, Noppe H, Boon N and Verstraete W (2009) Nitrifying membrane bioreactor as affective effluent polishing technique for instant 17α-ethinylestradiol removal. Poster at Ecohazard and Micropoll conference 2009, San Francisco CA, USA.
- Forrez I, Carballa M, Boon N and Verstraete W (2009) **Removal of 17α-ethinylestradiol** (EE2) in an aerated nitrifying fixed bed reactor: influence of manganese and ammonium oxidation. In: Proceedings, International Conference on Xenobiotics in the Urban Water Cycle, Xenowac, Cyprus. Presentation.
- Forrez I, Carballa M, Verbeken K, Schlüsener M, Ternes T, Boon N and Verstraete W (2009) **Diclofenac removal with biogenic manganese oxides.** Presentation at Ecohazard and Micropoll conference 2009, San Francisco CA, USA.
- Lagacé E., Corominas Ll., Vanrolleghem P.A., Rieger L. (2009) Improving design of measuring and control systems by introducing sensor models into dynamic WWTP simulation. Americana conference, Montreal, 17-19 March.
- Larsen H.F., Hansen P.A. (2009) Environmental sustainability of ozonating municipal waste water. Poster presented at the 19th annual meeting of SETAC-Europe, 31 May 4 June 2009 in Göteborg, Sweden. Abstract No.: WE 370.
- McArdell C.S., Kovalova L., Weissbrodt D., Ort C. Moser R., Hollender J., Siegrist H. (2009) Hospital Wastewater: Input and Elimination of Pharmaceuticals. Micropol and Ecohazard Conference. 6th International Water Association IWA and Groundwater Association of California, San Francisco, USA, June 8-10.
- McArdell C.S., Weissbrodt D., Kovalova L., Ort C., Moser R., Hollender J., Siegrist H. Mass (2009) Flow Analysis of Pharmaceuticals in Hospital Wastewater. XENOWAC, International Conference on Xenobiotics in the Urban Water Cycle, Paphos, Cyprus, March 11-13.
- Mininni G., Braguglia, C.M. Mascolo G. & Gianico A. (2009) Sustainable sewage sludge management based on separated processing of primary and secondary sludge. Proceedings of the 14th European Biosolids and Organic Resources Conference and Exhibition, Leeds (UK) 9-11 November 2009,1-14.

- Moldovan Z., Avram V., Marincas O. Giurgiu M. (2009) Characterization of water contaminants molecular distribution downstream of WWTP by GC/MS ion chromatograms. Workshop "Water Framework Directive and Emerging Pollutants. Measures to minimize river contamination by WWTP discharges", 21–22 April, Federal Institute of Hydrology (BfG) Koblenz, Germany.
- Morgan-Sagastume F. Karlsson A., Bengtsson S., Werker A., Pratt S., Lant P., Magnusson P., Johansson P. (2009) Production of polyhydroxyalkanoate bioplastics as by-products of waste treatment. Proceedings of 17th European Biomass Conference & Exhibition, Hamburg, Germany, June 29-July 2009.
- Oehlmann J. (2009) Effects of endocrine disrupting chemicals in the environment in the environment. Invited presentation at Colloquium of the faculty of Biology, University Giessen, Germany.
- Oehlmann J., Galluba S., Magdeburg A., Stalter D., Oetken M., Schulte-Oehlmann U. (2009) **Tests mit Mollusken zum Nachweis hormonaktiver Sunstanzen.** Invited presentation at the workshop "Biologische Nachweisverfahren hormonaktiver Substanzen in aquatischen Systemen: Basis fer die Regulatorik". Eawag, Ecotox Centre, Duebendorf, Switzerland, 11th-12th June.
- Oehlmann J., Magdeburg A., Stalter D., Weil M., Knacker T. (2009) Ecotoxicological impact assessment of upgrading technologies. Invited presentation at the workshop "Water framework directive and emerging pollutants Measures to minimise river contamination by WWTP discharges". Federal Institute of Hydrology (BfG), Koblenz, Germany, 21st-22nd April.
- Siegrist H. (2009) Full scale post-ozonation followed by sand filtration at WWTP Regensdorf (CH) for micropollutant removal and disinfection. Advanced Oxidation Process Conference (AOP5). Berlin, Germany, 2 April.
- Stalter D., Magdeburg A., Weil M., Knacker T., Oehlmann J. (2009)Vergleichende
oekotoxikologischeoekotoxikologischeUntersuchungvonerweitertenAbwasseraufbereitungsmethoden.Platformpresentationatthe4thDresdnerSymposium"EndokrinaktiveStoffeinAbwasser, KlaerschlammundAbfaellen,Dresden, Germany, 25th March.
- Stalter D., Magdeburg A., Weil M., Knacker T., Oehlmann J. (2009) Ozon oder Aktivkohle? Eine oekotoxikologische Vergleichsstudie zur erweiterten Abwassserreinigung. Platform presentation at the 4th annual meeting of SETC-GLB, Freising, Germany, 5th-7th October.
- Stalter D., Magdeburg A., Weil M., Knacker T., Oehlmann J. (2009) Toxicity assessment of micropollutant removal strategies via upgrading wastewater treatment technologies: Ozonation vs. activated carbon treatment. Platform presentation at the SETAC Europe 19th annual meeting, Goetteborg, Sweden, 31st May-4th June.
- Thomas T., Wick A., Schulz M., Kormos J., Fink G., Schlusener M., Marincas O., Moldovan Z., Joss ., Siegrist A. (2009) Occurrence and fate of emerging contaminants in the aqueous environment. Workshop "Water Framework Directive and Emerging Pollutants. Measures to minimize river contamination by WWTP discharges", 21–22 April, Federal Institute of Hydrology (BfG) Koblenz, Germany.
- Siegrist H. (2009) **PAC Additon to flocculation filtration to improve micropollutant removal.** Micropol and Ecohazard conference, San Francisco, 8-10. June.
- Voltolini M, Morgan-Sagastume F, Nymann J, Boon N, Nielsen PH, Werker A (2009). Influence of volatile fatty acids and carbohydrates on mixed cultures for PHA production. International Water Association Specialised Conference: Microbial population dynamics in biological wastewater treatment. Aalborg, Denmark, May 24-27. Poster.

- Wick, A., Schulz, M., Fink, G., Wagner, M., Joss, A., Siegrist, H., Ternes, T.A. (2009) Fate of psycho-active drugs in biological wastewater treatment: Examining removal processes and formation of transformation products. Micropol and Ecohazard Conference, 8-10 Jun 2009, San Francisco, CA, USA.
- Zimmermann S., Wittenwiler M., Koepke S., Krauss M., Salhi E., Traber J., Hammes F., Gansner E., Koch M., Ort C., Hollender J., Siegrist H., von Gunten U. (2009) Assessment and modeling of a full-scale ozonation step of municipal secondary wastewater effluent. Micropol and Ecohazard Conference, 8-10 Jun, San Francisco, CA, USA.
- Zimmermann S., Wittenwiler M., Koepke S., Krauss M., Salhi E., Traber J., Hammes F., Gansner E., Koch M., Ort C., Hollender J., Siegrist H., von Gunten U. (2009) Spurenstoffoxidation und Desinfektion in einer Ozonungsstufe zur Behandlung kommunalen Abwassers: Messungen und Modellierung. GdCh Tagung, Fachgruppe Umweltchemie und Ökotoxikologie, 23-25 Sep, Trier, Germany.
- Siegrist H. (2008) Fate of micropollutants in wastewater treatment and consequences for process design. Workshop at the Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences, Beijing, 28-30 October.
- Batstone, DJ, Keller, J., and Darvodelsky, P.S. (2008) Trends in Biosolids Handling Technologies: Economics and Environmental Factors. AWA Biosolids Conference June 7-10, Adelaide.
- Forrez I., Pauwels B., Vanhaecke L., Carballa M., Sabirova J., Boon N. And Verstraete W. (2008) Process technical oriented aspects of biological removal of 17alfaethinylestradiol in an aerated fixed bed reactor. Poster and short presentation at IWA World Water Congress 2008, Vienna, September 9. Poster presented at the technical visit of the water reclamation and treatment facility of "La Transhennuyère" organized by the Belgian committee of the International Water Association (B-IWA), Doornik, Belgium, October 20, 2008.
- Hansen P. A., Larsen H. F. (2008) Sustainable treatment of municipal waste water. Poster presented at the 18th annual meeting of SETAC-Europe, in Warsaw, Poland, 25. -29. May 2008 (Abstract No.: MO 191).
- Hollender J. Steimen I., Asmin J., Koepke S., Krauss M., McArdell C.S., Escher B., Zimmermann S., von Gunten U., Ort C., Siegrist H. (2008) Elimination of toxic micropollutants in a whole treatment plant using ozonation. 5th IWA Leading-Edge Conference, Zurich, June 1 4.
- Larsen H., F., Hauschild M. (2008) **Review of existing LCA studies on waste water treatment technologies**. Poster presented at the 18th annual meeting of SETAC-Europe, in Warsaw, Poland, 25. - 29. May 2008 (Abstract No.: TUPC4-3)
- Magdeburg A., Stalter D., Weil M., Knacker T., Oehlmann J. (2008) Vergleichende oekotoxikologische Untersuchung von ozoniertem und konventionell behandeltem Abwasser. Platform presentation at the 3rd joined annual meeting of SETC-GLB and GDCh, Frankfurt, Germany, 23rd-26th October
- Magdeburg A., Stalter D., Weil M., Knacker T., Oehlmann J. (2008) Comparative in vivo toxicity assessment of ozonation as advanced wastewater treatment method. Platform presentation at the 1st Young environmental scientists meeting, Landau, Germany, 16th-18th March.
- Moldovan Z., Marincas O., Ternes T. (2008) Fragmentation of some Linear Alkylbenzenesulfonates Compounds under Electron Impact. The 18th International Mass Spectrometry Conference, 30.09-04.09., Bremen, Germany.
- Morgan-Sagastume F., Karlsson A., Bengtsson S., Werker A. (2008) **Biopolymer production** from a high-strength waste stream: waste sludge treated with high-pressure thermal

hydrolysis. 4th International Conference on Renewable Resources and Biorefineries, Rotterdam, The Netherlands, 1. - 4. June 2008.

- Oehlmann J., Magdeburg A., Stalter D. (2008) **Ecotoxicology of emerging contaminants in the aquatic environment.** Invited presentation at the LET conference on water and wastewater treatment technologies, Zurich, Switzerland, 1st-4th June.
- Oehlmann J., Magdeburg A., Stalter D., Oetken M., Schulte Oehlmann U. (2008) Effects of sewage born emerging contaminants in aquatic ecosystems. Invited presentation at the Colloquium of the institute for hydrobiology, Technical university Dresden, Germany, 17th June.
- Vanrolleghem, P.A., Beaupré, M., Boudreault, M.-C. and Rieger, L. (2008) Comparing online sensors: Application and critical review of ISO standard 15839. Presentation at 2008 National Water Quality Monitoring Conference, May 18-22, Atlantic City, New Jersey, USA.
- Weissbrodt D., Kovalova L-, Ort C., Moser R., Hollender J., Siegrist H., McArdell C.S. (2008) Hospital Wastewater: Mass Flow Modelling, Analysis and Treatment of Pharmaceuticals and Disinfectants. 5th IWA Leading-Edge Conference, Zurich, June 1 -4.
- Zimmermann S., Lee Y., Trung Kieu A., von Gunten U. (2008) Oxidation of micropollutants and removal of phosphate during treatment of municipal wastewaters by ferrate (Fe(VI)): Comparison with ozonation. IWA, 5th Leading Edge Technology Conference, 1-4 Jun, Zürich, Switzerland.
- Zimmermann S., Salhi E., Koepke S., Hollender J., Hammes F., Gansner E., Koch M., Traber J., Ort C., Siegrist H., von Gunten U. (2008) Assessment of a full scale ozonation to reduce micropollutant concentrations in municipal wastewater. IWA, 5th Leading Edge Technology Conference, 1-4 Jun, Zürich, Switzerland.
- Forrez I., Pauwels, B., Carballa, M., Sabirova J., Boon, N. and Verstraete, W. (2007) **Process** technical approach of EE2 removal in WWTP effluent: direct biodegradation respectively indirect by mineral or biogenic manganese oxides. Presentation at Aquabase workshop "Mitigation Technologies" November 28.
- Joss, A., Siegrist, H., Ternes, T. A. (2007) Are we about to upgrade wastewater treatment for removing organic micropollutants? Micropol & Ecohazard Conference, 17 - 20 June 2007 Frankfurt, Germany.
- Kaelin D., Siegrist H., Rieger L., J. Eugster J., K. Rottermann K., C. Bänninger C. (2007) Real time aeration control in wastewater treatment plants using in-situ sensors with ion-selective electrodes. 3rd International IWA Conference on Automation in Water Quality Monitoring - AutMoNet2007, Gent - Belgium, September 5-7, 2007.
- Larsen H. F., Wenzel H., Hauschild M. (2007) New methodology in life cycle impact assessment (LCIA) of waste water treatment. Poster presented at 17th annual meeting of SETAC-Europe, 20-24 May 2007 in Porto, Portugal. Abstract No.: MO 463 Poster presented at the Micropol&Ecohazard Conference, 17-20 Jun 2007, Frankfurt, Germany. Poster E4.
- Moldovan Z., Marincaso. (2007) Development of method for determination of polar herbicide residues in water samples using GC/IT-MS system after SPE preconcentration. EUROANALYSIS XIV, Antwerp, Belgium, 9-14, September 2007.
- Moldovan Z., Marincaso., Avram V. (2007) Mass spectrometric methods for determination of synthetic antioxidants. Fifth Conference on Isotopic and Molecular Processes, 20-22 September, Cluj-Napoca, p 194.
- Moldovan Z., Marincaso. (2007) Determination of pesticide residues like triazine herbicides in waters samples using GC/MS system after SPE pre-concentration. Fifth Conference on Isotopic and Molecular Processes, 20-22 September, Cluj-Napoca, p 195.

- Siegrist, H., Joss, A., Ternes, T. A. (2007) Fate of Micropollutants in Drinking and Wastewater Treatment and Consequences for Process Design. Leading Edge Technology Conference, 4 7 June 2007 Singapore.
- Siegrist H., Salzgeber D., Eugster J. and Joss A. (2007) Anammox brings WWTP closer to energy autarky due to increased biogas production and reduced aeration energy for N-removal. Proceedings of 11th IWA World Congress on Anaerobic Digestion (AD11) in Brisbane Australia, 23-27 September 2007.
- Ternes, T. A., Joss, A., Siegrist, H. (2007) Contaminants of emerging concern a challenge for urban water management. WEF Symposium "Compounds of emerging concern", USA, 29. - 30. July 2007.
- Wenzel H., Larsen H. F., Clausson-Kaas J., Hoibye L. (2007) Weighing environmental advantages and disadvantages of advanced wastewater treatment of micropollutants using environmental life cycle assessment. Micropol&Ecohazard Conference, 17-20 Jun 2007, Frankfurt, Germany.
- Werker A. (2007) The next generation of wastewater and sludge treatment: biorefineries producing bioplolymer. Water 21, Magazine of the International Water Association, December 2007.
- Zimmermann, S, Lee, Y, von Gunten, U. (2007) Oxidation of Pharmaceuticals and Removal of Phosphate during Treatment of Municipal Wastewaters by Ferrate (Fe(VI). Aquabase workshop "Mitigation Technologies" 27-28 Nov, Aachen, Germany.
- Siegrist H. (2006) Leading-edge processes on urban wastewater treatment Presentation of the European Project NEPTUNE. ECOMONDO, 10th International Trade Fair on Material & Energy Recovery and Sustainable Development" Rimini, Italy, 8-11 November.

2.5.6 Catalogue of technologies (Deliverable 5.4)

A catalogue is compiled for stakeholders on the suitability of different technologies for the following wastewater treatment scopes:

- to control toxicity and pathogens
- for process optimization and energy recovery
- to control nutrient removal and recovery
- for safe handling and reuse of sludge.

The following technologies are covered:

- Ozone for micropollutant removal
- Ferrate addition for micropollutant and P removal
- Powdered activated carbon for micropollutant removal
- BioMAC for micropollutant removal
- Biometals for micropollutant removal
- Nitrifiers for micropollutant removal
- Separate hospital wastewater treatment
- Zeolites to improve performance of overloaded WWTP
- Sludge triage: segregation of primary and secondary sludge

- Pyrolysis of sludge
- Wet oxidation of sludge
- Thermal hydrolysis of sludge as pretreatment for anaerobic digestion
- Biopolymer production from sludge
- Instrumentation control and automation (ICA) for process optimization in WWTP
- Combined nitritation/anammox for digestor supernatant deammonification
- Microbial fuel cells for energy and resource recovery

The catalogue will be distributed via the website and by electronic letters to stakeholders from the project interest group and the attendees of the end-user conference.

2.6 WP 6: Project management

Major task of this WP is the scientific, financial and administrative coordination of the project. Meetings as well as related workshops are planned and coordinated within this WP.

Major objectives of WP6 included the following:

- project formulation and amendment (prolongation by 5 months)
- organizing and formulating the consortium agreement
- compilation and submission of the first second and third periodic reports, as well as the project deliverables
- to distribute the financial support from the EU to the partners
- organisation of project meetings:
 - kick-off meeting with EU Project Innowatech (November 1st-4th, Rome, Italy)
 - o 1st meeting: 20-22 May 2007 Cluj, Romania (host partner: INCDTIM)
 - 2nd meeting: 8-10 November 2007, Lund, Sweden (host partner: AnoxKaldnes, DTU, IPU)
 - LCA and micropollutants removal workshop, 10th-11th September, 2007, Koblenz, Germany
 - 3rd meeting: 4th-7th 2008, Zurich, Switzerland, which was a joint meeting of Neptune-Innowatech and interested end users (host partner: Eawag)
 - 4th meeting together with workshop for end users from Bulgaria (simultaneous translation was provided by host partner): 22nd-24th October 2008, Varna, Bulgaria (host partner Siluet B)
 - 5th meeting with the Workshop on water Framework Directive and Emerging Pollutants, 21-22 April, Koblenz (host partner BfG, Germany).

- 6th meeting (which was a joint meeting of Neptune-Innowatech and interested end users) together with workshop for end-users *Innovative and Sustainable Technologies for Urban and Industrial Waste* for end users, 26th - 28th January 2010, Ghent, Belgium (host partner Aquafin with help of LabMET, Belgium)
- workshop on *Technical Solutions for Nutrient and Micropollutants Removal in WWTPs*, 25th-26th March, Quebec, Canada (host partner Model*EAU*, Canada)
- maintaining of the project web site: <u>www.eu-neptune.org</u>, including the internal section for data exchange
- supporting the partner in project related administration

The objectives of the work package set up for the whole project period were successfully accomplished.

3 Consortium management

Neptune project lasted from 1st November 2006 - 31st March 2010. During the whole project no problems were reported regarding consortium management.

The consortium management has been carried out by Eawag with Hansruedi Siegrist as a project manager supported by his team and Eawag's general administration.

Scientific and administrative support was provided to all WPs through the project meetings via frequent communication with WP leaders.

Transfer of funds and advice on administrative issues has been carried out successfully.

3.1 Changes during the project

3.1.1 **Project prolongation**

After preceding discussion with the project officer Mr. Avelino Gonzales during the spring meeting in Zurich (May 2008) and in autumn in Varna (October 2008) the consortium agreed to ask Commission for 5 months project prolongation (totally 41 months instead of the originally planned 36) due to the following reasons:

- WP4 was delayed;
- AWMC and model EAU started late due to EU external funding issues;
- prolongation normally results in more publications being achieved during official project duration (better project evaluation).

The prolongation was approved.

3.1.2 Change of the WP leaders

- Henrik Fred Larsen, new WP4 leader instead of Henrik Wenzel
- Ilse Forrez, new WP2 leader instead of Willy Verstraete

3.1.3 Funding of non-EU partner

After delay of 16 months, the **Canadian partner model***EAU* was able to secure funding from the Natural Sciences and Engineering Research Council of Canada (NSERC) under the Special Research Opportunity program. A total amount of 180,000 CAD was made available for model*EAU*'s contribution to the NEPTUNE project.

3.1.4 Financial issues

Money transfer from Eawag to BfG

For the upscaling of the single SBR nitritation/anammox less consumables have been required by Eawag than initially planned. On the other hand, lab scale experiments (done by BfG in cooperation with INCDTIM) and pilot as well as full scale experiments (done by Eawag and DPU) show that more effort is required for characterizing the micropollutant removal capability of PAC addition (e.g. impact of background DOC on the required activated carbon addition) and the process technology required for PAC retention. Therefore, deemed to represent the best use of the Community's contributions to Neptune's funding by € 18,000.- from Eawag's budget was relocated to BfG, for allowing additional capacity for analysing micropollutant samples.

Money transfer from Siluet B to Eawag, BfG, Aquafin and DTU

Part of the funds from Partner, Siluet B has not been spent. The Neptune Management Committee agreed on **distributing these extra funds** (10 100€) equally to the following partners:

- Eawag
- BfG
- Aquafin
- DTU

The decision was based on the extra costs induced by the two workshops (Ghent and Quebec) as well as by extra work in the area of micropollutants removal with PAC addition (plant operation and analytical costs).

3.1.5 Cooperation with Innowatech

The EU project Innowatech had a similar topic with focus on industrial instead of municipal wastewater. The cooperation has been maintained during the whole project duration through the following activities:

- linked web pages
- agreement to publish and distribute newsletter jointly
- common meetings and workshops in Zurich, May 2008 and Ghent, January 2010
- exchange of data regarding endusers and stakeholders
- cooperation to a common approach on life cycle assessment (WP4)

4 Annex I - Confidential parts of the report

Partner 1: Eawag (page 26)

Task 8: Identify transformation products of tramadol as a model compound for tertiary amines during treatment with ferrate and compare them to those formed by ozone. Four transformation products of tramadol with ferrate were identified and compared to those formed by ozone. Both oxidants attack at the tertiary amine moiety. Still, ferrate seems to be a milder oxidant not able to break up moderately activated aromatic ring systems compared to ozone (<u>Third periodic report, Deliverable 3.3, Zimmermann et al., *in prep.*).</u>

Partner 1: Eawag (page 33))

Ferrate and ozone both attack electron rich moieties

Even in conventional WWTPs with elevated SRT>10 d the majority of micropollutants are either not removed at all, or only transformed to slightly modified TPs with similar chemical structures and mode of actions. In order to appreciable remove micropollutants, post-treatment processes such as activated carbon filtration or chemical oxidation (e.g. ozonation and ferrate) have been tested. It is already known from the EU project Poseidon (Huber et al., 2005, Ternes et al. 2003) that micropollutants containing electron-rich moieties such as amine groups or double bonds are oxidized by ozone. However, it was unknown which oxidation products are formed. In addition to ozone the innovative oxidant ferrate (Fe (VI)) was applied as post treatment in Neptune. Similar to ozonation micropollutants containing electron-rich moieties are oxidized by ferrate. Although the secondary rate constants obtained with ferrate are significantly lower, the oxidation efficiency might be comparable to ozone due to the longer exposure times of ferrate.

Oxidation products formed by ferrate and ozone differ only slightly

In order to elucidate the chemical structure of the oxidation products (OPs) formed by ozonation and ferrate, the weak opioid analgesic tramadol was selected as model compound. Tramadol is not significantly removed during biological treatment (Wick et al., 2009), and concentrations in the mid ng L^{-1} range up to 6 µg L^{-1} were detected in secondary effluents of different WWTPs (Hummel et al., 2006; Wick et al., 2009).

The OPs were formed in bench-scale experiments by adding ozone or ferrate to a tramadol solution in Milli Q water buffered at pH 8.5 (Zimmermann, et al., in prep.). The OPs were identified by HPLC fractionation in combination with fragmentation patterns of mass spectrometry formed in MS², MS³ scans, precursor scans using LC tandem MS with linear

ion trap (LC/Qq-LIT-MS). LC Fourier transform (FT)-MS/linear ion trap mass spectrometry was used for determinations of exact masses, i.e. their molecular formula.

Since ferrate is a much milder oxidant than ozone, no OPs are formed which contain a bialdehyde group as found with ozonation due to the attack of the aromatic ring system (Zimmermann, et al., in prep.). With both oxidants tramadol N-oxide was identified as well as a demethylation of the tertiary amine group. However, for ferrate the pure N-desmethyl tramadol was identified as OP, while the N-desmethyl-N-oxide was detected with ozone. Hence, both oxidants attack tertiary amines. The OPs identified for ozone and ferrate were similar (N-oxides) or slightly different.

Ferrate and ozone generate toxic by-products, degraded in sand filter

Whether one of the oxidants form more or less toxic TPs cannot be assessed. However, it is known that N-oxides (formed by both oxidants) have been shown to be toxic to human cells and to cause haemolysis (breaking-up of red blood cells). Furthermore, aldehydes formed with both oxidants (although different ones) are known to interact with DNA leading to genotoxic and carcinogenic effects. Bifunctional aldehydes formed during ozonation, are even known to cause DNA-protein cross-linking. The presence of bifunctional aldehydes might even to lead to false negative results in the comet assay measuring genotoxicity. The ecotoxicological assessment (see below) revealed a significant increase of in-vivo toxicity and in-vitro mutagenicity after ozonation. Therefore, based on the Neptune results the oxidation processes should not be applied as the last treatment step. In order to remove the toxic OPs formed, an appropriate post treatment process (e.g. biologically active sand filter) is needed.