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NEWSLETTER EU Project Neptune



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Foreword from the coordinator, H. Siegrist Eawag, Switzerland

Dear Reader,

The scope of sewage treatment is changing: today municipal WWTP are seen as endof-pipe treatment before discharge to avoid eutrophication, toxic effects and hygienic health hazard in surface water. Due to global demographic trends, climate change and new legislations, the future focus is put on resource recycling and on improving quality

of products, e.g. reuse of effluent and sludge. The focus of EU project Neptune is put on removal and recycling of nutrients, micropollutant and ecotoxicity removal, energy optimization and production, sludge inertisation as well as reuse of sludge and of its resources. The structure of Neptune is described in the figure (right). It consists of two work technical packages: WP1 investigates the upgrading of existing technologies, WP2 deals with novel technologies mainly at laboratory scale, WP3 assesses the effluent quality of the processes investigated in WP1 and WP2 while in WP4 these processes are evaluated with Life Cycle Assessment (LCA).



The EU-projects Neptune and Innowatech were the only two projects supported by the EU commission within subtopic II.3.2 "New concepts and processes in wastewater treatment" of the 4th Call in the 6th EU-Framework ,"GLOBAL CHANGE AND ECOSYSTEMS" Area II: Water cycle, including soil related aspects.

Whereas Innowatech concentrates on industrial wastewater Neptune is dealing with municipal wastewater treatment.

In April, Neptune is organizing a workshop on Water Framework Directive and Emerging Pollutants. This workshop will highlight how to implement sustainable technical solutions for wastewater treatment plants as well as source control measures to minimize contamination of waterways with priority and emerging pollutants (see page 3). The workshop will be organized at the BfG in Koblenz, where you are warmly welcome!



Full scale ozonation of municipal secondary wastewater effluent for eliminating micropollutants

A full scale ozone reactor was installed at wastewater treatment plant (WWTP) Regensdorf (Switzerland, 25.000 PE) to treat the secondary effluent. A rapid sand filter acted as biological polishing step after ozonation. In nine sampling campaigns, different ozone doses were added to the wastewater stream ranging from 0-1200 g O₃/kg DOC (0-6 mgO₃/L). During each campaign, 24 h or 48 h flow proportional composite samples were taken in the effluent of the primary and secondary clarifier, after ozonation and in the final effluent after sand filtration. More than 50 persistent pharmaceuticals and biocides with different second-order rate constants for the reaction with ozone were selected as suitable indicators for the evaluation of the elimination efficiency by ozone. They were measured by LC-tandem mass spectrometry after offline or online solid phase extraction. The results show that many of the compounds with aromatic moieties, amine functions or sulfamethoxazole, such as diclofenac olefines or carbamazepine were eliminated to concentrations below the limit of detection using 600 g O₃/kg DOC. Compounds more resistant against oxidation by ozone such as atenolol and benzotriazole were increasingly eliminated with increasing ozone doses. Only few pollutants such as x-ray contrast media persisted almost completely against oxidation. The kinetic behavior of the elimination process of micropollutants during ozonation could be well described by detailed full-scale sampling campaigns taking grab samples along the ozone reactor.



Concerning oxidation by-products, low concentrations of about 5-10 ng L⁻¹ of the carcinogenic NDMA were produced but ~50% were removed during the following sand filtration. Bromate formation from bromide was only 7.4 μ g L⁻¹ at the highest ozone dose applied (1240 gO₃/kg DOC) and hence always remained below the ecotoxicologial guideline value of 3 mg/L and even below the drinking water standard of 10 μ g/L.



The simultaneous toxicity reduction during the ozonation process was determined by a battery of ecotoxicological bioassays (see page 3). Ozonation led to a reduction of both specific and non-specific toxicity indicating that no relevant amount of toxic by-products is formed. The secondary effluent still exceeded the proposed environmental quality standard EQS of 1 ng L⁻¹ estradiol equivalent concentration, while final effluent was below this EQS for ozone concentrations higher than 470 g O_3 /kg DOC.

As an additional benefit, the total cell number was slightly decreased and the number of the indicator organism *E. coli* was significantly reduced by up to $2.5 \log$ units during ozonation.

Concerning energy consumption, the ozonation step was optimized during the study resulting in approx. 0.04 - 0.06 kWh/m³ wastewater at an ozone dose of ~800 g O_3 /kg DOC. This corresponds to 20-30% of the total energy consumption of a conventional nutrient removal plant. Additionally, 0.02 kWh/m³ wastewater electrical energy was needed for pure oxygen production.

In conclusion, the full scale reactor proves ozonation to be an efficient technique for the elimination of micropollutants from secondary effluent as well as for disinfection and toxicity decrease at feasible additional energy consumption. A subsequent rapid sand filter is useful for the elimination of NDMA and biodegradable compounds formed during ozonation.

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In vivo testing for ecotoxicological evaluation of ozonation as advanced wastewater treatment step

Ozonation as advanced wastewater treatment method for the removal of micropollutants was evaluated at the wastewater treatment plant (WWTP) Wüeri (Regensdorf, Switzerland). Besides the extensive chemical analysis comparative ecotoxicological а assessment of ozonated wastewater is essential for an appraisal of ozonation for advanced wastewater treatment. Long term in vivo exposure of test animals to whole effluent is indispensable to gain a comprehensive estimation of risks and advantages for the environment due to the integration of concentration fluctuations of micropollutants as well as of oxidation byproducts.



For the ecotoxicological evaluation of ozonation as advanced wastewater treatment method the following in vivo tests were performed: Fish early life stage toxicity test (FELST) with the rainbow trout, reproduction test with the snail Potamopyrgus antipodarum for testing endocrine active chemicals, sediment-water Chironomid toxicity test with the midge Chironomus riparius and sediment-water Lumbriculus toxicity test with the annelid L. variegatus. The tests were performed with wastewater from three different sampling points at consecutive treatment steps in a flow through system: after final sedimentation (FS), after ozonation (O) and after sand filtration (OS).

The FELST results showed а considerable developmental retardation in the test-water after the ozone reactor, accompanied by a significant decrease in bodyweight compared to the control (C) and the test-waters after FS and OS. In OS this effect was mostly annihilated. The reproduction test with Ρ. antipodarum revealed a significant reduction of the number of embrvos in all test-waters compared to C, but no differences among significant the treatments. This leads to the conclusion that the inhibited reproduction of the snails was probably a result of general toxicity.

The reproduction rate and biomass of *L.* variegatus was considerably decreased in all test-waters compared to C and significant decreased in O. Reproduction rate and biomass in O were also significant decreased compared to FS and OS.

As conclusion the ozonation of wastewater revealed significant adverse effects in the test with rainbow trout and the annelid. In both test systems the effects were annihilated after sand filtration. This probably is a result of the formation of oxidative byproducts (e.g. aldehydes, carboxylic acids, ketones and brominated organic compounds). These compounds are rapidly biodegradable or bound to suspended particular matter so that they were largely removed through sand filtration, which could explain the lessened effect in OS. However no compound could be clearly identified for these effects. Possibly the sum of (e.g. aldehydes formaldehyde), carboxylic acids, ketones and brominated organic compounds formed due to ozonation led to such effects, although no toxicity literature data are accessible for all these compounds for juvenile rainbow trouts after long term exposure.

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Workshop: Water Framework Directive and Emerging Pollutants *Measures to minimize river contamination by WWTP discharges*

21– 22 April 2009 Federal Institute of Hydrology (BfG) Koblenz, Germany

Based on the outcomes of the EU project *Neptune*, this workshop will highlight how to implement sustainable technical solutions for wastewater treatment plants (WWTPs) as well as source control measures to minimize contamination of waterways with priority and emerging pollutants. The workshop will allow researchers, governments, industry and other stakeholders to discuss the upgrading of existing municipal processes and the application of innovative techniques.

The final programme and registration form of the workshop are attached to this newsletter and can also be found on www.eu-neptune.org

Ultra high temperature sludge gasification for SYNGAS production

In ultra high temperature gasification (pyrolysis) sludge is mineralized at temperatures up to the 1300°C in the absence of oxygen. The process results in conversion of all organic material to valuable SYNGAS (more than 90% of content is mixture of CO and H₂) with the energy content of around 3.5 kWh/m³.

The key element of technology is the ability to create intense heat at low cost through a specially developed heating induction system. To achieve this goal, special metal mixture was developed which can withstand such elevated temperatures over a long period of time without corrosion. Since a clean gas and solid residue result from the ultra-high temperature exposure, no expensive gas scrubbers should be necessary and high fees for final storage of toxic residues should be avoided as well.

The pilot plant was constructed and delivered by Pyromex, Switzerland and the first trials for the goal of the Neptune project were performed in cooperation with Eawag, Switzerland.

So far the following process conditions were tested:

Temperature:1200°C, 1400°C;Total solids content of the sludge:70%, 80%;Residence time in the reactor:5min, 10min, 15min.



The obtained results are as follows:

- □ The obtained gas was free of tar and consisted of CO (~40%), H₂ (~50%), CH₄ and CO₂;
- □ Higher temperature and longer residence time reduced the amount of the solid residue coming out of reactor and increased the gas production, but did not reduce the concentration of heavy metals in the residue. Its concentration is below the value set by the EU standards for sludge use in agriculture.



- Phosphorus behaves similar to the heavy metals (either staying in the solid residue or in the gas). However, results indicate that the phosphorus in the solid residue at lower temperature and shorter reaction time is more bioavailable; (at 1200°C and 5 min 12.3 % of total amount of phosphorus entering the reactor proved to be bioavailable based on the leaching experiments in citric acid, compared to only 3.7% at 1400°C and 10min).
- Heavy metal volatilization can be increased by addition of chlorides to the feeding material due to the formation of volatile metal-chlorides.
- □ The heavy metals **water leaching** properties of the solid residue obtained after high temperature pyrolysis (gasification) were compared with the ones of other sludge inertisation methods (wet oxidation process and middle temperature gasification; T<900℃). Based on the absolute amount of heavy metals in the solid residues as well as the percentage leached after five days in the water solution, the conclusion is that the product of the high temperature pyrolysis (gasification) has the least effect on the environment after disposal or further use.
- More trials with variation of temperature, sludge water content as well as the exposure time are planned for the next project year. A full scale plant (capacity 25t/day) should be operational by the middle of the year 2009

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Constructed wetlands: An alternative for the elimination of organic micropollutants in urban wastewater?



The main goal of the sustainable approach in NEPTUNE is to carry out a holistic environmental performance ranking (optimisation) of different waste water treatment technologies (WWTTs). One of these WWTTs include end-of-line technologies involving wetlands. The objective is to assess post-treatment of municipal wastewaters to remove focus micropollutants and pathogens.

The wetland treatment of a municipal WWTP effluent was assumed to be an interesting ecological and economical alternative for pathogen and micropollutant removal if sufficient space (1-2 m² per capita) is available. Main removal processes may be photochemical processes in combination with biological degradation and sorption to particulates and plants, enhanced by grazing of filtering zooplankton (e.g. Daphnia) on free bacteria (e.g. fecal coli) and sludge particles.

The elimination of psychoactive drugs, iodinated contrast medias. X-ray phosphororganic flame retardants. antibiotics and biocides was investigated along a three stage constructed wetland plant (pre-settling basin with Daphnia, reed ditches and fish ponds) attached to the effluent of a conventional WWTP. In addition. the amount of microbial indicators such as coliform bacteria,

faecal enterococci and somatic bacteriophages was determined at five sampling points along the wetland. Biodegradation and sorption onto particles are the main elimination mechanisms in the constructed wetlands. Therefore, significant elimination was only observed for substances which were alreadv significantly eliminated in conventional WWTPs processes and compounds which have strong sorption affinity to particles, such as diclofenac, triclosan, diuron, ibuprofen and codeine. However, most of the tested micropollutants achieve no significant removal (<25%) in reed bed and pond. Based on the monitoring campaign it seems that the wetland treatment adds only marginal extra removal of the micropollutants studied compared to the well-functioning tertiary activated sludge treatment plant

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Life Cycle assessment for prioritising use of wastewater carbon

Several strategies may exist for the wastewater treatment plant configuration with respect to primary settling and the use of the primary sludge, namely today's main reference in terms of using it for biogas production, closing down primary settling in order to enhance nitrogen removal, or as an upcoming technology: using it for biopolymer production in the form of polyhydroxyalkanoates, PHA.

Within NEPTUNE, a Life Cycle Assessment was carried out for a holistic assessment comparing the environmental aspects of these strategies.

The enhanced nitrogen removal will take place at a somewhat higher energy consumption. Biogas was assumed to be used for co-production of electricity and heat with a partial use of heat internally at the plant and connection to the grid in the case of the electricity. PHA was assumed to replace a polymer of petro-chemical origin.

Comparing biogas and PHA, the energy balance showed biogas from one m³ of sludge to lead to an overall saving of 270 to 380 MJ of fossil energy, whereas the PHA solution would lead to an overall saving of 190 to 250 MJ of fossil energy. This energy balance was accordingly reflected by a higher CO_2 reduction from the sludge in the biogas application when comparing the greenhouse gas balances.

The explanation behind these differences were found to be that PHA production is aerobic leading to a higher in-plant electricity consumption, that biomass production aerobic leading to a higher sludge production, low yield of PHA compared to methane, and a higher CO₂ replacement from biogas per MJ when substituting coal based electricity. Data for the PHA technology represented an early stage of technology development and will change in the future. Comparing biogas and nitrogen removal, it was found that the nitrogen removal, of course happens at the expense of lost biogas production. The increased denitrification, however, removes 10 PE of nutrient enrichment potential per PE of global warming potential increase by the loss of biogas. Today's political weighting in terms of policies for nutrient enrichment and global warming reduction both require around 20% reduction over 10 years time. In a 'distance-to-target' based weighting, nitrogen removal, thus, has priority over biogas formation from the primary sludge. Global warming needs about 10 times higher weight to change the priority and make biogas preferable to denitrification.

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Anammox: All full scale SBRs in successful operation and further installations planned



The full scale sequencing batch reactors (SBR) for deammonification of municipal digester supernatant with the combined nitritation/anammox process are running reliably since their initial put into operation between August 2007 and June 2008: the operation of all five full scale reactors (between 150 and 1400 m³ reactor volume each) is completely handled by the plant operators, as after the startup procedure no further contribution from Neptune was required. This confirms the robustness of the process and its control strategy.

Parallel operation of the two reactors at Zurich-Werdhölzli using different sensors for cycle control confirmed the online ammonia sensor as superior compared to the conductivity signal. Under regular operation the two signals perform comparably. But in case of a decrease of anammox activity leading to a nitrite accumulation (e.g. toxic shock), the control with ammonia sensor increases correctly the non-aerated time for anammox, while the conductivity based control requires offline nitrite measurement and manual intervention by the operator.

Parallel operation of two reactors either with continuous or with intermittent aeration confirms that the two operation strategies do not differ in terms of nitrite oxidizer growth. Since continuous aeration allows slightly higher throughput, simpler operation and better control, it is considered slightly superior.

The total costs for the operation at Zurich-Werdhölzli confirm considerable savings of 1.5 instead of 2.5€ per kg N eliminated compared to conventional heterotrophic denitrification with methanol.

The positive experience has been presented at conferences as well as by direct contact with stakeholders, resulting in several additional projects currently in the planning phase in Germany and Austria. A publication describing the process and its control strategy has been submitted for peer review and publication at the journal Environmental Science and Technology.





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Let us know your opinion!

The goal of this newsletter is to inform our readers of the progress of our project, adressing New Sustainable Concepts and Processes for Optimization and Upgrading Municipal Wastewater and Sludge treatment

Since we appreciate very much your opinion, please send us your feedback, comments and questions!

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