SMARTDETOX – Removal of Organic Micropollutants from Water

Executive Summary (version June 2019)

Introduction

SMARTDetox is an SBO project proposal. SBO ('Strategisch Basisonderzoek') is a Flemish funding that aims at supporting new and challenging innovations with a relevant economical or societal application.

Problem Statement

Adequate supply of freshwater is an immense growing problem worldwide due to increasing demands and **pollution**. An **increasing problem** is the occurrence of **organic micro-pollutants (OMPs)** in surface and groundwater. OMPs are organic chemicals with complex and highly variable structures that occur at trace concentrations (µg–ng/L) and often have unknown eco-toxicological and/or human health effects. OMPs include pesticide residues, pharmaceuticals, personal care products, (synthetic) hormones, and others. They enter surface and ground waters through diffuse and point sources such the use of pesticides, manure, municipal and industrial wastewater treatment plants. Till recently, target OMPs mainly were pesticide residues. However, several other OMP chemicals were recently added to the EU surface water watch-list emphasizing the importance of OMP pollution in water. Similarly, while current quality standards for OMPs in drinking water only relate to pesticide residues, drinking water companies are already monitoring other OMP groups in influent and finished drinking water.

Changes in regulations and consumer behavior are likely insufficient to fully control the complex OMP discharge routes. **End of pipe removal** of OMPs from wastewater and **treatment of raw intake water for drinking water** require so-called advanced water treatment (AWT). Current commercialized AWTs are physicochemical processes, such as membrane filtration (including nanofiltration (NF) and reverse osmosis (RO)), adsorption on activated carbon (AC) and advanced oxidation processes (AOP). They show satisfying removal efficacies, but **are energy-intensive, use high amounts of chemicals, or result in toxic waste**.

General Goal of the Project

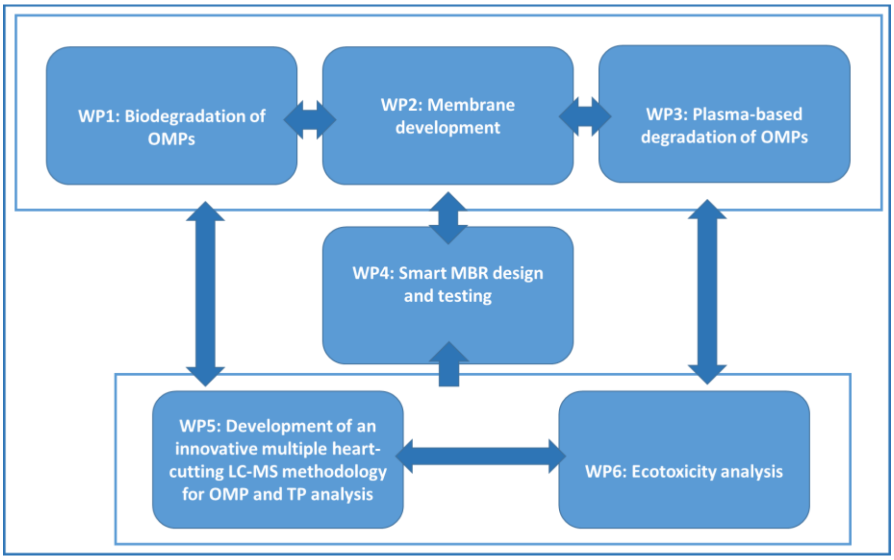
To improve sustainability, a technology combining retention and destruction of the OMPs with a minimal input of energy and chemicals is required. The SMARTDETOX project **aims at developing such technology and assessing/optimizing its feasibility by combining technological developments with an in-depth understanding of the underlying processes.**

The **main challenges** for the development of such treatment technology are:(i) the extreme low concentrations at which the OMPs occur and that will impact degradation rates, (ii) their presence as complex mixtures and (iii) the possibility of creating toxic transformation products (TPs).To tackle these challenges, the main aim of this project is to develop a knowledge-based state-of-the-art membrane technology that is customized to subsequently improve OMP destruction by biodegradation and/or plasma-based oxidative degradation (POD). POD will be used to treat effluents from municipal WWTPs while biodegradation will focus on groundwater treatment in drinking water treatment plants (DWTPs). To guide the optimization of these technologies, innovative analytical techniques will be developed.

Contributing Technologies and Research Groups

1. **Membrane Technology for the OMP-enrichment** (Membrane Technology Group (cMACS) – prof. Ivo Vankelecom)

Based on a combination of steric exclusion and charge repulsion, **nanofiltration membranes** typically retain compounds with a molecular weight between 200 and 1000 Da, while tighter RO-membranes retain all solutes. To adequately remove typical OMPs (150-300 Da), very dense membranes are thus required. Obviously, these membranes will also retain (inorganic) ions. Ideal membranes should retain OMPs and allow passage of salts and water at low pressure. Such membranes are currently not available on the market but preliminary academic research exists, i.e. using so-called '**mosaic membranes**', showing patches of negatively charged polymers in a matrix of a positively charged polymer or vice versa, prepared via e.g. inkjet printing, counter diffusion, or phase inversion. Each phase allows the passage of the oppositely charged ions. Water can pass through both regions, while these charged regions simultaneously are dense enough to retain organics.



Overview of technologies used and developed in the SmartDETOX project.

2. **OMP Biodegradation** (Division of Soil and Water Management - prof. Dirk Springael)

Biodegradation is considered an attractive, economically-sound alternative for removing OMPs from dilute waters. Most studies examine aerobic OMP biodegradation at concentrations far above the trace concentrations at which OMPs typically occur and hence the **mechanisms** that govern OMP degradation at trace concentrations are not yet well-understood. Recent pure culture studies show that while short-term degradation of OMPs at trace concentrations in dilute waters can be achieved, **long-term degradation** is more challenging as OMP degradation rates diminish in time. This appears linked to the oligotrophic nature of typical dilute waters that are **limited in dissolved organic carbon** (DOC) (including OPMs) required for energy and growth, resulting into energy constraints, starvation and reduced OMP degradation. Mixed substrate utilization refers to the simultaneous use of two C-sources and might be a solution for sustaining OMP biodegradation activity by fueling the organisms with auxiliary organic carbon. Moreover, several studies show that the availability of more recalcitrant DOC improves OMP degradation in both individual degraders and in communities. These observations indicate that microbes and even communities can be **steered towards increased OMP degradation by managing the organic feed.** However, evidence for this is lacking and the mechanisms are unknown.

3. **Plasma oxidative degradation (POD) of OMPs** (The Process and Environmental Technology Lab – prof. Raf Dewil)

Different types of non-thermal POD have been evaluated as a breakthrough AOP technology for the effective degradation of OMPs in water. A fast and non-selective degradation of a wide range of OMPs is feasible due to a variety of degradation mechanisms, including (*i*) the generation of chemically oxidative species like ozone (O_3), hydrogen peroxide (H_2O_2) and oxidative radicals (mainly hydroxyl radicals (OH*)), and (*ii*) physical effects, like high-energy electrons (e^-) and UV-light. The in-situ generation of the oxidative species omits the need for chemicals dosage, rendering the technique **highly environmentally friendly**. The **fundamental link** between plasma excitation, oxidative species production and pollutant degradation however remains elusive. In addition, for the vast majority of POD, the plasma is directly generated in the water phase, limiting the flexibility towards upscaling and oxidative species generation. An innovative approach to overcome these issues is **a gas phase surface discharge plasma reactor**, in which the oxidative species are generated in a carrier gas that flows through the plasma generator and is thereafter injected in the wastewater. Only proof-of-concept results using air as plasma carrier gas and oxytetracycline as OMP have so far been reported. Various parameters that influence the type and amount of oxidative species generated, neither the role of OMP concentration and composition, remain unexplored yet and knowledge on the actual degradation mechanism is missing.

4. **Chemical and toxicological analysis of OMP/Toxic Product (TP) mixtures –** (Pharm AI – prof. Deirdre Cabooter and the Laboratory for Molecular Bio-Discovery – prof. Peter de Witte)

Degradation of mixed OMPs, obtained either by biodegradation or by POD, is expected to result in a variety of TPs with a **wide range of physicochemical properties**. The identity of these TPs is often unknown as is their contribution to the environmental risk. To identify and quantify these unknowns, together with known OMPs, salts and other compounds of interest, **highly efficient analysis methods with orthogonal separation capabilities** are required. Multidimensional liquid chromatography (LC) methods are gaining popularity for the analysis of complex mixtures in different application fields. Their implementation is currently, however, still largely confined to academic research groups, due to the expert know-how and complex hardware and software required to use them. There is hence a pressing need to develop more robust, highly efficient and sensitive multidimensional separation techniques for complex samples to advance the field.

At the same time, the identity of these TPs needs to be related to toxicity in a pragmatic way. Several cheap, and relevant high-throughput ecotoxicity tests based on zebrafish-related methodology are available that can **relate OMP/TP ecotoxicity to structure.** This is particularly relevant for the assessment of mixture effects of parent OMPs and TPs acting jointly, which is a new and challenging approach. It can lead to new concepts about how to deal with OMP/TP mixtures in waters regarding risks.