Toxicity of coastal waters: use of a quick algal bioassay


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Optimization of the SPE step in the analysis of β-blockers and β-adenomodinetics in natural water samples by SPE–GC technique

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Environmental samples, especially sewage and marine-water samples are complex and often contain interfering elements that can mask or interfere with the analysed pharmaceuticals. In this study directly generalise these analyses may not be possible. Additionally, the low concentrations in which the pharmaceuticals are generally found cause that an initial stage of concentration and clean-up analysis is necessary. Fractionation methods (extraction (SPE)) is the most common sample preparation technique used in environmental areas. Choice of sorbent is a crucial in SPE because it can control such parameters as selectivity, affinity and capacity. This choice depends strongly not only on the target analytes and the interactions of the chosen sorbent through the functional groups of the analytes, but also on the kind of sample matrix and its interactions with both the sorbent and the analytes. This work describes the application of the different kinds of SPE sorbents: C18 bonded silica gel (Strata C18), copolymers (Osiris HLB, Strata X, and Lichrolut EN), functionalized copolymers (Isolute ENV+), mixed-mode (mixed-modeenanodinetics MCX) and a function sorbent (Strata SCX) for extraction of six β-blockers (acebutolol, atenolol, metoprolol, nadolol, propranolol, pindolol), and two β-adenomodinetics (terbutaline, salbutamol) from natural water samples. Parameters such as pH of the loading samples, the amount and the kind of solvents used in conditioning, washing and eluting steps, were selected and optimized. The obtained extracts were evaporated to dryness, subjected to silylation using BSTFA, and finally analysed by GC–FID technique. The recovery of the analytes form natural water samples in the mentioned above SPE conditions will be discussed.

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TU 082

Butterfly fractionation based on normal phase GC and reverse phase HPLC (RP–HPLC) for isolation of endocrine disrupting chemicals in environmental extracts

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Directed Extracted (EDA) approach aims to identify adverse pollutants by reducing the complexity of environmental matrices. Simple hyperfractionation combined to biosays is helpful to link direct active chemicals and to direct chemical knowledge to these “classical” pollutants. However, although the emergence of promising chemical tools (e.g. Orbitrap®), identification of unknown active chemicals is still time and cost consuming due to the complexity of each active fraction (e.g. mixture effect). Hence, further fractionation steps are often needed. The aim of this study was to develop and to test the use of a first pre-fractionation step on SPE that will be followed by a RP-HPLC fractionation. First the separation of 12 EDCs have been evaluated with several elution conditions. Silica cartridges with 4 step elution - heptane, heptane/dichloro methane (50/50 v/v), ethyl-acetate and methanol/water (50/50 v/v) - have been chosen for further investigations. For these conditions, recoveries were assessed for the mixture alone and for a blank sediment extract spiked with this mixture. Finally, a natural sediment known to exert estrogentic, PXR-like, anti-androgenic and dioxin-like activity in in vitro conditions. Good mixture recoveries (74–110 %), were obtained. The fractionation F1 contained only the PCBs and the PAHs, while 4-tert-octylphenol, triphenyl phosphate and fenofibrate were detected only in F2. Finally, steroids, bisphenol A and clotrimazole were found in F3 while F4 contained more polar chemicals. Fractionation on natural sediment allows isolation of TCDD-like activity in F1 and F2 while PAH-like activity was detected in F1, F2 and F3. Then estrogenic compounds were only detected in F2 and F3. Interestingly, the sum of the estrogenic activity found in these 2 fractions is higher than the active steroid crude extract, which is an indication of anti-estrogenic chemicals. Finally, PXR-like activity was mainly detected in F3.

This pre-fractionation protocol allows, in the present case study, the isolation of several biological activities. Based on this first isolation directed hyperfractionation has then been undergone. RP-HPLC hyperfractionation and a three-function sorbent (MCX) have been chosen for further investigations. For these investigations, recoveries were assessed for the mixture alone and for a blank sediment extract spiked with this mixture. Finally, a natural sediment known to exert estrogentic, PXR-like, anti-androgenic and dioxin-like activity in in vitro conditions. Good mixture recoveries (74–110 %), were obtained. The fractionation F1 contained only the PCBs and the PAHs, while 4-tert-octylphenol, triphenyl phosphate and fenofibrate were detected only in F2. Finally, steroids, bisphenol A and clotrimazole were found in F3 while F4 contained more polar chemicals. Fractionation on natural sediment allows isolation of TCDD-like activity in F1 and F2 while PAH-like activity was detected in F1, F2 and F3. Then estrogenic compounds were only detected in F2 and F3. Interestingly, the sum of the estrogenic activity found in these 2 fractions is higher than the active steroid crude extract, which is an indication of anti-estrogenic chemicals. Finally, PXR-like activity was mainly detected in F3.

TU 083

Towards a common mass spectra database for the identification of unknowns in environmental samples

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Environmental water sample matrices, especially sewage and marine-water samples are complex and often contain interfering elements that can mask or interfere with the analysed pharmaceutica. The ultimate aim is to develop a sensor that measures several types of toxicity and that can be applied continuously in the field, both at surface water inlets and in the distribution network.

TU 084

Construction of a water toxicity sensor based on luminescent bacteria

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Microcystis, highly toxic cyaelic peptides, are a group of hepatotoxins produced by a number of aquatic species of cyanobacteria, such as Microcystis, Anabaena and Plankothrix. Worldwide contamination in water has prompted the development of detection methods for their identification and quantification. A massive seasonal development of Plankothrix rubescens in a reservoir destined for crop irrigation located in Southern Italy has lead to quantify algal toxin content in water to evaluate the possible health risk. Microcystins dissolved into the water were collected episodic events into account. The concentrated extracts are tested in an algal bioassay with different marine algae species (e.g. Dunaliella tertiolecta, Phaeodactylum tricornutum) to include differences in algal sensitivity. Use of Pulse Amplified Modulation (PAM) fluorometry provides a quick (4 h) method to determine toxicity to algae based on changes in photosynthetic ef- ficiency. An Effect Directed Analysis (EDA) will be performed to unravel which chemical compounds are responsible for the toxic effect on the algae. In 2010-2011 passive samplers are exposed at Hansweert (Westerscheldt, The Netherlands) and collected every 6 weeks to include the seasonal dynamics of both anthropogenic as well as natural compounds. Here, first results of this sampling campaign are presented and discussed. The results of the EDA analysis will be used in experiments where mixture toxicity, multi stress and community effects are taken into account to describe the overall toxic effect under relevant field conditions.

TU 085

Toxicity of coastal waters: use of a quick algal bioassay

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Little knowledge on chemical compounds causing phytotoxic effects is lacking, while in the field many confounding factors (e.g. changing nutrient and light regimes) may affect microalgal responses. The first step to unravel the complex interaction between algae and toxic pressure is to provide knowledge on chemical compounds causing phytotoxic effects. In this study we use passive samplers which extract the freely dissolved concentration in the water during a period of 6 weeks to take episodic events into account. Extracted concentrations are tested in an algal bioassay with different marine algae species (e.g. Dunaliella tertiolecta, Phaeodactylum tricornutum) to include differences in algal sensitivity. Use of Pulse Amplified Modulation (PAM) fluorometry provides a quick (4 h) method to determine toxicity to algae based on changes in photosynthetic efficiency. An Effect Directed Analysis (EDA) will be performed to unravel which chemical compounds are responsible for the toxic effect on the algae. In 2010-2011 passive samplers are exposed at Hansweert (Westerscheldt, The Netherlands) and collected every 6 weeks to include the seasonal dynamics of both anthropogenic as well as natural compounds. Here, first results of this sampling campaign are presented and discussed. The results of the EDA analysis will be used in experiments where mixture toxicity, multi stress and community effects are taken into account to describe the overall toxic effect under relevant field conditions.