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Ecotoxicological evaluation of three tertiary wastewater treatment techniques via meta-analysis and feeding bioassays using *Gammarus fossarum*

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ABSTRACT

Advanced treatment techniques, like ozone, activated carbon and TiO_2 in combination with UV, are proposed to improve removal efficiency of micropollutants during wastewater treatment. In a meta-analysis of peer-reviewed literature, we found significantly reduced overall ecotoxicity of municipal wastewaters treated with either ozone (n = 667) or activated carbon (=113), while TiO_2 and UV was not yet assessed. As comparative investigations regarding the detoxification potential of these advanced treatment techniques in municipal wastewater are scarce, we assessed them in four separate *Gammarus*-feeding trials with 20 replicates per treatment. These bioassays indicate that ozone concentrations of approximately 0.8 mg ozone/mg DOC may produce toxic transformation products. However, referred effects are removed if higher ozone concentrations are used (1.3 mg ozone/mg DOC). Moreover, the application of 1 g TiO_2/l and ambient UV consistently reduced ecotoxicity. Although activated carbon may remove besides micropollutants also nutrients, which seemed to mask its detoxification potential, this treatment technique reduced the ecotoxicity of the wastewater following its amendment with nutrients. Hence, all three advanced treatment techniques are suitable to reduce the ecotoxicity of municipal wastewater mediated by micropollutants and may hence help to meet the requirements of the European Water Framework Directive.

1. Introduction

Wastewater treatment plants (WWTPs) equipped with secondary treatment, i.e. mechanical and biological methods, are not capable of degrading all contaminants present. Such contaminants, or micropollutants, are hence detected frequently at concentrations of up to a few microgram per liter in surface waters [1]. Thus, WWTP effluents are considered as one of the major pathways for micropollutants into aquatic ecosystems [2]. There, they may affect macroinvertebrate communities [3] as well as ecosystem functions, such as leaf litter breakdown [4,5].

To counteract the continuous release of such (in)organic micropollutants into surface waters – and the accompanied potential ecotoxicological implications – the European Commission, under the umbrella of the Water Framework Directive, requires a good status in terms of quantity and quality (=chemical and ecological) by implementing the best technique available to control their emission [6]. To achieve these requirements, end of pipe technologies may be useful in the medium term to reduce the release of micropollutants via point sources like WWTP effluents [7]. Ozonation, for instance, is an end of pipe technology that is economically feasible and technically realisable [8]. Moreover, it is capable of reducing the concentration of organic micropollutants in municipal wastewater [9,10]. Another option for chemical oxidation is photocatalysis, where reactive oxygen species are formed. TiO_2 is widely used as catalyst since it is photostable, non-toxic and insoluble [11]. Furthermore, the combined application of TiO_2 and ultraviolet (UV) irradiation is effectively degrading endocrine disrupting chemicals [11], organic chemicals in general [12], and was successfully applied in industrial wastewaters [13]. Hence, this technology may also be considered for implementation in municipal WWTPs. Besides these advanced oxidation technologies also the application of activated carbon – either granular or powdered – is currently under consideration as an additional treatment step to reduce concentrations of micropollutants [14]. In contrast to ozone or TiO_2 and UV, activated carbon adsorbs (in)organic chemicals from the water phase (i.e. wastewater) and hence, does not produce transformation products that may exhibit an even higher ecotoxicological potential than their parent compounds [15].

Especially this potential formation of transformation products makes it difficult to predict the ecotoxicological net effect of advanced treatment technologies in municipal WWTPs [16]. Thus, the main objective of the present study was to comparatively investigate the ecotoxicological consequences of the application

Abbreviations: COD, chemical oxygen demand; WWTP, wastewater treatment plant; TZW, water technology centre; SPE, solid phase extraction; DOC, dissolved organic carbon; TiO_2, titanium dioxide; UV, ultraviolet; PAC, powdered activated carbon; CI, confidence interval.

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of advanced treatment techniques – namely ozonation, TiO_2 and UV, and activated carbon – in municipal wastewaters. This issue was addressed (I) by conducting a meta-analysis of ecotoxicological data in literature dealing with these advanced treatment techniques and (II) by applying laboratory experiments. The feeding rate, a sublethal endpoint, of the leaf shredding amphipod *Gammarus fossarum* was selected as endpoint since former experiments suggest shifts in the organic matrix – potentially caused by ozone application – not to be the trigger of alterations in the feeding rate of *G. fossarum* [17]. In the same publication it was discussed that recolonization of leaf material by microorganisms (especially aquatic hyphomycetes), which may finally indirectly affect the investigated endpoint, are highly unlikely due to a lack of sources of such hyphomycetes and the short study duration [17]. Moreover, during a population level experiment it was displayed that levels of nutrients (e.g. NH_4^+) are not meaningfully affected by ozonation. Hence, this potential cause for effects is also considered to be of minor importance [18]. These insights were supplemented by an experiment, which used ten-fold enriched eluates of solid phase extraction (SPE) cartridges. The results suggested the fraction purified by the SPE-method applied, and hence not nutrients or heavy metals, are the trigger for the alterations in the feeding rate displayed by the test species *G. fossarum* [17]. Due to these explanations it can be assumed that shifts in the feeding rate of *G. fossarum* most likely display a reduction in the load of micropollutants. Therefore, *G. fossarum* was exposed to secondary treated wastewater from two different WWTPs, which were additionally treated with the above mentioned methods.

2. Material and methods

2.1. Meta-analysis

In order to locate studies assessing ecotoxicological properties of municipal wastewater treated with ozone, the combination of TiO_2 and UV irradiation (TiO_2 and UV), or activated carbon, a literature search was performed using the online database ISI Web of Science (Thomson Reuters; date 31st January 2011). The search strings used and the resulting number of paper hits are given in Table S1 of the supplementary data. In total more than 5000 articles were returned. However, only 16 dealt with ecotoxicological effects on various biomarkers and 25 used whole organism toxicity tests assessing the impact of ozone or activated carbon application, while in this context the employment of TiO_2 and UV was not yet investigated. The reference lists of the retained articles were inspected for pertinent additional publications [19]. However, only peer-reviewed publications were included from which information on treatment and control means, standard deviations and number of replicates could be deduced. All ecotoxicological effects were considered irrespective whether they assessed acute or chronic endpoints. Each comparison of the ecotoxicological mean effect, e.g. the proportion of dead organisms or any other measure of an adverse effect, caused by a given wastewater treatment (ozone or activated carbon treated or untreated) was considered as a separate observation (number of replicates = n). This approach resulted in a total of 780 comparisons used in the meta-analysis, 667 for ozonation and 113 for activated carbon.

Mean values and standard deviations were rescaled by dividing these original values by the largest value reported for each species, separately for each publication. Subsequently, Hedges' g, calculated from rescaled original values, was used as a standardised effect size, which is based on the difference between the mean effects caused by both treatments divided by the within groups standard deviations [20]. To be able to include all data in the analysis, for 21 cases from a range of biomarker and whole organism bioassays (e.g. bacteria, *Daphnia*, fish, yeast-based assays), where means and standard deviations of the original data were zero, rescaled values were set at zero and standard deviations were assumed to have an arbitrarily low value. Exclusion of these data pairs did not noticeably change results. Random-effects models were applied throughout because differences among observations in test species, experimental conditions and endpoints introduced substantial variation in addition to sampling error [20]. Large heterogeneity, which is defined as variation in the true effect size, suggested structure in the data set. Therefore, additional meta-analyses were performed that differentiated among biomarker, whole-organism tests, experiments conducted using eluates of SPE-cartridges loaded with the different types of wastewater, whole wastewater samples, and among groups of test organisms. Mean effect sizes are reported with 95% confidence intervals (CI).

Table 1
Quality parameter of secondary treated wastewater from WWTP Vidy (n = 3) and WWTP Wüeri (n = 3).

Parameter	Secondary treated wastewater from WWTP Vidy (mean ± SD)	WWTP Wüeri (mean ± SD)
COD (mg/l)	29.75 (±6.13)	17.16 (±2.71)
NH_4-N (mg/l)	2.93 (±0.31)	0.05 (±0.02)
NO_2-N (mg/l)	0.43 (±0.16)	0.05 (±0.08)
NO_3-N (mg/l)	14.43 (±2.14)	9.75 (±2.19)
pH	7.56 (±0.12)	7.38 (±0.13)
DOC (mg/l)	7.5 (±2.12)	5.64 (±0.76)

COD = chemical oxygen demand; DOC = dissolved organic carbon.

2.2. Tertiary wastewater treatment techniques applied at pilot-scale

Wastewater composite samples (48 h) were taken from 11th to 13th January and 3rd to 5th May 2010 below the biological treatment (=secondary treated), below the sand filtration (=ozone treated; 0.84 and 0.72 mg O_3/mg dissolved organic carbon (DOC), respectively) and below the powdered activated carbon treatment (=PAC treated; 10 and 12 mg PAC/l, respectively; Norit SAE-Super) at WWTP Vidy (Fig. 1). This WWTP is located in Lausanne, Switzerland, and treats wastewater of a population equivalent of 200,000. Its average discharge is approximately 1300 l/s and the water quality parameters are provided in Table 1. The composite samples were taken time proportional and stored in stainless steel containers at 4 °C. Eight liters of the wastewater sampled below the biological treatment in May 2010 were subjected at the lab-scale to a treatment consisting of a combination of 1 g TiO_2/l (P25 Degussa, average particle size: 21 nm; average surface area: 51 m^2/g) and UV irradiation. The UV irradiation was realized with the laboratory weathering testing system Suntest XLS+ equipped with a daylight filter accompanied by the coupled air conditioning unit SunCool (ATLAS®, Linsengericht, Germany). The irradiation with a wavelength range of 300–400 nm took place at an intensity of 40 ± 5 W/m^2 for 60 min at 20 ± 3 °C. The intensity applied was slightly below values reported for southwestern Germany during summertime [21] and thus is considered an ambient UV irradiation. Subsequently, all wastewater samples were filtered (Whatman, GF/6, pore size <1 μm) to remove particulate organic matter, although this procedure may have removed some organic micropollutants, and TiO_2 present and were afterwards aerated for another 12 h. In both experiments, river water from the Hainbach (49°14′ N; 8°03′ E) – a near natural stream upstream of any settlement, WWTP effluent or agricultural activity – served as control water. Gammarids were exposed to river water (=control), ozone treated, PAC treated, TiO_2 and UV treated (only for samples from May 2010) and secondary treated (=biology) wastewater.