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(K6) Removal of Micropollutants from Secondary Effluents and Sludge by Various Processes in Rural and Peri-urban Areas

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Abstract
The present work details the results of a comprehensive study dealing with the fate of several families of micropollutants (with various physicochemical properties) through tertiary treatment processes of water and through sludge treatments. Powerful and sensitive analytical techniques were used: 16 metals and 39 organics (pharmaceuticals, polycyclic aromatic hydrocarbons, alkylphenols, pesticides) were analysed in wastewaters; 14 metals and 62 organic hydrophobic micropollutants were measured in sludge (estrogenic hormones, polychlorinated byphenyl, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons, alkylphenols and other organics).
We studied treatment processes adapted for rural areas involving low energy-consumption: trench system, polishing pond, horizontal subsurface flow constructed wetlands with various adsorbing materials (i.e. expanded clay, zeolite, activated carbon, apatite, gravels) running at tertiary stage of water treatment; and sludge drying reed-bed operated at two different resting periods.
Our results show that the trench system was not efficient for additional removal of refractory micropollutants. The polishing pond had higher removal efficiencies (between 30 and 70%) for some pharmaceuticals due to indirect photodegradation. The horizontal subsurface flow constructed wetland (HSSF-CW) built with activated carbon showed almost full-removal during more than 330 days for pharmaceuticals, pesticides, several metals and nonylphenoxyacetic acid. For the HSSF-CWs built with expanded clay or zeolite, we obtained removal efficiencies of 70% for half of studied pharmaceuticals and alkylphenols mono- and di-ethoxylates. The removal efficiencies of other substances were much lower than the ones measured with activated carbon, but they were still higher than the ones measured with gravel (filter designed for denitrification) or apatite (designed for phosphorus removal). Due to better oxygen conditions, the sludge drying reed-bed with low frequency of sludge input resulted in better removal for organic micropollutants than the sludge drying reed-bed with high frequency of sludge input.
Keywords
Emerging and priority micropollutants, energy-free process, rural areas.

INTRODUCTION

Reducing the inputs of micropollutants to the environment by wastewater treatment facilities is expected to protect the quality of aquatic systems and drinking water resources. Conventional treatments plants usually remove several micropollutants by biodegradation and/or by adsorption onto sludge (Miège *et al.*, 2009; Martin Ruel *et al.*, 2010; Choubert *et al.*, 2012). But several refractory micropollutants are always measured in treated effluents discharged to the environment (e.g., several pharmaceuticals, pesticides and nonylphenoxyacetic acid). Energy-consuming processes involving oxidation or adsorption on activated carbon are widely studied (Lester *et al.*, 2011) and proposed to stakeholders as a solution to face micropollutants problem in urban areas. Alternatively, in the context of rural and peri-urban areas, energy-free tertiary treatment processes like ponds or constructed wetlands were shown to remove pharmaceuticals in planted or unplanted systems

(Matamaros *et al.*, 2008; Tchobanoglous and Leverenz, 2011; Li *et al.*, 2014) or adsorbent materials (Dordio *et al.*, 2010; Tahar *et al.*, 2013). Nevertheless, the fate of other families of micropollutants in these processes is still poorly documented. Also, sludges from secondary wastewater treatment are often treated by drying reed-beds in small treatment plants, before being applied on land for crop growth. The possible reduction of hydrophobic micropollutants like hormones, polycyclic aromatic hydrocarbons (PAH), alkylphenol (AKP), polychlorinated byphenyl (PCB) and polybrominated diphenyl ethers (PBDE) in such process is of particular concern.
The present work determines the removal efficiencies of various priority and emerging substances by a wide range of energy-free processes devoted to the context of rural areas (involving passive aeration supply) for tertiary water treatment and for sludge treatment. Special care was taken to ensure the reliability of sampling, analysis and calculation of removal efficiencies.

MATERIAL AND METHOD

Studied processes

Seven tertiary treatment processes were evaluated:

- 1 trench system of 80 meters-long, built on not-permeable soil (450 P.E.), hydraulic retention time (HRT) of 10 minutes;
- 1 polishing pond of 2,570 m^2 (1000 P.E.), HRT of 15 days;
- 3 unplanted horizontal subsurface flow constructed wetlands (HSSF-CW) at pilot-plant scale, one was filled with activated carbon (HRT = 1.5 h), one with expanded clay and one with zeolite (HRT = 24 h);
- 2 unplanted HSSF-CW of 60 m^2 each (50 P.E), one filled with gravel designed for denitrification, and one filled with apatite designed for phosphates precipitation (HRT = 24h).

Two sludge drying reed-beds were evaluated: one operated with a high frequency of sludge input (with 2 days feeding period and 14 days resting period), and the other one with a low frequency of sludge input (with 2 weeks feeding period and 14 weeks resting period).

Sampling

Influent and effluent water samples were taken in the inlet and outlet of each studied treatment stage. Automatic refrigerated samplers equipped with Teflon tubings and glass containers were used to set-up flow-proportional composite samples during dry weather conditions for each treatment plant. Sludge samples were collected at 2 depths (middle and bottom of a sludge blanket of 70 cm), twice for each site at 2-year interval.

Chemical analysis

Reliable analytical methods with low limits of quantification (LQ) were applied for the analysis of 55 micropollutants in the dissolved phase of wastewater: 16 metals, 19 PAH, 5 AKP, 4 pesticides and 11 pharmaceuticals (2 antibiotics, 4 betablockers, 5 analgesics/antidepressors), and among them 17 are priority substances of the water framework directive (WFD). Also, 76 micropollutants were analysed in the particulate phase of sludge, including 14 metals, 19 PAH, 4 AKP, 5 estrogenic hormones, 7 PCB, 18 PDBE and 9 other organics including di-2-ethylhexyl phthalate (DEHP), di-butylphtalate, triclosan, galaxolide, tonalide and bisphenol A.

RESULTS AND CONCLUSIONS

Concentrations of micropollutants in tertiary influents and sludge

In the 14 samples of tertiary influents (=secondary effluents) of rural areas, we quantified 14 metals and 31 organic micropollutants. Moreover, 10 organic micropollutants were always quantified at concentrations above 0.1 µg/L, including 8 pharmaceuticals (metoprolol, propranolol, sotalol, sulfamethoxazole, carbamazepine, ibuprofene, paracetamol, diclofenac), one AKP

(nonylphenoxyacetic acid (NP1EC)) and the aminomethylphosphonic acid (AMPA). Other measured micropollutants were never quantified (e.g. 6 PAH and 12 antibiotics). Two metals (tin, uranium) and 2 pesticides (isoproturon, glyphosate) were measured in 50% of influent samples.

In the 6 samples of sludge from drying reed-beds, we quantified all metals and 48 organic micropollutants. We only quantified one hormone (estrone) and the 4 other studied were never quantified (17β-estradiol, 17α-ethinylestradiol, estriol and 17α-estradiol) for which the limit of quantification (LQ) was below 5 ng/g of dry matter (DM). PCB and most PBDE were always quantified at very low concentrations, respectively below 20 ng/g DM and 50 ng/g DM (except BDE209 between 800 and 6000 ng/g DM). Benzothiazole, tertbutylphenol and pentachlorophenol were never quantified (LQ of 200 ng/g); whereas galaxolide, tonalide and triclosan were always quantified, with a maximum concentration of 350, 16 and 12 ng/g DM, respectively. Di-butylphtalate, DEHP and bisphenol A were quantified in 50% of sludge samples.

Removal efficiencies of micropollutants by tertiary treatment processes
For the overall tertiary treatment processes, removal efficiencies (Rw) could be determined for up to 15 metals and up to 18 organic micropollutants. The numbers of Rw in each range (<30%; 30-70%; 70-90%; >90%) are shown Figure 2 for each studied tertiary treatment.

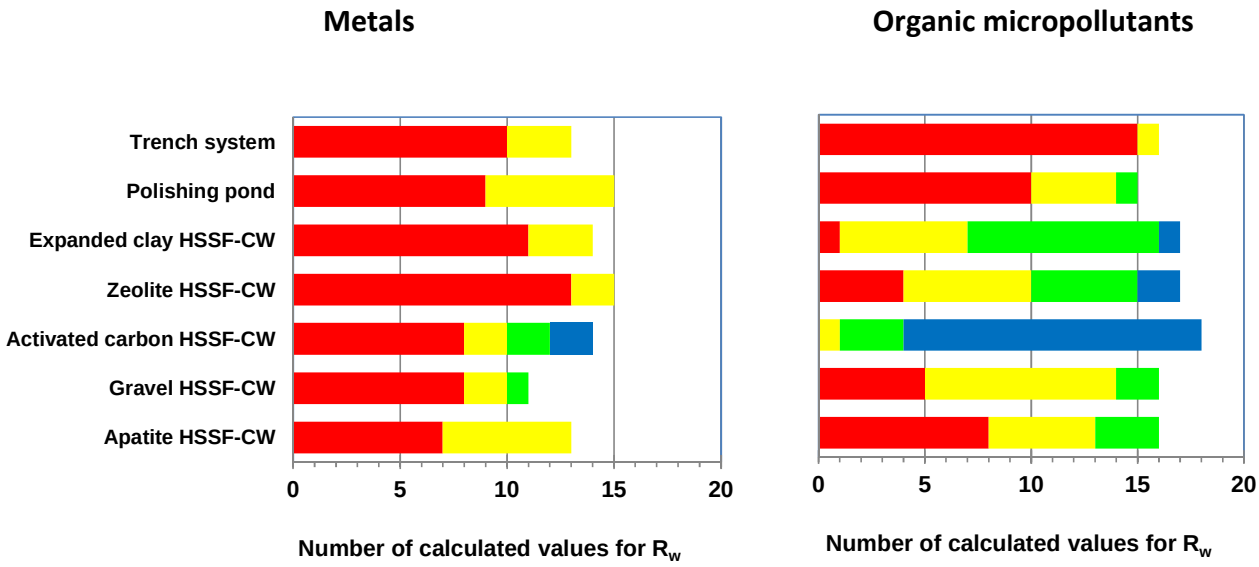

Figure 2. Classification of removal efficiencies (Rw) for various tertiary water treatments
<30% (■); 30-70% (■); 70-90% (■); >90% (■)

The trench system showed low removal efficiencies (Rw<30%) for a majority of refractory micropollutants. Only some Rw were between 30 and 70% due to adsorption on clay (cobalt, zinc, cadmium) or photodegradation (ibuprofen, paracetamol). The polishing pond showed higher Rw values (between 30 and 70%) for 5 pharmaceuticals (diclofenac, sotalol, propranolol, atenolol, roxythromycin) due to indirect photodegradation (half-life time around 4 to 20 h) during the HRT of 15 days. Other micropollutants had their concentrations unchanged in the process and stil above 0.5 µg/L (e.g. carbamazepine, AMPA and NP1EC).

For activated carbon horizontal subsurface constructed wetlands (HSSF-CW), removal efficiencies of organic micropollutants around 100% during more than 330 days for 3 metals (chrome, cobalt, cuivre), all studied pharmaceuticals, pesticides and NP1EC (by-product of alkylphenol

polyethoxylates). Only nonylphenol and other metals obtained lower removal efficiencies. For expanded clay HSSF-CW or zeolite HSSF-CW, removal efficiencies of micropollutants were > 70% for half of the studied pharmaceuticals (propranolol, sotalol, sulfamethoxazole, diazepam, ibuprofen, carbamazepine (except zeolite)) and 2 alkylphenols (octyl- and nonylphenol). The removal of other substances were much lower than the ones measured with activated carbon; nonetheless, Rw were much higher for expanded clay HSSF-CW than for gravel HSSF-CW designed for denitrification, or apatite HSSF-CW designed for phosphorus removal.

Removal efficiencies of micropollutants by sludge drying reed-beds

For the sludge treatment, removal efficiencies (Rs) could be determined for up to 15 metals and up to 34 organic micropollutants. The numbers of Rs in each range (<-30%;-30 to +30%; >30%) are shown on Figure 3 for each sludge treatment.

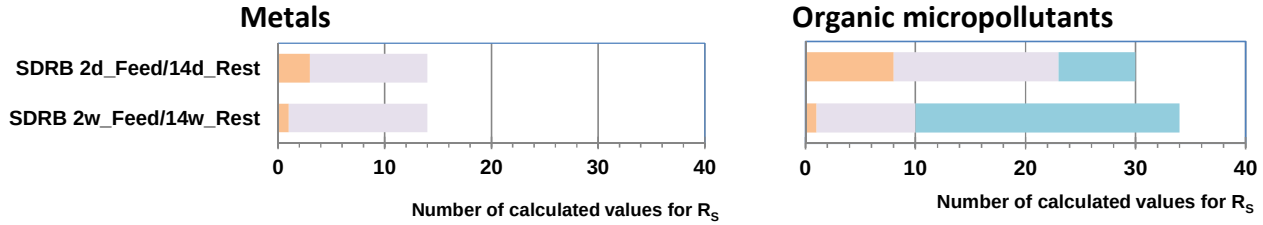

Figure 3. Classification of removal rates (RS) for the 2 sludge drying reed-beds <-30% (■);-30 to +30% (■); >30% (■)

Due to good oxygen conditions in the SDRB with low frequency of sludge input (2w_Feed/14w_Rest), this process had a majority of Rs > 30% due to biotransformation in aerobic conditions (i.e., for estrone, nonylphenol, 7 PAH, 7 PCB, 5 PBDE and 3 other organics (galaxolide, tonalide, triclosan)). Nevertheless, the Rs values only reached a maximum of 50% for some of the substances concerned (e.g. PAH, nonylphenol, estrone, galaxolide, triclosan, DEHP). The SDRB with high frequency of sludge input (2d_Feed/14d_Rest) had a majority of Rs values between -30% and +30% (as oxygen was lacking, micropollutants could not be biotransformed and concentration were unchanged,). Similar Rs values were measured whatever the studied SDRB: >30% for nonyphenol mono- and diethoxylates, DEHP; between -30% and +30% for metals.

Future research

In addition to source-reduction policy, we demonstrated the efficiency of some low-cost treatment processes for removal of refractory micropollutants before release of effluents in the environment. Future research will focus on the economic and environmental benefits of low-cost adsorbents in horizontal subsurface flow constructed wetlands. Also, other tertiary treatments are under study for refractory micropollutants, like successive low depth natural basins or trench with soil infiltration.

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