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Occurrence of selected micropollutants in treated wastewater and removal with optimised tertiary treatments

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Introduction. One of the next major challenges of wastewater treatment is to reliably remove micropollutants and the toxicity associated to them from treated water. Although they were initially designed to remove macropollutants, conventional wastewater treatment plants can eliminate part of the micropollutants by adsorption on sludge, bio-degradation and/or volatilisation [1]. However, some micropollutants remain in treated wastewater at the outlet of the plants. To reach values compatible with a good state of the environment, tertiary treatments can be implemented. They rely on an oxidation, an adsorption or a filtration of the micropollutants.

Two tertiary treatments were studied at pilot scale in three different plants. An advanced oxidation processes (AOP) pilot (O₃/UV/H₂O₂) [2] was tested in two plants with two different upstream treatment processes: plant A, a membrane bioreactor (MBR), and plant B, a low load activated sludge followed by a sand filter (CAS + SF). An activated carbon pilot was tested in one plant, plant C, a low load activated sludge followed by a sand filter and an ozone reactor (CAS + SF+ O₃). The objectives of the study were to assess the occurrence of micropollutants in treated wastewater after a full scale upstream treatment, to evaluate and compare the performance of oxidation and adsorption for micropollutants removal and to assess the toxicity of the effluents before and after a tertiary treatment.

Material and Methods: Micropollutants studied. 64 micropollutants were analysed in the samples of this study with different analytical techniques including HPLC-MS-MS (high performance liquid chromatography coupled with tandem mass spectrometry) for organic compounds and ICP-MS (inductively coupled plasma mass spectrometry) for metals. The selected substances and the analytical techniques are presented in table 1.

Family of substances	Substances	Preparation/Extraction	Analytical techniques	Limits of quantification (��g/L)
Betablockers (4)	Atenolol, metoprolol, propranolol, nebivolol	SPE	HPLC/MS/MS	0.5 to 1
Antibiotics (10)	Sulfamethoxazole, sulfadiazine, sulfamethoxazole, sulfadiazine, trimethoprim, erythromycin, amikacin, rifampicin, florfenicol, tylosin	SPE	HPLC/MS/MS	5 to 280
Other drugs (4)	Carbamazepine, diazepam, ibuprofen, diclofenac	SPE	HPLC/MS/MS	0.5 to 1
Herbicides, pesticides (3)	Glyphosate, AMPA	Derivation	HPLC/MS/MS	100
Herbicides, pesticides (4)	Atrazine, simazine, diuron, isoproturon	SPE	HPLC/MS/MS	5 to 15
Alkylphenols (6)	4-nonylphenol monoethoxylate, 4-nonylphenol diethoxylate, 4-nonylphenol, 4-tert-octylphenol, 4-nonylphenoxysuccinic acid, 4-tert-butylphenol	SPE or SPEE	LC/MS/MS and GC/MS	1 to 10
Polycyclic Aromatic Hydrocarbons (19)	Naphthalene, dibenzothiophene, phenanthrene, anthracene, acenaphthylene, acenaphthene, fluorene, fluoranthene, pyrene, benzo(a)anthracene, chrysene + triphenylene, 2,1-benzo-caphothiophene, benzo(b+j+k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-cd)pyrene, dibenzo(a,h+i,j)anthracene, benzo(ghi)perylene	SPEE	GC/MS	0.1 to 1
Metals (15)	B, Ti, V, Cr, Cu, Ni, Co, Zn, As, Mn, Cd, Sn, Ba, Pb, U	-	ICP-MS	10 to 2000

Table 1. Micropollutants analysed in this study classified by compounds families and quantification methods.

Results and Discussion. Occurrence of micropollutants. At the MBR outlet, concentrations were lower and more constant than after CAS + SF. Metals were the substances detected in highest concentrations in the three plants: bore over 100   g/L; zinc and barium over 10   g/L; titanium, nickel, copper, lead and vanadium over 1   g/L; arsenic, tin, cobalt, chromium, uranium and molybdenum over 0.5   g/L and under 0.1   g/L for cadmium. Aminomethylphosphonic acid (AMPA), which is notably the major degradation by-product of glyphosate, was the organic substance detected at the highest concentrations for plants A (from 450 to 950 ng/L), B (50 to 5400 ng/L) and C (2400 to 6500 ng/L). Betablockers are the second group of organic micropollutants detected in high concentrations (always over 100 ng/L, except metoprolol). Alkylphenols were detected in concentration ranges from

3 to 519 ng/L for plant A, 15 to 402 ng/L for plant B and 8 to 1204 ng/L for plant C. Carbamazepine and diclofenac were detected in concentrations over 350 ng/L for plants A and B but not plant C (< 70 ng/L). Glyphosate was not always detected. The other pesticides and drugs were found at lower concentrations (< 50 ng/L). PAH were detected at very low levels (always under 4 ng/L).

Results and Discussion. Micropollutants removal.

- Drugs were well removed by GAC (from 88% to 100% removal). The activated carbon was still efficient for the removal of these molecules after 6 months functioning 24/24h. Ozone alone, although the residence time and ozone dose were relatively low, was sufficient to remove over 98% betablockers, diclofenac, trimethoprim, sulfadiazine and carbamazepine. For these molecules, that are very sensitive to ozone, a radical oxidation pathway promoted by AOP did not improve the elimination yield. The other drugs analysed were not completely removed by ozone. The addition of H₂O₂ to O₃ increased the removal yield. In combination with ozone, the increase of UV dose and residence time allowed a better removal of roxithromycin, erythromycin and sulfamethoxazole.
- Pesticides (except glyphosate and AMPA) were well removed by GAC (from 85% to 100%) during all the 6 months of the tests. AMPA was removed during the first two days but after three weeks the removal was around 60% and this molecule was no longer removed after 3 months. Glyphosate was also partly removed until month 3 but was no longer removed at month 6. Ozone alone was not sufficient to remove the pesticides AMPA and atrazine (<70%), which are refractory to molecular ozone. For all the pesticides, an addition of H₂O₂ to ozone increased the removal yield by 5 to 50% and the removal increased with the H₂O₂ dose.
- PAH, although in very low concentrations at the pilot's inlet, were partly removed by GAC. Ozone pre-treatment before the GAC optimised the removal of some PAHs, especially at higher ozone dose (10 mg/L). Ozone alone was not sufficient to remove PAHs. Except for acenaphthylene and pyrene, the addition of H₂O₂ to ozone increased the removal yield of PAHs by 4 to 50%. UV/ H₂O₂ combinations were less efficient except for acenaphthylene and pyrene that were well removed. Ozone/UV combinations resulted in the lowest removal yields.
- 4-nonylphenoxyacetic acid was well removed by GAC during all the tests (>97% at the sixth month) as well as 4-nonylphenol mono- and di-ethoxylates (>90% at month 3). 4-nonylphenoxyacetic acid is also well removed by any combination of AOP tested or by ozone alone. The removal of nonylphenol by GAC was around 50% during all the tests and 4-ter octylphenol was decreasingly removed (69% at week 3 and only 6% at month 6).
- Some metals were removed by GAC (chromium, bore, zinc & lead) at the beginning of the tests but were no longer removed after three months. The other metals were not removed by GAC. Copper, zinc, lead and cadmium were partly removed by AOP but the other metals were unaffected or found in higher concentrations at the outlet.

Conclusions.

- The 64 selected micropollutants were detected at the outlet of an MBR, a CAS + SF and a CAS + SF + O₃.
- The tertiary treatments studied, ozone, AOP and activated carbon, were efficient for the removal of most of the micropollutants analysed in this study, except metals.
- Addition of H₂O₂ to O₃ increased significantly the number of substances well removed (>70%), but did not improve the removal of ozone-reactive compounds.
- In AOP processes (O₃/H₂O₂/UV), the applied doses must be optimized according to the refractory pollutants targeted.
- Granular Activated Carbon was still efficient (removal > 70%) after 6 months, especially for most drugs, urea pesticides & triazines.

Perspectives.

In a parallel study (ECHIBIOTEB research program), *in vitro* and *in vivo* biological tests were applied. The goal was to link the presence of contaminants to their effect on biological receptors or living organisms on the samples at the inlet and the outlet of the tertiary treatment processes studied. This approach is described in the abstract "Innovative chemical and biological tools for the evaluation of the efficiency of wastewater advanced treatments".

References

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Other drugs (4)	Carbamazepine, diazepam, ibuprofen, diclofenac	SPE	HPLC/MS/MS	0.5 to 1
Herbicides, pesticides (2)	Glyphosate, AMPA	Derivation	HPLC/MS/MS	100
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Polycyclic Aromatic Hydrocarbons (19)	Napthalene, dibenzothiophene, phenanthrene, anthracene, acenaphthylene, acenaphthene, fluorene, fluoranthene, pyrene, benzo(a)anthracene, chrysene + triphenylene, 2,1 benzo-naphthothiophene, benzo(b+j+k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-cd)pyrene, dibenzo(a,h + a,c)anthracene, benzo(ghi)perylene	SPME	GC/MS	0.1 to 1
Metals (15)	B, Ti, V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Sn, Ba, Pb, U	-	ICP-MS	10 to 2000