Limiting the emissions of micro-pollutants: what efficiency can we expect from wastewater treatment plants?

J. M. Choubert, S. Martin Ruel, M. Esperanza, H. Budzinski, C. Miège, C. Lagarrigue and M. Coquery

ABSTRACT

The next challenge of wastewater treatment is to reliably remove micro-pollutants at the microgram per litre range in order to meet the environmental quality standards set by new regulations like the Water Framework Directive. The present work assessed the efficiency of different types of primary, secondary and tertiary processes for the removal of more than 100 priority substances and other relevant emerging pollutants through on-site mass balances over 19 municipal wastewater treatment lines. Secondary biological processes proved to be in average 30% more efficient than primary settling processes. The activated sludge (AS) process led to a significant reduction of pollution loads (more than 50% removal for 70% of the substances detected). Biofilm processes led to equivalent removal efficiencies compared to AS, except for some pharmaceuticals. The membrane bioreactor (MBR) process allowed to upgrade removal efficiencies of some substances only partially degraded during conventional AS processes. Preliminary tertiary processes like tertiary settling and sand filtration could achieve significant removal for adsorbable substances. Advanced tertiary processes, like ozonation, activated carbon and reverse osmosis were all very efficient (close to 100%) to complete the removal of polar pesticides and pharmaceuticals; less polar substances being better retained by reverse osmosis.

Key words | activated sludge, biofilms, emerging substances, membrane bioreactor, priority pollutants, tertiary treatment

S. Martin Ruel (corresponding author)
M. Esperanza
CIRSEE, Suez Environnement,
38 rue du Président Wilson,
78230 le Pecq,
France

J. M. Choubert
C. Miège
M. Coquery
Cemagref,
UR MALY,
3bis quai Chauveau – CP220,
F-69336 Lyon Cedex 09,
France

H. Budzinski
ISM-LPTC, Université Bordeaux 1,
351 Cours de la libération,
33405 Talence cedex,
France

C. Lagarrigue
Agence de l'Eau Rhône Méditerranée & Corse,
2-4 allée de Lodz,
69363 Lyon cedex 07,
France

INTRODUCTION

Conventional wastewater treatment plants are currently designed to remove macro-pollutants at the mg per litre range, but an increasing number of regulations are pushing to find reliable solutions to remove substances at the microgram per litre level. The European Water Framework Directive (WFD, 2000/60/EC) may be the most representative example, with a list of priority substances for which emissions into the environment have to be reduced or stopped by 2015 and which concentrations in surface waters need to be below defined Environmental Quality Standards (EQS) to reach a good status of the water bodies. Since the diffuse sources of pollution are more difficult to control and to treat than point sources like WWTPs, water operators will probably be strongly impacted by these new rules. The fate of some organic contaminants during wastewater treatment has been documented in the scientific literature (Rogers 1996; Clara *et al.* 2005; Joss *et al.* 2005; Martin Ruel *et al.* 2008; Janex-Habibi *et al.* 2009; Miège *et al.* 2009), as well as the potential removal improvement through specific secondary processes like membrane bioreactors (MBR) (Bernhard *et al.* 2006; Gonzalez *et al.* 2007; Snyder *et al.* 2007; Joss *et al.* 2008) or tertiary treatments (Huber *et al.* 2005; Pereira *et al.* 2007). However, the reported removal efficiencies can be quite variable, and often lack of supporting information about sampling, analysis and process conditions.

doi: 10.2166/wst.2011.009

The present work aims to assess, through on-site mass balances over 19 municipal WWTPs, the efficiency expected with the most representative primary, secondary and tertiary treatments for the removal of priority substances and other relevant organic pollutants. A special care was taken to obtain extended information about process operating conditions, to ensure the reliability of the sampling and analytical protocols and to evaluate global removal efficiencies, taking into account the transfer of micro-pollutants to sludge.

MATERIALS AND METHODS

Substances studied

The list of 33 priority substances of the WFD was considered in this study. The 8 additional substances for which an environmental quality standard (EQS) has been defined were also added (E.C. 2008). Additional substances that could potentially be defined as priority substances in the future have also been included (Table 1). This choice has been set-up according to their potential harmfulness, and their reported occurrence based on French national inventories on dangerous and priority substances. Pharmaceutical compounds (emerging substances) were chosen considering their consumption and their occurrence in wastewater and surface water (GWRC 2008; Miège *et al.* 2009). A total of 125 substances (45 with EQS and 70 without EQS) has finally been selected.

Wastewater treatment plants selection

Nineteen WWTP treatment lines were studied, chosen as representative of various sizes and of various types of treatment processes (Table 2), including:

- seven activated sludge (AS) lines with different operating conditions (loading rate, sludge retention time, temperature), two of them with primary settling (PS);
- three biofilm biological treatment processes for WWTP > 10,000 P.E.: two submerged biofilters (BF, with one and two reactors) and one Moving Bed-BioReactor (MBBR, Biochip 1200 m^2/m^3; filling ratio 50%), all placed after primary settling with chemical addition (PSc);
- three biofilm biological treatment processes for WWTP < 2000 P.E.: Stabilization pond (SP, 3000 m^2) + vertical reed-bed filter (RBF, 100 m^2/filter), Rotating Biological Contactors (RBC, 1468 discs, 8647 m^2) + vertical RBF, and vertical RBF (30 m^2/filter) + horizontal RBF (60 m^2/filter);
- one membrane bioreactor (MBR) process (Ultrafor) equipped with four Zenon ZWD500 modules for a total membrane surface of 10,000 m^2;
- five advanced tertiary treatment lines, including fast tertiary settling and sand filtration as first tertiary steps, UV oxidation (100 Wedeco lamps, 125 W, UV-C, but only 20 in operation), ozonation, micro-filtration (MF, 84 modules, 1350 m^2, hollow polypropylene fibers) + reverse osmosis (RO, 90 modules filmtec BW30-365FR/polyamide); activated carbon filtration (Filtrasorb-400, height = 1.4 m) and ultrafiltration (UF, Norit X-flow, membrane 8" SXL-225 FSFC Aquaflex, polyestersulfone) + RO (Trisep, three membranes 8" 8040-X201-TSA, polyamide urea).

Sampling and analysis

Mass balances were performed based on measurements on the influent, effluent, waste activated sludge and return of sludge dewatering during 2 or 3 successive 24 h-periods under dry weather flow conditions, with refrigerated samplers equipped with Teflon pipes and glass containers. Strict procedures of cleaning, sampling, and field blanks were carried out (US Geological Survey 2002; Choubert *et al.* 2009).

Thirteen methods were developed for the analysis of the selected substances (Table 3). Dissolved and particulate phases were analysed in wastewater, except for VOCs (only raw samples) and some pesticides (only dissolved phase). Particulate phases were analysed in sludge.

Data processing

The calculation of removal efficiency for micro-pollutants proved to be specially complex due to the high variability of concentrations in raw wastewater, to the variation of operating conditions and to high analytical uncertainties associated to very low concentrations of substances in complex matrices.

Several choices were made in order to secure the data produced.

- Two concentrations levels (high level/low level) were defined for each compound and each type of matrix (raw inlet wastewater, treated outlet wastewater and sludge) with respect to their associated limit of quantification (LoQ). When concentration values of the inlet and outlet of the considered process were comprised within the low level or lower than the LoQ, the removal efficiency value was not processed. This resulted from the fact that the analytical uncertainty gets higher for values close to the LoQ. The low concentration level generally

Table 1 | List of substances analysed in this study, with concentration ranges measured in raw and treated wastewaters

	Concentration always < 0.1 µg/l
	Concentration > 0.1 µg/l in raw wastewater
	Concentration > 0.1 µg/l in raw and treated wastewater

	Priority substances (WFD)		Other substances with EQS (WFD)
	Priority substances (to be reduced)	Hazardous priority substances (to be stopped)	
Metals	Nickel Lead	Cadmium Mercury	
PAH	Naphtalene	Anthracene Fluoranthene Benzo(a)pyrene Benzo(b)fluoranthene Benzo(g,h,i)perylene Benzo(k)fluoranthene Indeno(1,2,3-cd)pyrene	
Pesticides	Alachlor Chlorfenvinphos Chlorpyrifos Diuron Isoproturon Atrazine Trifluraline Simazine Pentachlorophenol	Hexachlorocyclohexane Endosulfan	Aldrin DDT Dieldrin Endrin Isodrin
Industry	Benzene Trichlorobenzene DEHP	Hexachlorobutadiene C10-13 Chloroalcanes Pentachlorobenzene Hexachlorobenzene Pentabromodiphenylether	
Solvents and surfactants	Dichloroethane Dichloromethane Chloroform	Nonylphenols Octylphenols	Carbon tetrachloride Tetrachloroethylene Trichloroéthylène

Other relevant and emerging substances in this study					
	β- Blockers	**Antidepressors**	**Analgesics**	**Antibiotics**	**Broncho-dilatants, hypolipemiants**
Pharmaceuticals	oxprenolol metoprolol timolol propranolol nadolol betaxolol bisoprolol acebutolol atenolol sotalol	carbamazepine diazepam nordiazepam Amitriptyline doxepine imipramine Alprazolam Bromazepam Fluoxetine	ibuprofene paracetamol aspirine diclofenac ketoprofen naproxen	Sulphamethoxazole Roxytromicine	clenbuterol salbutamol terbutaline gemfibrozil
Hormones	Estrone (E1)	17a-estradiol (Ea2)	17b-estradiol (Eb2)	Estriol (E3)	Ethinylestradiol (EE2)
Metals	Zn, Li, B, Al, Ti, V, Cr, Fe, Co, Cu, As, Se, Rb, Sb, Mo, Ag, Sn, Ba, U				
Pesticides	Glyphosate	AMPA	Triclosan	Mono-, di-, *tri-, tetra-* chlorophenols	
Industry /solvents / additives	Tri-, Tetra-, *Hexa-,* nonylphenol polyethoxylates	*Octa-*, deca- bromodiphenylether	Tributylphosphates alkylphenol polyethoxyacids	Bisphenol A	Benzothiazoles 4 tertbutylphenol

presented an uncertainty between 30% and 100%, while for the high concentration level the uncertainty was below 30%. The limit between both concentration levels was comprised between 2.5 and 10 times the limit of quantification.

- When only one measurement (inlet or outlet) was lower than the LoQ, a value equal to LQ/2 was adopted for removal efficiency calculation.
- Results were displayed as a removal efficiency range: 0–30%, 30–70% or 70 – 100%.

Table 2 | Characteristics of the WWTPs studied

Code	Size (PE)	Treatment process	Operating conditions
A	2,900	AS (extended aeration)	$L_R = 0.07$ kg BOD/ kg VSS/d, SRT = 25 days, T = 9°C
B	13,000	AS (extended aeration)	$L_R = 0.10$ kg BOD/ kg VSS/d, SRT = 16 days, T = 13°C
C	700,000	PS + AS (high load)	$L_R = 0.35$ kg BOD/ kg VSS/d, SRT = 4.5 days, T = 20°C; Filter: 3 m/h, HRT = 1 h
D	36,000	AS (extended aeration)	$L_R = 0.04$ kg BOD/ kg VSS/d, SRT = 27 days, T = 15°C
E	250,000	PS + AS (low load)	$L_R = 0.08$ kg BOD/ kg VSS/d, SRT = 13 days, T = 20°C
F	50,000	AS (extended aeration)	$L_R = 0.05$ kg BOD/ kg VSS/d, SRT = 26 days, T = 24°C
G	110,000	AS (extended aeration)	$L_R = 0.06$ kg BOD/ kg VSS/d, SRT = 18 days, T = 20°C
H	80,000	PSc + BF 1 stage	Chemical addition: 70 mg/l $FeCl_3$; Filter: 1.4 m/h, HRT = 0.5 h
I	26,000	PSc + BF 2 stages	Chemical addition: 29 mg/l $FeCl_3$; Filter (stage 1 & 2): 1.7 m/h, HRT = 1.4 h
J	17,000	PSc + MBBR	Chemical addition: 72 mg/l $FeCl_3$; Filter (1^{st} stage): HRT = 2.9 h; Filter (2^{nd} stage): HRT = 5.4 h
K	300	PS + SP + vertical RBF	$L_R = 3$ gBOD_5/m^2.d; HRT = 80 d
L	1000	RBC + vertical RBF	$L_R = 5$ gBOD_5/m^2.d; HRT = 5.3 h
M	100	Horizontal RBF + vertical RBF	Horizontal: $L_R = 100$ gBOD_5/m^2.d; HRT = 2 h
N	24,000	MBR	$L_R = 0.06$ kg BOD/ kg VSS/d, SRT = 17 days, T = 24°C, Membrane flux = 23 L/h/m^2
O	300,000	Fast settling + sand filter + UV	Fast settling: 30 mg/l aluminium sulfate, 0.5 mg/l polyelectrolite, lamellar velocity = 3.2 m/h; Sand filter: velocity = 20 m/h; UV dose: 30 mJ/cm^2 (problem in the plant)
P	97,000	Sand filter + O_3	Sand filter: 3.6 m/h; Ozone dosage = 10 g O_3/m^3, contact time = 40 min
Q	25,000	Sand filter + MF + RO	Sand filter: 3.5 m/h; MF: 80 l/m^2/h, 1.6 bar; RO: 20 l/m^2/h, 21 bar
R	500	Silex filter + UF + RO (pilot)	Filter: 7.2 m/h; UF: 50 l/m/h, 2 bar; RO: 23 l/m^2/h, 8 bar
S	470,000	Fast settling + activated carbon filtration (pilot)	Fast settling: 70 mg/l $FeCl_3$, 1 mg/l polyelectrolite, 1 g/l sand, lamellar velocity = 6 m/h; Activated carbon: velocity 0.33 m/h, contact time = 2.1 h

RESULTS AND DISCUSSION

Concentrations in wastewater and sludge

In raw wastewater, about half of the substances with EQS and about 80% of the other relevant substances selected were found at significant concentrations (> 0.1 μg/l) (Table 1). Individual concentrations of substances in raw wastewater could be highly variable from one day to another in the same WWTP, reaching frequently 100%, except for hormones and for most pharmaceuticals. In addition, mean concentrations for each compound were extremely variable from one plant to another, with relative standard deviations often higher than 100%. The substances that could appear at concentration higher than 1 μg/l, were DEHP, some COVs (di- and tri-chloromethane, tri- and tetra- chloroethylene), some flame

Table 3 | Description of analytical methods and limit of quantification (LoQ)

Method	Extraction	Analytical technique	LoQ wastewater (ng/L)	LoQ sludge (µg/kg)
Multiresidue (semi-volatile organics)	Liquid-liquid + Florisil	GC-MS-MS	50 (except DEHP: 1000)	20–100 (except DEHP: 1000)*
COVs (ISO 15680:2003)	Purge & trap	GC-MS	100	Not analysed
Chlorophenols	SPME	GC-MS	50–150*	Not analysed
Pesticides - antibiotics	SPE	HPLC-MS-MS	1–2*	4
Glyphosate/AMPA	SPE	HPLC-MS-MS	100	Not analysed
Chloroalkanes	SBSE	TD-GC-EDC	500	1000
PBDEs / Bisphenol A	SBSE	TD-GC-MS	1–100*	4–50*
Alkylphenols + ethoxylates	SPE	LC-ESI-MS	10	100
Analgesics, antidepressors, broncho-dilatants, hypolipemiants	SPE	LC-MS-MS, UPLC-MS-MS	0.5–2	1–5
Beta-blockers	SPE	LC-ESI(+)-MS/MS	1–5*	Not available yet
Hormones	SPE + Florisil	LC-ESI(-)-MS/MS	1	Not available yet
Mercury	-	AFS	0.5	10
Other metals and metalloids	-	ICP-MS	10–5000	300–3000

*Depending on compound.

retardants (tetra- and decaBDE), AMPA, C10-C13 chloroalkanes, alkylphenols (plus ethoxylates and carboxylates), dichlorophenols, some pharmaceuticals (sulphamethoxazole, carbamazepine, ibuprofen, paracetamol, ketoprofene, naproxene, aspirin, diclofenac, gemfibrozil, acebutolol, atenolol, sotalol) and almost all metals (except Cd, Hg, Sb and U).

In treated water released by biological treatment, about 30% of priority substances and about 60% of substances without EQS were still found at concentrations higher than 0.1 µg/l (Table 1). Even if a significant reduction of concentrations with respect to raw wastewater was generally observed, concentrations higher than 1 µg/l were still frequently found.

All the molecules that were removed from wastewater were not necessarily biodegraded, most of them being adsorbed on sludge. In withdrawn activated sludge (excess sludge), about 35% of the priority substances and 65% of the others substances selected for this study were found at concentrations higher than 100 µg/kg (dry matter). Moreover, concentrations higher than 1000 µg/kg were measured for DEHP, decaBDE, benzothiazole, some PAH (fluoranthene and benzo(a)pyrene), most of the metals (including Hg), alkylphenols (plus ethoxylates and carboxylates), and 3 pharmaceuticals that were present at high concentration in raw wastewater (paracetamol, aspirin, ketoprofen).

Removal efficiencies with primary treatments

Primary settling processes (with or without addition of chemicals) allowed a first removal of about 35% of the 93 substances (20 priority substances and 73 other relevant substances) for which removal efficiencies could be calculated. In particular, adsorbable substances like polybromodiphenylethers, C10-C13 chloroalkanes, PAH and some metals (Al, Ti, Cr, Cu, Zn, Ag, Cd, Sn, Ag, Ba, Pb) were efficiently removed (>70%). However, for the majority of substances, removal efficiencies were about 30% lower for primary treatments in comparison to biological secondary treatments.

Removal efficiencies with conventional secondary treatments (activated sludge)

The ranges of removal efficiencies calculated for the six low load activated sludge plants of this study are presented in Table 4 (mean values).

Table 4 | Comparison of removal efficiencies of the activated sludge process (AS, low load) and of the biofilm biological processes.
PSc: Primary settling with chemical addition; **BF**: Biofilter; **MBBR**: Moving Bed Bioreactor; **RBF**: Reed-bed filter; **SP**: Stabilization pond; **RBC**: Rotating biological contactor. **Compounds in bold** : priority substances; *compounds in italics*: concentration < 0.1 g/l

removal efficiency > 70%
removal efficiency 30 - 70%
removal efficiency < 30%
not determined

Compounds in bold : priority substances; *compounds in italics*: concentration < 0.1 µg/l.

	Biological Biofilm Processes					
	Processes for > 10.000 P.E.			Processes for < 2.000 P.E.		
Low loaded activated sludge process (CAS) [data from 5 WWTP]	**PSc + BF** (1 stage)	**PSc + BF** (2 stages)	**PSc + MBBR** (2 stages)	**SP + vertical RBF** (2 stages)	**RBC + vertical RBF** (2 stages)	**horizontal RBF + vertical RBF** (2 stages)
di-, tri- chlorométhane, tri-, tetra- chloroéthylène						
glyphosate, AMPA, **diuron**, *isoproturon, atrazine, simazine*						
Chlorpyrifos						
Mono-, di- chlorophenols						
Triclosan						
tri-, tetra-, **penta-**, *hexa-*, deca- bromodiphenylether						
DEHP						
4-tert-butylphenol, **nonylphenols, octylphenols**, NP1EO, NP2EO						
Alkylphenol carboxylates						
Bisphenol A						
C10-13 Chloroalcanes, tributylphosphates, benzothiazoles						
Trichlorobenzene						
Naphtalene						
Fluoranthene, Benzo(b)fluoranthene, Benzo(k)fluoranthene						
Li, B, V, Co, As, Rb, Sb						
Ni, Zn, Se, **Cd**, Ba, U, Mo						
Al, Cr, Fe, Cu, Ag, Sn, **Hg**, Ti, **Pb**						
diclofenac						
ibuprofene, paracetamol, ketoprofene, naproxene, aspirine						
sulfamethoxazole, roxithromicine						
carbamazepine, *diazepam, nordiazepam, doxepine*						
Amitriptyline, fluoxetine						
imipramine, bromazepam						
Gemfibrozil						
clenbuterol						
salbutamol, terbutaline						
oxprenolol, propranolol, sotalol						
metoprolol, *timolol*, atenolol						
nadolol, acebutolol, bisoprolol, betaxolol						
estrone, estriol, *estradiol (Ea2, Eb2)*						

The 24 substances removed to less than 30% with activated sludge, therefore passing through the process almost unaffected, include: polar pesticides (e.g., glyphosate, AMPA, diuron) and polar pharmaceuticals (e.g., carbamazepine, diclofenac, sotalol), these molecules are often found at higher concentration at the outlet than at the inlet of secondary treatments (negative yields), mainly due to the degradation of precursors or conjugated forms; alkylphenol carboxylates, also presenting negative yields since they are produced during biological oxidation of alkylphenols; and metals like lithium, arsenic or cobalt.

At the opposite, 48 substances were removed at more than 70%, but their fate (checked through a global mass balance including the inlets and outlets from the sludge line) could be very variable: mainly biodegradation (triclosan, analgesics) or mainly adsorption on sludge (PBDEs, C10-C13 chloroalcanes, heavy PAHs or metals like Al, Fe, Cu, Cr), with the expected contribution of some volatilization. The 21 substances presenting intermediate removal efficiencies also combine these different types of removal mechanisms (with high proportion of volatilization expected for COVs).

It was shown previously that parameters like the sludge age or the loading rate had a great influence on the removal efficiency of micro-pollutants, but no significant influence of temperature could be demonstrated (Martin Ruel *et al.* 2009).

Removal efficiencies with biofilm biological treatment systems

The number of data available for removal efficiencies for biofilm treatment systems are 30% less numerous than the ones measured for low loaded activated sludge. Removal efficiencies obtained are in the same range as those of AS for more than 70% of the substances. Then, about 10% of substances presented significantly lower removal efficiencies than AS (ex : chorophenols, bisphenol A, imipramine, bromazepam, sulphamethoxazole, roxithromicine and gemfibrozil) and about 10% presented significantly higher removal efficiencies than AS (e.g., fluoxetine, metoprolol, atenolol).

Globally, it is therefore difficult to conclude on a difference between attached growth and suspended growth processes. However, it can be observed that extended processes intended for small communities (stabilization ponds, reed beds) tended to achieve higher removal efficiencies than intensive processes intended for high capacity WWTPs (biofilters, MBBR). In addition, two stages biofilm processes are more efficient for substances removal than one stage processes.

Removal efficiencies with advanced secondary treatments (membrane bioreactor)

Removal efficiencies were higher (more than 20% difference) at the MBR plant than at the 6 activated sludge plants studied for 22 of the substances (about 25% of all calculated removal efficiencies), although the sludge age was comparable for all plants. However, the large confidence interval associated to activated sludge data does not allow to confirm definitely this observation.

An increased removal efficiency appeared clearly for adsorbable substances such as decabromodiphenylether or lead, probably due to a slightly higher sludge concentration in the biological tank of the MBR process (5 g TSS/l in MBR vs. 2–4 g TSS/l in AS). The most interesting improvements appear for substances only partially removed (i.e., trichlorobenzene, naphthalene, chlorpyrifos, sulfamethoxazole, metoprolol) during activated sludge processes. The transfer on sludge, assessed by taking into account the concentration of micro-pollutants in sludge, was even reduced for a majority of substances in the MBR process (results not shown). The higher sludge concentration and the specific bacterial population of MBR process may favour biodegradation processes. (See figure 1)

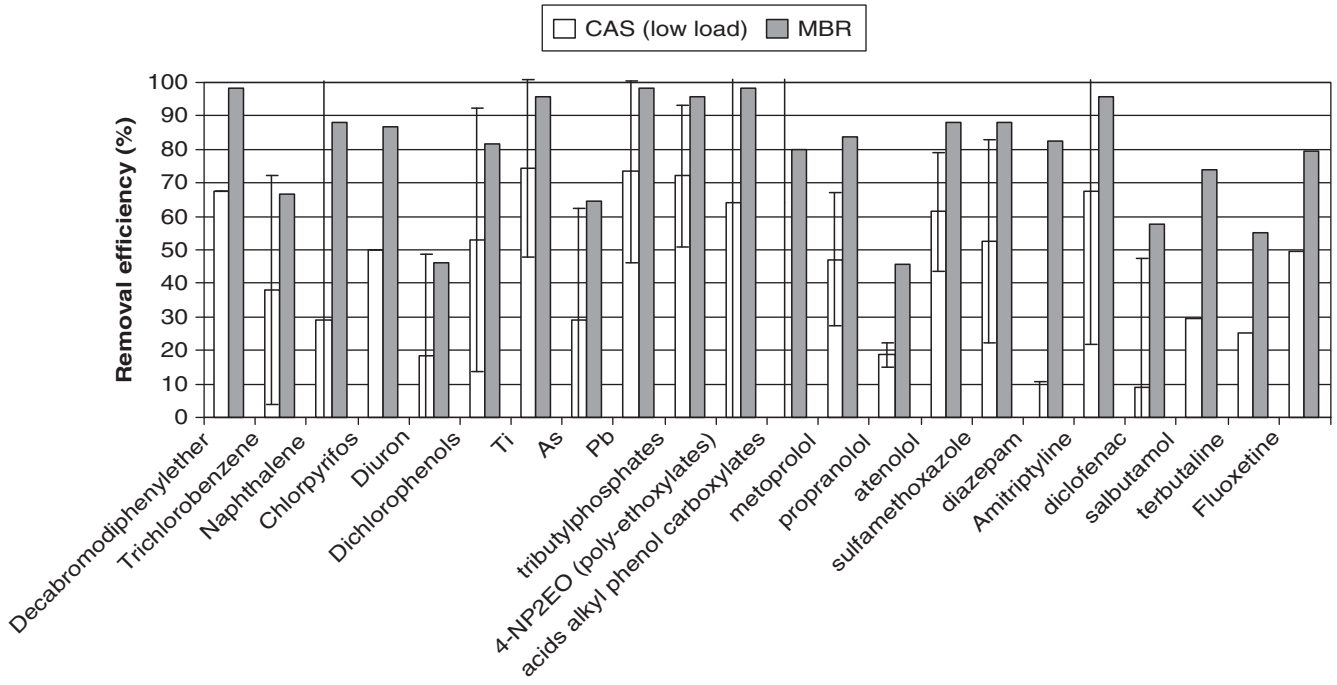

Figure 1 | Removal efficiency of selected substances with conventional activated sludge processes (AS, low load, n = 5) and with MBR process.

Additional removal with advanced tertiary treatments

For the substances present at high concentrations at the outlet of secondary treatments, tertiary treatment solutions may be applied to obtain complementary removal of micro-pollutants. After advanced tertiary treatments, only between 20 and 25% of the selected substances remain in the released treated wastewater at concentrations higher than 0.1 μg/l. Figure 2 presents the proportion of additional removal efficiencies obtained with different tertiary processes.

Some tertiary processes, like fast physico-chemical tertiary settling, sand filtration or micro-filtration, are generally intended to protect more advanced processes located downstream which are quite sensitive to suspended solids. It could be observed that partial removal occurred at this preliminary stage for COVs (40–50%) alkylphenols (60–80%) and metals (35–100%).

Concerning advanced tertiary processes, UV oxidation did not induce any additional removal, at least at the low dose applied on the site studied. At the opposite, ozone oxidation, activated carbon and reverse osmosis all show very high performances towards organic refractory substances: removal efficiencies higher than 75% for polar pesticides and close to 100% for most pharmaceuticals (except aspirin). However, some differences exist between these processes. Reverse osmosis proved to allow the retention of an extended range of substances (especially metals and COVs). Ozone oxidation allowed higher removal for DEHP (75%), not retained by reverse osmosis in this study, but with double bonds accessible to ozone and hydroxyl radicals. Activated carbon adsorption retained a comparable number of substances compared to reverse osmosis (except metals and COVs), but with slightly lower removal efficiencies.

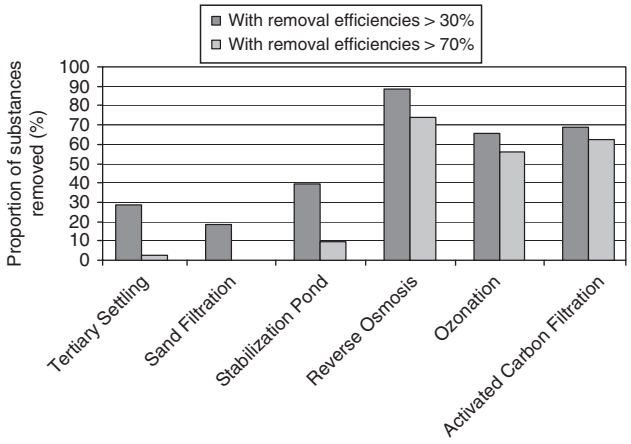

Figure 2 | Proportion of substances presenting additional removal efficiencies with different tertiary processes, of 30% or 70%,with respect to concentrations measured at the outlet of biological secondary processes.

CONCLUSIONS

From on-site mass balances on more than 100 micro-pollutants over 19 treatment lines, the occurrence of relevant micro-pollutants for wastewater treatment could be measured, and expected removal efficiencies of primary, secondary and tertiary processes were assessed.

- About 50% of the priority substances are detected at low concentrations (<0.1 μg/L) or not detected.
- Primary settling processes show removal efficiencies above 70% for a few very adsorbable substances, but about 30% lower removal efficiencies than secondary biological processes.
- The conventional activated sludge process (AS low loaded) and biological attached growth processes show comparable removal efficiencies, with more than 30% removal efficiency for about 70% of the substances quantified in inlet raw water.
- The design parameters of biological processes (e.g.,1 stage/2 stage biofilters, size of biological tanks), which influence the loading rate, have a measurable impact on removal efficiency towards micro-pollutants.
- The MBR process studied present an increased efficiency for about 25% of the substances quantified in inlet raw water, especially those partially degraded during activated sludge processes, but the removal mechanisms still need to be fully understood.
- Preliminary tertiary processes like tertiary settling and sand filtration can already achieve significant removal for selected substances.
- Advanced tertiary processes, like ozonation, activated carbon and reverse osmosis are all very efficient (close to 100%) to complete the removal of polar pesticides and pharmaceuticals. Reverse osmosis allows the retention of a wider range of substances, but it is also the most costly and the fate of the concentrate should be mastered to get a sustainable process. Ozone oxidation is the cheapest option but the fate and toxicity of by-products still remaining an issue to be investigated. Activated carbon filtration appears as well as an interesting alternative, but returns of experience in terms of reliability and life duration of adsorbing material for removal of micro-pollutants in wastewater are presently lacking.

Conventional processes such as load loaded AS can therefore lead to a significant reduction of pollution loads, but complementary treatments would be required to more efficiently decrease the concentrations of refractory substances in treated waters. The choice of the most appropriate technology should be made by balancing the affordable cost with water quality objectives.

ACKNOWLEDGMENTS

This study was supported by the French National Research Agency, in the framework of the AMPERES project and by the RI Alliance research foundation. We especially thank all technical staff of analytical laboratories and process teams for their contribution to the production of the data presented.

REFERENCES

Bernhard, M., Mueller, J. & Knepper, T. 2006 Biodegradation of persistent polar pollutants in wastewater: comparison of an optimised lab-scale membrane bioreactor and activated sludge treatment. *Water Res.* **40**(18), 3419–3428.

Choubert, J.-M., Martin-Ruel, S. & Coquery, M. 2009 Prélèvement et échantillonnage des substances prioritaires et émergentes dans les eaux usées. Les prescriptions techniques du projet de recherche AMPERES. Techniques Sciences et Méthodes n°4, 88–98.

Clara, M., Kreuzinger, N., Strenna, B., Gansb, O. & Kroiss, H. 2005 The solids retention time–a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. *Water Res.* **39**, 97–106.

European Community 2008 Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86.

Gonzalez, S., Petrovic, M. & Barcelo, D. 2007 Removal of a broad range of surfactants from municipal wastewater – comparison between membrane bioreactor and conventional activated sludge treatment, *Chemosphere* **67**, 335–343.

GWRC 2008 Development of an international priority list of pharmaceuticals relevant for the water cycle. April 2008. 23p.

Huber, M., Göbel, A. & Joss, A. 2005 Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents : a pilot study. *Environ. Sci. Technol.* **39**, 4290–4299.

Janex-Habibi, M. L., Huyard, A., Esperanza, M. & Bruchet, A. 2009 Reduction of endocrine disruptor emissions in the environment: The benefit of wastewater treatment. *Water Res.* **43**, 1565–1576.

Joss, A., Keller, E., Alder, A. C., Göbel, A., McArdell, C. S., Ternes, T. & Siegrist, H. 2005 Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Res.* **39**(14), 3139–3152.

Joss, A., Siegrist, H. & Ternes, T. A. 2008 Are we about to upgrade wastewater treatment for removing organic micropollutants? *Water Sci. Technol.* **57**(2), 251–255.

Martin Ruel, S., Choubert, J.-M., Ginestet, P. & Coquery, M. 2008 Semiquantitative analysis of a specific database on priority substances in wastewater and sludge. *Water Sci. Technol.* **57**(12), 1935–1944.

Martin Ruel, S., Esperanza, M., Choubert, J. M., Bruchet, A. & Audic, J. M. 2009 On-site evaluation of the efficiency of the activated sludge process for the removal of 60 organic micropollutants. Xenowac Conference (Cyprus, 11–13 March 2009), 8p.

Miège, C., Choubert, J.-M., Ribeiro, L., Eusebe, M. & Coquery, M. 2009 Removal efficiency of pharmaceuticals and personal care products with varying wastewater treatment processes and operating conditions : conception of a database and first results. Environmental Pollution **157**, 1721–1726.

Pereira, V. J., Linden, K. G. & Weinberg, H. S. 2007 Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Res.* **41**, 4413–4423.

Rogers, H. R. 1996 Sources, behaviour, fate of organic contaminants during sewage treatment. *Science of the Total Environment* **185**(1-3), 3–26.

Snyder, S. A., Adham, S., Redding, A. M., Cannon, F. S., DeCarolis, J., Oppenheimer, J., Wert, E. C. & Yoon, Y. 2007 Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* **202**(1–3), 156–181.

US Geological Survey 2002 National Field Manual for the Collection of Water-Quality Data. TWRI BOOK 9. 180p.