"Ozone" and "GAC filtration" synergy for removal of emerging micropollutants in a drinking water treatment plant?

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ABSTRACT

Ozonation plays an essential role in water disinfection to inactivate viruses, bacteria and some parasites (*Giardia*). Ozone treatment rates to attain disinfection goals also result in oxidation reactions of emerging pollutants. Pharmaceuticals–except Ciprofloxacin–are very reactive to ozone: they are removed as early as the transfer compartment outlet even at an ozone treatment rate of less than 1 g/m^3. Glyphosate, AMPA, Amitrole and Diuron–the four major pesticides in the Seine, Marne and Oise rivers–are reactive to ozone. Twenty-one pesticides are only partially reactive to ozone and an additional "GAC filtration" is needed to remove them. Further investigations have been planned to study the removal of Phthalates, Nonylphenols and Hormones by combining the "Ozone" and "GAC filtration" process units.

Key words | GAC, micropollutants, ozone, pesticides, pharmaceuticals

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INTRODUCTION

On behalf of the Syndicat des Eaux d'Ile de France (SEDIF), Veolia Water operates three major Drinking Water Treatment Plants (DWTP) located in the cities of Neuilly-sur-Marne, Choisy le Roi and Mery-sur-Oise. These treatment plants use water from respectively the Marne, Seine and Oise rivers and produce 800,000 m^3 of drinking water daily for 4 million people (144 towns in the Paris region).

Surface water of the Paris region remains vulnerable and contaminated by a wide range of micro-organisms and emerging micropollutants. Therefore, water sanitation has to be guaranteed by multiple treatment units in a strategic "multi-barrier" approach involving coagulation-flocculation-filtration units and specific disinfection steps (ozone, UV and chlorine steps).

Ozonation is implemented for disinfection purposes, but produces by-products like bromate as well. Engineering and process modifications have to be carried out to comply with bromate regulations without compromising disinfection goals. At ozone treatment levels used, oxidation reactions have a significant impact on pesticides, emerging micropollutants (pharmaceuticals, phthalates, nonylphenols and hormones), taste precursors and organic matter.

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MICROPOLLUTANTS IN SEDIF DWTP: CONTEXT

The water treatment process of the Neuilly-sur-Marne DWTP (see Figure 1) consists of clarification (coagulation-flocculation-settling and sand filtration), ozonation, Granular Activated Carbon (GAC) filtration and chlorination (with sodium hypochlorite)-dechlorination (with sodium bisulfite) prior to distribution.

Regarding raw water microbiological contamination levels, ozonation remains an essential disinfection step in the multi-barrier context.

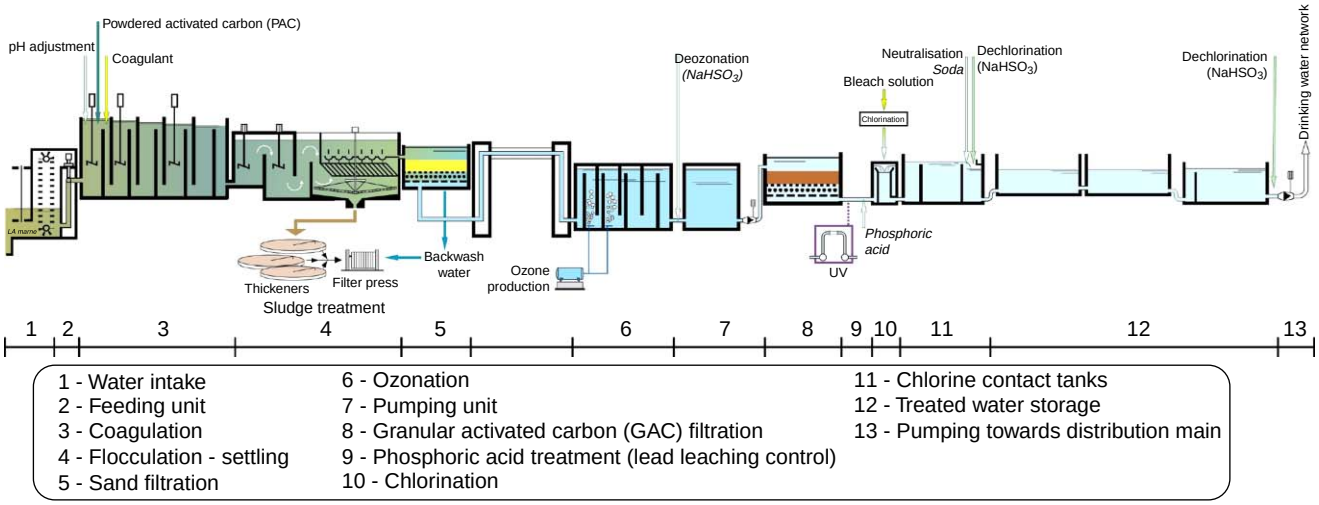

Figure 1 | SEDIF Neuilly-sur-Marne DWTP flowsheet.

Micropollutants contamination levels in the Seine, Marne and Oise rivers

The 98/83 European Directive introduced a duty of care to any substance that may cause a human health hazard. Monitoring the presence of emerging micropollutants in rivers is essential for the water industry. Studies on pesticides, pharmaceuticals, phthalates, nonylphenols and hormones have been implemented several years ago (Branchereau *et al.* 2006; Paffoni *et al.* 2006).

Pesticides: in 2007, 32 pesticides were detected at least once in raw water of one of the rivers. Among them, 11 were detected in a river with a concentration exceeding at least once the maximum threshold of 0.10 µg/L. Important pesticides in the Seine, Marne and Oise rivers are Glyphosate, Aminomethylphosphonic Acid (AMPA), Amitrole and Diuron (see Figure 2).

Pharmaceuticals: over the reference period 2004–2008, among the 20 substances analysed, analgesic Paracetamol, antiepileptic Carbamazepin and lipid regulator Bezafibrate are the most frequently detected compounds in the Seine, Marne and Oise Rivers (see Figure 2).

It is necessary to carry out pilot scale tests to quantify the efficiency of the "ozonation" followed by "GAC filtration" to remove such pesticides and emerging micropollutants from surface water. This article presents experimental results from an "ozonation" and "GAC filtration" pilot plant fed by Sand Filtered Water (SFW) spiked with targeted micropollutants.

MATERIAL AND METHODS

The pilot unit consists of an ozonation-deozonation step linked to a GAC filtration column (see Figure 3). The system is continuously fed by SFW from the Neuilly-sur-Marne drinking water plant. Bromide or micropollutants are injected into the feeding line via a static mixer. Moreover the pH can also be automatically controlled by

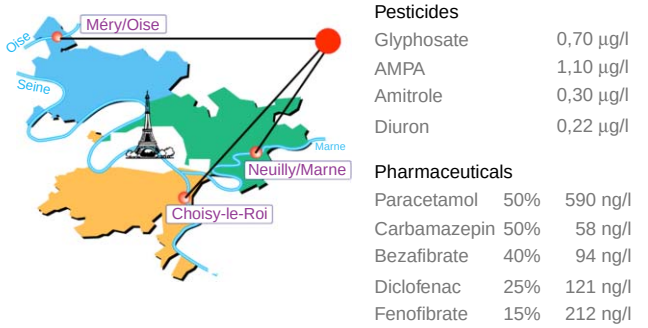

Figure 2 | Seine, Marne and Oise pesticides and pharmaceuticals contamination levels (extracts)–2007 Data–Detection frequency (%) and-or Maximum concentration observed (ng/L or µg/L).

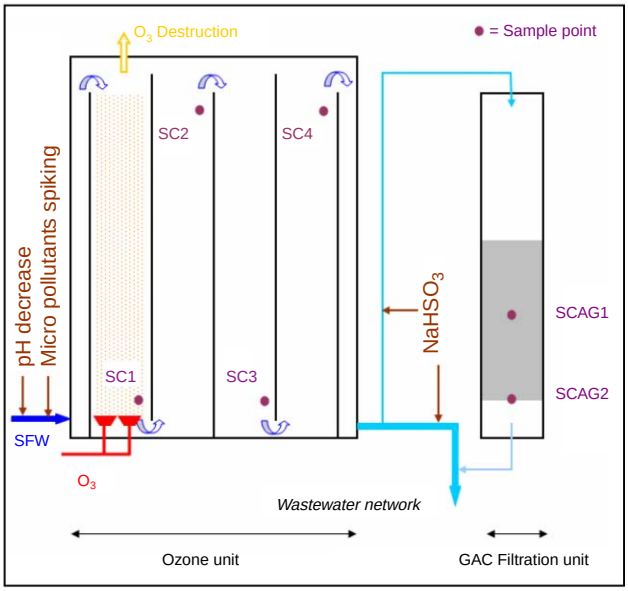

Figure 3 | Pilot used for ozonation combined with GAC filtration studies.

online sodium hydroxide or sulphuric acid injection. The pilot geometry is a rectangular tank with one transfer chamber and three contact chambers and the following characteristics: hydraulic efficiency ratio of 0.70[1] and hydraulic residence time of 17 minutes for a mean flow rate of 12 m^3/h. Gas/Liquid ozone transfer is achieved in the first chamber working as a bubble column with two porous diffusers and counter current ozonated gas and SFW flows. The 300 mm diameter GAC column contains a two metres GAC filter bed. The substrate of this filter bed comes from one full scale GAC filter in Neuilly-sur-Marne plant with an operating life equivalent to 21,000 bed volumes processed. The column is fed with ozonated-deozonated water from the ozonation unit with 750 L/h mean flow rate and 11 minutes mean contact time between water and filtering medium. The GAC unit is backwashed weekly (air, water and air + water backwash steps).

The operator of the pilot unit uses a man-machine interface system. This system includes specific automatic regulation loops to control SFW Flow rate, SFW pH, Ozone production or Ozone residual outlet and Ozone quenching upstream GAC filtration. At the beginning of each test, the operator can select a specific test level of ozone or instruct the pilot unit to fix the end-level of ozone. Then spiking of micropollutants is carried out to simulate medium or maximum concentrations found in the Seine, Marne and Oise rivers.

Samples are collected for analysis after a period of two hydraulic residence times, in order to reach a steady state. Some analyses – pH, Temperature, Alkalinity (AT), UV_{254}, ozone gas and liquid residual – are carried out on the spot. Ozone concentration measurements in "Air" and "Vent" gases are continuously monitored with sensors "Uvozon" and "BMT 964". Daily controls are also carried out using an iodometric method to assess the ozone concentrations in gases. A sensor "Depolox" continuously monitors the ozone concentration of the water at the pilot outlet. Two or three samples are made per outlet chamber per test based on the method described by Bader & Hoigné (1981). Micropollutants analyses are carried out using High Performance Liquid Chromatography (HPLC) or Gas Chromatography (GC) methods followed by either fluorescence, or mass spectrometry or UV detection.

[1] The hydraulic efficiency ratio α is the ratio between the time required for 10% of the water to pass through the contactor and the Hydraulic Residence Time (HRT = V/Q, where V is the volume of the contactor and Q is the flow through this contactor).

RESULTS AND DISCUSSION

Pharmaceutical tests

Seven tests have been carried out with an ozone treatment level ranging from 0 to 2.1 g/m^3 and with the following experimental conditions: $7.3 < pH < 7.4$, $17.2 < T(°C) < 17.6$, $0.097 < UV_{254}$ (cm^{-1}) < 0.130 and $A_T = 4.0$ meq/L. Table 1 shows the concentrations of pharmaceuticals tested in the spiked SFW. These concentrations remained constant during the three days test runs.

During the first test, without ozone, a very significant potential of GAC adsorption with a 10 minutes contact time (see Table 1) was measured. If we extrapolate these results, effective removal of pharmaceuticals in the DWTP can be guaranteed by GAC filtration. Erythromycin is partially adsorbed on a layer of GAC, but the initial concentration of Erythromycin spiking of 3 μg/L is too high compared to normal concentrations measured in the Seine, Marne and Oise rivers.

The tests with ozone show a very significant reactivity of these compounds to ozone. However, we would like to point out (see Table 1):

1. Very reactive molecules are removed as early as the transfer chamber outlet: Paracetamol, Diclofenac, Phenazone, Carbamazepin, Metoprolol, Propranolol, Sulfamerazine, Sulfamethoxazole, Sulfachloropyridazine, Ofloxacin, Spiramycin, Roxithromycin and Tylosin.
2. Less reactive molecules are only partially removed at the outlet of the contact chambers: Ketoprophen, Fenofibrate, Bezafibrate and Ciprofloxacin. Complete removal of these compounds is achieved downstream in the GAC filters, except for Ciprofloxacin.

These results are comparable to the results found in the literature concerning "batch", "pilot" or "full scale" studies (Ternes *et al.* 2002; Huber *et al.* 2003; Uvbiama & Craik 2004; Westerhoff *et al.* 2005; Hua *et al.* 2006; Jasim *et al.* 2006; Snyder *et al.* 2006*b*; Snyder *et al.* 2007; Ternes 2007; Vieno *et al.* 2007; Kim *et al.* 2008; Sein *et al.* 2008; Snyder 2008). The European project POSEIDON (Ternes 2007) established basic knowledge on removal of pharmaceuticals in drinking water treatment: "Ozonation", "GAC filtration" and "Nanofiltration" are very effective processes to remove pharmaceuticals, with the exception of iodinated contrast substances. (Snyder *et al.* 2006*a*,*b*; Snyder *et al.* 2007; Snyder 2008) described the removal of pharmaceuticals observed in full scale DWTP. "Clarification" or "UV" units don't eliminate these molecules. "Ozonation", "GAC filtration", "Membrane filtration" and "Chlorination" can be very effective processes to fully eliminate these molecules. (Vieno *et al.* 2007) studied the behaviour of pharmaceuticals in a pilot treatment file fed by river water. This unit combined "Coagulation with ferric salts", "Settling", "Sand filtration", "Ozonation", "GAC filtration" and "UV". Only Ciprofloxacin was able to pass all these steps. These results match our observations of partial removal by ozone as well as partial adsorption by the GAC filter (see Table 1).

Our results confirm the results of previous works dealing with the efficiency of "Ozonation" and "GAC filtration" to remove pharmaceuticals: most of the targeted compounds in our study are very reactive with ozone and are removed as early as the transfer chamber outlet even with an ozone treatment rate lower than 1 g/m^3; a synergetic effect appears by combining "Ozonation" and "GAC filtration". Thus, Ketoprofen, Bezafibrate and Fenofibrate compounds which are only partially oxidized by ozone can be removed from treated water. Only Ciprofloxacin molecule would be able to pass through these process units and could be found downstream in the DWTP.

Pesticides tests

Six tests have been carried out with an ozone treatment level ranging from 0 to 2.3 g/m^3 and with the following experimental conditions: $pH = 7.3$, $16.9 < T(°C) < 17.7$, $0.143 < UV_{254}$ (cm^{-1}) < 0.184 and $A_T = 4.4$ meq/L. Tables 2a & 2b show the concentrations of pesticides tested in the spiked SFW. These concentrations remained constant during the test runs which lasted three days.

During the first test, without ozone, a very significant potential of GAC adsorption with a 10 minutes contact time was measured. Shorter contact time – about 5 minutes – would imply only partial retention for these pesticides: 16 compounds on a total of 36 would be able to pass through this GAC filtration process unit (see Tables 2a and 2b).

Furthermore, the presence of Glyphosate, AMPA, Bentazone and Carbofuran downstream GAC filtration

Table 1 | Average pharmaceuticals concentrations in spiked Sand Filtered, ozonated and GAC filtered water matrix

			Water flow rate = 12 m^3/h & 7.3 < pH < 7.4 & 17.2 < T (°C) < 17.6 & 0.097 < UV_{254} (cm^{-1}) < 0.130 & A_T = 4.0 meq/L					
			Ozone treatment rate = 0 g/m^3		Ozone treatment rate: 0.8–2.1 g/m^3 Dissolved ozone residual: 0.11–0.79 mg/L CT: 0.9–6.2 mg min/L			
Pharmaceuticals	**Limit of quantification (ng/L)**	**Average SFW* concentration (ng/L) ($n = 2$)**	**SCAG1† concentration (ng/L) $\tau \sim 5$ min**	**SCAG2† concentration (ng/L) $\tau \sim 10$ min**	**SC1‡ concentration (ng/L) Minimum–Maximum ($n = 3$)**	**SC4§ concentration (ng/L) Minimum–Maximum ($n = 6$)**	**SCAG2† concentration (ng/L) Minimum–Maximum ($n = 2$)**	**Ozone removal (%) Minimum–Maximum**
Bezafibrate	10	825	36	<10	205–266	<10–66	<10	92–99
Carbamazepin	10	486	33	<10	<10	<10	<10	>98
Ciproflexacin	10	57	<10	<10	<10–21	<10–21	<10–22	63–82
Diclofenac	10	542	33	<10	<10	<10	<10	>98
Erythromycin	25	2,862	805	289	29–75	<25–143	<25–218	>95
Fenofibrate	25	112	<25	<25	<25–55	31–93	<25	17–72
Ketoprofen	25	842	66	<25	478–480	262–425	<25	50–70
Metoprolol	25	297	<25	<25	<25–35	<25	<25	>92
Ofloxacin	10	58	<10	<10	<10	<10	<10	>83
Paracetamol	10	1,073	<10	<10	13–33	<10	<10	>99
Phenazone	25	591	32	<25	<25	<25	<25	>96
Propanolol	10	222	<10	<10	<10	<10	<10	>95
Roxithromycin	10	149	38	<10	<10	<10	<10–24	>93
Spiramycin	10	170	20	<10	<10	<10	<10	>94
Sulfachloropyridazine	10	1,241	175	28	<10–40	<10	<10	>99
Sulfamerazine	25	501	62	<25	<25	<25	<25	>95
Sulfamethoxazole	10	428	132	31	<10–20	<10	<10	>98
Tylosine	10	240	44	14	<10–13	<10	<10	>96

*Spiked sand filtered water.
†GAC filtration outlet.
‡Transfer chamber outlet.
§Contact chambers outlet.

Table 2a | Average pesticides concentrations in spiked Sand Filtered, ozonated and GAC filtered water matrix

			Water flow rate = 12 m^3/h & pH = 7.3 & 16.9 < T (°C) < 17.7 & 0.143 < UV_{254} (cm^{-1}) < 0.184 & A_T = 4.4 meq/L					
			Ozone treatment rate = 0 g/m^3		Ozone treatment rate: 1.2–2.3 g/m^3 Dissolved ozone residual: 0.13–0.68 mg/L CT: 1.1–5.4 mg min/L			
Pesticides	**Limit of quantification (μg/L)**	**Average SFW* concentration (μg/L) (n = 3)**	**SCAG1† concentration (μg/L) τ ~ 5 min**	**SCAG2† concentration (μg/L) τ ~ 10 min**	**SC1‡ concentration (μg/L) Minimum–Maximum (n = 5)**	**SC4§ concentration (μg/L) Minimum–Maximum (n = 5)**	**SCAG2† concentration (μg/L) Minimum–Maximum (n = 5)**	**Ozone removal (%) Minimum–Maximum**
Acetochlore	0.02	0.28	0.05	<0.02	0.14–0.19	0.08–0.14	<0.02	50–71
Alachlore	0.02	0.17	0.03	<0.02	0.09–0.12	0.02–0.11	<0.02	34–88
Amitrole	0.10	1.17	<0.10	<0.10	<0.10	<0.10	<0.10	>91
AMPA‖	0.10	0.80	0.70	0.60	0.20–0.70	<0.10	<0.10	>88
Atrazine	0.02	0.16	<0.02	<0.02	0.12–0.15	0.10–0.13	<0.02	19–38
Azoxystrobine	0.02	0.22	0.04	<0.02	<0.02	<0.02	<0.02	>91
Bentazone	0.02	0.26	0.12	0.10	<0.02	<0.02	<0.02	>92
Bromuconazole	0.02	0.20	<0.02	<0.02	0.06–0.16	0.08–0.16	<0.02	21–61
Carbendazime	0.02	0.41	<0.02	<0.02	<0.02	<0.02	<0.02	>95
Carbetamide	0.02	0.35	<0.02	<0.02	0.15–0.21	0.07–0.11	<0.02	69–80
Carbofuran	0.02	0.97	0.29	0.06	0.18–0.54	<0.02–0.07	<0.02	93–> 98
Chloridazone	0.10	1.40	<0.10	<0.10	0.24–0.73	<0.10–0.21	<0.10	85–> 93
Chlortoluron	0.02	0.23	<0.02	<0.02	<0.02	<0.02	<0.02	>91
DCPMU¶	0.02	0.09	<0.02	<0.02	<0.02	<0.02	<0.02	>77
DEA**	0.02	0.29	<0.02	<0.02	0.27–0.32	0.29–0.54	<0.02	–
DEDIA††	0.02	0.27	<0.02	<0.02	0.28–0.33	0.30–0.35	<0.02	–
Deethylterbumeton	0.02	0.26	0.03	<0.02	0.21–0.28	0.22–0.26	<0.02	1–16
DIA‡‡	0.02	0.28	<0.02	<0.02	0.23–0.30	0.22–0.26	<0.02	6–20

*Spiked sand filtered water.
†GAC filtration outlet.
‡Transfer chamber outlet.
§Contact chambers outlet and.
‖Aminomethylphosphoric acid.
¶3,4-dichlorophenyl-methylurea.
** Deethylatrazine.
††Deethyldeisopropylatrazine.
‡‡Deisopropylatrazine.

Table 2b | Average pesticides concentrations in spiked Sand Filtered, ozonated and GAC filtered water matrix

			Water flow rate = 12 m^3/h & pH = 7.3 & 16.9 < T (°C) < 17.7 & 0.143 < UV_{254} (cm^{-1}) < 0.184 & A_T = 4.4 meq/L					
			Ozone treatment rate = 0 g/m^3		Ozone treatment rate: 1.2–2.3 g/m^3 Dissolved ozone residual: 0.13–0.68 mg/L CT: 1.1–5.4 mg min/L			
Pesticides	**Limit of quantification (μg/L)**	**Average SFW* concentration (μg/L) (n = 3)**	**SCAG1† concentration (μg/L) τ ~ 5 min**	**SCAG2† concentration (μg/L) τ ~ 10 min**	**SC1‡ concentration (μg/L) Minimum–Maximum (n = 5)**	**SC4§ concentration (μg/L) Minimum–Maximum (n = 5)**	**SCAG2† concentration (μg/L) Minimum–Maximum (n = 5)**	**Ozone removal (%) Minimum–Maximum**
Dichloroprop	0.05	0.20	0.05	<0.05	0.14–0.18	0.11–0.13	<0.05	35–45
Difenoconazole	0.04	0.19	<0.04	<0.04	0.04–0.16	<0.04–0.14	<0.04	25– > 79
Dimetachlore	0.02	0.22	0.04	<0.02	0.08–0.14	0.06–0.11	<0.02	50–73
Diuron	0.02	0.47	<0.02	<0.02	<0.02–0.13	<0.02	<0.02	>96
Ethofumesate	0.02	0.28	<0.02	<0.02	0.16–0.24	0.10–0.21	<0.02	26–65
Fluquinconazole	0.02	0.14	<0.02	<0.02	<0.02–0.11	<0.02–0.07	<0.02	50– > 86
Flusilazole	0.02	0.15	<0.02	<0.02	0.03–0.10	0.04–0.10	<0.02	32–73
Glyphosate	0.10	1.07	0.60	0.50	<0.10	<0.10	<0.10	>91
Hydroxyatrazine	0.02	0.12	<0.02	<0.02	0.11–0.12	0.09–0.10	<0.02	19–27
Imazamethabenz-methyl	0.02	0.21	0.07	0.02	0.15–0.21	0.14–0.19	<0.02	10–33
Isoproturon	0.02	0.45	<0.02	<0.02	<0.02	<0.02	<0.02	>96
MCPA‖	0.05	0.42	0.06	<0.05	0.12–0.19	<0.05–0.06	<0.05	86– > 88
Mecoprop	0.05	0.15	0.05	<0.05	<0.05–0.06	<0.05	<0.05	>67
Metazachlore	0.02	0.13	0.03	<0.02	0.03–0.08	0.02–0.07	<0.02	46– > 85
Metolachlore	0.02	0.30	0.06	<0.02	0.17–0.20	0.11–0.15	<0.02	50–63
Piclorame	0.05	0.15	<0.05	<0.05	0.10–0.16	0.09–0.14	<0.05	7–40
Prochloraze	0.02	0.14	<0.02	<0.02	<0.02	<0.02	<0.02	>86
Propazine	0.02	0.16	0.03	<0.02	0.13–0.16	0.11–0.16	<0.02	0–30

*Spiked sand filtered water.
†GAC filtration outlet.
‡Transfer chamber outlet.
§Contact chambers outlet and.
‖(4-chloro-2-methylphenoxy)acetic acid.

has to be noticed. These results match with previous works dealing with "batch" data (Roche *et al.* 2004).

The tests with ozone show that three groups of components could be distinguished according to their reactivity to ozone:

1. Very reactive molecules are removed as early as transfer chamber outlet: Azoxystrobine, Amitrole, Bentazone, Carbendazime, Chlortoluron, DCPMU, Glyphosate, Isoproturon and Prochloraz.
2. Less reactive molecules are removed at contact chambers outlet: MCPA, AMPA, Carbofuran, Chloridazone, Diuron and Mecoprop.
3. Weak reactive molecules are only partially removed at contact chambers outlet: Acetochlore, Alachlore, Atrazine, DEDIA, Bromuconazole, Carbetamide, DIA, DEA, Deethylterbumeton, Dichlorprop, Difenoconazole, Dimethachlore, Ethofumesate, Fluquinconazole, Flusilazole, Hydroxyatrazine, Imazamethabenz-methyl, Metazachlore, Metolachlore, Piclorame and Propazine.

Our experimental results emphasize the need to combine "Ozonation" and "GAC filtration" process units to remove such micropollutants. Concerning our initial spiking compounds, we would like to point out that 9 molecules are very reactive to ozone and are already removed at the transfer chamber outlet, 6 molecules are reactive to ozone and are removed at the outlet of the contact chambers. On the other hand, 21 molecules remain partially reactive to ozone with very variable removal rates, ranging between 10% and 70%, even for favourable ozonation conditions such as an ozone treatment rate of 2.3 g/m^3 and a temperature of 17°C. It is also important to point out that the 4 pesticides which are not adsorbed in GAC filter (Glyphosate, AMPA, Bentazone and Carbofuran) are reactive or very reactive to ozone (Ikehata & Gamal El-Din 2005; Lau *et al.* 2007). Consequently, the synergy of "Ozonation" and "GAC filtration" process units is necessary to remove such compounds.

CONCLUSIONS

In the context of a multi-barrier DWTP, ozonation remains an essential disinfection step: its capacity to inactivate viruses is necessary to control health risks. The ozone treatment levels needed to reach disinfection targets can also remove several emerging pollutants by oxidation like pesticides, pharmaceuticals, phthalates, nonylphenols and hormones. GAC filtration removes micropollutants which are weakly reactive to ozone. The synergy of the two process units is necessary to eliminate such emerging micropollutants.

Pharmaceuticals are reactive or very reactive to ozone. They are removed at the transfer compartment outlet even at an ozone treatment level below 1 g/m^3. We will retain that Ciprofloxacin can pass through the "Ozonation" and "GAC filtration" process units and can be detected downstream in the DWTP.

Glyphosate, AMPA, Amitrole and Diuron are reactive or very reactive to ozone. The ozonation process unit is necessary to remove the four major micropollutants of the Seine, Marne and Oise rivers since GAC filtration is not efficient in removing Glyphosate and AMPA. Nevertheless, 21 pesticides–micropollutants which are less common in rivers–remain only partially reactive to ozone and an additional GAC filtration is needed to remove such compounds.

But, this work has to be completed with the investigation of the disinfection by-products formed during ozonation of sand filtered water spiked with pesticides or pharmaceuticals.

REFERENCES

Bader, H. & Hoigné, J. 1981 Determination of ozone in water by the indigo method. *Water Res.* **15**, 449–456.

Branchereau, V., Fauchon, N. & Thibert, S. 2006 Perturbateurs endocriniens et résidus médicamenteux dans les rivières d'Île-de-France. *Tech. Sci. Méthodes* (12), 69–78.

Hua, W., Bennet, E. R. & Letcher, R. J. 2006 Ozone treatment and the depletion of detectable pharmaceuticals and atrazine herbicide in drinking water sourced from the upper Detroit River, Ontario, Canada. *Water Res.* **40**(12), 2259–2266.

Huber, M. M., Canonica, S., Park, G.-Y. & von Gunten, U. 2003 Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ. Sci. Technol.* **37**(5), 1016–1024.

Ikehata, K. & Gamal El-Din, M. 2005 Aqueous pesticide degradation by ozonation and ozone-based advanced oxidation processes: a review (part I). *Ozone Sci. Eng.* **27**(3), 173–202.

Jasim, S. Y., Irabelli, A., Yang, P., Ahmed, S. & Schweitzer, L. 2006 Presence of pharmaceuticals and pesticides in Detroit River water and the effect of ozone on removal. *Ozone Sci. Eng.* **28**(6), 415–423.

Kim, I. H., Tanaka, H., Iwasaki, T., Takubo, T., Morioka, T. & Kato, Y. 2008 Classification of the degradability of 30 pharmaceuticals in water with ozone, UV and H_2O_2. *Water Sci. Technol.* **57**(2), 195–200.

Lau, T. K., Chu, W. & Graham, N. 2007 Degradation of the endocrine disruptor carbofuran by UV, O_3 and O_3/UV. *Water Sci. Technol.* **55**(12), 275–280.

Paffoni, C., Welte, B., Gousailles, M. & Montiel, A. 2006 Nouvelles molécules mises en cause par les directives européennes: de la station d'épuration à l'usine de traitement d'eau potable. *Eur. J. Water Qual.* **37**(1), 21–38.

Roche, P., Lescouret, A.-S. & Suty, H. 2004 *Traitabilité de composés phytosaniataires sur une filière de traitement*. 16èmes Journées Information Eaux, Poitiers.

Sein, M. M., Zedda, M., Tuerk, J., Schmidt, T. C., Golloch, A. & von Sonntag, C. 2008 Oxidation of diclofenac with ozone in aqueous solution. *Environ. Sci. Technol.* **42**(17), 6656–6662.

Snyder, S. A., Adham, S., Redding, A. M., Cannon, F. S., DeCarolis, J., Oppenheimer, J., Wert, E. C. & Yoon, Y. 2006*a* Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* **202**(1–3), 156–181.

Snyder, S. A., Wert, E. C., Rexing, D. J., Zegers, R. E. & Drury, D. D. 2006*b* Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. *Ozone Sci. Eng.* **28**(6), 445–460.

Snyder, S. A., Wert, E. C., Lei, H., Westerhoff, P. & Yoon, Y. 2007 *Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes*. American Water Works Association (AWWA) & AWWA Research Foundation & IWA Publishing.

Snyder, S. A. 2008 Occurence, treatment, and toxicological relevance of EDCs and pharmaceuticals in water. *Ozone Sci. Eng.* **30**(1), 65–69.

Ternes, T. 2007 The occurence of micropollutants in the aquatic environment: a new challenge for water management. *Water Sci. Technol.* **55**(12), 327–332.

Ternes, T. A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H.-J., Haist-Gulde, B., Preuss, G., Wilme, U. & Zulei-Seibert, N. 2002 Removal of pharmaceuticals during drinking water treatment. *Environ. Sci. Technol.* **36**(17), 3855–3863.

Uvbiama, D. R. & Craik, S. A. 2004 *Degradation of Diclofenac–a Pharmaceutical Drugs–in Drinking Water Using Advanced Treatment Processes*. Annual conference of the Western Canada Water and Wastewater Association, Calgary, Alberta.

Vieno, N. M., Härkki, H., Tuhkanen, T. & Kronberg, L. 2007 Occurence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant. *Environ. Sci. Technol.* **41**(14), 5077–5084.

Westerhoff, P., Yoon, Y., Snyder, S. & Wert, E. 2005 Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environ. Sci. Technol.* **39**(1), 6649–6663.