

## By-products in surface and reclaimed water disinfected with various agents

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### Abstract

Pollution of natural water resources and water shortages make it difficult to cope with the total demand for water (potable, industrial, agricultural uses). As a consequence, the interest for alternative resources, such as reclaimed wastewater, is growing. In this field, new needs are coming to the attention of researchers, especially with respect to compounds potentially toxic for the environment and human health. Disinfection by-products (DBPs) formation is therefore a subject to be closely examined since the disinfection process is the final step of nearly all post-treatment schemes. Information on DBPs formation, when biologically treated and filtered wastewater is disinfected with sodium hypochlorite (NaClO), peracetic acid (PAA) or UV irradiation, is given with reference to the results of long-term pilot-scale research on disinfection for wastewater reclamation and reuse. When NaClO was used, total trihalomethanes (TTHMs) concentration did not comply with the new Italian law for direct agricultural reuse, despite the good quality of the effluent to be reclaimed. On the contrary, the use of PAA, quite frequently utilised as a NaClO substitute in Italy, led to no significant DBPs formation. A set of tests using UV irradiation confirmed, also in this field, the overall safety of this disinfection agent with respect to DBPs formation. This work deals also with drinking water treatment, giving information on the risk of DBPs formation when PAA is used for surface water pre-disinfection. In this case, very low concentrations of aldehydes were observed and no formation of halogenated by-products was evidenced, even at high TOC content.

*Keywords:* DBPs; Disinfectants; Surface water; Drinking water; Pre-disinfection; Reclaimed water; Reuse

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## 1. Introduction

Disinfection by-products (DBPs) have been recognised for a long time as a major problem, especially when surface water has to be disinfected to produce safe drinking water. However, more recently, the interest has been focused not only on drinking water disinfection, but also when disinfection is the key factor of a reclamation train used to produce renovated water for irrigation, while reducing the possible risk of contaminating water aquifers.

The recent Italian legislation for wastewater reclamation and reuse provides a good example of this trend. In fact, the original Water Quality Act [1] was substituted in 1999 by a new act [2], which displayed a better focus on reuse practices; the implementation of specific standards for reuse was nevertheless transferred to a future decision and finally, after 4 years of debate, a new set of standards was approved last year [3]. In Table 1 the main parameters are summarised. The new Italian regulations for wastewater reclamation and reuse apply to various reuse practices (urban,

Table 1

Reuse of reclaimed water for irrigation in Italy: examples of regional guidelines compared with present and proposed national standards (excerpt: 23 out of the 54 parameters listed)

No.	Parameters	Previous standards [1]	New standards [3]	
			Reference values	Sampling interval
1	pH	—	6.0, 9.5	W <sub>24h</sub>
2	SAR	<15	10	W <sub>24h</sub>
4	TSS (mg/L)	<sup>a</sup>	10 <sup>b</sup>	W <sub>24h</sub>
5	BOD <sub>5</sub> (mg/L)	—	10 <sup>b</sup>	W <sub>24h</sub>
6	COD (mg/L)	—	50 <sup>b</sup>	W <sub>24h</sub>
7	Phosphorus (mg P/L) (total)	—	10 <sup>d</sup>	W <sub>24h</sub>
8	Nitrogen (mg N/L) (total)	—	35 <sup>d</sup>	W <sub>24h</sub>
10	EC <sub>w</sub> (µS/m)	—	3,000	W <sub>24h</sub>
12	Arsenic (mg As/L)	—	0.02 <sup>b</sup>	W <sub>24h</sub>
14	Boron (mg B/L)	—	1.0	W <sub>24h</sub>
15	Cadmium (mg Cd/L)	—	0.005	W <sub>24h</sub>
17	Chromium (mg Cr/L) (total)	—	0.1 <sup>b</sup>	W <sub>24h</sub>
31	Sulphate (mg SO <sub>4</sub> /L)	—	500	M
34	Chlorine residual (mg/L)	—	0.2	M
35	Chloride (mg Cl/L)	—	250	M
<b>41</b>	<b>Total aldehydes (mg/l)</b>	—	<b>0.5</b>	<b>M</b>
43	VOC (mg/L)	—	0.04	M
<b>44</b>	<b>TTHMs (mg/L)</b>	—	<b>0.03</b>	<b>M</b>
49	Surfactants (mg/L) (total)	—	0.5	M
50	Chlorinated biocides (mg/L)	—	0.00001 <sup>e</sup>	M
53	<i>E. coli</i> (CFU/100 mL)	—	10 <sup>b,e</sup>	D <sup>b</sup> /W
54	<i>Salmonellae</i> (CFU/100 mL)	—	Absent	D <sup>b</sup> /W
	<i>T. coliforms</i> (MPN/100 mL)	2 <sup>b</sup> /20	—	—

D/W/M: daily/weekly/monthly sample; W<sub>24h</sub>: weekly, on a 24-h sample.

<sup>a</sup>Low enough to avoid soil clogging. <sup>b</sup>Unrestricted irrigation (spray irrigation not allowed, also in public parks). <sup>c</sup>0.03 µg/L for Aldrin, Dieldrin, Eptachlor epoxide. <sup>d</sup>Depending on crop requirements and aquifer characteristics. <sup>e</sup>80% of samples, never higher than 100 UFC/100 mL for single samples; this figure will be accepted as reference standard for the first 3 years of application.

agricultural and industrial, with the exception of internal recycles) and refer various distribution systems (dedicated networks or small surface bodies with low natural flows). As shown in Table 1, wastewater reuse standards take into account at least two possible DBPs: TTHMs and aldehydes, which, respectively, are derived mainly from chlorination and ozonation. Other possible DBPs like chlorites and chlorates, coming from chlorine dioxide, are not taken into account.

TTHMs appear to be a particularly limiting parameter, which will in most cases prevent the future use of chlorination for wastewater reclamation, as outlined from the experimental studies described in this paper.

In the following, the main results referring to DBPs formation during disinfection of surface and reclaimed water are reported. All experimental data were collected using the same pilot plant, with various disinfecting agents: for reclaimed water, NaClO, PAA and UV rays were compared; for surface water, PAA was evaluated as a NaClO substitute for water pre-disinfection.

## 2. Materials and methods

### 2.1. Overall pilot plant description

Research trials were performed on a large modular pilot plant (see Fig. 1 for layout), oper-

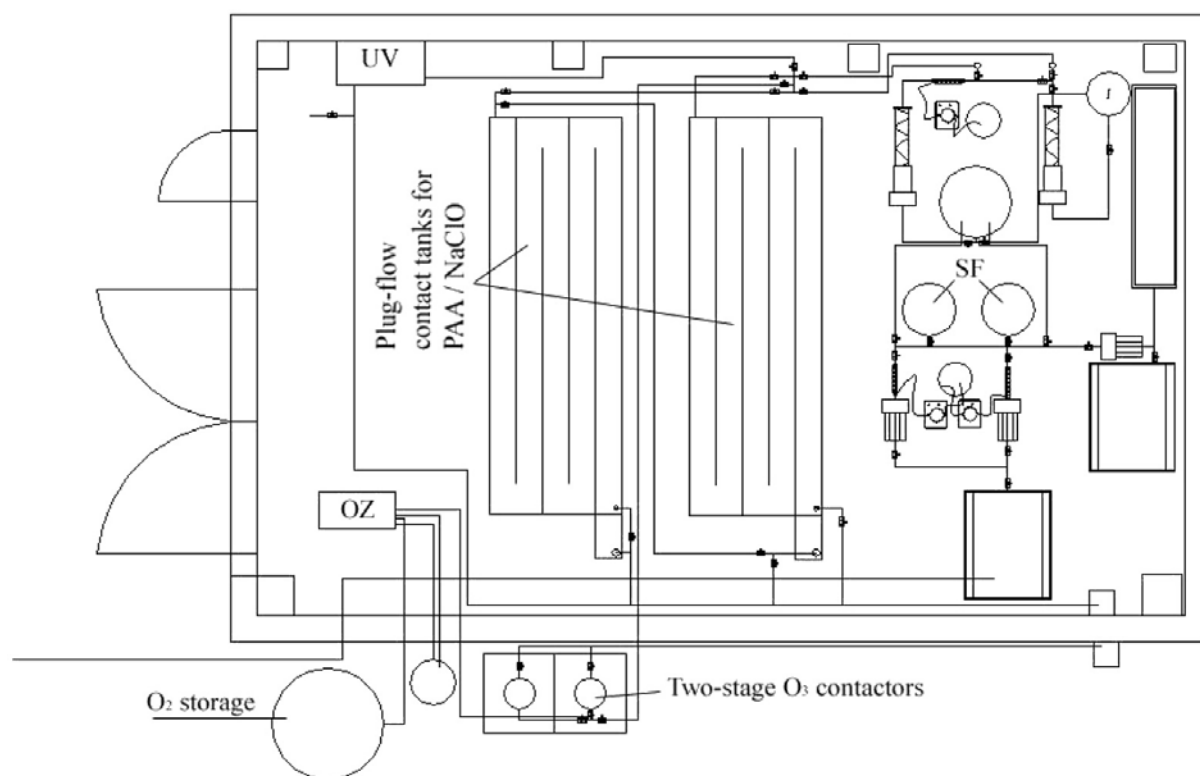


Fig. 1. Sketch scheme of the pilot plant in its complete configuration. I, flash-mixer; SF, sand filters; OZ, ozonator; UV, UV plant) [4].

ating at a continuous flow-rate up to 4.5 m<sup>3</sup>/h; the different modules were operated or not, depending on the type of trials to be performed. In its complete layout, the plant is based on a rapid sand filtration (or contact filtration) step (1st module) — working at 10.6 m/h as a maximum — followed by a disinfection module (four alternative disinfection sections in-parallel, not simultaneously operated: NaClO, PAA, ozone and UV irradiation).

When NaClO and PAA were used, contact took place in two “chicane” in-series tanks having a volume of 2.2 m<sup>3</sup> each. The hydrodynamics of the tanks was preliminary evaluated through impulsive tracer (KCl) tests at the same conditions (temperature, flow-rate, water characteristics) of disinfection tests, and the behaviour of the tanks was confirmed to be very similar to that of an ideal plug-flow reactor. Both agents were dosed by peristaltic pumps and mixed with water using, respectively, an in-line static mixer and a flash-mixing tank.

Ozone was produced from pure oxygen and contact took place in two in-series columns (diameter: 350 mm; height: 5 m; volume: 0.48 m<sup>3</sup>) and was counter-currently injected through fine ceramic diffusers at the bottom of each column.

UV radiation was applied thorough a 4.5 L quartz reactor, equipped with six low-pressure Hg lamps (active emission length: 789 mm; power: 30 W), vertically mounted around the reactor.

### 2.2. Reclaimed water tests

The pilot plant was fed with the biological effluent (nitrification–denitrification) of the Pero municipal wastewater treatment plant (WWTP), located near Milan (Italy); its influent wastewater was highly diluted, both in terms of physico-chemical and microbiological parameters, due both to high water consumption and to a relevant contribution of industrial cooling waters. As a consequence, the Pero WWTP effluent showed COD concentrations usually below 25 mg/L (the

peak values registered were on the order of 90 mg/L); TOC, TSS, turbidity and transmittance at 254 nm wavelength were, respectively, in the range of: 2.4–12 mg/L; 3–24 mg/L; 2–9 NTU and 51–84%. *E. coli*, *F. coli* and *T. coli* were, respectively, in the 60–65,000, 350–640,000 and 20,000–1,200,000 CFU/100 mL range. In all the trials, the sand filtration step was used and three disinfectant agents were dosed: NaClO, PAA and UV irradiation.

### 2.3. Surface water tests

The pilot plant was fed with water coming from an irrigation canal (Canale Villoresi), distributing the water derived from the Ticino River to a large area north of Milan (Consorzio di Bonifica Est Ticino). The raw water characteristics were: TOC, 1.7–4.9 mg/L; TSS, 1–6 mg/L; turbidity, 1–5 NTU; *T. coli*, 600–22,000 CFU/100 mL; *F. coli*, 100–8,000 CFU/100 mL.

In this case, the filtration step was by-passed and only PAA was dosed into one of the two plug-flow tanks previously described.

### 2.4. Analytical procedures

Samples were collected in glass bottles, completely filled up and in case stored at 4°C until analysis. With respect to samples collected after disinfection, when chemical agents were used, sodium thiosulphate 0.2 N was added to stop the oxidation process; when UV radiation was applied, dark glass bottles lined with an aluminium sheet were used.

Temperature, pH, turbidity, TSS, COD, TOC and absorbance/transmittance (detected at 254 nm wavelength or as UV/visible spectrum) were measured on the influent to the pilot plant, on the effluent from the filtration step (when used) and on the effluent from any specific disinfection section. When disinfection was performed using chemical agents, residual disinfectant was also measured at different contact times. THMs and

aldehydes were determined on samples collected before and after the disinfection step. All the analyses were performed according to the Italian Standard Methods [5], very similar to American Standard Methods [6].

TOC was measured on an analyzer (Shimadzu, TOC 5050A), having a 1 mg/L detection limit and 10% RSD. Absorbance/transmittance were measured by UV/visible spectrophotometer (Pye Unicam UV2).

Qualitative analyses on other DBPs were carried out by the GC–MS (HP GCD mass analyser): the same sample was extracted with two different methods: (1) by solid phase micro-extraction, with a 100  $\mu\text{m}$  polymethylsiloxane fibre for low molecular weight compounds; and (2) by liquid–liquid extraction of the acidified sample ( $\text{pH} < 2$ ) with dichloromethane for high molecular weight compounds.

### 3. Wastewater disinfection tests for reclamation and reuse

A long-term pilot-scale study on disinfection, partially funded by the Italian Ministry for University and Scientific Research, was performed on secondary wastewater to be reclaimed for reuse in agriculture; the work was mainly aimed at checking the technical and economical feasibility of alternative disinfectants to chlorine. Various agents were tested and compared:  $\text{NaClO}$ , PAA, UV radiation and ozone; due the limited number of data on ozonation available till now, they will not be discussed here.

Many aspects were examined closely to investigate the influence of operational parameters and influent characteristics on microbial inactivation kinetics (*T. coli*, *F. coli* and *E. coli*) and to check possible by-products formation. Microbial re-growth potential was also evaluated to monitor the possible quality changes of disinfected water at the reutilisation point.

The approach to the DBPs study was both qualitative and quantitative, through the measure

of specific compounds, generally known as typical by-products and non-specific ones (TOC). TTHMs formation potential was always evaluated as absorbance measured at 254 nm wavelength ( $\text{UV}_{254}$ ).

#### 3.1. $\text{NaClO}$ disinfection

Quantitative measurements were used to evaluate THMs formation, particularly chloroform, bromodichloromethane, dibromochloromethane and tribromomethane. Typical results are summarised in Fig. 2 for different contact times (HRT: 6, 12, 18, 36 min) and two chlorine doses (5 and 7.5 mg/L), capable of complying with the requested microbiological standards at contact times exceeding 30 min. More in detail, it is easy to recognise that the data summarised in Fig. 2 are at any contact time unable to comply with the fixed standard for TTHMs (see Table 1, No. 44). It must be noted that the lowest TTHM values obtained after 36 min were 40.6  $\mu\text{g/L}$  and 44.4  $\mu\text{g/L}$  (at a 5 and 7.5 mg/L dose, respectively). In any case, these values are higher than the requested standard (30  $\mu\text{g/L}$ ), even if the tests were performed on quite diluted biological effluents (like every modern biological plant, however, Pero WWTP produces well nitrified effluents) [7].

In Fig. 3 the evolution of TTHMs formation and of total and free chlorine is summarised. After the initial chlorine consumption, the decay rate decreases significantly, tending to an asymptote. The difference between total and free chlorine appears to be almost constant in the first 36 min. In parallel, TTHMs concentration increases rapidly in the first 6 min, attaining more than 50% of the value measured after 36 min. Probably due to the narrow ranges of variation of water physicochemical parameters, formation of TTHM seems not strongly influenced by the increase of  $\text{NaClO}$  dose: the ranges are 40.6–56.3  $\mu\text{g/L}$  and 44.4–62.0  $\mu\text{g/L}$  at 5 and 7.5 mg/L, respectively.

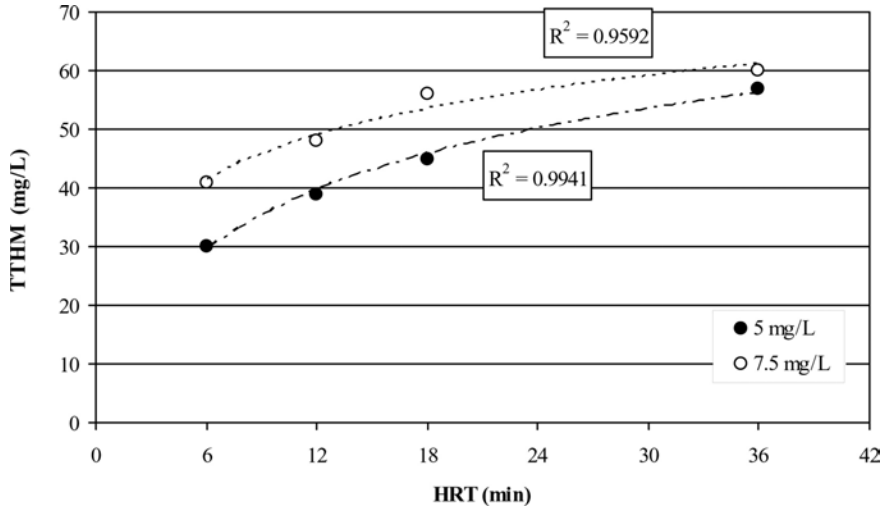


Fig. 2. TTHMs average production after chlorination (two doses: 5 and 7.5 mg/L) of a diluted nitrified effluent ( $N-NH_4 = 0.4\text{--}1.8$  mg/L;  $UV_{254} = 0.32\text{--}0.87$ ) [7].

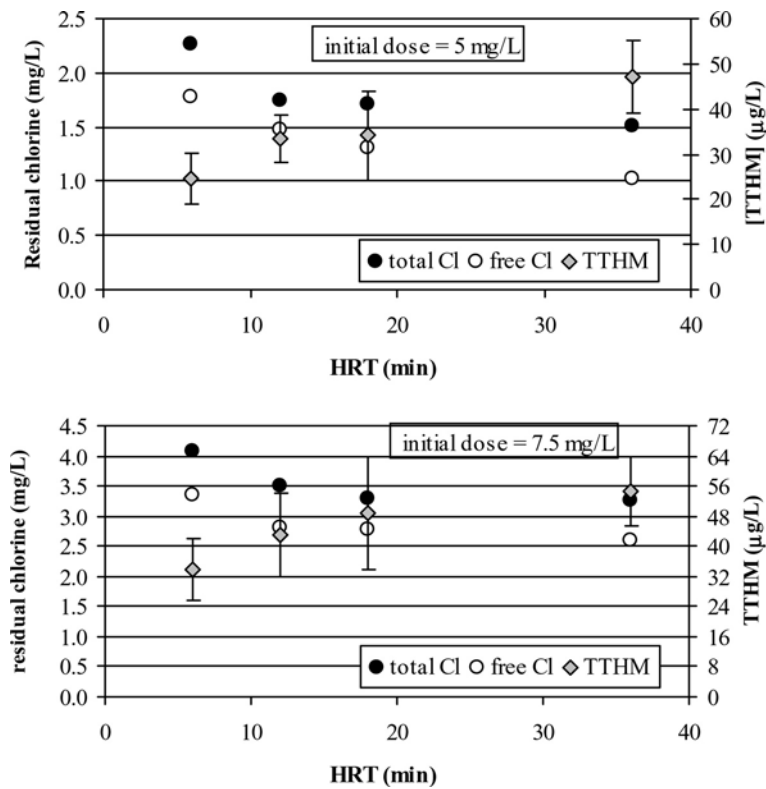


Fig. 3. TTHMs, total and free chlorine concentrations vs. contact time during chlorination, respectively, at 5 mg/L and 7.5 mg/L (applied doses).

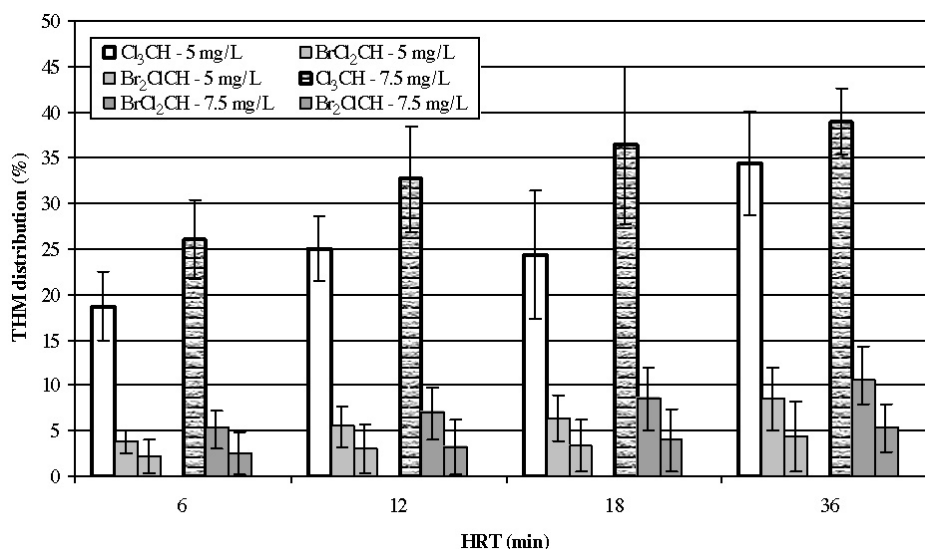


Fig. 4. TTHMs distribution vs. contact time after chlorination of a diluted nitrified effluent.

As far as speciation of TTHMs is concerned, tribromomethane was never detected, while chloroform was the main by-product formed (28.0–39.0  $\mu\text{g/L}$  and 35.0–42.0  $\mu\text{g/L}$  for the NaClO doses previously cited). As shown in Fig. 4, TTHMs distribution does not vary very much with the disinfectant dose applied. Furthermore, it can be noted that chloroform formation kinetics is very fast and its concentration tends to be constant or to slightly decrease. On the contrary, the percentages of bromodichloromethane and dibromochloromethane seem to slowly increase during tests.

Brominated species were produced by electrophilic reaction involving hypobromous acid. On the other hand, hypochlorous acid reacts with organic matter by a radical transfer mechanism so formation rates of brominated compounds were derived to be slower than chlorinated compounds. The absence of tribromomethane is likely to be ascribed both to the low bromine concentration in the Pero WWTP effluent and to the insufficient time for the completion of the reaction (monitoring was stopped at 36 min).

Qualitative analyses performed on samples collected after chlorination at 7.5 mg/L and for 6 and 36 min contact times did not show evidence for the formation of high molecular weight by-products. In fact, only in one of the samples collected, another possible by-product (polypropylene, at 6 min contact time) was detected, but this finding cannot be considered significant.

### 3.2. PAA disinfection

In Italy, PAA is being considered as a suitable substitute for chlorine-based disinfectants. This takes advantage of some useful characteristics of this compound: it can be used in a similar way to NaClO (using similar contact tanks), it is available as a ready-to-use agent and it displays acceptable disinfectant properties, even if at increased operational costs. Nevertheless, the studies referring to its capability of producing DBPs are not yet sufficient [8–10].

Generally speaking, high concentrations of chloride, PAA, organic and mineral compounds seem to be needed for the formation of chlorine-

based by-products. The formation of chlorine-based free radicals may occur if PAA is dosed in the presence of catalysts (such as organic compounds and mineral salts) which favour chloride oxidation into water having a sufficient amount of chloride (NaCl: 100–400 mg/L) and containing enough organic matter. PAA is a strong oxidant so it can react with organic compounds such as amino acids, phenols, anilines and other aromatics present in a wastewater effluent forming aldehydes as DBPs [9]. At PAA doses of 6–30 mg/L, phenol can act as an acceptor of free radicals. In deionised water, in the presence of 400 ng/L of phenol, used as a model compound, PAA does not oxidise  $\text{Cl}^-$  to HClO or free radicals able to lead to the formation of chlorine-based by-products [8]. The addition of PAA to an aqueous solution of humic acids enriched with chlorides does not produce an increase of absorbable halogenated organics (AOX) nor of total halogenated organics (TOX), suggesting that chlorides are not oxidised to HClO. On the contrary, if the solution is enriched with bromides, an increase of AOX and bromoform can be observed, suggesting that PAA can oxidise bromides to HBrO leading to the formation of brominated by-products [9]. The insufficient amount of information has therefore led to the need to perform research on DBPs formation during disinfection with PAA, not only with respect to nitrified effluents to be reclaimed, but also especially with reference to the pre-disinfection of surface water using PAA as a substitute for chlorine-derived agents.

As far as reclaimed water disinfection is concerned, only qualitative analyses were performed on samples collected for the highest PAA applied doses (15 and 25 mg/L, as pure agent) and for different contact times (6, 12, 18, 36 min). These doses were chosen since the probability of DBPs formation increases with the amount of the agent. Only for samples treated with the highest dose were some DBPs detected. In fact, two aldehydes,

nonanal and decanal, were confirmed — the former being present in a slightly higher percentage of abundance. The formation kinetics for both aldehydes seems to follow a Gaussian trend. However, available data are not sufficient to explain the shifts of the peak position (for contact times equal or higher than 12 min) observed in different tests. The low DBPs production observed can also be related to the low precursor concentration, correlated to the overall good quality of the effluent used for reclamation tests.

### 3.3. UV disinfection

Inactivation of microorganisms by UV radiation, unlike chemical agents, is based on photo-chemical reactions capable of modifying DNA and RNA structures. As a consequence, it is possible to suppose that UV radiation by similar photo-chemical reactions is able to modify the structures of some compounds present in water, thus producing potentially toxic DBPs [11,12]. It was noted that many organic compounds — especially compounds containing ring structures such as phenols, benzene, pyrimidine (heterocyclic nitrogen compounds) — can absorb UV radiation at 254 nm, which is the wavelength of the radiation emitted by Hg lamps used for water disinfection, reacting either directly or indirectly. In a direct reaction, a molecule (named chromophore, such as amine-based and phenol-based ones) can be chemically modified via direct absorption of UV radiation, while in an indirect reaction of UV, radiation is significantly absorbed by photosensitive species (such as nitrite/nitrate ions and humic compounds) and radicals, able to react with other organics, are produced [13,14]. UV radiation at low doses ( $<50 \text{ mJ/cm}^2$ ), often used for diluted wastewater, influences the decomposition of organic compounds only marginally [15]. Nevertheless, when UV irradiation is used to degrade organic compounds (e.g., pesticides), therefore operating at high intensity



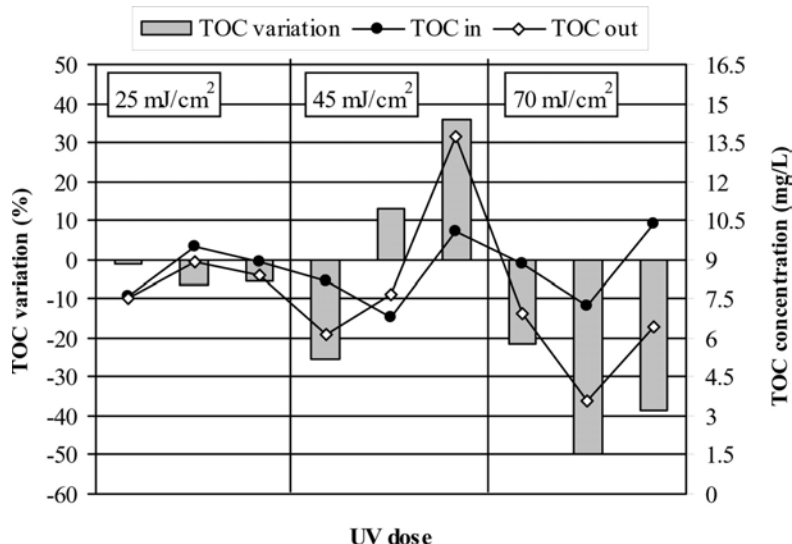


Fig. 5. TOC variation before and after UV ray disinfection of a filtered effluent.

(>1,000 mJ/cm<sup>2</sup>), it can generate DBPs [16,17]. Disinfection of clarified and filtered effluent by UV radiation at 100–160 mJ/cm<sup>2</sup> has not determined the respective formation of N-nitrosamine and nitro-phenols [10].

Some qualitative tests were therefore performed disinfecting Pero WWTP effluent at various UV doses (25, 45, 70 mJ/cm<sup>2</sup>). TOC variation and the UV/visible spectra were recorded in this phase of the study, but no specific compounds were investigated. Results in terms of TOC concentrations are summarised in Fig. 5. At the lowest UV dose (25 mJ/cm<sup>2</sup>), no significant TOC variation was observed. However, TOC reductions >25% always occurred at the highest dose used (70 mJ/cm<sup>2</sup>). Data related to the 45 mJ/cm<sup>2</sup> dose do not show any stable trend, but it must be pointed out that this set of samples showed considerable variability with respect to the characteristics of the effluent. The UV/visible spectra of samples before and after 70 mJ/cm<sup>2</sup> irradiation were determined, but no significant difference could be found, possibly suggesting that no organic compound transformation took place

during the disinfection process. As a consequence, TOC reduction could be explained assuming some mineralization of organic carbon to CO<sub>2</sub>, but clearly further research is needed to obtain more sound results.

#### 4. Surface water pre-disinfection

A set of tests was also performed on surface water, using the water of the Canale Villoresi and directly disinfecting it at relatively low PAA doses, without any previous type of treatment. The aim of this part of the study was to investigate the possible use of PAA as a NaClO substitute in the plants having a pre-chlorination facility, taking advantage of the capability of this agent to be used with contact techniques quite similar to those of NaClO. Investigations were related only to bromine-based by-products and to aldehyde formation (CHCl<sub>3</sub>, CHBr<sub>3</sub>, TTHM, formaldehyde, acetaldehyde, 2-heptenal, bromate), considered potentially toxic for human health. PAA doses, used to simulate pre-disinfection of surface water at different contact times (30 and

45 min) were, respectively, 1, 3, 5, and 10 mg PAA/L (as pure agent). Trials were organised to investigate the influence of PAA doses, bromides and organic carbon content in the water to be disinfected, so that two different sets of trials were performed modifying initial water characteristics.

Trial set 1: bromide content was varied (baseline value: 0.01 mg/L) with the addition of KBr, to reach a Br final content of 0.9 mg/L, while the organic content was not modified (see Table 2 for TOC concentration; pH = 8.2). With the exception of seawater intrusion cases or of anthropogenic pollution, a bromide value greater than 0.1 mg/L is not common in surface waters. Therefore, the situation implemented represents an extreme case, experimentally useful to examine closely PAA behaviour in case of quite high bromide concentration. Samples were collected after 30 min of disinfection and residual PAA was inactivated after 3.5 h from sampling to simulate the time asked by subsequent normal treatments for TSS removal.

Trial set 2: the organic content of surface water was increased (TOC = 3.2–4.9 mg/L; pH = 8.9–9.1) mixing it, just before the inlet section of the contact tank, with a concentrated solution (TOC = 2,000 mg/L), obtained by a prolonged

contact (some days) in alkaline conditions (NaOH = 0.1 M) with acid peat and soil rich in organic carbon, simulating in this way a water rich in humic and fulvic acids. Samples were collected after 45 min contact time. Inactivation of residual PAA was performed as before, with the exception of tests at 10 mg PAA/L, for which some samples were not inactivated; the analyses on these samples were postponed for 2 weeks after sampling.

Results obtained are hereafter summarised: Trial set 1 — As summarised in Table 2, there was no significant formation of monitored by-products; TTHMs and bromate maintained concentrations lower than analytical detection limit (0.1 µg/L and 2 µg/L, respectively). However, an appreciable amount of formaldehyde (detection limit: 1 µg/L) could be observed. These considerations remain valid for both of the examined conditions (bromides at baseline value and at the increased value). In conclusion, despite a very high bromide concentration, when organic content is low and probably not very oxidable, there is no evidence of DBPs formation.

Trial set 2 — The higher amount of oxidable organic carbon, at similar bromide concentrations, led to a significant increase in by-products, especially of aldehydes (see Fig. 6). No appreciable formation of THMs was ever observed,

Table 2

Initial characteristics and DBPs formed after pre-disinfection of surface water with PAA (applied doses: 1, 3, 5 mg/L)

Br <sup>-</sup> mg/L	TOC mg/L	Cl <sup>-</sup> mg/L	PAA mg/L	TTHMs µg/L	FA <sup>a</sup> µg/L	AA <sup>b</sup> µg/L	2-heptenal µg/L	Bromate µg/L
0.01	1.7	3	0	<0.1	1.1	14.5	1.1	<2
0.01		3	1		1.1	14.5	1.3	
0.01		3	3	<0.1				<2
0.01	1.7	3	5	<0.1	2.0	14.4	1.2	
0.9	2.0	3	1	<0.1	1.2	14.4	1.3	
0.9	2.9	3	3	<0.1	1.5	13.3	1.2	<2
0.9		3	5	<0.1	1.9	13.1	1.3	

<sup>a</sup>Formaldehyde. <sup>b</sup>Acetaldehyde.

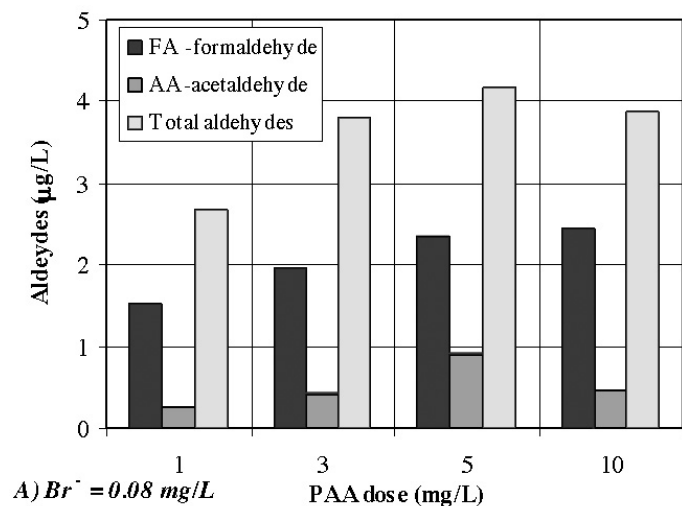
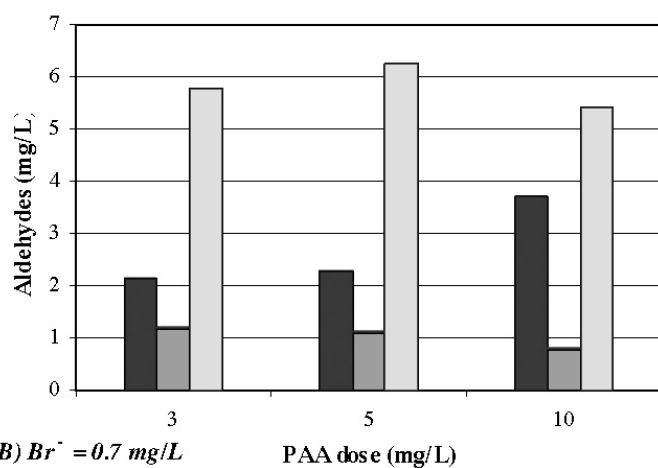
A)  $Br^- = 0.08 \text{ mg/L}$ B)  $Br^- = 0.7 \text{ mg/L}$ 

Fig. 6. Aldehydes vs. PAA dose in pre-disinfection of surface water (TOC = 3.2–4.9 mg/L) at two bromide concentrations (A, baseline: 0.08 mg/L; B, artificial increase: 0.7 mg/L).

Table 3

Initial characteristics and formed DBPs after pre-disinfection of surface water with PAA at various doses

$Br^-$ mg/L	TOC mg/L	PAA mg/L	$CHCl_3$ $\mu\text{g/L}$	$CHBr_3$ $\mu\text{g/L}$	TTHMs $\mu\text{g/L}$	FA <sup>a</sup> $\mu\text{g/L}$	AA <sup>b</sup> $\mu\text{g/L}$	Tot. aldehydes $\mu\text{g/L}$
0.08	3.2	0				< 1	0.18	1.9
0.08	3.4	1				1.5	0.26	2.7
0.08	3.9	3				2.0	0.41	3.8
0.08	4.3	5	0.4	< 0.1	0.4	2.4	0.91	4.2
0.08	4.9	10				2.4	0.47	3.9
0.7		3	0.4	< 0.1	0.4	2.1	1.2	5.8
0.7		5	0.4	< 0.1	0.4	2.3	1.1	6.2
0.7		10	0.4	< 0.1	0.4	3.7	0.78	5.4
0.7		10 <sup>c</sup>	0.6	0.2	0.8	6.1	15.1	24.8

<sup>a</sup>Formaldehyde. <sup>b</sup>Acetaldehyde. <sup>c</sup>This row reports data obtained from samples where PAA was not inactivated.

especially with respect to brominated compounds. Operating at 10 mg/L of PAA (see Table 3), without PAA inactivation after 3.5 h, the prolonged contact time led to a more complete oxidation of organic carbon and to a significant increase (over 100%) of DBP formation. Therefore, at the same conditions, both in terms of the physicochemical characteristics of water and operational parameters of the disinfection process, reaction time is a fundamental factor in DBP formation.

## 5. Conclusions

In summary, the following considerations can be made:

1. Disinfection for water reclamation: At the experimental conditions previously indicated, DBP formation was — as expected — evident when NaClO was used. Therefore, the TTHMs standard implemented by the new Italian regulations for water reuse will likely lead to the practical unfeasibility of chlorine disinfection, even if employed in very high-quality effluents. The use of PAA led, on the contrary, to quite negligible DBP formation (only two kinds of aldehydes). Referring to UV disinfection, the trials carried out were in this phase limited to low to medium doses, at which the presence of DBPs was not detected. For higher doses (up to 100 mJ/cm<sup>2</sup>), the TOC variations evidenced require further specific testing. In conclusion, both PAA and UV appear to be, from this point of view, suitable disinfecting agents. However, the high cost of PAA would probably hinder its widespread use on the Italian market.

2. Pre-disinfection of surface water: A moderate risk of DBP formation (mainly aldehydes) when PAA is used for raw surface water pre-treatment was evidenced. Levels detected were quite low, especially if compared with those typical of ozone treatment; if TOC is low, the amount of DBPs falls around the detection limits.

Moreover, there was no experimental evidence of chlorinated and brominated DBPs production, even when the concentration of bromides in water was high and pH fell in the alkaline field, a condition capable of promoting their formation. In any case, the practical applicability of PAA for pre-disinfection of surface water requires further studies, taking into account the peculiar characteristics of this agent, especially with reference to its decomposition characteristics.

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