



## DBPs formation and toxicity monitoring in different origin water treated by ozone and alum/PAC coagulation

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### Abstract

In this study, aluminium sulphate (alum) and polyaluminum chloride (PAC) coagulation were used for coagulation of different origin water (Buyukcekmece, BC and Omerli, OM in Istanbul, Turkey and Carmine, CR in Salerno, Italy) treatment. The effect of pre-ozonation alone and combined with coagulation on NOM removal which was characterized by TOC, UV<sub>254</sub> was investigated. DBPs formation and acute toxicity on *Daphnia magna* of chlorinated raw and treated samples were defined in parallel. Moreover, bromide spiking was evaluated for DBPs speciation. Optimum alum dose for TOC removal was found to be 40 mg/L for OM while 80 mg/L of alum exhibited the lowest total trihalomethane formation potential (TTHMFP). Pre-ozonation enhanced the removal of TOC and reduction of TTHMFP when it was used in combination with both coagulants. In contrast, total haloacetic acid formation potential (THAAFP) increased after each coagulation, ozonation and their combination. 300 µg/L bromide spiking (around the same level with BC) in raw sample collected from CR increased the formation of brominated disinfection by-products. Raw and treated samples displayed acute toxicity on *Daphnia magna* in different pattern and practically “no dose-response behavior” was observed.

**Keywords:** Disinfection by-products; Alum; Polyaluminium chloride; Drinking water; Coagulation; Pre-ozonation; Combined treatment; *Daphnia magna*

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## 1. Introduction

The coagulation and subsequently chlorination is the most common method for the treatment of drinking water [1–5]. However, the reaction between chlorine and the natural organic matter (NOM) forms disinfection by-products (DBPs) [6–9]. Epidemiological studies reported that the presence of DBPs may adversely affect human health, in particular, chloroform ( $\text{CHCl}_3$ ), the major and most dominant trihalomethane species (THMs) [9]. Human exposure to THMs in chlorinated water has been implicated epidemiologically to cancers of the lower intestinal tract and bladder [10–12] and adverse birth outcomes [13]. The USEPA classified  $\text{CHCl}_3$ , dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ) and bromoform ( $\text{CHBr}_3$ ) as possible carcinogens to humans [14]. The developmental toxicity of individual and combined haloacetic acids (HAAs) has been reported [15]. However, further investigations are required into DBPs toxicity as a complex mixture problem [16], including newly detected DBPs such as chlorinated furanones [17]. *Daphnia magna* was used to monitor the toxicity of chlorite [18] as well as testing many chemicals and accurately simulating their effects on mammals [19]. Recently, it was used to evaluate enhanced coagulation [20] and advanced oxidation technologies [21] for reducing DBPs formation.

The maximum contaminant level for THMs was set at different levels in developed countries (80  $\mu\text{g/L}$  in US, 250  $\mu\text{g/L}$  in Australia, 100  $\mu\text{g/L}$  in Canada, and 10  $\mu\text{g/L}$  in Germany, 100  $\mu\text{g/L}$  in the EU countries). In Italy, which has 80–85% of water demand supplied by groundwater, 30  $\mu\text{g/L}$  was set for THMs [22], while Turkish Consumable Water Regulation enforces water utilities to meet 100  $\mu\text{g/L}$  THM limit within the distribution system [23]. Moreover, USEPA set 60  $\mu\text{g/L}$  and 10  $\mu\text{g/L}$  limits for the total of five haloacetic acids and bromate, respectively [9].

The risks related to DBPs force the community to seek alternative water sources or treatment

methods of drinking water. To improve coagulation efficiency has become the main target to decrease the use of final chlorine dose and the formation of DBP [20,24–26]. Ozone ( $\text{O}_3$ ) offers municipal water purveyors the benefits of being the strongest commercially available oxidising agent being superior to chlorine, chlorine dioxide, or chloramines for the inactivation of water-borne pathogens such as *Giardia* and *Cryptosporidium* which have been recognised as a serious cause of water-borne diseases in humans [27]. Thus, it has become common using  $\text{O}_3$  as pre-oxidation in water treatment plants [28,29]. However, it has also many disadvantages of the corrosion related to increasing biodegradable organic carbon and formation of brominated disinfection by-products such as bromate. On the other hand, because  $\text{O}_3$  is not stable for the protection of the treated water in distribution system, chlorination is still required to ensure residual disinfection. Heterogeneous catalytic  $\text{O}_3$  treatment is a novel type of advanced oxidation, which demonstrates promising prospects for the elimination of organics. Catalytic ozonation combines  $\text{O}_3$  with the adsorptive and oxidative properties of solid phase metal oxide catalysts (i.e.  $\text{TiO}_2$ , Mn, CuO) to achieve mineralization of organics [30]. The  $\text{O}_3$  preoxidation followed by coagulation was optimized for bromate formation in bromide containing water [31]. The other promising advanced oxidation methodologies such as photocatalysis and photoelectrocatalysis have been used for NOM removal [21,32].

Istanbul which is the largest city of Turkey with its current population of 12 million people currently receives 90% of its water demand from six water reservoirs. Omerli (OM) and Buyukcekmece (BC) reservoirs supply 35% of the total water demand. Poor water quality in most of reservoirs is attributed to the urban settlement, industries [33] and agricultural activities [34] in the catchment areas [35]. The Carmine (CR) constructed basin supplies drinking water demand of more than 500,000 people during summer in

Salerno district (Italy). However, the use of chlorine dioxide leads to high chlorite formation in the effluent ( $> 0.2$  mg/L), which meets the present maximum contaminant level (MCL) set by Italian regulation, but it is not able to meet MCL which is going to come in force by 25 December 2006 [36]. DBPs were found high in the above mentioned water resources [36].

The effect of pre-ozonation on aluminum sulphate (alum) and polyaluminum chloride (PAC) coagulation is studied in detail on the raw water samples collected from BC, OM and CR water resources (Fig. 1) in relation to DBPs formation potential (DBFP), NOM removal (TOC and

$UV_{254}$ ) and acute toxicity on *D. magna*. The effect of bromide spiking at (300  $\mu$ g/L) on DBPs speciation in the CR water up to the level of BC water was also investigated.

## 2. Materials and methods

### 2.1. Water samples

The raw water samples were collected from the influent of the treatment plants of all sources. The raw water of BC is treated by coagulation (60 mg/L alum), sedimentation and sand filtration and chlorine gas (3–3.5 mg/L) is applied both



Fig. 1. The location of water resources.

for pre- and post-chlorination. The water of OM is treated by pre-ozonation followed by coagulation (40–60 mg/L alum), flocculation, sedimentation, sand filtration and post-chlorination. The existing water treatment plant in the CR basin consists of pre-oxidation with  $\text{ClO}_2$ , on line coagulation with 20 mg/L of PAC addition, filtration and final disinfection with the use of  $\text{ClO}_2$ . All water samples were taken from the influent of the treatment plants and kept refrigerated at +4°C during the experiments.

## 2.2. Treatment methods

### 2.2.1. $\text{O}_3$ treatment

A Corona discharge ozone generator (PCI Model GL-1 type) was used. The ozone gas was transferred into a 10 L cylindrical reactor using a 10 cm ceramic porous tube type of commercial ozone diffuser [21]. The system was operated in a semi-batch mode. Teflon tubing was used for the ozone gas lines. In this study 10.5 mg/L.min ozone dose was applied during 5 min reaction time period.

### 2.2.2. Coagulation

Coagulation experiments were performed at room temperature by applying rapid mixing for 1 min at 100 rpm, than slow mixing without adding polymer for 30 min at 30 rpm, and finally settling for 60 min [24].

### 2.2.3. Chlorination

Raw and treated water samples (250 mL) were chlorinated according to Standard Methods [37].

## 2.3. Toxicity measurement

*D. magna* acute toxicity test was conducted on raw, treated and treated-chlorinated water samples using 24 h newborn daphnids for the end point of immobilization of the animals. The details are explained elsewhere [20]. Experiments

were carried out quadruplicate without diluting the sample [20].

## 2.4. Analytical methodology

$\text{UV}_{254}$  values of raw and treated samples were recorded by Perkin Elmer Spectrophotometer (Lamp 12, USA) with 1.0 cm quartz cells. TOC of the samples were measured using a Shimadzu 500A Total Carbon Analyzer. The THMFP, THAAFP (nine HAAs) and other DBPs (chloral hydrate, haloacetonitriles, halo ketones) formation potential measurements were performed according to a standard procedure using a Hewlett Packard Gas Chromatograph (GC) 5890 Series II with a  $^{63}\text{Ni}$  Electron Capture Detector as described elsewhere [38,39]. These DBPs were selected for investigation because they are the most commonly encountered species worldwide [40]. The recoveries of the analytical methods used ranged from 72 to 127% for THMs and other DBPs and from 77.5 to 121.3% for HAAs for concentration levels ranging from 2 to 50 ug/l [40]. Source water parameters as pH, alkalinity, bromide and chloride were also measured according to the Standard Methods [37].

## 3. Results and discussion

### 3.1. Characterization of raw water samples

The characteristics of the raw water samples were quite different than each other. The raw sample collected from BC was characterized by high bromide and chloride concentrations, relatively high alkalinity and the highest TOC (Table 1). The quality of raw water from OM was relatively better than the BC sample by means of TOC and turbidity. On the other hand, the raw water sample from carmine was characterized by low TOC (2.06 mg/L),  $\text{UV}_{254}$  (0.096 1/cm), and turbidity, and relatively high pH and alkalinity. The samples were collected during summer season (July 2004).

Table 1

Water characteristics of the investigated raw water samples from Buyukcekmece (BC), Omerli (OM) and Carmine (CR) reservoirs

Parameter	OM	BC	CR
Alkalinity, mg CaCO <sub>3</sub> /L	70	150	111
Turbidity, NTU	2.7	3.2	2.7
UV <sub>254</sub> , 1/cm	0.097	0.1	0.096
TOC, mg/L	3.05	3.60	2.05
Bromide, µg/L	95	274	—
Chloride, mg/L	45	98	17.3
pH	7.18	7.65	7.73

3.2. Optimization of coagulation process and DBPs formation

As can be seen from TOC removal (Fig. 2) 80 mg/L alum dose resulted in the highest TOC removal (>50%). According to the enhanced coagulation procedure from USEPA the required TOC removal is >25% for the range of TOC between 2 and 4 mg/L and source water alkalinity >60 to 120 mg/L CaCO<sub>3</sub> [24]. Hence this value was already obtained using 40 mg/L of alum in the OM sample. On the other hand, coagulation by 40 mg/L alum dose did not decrease THMFP, in contrast, the amount of brominated THMs increased

after coagulation. No significant change was observed for the other DBPs except dichloroacetic acid (DCAA), for which the formation was doubled after coagulation (Fig. 3). The removal of UV<sub>254</sub> by ozonation, coagulation (60 mg/L) and combination of ozone and coagulation was recorded as 46%, 38% and 61% respectively [4].

The removal of TOC and UV<sub>254</sub> using 60 mg/L of alum and PAC, O<sub>3</sub> alone, O<sub>3</sub> and 60 mg/L of alum and PAC for the BC sample is shown in Fig. 4. PAC coagulation resulted in slightly less TOC removal than alum [20] while O<sub>3</sub> treatment exhibited the least TOC removal which was enhanced after coagulation treatment. According to the above result, O<sub>3</sub> and PAC coagulation resulted in less TOC removal than O<sub>3</sub> and alum coagulation combination. Pre-ozonation decreased THMFP/TOC ratio of coagulated water from 44 µg/mg to 22 µg/mg after alum coagulation [21] and to 27 µg/mg after PAC coagulation. Both alum and PAC coagulation of raw water slightly increased TTHMFP in the treated water samples (Fig. 5), while O<sub>3</sub>+alum and PAC decreased TTHMFP by 62% and 53% respectively, whereas all treatment methods increased THAAFP by almost two fold (Fig. 6). The phenomenon of increase of TTHMFP and THAAFP after coagulation raised the hypothesis that removal of precursors could form DBPs

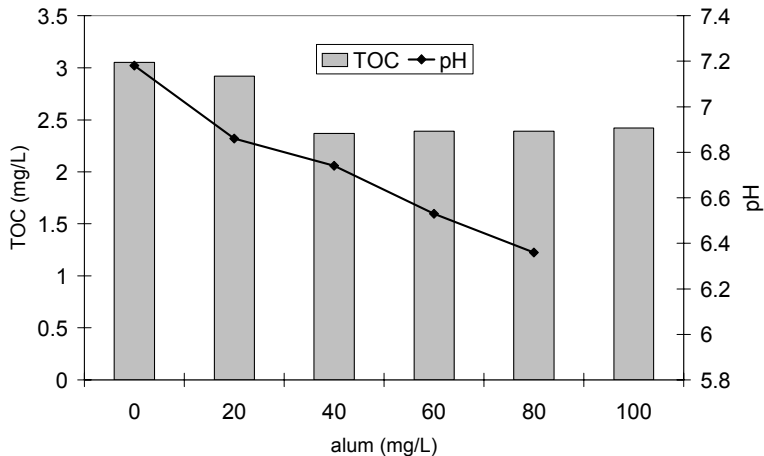


Fig. 2. TOC removal and pH behavior for Omerli (OM) water sample by alum coagulation.

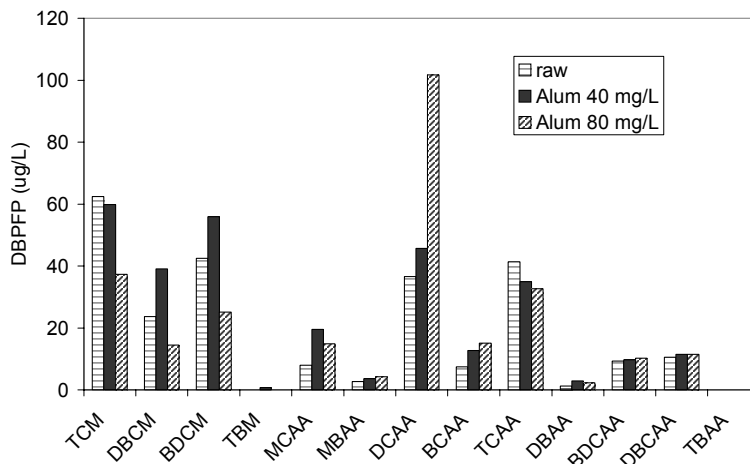


Fig. 3. THMs and HAAs formation potentials for the OM water samples.

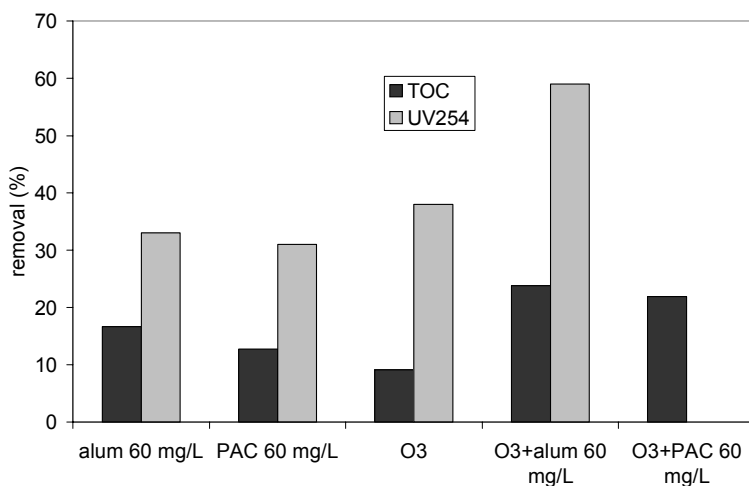


Fig. 4. TOC and UV<sub>254</sub> removal for the BC water samples by ozonation and/or coagulation.

(detected >500 species) other than those measured in this study [41], resulting in higher THMs and HAAs formation during chlorination.

The raw water collected from CR was spiked with 300 µg/L Br<sup>-</sup> to evaluate DBPs formation. TOC and UV<sub>254</sub> removal is shown in Fig. 7. TOC decreased from 2.05 to 1.54, 1.37 and 1.18 mg/L using PAC-bromide spiked doses of 80, 120 and 200 mg/L, respectively. Raw water sample

showed different character by higher THAAFP than both BC and OM water samples. TTHMFP increased two fold when 80 mg/L of PAC was used while THAAFP decreased. The ratio of brominated species to total DBPs increased after coagulation (Fig. 8). DBPs formation decreased due to the increase of PAC concentration. As can be seen from Fig. 9, showing DBPs for 120 mg/L PAC coagulation with or without bromide spik-

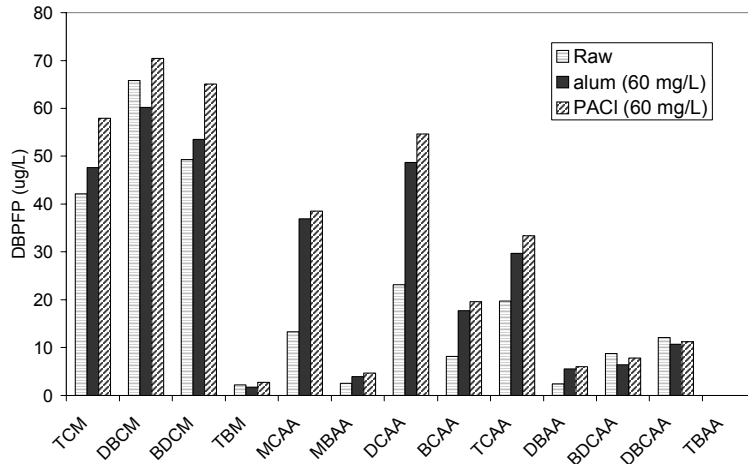


Fig. 5. THMs and HAAs formation potentials for the BC water samples, comparison between alum and PAC coagulation.

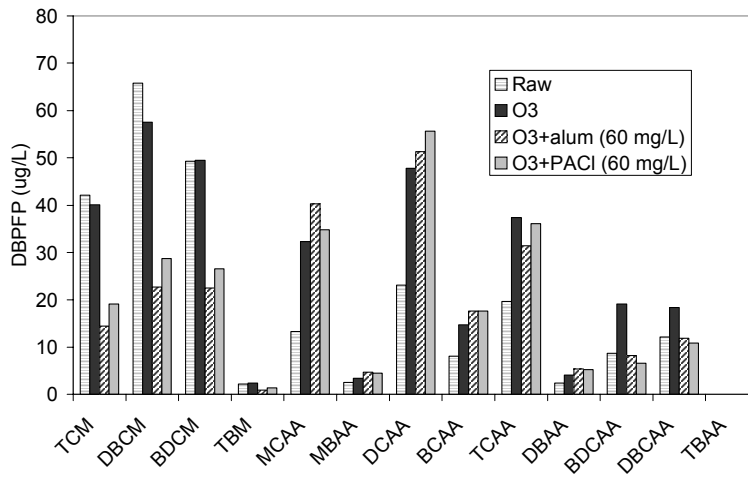


Fig. 6. THMs and HAAs formation potentials for the BC water samples, comparison among O<sub>3</sub> and O<sub>3</sub>-alum/PAC coagulation.

ing, all brominated THMs increased in the presence of Br<sup>-</sup> due to the increasing Br–TOC–chlorine interaction [27,42].

Besides THMs and HAAs, some other volatile DBPs were detected at small amounts in all water samples except chloral hydrate (CH) which was detected as the highest one in the raw CR sample. CH formation was reduced effectively by alum coagulation in the BC samples whereas O<sub>3</sub>

use alone and PAC were not effective (Table 2). It is worthwhile mentioning that also O<sub>3</sub>+alum coagulation resulted in higher CH level than alum coagulation while CH formation decreased when O<sub>3</sub> was used before PAC coagulation.

### 3.3. Evaluation of toxicity tests

Immobilization of *D. magna* for BC water is

Table 2  
DBPs ( $\mu\text{g/L}$ ) concentrations in the raw and treated waters from BC and CR

	BC (raw)	BC (alum 60 mg/L)	BC (PAC 60 mg/L)	BC ( $\text{O}_3$ )	BC ( $\text{O}_3$ +alum 60 mg/L)	BC ( $\text{O}_3$ +PAC 60 mg/L)	CR (raw)	CR* (PAC 80 mg/L)	CR (PAC 120 mg/L)	CR* (PAC 120 mg/L)	CR* (PAC 200 mg/L)
Monochloroacetonitrile	2.4	2.1	2.3	2.1	1.6	1.7	1.8	1.6	1.3	1.8	1.3
Dichloroacetonitrile	3.5	3.2		3.4	N.d	N.d	N.d	N.d	N.d	N.d	N.d
1,1-dichloropropanone	0.6	1.	N.d	0.8	N.d	0.4	N.d	0.2	N.d	0.4	0.4
1,1,1-trichloropropanone	0.7	0.9	1.9	0.8	0.6	1.1	0.9	0.6	0.9	0.6	0.5
Monobromoacetonitrile	1.6	3.5	1.6	1.2	0.5	0.7	N.d	1.3	0.4	1.2	1.2
Dibromoacetonitrile	1.1	0.9		0.9	N.d	N.d	N.d	N.d	N.d	N.d	N.d
Chloropicrin	0	3.6	3.5	N.d	3.5	3.6	N.d	3.5	3.5	3.5	3.5
Chloral hydrate (CH)	69.2	0.3	61.2	56.9	19	32.3	121.4	20.1	56.6	21.4	22.8

\*300  $\mu\text{g/L}$  bromide spiked

Nd: not detected



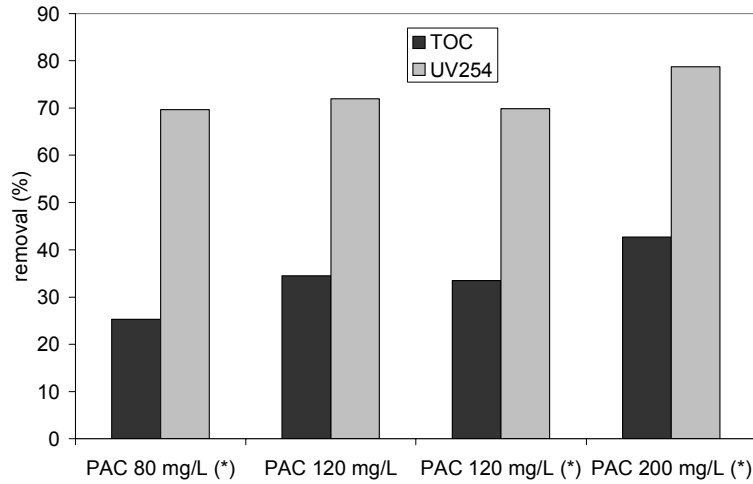


Fig. 7. TOC and UV<sub>254</sub> removal for CR water samples by PAC coagulation.

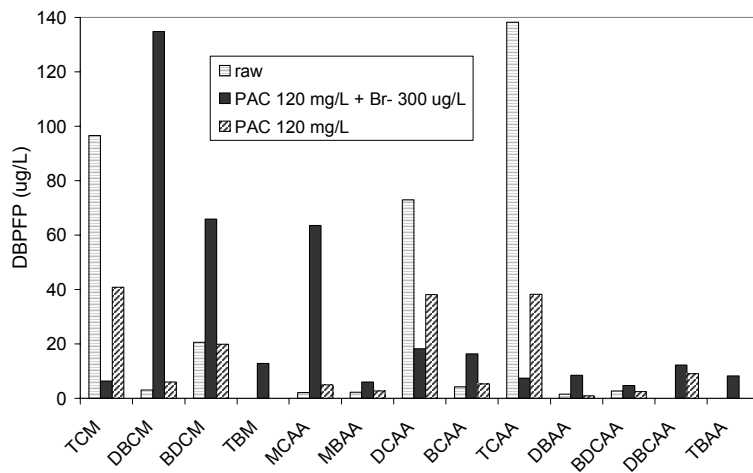


Fig. 8. THMs and HAAs formation potentials for CR water samples before and after coagulation with different PAC doses added after 300 µg/L Br<sup>-</sup> spiking.

shown in Fig. 10. The BC raw water exhibited the highest toxicity (70%) on *D. magna* while the raw water of CR did not display any toxicity although it yielded higher DBPs (467 µg/l) than the BC (318 µg/l) and OM (323 µg/l) which exhibited 20% of immobilization. *D. magna* toxicity decreased in the OM water by increasing alum dose and no immobilization was observed at 80 mg/L

alum dose [21]. The same tendency was observed for the BC samples after coagulation whereas after pre-ozonation PAC coagulation was found to be efficient for the reduction of toxicity in the BC sample. As expected, Br<sup>-</sup> just resulted in higher brominated DBPs and increase in the immobilization of *D. magna* for the CR samples (Fig. 11). No dose-response relationship was observed be-

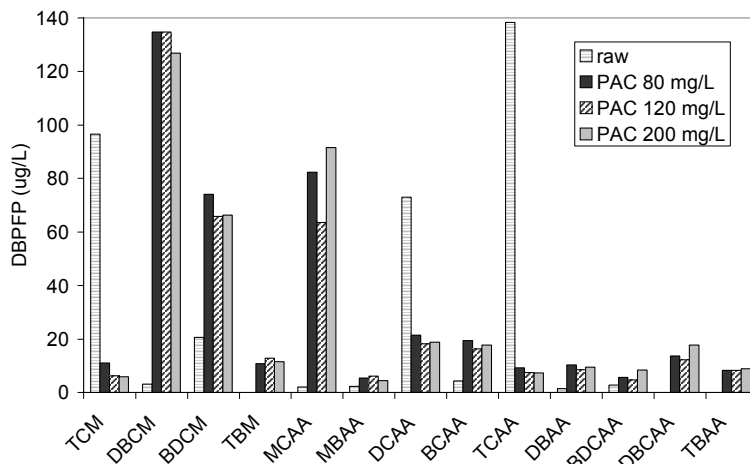


Fig. 9. THMs and HAAs formation potentials for CR water samples before and after coagulation with 120 mg/L PAC dose, with and without 300 µg/L Br<sup>-</sup> spiking.

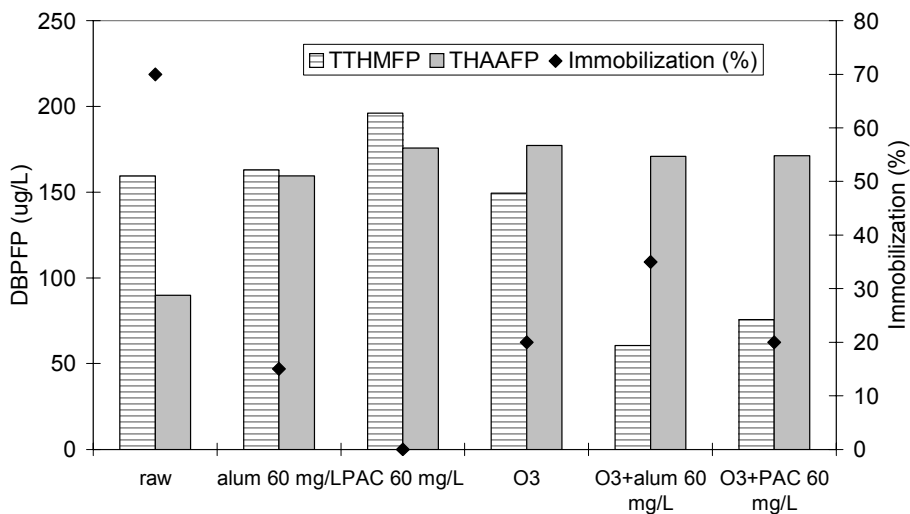


Fig. 10. Comparison among TTHMFP, THAAFP and *D. magna* toxicity for the BC water samples.

tween DBPs and *D. magna* toxicity test which urges one to focus on the complex mixture toxicity evaluation of the DBPs [16] although strong evidence was obtained on different bioassays with different end-points of the individual DBPs such

as dichloro-, dibromo-, and bromochloro acetic acid in rat embryo culture [15], or di- and trichloroacetic acid and chloral hydrate in mouse cells [43] or chromosomal aberrations of Chinese hamster lung cells by bromide spiking [42].

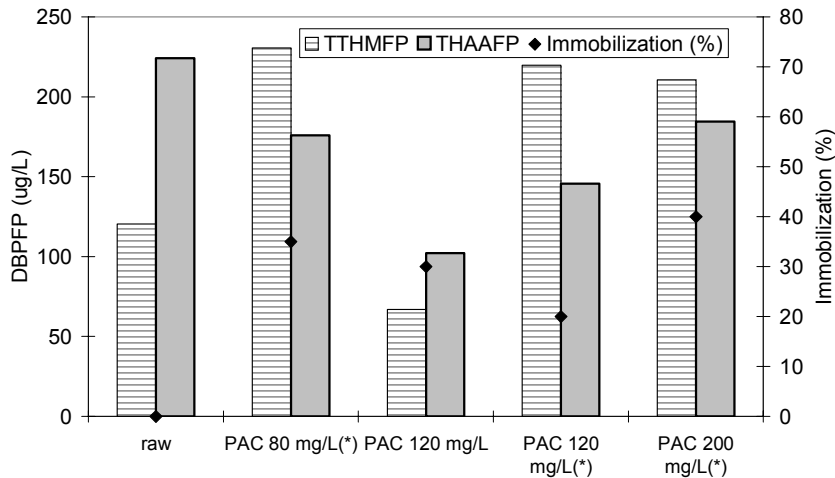


Fig. 11. Comparison among TTHMFP, THAAFP and *D. magna* toxicity for CR water samples (\* 300  $\mu\text{g/L}$  Br<sup>-</sup> spiked).

#### 4. Conclusions

Alum and PAC coagulation, ozonation and their combination were performed for the treatment of the raw water samples Buyukcekmece (BC) and Omerli (OM), Istanbul, Turkey and Carmine (CR), Salerno, Southern Italy. The efficiency of processes was evaluated by measuring DBPs, toxicity and TOC parameters. The following conclusions were drawn from the present work:

- TOC removal was almost the same at the alum doses over 20 mg/L (ranging from 40 to 100 mg/L) for the OM samples.
- TOC removal was almost the same at alum doses over 20 mg/L (ranging from 40 to 100 mg/L) for the OM samples. However, although the same TOC degradation (%22) was achieved using 40 mg/L alum, the change in TTHMFP was insignificant while TTHMFP decreased 40% after coagulation with 80 mg/L of alum.
- Pre-ozonation enhanced the efficiency of both alum and PAC coagulation.
- Bromide spiking at 0.15 Br<sup>-</sup>/TOC ratio affected drastically DBPs speciation, in particular THMs.

- The raw water samples of BC and OM exhibited significant toxicity on *D. magna*. Toxicity of raw water was reduced due to treatment.
- *No dose-response relationship* was observed between DBPs and *D. magna* toxicity test for all samples. As expected bromide adding just resulted in higher levels of brominated DBPs but no significant change was observed in the immobilization of *D. magna*.

To enhance the results obtained from this study, more multi-disciplinary studies including DBPs with new discovered species, treatment type, toxicity studies and NOM structure should be designed in different origin waters.

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