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Occurrence of carboxylic acids in different steps of two drinking-water treatment plants using different disinfectants

Beatriz Jurado-Sánchez [a], *Evaristo Ballesteros* [b,**], *Mercedes Gallego* [a,*]

[a] *Department of Analytical Chemistry, Campus of Rabanales, University of Córdoba, E-14071 Córdoba, Spain*
[b] *Department of Physical and Analytical Chemistry, E.P.S. of Linares, University of Jaén, E-23700 Linares, Jaén, Spain*

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ABSTRACT

The occurrence of 35 aliphatic and aromatic carboxylic acids within two full scale drinking-water treatment plants was evaluated for the first time in this research. At the intake of each plant (raw water), the occurrence of carboxylic acids varied according to the quality of the water source although in both cases 13 acids were detected at average concentrations of 6.9 and 4.7 μg/L (in winter). In the following steps in each treatment plant, the concentration patterns of these compounds differed depending on the type of disinfectant applied. Thus, after disinfection by chloramination, the levels of the acids remained almost constant (average concentration, 6.3 μg/L) and four new acids were formed (butyric, 2-methylbutyric, 3-hydroxybenzoic and 2-nitrobenzoic) at low levels (1.1–5 μg/L). When ozonation/chlorination was used, the total concentration of the carboxylic acids in the raw water sample (4.7 μg/L) increased up to 6 times (average concentration, 26.3 μg/L) after disinfection and 6 new acids (mainly aromatic) were produced at high levels (3.5–100 μg/L). Seasonal variations of the carboxylic acids under study showed that in both plants, maximum levels of all the analytes were reached in the coldest months (autumn and winter), aromatic acids only being found in those seasons.

1. Introduction

Carboxylic acids are an important group of disinfection by-products (DBPs) that can originate when chlorinated agents and ozone are applied during water treatment (Peldszus et al., 1998; Richardson, 2002; Von Gunten, 2003; Krasner et al., 2006; Richardson et al., 2007). As the degradation rate of these compounds is usually lower than their formation rate, they accumulate during disinfection, leading to bacterial regrowth and biofilm formation in distribution systems (Chu and Lu, 2004; Meylan et al., 2007). In a review of 252 DBPs, dicarboxylic acids have been considered potential rodent carcinogens because of potential peroxisome proliferating activity (Moudgal et al., 2000). These results have been later corroborated in a similar study of ~210 halogenated and non-halogenated DBPs (Woo et al., 2002).

Several studies have documented the formation of carboxylic acids (17 aliphatic and 6 aromatic acids) in laboratory reactions of ozone with isolated humic substances or organic pollutants in water (Vincenti et al., 2005; Huang et al., 2005; Miao and Tao, 2008; Zhang et al., 2008). In drinking-water treatment plants (DWTPs), the occurrence of carboxylic

* *Corresponding author*. Tel./fax: +34 957 218614.
** *Corresponding author*.
E-mail addresses: eballes@ujaen.es (E. Ballesteros), mercedes.gallego@uco.es (M. Gallego).

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acids varies according to the quality of the water source and the operations carried out. Thus, in a comprehensive study of 6 water treatment facilities using ozone and chlorine dioxide as disinfectants, up to 33 aliphatic and 10 aromatic ones were formed (Richardson et al., 2000). More recently in a similar survey conducted in 12 American full-scale DWTPs, up to 24 aliphatic acids as well as one aromatic one have been identified as ozone/chlorine and ozone/chloramines DBPs (Krasner et al., 2006). Neither survey provides information on the effect of the treatments applied on the formation/removal of these acids, nor on the levels found (Richardson et al., 2000; Krasner et al., 2006). Gagnon et al., have performed a more extensive study about the occurrence of 4 short-chain aliphatic acids in the different steps (*viz.* raw water, sedimentation, ozonation and filtration through granular activated carbon filters) of a full-scale DWTP that uses ozone as the main disinfectant as well as sodium hypochlorite at the exit of the plant. This study spread to the influence of different water temperatures from 3 to 22 °C on both the formation of the acids after ozonation and their removal by biofiltration. Concentrations of all acids increased substantially after ozonation at the highest water temperature evaluated. The acids were completely removed after biofiltration with the sole exception of formic acid, although its concentration decreased ~5 times (Gagnon et al., 1997). A similar study performed on different steps (*viz.* raw water, ozonation, sand filtration and finished water) of a DWTP using the ozonation process corroborates the findings observed above since acetic and formic acids are the compounds that experienced a major increase in their concentrations after ozonation along with oxalic and pyruvic acids (up to 48 times). In addition, the acids formed after ozone application can be removed by biofiltration but in this case using sand-media filters (Hammes et al., 2006). The most recent and complete study to date compared the occurrence of 6 aliphatic dicarboxylic and 9 aromatic (mono- and dihydroxy-) acids in raw and finished water samples collected from a DWTP that uses ozone in combination with a chlorinated agent (Vincenti et al., 2010). After water treatment, two new acids (maleic and itaconic) were formed, while the levels of some aliphatic acids and all aromatic acids decreased.

To date, there is little information about the occurrence of a wide range of carboxylic acids because the studies concerning the largest number of compounds provide little data at the different steps of a DWTP (Richardson et al., 2000; Krasner et al., 2006). In addition, the reports that explore the influence of different disinfectants, water temperature and removal by filtration only cover 4–5 aliphatic acids (Gagnon et al., 1997; Hammes et al., 2006). The most recent and comprehensive paper, which includes 15 acids (Vincenti et al., 2010), is somewhat complex with respect to the above studies, since after ozonation there is a decrease in concentration of some acids found in raw water. Furthermore, there is no information about the behaviour and fate of these compounds in DWTPs that use only chlorinated agents (without combining them with ozone). Therefore, the aims of this paper were: i) to establish the behaviour of 35 (22 aliphatic and 13 aromatic) carboxylic acids within two full scale DWTPs that employed chloramines or ozone and chlorine as disinfectants, ii) to obtain information about the effect of the various treatment stages on the removal/increase of acids present in raw water, and iii) to evaluate the effect of seasonal changes (water temperature and rainfall) on the occurrence of acids through both DWTPs.

2. Materials and methods

2.1. *Description of DWTPs and sample collection*

Two surface DWTPs located in SE Spain (separated by a distance of ~250 km) were selected for this study since they employed different disinfectants. The schematics diagrams of the potabilization process employed in each facility as well as the location of the 5 sampling points are depicted in Fig. 1. DWTP 1 (Fig. 1a) treated and provided 30 million L/day from a reservoir to about 100,000 people. The reservoir (medium pluviometry, 320 mm/year) received water from a tributary river with an average flux of 1.72 m^3/s and had a total water

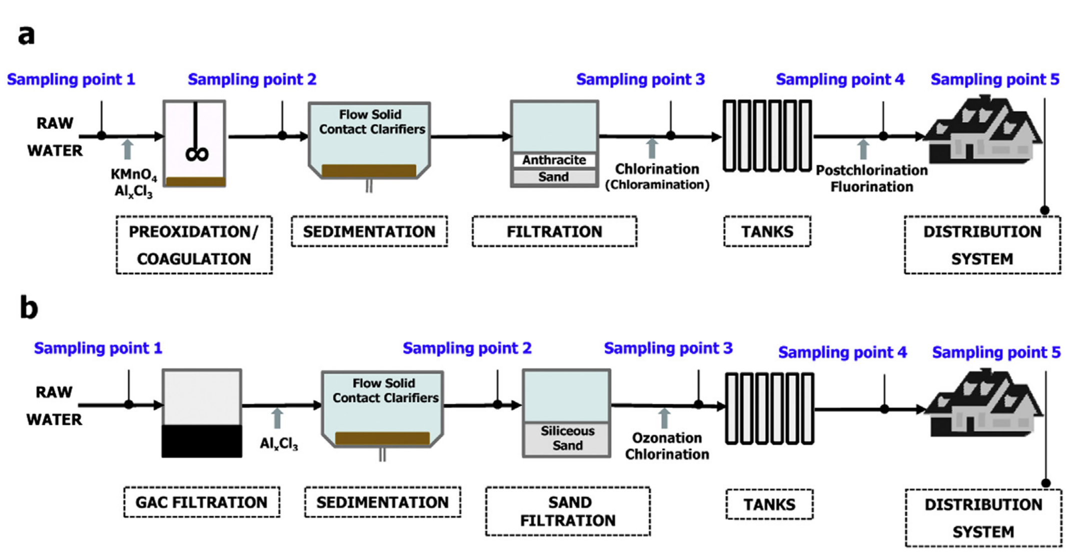

Fig. 1 – Schematic diagrams of the two drinking-water treatment plants studied and locations of sampling points. (a) DWTP 1 (chloramination); (b) DWTP 2 (ozonation/chlorination).