ABSTRACT

The drinking water disinfection procedures may affect the water quality. The addition of Na hypochlorite induces strong modifications in the chemical-physical characters of drinking waters, that involve the humic substances (HS) activity and, indirectly, the fate of the elements associated to HS. The case studied is a drinking water distribution net in Italy, in the town of Castelfranco Emilia (Modena, Northern Italy). Ten water samplings were performed from June 2000 to July 2001. The drinking water samples were collected at the input of the net, before the addition of disinfectants (station 1), and at two sites corresponding to 2 hours (station 2) and 10 hours (station 3) of way for the water flow from the input of the net. The experimental approach here presented is based on the enrichment of HS at the water-air interface, obtained by means of a suitable laboratory apparatus in which the water sample aerosolization is produced. The original samples, the collected aerosols and the water samples depleted by the aerosolization process were submitted to PIXE (Particle Induced X-ray Emission) analysis for the element determination at concentration level of fractions of μg/l, and to spectrofluorimetric and dynamic surface tension measurements. The largest volumes of aerosol were obtained in the treatment of the samples collected at the first station, before the addition of Na hypochlorite, while a lower mass of elements was evaluated in the aerosol produced by the samples of the second station respect to the other two stations. The wavelength values of the fluorescence intensity maximum suggested the presence of lignin and aromatic groups for the first and the second station samples, and of terrestrial humic acids for the third station samples. The dynamic surface tension values resulted generally anti-correlated with the fluorescence intensities. It may be concluded that, in the tested aqueduct net, the disinfection procedure depletes the HS activity, but, ten hours after the addition of disinfectants, the HS have reproduced humic acids in solution.

KEYWORDS: Drinking Water, Humic Substances, Water-Air Interface, PIXE, Trace Elements.

INTRODUCTION

In the last decade studies regarding the presence of small quantities of natural organic compounds, as humic substances (HS), in drinking water, have been always considered as an important topic with relationships to the drinking water quality. Humic substances themselves cannot be considered as dangerous, but their association with other components (Suffet and MacCarthy, 1989) during the water purification processes, including the water disinfection stage (especially for some class of disinfectants), can originate reactivity phenomena able to worse the water quality during time. This aspect also concerns human health.

The humic substances characteristics, studied for many years, show many particularities due to their structure, their refractory behaviour and their surface active properties. At the same time, for waters involved in the drinking water distribution net, the HS large molecular dimension range, from 5000 to
200000 Daltons, (Beckett, R., 1990) give them, also in low concentrations (1 mg/l), the typical colloidal dispersion properties. On the other hand, in view of the ubiquitous character of HS as well as their ability to interact with a large number of components, the humic substances play an important role during the purification process and the quality control procedures of the drinking water.

It is important to point out that both the micellization-demicellization HS equilibrium (Loglio et al., 1986, 1989, 1991) and their enrichment at the air-water interface are an important aspect during the autodepuration process in natural waters. In particular, both breaking-waves and water-fall (Resch, F., 1986) are able to generate a large absorption and floatation beds constituted by a well continuously collapsed gas-bubble distribution. Such gas bubble collapses and the consequent aerosol formation are responsible of a complex phenomenon which allows to get further information related to the origin and the transformation of microcomponents present in water. The study of these processes by means of parameters used as pollutant tracers through the drinking water distribution net, have given very encouraging results (Loglio et al., 1984).

The fate of heavy metals (Cecchi et al., 1990, Ghermandi et al., 1991, 1994) associated with HS, together with their decay during the disinfection stage, seems to be a suitable information to support water quality studies. The heavy metals, among which dangerous elements for human health are included, are frequently scavenged by HS in water, and involved in the natural autodepuration process described above. Given that the trend of heavy metals bounded to HS is affected by the phenomena that interact with HS activity, the enrichment of these elements in the aerosol, artificially produced from drinking water, is an important parameter to evaluate the impact of purification and disinfection processes on the water quality.

The case studied (project co-financed by Italian Ministry for University and Research, 1999-2001) is a simple drinking water distribution net in the town of Castelfranco Emilia (close to Modena, Northern Italy). Water samples were collected before the addition of the disinfectant to the water and along the net, at increasing distance from its start point. Ten samplings were totally performed in a year. By means of a suitable laboratory apparatus, an aerosol was artificially produced from each water sample; in this aerosol the HS and the scavenged metals contained in the water sample were concentrated. The aerosols were collected and submitted to PIXE (Particle Induced X-ray Emission), spectrofluorimetric and dynamic surface tension measurements.

**EXPERIMENTAL**

The Castelfranco Emilia (Modena, Northern Italy) drinking water distribution net collects water by means of wells at 100m depth. The mean pumped water temperature is 10°C, that is quite constant during the year. The mean discharge is 50 l/s. The water pH generally ranges from 6 to 7. The disinfection process consists of the addition of Na hypochlorite, at the input of the net. The Na hypochlorite concentration is kept constant at the start point of the net, and equal to 0.1 mg/l. The distribution net runs underground at 1 m depth, and the water temperature along the net ranges from about 8° in winter to about 18° in summer time.

The drinking water samples were collected at the wells that supply the net, before the disinfection procedure, station 1, and at two sites corresponding respectively to 2 hours, station 2, and 10 hours, station 3, of way for the water flow from the input of the net. The samplings have been performed in the months of June (test), July, September, October, November 2000, and monthly from March to July 2001. The samples were collected in polyethylene 20 l tanks, cleaned following the standard procedure for trace element analysis (Ghermandi et al., 1996). The samples were kept refrigerated up to the following treatments.

The production of aerosol from the drinking water samples (non-foaming gas-bubble process) was performed by means of an especially made laboratory apparatus (Cini et al., 1994). It consists of a pyrex glass column, that is filled not completely with the water to treat; a laminar flow of bubbles is achieved in the water by means of pure nitrogen (to avoid oxidation phenomena) injection from the column bottom. The water drops ejected from the water sample surface form a liquid film impacting on the inner surface of the column head, that is expanded to prevent foam formation. The surface of the column head is conical with an angle of 15° and collects the liquid films formed by the ejected drops in a tube, which is in contact with the central point of the conical impact surface.

For the treatment of about 14 l of water samples, a constant laminar nitrogen flow of 150 ml/min was used, and the aerosolization process was carried on for 6 hours. If different experimental conditions were used, the results were normalized to the sample volume (14 l) and to the treatment duration (6 hours).
The original water samples, the collected aerosols and the water depleted by the aerosolization process, i.e. three sub-samples from each sampled water, 90 sub-samples totally, were submitted to PIXE (Particle Induced X-ray Emission) analysis, and to spectrofluorimetric and dynamic surface tension measurements.

The PIXE technique is a multi-element methodology widely applied to the evaluation of element concentration in environmental samples (Ghermandi G., 2000), and is based on the detection of the characteristic X-rays emitted by a sample bombarded by a particle beam of adequate energy. A PIXE measurement allows the simultaneous determination of several elements (Na ≤ Z ≤ U), with low detection limits (a p.p.m. of the bombarded target).

The PIXE measurements were performed at the National Laboratories of Legnaro (Padua, Italy), by means of a proton beam accelerated to 1.8 MeV by a Van de Graaff, in a previously experimentally calibrated set-up. The targets for PIXE analysis from liquid samples were prepared by preconcentration and precipitation of the elements of interest as carbamates on Nuclepore polycarbonate membranes (0.4 µm pore size, 1 mg/cm² surface density), with Pd as internal standard (Ghermandi et al., 1996). The target preparation procedure was performed in a clean-room, using ultra pure reagents. The use of carbamate salts and of Pd in the target preparation hinders the determination of elements with Z < Cl; however, their concentration in the tested samples was strongly affected by the introduction of the commercial disinfectants. K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Hg, Pb concentrations, up to level of fractions of µg/l, were measured with errors ranging from 5% to 10%. The GUPIX98 software (Maxwell et al., 1995) was used for PIXE spectra processing. Blank samples of high purity water were prepared as the studied samples and analysed during each PIXE measurement session; their average contribution was subtracted to the sample compositions. The PIXE concentration data (ng/cm²) were transformed in µg/l (p.p.b.) in the tested liquid samples by means of the treated water volumes, that ranges from 15 ml (for the original drinking water samples and the depleted waters, after the aerosolization procedure) and 1-5 ml (for the collected aerosols).

The fluorescence spectra, for all the sub-samples, were obtained with a Perkin Elmer Luminescence Spectrometer mod. LS50B. The resulting values are the maximum fluorescence intensities (I_max) of organic matter in an emission spectrum that ranged from 320 to 630 nm (wavelength). All the values are normalised (I_norm) to the intensity of the peak of Raman fluorescence (I_Raman), typical of aqueous solutions, as : I_norm = I_max/I_Raman x 100.

The dynamic surface tension measurements were performed by a Mettler balance, equipped with a special apparatus in order to evaluate the weight of the meniscus. The measurement was repeated, to obtain the average value of the meniscus weight, from which the dynamic surface tension of the sample was calculated.

RESULTS AND DISCUSSION

The described non-foaming gas-bubble process provided the aerosol production from each water sample. From the examination of the experimental data, it clearly results that the volumes of aerosol produced from the thirty drinking water samples collected during this study, normalized to 14 l of treated water and to 6 hours of treatment duration, are strongly variable. The largest volumes of aerosol have been obtained from the waters collected at the first site (station 1). These samples were taken directly at the pumps of the aqueduct wells, before the addition of Na hypochlorite. The aerosol volume obtained from the station 1 samples is generally higher than the other two stations, while the aerosol volume extracted from the station 2 samples is generally the least among the three stations (Fig. 1). In addition, the station 2 aerosol volume values are not very variable respect to the other two stations. The average value of aerosol volumes obtained from the station 1 samples is 39.1 ml (st.dev. 22.0 ml) and for station 3 is 19.4 ml (st.dev . 16.4 ml), while for station 2 is 11.2 ml (st.dev. 6.3 ml); but if the July 2001 datum (see Fig. 1) is not included in the calculation, the average value for station 2 is 9.4 ml (st. dev. 3.6 ml). The addition of disinfectant to the water affects the surface activity of the organic substances that results in a reduced efficiency in the aerosol production.
The total mass of elements detected in the aerosol, obtained from each water sample, has been calculated from the element concentrations measured by PIXE and the collected aerosol volumes, normalized as reported above. The Cl concentration, coming mainly from the added disinfectant, was not accounted. The comparison of the trends of the total element mass for the three stations (Fig. 2) shows that the samples collected from the station 2 generally contain a lower amount of elements respect to the other two stations. The total mass average value for the samples of station 2 is 0.6 µg (st.dev. 0.4 µg), while for station 1 samples is 1.5 µg (st.dev 1.6 µg) and for station 3 is 1.9 µg (st.dev 1.5 µg). The data of Sept. 2000 were not included in the calculation, because of the exceptionally high value for station 1, reported (x 10^{-1}) in Fig. 2, probably due to an anomalous quantity of soil particles.

These results are in agreement with the aerosol volume behaviour: based on the total mass of element value for station 1, before the addition of disinfectant, at the station 2 the HS appear depleted in their surface activity and consequently in the scavenger capability respect to the elements in solution. Nevertheless, these capabilities are restored at the station 3.

The concentration of the measured elements, Cl a part, are generally in the range units-tens of p.p.b., far from the values dangerous for human health. Fe and Zn concentration are higher than 100 p.p.b. only for the Oct. 2000 water sample collected at station 1, and are probably due to solid particles coming from the pumping system: in fact in the corresponding aerosol an exceptional concentration of these elements was not found.

The spectrofluorimetric analysis results are expressed in terms of the enrichment ratio (ER) between the fluorescence intensity measured in the produced aerosol and in the original sample. The ER values are always $\geq 1$, because the organic matter concentration in the aerosol samples is higher than in the original.
The calculated ER values range from 1 to 6 for the station 1, May 2001 sample, for which ER = 20.99 (the aerosol was very turbid), while the average $I_{norm}$ value for the aerosol samples is about double respect to original samples.

The wavelength values of the fluorescence intensity maximum are close to 360 nm for station 1 samples (both the original ones and the aerosols), that may indicate the presence of lignin and aromatic groups, that precede the formation of more stable humic compounds.

The calculated ER values for the station 2 are in the range 1.3 - 13.3. The average $I_{norm}$ for the aerosol samples is about seven time the value for original samples. This is mainly due to the very small aerosol volumes produced from the station 2 samples. Even if the efficiency of the aerosol production procedure is assumed as linear with time, it probably decreases in the last part of the treatment. When the HS activity in the original sample is low, the efficiency of the procedure rapidly decays, and may stop during the treatment time, so that the produced aerosol volume is quite little. When the HS activity in the original sample is high, the efficiency of the procedure slowly decays, and the aerosol production continues providing larger aerosol volumes, even if in them the fluorescent organic matter concentration progressively decreases.

The wavelength values of the fluorescence intensity maximum are close to the station 1 data.

The calculated ER values for the station 3 range from 1.0 and 23.1, but, two samples a part, ER is lower than 4.3, so that its variability is comparable with station 1 values, while the station 2 values result more variable. The wavelength values of the fluorescence intensity maximum are in the range 360 - 417 nm, and also in the original samples the wavelength value is frequently close to 400nm, that is typical of terrestrial humic acids.

The dynamic surface tension values ($\text{mN m}^{-1}$) result generally anti-correlated with the fluorescence intensities, to confirm that the increasing concentration of fluorescent matter at the water surface involves a surface tension reduction.

The comparative behaviours of dynamic surface tension and of fluorescence intensity ($I_{norm}$) for the aerosols produced from station 1 drinking water samples are reported in Fig. 3. The missing June 2000 data depend on an error in the surface tension measurements.
The examination of all the experimental results may support this interpretation: the addition of Na hypochlorite to the well waters soon pumped, and therefore enriched in lignin and in the unstable aromatic compounds that precede the humic substances formation, kept rapidly the water pH to low values (probably < 2.2) (Petronio, B. M., 1997) that induce the precipitation of humic and fulvic acids. The humines principally remain in solution: if the original chemicalophysical conditions are restored, these humines may contribute to the production of new humic substance in solution.

It is in agreement with the higher aerosol volumes collected and the high mass of elements determined from the station 1 samples. In addition, the fluorescence intensity maximum wavelength of the station 1 samples indicates that they contain mainly lignin. Two hours after the disinfection procedure, the water flow in the net arrives at station 2: in the station 2 samples, the humic substance activity results depleted (small aerosol volumes, low element mass), while their composition (from the fluorescence intensity maximum wavelength) is not changed. Ten hours after the disinfection procedure, at station 3, the humic substances have reproduced humic acids in solution, as confirmed by fluorescence intensity maximum wavelength typical of terrestrial humic acids. The restored activity of the humic substances determines an increase of the aerosol volumes produced by sample treatment and of the mass of scavenged elements measured by PIXE, that return to values comparable with station 1.

CONCLUSIONS

A new approach for the study of some aspects of the disinfection procedure impact on potabilized water quality has been here presented. The variability of humic substance surface activity has been investigated along a drinking water distribution net, by means of a suitable experimental apparatus that artificially produces an aerosol from the water sample. The collected aerosol volumes and the mass of elements determined by PIXE in these aerosols, principally heavy metals scavenged by humic substances, indicate a depletion of HS activity in the water flowing in the net two hours after the disinfection procedure. The spectrofluorimetric analyses suggest that the addition of disinfectant probably hinders the production of new humic substance in solution. Nevertheless, the HS activity results restored in the water sampled along the distribution net about ten hours after the disinfection procedure.

In this work only some relevant aspects of the complex and variable HS behaviour has been examined; however, the experiments and the analytical measurements show that in a simple aqueduct net, as the tested one, the impact of disinfection by addition of Na hypochlorite on HS activity is limited and transitory for what concerns the auto-depuration capability of humic substances.
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