Control and monitoring disinfection by products by POX and UV-254 parameters in Friuli (Italy) drinking waters

DANIELE GOI*, VICTOR TOSORATTI*, GIULIANO DOLCETTI* & IGINIO COLUSSI#

Abstract. This study reports on a monitoring program carried out on 25 drinking water sources in the Friuli Venezia Giulia (Italy) district. In this area, particular heavy potable water resources contamination does not seem to occur; therefore, chemical disinfection and disinfection byproducts (DBPs) formed during chlorination should be considered as a noticeable potential drinking water hazard.

The presence of volatile chlorination byproducts is investigated by the sum parameter POX (Purgeable Organic Halogen), while the content of organic matter content (DBPs precursor) is assayed with the surrogate parameter UV-254. The introduction of these analytical procedures has a two-fold interest, concerning first the simplicity in analyzing and second the proof of these parameters in predicting organic halogen content in chlorinated drinking water. Water samples were taken on the catch systems (sources and wells) in order to detect the natural contamination by halorganics, and a monitoring of POX was also made on the distribution systems. In a second phase of the study these samples were chlorinated to determine SDS – POX (Simulated Distribution Systems POX) and POXFP (POX Formation Potential) parameters.

The measurements showed no natural POX contamination and low POX concentration in the distribution systems, generally small SDS-POX content but a measurable POXFP that evidences DBPs precursor content.

A correlation between the POXFP and UV-254 as shown by a linear regression curve confirms a relationship between these measures of halorganic precursors.

Keywords. Chlorination, drinking water, POX, Organic-Halogen.

* Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, Italy. E-mail: clsgoi@dstc.uniud.it; victor.tosoratti@dstc.uniud.it
# Dipartimento di Ingegneria Chimica, dell’Ambiente e delle Materie Prime, Università di Trieste. E-mail: iginioc@dicamp.univ.trieste.it
**Introduction.** The Friuli Venezia-Giulia region is located in the North-East of Italy, covers an area of 7,844 Km\(^2\); 43% of the territory are mountains, 19% are hills, 38% is plain. In this territory fresh water comes both from mountain sources and wells placed on the alluvial plain. Since this zone is not very industrialized, the water quality distributed by local aqueducts is generally excellent. To avoid bacteriological contamination of fresh and distribution system tap waters, disinfection by chlorination is conventionally used. For this reason, particular attention is given to control the pollution induced by Disinfection ByProducts (DBPs).

The bacteriological contamination can be intended as a natural one, but as it is the most dangerous pollution from an epidemic point of view, it is always controlled from the drinking water caption plant to the distribution system (Minear and Amy, 1996). Disinfection is the typical methodology to control bacteriological contamination, and the most extensively used disinfectant remains chlorine.

From the beginning of the eighties, many authors investigating drinking waters disinfected by chlorine and other chlorine products, found measurable concentrations of organic halogen disinfection byproducts (Rook 1974), which can be either volatile or not volatile (Stevens et al., 1989). The most common volatile DBPs are Trihalomethanes (THMs) that include Chloroform, Bromoform, Bromodichloromethane, Chlorodibromomethane (Yu and Cheng, 1999).

Several studies were made by many authors about formation of these compounds in water (Singerand and Chang, 1989; Merlo et al., 1993; Pomes et al., 1999), where it was confirmed that organic matter (in particular humic and fulvic acids) react with chlorine to generate DBPs. A correlation between organic matter and DBPs is well defined in most of the research carried out, confirming the organic matter as the precursor of the DBPs formation.

Toxicological investigations have shown that THMs and many other volatile compounds are animal carcinogens and have mutagenic proprieties (Bull, 1982). Other studies proved that numerous non-volatile chlorination byproducts, also identified at trace levels, are contributors to the overall mutagenicity of chlorinated drinking water (Kool, 1984).

Subsequent to new health-related importance of this water contamination, the European Commission have proposed new guidelines of drinking waters that consider controls for many volatile organic halogens (among these THM, 1,2 dichloroetane, tetrachloroethylene, trichloroethylene). Moreover, new analytical methods to measure organic halogen concentration in water and new removal technologies (Backlund, 1994) have been developed. The coulometric tritiation method is an analytical procedure which allows global measure of organic halogen compounds in water by parameters as POX (Purgeable Organic Halogen) and NPOX (Not Purgeable Organic Halogen). The first one represents the amount of organic halogen that can be globally purged from a water sample (e.g.
Control and monitoring in Friuli drinking waters

THMs), while NPOX generally refers to an estimation of the heavy halo-
genated organics (HAA-Haloacetic acids, haloketones, any others not
identified) (Jekel, 1980).

POX is a collective parameter useful for the evaluation of potentially harmful volatile organic halogen substances formed as DBPs in drinking water.

This parameter can be used to characterize pollution induced by chlorination, when chlorine and chlorine products are used in drinking water treatment.

Different waterworks distributed around the Friuli region in the north-
est of Italy were monitored for present and potential DBPs, and for each aqueduct, POX, SDS-POX (Simulated Distribution Systems POX) and POXFP (Total Trihalomethane Formation Potential) were determined.

These parameters were obtained following a procedure that consists in measuring POX in samples treated as described beyond, these procedures are similar to those utilized to determine SDS – THM (Simulated Distribution Systems Trihalomethanes) and TTHMFP (Total Trihalomethane Formation Potential) described in Standard Methods for the Examination of Water and Wastewater 20th Ed./part 5710.

During the monitoring an organic matter content measurement was taken using the Total Organic Carbon (TOC) surrogate parameter UV-254 (Dobbs et al., 1972), referring again to Standard Methods for the Examination of Water and Wastewater 20th Ed./part 5910. A correlation between the last two parameters was found.

Materials and Methods

Sampling and study area. The area of the Friuli region investigated includes the Province of Udine in which 4 great water supply organisms provide and treat water for up to 70% of the population (about 400000 inhabitants). The rest of the inhabitants are supplied by municipal waterworks with lower capabilities (Figure 1).

In this province 25 water supply points were chosen for monitoring, some of them are mountain sources intakes, others are wells with a deep range from 30 to 150 m.

Some samples were taken directly from mountain sources and wells, paying attention to collect fresh water, others along the distribution system far from the chlorination point (Table 1).

Four 0.5 L glass bottles were collected for each sample at the supply station, two for natural POX content in water source and UV-254 measurement, the remaining for POXFP and SDS-POX determination. To assay POX content in the distribution system one sample of tap water far from the source network was also taken. According to procedures for sample treatment, bottles were fully filled and sealed with TFE-lined screw cups; the analytical determinations were completed within five hours from withdrawal.

Procedures and instrumentation. Organic matter content was evaluated by means of UV-254 surrogate parameter using a JASCO UVIDEC-505 UV-Vis spectrophotometer with
The POX measurement was carried out by an Euroglas ECS1000 analyzer by microcoulometric titration, following the ISO 9562 standard method.

This procedure consists in purging the sample contained in a 100 ml purge-bottle immersed in a water bath at 60°C. An oxygen flow passing through the purge-bottle releases purgeable organic halogens which enter an oven maintained at 950°C, so all organic halogen material is converted in hydrogen halides (HCl, HBr, etc.). A scrubber with sulfuric acid brings temperature to low values and eliminates water vapors in flow that come into an electrolytic cell, here halogen charges are converted to electric current (I) with the aid of a microcoulometer. This current over a specified period of time (the titration time) is a measurement of the quantity of organic halogen content of the sample. The integration of current versus time gives electric charge:

$$Q(\text{el}) = \int_0^t I dt$$

The final value of POX concentration (µg/L as Chloride) follows the expression:

$$\text{POX} = \frac{Q(\text{el}) \cdot M \cdot n(\text{el})}{V \cdot F}$$

where:

- POX = Mass concentration [µg/L as Cl⁻]
- Q(\text{el}) = Electric charge of organic halogens purged [C]
- V = Sample volume [L]
- M = Molar mass of chloride: 35.45 x 10⁶ µg/mol
- F = Faraday constant: 96487 C/mol
- n(\text{el}) = Yield of electrolytic cell

Figure 1. Map of Friuli region with main hydrology and location of sampling sites.
### Table 1. Monitoring data, water supply organisms and chlorination typology.

<table>
<thead>
<tr>
<th>Water supply organism</th>
<th>Sample</th>
<th>Chlorine¹</th>
<th>POXNC²</th>
<th>POX³</th>
<th>SDS-POX</th>
<th>POXFP</th>
<th>UV 254 nm (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMGA W1</td>
<td>0.10</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>3.20</td>
<td>14.15</td>
<td>5.80E-03</td>
<td></td>
</tr>
<tr>
<td>W2</td>
<td>0.10</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>2.45</td>
<td>12.42</td>
<td>7.90E-03</td>
<td></td>
</tr>
<tr>
<td>W3</td>
<td>0.10</td>
<td>3.4</td>
<td>5.3</td>
<td>9.10</td>
<td>39.20</td>
<td>1.14E-02</td>
<td></td>
</tr>
<tr>
<td>W4</td>
<td>0.10</td>
<td>n.d.</td>
<td>3.1</td>
<td>2.20</td>
<td>10.58</td>
<td>4.30E-03</td>
<td></td>
</tr>
<tr>
<td>Municipal aqueduct -</td>
<td>S5</td>
<td>0.20</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>8.90</td>
<td>48.28</td>
<td>8.00E-03</td>
</tr>
<tr>
<td>Bordano S6</td>
<td>0.10</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>10.50</td>
<td>45.36</td>
<td>6.30E-03</td>
<td></td>
</tr>
<tr>
<td>Udine municipal aqueduct society with automatic HClO chlorination device</td>
<td>W4</td>
<td>0.10</td>
<td>n.d.</td>
<td>5.1</td>
<td>1.65</td>
<td>17.82</td>
<td>1.03E-02</td>
</tr>
<tr>
<td>W4</td>
<td>0.10</td>
<td>n.d.</td>
<td>3.9</td>
<td>5.65</td>
<td>23.11</td>
<td>6.60E-03</td>
<td></td>
</tr>
<tr>
<td>Cornappo River consortium - AMGA - Tricesimo</td>
<td>S8</td>
<td>0.10</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>7.70</td>
<td>42.55</td>
<td>9.50E-03</td>
</tr>
<tr>
<td>Central Friuli Aqueduct W9</td>
<td>0.10</td>
<td>n.d.</td>
<td>3.5</td>
<td>6.60</td>
<td>27.00</td>
<td>8.50E-03</td>
<td></td>
</tr>
<tr>
<td>W10</td>
<td>0.05</td>
<td>n.d.</td>
<td>4.8</td>
<td>2.10</td>
<td>10.80</td>
<td>7.60E-03</td>
<td></td>
</tr>
<tr>
<td>W11</td>
<td>0.10</td>
<td>n.d.</td>
<td>2.8</td>
<td>2.00</td>
<td>11.70</td>
<td>1.26E-02</td>
<td></td>
</tr>
<tr>
<td>W12</td>
<td>0.10</td>
<td>n.d.</td>
<td>5.1</td>
<td>1.65</td>
<td>17.82</td>
<td>1.03E-02</td>
<td></td>
</tr>
<tr>
<td>Poiana aqueduct consortium - Cividale del Friuli</td>
<td>W13</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>4.20</td>
<td>19.44</td>
<td>5.50E-03</td>
</tr>
<tr>
<td>S14</td>
<td>0.25</td>
<td>n.d.</td>
<td>5.0</td>
<td>8.50</td>
<td>33.16</td>
<td>1.10E-02</td>
<td></td>
</tr>
<tr>
<td>Municipal aqueduct -</td>
<td>S15</td>
<td>0.20</td>
<td>n.d.</td>
<td>3.4</td>
<td>7.40</td>
<td>27.32</td>
<td>1.14E-02</td>
</tr>
<tr>
<td>Forni Avolti</td>
<td>S16</td>
<td>n.d.</td>
<td>n.d.</td>
<td>5.80</td>
<td>22.14</td>
<td>1.75E-02</td>
<td></td>
</tr>
<tr>
<td>Municipal aqueduct -</td>
<td>W17</td>
<td>n.d.</td>
<td>n.d.</td>
<td>3.10</td>
<td>16.74</td>
<td>1.10E-02</td>
<td></td>
</tr>
<tr>
<td>Forni di Sopra</td>
<td>S18</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2.70</td>
<td>15.23</td>
<td>1.40E-02</td>
<td></td>
</tr>
<tr>
<td>Palmanova - CAFC</td>
<td>S19</td>
<td>0.10</td>
<td>2.5</td>
<td>&lt;2</td>
<td>5.40</td>
<td>20.52</td>
<td>1.71E-02</td>
</tr>
<tr>
<td>Municipal aqueduct -</td>
<td>S20</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>6.30</td>
<td>21.60</td>
<td>1.26E-02</td>
</tr>
<tr>
<td>Ravascletto S19</td>
<td>S21</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>6.90</td>
<td>40.50</td>
<td>1.51E-02</td>
</tr>
<tr>
<td>Seazza aqueduct -</td>
<td>S22</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>5.10</td>
<td>20.52</td>
<td>1.37E-02</td>
</tr>
<tr>
<td>Preone</td>
<td>S23</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>9.80</td>
<td>47.74</td>
<td>1.74E-02</td>
</tr>
<tr>
<td>Municipal aqueduct -</td>
<td>S24</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>7.40</td>
<td>39.10</td>
<td>2.01E-02</td>
</tr>
<tr>
<td>Tarvisio</td>
<td>S25</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt;2</td>
<td>5.40</td>
<td>32.40</td>
<td>1.87E-02</td>
</tr>
</tbody>
</table>

W= Wells;  S= Springs;  n.d. = Not detected.

1. Chlorine is referred to the far from source sample.
2. POXNC= POX Natural Content.
3. POX in distribution system far from chlorination point.
SDS-POX and POXFP procedures suggest use of 250 mL bottles and pretreatment of sample as follows:

SDS-POX samples were buffered within the pH range 7.0±0.2 by NaOH 0.1 N or HNO₃ 0.1 N and added with 0.5 mL of phosphate buffer solution. Then, a calculated volume of NaClO solution (100 mg/L) was added. This chlorine concentration was calculated considering a 0.2 mg/L chlorine free value in any waterwork distribution point of the simulated network (as established by Italian guidelines for drinking water DPR 236/88).

Temperature, pH, chlorine dose, residual concentration and storage time (estimation on average water retention time) were adjusted to simulate conditions in distribution systems.

For POXFP determination samples were treated as above with a chlorine dose providing an excess of 2-4 mgCl₂/L, a temperature maintained at 25°C for 7 days of reaction time. All reagents used were of high purity.

Results. Data collected during the last 20 years by the Italian drinking water quality control office put in evidence the good quality of all potable waters considered in this monitoring, where both spring and well waters have optimal characteristics for drinking purposes. Risks of microbiological contamination and, in particular, use of chlorination in its treatment seem to be the most important problem. Most efforts of waterwork management in this situation are geared to achieve an economic equilibrium between chlorination practice and microbial pollution control without compromising tap water quality.

The experience of this study was organized to assay potentiality of
POX and UV-254 parameters in procedures to routine control DBPs formation in monitored drinking waters (Figure 2).

All samples considered seem to have no microbial contamination and not detectable value of natural POX content. However, W3 and S19 show a POX contamination likely caused by a local contamination via organic halogen compounds leaching from ground drainage of industrial activities.

Most waters coming from high mountain springs seem to be less suitable for disinfection by chlorine considering POXFP values (S5-S6, S8, S21, S23-S24) while plain wells seem to have a lower DBPs precursor content (W1, W10, W11, W22).

Any samples taken in the network far from source points have a measurable POX content (W3, W4, S7, W9-11, S12, S14-15, S19), in other points values approaching instrument detection limits are observed.

The SDS-POX of all monitored regional waterworks is very low but larger aqueducts, where better controls on chlorine distribution and dosage are performed (W1-W4, W9-S12, W13-S14), seem to be in a better situation. In fact, chlorination, if not controlled and discontinuous, can bring about larger DBPs formation.

Mild chlorination assumed (0,05-0,2 mg/l free Cl₂) in estimation of organic halogen content in simulated distribution system, result in limited concentration of SDS-POX parameter too (2-10 µgCl/L), but POXFP has an observable value indicating a diffused presence of organic halogen precursors in monitored waters.

Surrogate parameter UV-254 on UV-spectrophotometer reveal organic matter content in the examined waters (mainly humic and fulvic acids). A relation between this parameter and POXFP is found, confirming presence of organic matter as precursors of the

Figure 3. Linear regression constructed by UV-254 and POXFP values.
organic halogen compound formation in chlorinated water.

A linear correlation is investigated between these last two parameters, resulting in a correspondence between potential formation of organic halogens and natural organic content measured with surrogate parameter UV-254 as depicted by other authors (Edzwald et al., 1985) (Figure 3).

Discussion. The waters analyzed can be considered of good quality following European Community and Italian Guidelines, so that the major source of drinking water contamination, potentially, could be a harmful organic halogen content as a result of chlorination.

The analyses conducted on spring and well water in the Friuli Region show the presence of POXFP in all points assayed, while the POX natural content or SDS-POX seem to be low or negligible. The two parameters POX and UV-254 can be considered an easy and cost-effective approach to monitoring and estimate volatile DBPs in this kind of waters.

Another important result seem to be the lower concentration of UV-254 organic content and POXFP found in well samples vs. spring samples. This is probably connected to the topology of intake catchments to reach a supply of water that let organic matter (dissolved matter in particular) drain into catchment tank, during particularly strong rainfall. Less organic matter content is observed in deep wells.

Acknowledgements. The authors are grateful to all the persons who have collaborated at this work, and in particular to Dr. R. Mattioni (A.R.P.A. - F.V.G.) and the Region F.V.G.
References/ Bibliografie


