Natural Organic Matter from Surface Water: Potential Risk for Drinking Water

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Summary

Natural organic matter (NOM) of surface water is investigated in relation to humic matter. NOM can be divided into two fractions: humic substances (HS) and non humic substances (non-HS). MON is used as generic name for all natural organic compounds which include carbohydrates, lipids and amino acids. Surface water represents a source of drinking water for human communities and is the result of the water trail, which contained both allochthonous influences (washing of the agricultural land from adjacent river in the area, and washing in case of the flood meadows) and autochthonous influences (from the death aquatic fauna and flora and their metabolic transformations). Removal of natural organic matter from water is directly proportional to the decrease potential of the formation of trihalomethanes (THM) and haloacetics (HAA), compounds with carcinogenic risk, which are formed during chlorine disinfection. In this study, the natural organic load in waters from the upper river Bega, was examined by usually parameters: chemical oxygen demand (COD), turbidity, color and organic matter status, respectively: total organic carbon (TOC), dissolved organic carbon (DOC) and UV-VIS absorbance at 250-450 nm, in reference to the absorbance at 254 nm (A254), 280 nm (A280), and 365 nm (A365). A254 is the parameter selected for the overall evaluation of humic material and A365 is useful for evaluating the compounds with pronounced aromatic and hydrophobic character, and higher molecular weight, respectively. Evaluation of new analytical methods of humic matter in water is necessary for understanding the structure of these compounds and their chemistry on the stages for obtaining drinking water.
Keywords: humic matter, surface water, natural organic matter, UV-VIS absorbance.

**Introduction**

Surface water represents a source of drinking water for human communities and is the result of the water trail, which contained both allochthonous influences (washing of the agricultural land from adjacent river in the area, and washing in case of the flood meadows) and autochthonous influences (from the death aquatic fauna and flora and their metabolic transformations). In the surface water naturally occurring animal and vegetable matter transformations of death materials occur in the metabolic activity of specific aquatic biocenosis.

The biological decomposition of dead material results in a heterogeneous mixture of organic compounds. They have a varied chemical composition both in terms of the presence of functional groups (phenol, carboxylic, alcohol, amine, etc.), molecular weight, degree of polymerization etc. [1-4]

Mixture of the formed organic compounds humic substances (HS) and non humic substances (non-HS) is known as humic matter and has strong aromatic character. The humic matter also possesses hydrophilic/hydrophobic properties, being determinates by means of humic compounds formation, climatic and geographical conditions, soil quality etc. The presence of humic matter in water can dramatically affect its quality by:

- Major contributions to water color changes;
- Complexation with metals, forming soluble complexes that ultimately cause increased metal content of the water;
- Formation of carcinogens produced in the phase of water disinfection with agents based on chlorine, for example: trihalomethanes (THM) and haloacetics (HAA). [5,6]

The characterization of water composition is difficult due to complexity of mixture of organic compounds.

The control parameters analyzed in terms of conventional treatment process are: pH, turbidity, chemical oxygen demand (COD), color intensity by absorbance at 436 nm wavelengths, (A436), taste and smell. These analyses are imposed by the rigors of drinking water quality.

The parameters used in advanced control stages of treatment of drinking water are expressed by TOC (total organic carbon) and DOC (dissolved organic carbon), in samples filtered through 0.45 µm filter. All these parameters give quantitative information about water quality [7,8,9,10]

It sought a quick analyze method of the raw and treated water, as well as a method capable to find compounds in water that are in greater quantities than usually, to detect the
appearance of unwanted, toxic compounds detectable by UV-VIS analyze. Because in UV-VIS domain could be find $\pi-\pi^*$ and $n-\pi$ electron transitions caused by unsaturated bonds and aromatic ring as well, an analytical method is used for natural and waste waters since 1930. The domain between 250 nm and 450 nm has a particular interest because the intensity of A254 is directly connected with some organic functional groups found in humic matter and because the necessary low pressure mercury lamp emits an intense ray of wavelength and it is a low-cost one.

Between the absorbance value at $\lambda = 254$nm and other parameters like TOC, DOC, etc. have been established some useful correlations for raw water characterization and guidance on the process of coagulation. The increase of the molecular size of compounds is directly proportional to the intensity at higher wavelengths.

The absorbance at 280 nm, A280, was introduced because it gives an indication of the presence of fully aromatic compounds, through $\pi-\pi^*$ electron transitions.

The absorbance at 365 nm, A365, was introduced because it gives an indication of the presence of aromatics and hydrophobic compounds with high molecular weight, and with low humidification process of organic matter, respectively.

The ratio A254/A365 is the property of aquatic humic substances, and increases as the aromaticity and hydrophobic character and molecular size decreases. [5,11,12].

**Materials and Methods**

Four water samples collected from the upper and medium section of a river used downstream for drinking water production were analyzed.

The collection and transport of samples are made under current rules. Water samples were taken between 8-12 a.m., after a period of torrential rainfall. The sampling date was 04.21.2010.

The conventional parameters analyzed for the control of the treatment process are: pH, turbidity, chemical oxygen demand (COD), color intensity by measurement of the absorbance at $\lambda = 436$ nm (A436), taste, smell - all these parameters being forced by the rigors of quality standards for drinking water.

The turbidity was measured using a HACH 2100 device and the pH values with an Thermo Orion pH-meter.

COD is carried out by oxidation with an oxidizing agent (potassium permanganate) and represents the demand of oxygen for oxidation of the organic compounds in acidic conditions.

To control the advanced stages in the treatment of drinking water, the following parameters were used: total organic carbon (TOC), dissolved organic carbon (DOC) in
samples filtered through 0.45 µm filter, and absorbance at different wavelengths (A254, A280, A365, A436), respectively.

Parameters TOC, DOC were determined with a carbon analyzer Multi C/N 2100 Analytik Jena device.

A254 is the value of absorbance at 254 nm. This wavelength was chosen because organic compounds with aromatic character or with conjugated double bond have absorption in bands B and K. The functional groups -O-, -CH=O, -COCH3, -COOH,-COO-, -CH=CH2, -OH, -NH2 present in humic compounds have absorption at this wavelength.

A280 is the value of absorbance at 280 nm, and represents another parameter that indicates the aromatic character of humic matter containing aniline derivatives, benzoic acid, polycyclic aromatic hydrocarbons with two or more rings, arenas, phenols, etc. This humic matter is responsible for the harmful disinfection by-products (DBPs).

A365 it is a parameter correlated with the presence of humic substances in water. It was selected as indicating the presence of compounds resulting from aquatic heterotrophic metabolism, compounds with aromatic character and nitrogen functions.

A436 is a parameter measuring the absorbance at λ = 436nm and indicates the degree of coloration of the water by chromophore groups [5].

The absorbances were measured with a Specord 205 spectrophotometer Analytik Jena device, in quartz cuvettes of 1 cm at prescribed wavelengths.

The ratio A254/A 365 indicates the proportion of high molecular weight aromatic substances and the total N content of aromatic substances and it is a useful parameter to measure indirectly the distribution of humic material with low molecular weight comparing it with the hydrophobic compounds.

Results

Table I presents the characteristics of water samples noted with L1, L2, L3, L4, in terms of traditional parameters in water analysis: pH, COD, color and turbidity.

Samples are taken from different points situated on the upper stream of water, before the impact with human activities.
Table I. Characterization of water samples taken from the upper stream of water following a rainfall period by conventional parameters pH, COD, color and turbidity

<table>
<thead>
<tr>
<th>Source water</th>
<th>pH</th>
<th>COD [mg O₂/L]</th>
<th>Turbidity [NTU]</th>
<th>Absorbance λ= 436 nm [m⁻¹]</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>6.87</td>
<td>2.48</td>
<td>12.5</td>
<td>&lt;0.1</td>
<td>Turbid water area</td>
</tr>
<tr>
<td>L2, Influent</td>
<td>6.76</td>
<td>14.13</td>
<td>65</td>
<td>&lt;0.1</td>
<td>High turbidity water area</td>
</tr>
<tr>
<td>L3</td>
<td>6.93</td>
<td>2.23</td>
<td>8.5</td>
<td>&lt;0.1</td>
<td>Relatively clear water area</td>
</tr>
<tr>
<td>L4</td>
<td>6.98</td>
<td>2.22</td>
<td>12</td>
<td>&lt;0.1</td>
<td>Turbid water area</td>
</tr>
</tbody>
</table>

The characteristics of water samples noted L1, L2, L3, L4, conducted by state parameters COD, TOC, DOC and ratio DOC/TOC are presented in Table II.

Table II. The organic load expressed by TOC and DOC in water samples taken from the upper stream of water following a rainfall period

<table>
<thead>
<tr>
<th>Source water</th>
<th>TOC [mg C/L]</th>
<th>DOC [mg C/L]</th>
<th>Ratio DOC/TOC</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>3.71</td>
<td>1.96</td>
<td>0.52</td>
<td>Solid organic matter is similar to the dissolved matter</td>
</tr>
<tr>
<td>L2, Influent</td>
<td>15.89</td>
<td>5.64</td>
<td>0.33</td>
<td>Predominant solid organic and fine colloidal matter</td>
</tr>
<tr>
<td>L3</td>
<td>2.48</td>
<td>2.13</td>
<td>0.85</td>
<td>Predominant dissolved organic substances</td>
</tr>
<tr>
<td>L4</td>
<td>2.51</td>
<td>2.17</td>
<td>0.86</td>
<td>Predominant dissolved organic substances</td>
</tr>
</tbody>
</table>

Above analysis mainly gives information about the quantity of matter found in water. Introducing the UV-VIS spectral analysis we were allowed to estimate the abundance of aromatic compounds, finding information about the presence of some classes of organic compounds and about the stage of humic matter in natural materials, fine particles, colloidal systems, soluble compounds etc.

Table III contains the values of absorbance A254, A280, and A365 and A254/A365 ratio determined for water samples L1, L2, L3, L4.
Table III. Organic load expressed by absorbance A254, A280, A365 and A254/A365 ratio of water samples taken from the upper stream of water following a rainfall period

<table>
<thead>
<tr>
<th>Source water</th>
<th>A254 [m⁻¹]</th>
<th>A280 [m⁻¹]</th>
<th>A365 [m⁻¹]</th>
<th>Ratio A254/A365</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>2.21</td>
<td>1.88</td>
<td>0.27</td>
<td>8.18</td>
</tr>
<tr>
<td>L2</td>
<td>2.12</td>
<td>1.63</td>
<td>0.27</td>
<td>7.85</td>
</tr>
<tr>
<td>L3</td>
<td>2.57</td>
<td>2.37</td>
<td>0.31</td>
<td>8.29</td>
</tr>
<tr>
<td>L4</td>
<td>2.58</td>
<td>2.36</td>
<td>0.31</td>
<td>8.32</td>
</tr>
</tbody>
</table>

**Discussion**

From Table I: samples L1, L3, L4 are sampled in the main stream of river km 0, Km7.0 and Km 10.0 and L2, influent at km 3.0.

Sampled water had a small amount of organic compounds, COD ranging from 2.22 to 2.48 mgO₂/L and the turbidity values, even after heavy rainfall, are relatively low, being in the range from 8 to 12.5 NTU.

Influent point L2 originates from a steep slope covered with leaves, twigs, shoots etc. washing the soil, actually resulted in a large amount of organic compounds, having COD of 5.7 to 6.4 times greater than other samples of water, and an amount of 5 to 6 times higher of fine and colloidal suspensions, expressed as turbidity.

Dissolved organic matter and solid compounds consist of heterotrophic decomposition of plant debris and is driven mainly by slope wash.

From Table II: samples L1, L3, L4 from the main stream are less loaded with organic matter which varies between 2.51 and 3.71 mg C/L, containing organic compounds, solids and dissolved solids (over 50% from the dissolved material). Sample L2 washing slopes, contains an amount of organic carbon expressed as TOC, 4-6 times larger than water samples from the main stream water.

Share of total organic carbon compounds in the sample influent L2 is the solid organic matter, driven on the basis of fine suspended colloidal systems is two thirds and only one third dissolved compounds.

From Table III: note that the range of variation for parameters A254, A280, A365 is insignificant, being in conjunction with conventional features and water status. Absorbance at λ = 254 nm is between 2.12 and 2.58 m indicating the presence of organic matter with aromatic rings and organic functions in small amount as a result of lower activity of organic decomposition.
A280, absorbance at $\lambda = 280$ nm were recorded between 1.63 and 2.37 m and shows a low quantity of polycyclic aromatic hydrocarbons with two or more rings, arenes, and phenols.

A365, absorbance at $\lambda = 365$ nm indicates the presence of material with high molecular weights, but in small quantities, 7-8 times lower than that indicated by A254. The ratio A254/A365 located from 7.85 to 8.32, due to large value of A254 and low for A365 indicate a high degree of conversion of organic matter in mixed function compounds and the preponderant aromatic character of the heterogeneous mixture compounds.

**Conclusion**

Natural analyzed waters, in the upper stream, have COD less than 5 mg O$_2$/L.

Waters are loaded with dissolved organic matter, except the water washing the slopes; in this case the stream brings dissolved compounds that represent up to 2/3 of TOC and are fine and colloidal suspensions.

Expression of organic load of water by UV-VIS properties increases the possibilities of overall characterization of water quality by absorbance measurements of selected classes of compounds.

The high A254/A365 ratio, mainly gives indications about the presence of dissolved organic matter, with aromatic and hydrophobic character, found in areas exposed to heavy rains washing.

Water brings low quantity of high weight molecular compounds (indicated by A365, A436) because the processes of humic matter production are in an early stage due to lower temperatures, so these compounds are in water mainly from the previous year.

**References**