Chemical Analysis and the River Mura Water Quality

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ABSTRACT

The environment contains several water sources such as brooks, rivers and lakes, that indirectly or directly contribute to human wellbeing and a variety of water ecosystems. Rivers are, unfortunately, still the main domestic and industrial waste-water transmission source, creating both the permanent and largest pollution source. From among other significant pollution sources, outflows from agricultural areas, also have an influence on climatic changes. Rivers are regarding pollution easily accessible, therefore it is very important to supervise water-pollution, the quality of river-basins' waters, and to assess water quality according to time and space influences.

This paper presents the physical and chemical parameters of the River Mura's water for the period 1996 to 2009. Samples of water were taken at four diverse measuring places; analyses being performed in two independent laboratories. The parameters that characterized the 336 samples were: water temperature, pH, electrical conductivity, dissolved oxygen, oxygen saturation, oxygen deficiency, biochemical and chemical oxygen demand in filtered and non-filtered samples, total and carbonate hardness, suspended substance share, AOX, TOC and phosphate, ammonium, nitrite, nitrate, calcium, magnesium, sodium, potassium, chloride, sulphate and phosphate ions contents.

The seasonal and space influences of pollution on the River Muras’ were researched using linear regression. Special attention was devoted to the monitoring of those individually measured parameters that most reflected river’s quality. Monitoring of the River Mura’s water pollution and the results from particular measured parameters, can also be used when searching for pollution causes and when planning preventive measures for protective purpose.

KEY WORDS:
River, Water quality, Pollution, Physical-chemical parameters, Linear regression.
INTRODUCTION

1.1 The River Mura

A river-based landscape is often an area within, people live and which is constantly being changed by its inhabitants. This process has been evolving over millennia, as great rivers are sources for sustaining life. These sustainable activities have more recently begun to destroy the rivers, and the natural dynamics and diversities of the many life-forms associated with them. However, the lower-flow of the River Mura has managed to preserve many rare parts of its landscape. Conservation of the river’s flow, has in addition to exceptional ecological functions and the role of huge water restraint, providing better flood-safety, had a decisive influence on underground water-quality and the supply of clean drinking water.

Rivers can generally be classified as either alluvial, bedrock, or some mix of the two. Alluvial rivers have channels and flooded-plains that are self-formed in non-consolidated or weakly-consolidated sediments. Bedrock rivers form when the river breaks’ through the newer sediments and into the underlying bedrock.

Rivers are used as a source of water, for obtaining food, for transportation and defense purposes, as a source of hydropower for driving machinery, for bathing, and as a means of waste-disposal. They can provide a rich source of fish and other edible aquatic life, and are a major source of fresh water, which can be used for both drinking and irrigation.

The flora and fauna of rivers use the aquatic habitats available, from torrential waterfalls through to lowland mires. The organisms in the riparian zone respond to changes in river-channel locations and flow-patterns. The basic idea is that the river can be described as a system that is continuously changing along its length in regard to physical parameters, the availability of food particles, and the composition of the ecosystem.

The chemistry of rivers is complex and depends on inputs from the atmosphere, the geology through which it travels, and inputs from humans’ activities. The chemistry of the water has a large impact on the ecology of that water for both plants and animals, and also affects any usage that may be made of the river’s water. Understanding and characterizing river water chemistry requires a well-designed and managed programme of sampling and analysis.

Like many other Aquatic ecosystems, rivers are also under increasing threat of pollution.

The River Mura, 444 km in length, rises in Austria (1898 m above sea-level) and as a border river between Croatia and Hungary, before it flows into the River Drava. The size of its basin is 14,304 km². More than half of its surface is in Austria. The Slovenian section of the basin is 1,393 km² in area, the Croatian 987 km², and Hungary 1911 km². The average fall of the river is 0.21 %. The average fall in Slovenia is 0.1 % and less than 0.06 % at the border between Croatia and Hungary.
The River Mura can be divided according to the regions through which it flows:

- Mountain section (source - Bruck) over 216 km (46 %) within a catchment area of 4,700 km² (34 %),
- Transitional section (Bruck - Mureck) over 119 km (26 %) within a catchment area of 5,070 km² (36 %),
- Lowland section (Mureck - Legrad) over 130 km (28 %) within a catchment area of 4,255 km² (30 %).

Its major left tributaries are Murica and Ledava and right tributaries Ščavnica and Trnava which were, under regulation, redirected from the Drava into the Mura.

The average flow-distribution over the year mainly depends on any snowfall and the duration of the snow-blanket in Austria. Above-average flows occur in Spring, (March-May), whilst the late Autumn and Winter months have low-flows.

In the Autumn the volume of water increases in the channel due to rain, and during that period the river occasionally floods the hills, very occasionally embankment which protects the cultivated areas. Flooding is a natural part of a river's cycle. The majority of river channels' erosion and the erosion and deposition on the associated flooded-plains occur during the flooding stage. In many developed areas, human activity has changed the formations of river's-channel, altering different magnitudes and frequencies after flooding. In many cases human activities regarding rivers and flooded-plains have dramatically increased the risk of flooding. Due to the needs for flood protection and the exploiting of energy potential, the Mura in Austria (315 km) is mainly regulated, high water dams have been built, and 31 hydroelectric power plants are situated on it.

In the Summer the level of water decreases considerably due to high temperatures and strong evaporation, and in the Winter due to low rainfall.

Despite the relative slow current of the Mura, it does flow much faster than it once did, which also deepens it. Regulations in Slovenia have been introduced gradually and less systematically than in Austria. In the past on River Mura and its subsidiaries several hydro-technical facilities were built (regulated channels, shore protection, transverse steering structures) but in this section there are no hydroelectric installations. Before the regulations, only about 40 % of water went under the main river-bed, now almost all the water runs there and, due to its stronger flow it loosens more gravel away. The main riverbed is otherwise balanced and deepened, but within high water dams there are still preserved (many former branches and legacies of the river). The middle and lower parts of the River Mura, which begin at the border between Slovenia and Austria, some natural morphological and ecological characteristics of the river area have been preserved.

The region from the left bank of the River Mura, in the northeastern part of Slovenia is called Prekmurje and together with Prlekija on the
right bank, forms Pomurje. There is no doubt that River Mura gives life to the whole of Pomurje, especially to flooded forests, gravel pits, animals, plants, as well as people.

In order to protect settlements and agricultural land from flooding in the flat part of the river’s basin and in order to facilitate construction and intensive farming, the River Mura and its three major tributaries were continuously regulated in the past. The consequences of urbanization, primarily dispersed basin settlement, and a large proportion of agricultural land has caused excessive nutritive substances (nitrogen and phosphorus compounds) in the water, and a significant hydro-morphological burden on most water bodies. Organic pollutants can also be present in the surface water. The hydro morphological burden on the surface water of the River Muras’ basin and the burdening of the environment with heavy metals, organic matter and nitrogen and phosphorus compounds that plants don’t take-up had an influence on the quality and quantity of groundwater in aquifers. Therefore from the environmental point of view, lowland alluvial forests, old overgrown channels, river islands, gravel deposits, and the erosive areas in river channels, are extremely important because they not only represent a habitat for existing endangered species of animals and plants, but also provide long-term infiltration of surface water in the soil, the allocation of high water over more surface area, and the chemical-intensive processes, (micro) biological degradation of nitrogen and phosphorus compounds, together with other dangerous chemical substances in the water. Reduction of flood risks and human health, the environment, economic activities and cultural heritage, safer care for residents when drinking water, ensuring the biodiversity of the River Mura area and its wetlands and river basins are, thus, the most important objectives of water management [1-6].

1.2 Linear regression

Linear regression demonstrates the relationship between two variables by fitting a linear equation to observed data. One variable is considered to be an explanatory-variable, and the other a dependent variable.

Before attempting to fit a linear model to observed data, it should first be determined whether or not there is a general relationship between the variables of interest. A scatter plot can be a helpful tool in determining the strength of the relationship between two variables. A valuable numerical measure of the association between two variables is the correlation coefficient, which is a value between -1 and 1, indicating the strength of the observed data’s association for the two variables.

The most common method for fitting a regression line is the method of “least-squares”. This method calculates the best-fitting line for the observed data by minimizing the sum of the squares of the vertical deviations from each data point to the line (if a point lies on the fitted line exactly, then its vertical deviation is 0). Because the deviations are first squared, then summed, there are no cancellations between positive and negative values.
The purpose of this work was to find any correlation between different designated places (sample places) and their variables, obtained using physico-chemical measurements.

After a regression line has been computed for a group of data, a point which lies far from the line (and thus has a large residual value) is known as an “outlier”. Such points may represent erroneous data, or may indicate a poorly-fitting regression line. The reason for this distinction is that these points may have a significant impact on the slope of the regression line [7].

River Mura water analysis, which took into consideration the physical and chemical characteristics, was sampled at four designated places. Data collected within the period 1996 to 2009 was first discussed. The purpose of this work was to find any correlation between different designated places (sample places) and their variables, obtained using physico-chemical measurements. These parameters were used to form a model, which was a basis for the separation and classification of diverse water samples over different time-periods.

Chemometric techniques can be used for the classification and comparison of diverse samples. Linear regression, helps to interpret these complex database, which result from long-term monitoring programmes of water quality and when determining several parameters to be used for the presentation of monitoring effectiveness. During the last period several chemometric techniques were used for fresh water characterization and when estimating, groundwater and sea water. The application of different statistical and chemometric techniques is one of the more applied instruments for presenting representative important information from extensive databases.

Quality River Mura monitoring has been performed continuously for over 30 years, but this contribution only presents the results of the last period between 1996-2009. The measurements were performed weekly between October – April, on the same day and the same time, at precisely determined place. Samples were not collected, during the summer months namely, the samples would not be representative due to increased flow. Additional sampling was performed twice a year at four different places along the river-stream. The first sample was taken in the middle of the river in Šentilj. The other three sampling places were 10 km further along the river-stream, in the middle and on both banks (left side in Austria – Bad Radkesburg and the right side in Slovenia – Gornja Radgona). Measurements were performed and exchanged over equal periods by two laboratories: Laboratory for Analytical Chemistry and Industrial Analysis at Faculty of Chemistry and Chemical Engineering, University of Maribor and Amt der Steiermarkischen Landesregierung in Graz, Austria. The intention was to compare the results and both laboratories performed samples contemporarily, twice a year [8-13].

2. EXPERIMENTAL PART

2.1 Samples and sample analyses

For sampling and sample transportation we used the standard sample ISO method [ISO 5667-11:1992 (E)]. [14] Water samples were taken half a meter under the surface in polyethylene containers. All plastic
and glass containers used for the samples and analyses were previously washed off with distilled water. Filtration was accomplished through glass-filters. All measurements were carried out on the same days, as the samples were taken.

2.2 Instruments and reagents
A Dionex CD 20 ion chromatograph a Perkin Elmer 552 UV-VIS spectrophotometers and a Cary 1E Varian were used for the determining the ions specified below. A WTW LF 537 conductivity meter an OXI 96 WTW oximeter and an Orion 920 mV/pH meter were used for conductivity, oxygen, and pH measurements. All the used reagents were analytically graded. The detailed measurement procedures are described in the literature [14-29].

2.3 Analytical methods
For the definition of AOX we applied [ISO 9562:1989], [16] for COD [ISO 6060:1989], [17] and for BOD5 [ISO 5815:1989],[18] The suspended solids were determined by filtration through glass-fibre filters (ISO/DIS 11923). [19] Conductivity and pH were measured using the standard methods [ISO 7888 1985; ISO 10523 1994]. [20] Ammonium and nitrate were determined spectrophotometrically. Reaction with salicylate and hypochlorite ions in the presence of sodium nitrosopentacyanoferrate was used for ammonium determination, [ISO 7150/1 1984]; [21] and 2,6-dimethylphenol was used as a reagent for determining nitrate [ISO 7890/1 1986] [22]. Most anions were determined by the ISO standard method using ion chromatography [ISO 10304-1 1996] [23]. Nitrite was determined with NO₂ ion reaction with sulphanilamide where the results intensively coloured the diazonium salt, [24] meanwhile, orthophosphate was determined using ammonim molybdate method [25]. Sodium and potassium were determined using flame-emission spectrometry [ISO 9964-3 1993]. [26] Calcium, magnesium and sulphate were determined using EDTA titrations [ISO 6058 1984; ISO 6059 1984; SIST ISO 9280 1996] [27,28].

Oxidation to carbon dioxide by the addition of an appropriate oxidant was applied for the determination of TOC and DOC (ISO 8245:1999) [29].
2.4 Data analysis

336 samples were characterized within following physical-chemical variables.

<table>
<thead>
<tr>
<th>Num.</th>
<th>Code</th>
<th>Physical-chemical variables</th>
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<tbody>
<tr>
<td>1</td>
<td>V2</td>
<td>Filtered solids (mg/L)</td>
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<tr>
<td>2</td>
<td>V3</td>
<td>Absorbable organic halogens (μg/L)</td>
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<tr>
<td>3</td>
<td>V4</td>
<td>Alkaine (mmol/L)</td>
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<td>V6</td>
<td>Ammonia (mg/L)</td>
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<td>V14</td>
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<td>V18</td>
<td>Electrical conductivity (mS/m)</td>
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<td>V19</td>
<td>Dissolved organic carbon (mg/L)</td>
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<td>V20</td>
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<td>V37</td>
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<td>pH</td>
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<td>V43</td>
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<td>V44</td>
<td>Biochemical oxygen demand after 5 days (BOD5) in unfiltered samples (mg/L)</td>
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<td>V45</td>
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<td>32</td>
<td>V59</td>
<td>Suspended solids (mg/L)</td>
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</table>

3. RESULTS AND DISCUSSION

When monitoring the water quality of the river, special attention was paid to those parameters that had maximal influence, namely AOX, nitrate, nitrite, phosphate, and ammonium.

Figure 1 presents the non-linear time dependence for AOX variable from 1996 to 2009. The AOX content had already been monitored in the period 1990 to 1996 [8]. After 2006, the AOX content decreased below the limit value, 20 mg Cl/L. Reduction grounding on the already-mentioned reduction of paper industry efflux, which had the greatest impact on the parameters' high-values. A further course of AOX values is difficult to foresee, but the collected data suggests that the values could decrease in the future.

The bulk of phosphorus in the water is a consequence of human activities such as erosion, ablation of fertilizer, and the effusion of industrial and municipal wastewaters. Phosphorus in the water occurs predominantly in the form of phosphates. The most common forms are ortho-
phosphate, condensed phosphates, and organic phosphates. An increased flow of phosphorus in the water causes increased primary production of algae and their decomposition as secondary pollution. Therefore, the determination of phosphorus in the water is important in order to evaluate the potential biological productivities of surface waters.

From 1996 to 2009, the critical value for orthophosphate was placed at concentration of 0.5 mg P/L. In 1998 and 2002 at two locations the value exceeded 0.8 mg/L (Figure 2). From 2005 the concentrations were surprisingly low, but by 2008 they began to increase again. The quantities of industrial and municipal discharges and water-wash of mineral fertilizers had a significant impact on orthophosphate content oscillation.

Figure 1:
AOX concentrations (mg/L) versus time.

Figure 2:
Orthophosphate concentration (mg P/L) versus time.
An concentrations of total phosphorus in the filtered samples had been under monitoring since 2004. Figure 3 present a deviation for the period 2004 to 2005 and the year 2009. As already-mentioned, increased content of total phosphorus in the filtered samples is also a result of agricultural land ablation and the discharges of industrial and municipal wastewater. Similar deviation (maximal value over 0.7 mg P/L) can be observed in 2005 for the concentration of total phosphorus in unfiltered samples – Figure 4.

Nitrate and nitrite are present naturally in water and are widespread in the environment. Microbial action in soil or water decomposes wastes
containing organic nitrogen into ammonia, which is then oxidized to nitrite and nitrate. Because nitrite is easily oxidized to nitrate, nitrate is the compound predominantly found in ground and surface waters. All sources of nitrogen are potential sources of nitrate. In water, especially groundwater, these sources include decaying plant or animal material, agricultural fertilizers, manure, domestic sewage, industrial wastewaters, precipitation, or geological formations containing soluble nitrogen compounds. The nitrate concentration in groundwater and surface water is normally low, but can reach high levels from agricultural runoffs, or from contamination by human or animal wastes.

Nitrate is less toxic than the other forms of nitrogen in the aquatic environment, such as nitrite or ammonia. There is growing evidence, though, that nitrate can have a harmful impact on the development of early life stages in aquatic organisms, by reducing the oxygen-carrying capacity of the blood, or by disrupting the ability to maintain a proper balance of salts.

Increased levels of nitrogen in the water, combined with phosphorus, can cause excessive plant and algal growth that depletes oxygen levels, possibly to lethal levels. Some algal blooms also produce toxins that can affect aquatic life or the humans that consume them.

Currently, there are some guidelines for the protection of aquatic life concerning nitrogen compounds in surface water. In order to limit nitrate in the water supply it is necessary to: limit fertilizer use and apply it only at appropriate times, control runoffs and soil erosion, start a compost pile, and recycle yard waste [30,31].

The concentrations of nitrite in the River Mura were, until 2003, constant at up to 0.125 mg/L, maximum values were obtained in 1997, 1999, and 2003 (over 0.15 mg/L) (Figure 5). After 2004 the concent-

There is growing evidence, though, that nitrate can have a harmful impact on the development of early life stages in aquatic organisms, by reducing the oxygen-carrying capacity of the blood, or by disrupting the ability to maintain a proper balance of salts.

Figure 5: Nitrite concentration versus time (1996-2009).
Monitoring nitrite and nitrate content together with ammonia content is essential in order to evaluate nitrogen equilibrium in water.

In the River Mura, the concentrations of nitrate have periodically fluctuated (Figure 6), reaching maximum values at up to 16 mg/L. The reduction in nitrate content started in 2005 over a short period, but from 2007 the concentrations increased almost to their primary values. Monitoring nitrite and nitrate content together with ammonia content is essential in order to evaluate nitrogen equilibrium in water.

Ammonia levels in excess of the recommended limits may harm aquatic life. Toxic levels are pH and temperature dependent; toxicity increases as pH, and the temperature decreases. Plants are more tolerant to ammonia than animals, and invertebrates are more tolerant than fish. Ammonia is the typical result of water pollution caused by municipal and industrial effluent and agricultural land ablation. Figure 7 presents the concentrations of ammonia from 1996 to 2009. These concentrations were within the range of 0.5 to 1.0 mg/L until 2003, the maximum values were obtained in 2001 (over 1.2 mg/L). After 2004 the concentrations of ammonia started to decrease below 0.6 mg/L and had, in 2009, reached the value of approximately 0.3 mg/L.

4. CONCLUSION

These parameters that we have studied in detail are among the main indicators of water pollution. Based on the monitoring of complete parameters’ trends of the concentrations of ammonia, nitrite, nitrate and orthophosphate from 1996 to 2009, have, without any doubt, definitely decreased. We can give an assurance that the chemical and physical
state of the River Mura quality, based on the reduction in concentration content, has improved. This significant impact on reduction has increased the awareness of industry when referring discharges into the river and a more rational use of plant protection products on agricultural land.

Compared to the period 1990-1996 AOX values over the period 1996-2009 had stabilized. The content of total phosphorus in the filtered and unfiltered samples had been under monitoring from 2004. Two perceivable deviations, which may be a consequence of the coincident increase when referring to industry and agriculture impact, from the data collected from 2004 to 2009, were observed. In order to determine the trend regarding phosphorus more data needs to be collected, therefore, a monitoring programme is also planned for future years.

Sampling and analyses were performed and exchanged over equal periods between the Slovene and Austrian laboratories; the programme was prepared in advance. Sampling was performed together - twice a year - for comparing measurement capabilities of both laboratories but samples were then analyzed separately. Within the studied period both laboratories performed reliable and comparable results according to the prescribed measurement uncertainties of the methods used.

The performed analyses of River Mura’s water samples, have certainly contributed to people’s and industry’s awareness regarding emissions, because the reduced amount of emissions ensured an improvement in the water quality of the River Mura.
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