Project:

Vltava - the River in Our Capital City

School: Secondary Chemical School, Prague
Masarykova støední škola chemická Praha

Class/Grade: Grade 1 - 14/15 years

Teacher: Blanka Jelínková and colleagues

Judges Comment:

Contents:

Vltava - the River in Our Capital City

1. Introduction

The project "Vltava - the River in our Capital City" has been carried out by students of the 1st grade of the Secondary Chemical School in Prague and their teachers. These students study analytical chemistry extended to include also environmental monitoring. They are aged 14 - 15 years, and are thus at the very beginning of their professional studies. They themselves chose the subject of the project since they wanted to learn various facts about the river, especially regarding its pollution.
The chemistry teacher divided the students into four groups. Each group received a separate task which was to be independently carried out, and had to inform the whole class about the results. This made all participating students gather pieces of information, take up contacts with experts and participate in teamwork. They also learned to combine individual pieces of data and to process them so as to obtain a final written and graphical form with the use of a computer.

Individual group tasks:

- Group 1 collected general information about the river and its history, geography and water management, and measured the concentration of nitrates and phosphates in the water.
- Group 2 was concerned with the principle of measurement of these two parameters and the principles of function of the measuring apparatus.
- Group 3 studied the technology of sewage water treatment.
- Group 4 addressed the production of drinking water from the river water.

The students collected samples of water under field conditions and performed the measurement of nitrate and phosphate level in the school lab. Other tasks could be carried out only in collaboration with several enterprises. The students and their teachers visited, and were given detailed information about, the following enterprises:
Povodí Vltavy, Inc. - water management laboratories
Central Waste Water Treatment Plant in Prague
The Podolí water works
The 16 students participating in the project worked with great enthusiasm and motivation. In the course of the work they collected further data and their interrelations, so that in the end the scope of the collected material had to be reduced.

2 History of the Vltava river

Where did the ancient Vltava flow
The Prague basin and its present appearance has been modelled mostly by the Vltava river (Fig. 1). Its course also determined, or at least strongly affected, the development of the human settlement. Yet the river had not always been as we know it today. In the Tertiary, i.e. about 50 million years ago, its water flowed 120 - 150 metres above the today's level. Later, as the water level gradually declined, the river flowed approximately through the today's Peace Square and Tyl Square northwards to the Letná Plain and to Podbaba. Later still, about 20 metres above the present level, the water streamed across the Wenceslaus Square at the level of today's Charles Square. The stream was very wide, far wider than today. As the river level dropped, it left behind a number of terraces recognized and named by geologists (Fig. 1).

3 The Vltava river basin today

1. Description of the river course:
Vltava is the longest Czech river, with the largest water flow rate. Its source is in the Šumava mountains underneath the Èerná hora (Black Mountain) at an altitude of 1 172 m, and it forms the main backbone of the Czech river system. Its length from the origin to the confluence with the Labe river is 430.3 km and the total area of the Vltava river basin is 28 090 km^2.
The part of the river crossing the region of the capital city of Prague is 30.9 km long. The narrowest part of the stream, 40 m wide, is just upstream of its junction with the Berounka river, the widest span of 300 m being at the Šítkovský weir. The greatest depth, 9 m, is underneath the Vyšehrad Rock, varying between 3 and 4 m at other places. Vltava has a total of 23 tributaries and its long-term average water flow rate is 147 m^3/s.
At Mìlník, Vltava flows into Labe which in turn empties its waters into the North Sea in Hamburg. Vltava´s system of tributaries is an example of a symmetric river system, with left--hand and right-hand tributaries being finely balanced as to their spacing and number.

2. Uses of Vltava by the human population
Vltava serves as a drinking water reservoir, as a river transport highway, and is used for electricity production in power plants. In addition, it serves as a place of recreation, water sports and fishing. Vltava is straddled by a number of large dams, the so-called Vltava Cascade, which brought drastic changes to the original ecosystems. The largest dams are at Lipno, Orlík, Kamýk, Slapy, Štìchovice and Vrané.

3. Pollution
The pollution is both regional (drain from fields and roads) and point-like (factories, human settlements). Insufficiently treated waste waters from point sources contribute to the loading of water with nutrients that bring about excessive growth of algae (eutrophization) of the dam lakes of the Vltava Cascade.
Considerable pollution load in some reaches is due to roads skirting the river. The roads are a source of heavy metal pollution from the actual motor vehicle traffic and from the road strewing materials. Other activities adversely affecting the river include building and construction, real estate utilization, waste dumps, mineral mining and also intensive recreation activities.
The nuclear power plant at Temelín is expected to begin its operation in 1997. The power plant is situated near the river and its effluent waste waters will therefore have to be monitored for tritium, the radioactive hydrogen isotope. The rise in the river water temperature caused by this effluent water will also have a negative impact on the river wildlife.

A survey of important point pollution sources along the Vltava river:

Source name	Quantity thousands m^3 /year	Pollution due to effluent t BOD_5 /year
UNILEVER PTZ Nelahozeves	1 189.0	335.7
Kauèuk Kralupy n. Vlt. ÈOV NRK	1 574.1	22.0
VKM a.s. ÈOV Kralupy n. Vlt.	3 710.6	80.0
Obilní lihovar Kralupy n. Vlt.	431.9	218.0
VÚAB Roztoky u Prahy	1 009.1	124.0
StèVaK Praha-záp, ÈOV Roztoky	613.3	95.5
PKVT Praha ÚÈOV Praha	184 966.4	5 988.0
PKVT Praha odlehèení Prahy	3 410.8	448.6
Pražské vodárny Podolí	501.7	11.0

SEMOS Modøany	322.0	12.0
Cukrospol Praha Modøany	484.7	188.3
Papírny Vrané n. Vlt.	1 402.0	18.0
StèVaK Pøíbram ÈOV Kamýk n. Vlt.	74.4	9.8
VaKJè, d. ÈB Týn nad Vltavou	860.0	20.0
VaKJè, d. ÈB Hluboká n. Vlt.	184.3	9.8
VaKJè, d. ÈB Èeské Budìjovice ÈOV	22 241.3	1 348.0
VSB 0227 Planá u È Budìjovic	160.0	5.2
Obec Vèelná	57.6	17.3
JIP Papírny Vìtøní (È. Krumlov)	14 226.1	71.1
VaKJè, d. ÈB Èeský Krumlov	79.0	14.0
JIP Papírny Louèovice	3 330.0	86.6
VaKJè, d. ÈB Horní Planá	174.0	37.0

4. Water basin management

The enterprise Povodí Vltavy (Vltava River Basin Management) fulfils water management and environmental functions in an area of 28 708 km^2, i.e. 55 % of the acreage of Bohemia. It is divided into three branches under a common head office in Prague:

a) branch Upper Vltava (Horní Vltava) based in Èeské Budìjovice: a staff of 154 manages 1 533 km waterways in an area of 12 198 km^2

b) branch Lower Vltava (Dolní Vltava) based in Prague: a staff of 304 are responsible for the management of 1 464 km waterways in an area of 7 169 km^2

c) branch Berounka located in Plzeò: a staff of 178 administers 1 636 km waterways in an area of 9 341 km^2 (Fig. 2).

We visited the fine new laboratories in Prague. We saw the preparation of sample containers and learned about the sample collection schedule and sampling locations. We could inspect individual establishments equipped with many up-to-date instruments. The laboratories carry out determinations of chemical, microbiological and radiochemical parameters of water and analyses of sediments. Some analyses are being performed in a mobile field laboratory. The laboratories are subject to control by the ASLAB accreditation centre.

4 Water

In nature, water is not found in a chemically pure form. It always contains dissolved gases and soluble or insoluble inorganic and organic substances. Various compounds enter the water vapour already in the atmosphere but the main enrichment with dissolved substances takes place during its seepage through soil and various minerals. An artificial source of organic and inorganic compounds in nature water is industrial and sewage waste water.

Water contains many compounds but we concentrated on phosphates and nitrates since both these compounds are closely monitored; in higher quantities they can considerably affect the quality of water in nature (eutrophization) and thereby also the quality of drinking water, and can thus pose a health risk for all living organisms.

One of the sources of raw water for Prague, which is treated to obtain drinking water, is the surface water from Vltava. We therefore tested the drinking water for its content of phosphates and nitrates.

We also tested the concentrations of these ions at the Prague Central Waste Water Treatment Plant because this facility treats wastewater from the whole Prague municipal area and returns the treated water back to the Vltava.

5 The Prague Waterworks Podolí

The water works producing drinking water from the river water is situated about 5 km from our school. The works buildings were designed by the outstanding architect Antonín Engl. They do not resemble an industrial plant at all but, rather, a theater or a museum. The water works building has been proclaimed a National Technical Monument.
The works has long ago ceased to meet the demands posed by rising municipal water consumption. Most of the water for Prague is brought in from the Želivka dam lake about 100 km south of Prague, and from a system of wells bored in alluvial sands around the Jizera river about 60 km north of Prague.

The technological water treatment process
The water is pumped in through screens that trap crude floating debris. Then it passes into aerated grit chambers and is pumped up to the highest works storey and brought into clarifiers. One of the clarifiers was empty at the time of our visit and we had the chance to have a look at its construction. A coagulant is fed into the clarifiers; the Prague plant uses the cheap iron (II) sulphate $FeSO_4.7H_2O$ which is oxidized by chlorine

$$6\ FeSO_4 + 3\ Cl_2 \longrightarrow 2\ Fe(SO_4)_3 + 2\ FeCl_3$$

Ferric salts hydrolyze in water to yield russet-coloured flakes of ferric hydroxide.

$$FeCl_3 + 3\ H_2O \longrightarrow Fe(OH)_3 + 3\ HCl$$
$$Fe_2(SO_4)_3 + 6\ H_2O \longrightarrow Fe(OH)_3 + 3\ H_2SO_4$$

These flakes entrap fine and strongly hydrated particles which then sediment together with the flakes and are drawn off from the clarifier bottom into the sewer system. An auxiliary coagulant, polyacrylamide, is added to increase the clarification efficiency. Clarified water flows away over a weir around the clarifier circumference.
As seen from the equations describing the hydrolysis, the clarified water is acidic. It has to be alkalinized to a pH value of around 7. This is achieved by adding to the water milk of lime, $Ca(OH)_2$. The whole process of clarification and alkalinization is continuously checked in the laboratory.
The effluent water is then brought via a large-diameter (∅ 1200 mm) pipeline into the other plant building to grit pits housed in a huge hall. These filter pits trap the remaining impurities and entrained flakes. The grit pit becomes gradually clogged and its resistance rises. At certain intervals, it is therefore flushed from below by pressurized water. After filtration the water is disinfected by chlorination.
The water then passes into storagetanks and from there into water supply tanks, where it is mixed with water from other sources (Fig. 3).
It was interesting to learn about the source of the chlorine used at the water works. The chlorine is produced by hydrolysis of salt brine at a large chemical plant, Spolana Neratovice (25 km north of Prague). The water works imports once monthly five 500-l barrels of chlorine. Strict safety measures have to be kept during the transport of the chlorine.
Another task we had was to measure the amount of PO_4^{3-} and NO_3^- in drinking water. The measurement was carried out on an RQ reflectometer.

Average results of our measurement: PO_4^{3-} = 0 $mg.dm^{-3}$
NO_3^- = 20 $mg.dm^{-3}$

These results correspond to the Czech Standard.

6 The Prague Central Waste Water Treatment Plant

A part of our project was to learn about the waste water treatment in our city. We therefore visited the Prague Central Waste Water Treatment Plant (CWWTP) in the Trojský Isle.
CWWTP was built in 1967 on one of the Vltava isles, on a site where the Vltava in fact leaves the city. The management of the sewer network that brings waste water to the plant is based on the Sewage Regulations of the Prague sewer network for the CWWTP-controlled area. According to the Regulations, waste water producers are divided into two principal groups.
The first group comprises most key producers of industrial waste water that have their own permits from the water management authority regulating the quality of their effluent waste water. This group includes machine, electric engineering, chemical and pharmaceutical factories, power plants, public transport facilities and printing works.
The other group comprises the so-called general polluters, i.e. all other waste water producers that have effluent waste water quality parameters imposed by the water management authority.
At the plant, we saw the mechanical waste water treatment which includes removal of insoluble substances. The mechanical stage includes screens, oil and fat traps, aerated grit chambers and settling tanks.
The biological stage represents a biochemical degradation of organic compounds by microorganisms in aeration tanks. A mixture of the treated water with activated sludge is brought into final settling tanks. After control checks, the water is then discharged back into the river. A part of the sludge is taken back into the settling tank inlet and its surplus is processed in the so-called sludge processing unit. We learned that, until 1988, the digested sludge was shipped to agricultural establishments and was used for composting. This type of sludge utilization was abandoned owing to its high content of cadmium. Nowadays, the sludge is dehydrated in filter presses or pumped to sludge dumps, or, alternatively, is shipped via the river to sludge lagoons along the Vltava river.
An integral part of the CWWTP is laboratories where the physico-chemical and biological efficiency of individual stages of the treatment process is assessed. There we had the chance to get familiar with the methods of determining individual parameters such as BOD_5, individual forms of nitrogen, etc. We were particularly interested in phosphate and nitrate assays.
In view of its insufficient capacity, the WWTP itself is at present one of the major Prague water polluters. Work has therefore commenced to increase its capacity and, at the same time, the building of a new municipal waste water treatment plant is planned (Fig. 4).

7 Determination of nitrate and phosphate content in water

Closed nitrogen and phosphorus turnover exists in nature under normal conditions, i.e. without human activities. Human activities give rise to nitrogen and phosphorus compounds which join this turnover and disturb it by bringing in an extra load. The main source of the undesirable increase in the level of these substances is the use of high amounts of industrial fertilizers and failure to keep sound agrotechnical measures. Moreover, waste water treatment plant effluents as well as some industrial and household waste waters contain higher concentrations of nitrogen and phosphorus in the form of nitrates and phosphates. Another source of contamination in addition to these phosphate sources in water comes from washing powders.

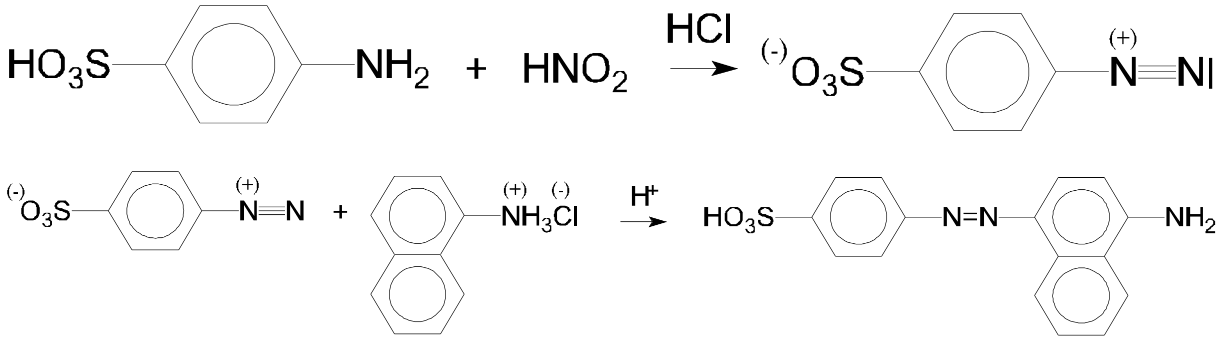
Nitrates

Nitrates represent the final form of nitrogen compounds in the water. The sequence of individual degradation steps of nitrogen-containing compounds includes organic nitrogen, ammonia, nitrites and nitrates. The interconversion of individual forms occurs under the participation of

microorganisms and the final form is always associated with the amount of oxygen dissolved in the water.
Nitrate ions in a daily dose of 200 mg are not deleterious for the body and their toxicity is usually compared with that of sodium chloride. In higher doses they may cause disorders of the digestive tract. The most important factor is, however, their ability to serve as a source of nitrites which are clearly toxic. The reduction of nitrates to nitrites takes place enzymatically partly in the digestive tract and partly in foods with a high content of nitrates, especially after kitchen treatments that lead to the proliferation of denitrification bacteria.
Nitrites can participate in the formation of carcinogenic nitroso compounds or may themselves have a toxic effect. One of the direct negative effects of nitrites is the alimentary nitrate methemoglobinemia of formula-fed in facts up to 5 months of age. The actual cause is the oxidative action of nitrites on hemoglobin, which yields the derivative methemoglobin that no longer functions as oxygen carrier. Infants therefore cannot drink water containing more than 15 $mg.dm^{-3}$ nitrates while the tolerable dose in drinking water for adults is 50 $mg.dm^{-3}$.
Tens of methods exist for nitrate assay in water. The largest group of the methods includes spectroscopic techniques.
We carried out the nitrate assays on the RQ reflectometer from Merck.

Principle of the assay: The nitrate ion is reduced to a nitrite ion. In the presence of a buffer, this nitrite ion reacts with an aromatic amine to yield diazonium salt. The diazotation is followed by coupling and the colour intensity of the resulting azo dye is measured.

$$NO_3^- + e^- \longrightarrow NO_2^-$$



We collected the samples for the assay before the waste water treatment plant and after final settling tanks, i.e. prior to the discharge of the treated water into Vltava. The results of the measurements are given in the table.

Phosphates

Phosphates are basically nontoxic for humans or for animals, the limit value for drinking water being 1 $mg.dm^{-3}$. However, they participate in water eutrophization, i.e. natural and artificial enrichment of the water with nutrients which cause striking changes in the physico-chemical properties of water and in the biological regime of aquatic ecosystems. This process is reflected in an increasing production of algal biomass and excessive proliferation of zooplankton which feeds on these algae. The dead remnants of both the zooplankton and the algal biomass sediment on the bottom along with considerable amounts of organically bound phosphorus. After aerobic bacterial decomposition, the phosphate is converted to insoluble iron (III) phosphate with a concomitant consumption of oxygen dissolved in the water. This reduces the self-cleaning ability of the water stream. When the oxygen has been depleted, aerobic processes are replaced by anaerobic ones that result in the production of methane and ammonia. All these processes adversely affect the quality of the surface water.

All types of phosphorus compounds in waters are converted into soluble organic orthophosphates, which are then assayed by absorption spectrophotometry. Total phosphates can be determined after an oxidative decomposition.

<u>Principle of assay:</u> In a solution acidified with sulphuric acid the phosphate ion reacts with molybdate to form phosphomolybdenic acid. This is then reduced to phosphomolybdate blue and the colour intensity of this dye, which is proportional to phosphate concentration, is measured on a reflectometer.

$PO_4^{3-} + (NH_4)_2MoO_4$ ¾ ® $H_4P(Mo_{12}O_{40})$ $\longrightarrow$ phosphomolybdate blue

Samples for measurement were again collected before the water treatment plant and after the final settling tanks, i.e. before the discharge of the treated water into Vltava. The results of the measurements are given in the table.

<u>Table of mean values for waste water:</u>

	Before water treatment plant		After water treatment plant		Reduction in ion content in %	
	Our data	CWWTP	Our data	CWWTP	Our data	CWWTP
NO_3^- mg.dm^{-3}	26	10	4	3.3	84.6	33
PO_4^{3-} mg.dm^{-3}	10	9	3	2.5	70	72.3
t °C	11.6		11.7			
pH	8		7.7			

Evaluation of results:

The measurements were carried out in January 1996. The measured values of PO_4^{3-} are in keeping with the values given by CWWTP whereas our values for NO_3^- are higher than those provided by the CWWTP. This is because our RQflex responded to the presence of other forms of nitrogen (NO_2^-, etc.) and we had no possibility to remove these interfering ions. As pointed out by the supplier of the indicator strips, NO_2^- interfere with the assay.

8 The pocket laboratory Merck RQflex

The system Reflectoquant Merck makes it now possible to assay a variety of parameters without heavy instrumentation. The RQflex reflectometer is based on the principle of reflectometry (remission photometry). The instrument provides an exact measurement of light refracted from a zone of an analytical strip. As in classical photometry, the difference between the incoming and reflected light permits a quantitative determination of concentration of the compound to be analyzed.
The RQflex reflectometer, with its dimensions of 19 x 8 x 2 cm, weight of 275 g, working temperature range of 5 - 40 °C and the ability to store up to 50 data in a memory is excellently suited for field work.
The instrument is supplied with a set of analytical strips which form the basis of its mobility. The Reflectoquant strips respond to ammonia, water hardness, chlorine, chromates, tin, potassium, nitrates, formaldehyde, phosphates, aluminium, magnesium, cobalt, cyanides, ascorbic acid, peracetic acid, manganese, copper, molybdenium, nickel, lead, peroxides, pH, sulphites, silver in

fixative baths, calcium, zinc and iron. The polyester foil is biodegradable and the total content of agents in the strip is so low that the strips do not require dumping into special containers.
A part of the system is a line code which is the central unit of the Reflectoquant analytical system. The line code serves for feeding into the instrument all information needed for manipulation and calibration. The data are specific for a particular batch of strips and are recorded during their manufacture. The batch-specific calibration, correction for wavelength drift and doubled optics ensure the highest possible precision of the instrument.

What are the interesting features of the system?

- High precision due to the doubled optics and batch-specific calibration
- Mobility caused by the small size
- Absence of problems with wastes and recycling
- Speed of assay.

(Fig. 5)

9 Conclusion

The work of our student group on the project "Vltava, the river in our capital city" has ended for this year. It brought us a number of new pieces of information from the fields of environmental protection, water management, chemistry, technology, and also regarding languages.
We learned how to work with specialized literature, became aware of the principles of teamwork, acquired a new view of life environment, established contacts with professionals both in the laboratory and in plant departments, and improved our insight into our intended line of study.
We are proud of the work we have accomplished, but at the same time sad at the current level of pollution of our river, at the many pollution parameters that are still not being measured in waste and drinking water, and at how insufficient still is the technology of drinking water treatment and waste water processing.

The following students participated in the project:

Kateøina Knìžourková, Jiøina Venhauerová, Dana Grygarová, Katøina Zugárková, Šárka Kocová, Tereza Høíchová, Jakub Hodaò, Lenka Havlíèková, Perla Bìhalová, Martina Döbertová, Miriam Lehocká, Ivana Sejpková, Petr Kelbl, Martin Váòa, Jiøí Gregor, David Kosiner.

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