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Water Pollution Abatement Programme, The Czech Republic

Environmental Improvement of Areas Polluted by Metal Ore Mining



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Water Pollution Abatement Programme, The Czech Republic

Project 3.4

Environmental Improvement of Areas Polluted by Metal Ore Mining

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Abstract:

The report discusses water pollution from mining in the Zlaté Hory area in the Czech Republic. The Zlaté Hory Mining District is the largest mineral deposit of base metals in this country, and the results obtained in this study will be of practical value for the solution of similar problems in other parts of the Czech Republic. The creeks draining the mining areas (Castle Creek and Golden Creek) are both polluted with heavy metals. In Castle creek the concentration is 8000 μg/l zinc and 700 μg/l copper. Most of the water from polluted areas draining to Golden Creek is treated by liming and sedimentation. The concentration in this creek is still 700 µg/l zinc and 20 µg/l copper downstream the town of Zlaté Hory. There is little fish and only some pollution-resistant organisms present in this part of the Golden Creek.

The report is based both on co-operate field work between NIVA and The Mining University, and on the results from the monitoring programme of Pvodi Odry. The results from the work from different institutions are in good accordance. It is recommended that possible pollution sources in the town of Zlaté Hory and in other parts of the area are given more attention.

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1. Preface

As part of the bilateral environmental agreement signed by the governments of the Czech Republic and Norway, several collaborative projects were identified.

"Abatement strategies in the River Odra catchment" was a programme area discussed in Ostrava and Prague in April 1992. As a result of these discussions the project "Improvement of the Environment Deteriorated by Metal Mining Activity" was started. During the further work the name of the project was changed to "Environmental improvement of areas polluted by metal ore mining", but the objectives have been the same all the time.

The text in this report has mainly been prepared by Rolf Tore Arnesen NIVA, Magne Grande NIVA, Konstantin Raclavsky and Helena Raclavska The Mining University, Ostrava. Petr Brezina has contributed to the work by putting the data collected by Povodi Odry in the Zlaté Hory area at our disposal.

This report will finish NIVA's engagement in Zlaté Hory for the time beeing. The water pollution in this area may, however, go on for many years still, depending upon how the measures against water pollution are managed in the future.

Oslo and Ostrava

October 1995

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2. Summary

The Zlaté Hory Mining District is the largest mineral deposit of base metals in the Czech Republic. The mining which has been going on for many centuries have polluted the ground and the water around the mining operations. The most abundant mineral in the ore is pyrite and pyrrhotite. Other important minerals are sphalerite, chalcopyrite, and galena - sulphide minerals of iron, copper, zinc and lead.

Zlaté Hory is a renown recreational centre and the quality of surface and ground water is of importance in the development of this activity. The nearness to the international border between the Czech Republic and Poland, and the fact that the river collecting the drainage from the mining area crosses this border and enters into the Odra River, makes measures against pollution an issue of special importance.

Most of the area of The Mining District Zlaté Hory is drained by Golden Creek (Zlaty potok) and its tributaries. Golden Creek originates in the wetlands north-east of the village Hermanovice and flows to the north through the wide valley. Golden Creek is the main tributary to Castle Creek, entering from west in the southern part of the town Zlaté Hory. The Creek is polluted mainly from the mining gallery Mir and water percolating through the waste rock dump in this area.

In co-operation with Mining University, Ostrava and Povodi Odry, Norwegian Institute for Water Research (NIVA) have performed investigations of surface water in this area. For some years Povodi Odry has been monitoring the water quality in some of the Creeks influenced by mine drainage. Data from this work have also been included in this report. In 1993 NIVA and the Mining University, Ostrava performed co-operative field work in the area, with sampling for chemical analysis and some biological studies.

The available data have been discussed in this report, both by comparing results from different institutions and by discussing pollution problems in surface water.

The chemical results obtained by Povodi Odry, NIVA and The Mining University is in quite good accordance with each other, but there is still need for more work. Some of the observed differences or variations in chemical data may be real, but analytical errors may also be the case.

The influence of pollution from mining activities are very marked in Castle Creek (zinc $8000 \mu g/l$, copper $700 \mu g/l$), but also in Golden Creek downstream the mining area, the heavy metal concentrations are high. Even upstream the waste rock dump at the mine "Mir", the zinc and copper concentrations are high from mines which have not been operated for very many years ago. The concentrations of mercury were reported quite high from Povodi Odry. NIVA's results indicate that these figures are too high, due to analytical errors. Downstream the town of Zlaté Hory the concentrations of zinc and copper were about $700 \mu g$ Zn/l and $20 \mu g$ Cu/l.

When the water from the tailings area is limed in the existing treatment plant, the most important source of pollution will probably be the waste rock dump at the mine Mir. There may also be diffuse sources of metal pollution in the area, i.e. within the town of Zlaté Hory.

Due to heavy metal pollution from the mining areas, there was no fish and very few bottom animals and other organisms in Castle Creek and in the upper part of Golden Creek. Observations in Black Creek showed a normal fauna with a variety of bottom animals and a dense population of trout. Downstream the town of Zlaté Hory, there were quite a few pollution-resistant organisms present, and local people had observed some fish in 1993.

Tests at NIVA with water from this lower part of Golden Creek showed no acute toxicity to fish, but there was an inhibition of growth of algae.

At present the mine water and seepage from the tailings pond are limed. If this is reduced or stopped, the concentrations of heavy metals, especially copper and zinc would rise in Golden creek. In that case other measures would be necessary. Mine waste might then be removed or covered to reduce contact with oxygen. Partial or complete flooding of the mine may reduce the heavy metal content in the mine water. Before any such changes are made, thorough studies should be performed.

The investigations in Zlaté Hory have been very interesting for NIVA and have given useful experience in our work with water pollution from mining of sulphide minerals.

At present a further engagement from NIVA in Zlaté Hory would require quite large resources to be of any use. The contacts established during the project, should, however, be maintained, and hopefully result in new co-operate projects, i.e. if the situation in the area should change in any way.



Figure 1 Golden Creek downstream the mine area (April 1992).



Figure 2 Tailings pond 03 in operation at Zlaté Hory-South (April 1992).



Figure 3 Castle Creek downstream the mine "Mir" (April 1992).

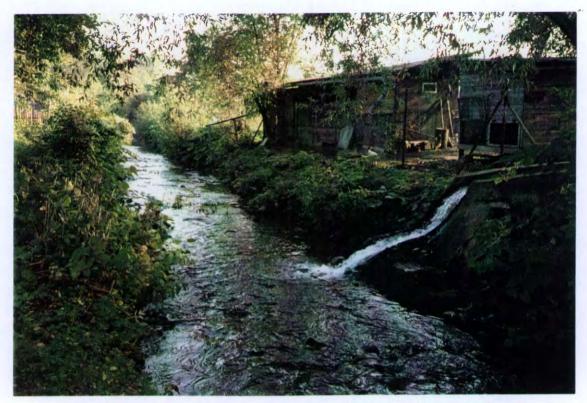


Figure 4 Golden Creek downstream the town of Zlaté Hory. The outlet from the sewage treatment plant is seen to the right (September 1993).

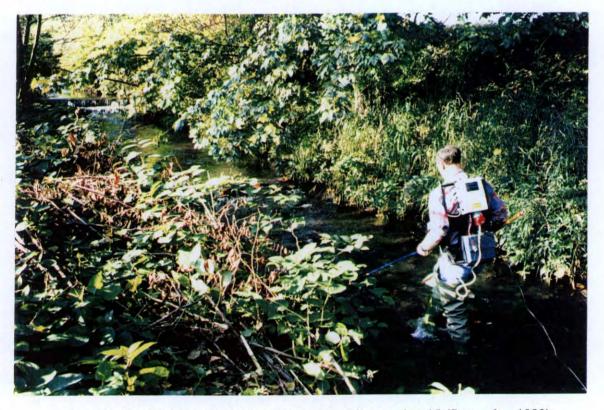


Figure 5 Electrofishing in Golden Creek at sampling station 15 (September 1993).

3. Introduction

3.1 Background

The Zlaté Hory Mining District is the biggest mineral deposit of base metals in the Czech Republic. The mining which has been going on for many centuries have polluted the ground and the water around the mining operations. The most abundant mineral in the ore is pyrite and pyrrhotite. Other important minerals are sphalerite, chalcopyrite, and galena - sulphide minerals of iron, copper, zinc and lead.

During discussions with Czech co-workers in the project it has been pointed out that the Zlaté Hory area may be considered as a model area for dealing with metal mining problems in The Czech Republic. The results obtained will therefore be of practical value to the solution of similar problems in other parts of the country.

Norwegian Institute for Water Resarch (NIVA) has planned and executed the project in cooperation with Institute for Industrial landscape Ecology (ILE) and the Mining University in Ostrava. Field work in the Czech republic was carried out by Czech co-workers partly assisted by scientists from NIVA.

The creeks draining the mining areas are polluted with heavy metals. The concentrations are comparable to those found in Norwegian rivers in mining areas. The levels of copper and zinc especially are high, and in the brooks near the mines the biology is affected. The main river from the area, Golden Creek (Zlatý Potok), is a tributary to the Odra river, entering Poland near the town of Zlaté Hory.

The main objectives for the total project have been:

- Assess the present environmental impact of metal mining effluents on water courses in the Zlaté Hory area.
- Identify and characterize main sources of pollution, evaluate water quality in the area and describe the impact of the mine pollution on the biology in the watercourse.
- From a realistic description of the present situation, propose alternative measures for the abatement of the mine pollution in the Zlaté Hory area.

In 1993 the following tasks were performed:

Sites for sampling and water flow measurements were selected and sampling was done by Czech institutions and by NIVA. Analysis of samples were performed both at NIVA and in the Czech Republic.

During a visit to the mining area the team from NIVA studied water quality and the biology in a number of places within the area. Samples were brought to NIVA for studies and toxicity tests with fish and algae were performed.

Studies of groundwater pollution should be done. The special local conditions makes it necessary that the practical part of this work is carried out by Czech experts.

In 1993 it was considered most important to perform co-operative field work in the area and R.T. Arnesen, M. Grande and E.R. Iversen from NIVA visited the area in September together with K. Raclavsky, H. Raclavska and D. Matysek from Mining University in Ostrava. Water samples were taken, measurements of water flow were performed and samples of bottom fauna were collected. A simple registration of fish status was also done.

In 1994 Konstantin Raclavský and Helena Raclavská visited NIVA, discussing the results obtained and preparing parts of this report.

3.2 Earlier work

There have been programs for monitoring rivers and soil influenced by the mining activities going on for many years. Povodi Odry, responsible for the monitoring of the quality in surface water, has submitted their data from the years 1990, 1991 and 1992 to NIVA. The data from 1990 and -91 were to some extent processed and presented in our report in 1993 (Arnesen *et al.* 1993).

Raclavská and Raclavský (1992) have made a geological and hydrogeological description of the area, and shown that groundwater, sediments and soil is markedly influenced by mine pollution downstream the mining area.

Povodi Odry has done leachability tests of materials from the slurry pond. The results of these tests are referred in Chapter 1.3.4.

The project reported here has been described, and the main tasks discussed in the above mentioned NIVA-report (Arnesen 1992). In the report, an intercalibration of chemical analyses between NIVA and Czech laboratories is also discussed.

3.3 The local situation of Mining in Zlaté Hory

3.3.1 Location of the mining district

The Zlaté Hory Mining District is located in the north-eastern part of Hruby Jesenik Mts., (northern Moravia) near the border with Poland. The mining district covers an area of approximately 20 km² between the town of Zlaté Hory in the north, the village Hermanovice in the south and villages Dolni Udoli and Horni Udoli in the west. The mining activity is concentrated in valley of Zlaty potok (Golden Creek) and on the slopes of Pricny vrch Hill (Querberg).

Geologically the mining district is situated in the northern part of the Devonian belt formed by Vrbno Group - volcanosedimentary complex of sedimentary quartzites, metamorphosed quartz keratophyres and their tuffs ("ore-bearing quartzites"), graphite phyllites and chlorite-sericite schists. The whole area lies a little to the east of the central part of Hruby Jesenik Mts. (High Jesenik Mts.), formed by crystalline core units. Farther to the east Devonian plunges below Lower Carboniferous developed in flysch culm facies of Nizky Jesenik Mts. (Low Jesenik Mts.). Stratiform polymetallic ores belong to the disseminated type and they have variable content of main mineral phases - chalcopyrite, sphalerite, galena, pyrite and pyrhotite.

3.3.2 History of mining

The mining town Zlaté Hory (former name Zuckmantl) was mentioned in written record for the first time in 1224 as a mining settlement. Panning of gold from placers started probably in 11th century. Mining of primary ores dates from the end of the 13th century, later mostly for copper. Two important mining adits were opened on the slopes of Pricny vrch Hill in the 13th century. The Mining Gallery Old Hackelberg is still draining water from a large area of mining works at Pricny vrch Hill. The mining activity culminated in the 16th century when also the largest pieces of gold were found in placer deposits (1.39 and 1.78 kg). Copper was exploited from polymetallic deposits and iron from volcanosedimentary deposits of Lahn-Dill type. The decline of the mining activity was caused by difficulties in pumping water from deep mines, and at the close of 18th century the mining activity was stopped for 150 years. The total amount of ore extracted during this historical period, is estimated to be 300 to 500 thousands of tons.

In 1951 a new geological exploration started. This led to the construction of mine Zlaté Hory-South where exploitation of copper began in 1962. Besides this main area of mining activity exploration was performed on the territory of the whole mining district and many mining galleries were prepared for exploitation of complex polymetallic ores (Cu-Pb-Zn). New economical conditions led to the closure of the mines, which started in 1991.

3.3.3 The present situation

Figure 1 shows a map of the mining area of Zlaté Hory. Exploitation was most intensive at the mineral deposit Zlaté Hory-South which was formed mostly by copper ores. Other deposits were exploited partly: Zlaté Hory-Hornicke Skaly (Mining Rocks - mostly Cu), and polymetallic deposits (Cu, Pb, Zn): Zlaté Hory-Kozlin, Zlaté Hory-East, Zlaté Hory-West (with Mining Gallery Mir - Peace). Tailings from the flotation plant were deposited at the tailings pond 01 which was entirely filled, covered by waste rocks, subsoil and topsoil and planted by seedlings of trees. Tailing pond 02 is now used as a purification basin for water output from waste water treatment plant. The biggest tailing pond 03 was in use until the closing of the mines and a program for land reclamation of the whole area was started.

Exploitation of selected parts of the deposits continued until March 1994. The closing of mines which began in 1991 made the environmental problems more pronounced. Reclamation of the polluted areas and restoration of the landscape, soils and streams to a state which is as near as possible to the natural require more information on pollution, its sources and the behaviour of pollutants in the environment than that found necessary during the period of full activity in the mine.

3.3.4 The tailing pond

The material deposited in the slurry pond can be described as fine and very fine sands (particle size class 0.040 - 0.071 mm is prevailing). The petrographical composition of this fine grained material is corresponding to the geological conditions in the deposits: quartzites, phylite rocks (graphite-muscovite schists, graphite schists, muscovite-chlorite + biotite schists). The most common mineral is quartz. Phyllosilicates (muscovite, chlorite, biotite), feldspars and locally carbonates are also abundant. From the ore minerals, almost exclusively pyrite is present. The flotation tailings are mainly from dressing of chalcopyrite ore with pyrite and contents of other sulphides (sphalerite, galena). Mineral deposits of complex Cu-Pb-Zn ores were prepared for exploitation, but the extraction of ore was very limited.

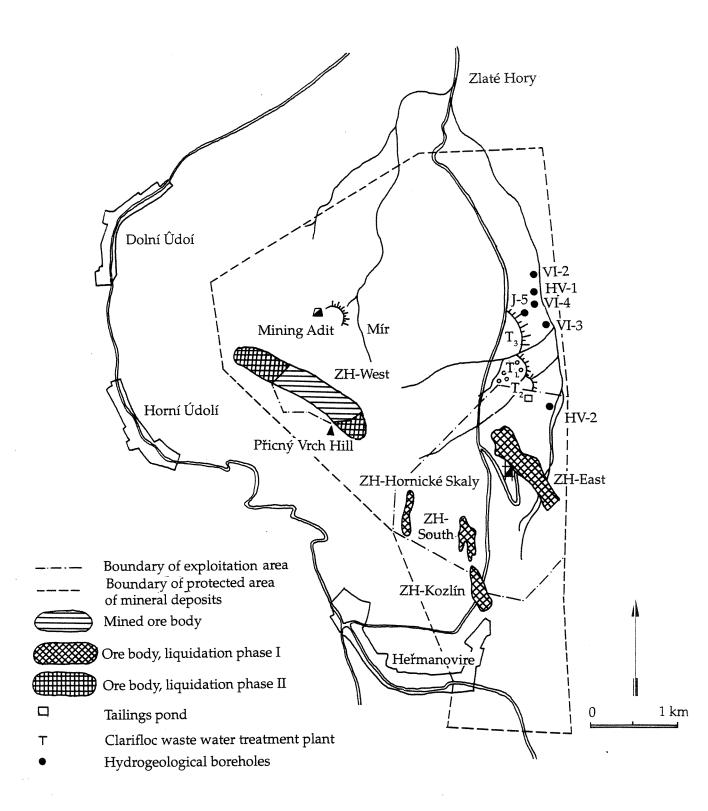


Figure 6 Map of the mining area in Zlaté Hory

Leachability and toxicity of leachates have been tested in connection with the study of land reclamation of the tailings pond (Konupcikova et al. 1993). The test of leachability was performed in the laboratories of Povodi Odry, Ostrava and the results are presented in table 1. The ecotoxicological assessment of the leachate on the green alga *Scenedesmus quadricauda* (72 h) and *Daphnia magna* (48 h), was performed by the laboratory of the Water Research Institute. According to these results the tailings deposited in the slurry pond corresponds to the class III in the Czech environmental laws (Regulation of Government of Czech Republic No. 513/92), which classifies this material as a type of waste where special precaution are needed for its disposal. Wastes belonging to class I and II represent lower danger to the environment.

Parameter	Unit	Value	Leach- ability			Value	Leach- ability
рН		5.6	Ic	Co	μg/l	15	Ia
Conductivity	mS/m	406	Шa	Cu	μg/l	14	Ia
COD - Cr	mg/l	20		Mn	μg/l	550	Ia
PCB	mg/l	20		Ni	μg/l	40	Ia
Al .	mg/l	100	Шa	Se	μg/l	<0.2	Ia
Sb	μg/l	<5	Ia	Ag	μg/l	<10	Ia
As	μg/l	10	Ia	Zn	μg/l	300	IIa
Ba	μg/l	50	Ia	V	μg/l	<20	Ia
Be	μg/l	<0.2	Ia	Sn	μg/l	<5	Ia
В	μg/l	<10	Ia	Fluorides	mg/l	1.90	
Pb	μg/l	<20	Ia	Chlorides	mg/l	-	
Cd	μg/l	9	Па	Nitrites	mg/l	0.05	Ia
Cr-total	μg/l	<10	Ia	Phosphates	mg/l	0.03	Ic
Fe	μg/l	200	Ia	Sulphates	mg/l	460	

Table 1 Leachability of tailings from the pond near Zlaté Hory

3.3.5 Pollution - local interests

The pollution of surface waters caused by the mining activity in the Zlaté Hory area was from the exploitation started in the early sixties, a source of conflicts between citizens and the town council of Zlaté Hory on one side, and the company Rudne Doly (Ore Mines) Jesenik, Enterprise Zlaté Hory on the other side. Extraction of ores by the government-owned company had a much higher priority and all demands from the public and The Society of Anglers to improve the protection of surface waters were rejected. The pollution of Golden Creek increased as the slurry pond was filled with tailings, causing an increase in the seepage from the slurry pond. The result of the combined pollution from mine water and leakage from the slurry pond was the total disappearance of fish from Golden Creek on Czech territory. The liming of mine waters discharged from The Mining Gallery Mir was only partly successful and the water in Castle Creek remained highly polluted by mine water and by water seepage from the waste rock dumps.

3.3.6 Pollution - regional/international interests

Zlaté Hory is a renown recreational centre and the contribution of this activity to the regional economics is growing. This is especially important in this part of the country in relation to the decline of mining and restructuring of agriculture. Therefore the importance of a clean-up of surface water

in the Zlaté Hory mining area is increasing. The international border crossing to Poland is planned at Zlaté Hory, which may bring even more visitors to the area. Their interest in spending some time here depends however largely on the quality of the environment.

The water quality in Golden Creek is important also because it is crossing the border of The Czech Republic to Poland approximately 1 km downstream Zlaté Hory. It has repeatedly been demands to reduce the pollution of water entering Poland.

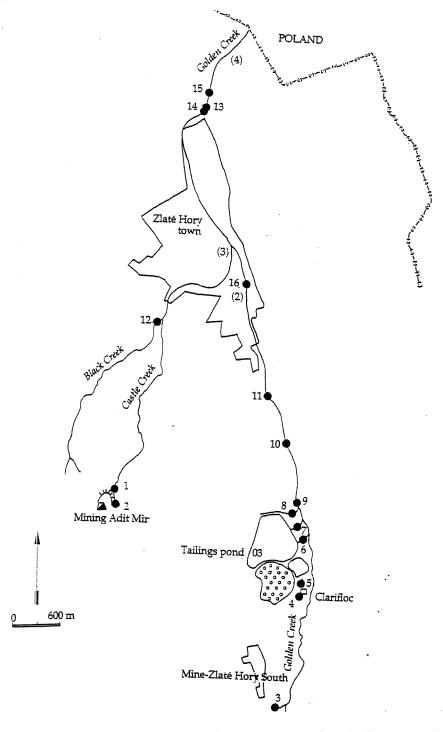


Figure 7. Map of the watercourses in the Zlaté Hory-area. Numbers indicate sampling stations in september 1993. Numbers in paranthesis indicate sampling stations for Povodi Odry.

4. Hydrology

4.1 General - Water courses, precipitation, drainage etc.

A simple sketch of the creeks draining the mining area and the town of Zlaté Hory is shown in figure 7. The sampling points in the water system are also presented in this figure.

Most of the area of The Mining District Zlaté Hory is drained by Golden Creek (Zlaty potok) and its tributaries. Golden Creek originates in the wetlands north-east of the village Hermanovice and flows to the north through the wide valley.

The main mine Zlaté Hory-South is located in this valley together with the ore-dressing plant and tailings ponds. Other mining galleries are situated at the eastern slopes of Pricny vrch Hill also draining to Golden Creek. A number of small unnamed tributaries polluted by mine water and water from other mining activities are running into Golden Creek from the left side (slopes of Pricny vrch Hill). From the left side some small streams originating as seepages from the tailings pond 03, are also going into Golden Creek.

The unnamed tributaries coming from the eastern part of the drainage area, where there have been no ore bodies or mining activities, are unpolluted. Under normal conditions (with exceptions of very high water flow in spring) the water in Golden Creek upstream the main shaft in Zlaté Hory-South disappears underground into the mine through, cracks to the surface.

The water in Golden Creek downstream the mining area, comes from the "Clarifloc treatment plant". Water from the third level in the mine is pumped to the surface at the entrance of the drainage adit near the Clarifloc. The water is limed, before passing through the Clarifloc. After final settling in two sedimentation basins (former tailings pond 02), the mine water is discharged into Golden Creek.

The water from the mining gallery Mir (mineral deposit Zlaté Hory-West) is led underground to the main centre of mining (Zlaté Hory-South). Only a small amount of mine water collected near the entrance of this mining gallery is now discharged directly to Zamecky potok (Castle Creek). Seepages from the tailings pond are bringing much iron into Golden Creek which results in a brown colour downstream the tailings pond.

The main tributary to Golden Creek, Castle Creek, is entering from west in the southern part of the town Zlaté Hory. The creek is polluted mainly from the mining gallery Mir and water percolating through the waste rock dump in this area.

Cerny potok (Black Creek) is the main tributary to Castle Creek, coming in from the left side at the southern boundary of the town Zlaté Hory. The catchment area of the Black Creek is mainly located outside the mining area. Water from a small reservoir in the upper part of this creek is used as a source of drinking water.

Golden Creek downstream the confluence with Castle Creek is flowing through Zlaté Hory from the south, and about 1 km from the northern boundary of the town it crosses the international boundary into Poland. In Poland the river is called Prudnik a name used on some maps over this part of the Czech territory.

The western slopes of Pricny vrch Hill are drained into the creek Olesnice which flows towards the north through the villages Horni Udoli and Dolni Udoli (former name Olesnice). Mining was

intensive in this historical Olesnice Mining District in mediaeval times but today there is no new mining activity in this area. Olesnice Creek enters the river Bela which is flowing into Poland.

The southern slopes of Pricny vrch Hill (Hornicke skaly Rocks) are drained into Opavice Creek which is growing to a small river joining the Opava River - one of the most important tributaries to the Odra River.

All these streams belong to the catchment area of the River Odra running to The Baltic Sea.

The mining district is located in a hilly area, and from the level approximately 400 m a.s.l. at the town Zlaté Hory it ranges up to 975 m a.s.l. at the highest summit Pricny vrch Hill. The slopes of the hills are covered by coniferous forests formed by spruce (*Picea abies*). The town Zlaté Hory lies at the northern foot of the hills and further to the north the flat land is used for agriculture. The soils in the area belong to the group of cambisols, in some places podzol cambisols and locally humic podzols.

In Table 2 the theoretical run-off for different parts of the catchment area of Golden Creek are listed. These values are based on annual precipitation and does not include evaporation. The values are probably to high, but they indicate the order of magnitude.

Table 2 Hydrological data for the separate catchment areas of Golden Creek. The values have not been adjusted for evaporation.

	Ann.	Catchm.	Annual	Water
Water course	prec.	area	run-off	flow
	mm	km ²	$10^3 \mathrm{m}^3$	1/s
Black Creek	900	2.27	2043	66
Castle Creek	930	2.47	2297	74
Golden Creek				
Part 1 - Upstream tailings pond	880	8.2	7216	232
Part 2 - Tailings pCastle Creek	880	6.17	5430	175
Part 3 - Downstr. Castle Creek	800	6.3	5040	162
Golden Creek (Parts 1+2+3)		20.67	17686	569
Golden Creek (with Castle Creek)		25.41	22026	708

The water flow in Golden Creek is monitored by Povodi Odry. In Table 6 the annual average of values given for the sampling stations are listed.

4.2 Field observations - 1993

In September 1993 a team from NIVA visited the area together with a team from The Mining University, Ostrava. The sites for observations during the field work in September 1993 are shown in figure 7. At most stations the water flow was either measured or estimated subjectively at the time of water sampling for chemical analysis. Only at the points 4 and 5 the water flow is registered continuously by the mining company. At the other points in the field, estimation of water flow was done at the time of sampling.

Measurement done with a bucket and a stop-watch was used at the points 1 and 3. This method is quite accurate.

At the points 4 and 5 the flow was measured continuously, and the value was read from the instrumentation in the control room for the "Clarifloc"-basin.

At the points 9, 11 and 15 the water flow was estimated by measuring the area of a cross-section of the creek, combined with measurement of the velocity of the current at some points across the river. This method may be very accurate, but then many points of measurements are needed, and the structure of the bottom substrate of the river and the river bank must be known. Accurate measurement of the area of the cross-section is also needed. The creeks were quite shallow and the cross-sections were not quite regular. The water flows calculated from these data may deviate from the true water flow at the time of sampling. We have not made any corrections for the structure of the river bed and the shallow water in some locations. The estimated water flow may therefore be to high.

5. Water chemistry

5.1 Sources of data

5.1.1 The Mining University, Ostrava

During August and September 1993 The Mining University, Ostrava analysed samples of surface and mine water from the Zlaté Hory area. Data from these samples are presented in table 5 and 6 together with results for samples taken from the same localities analysed by NIVA.

pH and conductivity were measured electrometrically by instruments produced by WTW Weilheim, Germany (pH-96, LF-96). Sulphates were determined by capillary isotachophoresis. Chlorides were determined by argentometric titration according Czech Standard CSN 83 0520. Procedures according this standard were used also for determination of dissolved matter, particulate non-dissolved matter (gravimetrically on Synpor filter). Trace elements (Cd, Cu, Pb, Zn) were determined by flameless atomic absorption Spectrophotometry with graphite rod atomizer. Fe and Mn were analysed by atomic absorption Spectrophotometry (AAS 3 Carl Zeiss, Jena).

5.1.2 Povodi Odry, Ostrava

NIVA received data from Povody Odri (PO) in July 1992. The data from Povody Odri represents samples taken every month at sites comparable to station 16 (fig. 2) and station 15 twice a month. Samples have also been taken from Castle Creek upstream Black Creek. This station is not directly comparable to any of the sites chosen during the sampling in September 1993. In this report these data have been compared to our station 1, but due to the dilution, the concentrations measured by Povodi Odry should be expected to be a little lower. The samples have been analysed for many different parameters. To be able to compare the conditions in Zlaté Hory with other mine polluted rivers, NIVA have processed the data to some extent. The yearly arithmetic mean is often used for such purposes and this has been calculated for the most relevant parameters. This extract of the data from PO together with data from The Mining University, Ostrava and from NIVA is presented in table 5 and 6.

5.1.3 NIVA - Field data 1993

According to the tasks described in Chapter 1.1, scientists from NIVA visited the Zlaté Hory-area in September 1993, together with the Czech co-workers from the Mining University of Ostrava. The team from NIVA brought the necessary equipment to determine water flow, take samples for chemical analysis and to investigate the biological conditions in the water system. A special ground water sampler was demonstrated during this visit to initiate the ground water part of the programme.

During the stay in Zlaté Hory, 16 water samples were taken from creeks in the mining area, outlets from industrial plants, from the local sewage treatment plant and from the plant treating parts of the mine water.

The samples were samples were taken to Norway where they were analysed in different ways. pH and conductivity were measured electrometrically at NIVA. The sulphur and metals were analysed at NIVA with an ICP-instrument with an optical sensor. Samples were also analysed at NILU (Norwegian Institute for Air Research) with an ICP-instrument with a mass spectrometer. Sulphate

has been determined as total sulphur recalculated to sulphate. Mercury was determined at NIVA in some samples. These samples were taken on special bottles prepared for this type of analysis. The analysis was performed at NIVA by reducing the mercury to metallic form with tinchloride. The metal was then driven off with helium and amalgamated on gold. The mercury was vaporized by electric heating and detected by atomic absorption on an instrument especially made for this analysis.

For most metals the ICP-MS-instrument gives the most reliable results, because this method is more sensitive and there are less problems with interference from other components.

Table 3 Sampling sites during the co-operate field-work in September 1993 The stations are marked on the map in figure 2.

Station	Description
1	Castle Creek - Downstream the waste-rock dump at the Mine "Mir". Road bridge crossing.
2	Castle Creek - Upstream waste-rock dump at the Mine "Mir". Virtually unpolluted.
3	Mine-water from level 2. Untreated, discharged into the ground. No surface water reaching Golden Creek.
4	Mine-water from level 3. Limed before it is discharged to the "Clarifloc"-basin.
5	Outlet from the "Clarifloc"-basin.
6	From pump station - outlet from tailings dam.
7	Leakage from tailings dam.
8	Leakage from tailings dam.
9	Golden Creek downstream all tributaries in the mining area around the tailings dam.
10	Ground-water, Near Golden Creek, upstream the channel near the Forester's house
11	Golden Creek at Strelnice, downstream the Forester's house. Sampling point for Povodi Odry
12	Black Creek just before entering Castle Creek.
13	Waste water from the bicycle factory "Velamos"
14	Waste water from the sewage treatment plant in Zlaté Hory
15	Golden Creek downstream the town of Zlaté Hory
16	Waste water from the textile factory in Zlaté Hory

Results from chemical analysis of some samples from Zlaté Hory, taken in September 1993. Analysed by NIVA Table 4

Lead	1	µg/l	1.12	2.11	96.0	ı	0.7	3.26	3.02	7.94	11.8	3.49	6.15	5.1			31.2
Copper	!	µg/l	785	6.67	14.3	09 <i>LL</i>	9.01	5.55	32.2	97.6	106	< 0.1	54.1	1.47			13
Cadmium		µg/1	31.7	11.5	< 0.01	100	90:0	< 0.01	< 0.01	1.64	1.91	98.0	0.78	< 0.01			2.51
Zinc		µg/l	2508	3433	47	16200	34	725	45.4	1206	335	65.4	219	17			<i>11</i> 0
Iron		mg/l	< 0.01	0.01	0.35	57.6	90:0	24.4	37.7	12	2.26	0.02	1.42	0.24	0.21	0.1	0.09
Magne-	sium	mg/l	12.5	7.75	6.05	30.6	0.04	11.2	16.7	18.3	12.8		12.4	2.28	10.6	5.46	8.23
Calcium		l/gm	41.6	35	35.6	494	225	212	284	242	172	112	158	11.5	57.9	34.6	88.4
Sulphate		mg/l	151.8	93	53.1	372	303	576	885	969	4	253	396	11.79	54	33	193.5
Cond.	mS/m	25 °C	36.8	26.6	23.7	282	276	113.9	163.2	136	93.4	60.1	82.2	9.45	52.9	34.1	53.4
Hd			5.08	6.5	7.61	12.26	12.2	4.86	3.69	3.63	6.32	98.9	6.88	7.26	7.15	7.04	7.04
Water	flow	l/sec.	4.0	4.0	0.73	09	09	3.0	< 1.0	< 1.0	68		175				222
Station	_	_		7	ĸ	4	8	. 9	7	∞	6	10	=	12	13	14	15

Table 5 Data from chemical analysis of samples from the Zlaté Hory area. Numbers in the reference column are referring to stations listed in Table 3. The letter indicates the institution responsible for the analysis U. Mining University, Ostrava, N: NIVA, P: Povodi Odry (Continues)

Refere	nce	Date	рН	Cond.	SO4	Ca	Mg	Zn	Cu	Fe	Cd	Pb	Hg
				mS/m	mg/l	mg/l	mg/l	μg/l	μg/l	mg/l	μg/l	μg/l	μg/l
1	U	08.08.93						2940	510	0.08	28.6	0.1	
	υ	09.09.93	4.32	38.9	608.5			7045	564	0.31	20	0.1	
	υ	23.09.93	4.86	38.2	456.2			7960	684	0.1	42.3	0.2	
	N	23.09.93	5.08	36.8	151.8	41.6	12.5	8057	785	< 0.01	31.7	1.12	< 0.002
	Р	1990	7.46	19.8	46	27	4.1	565	15	0.25	4.0	< 20	0.3
	Р	1991	7.35	20.8	49	27	4.4	1097	29	0.17	6.6	< 20	0.2
	Р	1993	7.10	26.5	99	34	5.9	6190	247	0.48	26.1	< 20	< 0.2
2	U	23.09.93	6.56	24.6	160.2			3512	104	0.015	9.6	2.5	
	N	23.09.93	6.5	26.6	93	35	7.75	3433	79.9	0.01	11.5	2.11	< 0.002
3	U	08.08.93						100.5	9.52	0.32	<0.01	1.1	
	υ	09.09.93	6.07	28.6	28.2			68	11.5	0.35	<0.01	1.12	
	U	23.09.93	6.96	22.8	46.5			52.5	12.2	0.42	<0.01	1.15	
	N	23.09.93	7.61	23.7	53.1	35.6	6.05	47	14.3	0.35	< 0.01	0.96	
4	U	23.09.93	12.56	291	451			17230	7910	51.28	125		
	N	23.09.93	12.26	282	372	494	30.6	16200	7760	57.6	100	•	
5	U	23.09.93	12.5	286	440			52	8.6	1.54	0.05	1	
	N	23.09.93	12.2	276	303	225	0.04	34	9.01	0.06	0.06	0.7	
6	U	08.08.93						910	6.8	17.2	<0.01	4.5	
	υ	09.09.93	5.53	114	478.8			690	5.7	24.4	<0.01	10.2	
	U	23.09.93	4.89	115	456			745	6.8	25.2	<0.01	8.8	
	N	23.09.93	4.86	113.9	576	212	11.2	725	5.55	24.4	< 0.01	3.26	< 0.002
7	U	08.08.93						2110	5.6	53	0.02	5.12	
	υ	09.09.93	2.6	195	770.5			42.5	3.86	45	0.02	7.2	
	U	23.09.93	3.56	186	652.5			51.2	3.57	41.2	0.01	6.5	
	N	23.09.93	3.69	163.2	885	284	16.7	45.4	(32.2)	37.7	< 0.01	3.02	
8	U	08.08.93						2950	106	20.7	2	6.54	
	U	09.09.93	2.85	152	854.9			1960	98.5	17.6	1.8	8.2	
	U	23.09.93	3.56	136	889.2			1308	92.4	18.2	1.1	7.1	
	N	23.09.93	3.63	136	696	242	18.3	1206	92.6	12	1.64	7.94	
9	U	08.08.93						76.2	85.6	1.86	2	5.86	
	υ	09.09.93	6.13	125	465.9			72.8	120.2	3.25	i 1	9.23	
	υ	23.09.93	6.4	96.2	492.5			61.5	124.8	2.82	2	8.56	
	N	23.09.93	6.32	93.4	441	172	12.8	335	106	2.26	1.91	11.8	
10	U	23.09.93	6.92	62.4	48.2			61.8	2.12	0.05	<0.01	2.8	
	N	23.09.93	6.86	60.1	253	112	11	1	< 0.1	0.02		3.49	l

Table 5 Data from chemical analysis of samples from the Zlaté Hory area. Numbers in the reference column are referring to stations listed in Table 3. The letter indicates the institution responsible for the analysis U. Mining University, Ostrava, N: NIVA, P: Povodi Odry (Continued)

Refer	ence	Date	рΗ	Cond.	SO4	Ca	Mg	Zn	Cu	Fe	Cd	Pb	Hg
				mS/m	mg/l	mg/l	mg/l	μg/l	μg/l	mg/l	μg/l	μg/l	μg/l
11	U	09.09.93	6.41	92.7	446.4			234	39.1	1.58	1.12	8.5	
	U	23.09.93	6.66	88.6	462.2			228	42.2	1.65	0.92	7.2	
	N	23.09.93	6.88	82.2	396	158	12.4	219	54.1	1.42	0.78	6.2	< 0.002
	Р	1990	7.48	53.7	209	79	7.3	100	43	0.46	4.0	< 20	0.7
	Р	1991	7.53	48.5	195	83	6.2	112	40	0.54	4.8	20	0.2
	Ρ	1993	7.41	55.3	236	104	8.9	127	33	0.81	3.1	< 20	< 0.20
12	U	23.09.93	.7.35	10.12	21.1			16.2	2.5	<0.1	<0.01	4.26	
	N	23.09.93	7.26	9.45	11.8	11.5	2.28	17	1.47	0.24	< 0.01	5.1	< 0.002
13	N	24.09.93	7.15	52.9	54	57.9	10.6			0.21			0.0035
14	N	24.09.93	7.04	34.1	33	34.6	5.46			0.1			
15	N	24.09.93	7.04	53.4	193.5	88.4	8.23	770	13	0.09	2.51	31.2	0.0025
	Р	1990	7.50		133			172	50	0.92		< 20	
	Р	1991	7.52		132			276	26	0.40		< 20	
16	N	24.09.93	7.02	49									

Table 6 Data from chemical analysis of samples from the Zlaté Hory area. Numbers in the reference column are referring to stations listed in Table 3. The letter indicates the institution responsible for the analysis U. Mining University, Ostrava, N: NIVA, P: Povodi Odry (Continues)

Refer	ence	Date	Water flow	CI	Diss. ma.	Nond. Ma.	Mn	Ni
			l/s	mg/l	mg/l	mg/l	μg/l	μg/l
1	U	08.08.93					2160	49.5
-	υ	09.09.93		14.18	782.5	14	1450	48.6
	υ	23.09.93					1360	46.2
	N	23.09.93	4				1708	78
	Р	1990	78	7.9	152	11.8	70	13
	Р	1991	112	7	151	17.2	122	14.7
	P	1993	-	6.5	213	21.2	-	42.3
2	U	23.09.93					89.6	•
	N	23.09.93	4				57.6	46.4
3	U	08.08.93					87.5	4.2
	U	09.09.93		4.43	149.2	7.5	212	4.6
	U	23.09.93					193	
	N	23.09.93	0.73				168.6	4.07
4	N	23.09.93	60				5820	
5	U	23.09.93					107	
	N	23.09.93	60				11.4	5.73
6	U	08.08.93					4600	42.2
	υ	09.09.93	-	14.18	907.52	39	3250	45.5
	U	23.09.93					3660	
	N	23.09.93	3				4222	22.4
7	U	08.08.93					18200	40.3
	U	09.09.93		21.27	1473.3	88.56	13500	42.3
	U	23.09.93					12820	
	N	23.09.93	< 1.0				10857	25.6
8	U	08.08.93					6800	50.6
ļ	U	09.09.93		15.07	1630.5	99.3	11200	81.2
	U	23.09.93					12280	
	N	23.09.93	< 1.0				14300	73.9
9	U	08.08.93					1960	36.5
	U	09.09.93		9.75	861.2	18.5	3850	38.7
	U	23.09.93					3254	
	N	23.09.93	89			<u></u>	3418	39.8
10	U	23.09.93					2234	
	N	23.09.93					8.5	7.41

Table 6 Data from chemical analysis of samples from the Zlaté Hory area. Numbers in the reference column are referring to stations listed in Table 3. The letter indicates the institution responsible for the analysis U. Mining University, Ostrava, N: NIVA, P: Povodi Odry (Continued)

Refe	rence	Date	Water flow	Cl	Diss. ma.	Nond. Ma.	Mn	Ni
			l/s	mg/l	mg/l	mg/l	μg/l	μg/l
11	C	09.09.93		12.41	798.25	6	3500	32.6
	υ	23.09.93					3412	
	N	23.09.93	175				2158	30
	Р	1990	145	12.8	367	14.3	1298	24
	Р	1991	202	8.2	357	20	773	17
	Р	1993	209	7.2	420	25	1030	20.7
12	U	23.09.93					82	
	N	23.09.93					45.2	< 0.5
15	N	24.09.93	222				538	12.2
	Р	1990	339	14.8	306	27	-	28
	Р	1991	460	12	306	15	-	27

5.2 Presentation of chemical data

5.2.1 All available data

The results of the analyses of the samples taken to Norway for analysis are shown in Table 4.

In table 5 the most important results obtained at NIVA/NILU, at The Mining University, Ostrava and an extract of the yearly averages for 1990, 1991 and 1993 from Povodi Odry are presented together.

5.2.2 Discussion of chemical data

The samples from the co-operate field-work in September 1993 have not been analysed sufficiently detailed to test anion/cation balance or theoretical conductivity against measured. For data from Povodi Odry we have calculated the ion balance for all samples with sufficient information. For some randomly chosen samples the theoretical conductivity was also calculated.

The results of these calculations showed that the ion-balance is quite good for most samples within 10 % of sum anions or cations (miliequivalents). A few samples had ion balances far from this. We have not investigated this further, but when possible such tests should be performed as part of the laboratory quality assurance routines. For the samples tested, the theoretical conductivity is higher than the measured value. This may be expected in this type of water, with quite high ion concentrations. The values used for this type of calculations are found in Appendix I

In rivers polluted from metal mines, the main anion usually is sulphate, generated as sulphuric acid by the oxidation of sulphide minerals. The main cation is usually calcium, dissolved from basic minerals as limestone and dolomite. As a consequence of this, there should be a near correlation between sulphate concentration and electric conductivity in samples with pH not too far from neutral. In Figure 8 and 9 these relations are presented graphically for data from Golden Creek upstream Castle Creek and Castle Creek, the Povodi Odry stations 2 and 3 (Figure 7). The correlation is quite obvious, but for some samples the deviations is more than the expected "random variations" can explain. At station 3 the sulphate concentration is quite low, so sodium and chloride will also have an influence on the conductivity. In figure 10 the measured and calculated conductivities for a few samples from the Povodi Odry station 2 (NIVA, 11) are presented graphically.

The samples analysed in Norway could not be tested on ion balance or theoretical conductivity. In figure 11 however, the sulphate concentration is presented as a function of the measured conductivity. Apart from 4 samples there is an excellent correlation. The samples not in accordance with this correlation have been marked with the sample numbers. The sample 4 and 5 from the Clarifloc have a much higher conductivity than expected from the sulphate values. This is obviously due to the high pH in the samples. The samples 13 and 14 are the outlet from the bicycle factory and the effluent from the sewage treatment plant respectively.

The sample 3 did also have a high sulphate concentration compared to the measured conductivity in the report from the NIVA-laboratory. It seems however that a decimal point was missing. A good illustration of the importance of making such tests on the analytical results.

The difference between the results from the virtually unpolluted water in Black Creek and that in Castle Creek and Golden Creek is quite evident. The main heavy metal pollution is from zinc, but

cadmium and copper is also quite high. Mercury, on the other hand was low on all sampling stations. This is an important result, as the results for mercury in the data from Povodi Odry indicated in our former report (Arnesen et al. 1993) were quite high.

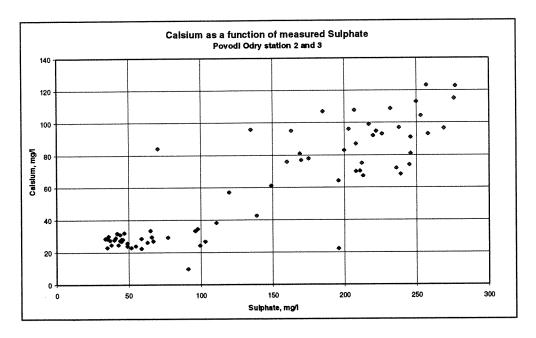


Figure 8 Concentration of calcium as a function of measured sulphate at the Povodi Odry stations 2 and 3 (Figure 7). Data from Povodi Odry

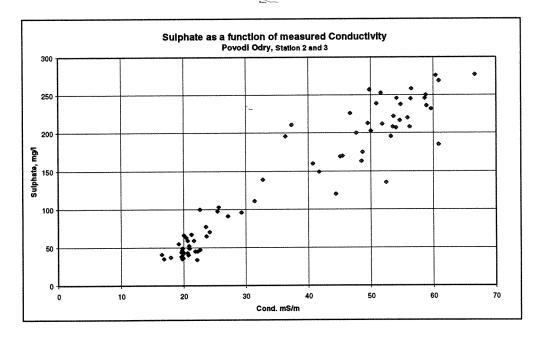


Figure 9 Concentration of sulphate as a function of measured conductivity at the Povodi Odry stations 2 and 3 (Figure 7). Data from Povodi Odry

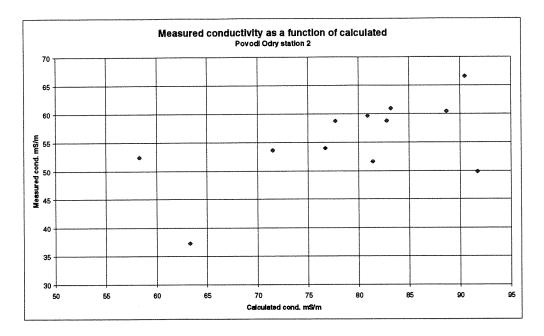


Figure 10 Comparison of calculated and measured conductivities for some randomly chosen samples from Povodi Odry station 2 (Figure 7). Data from Povodi Odry.

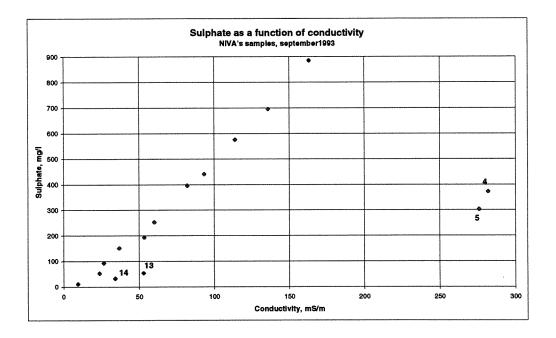


Figure 11 Concentration of sulphate as a function of electrical conductivity in samples for Zlaté Hory. Data from NIVA's samples, September 1993. All stations. Numbers in plot indicates sampling station (Table 3).

The results from Povodi Odry have been changed a great deal over the years from 1990 to 1993. If the analytical procedure have been the changed, this may be the reason, but it seems that the concentration of sulphate, zinc, copper and cadmium have increased with a factor varying from 2 to 10 for the different components.

It is difficult to give any conclusive remarks about these changes, as long as NIVA only have analysed one sample from each station. It seems, however, that NIVA's results for heavy metals confirms the results for Povodi Odry in 1993.

Even if there are some differences, the results from the Mining University and those from NIVA are in quite good accordance for heavy metals. For sulphate most of the results from The Mining University are too high.

The concentrations of cadmium and mercury found by Povodi Odry seems to be too high, compared to the results found by NIVA. These metals are found in very low concentrations and the analysis requires special methods. One single sample from each locality is however too little to make the data from NIVA sufficiently reliable to conclude on this question. The samples brought to Norway for analysis, showed all concentrations below or around the detection limit for mercury, while the concentration of cadmium was high in samples with high concentrations of the other heavy metals.

Altogether the chemical data presented in this report seems to give a reliable picture of the situation, when the remarks above are taken into consideration.

The mining activity have great influence on the water quality in the area. Especially in Castle Creek the concentrations of heavy metals are very high and may certainly influence the use of the this stream. The main source of pollution in Castle Creek seems to be the waste rock dump at the mine gallery "Mir". However, the old mining area upstream the mine also have some influence on the heavy metal content.

In Golden Creek, the all mining activities attributes to the pollution. As long as the mine water from "Level 3" is limed, the heavy metal concentration in the upper part of Golden Creek will be low. Mine water form level 2 is less polluted an will have little effect on the aquatic environment.

The outlet and the seepage from the tailings dam is acid and have high concentrations of heavy metals and were the main contribution of heavy metals to Golden Creek at the time of sampling. At that time work was going on to transfer these outlets to the Clarifloc plant. If this is done effectively, the water in the stream will improve.

In September 1993 the tailing pond seemed to be the main source of pollution. The water pumped from the mines or discharged from mining galleries were also a source of pollution but most of the mine water was limed and the heavy metals precipitated in the sedimentation pond. The waste rock dump at Mir and mines abandoned very many years ago may also be sources of pollution to Castle Creek. Possibly there may be diffuse sources of pollution in the area, i.e. within the town of Zlaté Hory.

5.3 Ground water

During the field work in September 1993 the BAT groundwater sampler was demonstrated. It was attempted to take out ground water samples, but we did not succeed. The quality of ground water in the area will therefore not be discussed. It has been shown (Raclavská and Raclavský 1992) that the ground water in the area is polluted with heavy metals, especially zinc.

6. Transport of pollutants

One of the main tasks for the work in 1993 was to identify the most important sources of pollution in the area. To do this we have tried to calculate the transport of pollutants in the different parts of the water system draining the mining area.

Transport of pollutants may be measured or estimated in different ways. In this report we define transport as the product of concentration and water flow at the time of the sampling. The value has been calculated on a 24 hour basis as kg/day. As a basis for these calculations we have used the results obtained by NIVA on the samples collected in September 1993. The transported amounts of pollutants at the different sampling points, estimated in this way, are listed in table 7.

Station	Water	Conduc-	Sulphate	Zinc	Cadmium	Copper	Lead
	flow	tivity					
	l/sec.	mS/m	kg/day	kg/day	kg/day	kg/day	kg/day
1	4	36.8	52	2.8	0.011	0.27	0.000
2	4	26.6	32	1.2	0.004	0.03	0.001
3	0.73	23.7	3	0.0	0.000	0.00	0.000
4	60	282	1928	84.0	0.518	40.23	
5	60	276	1571	0.2	0.000	0.05	0.004
6	3	113.9	149	0.2		0.00	0.001
7	< 1.0	163.2					
8	< 1.0	136					
9	89	93.4	3391	2.6	0.015	0.82	0.091
10		60.1					
11	175	82.2	5988	3.3	0.012	0.82	0.093
12		9.45					
13		52.9					
14		34.1					
15	222	53.4	3711	14.8	0.048	0.25	0.598

Table 7 Estimated momentary transport values during the sampling in the Zlaté Hory-area. September 1993. Data from NIVA.

6.1 Sulphate

The transport of sulphate is quite high in the mine water from gallery 3 level (4). In the outlet from the "Clarifloc" basin (5) the transport of sulphate is a little less, possibly because of precipitation of some calcium sulphate (gypsum). In Golden Creek downstream all tributaries from the tailings pond, the transport of sulphate is approximately doubled from that found at point 5. This may to some extent be due to errors in the water flow measurement, but it is quite certain that the sulphate transport is much higher in Golden Creek than that coming from the mine water from gallery 3 level. The sum of sulphate transport in the three small creeks from the tailings dam area is only responsible for a small part of the total transport at this point.

In Golden Creek at Strelnice (11) the transport is again much higher than at point 9. Possibly this is due to some error in measurement. If not it seems that there is some source of sulphate in the area, possibly groundwater seepage. The groundwater well (10) upstream Strelnice is however quite low in sulphate.

At point 15, Golden Creek downstream Zlaté Hory, the sulphate transport is about the same as at point 9 or a little higher. Sulphate is very nearly conservative in natural water, and it seems that the value found at Strelnice is to high. This may be due to the water flow measurement, or to a to high sulphate concentration.

There should be done more measurements to investigate this further. It may give useful information about other sources of pollution in the area.

6.2 Zinc

Even upstream the waste-rock dump at the "Mir"-mine (point 2), the transport of zinc is significant. The transport is a little more than doubled downstream the dump - 1.6 kg/day - (point 1).

The mine water from level 3 is limed and the heavy metals are precipitated in the "Clarifloc"-basin. In the mine water the transport of zinc is about 84 kg/day, while transport of zinc going to Golden Creek from the Clarifloc is about 0.18 kg/day. This means a reduction of about 99,8 %.

In Golden Creek downstream the Tailings pond area (9) the transport of zinc is about 3.3 kg/day. The groundwater in the area is also quite high in zinc, and this is in quite good agreement to what has been found at point 9 and 11.

The value at point 15 is very much higher and indicates other sources between this point and sampling points in Castle Creek and Golden Creek upstream Zlaté Hory. Possible sources in the town of Zlaté Hory should be investigated. There may for instance be diffuse sources as road beds, dumps in housing areas etc. A sampling programme over some time should give the answer. The programme should include water flow measurements.

6.3 Copper

The transport of copper is not very high. The sum coming from Castle Creek and Golden Creek together should be about 1 kg/day. The transport found at point 15 is much less. This may be due to adsorption in organisms, sedimentation of particles, etc. Relatively the difference is quite high, but the absolute values are low.

6.4 Cadmium

The transport of cadmium in Golden Creek is about 12 g/day at point 11. In the river at point 15 the transport is about 50 g/day. This difference may be significant, but the values are low and the uncertainty in flow-measurement and concentrations will be quite high. The transport is quite certain above background values but it is difficult to point out the most important source.

A sampling programme over time based on the results from this investigations should identify the sources more clearly.

6.5 Lead

The lead concentration in Golden Creek at point 15 is quite high. It is also high at the points 9 and 11, but much lower than at the point downstream the town of Zlaté Hory. This should be investigated further, and there should be looked for sources inside the town. If roofs or other building details are made from lead or copper this might give an explanation.

7. Biological observations

7.1 Observations done in September 1993

7.1.1 Bottom animals

Methods

Bottom animals were sampled from different localities in Golden Creek, Castle Creek and Black Creek by using a hand net with 250 μ m mesh size. The so called "Kick-method" is used by kicking bottom materials upstream the hand net which is pressed against the bottom. The animals will then drift into the net together with some bottom material. The sampling period on each station was 1 minute. The animals were first observed in a white plastic disk and thereafter conserved in ethanol for further analysis. The animals from 1/10 of the sample were sorted in the laboratory into main groups and counted.

Results

The results are shown in Table 8 and Figure 12.

Table 8 Bottom animals from Golden Creek, Castle Creek and Black Creek in Zlaté Hory. Number of animals counted in 1/10 of the sample x 10. Sampling period was 1 minute on each station.

Group	G	olden Cr	eek	Castle	Creek	Black Creek
	No 5	No 11	No 15	No 2	No 1	No 12
Oligochaetae			80			
Hirudinea				290	170	,
Collembola					30	
Plecoptera	40	30		1710	20	230
Ephemeroptera		10	440			120
Neuroptera						40
Trichoptera	20	10	40	10		
Coleoptera				20		
Tipulidae						10
Chironomidae	40	10	2830	2230	20	1270
Ceratopogonidae	30	20	10			
Simulidae			4220			20
Number of groups	4	5	6	6	4	6
Total number of	130	80	5820	4260	240	1690
animals						

Golden Creek

The results from Golden Creek showed that the two upper localities (No 5 and No 11) were strongly affected by pollutants. Only a few animals were found, mainly insect larvaes as stoneflies (*Plecoptera*) and chironomids. On both localities the water was running swiftly over a bottom material of stones and gravel which would normally consist of a great variety of animals. However,

the bottom was partly covered with a white-brownish precipitation (ochre etc.) characteristic for mine drainage. According to the water analysis the lack of animals at station 5 is probably due to the high pH. The pH was here measured to be 12.2 which is far above the upper threshold for acute effects on evertebrates and fish (≈ 10-10.5). At station 11 the concentrations of metals and other components may not fully explain the lack of animals. However, episodic situations with more unfavourable conditions or chemical non-equilibrium due to mixing zones may be explanations. Station No 15 in Golden creek was located about 50 m downstream the outlet of the sewage plant of Zlaté Hory. Here the fauna consisted of a great number of chironomids and black gnats (Simulidae). Also other groups as the more sensitive mayflies, Ephemeroptera, were represented. These observations indicate organic enrichment which results in a high production of some animals. This was also supported by a rather heavy growth of bacteria and/or fungi and some algae at the bottom substrate. However, the high number and variety of benthic organisms also shows that the water has a low if any toxicity. The tests and chemical analysis give further light to these questions.

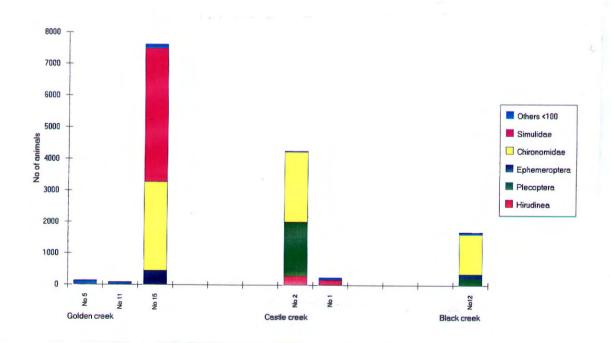


Figure 12 Bottom animals in Golden creek, Castle creek and Black creek. Number of animals sampled in 1 min.

Castle Creek

As shown in table 8, two localities were sampled in this little creek draining the mine gallery Mir. The upper station (No 2), supposed not to be influenced by the mine, had a rather high number of animals in spite of the little water flow. Dominant groups were the chironomids and stoneflies which were found in rather great numbers. It is somewhat astonishing that these animals could exist here in the high concentrations of zinc (3433 μ g/l), cadmium (11.5 μ g/l) and copper (80 μ g/l). They were for example far above the concentrations observed at station 11 where the fauna was very poor. Calcium, which is a strongly modifying element, was also higher at station 11. The mayflies, however, which is a sensitive group were absent. The water was clear and the stony bottom mostly covered with newly fallen leaves. The next station downstream the mine dump (No 1) was strongly affected by pollutants. Only some few leeches and insect larvaes were found. The stony bottom was covered with a white/brownish layer. The high concentrations of heavy metals (8057 μ g Cu/l, 32 μ g Cd/l and 785 μ g Cu/l) were undoubtedly responsible for the toxic effects on this locality.

Black Creek

Only one locality (No 12) was sampled in this creek which is supposed to be unaffected of any mining activities. The chemical analysis, however, showed that lead and zinc were present in concentrations slightly above those expected to be background levels. The water running swiftly through small rapids and pools was also clear and the bottom substrate of small stones and gravel was clean with only little growth of vegetation. The bottom fauna was dominated of chironomids which were found in considerable numbers. Mayflies and stoneflies were found in normal quantities and the benthic fauna as a whole was as one could expect in a unpolluted locality like this. It should be mentioned that predation from the fish (*Salmo trutta*) observed may significantly reduce the number of animals.

7.1.2 Fish

Methods

Observations for fish were made on all locations. In addition fishing with an electric apparatus was made in Black Creek (No 12) and in Golden Creek at the location downstream Zlaté Hory (No 15). The apparatus is designed for use in small water systems (F. Paulsen, Type FA 2, Trondheim, Norway) and can be operated by one person wearing the whole equipment in a special construction on the back. A battery of 12 V is used. The fishes after being paralysed were picked up by a handnet and placed in a bucket with water. After being measured the fishes were put back in the locality where they were caught.. The fishing lasted for 5 minutes in Golden Creek and 10 minutes in Black Creek. This would be sufficient to verify if there was any fish present in these small water systems.

Results

Even if the physical habitat should be optimal for brown trout or other salmonids no fish were seen or caught in Golden Creek from the upper parts down to station No 15 downstream Zlaté Hory. Fishing for 5 minutes at this locality resulted in no catch. According to local people some fish, probably trout, had been observed at station 15 earlier in the summer 1993. This suggest that the

water quality at least periodically must be good enough for fish survival. The high content of lead, however, may be questioned. At the sampling time there was a great quantity of food available for fish.

In Castle creek also the physical habitat should be well suited for fish. No fish, however, was observed on the localities visited down to the meeting with Golden creek.

At station 12 fish were observed during sampling of bottom animals. Electrofishing for 10 minutes resulted in a catch of 20 brown trout. The length distribution of these fishes is presented in Figure 13. This result shows that the biomass of trout in this little creek was rather high. The fishes were rather small with lengths of 6-20 cm. Age was not determined but most of the fishes were probably from 1-2 years old. Black creek may be considered as an important tributary for producing recruits to Castle and Golden creek if the water quality becomes satisfactory for fish in these areas in the future.

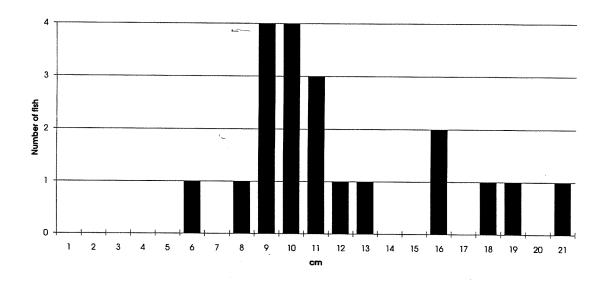


Figure 13 Length frequency of trout from Black creek.

7.1.3 Toxicity test

100 litres of water was sampled in plastic jars in Golden creek at station No 15 downstream Zlaté Hory. The water was transported to the laboratory and 4 days later tests with fish were started. Some days later test with algaes were performed.

Toxicity test with algae

The effect of water from Zlaté Hory (24.9.93) on the growth of algae was tested according to OECD Guideline 201; "Alga growth inhibition test", with the green alga *Selenastrum capricornutum* as test organism. The water sample, and a sample of distilled water was enriched with an inorganic nutrient solution (ISO 8692). A third sample was prepared by mixing these two samples 1:1 to obtain a 50% dilution of the Zlaté Hory water sample. The three samples were inoculated with algae from an exponentially growing culture and split into 3 parallel cultures in 100 ml flasks, that were incubated on a shaking table under continuous illumination (70 μ E m⁻²s⁻¹) at 20 °C. The growth of algae in each flask was monitored by daily counting of cell density for three days, using a Coulter Multisizer.

The growth curves obtained from the test are shown in Fiure 14. A significant inhibition of the growth of algae was observed in both cultures in water from Zlaté Hory. At 90% concentration, the growth was totally inhibited after 1 day of exposure, while the growth prevailed at a low rate at 50% concentration. The inhibition of the average algal growth rate during the test was 73% at 50%. concentration and 97% at 90% concentration. The effect on algal growth may be well explained by the concentration of zinc $(770 \,\mu\text{g/l})$ alone.

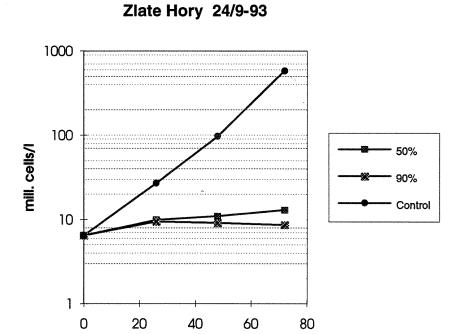


Figure 14 Growth curves for cultures of *Selenastrum capricornutum* in control growth medium and dilutions of water from Zlaté Hory (mean values for parallels).

hours

Toxicity test with fish

The tests were performed according to OECD Guidelines for Testing of Chemicals, No 203; Fish, acute toxicity test. Fry (O+) of brown trout, Tunhovd strain, with mean weight of 1.5 g were used as test fish. The test was carried out in glass aquaria with 101 of water and 7 fishes. The test fishes

were transferred to new solutions each day (semistatic method) and the test lasted 4 days. The fishes were observed each day. Natural lake water was used as a control. Gentle aeration was used to maintain the gas equilibrium with the atmosphere. The temperature was held at 11 ± 0.5 °C. During the four days no effect on the fish was observed. No mortality occurred and the fishes in the water from Golden Creek was evidently of the same health and condition as the fishes in the control at the end of the experiment. The water from Golden Creek showed thus no acute toxicity to trout, even if the zinc and lead concentrations were high. An explanation for this is the high concentration of calcium which modify the toxic effect of the metals on fish (table 9). The values presented in table 9 refer to long term effects of "soluble" metals. Fish and other aquatic organisms may tolerate considerable higher concentrations of "total" metal as measured in this investigation.

Table 9 Approximate maximum annual 50-percentile concentrations of "soluble" copper, zinc and cadmium for salmonids (μg/l). Modified after Alabaster and Lloyd (1982).

	Hardness, μg CaCo ₃ /l				
Metal	10	50	100	300	
Copper	1	6	10	28	
Zinc	15	50	75	125	
Cadmium	0.3	0.4	0.5	0.75	

7.1.4 Conclusive remarks

Castle Creek and the upper part of Golden Creek down to the town of Zlaté Hory were strongly affected by the mine drainage. The bottom substrate was partly covered by a white/brownish precipitate and there was no fish and very few bottom animals and other organisms present. Undoubtedly the heavy metals, as copper and zinc are most responsible for these effects. The difference between these localities and a normal one was clearly demonstrated by the observations in Black Creek. Here the fauna was quite normal with a variety of bottom animals and a dense population of trout present.

After passing the town of Zlaté Hory Golden Creek evidently became less toxic and there was a great deal of pollution resistant organisms present. The water was not acute toxic to trout according to the test, and local people had observed some fish earlier this year. However, the alga test showed that there was an inhibition on the growth of the green algae. Selenastrum capricornutum which was significant even at a dilution of 50 %. It may therefore be concluded that the water quality at this point must be nearly good enough to support fish in periods even if sensitive organisms as for example some algaes may be more chronically affected by the metals.

7.2 Microbiology

Microbiological analysis of water from this area has been used to estimate the intensity and speed of the weathering process in environments with high concentrations iron (Raclavsky et al. 1993). In the mining area of Zlaté Hory, *Thiobacillus ferrooxidans* represents the most important acidophile bacterial organism with optimum growth at pH values below 3. Water for microbiological analysis were sampled 9 September 1993, at localities for surface water sampling (Table 3). Technique according to Brauckmann (1986) was used for isolation of bacteria and their abundances were determined by the method according to Meynell (1986), which is based on the

determination of Fe³⁺ oxidized by bacteria. The results which are presented in Table 10 show very pronounced differences in bacteria abundance in surface water from the area. The highest values are found in samples in water directly related to the weathering process in the tailings pond. Relatively lower values were found in diluted water in Golden Creek and at the mining adit Mir.

Table 10 Abundance of *Thiobacillus ferrooxidans* in water samples from Zlaté Hory ore district.

Locality	Number	
1	$0.5 \cdot 10^3$	
6	$0.5 \cdot 10^6$	
7	11.10^{6}	
8	35·10 ⁹	
9	$1.1 \cdot 10^4$	
11	$0.8 \cdot 10^4$	

8. Further work

Chemistry

This report will conclude NIVA's present engagement in Zlaté Hory. It is, however, important to keep up the work initiated by this co-operate project.

It seems that the work going on to reduce the impact on Golden Creek from the seepage from the tailings deposits, will reduce the concentrations of heavy metals in the river crossing the border to Poland. The available data does not give enough information to identify all sources of heavy metal pollution in the area. This can only be done by monitoring a number of stations in the water-system with sampling for chemical analysis, and frequent measurements of water flow. Such intensive monitoring should be done for at least one year.

The existing data seems to indicate some change in transport of heavy metals through the town of Zlaté Hory. The monitoring should therefore include some stations within this area.

A programme for study of ground water pollution should also be initiated. The primary objective of this programme should be to identify the area where ground water is influenced by mine pollution. The extent and ways of transport of pollution through ground water should also be investigated.

The need for measures against water pollution will depend upon the future management of the mining area and the watercourses influenced by the mines. As long as the liming of mine water and the seepage from the tailings pond is maintained, the concentration of copper and zinc in Golden Creek may be low enough to allow fish in the lower part. If the liming is stopped or if there is need for further reduction in heavy metal concentrations in the recipient, other measures are needed.

NIVA would very much like to participate in the programme for planning such measures, but before this can be started, more detailed investigations of pollution sources and transport should be completed.

Possible measures in case the liming should be stopped, are either removal of mine wastes to dispose it in a safe place, or covering up with materials which will reduce contact with oxygen virtually to zero.

Biology

The biological investigation made in connection with the field work in this project is simple and gives only a rough idea about the situation. For practical purposes, however, such simple biological studies may be satisfactory. To get a more realistic picture of the connection between the water quality and the biological conditions, more thorough investigations are necessary. These should include more localities and the analysis of organisms should go further down to families, genera and species, if possible. Toxicity tests with actual water quality, fish and metals may also be performed. Sampling for two or more times a year would be preferable. The results would be of scientific interest and would give a better understanding of what effects one may expect in the water system after rehabilitation of the mines.

However, whether such more thorough investigations can be done or not, the development of biological conditions in the water system should at least be followed by one simple yearly field

investigation as described in this report. The same locations and methods may be used. Of special importance are the bottom fauna and fish. By use of the "kick" method with a hand net and electrofishing these animals should be adequately monitored. One day of field work would be sufficient and the analysis of the bottom animals may be reduced to sorting into main groups. Together with water quality data the results may be presented in a simple yearly report. In this way it should be possible to get a rough idea about the effects of the rehabilitation of the Zlaté Hory metal mine.

9. Conclusions

- With less than two days of co-operate field work there are still many unanswered questions
 concerning the pollution of water in the Zlaté Hory area. The samples taken and the
 studies done during these days have, however, given a good view of the situation, even if
 many important factors vary with time and situation.
- The chemical results obtained by Povodi Odry, NIVA and The Mining University is in quite good accordance with each other, but there is still need for more sampling both at the places mentioned in this report and others. Some of the observed differences or variations may be real, but analytical errors may also be the case.
- The influence of pollution from mining activities are very marked in Castle Creek, but also in Golden Creek downstream the mining area, the heavy metal concentrations are high. Even upstream the waste rock dump at the mine "Mir", the zinc and copper concentrations are high from mines which have not been operated for very many years ago. The concentrations of mercury were reported quite high from Povodi Odry. NIVA's results indicate that these figures are to high, due to analytical errors.
- NIVA have only one set of samples from the area, Mining University, Ostrava have some samples from a short period of time, while Povodi Odry have been sampling regularly over for years. In Castle Creek there seems to be an increasing trend for copper and zinc, while the concentrations have been quite stable in the Golden Creek.
- At the time of our co-operate field work preparations for the transfer of seepage from the
 tailings disposal area to the "Clarifloc" plant for liming, were made. When this is finished,
 the most important source of pollution will probably be the waste rock dump at the mine
 Mir. There may also be diffuse sources of metal pollution in the area, i.e. within the town
 of Zlaté Hory.
- Due to heavy metal pollution from the mining areas, there was no fish and very few bottom animals and other organisms in Castle Creek and in the upper part of Golden Creek. Observations in Black Creek showed a normal fauna with a variety of bottom animals and a dense population of trout. Downstream the town of Zlaté Hory, there were a quite a few pollution resistant organisms present, and local people had observed some fish in 1993.
- Tests at NIVA with water from this lower part of Golden Creek showed no acute toxicity to fish, but there was an inhibition of growth of algae.
- Observations of *Thiobacillus ferrooxidans* show that there are quite high activities in water coming from the tailings pond, indicating an oxidation of sulphide minerals.
- How to deal with the water pollution from the Zlaté Hory area will depend upon how the mining area and the surroundings are administered. If the liming of mine water is maintained, as much polluted water from the area as possible should be treated here. Also seepage from the waste rock dump at Mir might perhaps be transferred to the treatment plant.
- If the present liming is reduced or stopped, the concentrations of heavy metals, especially copper and zinc would rise to a very high level in Golden Creek. In that case other measures would be necessary. Theoretically two possibilities may be considered. Either the mine waste should be removed and secured in a safe place, or it should be covered by some material which can reduce the contact with oxygen to virtually zero. Partial or complete flooding of the mine may reduce the heavy metal content in the mine water.

• Before any such changes are made. There should be a thorough study, quantify all sources of pollution and discussing all possible solutions economically and in relation to the possible reduction in total pollution from the area.

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11. Appendix

Data for calculation of ion-balance and theoretical electrolytic conductance in water samples

Table 11 Atomic, molecular and equivalent weight of some important elements

Crombal	Ionio	Atomio	Molo	Chargo	Equivalent
Symbol of	Ionic form	Atomic weight	Mole- Charge cular		weight
element	101111	weight	weight		weight
Ba	Ba ⁺	137.34	137.34 1		137.34
Be	Be ⁺⁺	9	9 2		4.5
C		12.01			
	HCO ³⁻	12.01	61.01	-1	-61.01
	CO ³⁻		02.02	_	02.02
Ca	Ca ⁺⁺	40.08	40.08	2	20.04
Cd	Cd ⁺⁺	112.4	112.4	2	56.2
Cl	CI ⁻	35.45	35.45	-1	-35.45
Cu	Cu ⁺⁺	63.55	63.55	2	31.775
Н	H ⁺	1.008			
	OH.		17	-1	-17
	H_2O				
Fe	Fe ⁺⁺⁺	55.85	55.85	3	18.62
	Fe ⁺⁺	55.85	55.85	2	27.925
Hg	Hg ⁺	200.59	200.59	1	200.59
	Hg ⁺⁺	200.59	200.59	2	100.3
K	K ⁺	39.1	39.1	1	39.1
Mg	Mg ⁺⁺	24.31	24.31	2	12.16
Mn	Mn ⁺⁺	54.9°	54.9	2	27.45
N	N	14.01			
	NO ²⁻		46.01	-1	-46.01
	NO ³⁻		62.01	-1	-62.01
	NH ⁴⁺		18.01	1	18.01
Na	Na ⁺	23	23	1	23
Ni	Ni ⁺⁺	58.71	58.71	2	29.36
0	O_2^+	16			
	OH.		17	-1	-17.0
P	P	31			
	PO ₄		95	-3	-31.67
Pb	Pb ⁺⁺	207.2	207.2	2	103.6
S	S	32.1	32.1	-2	-16.05
	SO ₄ -		96.1	-2	-48.05
Si		28.09			
Sn	Sn ⁺⁺	118.69	118.69	2	59.35
Ti	Ti ⁺⁺	47.9	47.9	2	23.95
Zn	Zn ⁺⁺	65.38	65.38	2	32.69

Table 12 Equivalence conductance of some iportant ions.

Ion (Symbol)	Equivalent conduc-	Ion (Symbol)	Equivalent conduc-
(Byllioor)	tance	(2) 222001)	tance
H+	350	OH-	198
Na+	50	Cl-	76
K+	74	NO3-	71
NH4+	74	HCO3-	45
1/2Ca2+	60	1/2CO32-	69
1/2Mg2+	53	1/2SO42-	80
1/2Fe2+	54	SiO(OH)3-	68
1/3Fe3+	52		

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