

Enhanced Arsenic Contents in Spring Water within the Engadine Valley (South-eastern Switzerland; Canton of Graubünden)



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Abstract

Near the city of St. Moritz (Figure 1, Canton of Graubunden, Switzerland) were measured enhanced arsenic concentrations in the spring water which is used for drinking water. The investigated area is mainly formed of silicate rocks, which regionally contain arsenic-bearing minerals such as pyrite and haematite. The soil percolation water is contaminated with arsenic up to 120 micrograms per litre. These observed concentrations are largely above the internationally recommended limiting value of 10µg/l. The sources of arsenic are supposed to be related to the occurrence of pyrite iron ore minerals and arsenic sulphur-minerals, such as arseno-pyrite (FeAsS) and CoAsS, within the crystalline rocks



Figure 1: Map of Switzerland, St. Moritz (red mark).

Keywords: Arsenic; Groundwater; Crystalline rocks; Ore deposits; Water rock interaction

Introduction

Enhanced arsenic contents were observed (at the Chemical laboratory of the Canton Graubunden in Chur) in the water of some mountainous springs of the Upper Engadine Valley in the vicinity the alpine resort of St. Moritz. In the investigated springs situated within the zone of crystalline rocks belonging mainly to the Bernina crystalline unit concentrations of up to 120 micrograms per litre were measured. In this area the outcropping crystalline units are overlapped by mesozoic sediments, mostly sandstone, dolomite, limestone and nair-porphyroide. The Building Authorities of St.

Moritz asked us to find the source of these arsenic contents. The water of the affected springs is no longer used as drinking water and they have cut it off from the main water supply.

Geology

Geographically speaking, St. Moritz is situated in the south-eastern Alps of Switzerland in the canton of Graubünden. St. Moritz is a well-known winter sports area. The mountains in the northwest are called Piz Nair (3056 m) and Piz Nair Pitschen (2876

m). The observed area is a part of the Lower Austroalpine nappes, which overlay the Penninic nappes. They are affected by two large fault-lines: the Tonale fault to the south, which marks the boundary between the main body of the Alps and the Southern Alps, and the SW-NE trending Engadine fault, which cuts through the Penninic, Lower and Upper Austroalpine nappes (Figures 2 & 3).

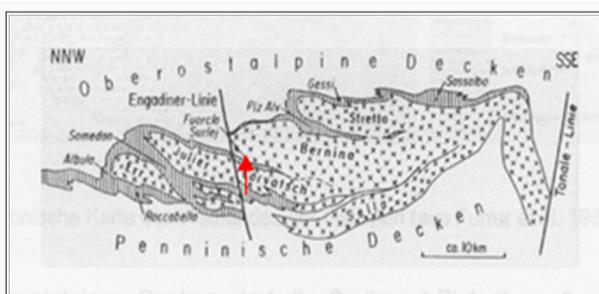


Figure 2: Cross section of the Alpine Area crossing the Engadine Valley indicating the main tectonic units and the Engadine Fault (Engadiner Linie).

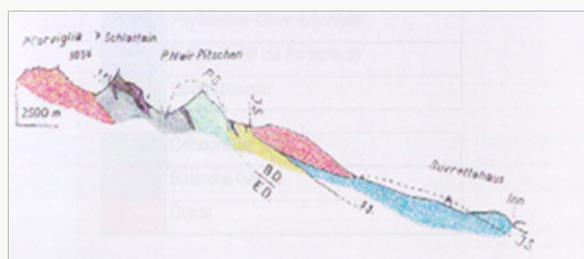


Figure 3: Schematic cross section of the investigated area stretching from St. Moritz to Piz Nair Pitschen.

Table 1: Main lithological units of the investigated area.

Jura		Radiolarite
		Aptychus limestone
Trias		Dolomite
		Gypsum
		Arkosic sandstone
Paleozoicum		Nairporphyroide
Basement Rocks		Quartzphyllite
		Gneiss
		Granite
		Basic dykes

The Lower Austroalpine nappes build the high mountains of the Bernina group, which form the southern part of the Engadine. Several sheets of basement rocks, especially Variscan granitoids, can be distinguished: from bottom to top (Figure 3), Sella, Corvatsch, Bernina and Stretta. A lot of mesozoic sediments are found in this area. North of the Engadine Line, there are again two Lower Austroalpine basement nappes: Err nappe below and Julier nappe above. The stratigraphic succession was established by HP Cornelius [1] and is updated by the first author. Table 1 shows the main lithologies.

Hydrogeology

In the region of the Upper Engadine no thermal water has been observed. But in some areas in the valley itself, mineral springs with high CO_2 contents exist, e.g. the famous St. Moritz spa spring. The springs mentioned above are situated on the north-eastern hillside below Piz Nair Pitschen (Figure 3) in an altitude range of about 2000 to 2200 m (about 500 to 900 m above the level of St. Moritz-lake. The different spring sites are all located within loose deposits of a local moraine. But above the spring sites, outcrops of granite rocks containing mafic dykes are observed.

Materials and Methods

Within the present study, a combined approach of hydro geological mapping with hydro chemical and isotope analyses, as well as mineral studies, was applied. Analyses of general chemistry were performed with ion chromatography (ions and cations), whereas the arsenic speciation was achieved by ICP-MS technique. Water was analysed for ions, temperature, acidity, alkalinity, pH, oxygen-content, isotopes and arsenic-concentration. The measurements of the water temperature, pH and electrical conductivity as also the analyses of oxygen concentration, acidity and alkalinity were made directly in the field, whereas the arsenic concentration and the ionic- state were measured at the EAWAG (Chemistry of Water Resources Section). In the following sections the methods and results are presented:

Chemistry

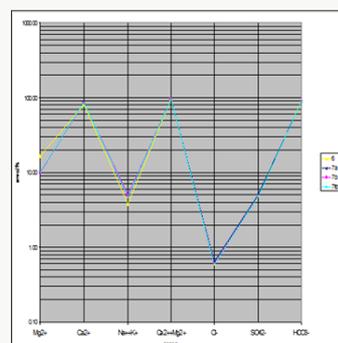


Figure 4: Schoeller - diagram for for springs 6, 7a, 7b and 7tot (average values).

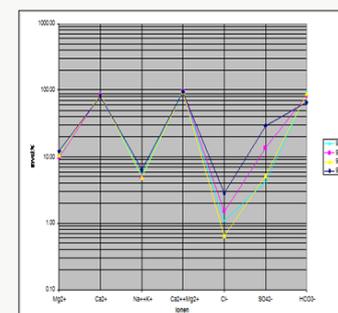


Figure 5: Schoeller - diagram for springs 9a, 9b, 9c and 9tot (average values).

The main ions are illustrated in the Schöller-diagrams in Figures 4 & 5. The axes are: horizontal axis represents Mg^{2+} , Ca^{2+} , $\{Na^{+} + K^{+}\}$, $\{Mg^{2+} + Ca^{2+}\}$, Cl^{-} , SO_4 , and HCO_3 and the vertical axis represents the concentration of the represented ions in mval%.

Physical Parameters?

Most of the physical parameters were measured in the field, like temperature, oxygen-content, acidity, alkalinity and pH. The results are illustrated in Table 2 & 3. Low Conductivity indicates water circulating through crystalline rocks. Evidence of oxygen concentrations near 100%, thereby indicate water saturated with oxygen, means that the water of this spring hasn't been circulating for a long time through the rocks. Arsenic-concentrations were measured in the water samples, in the different rock types and in the powdered rock samples. The arsenic-concentration in drinking-water was measured twice, once in 2000 and again in 2001. The main spring collector has several influxes, which were analysed separately and are presented below.

Table 2: Physical parameters.

Spring-Number	Conductivity	Temperature	Alkalinity
	[μ S/cm]	[°C]	[mmol/l]
6	127	4.4	1.5
7a	119	3.5	1.4
7b	118	3.8	1.5
8	128	3.9	n.a
9a	118	3.8	1.7
9b	118	4	1.1
9c	119	5.6	1.4

Table 3: Physical parameters.

Spring-Number	Acidity	O2-Content	Flow	pH
	[mmol/l]	[mg/l]	[l/min]	
6	0.3	7.7	187	7.63
7a	0.3	7.8	n.a.	7.70
7b	0.4	9.6	n.a.	7.61
8	n.a.	n.a.	830	n.a.
9a	0.2	8.5	n.a.	7.46
9b	0.3	9.0	n.a.	7.43
9c	0.3	9.3	n.a.	7.27

Arsenic-concentrations varied between 100 and 120 μ g/l and were above the internationally recommended limiting value of 10 μ g/l. The powdered rock sample has been analysed at the University of Lausanne and the results are represented in the Tables 4 & 5. The average concentration of arsenic in igneous and sedimentary rocks is 2mg/kg, and in most rocks it ranges from 0.5 to 2.5mg/kg. Arsenic is concentrated in some reducing sediments,

in iron deposits and in crystalline rocks. Since the water which was found to have high arsenic-concentrations is circulating through crystalline rocks, the arsenic seemed to be coming from these rocks. In order to determine from which minerals the arsenic is coming, rocks were analysed with a microscope. Lots of ore-minerals were observed and three different ores were distinguished: pyrite, haematite and copper- and magnesium-gravel.

Table 4: Arsenic content in drinking water.

Spring-Number	μ g As/l (2000)	μ g As/l (2001)
6	108	105
7a	108	107
7b	119	117
8	127	111
9a	110	110
9b	99	113
9c	100	110

Table 5: Arsenic content in rocks.

Type of Rock	Arsenic Content [ppm]
Gneiss	35
Quartzphyllit	42
Quartzphyllit	55
Gneiss	11
Lamprophyre	54
Nairporphyroid	65
Gneiss	67
Granite	4

Arsenic

Arsenic is a metalloid element that is ubiquitous in the environment, usually being present in small amounts in all rock, soil, dust, water, air and biological tissues. Inorganic arsenic species in contaminated industrial sites exist in the arsenate (oxidation form=V), arsenite (oxidation form=III), arsenic sulfide (HAsS₂), elemental arsenic (As₀) and arsine (oxidation form=-III) forms. Although in acute poisoning the trivalent form of inorganic arsenic is considered to be more toxic than the pentavalent form, in cases of chronic exposure to lower doses such as consumption of contaminated drinking-water, reduction of As₅₊ makes the distinction less important. The minimum lethal dose in humans has been estimated to be 2mg/kg weight [2].

Arsenic occurs in the lithosphere, atmosphere, biosphere and hydrosphere. Human exposure to arsenic occurs from natural, industrial and agricultural sources. Sources of arsenic into drinking waters and into soils, dust, and the food chain may be derived from:

- a) Naturally occurring arsenic-rich minerals and rocks, such as pyrite,
- b) From sulfide mineralisation and waste materials resulting from mining and smelting activities, and
- c) From the burning of arsenic-rich coal [3].

Because in the city of St. Moritz there were neither smelting activities, nor burning of coal, nor waste materials, the arsenic has to be from different minerals and rocks. Thornton [4] has recently reviewed the geochemistry of arsenic. Arsenic occurs in different species and in more than 200 minerals. The most common minerals with an arsenic-content of up to 4% are arsenopyrite and pyrite.

As was shown in the section before, arsenic-rich minerals, such as pyrite and haematite, which can be a source of arsenic in drinking water, are likely to come from the rock components of the underlying geological strata. Numerous reports indicate that chronic exposure to arsenic in drinking-water can be harmful to health. These include hyper pigmentation, keratosis (horny growth), and cancer of the skin, the liver, the lungs and any other internal organs [5].

Limiting Value

The internationally recommended limiting value of arsenic in drinking-water amounts to 10 µg/l in the US and the EU [6]. Unfortunately the limit in Switzerland is 50 µg/l. That means that in Switzerland and therefore also in the city of St. Moritz concentrations between 10 and 50 µg/l were allowed, whereas in all other countries of Europe and the US, this water would not be allowed be drunk.

Results and Discussion

From the first results of the ongoing study (2000-2001) the sources of arsenic in the Upper Engadine Valley are supposed, (as observed by the high arsenic contents of the analysed spring waters), to be related to the occurrence of pyrite iron ore minerals within the crystalline rocks. Within the frequently observed two-mica para gneisses of these area arsenic concentrations of up to more than 600ppb were observed. The observed rocks contain also combined arsenic sulphur-minerals, such as arseno-pyrite (FeAsS) and CoAsS [7-15].

As a result of the recently reduced legal limit of arsenic concentration (in the EU and also in Switzerland), all affected springs were detached from the domestic water supply network in order to avoid any overdose of the concerned commercial product. Although such first prevention has been made, the observed enhanced levels of arsenic presents the Upper Engadine Valley with a severe problem which is still under discussion [15-22].

Acknowledgement

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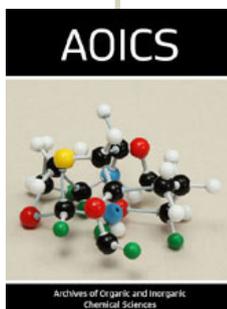
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