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Occurrence of arsenic in drinking water of the canton of Valais

Part I: Overview of arsenic concentration and geographic distribution

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Introduction

Arsenic is a toxic element which is known and used since antiquity. For a long time arsenic compounds were used in agriculture as herbicide and pest control but these applications are forbidden since at least 20 years in many countries because of toxicity and of environmental contamination (1). The last major wood preservative used in the USA, the chromated copper arsenate, was banned in 2004. Medicinal and veterinary drugs based on arsenic are nowadays uncommon. Today, the principal uses of arsenic are metallic arsenic in non-ferrous alloys and semiconductor materials and arsenic trioxide as decolourizing agent in glass manufacturing.

All together, the world consumption of arsenic is rather steady and should even tend to decline. The environmental contamination by anthropogenic arsenic is reduced and controlled by the environmental legislation. Health hazards may also originate from naturally occurring arsenic. Inorganic arsenic can be present in drinking water. Minerals, often concentrated as ores dissolve in contact with water and arsenic concentration can increase up to a level of toxicological concern (2). Very dramatic cases of natural arsenic occurrences in water were reported from India and Bangladesh (3, 4) but the arsenic problem is not confined to developing countries (5, 6, 7). With an average of ca. 2 ppm, this element is not particularly abundant in the earth's crust but arsenic minerals are widely distributed in the world (8). High natural concentrations of arsenic can potentially occur in any country of the world. In Switzerland, the geology of arsenic is well documented, and the

Alpine region is known to be the most problematic, especially the cantons of Ticino, Valais and Grisons (9).

Based on a risk evaluation set out by the Joint FAO/WHO Expert Committee on Food Additives (JECFA, 10), the World Health Organisation (WHO) decided in 1993 to reduce the provisional guideline value for arsenic in water from 50 µg/l to 10 µg/l (11, 12). The European Commission (EC) followed this recommendation in 1998 and implemented this value as a limit value in its Directive on the quality of water intended for human consumption (13). The Swiss Federal Office of Public Health (SFOPH) did not follow the WHO risk assessment, considering that the dietary intake of inorganic arsenic from solid food was not significant (14). Arsenic exposure in Switzerland was attributed mainly to drinking water. The SFOPH considered that the limit of 50 µg/l for As in water (15) was still adequate to protect the Swiss consumers.

Toxicology and epidemiology data on arsenic are revised periodically and the U.S. National Research Council (NRC) confirmed in 2001 an increased health risk with an arsenic level which is below 50 µg/L water (16). Such new evidence put some pressure on the SFOPH to reassess the situation. The scientific data on the arsenic level in natural water are, with the exception of Ticino, regretfully unsatisfactory and do not permit an accurate risk assessment. To address the lack of data, a study was designed to survey systematically the drinking water in every commune of the canton of Valais. Besides arsenic, 17 other elements (Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Se, Sr, Th, Tl, U, V and Zn) were monitored but only data on arsenic are discussed in this article. Sector field ICP-MS was used to perform the measurements because it allows precise and accurate determination of elements at ultra trace levels in water samples (17).

In a second article the arsenic data will be related to the incidence registry of the canton of Valais (18)

Materials and Method

Reagents

High purity (<0.1 ng/ml arsenic) nitric acid 65 % Suprapur® was obtained from Merck (Darmstadt, Germany). All blank, standard, sample and reference solutions were prepared in 0.2 % nitric acid. Water for preparation and dilution of solutions was purified and deionized using a cartridge system Easy Pure LF (Barnstead, Dubuque, IA, USA) to obtain specific conductivity of 18 MΩ/cm. All calibration standard solutions were prepared by diluting the ICP multi-element standard VI Certipur (Merck, traceable to NIST), which has a certified arsenic concentration of 104±5 mg/l. The standard reference materials NIST1640, Natural Water (National Institute of Technology, USA), and NWRI-TMRAIN-95, simulated water (National Water Research Institute, Canada), were used as quality control samples.

Water samples

A total of 1297 drinking water samples were collected from across the canton of Valais. The sampling took place from June to November 2003. The samples were taken mainly at different locations of public water supplies, which normally depend on spring water. Bigger cities or communes provided samples from different sections of their water supply network. Other sampling locations were water reservoirs (n=46), near or at springs (n=251) and wells (n=219). From 1 to 53 samples were obtained from each of the 160 communes of the canton. A few samples (n=37) originated from private sources such as wells or springs.

Local food inspectors or official representatives of the communes collected the water samples. 50 ml polypropylene-tubes were filled, subsequently acidified with 0.5 ml 65 % nitric acid at the Cantonal Laboratory of Valais in Sion and sent to the laboratory in Bern. The samples were stored at cool temperature (4 °C) in darkness until measurement. No specific sample preparation procedures were required for the measurement except for a simple dilution and addition of the internal standard element.

Preparation of standards, references and samples

The analysis was carried out using external calibration for quantification. Calibration solutions were prepared at arsenic levels of 1.0, 2.5, 5.0, and 10 µg/l in 0.2 % nitric acid. A 0.2 % nitric acid was used as blank. The standard reference materials NIST1640 and NWRI-TMRAIN-95 were measured after 10- and 2-fold dilution, respectively, with 0.2 % nitric acid. The water samples were measured after 3-fold dilution with 0.2 % nitric acid. Rhodium was added (1 µg/l) to all solutions, including the calibration blank, to correct for time-dependant parameters such as instrumental drift or changes in matrix (related to predominant elements such as calcium). Blank measurements were repeated after each series of five samples to monitor contamination and memory effects. If a concentration was well above the highest calibration point the sample was rerun.

Instrumentation

The sector field instrument used was an Element 2 (Finigan-MAT, Bremen, Germany) equipped with a Cetac ASX-100 autosampler (Omaha, NE, USA). It was operated in low (m/Δm=300) and high resolution mode (m/Δm=10000). These resolution settings were approximate nominal values. Ion intensity optimization and mass calibration were carried out daily using a tuning solution containing elements covering the whole mass range at a concentration of 1 ng/ml. The optimization was usually restricted to adjustments of sample and auxiliary gas flow rates to obtain a stable response at a maximum signal. Details of instrument operating conditions are summarized in table 1.

For the control measurements an atomic absorption spectrometer 4100ZL (Perkin-Elmer, Germany) was used. Details are described elsewhere (19).

Table 1
Instrumental operating conditions and instrumental parameters

Rf-power	1200 W
Argon flow rates:	
– plasma	15.5 l/min
– auxiliary	0.8–0.9 ml/min
– nebulizer	0.9–1.0 ml/min
Sample uptake rate	0.3 ml/min
Nebulizer	Sea Spray (Glass Expansion)
Spray chamber	Mini cyclonic with central tube (Glass Expansion)
Acquisition mode	E-scan
Number of replicate measurements	3
Number of scans per replicate	3
Acquisition time per nuclide	1.35 s
Resolution settings	300, 4000, 10000
Take-up time	2 min
Wash time	5 min

Results and Discussion

Quality control

The spectral interference of arsenic signal

Interferences caused by the plasma are, to a large extent, dependent on the isotopic composition of the sample matrix and the plasma gas, the latter has the most abundant isotope ^{40}Ar. As a result, spectral overlap of the molecular ion $^{40}Ar^{35}Cl^+$ on $^{75}As^+$ is observed. While in general an alternative isotope can be chosen, arsenic is mono-isotopic. In waters with a high chloride and a low arsenic content, the intensity of the ArCl-signal may be a substantial fraction of the peak at $m/z=75$. For the interference free determination of arsenic, a high resolution of $m/\Delta m=10000$ is necessary to separate the $^{75}As^+$ signal from $^{40}Ar^{35}Cl^+$; however, the loss in sensitivity hampers the determination of low arsenic concentrations. The potential bias between both resolution settings, i.e. the interference effect itself, was estimated in the ranges from 0–0.5 and 2–15 µg/l, the latter includes the proposed guideline value of 10 µg/l, using maximum-likelihood fitting of the functional relationship (20). There is no statistically significant deviation between the low and high resolution mode because the individual 95 % confidence intervals (CI) of the intercept and the slope include the ideal values 0 and 1, respectively (figure 1).

Accuracy and detection limit of the method

The results presented in this paper are based on measurements of total arsenic in the drinking water samples; no information on valence states or compounds was obtained. To ensure confidence and accuracy of the data, quality assurance measurements for water concentration data on the target element arsenic were included. Analytical results for the reference materials that were measured at the start and the

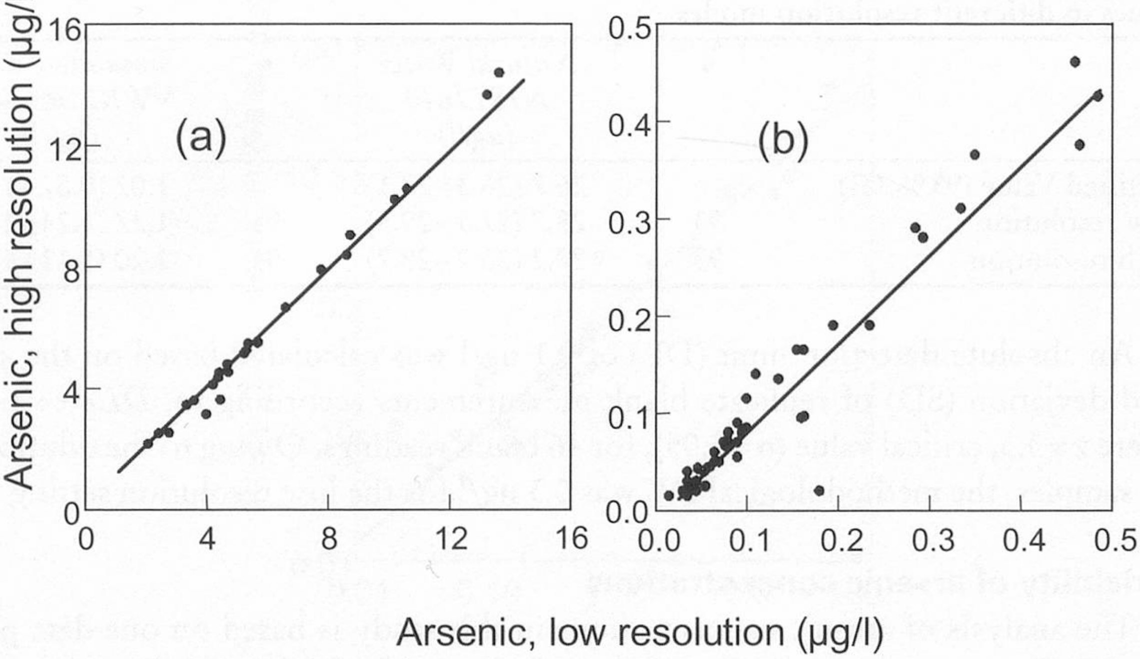

Figure 1 **Relation between two resolution modes. Arsenic was measured repeatedly (n=3) in selected water samples that cover the ranges 2–15 µg/l (a) and 0–0.5 µg/l (b).** The solid line represents the maximum-likelihood fitting of the functional relationship with the 95 % CI for intercept and slope, respectively:
(a) As_{high}=0.02 µg/l (–0.054–0.097 µg/l)+0.989 (0.974–1.004) As_{low},
(b) As_{high}=–0.01 µg/l (–0.024–0.006 µg/l)+0.899 (0.735–1.062) As_{low}

end of each sample series to monitor the performance of the method are presented in table 2. Erratic values were not included and the corresponding series were rerun. The differences between measured and certified values are acceptable. The 95 % CI of the certified value is comparatively narrow for the NIST1640 sample. Conversely, the estimated CI takes into account the fact that the analyses of reference water samples were carried out on different days over a period of several months and therefore represent a larger uncertainty. There are some limitations to the usefulness of the reference materials compared to the water samples from Valais: the matrix is similar but the concentrations differ considerably.

In addition, selected samples (n=13) that showed very high values in the range 20–100 µg/l were measured by graphite furnace atomic absorption spectrometry (GF-AAS). Maximum likelihood estimation was also used to compare the methods. There is no statistically significant deviation between GF-AAS and ICP-MS in this concentration range: [GF-AAS]=1.17+0.946 [ICP-MS]. The 95 % CI for intercept and slope ranged from –4.56 to 6.90 µg/l and 0.845 to 1.039, respectively.

Table 2

Comparison of reported arsenic values of certified reference materials with measured values in different resolution modes

	n	*Natural Water NIST1640 (µg/l)*	*n*	*Simulated Water NWRI tmrain-95 (µg/l)*
Certified Value (95 % CI)		26.7 (26.3–27.1)		1.07 (0.82–1.32)
Low resolution	93	28.7 (27.9–29.5)	94	1.27 (1.24–1.31)
High resolution	93	27.2 (25.7–28.7)	94	1.20 (1.13–1.28)

An absolute detection limit (DL) of 0.1 ng/l was calculated based on the standard deviation (SD) of replicate blank measurements according to: $DL \approx \bar{x} + z \cdot SD$, where $z = 3.3$, critical value ($\alpha = 0.05$), for 46 blank readings. Owing to the dilution of the samples, the methodological DL was 0.3 ng/l for the low resolution setting.

Variability of arsenic concentrations

The analysis of arsenic concentrations in this study is based on one data point per sampling source, which may not be representative if the variability of concentration over time is significant. Consequently, the variation of arsenic concentrations is an important consideration because toxicological effects may result from chronic exposure rather than short-term exposure.

Variation in arsenic concentration is related to natural fluctuations in water supply systems and laboratory analytical variability. Natural fluctuations in arsenic levels of well water for example, can be associated with rainfall or the season (21). Although the data of this study were not collected with the specific intent of revealing temporal variation, it was possible to evaluate a series of samples (n=40) that originate exactly from the same sampling source as in previous studies (22, 23). In the former studies arsenic was measured by AAS and ICP-MS as well. The data were compared as shown in figure 2.

Only four samples ranging from 5–12 µg/l presented relevant differences in arsenic concentration. These data suggest altogether that the magnitude of difference in arsenic concentrations between the two studies is very small and that there was little variation over the four-year period. The values from the two sets of samples were highly correlated (r=0.97) and the position of the linear regression line does not reveal any methodological bias because the slope is not statistically different from unity.

Overview and distribution of the arsenic concentrations

Descriptive statistics were computed for each commune and summarized in table 3. Arsenic values as obtained by the low resolution measurements were used throughout the study. The concentrations of arsenic found in drinking water from the Valais were typically <10 µg/l and within the ranges reported nationwide (9, 24). Arsenic was detected in virtually every sample, however, in more than half of the

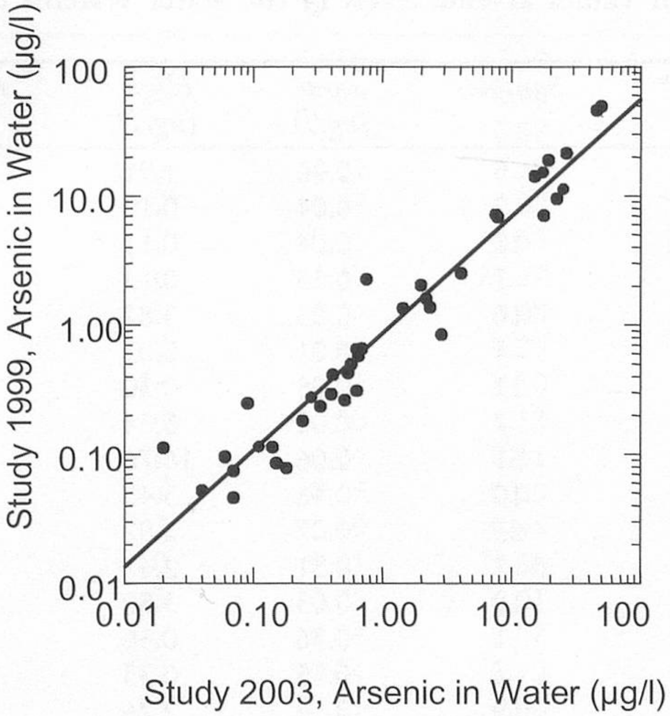

Figure 2 **Relation between arsenic concentrations measured in 1999 and 2003.** The linear regression line was calculated based on logarithmically transformed values. A slope of 1.04 (0.95–1.12) and an intercept of 0.07 (–0.01–0.14) were obtained

samples at very low concentrations (<1 µg/l) that are less relevant. The maximum concentration found was 101 µg/l. The distribution of the concentrations of arsenic in drinking water is provided in a percentile diagram (figure 3), in order of the lowest to the highest concentration. The distribution is right-skewed and the values range over approximately four orders of magnitude. The shape of the curve shows the distribution of concentrations, with steeper slopes indicating a narrower spread of concentrations. The S-shaped plot indicates the approximation of a lognormal distribution. It is interesting to note that arsenic concentration in springs and ground water from the canton of Grisons follows approximately the same kind of distribution (25). Evidently, the 50th percentile, the median, corresponds to the relatively low arsenic concentration of 0.52 µg/l. About half of the samples had concentrations below 0.5 µg/l, which are typical background levels (26). 93 % of all water samples analyzed fall below the WHO guideline value of 10 µg/l while 6.4 % have arsenic concentrations between 10 and 50 µg/l. Only 0.5 % (7 samples) exceed the current legal limit in Switzerland (Table 3).

Table 3

Low, high and mean values arsenic levels in the water systems of 160 communes of Valais

*Commune/map code**	*Samples*	*Low (µg/l)*	*High (µg/l)*	*Median (µg/l)*	*Mean (µg/l)*
Agarn	5	0.26	1.91	1.51	1.35
Albinen	2	0.04	0.19	0.12	0.12
Arbaz	10	0.04	0.11	0.07	0.08
Ardon	1	0.13	0.13	0.13	0.13
Ausserberg	10	0.03	3.82	0.16	0.82
Ausserbinn	4	0.01	0.03	0.02	0.02
Ayent	17	0.05	0.30	0.17	0.17
Ayer	7	0.03	5.34	2.86	3.04
Bagnes/16	51	0.06	16.76	0.43	2.40
Baltschieder	10	0.48	3.45	1.22	1.61
Bellwald	25	0.07	2.92	0.30	0.64
Betten	7	0.31	2.47	0.82	1.12
Binn	10	0.03	3.50	0.11	0.68
Birgisch	1	0.36	0.36	0.36	0.36
Bister	1	0.35	0.35	0.35	0.35
Bitsch	9	0.14	2.26	1.40	1.25
Blatten	6	0.07	2.18	0.79	1.00
Blitzingen	10	0.41	4.09	0.51	0.95
Bourg St. Pierre	3	0.24	4.90	1.98	2.37
Bovernier	2	0.32	0.63	0.48	0.48
Bratsch	4	0.04	0.09	0.06	0.06
Brig-Glis	21	0.06	3.80	0.78	1.35
Bürchen	11	0.88	8.87	1.85	2.99
Chalais	2	0.41	0.63	0.52	0.52
Chamoson	10	0.02	0.11	0.07	0.06
Champéry	4	0.05	0.36	0.08	0.15
Chandolin	3	1.12	1.85	1.69	1.55
Charrat	4	0.44	4.82	1.46	2.05
Chermignon[1]	7	0.04	0.07	0.05	0.05
Chippis	1	1.01	1.01	1.01	1.01
Collombey-Muraz	4	0.06	0.41	0.20	0.22
Collonges/1	3	0.11	18.65	10.69	9.82
Conthey	18	0.03	0.33	0.08	0.10
Dorenaz/2	1	19.31	19.31	19.31	19.31
Eggerberg	2	1.49	1.79	1.64	1.64
Eischoll	1	7.80	7.80	7.80	7.80
Eisten/25	10	1.67	24.06	11.40	11.21
Embd/22	10	0.85	10.26	4.69	4.92
Ergisch	2	2.01	2.10	2.06	2.06
Ernen/30	10	0.04	25.17	0.56	6.09
Erschmatt	2	0.23	0.24	0.24	0.24
Evionnaz	2	0.31	0.75	0.53	0.53
Evolène	20	0.10	3.71	0.55	0.66
Ferden	3	0.93	5.32	3.95	3.40
Fiesch	8	0.10	2.71	0.45	0.92
Fieschertal	8	0.03	2.31	0.23	0.46
Filet	7	0.02	1.55	0.49	0.60

*Commune/map code**	*Samples*	*Low (µg/l)*	*High (µg/l)*	*Median (µg/l)*	*Mean (µg/l)*
Finhaut/7	4	22.56	27.30	24.72	24.82
Fully	19	0.09	8.70	0.39	1.19
Gampel	1	6.07	6.07	6.07	6.07
Geschinen	3	0.11	0.39	0.17	0.22
Gluringen[2]	2	1.57	2.08	1.83	1.83
Goppisberg[3]	7	0.06	1.53	1.08	0.82
Grächen/23	16	1.61	20.27	5.38	7.93
Grafschaft[2]	2	1.57	2.08	1.83	1.83
Greich[3]	2	1.42	2.25	1.84	1.84
Grengiols	16	0.01	1.30	0.14	0.31
Grimentz	4	0.30	1.13	0.53	0.62
Grimisuat[4]	10	0.04	0.11	0.07	0.08
Grône	1	0.65	0.65	0.65	0.65
Guttet-Feschel	2	0.19	0.45	0.32	0.32
Hérémence/15[5]	10	0.21	29.56	5.11	6.81
Hohtenn	15	0.75	6.01	3.06	2.94
Icogne	7	0.04	0.07	0.05	0.05
Inden	4	0.04	0.10	0.05	0.06
Isérables	13	0.21	4.60	2.41	2.55
Kippel	6	1.08	6.95	3.76	3.84
Lalden	3	0.51	1.01	0.69	0.74
Lax	12	0.03	1.46	0.25	0.46
Lens	8	0.03	0.09	0.05	0.06
Les Agettes/13	10	1.18	14.39	6.89	7.48
Leuk/19	34	0.04	18.47	1.29	1.72
Leukerbad	12	0.03	0.12	0.05	0.06
Leytron	11	0.05	2.67	0.23	0.53
Liddes	3	0.56	4.06	0.85	1.82
Martigny/4	8	0.06	10.62	7.82	6.58
Martigny-Combe/6	4	0.69	17.78	8.26	8.75
Martisberg	5	0.05	0.33	0.07	0.14
Mase	1	0.59	0.59	0.59	0.59
Massongex	2	0.42	0.80	0.61	0.61
Mex	1	0.32	0.32	0.32	0.32
Miège	2	0.05	0.07	0.06	0.06
Mollens	10	0.04	0.20	0.06	0.08
Montana	12	0.01	0.13	0.03	0.04
Monthey	10	0.04	0.68	0.11	0.15
Mörel	6	0.24	2.37	0.30	0.83
Mühlebach/31	2	7.53	10.16	8.85	8.85
Mund	11	0.07	1.69	0.50	0.65
Münster	5	0.59	4.72	3.49	2.97
Naters	22	0.04	1.27	0.17	0.36
Nax	1	1.79	1.79	1.79	1.79
Nendaz	17	0.11	6.08	1.14	1.83
Niedergestel	5	0.79	1.24	1.06	1.03
Niederwald	6	0.15	3.64	0.34	0.89
Oberems	10	1.24	7.87	3.64	3.86
Obergesteln	1	0.38	0.38	0.38	0.38
Oberwald/33	12	0.06	101.42	16.87	29.01

*Commune/map code**	*Samples*	*Low (µg/l)*	*High (µg/l)*	*Median (µg/l)*	*Mean (µg/l)*
Orsières	10	0.02	1.60	0.21	0.38
Port-Valais	4	0.18	0.44	0.21	0.26
Randa/27	7	1.64	10.09	3.39	4.54
Randogne	22	0.01	0.17	0.07	0.08
Raron	2	0.17	0.66	0.42	0.42
Reckingen	6	0.11	2.08	0.25	0.73
Riddes/9	13	0.05	13.69	0.81	1.80
Ried-Brig	6	0.02	0.23	0.08	0.10
Ried-Mörel	3	0.13	0.18	0.14	0.15
Saas Fee	4	0.13	0.92	0.50	0.51
Saas-Almagel	5	0.18	1.60	0.34	0.61
Saas-Balen	9	0.61	5.22	1.30	1.65
Saas-Grund/28	4	0.26	11.21	0.86	3.30
Saillon	2	0.33	1.15	0.74	0.74
Salgesch	1	0.09	0.09	0.09	0.09
Salins	7	0.50	9.52	1.76	2.58
Salvan/5	9	0.63	25.91	14.02	12.33
Savièse	6	0.04	0.14	0.07	0.07
Saxon	8	0.05	0.56	0.18	0.20
Sembrancher	4	0.05	0.62	0.24	0.29
Sierre	5	0.20	0.60	0.31	0.35
Simplon/29	19	0.10	16.33	0.50	1.51
Sion/10	36	0.05	79.47	0.08	6.30
St Gingolph	4	0.09	0.23	0.17	0.17
St Jean	4	0.99	3.25	2.07	2.10
St Léonard	1	0.48	0.48	0.48	0.48
St Luc	1	1.60	1.60	1.60	1.60
St Martin/14[5]	22	0.15	29.56	0.79	2.89
St Maurice	1	0.67	0.67	0.67	0.67
St Nicklaus/26	16	0.90	43.77	12.64	15.38
Stalden	9	0.77	4.80	1.82	2.48
Staldenried/24	19	0.37	17.15	2.58	3.55
Steg/18	4	1.98	13.89	2.39	5.16
Steinhaus	8	2.57	8.26	5.47	5.45
Täsch	2	0.20	0.62	0.41	0.41
Termen	6	0.01	0.52	0.03	0.13
Törbel/21	6	4.91	24.72	6.79	9.54
Trient/8	5	0.26	22.40	0.65	9.12
Troistorrents	14	0.03	0.14	0.05	0.06
Turtmann	15	0.23	1.74	1.03	0.98
Ulrichen/32	6	0.67	20.44	6.87	8.00
Unterbäch/20	5	0.42	22.42	4.38	7.04
Unterems	5	0.78	2.53	1.25	1.41
Val d'Illiez	8	0.01	0.20	0.09	0.09
Varen	6	0.07	0.15	0.08	0.10
Venthône	3	0.07	0.45	0.21	0.24
Vernamiège	1	0.57	0.57	0.57	0.57
Vernayaz/3	2	17.50	25.17	21.34	21.34
Vérossaz	3	0.05	0.17	0.08	0.10
Vétroz	3	0.11	0.57	0.14	0.27

*Commune/map code**	*Samples*	*Low (µg/l)*	*High (µg/l)*	*Median (µg/l)*	*Mean (µg/l)*
Vex/11	53	0.11	98.53	2.32	8.22
Veyras	1	0.28	0.28	0.28	0.28
Veysonnaz/12	11	0.19	12.04	2.23	4.27
Vionnaz	2	0.29	0.33	0.31	0.31
Visp	23	0.07	6.40	1.18	1.31
Visperterminen	33	0.04	3.74	0.51	0.80
Vissoie	1	1.99	1.99	1.99	1.99
Vollèges	14	0.06	0.49	0.25	0.26
Vouvry	3	0.13	0.24	0.21	0.19
Wiler/17	5	1.15	10.39	3.86	4.15
Zeneggen	1	0.21	0.21	0.21	0.21
Zermatt	23	0.03	1.91	0.27	0.46
Zwischbergen	20	0.03	5.73	0.33	0.85

[1] Water supplied from Icogne

[2] Water supplied from two supply systems from Reckingen (2 data points)

[3] One common supply

[4] Water supplied from Arbaz

[5] One common supply

*The map code denotes the communes in which water with arsenic concentration above the guideline value of 10 µg/l is supplied (figure 5)

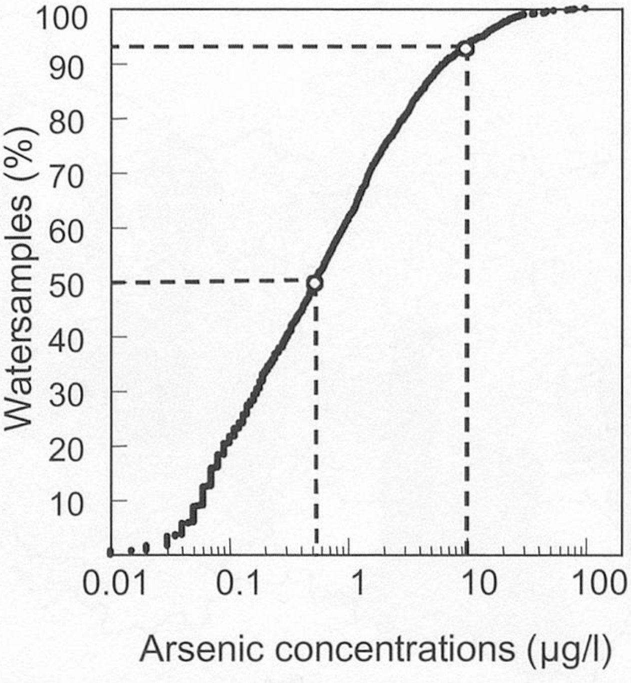

Figure 3 **The distribution of the arsenic concentrations (percentile plot). The values are displayed on a logarithmic scale.** For any given percentage of measured samples plotted on the y-axis, a maximum arsenic concentration can be read off the graph. The dashed lines indicate the median value or the fractions that are either below or above the WHO guideline value of 10 µg/l

Figure 4 shows an overview of the geographic distribution of the arsenic concentrations. The graduated coloration indicates that the occurrence of arsenic in community water supplies is a regional phenomenon, which is similar in other cantons (9). The map does not identify whether a particular water supply network has an arsenic problem, because it is generated on the basis of average values from all water samples collected in a commune. While many networks do not have high arsenic concentrations in their drinking water, there may be "hot spots" with water supplies higher than the average occurrence for a certain area. Generally, the sampling coverage of the canton of Valais indicates little arsenic present in water from the area north of the river Rhone. The most arsenic rich water was found in the Northeastern Region of Oberwald. Other areas where higher arsenic concentrations were found are clustered around the communes of Finhaut or St. Niklaus. Also, a few sources with unexpected high concentration (>50 µg/l) were detected in the communes of Vex and Sion (Les Mayens de Sion).

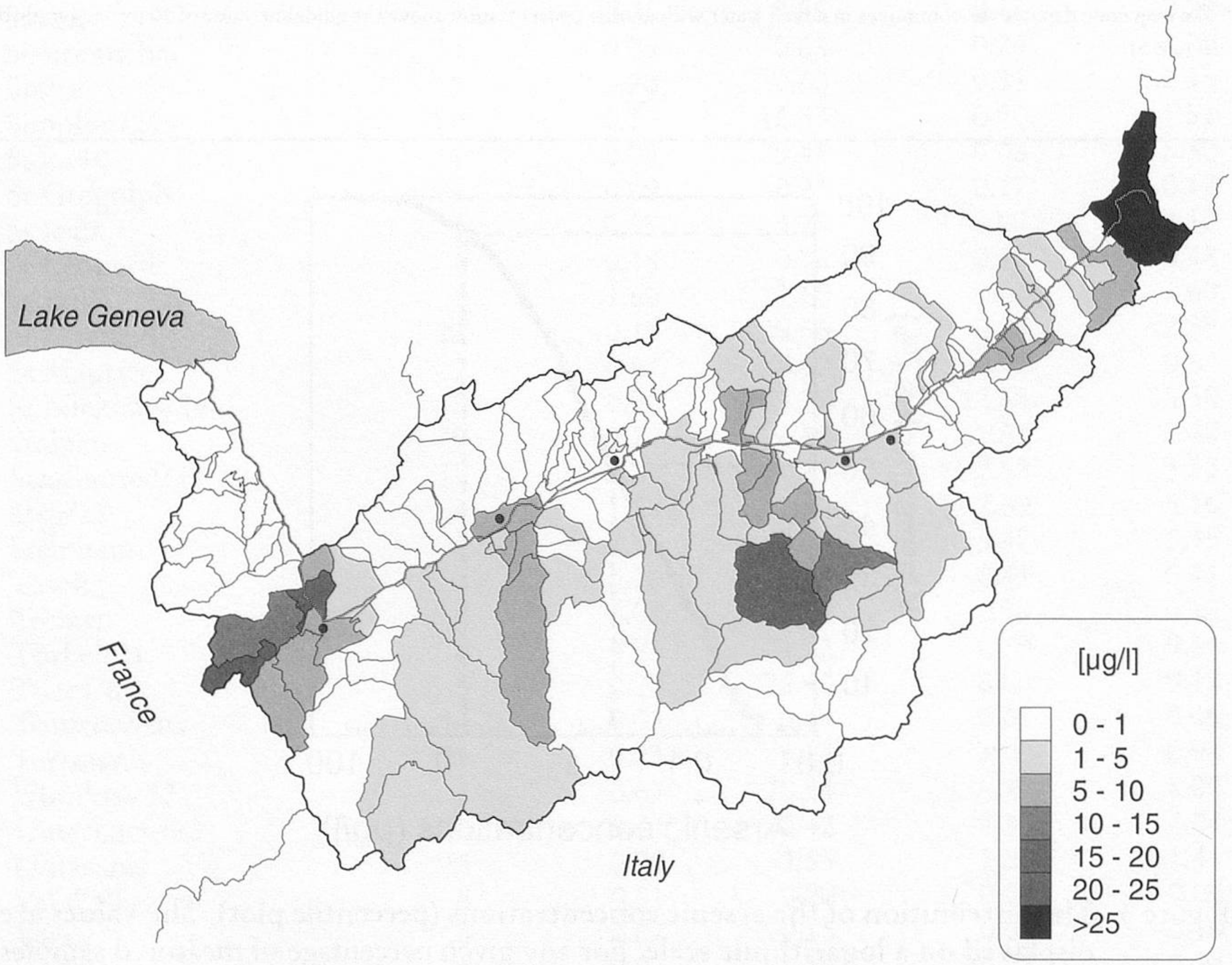

Figure 4 **Average concentration of arsenic in the communes of the canton of Valais.** The river Rhone and the largest cities are depicted to ease orientation (black points, from left: Martigny, Sion, Sierre, Visp, Brig)

The arsenic concentrations in water displayed on the map (Figure 4) agree in a general way with the spatial distribution of arsenic rich sediments, which reflect the composition of the parent rock (24). Furthermore, this map (Figure 4) basically agrees with a previous cantonal-scale survey of arsenic in drinking water (22).

Figure 5 depicts the delineation of the 10 μ/l WHO criterion for arsenic in drinking water. If Switzerland adopts this WHO guideline value, 33 communes should take measures to reduce arsenic levels in their water supply in order to comply with the new legal limit. This can be achieved by introducing new springs in problematic networks or through consolidation (dilution) with other water supplies. If alternative sources are not available, a variety of water treatment techniques can be used to essentially eliminate arsenic, such as filtration with iron oxide filters or ultrafiltration on membranes (27, 28).

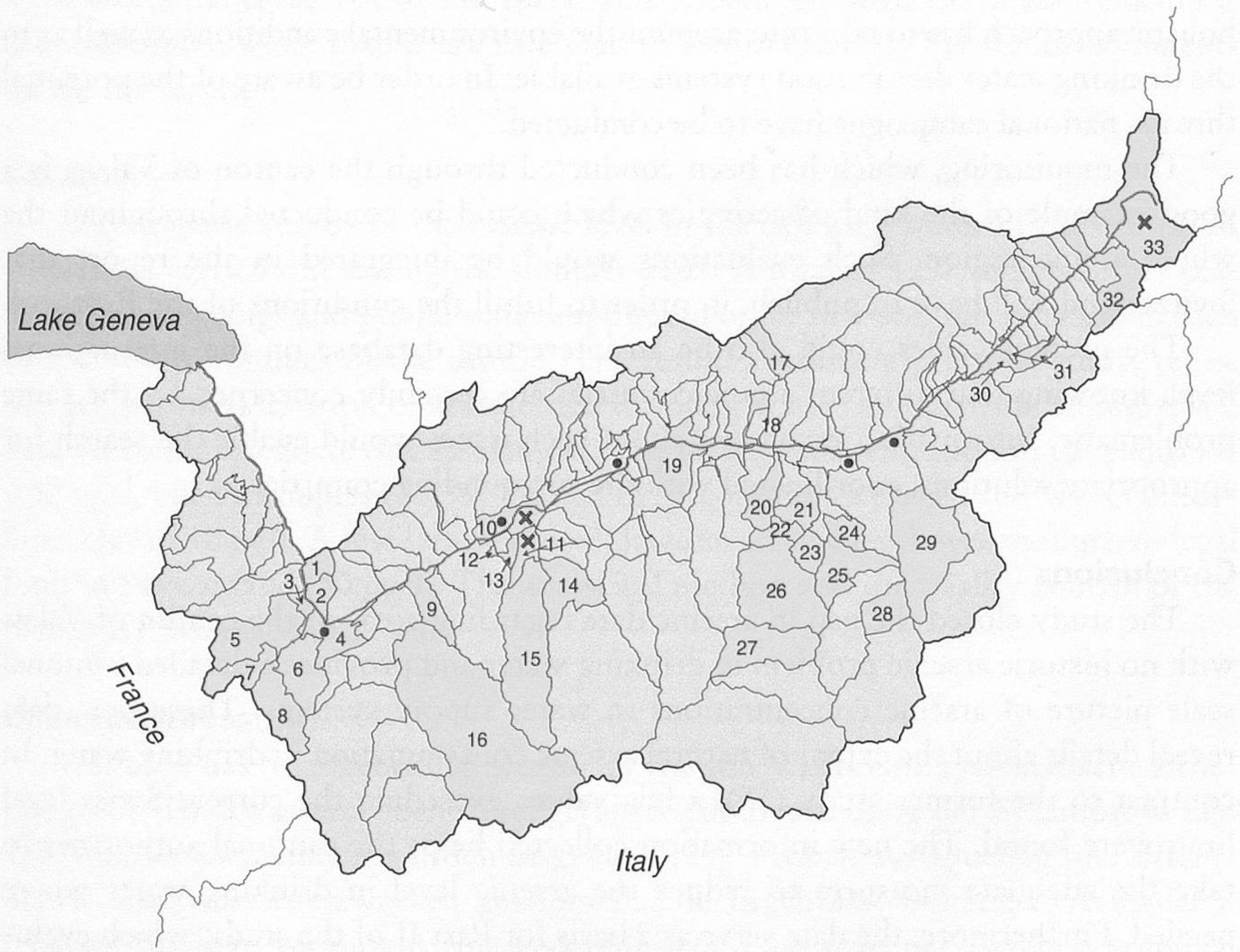

Figure 5 **Communes of the canton of Valais possessing at least one drinking water with an arsenic concentration over 10 μg/l (depicted in yellow).** The red crosses indicate locations of springs with a level which is higher than 50 μg/l. Numbers refer to commune names given in table 3

An arsenic concentration of over 10 µg/l was assessed in 89 samples. It should be noted that many of these samples (n=15) are supplying residences with only a seasonal activity (permanent residence in summer only, e.g. Les Mayens de Sion). These samples were not taken into account to estimate that the problem could potentially affect ca. 14000 persons, roughly 5% of the overall population of the Valais.

Relevance to the WHO Protocol on water and health

This Protocol, signed in 1999 by 52 countries, is an instrument set to get an overview concerning water management throughout Europe. The goal of this management is the prevention and control of water-related diseases. That implies that each country will take appropriate measures in order to ensure a safe drinking water supply.

These measures will be based on a monitoring program where relevant parameters are established for a countrywide evaluation of the drinking water quality. This holistic approach has to take into account the environmental conditions as well as to the drinking water distribution systems available. In order be aware of the potential threats, national campaigns have to be conducted.

The monitoring, which has been conducted through the canton of Valais, is a good example of the kind of activities which could be conducted throughout the whole alpine region. Such evaluations would be integrated in the report that Switzerland will have to publish, in order to fulfill the conditions of the Protocol.

The present values could also be an interesting database on the international level, knowing that different alpine countries are certainly concerned by the same problematic. Information exchanges about such issues would enable the search for appropriate solutions, coordinated with the surrounding countries.

Conclusions

The study closed the gap in arsenic data regarding areas of the canton of Valais with no historic arsenic problem in drinking water and provides a detailed cantonal scale picture of arsenic concentrations in water supply systems. These new data reveal details about the extent of natural arsenic contamination in drinking water. In contrast to the former study (15), a few values exceeding the current Swiss legal limit were found. The new information collected helps the cantonal authorities to take the adequate measures to reduce the arsenic level in drinking water where needed. Furthermore, the data serve as a basis for Part II of the study, which evaluates the relation between arsenic in drinking water and cancer incidence (18).

As previously mentioned, the arsenic concentration data were based on samples collected from a variety of different sources. The measured arsenic concentration for a given water supply is a function of the number of samples collected and where these samples were collected along the water network. The regional distribution of samples may be somewhat more representative of the arsenic concentration from small water supplies than that of large and complex supply systems where abundant water sources are available. However, this deficit in the sampling is compensated by a large number of samples and a consistent data-collection. The results provide a preliminary basis for evaluating the consequences of adopting a particular limit value for drinking water in Switzerland. Except for a few cantons, there is still little or no data in large parts of Switzerland. The arsenic concentrations found in the mainly alpine terrain of the canton of Valais do not necessarily conform to patterns shown at the national scale. Although concentrations of arsenic are likely to be higher in certain geographic regions compared to others, there can be a high degree of local variability. The only way to be certain of the arsenic concentration in the water supplied by any given system is to have the water tested. This type of systematic survey should be carried on with other cantons in the future.

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Summary

A systematic survey of the arsenic level in the drinking water of the canton of Valais was carried out during the summer 2003. A total of 1297 samples were collected from springs and public water supplies in order to assess the situation in each of the 160 communes of the canton. The results confirm a previous study, refine the geographical location of arsenic rich drinking waters and provide an improved data set for an adequate risk assessment. The median concentration in the canton is 0.52 µg/l, but 89 samples (6.9 %) located in 33 communes exceed the WHO guideline value of 10 µg/l. A few samples (n=7) have an arsenic level over the current legal limit in Switzerland (50 µg/l). The analytical method and the quality control of the results are discussed in detail.

Zusammenfassung

Während des Sommers 2003 wurde im Kanton Wallis eine systematische Erhebung von Trinkwasserproben durchgeführt. Zur Beurteilung der Situation in den 160 Walliser Gemeinden wurden insgesamt 1297 Proben aus Quellen und öffentlichen Trinkwassernetzwerken gesammelt. Die Ergebnisse bestätigen Arsendaten früherer Studien, vermitteln eine geographische Übersicht der Arsenvorkommen und können als erweiterte Datenbasis für die Risikoanalyse genutzt werden. Der Median der Arsenkonzentration beträgt 0,52 µg/l. 89 Proben (6,9 %), die aus 33 Gemeinden stammen, überschritten den WHO-Richtwert von 10 µg/l. Nur wenige Proben (n=7) wiesen eine Arsenkonzentration auf, die über dem gegenwärtig in der Schweiz gültigen Grenzwert von 50 µg/l lag. Die Messmethode (ICP-MS) und die analytische Qualitätssicherung sind detailliert beschrieben.

Résumé

Une surveillance systématique du niveau d'arsenic dans l'eau potable du canton du Valais a été réalisée durant l'été 2003. Un total de 1297 échantillons ont été collectés dans les sources et les réseaux de distribution afin d'établir la situation dans chacune des 160 communes du canton. Les résultats confirment une étude antérieure, permettent d'affiner la distribution géographique des eaux riches en arsenic et fournissent un ensemble de données amélioré pour une évaluation du risque appropriée. La concentration médiane dans le canton est de 0,52 µg/l mais 89 échantillons (6,9 %) situés dans 33 communes présentent une concentration supérieure à la valeur de 10 µg/l recommandée par l'OMS. Quelques échantillons (n=7) ont un niveau d'arsenic supérieur à la valeur limite légale en Suisse (50 µg/l). La méthode analytique ainsi que le contrôle de qualité des résultats sont discutés en détail dans cet article.

Key words

ICP-MS, arsenic, drinking water, inorganic contaminant, risk assessment

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