Arsenic in rocks and groundwaters in Trentino (Italy). Arsenic removal from water for human consumption: state of compliance activities.

Dr. Gianfranco Bazzoli – Dr. Marco Visintainer Trentino Servizi S.p.A.

We shall report here on the studies and the activities performed in Trentino in order to comply with the law requirement to lower the Arsenic concentrations in the water supplied for human consumption, where it is above the limit of 10 micrograms per liter.
The activities that were performed followed two paths:

- studies and investigations in order to improve our knowledge of the distribution of Arsenic as natural contaminant in the surface waters and groundwaters of the central Trentino area and in order to understand how As is brought into solution. The studies were coordinated by prof. A. Fuganti of the University of Trento, Engineering Department. Prof. G. Morteani was also involved in the study.
- experimental testing of arsenic- removal technologies to choose the treatment solution that best fit to Trento waters.

The scientific investigations were centered on the Adige valley area , between Mattarello (Trento) and Mezzolombardo and Roverè della Luna, at the border between Trento and Bozen province, where the Arsenic problem is not widespread, but the contamination mechanism was not explained. Elsewhere, as in the upper Val Sugana area, east of Trento, many municipalities deal with high Arsenic contens in the sources, but for this area it is well known that Arsenic in waters is due to the presence of metallic sulphides ores in the recharge areas of the sources. The Arsenic is in the crystalline lattice of the minerals, and it is leached by running and infiltration water.
To investigate the reasons of Arsenic presence in Adige valley waters, many samples were analyzed: rocks, surface waters and groundwaters.

Arsenic in rocks

Rock samples were collected mainly from the eastern flank outcrops of the Adige valley. In fact, at the western slopes the outcrops are mainly carbonatic rocks of coral reef environment (limestones and dolomites): in this type of rocks, Arsenic is usually not found. On the eastern slopes, the rocks are mainly sedimentary rock of shallow sea environment, then formed from wheathering of continental rocks, and volcanic rocks.
The samples analysis interpretation was made taking into account the age and sedimentary environment of the rocks. Higher arsenic concentrations are found in the rocks from coastal and shallow sea, evaporitic, environment, and in the older volcanic rocks, while the rocks formed in deep sea environment have little arsenic content.
Investigations were made on the Arsenic contents of alluvial sediments at a drilling site in the area of Roverè della Luna, near the border between Trento and Bozen provinces. Here, until the second part of 19th century the valley bottom was flat, with Adige meanders and marshes. In this low-enrgy environment peat deposition was intense.The investigations were made on two samples from a borehole drilled until a depht of 80 meters. The drilling crossed sands and silts, with peat layers and methane gas emissions. A sample of peat from 32 m was analyzed: the As concentration in it was 115 mg/kg of dry substance, that is more than double of the maximum concentration limit admitted in Italy for soils in industrial areas: above the limit of 50 mg/kg As, the area is considered as polluted. In a sand sample from 33.5 m depth, As was 4.9 mg/kg.

Arsenic in surface waters

Samples were collected from the main rivers in the area. We took into account also analyses made in former times. Arsenic concentrations above the 10 micrograms limit were found only in Fersina river waters, while the other rivers have As concentration below the limit. Fersina is the river draining the metallic sulphides ore area. One of sampled rivers, Carpine river, is draining a basin where shallow sea and evaporitic rocks are dominant, but the As concentrations were low in its water.

Arsenic in groundwaters

Groundwater sampling involved two different aquifers of the Adige valley:
the unconfined or leaky aquifers, that is the shallow groundwater of the valley;
the confined and deeper aquifers, found at dephts of over 150 meters.
The most of the water drawn from wells for public supply and agricultural use in Adige valley comes from shallow unconfined aquifers. For Trento town, about 60% of tap water supplied to the over 112000 residents comes from shallow aquifers. Only in the last years water research and new wells were aimed at deep aquifers. The higher As concentrations are found in deep aquifers, and repeated samples confirm the first data. Samples from shallow aquifers are low in Arsenic, with some exception: a well near the Trento urban landfill, and wells pumping water from the underflow aquifer of Fersina river The concentration of As in the underflow water of Fersina river is due to the content of arsenic in its surface water, that we explained before.
At deep aquifer depht, we find reducing conditions, wich cause the mobilization of Arsenic through desorption from iron and manganese hydroxides that are attached to the grains of aquifer matrix. The Arsenic release process is just the reverse of one of the removal technologies we will discuss hereinafter.
Reducing conditions are present also in the aquifer at the urban landfill. Here we find As concentrations up to 60 micrograms/liter, that are clearly associated with the reduction zones of a contaminant plume. Reducing conditions in the aquifer are easily recognized in Roverè della Luna area, where groundwater samples have high concentrations of iron and manganese. Methane emissions were observed in the borehole.
The hydrogeochemical investigations point out that the Arsenic concentrations in Adige valley aquifer are associated with reducing conditions, in deep anoxic environments or in former palustrine environments, where organic matter avalaibilty may mediate the As release processes. The As content in the rocks outcropping in the slopes of the area seems to have no direct relevance.

Arsenic removal from Trento water

The Arsenic problem for Trento town comes from the fact that 110 l/s out of 600 l/s of supplied tap water is from Fersina river underflow. From tunnels excavated in rock in the years from 1950 to 1960, horizontal and sloping drains were drilled in the alluvials of the river, and underflow water flows by gravity to a collector pipe and from here to the supply structures.
The average concentration of As in the water is around 15 micrograms, varying of about 7 micrograms/liter with the river discharge, and then with the season. Due to the characteristics of the supply system, Trentino Servizi S.p.A. was concerned about the costs and viability of mixing this water with groundwaters from Adige valley wells, to lower

the As concentration by dilution, and it was decided to acquire a treatment plant for Arsenic removal.
In order to choose the treatment technology that best fit for the Fersina river underflow water, Trentino Servizi tested three different technologies, in pilot plants built and operated by the producing firms, while T.S. technicians and chemical laboratory were checking the system and the results.The three technologies tested are:

- Flocculation/filtration: where Arsenic is oxydized, then flocculated using ferric chloride or aluminum polychloride, then filtered on sand beds;
- Osmosis/nanofiltration: where the water is passed under pressure through membranes: As molecules do not pass through the membranes;
- Adsorption: As is removed from solution and adsorbed on iron hydroxide–based adsorptive media: four different products were tested

The selection of the technology to apply was made taking in to account many parameters of evaluation, first of all the efficiency in arsenic removal. After about 6 months of testing (not continued, indeed), the flocculation/filtration technology proved itself not effective. This technology appears to be very effective when starting from very high concentration of arsenic, but when starting concentrations are just few micrograms over the limit, as in our case, efficiency is low.
The other technologies considered resulted to be effective in lowering As concentrations below the limits, and the final choice was made according to other evaluations, as reported in the following table.

Evaluation items	Membranes/nanofiltration	Adsorption
General costs (plant + running)	Costs are similar	
Operational characteristics	Requires more water pressure at inflow (5-8 bar). Turbidity of water may cause efficiency reduction. Other elements are removed: more aggressive water	Requires lower water pressure at inflow (1.5 - 2 bar). Turbidity is not a problem
Technological complexity	More complexity	Low maintenance requirements
Reliability	Reliability is high in both technologies	
Water not available after treatment	1.5 % of water discarded after treatment	No water discarded
Chemicals **Process control**	Chemicals must be carefully dosed for optimal results; process parameters must be controlled. Reject waste must be disposed of	No chemicals added; Exhaust material must be disposed of (possible regeneration). Periodic recharge
Space required/ costs of building structures	More compact	Requires more space and higher rooms

At the end, the adsorption technology was selected, but it was not an easy decision.
The choice was mainly due to lower technological complexity.
A project has been prepared and financed for two plants in two different sites, able to treat 90 l/s and 60 l/s each, and for service buildings. A tender for the plants in on the way. The costs of the two plants, building and pipe costs excluded, is of about 1,290,000 euro.
Other municipalities in Trentino are dealing with the As-lowering compliance.
Tenna municipality, at about 20 km east of Trento, in Valsugana, just built an As removal plant and a plant for increase the degree of mineralization of the water, that were too low, at a cost of 200,000 euro.
Roverè della Luna municipality is evaluating non-treatment alternatives: lowering the As concentration by blending with low-As water, or replacing it with new sources.

Innsbruck

June,23, 2006

Arsenic in rocks and groundwaters in Trentino (Italy).

Arsenic removal from water for human consumption: state of compliance activities

Trentino Servizi S.p.A.

Dr. Marco Visintainer Dr. Gianfranco Bazzoli

INNSBRUCK

23.06.2006

Arsenic in rocks and groundwaters in Trentino (Italy)

Intro

Rocks

Surface water

Ground water

Treatment

Study area: Adige valley between Trento town and Bozen province border

Project purposes:

1. Screening of As concentrations in rocks, surface waters and groundwater in **Adige valley bottom**

2. Understand the origin and conditions of As-enrichment in the **groundwater** tapped for human consumption

3. Define the treatment technology to be applied to reduce As in tap water

27 rock samples
6 surface water samples
38 groundwater samples

mineralizations near Trento: red containing As – pyrite: up to 3000 ppm As in ZnS and PbS minerals

ARGE ALP

INNSBRUCK

23.06.2006

Arsenic in rocks and groundwaters in Trentino (Italy)

Intro

Rocks

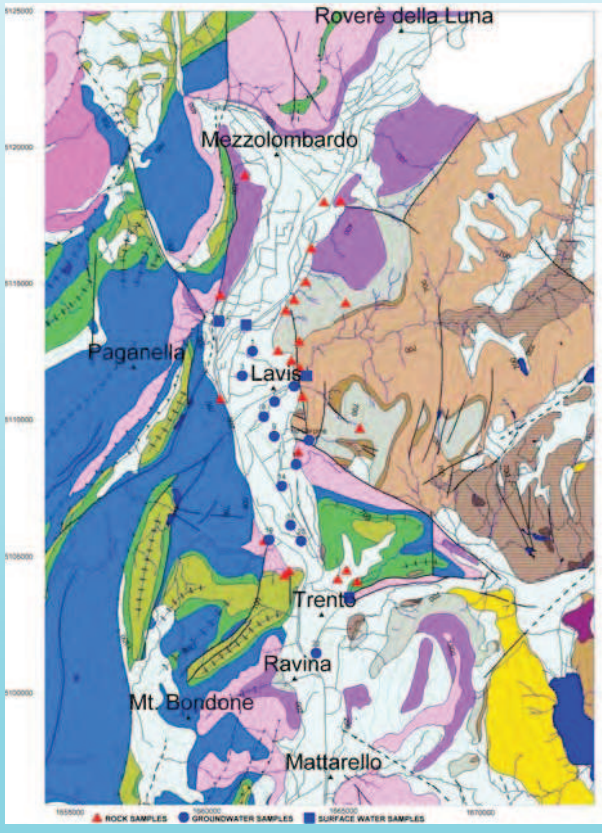
Surface water

Ground water

Treatment

GRUPPO Trentino Servizi

Geological map of study area and sampling points.



ARGE ALP

INNSBRUCK

23.06.2006

Arsenic in rocks and groundwaters in Trentino (Italy)

Intro

Rocks

Surface water

Ground water

Treatment

GRUPPO Trentino Servizi

Era	Period	Subperiod	Epoch (Harland)	Age	My	Sedimentary environment of Central Trentino	As content in sampled rocks (ppm)
Mesozoic	Jurassic		Malm	Tithonian		deep sea	<1
				Kimmeridgian			
				Oxfordian	161		
			Dogger	Callovian			
				Bathonian			
				Bajocian			
				Aalenian	176		
			Lias	Toarcian			
				Pliensbachian			
				Sinemurian			
				Hettangian	200		
	Triassic		Tr3	Rhaetian		coral reef	<1, <1
				Norian			
				Carnian	228		<1, 1, 1, <1
			Tr2	Ladinian			
				Anisian	245		3, <1, <1
			Scythian	Spathian		shallow sea	2, <1, <1, 13, 12, <1, 9
				Nammalian			
				Griesbachian	251		
Paleozoic	Permian		Zechstein	Changxingian		coastal, evaporitic gypsum, marls, dolostones	39, 24, 11, 11
				Longtanian			
				Capitanian			
				Wordian		continental sandstones	
				Ufimian	276	ignimbritic plateau lavas and conglomerates	4, 8
			Rotliegendes	Kungurian			
				Artinskian			
				Sakmarian			
				Asselian	299		

ARGE ALP

INNSBRUCK

23.06.2006

Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment

Era	Period	Subperiod	Epoch (Harland)	Age	My	Sedimentary environment of Central Trentino	As content in sampled rocks (ppm)
Cenozoic	Quaternary		Holocene		0.01		
			Pleistocene		1.8		
	Tertiary	Neogene		Piacenzian			
				Zanclean			
				Messinian			
			Pliocene	Tortonian	5.3		
				Serravallian			
				Langhian			
				Burdigalian			
			Miocene	Aquitanian	23		
		Paleogene		Chattian			
			Oligocene	Rupelian	34		
				Priabonian		deep sea, submarine volcanoes	
				Bartonian			
				Lutetian			
			Eocene	Ypresian	56		3
				Thanetian			
			Paleocene	Danian	65		
Mesozoic	Cretaceous			Maastrichtian		deep sea	<1, <1
				Campanian			
				Santonian			
			Senonian	Coniacian	89		
				Turonian			
				Cenomanian			
				Albian			
				Aptian			
			Gallic	Barremian	130		
				Hauterivian			
				Valanginian			
			Neocomian	Berriasian	146		

GRUPPO Trentino Servizi

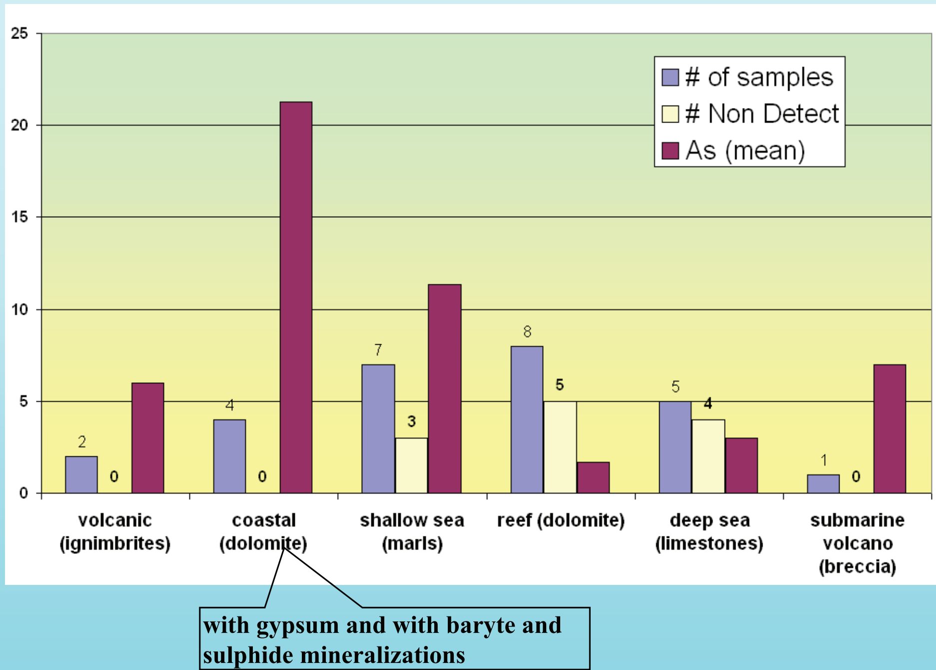
ARGE ALP

INNSBRUCK

23.06.2006

Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment



No. of samples per sedimentary environment and resulting As concentration values (ppm)

GRUPPO Trentino Servizi

ARGE ALP

INNSBRUCK

23.06.2006

Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment

peat sample collected at 32 mt depth. As: **115.6 mg/kg** (dry substance)

alluvial sand sample collected at 33.5 mt depth. As: **4.9 mg/kg** (tout venant)

Quaternary alluvium : old marsh area between Salurn and Roverè della Luna. Anoxic environment, with methane emissions and reducing conditions

GRUPPO Trentino Servizi

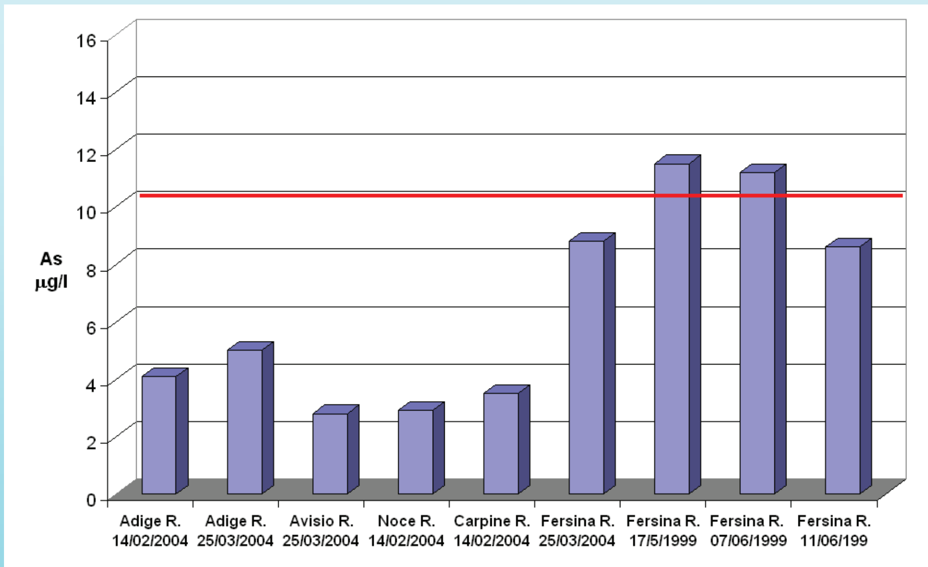
ARGE ALP

INNSBRUCK

23.06.2006

Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment



High As contents were detected only in the water of Fersina river, draining the sulphide mineralization area.

GRUPPO Trentino Servizi

ARGE ALP

INNSBRUCK
23.06.2006
Arsenic in rocks and groundwaters in Trentino (Italy)

Groundwater sampling involved:

unconfined/leaky aquifers ↔ shallow groundwaters

confined aquifers ↔ deep (>150 m) groundwaters

More than 60% of tap water of Trento town (112 000 residents) comes from wells drilled in unconfined/leaky aquifers.

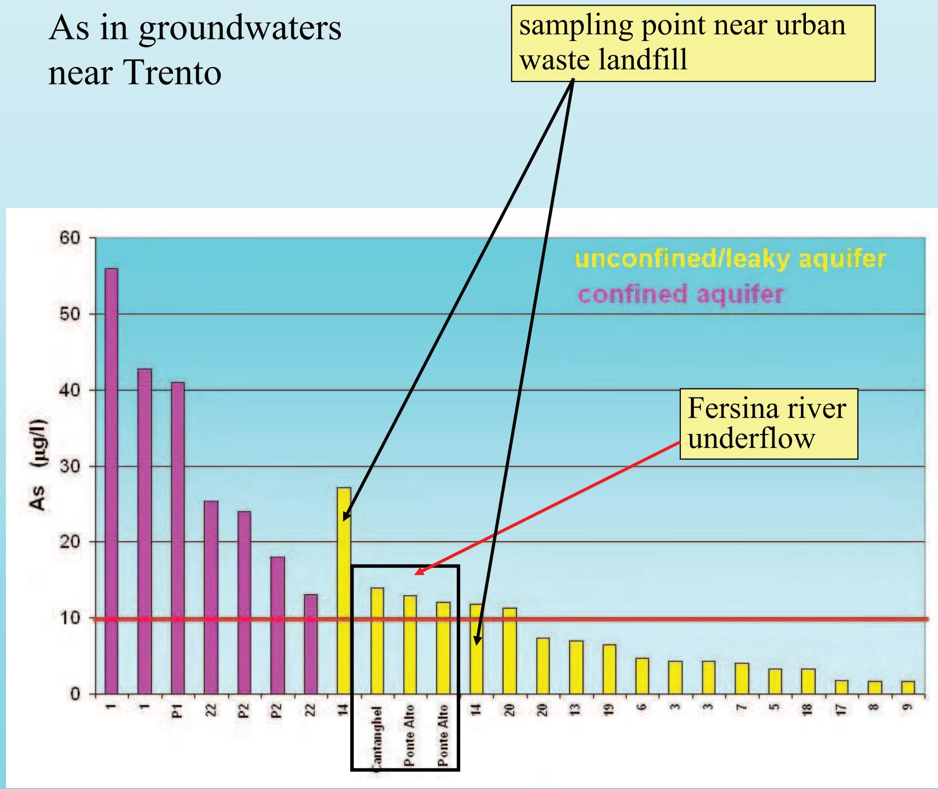
In the last years investigation and production water wells for water supply have been drilled in confined aquifers.

GRUPPO Trentino Servizi

ARGE ALP

INNSBRUCK
23.06.2006
Arsenic in rocks and groundwaters in Trentino (Italy)

As in groundwaters near Trento



GRUPPO Trentino Servizi

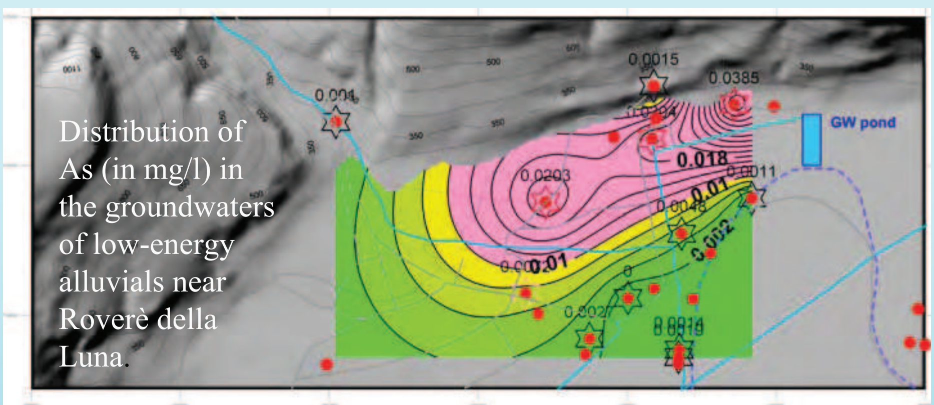
INNSBRUCK

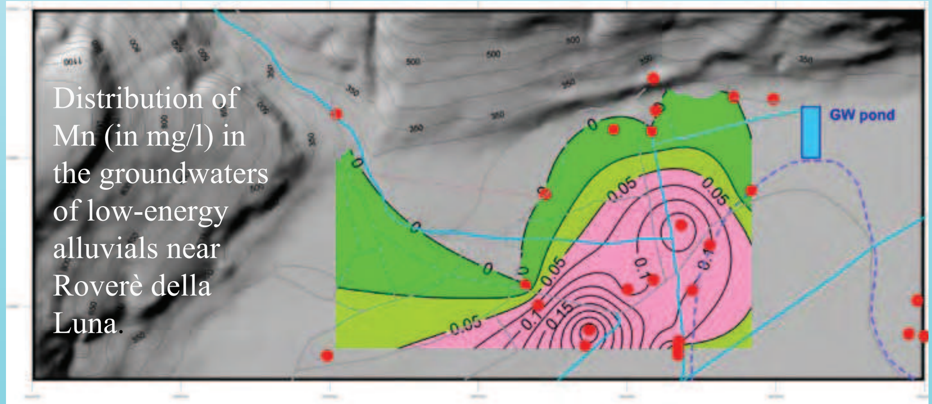
23.06.2006

Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment

Gruppo Trentino Servizi





INNSBRUCK

23.06.2006

Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment

Hydrogeological and geochemical evidences point out:

that in Adige valley groundwater arsenic concentrations above law limits are generally due to the presence of reducing environments, that is:

- in areas where peat deposits are observed (old marshes, abandoned river meanders);
- in deep anoxic sediments;
- at the reduction front of contaminated areas.

The aquifer of Fersina river (underflow water and alluvial fan groundwater) As-contents are instead due to leaching and transport of As from ores in river basin.

Gruppo Trentino Servizi

INNSBRUCK
23.06.2006
Arsenic in rocks and groundwaters in Trentino (Italy)

The problem at Trento

150 l/s out of 600 l/s of water supplied to Trento town come from plants tapping Fersina river underflow, having an average As concentration of 15 µg/l.

Dilution of As concentration by mixing with groundwater from Adige valley is not viable, and treatment is then necessary.

Trentino Servizi

INNSBRUCK
23.06.2006
Arsenic in rocks and groundwaters in Trentino (Italy)

The technical solution by Trentino Servizi

The selection of treatment technology to apply was made **after testing three technologies**, in pilot plants built and operated in situ by the producing firms, our technicians and lab checking the results

Flocculation/filtration: As is oxydized, then flocculated using ferric chloride or aluminum polychloride, then filtered on sand beds

Osmosis/nanofiltration: water is passed under pressure through membranes : As molecules do not pass through

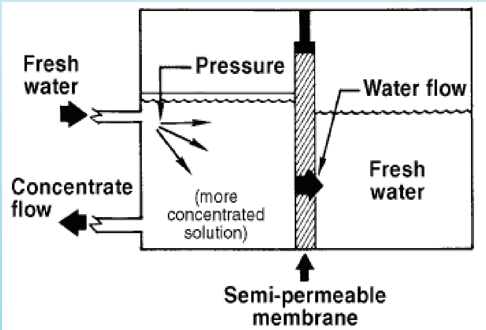
Adsorption: As is removed from solution and adsorbed on iron hydroxide – based adsorptive media: four different products were tested.

Trentino Servizi

INNSBRUCK
23.06.2006
Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment

Membrane/nanofiltration pilot plant for As removal



Testing duration:
2 months

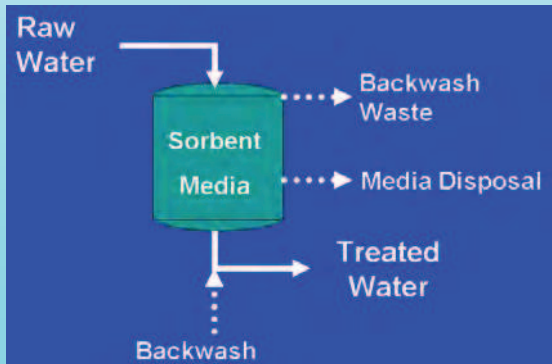
Trentino Servizi

INNSBRUCK
23.06.2006
Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment

Adsorption pilot plant for As removal at Trento water supply structures

Testing duration:
2 months per sorbent product tested



Trentino Servizi

ARGE ALP

INNSBRUCK
23.06.2006
Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment

GRUPPO Trentino Servizi

Parameters considered for the selection of treatment plant.

No. 1: Efficiency

flocculation/filtration resulted not effective due to low As concentration in inflow water: only in 1 day of testing period the Arsenic concentration was lowered under the 10 µg/l limit

osmosis/nanofiltration and **adsorption** on iron hydroxide – based products were both effective . More testing and evaluation were performed to choose between these alternative technologies

ARGE ALP

INNSBRUCK
23.06.2006
Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment

GRUPPO Trentino Servizi

Other evaluations

Evaluation items	Membranes/nanofiltration	Adsorption
General costs (plant + running)	Costs are similar	
Operational characteristics	Requires more water pressure at inflow (5-8 bar). Turbidity of water may cause efficiency reduction. Other elements are removed: more aggressive water	Requires lower water pressure at inflow (1.5 - 2 bar). Turbidity is not a problem
Technological complexity	More complexity	Low maintenance requirements
Reliability	Reliability is high in both technologies	
Water not available after treatment	1.5 % of water discarded after treatment	No water discarded
Chemicals Process control	Chemicals must be carefully dosed for optimal results; process parameters must be controlled. Reject waste must be disposed of	No chemicals added; Exhaust material must be disposed of (possible regeneration). Periodic recharge
Space required/ costs of building structures	More compact	Requires more space and higher rooms

ARGE ALP

INNSBRUCK
23.06.2006
Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment

Adsorption technology was finally chosen , a project has been prepared for building As - removal plants in two sites, able to treat 90 l/s and 60 l/s, and financed.

A tender is on the way.

Project costs : two arsenic removal plants, with adsorption beds : **1.290. 000 €**

building and pipe costs excluded

GRUPPO Trentino Servizi

ARGE ALP

INNSBRUCK
23.06.2006
Arsenic in rocks and groundwaters in Trentino (Italy)

Intro
Rocks
Surface water
Ground water
Treatment

Tenna municipality, 20 km E from Trento, has built in 2006 a **As-removal and mineralization** plant (inflow project: 2 l/s), at a cost of about **200.000 €.**

Roverè della Luna municipality is evaluating **non-treatment alternatives** :

- blending (dilution)
- new sources (mountain springs, new wells).

GRUPPO Trentino Servizi

Thank you for attention

Danke für Ihre Aufmerksamkeit

Grazie per l’attenzione

Innsbruck, June 2006
Arsenic in rocks and groundwaters in Trentino (Italy)
Arsenic removal from water for human consumption: state of compliance activities