

Arsenic in groundwater: *Probability of occurrence of excessive concentration on global scale*

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1 Introduction

1.1 Special projects of IGRAC

The International Groundwater Resources Assessment Centre (IGRAC) aims to facilitate and promote world-wide exchange of groundwater knowledge. Within its fields of activity, IGRAC prioritise those activities that are prompted by the international groundwater community.

IGRAC's special projects intend to collect, analyse and display information on specific groundwater issues relevant to development of groundwater resources on various scales.

The aim of this IGRAC's special project is to review available information about groundwater contaminated with arsenic and to display the probable occurrence of arsenic on continental maps.

1.2 Arsenic in groundwater

Arsenic has become increasingly important in environmental geochemistry because of its significance to human health. Long-term exposure to arsenic through drinking contaminated water can result in a chronic arsenic poisoning. Known symptoms are: cancer of the skin, lungs, urinary blades, and kidney as well as other skin changes such as pigmentation and thickening (WHO on <http://www.who.int/mediacentre/factsheets/fs210/en/index.html>)

The concentrations vary markedly in the environment, partly in relation to natural conditions and partly as a result of human activity (Plant et al, 2004). Natural sources are connected to various types of rocks and to geothermal activity. Industrial activities, especially mining can also contribute to an increased arsenic concentration in groundwater.

2 Sources of arsenic

2.1 Abundance in hard rocks and unconsolidated sediments

The average crustal abundance of arsenic is 1.5 mg/kg. The element is strongly chalcophile. Approximately 60% of natural arsenic minerals are arsenates, 20% sulphides and sulfosalts, and the remaining 20% are arsenides, arsenites, oxides, alloys and polymorphs of elemental arsenic. Arsenic concentrations of more than 10^5 mg/kg have been reported in sulphide minerals and up to 7.6×10^4 mg/kg in iron oxides (Smedley and Kinniburgh, 2002). However, concentrations are generally much lower. Arsenic is incorporated into primary rock-forming minerals only to a limited extent, for example, by the substitution of As^{3+} for Fe^{3+} or Al^{3+} . Therefore, arsenic concentrations in silicate minerals are typically ~1 mg/kg or less (Smedley and Kinniburgh, 2002). Many igneous and metamorphic rocks have average arsenic concentrations of 1-10 mg/kg. Similar concentrations are found in carbonate minerals. (Plant et al, 2004).

Arsenic concentrations in sedimentary rocks can be more variable. The highest arsenic concentrations (20-200 mg/kg) are typically found in organic-rich and sulphide-rich shales, sedimentary ironstones, phosphatic rocks, and some coals (Smedley and Kinniburgh, 2002). In sedimentary rocks arsenic is concentrated in clays and other fine-grained sediments. The average concentration of arsenic in shale is an order of magnitude greater than in sandstones, limestones and carbonate rocks. Arsenic is strongly sorbed by oxides of iron, aluminium and manganese as well as some clays, leading to its enrichment in ferromanganese nodules and manganiferous deposits (Plant et al, 2004). Alluvial sands, glacial till and lake sediments typically contain <1-15 mg/kg arsenic (Plant et al, 2004).

2.2 Abundance in soils

The arsenic concentrations in soils show a similar range to that found in sediments except where contaminated by industry or agricultural activity (Plant et al, 2004). By and large, the arsenic release potential seems to be correlated with three soils or hydrogeological situations (this does not mean, however, that all soils of these types necessarily carry measurable levels of arsenic) (Alaerts and Khouri, 2004):

- Peaty or peaty-clayey soils with high humic organic content and with a high water table, which contain arsenopyrite crystals. When these soils, often associated with wetlands and marshes, are drained to bring them into production, oxygen penetrates the peat and oxidises the arsenopyrite crystals, thus releasing a sulphate-rich acid as well as dissolved arsenic into ground and drainage water. Arsenic concentrations are usually below 100 µg/l. Such conditions are found for example in England, Germany, The Netherlands and many tropical peaty lowlands.
- Young volcanic deposits or thermal water sources. These often contain elevated dissolved arsenic concentrations that can well exceed 1 mg/l. This water usually enters surface water streams as experienced for example in Argentina, Bolivia, Chile, Greece and Taiwan.
- Loamy and clayey deposits (especially in deltaic areas) that may contain arsenic in dissolved state and/or adsorbed onto clay particles. The release of the arsenic is thought to be primarily governed not by changes in the redox potential, but by the physical-chemical circumstances that control desorption equilibria. Arsenic concentrations can vary from high to low. Such conditions are found for example in Bangladesh and China (Inner Mongolia and Xinjiang).

- Anthropogenic arsenic sources. Mine tailings and soil under factories processing arsenic-based pesticides or under fields where these pesticides are applied can contain arsenic. This contamination commonly is of much localised nature. Tailing drainage may seep into rivers and aquifers. Concentrations can vary from low to medium. Pollution from mines was reported for example in Ghana and Thailand.

2.3 Abundance in groundwater

The concentration of arsenic in most groundwaters is lower than 10 µg/l and often below the detection limit of routine analytical methods. The physicochemical conditions favouring arsenic mobilisation in aquifers are variable, complex and poorly understood, although some of the key factors leading to high groundwater arsenic concentrations are known. Mobilisation can occur under strongly reducing conditions where arsenic, mainly as As(III), is released by desorption from and/or dissolution of iron oxides. Immobilisation under reducing conditions is also possible. Some sulphate-reducing microorganisms can respire As(V) leading to the formation of an As₂S₃ precipitate. Some immobilisation of arsenic may also occur if iron sulphides are formed (Plant et al, 2004).

Reducing conditions favourable for arsenic mobilisation have been reported most frequently from young (Quaternary) alluvial, deltaic sediments. The interplay of tectonic, isostatic and eustatic factors have resulted in complex patterns of sedimentation and rapid burial of large amounts of sediment together with fresh organic matter during delta progradation. Thick sequences of young sediments often contain groundwater with a high arsenic concentration (Plant et al, 2004). Recent groundwater extraction, either for public supply or for irrigation, has induced increased groundwater flow. This could induce further transport of arsenic (Harvey et al, 2002).

High concentrations of naturally occurring arsenic are also found in oxidising conditions where groundwater pH values are high (>8) (Smedley and Kinniburgh, 2002). In such environments, inorganic As(V) predominates and arsenic concentrations are positively correlated with those of other anion-forming species such as HCO₃⁻, F⁻, H₃BO₃, and H₂VO₄⁻. The high-arsenic groundwater provinces are usually in arid or semi-arid regions where groundwater salinity is high. Evaporation has been suggested to be an important additional cause of arsenic accumulation in some arid areas (Welch and Lico, 1998).

High concentrations of arsenic have also been found in groundwater from areas of bedrock and placer mineralization which are often the sites of mining activities. Arsenic concentrations of up to 5000 µg/l have been found in groundwater associated with the former tin-mining activity in the Ron Phibun area of Peninsular Thailand, the source most likely being oxidised arsenopyrite (FeAsS) (Plant et al, 2004).

2.4 International standards for drinking water

The standards for maximum concentrations of arsenic in drinking water have been sharpened since the high toxicity of arsenic has become apparent. The 1903 report of the Royal Commission on Arsenic Poisoning in the UK set a standard at 150 µg/l. In 1942, the US Public Health Service set a drinking water standard at 50 µg/l for interstate water carriers.

The WHO guideline value for arsenic in drinking water was reduced from 50 µg/l to a provisional value of 10 µg/l in 1993. Most western countries adopted this limit in their current drinking water standards (Yamamura, 2003). On the other hand, many affected countries still operate 50 µg/l standard due to lack of adequate testing facilities.

3 Probability of occurrence of excessive arsenic concentrations

Various publications and web-sites were consulted to obtain information about the occurrence of arsenic in groundwater. An overview of regions with groundwater containing arsenic in excess of 50 µg/l is given in Appendix 1. Known aquifer types and sources of contamination are also included.

Geographical extent of areas contaminated with arsenic is shown on six continental maps (Figure 1 through 6). Probability of occurrence of excessive concentrations in these areas is indicated by three different colours:

- The areas indicated in red, have a relative high probability to contain arsenic in the groundwater. The locations of these areas are often well defined and many groundwater samples of these areas contain high concentrations of arsenic.
- The areas indicated in pink, have a relative low probability to contain arsenic contaminated groundwater. The precise location of the contaminated groundwater is not known and only few groundwater samples contain high concentrations of arsenic.
- Grey hatched areas are mentioned in the literature as contaminated areas, but no detailed information is available.

For the remaining areas (indicated in yellow), no information about arsenic contamination has been found so far.

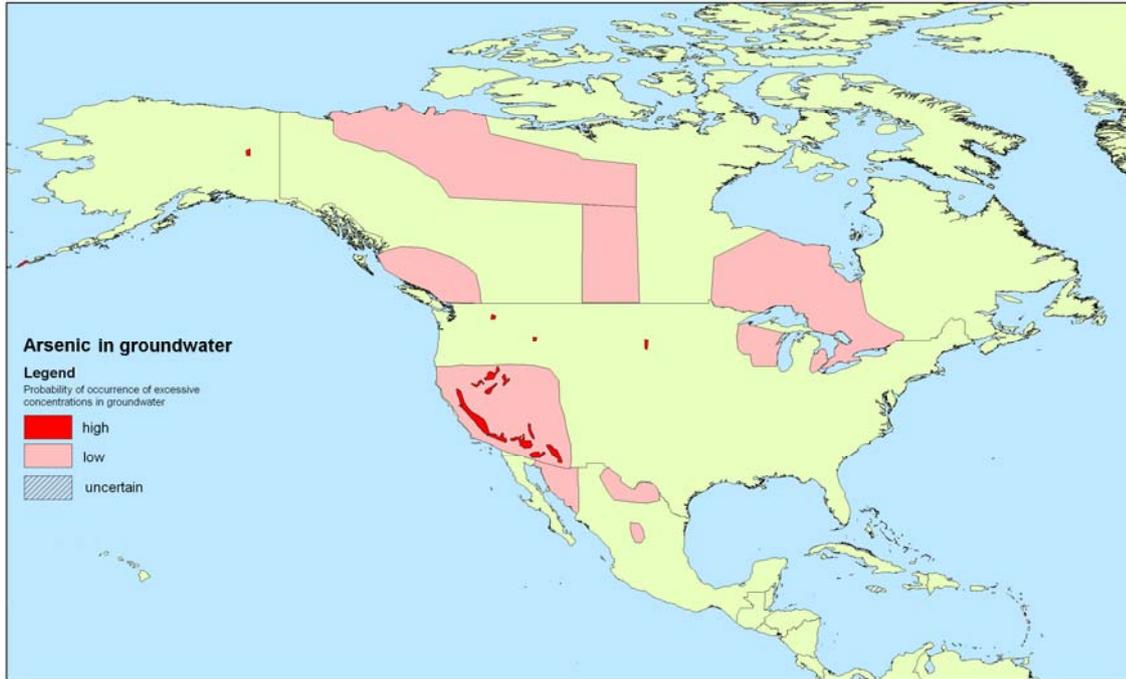


Figure 1 Arsenic in groundwater in North and Central America



Figure 2 Arsenic in groundwater in South America

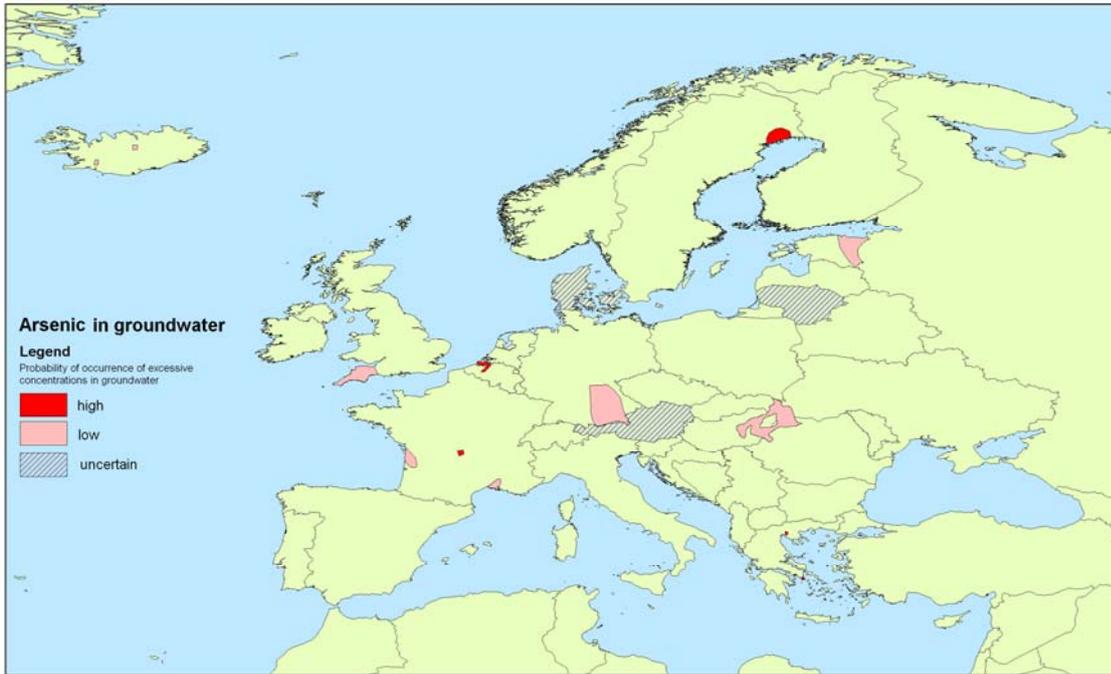


Figure 3 Arsenic in groundwater in Europe



Figure 4 Arsenic in groundwater in Africa

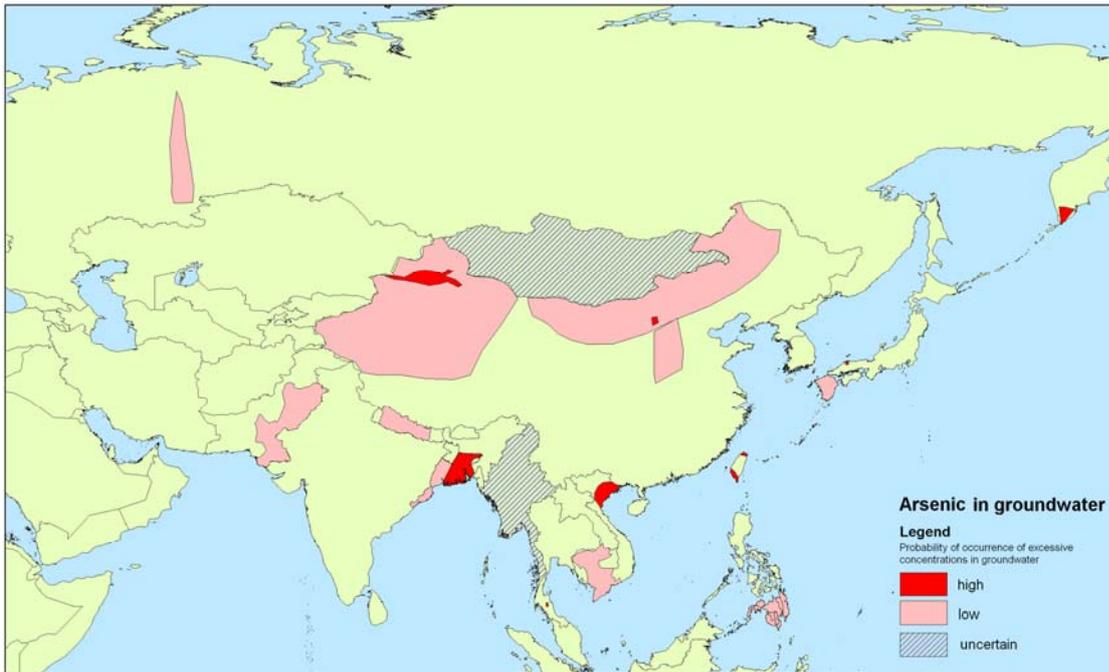


Figure 5 Arsenic in groundwater in Asia

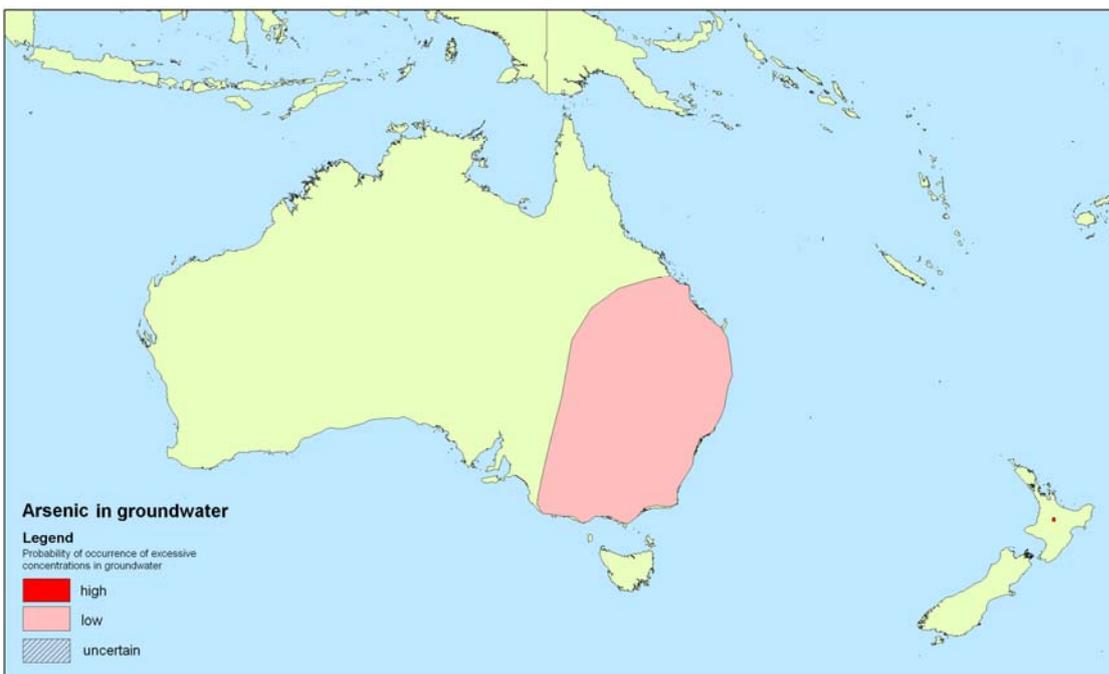


Figure 6 Arsenic in groundwater in Australia

4 Concluding remarks

This special IGRAC project resulted in refining of (administrative) boundaries of regions which have been reported as having problem with high arsenic concentrations in groundwater. In this stage, more detailed mapping of global distribution of arsenic-rich groundwater by using existing geological maps is not yet possible.

Areas with arsenic-rich groundwater are often associated with unconsolidated alluvial sediments. As rivers eroded and silted up, sediments packets of varying composition and grain size were deposited and shifted along. Therefore, their arsenic content and release potential may vary, even within a distance of 10 m (Alaerts and Khouri, 2004). This makes it difficult to locate the precise arsenic contaminated area.

The depth of the arsenic contaminated groundwater was also not taken into account. Deeper groundwater can travel a longer distance through different aquifers. Consequently, deeper groundwater has a higher chance to contain arsenic. The aquifer rocks found at the places where groundwater is contaminated with arsenic, do not necessarily have to be the source of the arsenic. The source can be just the layer on top, or a formation much further away upstream.

Input from regional experts will result in additional information and consequently more detailed specification of areas (aquifers, geological formations) contaminated with arsenic.

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- www.epa.gov/glnpo/solec/2002/d2/Groundwater.Norm.Final.pdf
- www.igrac.nl
- www.umeciv.maine.edu/MacRae/where_is_arsenic_a_problem.htm
- www.wateraid.org
- <http://www.who.int/mediacentre/factsheets/fs210/en/index.html>

Appendix 1 Regions with an arsenic concentration above 50 µg/l specified per continent

<i>Country</i>	<i>Region</i>	<i>Origin, natural or anthropogenic (concentration ranges (µg l⁻¹))</i>	<i>Reference</i>
Asia			
Bangladesh	Bengal basin	Holocene alluvial/deltaic sediments. Abundance of solid organic matter (<0.5-2500)	Smedley et al, 2002, Alaerts and Khouri, 2004
Cambodia	Mekong delta	Holocene alluvial/deltaic sediments.	Smedley et al, 2002
China	Inner Mongolia (Tumet plain, Huhhot basin, Ba Men, Bayingao, Hexi)	Holocene alluvial and lacustrine sediments (<1-2400)	Smedley et al, 2002, Alaerts and Khouri, 2004
	Xinjiang Provinces (Tianshan plain)	Holocene alluvial plain (40-750)	Smedley et al, 2002, Alaerts and Khouri, 2004
	Shanxi Province	Alluvial plain	Smedley et al, 2002, Alaerts and Khouri, 2004
India	West Bengal (Bengal Basin)	Holocene alluvial/deltaic sediments. Abundance of solid organic matter (<10-3200)	Smedley et al, 2002, Alaerts and Khouri, 2004
Japan	Matsu&Turoko	Industrial	www.dchtrust.org/arsenic%20country%20to%20country.htm
	Kyushu	Geothermal field	Smedley et al, 2002
Mongolia			www.dchtrust.org/arsenic%20country%20to%20country.htm
Myanmar			Smedley et al, 2002
Nepal	Nawalparasi (Western region), Rautahat and Bara (Central), Bardia (Midwestern), Parsa, Rupandehi, Kapilbasthu and Banke	Recent sediments of the Terai region and groundwater of the active floodplain of the River Koshi	www.wateraid.org
Pakistan	Indus River		Tariq et al, 1996
Philippines	Mindanao island		Webster, 1999
Russia	Ural Mountain range	Mine drainage (400.000)	Smedley et al, 2002
	Kamchatka	Geothermal field	Smedley et al, 2002
Taiwan	Southwest and Northeast coastal zones	Sediments, including black shales (10-1820)	Smedley et al, 2002, Alaerts and Khouri, 2004
Thailand	Ron Phibun district, Nakhon Si Thammarat Province	Dredged Quaternary alluvium (some problems in limestone), tailing (1-5000)	Smedley et al, 2002
Vietnam	Mekong delta, Red River delta	Holocene alluvial/deltaic sediments. (1-3050)	Smedley et al, 2002

Europe			
Austria			www.umeciv.maine.edu/MacRae/where_is_arsenic_a_problem.htm , www.igrac.nl
Belgium	Schelde estuary	Mining and industry (up to 30)	Smedley et al, 2002, Alaerts and Khouri, 2004 www.igrac.nl
Denmark			
England	Parts of SW England	Mining Pb, Ag	Smedley et al, 2002
Estonia	Parts of NE Estonia	Industrial	Häsänen et al, 1997
France	Massif Central	Geothermal field	Smedley et al, 2002
Germany	Bavaria	Upper Triassic Keuper Sandstone (<10-150)	Smedley et al, 2002
Greece	Lavrion	Mining Pb, Ag	Smedley et al, 2002
	Thessaloniki	Geothermal field	Alaerts and Khouri, 2004
Hungary	Great Hungarian Plain	Alluvial Quaternary sediments (<2-176)	Smedley et al, 2002, Alaerts and Khouri, 2004
Iceland		Geothermal field	Smedley et al, 2002
Lithuania			www.igrac.nl
Netherlands	Schelde estuary	Mining and industry	Alaerts and Khouri, 2004
Romania	Great Hungarian Plain	Alluvial Quaternary sediments (<2-176)	Smedley et al, 2002
Sweden	Kalix River estuary	Sediment pore water	Plant et al., 2004
North and Central America			
Canada	British Columbia	Mining (0.5-580)	Smedley et al, 2002
	Saskatchewan	Clay sediments, sediment pore water	Plant et al., 2004
	Ontario	Mining (35-100)	Smedley et al, 2002, Alaerts and Khouri, 2004
	Northwest Territories	Mining (64-530)	Smedley et al, 2002, Alaerts and Khouri, 2004
Mexico	Lagunera region, Sonora province, other parts of northern Mexico	Volcanic sediments (Lagunera), calcareous formations (aquifer) (8-620)	Smedley et al, 2002, Alaerts and Khouri, 2004
	Zimapan valley	Mining	Smedley et al, 2002
USA	San Joaquin valley, Tulare Basin, California	Holocene and older basin-fill sediments (<1-2600)	Smedley et al, 2002
	Southern Carson desert, Nevada	Holocene mixed aeolian, alluvial, lacustrine sediments, some thin volcanic ash bands (up to 2600)	Smedley et al, 2002

	Basin and Range, Arizona	Alluvial basins, some evaporates (<1300)	Smedley et al, 2002
	Coeur d'Alene district of Idaho	Valley-fill deposits (<1400)	Smedley et al, 2002
	Lake Oahe, south Dakota	Lake sediments (<2000)	Smedley et al, 2002
	Fairbanks mining district of Alaska	Schist, alluvium, mine tailings (<10000)	Smedley et al, 2002
	Coeur d'Alene, Idaho	Pb-Zn-Ag mining	Smedley et al, 2002
	Leviathan mine, California	Mining	Smedley et al, 2002
	Kelly Creek Valley, Nevada	Mining	Smedley et al, 2002
	Clark Fork River, Montana	Mining	Smedley et al, 2002
	Lake Oahe, south Dakota	Mining	Smedley et al, 2002
	Geyser Bight Umnak Island, Alaska	Geothermal field	Smedley et al, 2002
	Honey Lake Basin, California	Geothermal field	Smedley et al, 2002
	Coso Hot Springs, California	Geothermal field	Smedley et al, 2002
	Imperial Valley, California	Geothermal field	Smedley et al, 2002
	Long Valley, California	Geothermal field	Smedley et al, 2002
	Steamboat Springs, Nevada	Geothermal field	Smedley et al, 2002
	Yellowstone National Park	Geothermal field	Smedley et al, 2002
	Lassen Volcanic National Park, California	Geothermal field	Smedley et al, 2002
	South-eastern Michigan		www.epa.gov/glnpo/solec/2002/d2/Groundwater_Norm.Final.pdf
South America			
Argentina	Chaco-Pampean Plain	Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash, often situated in closed basins (<1-5300).	Smedley et al, 2002, Alaerts and Khouri, 2004
	Parts of Salta and Jujuy Provinces	Geothermal field	Smedley et al, 2002, Alaerts and Khouri, 2004
Bolivia	Southern Altiplano (dept. Potosi)	Geothermal field	Alaerts and Khouri, 2004
Chile	Antofagasta area	Quaternary volcanogenic sediments (100-1000)	Smedley et al, 2002, Alaerts and Khouri, 2004
	El Tatio system in the Antofagasta region	Geothermal field	Smedley et al, 2002, Alaerts and Khouri, 2004
Dominica		Geothermal field	Smedley et al, 2002
Jamaica			www.umeciv.maine.edu/MacRae/where_is_arсениc_a_problem.htm
Peru		Mining	Bech et al, 1997

Australia			
New Zealand	Lake Ohakuri	Geothermal field	Smedley et al, 2002
	Wairakei	Geothermal field	Smedley et al, 2002
	Broadlands	Geothermal field	Smedley et al, 2002
	Orakei Korako	Geothermal field	Smedley et al, 2002
	Atiamuri	Geothermal field	Smedley et al, 2002
Australia	Southeast Queensland		Preda and Cox, 2002
	New South Wales	Industry	Smith et al, 2003, Barwick and Maher, 2003, Martley et al, 2004
Africa			
Ghana	Ashanti Region, Central Ghana	Au mining	Smedley et al, 2002, Alaerts and Khouri, 2004
Zimbabwe		Mining	Smedley et al, 2002
South Africa		Mining	Smedley et al, 2002