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resources
assessment
centre

Fluoride in groundwater:

Probability of occurrence of excessive concentration on global scale

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Utrecht
April 2004

Report nr. SP 2004-2

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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 fluoride and to display the probable occurrence of fluoride on continental maps. Approach used in this project combines the results of the literature study (fluoride analyses and geochemical knowledge) with spatial information on geology and climate.

1.2 Fluoride in groundwater

Fluoride is an ion of the chemical element fluorine which belongs to the halogen group.
Fluoride has a significant mitigating effect against dental caries if the concentration is approximately 1 mg/l. However, continuing consumption of higher concentrations can cause dental fluorosis and in extreme cases even skeletal fluorosis. High fluoride concentrations are especially critical in developing countries, largely because of lack of suitable infrastructure for treatment (http://www.wateraid.org).

Fluoride is a common constituent of groundwater. Natural sources are connected to various types of rocks and to volcanic activity. Agricultural (use of phosphatic fertilizers) and industrial activities (clays used in ceramic industries or burning of coals) also contribute to high fluoride concentrations in groundwater.

2 Factors affecting the natural fluoride concentrations

2.1 Geology

During weathering and circulation of water in rocks and soils, fluorine can be leached out and dissolved in groundwater and thermal gases. The fluoride content of groundwater varies greatly depending on the geological settings and type of rocks. The most common fluorine-bearing minerals are fluorite, apatite and micas. Therefore fluoride problems tend to occur in places where these minerals are most abundant in the host rocks.

Igneous and volcanic rocks have a fluorine concentration from 100 ppm (ultramafic) up to >1000 ppm (alkalic) (Frencken, 1992). In general fluorine accumulates during magmatic crystallization and differentiation processes of the magma. Consequently, the residual magma is often enriched in fluorine. Groundwaters from crystalline rocks, especially (alkaline) granites (deficient in calcium) are particularly sensitive to relative high fluoride concentrations. Such rocks are found especially in Precambrian basement areas.
The fluorine, which cannot be incorporated in crystalline phase during crystallization and differentiation of magmas, will be accumulated in hydrothermal solutions. These fluids may form hydrothermal fluorite deposits and veins. Fluorine transport in these aqueous solutions is controlled mainly by the solubility of CaF_2 (Allmann et al, 1974).
Further, of the volcanic series, the (calc-) alkaline volcanoes, typical of a continental rift (East Africa), hot spot, continental margin (Andes) or island arc (Japan), produce relative fluorine rich lava. (Rosi et al, 2003).

Sedimentary rocks have a fluorine concentration from 200 ppm (limestone) up to 1000 ppm (shales) (Frencken et al, 1992). In carbonate sedimentary rocks the fluorine is present as fluorite. Clastic sediments have higher fluorine concentrations as the fluorine is concentrated in micas and illites in the clay fractions. High concentrations may also be found in sedimentary phosphate beds (shark teeth) or volcanic ash layers (Frencken et al, 1992).

Metamorphic rocks have a fluorine concentration from 100 ppm (regional metamorphism) up to more than 5000 ppm (contact metamorphism). In these rocks the original minerals are enriched with fluorine by metasomatic processes (Frencken et al, 1992).

2.2 Contact time

The ultimate concentration of fluoride in groundwater largely depends on reaction times with aquifer minerals. High fluoride concentrations can be built up in groundwaters which have long residence times in the aquifers. Such groundwaters are usually associated with deep aquifer systems and a slow groundwater movement.

Shallow aquifers which contain recently infiltrated rainwater usually have low fluoride. Exceptions can occur in shallow aquifers situated in active volcanic areas affected by hydrothermal alteration. Under such conditions, the solubility of fluorite increases with increasing temperature and fluoride may be added by dissoluition of HF gas (Frencken et al, 1992 and http://www.wateraid.org.uk/in_depth/in_depth_publications/groundwater/default.asp).

2.3 Climate

Arid regions are prone to high fluoride concentrations. Here, groundwater flow is slow and the reaction times with rocks are therefore long. The fluoride contents of water may increase during evaporation if solution remains in equilibrium with calcite and alkalinity is greater than hardness. Dissolution of evaporative salts deposited in arid zone may be an important source of fluoride.

Fluoride increase is less pronounced in humid tropics because of high rainfall inputs and their diluting effect on the groundwater chemical composition (Frencken et al, 1992 and (http://www.wateraid.org.uk/in_depth/in_depth_publications/groundwater/default.asp).

2.4 Chemical composition of groundwater

High-fluoride groundwaters are mainly associated with a sodium-bicarbonate water type and relatively low calcium and magnesium concentrations. Such water types usually have high pH values (above 7).

Information on chemical composition of groundwater can be used as an (proxy) indicator of potential fluoride problems. The formation of fluoride rich waters is described by Frencken et al., (1992) and on http://www.wateraid.org.uk/in_depth/in_depth_publications/groundwater/default.asp.

2.5 International standards for drinking water

The WHO guideline value for fluoride in drinking water is 1.5 mg/l. Above 1.5 mg/l mottling of teeth may occur to an objectionable degree. Concentrations between 3 and 6 mg/l may cause skeletal fluorosis. Continued consumption of water with fluoride levels in excess of 10 mg/l can result in crippling fluorosis.

In many arid regions, drinking water is such a scarce commodity that governments have been forced to set the standard at higher levels, in order to have any drinking water at all.

3 Probability of occurrence of excessive fluoride concentrations

Various publications and web-sites were consulted to obtain information about the occurrence of fluoride in groundwater. An overview of regions with groundwater containing fluoride in excess of 1.5 mg/l is given in Appendix 1. Table in Appendix 1 contains also information on the fluoride source rock and the climate.

As already outlined in section 2.1, the potential fluoride rich environments are mainly linked with the Precambrian basement areas and areas affected by recent volcanism.

The Meig's classification adapted by Milich (1997) was used to characterize main climatic types according to precipitation/potential evaporation ratio (P/PE):

- hyper arid (P/PE<0.03)
- arid (P/PE<0.20)
- semi arid (P/PE<0.50),
- dry subhumid (P/PE<0.65),
- moist subhumid (P/PE<0.75)
- humid (P/PE>0.75).

Published country-based information about fluoride was combined with information regarding the geology and climate to assess the probability of occurrence of excessive fluoride concentrations. Four probability classes are distinguished:

I. High-probability:
   - Geological formation with a fluoride contaminated groundwater area, situated in a hyper-arid or arid zone.

II. Medium-probability:
   - Geological formation with a fluoride contaminated groundwater area, situated in a semi-arid or dry-subhumid zone.
   - Geological formation or area, which has the characteristics of a potential fluoride rich environment, and is either a) located in a known fluoride problem country (according to IGRAC and/or Unicef) or b) adjoined to a fluoride problem country with the same geological formation crossing the border. In the second case no further evidence of fluoride contaminated groundwater is found in the literature so far. The climate is hyper-arid, arid or semi-arid in both cases.

III. Low-probability:
   - Geological formation with a fluoride contaminated groundwater area, which continues in a moist subhumid or humid climate.
   - Geological formation or area, which has the characteristics of a potential fluoride rich environment, and is either a) located in a known fluoride problem country (according to IGRAC and/or Unicef) or b) adjoined to a fluoride problem country with the same geological formation crossing the border. In the second case no further evidence of fluoride contaminated groundwater is found in the literature so far. The climate is dry-subhumid, moist- subhumid or humid in both cases.

IV. Assumed-probability:
   - Geological formation or area, which has the characteristics of a potential fluoride rich environment, but is not located in a known fluoride problem country (according to IGRAC

and/or Unicef), and no further evidence of fluoride contaminated groundwater is found in the literature so far. The climate is hyper-arid, arid, semi-arid or dry-subhumid.

The above categories were used in preparation of continental maps showing the probability of occurrence of excessive fluoride concentrations. A fifth class "not confirmed" was added. This class refers to those countries which were indicated by IGRAC (**www.igrac.nl**) and/or Unicef (**http://www.unicef.org/wes/fluoride.pdf**) as having problem with fluoride in groundwater but which have no specific information on fluoride source and its distribution.

The probability classes and corresponding colours appearing on the maps are summarized in Table 1.

Table 1 Probability classes used on the continental maps

Probability	**Hydrogeology**	**Climate**	**Additional references**
	Formation with F-rich groundwater	Hyper-arid/arid	yes
	Formation with F-rich groundwater	Semi-arid/dry-subhumid	yes
	Potential F-rich + known fluoride-problem country (or neighbouring)	Hyper- to semi-arid	no
Low	Formation with F-rich groundwater	Moist-subhumid/humid	yes
	Potential F-rich in known fluoride-problem country (or neighbouring)	Dry subhumid to humid	no
	Potential F-rich *not* in known fluoride-problem country	Hyper-arid/dry-subhumid	no
	Not known	Not known	no

The geological world map (CGMW/UNESCO, 2000) was used to delineate the extent of endogenous (plutonic and metamorphic) rocks and extrusive volcanic rocks, which are assumed to be the main source of fluoride.

Information on spatial extent of climatic zones for individual continents was obtained from Milich (1997).

The six continental maps are shown in figures 1 to 6.

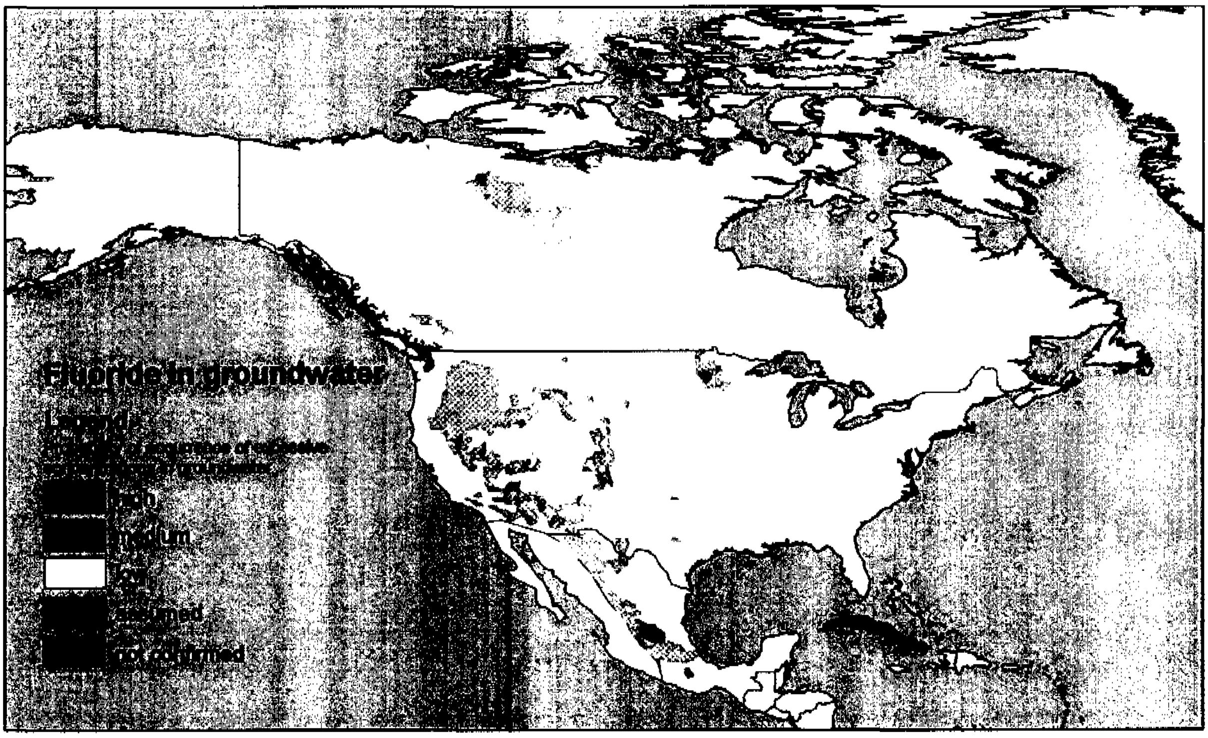

Figure 1: Fluoride in groundwater in North and Central America

Figure 2 Fluoride in groundwater in South America

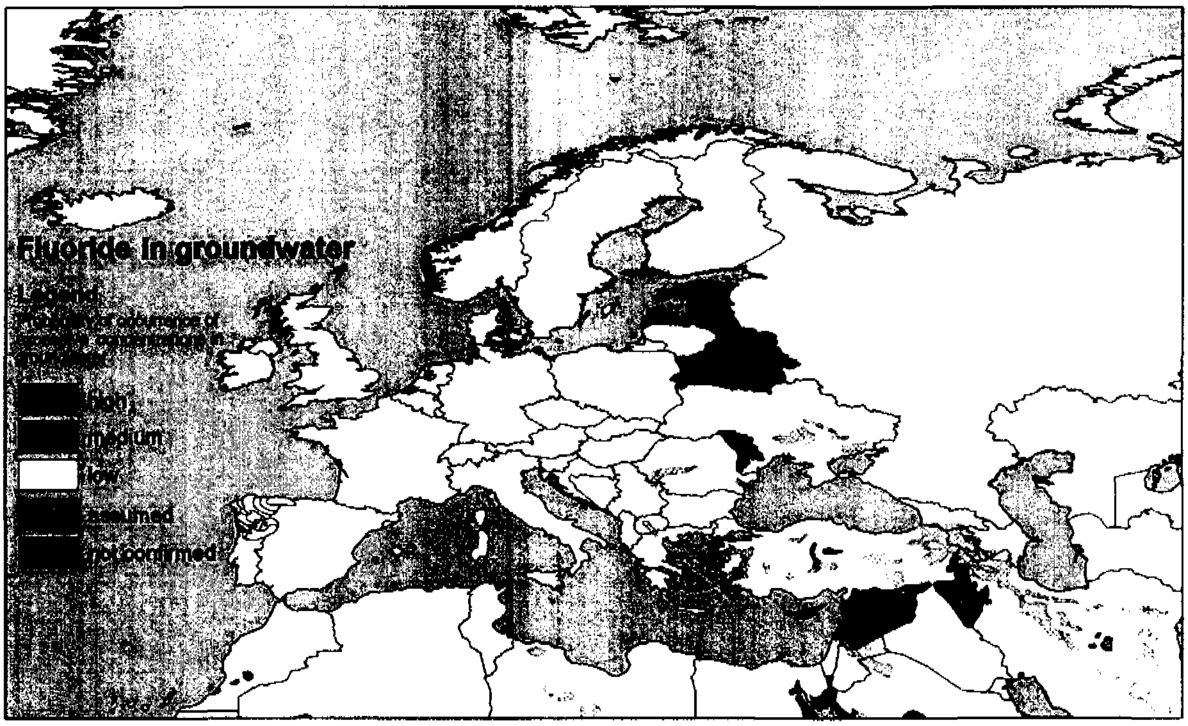

Figure 3 Fluoride in groundwater in Europe

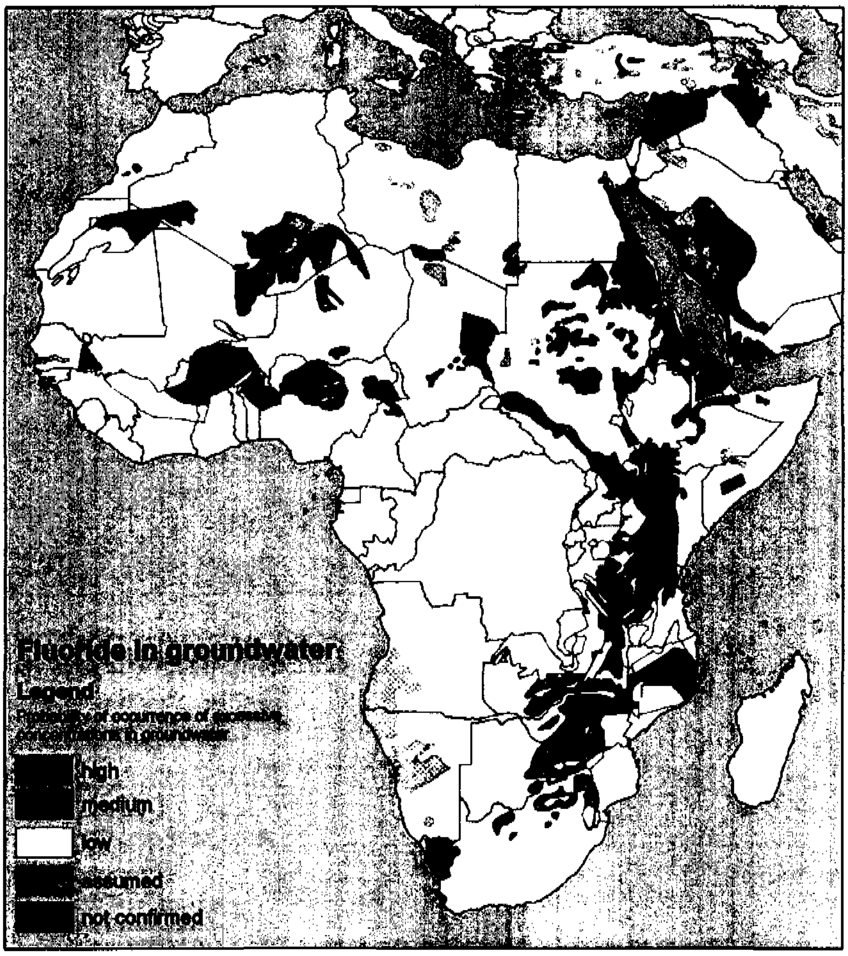

Figure 4 Fluoride in groundwater in Africa

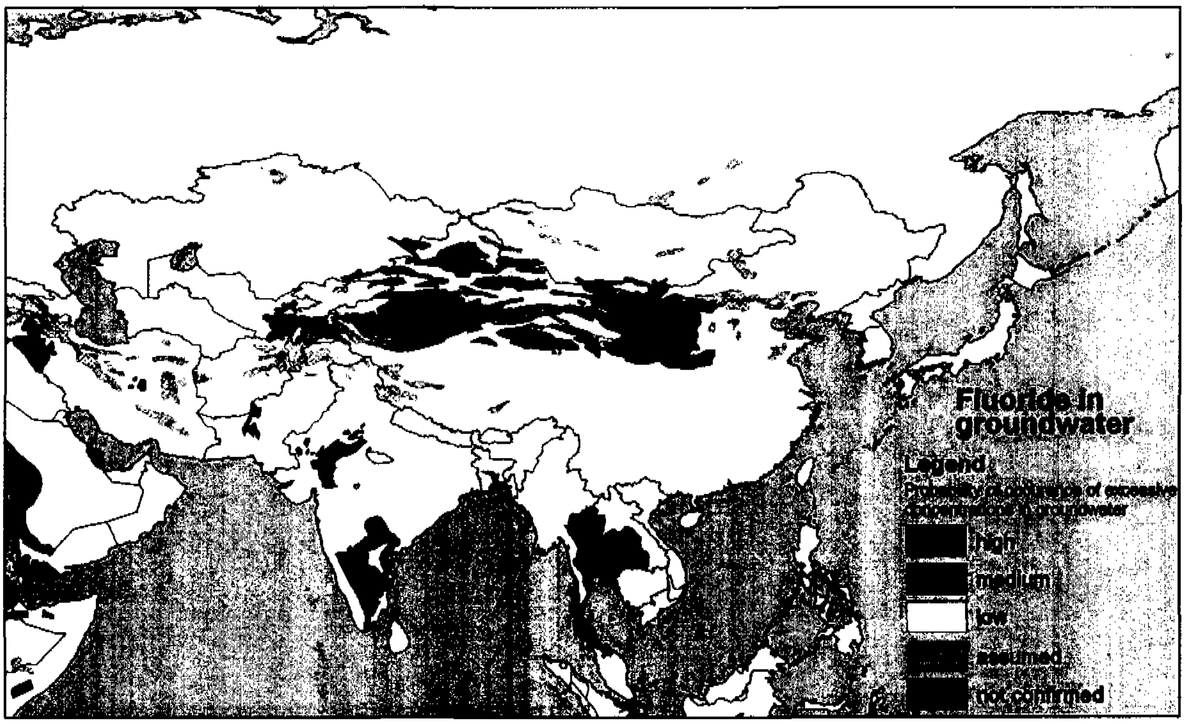

Figure 5 Fluoride in groundwater in Asia

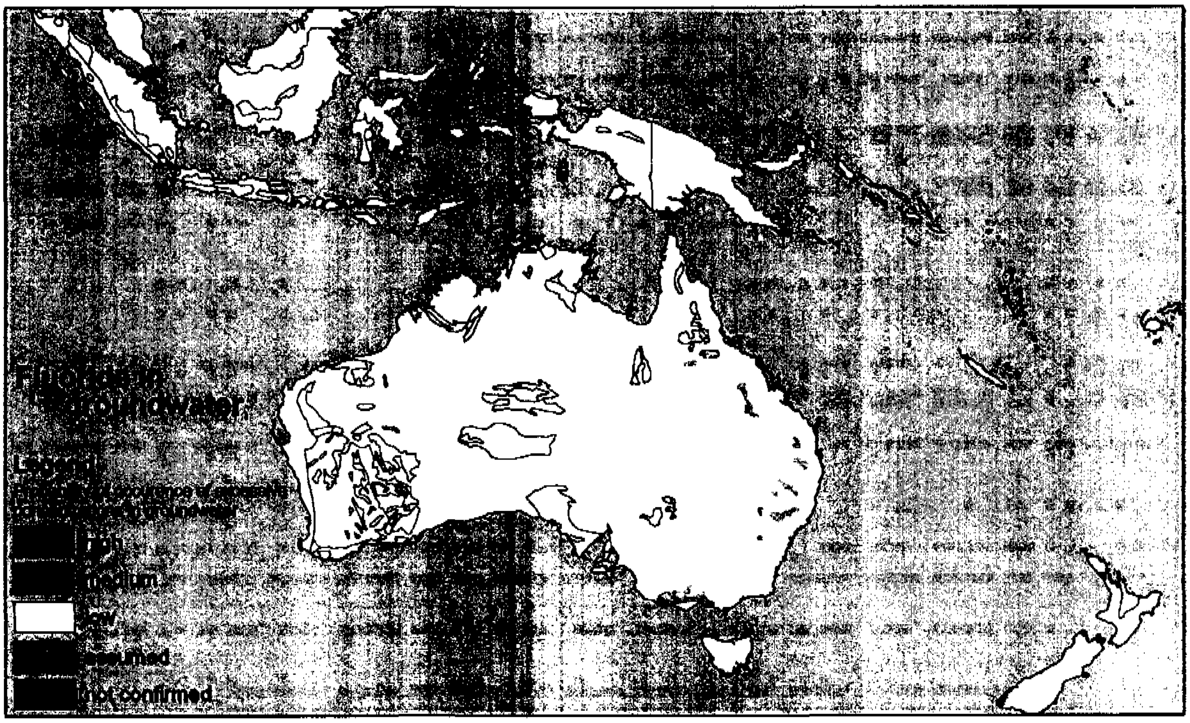

Figure 6 Fluoride in groundwater in Oceania

4 Concluding remarks

This IGRAC's special project resulted in refining of boundaries of regions which have been reported as having problems with high fluoride concentrations in groundwater. Additional regions were defined as potential sources of fluoride rich groundwater on the basis of a geological map of the world, distribution of climatic zones and geochemical knowledge.

The geological map used, distinguishes only four types of formations: sedimentary rocks, endogenous rocks (plutonic and metamorphic), extrusive volcanic rocks and Quaternary (unconsolidated) sediments and focuses rather on chronostratigraphy than on lithostratigraphy. The large scale of the map (1:25 000 000) allows only for a general insight in distribution of potential fluoride rich formations. More detailed lithological information is therefore needed, especially on the distribution of granitic rocks. As outlined in section 2.1, granites often consist of residual magma melts, and during the intrusion, contact metamorphism will enrich the host rock with fluorine by metasomatic processes.

The available geological map largely indicates only the rocks at the surface. A multilayered aquifer system may include rock formations which act as sources of fluoride at various depths. Cross sections of potential contaminated areas would increase the accuracy of the fluoride maps as well.

Depending on the flow direction of the groundwater, also aquifers neighboring fluorine-rich formation can be contaminated with fluoride. However, the groundwater flows were not taken into account during this study.

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

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http://www.wateraid.org.uk/in_depth/in_depth_publications/groundwater/default.asp

Appendix 1 Regions with a fluoride concentration above 1.5 mg/l

Country	Region	Source rock	Climate*	Prob**	References
Asia					
China	Northwest (over 5 mg/l)	Sandstone (Jurassic, Cretaceous and Tertiary) and (semi-)cemented or loose sand -graval rocks (Quaternary)	1,2,3	H-M-A	Genxu et al, 2001
	Huhhot basin (up to 6.8 mg/l)	Lacustrine and fluvial sediments (Quaternary)	3	M-A	Smedley et al, 2003
India	Southern provinces: Andra Pradesh, Tamil Nadu and Karnataka (up to 20 mg/l)	Archean basement	3,4	M-A	http://www.wateraid.org/in_depth/in_depth_publications/groundwater/default.asp
	Northwest	Archean basement	2,3,4,5	M-L-A	***
Indonesia	Locally possible	Volcanic (ash, hydrothermal, lava)	4,5,6	L	***
Iraq	Northeast	Calc-alkaline to alkaline igneous rocks (Upper Cretaceous-Miocene)	2,3,4	M	Al-Hafdh et al, 1992
Iran	North and Central	Alkalic granites (Precambrian)	2,3,4	M-A	Samani, 1988
Israel	South	Alkalic granites (Precambrian)	1,2	M-A	Beyth et al, 1994
Japan	Kitakami Mountains	Mesozoic granites	6	L	Kanisawa, 1979
	Hokkaido	Volcanic (Cenozoic)	6	L	Africano et al, 2000
Jordan	Southern point	Crystalline Precambrian basement (granites)	1,2	M-A	***
Kazakhstan	Southeast	Cenozoic sediments	3	M-A	***
Lebanon			3,4	A	Http://www.unicef.org/wes/fluoride.pdf
Pakistan	Nearby Quetta	Calc-alkaline granitic plutons (Cret.)	2	M-A	Lawrence et al, 1981
Qatar			1,2		Http://www.igrac.nl
Saudi Arabia	West	Precambrian granites	1,2	M-A	***
Sri Lanka	Almost entire country	Precambrian granites	4,5,6	L	Dissanayake et al, 1986
Syria			2,3,4	A	Http://www.unicef.org/wes/fluoride.pdf
Tajikistan			2,3,4,5,6	A	Http://www.igrac.nl
Thailand			5,6		Http://www.igrac.nl
Vietnam	South	Mesozoic granites	6	L	Nguyen Thi Bich Thuy, et al, in press, and ***
Yemen	West	Volcanic (hydrothermal) and Precambrian granites	1,2,3	M-A	Fara et al, 1999, and ***

Appendix 1 (continued)

Country	Region	Source rock	Climate*	Prob**	References
Africa					
Angola	Southwest and East	Crystalline Precambrian basement (granites)	2,3,4,5,6	L-A	***
Algeria	South and West	Crystalline Precambrian basement (granites)	1,2,3	H-M-A	***
Benin	North	Crystalline Precambrian basement (granites)	3,4,5,6	M	***
Botswana	East	Crystalline Precambrian basement (granites)	3	M	***
Burkina Faso	Almost entire country	Crystalline Precambrian basement (granites)	3,4,5	M-L	Http://www.wateraid.org/in_depth/in_depth_publications/groundwater/default.asp
Cameroon	North	Crystalline Precambrian basement (granites)	2,3,4,5,6	M-A	***
Central African Republic	Eastern parts	Crystalline Precambrian basement (granites)	3,4,5,6	L	***
Chad	Border with Libya and Sudan	Crystalline Precambrian basement (granites)	1,2,3,4	M-A	***
Egypt	Border with the Red Sea	Crystalline Precambrian basement (granites)	1,2	M	***
Eritrea	Almost entire country	Crystalline Precambrian basement (granites) and Rift volcanics	2,3	H-M	***
Ethiopia	Central and Western parts	Crystalline Precambrian basement (granites) and Rift volcanics	2,3,4,5,6	H-M-L-A	Http://www.wateraid.org/in_depth/in_depth_publications/groundwater/default.asp
Ghana	Upper Regions	Crystalline Precambrian basement (granites)	4,5,6	M-L	Http://www.wateraid.org/in_depth/in_depth_publications/groundwater/default.asp
Guinea	Northeast	Crystalline Precambrian basement (granites)	4,5,6	L	***
Ivory Coast	Upper Regions	Crystalline Precambrian basement (granites)	5,6	L	***
Kenya	West	Crystalline Precambrian basement (granites) and Rift volcanics	2,3,4,5,6	H-M-L	***
Libya	Border with Chad	Crystalline Precambrian basement (granites)	1,2,3	M-A	***
Malawi	Almost entire country	Crystalline Precambrian basement (granites)	4,5,6	M-L	***
Mali	Northeast	Crystalline Precambrian basement (granites)	1,2,3,4,5,6	H-M-L	Http://www.wateraid.org/in_depth/in_depth_publications/groundwater/default.asp
Morocco	Few areas in the Middle and South	Crystalline Precambrian basement (granites)	1,2,3,4	M-L	***
Mozambique	Central and Northern parts, border with Malawi	Crystalline Precambrian basement (granites) and Rift volcanics	3,4,5,6	M-L	Http://www.wateraid.org/in_depth/in_depth_publications/ground

Appendix 1 (continued)

Country	Region	Source rock	Climate*	Prob**	References
Africa					
Namibia	North, Central and South	Crystalline Precambrian basement (granites)	1,2,3	M-A	***
Niger	North and Southwest	Crystalline Precambrian basement (granites)	1,2,3	M	***
Nigeria	Northern, Eastern and Western parts	Crystalline Precambrian basement (granites)	2,3,4,5,6	M-L	***
Senegal	Eastern parts	Crystalline Precambrian basement (granites)	2,3,4,5,6	M	***
Somalia	Relative small areas in the North and South	Crystalline Precambrian basement (granites)	1,2,3	M-A	***
South Africa	Several areas in the North and West	Crystalline Precambrian basement (granites)	2,3,4,5,6	M-L	***
Sudan	Several areas in the Central, Southern and Eastern part	Crystalline Precambrian basement (granites)	1,2,3,4,5,6	H-M-A	***
Swaziland	Almost entire country	Crystalline Precambrian basement (granites)	3,4,5,6	M-L	***
Tanzania	Almost entire country	Crystalline Precambrian basement (granites) and Rift volcanics	3,4,5,6	M-L	Http://www.wateraid.org/in_depth/in_depth_publications/groundwater/default.asp
Uganda	Western and Central parts and border with Kenya	Crystalline Precambrian basement (granites)	3,4,5,6	M-L	Http://www.wateraid.org/in_depth/in_depth_publications/groundwater/default.asp
Zambia	East and Central	Crystalline Precambrian basement (granites) and Rift volcanics	3,4,5,6	M-L	Http://www.wateraid.org/in_depth/in_depth_publications/groundwater/default.asp
Zimbabwe	Almost entire country	Crystalline Precambrian basement (granites)	2,3,4,5,6	M-L	***
Australia					
Australia	Mainly areas of Western and Central Australia	Precambrian basement	2,3,4,5,6	L-A	***
New Zealand	Ruapehu and Taupo volcano, North Island	Volcanic gases and ash	6	L	Http://www.gns.cri.nz/

Appendix 1 (continued)

Country	Region	Source rock	Climate*	Prob**	References
Europe					
Belarus			5,6		Http://www.igrac.nl
Cyprus			3		Http://www.igrac.nl
Estonia			6		Http://www.igrac.nl
Latvia			6		Http://www.igrac.nl
Moldova			3,4,5		Http://www.igrac.nl
Portugal	North	Calc-alkaline granites, Paleozoic	3,4,5,6	L	Dias et al, 1998
Spain	Northeast	Endogenous rocks, Upper Paleozoic	4,5	L	Schwartz et al, 1973
	Nortwest	Calc-alkaline granites, Paleozoic	3,4,5,6	L	Galan et al, 1989, Roman-Berdiel et al, 1995
	Southeast	Calc-alkaline volcanism	3	M	Weijermars, 1991
Turkey	Mid Anatolia	Calc-alkaline granites, Cretaceous	3	M-A	Ilbeyli et al, 2004
	Southeast	Calc-alkaline to alkaline igneous rocks, Proterozoic	3,4	M-A	***
America's					
Argentina	Andes	Calc-alkaline volcanism Mesozoic, Cenozoic	2,3,4,5,6	M-L	Franchini et al, 2003, Coira et al, 1982, Francis et al, 1980, Siebel et al, 2001
	Southwest of Buenos Aires province	Bedrock and clastic sediments, Upper Paleozoic	3,4	M	Ainchil, 2003, and ***
	Central West	Calc-alkaline granites, Upper Precambrian to Lower Paleozoic	2,3,4	M-L	Lira et al, 1997
	South	Calc-alkaline volcanism Mesozoic, Cenozoic	2,3,4	L	***
Bolivia	East	Crystalline Precambrian basement (calc alkaline granites)	4,5,6	L	***
	West	Calc-alkaline volcanism Mesozoic, Cenozoic	2,3	M	***
Brazil	North	Crystalline Precambrian basement (calc alkaline granites)	6	L	Lamarao et al, 2002, and ***
	Central	Crystalline Precambrian basement (calc alkaline granites)	6	L	Lamarao et al, 2002, and ***
	East	Crystalline Precambrian basement (calc alkaline granites)	3,4,5,6	M-L	Lamarao et al, 2002, and ***
	South	Crystalline Precambrian basement (calc alkaline granites)	6	L	Lamarao et al, 2002, and ***
Chile	Andes	Calc-alkaline volcanism Mesozoic, Cenozoic	1,2,3,4,5,6	M-L	D'Orazio et al, 2003, Breitkreuz, 1989, and ***

Appendix 1 (continued)

Country	Region	Source rock	Climate*	Prob**	References
America's					
Colombia	Andes	Calc-alkaline volcanism Cenozoic	6	L	Calvache et al, 1997, Droux et al, 1996, and ***
	Nevado del Ruiz volcano, Andes	Hydrothermal waters	6	L	Williams et al, 1990
Cuba			4,5,6		http://www.igrac.nl
Ecuador	Andes	Calc-alkaline volcanism Cenozoic	3,4,5,6	M-L	van Thourhout et al, 1992, Lavenu et al, 1992.
French Guiana	Almost entire country	Crystalline Precambrian basement (calc alkaline granites)	6	L	Vanderhaeghe et al, 1998
Guyana	North and South	Crystalline Precambrian basement (calc alkaline granites)	6	L	***
Mexico	San Luis Potosi (province)	Deep (thermal) groundwater, volcanic	3	M-A	Carrillo-Rivera et al, 1996
	West	(deep) Continental crust consist of high-K calc alkaline basalts, Cretaceous	1,2,3,4,5,6	L-A	Tardy et al, 1994
Paraguay	South	Crystalline Precambrian basement (calc alkaline granites)	6	L	***
Peru	Andes	Calc-alkaline volcanism Mesozoic, Cenozoic	2,3,4	M-L	Sandeman et al, 2004, and ***
Suriname	Central and South	Crystalline Precambrian basement (calc alkaline granites)	6	L	***
Uruguay	South and East	Crystalline Precambrian basement (calc alkaline granites)	6	L	***
Venezuela	South and East	Crystalline Precambrian basement (calc alkaline granites)	5,6	L	Dougan, 1977, and ***

* Climate	** Probability	*** No direct references.
1 = hyper-arid 2 = arid 3 = semi-arid 4 = dry-subhumid 5 = moist-subhumid 6 = humid	H = high-probability documented M = medium-probability documented L = low-probability documented A = assumed-probability	These areas are interpreted as a potential fluoride rich environment, based on their climate and geology, and often also based on neighboring fluoride-contaminated countries with comparable climate and geology

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