Essential and toxic elements in karst springs of Kashmir

Apart from air and dietary sources, drinking water serves as an important source of minor and trace elements for human consumption. More than 80% of trace elements are supplied through diet and 1–20% through water[1]. Of more than 80 trace elements, 14 are considered essential for good health. These elements in combined form affect bone and membrane structure (Ca, P, Mg, F), water and electrolyte balance (Na, K, Cl), metabolic catalysis (Zn, Cu, Se, Mg, Mn, Mo), oxygen binding (Fe) and hormone functions (I, Cr)[1]. B, Mn, Ni, Si and V may also be considered essential based on emerging information. Pb, Cd, Hg, As, Al, Li and Sn are considered as potentially toxic elements[2–5]. Though trace elements are present in small quantities, they play a crucial role in the human body. Inadequate intake of essential elements leads to impairment of relevant physiological functions, increased morbidity, mortality due to reduced immune defence systems and impaired physical and mental development[1,6].

Though of a great concern for health, data is not available on the levels of trace elements in the spring waters, which are the sole source of public water supplies in the southeastern part of Kashmir Valley. Here, we present a preliminary report on the levels of some minor and trace elements in these karst spring waters of this region. The objective of the study is to determine the aforesaid elements in the spring waters, verify their abundance with reference to the international standards for drinking water as established by WHO and ascertain that the elemental levels are in no way detrimental to the overall well-being of the populace consuming these spring waters.

Eighteen water samples from nine karst springs in the SE Kashmir valley (Figure 1) were collected in May 2008 (representing peak flow period) and November 2008 (representing lean flow period) and analysed for 18 trace elements (Zn, Cu, Se, Mn, Mo, Fe, Cr, B, Ni, Si, V, Pb, Cd, Hg, As, Al, Li and Sn) and four minor elements (Na, K, Mg and Ca). Most of these chemical constituents were determined using ICP–MS (PerkinElmer Sciex ELAN DRC II) at the Geochemistry Division, National Geophysical Research Institute (NGRI), Hyderabad. The detection limit of these elements is given in Table 1 and the accuracy is better than 5% (ref. 7). Concentrations of F and NO_3 were determined using a spectrophotometer, whereas Cl was determined using standard $AgNO_3$ titration technique following standard procedures[8].

A summary of the results is shown in Table 1.

The concentrations of group-I elements Na, K and Li in karst springs range from 1.1 to 13.4, 0.2 to 1.3 and 0.2 to 3.6 mg/l, with a mean value of 4.8, 0.6 and 1.5 mg/l respectively. It may be noted that average concentrations of Na and Li in these spring waters are lower than those reported in natural freshwater (groundwater) at 5.2 (ref. 9) and 10 μg/l (ref. 10) respectively. Potassium is usually not found in natural drinking water at significant levels. The concentrations of Ca and Mg, important for bone and cardiovascular health, range from 6.2 to 37.1 and 1.8 to 12.5 mg/l, with a mean value of 4.8 and 0.6 mg/l respectively. These concentration levels are higher than those in natural freshwater, i.e. 13.4 and 3.4 mg/l respectively[9].

B and Al (group-III elements) vary from 6.3 to 110.8 and 1.1 to 156.1 μg/l respectively; their average values are 35.5 and 34.9 μg/l. The average aluminium content which is a toxic element in natural freshwater is less than 50 μg/l. The average B content is higher than the average of 10 μg/l in natural waters.

Concentration of F ranges between 0.4 and 1.5 mg/l, with a mean value of 1.0 mg/l. Most of the samples fall within the optimal concentration required for dental health (0.5–1.0 mg/l). Chloride concentration in the water samples ranges from 1.2 to 8.5 mg/l, with an average of 3.7 mg/l, lesser than that characteristic of natural freshwater (5.2 mg/l)[9]. The concentrations of Se and

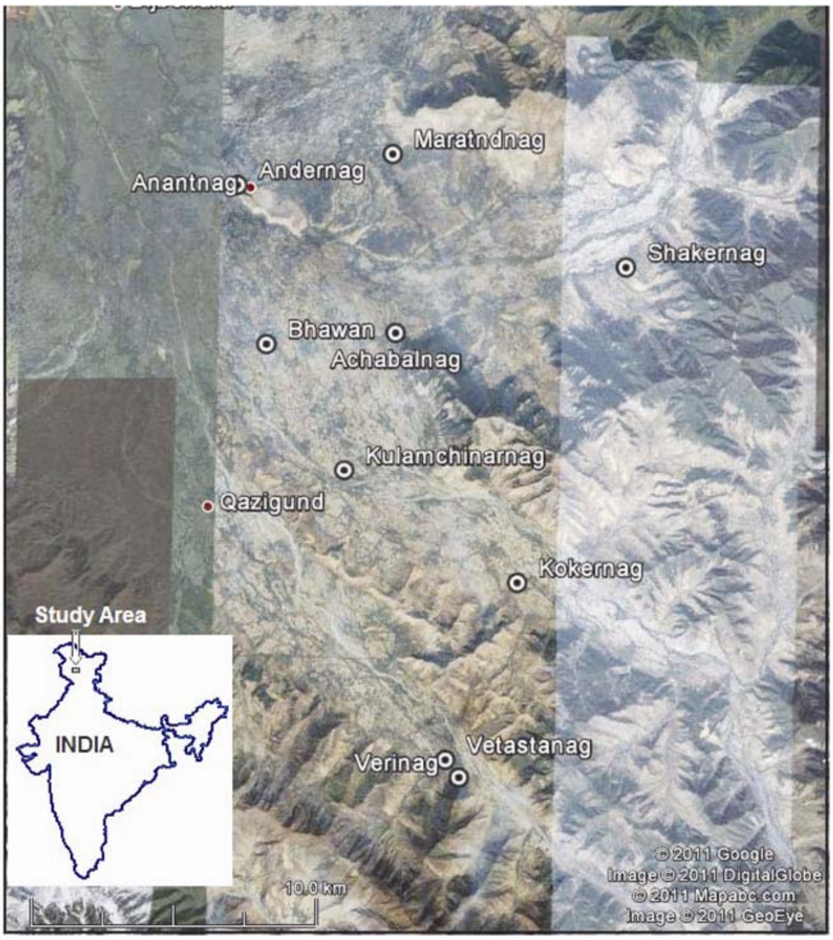

Figure 1. Map of SE Kashmir showing the location of the springs.

Table 1. Data on minor and trace elements in karst springs of Anantnag, Kashmir

Chemical species[#]	Detection limit (ppt)[7]	Minimum	Maximum	Average	SD	WHO Permissible limit	Bottled water
Ca	400	6.2	37.1	20.4	10.2	75–200	17.2[$]
Mg	20	1.8	12.5	7.1	3.3	50	7.5[$]
F	–	0.4	1.5	1	0.2	1.5	0.24[$]
Na	50	1.1	13.4	4.8	3.8	20	22.6[$]
K	500	0.2	1.3	0.6	0.2	12	3.4[$]
Cl	–	1.2	8.5	3.7	1.8	250	14.8[$]
Zn	40	2.5	138.2	24.3	32.9	5000	7.9[$]
Cu	5	0.4	32	4.8	9	2000	0.73[$]
Se	50	0.1	0.7	0.3	0.2	10	BD[€]
Mn	5	0.1	231.1	21	56.6	100	–
Mo	80	0.2	28.8	4.5	9.3	70	BD[€]
Fe	500	37.7	173.1	89.5	37	300	–
Cr	5	0.6	16.4	2.8	4.1	50	–
B	12	6.3	110.8	35.5	38.1	500	–
Ni	10	1.6	14.6	11.1	18.2	20	–
Si	–	0.2	8.3	3	2.2	–	–
V	10	0.2	23.4	2.9	5.9	–	BD[€]
Pb*	10	0	1.8	1	0.5	15	14.25[$]
Cd*	5	0	0.7	0.2	0.2	5–10	0.46[$]
Hg*	5	0.2	1	0.4	0.2	6	–
As*	5	0.1	8.3	1.2	2	10	–
Al*	10	1.1	156.1	34.9	41.9	200	–
Li*	10	0.2	3.6	1.5	1	–	–
Sn*	–	0	20.1	2.9	6.7	–	–
NO_3^*	–	1.3	4.9	3.5	0.9	50	1.35[$]

[#]Concentration units for Na, K, Ca, Mg, F, Cl and NO_3 in mg/l, other elements in μg/l.
BD, Below detection limit; *Potentially toxic elements; others are essential elements.
[$]Mahajan *et al.*[13]; [€]Babaji *et al.*[14].

Si range from 0.1 to 0.7 μg/l and 0.2 to 8.3 μg/l respectively.

V, Cr and Mo, essential trace elements, are in the range 0.2–23.4, 0.6–16.4 and 0.2–28.8 μg/l respectively, with mean concentration of 2.9, 35.5 and 4.5 μg/l respectively. Mean V, Cr and Mo concentration in freshwater is 0.5, 1.0 and 1.0 μg/l respectively. Therefore, there is relative enrichment of these elements in spring waters.

High levels of Fe and Mn in water are of concern (staining, odour, taste, etc). Fe and Mn concentrations in the karst springs of SE Kashmir range from 37.7 to 173.1 μg/l (average: 89.5 μg/l) and 0.1 to 273.1 μg/l (average: 21 μg/l) respectively. The mean concentration of Fe in the spring waters is lower than the maximum acceptable WHO limits (300 μg/l)[10] and that in natural freshwaters (500 μg/l)[9]. However, the mean concentration of Mn in the spring waters is higher than those in natural freshwaters (10 μg/l)[9] and the maximum acceptable WHO limits (100 μg/l)[10]. Concentration levels of Cu and Ni of 0.4 to 32 μg/l and 1.6 to 54.6 μg/l respectively, are also higher than their mean values in natural freshwaters[9].

Cd, Pb and Zn concentrations range from 0 to 0.7, 0 to 1.8 and 2.5 to 138.2 μg/l, the mean values being 0.2, 1.0 and 24.3 μg/l respectively. While mean concentrations of Cd and Pb are lower, Zn concentrations are higher than those in natural freshwaters[10].

Concentrations of highly toxic elements, Hg and As, are very low in the spring waters of the study area. Nitrate is low too.

The source of both essential and toxic elements in spring waters may be taken as lithogenic, as the area of study has not witnessed industrialization or any other significant anthropogenic activity, except, of course, limestone quarrying on a limited scale. Continuous monitoring of springs has revealed that elemental concentrations during the low discharge period are higher than those during the high discharge period. This may be simply related to dilution by glacial melt, snow melt and precipitation. Lower concentration of Ca (~6 to 37 mg/l) and/or Mg (~2 to 13 mg/l) is found in the karst springs. This is attributed to the less residence time of the infiltrating waters to interact with the host carbonate lithology[11]. This interpretation is supported by the highly fluctuating and dynamic nature of the karst spring discharges. However, the levels of all the trace and minor elements remain well within the permissible limits prescribed by WHO for drinking water[3].

It is worth mentioning here that bottled water contains only the major ions and the trace elements are generally below detection limit (Table 1). In comparison, karst spring waters are characterized by relatively moderate TDS, appreciably high and appropriate concentrations of minor elements and presence of necessary and vital trace elements. Therefore, they are not only good for drinking purposes, but are also more nutritious and conducive for human metabolism.

This precious source of drinking water, in the form of karst springs, which is the lifeline of the populace in SE Kashmir, needs to be conserved by judiciously restricting and monitoring anthropogenic activities, including limestone quarrying and spread of human settlements. This is particularly relevant as karst areas are more vulnerable to pollution[12].

1. National Academy of Sciences (NAS), *Drinking Water and Health*, National Academy Press, Washington, DC, 1977.
2. NAS, *Drinking Water and Health*, National Academy Press, Washington, DC, 1980, vol. 3.
3. WHO International Programme of Chemical Safety, *Guidelines for Drinking-Water Quality. Health Criteria and other Supporting Information*, World Health Organization, Geneva, 1996, vol. 2, 2nd edn.
4. WHO/FAO/IAEA. Trace elements in human nutrition and health. WHO, Geneva, 1996.
5. Pier, S. M. and Moon, K. B., *Environment and Health*, Ann Arbor Science Publishers Inc., The Butterworth Group, 1980, p. 367.
6. Faure, G., *Principles and Applications of Inorganic Geochemistry*, Maxwell Macmillan International, 1992.
7. Balaram, V. and Tao, T. G., *At. Spectrosc.*, 2003, **24**, 206–212.
8. APHA, AWWA, WEF, Standard methods for the examination of water and waste water. APHA-AWWA-WEF, Washington, 2001.
9. Ward, N. I., *Environmental Analytical Chemistry* (eds Fifield, F. W. and Haines, P. J.), Blackie Academic and Professional, Chapman and Hall, 1995.
10. WHO, Nutrients in drinking water. World Health Organization, Geneva, 2005.
11. Jeelani, G., Bhat, N. A., Shivana, K. and Bhat, M. Y., *J. Earth Sys. Sci.*, 2011, **120**, 921–932.
12. Ford, D. and Williams, P., *Karst Hydrogeology and Geomorphology*, John Wiley, 2007.
13. Mahajan, R. K., Walia, T. P. S. and Lark, B. S., *Int. J. Environ. Health Res.*, 2006, **16**, 89–98.
14. Babaji, I., Shashikiran, N. N. and Reddy, S. V. V., *J. Indian Soc. Pedo. Prev. Dent*., 2004, **22**, 201–204.

ACKNOWLEDGEMENTS. We thank the Head, Geochemistry Division, National Geophysical Research Institute, Hyderabad for providing the laboratory facilities. The work is a part of first author's INSA-Visiting fellowship.

Received 12 December 2011; revised accepted 6 September 2012

GH. JEELANI[1,*]
SHAKEEL AHMED[2]
A. ABSAR[3]

[1]*Department of Geology and Geophysics, University of Kashmir, Srinagar 190 006, India*
[2]*Indo-French Centre for Groundwater Research, National Geophysical Research Institute, Uppal Road, Hyderabad 500 007, India*
[3]*Thermax India Ltd, Pune 411 019, India*
**For correspondence.*
e-mail: geojeelani@gmail.com