with scan size  $3.3 \,\mu\text{m} \times 3.3 \,\mu\text{m}$  ( $256 \times 256 \,$  pixels resolution). The image cleary identifies 200 nm diameter perforations in the filter. Similarly, Figure 9 is a 200 nm  $\times$  200 nm ( $128 \times 128 \,$  pixels) scan of a polymer macromolecule with Trintoni X as surfactant.

- 1. Binnig, G., Quate, C. F. and Gerber, Ch., Phys. Rev. Lett., 1986, 56, 930.
- 2. Ferrell, T. L., Goundonnet, J. P., Reddick, R. C., Sharp, S. L. and Warmack, R. J., J. Vac. Sci. Technol., 1991, B9, 525-530.
- Hansma, P. K., Drake, B., Marti, O., Gould, S. A. and Prater, C. B., Science, 1989, 243, 641-643.
- 4. Williams, C. C. and Wickermasinghe, H. K., Appl. Phys. Lett., 1986, 49, 1587-1589.
- 5. Martin, Y. and Wickeramasinghe, H. K., Appl. Phys. Lett., 1987, 50, 1455-1458.
- 6. Sarid, D., Iams, D., Weissenberger, V. and Bell, L. S., Opt. Lett., 1980, 13, 1057.
- 7. Martin, Y., Williams, C. C., Wickramasinghe, H. K., J. Appl. Phys., 1987, 61, 4723.
- 8. Meyer, G. and Amer, N. M., Appl. Phys. Lett., 1986, 53, 2400.
- 9. Roher, H., Jpn. J. Appl. Phys., 1993, 32, 1335.
- 10. Hansma, P. K., Phys. Today, October, 1990.
- McClelland, G. M., Erlandsson, R. and Chiang, S., in Review of Progress in Quantitative Nondestructive Evaluation (eds Thompson, D. O. and Chimenti, E. E.), Plenum, New York, 1987, vol. 6B, p. 307.
- 12. Meyer, G. and Amer, N. M., Appl. Phys. Lett., 1988, 53, 1045.
- 13. Alexander, S., Hellenmans, L., Marti, O., Schneir, J., Elings, V.,

- Hansma, P. K., Longmire, M. and Gurley, J., J. Appl. Phys., 1989, 65, 164.
- 14. Rugar, D., Mamin, H. J., Erlandsson, R., Stern, J. E., Terris, B. D., Rev. Sci. Instrum., 1988, 59, 2337.
- 15. Sarid, D., Iams, D. and Weissenberger, V., Optics Lett., 1989, 13, 164.
- 16. Schonenberger, C. and Alvardo, S. F., Rev. Sci. Instrum., 1989, 60, 3131.
- 17. Burnham, N. A. and Colton, R. J., in Scanning Tunneling Microscopy and Spectroscopy: Technique and Applications (ed. Bonell, D. A.), VCH, New York, 1993.
- 18. Burnham, N. A., Colton, R. J. and Pollock, H. M., Nanotechnology, 1993, 4, 64.
- 19. Altman, E. I., Dilella, D. P., Ibe, J., Lee, K. and Colton, R. J., Rev. Sci. Instrum., May 1993, 64, 000.
- 20. Drake, B., Prater, C. B., Weisenhorn, A. L., Gould, S. A. C., Albrecht, T. R., Quate, C. F., Cannell, D. S., Hansma, H. G. and Hansma, P. K., Science, 1989, 243, 1586.
- 21. Marti, O., Drake, B. and Hansma, P. K., Appl. Phys. Lett., 1987, 51, 484.

ACKNOWLEDGEMENTS. We thank all the members of the STM/AFM group in CSIO, particularly Mr Vijay Mohal, Ms Jasjit Kaur, Mr Joginder Singh and Mr S. S. Bhiwani for experimental and technical support. The work done by Institue of Microbial Technology, Chandigarh in preparing biological samples is gratefully acknowledged. Our special thanks are for Dr R. J. Colton of Naval Research Laboratory, Washington DC for his advice on the design aspects of AFM. This development was sponsored by Instrumentation Development Programme (IDP) of Department of Science and Technology (DST), Govt of India. We are grateful to IDP-DST.

# Groundwater quality: Focus on fluoride and fluorosis in Rajasthan

Vinod Agrawal, A. K. Vaish and Prerana Vaish

The problem of high fluoride concentration in groundwater resources has now become one of the most important health-related geo-environmental issues in India. Rajasthan is one state where high fluoride groundwater is distributed in all the 31 districts and is influenced by the regional and local geological setting and hydrological conditions for the fluoride contamination. Studies have shown that nearly three million people are consuming excess fluoride-containing water; as such, the problem of both dental and skeletal fluorosis is widespread, specially in the rural population and in children.

FLUORINE is the most electronegative of all chemical elements and is therefore, never encountered in nature in the elemental form. It is seventeenth in the order of

frequency of occurrence of the elements, and represents about 0.06 to 0.09% of the earth's crust<sup>1</sup>. Fluoride is an essential ion for all living beings from the health point of view. It helps in the normal mineralization of bones and formation of dental enamel. Fluoride when consumed in inadequate quantities (less than 0.5 mg/l) causes health problems like dental caries, lack of formation of dental enamel and deficiency of mineralization

Vinod Agrawal is in the Department of Geology, M.L. Sukhadia University, Udaipur 313 002, India; A. K. Vaish is in the Department of Mines and Geology, Government of Rajasthan, Jaipur 302 004, India; and Prerana Vaish is in SARITA (NGO), 12 Rajendra Nagar, Gariawas Road, Udaipur 313 001, India.

of bones, specially among the children. On the contrary, if fluoride is consumed or used up in excess (more than 1.0 mg/l), it can cause different kinds of health problems which equally affect both young and old. Higher fluoride concentration exerts a negative effect on the course of metabolic processes and an individual may suffer from skeletal fluorosis, dental fluorosis, non-skeletal manifestation or a combination of the above<sup>2-5</sup>. The incidence and severity of fluorosis is related to the fluoride content in various components of environment, viz. air, soil and water. Out of these, water (specially groundwater) is the major contributor to the problem<sup>6</sup>.

# Distribution of fluoride in groundwater

Groundwater is an important resource for mankind's existence and economic development. Due to the scarcity of surface water, Rajasthan has to depend on groundwater resources to a great extent. In arid and semi-arid areas of the state, groundwater is the only water resource for drinking and agriculture purposes. The total groundwater resources of the state are 11,715.11 mcm, which appear to be inadequate compared to the rapidly increasing

Table 1. Number of villages and population exposed to high fluoride groundwater in Rajasthan

| Fluoride<br>content<br>(mg/l) | No. of affected villages | Total population under threat | No. of affected children below 7 years |
|-------------------------------|--------------------------|-------------------------------|--|
| 0.8–1.4                       | 269                      | 262,800                       | 54,183                                 |
| 1.5-2.9                       | 1467                     | 1,643,542                     | 331,754                                |
| 3.0-4.9                       | 668                      | 719,309                       | 146,168                                |
| 5.0-9.9                       | 255                      | 238,447                       | 51,659                                 |
| Above 10.0                    | 43                       | 35477                         | 7525                                   |
| Total                         | 2702                     | 2,899,581                     | 591,289                                |

Table 2. Number of villages (district wise) and the fluoride level in Rajasthan (value in mg/l)

| District    | 1.5–2.9 | 3.0-4.9     | 5.0–9.9 | 10.0 and<br>above | Total |
|-------------|---------|-------------|---------|-------------------|-------|
| Alwar       | 8       | 11          | 9       | _                 | 28    |
| Dausa       | 18      | 49          | 36 .    |                   | 103   |
| Jaipur      | 126     | 175         | 116     | 18                | 435   |
| Pali        | -       |             | _       | 4                 | 4     |
| Sikar       | 2       | 11          | 5       | i                 | 19    |
| S. Madhopur | 4       | <del></del> | 6       | 5                 | 15    |
| Bikaner     | 6       | 6           | 4       | _                 | 16    |
| Bharatpur   | 48      | 8           | _       | -                 | 56    |
| Dholpur     | 11      | 2           |         | _                 | 13    |
| Dungarpur   | 27      | 7           | 2       | <del>-</del> ·    | 36    |
| Jaisalmer   | -       | 85          | 3       | 3                 | 91    |
| Jalore      | 3       | 16          | 7       | 3                 | 29    |
| Nagaur      | 250     | 70          | 11      | 2                 | 333   |
| Sirohi      | 11      | 8           | 1       |                   | 20    |

demands for domestic and industrial uses<sup>7</sup>. The depth of water varies widely throughout the state. To the east of Aravalli, the depth is comparatively shallower than in the west. It generally varies between less than 10 and 25 m in the eastern part, whereas in the western part, it ranges between 20 and 80 m. The water level slopes towards the east and south-east on the eastern side, whereas to the west of the Aravalli, it slopes towards west and the north-west.

The problem of high fluoride concentration in ground-water resources has now become one of the most important toxicological and geoenvironmental issues in India. During the last three decades, the high fluoride concentration in water resources and the resultant disease 'fluorosis' is being highlighted considerably throughout the world. India is also confronting the same problem and about 25 million people in 8700 villages are consuming water having high fluoride<sup>8.9</sup>. According to the 'Survey of Status of Drinking Water Supply in Rural Habitation' conducted by the Rajiv Gandhi National Drinking Water Mission in 1993, there are 9741 villages and 6819 habitations having fluoride content more than 1.5 mg/l in groundwater sources.

Rajasthan is one state where fluoride in high level is present in all the 31 districts and has become a serious health-related issue in 23 districts, contrary to the earlier belief that only those districts coming under the 'Banka Patti' were affected<sup>10</sup>. The studies carried out by the Rajasthan Voluntary Health Association (RVHA) noticed that the total number of problem villages is 2702 which have high fluoride content in groundwaters and a substantial proportion of the population (i.e. around 3 million people) are using high-fluoride water sources. Moreover, nearly 35,000 people are consuming water having more than 10 mg/l of fluoride. The most interesting fact of the study is that one-fifth of the affected population are children below seven years of age. According to a survey conducted by the Public Health and Engineering Department under the Rajiv Gandhi National Drinking Water Mission, New Delhi, (between 1991 and 1993), the drinking water sources in 9741 (25.7%) out of 37,889 villages and 6819 (15%) out of 45,311 habitations were found to contain more than 1.0 mg/l of fluoride (the permissible limit according to WHO) in the water sources. Table 1 summarizes the number of villages and

Table 3. Fluoride content in various rocks

| Rocks                 | Fluoride range<br>(in ppm) | Average<br>(in ppm) |
|-----------------------|----------------------------|---------------------|
| Basalt                | 20–1060                    | 360                 |
| Granites and gneisses | 20-2700                    | 870                 |
| shales and clays      | 10-7600                    | 800                 |
| imestone              | 0-1200                     | 220                 |
| andstone              | 10-880                     | 180                 |
| Phosphorite           | 24,000-41,500              | 31,000              |
| Coals (ash)           | 40-480                     | 80                  |

Table 4. Fluorosis-affected districts and the prevailing geological setup

| _   | 50ttip                                       |   |
|---|--|---|
| District  | Most affected region/tehsil                  | Lithology   |
| Ajmer   | Kekri, Kishangarh                            | Mica-tourmaline pegmatites, alkali igneous rocks, mica-schists  |
| Alwar   | Lachmangarh, Rajgarh                         | Mica-bearing quartzite, lime-<br>stone (marble), granites,<br>calc-gneisses                                   |
| Banswara  | Bagidora, Ghatol,<br>Kushalgarh              | Basalts, limestone, granites, schist, carbonaceous phyllite   |
| Bhilwara  | Shahpura, Banera,<br>Mandal, Jahazpur, Asind | Mica-tourmaline pegmatite,<br>gneisses, mica-schists, lime-<br>stone, granites, sandstone,<br>fluorspar veins |
| Barmer  | Balotra, Chohtan, Sheo                       | Acid igneous rocks (apatite<br>and biotite bearing), mica<br>bearing sand, limestone,<br>clays                |
| Bikaner   | Bikaner, Kolayat                             | Clays, lignite, evaporites, sand  |
| Bundi   | Hindoli, Nenwa                               | Limestone, quartzite, sand-<br>stone  |
| Baran   | Anta .                                       | Quartzite, mica-schists   |
| Bharatpur   | Bayana, Deeg, Kaaman                         | Mica-bearing sandstone, quartzite   |
| Chittorgarh   | Begu, Chittorgarh,<br>Rashmi                 | Limestone, shale, clays, mica-schists   |
| Churu   | Ratangarh                                    | Lime kankar, granites, mica-<br>sand  |
| Dungarpur   | Aspur, Dungarpur,<br>Sagwara                 | Granite gneisses, mica-<br>schists, asbestos-bearing<br>ultra-basics, fluorspar<br>mineralization             |
| Dholpur   | Dholpur, Bari                                | Sandstone, quartzite  |
| Dausa   | Lalsot, Dausa                                | Dolomite, schists, quartzites   |
| Ganganagar  | Suratgarh                                    | Evaporites, mica-bearing sand   |
| Jalore  | Ahor, Sanchor                                | Granites, acid volcanics, mica-bearing sand, fluorspar mineralization   |
| Jhunjhunu   | Alsisar, Jhunjhunu,<br>Khetri                | Mica-bearing sand, mica-<br>hornblende-chlorite schists,<br>granites, limestone                               |
| Jaipur  | Bassi, Chaksu, Dudu,<br>Phagi                | Mica-quartzites, mica-bearing sand, clays, limestones   |
| Jodhpur   | Bilara, Phalodi                              | Sandstone, acid igneous rocks   |
| Jaisalmer   | Jaisalmer, Sanu                              | Limestone, sand, clay, shale  |
| Jhalawar  | Jhalrapatan, Dag                             | Basalts, limestone, sandstone   |
| Nagaur  | Didwana, Degana,<br>Makrana                  | Limestone, clays, mica-<br>bearing sand   |
| Pali  | Bali, Pali                                   | Mica-schists, acid igneous rocks, fluorspar minera-<br>lization   |
| Rajsamand   | Deogarh, Bhim                                | Gneisses, mica-schists, horn-<br>blende schists, crystalline<br>limestone                                     |
| Sirohi  | Pindwara, Reodar                             | Granites, gneisses, mica-<br>schists, acid igneous rocks,<br>fluorspar mineralization                         |
| Udaipur   | Sarada, Salumber                             | Gneisses, schists, amphi-<br>bolites, limestone, dolomite,<br>granites  |
| ر سیستند کی در بروی کاری در بروی کاری در بروی کاری در | · · · · · · · · · · · · · · · · · · ·        |   |

population affected by high fluoride groundwater in Rajasthan<sup>10</sup>. Village-wise distribution of fluoride level in the groundwater in some of the districts is given in Table 2.

### Status of fluorosis

The problem of fluorosis in the state has been known for a fairly long time. The term 'Banka Patti' (a strip of land where deformed people reside) has been in use in Rajasthan for over a century and refer to a specific belt near Makrana. The first case of skeletal fluorosis was reported in 1959 from Jobner (Jaipur district)<sup>11</sup>. Later Thergaonkar and Bhargava<sup>12</sup> reported the prevalence of dental fluorosis in parts of Jhunjhunu district. In the last few years many studies on the fluoride issue have been carried out and fluorosis was correlated with high concentration of fluoride in drinking water and a number of cases of fluorosis, both in human beings and domestic animals were reported from the state<sup>13-17</sup>.

'SARITA Udaipur', and we have carried out detailed assessment of fluoride content in groundwater sources in Dungarpur district and found that 150 villages are affected by the fluoride problem where the fluoride concentration was found between 1.5 mg/l and 8.5 mg/l. A number of cases of both skeletal and dental fluorosis were reported in these villages<sup>15,16</sup>. Besides, a substantial animal population is also suffering from the disease. The micro-level study reveals that the dental fluorosis is pronounced in those areas where fluoride content in groundwater is above 2.00 mg/l. But the skeletal fluorosis symptoms were observed only where the water contained more than 5.00 mg/l of fluoride. The non-skeletal manifestations are, however, commonly complained of by people living where fluoride is above 1.5 mg/l. It is estimated that nearly one lakh rural population in the district is being affected from the ill effects of the disease, whether it is dental fluorosis, skeletal fluorosis and/or non-skeletal manifestations. Similar studies are underway in Bhilwara district, where in 377 villages, the fluoride level in groundwaters ranges between 1.5 mg/l and 13 mg/l, thus affecting a population of nearly two lakhs<sup>18</sup>.

## Fluoride incidence and geological influence

Fluoride incidence in groundwater is mainly a natural phenomenon, influenced basically by the local and regional geological setting and hydro-geological conditions. The chief sources of fluoride in groundwaters are the fluoride-bearing minerals in the rocks and sediments. The important fluoride-bearing minerals are: fluorite (fluorspar), fluorapatite, cryolite, biotite, muscovite, lepidolite, tourmaline, hornblend series minerals, glucophane-riebeckite, asbestos (chrysotile, actinolite, anthophyllite),

sphene, apophyllite, zinnwaldite, etc. These minerals have sufficient amount of fluorine in their composition. Even in some minerals like micas where fluorine is present as minor constituent, the fluoride content is very high.

Biotite – Fluoride ranges from 970 to 3500 ppm. Phlogophite – Fluoride ranges from 3300 to 37,000 ppm. Lepidolite – Fluoride ranges from 19,000 to 68,000 ppm. Muscovite – Fluoride ranges from 170 to 14,800 ppm.

Since rocks are made up of minerals and the soil is derived from parent rocks, fluoride is fairly abundant in rocks and soil. Keller<sup>19</sup> gave the values of fluoride in various rocks (Table 3).

The weathering and leaching processes, mainly by moving and percolating water, play an important role in the incidence of fluoride in groundwater. The various factors that govern the release of fluoride into water by the fluoride-bearing minerals are (i) the chemical composition of water, (ii) the presence and accessibility of fluoride minerals to water, and (iii) the time of contact between the source mineral and water.

In Rajasthan the widespread fluoride-rich water and the prevalence of fluorosis in certain areas are also indicative of features of regional and local geological significance. Table 4 lists some of the important districts having fluoride-rich groundwater, along with the important geological features responsible for the fluoride incidence.

### Conclusion

The problem of high fluoride concentration in ground-waters in Rajasthan has to be tackled on a war footing<sup>18</sup>. It is high time that an affordable solution is found to minimize the fluoride contamination for maintaining the good health of the large population of the state. There is an immediate need to defluoride the water system either by community or by domestic defluoridation techniques. Demonstration-cum-awareness camps for the pur-

pose should be arranged in fluorosis-endemic areas. There is a need to carry out detailed fluoride mapping, hydrological studies for existing water sources to show flow lines and hydro-geochemical survey in areas where fluorosis is endemic. In the affected areas, the government should apply firm guidelines for the utilization of groundwater so that tube wells/hand pumps in high-fluoride zones could be discouraged. The short-term solution to minimize the fluoride level in drinking water could be the use of domestic defluoridation equipments or filters. An effort in this regard has been attempted by SARITA in a few villages of Aspur Panchayat Samiti in Dungarpur district which proved satisfactory and effective.

- I. WHO, WHO Geneva Report, 1994, 1-37.
- 2. Underwood, E. J., Trace Elements in Human and Animal Nutrition, Academic Press, New York, 1977, pp. 545.
- 3. WHO, WHO Geneva Publication, 1984, No. 36.
- 4. Singh, C. and Saimbi, C. S., Indian J. Environ. Health, 1988, 30, 163-167.
- 5. Machoy, Z., Dabkowska, E. and Nowicka, W., Env. Geochem. Health, 1991, 13, 161-163.
- 6. Gupta, M. K., Singh, V., Rajwanshi, P., Srivastava, S. and Das, S., Indian J. Environ. Health, 1994, 36, 43-46.
- 7. DST Rajasthan Publ., 1994, pp. 231.
- 8. Report on Control of Fluorosis Submission II, APPRR, 1987.
- 9. Handa, B. K., BHU Jal-News, 1988, 3, 31-34.
- 10. Rajasthan Voluntary Health Association Report, 1994, pp. 123.
- Kasliwal, R. M. and Solomon, S. K., J. Assoc. Phys., 1959, 7, 56-59.
- Thergaonkar, V. P. and Bhargava, R. K., Indian J. Environ. Health, 1974, 16, 168–180.
- 13. Mathur, G. M., Tamboli, B. L., Mathur, R. H., Roy, A. K., Mathur, G. L. and Goyal, O. P., *Indian J. Prev. Soc. Med.*, 1976, 7, 90-93.
- 14. Susheela, A. K., Rajiv Gandhi Drinking Water Mission Health Abst., 1993, vol. I.
- 15. Vaish, A. K., Ph D thesis, ML Sukhadia Univ., 1995, pp. 209.
- Vaish, A. K., Gyni, K. C. and Agrawal, V., MIN-ENV-95 Publ., 1995, pp. 38-46.
- 17. Choubisa, S. L., Sompura, K., Bhatt, S. K., Choubisa, D. K., Pandya, H., Joshi, S. C. and Choubisa, L., *Indian J. Environ. Health*, 1996, 38, 119–126.
- 18. SARITA Udaipur Project Report, SARITA, 1996, pp. 104.
- 19. Keller, E. A., Environmental Geology, Charles & Merril Publ. Co., Ohio, USA, 1979, pp. 548.