Phosphate pollution in the groundwater of lower Vamsadhara river basin, India

N. Srinivasa Rao · P. Rajendra Prasad

Abstract The lower Vamsadhara river basin, spreading over an area of 817 sq.km in northern Andhra Pradesh, represents a typical rural setting. The occurrence of phosphorus-bearing minerals reported in literature, and the increasing application of phosphatic fertilizers in the area have prompted these studies. Water samples from 113 wells were analysed for Ca, Mg, Na, K, Cl, SO_4, HCO_3, F, NO_3 and PO_4. The results indicate the presence of phosphate in the groundwater ranged from 0.72 to 7.07 mg/l, which is beyond the limits recommended for domestic and water treatment purposes. Samples of soils and weathered rocks were analyzed for their water-soluble phosphate and other chemical parameters. The water-soluble phosphate in the widely used fertilizers of the area was determined. The spatial variation of phosphate in the aquifer and the soil leachate characteristics supplemented by the chemical equilibrium calculations clearly indicate the dominance of geological sources over the fertilizer sources in contributing PO_4 to the groundwaters.

Key words Phosphate · Leachate · Vamsadhara river basin · Apatite

Introduction

Groundwater has become the major source of water supply for domestic, industrial and irrigation sectors of many countries. As a result, water quality and its management strategies have gained popularity in developing nations for the past two decades. The water quality management mainly involves the identification and analysis of the contaminants, their sources and possible remedial measures. In recent years there has been a phenomenal growth in the application of fertilizers in the agricultural sector. High concentrations of nitrate, phosphate and fluoride in groundwaters have been reported by several investigators (Gaumat and others 1992; Hamilton and Shedlock 1992; Handa 1983, 1990; Helgesen and others 1994; Jha and Jha 1982; Klimas and Paukstys 1993; Raju and others 1979), the sources of which are attributed to the increase in fertilizer application. Although phosphorus is not a harmful constituent in drinking water, its presence in groundwater can be of considerable concern and environmental significance. Phosphorus additions to waterbodies even in small amounts can produce accelerated growth of algae and aquatic vegetation, thereby causing eutrophication of the aqueous system (Handa 1990). This further causes problems in respect to odor and taste. The Canadian Department of National Health and Welfare (1969) has suggested a maximum limit of 0.2 mg/l for PO_4 in water, while that of the European Economic Community (Smeats and Amavis 1981) is 0.54 mg/l. In this context, the lower Vamsadhara river basin in India, representing a typical rural setting where fertilizer application has only been significant for the past 10 years, has been systematically studied for the occurrence and movement of phosphorus in the groundwater regime.

The Vamsadhara river basin, enclosed between Long. 83°50′–84°10′E and Lat. 18°15′–18°38′N, is a medium-sized, narrow, elongated, mature basin with its basin order reaching ‘six’ as per Strahler stream ordering method (Gardiner 1975). The study area (Fig. 1), spreading over 817 sq.km, is mostly covered by recent alluvium. The alluvial cover is underlain by rocks of varied petrological characteristics. Garnetiferous granite gneiss is the most abundant rock type (Padmanabhayya 1958; Suryanarayana 1957), while granite gneiss and khondalites (Rao personal comm. 1995) follow the sequence. The presence of pegmatite veins in these formations is common. Though the Vamsadhara is a perennial river, due to insufficient canal and drainage networks, inadequate quantities of surface water and poor management strategies, 80% of the domestic and agricultural needs of its catchment area are met from groundwater. The rich alluvial cover, comprising mostly black cotton soils, has facilitated agricultural activity. Apart from paddy, commercial crops like jowar, black gram, green gram, sugarcane, groundnut and gingelly are grown in the region. The farmers normally depend on conventional farmyard, pig and sheep, manure. However, in recent years indiscriminate use of fertiliz-

Received: 4 March 1996 / Accepted: 29 July 1996

N. S. Rao (✉) · P. R. Prasad
Department of Geophysics, Andhra University,
Visakhapatnam – 530 003, India

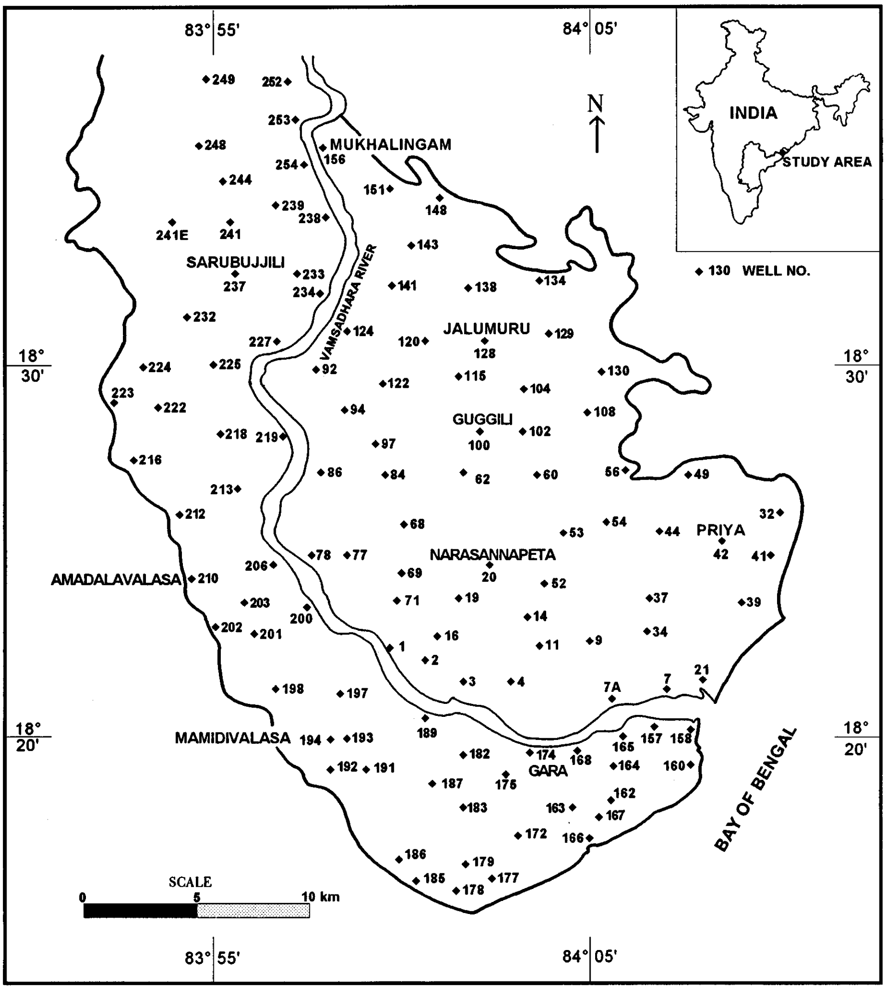


Fig. 1
Location map

ers such as Urea(CH_3CONH_2), NPK(nitrate, phosphorus, potassium:15,15,15) and superphosphate ($CaH_4(PO4)_2$) has become prevalent in the area. In general, the climate is dry with the temperatures ranging from 18 °C in winter to 40 °C in summer. The average annual rainfall is 910 mm.

Occurrence of phosphate

Phosphorus is an important constituent of the lithosphere. There is not a single living cell that can survive without phosphoric acid (Handa 1990). The strong bond of phosphate with clay minerals and metal hydroxides, particularly iron hydroxide, as well as its involvement in the biological cycle, are responsible for low concentrations of phosphate in groundwater (Matthess 1982).

Phosphorus occurs chiefly in apatite which is a calcium phosphate mineral with variable amounts of OH, Cl and F and various impurities (Matthess 1982; Hem 1986; Handa 1990). The modal composition of apatite at Kasipatnam near the study area located in the Eastern Ghat belt is as follows:

Apatite Composition (After Narasayya 1970)

CaO	54.06	F	3.29
MnO	0.05	Cl	0.35
P_2O_5	42.43	H_2O^+	0.16
CO_2	0.40	H_2O^-	0.02

The phosphorus content (as P) of various rocks, namely pyroxene, plagioclase, garnet, amphibole and biotite, is 89, 27, 185, 77 and 58 ppm, respectively (Handa 1990). These rocks are reported in the study area by Padmanabayya (1958), Suryanarayana (1957) and Rao (personal comm. 1995). The superphosphate and NPK(15,15,15) fertilizers may also act as important external source of phosphorus in groundwater in the area.

Methods

The groundwater samples (113) were collected mostly from open dug wells during the summer season (April 1993). The WHO and UNESCO standards were followed for collection and preservation of these samples while the vanadomolybdophosphoric acid colorimetric method

(American Public Health Association 1985) was used to determine the phosphorus content. Other major ionic concentrations namely chloride, sulphate, bicarbonate, calcium, magnesium, sodium, potassium, fluoride, iron, nitrate were also determined in the laboratory using standard methods (American Public Health Association 1985). In situ measurements were made for electrical conductivity, temperature, pH and dissolved oxygen. To determine the water-soluble phosphate content in the soils, 30 gm of the soil or powdered weathered rock sample is added to 300 ml distilled water and rigorously stirred for 6 h using a magnetic stirrer. The sample is filtered and then analysed for phosphate and the other chemical parameters. The saturation indices of related mineral and chemical facies are calculated through a computer programme, WATEQF, developed by the U.S. Geological Survey.

Results and discussion

The phosphorus content in groundwater, expressed as PO_4 for the pre-monsoon season (April 1993) varies from a minimum of 0.72 mg/l to a maximum of 7.07 mg/l (Fig. 2). Pockets of higher concentration are distributed in the entire area. The frequency distribution chart (Fig. 3) indicates that 44% of the samples contain PO_4 in the range 3.0–4.0 mg/l while 35% of them contain up to 2 mg/l. However, only 4 samples out of 113 contain PO_4 between 2.0 and 3.0 mg/l and hence are not considered. The distribution of PO_4 as can be seen from Figs. 3, 4a and 4b falls into three groups, i.e. ≤ 2.0 mg/l, 3.0–4.0 mg/l and >4.0 mg/l. A critical comparison of the distribution of PO_4 with the water table conditions and physiography of the area do not show any specific relationship.

The three major ranges of distribution of PO_4 have an apparent correlation with the surface and subsurface geology. The regions marked with $PO_4 \leq 2$ mg/l coincide either with thick sandy formations or with red sandy soils while the zones with 3.0–4.0 mg/l of PO_4 can be identified with the clayey horizons. The regions containing $PO_4 > 4$ mg/l are associated with thick weathered horizons of gneisses. To understand the overall quality of groundwater in the area, the other parameters in the above three horizons are given in Table 1.

The poor adsorption characteristics of PO_4 in sands are responsible for lower concentrations in the sand and red soil zones. The high concentrations of PO_4, recording more than 4 mg/l, are associated with weathered layers containing substantial quantities of apatites and pyroxene amphibolites. Of the region, 60% covered with a surface clay layer contains 3.0–4.0 mg/l of PO_4 in the groundwater. In this region, the water table is observed to fluctuate mostly within the clay zone and occassionally between the clay zone and the underlying sand layer. Phosphates are strongly adsorbed by fine-grained soils and are enriched due to the application of fertilizers in the region to the top layer. However, in this region the weathered gneisses, with or without the presence of apatite and pyroxene amphibolites, underlies the clay or sand layer. In a majority of the wells, the water table fluctuates between the weathered layer and the overlying clay layer, providing the suitable conditions for adsorption and enrichment of PO_4 in clay and subsequent partial release of PO_4 in groundwater. As a result, the groundwater in this formation records a PO_4 range of 3.0–4.0 mg/l.

As far as the use of fertilizers is concerned, the entire area receives more or less uniform doses of PO_4 and the irrigation practices do not differ significantly. A quantitative evaluation of the application of fertilizer in the area indicates a maximum supply of 2.35 mg/l PO_4 if the irrigation does not exceed 10 cm water column (50 kg/acre),

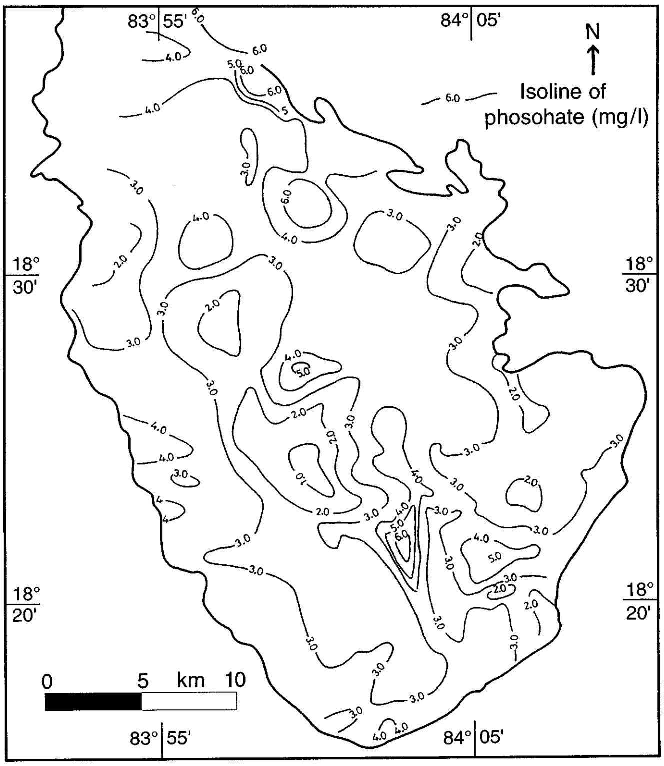


Fig. 2
Distribution of phosphate

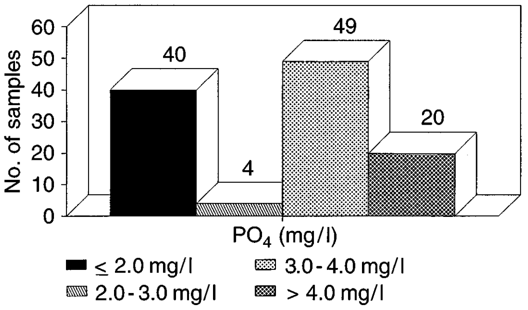


Fig.3
Frequency distribution of phosphate

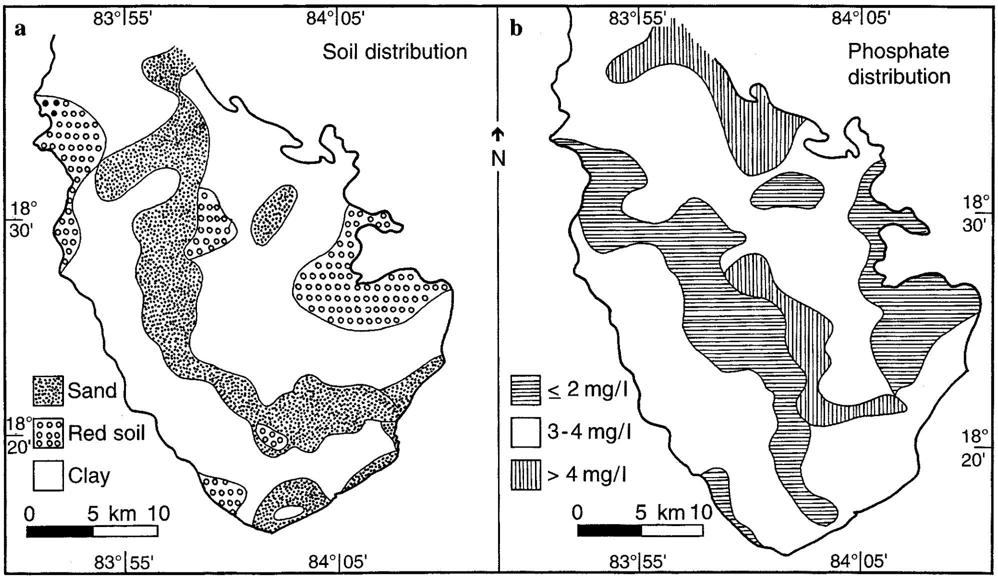


Fig. 4a, b
Distribution of (**a**) soil and (**b**) phosphate

Table 1
Water quality parameters in three different hydrogeological formations. Average values are given in parentheses. Electrical conductivity is given in μS/cm at 25 °C. All ion concentrations are given in mg/l. BDL – Below detection limit

Parameter	Sand/red soil region	Clayey soil region	weathered rock region
pH	6.2–7.2 (6.8)	6.8–7.9 (7.1)	6.8–7.7 (7.2)
Electrical conductivity	218–665 (458)	2032–4273 (2639)	713–1868 (1123)
Dissolved oxygen	1.6–6.1 (3.3)	1.4–3.8 (2.7)	2.4–6.9 (3.7)
Calcium	22–85 (37)	45–160 (117)	15–63 (40)
Magnesium	33–42 (38)	64–183 (104)	40–80 (60)
Sodium	14–72 (43)	120–1245 (368)	35–360 (157)
Potassium	BDL-34 (8)	22–455 (160)	BDL-41 (10)
Chloride	15–80 (48)	460–2170 (768)	55–345 (132)
Sulphate	BDL-34 (20)	33–521 (156)	16–80 (39)
Bicarbonate	103-367 (236)	235–926 (551)	338–926 (533)
Fluoride	BDL-0.7 (0.4)	BDL-0.5 (0.25)	1.1–3.4 (1.7)
Total iron	0.4–2.5 (1.0)	0.2–1.1 (0.5)	0.2–6.6 (1.0)
Nitrate	4–20 (10)	22–146 (76)	2–22 (12)

assuming that only superphosphate and NPK fertilizers are applied. These two fertilizers, on analysis of the supernatant liquid, yield the highest concentration of PO_4. Though the use of fertilizer cannot be treated as a point source, the contribution of $PO_4$from the fertilizers cannot perhaps be ignored over a period of continuous usage.

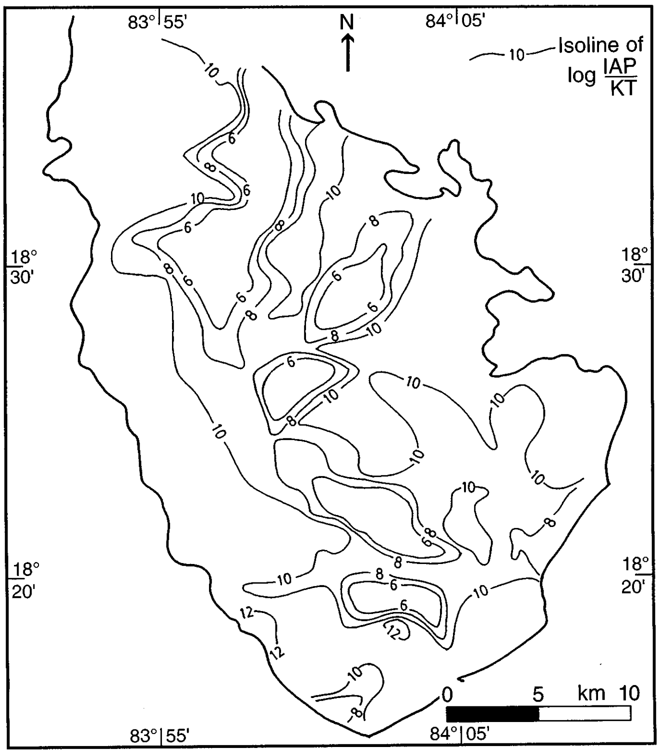
Groundwater quality modelling studies based on thermodynamic equilibrium concepts of various mineral and chemical facies were made using the WATEQF computer programme (Plummer and others 1976). Weathered rock samples collected from the sections of the wells containing >5.0 mg/l of PO_4 in groundwater were mixed with water and stirred. The PO_4 from the extract reaches 7.5 mg/kg when 30 g of weathered rock was mixed in 300 ml distilled water. This observation has provided substantial support to the results of equilibrium model studies.

The saturation status of fluorapatite and hydroxylapatite in groundwater are shown in Fig. 5 and 6, respectively. The results revealed the possibility of a state of supersaturation of fluorapatite (Fig. 5) in the entire region while the hydroxylapatite exhibits all three states of equilibrium in the region (Fig. 6). Further release of PO_4 into the groundwater in this region also cannot be ruled out.

Though it is realized that the modelling studies merely indicate the occurrence of precipitation reaction, while the actual precipitation is also guided by kinetic considerations, it is interesting to record the abundant occurrence of apatite mineral that supports the above results.

Conclusions

The significant enrichment of PO_4 in clay zones is due to its adsorption capabilities associated with water table fluctuation. Though the application of phosphatic fertiliz-

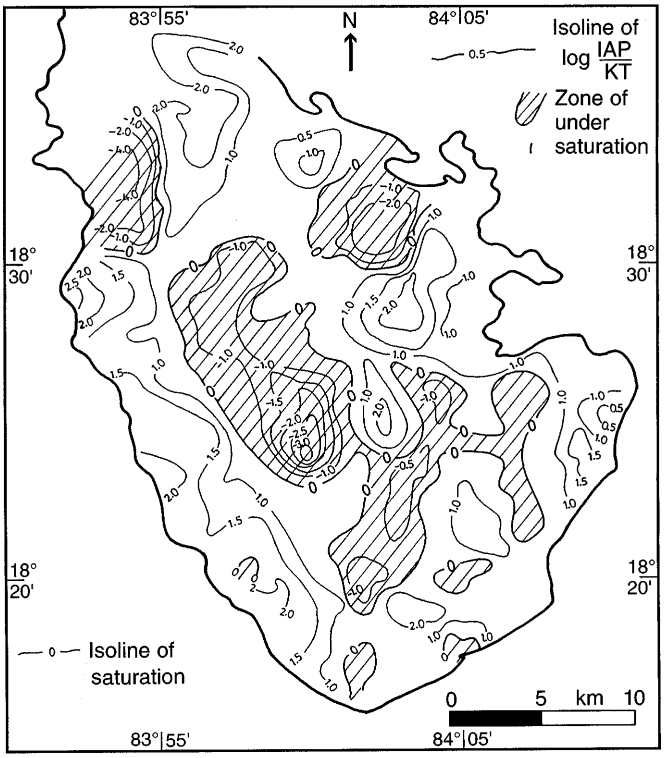


i) Under saturation → $\log \frac{IAP}{KT} < 0$

ii) Saturation → $\log \frac{IAP}{KT} = 0$

iii) Super saturation → $\log \frac{IAP}{KT} > 0$

Fig. 5
Saturation index of fluorapatite



i) Under saturation → $\log \frac{IAP}{KT} < 0$

ii) Saturation → $\log \frac{IAP}{KT} = 0$

iii) Super saturation → $\log \frac{IAP}{KT} > 0$

Fig. 6
Saturation index of hydroxylapatite

ers has increased considerably in recent years, the abundance of phosphate in the groundwater has increased due to geological sources rather than the application of fertilizers. The weathered apatite mineral releases significant quantities of phosphate into the groundwater. The thermodynamic model studies reveal the contributing sources and the possible changes that are likely to occur in groundwater quality.

Acknowledgements Authors are grateful to Dr. B. K. Handa, Supdt. Chemist(Retd.), Water Research Centre, Chandigarh for critical evaluation of this paper.

References

American Public Health Association (1985) Standard methods of analysis of water and waste water, 16th ed. Washington DC

Dept. of National Health and Welfare (1969) Canadian drinking water standards and objectives, 1968. Canada

Gardiner V (1975) Drainage basin morphometry. British geomorphological research group. Technical Bulletin no. 14. ENGLAND: Geo-Abstracts Ltd. 48pp

Gaumat MM, Rastogi R and Mistra MM (1992) Fluoride level in shallow groundwater in central part of Uttar Pradesh. Bhujal News 7:17–19

Hamilton AP and Shedlock JR (1992) Are fertilizers and pesticides in the groundwater? A case study of the Delmarva Peninsula, Delaware, Maryland, Virginia. U.S. Geological Survey Circular 1080. 16 pp

Handa BK (1983) Effect of fertilizer on groundwater quality in India. In: Symposium on groundwater development – A perspective for the year 2000 A.D. University of Roorkee, India. pp 451–462

Handa BK (1990) Contamination of Groundwaters by Phosphates. Bhu-Jal News 5:24–36

Helgesen JO, Stullken KE and Rutledge AT (1994) Assessment of non-point source contamination of the High plains aquifer in south-central Kansas, 1987. U.S. Geological Survey Water-Supply Paper 2381-C. 51 pp

Hem JD (1986) Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water-Supply Paper 2254. 264 pp

Jha LB and Jha M (1982) Fluoride pollution in India. Int J of Environ Stud 19:225–230

Klimas A and Paukstys B (1993) Nitrate contamination of groundwater in the Republic of Lithuania. NGU Bull 424:75–85

Matthess G (1982) The properties of groundwater. New York: Wiley and Sons. 498 pp

Narasayya BL (1970) Mineralogy of chromite, magnetite and apatite deposits of parts of eastern ghats, Andhra Pradesh, India. Ph.D thesis. Andhra University, 228 pp

Padmanabhayya K (1958) Geology of Parts of Srikakulam district. MS thesis. Andhra University, 80 pp

Plummer LN, Jones BF and Truesdell AH (1976) WATEQF – A Fortran IV version of WATEQ – A computer program for calculating chemical equilibrium of natural waters. U.S. Geological Survey Water-Resources Investigations Report, 76–13. 70 pp

Raju KCC, Kareemuddin M and Prabakhara Rao P (1979) Operation Anantapur. Geological Survey of India, Miscellaneous publication no. 47. 57 pp

Smeats J and Amavis P (1981) European Community directives relating to the quality of water intended for human consumption. Water Air Soil Pollut 15(4):483–502

Suryanarayana L (1957) Geology of Parts of Srikakulam district. MS thesis. Andhra University, 91 pp