Trace element concentration in groundwater of Pesarlanka Island, Krishna Delta, India

N. C. Mondal · V. S. Singh · S. C. Puranik · V. P. Singh

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Abstract There is a growing concern over the potential accumulation of trace element concentration in groundwater of coastal aquifer owing seawater encroachment in the last several decades. A total of 29 groundwater samples collected from Pesarlanka Island, Krishna delta, Andhra Pradesh, India were analyzed for 13 trace elements (B, V, Mn, Fe, Ni, Co, Cu, Zn, As, Sr, Cd, Ba, and Pb) using inductively coupled plasma mass spectrometry. The results reveal that B, Fe, Ni, As, Sr, and Pb vary from 11.22 to 710.2, 1.25 to 684.6, 0.02 to 37.33, 27.8 to 282.3, 164.1 to 7,009, and 1.97 to 164.4 μg/l, respectively. Ba, Cd, Co, Cu, Ni, V, and Zn are almost within permissible limits for drinking water, but As, Fe, Mn, Pb, B,

N. C. Mondal $(\boxtimes) \cdot V$. S. Singh National Geophysical Research Institute (Council of Scientific & Industrial Research), Uppal Road, Hyderabad, 500 606, India e-mail: ncmngri@yahoo.co.in

S. C. Puranik Karnatak University, Dharwad, 580 003, Karnataka, India

V. P. Singh · N. C. Mondal Department of Biological and Agricultural Engineering, 321 Scoates Hall, 2117 TAMU Texas A & M University, College Station, TX 77843-2117, USA

and Sr are above the permissible limit. The toxic element Pb is 1.64 times more than the maximum permissible limits of drinking water. The minimum value of As is also 2.78 times more, whereas the maximum is 28.2 times the permissible limit. The spatial distributions of alkaline earths (Sr, Ba), transition metals (V, Co, Ni, Fe), metallic elements (Cu, Pb), and (As) were found in considerable variation in the entire Island. Good crosscorrelations were found between As, B, Co, and Sr with total dissolved solids and among other trace elements such as B, As, Co, and Sr. The variability observed within the groundwater samples is closely connected to the sea spray input; hence, it is primarily a consequence of geographical and meteorological factors, such as distance from the ocean and time of year. The trace element levels, in particular those of heavy metals, are very low, suggesting an origin from natural sources rather than from anthropogenic contamination. A few trace elements (Sr and B) are found as sensitive parameters responding to changes in fresh to saline groundwater environment. The highly elevated trace elements in this area which may be attributed to marine sediments or death and decay of plants are presented in this paper.

Keywords Distribution of trace elements **·** Seawater intrusion **·** Pesarlanka Island **·** Krishna delta **·** India

Introduction

Trace element studies are of wide application in varied branches of scientific discipline. Concentration of trace elements in water helps in the circulation and distribution of minerals in rock and waters. It has some relationship between water composition and public health, which may be either related to groundwater pollution or to natural condition (Karant[h](#page-11-0) [1989\)](#page-11-0). Trace elements are contributed to groundwater from a variety of natural and anthropogenic sources (Ramessu[r](#page-11-0) [2000;](#page-11-0) Newcomba et al[.](#page-11-0) [2002](#page-11-0); Abollino et al[.](#page-11-0) [2004;](#page-11-0) Leung and Jia[o](#page-11-0) [2006\)](#page-11-0). Some of the trace elements like Fe, Mn, Ni, Cu, Zn, and As are needed by the human body to activate vital functions and biological processes. Iron deficiency leads to anemia and

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Fig. 1 Key map of Pesarlanka Island (India) showing the sampling points

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iodine deficiency causes goiter. The FAO-WHO Expert Committee on Food Additives (Code[x](#page-11-0) [1984\)](#page-11-0) recommended a maximum acceptable daily intake of inorganic arsenic of 2.0 mg/kg needed for body weight. But it is well established that an accrue in trace element beyond the permissible limit can cause several health hazards (WH[O](#page-12-0) [1984\)](#page-12-0). Generally, trace elements are categorized as toxic element (Pb, As), alkaline earths (Sr, Ba), transition metals (Mn, Co, Ni), metallic elements (V, Cu, Cd, Fe, Zn), and non-metallic elements (B; Hem [1991](#page-11-0)).

A lot of work has been done worldwide in this field in the Atlantic, Pacific, and Indian Ocean. Dodge and Bras[s](#page-11-0) [\(1984\)](#page-11-0) have documented the increase in lead levels in the coral reef of Virgin Island with time due to the increase in lead availability from global pollution. Xie et al[.](#page-12-0) [\(2005](#page-12-0)) reported that the contamination of groundwater of Coral Island (Xi Sha Island in South China Sea) is due to saltwater intrusion, leaching of heavy metals, and toxic elements from granitic rock and guano-soil, respectively. Analysis of groundwater from some crystalline rocks in the upper region of Ghana indicated that most trace elements (Al, Fe, Zn, Sr, and Ba) were excessively higher in natural water systems (Pelig-B[a](#page-11-0) [1998](#page-11-0)).

Fig. 2 Fence diagram of Pesarlanka Island represents the distribution of sandy slit, clay, fine, and coarse sand

all trace elements in

μg/l, *BDL* below detection limit

Parameters	Min.	Max.	Av.	SD	WHO guideline	ISI (1983)		
					value (1984)	Highest desirable	Maximum permissible	
pH	6.9	7.8	7.4	0.24	$6.5 - 8.5$	$7.0 - 8.5$	$6.5 - 9.2$	
EC	790	6000	2798	1535	1,500	—	-	
TDS	476	4200	1929	1105	< 1,000	500	1,500	
As	27.8	282.3	114.3	86.4	10	50	50	
B	11.22	710.2	254.9	180.7	300			
Ba	5.08	250.2	101.6	73.09	700			
Cd	0.01	5.94	1.62	1.79	3			
Co	2.08	21.53	9.07	6.54				
Cu	0.58	58.49	11.5	11.64	100	50	1,500	
Fe	1.25	684.6	154.51	150.04	300			
Mn	1.21	1766	444.2	509.12	100			
Ni	0.02	37.33	7.35	14.7	20			
Pb	1.97	164.4	26.21	35.62	100	300	300	
Sr	164.1	7009	2000.9	1811.1	70			
V	3.5	10.72	6.32	3.27	5,000			
Zn	1.39	4928	453.5	1017.2	3,000	5,000	15,000	

Table 2 Statistical parameters of trace elements of Pesarlanka Island, Krishna delta, India

All elements: in μg/l; EC: in μS/cm, TDS: in mg/l, pH: $-\log_{10}H^{+1}$

Min. minimum, *Max*. maximum, *Av*. average, *SD* standard deviation

A large number of researchers have also worked on trace element contents of groundwater in the Indian subcontinent and along its coastal area. Ramesh et al[.](#page-11-0) [\(1995\)](#page-11-0) revealed that the toxic element (As and Se) and other trace elements in groundwater of Madras city are due to anthropogenic activities and saltwater intrusion. On the basis of spatial and temporal variation, Da[s](#page-11-0) [\(2003\)](#page-11-0) reported that weathering of rocks and anthropogenic input were the main sources of trace elements in the groundwater of Cuttack district in the eastern coast of India. Mandal and Sengupt[a](#page-11-0) [\(2005,](#page-11-0) [2006](#page-11-0)) reported that the contamination of groundwater at Mecheda in Midnapur District, West Bengal is from the toxic elements leached from the ash pile of thermal power plant.

So far, no study has been done to examine trace element content in the groundwater of the coastal island (Pesarlanka) of the eastern coast of India. The pristine groundwater of this island is at peril due to the deterioration of groundwater quality. The fragile nature of the aquifer and thin groundwater lenses allow the waters of this island to be vulnerable to saline water encroachment. In this study, the concentration of various trace elements and their sources were discussed in details.

Location

Pesarlanka Island is located on the southern part of Krishna delta in Andhra Pradesh, India (Fig. [1\)](#page-1-0). This location is mostly covered by clay, slit, sand, etc. The western side of this island is an upper deltaic plain, with an elevation of about 13.0 m above mean sea level. The quaternary formation, comprising clay, silt, and sand, is shown in Fig. [2.](#page-1-0) The channel deposits are of fine medium quartz sand (Biksham et al[.](#page-11-0) [1991](#page-11-0); Saxena et al[.](#page-11-0) [2004;](#page-11-0) Mondal et al[.](#page-11-0) [2008a](#page-11-0)). Mostly groundwater of this area recharges from precipitation; however, a canal is also available. The average annual rainfall is 1,010.7 mm and the rains come from the southwest monsoon, usually in June–October. Some rains also occur during the month of February.

Methodology

Twenty-nine groundwater samples were collected in October 2006 in 1-l polyethylene bottles scattered over the entire island based on the methods described by He[m](#page-11-0) [\(1959](#page-11-0)). pH, temperature, total dissolved solids (TDS), and conductivity tests were conducted in situ on the samples using portable kits. The trace elements were analyzed using inductively coupled plasma mass spectrometry by the methods described by Balaram and Ra[o](#page-11-0) [\(2004\)](#page-11-0) at Geochemistry Laboratory, NGRI, Hyderabad, India. Location map of the sampling points is shown in Fig. [1.](#page-1-0) The results of the trace element are presented in Table [1.](#page-2-0) Statistical parameters of the trace elements in the samples are presented in Table [2.](#page-3-0)

Results and discussion

Twenty-nine groundwater samples were collected from the small island and were analyzed for their trace elements content and physiochemical parameters mentioned in Table [1.](#page-2-0) Table [2](#page-3-0) shows the statistics of the groundwater samples. The results of the physiochemical parameters show that pH varies from 6.9 to 7.8 in the groundwater of the study area, revealing a mildly acidic to alkaline water. Electrical conductivity (EC) and TDS vary from 790 to 6,000 μS/cm and

Fig. 3 TDS contours (in mg/l) of groundwater in Pesarlanka Island during October 2006

476 to 4,200 mg/l, respectively. The contour map of the TDS values clearly showed that higher value of TDS occur in the middle part of this island, especially close to Tadikalapudi (C) and Tippalakatta (Fig. 3). Similarly, higher TDS values were noticed in Pesarlanka (Southern part) and Krishkindapaleum (western part). This may indicate the possibility of high rate of ingression/ intrusion in the middle, southern, and western parts of the island where high rate of withdrawal of groundwater were observed. It is also noticed that the central part of this island is comparatively more populated, has larger agricultural fields and also numerous dug and bore wells. TDS value of groundwater is observed as low as 476 mg/l in the vicinity of Donipudi and along the river sides, which indicate the availability of fresh groundwater aquifer systems in these places.

The status of trace elements in the groundwater of this island have been discussed in different groups like toxic elements (Pb and As), alkaline earths (Sr and Ba), transition metals (Mn, Co, and Ni), metallic elements (V, Cu, Cd, Fe, and Zn), and other non-metallic elements (B).

Toxic Elements (Pb and As)

Lead (Pb) For the first time, an attempt was made to assess the area severely affected by lead (Pb) pollution. Its concentrations vary from 1.97 to 164.4 μg/l, with an average of 26.21 μg/l. Mean Pb concentrations in freshwater and rivers are 1.0 and 3.0 μg/l, respectively. The maximum value of Pb found at Pallepalem (near canal) is 1.64 times more than the maximum permissible limit (WH[O](#page-12-0) [1984\)](#page-12-0). The contour map of Pb distribution is shown in Fig. [4a](#page-5-0). The occurrence of Pb in groundwater may be attributed to release of lead adsorption of marine sediments, from dust transported via atmosphere and continental crust erosion, precipitation and deposition of airborne aerosols, and lead availability in global pollution (Schaule and Patterso[n](#page-12-0) [1981;](#page-12-0) Dodge and Gilber[t](#page-11-0) [1984;](#page-11-0) He[m](#page-11-0) [1991](#page-11-0); Hunt and Howar[d](#page-11-0) [1994](#page-11-0)). Lead concentration is within permissible limit in the entire island except at Pallepalem (near canal) hand pump. The high content of Pb in groundwater of this Island may have been sourced from

Fig. 4 Pb (**a**) and As (**b**) contours map (in μg/l) of groundwater in Pesarlanka Island during October 2006

either Pb released from death and decay of marine organisms and/or through precipitation.

Arsenic (As) Arsenic concentration in the groundwater of Pesarlanka Island is exceedingly high at all locations in the island (shown in Fig. 4b). The maximum As value recorded for the island is over 28.2 times more than the maximum permissible limit (WH[O](#page-12-0) [1984\)](#page-12-0), and minimum value is also found more than 2.78 times of that. In water, As concentration is in the form of arsenic compounds. It is also adsorbed onto clay colloids bound to organic matter to form water-soluble complexes, Fe, Ca, and Mg. There is sufficient evidence to suggest that there is a geological control in the distribution of As with alluvium sediments. Anthropogenic sources of As are numerous, both in the form of organic metal complexes and inorganic ions (Pal and Mukherje[e](#page-11-0) [2009\)](#page-11-0). Arsenic compounds are used in paint industries as paint pigments and in textile and tanning industries. Household detergents may also contain about 10–70 mg/l of As. Generally, elevated As concentration is recorded for the groundwater of the entire island. The occurrence of As in natural waters is usually associated with sedimentary rocks of marine origin, weathering of volcanic rocks, fossil fuels, mineral deposits, mining wastes, agricultural use, and irrigation practices (Hunt and Howar[d](#page-11-0) [1994\)](#page-11-0). Arsenic is also adsorbed onto clay colloids bound to organic matter to form water-soluble complexes with Al, Fe, Ca, and Mg (Ganje and Rain[s](#page-11-0) [1982;](#page-11-0) Government of Indi[a](#page-11-0) [1993\)](#page-11-0). However, the elevated As except in groundwater of this island could be from marine sediments and fossil fuels.

Alkaline earths (Sr and Ba)

Strontium (Sr) High concentration of Sr is observed in the area, indicating that the source could be fossils found in the sedimentary rock. Sr concentrations in the groundwater of the study with the central and southern parts of the island are

Fig. 5 Sr (**a**) and Ba (**b**) contour maps (in μg/l) of groundwater in Pesarlanka Island (October 2006)

elevated. It varies from 164.1 to 7,009 μ g/l (shown in Fig. 5a). War[d](#page-12-0) [\(1995](#page-12-0)) reported the mean concentrations of Sr in freshwater and river water as 70 and 60 μg/l, respectively. Simultaneously, Saxena et al[.](#page-11-0) [\(2004](#page-11-0)) have established that Sr content could be linked to various water types. They further suggested Sr values of $\langle 1,600 \,\mu g/l$ for fresh groundwater, 1,600–5,000 μg/l for brackish water, and >5,000 μg/l for saline groundwater in the coastal aquifers. The Sr values obtained indicated that the groundwaters have 17% and 38% contents of saline and brackish waters, respectively. This suggests that the aquifer system is under interaction with seawater and that the source of Sr content may be linked solely to marine in origin.

Barium (Ba) Ba content in the groundwater ranges from 5.08 to 250.2 μg/l, which is within permissible limit (Fig. 5b).

Transition metals (Ni, Co, Mn)

Nickel (Ni) and cobalt (Co) The samples contain Ni lesser than permissible limit. Ni and Co range from 0.02 to 37.33 μg/l and 2.08 to 21.53 μg/l, respectively. Ni and Co tend to be co-precipitated with iron oxides and especially with manganese oxides. High Ni content of marine manganese nodules present in part of the Pacific Ocean suggests that co-precipitation processes may be involved in controlling the amount of element present in seawater, as co-precipitation with manganese oxides probably can maintain lower dissolved nickel activities than any of the simple direct precipitation mechanisms for $Ni²⁺$.

Manganese (Mn) In this study, Mn concentration range between 1.214 and 1,766 μg/l, while the respective mean value is 444.2 μg/l. The mean concentration of Mn is 4.4 times higher than

Fig. 6 Mn contour map (in mg/l) of groundwater in Pesarlanka Island

the WH[O](#page-12-0) [\(1984\)](#page-12-0) guideline limit. The spatial distribution of Mn revealed that the entire Island is highly elevated in manganese concentration (Fig. 6). However, higher concentration of Mn is found in linking the possible origin to the marine environment.

Metallic elements (Cu, Cd, Zn, Fe, V)

The concentration of Cu in groundwater ranges from 0.58 to 58.49 μg/l, with a mean value 11.5 μg/l. The concentration of Cu in freshwater and rivers are 3 and 5 μg/l, respectively. In comparing the data, the groundwater was more enriched in Cu than in natural waters, probably suggesting possible enrichment from aquifer materials such as feldspar, biotite, and muscovite minerals. The WH[O](#page-12-0) [\(1984\)](#page-12-0) guideline value for Cu is 100 μg/l, which was above the concentrations obtained in the groundwater. Vanadium concentration ranges from 3.5 to 10.72 μg/l, values that fall within permissible limit.

Cd and Zn concentrations range from 0.01 to 5.94 and 1.39 to 4928 μg/l, respectively. For drinking water are 3 and 3,000 μg/l, respectively. This revealed that Cd and Zn exceed the WHO guideline values in some villages. Mean concentrations of Cd in freshwater and rivers are 0.03 and 0.02 μg/l, respectively, whereas 15 and 20 μg/l for Zn. Generally, Cd is used as a coating material, paint pigment, in plastics, fungicide, and is a constituent of some fertilizers. But Zn is used as an anticorrosion agent where it is coated on iron pipelines to protect them against corrosion. During the construction of the boreholes, galvanized pipelines are used. Corrosion of pump parts could also lead to Zn being released into the groundwater. However, a level of 4,928 μg/l of Zn is found in Chintamudi (North) borehole. Even though in other sides its value is less than the WH[O](#page-12-0) [\(1984](#page-12-0)) guideline limits, the high concentration of this metal is alarming and should pose concern to the groundwater users.

About 14% of the samples contain concentration of Fe higher than 300 μg/l (WH[O](#page-12-0) [1984](#page-12-0)) guideline (shown in Fig. [7a](#page-8-0)). The concentration of Fe in water usually gives aesthetic problems to water consumers. However, according to War[d](#page-12-0) [\(1995\)](#page-12-0), the mean concentrations of Fe in both freshwater and rivers are 500 and 50 μg/l, respectively. In this study, Fe concentration ranges from 1.25 and 684.6 μg/l, while the respective mean value is 154.51 μg/l. It suggests that the studied wells were highly enriched in this metal. It is possible that some of the increase of Fe concentration could be attributed to the corrosion of pump parts as was shown by Langanege[r](#page-11-0) [\(1987\)](#page-11-0). Higher Fe concentrations in the aquifers might have resulted from interaction of oxidized Fe minerals and organic matter and subsequent dissolution of $Fe₂CO₃$ at a comparatively lower pH. This type of water is clear when first drawn from the well, but soon becomes cloudy and then turns brown by the precipitation of $Fe(OH)_3$, which is a common problem in some parts of the area. Another reason for the high Fe concentration may be the removal of dissolved oxygen by organic matter, leading to

Fig. 7 Fe (**a**) and B (**b**) contour maps (in μg/l) of groundwater in Pesarlanka Island (October 2006)

reduced conditions. Under reducing conditions, the solubility of Fe-bearing minerals (siderite, marcacite, etc.) increases, leading to enrichment of dissolved iron in the groundwater (Applin and Zha[o](#page-11-0) [1989;](#page-11-0) White et al[.](#page-12-0) [1991](#page-12-0)).

Non-metallic (B)

The toxic effect for B in humans is found to occur above 20 mg/l (Bolt and Bruggenwer[t](#page-11-0) [1978\)](#page-11-0). Boron usually occurs as a non-ionized form as

Table 3 Cross-correlation coefficients of trace elements in Pesarlanka Island (India)

	EС	TDS	As	B	Ba	Cd	Co	Cu	Fe	Mn	Ni	Pb	Sr	V	Zn
EC	1.00														
TDS	0.99	1.00													
As	0.86	0.86	1.00												
В	0.89	0.89	0.81	1.00											
Ba	0.58	0.58	0.67	0.57	1.00	$\qquad \qquad -$									
C _d	0.42	0.42	0.48	0.43	0.43	1.00									
Co	0.88	0.88	0.90	0.73	0.55	0.40	1.00								
Cu	0.18	0.18	0.34	0.08	0.13	0.47	0.40	1.00							
Fe	-0.16	-0.16	0.05	-0.10	0.01	0.15	0.01	0.79	1.00						
Mn	0.38	0.37	0.45	0.41	0.45	0.45	0.36	0.28	0.20	1.00					
Ni	0.11	0.11	-0.07	0.12	0.41	0.98	-0.19	0.40	-0.51	-0.02	1.00				
Pb	0.04	0.04	-0.03	-0.11	0.02	0.18	-0.01	0.09	0.15	-0.17	-0.03	1.00			
Sr	0.90	0.89	0.76	0.86	0.65	0.39	0.70	0.00	-0.22	0.37	0.48	-0.07	1.00		
V	-0.50	-0.50	-0.67	-0.30	0.00	-0.40	-0.12	0.77	0.87	-0.31	0.00	-0.30	-0.50	1.00	
Zn	0.37	0.37	0.58	0.23	0.42	0.42	0.55	0.73	0.60	0.45	-0.25	0.08	0.18	-0.15	1.00

 H_3BO_3 in soils at pH < 8.5, but above this pH, it [e](#page-11-0)xists as an anion, $B(OH)_4$ (Miller and Donahue [1995\)](#page-11-0). It is very soluble in soils and can be leached especially in sandy soils (Brad[y](#page-11-0) [1984](#page-11-0)). It is also dispersed in the environment through fertilizer application. Since the pH was less than 8.5 for all the samples, it is more likely that B would be in the non-ionized than the ionized state. It varies from 11.22 to 710.02 μ g/l (as shown in Fig. [7b](#page-8-0)) in the study area.

Interrelationship and identification saline zones

Seawater intrusion is a common phenomenon in the coastal aquifers. In coastal aquifers, this island is not an exception (Mondal et al[.](#page-11-0) [2008b](#page-11-0)) because it lies in the coastal belt. A cross-correlation chart was prepared in order to visualize the correlations between the different trace elements which are depicted in Table [3.](#page-8-0) It shows that there are good correlations between As, B, Co, and Sr with TDS and among other trace elements such as B, As, Co, and Sr. The trace elements of groundwater revealed good correlations between TDS, Sr, and B (Fig. 8). In general, Sr and B concentrations

Table 4 Basis of groundwater classification

Parameter	Freshwater	Brackish water	Saline water
TDS	< 1.500	1,500–3,000	> 3,000
-Sr	< 1600	$1,600 - 5,000$	> 5,000
^B	< 200	$200 - 500$	> 500

TDS: in mg/l; Sr and B in μg/l

were low in fresh groundwater (Saxena et al[.](#page-11-0) [2004\)](#page-11-0), but high in brackish and saline waters (Table 4). It is observed that the effects of seawater intrusion are less in the northern and eastern parts of the Island close to Donipudi, Potharlanka, Tippalakata (E), Pallepalem, Peddalanka, and Khadagudam villages. Groundwaters near Pesarlanka, Tippalakatta, and Krishkindapaleum regions indicate elevated concentrations of both Sr and B and revealed seawater intrusion. It shows that seawater intrusion is more in the central part; however, the groundwater withdrawal is also indicated more. Freshwater zones identified by strontium (Sr) and boron (B) are compared (Table [5\)](#page-10-0) with TDS. About 43% of Pesarlanka Island is not under the influence of seawater intrusion. This study indicates the applicability of Sr and B as useful parameters for the identification of fresh groundwater resources in the coastal aquifers.

Conclusions

- Groundwater is slightly acidic to neutral to mildly basic (pH 6.9–7.8). Electrical conductivity varies from 790 to 6000 μs/cm and trace elements show that the southern and central parts of Pesarlanka Island are under seawater intrusion.
- About 57% of the Island is under the influence of seawater intrusion.

- *F* freshwater, *B* brackish water, *S* saline water
- The concentration of most trace elements in the studied groundwater exceeded the WH[O](#page-12-0) [\(1984](#page-12-0)) guideline limits. The main source of most elements is the marine sediments. Anthropogenic sources are quite few and limited and should therefore be less significant sources of these elements. However, groundwater from boreholes construction where Fe and Zn metals are used as pipeline and pump materials in somewhat enriched in these metals due to corrosion.
- Toxic element Pb is 1.64 times more than the maximum permissible limits of drinking water. Arsenic is found 27.8 to 282.3 μg/l in this island. The minimum value is also 2.78 times more, whereas the maximum is 28.2 times the permissible limit.
- Good cross-correlations are found in between As, B, Co, and Sr with TDS and among other trace elements such as B, As, Co, and Sr.
- Alkaline earth element (Sr) and non-metallic element (B) are found as sensitive trace elements responding to changes in fresh to saline water environment in this island.

The highly elevated trace elements (i.e. Pb, As) and saline water environment in Pesarlanka Island indicate that there are immediate steps to be taken like rainwater harvesting and artificial recharge to arrest the seawater ingress and its further encroachment/spread on the island.

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