

ESTIMATION OF WATER QUALITY CHARACTERIZATION PARAMETERS FOR LOCAL SPRING WATERS

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Physico-chemical parameters and trace metal levels have been reported for selected natural spring waters from rural areas of Azad Kashmir and Northern Hill Tracts. Standard analytical methods, augmented by the atomic absorption technique, have been used for the estimation of quality characterization parameters such as conductance, hardness (CaCO_3), alkalinity, phosphate (PO_4), nitrate/nitrite (NO_3/NO_2), dissolved oxygen and other relevant parameters in addition to trace metals. Estimated metals include sodium, potassium, cadmium, zinc, iron, lead, mercury, strontium, copper, chromium, barium, nickel and cobalt. The results are discussed in terms of internationally recognised water quality limits for human consumption.

Key words: Spring water analysis, Physico-chemical parameters, Trace metal analysis.

INTRODUCTION

An increasing consciousness of water pollution since the sixties has led to the recognition that during the course of fast urbanization and industrialization man has severely upset the natural biologic balance of his environment. Among the various sources of pollutants in surface and ground waters atmospheric emissions from industry and households and run-off from agriculture have contributed to water pollution. It is estimated that industrial and domestic waste waters introduce a very large number of different pollutants into natural waters, such as polycyclic aromatics, pesticides, radioactive matter and trace metals. The latter group of pollutants is specially dangerous for human health as trace metals are not usually eliminated from aquatic ecosystems by natural processes and tend to accumulate in bottom sediments from which they may be released through remobilization processes and thus move up the biologic chain to reach human beings, thus causing chronic and acute ailments. Extensive studies have been undertaken by various workers [1,2] to characterize water pollution in terms of various trace metals in natural surface and underground waters.

More recently, the behavioural role of trace metals has been studied in great depth subsequent upon growing public concern over the deteriorating water quality [3,4]. Concern to this effect has now arisen in developing countries where in the wake of urbanization and rapid industrial/agricultural development, natural surface and underground waters even are not secure from the adverse effects of

trace metals. Some recent local data on the abundance of certain metals in public utility waters in rural areas have shown abnormal contamination of some of the trace metals in surface and ground water resources that serve, on an average, a large population density in these areas [5].

In order to determine the extent of this pollution, background concentrations are most desirable as these may serve as guidelines for water quality control and, at the same time, as indicators of the extent and possible consequence of contamination wherever they are exceeded. An attempt has been made in the present work to obtain data on water quality parameters and trace metal levels for natural spring waters collected from a radial periphery of 80 km around Islamabad from areas belonging to Azad Kashmir and certain Northern Hill Tracts. The composition of spring waters is particularly valuable in providing a standard for assessing the contamination of certain waters. Also, by including regional and/or local lithogenic influence into consideration, the anthropogenic effects can be determined with accuracy [6]. Thus, a study of water quality parameters becomes imperative in view of the fact that spring waters belonging to these areas serve large remotely located population having no other water source. In line with the demand of water quality characterization for personal hygiene and domestic use the following parameters are estimated for these spring waters; temperature, pH, conductance, alkalinity, hardness, phosphate, nitrite, nitrate, total dissolved solids (TDS), dissolved oxygen (DO) and chemical oxygen demand (COD). Trace metals estimated include sodium, potassium, zinc,

cobalt, nickel, strontium, copper, iron, cadmium, chromium, lead, mercury and barium.

EXPERIMENTAL

For the purpose of sampling, plastic cans (2.5 litre capacity) were used. These cans were prewashed first with chromic acid and then with distilled water to remove any organic matter. Prior to sampling, a blank check on these cans was performed using distilled water as the leaching solvent in order to verify that these cans were uncontaminated at the detection level of the individual trace metals, especially with respect to chromium. The lower detection limit achieved under optimized operational conditions for potassium, cobalt, strontium, nickel, iron and chromium is $2 \mu\text{g/l}$; for sodium, zinc and copper it is $1 \mu\text{g/l}$ and for lead and barium $5 \mu\text{g/l}$. Cadmium has the lower detection limit at $0.5 \mu\text{g/l}$. The cans were found to be capable of retaining the samples for a period of four to six days without undergoing detectable change in trace metal level or major anionic/cationic concentrations. After collection, the samples were directly transported to the laboratory where the analytical work was completed within 72 hr. Conductance, temperature and pH were measured as filed parameters through the use of precalibrated portable pH meter, conductance bridge and mercury thermometer ($0\text{-}50^\circ$ range). Dissolved oxygen was also measured on the sampling site using the YSI oxygen meter, Model 53.

Before estimating trace metal concentrations, optimum atomic absorption measuring conditions were determined as a function of acetylene flow rate, air flow rate, burner height and lamp current for all trace metals. A Hitachi atomic absorption spectrophotometer, Model 170-10, was used in this investigation. A Servogor recorder, Model 310, was used to record the absorption signals. Samples were run in triplicate.

Research grade chemicals were used for the purpose of preparation of standards. Normally, Merck chemicals of guaranteed 99.9 % purity were used to prepare aqueous standard solutions for each trace metal by dissolving an accurately weighed quantity of the relevant salt in doubly distilled water so as to yield a metal ion concentration of 100 mg/l . Appropriate aliquots were taken from these standards for subsequent dilution to the desired concentration level. Each time the standards were prepared afresh, they were calibrated against the previous standards in order to check any probable discrepancy in the finished concentration. These standards were also checked against WHO standards. The experimental procedure for the estimation of physico-chemical parameters, and the trace metal con-

centrations in waters, together with the APDC/MIBK solvent extraction method for lead and cadmium is described in detail elsewhere [7,8].

RESULTS AND DISCUSSION

The sampling site distribution is shown in Figure 1, and the estimated physico-chemical parameters and trace metal are given in Tables 1 and 2 respectively. The maximum tolerable levels for various water quality parameters and trace metals are presented in Table 3. The overall precision pertaining to replicate trace metal measurements is found to be within $\pm 1.5 \%$. The quoted results appear at 2S confidence level.

It may be noted that the measured temperatures for samples S-1 through S-10 are all ideal in that they are well below the stipulated temperature requirement. Samples S-11 through S-15, belonging to the Azad Kashmir zone have relatively higher temperatures. Data on pH, conductance, alkalinity and total dissolved salts show that the values are within the permissible safe range set for these parameters. The estimated hardness values (mg/l CaCO_3) range between $100\text{-}188 \text{ mg/l CaCO}_3$. In view of the bicarbonate type of alkalinity present in these waters, the hardness may be effectively reduced, if required, by simple boiling. The cumulative nitrate/nitrite level allowed for drinking waters does not allow a safe use of samples S-2, S-3, S-4, S-7 and S-8. The observed high concentration

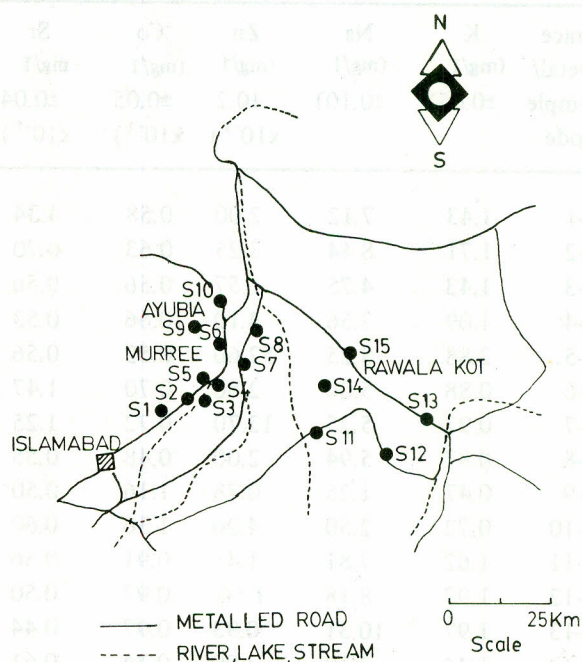


Fig. 1. Sampling site distribution for the area under investigation.

level of these anions may be attributed to nitrogen sources emanating either from local organic contamination or nitrogen fertilizers used in nearby fields adjoining main spring ponds for raising crops. Hence, it may be expected that during rainy season the natural run-off would lead to

an enriched nitrate/nitrite content of these waters. Work on the estimation of these anions in waters belonging to Company Bagh and Ghora Galli is already under way in our laboratory, and it has been observed that these waters undergo contamination of this sort during rains.

Table 1. Estimated water quality characterization parameters for various spring waters.

Sample Code	Location/ Nature*	Temperature (°C±0.1)	pH ±0.1	Conductance (µS/cm ±10)	Alkalinity (mg/l ±5)	Hardness (mg/l ±6)	Phosphate (mg/l ±0.08)	Nitrite (mg/l ±0.008)	Nitrate (mg/l ±0.1)	TDS (mg/l ±5)	DO (Mg/l ±0.2)	COD (mg/l ±0.3)
S-1	Salgran	5.3	8.0	315	242	176	1.72	0.041	2.9	325	3.2	15.2
S-2	Charrah Paani	5.6	7.8	400	255	135	3.42	0.102	13.4	324	4.3	9.6
S-3	Company Bagh	3.4	7.8	370	268	140	1.00	0.083	12.4	332	2.3	6.8
S-4	Ghora Galli	4.5	8.2	280	212	137	2.30	0.071	15.3	306	1.8	10.6
S-5	Ghitta Moor	5.0	7.7	320	206	142	1.22	0.032	7.2	301	4.2	17.2
S-6	Murrée	4.0	8.1	240	175	141	1.72	0.100	8.9	240	3.2	14.5
S-7	Jheenga Galli	3.0	8.1	225	172	143	1.31	0.131	12.4	242	1.9	11.2
S-8	Bhoor Bun	5.0	7.6	340	192	155	3.11	0.090	10.7	328	2.3	17.6
S-9	Changla Galli	4.5	7.3	260	189	148	1.10	0.012	1.9	153	3.7	7.8
S-10	Ayubia	5.0	7.2	240	185	145	0.30	0.041	6.7	238	2.8	9.2
S-11	Azad Pattan	17.0	8.0	190	137	100	2.31	0.030	3.4	174	3.7	7.2
S-12	Plundari	16.0	7.8	270	167	108	0.99	0.090	9.7	182	4.3	10.2
S-13	Tarar Khal	15.0	7.8	300	207	128	0.91	0.080	8.2	106	4.3	11.2
S-14	Mung	16.0	7.5	460	275	188	1.31	0.071	7.3	147	4.8	11.3
S-15	Rawala Kot	15.0	7.4	350	196	152	2.11	0.060	9.3	190	5.3	9.8

* All waters are non-treated.

Table 2. Estimated average concentrations of Trace Metals at 2S Confidence Level.

Trace Metal/ sample Code	K (mg/l ±0.05)	Na (mg/l ±0.10)	Zn (mg/l ±0.2 x10 ⁻¹)	Co (mg/l ±0.05 x10 ⁻¹)	Sr (mg/l ±0.04 x10 ⁻¹)	Ni (mg/l ±0.02 x ⁻¹⁰)	Cu (mg/l ±0.01 x10 ⁻¹)	Fe (mg/l ±0.1 x10 ⁻¹)	Cd (mg/l ±0.2 x10 ⁻¹)	Cr (mg/l ±0.3 x10 ⁻²)	Pb (mg/l ±0.2 x10 ⁻²)	Hg (mg/l ±0.2 x10 ⁻⁴)	Ba (mg/l ±0.0 x10 ⁻³)
S-1	1.43	7.12	2.00	0.58	4.34	0.95	0.64	0.47	0.62	2.34	4.76	11.70	18.7
S-2	1.71	8.44	3.25	0.63	0.70	1.56	1.12	0.32	1.48	2.53	5.54	8.38	16.7
S-3	1.43	4.75	1.57	0.56	0.56	0.78	0.64	0.58	0.97	1.95	3.12	15.60	25.6
S-4	1.09	7.56	4.10	0.66	0.53	0.58	0.94	0.39	0.39	1.56	3.12	8.38	23.2
S-5	2.88	8.25	52.60	0.52	0.56	0.27	0.80	0.32	0.19	1.64	4.80	8.38	19.1
S-6	0.88	5.06	2.80	0.70	1.47	0.78	0.80	0.74	0.39	0.78	4.68	5.26	8.7
S-7	0.97	5.25	12.70	0.72	1.25	0.78	0.62	1.40	0.39	1.17	6.25	8.77	18.9
S-8	0.87	5.94	2.00	0.48	0.55	1.05	1.02	0.39	0.39	1.56	6.05	7.80	17.2
S-9	0.47	1.25	0.78	1.16	0.50	2.38	0.49	0.17	0.29	5.23	3.60	6.87	32.0
S-10	0.72	2.50	4.20	1.36	0.60	2.46	0.48	0.17	0.34	5.93	4.05	6.37	34.3
S-11	1.62	7.81	1.41	0.91	0.56	1.75	0.39	0.25	0.28	3.90	4.85	5.20	34.0
S-12	1.97	8.18	1.56	0.97	0.50	1.64	0.42	0.24	0.25	3.24	5.80	5.78	32.5
S-13	1.97	10.31	0.93	0.97	0.44	1.71	0.45	0.21	0.25	3.93	5.33	6.46	32.5
S-14	1.44	7.19	3.90	0.74	0.61	1.95	0.60	0.24	0.29	3.28	3.28	5.20	28.8
S-15	0.64	6.62	1.71	0.74	0.39	2.53	0.59	0.22	0.27	2.66	6.15	5.41	30.5

Table 3. Maximum tolerable levels for various parameters and trace metals for public utility waters (19,20).

Parameter	Maximum permissible level/range	Trace metal	Maximum permissible level (mg/l)
Temperature	15°	Sodium	25
pH	6.5-9.5	Potassium	10
Conductance	50-500 μ mho/cm	Cadmium	0.01
Hardness	50-150 mg/l CaCO ₃	Zinc	5
Alkalinity	50-500 mg/l CaCO ₃	Iron and lead	0.10
Phosphate	1-5 mg/l	Mercury	0.001
Nitrate/Nitrite	10 mg/l	Strontium and barium	0.5
TDS	500 mg/l	Copper	0.05
DO	3-4 mg/l	Chromium	0.05
COD	Variable	Nickel and cobalt	0.5

Both dissolved oxygen and chemical oxygen demand parameters show minor organic matter contamination in these waters. The overall total phosphate is on the higher side of allowed upper limit. A probable source to this effect may be attributed to underground phosphate minerals in addition to a possible phosphate contamination through mixing of the field drain water with that of spring reservoir. This is specifically true for S-2, S-8 and S-15 springs located at a steep terrain.

As for the trace metals, both sodium and potassium (although strictly these two are macro-constituents) have levels well within the stipulated limits. Zinc, too, possess no physiological problem in these waters except for S-5 for which the estimated amount is 5.26 mg/l. The cobalt, strontium and nickel contents of all the samples are within the allowed levels. Similarly, in the case of copper and iron, all the samples are found to be safe except for sample S-7 for which the iron content (0.14 mg/l) exceeds the upper permissible limit. Samples S-9 and S-10 have been found to contain amounts of chromium in excess to the permissible upper limit rendering these waters unfit for human consumption.

The data also reveal that these spring waters have lead contents well below the upper limit. The same is true for mercury content except for S-1 and S-3 in which case the upper allowed limit is exceeded rendering them unfit for human consumption. Barium, too, is found to be within the safe limit. The case of cadmium, however, needs serious consideration since its concentration level in these waters exceeds the maximum permissible limit by about an order of magnitude. As these springs are quite distant from any urban population, a human befolement factor does not

come into the picture. Underground cadmium mineral resources may be one of the causes to this effect.

On the basis of the present study it can be seen that the trace metal content of the spring waters under investigation are generally high compared with natural surface/underground waters. This is specifically true about zinc in sample S-5, iron in sample S-7, chromium in samples S-9 and S-10 and mercury in samples S-1 and S-3. In fact, the waters belonging to these sampling sites are not truly spring waters: rather they must be labelled as mineralized waters. There are many instances available in literature where Zn, Fe, Cr and Hg are present in excessive amounts in the so-called spring waters. For example, zinc has been found to be present upto 177 mg/l in groundwaters close to mineralized zones, so being true about Cr, Fe and Hg [9,10,11,12]. The main factors influencing the contents of trace metals in spring waters are the composition of the surrounding rocks, the degree of mineralization, water temperature interior pressure and dissolved gases in water [13]. Survey of the water quality and trace metal analysis in Shishan area in China has revealed that the trace metal contents in spring waters are higher in rocky areas than in clay areas [14]. For instance, a mercury concentration of 0.04 mg/l has been found in rocky spring waters [15]. In the same waters, iron is estimated at 7-10 mg/l and strontium at 5-9 mg/l. It is also established that cadmium concentrations in natural fresh waters are ~ 100 times the value in sea waters [16]. The anomalous amounts of various trace metals present in spring waters as arising from complexation is also well known [17]. In short, it is the local geology and internal hydrothermal activity within a given field that defines the trace metal dispersion patterns in a given spring system. Even various subsystems of a large underground reservoir may differ widely with respect to each other in terms of trace metal concentration distribution [18]. It is, therefore, only through the inclusion of local and regional factors that an assessment as to the extent of trace metal pollution may be ascertained. Temporal studies on these sources are, therefore, the first prerequisite to this end.

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