

## ESTIMATION OF QUALITY CONTROL PARAMETERS AND TRACE METAL LEVELS IN VARIOUS PUBLIC UTILITY WATERS: PART I. — N.W.F.P.

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Water quality control parameters and trace metal levels for public utility waters belonging to a selected area in NWFP have been estimated and reported. Physicochemical parameters, measured include temperature, pH, conductance, alkalinity, hardness ( $\text{CaCO}_3$ ), chemical oxygen demand (COD), dissolved oxygen (DO), phosphate, nitrate, nitrite and total dissolved solids (TDS). Trace elements estimated by the atomic absorption method are sodium, potassium, copper, iron, zinc, strontium, nickel, cobalt, lead, cadmium, chromium, barium and mercury. Duplicate runs were conducted at predetermined optimum operating conditions with an overall precision of  $\pm 1.5\%$ . Parallel measurements on concentrations of lead and cadmium were carried out using the APDC/MIBK method to warrant a quantitative comparison of the results obtained. The data are reported at  $\pm 2S$  confidence level, and discussed in terms of the feasibility of the tested waters for human consumption.

*Key words:* Water Quality; Trace Metal Levels in Water; Water Quality, Parameter.

### INTRODUCTION

During the past two decades, concerted attention has been focused on the environment in specific relation to water pollution. This has been caused partly by increasing pollution of water resources. Many diseases are caused by the inability of the environment to support the mineral needs of plants and animals in adequate, safe, or non-toxic amounts. It has been established that both deficiencies and excesses of trace elements can terminate life [1]. Industrialization and urbanization, as well as man's own activities, have all adversely influenced the quality of water resources. Even natural waters are no exception; they have undergone undesirable changes in their physical, chemical or biological characteristics that may harmfully affect human life [2, 3].

The overall quality of a given water is not only a function of its trace metal content, but also of the physico-chemical parameters such as temperature, pH, alkalinity, hardness, nitrite/nitrate, phosphate, dissolved oxygen (DO), and certain biological characteristics [4, 5]. Although short and long-term studies on water pollution arising from trace metal pollutants have been extensively undertaken in developed countries [6-9], developing countries have just taken a humble start. An attempt has been made in the present work to ascertain the quality of local utility waters as to their suitability for public use in the NWFP area falling within a radius of 80 km from Islamabad. The water

sampling was restricted to wells and tubewells (about 30-45 ft. deep) and to springs as sources of non-treated water. These sources serve, on the average, a population of 2000 to 5000 people in the relevant rural sites which are apparently located far away from urban or industrial sites. Atomic absorption method is being used for the estimation of the trace metals, while the physico-chemical parameters are estimated by standard analytical methods.

### EXPERIMENTAL

*Collection, transport and storage of samples.* Plastic cans (2.5 litre capacity) were used for sampling. These cans were washed first with chromic acid and then with distilled water to remove any oxidizable/soluble sticking matter. Prior to sampling, a blank check on these cans was performed using distilled water as the leaching solvent in order to confirm that these cans were uncontaminated at detection level of individual trace metals. Through this procedure, the cans were found to be capable of retaining the samples without causing any adverse effect for a period of four to six days. After collection, the samples were transported to the laboratory and chemical analysis was started as soon as it was practicable. In almost all cases, the analytical work was completed within 72 hr. [10, 11]. Conductance, temperature and pH were measured as field parameters through the use of a portable pH meter, a portable conductance bridge and a precalibrated mercury thermometer.

Alkalinity, pH and hardness were estimated following standard methods [12, 14].

**Atomic absorption measuring conditions.** 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. The Hitachi atomic absorption spectrophotometer used in this investigation employed a single-slot, premix burner capable of producing acetylene-air flame at a supply pressure of 0.4 kg/cm<sup>2</sup> and 0.8 kg/cm<sup>2</sup>. A Servogor recorder was used for recording absorption spectra at high S/N ratio.

**Reagents and preparatory procedure.** GR chemicals (Merck) were used for the purpose of the preparation of standards. Aqueous standard solutions for each trace metal were in doubly distilled water so as to yield a metal ion concentration prepared at 100 mg/l concentration. Appropriate aliquots were taken from these standards for subsequent dilution to the desired concentration level. The standards were frequently calibrated against fresh standards in order to check any probable discrepancy in the finished concentration. Detailed experimental procedure for the estimation of physicochemical parameters, together with the APDC/MIBK solvent extraction method for lead and cadmium is described in detail elsewhere [10, 11].

## DISCUSSION

The sampling site distribution is shown in Fig. 1, and the estimated water quality parameters appear in Table 1. Water temperatures below 15°C (59°F) are preferred for drinking purposes. The tabulated data reveal that only

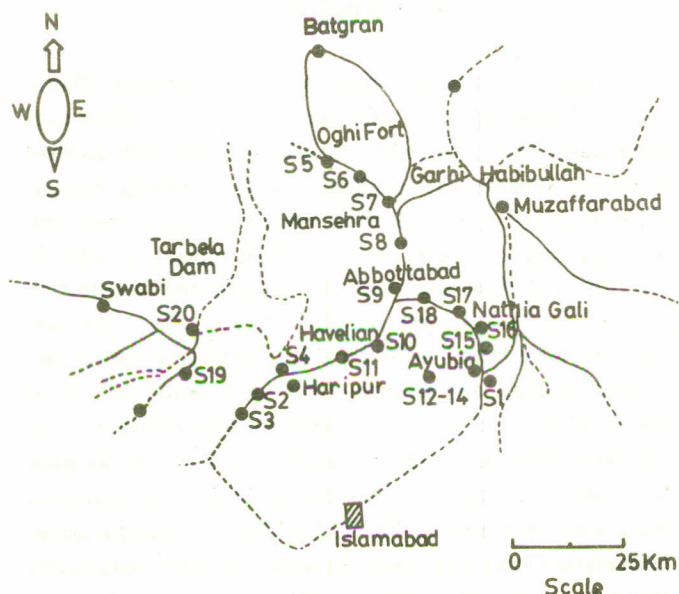


Fig. 1. Sampling site distribution for the area under investigation.

25 % of the collected water samples meet this low temperature requirement. This stems from the fact that the temperature of natural waters is environment dependent; for open lakes and wells the water temperature changes appreciably as a function of changing weather conditions prevailing in the area. For natural spring waters, the observed temperature has been found well below 15°C. The highest temperature is 18.5°C while the lowest one is 4.0°C. These limits are in consonance with the nature and origin of the relevant water sources and the attendant seasonal variations.

It is well known that waters of high pH tend to be scale forming, and waters of low pH are normally corrosive to certain metals and biosystems. The pH range encountered in the present investigation lies between 6.7 (S-6) and 8.3 (S-8). Obviously, all water samples fall within the prescribed pH limit (pH 6.5 – 9.5) and are basic in nature except sample S-6. Thus, only bicarbonate alkalinity is present in these waters, the acceptable range being between 50 and 500 mg/l as CaCO<sub>3</sub>.

The present data reveal that the waters under investigation are genuinely hard with the exception of sample S-17 with a hardness value falling close to the lower limit ( $\approx$  50 mg/l CaCO<sub>3</sub>) set for soft waters. Experiments during the present work have shown that reduction in hardness by 50-80 mg/l CaCO<sub>3</sub> can be achieved for any water by simple boiling for 5 min. Thus, these hard waters may be made suitable for human consumption through simple boiling.

For all practical purposes other than drinking the tolerable limit for phosphates is set at about 5 mg/l. The waters under investigation are rich in phosphate content, and can thus serve as a good irrigation source contrary to domestic applications. The observed phosphate enrichment exceeding 1 mg/l may be attributed to either underground phosphate minerals and/or to a probable absorption through surface runoff, or through industrial waste contamination. This last concern is specifically true for sample S-11 whose source lies in close vicinity of Messrs. Ali Match Factory in Baldhair.

Nitrogen in water systems enters from many sources, principally from the decomposition of organic waste, sewage, surface runoff and use of nitrogen fertilizers. The present investigation shows that even well waters are susceptible to these contamination sources. Examples to this effect are of samples S-4 and S-5 which have maximum nitrate/nitrite content indicating a probable serious sewage pollution of the aquifer. The maximum acceptable limit for nitrate and nitrite is set at 10 mg/l.

Table 1. Estimated physico-chemical parameters of various water samples.

Sample Code	Location/ Nature	Temperature °C ±0.1	pH ±0.1	Conduc- tance mho/cm x 10 <sup>-4</sup> ±0.2	Alkali- nity mg/l ±5.0	Hard- ness mg/l ±6.0	Phos- phate mg/l ±0.08	Nitrite mg/l ±0.008	Nitrate mg/l ±0.1	TDS mg/l ±5.0	DO mg/l ±0.2	COD mg/l ±0.25
S- 1	Gulehra Gali/NT (S*)	18.2	7.9	6.2	425	336	0.79	0.03	8.7	286	2.5	20.7
S- 2	Punyan/T (TS)	15.0	7.9	3.80	268	92	3.34	0.04	8.7	280	3.1	12.0
S- 3	Shahya Jhari Kuss/NT (W)	16.3	7.7	4.10	38	160	4.12	0.08	7.8	280	4.2	8.8
S- 4	Haripur/NT (W)	16.1	7.8	3.30	275	144	3.21	0.01	20.1	240	3.1	7.2
S- 5	Oghi Fort/NT (SW)	18.5	8.0	1.35	147	84	2.93	0.03	20.4	160	3.1	10.4
S- 6	Sussal Nara/NT (S)	18.0	6.7	1.7	145	174	2.80	0.03	9.5	220	2.9	11.2
S- 7	Mansehra/NT (W)	18.5	8.1	3.1	222	140	2.73	0.04	8.6	240	2.8	8.4
S- 8	Kalanderabad/NT (HP)	18.2	8.3	1.7	150	104	1.95	0.05	7.6	140	2.7	16.0
S- 9	DC Office											
	Abbottabad/NT (TS)	18.3	7.9	3.1	263	167	2.36	0.01	6.9	280	2.6	4.0
S-10	Hawelian/NT (W)	18.4	7.8	2.6	234	143	3.39	0.02	4.2	240	2.5	12.0
S-11	Baldhair/NT (TS)	18.5	7.9	2.6	207	200	4.51	0.03	9.2	220	2.4	13.6
S-12	Kali Matti/NT (S)	4.0	7.2	2.3	205	141	1.32	0.03	3.5	195	3.9	6.3
S-13	Barian/NT (S)	5.5	7.4	2.2	195	152	0.87	0.03	2.8	136	4.2	7.2
S-14	Kherra Galli/NT (S)	4.5	7.1	2.4	186	135	0.09	0.02	3.5	182	2.7	4.2
S-15	Donga Galli/NT (S)	16.0	7.8	2.3	122	110	1.10	0.01	7.3	165	5.9	7.2
S-16	Nathia Galli/NT (S)	15.0	7.5	2.9	167	128	1.20	0.01	2.3	181	4.8	7.3
S-17	Kala Bagh/NT (S)	17.0	7.6	0.5	157	48	4.12	0.01	2.3	130	3.6	6.5
S-18	Thai/NT (S)	16.0	8.1	2.2	141	116	3.79	0.10	3.1	182	2.9	4.1
S-19	Ghazi/NT (TS)	18.0	8.0	7.1	227	212	0.87	0.04	4.3	221	3.1	4.1
S-20	Tarbella Dam/NT (R)	16.0	8.1	2.3	180	80	0.81	0.01	4.3	153	4.2	7.1

S\* = Spring water; T = Treated; NT = Non-treated; W = Well water; TS = Tank supply; ST = Stream water; HP = Hand pump; R = Reservoir.

A minimum TDS content of 130 mg/l for sample S-17 and a maximum of 286 mg/l for S-1 is estimated, and this shows that the allowed range of 500-1000 mg/l is not exceeded. Both oxidizable matter and organic matter are measured in terms of dissolved oxygen (DO) and COD. The acceptable maximum limits of DO and COD are quite varied in relation to sources and environment of waters. The measured set of values for the levels of these parameters are satisfactory and they reveal no appreciable organic matter contamination. Only samples S-1, S-8 and S-11 have minor organic contamination problems.

The estimated trace metal levels are given in Table 2. Sodium is found in natural waters upto 25 mg/l and potassium upto 10 mg/l without being critical. Both metals are highly concentrated in bodily fluids, and are widely distributed throughout human body [15].

Only sample S-1 has a cadmium content falling close to the lower permissible limit of 0.01 mg/l; for all other samples, however, the cadmium content is about 2-6 times higher than this value. The cause of this high cadmium contamination may be traced in soil and vegetation where cadmium is normally present in much higher levels. Normal

human body burden of this metal is about 30 mg/l and its toxicity is based on the presence of other trace metals such as zinc and copper [8].

The maximum concentration of zinc met within the present investigation is for sample S-10 at 1.93 mg/l. The rest of the samples fall within the safe range of 5 mg/l, and hence they pose no physiological problem. As stated above, sample S-10 is found to be associated with a high cadmium content as well. Thus, this water is unsuitable for human consumption.

The desirable level of iron is set at 0.1 mg/l, with an upper limit of 1.0 mg/l. Seen in this perspective, all water samples are neat with respect to iron. Only sample S-3 has a higher iron content at 0.39 mg/l. For lead, 0.1 mg/l is the upper allowed limit in public utility waters. All water samples are thus safe with regard to lead. Also the mercury content of these waters is well below the allowed upper concentration limit of 0.001 mg/l.

The tolerable level for strontium is about 0.5 mg/l. Samples S-7 and S-9 have relatively higher strontium content than this permissible limit and as such are potential health hazards.

Table 2. Estimated concentrations of trace metals.

Trace Metal/ Sample Code	K mg/1 ± 0.150	Na mg/1 ± 0.100	Zn mg/1 $\times 10^{-1}$ ± 0.020	Co mg/1 $\times 10^{-1}$ ± 0.005	Sr mg/1 $\times 10^{-1}$ ± 0.035	Ni mg/1 $\times 10^{-1}$ ± 0.005	Cu mg/1 $\times 10^{-1}$ ± 0.001	Fe mg/1 $\times 10^{-1}$ ± 0.001	Cd mg/1 $\times 10^{-1}$ ± 0.002	Cr mg/1 $\times 10^{-2}$ ± 0.003	Pb mg/1 $\times 10^{-2}$ ± 0.005	Hg mg/1 $\times 10^{-4}$ ± 0.00002	Ba $\mu$ g/1 ± 0.50
S- 1	1.30	11.42	10.07	1.45	1.10	0.45	1.60	1.13	0.15	3.10	3.24	3.24	31.5
S- 2	2.80	13.00	1.86	0.93	0.88	2.07	0.14	0.40	0.64	2.10	2.40	2.11	68.5
S- 3	1.20	4.20	1.56	1.07	1.00	1.73	0.10	3.90	0.64	3.40	1.56	3.28	26.5
S- 4	4.20	2.00	1.56	1.23	0.62	1.56	0.20	0.40	0.62	3.90	0.62	2.34	35.5
S- 5	2.40	1.63	0.90	1.31	0.32	1.40	0.20	3.35	0.69	2.80	0.86	1.56	23.4
S- 6	3.45	4.28	3.42	1.05	1.20	1.56	0.14	0.06	0.69	3.90	1.17	1.64	23.5
S- 7	2.10	3.26	2.46	1.05	6.25	1.56	0.43	0.23	0.62	2.80	4.68	1.95	26.5
S- 8	1.30	0.51	13.70	0.92	1.56	1.75	0.36	0.04	0.54	2.80	0.78	2.34	29.6
S- 9	2.10	1.88	6.25	1.03	8.81	2.03	0.43	0.06	0.74	1.90	0.39	1.32	25.0
S-10	2.00	1.30	19.35	0.97	4.32	1.64	0.20	0.23	0.64	2.70	0.31	1.10	28.1
S-11	1.13	2.29	3.72	1.03	3.42	1.83	0.30	0.23	0.64	3.70	1.40	1.33	23.0
S-12	0.87	3.56	1.71	1.36	1.35	2.53	0.48	0.15	0.34	4.48	3.60	5.91	25.8
S-13	0.81	4.38	2.01	1.16	1.40	2.22	0.49	0.17	0.29	5.93	3.80	6.37	28.8
S-14	1.60	5.63	8.26	1.36	1.45	2.53	0.54	0.17	0.31	5.93	6.04	6.87	27.5
S-15	0.75	2.56	1.26	1.10	1.37	2.42	0.51	0.19	0.37	3.91	3.90	4.79	28.8
S-16	0.53	2.87	0.78	1.12	0.99	2.57	0.46	0.20	0.34	3.26	5.48	5.16	35.0
S-17	0.44	1.99	6.25	1.10	0.21	2.42	0.51	0.20	0.32	3.28	4.61	5.87	28.8
S-18	0.63	1.00	0.78	1.10	0.25	2.73	0.49	0.21	0.37	3.91	4.90	5.87	32.5
S-19	3.59	10.63	6.25	1.16	0.52	2.53	0.53	0.20	0.27	4.43	5.43	5.33	34.3
S-20	3.19	5.00	9.04	1.16	0.29	2.10	0.49	0.22	0.22	2.64	5.90	5.66	31.3

In the case of copper, the desirable level is 0.05 mg/l, with a maximum permissible limit of 1.0 mg/l. In this respect, all water samples are clean in terms of their copper content.

Samples S-13 and S-14 fall outside the prescribed range of 0.05 mg/l set for chromium. These waters therefore may pose health hazard.

Barium ions are not normally present in natural waters. Our data show that all the samples under investigation are clean with respect to barium for which the upper limit is 0.5 mg/l. In drinking waters, the safe allowed level of nickel and cobalt is set at 0.5 mg/l. The measured data on these metals indicate that all the water samples are clean with respect to them.

In conclusion, the waters in public utility in the investigated NWFP area are genuinely hard and possess certain trace metal levels in excess to the allowed levels. Therefore there is an urgent need of water quality control in these areas before these waters are accepted for human consumption.

All standard tolerable/maximum limits of concentrations for various parameters/trace metals included in discussion have been adopted from literature [16, 17].

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EXPERIMENTAL

The leaves and pods of the above three bean species were collected from plants growing wild in the sandy soil near the PNRK Laboratory Campus. The collected samples were washed for 2 days and this material was used for analysis.

The procedure was followed as described in [1]. The percentage in total sennoside is given in Table I.

Table I. Total sennoside content of *Cassia* species

Sl. No.	Species of the plant	Part of the plant examined	Total sennoside content (%)
1	<i>C. sennosida</i>	leaf	2.08
		pod	2.10
2	<i>C. fimbria</i>	leaf	1.30
		pod	1.18
3	<i>C. holosericea</i>	leaf	1.59
		pod	0.84

The absorption is wavelength curve of the sennosides in 0.1N KOH is shown in Figure 1. The maximum absorption is observed at 215 mμ. The absorption is low in the region of 200-220 mμ and increases sharply in the region of 220-240 mμ. The absorption is high in the region of 240-260 mμ and decreases sharply in the region of 260-280 mμ. The absorption is low in the region of 280-300 mμ and increases sharply in the region of 300-320 mμ. The absorption is high in the region of 320-340 mμ and decreases sharply in the region of 340-360 mμ. The absorption is low in the region of 360-380 mμ and increases sharply in the region of 380-400 mμ. The absorption is high in the region of 400-420 mμ and decreases sharply in the region of 420-440 mμ. The absorption is low in the region of 440-460 mμ and increases sharply in the region of 460-480 mμ. The absorption is high in the region of 480-500 mμ and decreases sharply in the region of 500-520 mμ. The absorption is low in the region of 520-540 mμ and increases sharply in the region of 540-560 mμ. The absorption is high in the region of 560-580 mμ and decreases sharply in the region of 580-600 mμ.

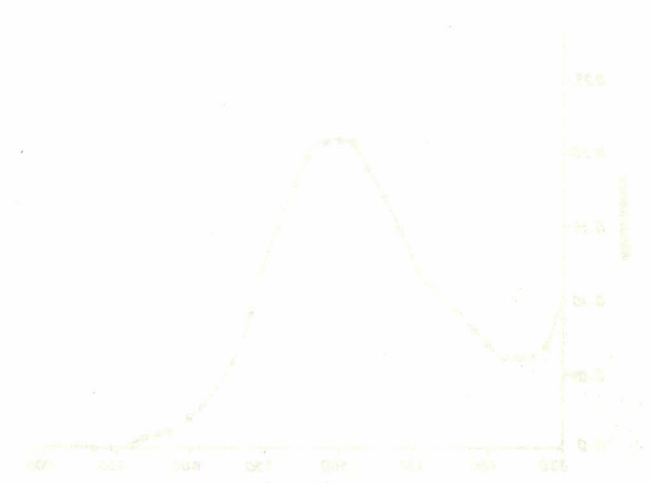


Fig. 1. Absorption is wavelength curve of the sennosides in 0.1N KOH.

The above three species are well known for their medicinal properties and are reported as being laxative and purgative in nature [2].