

CHEMICAL QUALITY ASSESSMENT OF MAJOR BRANDS OF BOTTLED WATER IN LAHORE

By

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ABSTRACT

Twenty five brands of commercially available bottled water were randomly collected from local markets to check the chemical quality for the confidence-building of the consumers. The suitability for human consumption was assessed according to WHO and EU guidelines/directives. Various water quality parameters along with anionic and cationic balance were analysed by standard APHA and AWWA methods. Forty percent of the samples had higher conductivity ranges as per EU directives while micronutrients (Cu^{+2} , Fe^{+2} , Mn^{+2} , Ni^{+2} , Zn^{+2}) were found entirely absent. Sodium was marginally higher in one sample as per WHO guidelines. Forty four percent of the samples had confirmed presence of arsenic (As) between the range of 1-11 ppb.

It is therefore, concluded that majority of the available bottled water brands conformed to the guidelines/directives of WHO/EU for the over all quality of drinking water.

Keywords: Bottled water, drinking water standards, maximum admissible concentration, atomic absorption spectrometer, ion chromatography

INTRODUCTION

Water is inevitable for life. It serves as the principal vehicle and mediator of physiological activities. It is a major source of all the essential minerals that play important role in human nutrition and proper functioning of various body systems (Versari *et al.*, 2002; Buchanan *et al.*, 2000). Calcium, magnesium, phosphate and fluoride, for instance, are needed for the proper teeth and bone development; calcium is also essential for activation of some enzymes that take part in blood clotting, and phosphate is an integral component of the energy transfer system (Buchanan *et al.*, 2000). Manganese and zinc are needed for the activation of a number of enzymes that are essential for the proper metabolic functioning of human body (Buchanan *et al.*, 2000). Copper is involved in the oxidative electron transport chain, while iron is the main constituent of haemoglobin and its deficiency causes anaemia (Murray *et al.*, 2000). Sodium is necessary for maintenance of osmotic and acid-base balance in the body, whereas potassium is involved in the rhythmic cardiac movements, and nerve and muscle irritability (Khan, 1998). Besides the essential need of minerals in human health, they become toxic when their intake exceeds the tolerance levels of the human body. Sodium, for example, is considered a contributory cause of dietary cancer (Jansson, 1996). The consumption of water with high fluoride and silica leads to multiple bone fracture (Fabiani *et al.*, 1999). Several other chemical contaminants identified in the drinking water, such as chloride, nitrate, sulphite, arsenic, toxic elements, organic compounds, and radionuclides can lead to cancer, human body malfunctioning, and chronic illnesses (Nickson *et al.*, 2005; Kuo *et al.*, 1997; Parslow *et al.*, 1997; Aral *et al.*, 1996; Tsezou *et al.*, 1996; Lester, 1995; Gabrielli and Geroffi, 1984).

The chemical quality of drinking water during recent years has deteriorated considerably due to the presence of toxic elements, which even in traces are a serious cause of health hazard (Ikem *et al.*, 2002). Besides the geochemical strata of groundwater sources, the problem is mostly traceable to the indiscriminated discharge of industrial effluents, leading to the chemical contamination of natural water bodies (Nickson *et al.*, 2005). It is now known that fluoride and arsenic contamination in groundwater in the vicinity of Lahore, Pakistan is traceable to geological formations of the region (Nickson *et al.*, 2005), while contamination of water with chromium, lead, cadmium and nitrite is traceable to agro-industrial activities (Nickson *et al.*, 2005). Because of the high risk and health hazards associated with intake of contaminated tap water, the consumption of bottled water is becoming popular worldwide, particularly due to ready availability at a reasonable cost, better taste, and the presence of fewer impurities. Bottled water not only serves the drinking purpose, it has also found wide usage in infant formula preparations, reconstitution of various food products, skincare formulations, and for filling humidifiers (Warburton, 1993). Since the availability of safe drinking water from the usual sources of supply in Pakistan has become a serious concern, a huge consumer demand for bottled water has been generated. This has led to the market flooding by a large number of commercial bottled water brands.

Various countries have enforced drinking water standards for the maximum permissible levels of different constituents, which may vary from country to country (Misund *et al.*, 1999). The quality of bottled drinking water in Pakistan is regulated by Pakistan Standards and Quality Control Authority (PSQCA, 2004), under which compulsory certification and the printing of PSQCA mark on the brand label is mandatory. Manufacturers are using various technologies, such as filtration, deionization, reverse osmosis, and ozonation for the preparation of their bottled water products (Allen *et al.*, 1989). Since these are non-selective procedures, while removing toxic chemicals, the essential micronutrients are also removed, thus creating a drinking water composition that may not have the desirable mineral balance as in the natural water. The present study, therefore, aims to conduct a survey of the chemical quality status of randomly collected 25 different bottled water brands vended in Lahore, Pakistan, inclusive of data on their physicochemical characteristics, essential minerals, micronutrients, and toxic elements.

MATERIALS AND METHODS

Sample Collection. Sets of three bottles each (volume: 0.5-1.5 liter) of commercially available bottled water brands vended in Lahore, Pakistan, were randomly purchased from stores and shops for assessment of their physicochemical quality. The chemical composition and expiry dates as printed on the brand labels were recorded. Details of the bottled water samples in terms of brand names, bottle volume capacity, container type and the code number allotted to each brand are given in Table 1.

Reagents. Reference standards for cations and anions used were from Merck (UK), while rest of the chemicals were of analytical reagent grade (Sigma-Aldrich, Germany).

Analytical Methodology and Quality Assurance. Bottled water samples were transported to the laboratory where most of the water quality parameters were analyzed

within 1-6 h. The pH and conductivity were respectively measured with pH meter (Knick 646, Germany) and conductivity meter (DiST 3, Hanna Instruments, Singapore), which

Table 1. Brand information about the commercially available brands of bottled water studied*.

Brand code#	Brand name	Bottle capacity (liter)
1	Ab-e-Hayat	1.5
2	Aqua Pak	1.5
3	Aqua Safe	0.5
4	Askari	0.5
5	Mitchell's Balane	0.5
6	Clear	0.6
7	Classic	0.5
8	Cool	1.5
9	Country	0.6
10	Empire	0.6
11	Everest	0.6
12	Ever Green	0.6
13	Fazal Din's Pharma Plus	0.5
14	Fresh	0.5
15	H ₂ O Plus	0.6
16	Maza	0.5
17	Minra	0.6
18	Mum	0.5
19	Naimat	1.5
20	Nation	0.6
21	Nestle Pure Life	0.5
22	Oas	0.5
23	Sparkletts	0.6
24	Springley	0.5
25	Sufi	0.625

*triplicate samples were analyzed; all brands used disposable plastic bottles as the container

were duly calibrated with standard pH buffers and conductivity standard solutions in accordance with standard procedures (PSQCA 2004; APHA 1998). Calcium carbonate alkalinity was measured by titration against standard 0.1N HCl, phosphate by colorimetric method, total dissolved solids (TDS) by evaporation, and total hardness (TH) by EDTA titration against calcium (Ca²⁺) ions (PSQCA, 2004; APHA, 1998). Total nitrate, nitrite, chloride, fluoride and sulphate were analyzed by an ion exchange column chromatography (HIC-6A series, Shimadzu, Japan) on shim pack column (IC-A1) and shim pack guard column using mobile phase of Tris buffer (2.5 mM phthalic acid and 2.4 mM Tris (hydroxymethyl) amino methane, pH 4.0) at flow rate of 1.5 ml/min; a conductivity detector (CDD-6A series, Shimadzu, Japan) was used with wavelength set at 195 nm (PSQCA, 2004; Shimadzu Operation Manual, 1999; APHA 1998). Atomic absorption spectrophotometer (Unicam 969, 2000, UK) was used to analyze metals, which included arsenic, cadmium, calcium, copper, iron, lead, manganese, magnesium, nickel, potassium, sodium and zinc (Unicam 969 Operation Manual Atomic Absorption Spectrophotometer, 2000).

Statistical Analysis. The data reported is the mean value of three separate analyses. Means were compared using Duncan's new multiple range tests at $p \leq 0.05$ (Steel *et al.*, 1997). Standard deviation (\pm) was accordingly calculated from the triplicate values.

Guidelines for Quality Control of Drinking Water. The chemical quality of the bottled water brands was evaluated and compared with the World Health Organization (WHO) guidelines for drinking water (WHO, 1993; 1981), the European Union (EU) maximum permissible directive for drinking water (Ikem *et al.*, 2002), and the Pakistan (PSQCA) standards specifications for bottled drinking water (PSQCA, 2004). A summary of WHO, EU and PSQCA values are given in Table 2.

Table 2. World Health Organization (WHO), European Union (EU) and Pakistan (PSQCA) drinking water standards.

Parameters	EU ^a (MAC) ^c	WHO ^b (MPL) ^d	Pakistan ^e (PS) ^f
pH	6.5-8.5GV*	6.5-8.5	-
Conductivity	400 μ S/cm	-	-
Total Dissolved Solids (TDS)	-	1000 ppm	500 ppm
Fluoride	-	1.5	-
Sulphates	250 ppm	250 ppm	250 ppm
Chlorides	-	250 ppm	250 ppm
Nitrate	-	50 ppm	-
Nitrite	-	0.5 ppm	1.0 ppm
Calcium	100 ppm GV	-	100 ppm
Magnesium	50 ppm	-	50 ppm
Sodium	150 ppm	200 ppm	-
Potassium	12 ppm	-	10 ppm
Iron	200 ppb	300 ppb	300 ppb
Copper	100 ppb GV	2000 ppb	-
Manganese	50 ppb	10 ppb	-
Zinc	100 ppb GV	3000 ppb	3000 ppb
Nickel	50 ppb	20 ppb	-
Phosphorous	5000 ppb as P ₂ O ₅ /l	-	-
Cadmium	5 ppb	3 ppb	3 ppb
Lead	50 ppb	10 ppb	-
Chromium	50 μ g/l (Total)	50 ppb	50 ppb
Arsenic	50 ppb	10 ppb	10 ppb

^aEuropean Union (EU) directives for drinking water (source Ikem *et al.* 2002)

^bWorld Health Organization (WHO) guidelines for drinking water (WHO 1993)

^cMAC = maximum admissible concentration

^dMPL = maximum permissible limit

^ePakistan standards specifications for bottled drinking water (PSQCA 2004)

^fPS = Pakistan Standards PS: 4639-2004 (R) under compulsory certification marks

scheme

*GV = guide value

RESULTS AND DISCUSSION

pH, conductivity, total hardness, total dissolved solids, alkalinity as CaCO_3 , carbonates, bicarbonates in all the brands are given Table 3. Most of the water quality constituents were within the acceptable limits of the respective guidelines, directives and the standard of WHO, EU and PSQCA. The only exception noted was in respect of conductivity, which in 10 brands (# 1, 2, 3, 8, 9, 10, 12, 15, 20, 24) was higher (411-946 $\mu\text{S/cm}$) than the maximum permissible limit of 400 $\mu\text{S/cm}$ of EU directive. The conductivity was exceptionally high (946 $\mu\text{S/cm}$) in brand #2. The level of conductivity is a useful parameter for the assessment of chemicals quality of drinking water, as conductivity indicates the total inorganic contents in the drinking water. Only one brand (# 25) had pH value of 6.5 (slightly acidic), which is the lowest limit in the acceptable range of 6.5-8.5, while all others had the pH value range of 7.1-8.1. However, brand #2 and 21 had pH 8.1 and 8.0, respectively, which may be rated to be on the alkaline side. Phenolphthalein alkalinity was zero, which is an indication that hydroxide alkalinity was absent (Ahmed, 1998), and bicarbonate was the major form of alkalinity (Table 3). High alkalinity is associated with high pH, which in terms of contribution in water is due to, in the order of, hydroxide < carbonates > bicarbonates. High alkaline water is unpalatable. The low pH range of 7.1-8.1 further indicates that bicarbonates were the major contributors of alkalinity in the water brands analyzed.

Table 3. Summary of some physicochemical parameters of the brands of bottled water studied.

Brand #	pH	TH* (ppm)	TDS* (ppm)	Alkalinity as CaCO_3 (mg/L)	Conductivity (µS/cm)	Total Carbonates as CaCO_3^* (ppm)	Bicarbonate* (ppm)
1	7.62±0.11	224±2.00	316±7.9	2.98±0.17	504±5.04	149	182.21
2	8.14±0.021	196±1.15	545±11.44	2.61±0.20	946±11.35	130.5	159.40
3	7.87±0.015	94±1.00	282±5.34	1.25±0.021	450±5.85	62.5	76.25
4	7.84±0.017	102±1.53	206±4.74	1.36±0.011	274±4.66	68	82.96
5	7.87±0.010	120±1.52	192±4.22	1.61±0.015	350±4.90	80.5	98.21
6	7.17±0.118	101.6±0.81	229±4.81	1.35±0.010	338±4.40	67.5	82.36
7	7.64±0.021	104±1.52	276±7.45	1.88±0.017	276±3.04	69	84.18
8	7.57±0.026	140±1.00	224±5.82	1.86±0.021	411±7.40	93	113.46
9	7.88±0.015	96±2.08	246±5.66	1.28±0.017	456±5.93	64	78.08
10	7.85±0.012	98±1.73	288±7.20	1.31±0.006	499±4.99	65.5	79.91
11	7.83±0.025	88±1.00	188±4.89	1.17±0.021	365±6.93	58.5	71.37
12	7.67±0.015	112±1.53	238±5.71	1.49±0.005	572±9.15	74.5	90.89
13	7.78±0.010	102±1.52	214±6.21	1.36±0.015	294±5.88	68	82.96
14	7.17±0.014	124±3.10	250±6.00	1.67±0.019	314±4.39	83.5	100.65
15	7.86±0.030	232±1.52	348±9.40	3.09±0.061	500±7.50	154.5	188.5
16	7.32±0.038	64±1.15	156±2.96	1.15±0.031	185±1.85	57.5	70.15
17	7.27±0.01	168±1.16	276±5.52	2.24±0.022	343±6.52	112	136.64
18	7.89±0.020	84±1.73	132±2.77	1.12±0.006	182±3.64	56	68.32
19	7.81±0.015	62±0.58	188±4.70	1.23±0.023	290±4.93	61.5	75.3
20	7.84±0.021	148±1.15	366±9.51	2.07±0.020	544±8.16	100	120.35
21	8.01±0.006	132±1.00	258±5.42	1.76±0.011	387±7.35	88	107.36
22	7.86±0.032	112±1.68	180±4.68	1.50±0.012	249±2.49	75	91.07
23	7.64±0.043	174±1.74	228±5.47	2.32±0.015	344±3.44	116	141.52
24	7.37±0.264	200±1.16	328±7.21	2.67±0.017	460±6.9	133.5	162.87
25	6.52±0.031	128±1.92	300±6.30	1.71±0.015	366±6.95	85.5	104.31

TH* = total hardness; TDS* = total dissolved solids; Carbonates* = by calculations from the mean value of alkalinity; Bicarbonates* = by calculations from the mean values of alkalinity

The amounts of essential nutrients such as calcium, magnesium, phosphorus, sodium, and potassium are reported in Table 4. As seen from Table 4, the values of calcium, magnesium and potassium were found with the range of WHO guidelines and EU directives. However, notable deviations were observed with respect to sodium (211 ppm in brand # 15 respectively), was higher as per WHO guideline of 200 ppm and the EU directive of 150 ppm (157.5 and 211 ppm in brand # 5 and 15 respectively). It may be noted that sodium-rich water may be detrimental to the health of heart and blood pressure patients (US EPA, 1998a), which may contribute to the occurrence of hypertension (Garzon and Eisenberg, 1998). Low salt diet patients may be affected by high intake of sodium-rich water. It is significant to note that though the values of calcium, magnesium, phosphorus and potassium were within the maximum limits, these in comparison were extremely low (compare Table 2 and Table 4). It may be observed in this regard that epidemiological and chemical studies have suggested that drinking magnesium-rich water is good for human consumption, as it reduces the frequency of sudden death (Garzon and Eisenberg, 1998). Calcium and phosphorus impart positive effect on proper bone and teeth development, while potassium is useful for rhythmic cardiac movements, for preventing muscle cramps, and irritability of nerves (Khan, 1998).

Table 4. Status of some minerals/macronutrients (calcium, magnesium, sodium, potassium, phosphorus) in the brands of bottled water studies.

Brand #	Sodium (ppm)	Potassium (ppm)	Calcium (ppm)	Magnesium (ppm)	Phosphorus* (ppm)
1	37.5±0.562	2.2±0.055	35±0.700	14.3±0.286	1025±14.35
2	140±1.540	5.2±0.119	30±0.660	28.8±0.720	1025±16.40
3	54±0.972	1.7±0.036	16±0.384	11.1±0.299	450±5.85
4	8±0.096	2.4±0.065	20±0.380	10.94±0.252	725±12.32
5	157.5±2.362	4.6±0.087	24±0.624	15.28±0.412	600±9.60
6	8±0.152	5.7±0.154	36±0.756	4.95±0.319	175±3.15
7	13±0.169	2.26±0.054	28±0.588	9.08±0.218	650±11.70
8	30±0.480	4.31±0.099	25±0.550	14.34±0.373	825±16.50
9	74±1.110	2.12±0.053	20±0.460	4.95±0.144	550±5.51
10	83±1.411	2.3±0.051	20±0.480	12.6±0.3024	600±7.80
11	50±0.900	1.8±0.038	15±0.285	8.7±0.183	800±12.81
12	86±1.376	2.9±0.084	24±0.600	13.5±0.351	850±12.75
13	44±0.440	3.6±0.097	15±0.315	11.2±0.280	340±4.08
14	23.5±0.399	2.5±0.067	12±0.240	14.2±0.383	950±18.05
15	211±3.165	5.3±0.154	30±0.750	22.5±0.518	1200±15.6
16	48±0.864	8.87±0.204	15±0.420	6.67±0.160	50±0.70
17	47.5±0.617	3.34±0.080	20±0.540	13.01±0.286	700±11.2
18	14.86±0.178	2.56±0.059	25±0.650	5.4±0.146	300±5.10
19	40.1±0.642	2.87±0.057	14±0.350	11.5±0.276	800±14.40
20	72±1.080	3.5±0.094	28±0.756	16.8±0.437	1050±12.60
21	20.3±0.365	0.23±0.005	37.5±0.937	5±0.125	10±0.15
22	6.2±0.111	3.4±0.088	30±0.780	5.8±0.116	375±6.00
23	26.3±0.394	1.1±0.026	31±0.744	10.4±0.270	875±15.75
24	54.8±0.877	1.96±0.045	37±0.999	16.9±0.406	1050±17.85
25	14.4±0.274	1.09±0.031	54±1.188	8.74±0.183	25±0.30

* as P₂O₅

All the brands analyzed for nitrate, sulphate and chloride had levels below the maximum acceptable limits of these anions (Table 5). Fluoride and nitrite was not detected in any sample. The presence of nitrate and nitrite in drinking water at high levels causes shortness of breath, blue babies syndrome in infants, and haemorrhaging of spleen (US EPA, 1998b). Fluoride-rich water is a cause of bone fractures and teeth disorders (Fabiani *et al.*, 1999).

Table 5. Level of some anions (chloride, nitrate, sulphate, nitrite*, fluoride*) in the brands of bottled water studied.

Brand #	Chloride (ppm)	Sulphate (ppm)	Nitrate (ppm)
1	10.13±0.203	50±1.05	17.4±0.021
2	38.89±0.739	111.1±2.22	2.83±0.042
3	34.92±0.733	46.91±1.17	nd
4	7.94±0.183	12.34±0.296	6.25±0.006
5	14.88±0.372	37.04±0.778	3.12±0.018
6	60.14±1.683	25±0.500	nd
7	39.22±0.784	35.63±0.998	nd
8	22.55±0.519	27.5±0.715	nd
9	30.4±0.760	41.25±1.114	13.1±0.029
10	34.64±0.831	46.25±1.063	2.1±0.028
11	5.82±0.122	11.06±0.243	5.49±0.005
12	30.25±0.756	66.67±1.600	11.07±0.032
13	2.4±0.062	19±0.380	0.6±0.009
14	4.2±0.966	27.04±0.730	7.05±0.015
15	5.34±0.133	31.45±0.786	6.52±0.021
16	21.52±0.602	12.58±0.264	12.08±0.006
17	6.31±0.183	28.93±0.694	nd
18	2.59±0.057	25.8±0.671	nd
19	2.26±0.054	18.68±0.411	nd
20	17.45±0.366	51.85±1.192	nd
21	79.19±1.900	15.43±0.386	nd
22	2.44±0.066	31.86±0.860	nd
23	3.84±0.084	9.8±0.186	8.82±0.004
24	6.1±0.122	18.2±0.364	12.94±0.007
25	98.7±1.877	0.5±0.011	nd

* = fluoride and nitrite were not detected in any of the bottled water brand studied

The observations on the detection of some essential micronutrients and toxic metals are recorded in Table 6. Manganese, nickel, zinc, chromium, cadmium and lead were not detected in any sample. However, among the essential micronutrients, copper was not detected in 15 brands, while in the remaining 10 brands the micronutrient was present in minor quantities (3.2-13.1 ppb as compared to the maximum acceptable limits of WHO, EU, PSQCA, Table 2). Likewise, iron was not detected in 4 brands, while the value detected for this essential micronutrient was also extremely low. It is noteworthy that the presence of both copper and iron in drinking water is good for human consumption to overcome the problems associated with their deficiencies, such as anaemia (Murray *et*

Table 6. Status of micronutrients and toxic metals (copper, iron, manganese, nickel, zinc, chromium, cadmium, lead)* in the brands of bottled water studied.

Brand #	Copper (ppb)	Iron (ppb)
1	Nd	152.7±3.054
2	5.3±0.106	106±2.226
3	Nd	22.5±0.562
4	Nd	10.38±0.249
5	Nd	41.5±0.871
6	13.2±0.251	76.7±1.764
7	Nd	65.1±1.627
8	Nd	5.5±0.121
9	Nd	nd
10	3.2±0.080	nd
11	7±0.154	52±1.040
12	Nd	3.8±0.072
13	Nd	33.4±0.835
14	4.6±0.092	1.3±0.025
15	Nd	8.3±0.174
16	Nd	21±0.525
17	Nd	17±0.391
18	Nd	nd
19	Nd	24±0.600
20	Nd	39±1.014
21	6±0.114	nd
22	4.8±0.110	28±0.588
23	4.7±0.117	29±0.638
24	13.1±0.249	28.1±0.759
25	10.7±0.257	18.1±0.416

nd* = manganese, nickel, zinc, chromium, cadmium, lead were not detected

al., 2000). The non-detection of cadmium and lead in any brand may be rated as a positive indicator, as both are extremely toxic and their ingestion causes nausea, vomiting, sensory disturbances, liver injury, shock and renal failure (US EPA, 1998c). From Fig. 1 arsenic, another toxic metal, was detected in 11 brands (44%). It may be noted, however, that except for brand # 5, the detected arsenic in all other brands was within the WHO, EU, PSQCA maximum acceptable limits for this toxic element (< 10 ppb). High concentration of arsenic in drinking water increases the ratio of still-births and spontaneous abortion, causes arsenism and black-foot disease, hyperpigmentation, cardiovascular diseases, and skin cancer (Jain and Ali 2000; WHO 1981).

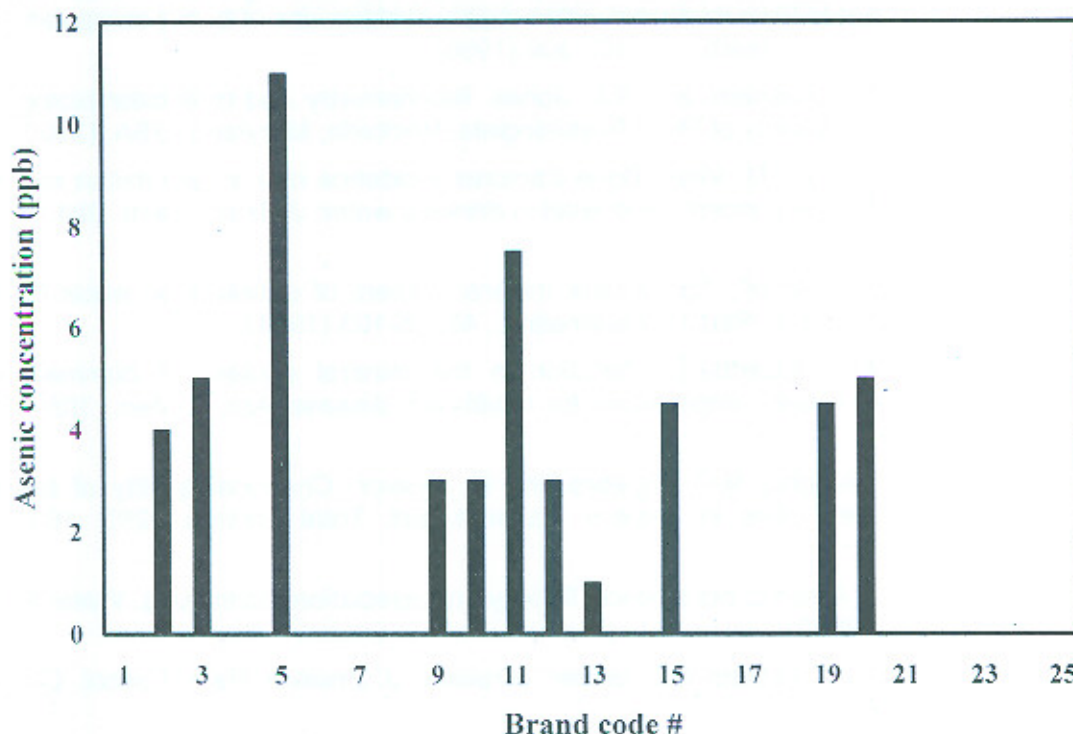


Fig. 1. Arsenic concentration detected in the bottled water brands studied.

CONCLUSION

The chemical quality of bottled water depends on the source and chemical composition of the raw water. It also depends on the treatment technologies used by various manufacturers. Most of the samples investigated for their chemical quality had values within the acceptable limits of WHO, EU and PSQCA. However, some bottled water brands had higher conductivity. The detection of high sodium content in 10 brands may be rated as a negative attribute. Arsenic was detected in 11 brands, one of which exceeded the acceptable limit. The brands exceeding the limits of conductivity, sodium and arsenic may not be good for human consumption. The low values of essential minerals and micronutrients is a grey area, which merits critical review by nutritionists and manufacturers.

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SHALLOW GROUNDWATER QUALITY OF UN-COMMANDED AREAS OF PUNJAB DOABS

By

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ABSTRACT

Pakistan is an agricultural country and agriculture is the mainstay of its economy. Due to limited surface irrigation supplies, groundwater is extensively being exploited and utilized to meet the crop water requirements.

Scarps Monitoring Organization being the main groundwater investigating agency carried out water quality monitoring under NDP to assess the groundwater quality status of un-commanded areas of Punjab Doabs. Water samples were collected from the private tubewells of Bari (78), Rechna (69), Chaj (71), Thal (169) Doabs and D.G. Khan Area (32). The collected water samples were analysed, in Water Testing laboratory of SMO. The analysis comprised of pH, EC, Cations, Anions, TDS, SAR and RSC. Analytical results were summarized doab-wise on different water quality parameters. In Bari Doab, 34(44%) water samples were usable, 21(27%) marginal and 23(29%) were hazardous.

In Rechna Doab, 42(61%) water samples were usable, 22(32%) marginal while 5(7%) were hazardous. In Chaj Doab, out of the collected water samples, 42(59%), 23(32%) and 6(9%) were usable, marginal and hazardous respectively. In Thal Doab 119(70%) water samples were usable, 44(26%) marginal while 6(4%) were hazardous. In D.G. Khan, out of the total collected water samples, 5(16%) were usable, 10(31%) marginal and 17(53%) were hazardous.

GEO-CHEMICAL CLASSIFICATION

Major geo-chemical types of groundwater underlain in Bari Doab are NaHCO_3 and $\text{Ca}(\text{HCO}_3)_2$. NaHCO_3 and $\text{Mg}(\text{HCO}_3)_2$ are major geo-chemical types of groundwaters underlain in Rechna Doab. In Chaj Doab, the major groundwaters underlain are NaHCO_3 and $\text{Ca}(\text{HCO}_3)_2$. The major geo-chemical type of groundwaters underlain in Thal Doab and D.G. Khan Area is Na_2SO_4 .

Key Words: Groundwater, Usable, Marginal, Hazardous, EC, SAR and RSC

1. INTRODUCTION

Water is one of the major constraints which limits agricultural production in the country, especially in Barani tract and effective water management is perhaps the biggest challenge to achieve rapid yield increase. The existing surface supplies are quite inadequate not only to meet the crop water requirements but also to bring more area under cultivation. Groundwater resources have played an increasingly important role in

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meeting the country's food and fiber requirements. Groundwater is approximately meeting around 45% of crop water requirements in the country. During the last few years, substantial increase in the number of private tubewells has changed the underground paradigm.

Water level has now declined due to private tubewells development. The impact on groundwater resources is alarming and causes the intrusion of saline water in the fresh zone through lateral or upward movement. Annual groundwater extraction through the tubewells is around 42 MAF while only in Punjab, it is 36 MAF.

2. METHODOLOGY

Keeping in view the problem of water quality in the un-commanded areas, groundwater monitoring program was carried out under Institutionalized Environmental Monitoring (IEM) of Land and Water Conditions under National Drainage Program (NDP) during 2001-04. Scarps Monitoring Organization (SMO) WAPDA conducted the water quality monitoring by sampling of the existing private tubewells in un-commanded areas of Bari, Rechna, Chaj, Thal Doabs and D.G. Khan Area.

The collected water samples were completely analysed in Water Testing laboratory for assessing their quality for pH, EC, Cation, Anion, TDS, SAR and RSC for irrigation purpose. Based on water analysis, the water samples were categorized as Usable, Marginal and Hazardous on the basis of EC, SAR and RSC.

The main objectives of the monitoring program were:

- Collection of necessary data forming sound base for the optimal and safe use of groundwater.
- Delineate fresh and saline groundwater zones.
- Provide necessary water quality data for future planning of groundwater exploitation.

3. RESULTS AND DISCUSSION

Water quality is assessed on the basis of salinity as EC and sodicity as SAR and RSC. Different parametric limits adopted by SMO, WAPDA for categorization of irrigation water are incorporated in Table-1.

Table-1: Water Quality Criteria

Water Quality Category	Parametric Limits		
	Salinity as EC ($\mu\text{S}/\text{cm}$) at 25°C	Sodicity as SAR	Sodicity as RSC (meq/l)
Usable	< 1500	<10	< 2.5
Marginal	1500 – 2700	10 -18	2.5 - 5.0
Hazardous	> 2700	>18	> 5.0

3.1 Groundwater Quality in Bari Doab

The collected data was processed / analysed on the basis of EC, SAR and RSC. In Bari Doab, the number of tubewells alongwith percentage falling in each category was as follows:

Table-2: **Number of Tubewells Falling under Different Water Qualities based on EC, SAR and RSC.**

Name of Doab	No. of T/Wells Sampled	Shallow Groundwater Quality based on EC, SAR and RSC					
		Usable		Marginal		Hazardous	
		Nos.	%age	Nos.	%age	Nos.	%age
Bari Doab	78	34	44	21	27	23	29

The above table indicates that out of 78 tubewells, 34(44%) produced usable, 21(27%) marginal and 23(29%) hazardous water on the basis of all parameters.

In Bari Doab, the water quality of each tubewell on the basis of all parameters was depicted on the map. After contouring, the area was calculated and is reproduced below in Table-3.

Table-3: **Area alongwith percentage falling under different categories based on EC, SAR and RSC in un-commanded Area of Bari Doab.**

(Million Acres)

Name of Doab	G.A	Area falling under different categories based on EC, SAR and RSC					
		Usable		Marginal		Hazardous	
		Area	%age	Area	%age	Area	%age
Bari Doab	0.184	0.080	44	0.050	27	0.054	29

The table reveals that out of 0.184 million acres, 44% was underlain as usable, 27% marginal and 29% hazardous.

3.2 Geo-Chemical Classification

Geo-Chemical classification was done by Stiff's method. In this method, the dominant radicals from cation and anions (50% or more) are combined together to establish the geo-chemical types. Some types of waters present in un-commanded area of Bari Doab are given in Table-4.

Table-4: Number of Tubewells alongwith Percentages falling under Different Geo-Chemical Types in un-commanded Area of Bari Doab.

Total No. of T/Wells Sampled	Geo-Chemical Types							
	NaHCO ₃		Na ₂ SO ₄		Ca(HCO ₃) ₂		Mg(HCO ₃) ₂	
	No.	%	No.	%	No.	%	No.	%
78	63	81	1	1	13	17	1	1

The above table reveals that majority of the tubewells produced Sodium bicarbonate 63(81%) type of water. The second major category was Calcium bicarbonate 13(17%). The third and fourth categories were Sodium sulphate and Magnesium bicarbonate 1(1%) each.

3.3 Groundwater Quality in Rechna Doab

In Rechna Doab, the number of tubewells falling under different categories based on EC, SAR and RSC alongwith percentage are summarized in Table-5.

Table-5: Number of tubewells falling under different categories based on EC, SAR and RSC

Name of Doab	No. of T/Wells Sampled	Shallow Ground Water Quality based on EC, SAR and RSC					
		Usable		Marginal		Hazardous	
		Nos.	%age	Nos.	%age	Nos.	%age
Rechna Doab	69	42	61	22	32	5	7

The table indicates that out of 69 tubewells, 42(61%) produced usable, 22(32%) marginal while 5(7%) yielded hazardous water.

The water quality of each tubewell was depicted on map. After contouring, the area was calculated as usable, marginal and hazardous and is reported in Table-6.

Table-6: Area alongwith percentage falling under different categories based on EC, SAR and RSC in un-commanded Area of Rechna Doab.

(Million Acres)

Name of Doab	G.A.	Area falling under different categories based on EC, SAR and RSC					
		Usable		Marginal		Hazardous	
		Area	%age	Area	%age	Area	%age
Rechna Doab	1.311	0.798	61	0.418	32	0.095	7

The above table reveals that 61% area was underlain by usable, 32% marginal while 7% hazardous water on all parameters basis.

3.4 Geo-Chemical Classification

Under this classification, three types of geo-chemical were present in Rechna Doab which are presented in Table-7.

Table-7: Number of tubewells alongwith percentage falling under different Geo-Chemical types in un-commanded Area of Rechna Doab.

Geo-Chemical Types	No. of T/Wells Sampled			69		
	NaHCO ₃	Ca(HCO ₃) ₂	Mg (HCO ₃) ₂	No.	%	No.
				45	65	2
						3
						22
						32

The table shows that most of the tubewells pumped out Sodium bicarbonate waters (65%). The next categories noticed were Magnesium bicarbonate (32%) followed by Calcium bicarbonate (3%).

3.5 Groundwater Quality in Chaj Doab

The analytical results were processed on all parameters basis as usable, marginal and hazardous. The number of tubewells alongwith percentage falling under each category is given below.

Table-8: Number of tubewells falling under different water quality categories based on EC, SAR and RSC

Name of Doab	No. of T/Wells Sampled	Shallow Ground Water Quality based on EC, SAR and RSC			Chaj Doab		
		Usable	Marginal	Hazardous	Nos.	%age	Nos.
					42	59	23
							32
							6
							9

The table reveals that out of 71 water samples, 42(59%) yielded usable, 23(32%) marginal and 6(9%) hazardous waters.

The water quality of each tubewell was depicted on the map. After contouring, the area was delineated in usable, marginal and hazardous waters which is produced below in

Table-9.

Table-9: Area alongwith percentage falling under quality categories based on EC, SAR and RSC in un-commanded Area of Chaj Doab

Name of Doab	G.A.	(Million Acres)					
		Shallow Ground Water Quality based on EC, SAR and RSC					
		Usable		Marginal		Hazardous	
Area	%age	Area	%age	Area	%age		
Chaj Doab	0.726	0.429	59	0.235	32	0.062	9

The table reveals that out of 0.726 million acres 59% was underlain by usable, 32% marginal and 9% hazardous water.

3.6 Geo-Chemical Classification

Under this classification, four types of geo-chemical types were established in the groundwater and reported in Table-10.

Table-10: Number of tubewells alongwith percentage falling under different Geo-Chemical types of un-commanded Area in Chaj Doab.

No. of T/wells Sampled	Geo-Chemical Types							
	NaHCO ₃		Na ₂ SO ₄		Ca(HCO ₃) ₂		Mg (HCO ₃) ₂	
	No.	%	No.	%	No.	%	No.	%
71	41	58	5	7	15	21	10	14

The table indicates that majority of the tubewells produced Sodium bicarbonate water (58%) followed by Calcium carbonate (21%) and Magnesium bicarbonate (14%) and Sodium sulphate (7%) waters.

3.7 Groundwater Quality in Thal Doab

Groundwater quality based on processed analytical data was summarized on basis EC, SAR and RSC is reported in Table-11.

Table-11: Number of tubewells falling under different categories based on EC, SAR and RSC.

Name of Doab	No. of T/Wells Sampled	Shallow Ground Water Quality based on EC, SAR and RSC					
		Usable		Marginal		Hazardous	
		Nos.	%age	Nos.	%age	Nos.	%age
Thal Doab	169	77	46	41	24	51	30