

Heavy metal burden in beverages consumed in the Kingdom of Saudi Arabia

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ABSTRACT

The levels of selected heavy metals (As, Ni, Cr, Fe, Mn, Cd, Cu, Hg, Pb and Zn) and macronutrients (Na, K, Ca and Mg) in local/imported carbonated waters, juices and mineral waters were determined. Relevant parameters like pH and TDS (total dissolved solids) were also measured. Atomic absorption spectrophotometric technique was applied for these estimations. The study revealed that the nutritional quality of local carbonated water was better than that of fruit juices, both in terms of heavy metal and macronutrient levels. Among the cardboard-packed juices, guava was found to contain maximum arsenic, whereas mixed fruit was found to contain maximum lead. Among the carbonated waters, Ribena was found to contain maximum chromium, whereas Sun Cola showed maximum levels of lead. Generally, most of the beverages showed heavy metal levels within the stipulated limits laid down by WHO.

KEYWORDS: beverages, safety, heavy metal, health effects.

INTRODUCTION

The use of beverages is deeply imbedded in the lifestyle of people. Soft drinks are linked to our social activities. These drinks are composed of water, carbon dioxide gas, acidulants, flavors, colors and sugars. This blend of ingredients provides a pleasant refreshment. Harmless coloring materials and additives lend a normal appearance to soft drinks and increase their aesthetic appeal. However, for health reasons,

water used in soft drinks and canned fruits juices must be soft and free from any appreciable amount of toxic trace metals and organic matter [1, 2]. Emulsifiers are widely used in many cardboard-packed items. Typically, they are used as solubilizers, emulsifiers and demulsifiers, detergents, crystallization modifiers, foaming and defoaming agents, wetting and lubricating agents and complexing agents. Their origin maybe synthetic or natural, and hence their toxic effects on human health cannot be ignored [3].

The role of heavy trace metals is very critical in determining the quality of soft drinks, especially that of chromium [4, 5]. Macronutrients also furnish a strong nutritional supplement in soft drinks, the same being true for canned juices. Several studies during recent years have underlined the importance of investigations aimed at monitoring heavy trace metals and macronutrients in non-alcoholic soft drinks [6, 7]. It was, therefore, imperative to explore the present status of locally manufactured and imported versions of soft drinks in terms of the above-cited toxic trace metals and the macronutrients (sodium, potassium, magnesium and calcium). Atomic absorption method was used to determine the levels of these toxic metals and macronutrients in various samples of carbonated soft drinks, juices, mineral, spring and natural waters using standard procedures.

MATERIALS AND METHODS

The investigation was carried out on eight carbonated drinks of local origin, nine carbonated drinks of imported origin, fourteen fruit juices of

local origin and three different natural waters. The beverage samples were procured from local markets and kept refrigerated until analysis. Chemical analysis was started as soon as it was practicable. Heavy metals and macronutrients were assayed by using a Shimadzu atomic absorption spectrophotometer (Model AA-670). Prior to analysis, the optimum measuring conditions were determined as a function of instrumental parameters as per the instructions given by the manufacturer. To validate the reproducibility of the measurements, each sample was run in triplicate and the average was reported. The precision achieved was better than $\pm 1.5\%$. Research grade chemicals were used throughout the investigation. Merck salts/standards of guaranteed purity ($> 99.9\%$) were used to prepare standards.

All carbonated beverage samples were degasified using dilute nitric acid (1:10, v/v) prior to aspiration. In case of fruit juices, a 100.0 mL aliquot was taken from a well-shaken container, in a 250.0 mL pyrex beaker. To this, 20.0 mL of 50% nitric acid was added, followed by 5.0 mL of 70% perchloric acid with constant shaking. The solution matrix was allowed to cool to room temperature after heating to about 60°C for thirty minutes. The clear digest so obtained was aspirated directly onto the atomic absorption spectrophotometer. The mineral, spring and natural waters were directly aspirated, without prior filtration. All these procedures were adopted

from standard literature [1-3]. Pb, Hg, Cd, Zn, Ni, Cr, Cu, As, Mn, Mg, Na, K, Ca, and Fe, were estimated in local/imported carbonated waters, juices, mineral, spring and natural waters by atomic absorption technique.

RESULTS AND DISCUSSION

The sampling codes, description and origin of both local and imported carbonated drinks, fruit juices and drinking waters analyzed are given in Table 1. Table 2 summarizes the concentrations of sodium, potassium, magnesium, calcium and heavy trace metals, expressed as average of triplicate subsamples of various local carbonated drinks. The total dissolved solids (TDS) along with pH value of various drinks are also listed in the same table.

The reported pH values for various carbonated drinks in Table 2 ranged between 2.1 and 3.3, while the corresponding TDS per 100 mL of the samples ranged between 7.2 and 13.3 mg/100 mL; the carbonated drink CWL-01 was found to be the most acidic while CWL-07 was found to have the least acidic character, but with high calcium content. Thus, the total dissolved salts could be considered to contribute towards higher pH as in the case of CW-07. The total dissolved solids normally comprise of sugar, sodium or potassium citrate, citric acid and chemical stabilizers. Therefore, as expected, it is always desirable to have minimal TDS to achieve good quality of the water to be used for the production of

Table 1. Basic data on sample codes, description and origin of local and imported carbonated drinks, local fruit juices and different types of drinking waters.

Sample code*	Sample description	Origin	Package type
CWL-01	Pepsi Cola	Local	Glass bottle
CWL-02	Pepsi Diet	Local	Glass bottle
CWL-03	Fanta	Local	Glass bottle
CWL-04	Mirinda	Local	Glass bottle
CWL-05	Sprite	Local	Glass bottle
CWL-06	7-Up	Local	Glass bottle
CWL-07	Dew	Local	Glass bottle
CWL-08	Coca-Cola	Local	Glass bottle

Table 1 continued..

Sample code*	Sample description	Origin	Package type
CWI-01	7-Up Diet	Imported	Tin
CWI-02	Sun cola	Local	Tin
CWI-03	Coca-Cola	Imported	Tin
CWI-04	Ribena	Imported	Tin
CWI-05	Pepsi Diet	Imported	Tin
CWI-06	Club Soda	Imported	Tin
CWI-07	Sprite	Imported	Tin
CWI-08	Soda Water	Imported	Glass bottle
CWI-09	Tonic Water	Imported	Tin
JL-01	Mixed Fruit	Local	Cardboard Carton
JL-02	Guava	Local	Cardboard Carton
JL-03	Falsa	Local	Cardboard Carton
JL-04	Mango	Local	Cardboard Carton
JL-05	Apple	Local	Cardboard Carton
JL-06	Orange	Local	Cardboard Carton
JL-07	Mixed Fruit	Local	Cardboard Carton
JL-08	Banana Cool	Local	Cardboard Carton
JL-09	Plum Cool	Local	Cardboard Carton
JL-10	Mixed Fruit	Local Shop	Glass Container
JL-11	Pomegranate	Local Shop	Glass Container
JL-12	Mango	Local Shop	Glass Container
JL-13	Apple	Local Shop	Glass Container
JL-14	Cane Sugar	Local Shop	Glass Container
W-01	Mineral Water	Locally produced	Plastic bottle
W-02	Sparkling Water	Imported	Glass bottle
W-03	Tap Water	Filtered well water	

*CWL-carbonated water (Local), CWI-carbonated water (Imported), JL-juice (Local), W-drinking water.

a carbonated drink. Table 2 clearly shows in general, low TDS is associated with low macronutrient content. Compared with natural drinking waters (W-03), the sodium content of CWL-01, CWL-02, CWL-04 and CWL-05 is on the higher side, reaching up to a maximum of 15.00 mg/L. The rest of the carbonated drinks have a lower sodium content of up to a minimum

of 6.5 mg/L. This variation pattern may also be seen for other nutrients such as magnesium and calcium. However, the case of potassium is uniquely different since all the carbonated water samples contained potassium higher than 7.5 mg/L which was detected for the tap water (W-03). The listed drinks have the same hardness as natural drinking water W-03, with a calcium

Table 2. Concentrations (mg/L) of macronutrients and heavy trace metals in local carbonated drinks.

Sample code + B3:RII	pH	TDS mg/100 mL	Na	K	Mg	Ca	Cr	Ni	As	Fe	Mn	Cd	Cu	Hg	Pb	Zn
CWL-01	2.1	09.6	14.0	16.0	09.5	28.80	0.053	0.007	0.146	1.25	0.004	0.010	0.10	0.535	0.187	*
CWL-02	3.1	10.4	14.7	17.5	08.1	23.70	0.007	0.052	0.105	1.25	0.001	*	0.15	0.150	0.012	*
CWL-03	2.8	12.6	09.0	19.0	06.8	24.70	0.010	0.041	0.028	1.50	0.001	0.004	0.10	0.042	0.006	*
CWL-04	2.6	12.7	15.0	49.0	10.0	35.60	0.010	*	0.340	1.25	*	0.030	0.25	0.130	0.040	*
CWL-05	3.2	07.2	14.8	16.0	09.5	24.60	0.012	0.045	0.180	1.25	0.008	0.030	0.10	0.024	0.160	*
CWL-06	2.9	07.2	06.5	16.0	07.0	20.80	0.013	0.117	0.139	1.20	0.013	0.001	0.01	0.290	0.176	*
CWL-07	3.3	13.3	07.5	47.0	09.0	35.50	0.006	0.065	0.837	1.70	0.007	0.030	*	0.420	0.302	*
CWL-08	2.4	09.8	07.7	23.0	07.7	36.10	0.024	0.089	0.390	1.60	0.014	0.030	0.10	0.346	0.300	*

* Not detected.

Table 3. Concentrations (mg/L) of macronutrients and heavy trace metals in various imported carbonated drinks.

Sample code	pH	TDS mg/100 mL	Na	K	Mg	Ca	Cr	Ni	As	Fe	Mn	Cd	Cu	Hg	Pb	Zn
CWI-01	3.1	13.7	13.70	15.40	12.60	52.90	0.010	0.039	0.253	0.086	0.023	0.016	0.005	0.123	0.188	0.079
CWI-02	2.7	09.2	14.69	45.30	04.70	20.10	0.007	0.008	0.408	0.658	0.006	0.008	0.005	0.202	0.445	0.001
CWI-03	2.6	10.2	08.90	22.00	01.70	38.20	0.015	0.038	0.037	0.434	0.002	0.010	0.003	0.224	0.263	0.010
CWI-04	2.8	13.2	08.30	55.00	08.20	32.60	0.025	0.084	0.129	0.866	0.149	0.008	0.004	0.276	0.211	0.048
CWI-05	3.1	06.2	13.30	19.00	02.20	19.80	0.017	0.103	0.194	1.625	0.008	0.010	0.016	0.550	0.105	*
CWI-06	4.7	09.1	13.70	51.00	04.70	13.30	0.018	0.002	0.091	0.600	0.004	0.008	0.018	0.133	0.053	*
CWI-07	3.0	11.3	10.90	19.00	01.40	31.60	0.015	0.050	0.065	0.366	0.007	0.012	0.010	0.121	0.083	*
CWI-08	4.2	07.1	10.30	15.40	09.20	31.80	0.011	0.028	0.207	0.126	0.009	0.011	0.022	0.162	0.046	*
CWI-09	2.6	08.1	02.00	13.50	01.20	38.10	0.004	0.057	0.319	1.970	0.002	0.013	0.015	0.280	0.147	*

* Not detected.

content of 38.1 mg/L. On the whole, these drinks were found to be quite rich in sodium, potassium, magnesium and calcium.

The heavy trace metal content (Table 2) of these beverages revealed that the incidence of occurrence of all the trace metals, except zinc, was almost 100%. Iron was found to have the maximum concentration among all the metals investigated; the observed range was 1.20-1.70 mg/L. This showed a relatively narrow variability in the iron content of various drinks, the minimum amount being in CWL-06 while the maximum was in CWL-07. When analyzed from the perspective of allowed limits of trace metal levels for lead, arsenic and mercury [7], none of the samples exceeded the recommended limit of concentrations of these metals. Copper, an essential trace element, was found to be present at a comparatively low level in all the samples, the same being true for manganese and zinc. Thus, among the essential trace elements, only iron was present at a maximum concentration level. The observed levels of chromium and manganese were comparably lower still. From the point of view of mercury contamination, sample CWL-01, though close to upper safe limit (1.0-1.5 ppm), cannot be recommended for human consumption on regular basis. This high level could be attributed to the mercury content of local waters used in the preparation process or chemical preservatives added to stabilize the drinks.

The macronutrient data for various imported drinks are summarized in Table 3. Here, the pH range of 2.6-4.7 was recorded along with the TDS range of 6.2-13.7 mg/100 mL. The data, thus, showed a wider range of pH for the imported drinks as compared with the local drinks. The corresponding levels of TDS for the two types of drinks were comparable, except for diet and club brands of drinks containing no salt constituents. These included CWI-02, CWI-05, CWI-06 and CWI-08. However, their macronutrient contents were found to be comparable. The maximum sodium content was found in CWI-02, the Mirinda sample from U.A.E., while the minimum sodium content (2 mg/L) was in CWI-09, a Tonic Water sample from Singapore. The potassium content ranged between 13.5 and 55.0 mg/L with minimum content in CWI-09, while the maximum

was in the drink from U.K. (CWI-04). The concentration of magnesium was comparable in samples CWI-03, CWI-07 and CWI-09 with a range of 1.2-1.7 mg/L, the same being true for CWI-02 and CWI-06 at 4.7 mg/L. Similarly, samples CWI-04 and CWI-08 had comparable magnesium content. The only sample having the peak magnesium content of 12.6 mg/L was CWI-01. This diet 7-Up sample was claimed to have a low calorie with no sweet blending agent, yet it had maximum TDS as compared with all the drinks in the category. The overall status of the macro-nutrients in these drinks was compatible with that required for human nutrition [8].

Unlike local drinks, the overall heavy metal burden in imported drinks was far smaller (Table 3), especially for chromium, arsenic, iron, calcium, copper and mercury. Of all the metals estimated, the maximum concentration was found for iron, as in the case of local carbonated drinks. However, the variation in the concentration range of iron was higher in the case of imported drinks. On the whole, the concentrations of essential trace elements such as manganese, iron, and zinc were well within the recommended limit of 1.0-1.5 mg/L. The overall nutritional status, both in respect of macronutrients and heavy trace metals, of the imported carbonated drinks was found to be better than that of local counterparts. It, therefore, could be inferred that the quality of chemicals and water used in the preparation of local drinks does not meet required standards.

The macronutrient study on local fruit juices (Table 4) reported a pH range 2.4-4.6, comparable to that of local carbonated waters. The TDS values indicated high sugar and macronutrient concentrations. Maximum sodium content was found in samples JL-03 and JL-10, from the Frost and Frooto products, respectively. However, there was no marked difference in the sodium content of the juices, which remained at about 15 mg/L. There was more variation in the concentration values of magnesium ranging between 8.30 and 15.2 mg/L as was the case for potassium ranging between 47.0 and 77.0 mg/L. The apple juice JL-05 was found to be rich in potassium, as was JL-11, the pomegranate juice, and JL-09, the plum cool juice. Nutritionally, these fruit juices were found to be remarkably rich in macronutrients.

Table 4. Concentrations (mg/L) of macronutrients and heavy trace metals in fruit juices of local origin.

Sample code	pH	TDS mg/ 100 mL	Na	K	Mg	Ca	Ni	Cr	As	Fe	Mn	Cd	Cu	Hg	Pb	Zn
JL-01	3.1	20.00	14.40	15.20	71.00	25.00	0.368	0.159	0.877	1.410	0.222	0.105	0.081	0.015	1.039	0.393
JL-02	3.0	18.30	15.10	11.00	69.00	24.90	0.070	0.074	1.080	1.100	0.260	0.004	0.047	0.087	0.009	0.067
JL-03	2.6	11.90	15.20	11.80	47.00	26.70	0.122	0.054	0.414	1.230	0.295	0.014	0.039	*	0.051	1.242
JL-04	3.3	18.00	15.00	11.70	61.00	25.30	0.137	0.027	0.399	1.860	0.220	0.009	0.117	0.021	0.065	0.052
JL-05	3.0	15.50	15.00	10.50	77.00	25.10	0.154	0.009	0.238	*	0.168	0.010	0.001	0.173	0.101	0.012
JL-06	2.7	12.50	15.10	10.80	69.00	25.30	0.276	0.007	0.146	*	0.198	0.170	0.027	0.115	0.119	0.122
JL-07	3.8	14.00	15.00	11.20	75.00	24.40	0.053	0.012	0.787	*	0.103	0.014	0.069	0.120	0.209	0.009
JL-08	4.3	11.80	14.20	11.20	71.00	28.30	0.056	0.099	0.132	3.370	0.161	0.017	0.046	0.152	0.364	0.113
JL-09	3.7	14.00	14.20	11.00	77.00	27.20	0.068	0.077	0.868	2.520	0.140	0.009	0.059	0.165	0.264	0.073
JL-10	2.9	11.10	15.20	11.10	70.00	25.50	0.132	0.032	0.342	0.550	0.119	0.010	0.087	0.093	0.163	0.025
JL-11	2.4	15.20	14.90	08.30	77.00	26.40	0.080	0.019	0.431	0.278	0.090	0.009	0.039	0.024	0.263	0.032
JL-12	3.0	14.40	14.60	09.20	76.00	25.40	0.103	0.095	0.113	1.440	0.159	0.013	0.047	0.020	0.338	0.290
JL-13	3.1	12.90	14.80	12.10	68.00	27.60	0.204	0.045	0.92	*	0.090	0.014	0.005	*	0.376	0.022
JL-14	4.6	19.70	14.01	09.10	58.80	26.50	0.606	0.061	*	0.550	0.709	0.020	0.140	*	0.386	1.633

* Not detected.

Table 5. Concentrations (mg/L) of macronutrients and heavy trace metals in various drinking water.

Sample code	pH	Na	K	Mg	Ca	Cr	Ni	As	Fe	Mn	Cd	Cu	Hg	Pb	Zn
W-01	7.4	8.2	7.0	25.0	5.1	0.004	0.093	0.575	0.141	0.014	0.014	0.027	0.124	0.074	*
W-02	7.4	7.9	7.5	11.8	1.4	0.008	0.022	0.291	0.151	0.013	0.015	0.002	0.287	0.040	0.003
W-03	7.3	13.8	7.5	7.2	38.1	0.009	0.007	0.480	0.021	0.024	0.001	*	0.464	0.084	1.647

* Not detected.

Table 4 also reports the heavy metal contents of the fruit juices. The observed levels were found to be higher than corresponding metal levels in carbonated waters, due perhaps to the presence of stabilizers and other chemical additives used as anticoagulants and life-enhancers. All the juice samples contained higher TDS, compared to other drinks. Moreover, they were rich in macronutrients as well. Levels of Hg and As were within the stipulated limits laid down by health agencies. The generally recommended safe limit of 1 mg/L arsenic was exceeded in one sample: 1.080 mg/L for JL-02. In the case of iron, this limit was exceeded in almost all the samples except JL-10, JL-11 and L-14. In the case of lead (Pb), JL-01 also crossed the safe limit. Finally, only one sample, JL-03 had a zinc content of 1.242 mg/L, in excess to the stipulated limit. In view of this analysis, the juice sample JL-01, could be labelled as undesirable from the viewpoint of health. The sample JL-02, was also observed to be undesirable from the viewpoint of its high arsenic and iron contents. Even though the upper limit of zinc concentration could be relaxed to 5 mg/L [7], the juice sample JL-03 had fairly high zinc and iron contents, the same being true for JL-08. Researchers from other parts of the world have reported similar levels of heavy metals in soft drinks [8-10].

A direct comparison of trace metal content of natural waters and these juices indicated that their high levels in juices could only be attributed to the chemicals used in the blending process. Problems arising from tin cans are no longer significant as the majority of these juices are cardboard-packed. The quality of drinking waters, as compared with quality of carbonated waters and juices was also evaluated. The relevant data in terms of macronutrients and heavy trace metals are summarized in Table 5. The mineral water W-01 and the spring water W-02, showed the same pH and comparable sodium and potassium contents. They both had a calcium content as low as 5.1 and 1.4 mg/L, as against 38.1 mg/L for W-03. The latter was found to have more sodium, but a comparable potassium content, as compared with W-01 and W-02. Also, magnesium content for W-03 was lower compared with two imported waters. The quality of imported waters can be adjudged on the

basis of their trace metal levels as well. In the case of chromium, manganese, mercury, lead and zinc for W-03, the corresponding levels for W-01 and W-02 are relatively much lower. In contrast, nickel in W-03 was found to be less than that present in W-01 and W-02, the same being true for arsenic in the case of W-03 and W-01, for iron and cadmium.

CONCLUSION

The current study revealed that nutritional quality of local carbonated waters is better than that of local fruit juices, both in terms of heavy trace metal and macronutrient levels. It was observed that local fruit juices normally conform with the international standards laid down for macro and micro trace metals in various drinks. Of the foreign carbonated waters, the diet or low-calorie versions are suitable for direct human consumption and in the category of mineral waters, the spring waters are suitable from the viewpoint of quality and nutrition.

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CONFLICT OF INTEREST STATEMENT

Authors declare that there is no conflict of interest.

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