Heavy Trace Metal and Macronutrient Levels in Various Soft Drinks and Juices

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Summary: The levels of selected heavy toxic trace metals (Cr, Ni, As, Fe, Mn, Cd, Cu, Hg, Pb and Zn) and macro-nutrients (Na, K, Mg and Ca), along with relevant pH and TDS (total dissolved solids) measurements on local/imported carbonated waters, juices, mineral, spring and natural waters are reported. The atomic absorption technique was applied for these estimations conducted on thirty four samples procured from local markets. The study revealed that nutritional quality of local carbonated waters was better than that of fruit juices, both in terms of heavy toxic trace metals and macro-nutrient levels. The local Pepsi Cola sample contained maximum mercury (0.535 mg/L) while Tops showed maximum arsenic (0.837 mg/L). Out of cardboard packed juices, apple juice was found to have maximum arsenic (2.920 mg/L). Local fruit juices were found not to conform with the standards allowed for safe ingestion of micro- and macro-metals in various drinks, as laid down by WHO.

Introduction

The use of beverages is deeply imbedded in life style of people. Soft drinks are linked to our social activities. It is in this category of edibles, determined more by social rather than nutritional factors, that soft drinks have always remained popular among users. These drinks are composed of water, carbon dioxide gas, acidulents, flavors, colors and sugars. This blend of ingredients provides a pleasant refreshment. Harmless coloring materials and additives lend usual appearance to soft drinks and increase their aesthetic appeal. However, for health reasons, water used in soft drinks and canning fruit 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 beverages including many cardboard packed items. Typically they are used as solubilisers, emulsifiers and demulsifiers, detergents, crystallization modifiers, foaming and defoaming agents, wetting and lubricating agents and complexing agents. Their origin may be synthetic or natural, and hence their toxic effects on human health cannot be ignored [3].

The role of heavy toxic trace metals is very critical in determining the quality of soft drinks, especially that of chromium [4,5]. Macro-nutrients 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 macro-nutrients 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 macro-nutrients (sodium, potassium, magnesium and calcium). Atomic absorption method was used to determine the levels of these toxic metals and macro-nutrients in various samples of carbonated soft drinks, juices, mineral, spring and natural waters using standard procedures.

Results and Discussion

The sampling codes, description and origin of both local and imported carbonated drinks, fruit juices and drinking waters analysed 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. 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 most acidic while CWL-07 was found to contain relatively

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

Sample Code*	Sample Description	Origin	Package Type
CWL-01	Pepsi Cola	Local	Glass bottle
CWL-02	Teem	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	Tops	Local	Glass bottle
CWL-08	Coca Cola	Local	Glass bottle
CWI-01	7-Up Diet	Nutra Sweet Blend, Searle & Co., Singapore	Tin
CWI-02	Mirinda	Dubai Refreshment Co.(Ltd), U. A. E.	Tin
CWI-03	Coca Cola	Fraser and Neave Ltd. Singapore	Tin
CWI-04	Ribena	Beectiam Products, U. K.	Tin
CWI-05	Pepsi Diet	Nutra Sweet blend, Singapore	Tin
CWI-06	Club Soda	Dubai Refreshment Co. U. S. A.	Tin
CWI-07	Sprite	Fraser and Neave Ltd. Singapore	Tin
CWI-08	Soda Water	London Soda Waters, U. K.	Glass bottle
CWI-09	Tonic Water	Loin (S) PTE, Ltd. Singapore	Tin
JL-01	Mixed Fruit	Frost, Milk Pak Ltd. Lahore, Pakistan	Cardboard Carton
JL-02	Guava	Frost, Milk Pak Ltd. Lahore, Pakistan	-do-
JL-03	Falsa	Frost, Milk Pak Ltd. Lahore, Pakistan	-do-
JL-04	Mango	Frost, Milk Pak Ltd. Lahore, Pakistan	-do-
JL-05	Apple	Frost, Milk Pak Ltd. Lahore, Pakistan	-do-
JL-06	Orange	Frost, Milk Pak Ltd. Lahore, Pakistan	-do-
JL-07	Mixed Fruit	Best Juices, Malik Food Ind. Ltd. Lahore	-do-
JL-08	Banana Cool	Country Juices, Maaher Food Ind. Ltd. Lahore	-do-
JL-09	Plum Cool	-do-	-do-
JL-10	Mixed Fruit	Frooto, Kamran distributors (PVT) Karachi	-do-
JL-11	Pomegranate	-do-	-do-
JL-12	Mango	-do-	-do-
JL-13	Apple	Bambino Food Ind. Ltd. D. G. Khan, Pakistan	-do-
JL-14	Cane Sugar	Local Shop	Glass Container
W-01	Mineral Water	Massafi Mineral Water, Co., U. S. A.	Plastic bottle
W-02	Spring Water	Emirate Water, U. A. E.	Plastic bottle
W-03	Tap Water	Simli Lake, Islamabad	

*CWL - Carbonated water (Local), CWI - Carbonated water (Imported), JL - Juice (Local) W- Drinking water

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

Sample Code	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	*

minimum 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 CWL-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 have a good quality of the water to be used for the production of a carbonated drink. Table 2 clearly shows that, in general, low TDS is associated with low macro-nutrient content. Compared with natural drinking waters of Simli Lake (Table 5), the sodium content of CWL-01, CWL-02, CWL-04 and CWL-05 is on the higher side, upto a maximum of 15.00 mg/L. The rest of carbonated drinks have lower sodium content upto a minimum of 6.5 mg/L. This variation pattern may also be seen for other macro-nutrients such as magnesium and calcium. However, the case of potassium is uniquely different since all the samples are above 7.5 mg/L potassium estimated

for the Simli Lake natural water. The listed drinks have the same degree of hardness as compared with natural drinking water W-03, with a calcium content of 38.1 mg/L (Table 5). 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 of 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 in CWL-07. Next to iron, were the concentrations of arsenic, mercury and lead. When seen from the perspective of allowed limits of trace metal levels for lead, arsenic and mercury [8], 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, same being true about manganese and zinc. Thus, out of 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 macro-nutrient data for various imported drinks are summarized in Table 3. Here, the pH range of 2.6 - 4.7 was recorded with a 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 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 macro-nutrient contents were found to be comparable. The maximum sodium content was found in CWI-02, the Mirinda sample from U.A.E., while minimum sodium (2 mg/L) was found 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 maximum 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 be 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, copper and zinc were well within recommended limit of 1.0 - 1.5 mg/L. The overall nutritional status, both in respect of macro-nutrients and heavy trace metal, of the imported carbonated drinks was found to be better than that of local

Table 3 Concentrations (mg/L) of macro-nutrients 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	0.988	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	0.017	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	0.025	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	*

* Below detection limit

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 macro-nutrient study on local fruit juices (Table 4) exhibited a pH range of 2.4 - 4.6, comparable to that of local carbonated waters. The TDS values indicated high sugar and macro-nutrient 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 all the juices, which remained at about 15 mg/L. There was more spread 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 macro-nutrients.

Table 4 also reports the heavy metal contents of the fruit juices. The observed levels were found to be higher than corresponding trace metal levels in carbonated waters, due perhaps to the presence of stabilizers and other chemical additives used as anticoagulants and life-enhancers. Iron and arsenic, and in a couple of cases, for mercury, lead and zinc showed maximum concentrations. The generally recommended safe limit of 1 mg/L arsenic is, thus, exceeded by many fruit juices: 1.080 mg/L for JL-02; 1.399 mg/L for JL-04; 2.132 mg/L for JL-08; 2.342 mg/L for JL-10, 1.431 mg/L for JL-11; 1.113 mg/L for JL-12 and 2.920 mg/L for JL-13. In the case of iron, this limit was exceeded by almost all the samples except JL-10, JL-11 and JL-14. In case of mercury, JL-01 and JL-02 crossed this limit and in case of lead again JL-01 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, a Frost mixed juice, could be labelled as highly undesirable from the viewpoint of health. The guava Frost juice sample, JL-02, was also observed to be undesirable from the viewpoint of its high arsenic, mercury and iron contents. Even though the upper limit of zinc concentration could be relaxed to 5 mg/L [8], the juice sample JL-03 had fairly high arsenic and iron contents; the same being true for JL-08, the banana cool. From the viewpoint of arsenic content, juices JL-08 and JL-13, having arsenic content greater than 2 ppm would be considered as highly undesirable from the viewpoint of human consumption [9].

A direct comparison of trace metal content of natural waters and these juices indicated that their high levels in juices could result only from chemicals used in the blending process. Problems arising from tinned caps are no longer significant as 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 are summarized in Table 5 in terms of macro-nutrients and heavy trace metals. The mineral

Table 4 Concentrations (mg/L) of macro-nutrients 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	0.205	0.081	3.405	2.039	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	1.887	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	1.399	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	0.215	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	0.220	0.209	0.009
JL-08	4.3	11.80	14.20	11.20	71.00	28.30	0.056	0.099	2.132	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	2.342	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	1.431	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	1.113	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	2.920	*	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

Table 5 Concentrations (mg/L) of macro-nutrients and heavy trace metals in various drinking waters.

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

* Below detection limit

water W-01 and the spring water W-02, both imported, showed the same pH and comparable sodium and potassium contents. They both had calcium content as low as 5.1 and 1.4 mg/L as against 38.1 mg/L for W-03, the Simli Lake water. 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 the Simli Lake water 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. Hence, in respect of these metals the imported waters claim a far superior quality. In contrast, nickel in W-03 was found to be less than that present in W-01 and W-02, same being true for arsenic in the case of W-03 and W-01, for iron and cadmium.

The 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 macro-nutrient levels. The local pepsi cola sample was found to contain maximum mercury (0.535 mg/L), while tops contained maximum arsenic (0.837 mg/L). Out of cardboard packed juices, apple juice contained maximum arsenic (2.920 mg/L). It was observed that local fruit juices normally do not conform with the standards internationally 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.

Experimental

The investigation was based 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 analyzed. Chemical analysis was started as soon as it was practicable. Before estimating the selected heavy toxic metals and macro-nutrients onto a Shimadzu Atomic Absorption Spectrophotometer (Model AA-670), the optimum measuring conditions were determined as a function of instrumental parameters as per instructions given by the manufacturer. The reproducibility was checked by undertaking absorption measurements for triplicate runs. The precision achieved was better than ±1.5%. Inter-laboratory comparison of finished data was conducted at NIH, Islamabad. 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 [10,11].

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. Sampling was conducted from within Islamabad and outside markets.

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