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Research Paper

An Evaluation of Metal cations and anions Concentration in Surface Water from Six selected areas of Coastal Guyana via Flame Atomic Spectroscopy

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Abstract: *The concentration of heavy metals such as Pb, Cu, Zn and Cd, and anions: Cl^-, NO_3^- and SO_4^{2-} and PO_4^{3-} were determined for six selected surface waters of coastal Guyana . It was found that the concentration was area dependent. Cl^- anion registered the highest value of 85.0 ± 1.0 mg/L at area (5). Area (3) registered a value of 0.15 ± 0.0 mg/L for NO_3^-. In areas such as (1) and (2), the surface waters showed negligible detection for NO_3^-. The highest value for SO_4^{2}- , 18.95 ± 0.97 mg/L was noted for area (2). The toxic heavy metals such as Pb and Cd showed low and no detection in some areas. For Cd, this range from 0.002 ± 0.00 to 0.03 ± 0.00 mg/L, with the highest occurring at area (3). Pb was undetected in most areas. In areas of detection, the highest concentration of 0.05 ± 0.0 11 mg/L was noted. With the exception of Pb in areas (4) and (5) and Cu in area (1), the concentration of these metal ions/element and anions are below the threshold limit in surface water as accepted by International accepted standards of the Environmental Protection Agency, EPA and thus are no threat to the national livelihood. However, the country surface water must be continually tested as anthropogenic activities increases.*

Keywords: Heavy metals, Concentration, Selected water, Coastal Guyana, Threshold limit, National livelihood.

Introduction

Surface water is water on the surface of the planet such as in a stream, river, lake, wetland, or ocean. It can be contrasted with groundwater and atmospheric water [1-7]. Providing sufficient quantities of high quality water to satisfy our domestic, industrial and agricultural needs is an ongoing global problem. Increasing population size, climate change and pollution will only exacerbate the global status. There is no physical shortage of water on the planet earth as it covers 70% of the globe. However, 97% of the world water is saline and is thus non-drinkable, 2% is locked in glaciers and polar ice caps, resulting in 1% to meet humanity needs [7]. Guyana's water need continual monitoring to assess the concentration of toxic elements[8].

There is an ongoing need to determine the concentration of toxic elements in water in view of the fact that some can be toxic, amongst other effects[1-10]. Also, to ensure that the concentration of these is below the threshold limit [1-7,11]. Some cations, anions are toxic beyond their threshold value because of their mobility in living systems and abilities to cross cell membranes. Toxic anions are poisonous and can cause harm or even death via malfunctioning of the organs such as the kidney etc. They enter the body via drinking waters, food, fruits and vegetables, fish and other foods in general that may have been exposed to such waters. Thus, the levels of concentration of cations/ anions must be controlled in our water bodies.

For example, lead is a lethal ubiquitous metal. Natural waters seldom contain more than 5 ug/L, even though much higher values have been reported. Lead in water may originate from industrial, mine, smelter discharges or from the dissolution of old lead plumbing [1-7, 9-10]. In Guyana, the deposition of lead batteries may also contribute to the lead been carried to water ways and is also a source of lead poisoning [8]. Other sources include lead based indoor paint, lead in air from the combustion of lead containing industrial emissions, lead glazed pottery, lead dust brought home by industrial workers on their shoes and clothes. Lead has neurological, hematological and renal effects. Amongst these are lethargy, vomiting, irritability, loss of appetite, dizziness and eventual death [1-7, 9,10].

Cadmium is used in electroplating, galvanizing and as a cathode material for nickel-cadmium batteries. It's also used as a colour pigment in paints and plastics and is a by product of zinc, lead mining and smelting. Cadmium is highly toxic and has been responsible for poisoning through food. Minute quantities are responsible for adverse changes in the arteries of human kidneys, resulting in proteinuria. Cadmium has also been responsible for human cancers, osteomalacia and osteoporosis. High concentration of cadmium may produce an acute chemical pneumonitis and pulmonaty edema. Cadmium concentration of 200 ug/L is toxic to fish. Cadmium can also enter the water via industrial discharges or the determination of galvanized pipe [9-10].

Zinc is an essential element to humans. More than 200 metalloenzymes, belonging to six major categories of which isomerases and lipases are included, require zinc as a cofactor. Zinc also stimulates the synthesis of metallothionein. Zinc chelates with cysteine and histidine, forming the so called "zinc fingers" which binds to specific DNA regions. Zinc is also necessary for the development and normal functions of the nervous systems and it also stabilizes membranes by binding to various ligands. In an aquatic environment, zinc concentrations above 5 mg/L may cause a bitter astringent taste and an opalescence in alkaline waters. Zinc usually enters the water from deterioration of galvanized iron and deterioration of brass. Lead and cadmium may also be present because they are impurities of the zinc in galvanizing[1-7, 9,10].

In humans, ingestion of drinking water with concentration of copper greater than 4mg Cu/L will produce gastrointestinal symptoms such as nausea, vomiting and diarrhea. Ingestion of large amounts of copper salts such as $CuSO_4$ may produce hepatic necrosis and death. Wilson's disease is characterized by an extensive accumulation of copper in the liver, brain, kidneys and corneas [9-13].

Dissolved copper can sometimes impart a light blue or blue-green colour and an unpleasant metallic, bitter taste to drinking-water. The taste threshold of copper as the sulfate or chloride salt in tap or demineralized water ranged from 2.4 to 2.6 mg/litre. The taste threshold increased in the presence of other solutes [9-13].

Chloride is spherical in shape and is one of the major inorganic anions in water and waste water. Cl^- anion has both positive and negative impact on human lives[14-16]. Biologically, chloride is the major intra and extra cellular anion found in the body. It is also responsible for maintaining acid/base balance, transmitting nerve impulses and regulating fluid in and out of cells.

Chloride is also an important component of the chloride-bicarbonate exchanger, also known as the anion exchange (AE) protein. In the absence of Cl^- ion, bicarbonate transport stops. Cl^- ion is also implicated in the genetic disease cystic fibrosis, in that Cl^- ion is responsible for the function of the chloride ion channel[14,15]. Chloride is an essential micronutrient for higher plants. Rainwater, dust and air pollution are natural inputs of chloride to soils. Human practices such as irrigation and chemical fertilizer contribute significantly to chloride deposition [21].

On the negative side, high Cl^- ion content has a corrosive effect on metal pipes, stainless steel, high alloyed materials, structures and is harmful to most trees and plants. Chlorides can also react with humic substances present in water to form trihalomethanes (THMs) which are very carcinogenic and can cause cancer during consumption. Organo chlorine can also be formed such as CFCs (chlorofluorocarbons), PCBs (Polychlorobiphenyls), Dioxin and others. These compounds are harmful to both humans and aquatic life. Chlorides can also contaminate freshwater streams and lakes. Fish and aquatic communities cannot survive in high levels of chlorides.

The phosphate anion (1) is a hypervalent molecule [15,16]. It is the conjugate base of the hydrogen phosphate anion, HPO_4^{2-}, which is the conjugate base of $H_2PO_4^-$, the dihydrogen phosphate ion, is the conjugate base of H_3PO_4, phosphoric acid. Organophosphate (2), Figure 1 is an ester of phosphoric acid, H_3PO_4. Phosphate can also form polymeric ion such as diphosphate (pyrophosphate, $P_2O_7^{4-}$, triphosphate, $P_3O_{10}^{5-}$etc. Metaphosphate ions which are long linear polymers have an empirical formula of PO_3^- and are found in many compounds.

Phosphates anion occurs in natural and wastewaters as Orthophosphates, Condensed or acid hydrolysed phosphates (Pyro-, meta-, and other polyphosphates), and organically bound phosphates. They occur in solution, in particles or detritus, or in the bodies of aquatic organisms. These forms of phosphates arise from a variety of sources. Phosphates may also occur in bottom sediments and in biological sludge [1-7]. Phosphate anion, PO_4^{3-}, (1) is a salt of phosphoric acid, H_3PO_4, Figure 1.

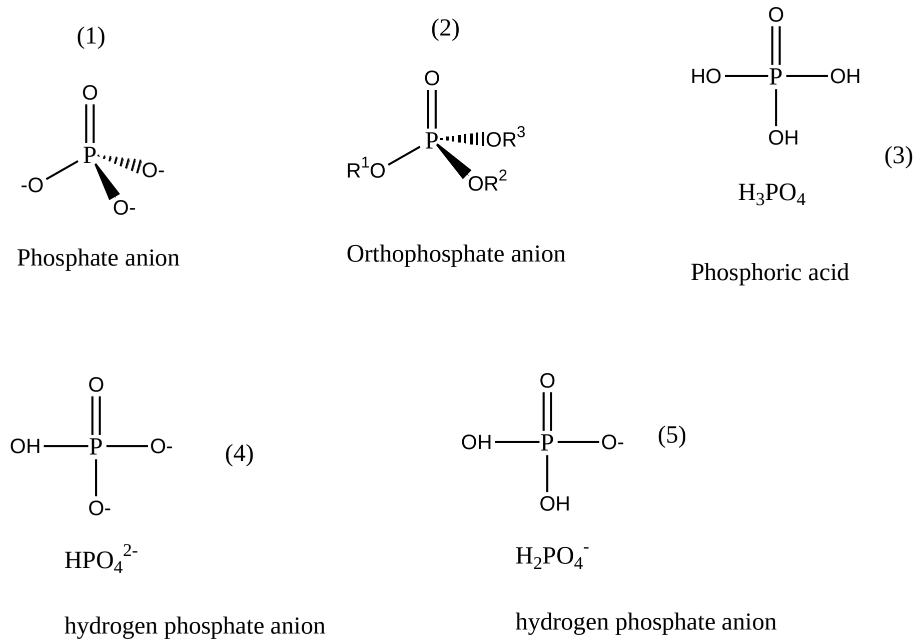
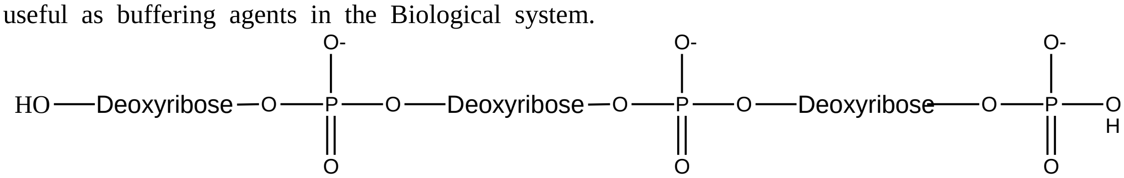


Figure 1

Biologically, Phosphates are found in the form of Adenosine Phosphates (AMP, ADP and ATP) and in DNA and RNA, Figure 2. Hydrolysis of these results in the release of phosphates. Phosphates are useful as buffering agents in the Biological system. These include Na_2HPO_4, NaH_2PO_4 and the corresponding potassium salts. Phosphates form the structural material of bone and teeth[1-7, 14-15].



(b)

Figure 2: Structure of Adenosine Triphosphate, ATP, (a) and a section of a single strand of DNA

Phosphorus in phosphates is essential for the growth of plants, animal and microorganisms. It is an essential part of the process of photosynthesis and can be the nutrient that limits the primary productivity of a body of water. In instances, where phosphate is a growth-limiting nutrient, the discharge of raw or treated wastewater, agricultural drainage, or certain industrial wastes to that water may stimulate the growth of photosynthetic aquatic micro and macro-organisms in nuisance quantities. Phosphorus is involved in the formation of all oils, sugars, starches etc. It helps with the transformation of solar energy into chemical energy, proper plant maturation, withstanding stress and it also encourages blooming and root growth [17-19].

Nitrates have both beneficial and harmful uses. On the positive side, nitrates (NO_3^-) are essential plant nutrients that are important for protein synthesis [20-22]. They are responsible for the growth of plants and nitrogen fixation. Nitrates are found in nature, since they are the end product of the aerobic decomposition of organic nitrogenous matter as well as the decomposition of organic micro-organisms.

Unpolluted natural waters contain only miniature amounts of nitrate. In surface water, nitrate is a nutrient which is taken up by plants and assimilated into nucleic acid. Nitrates have also been responsible for Eutrophication, the process of enriching water or algal blooms.

Biologically, high concentration of nitrate in drinking water is dangerous to small children, infants and fetuses[14, 22]. High concentrations of nitrate in drinking water can induce blood disorder in babies less than six months of age. In infants intestine, bacteria, notable *Escherichia coli*, reduce the nitrate ions (NO_3^-)

to nitrite ions (NO_2^-). The nitrite ions are absorbed into the bloodstream where they oxidized iron (ii) Fe^{2+} in the hemoglobin to iron (iii) Fe^{3+}. The presence of hemoglobin containing oxidized ion which is known as Met-hemoglobin reduce the oxygen carrying capacity of the blood. More Babies are more vulnerable to high nitrate levels than adults because their stomachs are less acidic. This allows the *E. coil* to colonize higher up the digestive tract and convert the nitrate ions to nitrite prior to absorption. A concentration of met-hemoglobin in the blood above 25% cause the skin and lips of the infected infant to take on a bluish hue, the 'Blue Baby Syndrome' or methanoglobianemia. If untreated, the condition can be fatal. Boiling water contaminated with nitrate increases the nitrate concentration and the potential risk [13, 22].

Internationally, the Helmholtz centre for environmental research in Germany have shown that Gazan (Gaza strip) groundwater contains level of nitrates (NO_3^-) ions up to eight times higher than the World Health Organisation (WHO) safe standard of 45 mg/L. The high level of nitrates could be poisoning many newborn babies. The high level of NO_3^- originate mainly from run off from manure used as fertilizer [22].

Sulphate, the polyatomic anion SO_4^{2-} is widely distributed in nature and may be present in natural waters in concentration ranging from a few to several thousand milligrams per liter. Many drainage wastes may contribute large amounts of SO_4^{2-} anion. Sulphate in water sources is often leached from rock or soil containing gypsum and other sulphate containing minerals. Sulphate can also originate from waste water plant or industrial plant discharges or from agricultural runoff. Diarrhea is the main health effect caused by the ingestion of drinking water with a high sulphate content. The threshold limit is 250mg/L[1-7, 9-10].

Material and Methods

Water samples that contain particulates organic matter requires treatment before analysis. Total metal includes all metals: inorganically and organically bound, both dissolved and particulate. To reduce interference by organic matter and to convert metal associated with particulates to a form such as the free metal, Flame Atomic Absorption Spectroscopy (AAS) is used [1-6].

The water samples were collected from the six selected areas of coastal Guyana (1)-(6) in plastic container and stored in a cool environment. A map of Guyana and the section of the Coastal plain where the surface water was collected is shown in Figure 3 and Figure 4 respectively. The samples were then submitted immediately for analyses at a certified laboratory. The water sample was filtered using a Pre-washed ungraded 0.4 to 0.45 um pore diameter membrane filter. After filtration, the filtrate was transferred to a beaker. 5ml of Conc. H_2SO_4 and several boiling chips were added. The contents of the beaker was brought to a slow boil and evaporated on a hot plate to the lowest volume (10ml) to initiate precipitation. Heating was continued with concomitant addition of HNO_3 until digestion was evident by the light coloured clear solution. Drying of the sample was avoided. The flask was washed with water and contents filtered. The filtrate was transferred to a 100ml volumetric flask and made up to the mark. Portions of the solution was then taken for metal determinations using Flame Atomic Spectroscopy. The analyses of the surface water for each selected area was done in triplicates and an average value recorded. For each metal analysed, appropriate standard solution of known metal concentration in the water with a matrix similar to the sample were prepared[1-5].

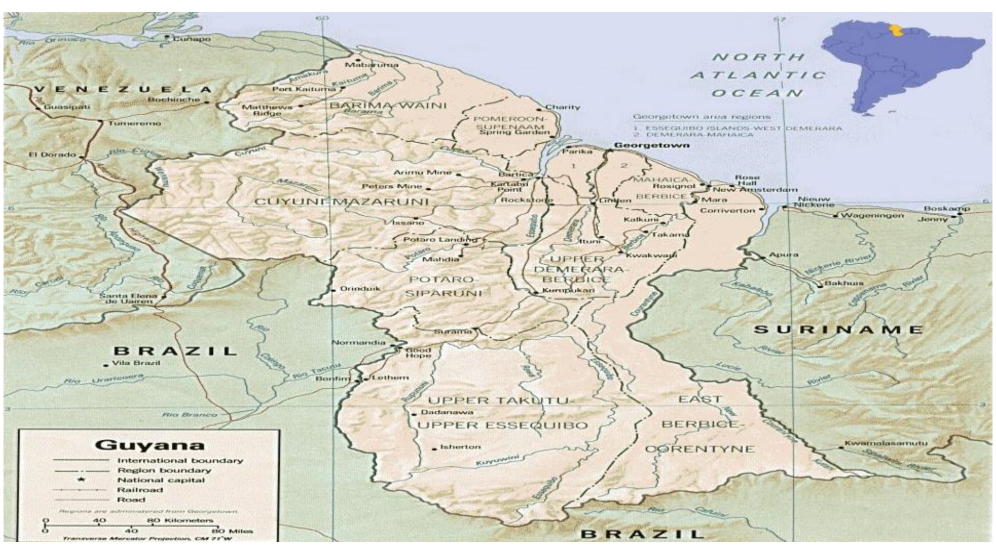


Figure 3: Map of Guyana

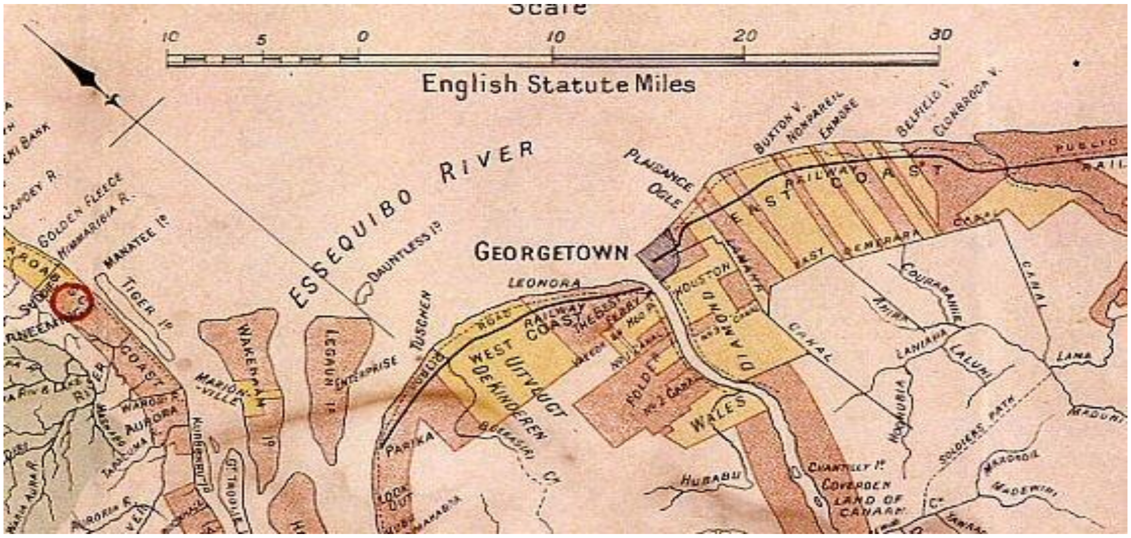


Figure 4: A Map of the Coastal Plain of Guyana

Results and Discussion

The following results were obtained for the six selected areas of Coastal Guyana chosen. Guyana is located on the mainland of South America and is divided geographically into three main regions/counties: Berbice, Demerara and Essequibo. It's usually call the "Land of Many Waters". However, it's water status needs to be monitored in light of global pollution. Metal ion/element and anion in surface water can be from natural or anthropogenic sources. The current status in the world is that anthropogenic sources usually exceed natural sources. Six selected surface water of coastal Guyana were analysed for metal cations and anions. These were: Abary River, West Coast Berbice (1), Mon-Repos Drainage Canal on East Coast Demerara (2), Surface water near Guyana Pharmaceutical Corporation (3), Turkeyen, Caricom Surface water on the right side (4), Turkeyen, Caricom Surface water on the left side (5) (left and Surface water from canal leading out of Ogle Sugar Estate on the East Coast of Demerara (6).

Table 1: Metal cations and anions concentration (mg/L) for selected areas (1)-(3) of coastal Guyana

Sample Description	Cl^- (mg/L)	NO_3^-	PO_4^{3-}	SO_4^{2}-	Pb	Cu	Zn	Cd
Abary River East Bank Berbice (1)	28	ND	0.15	5.27	ND	0.02	ND	0.03
	28	ND	0.23	5.39	ND	ND	ND	0.02
	21	ND	0.2	5.75	0.01	ND	ND	0.02
Average	25.67 ± 4.04	Nd	0.19 ± 0.04	5.47 ±0.25	0.01 ± 0.0	0.02 ± 0.0	Nd	0.023 ±0.006
CL (95%)	25.67 ± 4.58	Nd	0.19 ± 0.05	5.47 ±0.28	0.01 ± 0.0	0.02 ± 0.0	Nd	0.023 ±0.007
Mon-Repos-Drainage Canal, East Coast Demerara (2)	64	Nd	0.38	20.06	Nd	Nd	Nd	0.03
	57	Nd	0.38	18.36	0.01	Nd	Nd	0.02
	64	Nd	0.38	18.42	ND	ND	ND	0.02
Average	61.67 ± 5.72	Nd	0.38 ± 0.00	18.95 ±0.97	0.01	ND	ND	0.023 ±0.006
CL (95%)	61.67 ± 6.48	Nd	0.38 ± 0.00	18.95 ±1.90	0.01 ± 0.00	ND	ND	0.027 ±0.000
Farm-Drainage Canal, ECD near Guyana Pharmaceutical Corporation (3)	43	0.15	0.45	14.56	ND	ND	ND	0.02
	43	0.15	0.4	14.53	ND	ND	ND	0.03
	43	0.15	0.43	14.38	ND	ND	ND	0.03
Average	43 ± 0.0	0.15 ± 0.0	0.43 ± 0.143	14.49±0.097	ND	ND	ND	0.027 ± 0.00
CL (95%)	43 ± 0.0	0.15 ± 1.132	0.43 ± 0.162	14.49±1.099	ND	ND	ND	0.027 ± 0.00

Heavy metal ions analysed for were: Pb, Cu, Zn and Cd. Anions investigated were Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}. Analyses were done using Flame Atomic Absorption Spectroscopy[1-5]. Results were stastically analysed for mean value with standard deviation and the Confidence Limit (CL) at the 95% level[26-30]. These are listed in Tables 1 and 2. As can be seen, there is a variation in heavy metal cation and anion concentration for the selected water as per area. Results indicate that there was no detection of NO_3^- in the Abary river and Mon-Repos drainage surface water. The surface water (3) in the vicinity of Guyana Pharmaceutical Corporation registered a value of 0.15mg/L ± 0.00 mg/L. This value is below the international accepted value of 45 mg/L.

Table 2: Metal cation and anion concentration for areas (4)-(6) of coastal Guyana

Sample Area	Cl^- (mg/L)	SO_4^{2-} (mg/L)	Pb (mg/L)	Cd (mg/L)	Zn (mg/L)
Right side drain Caricom (4)	57.0 58.0 56.0	1.73 1.74 1.72	0.04 0.03 0.05	0.002 0.003 0.001	0.006 0.004 0.008
Average	57.0± 1.0	1.73 ± 0.01	0.04 ± 0.01	0.002± 0.00	0.006± 0.002
CL(95%)	57.0 ± 1.133	1.73 ± 0.011	0.04 ± 0.01	0.002±0.00	0.006 ± 0.003
Left side darin before Caricom (5)	85.0 86.0 84.0	1.82 1.83 1.81	0.05 0.04 0.06	0.002 0.001 0.003	0.005 0.03 0.07
Average	85.0 ± 1.0	1.82 ± 0.01	0.05 ± 0.01	0.002±0.0005	0.05±0.02
CL(95%)	85.0 ± 1.133	1.82 ± 0.011	0.05 ± 0.011	$0.002 \pm 5.67 \times 10^{-4}$	0.05 ± 0.023
From Canal leading out of Ogle Sugar Estate (6)	21.0 23.0 19.0	3.10 3.15 3.05	0.05 0.03 0.07	0.003 0.004 0.002	0.007 0.006 0.008
Average	21.0 ± 2.0	3.1 ± 0.05	0.05 ± 0.02	0.003± 0.0007	0.007 ± 0.064
CL(95%)	21.0 ± 2.26	3.1 ± 0.057	0.05±0.02	$0.003 \pm 7.93 \times 10^{-4}$	0.007± 0.073

CL: Confidence Limit at the 95% confidence

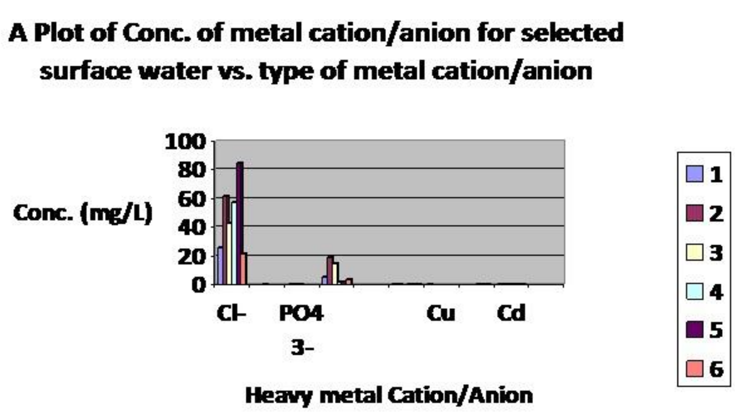


Figure 5: A plot of cation and anion concentration for the selected surface water versus type of cation/anions

Key:

Area	Description with Location
1	Surface water from Abary River, West Coast Berbice
2	Surface water from Mon-Repos Drainage Canal, East Coast Demerara, ECD
3	Surface Water near Guyana Pharmaceutical Corporation, East Coast Demerara, ECD
4	Surface water from Right Side Drain in front of Caricom building, Turkeyen, Georgetown
5	Surface water from Left Side Drain infront of Caricom building Turkeyen, Georgetown
6	Surface water from Canal, out of Ogle Sugar Estate ,East Coast Demerara,, ECD

No detection of zinc was noted for areas (1), (2) and (3). However, low values were registered for area (4), (5) and (6). These were 0.006 ± 0.002 mg/L, 0.05 ± 0.023 mg/L and 0.007 ± 0.064 mg/L respectively.

The highest value was recorded for chloride anion (Cl^-). These range from 21.00 to 85.00 mg/L. The lowest value of 21.00 ± 2.26 mg/L was recorded for area (6) and the highest value of 85.0 ± 1.13 mg/L was registered for area (5). However, these values are lower than the threshold limit of 250 mg/L.

Table 3: Threshold limit of cations and anions investigated in Surface Waters according to the International Standard, EPA (USAEPA)

Metals/cations/ anions	Threshold limit (mg/L)
Pb	Natural water < 0.02mg/L (USA, EPA)
Cu	Natural water < 0.017 mg/L (USA, EPA,)
Zn	Natural water < 0.11 mg/L
Cd	Surface water Natural water < 0.0037 mg/L
Cl^-	250mg/L in surface water
NO_3^-	45mg/L or 10mg/L nitrate nitrogen).
PO_4^{3}-	2.2 mg/L (UK). EU (5 mg/L) in surface water
SO_4^{2}-	Surface water:

Cu showed no detection for area (2), (3), (4), (5) and (6). However, area (1), registered a value of 0.02 ± 0.00 mg/L. This just exceed the threshold limit of 0.017 mg/L. Pb showed no detection for area (3), whereas the other areas registered value from 0.01 to 0.05 mg/L. The highest value of 0.05 ± 0.02 mg/L was noted for area (6). Thus, the concentration of Pb for areas (4), (5) and (6) exceed insignificantly, the International accepted threshold value of 0.02 mg/L.

Sulphate anion (SO_4^{2}-) was dectected for all areas and these ranged from 18.95 ± 1.90 mg/L to 1.82 ± 0.01 mg/L. The highest value of 18.95 ± 1.90 mg/L was noted for area (2), whereas the lowest value of 1.73 ± 0.01 mg/L was noted for area (1). Only areas (1) to (3) were analysed for phosphate, PO_4^{3}-. Value registered ranged were from 0.19mg/L ± 0.04 mg/L to 0.43 ± 0.14 mg/L. The latter was recorded for area (3) whereas the former for area (1).

Conclusion

The concentration of heavy metals such as Pb, Cu, Zn and Cd, and anions: Cl^-, NO_3^- and SO_4^{2-} and PO_4^{3-} were determined for six selected surface waters of coastal Guyana via Flame Atomic Spectroscopy. It was found that the concentration of these metal cations and anions was area dependent. Cl^- anion registered the highest value of 85.0 ± 1.0 mg/L at area (5). Area (3) registered a value of 0.15 ± 0.0 mg/L for NO_3^-. In areas such as (1) and (2), the surface waters showed negligible detection for NO_3^-. The highest value for SO_4^{2}- , 18.95 ± 0.97 mg/L was noted for area (2). The toxic heavy metal ions such as Pb and Cd showed low and no detection in some areas. For Cd, this range from 0.002 ± 0.00 to 0.03 ± 0.00 mg/L, with the highest occurring at area (3). Pb was undetected in most areas. In areas of detection, the highest concentration of 0.05 ± 0.0 11 mg/L was noted. With the exception of Pb in areas (4) and (5) and Cu in area (1), the concentration of these metal ions/element and anions are below the threshold limit in surface water as accepted by International accepted standards of the Environmental Protection Agency, EPA and thus are no threat to the national livelihood. However, the country surface water must be continually tested as anthropogenic activities increases.

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References

1. Young R.A., Bredehoeft J.D., Digital simulation for solving management problems with conjunctive groundwater and surface water systems, *Water Resources Research*, **8 (3)**, 533-56 (**1972**)

2. Eaton A.D., Clessicens S.L. and Greenberg E.A., Standard methods for the Examination of Water and Wastewater, 19th ed. United Book Press Inc. Baltimore, Maryland USA., 4-48 (**1995**)

3. Eaton A.D., AWWA, Chair, et al, Standard methods for the examination of Water and Wastewater**,** 19th ed. United Book Press Inc. Baltimore, Maryland USA, 4-67 **(1995)**

4. Booth R.L., Methods for the Chemical analysis of Water and Wastes, 2nd ed. Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati: Ohio., 352 (**1983**)

5. Hach company, Water Analyses handbook, 3rd ed. Loveland Colorado, USA., 304-307 (**1997**)

6. Radojevic M., Bashkin V.N., Practical Environmental Analysis, Royal Society of Chemistry, Cambridge UK. 1-466 (**1999**)

7. Elliot S., Testing the Water, Royal Society of Chemistry, RSC, News Magazine, **12(5)**, 12-13 (**2008**)

8. Williams N., Guyana Times, a News Magazine, **(11)**, 31-32 (**2010**)

9. Ho Yu, Ming., Environmental Toxicology: Biological and Health Effects of Pollutants, second edition, CRC Press, Boca Raton, London, 185-223 (**2005**)

10. Nordberg M., Nordberg F. G., Fowler, A.B and Friberg. L, Handbook on the Toxicology of Metals, Academic Press, Science, 1-1024 (**2011**)

11. Zacarias I., Yanez G C., Araya M., Oraka C., Olivares M. and Uauy R., Determination of the taste threshold of copper in water, *Chemical Senses*, **26 (1)**, 85–89 (**2001)**

12. Olivares M. and Uauy R., Limits of metabolic tolerance to copper and biological basis for present recommendations and regulations, *American Journal of Clinical Nutrition*, **63**, 846S–852S (**1996**)

13. Olivares M. and Uauy R., Copper as an essential nutrient, *American Journal of Clinical Nutrition*., 63, 791S–796S (**1996**)

14. Nelson D.L. and Cox M. M., Lehninger, Principles of BioChemistry, 4th ed. W.H. Freeman and Company, New York, NY, 834-835, 273-274, 763-774 (**2005**)

15. Murray R. K ., Granner D. K. and Rodwell V.W., Harper's Iilustrated BioChemistry, 27th Ed. Lange Medical Books/McGraw-Hill., 90-91 (**2006**)

16. Daintith J., The facts on File Dictionary of Inorganic Chemistry, Market House Books Ltd. 1st Edition., 51 (**2004**)

17. Bell C.F. and Lott K.A.K., Modern Approach to Inorganic Chemistry, 2nd ed, Butterworths, London., 260, (**1996**)

18. Devey D. G. and Hawkness, N., The Significance of Man-made sources of Phosphorous, Detergents and Sewage, *Water Research*, **7**, 35-54 (**1973**)

19. McCoy M., Goodbye Phosphates, Chemical and Engineering News, ACS., **5**, 12 (**2011**)

20. Smith V.H., Tilman G.D. and Nekota J.C., Eutrophication impacts of Excess nutrient in Freshwater, Marine and Terrestrial Ecosystems, *Environmental Pollution*, **100**, 179-196. (**1999**)

21. Tindale S.L. and Nelson W.L., Soil fertility and Fertilisers, 2nd ed. The Macmillan, New York, NY., 174-179 (**1970**)

22. Peplow M., Nitrates pollute Gaza's wells, *Chemistry World*, **5(10)**, 25 (**2008**)

23. Allen S.E., Grimshaw M.H., Parkinson J.A. and Quarmby C., Chemical Analysis of Ecological Materials. In: Allen SE (Ed). Blackwell Scientific Publications, Oxford London, Edinburgh, Melbourne, 386 (**1974)**

24. Daniel H.C., Quantitative Chemical Analysis, 6th ed. W.H. Freeman and Company, New York, 61-79 (**2003**)

25. Skoog A.D., Holler, J.F. and Nieman A.T., Principles of Instrumental Analysis, 5th ed. Thomson Learning, Inc., 329-353 (**1998**)

26. Skoog D.A., West, D.M., Holler F.J., Fundamentals of Analytical Chemistry, 7th ed. Thomson Learning, Inc; USA, (**1996**)

27. H. C., Quantitative Chemical Analysis, 6th ed. W.H. Freeman and Company, New York, 61-79 (**2003**).