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COLLEGE OF BASIC AND APPLIED SCIENCES

SPECIATION OF INORGANIC ANTIMONY IN POLYETHYLENE TEREPHTHALATE (PET) BOTTLED WATER USING HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROPHOTOMETRY (HG-AAS)

MARKWO ALI

DEPARTMENT OF CHEMISTRY

JULY 2015

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THIS THESIS IS SUBMITTED TO THE UNIVERSITY OF GHANA, LEGON

BY

MARKWO ALI

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DECLARATION

This is to certify that, this thesis is the outcome of a research undertaken by Markwo Ali towards the award of MPhil chemistry degree in the Department of Chemistry, University of Ghana and has neither in part nor in whole been presented for another degree elsewhere.

Markwo Ali	…………………….	………………………
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Professor Derick Carboo	………………………	……………………..
(Principal Supervisor)	Signature	Date
Professor Robert Kingsford-Adaboh	……………………...	………………..........
(Co-Supervisor)	Signature	Date

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DEDICATION

To the Almighty God and to the

Ali Kansake family, Buipe, Central Gonja District.

…… M. Ali

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I thank the Lord almighty for the wisdom and strength he has bestowed on me. I bless his name all my lifetime.

I am extremely grateful to my supervisor, Professor Derick Carboo for his patience, guidance and invaluable contributions to make this work a success. My sincere thanks to Dr. Walter Affo for seeing the potential in me and giving me the chance to soar further in education. Without your guidance and advice, this MPhil degree will not have started in the first place. You are an inspiration to me. God richly bless you. To my Co-Supervisor, Professor Robert Kingsford-Adaboh, I say thank you for your time and resources to make this labour an achievement.

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INTEGRI PROCEDAMUS

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ABSTRACT

Antimony (Sb) is a regulated drinking water contaminant that has been found to leach from polyethylene terephthalate (PET) plastic containers into the waters stored in them. The common inorganic species of antimony in water are Sb(III) and Sb(V), with the former being more toxic and the latter being more soluble. In order to assess the extent to which waters stored in PET bottles are contaminated with inorganic Sb and to further examine the effect of typical storage conditions on migration rates, speciation analysis of inorganic Sb using hydride generation atomic absorption spectrophotometry (HG-AAS) was undertaken on selected PET plastic bottled waters marketed in the Greater Accra Region of Ghana.

Six brands of PET plastic bottled waters were obtained at source on the day of packaging, and analyses undertaken on samples of the waters stored in the plastic containers at intervals of four weeks for twelve weeks, under three carefully chosen storage conditions distinctive of bottled water usage. Selected physicochemical properties of samples of the waters stored in the plastic containers and total Sb of samples of the plastic containers were also determined to discover the effect of some physical properties and certain major ions, and the influence of the different quality PET plastic types on Sb migration respectively.

The study revealed amounts of total Sb in the PET plastic containers of the 6 brands ranging from 123.46 mg/kg to 146.45 mg/kg. The selected physicochemical properties of the waters stored in the PET plastic containers considered were pH (6.78 – 7.43), Ca^{2+} (1.61 – 12.39 mg/L), Mg^{2+} (1.00 – 4.96 mg/L), HCO_3^- (6.18 – 55.41 mg/L) and TDS (8.70 – 70.40 mg/L)). PET bottled waters of 5 out of the 6 brands contained Sb (initial total Sb ranging from 1.11 – 14.65 µg/L) before storage. Total Sb concentrations of the waters stored in the plastic containers were observed to increase with storage time under all the three storage conditions for all the brands of PET plastic bottled waters. Sb(III) and Sb(V) of the waters stored in the

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plastic containers were observed to increase with storage time, with the latter in higher amounts in solution under all the three storage conditions. Waters stored in plastic containers exposed to harsh conditions of the weather like high air temperatures (average temperature for 12 weeks: 23.0ºC in the morning and 39.5ºC in the afternoon) and sunlight outdoors registered the highest Sb concentrations.

In conclusion, PET bottled waters marketed in the Greater Accra region were not found to be contaminated with Sb leaching from their packaging PET plastic containers within the one year limited time of expiry using WHO MCL. Notwithstanding that, harsh weather conditions outdoors is most likely to contribute to the rapid migration of the metalloid (Sb) from the plastic containers, making the bottled water unwholesome before its due expiry time is reached.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometry
AFS	Atomic Fluorescence Spectrometry
CI	Confidence Interval
CoV	Coefficient of Variation
CPE	Cloud Point Extraction
CRM	Certified Reference Material
CSIR	Council for Scientific and Industrial Research
EU	European Union
FDA	Foods and Drugs Authority
GEMS	Global Environment Monitoring System
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
LOD	Limit Of Detection
LOQ	Limit Of Quantification
MCL	Maximum Contaminant Level
PET	Polyethylene Terephthalate
SPE	Solid-Phase Extraction
TDS	Total Dissolved Solids
WEEE	Waste Electrical and Electronic Equipment
WHO	World Health Organisation

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CHAPTER ONE

1.0 GENERAL INTRODUCTION

1.1 Background

Access to safe drinking water is vital to human health, a basic human right and an element of effective policy for health protection (Graham, 1999). Germs and contaminants such as bacteria, viruses, heavy metals and pesticides when present in water, reduces its quality and as such can cause toxic effects (Fleeger, Carman, & Nisbet, 2003). This has influenced growing concerns, particularly with regards to municipal tap water, as contaminants such as lead (Pb), copper (Cu) and other toxic heavy metals through plumbings and fittings enter the water lowering its wholesomeness, and thus, making bottled water the most preferred and popular choice worldwide (Krachler & Shotyk, 2009; Osei, Newman, Mingle, Ayeh-Kumi, & Kwasi, 2013; Schmid, Kohler, Meierhofer, Luzi, & Wegelin, 2008).

For the past fifteen years, global bottled water market has witnessed tremendous annual growth, reaching a total value of about €66 billion in the year 2010. China became the largest market in the consumption of bottled water at 40 million tons in the year 2011. (Y. Y. Fan *et al.*, 2014; Rani, Maheshwari, Garg, & Prasad, 2012). The United Kingdom observed an increase in consumption of bottled water from 1415 to 2275 million litres between 2000 and 2006, spending about £1 billion. (Ward *et al.*, 2009). Italy tops as the greatest annual producer of bottled water, manufacturing about 10 billion litres per year with a consumption rate of 151 litres per capita per year annually (Krachler & Shotyk, 2009). There is, therefore, no doubt that, bottled water in few years to come will replace tap water completely.

In Ghana, the majority of the public consume drinking water that is stored in plastic container bottles or ‘sachets’. These bottled- and “sachet” waters are generally perceived to be clean, convenient, healthy and safer compared to tap water (Y. Y. Fan *et al.*, 2014; Grant &

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Yankson, 2003; Osei *et al.*, 2013; Ward *et al.*, 2009; Westerhoff, Prapaipong, Shock, & Hillaireau, 2008). Therefore, to satisfy domestic Ghanaian need for bottled- and "sachet" water, many manufacturers have proliferated the market, most of whom are suspected not to have permits. This leads to difficulty in estimating the exact number of bottled- and 'sachet' water companies in Ghana.

Bottled- and "sachet"-water companies to begin production will require three basic things: a water source, systems to purify the water and a packaging material for the finished product — purified water. Depending on the factory's location, some companies use water from aquifers and streams. Others depend on rivers, harvested rain or tap water supplied by urban or municipal water companies. Two water works are involved in the supply of pipe borne water to the city of Accra: Weija dam off the river Densu and Kpong water works off the Volta river (Machdar, van der Steen, Raschid-Sally, & Lens, 2013).

Waters from these various sources are then passed through purification systems, which are usually in stages, some up to fourteen depending on the type of manufacturing plant. Some of the purification steps involved are activated carbon filtration, reverse osmosis, ultra violet sterilisation and ozonation post carbon filtration (Belaqua.com.gh, 2015). Hence, most of the germs and particulate dirt are removed or reduced to a level that is harmless to the consumer. Nonetheless, most of the purification processes used are not directly involved in the removal of dissolved trace metallic contaminants. After purification, the waters are usually packaged in plastics or in glass containers.

The plastic material for drinking water packaging differ from country to country, but the common package material used is polyethylene terephthalate (PET) (Keresztes *et al.*, 2009). PET plastics have become the most preferred packaging material for drinking water and other beverages. This is due to its excellent material properties like unbreakability, good barrier

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properties towards moisture, high clarity, low migration trends for residuary constituents and very low weight of the bottles compared with glass bottles of the same filling capacity (Y. Y. Fan *et al.*, 2014; Sánchez-Martínez, Pérez-Corona, Cámara, & Madrid, 2013; Welle, 2011; Westerhoff *et al.*, 2008). In Ghana, most of the "sachet"-water companies use polyethylene plastics whilst the bottled water companies use PET plastics in packaging their treated waters.

PET is made from the polymerisation of monomers of terephthalic acid and ethylene glycol using antimony-, titanium-, or germanium-based catalysts (Westerhoff *et al.*, 2008). Over ninety percent of globally manufactured PET utilizes antimony-based catalysts, predominantly antimony trioxide (Sb_2O_3) with beneficial qualities like high catalytic activity, low tendency to catalyse side reactions, creates no colour in the final product and has low-cost price (Carneado *et al.*, 2014; Shotyk *et al.*, 2006; Welle, 2011; Westerhoff *et al.*, 2008). An estimated 150 billion plastic bottles are produced from PET resins annually (Shotyk, Krachler, & Chen, 2006). Commercialised PET resins produced from the use of antimony trioxide catalysts ordinarily have residual antimony concentrations ranging between 150 mg/kg – 300 mg/kg (Carneado, Hernández-Nataren, López-Sánchez, & Sahuquillo, 2015; Hureiki & Mouneimne, 2012; Keresztes *et al.*, 2009). These residual antimony concentrations are very high and raise concerns, considering earlier findings that, antimony can migrate into the waters and beverages stored in PET plastic containers (Carneado *et al.*, 2015; Y. Y. Fan *et al.*, 2014; Keresztes *et al.*, 2009).

1.2 Problem statement

Bottled water sales volume, popularity, and consumption have increased considerably in recent times. This raises worries about the quality of the stored water and the packaging container, as previous studies have suggested that, heavy metalloids like antimony leach into juice, drinking water and other beverages packaged with PET plastics over time (Carneado *et al.*, 2015; Y. Y. Fan *et al.*, 2014; Hureiki & Mouneimne, 2012; Keresztes *et al.*, 2009; Tostar,

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Stenvall, Boldizar, & Foreman, 2013). Critical public health concerns are therefore evoked, as antimony has been established as a regularised drinking water contaminant by monitoring organizations like United States Environmental Protection Agency (US EPA), European Union (EU), and World Health Organization (WHO) (Carneado *et al.*, 2015; Hureiki & Mouneimne, 2012; Keresztes *et al.*, 2009; Sánchez-Martínez *et al.*, 2013; Westerhoff *et al.*, 2008).

Antimony is a non-essential element for plants and animals which has no known biological or physiological function and on a long-term exposure has been suspected to be carcinogenic (Roberts & Orisakwe, 2011; Sayago, Beltrán, & Gómez-Ariza, 2000; Shotyk *et al.*, 2006; Tostar *et al.*, 2013; Westerhoff *et al.*, 2008). In cases of acute intoxication, conditions such stomach and muscle aches, diarrhoea, desiccation, shocks, anaemia, and uraemia may arise. These lead to serious myocardial inflammation, shivering, necrosis and finally death (Keresztes *et al.*, 2009). Other detrimental ailments associated with exposure to this metalloid include pneumonitis, fibrosis, bone marrow damage and carcinomas (Sayago *et al.*, 2000).

Within the last two decades, scientists have come to the realisation that, total concentrations of elements do not provide the requisite information about mobility, bioavailability and how they affect ecological systems or biological organisms. Knowledge about the chemical forms or species of these elements is paramount to understanding the chemical and biochemical reactions involving these species. Thus, providing information about toxicity, innocuousness or essentiality of the element (Caruso & Montes-Bayon, 2003; Michalke, 2003).

In water, the common antimony species reported are antimony (III) and antimony (V), with the former being more soluble as the pentavalent oxo-anion $Sb(OH)_6^-$ under oxic conditions and the latter as $Sb(OH)_3$, which is ten times more toxic probably because it has higher reactivity in living systems (Cornelis, Crews, Caruso, & Heumann, 2005; Krupka &

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Serne, 2002; Okkenhaug *et al.*, 2011; Quiroz *et al.*, 2013; World Health Organization, 2003). Total antimony concentrations only, will therefore not be sufficient in determining toxicity and subsequently contamination.

Several environmental factors affect the migration of antimony from the plastic container into the water stored inside. Effects of factors like temperature, sunlight, duration and physicochemical properties amongst others on migration have been studied in other parts of the world using total antimony concentrations (Bach *et al.*, 2013, 2014; Carneado *et al.*, 2015; Hureiki & Mouneimne, 2012; Keresztes *et al.*, 2009; Shotyk *et al.*, 2006; Westerhoff *et al.*, 2008). Climatic conditions or factors in our part of the world are very different and more severe with variations in seasons. Various ways in which consumers store plastic bottled water therefore becomes critical. Furthermore, the fate of the individual species *vis-à-vis* the effects of the factors studied based on the literature reviewed, has not been explored.

Thus, it becomes imperative antimony speciation under typical storage conditions be conducted on PET plastic bottled waters to determine the levels of inorganic antimony species and to ascertain whether migration rates are high leading to contamination.

1.3 Justification

Data obtained from antimony speciation in PET plastic bottled waters will be invaluable, as it will inform manufacturers, consumers and regulatory authorities on the extent to which the bottled waters are contaminated and how storage conditions typical of consumers may influence the release of antimony from the residual catalysts in the plastic containers into the waters stored inside.

Information on the residual antimony in the plastic containers and migration rates will advise PET plastics manufacturers on the quality of the plastics they are producing. This can

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be used to decide whether to use PET plastic bottles manufactured using catalyst other than antimony or to switch to other types of plastics entirely.

Typical conditions in which consumers store plastic bottled water affect antimony release under prevailing climatic conditions. Findings of this study will advise consumers on proper ways of storing plastic bottled water to avoid getting them contaminated before their due expiry date.

Lastly, plastic bottled water manufacturers will be informed on some the factors to take into consideration when specifying the duration period before expiry. This should be done in order to protect the consumer.

1.4 Hypotheses

H_0: Waters stored in PET plastic containers marketed in Greater Accra Region are contaminated with antimony leaching from the plastic containers within the limited time of expiry.

$H_{1:}$ Waters stored in PET plastic containers marketed in Greater Accra Region are not contaminated with antimony leaching from the plastic containers within the limited time of expiry.

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1.5 Objectives of the research

1.5.1 Aim

The aim of this study is to assess the extent to which waters stored in PET plastic containers are contaminated with inorganic antimony.

1.5.2 Specific objectives

The specific objectives comprise the following:

1. To determine total inorganic antimony in the PET plastic containers.
2. To determine inorganic antimony species in the source waters (within 12 hours after filling)
3. To determine inorganic antimony species of waters stored in PET plastic containers for twelve weeks (at intervals of four weeks).
4. To determine the impact of typical storage conditions on the migration rate of antimony from the PET plastic containers into the waters stored inside.
5. To establish the relationship between physicochemical properties and inorganic antimony species of the waters stored in PET plastic containers.

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CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Antimony occurrence and applications

Antimony (atomic number 51) is universally present in the environment as a result of natural developments and human activities (Filella, Belzile, & Chen, 2002). It belongs to group VA (symbol Sb from the latin word *stibium*) of the periodic table of elements and according to the Gold-Schmidt classical classification, is a strong chalcophile element that exists predominantly in nature as Sb_2S_3[1] and Sb_2O_3[2] (Ferreira *et al.*, 2014; Filella *et al.*, 2002). In the Earth's crust, antimony and its compounds have a mean crustal abundance of *ca* 0.20 to 0.3 mg/kg, and are released into the environment via natural discharges like windblown dust, volcanic eruptions, sea sprays, forest fires, and biogenic sources (Filella *et al.*, 2002; Kubota, Kawakami, Sagara, Ookubo, & Okutani, 2001; Sundar & Chakravarty, 2010). Anthropogenic sources of antimony in the environment include fossil fuel combustion, mining and smelting activities, waste incineration of plastic materials and vehicular emissions (Amereih, Meisel, Kahr, & Wegscheider, 2005).

The uses of antimony were already known from ancient times as it could dissolve precious metals. This attribute was used in the purification process of gold (Au) from copper (Cu) and silver (Ag) up to the 18th century (Filella *et al.*, 2002). It is very mobile in the environment and as such, has been used as a prospecting guide for ore deposits containing antimony-bearing minerals like gold (Au), silver (Ag), and some other metals (Krupka & Serne, 2002). In elemental form, the metalloid is sturdy, indissoluble in water and forms very hard and technically interesting alloys with tin (Sn), Cu and lead (Pb). Therefore, its presence

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[1] Stibnite (Antimony trisulphide) – Sometimes known in Geology as antimonite.

[2] Valentinite (Antimony trioxide) – Transformation product of Stibnite

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in metals like Pb greatly improves hardness and mechanical strength. This successively has resulted in its use in batteries, antifriction alloys, type-metal, small arms, tracer bullets, cable sheathing and in semiconductors for making infrared detectors, diodes and Hall-effect devices (Dessuy, Kratzer, Vale, Welz, & Dědina, 2011; Filella *et al.*, 2002; Kubota *et al.*, 2001; Sayago *et al.*, 2000; Sundar & Chakravarty, 2010; World Health Organization, 2003).

Various antimony compounds are used in industry for the manufacture of several products. Antimony trioxide (Sb_2O_3) is utilised in fire retardant preparations for plastics, rubbers, textiles, papers, and adhesives. It is correspondingly used as, a paint pigment (a turbidifier in white enamel paint), ceramic opacifier, catalyst (initiator or additive in the production of polyethylene terephthalate), mordant, and glass decolouriser (Cavallo *et al.*, 2002; dos Santos *et al.*, 2013; Filella *et al.*, 2002; Sayago *et al.*, 2000; Sundar & Chakravarty, 2010; World Health Organization, 2003). Other antimony compounds like Sb_4O_8[3] and Sb_2S_3 are also widely known, with the former being used as an oxidation catalyst in the oxidative dehydrogenation of olefins and the latter in break linings, vulcanisation process of rubber, production of explosives, antimony salts and ruby glass (Filella et al., 2002; Fujiwara, Rebagliati, Marrero, Gómez, & Smichowski, 2011; Sundar & Chakravarty, 2010). The pentavalent antimony compounds (stibosamine, sodium stibogluconate, pentostam, glucantime) are used in the biomedical field as therapeutic agents against parasitic tropical protozoan diseases like leishmaniasis, schistosomiasis, ascariasis, trypanosomiasis and bilharziasis (Filella *et al.*, 2002; Sundar & Chakravarty, 2010; World Health Organization, 2003). Certain compounds of antimony were also formally used to treat syphilis (Filella *et al.*, 2002).

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[3] Antimony tetra-oxide

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In conclusion, antimony is ubiquitously present in the environment and has many industrial applications for the production of goods for man's use.

2.2 Antimony species in speciation analysis

The speciation analysis of antimony takes into account two groups of species: inorganic antimonials which are evaluated using their oxidation states (trivalent (III) and pentavalent (V)) and the organic antimonials in environmental and biological matrices (mainly methylated species comprising monomethylated methylstibonic acid [$MeSbO(OH)_2$], dimethylated dimethylstibinic acid [$Me_2Sb(OH)$], monomethylstibine [$MeSbH_2$] and dimethylstibine [Me_2SbH]) (Cornelis *et al.*, 2005; Hernández-Nataren, Sahuquillo, Rubio, & López-Sánchez, 2011; Miravet, Hernández-Nataren, Sahuquillo, Rubio, & López-Sánchez, 2010).

In the urine of occupationally exposed humans, methylated forms like [$(CH_3)_3SbCl_2$] have also been reported (Quiroz *et al.*, 2011). Antimony is further observed to associate strongly with soil organic matter, oxyhydroxides of Iron (Fe), Manganese (Mn), Aluminium (Al) and clay minerals. These types of associations have resulted in subjects for several studies as different antimony species can be formed with organic chelating macromolecules (Thanabalasingam & Pickering, 1990; Tserenpil & Liu, 2011; Van Vleek, Amarasiriwardena, & Xing, 2011; Wilson, Lockwood, Ashley, & Tighe, 2010). In some rivers and marine waters, methylated forms have been discovered and usually constitute about 10% or less of the total dissolved antimony (Krupka & Serne, 2002).

Based on thermodynamic equilibrium considerations, the inorganic trivalent (III) and pentavalent (V) forms are the stable states under reducing and oxidising conditions respectively. Nonetheless, these two inorganic forms have been found to co-exist in natural aqueous systems (Krupka & Serne, 2002). In water, both species are strongly hydrolysed with antimony (V) existing as $Sb(OH)_6^-$ and antimony (III) as SbO_2^- (Serafimovska, Arpadjan, &

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Stafilov, 2011). Under oxic to slightly reducing conditions (pH > ~ 2.5), the hydrolytic pentavalent oxo anion $Sb(OH)_6^-$ exist. At averagely reducing conditions (pH 2 – 12), the dominant species is $Sb(OH)_3$. At pH < 2, the dominant species is $Sb(OH)_2^+$ and at pH > 12, the dominant species is $Sb(OH)_4^-$ (Krupka & Serne, 2002; World Health Organization, 2003).

The focus of this study will be on inorganic antimonials because of the major draw back of the lack of standard substances for calibration for organic antimonials (Ferreira *et al.*, 2014).

2.3 Synthesis of polyethylene terephthalate (PET)

Polyethylene terephthalate (PET) is a thermoplastic material that is made for a wide variety of applications, particularly food and beverage packaging, including drinking water bottles (Carneado *et al.*, 2015).

It is synthesised from the polymerization of the petroleum-derived monomers of terephthalic acid and ethylene glycol using Sb-, Ti-, or Ge-based catalyst. The use of Ti-based catalysts causes the formation of the PET resins to occur at higher temperatures whereas Ge-based catalyst are expensive compared to Sb-based catalyst. This makes the latter the best choice worldwide (over 90% manufactured PET) (Westerhoff *et al.*, 2008). Furthermore, Sb-based catalysts (specifically antimony trioxide (Sb_2O_3)) are widely used because, they are efficient, present minimal tendency to produce side effects and do not produce undesirable colour in the polymer material (Aharoni, 1998; Duh, 2002).

The first industrial step in the synthesis of PET involves a pre-polymerization reaction that generates low-weight oligomers and bis(hydroxyethyl) terephthalate (BHET) as an intermediate compound. A second poly-condensation reaction uses various catalysts such as the Sb-based ones to transform BHET to PET. Below is a scheme, showing the polycondensation reaction process adopted from Habaue *et al.* (2010).

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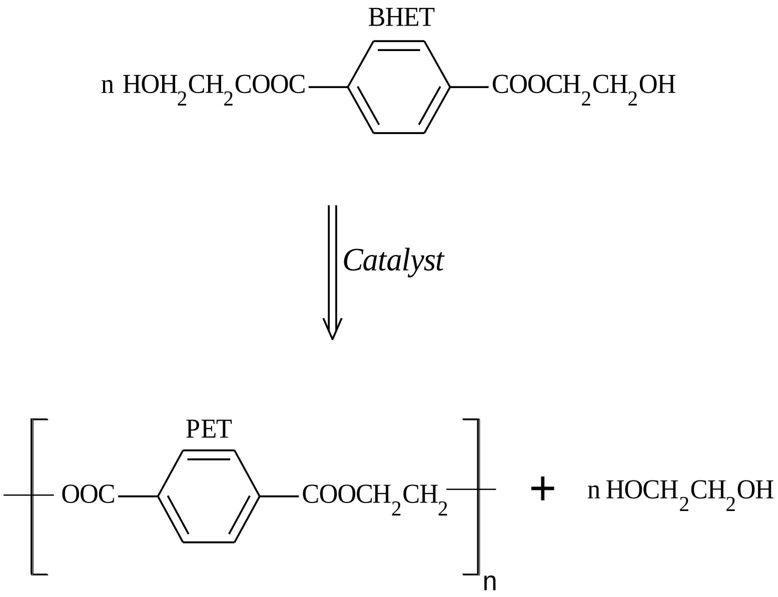

2.4 Effects of antimony toxicity

The toxicity of antimony and its compounds raises global health concerns (Amarasiriwardena & Wu, 2011). They are regarded as pollutants of priority by international statutory bodies like the United States Environmental Protection Agency (US EPA), European union (EU) and the World Health Organisation (WHO). This is because, antimony can accumulate in living organisms and stimulate health effects like nausea, vomiting, and diarrhoea. These occur when maximum contaminant levels (MCLs) are surpassed over comparatively short periods (Carneado *et al.*, 2015; Filella *et al.*, 2002; Kubota *et al.*, 2001; Mendil, Bardak, Tuzen, & Soylak, 2013; Miravet, López-Sánchez, Rubio, Smichowski, & Polla, 2007; Sánchez-Martínez *et al.*, 2013; Westerhoff *et al.*, 2008; Yousefi, Shemirani, & Jamali, 2010). Antimony also has biological properties similar to arsenic (As) and as such, may possess some carcinogenic tendencies (Tostar *et al.*, 2013). Therefore, to protect consumers of bottled water and other beverages store in PET plastic containers, these international bodies and governmental organisations provide guideline values derived from various experimental data. The maximum permissible concentration of antimony in drinking water signed by the WHO, EU and US EPA are 20 µg/L, 5 µg/L and 6 µg/L respectively (Carneado *et al.*, 2015;

Hureiki & Mouneimne, 2012; Sánchez-Martínez *et al.*, 2013; Tostar *et al.*, 2013; Westerhoff *et al.*, 2008; World Health Organization, 2003). There is no guideline value for the maximum allowable concentration of antimony in drinking water in Ghana.

Antimony toxicity chiefly comes into existence due to occupational exposure, domestic use or during therapy. Furthermore, the chemical form, oxidation state and water solubility of the species under consideration is a key function of toxicity (Amereih *et al.*, 2005; Hagarová, Kubová, Matúš, & Bujdoš, 2008; Sánchez-Martínez *et al.*, 2013; Sundar & Chakravarty, 2010; World Health Organization, 2003).

Antimony concentrations in air ordinarily range from nanogram per cubic meter to approximately 170 ng m^{-3}. In rivers and lakes, dissolved concentrations usually range less than 5 parts of the metalloid in 1 billion parts of water and are mostly found attached to dirt particles (Sundar & Chakravarty, 2010). Stibine (SbH_3), a lipophilic gas, when inhaled is the most toxic of the inorganic forms of the metalloid. Some of the diseases associated with inhalation exposure to antimony are pneumonitis, fibrosis, bone-marrow damage and carcinomas (Amereih *et al.*, 2005). The elemental form (Sb^0) of the metalloid is more toxic than its inorganic salts. Its inorganic salts are in turn more toxic than the organic forms (Sundar & Chakravarty, 2010; World Health Organization, 2003).

The inorganic Sb(III) and Sb(V) states constitute the predominant forms in inorganic environmental matrices with the former being more toxic because it has higher responsiveness in living systems (*i.e*, it expresses high affinity for red cells and thiol groups of cell components and has physicochemical properties similar to As (III) of known toxicity) (Amereih *et al.*, 2005; Cornelis *et al.*, 2005; Hagarová *et al.*, 2008; Kubota *et al.*, 2001; Quiroz *et al.*, 2013; Sánchez-Martínez *et al.*, 2013). Conditions like optical nerve destruction, uveitis, and retinal bleeding are linked to repeated oral exposure to therapeutic doses of antimony (III) with specific

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symptoms of intoxication generally followed by coughing, anorexia, troubled sleep and vertigo. Soluble antimony (III) salts have also been found to exert genotoxic effects *in vitro* and *in vivo* (World Health Organization, 2003).

Thus, antimony can pose serious health risks to humans and as such, must be regulated and monitored frequently in the environment.

2.5 Antimony migration from PET bottles

2.5.1 Effect of sunlight and temperature on antimony migration

Few studies have investigated the impact of sunlight and surrounding temperature on the migration of antimony from the PET plastic container into the water stored in it.

Bach *et al.* (2014) discovered that bottled waters on exposure to sunlight for 2, 4 and 10 days had migration dependent on the type of water (carbonated or non-carbonated) and the migration rates for formaldehyde, acetaldehyde and antimony increased. Bach *et al.* (2013) also recognised that, increase in temperature impelled the release of plastic constituents like antimony, formaldehyde and acetaldehyde. Carneado *et al.* (2014) further examined the influence of temperature and storage time on antimony migration from PET bottles into the mineral water in a short term and long term. Their study showed that waters stored in the temperature range of 4ºC to 20ºC were not subject to antimony migration whilst, at temperatures above 40ºC and 60ºC, there was a significant increase in migration. Hureiki and Mouneimne, in their study too realised that in outdoor conditions under sunlight at temperatures below 45ºC, there was no significant effect on antimony release from PET bottles into natural water (Hureiki & Mouneimne, 2012). Fan *et al.* (2014) considered the effect of storage temperature and duration on sixteen brands of PET bottled water. They discovered that, an increase in temperature from 4ºC to 70ºC increased antimony release from the PET plastic container for up to four weeks and then decreased. This indicates that, under long-term storage,

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release rates may probably stabilise. Westerhoff *et al.* (2008) investigated how sunlight affects the migration of antimony from PET plastics. Natural sunlight experiments were conducted with controls held at the same temperature, but wrapped in aluminium foils. Samples were exposed to natural sunlight for seven days. From their results, it was realised that the effect of sunlight irradiation on antimony migration was minimal (5 – 10% higher than the control). It was also discovered that, increasing storage temperatures from 22ºC to 80ºC led to higher rates of antimony migration.

Thus, exposure of plastic bottled water to sunlight and higher air temperatures tends to accelerate the migration process of antimony from the PET plastic container into the water stored in it.

2.5.2 Effect of storage condition and duration on antimony migration

The state in which PET plastic bottled waters are stored over time influences the migration of constituents like antimony from the packaging material into the water stored inside.

Carneado *et al.* (2014) storing bottled waters under conditions similar to refrigeratory and indoor settings (4ºC and 20ºC respectively) observed no antimony migration whilst at high-temperature conditions (above 40ºC) such as in outdoor exposed to high air temperatures and sunlight, significant increase in antimony concentration was witnessed. Hureiki and Mouneimne (2012) assessed eight Lebanese brands of bottled waters in the dark indoors (at 22ºC) and outdoor under sunlight (at a maximum temperature of 45ºC) for antimony migration. It was observed that the migrated antimony concentration of six of the brands increased reaching a concentration of 5.5 µg/L after 544 days of contact time with the PET packaging material. A study by Fan *et al.* (2014) revealed that storage duration affects the release rates of antimony from the PET plastic container. It was realised that release rates increased for a short

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period and then stabilise on a long-term. Modelling improper storage conditions by bottled water usage, Keresztes *et al.* (2009) stored purchased Hungarian mineral water for the duration of 10 to 950 days under various conditions. It was observed that the leaching rate increased with storage time and sparkling waters had higher migration rates than still mineral waters.

Thus, longer storage periods are likely to result in higher antimony concentrations in the stored water.

2.5.3 Effect of physicochemical properties of water on antimony migration

The presence of various degrees of ions in the stored water can affect the release of antimony from the PET plastic container. A small number of studies have considered the effect of physicochemical properties of the stored water on antimony release.

Hureiki and Mouneimne (2012) studied four physicochemical properties (pH, calcium, magnesium, and bicarbonate) on antimony release. It was realised that only calcium had a significant effect on antimony release. Keresztes *et al.* (2009) in their study realised that carbonated water had higher antimony leaching rates compared to non-carbonated water. This observation was attributed to the lower pH values (4.94 – 5.27) of sparkling mineral water, indicating that lower pH may accelerate the release of antimony from the packaging material. Bach *et al.* (2013, 2014) discovered that antimony migration was higher in carbonated compared with non-carbonated waters. Carbonated waters have lower pH values by virtue of the dissolution carbon dioxide (CO_2) to form carbonic acid. The carbonic acid then dissociates and contributes mores hydrogen ions in solution, thereby lowering the pH. A study by Westerhoff *et al.* (2007) showed that pH had no effect on antimony migration. They suggested that the typical pH range of 6 to 8 for drinking waters, regardless of the location would not influence antimony migration.

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In effect, lower pH (< 6) and few ions like calcium are likely to affect the release of antimony from the PET plastic container.

2.5.4 Effect of different plastic types on antimony migration

The quality of the PET plastic containers used in packaging differs from country to country. Information regarding the effect of the different types of plastics on antimony migration is scanty. Nonetheless, few workers as part of their studies have tried to assess the effect of the different plastic types on antimony release or migration.

Westerhoff *et al.* (2007) examined antimony migration between two types of PET plastic bottles (based on the colour of packaging material – clear and blue). Samples were incubated at 80°C over a ten-day period. The results indicated that clear PET plastics released about four times more antimony than blue-coloured PET plastics. In another study by Carneado *et al.* (2014) based on colour and the residual antimony content (191 – 268 mg/kg) in the PET plastic containers, dark blue plastics contained slightly higher antimony levels than clear and light blue plastics. It was realised that leaching of antimony (III) into water samples stored in dark blue, clear and light blue bottles at 60°C for 50 – 220 days had waters held in dark blue bottles having higher antimony levels in the stored water than clear and light blue bottles. The concentrations of stored waters (in dark blue plastics) increased from 5.61 at day 50, peaked at 7.12 at day 78 and decreased to 3.34 at day 220. Fan *et al.* (2014) determine total antimony in sixteen brands of PET drinking bottled waters in China. Comparing the maximum antimony concentrations in the stored waters if all the antimony in PET plastic containers were to be released into the stored waters showed that, the higher the total antimony in the PET packaging material, the higher the maximum antimony concentration released into the stored water.

In summary, based on the literature reviewed, the colour and the residual amount of antimony in the plastic material tends to affect the levels of antimony in the stored water.

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2.6 Analytical method employed in antimony speciation

Elemental speciation is outlined *'…as the analyses that lead to determining the distribution of an element's particular chemical species in a sample'* (Caruso & Montes-Bayon, 2003). Antimony speciation in plastic bottled water has been the topic of focus for the past decades. Nonetheless, few published works have been centred on identification, quantification and the fate of the species in the stored water and in the PET plastic container (Carneado *et al.*, 2015). Furthermore, the extremely low concentrations of the inorganic forms (Sb(III) and Sb(V)) in aqueous environments makes direct speciation more difficult (Z. Fan, 2005; Hagarová *et al.*, 2008). To understand the fate of antimony in the aquatic environment, low detection limits are usually required. This is accomplished by using speciation analysis methods which generally comprise a selective separation or pre-concentration technique and a sensitive detection method capable of determining analyte concentrations naturally in the range of 1 – 300 ng/L (Amereih *et al.*, 2005; Apte & Howard, 1986; Hagarová *et al.*, 2008; Krachler & Emons, 2001).

Some of the analytical methods employed are: high-performance liquid chromatography (HPLC) coupled to inductively coupled plasma mass spectrometry (ICP MS), HPLC coupled online to hydride generation AAS or to ICP-MS, ion chromatography (IC) coupled to hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP OES), cloud point extraction (CPE)/ atomic absorption spectrophotometry (AAS) and hydride generation coupled to atomic fluorescence spectrometry (AFS). Other techniques applied are anodic striping voltammetry, cathodic stripping voltammetry, X-ray fluorescence, microwave induced plasma atomic emission spectrometry (Ferreira *et al.*, 2014; Krachler & Emons, 2001). Most of these procedures are largely complicated, time-consuming and bear high operation costs. Hence, the need for a simple, express, efficient and cost effective analytical method.

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Hydride generation atomic absorption spectrophotometry (HG-AAS) is the analytical technique frequently used in the determination of trace amounts of antimony typically in the µg/L concentration range (Apte & Howard, 1986; Ferreira *et al.*, 2014). The hydride generation method has the benefit of being simple, rapid, is comparatively free from interference and by careful control of the reduction process, information of analyte oxidation state may be reached (Apte & Howard, 1986). The hydride generation process basically involves reacting antimony compounds with tetrahydroborate (III) in acidic medium to produce stibine (SbH_3). Antimony (V) cannot be completely reduced to stibine with tetrahydroborate (III) because it demonstrates poor sensitivity compared to antimony (III). Thus, to achieve total amounts of the metalloid, antimony (V) should be pre-reduced to antimony (III) first and then further reduced with the tetrahydroborate to generate the stibine. The reaction chemical equations adopted from Feng *et al.* (1999) are presented below:

$$4H_3SbO_4 + BH_4^- + H^+ \rightarrow 4H_3SbO_3 + H_3BO_3 + H_2O \text{ (Slow)}$$

$$H_3SbO_3 + 3BH_4^- + 3H^+ \rightarrow 4SbH_3 + 3H_3BO_3 + H_2O \text{ (Fast)}$$

The electrochemical equation of the reduction of antimony (V) to antimony (III) in acidic medium shows an important feature.

$$SbO_4^{3-} + 2H^+ + 2e^- \rightleftharpoons SbO_3^{3-} + H_2O \; E^o_{Sb(+5)/Sb(+3)} = +\,0.69 \text{ volts.}$$

The reduction process is highly favourable in acidic medium (Ferreira *et al.*, 2014). However, not all acids will favour this reduction process. The choice of the acid, therefore, becomes critical in speciation analysis of antimony, as acids like oxidising ones would not be suitable for the reduction process to proceed. Hydrochloric acid is the principal acidifying agent routinely used for extracting antimony in aqueous matrices (Ferreira *et al.*, 2014). Also from the reaction, the use of a reducing agent can be supportive in the reduction process. A variety of reducing agents have been utilised, but the most favoured is L-cysteine, as its solutions are

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usually more stable compared to other reducing agents (Z. Fan, 2005, 2007; Ferreira *et al.*, 2014). When in solution with antimony (V), L-cysteine reduces it to antimony (III) as follows:

$$2R–SH + H_3SbO_4 \rightarrow R–S–S–R + H_3SbO_3 + H_2O \text{ (Slow)}$$ (Feng, Narasaki, Chen, & Tian, 1999)

The antimony (III) is further reduced to stibine using tetrahydroborate (III) in acidic medium. A neutral inert gas then carries it for atomisation (by AAS or AFS) or excitation (using ICP or MIP).

AAS is a technique in which free gaseous atoms absorbs light of characteristic wavelength (monochromatic radiation) in a flame or furnace resulting in the quantification of the atoms. To measure the concentration of an element in the sample, a liquid sample of the element is first aspirated into a nebulizer system. The fine mist produced by the nebulizer system is mixed with an oxidant gas that is drawn under pressure, thus producing aerosols. These aerosols are then carried into a flame that is commonly produced by a mixture of air and acetylene (2400ºC) or nitrous oxide and acetylene (2800ºC). In the flame, the solvated aerosols lose their solvent (desolvation) and the gaseous metallic element undergoes excitation. At the same, a light beam from a lamp (usually a hollow cathode lamp whose cathode is made of the element being determined) is passed through the flame. A photomultiplier tube is then used to detect the reduction of light intensity due to absorption by the atoms of the analyte in the flame. Using the Beer-Lambert law, the absorbance is proportional to the concentration of the metal ions (Skoog, Holler, & Nieman, 1998).

In summary, inorganic speciation of antimony in the water samples can be undertaken by carefully controlling the reduction processes to determine total antimony and then antimony (III). Antimony (V) is the obtained from the difference between total antimony and antimony (III).

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CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Introduction

This chapter describes the sample selection and collection procedure, sample preparation, sample treatment and analyses carried out to speciate inorganic antimony in waters contained in PET plastic bottles stored under three distinct conditions.

3.2 Sample selection and collection procedure

PET plastic bottled water samples of six popular brands (shown in **Figure 3.2.2**) in Greater Accra were selected and purchased at source (bottling plant locations are shown in **Table 3.2.1** and geographically mapped out in **Figure 3.2.1**). Samples were obtained on the day of bottling in the month of January 2015. For each brand of plastic bottled water, forty samples were required. Thus for the six brands, two-hundred and forty bottled water samples were procured. All samples of a particular brand originate from the same batch of bottled waters bottled at that time of the day.

All brands of bottled waters had a transparent layer of PET material used in packaging and the waters stored in them had different degrees of mineral composition. The container capacity (volume) chosen was 0.5 L for all the six brands of plastic bottled water samples. Bottled water samples were not of the same bottling date but were all packaged in the period of two weeks in the month of January 2015. All bottled water samples remained sealed in their original containers until analysis and all antimony analysis (total antimony and antimony (III)) for each brand (water samples and PET plastic containers) were carried out in quadruplicate ($n = 4$). Thus, the obtained results will correspond to the mean of four independent measurements for both water samples and plastic material originating from bottled water samples of the same batch.

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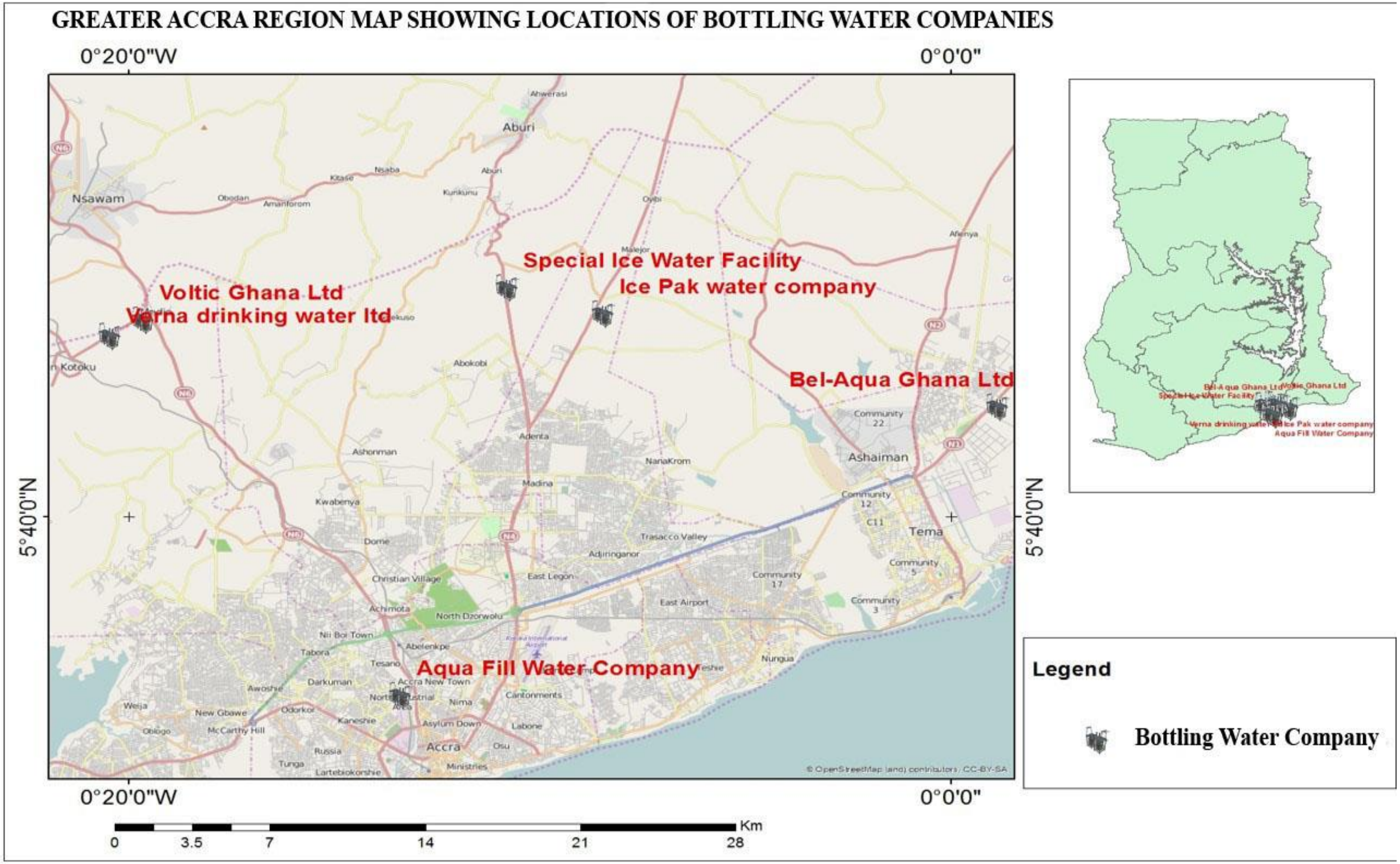

Figure 3.2.1: Geographical map showing the locations of the bottled water companies in Greater Accra.

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Table 3.2.1: Bottling plant sites in the Greater Accra Region

Bottled water establishment	Location (Off)	Latitude	Longitude
Voltic Ghana Limited	Nsawam Road	5º45’29.81”N	0º19’40.40”W
Special Ice water facility	Oyarifa Road	5º46’23.47”N	0º10’49.75”W
Bel-Aqua Ghana Limited	Tema heavy industrial Area	5º43’4.71”N	0º1’5.72”E
Verna water company	Nsawan Road	5º45’3.09”N	0º20’30.04”W
Ice Pak water company	Adenta-Dodowa Road	5º45’39.55”N	0º8’30.03”W
Aqua Fill water company	North industrial area	5º35’2.52”N	0º13’25.94”W

Figure 3.2.2: The six brands of bottled water samples displayed on a clean laboratory bench. *From left, bottled water coded names are VOL, AQF, VER, ICP, BQA, and SPI respectively.*

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3.3 Reagents and standards

The standards and reagents used in this study were prepared with ultrapure water (8 – 10 $M\Omega\cdot cm^{-1}$ at 24.5ºC) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). All chemicals were analytical-reagent grade unless otherwise stated.

The 1 mg/mL stock standard solutions of antimony (III) and antimony (V) were prepared by dissolving 0.274 g of dried (at 105ºC for 2 hours) antimony potassium tartrate hemihydrate (Sigma-Aldrich, 99%) in 0.1 L of 6 M HCl (Springer Shenstone Lichfield, 36% – 38%) and 0.216 g of potassium hexahydroxyantimonate (Sigma-Aldrich, 99%) in 0.1 L of 2.4 M HCl, respectively. Antimony stock solutions were stored in polyethylene plastic bottles in refrigerator at 4ºC and working solutions were prepared daily by dilution.

Sodium borohydride solution was prepared from dissolving 0.700 g granular $NaBH_4$ (to a 0.7% (w/v) concentration, KEM Light laboratory purpose reagent, >97%) in 0.4% (w/v) sodium hydroxide (prepared from 0.400 g NaOH pellets, Merck, 99%).

In the microwave digestion of the plastic samples, concentrated HNO_3 (Panreac, hyper-pure reagent grade, 69%) and H_2O_2 (Merck, 96%) were used. The 1 M citrate solution used was prepared by dissolving 2.940 g sodium citrate dihydrate (≥ 99%, Sigma-Aldrich) in 10 mL ultrapure water.

The 1 M L-Cysteine solution used to reduce antimony (V) in total antimony determination was prepared by dissolving 1.212 g of L-Cysteine (97%, Sigma-Aldrich) in 10 mL of HCl (2.4 M).

The 0.5 M aqueous sulphuric acid (Sigma-Aldrich, 99.99%) used in the titration determination of bicarbonate ion concentration was prepared by slowly adding 2.81 mL of the stock acid to 25 mL double distilled deionised water. The final volume of the mixture was then adjusted to 100 mL to obtain the required concentration.

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The 1 M potassium chloride used in the validation of the pH determination procedure was prepared by dissolving 0.750 g of KCl (Sigma-Aldrich, > 99%) in 10 mL of double distilled deionised water.

The ionisation suppression agent (1 M lanthanum chloride solution) used in the spectrophotometric determination of magnesium and calcium was prepared by dissolving 18.570 g of $LaCl_3 \cdot 7H_2O$ (Sigma-Aldrich, 99.99%) in 50 ml of 1.5 M HCl solution.

3.4 Instrumentation

A 240 FS AA spectrophotometer (New York, US) with an antimony hollow cathode lamp (Photron Super Lamp) was used in the determination of trace inorganic antimony, calcium and magnesium. Background absorption was corrected using a deuterium lamp. The operating conditions of the spectrophotometer during the determinations are shown in **Table 3.4.1**.

Table 3.4.1: Operating conditions of the spectrophotometer

Element	Wavelength, λ (nm)	Current (mA)	Spectral resolution (nm)	Gas
Antimony (Sb)	217.6	14	0.7	C_2H_2/air
Calcium (Ca)	422.7	10	0.5	C_2H_2/N_2O
Magnesium (Mg)	285.2	4	0.5	C_2H_2/air

Temperature measurements were done using a mercury (Hg) bulb thermometer (US Coater). The Hg-filled thermometer had a precision of ± 0.1°C.

All pH measurements were carried out using an HI 2210 basic Bench top pH meter.

Total dissolved solids (TDS) for the bottled water samples were measured using HANNA HI 4321 conductivity/TDS meter.

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Microwave digestion of the PET plastic container samples was performed using a Milestone Ethos Touch control digester instrument, with a temperature controller and a power of 1000W. For this procedure, eight Teflon pressure vessels were used simultaneously.

3.5 Sample preparation

Before analysis, water samples were allowed to stand an hour before treatment starts. This is to enable all the water samples held under the different storage conditions, re-adapt to the same experimental settings before treatment and subsequent analysis.

PET plastic containers were cut into approximately 5 × 5 mm^2 pieces using a ceramic blade. Each cut-out replicate of the PET plastic container weighed approximately 0.250 g.

3.6 Containers and cleaning process

Glassware and polyethylene containers were cleansed by soaking in 1.5 M HCl overnight and rinsing with double distilled de-ionized water. They were then placed in a clean oven overnight at 35°C. The moisture-free containers were then placed in a clean glass cabinet ready for use.

The ceramic blade used in cutting the plastic containers was pre-cleansed with 1.5 M HCl

3.7 Migration experiment

To simulate the effect of storage conditions typical of bottled water usage on the migration of antimony from the plastic containers into the waters stored inside, bottled water samples were assigned into three storage groupings, with each group comprising bottled waters from the six different brands.

Each group (excluding samples for analysis on the day of acquiring samples – day one) was further divided into three subgroups. The three subgroupings (containing four bottled water samples for each brand) will represent four weeks, eight weeks and twelve weeks under a specified storage condition. One group will be stored in a refrigerator at 4°C; the second group

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exposed to high air temperatures and sunlight light outdoor, and the third group in a closed cabinet away from sunlight indoor. The samples were held under these conditions from January to March 2015. During the study, temperatures of the bottled waters kept outside and indoors were monitored at regular intervals using the mercury bulb thermometer and those in the refrigerator maintained at 4ºC.

To establish the concentrations of the inorganic antimony species in the source waters, determinations were done on some of the bottled water samples for each brand on the day of acquiring the samples (within 12 hours after filling). The rest of the bottled water samples were then stored according to the group they were assigned into for the rest of the period of study.

3.8 Analysis of water samples

3.8.1 Physicochemical properties of the water samples

3.8.1.1 pH

The pH of the water samples of the six brands of bottled waters were taken using the basic Benchtop pH meter on the day the bottled water samples were acquired.

The meter was first calibrated with buffers at pH 4.70 and 10.01 at ambient temperature (24ºC). The probe of the meter was then inserted into specific volumes (10 mL) of the water samples and readings taken from the screen.

For validation purposes, the pH of 1 M KCl solution was similarly determined (APHA, 1998).

3.8.1.2 Total dissolved solids (TDS)

The total dissolved solids of the water samples were measured using the conductivity/TDS meter that was calibrated at ambient temperature (24ºC) using HANNA standards. The probe of the meter was inserted into specific volumes (20 mL) of the water samples. Total dissolved solids readings were then taken from the screen (HANNA, 2012).

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3.8.1.3 Calcium

The calcium content of the water samples was determined spectrophotometrically at 422.7 nm by atomic absorption.

Aliquots of the water samples were first mixed with lanthanum chloride ($LaCl_3$) solution and aspirated into nitrous oxide-acetylene flame. The absorbance was then measured and compared to identically-prepared standard and blank solutions from which concentrations were obtained (Environment Canada, 1979a).

3.8.1.4 Magnesium

The magnesium concentration was determined by atomic absorption spectrophotometry (AAS) – direct aspiration.

Aliquots (10 mL) of water samples were mixed with 5 mL of 1 M lanthanum chloride ($LaCl_3$) solution and aspirated into an air-acetylene reducing flame. The absorbance was measured at 285.2 nm and compared to prepared standards and blank solutions. From the absorbance, concentration is then obtained (Environment Canada, 1979b).

3.8.1.5 Bicarbonate

Bicarbonate ion concentration was determined by titration.

Aliquots (10 mL) of bottled water samples were titrated with 0.5 M sulphuric acid using phenolphthalein and mixed bromocresol green and methyl red indicators. The endpoints reached was used to evaluate the amount of hydrogen carbonate present in the water samples (APHA, 1967).

3.8.2 Total antimony determination

For total inorganic antimony determination, the pH of water samples (10 mL) were adjusted to 2 by adding 10 mL of 8 M HCl, after which 5 mL of 1 M L-cysteine was added to reduce all the antimony (V) to antimony (III). Solutions were then allowed to stand for 15

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minutes after which they were place in the auto sampler section of the atomic absorption spectrophotometer for analysis to begin.

Prior to the commencement of total antimony analysis, a calibration curve was generated using pre-reduced (by 1 M L-cysteine) working standards of antimony (V) prepared by serial dilutions of the stock antimony (V) standard. Blanks were also prepared and used to correct interferences originating from the matrices of the solutions.

A global environment monitoring system (GEMS) water standard reference material having the same matrix as the water samples was equally determine using the same procedure. The result obtained will be used to check the accuracy of the method.

3.8.3 Antimony (III) determination

In antimony (III) determination, 1 M citrate solution in HCl is used instead of L-cysteine. Thus, there was no pre-reduction. The rest of the procedure remains the same as in total antimony determination.

Calibration was done using working standards obtained by serially diluting the antimony (III) stock standard solution.

For quality control purposes, ultrapure water was spiked with 20 µg/L antimony (III) and determined using the same procedure.

3.8.4 Antimony (V) determination

Antimony (V) concentrations of the waters stored in the PET plastic containers were evaluated by subtracting antimony (III) concentrations from total antimony concentrations.

3.9 Analysis of PET plastic containers

Each cut-out replicate of the PET plastic containers was mixed with 10 mL of concentrated HNO_3 and 2 mL of concentrated H_2O_2 and digested in Teflon closed vessels using

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the Milestone Ethos Touch control digester instrument. The maximum temperature and pressure was 180ºC and 250 psi respectively for 15 minutes using 50% of the digestion system's maximum power of 1000 W. After digestion, 5 mL of 1 M L-cysteine was added to the digestates and solutions allowed to stand for 15 minutes to reduce all the antimony (V) to antimony (III). Solutions were finally topped to 25 mL with ultrapure water and analysed for antimony using the atomic absorption spectrophotometer.

Calibration of the spectrophotometer was done using working standards of antimony (V) that were prepared from serial dilutions of the stock antimony (V) standard. Concentrated HNO_3 and H_2O_2 were added to the antimony (V) standards and digested as in the determination of the unknown. Antimony (V) in these solutions were then pre-reduced using L-cysteine for the same time as in the unknown. Blanks were also prepared and used to eliminate interferences that may be coming from the matrices of the solutions.

For quality control purposes, cut samples of polyethylene plastic containers were spiked with 20 µg/L antimony (V) and determined the same way as in the total antimony determination in the PET container samples.

3.10 Data analysis

SPSS (IBM Corporation, 2012) and Excel (Microsoft Corporation, 2012) software tools were used to analyse data obtained in the study.

Means, standard deviations, the coefficient of variations and confidence intervals were carried out using Excel whilst, Pearson's correlations, Paired-Samples T Test, linear regressions, line and bar graphs were generated using SPSS.

To determine how total antimony concentrations of the water samples change with time under the typical storage conditions, linear regressions were used. The results will reveal how migration is occurring over time.

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Pearson's correlation analysis was used to highlight the relationship between the five selected physicochemical properties (pH, total dissolved solids, calcium, magnesium, and bicarbonate) and antimony content (total antimony, antimony (III) and antimony (V)).

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CHAPTER FOUR

4.0 RESULTS

4.1 Introduction

This chapter presents the results obtained in the speciation analysis of inorganic antimony in selected PET plastic bottled waters marketed in the Greater Accra Region.

Quality control methods used in validating the procedures used in the determination of the inorganic species of antimony are presented in **Table 4.2.1**.

The selected physicochemical properties of the waters stored in the PET plastic containers for the six brands of PET bottled waters are presented in **Table 4.3.1** and illustrated in **Figure 4.3.1**.

Total inorganic antimony concentrations of the PET plastic containers of the six brands of PET plastic bottled waters are displayed in a table in **Appendix F** and illustrated in **Figure 4.4.1**.

Inorganic antimony species of the waters stored in PET plastic containers exposed outdoor in the sun at high temperatures (average temperature: 23.0ºC in the morning and 39.5ºC in the afternoon – **Appendix D**), indoor in a closed cabinet at room temperature (average temperature: 20.4ºC in the morning and 25.3ºC in the afternoon – **Appendix D**) and in a refrigerator (at 4ºC) for twelve weeks at intervals of four weeks are presented in **Tables 4.5.1** – **4.5.5** and illustrated in **Figures 4.5.1** – **4.5.9**.

The results of correlation analysis depicting the relationships between the selected physicochemical properties and inorganic antimony species of the waters stores in PET plastic containers are presented in **Appendix A**.

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Linear regressions showing how total inorganic antimony concentrations of the waters stored in PET plastic containers vary with time under the selected unique storage conditions for the six brands of PET plastic bottled waters are presented in **Appendix C.**

4.2 Validation of analytical procedures used in inorganic antimony determination

Table 4.2.1: Quality control methods for the procedures used in inorganic Sb analysis

Procedure	Reference material	Certified amount (µg/kg)	Measured amount (µg/kg)	Recovery (%)
Total Sb determination in water samples	GEMS water standard	100	99.49	99.5
Total Sb determination in PET plastic container samples	Spiked polyethylene plastic	20	19.98	99.9
Sb(III) determination in water samples	Spiked ultrapure water	20	19.97	99.9

The certified total antimony content in the GEMS material used in validating the total antimony determination procedure was 100 µg Sb/kg ± 2%. This standard reference material was analysed in quadruplicate (*n* = 4), in order to establish the precision of the measurement. The quantified total antimony concentration matched the certified value considering the associated uncertainties, achieving a value of 99.49 µg Sb/kg ± 2% (**Table 4.2.1**).

Spiked ultrapure water samples and cut polyethylene container samples in the determination of antimony (III) in the waters stored in the PET plastic containers and total

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antimony in PET plastic containers respectively, had uncertainties within acceptable limits (**Appendix B**) and recoveries > 95% (**Table 4.2.1**).

4.3 Relationship between physicochemical properties and inorganic antimony species

The results for physicochemical properties of the bottled water samples are presented in **Table 4.3.1**. The properties considered are pH, bicarbonate ion (HCO_3^-) concentration, calcium ion (Ca^{2+}) concentration, magnesium ion (Mg^{2+}) concentration and total dissolved solids (TDS). These were measured on the day bottled water samples were acquired (day one – week 0).

Pearson correlation was used to highlight the relationship between the water physicochemical properties on one hand and total antimony, antimony (III) and antimony (V) concentrations on another hand. **Appendix A** shows the results for correlation analysis undertaken for each brand of bottled water.

4.3.1 pH *versus* antimony species

From **Table 4.3.1**, the pH of the six brands of bottled water ranged 6.78 – 7.43 with a mean and median value of 7.12 and 7.11 respectively. The range obtained was similar to those obtained in literature (Hureiki & Mouneimne, 2012; Westerhoff *et al.*, 2008).VOL recorded the highest pH value (7.43) and AQF the least (6.78). The rest of the brands had pH values varying between the figures 6.78 and 7.43.

pH statistically registered an insignificant positive correlation (P = 0.085, 0.091 > 0.05, 0.01) to total antimony and antimony (V) (**Appendix A**). This suggests that pH does not statistically affect total antimony and antimony (V) at the 0.05 and 0.01 significance level. On another hand, pH significantly correlated antimony (III) positively (P = 0.046 < 0.05). This suggests that pH statistically affects antimony (III) at 0.05 level.

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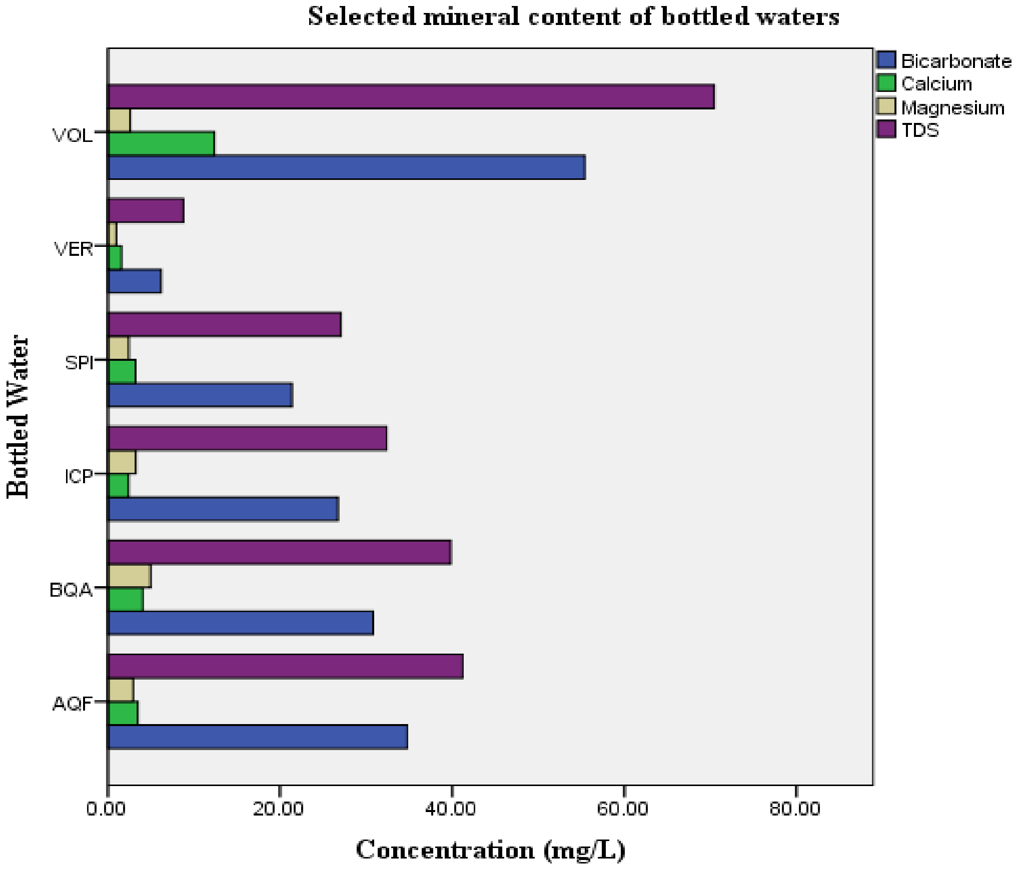

Figure 4.3.1: Selected ionic mineral content of bottled water samples. *Bars represent mean concentration values (n = 4).*

4.3.2 Bicarbonate content *versus* antimony species

The bicarbonate ion (HCO_3^-) concentrations of the waters stored in the PET containers are shown in **Table 4.3.1** and in Figure 4.1. Concentrations ranged from 6.18 – 55.41 mg/L. These range of concentrations are lower compared with those obtain by (Hureiki & Mouneimne, 2012; Keresztes *et al.*, 2009).

The bicarbonate ion concentration is positively correlated to total antimony, antimony (III) and antimony (V) concentrations (P = 0.344, 0.307, 0.351 > 0.05, 0.01 – **Appendix A**). The correlation is, however, insignificant. This suggests that the bicarbonate ion concentration statistically has no relationship with antimony content in the stored water. Hureiki and Mouneimne (2012) obtained similar results.

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Table 4.3.1: Physicochemical properties of the water samples

Bottled water	pH	TDS (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	HCO_3^- (mg/L)
AQF	6.78 ± 0.06	41.22 ± 0.19	3.49 ± 0.03	2.96 ± 0.04	34.77 ± 0.16
BQA	7.21 ± 0.04	39.82 ± 0.37	4.06 ± 0.05	4.96 ± 0.05	30.80 ± 0.30
ICP	7.02 ± 0.04	32.39 ± 1.29	2.40 ± 0.21	3.26 ± 0.07	26.73 ± 1.29
SPI	6.91 ± 0.07	27.05 ± 1.02	3.24 ± 0.06	2.43 ± 0.06	21.38 ± 0.93
VER	7.38 ± 0.08	8.78 ± 0.12	1.61 ± 0.07	1.00 ± 0.08	6.18 ± 0.06
VOL	7.43 ± 0.15	70.40 ± 0.33	12.39 ± 0.06	2.60 ± 0.06	55.41 ± 0.39

4.3.3 Calcium content *versus* antimony species

The calcium ion (Ca^{2+}) content of the six brands of bottled waters are shown in **Table 4.3.1**. The concentrations ranged from 1.61 – 12.39 mg/L with a mean and median value of 4.53 and 3.36 mg/L respectively. These are lower compared with those obtained by Hureiki and Mouneimne (2012) and Keresztes *et al.* (2009).

The calcium content registered statistically insignificant positive correlation to total antimony, antimony (III) and antimony (V) concentrations (P = 0.193, 0.064, 0.205 > 0.05, 0.01) at 0.05 and 0.01 significance level (**Appendix A**). Thus, the calcium content does not appear to affect the changing levels of the antimony content in the stored water.

4.3.4 Magnesium content *versus* antimony species

Figure 4.3.1 displays the magnesium ion concentration for the six brands of bottled waters. The concentrations ranged from 1.00 – 4.96 mg/L with a mean and median value of 2.87 and 2.78 mg/L respectively. This range of concentrations are lower compared to those obtained in a study by Hureiki and Mouneimne, (2012) and Keresztes *et al.*, (2009).

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The magnesium ion concentration is statistically correlated positively to total antimony and antimony (V) (*P* = 0.453, 0.429 > 0.05, 0.01 – **Appendix A**). These correlations are however insignificant. The magnesium concentration is also negatively correlated to antimony (III) concentration. The correlation is statistically insignificant (*P* = 0.708 > 0.05, 0.01). Therefore, the magnesium ion concentration does not statistically affect inorganic antimony species in the waters at the respective significance levels.

4.3.5 Total dissolved solids content *versus* antimony species

Results for the total dissolved solids for the six brands of bottled water are presented in **Table 4.3.1**. This range of concentration was lower compared to those obtained by Hureiki and Mouneimne, (2012) and Keresztes *et al.*, (2009).

TDS was found to be positively correlated to total antimony, antimony (III) and antimony (V) concentrations (**Appendix A**). This correlation was however found to be insignificant (*P* = 0.288, 0.264, 0.295> 0.05, 0.01). This suggests that the TDS content does not statistically affect the inorganic antimony species in the waters at the respective significance levels.

4.4 Effect of different plastics on antimony migration

Figure 4.4.1 displays the total antimony concentrations in the plastic containers the waters were stored in for the six brands of bottled water. Differences were clearly shown in the residual total antimony concentrations. The concentrations ranged from 123.5 mg/kg to 146.5 mg/kg. VER had the highest total antimony concentration (146.5 mg/kg) and AQF had the least (123.5 mg/kg).

These concentrations were lower compared to concentrations of PET bottles obtained in some previous studies (Carneado *et al.*, 2015; Keresztes *et al.*, 2009; Tukur, Sharp, Stern, Tizaoui, & Benkreira, 2012). However, the concentrations obtained were within the range of concentrations ((104 – 166 mg/kg) obtained in a study by Fan *et al.* (2014). Sanchez-Martinez

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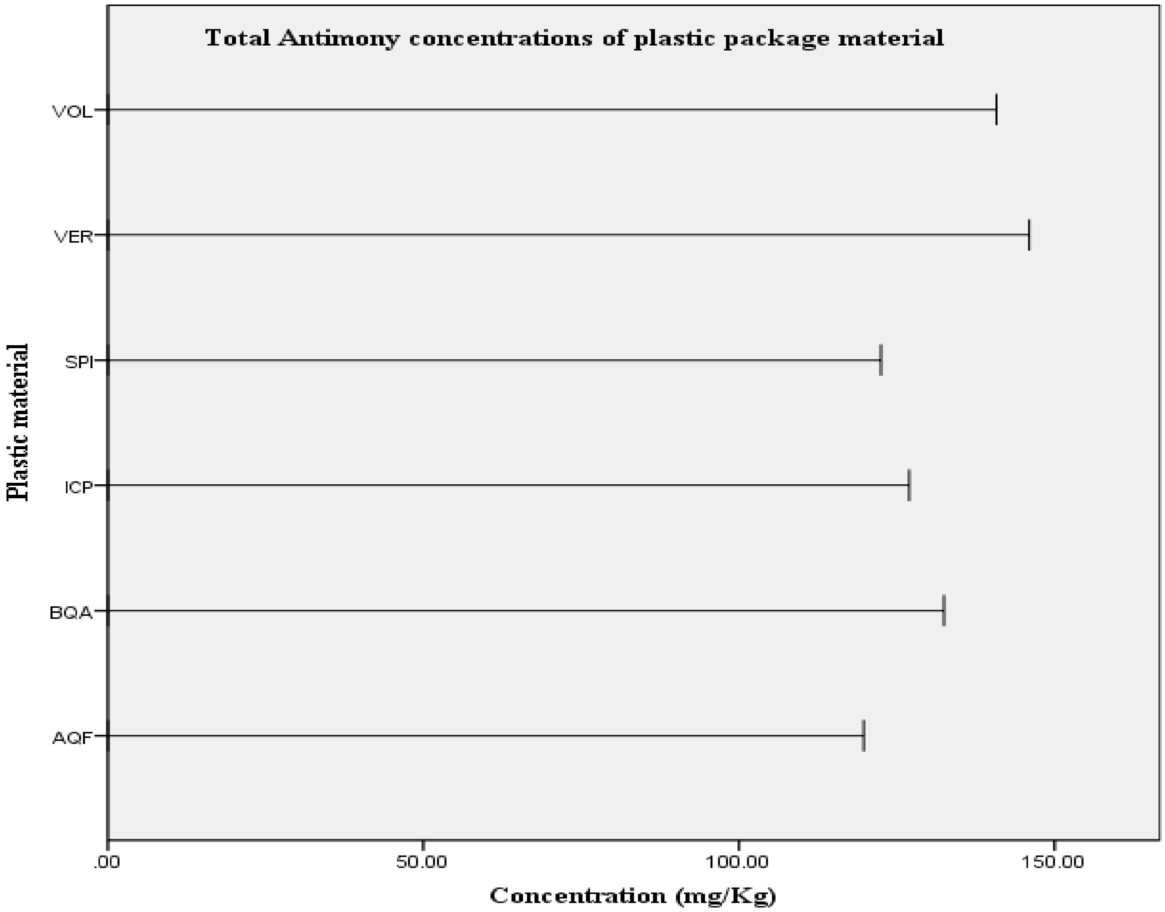

Figure 4.4.1: Total antimony concentrations of the plastic material used in making the bottles. *AQF – VOL represents the branded PET bottles used in packaging the waters. I-beams represent the mean total antimony concentrations of the plastic materials (n = 4).*

et al. (2013) recorded higher total antimony concentrations in the PET plastic containers used in their study. ICP-MS and HG-AFS were used in the determinations of antimony in PET plastic containers.

4.5 Effect of storage conditions on inorganic antimony species

4.5.1 Effect of storage conditions on total antimony

The **Figures 4.5.1** – **4.5.9** display the total antimony concentrations of water samples determined for twelve weeks at intervals of four weeks under the three selected storage conditions for the six brands of bottled waters. The three selected storage conditions (in a refrigerator at 4°C, indoor at room temperature and outdoor exposed to direct sunlight and high air temperatures) were specific and characteristic of bottled water usage in Ghana.

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Five (AQF, BQA, ICP, VER and VOL) out the six brands of bottled water samples already had some amounts of antimony present in them on the day their samples were acquired – day one (week 0). The total antimony concentrations ranged below the detection limit (0.05 µg/L) for SPI to 13.77 µg/L for VOL (**Table 4.5.1**).

The detected concentrations on the day of acquiring bottled water samples are about 1000 times higher compared to the analysis of twelve brands of PET bottled water from Canada (112 – 375 ng/L Sb) (Shotyk *et al.*, 2006). In another study by Westerhoff *et al.*, (2008), antimony concentrations of PET bottled waters ranged 0.095 – 0.521 µg/L. These concentrations were far lower compared to those obtained in this study. In Lebanese natural water bottled in PET, determined antimony concentrations ranged from 0.2 µg/L to about 5.12 µg/L after 544 days (Hureiki & Mouneimne, 2012). Concentrations ranging between 0.03 and 6.61 µg/L have also been obtained for 47 freshly purchased British bottled contents (Tukur *et al.*, 2012).These concentrations are similar to concentrations determined on the day the bottled water samples were acquired in this study. In the study of the influence of storage time and temperature on antimony migration from PET bottles into mineral water, Carneado *et al.* (2014) detected antimony in all tested water samples before storage (day 0). Detected total antimony concentrations ranged from 0.3 to 0.7 µg/L. These concentrations compared with detected antimony concentrations in this study for bottled waters on the first day (week 0), were far lower.

BQA, VER, and VOL registered total antimony concentrations greater than the maximum contaminant level specified by US EPA and EU but lower than the maximum contaminant level specified by WHO for day one.

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Table 4.5.1: Total Sb, Sb(III) and Sb(V) concentrations of water samples determined on first day and after four weeks in refrigerator

Bottled water brands	Bottling date (2015)	Week					
		0			4		
		$Sb^{Tot\,\text{ʁ}}$ (µg/L)	Sb^{III} (µg/L)	Sb^{V} (µg/L)	Sb^{Tot} (µg/L)	Sb^{III} (µg/L)	Sb^{V} (µg/L)
AQF	5th January	1.76 ± 0.09	0.14 ± 0.01	1.62 ± 0.09	1.89 ± 0.03	0.22 ± 0.01	1.67 ± 0.02
BQA	7th January	14.65 ± 0.14	0.24 ± 0.01	14.42 ± 0.14	15.51 ± 0.39	0.35 ± 0.02	15.16 ± 0.39
ICP	8th January	1.11 ± 0.04	< LD	1.11 ± 0.04	1.77 ± 0.09	0.38 ± 0.03	1.40 ± 0.09
SPI	9th January	< LD	< LD	< LD	1.33 ± 0.09	0.95 ± 0.06	0.38 ± 0.14
VER	10th January	6.12 ± 0.47	0.35 ± 0.02	5.78 ± 0.47	8.27 ± 0.37	0.86 ± 0.06	7.41 ± 0.42
VOL	12th January	13.77 ± 0.13	0.65 ± 0.07	13.12 ± 0.15	14.86 ± 0.37	1.21 ± 0.08	13.65 ± 0.38

Sb^{Tot}: Total antimony, Sb^{V}: antimony (V), Sb^{III}: antimony (III), $Sb^{V} = Sb^{Tot} - Sb^{III}$, Concentrations shown are expressed as mean ± standard deviation, n = 4. LD: Limit of detection. Week 0 (First day): day bottled water samples were acquired.

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Table 4.5.2: Total Sb, Sb(III) and Sb(V) concentrations of water samples determined after eight weeks and twelve weeks in refrigerator

Bottled Water brands	Week					
	8			12		
	Sb^{Tot} (µg/L)	Sb^{III} (µg/L)	Sb^{V} (µg/L)	Sb^{Tot} (µg/L)	Sb^{III} (µg/L)	Sb^{V} (µg/L)
AQF	2.02 ± 0.06	0.57 ± 0.04	1.45 ± 0.06	2.92 ± 0.08	1.09 ± 0.06	1.83 ± 0.08
BQA	16.67 ± 0.34	0.84 ± 0.08	15.84 ± 0.32	17.32 ± 0.10	1.50 ± 0.04	15.82 ± 014
ICP	1.96 ± 0.03	0.69 ± 0.06	1.27 ± 0.07	2.55 ± 0.20	1.05 ± 0.06	1.50 ± 0.22
SPI	1.43 ± 0.04	1.09 ± 0.06	0.34 ± 0.10	1.94 ± 0.04	1.76 ± 0.06	0.19 ± 0.09
VER	9.03 ± 0.05	1.07 ± 0.04	7.96 ± 0.06	10.16 ± 0.05	1.90 ± 0.05	8.26 ± 0.08
VOL	15.75 ± 0.21	1.37 ± 0.04	14.37 ± 0.18	16.79 ± 0.06	2.20 ± 0.05	14.60 ± 0.09

Sb^{Tot}: *Total antimony,* Sb^{V}: *antimony (V),* Sb^{III}: *antimony (III),* $Sb^{V} = Sb^{Tot} - Sb^{III}$, *Concentrations shown are expressed as mean ± standard deviation* $n = 4$.

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Table 4.5.3: Total Sb, Sb(III) and Sb(V) concentrations of water samples determined after four and eight weeks indoors

Bottled Water brands	Week 4			Week 8		
	Sb^{Tot} (µg/L)	Sb^{III} (µg/L)	Sb^{V} (µg/L)	Sb^{Tot} (µg/L)	Sb^{III} (µg/L)	Sb^{V} (µg/L)
AQF	2.86 ± 0.13	0.56 ± 0.06	2.30 ± 0.10	3.31 ± 0.11	0.96 ± 0.07	2.36 ± 0.13
BQA	15.11 ± 0.08	0.80 ± 0.06	14.32 ± 0.03	15.93 ± 0.09	1.27 ± 0.04	14.66 ± 0.11
ICP	2.14 ± 0.06	0.27 ± 0.04	1.87 ± 0.07	2.95 ±0.07	0.59 ± 0.03	2.36 ± 0.07
SPI	1.85 ± 0.06	1.17 ±0.05	0.68 ± 0.10	2.68 ± 0.10	1.82 ± 0.04	0.85 ± 0.07
VER	6.56 ± 0.07	0.77 ± 0.05	5.78 ± 0.08	6.90 ± 0.07	1.12 ± 0.03	5.78 ± 0.09
VOL	14.69 ± 0.08	1.08 ± 0.04	13.60 ± 0.07	15.70 ± 0.11	1.62 ±0.05	14.07 ± 0.07

Sb^{Tot}: Total antimony, Sb^{V}: antimony (V), Sb^{III}: antimony (III), $Sb^{V} = Sb^{Tot} - Sb^{III}$, Concentrations shown are expressed as mean ± standard deviation, $n = 4$.

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Table 4.5.4: Total Sb, Sb(III) and Sb(V) concentrations of water samples determined after twelve weeks indoors and four weeks outdoor

Bottled Water brands	Week					
	12			4		
	Sb^{Tot} (mg L^{-1})	Sb^{III} (mg L^{-1})	Sb^{V} (mg L^{-1})	Sb^{Tot} (mg L^{-1})	Sb^{III} (mg L^{-1})	Sb^{V} (mg L^{-1})
AQF	3.91 ± 0.07	1.53 ± 0.04	2.38 ± 0.08	3.51 ± 0.22	1.67 ± 0.05	1.84 ± 0.17
BQA	16.84 ± 0.06	1.79 ± 0.04	15.05 ± 0.06	17.56 ± 0.23	1.62 ± 0.06	15.94 ± 0.17
ICP	3.68 ± 0.13	1.01 ± 0.07	2.68 ± 0.17	3.47 ± 0.20	1.00 ± 0.05	2.47 ± 0.24
SPI	3.78 ± 0.11	2.30 ± 0.03	1.48 ± 0.12	3.57 ± 0.25	2.90 ± 0.06	0.68 ± 0.23
VER	7.94 ± 0.06	1.72 ± 0.05	6.22 ± 0.09	8.86 ± 0.17	1.81 ± 0.05	7.05 ± 0.16
VOL	16.86 ± 0.06	2.08 ± 0.05	14.78 ± 0.06	15.69 ± 0.23	1.91 ± 0.05	13.78 ± 0.21

Sb^{Tot}: Total antimony, Sb^{V}: antimony (V), Sb^{III}: antimony (III), $Sb^{V} = Sb^{Tot} - Sb^{III}$, Concentrations shown are expressed as mean ± standard deviation, n = 4.

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Table 4.5.5: Total Sb, Sb(III) and Sb(V) concentrations of water samples determined after eight and twelve weeks outdoor

Bottled Water brands	Time (weeks)					
	8			12		
	Sb^{Tot} (mg L^{-1})	Sb^{III} (mg L^{-1})	Sb^{V} (mg L^{-1})	Sb^{Tot} (mg L^{-1})	Sb^{III} (mg L^{-1})	Sb^{V} (mg L^{-1})
AQF	6.69 ± 0.18	2.70 ± 0.05	3.99 ± 0.14	8.63 ± 0.19	3.83 ± 0.04	4.79 ± 0.19
BQA	19.48 ± 0.27	2.25 ± 0.05	17.23 ±0.28	22.62 ± 0.13	3.48 ± 0.04	19.15 ± 0.17
ICP	6.83 ± 0.26	1.88 ± 0.04	4.96 ± 0.30	10.05 ± 0.14	2.81 ± 0.05	7.24 ± 0.10
SPI	7.63 ± 0.24	4.72 ± 0.06	2.92 ±0.24	11.99 ± 0.19	7.06 ± 0.06	4.93 ± 0.15
VER	11.69 ± 0.29	2.97 ± 0.07	8.72 ± 0.32	14.65 ± 0.22	4.06 ± 0.06	10.60 ± 0.20
VOL	19.57 ± 0.34	3.08 ± 0.09	16.49 ± 0.29	23.88 ± 0.16	4.18 ± 0.04	19.70 ± 0.18

Sb^{Tot}: Total antimony, Sb^{V}: antimony (V), Sb^{III}: antimony (III), $Sb^{V} = Sb^{Tot} - Sb^{III}$, Concentrations shown are expressed as mean ± standard deviation, n = 4.

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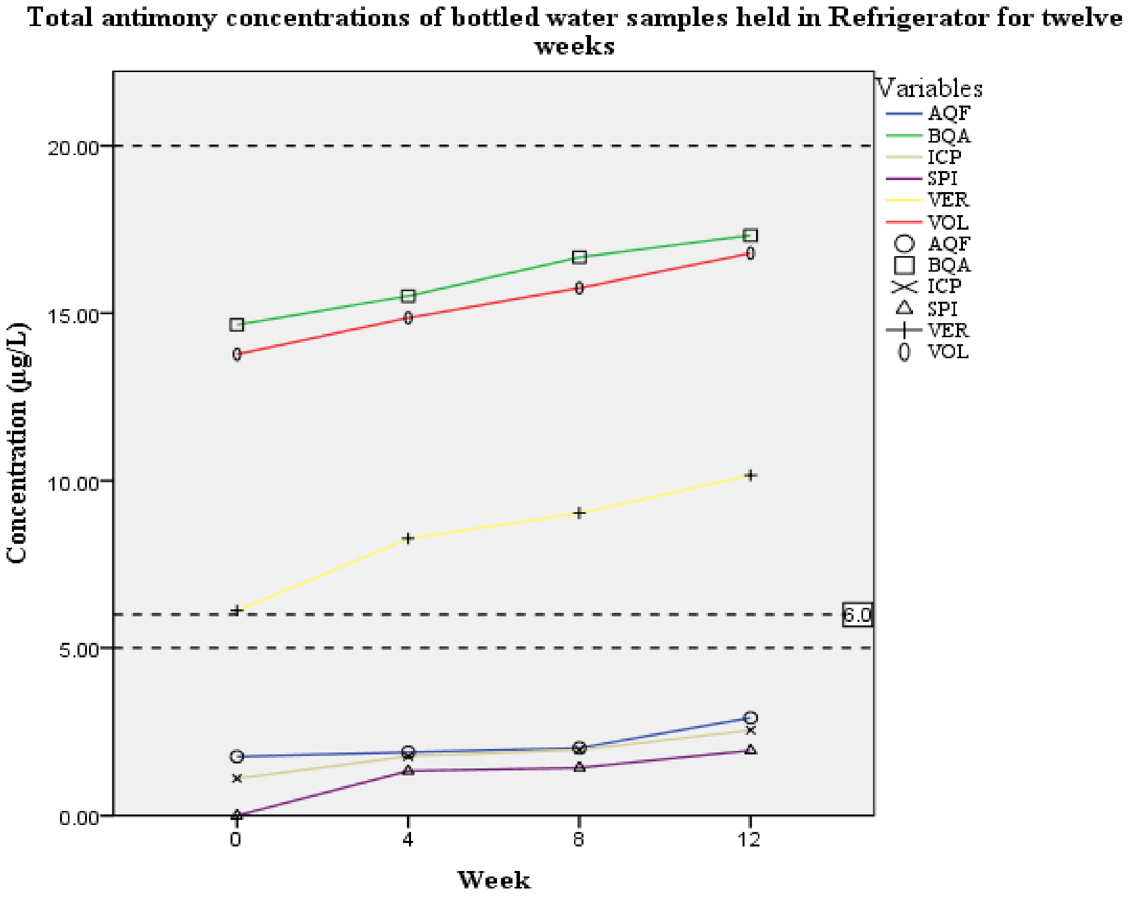

Figure 4.5.1: Total antimony concentrations of bottled water samples stored in a refrigerator for twelve weeks. *Horizontal reference lines represent maximum contaminant levels (MCL). AQF – VOL represents coded names of the brands of bottled water purchased.*

Water samples stored in the refrigerator witnessed an increase in total antimony concentrations from day one to the end of the twelve weeks for all brands of bottled water (**Figure 4.5.1**). Increments observed from week 0 – 4 for BQA, ICP, SPI, VER and VOL had a mean difference of total antimony concentration greater than 0.5 µg/L. Only AQF had a mean difference of total antimony between week 0 and 4 to be less than 0.5 µg/L. The mean difference between week 1 and 4 for BQA, VER and VOL exceeded 0.5 µg/L. The mean difference between week 1 and 4 for AQF, ICP and SPI were below 0.5 µg/L. For the mean difference between week 4 and 8, all the brands of bottled water exceeded the 0.5 µg/L value. BQA recorded the highest total antimony concentration at the end of week 12 under refrigeratory conditions. This was reached because of the major contribution from total

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antimony determined on day one. On the other hand, looking at the difference in mean total antimony concentrations between week 0 and 12 for the six brands suggested an interesting effect. VER recorded the highest difference (4.04) followed by VOL (3.02) (Table 4.2). BQA, SPI, ICP and AQF then followed in decreasing order of difference in mean total antimony concentrations. Despite the increments observed, none of the brands of bottled water had total antimony concentrations exceeding the MCL specified by WHO at the end of the twelve weeks under refrigeratory conditions.

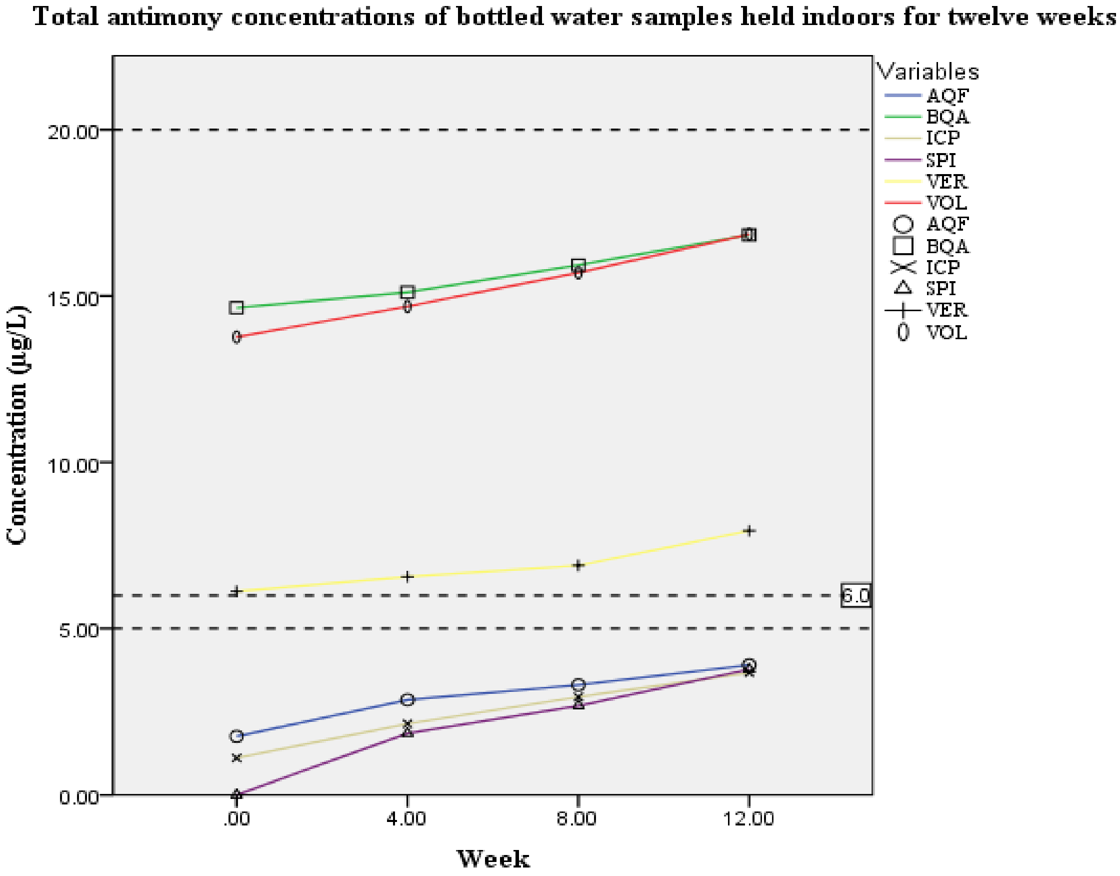

Figure 4.5.2: Total antimony concentrations of bottled water samples stored indoor for twelve weeks. *Horizontal reference lines represent maximum contaminant levels (MCL). AQF – VOL represents coded names of the brands of bottled water.*

Water samples stored indoor saw increase in total antimony concentrations from week 0 to 12 for all the six brands of bottled water (**Figure 4.5.2**). Increments observed from week 0 to 4 for AQF, ICP, SPI and VOL had a mean difference in total antimony concentrations

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exceeding 0.5 µg/L. The mean difference of total antimony for BQA and VER were below 0.5 µg/L from week 0 to 4. The difference in mean total antimony concentrations between week 4 and 8 for BQA, ICP, SPI and VOL were greater than 0.5 µg/L. On the other hand, AQF and VER had their mean difference in total antimony concentration between week 4 and 8 to be below 0.5 µg/L. For the mean difference in total antimony concentrations between week 8 and 12, all brands of bottled water samples had a difference in mean total antimony concentrations exceeding 0.5 µg/L. VOL recorded the highest total antimony concentration (16.86 µg/L) indoors at the end of week 12. The major contribution of total antimony was from concentration determined one the first day (day one). Considering the difference in mean total antimony

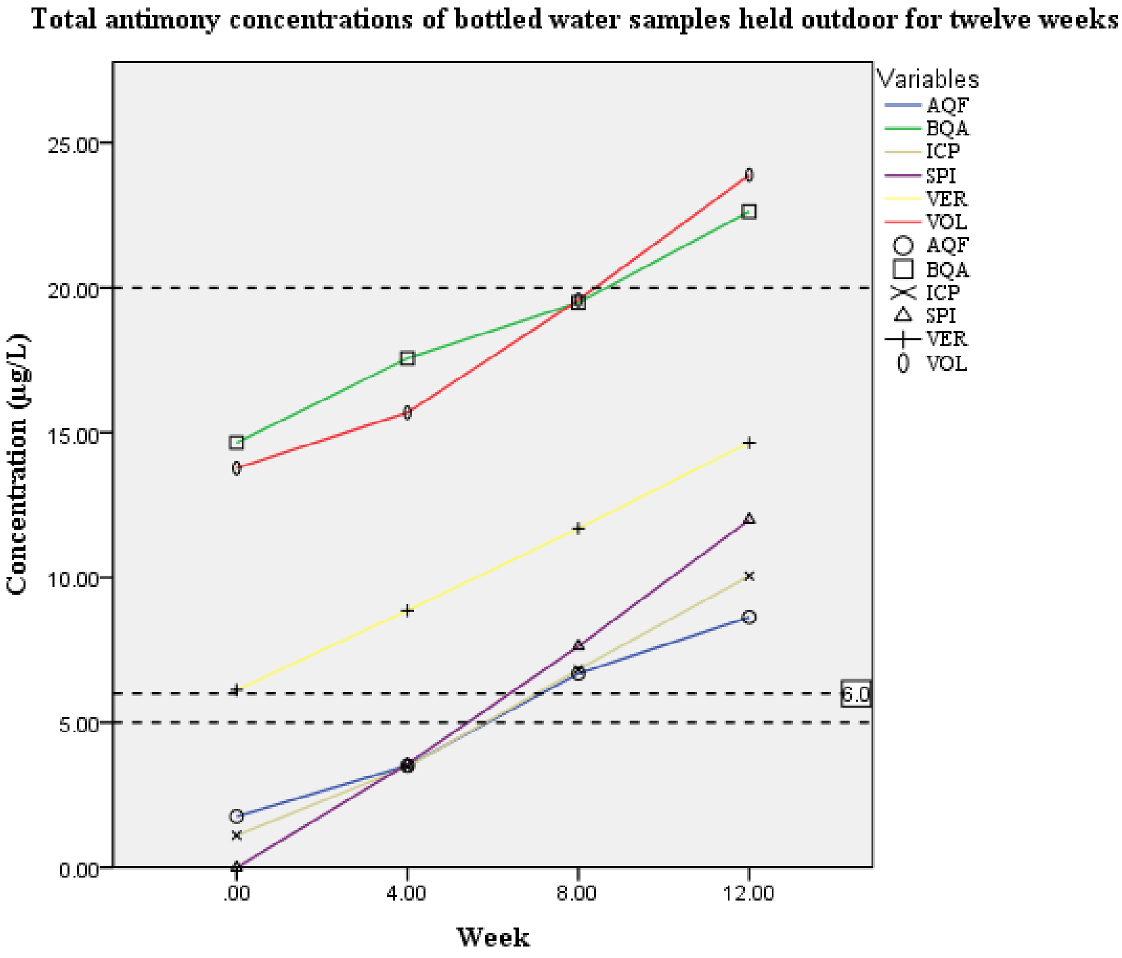

Figure 4.5.3: Total antimony concentrations of bottled water samples stored outdoor for twelve weeks. *Horizontal reference lines represent maximum contaminant levels (MCL). AQF – VOL represents coded names of the brands of bottled water.*

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concentrations between week 0 and 12, resulted in SPI registering the highest with a value of 3.78 difference. This was followed in decreasing order of difference in mean total antimony concentrations by VOL, ICP, BQA, AQF and VER. Bottled water brands BQA, VER and VOL had concentrations greater than the MCL defined by EU and US EPA but less than WHO MCL at the end of week 12 indoor.

Total antimony concentrations of water samples stored outdoor exposed to sunlight and high air temperatures increased from week 0 to 12 for all brands of bottled water (**Figure 4.5.3**). For the period from week 0 to 4, all bottled water brands recorded a difference in mean total antimony concentrations greater than 0.5 µg/L. The difference in mean total antimony concentration from week 4 to 8 and 8 to 12 were all found to be greater than 0.5 µg/L. At the end of week 12, VOL recorded the highest total antimony concentration (23.88 µg/L) followed by BQA. AQF recorded the least total antimony concentration (8.63 µg/L) at the end of week 12. Total antimony concentration obtained at day one were taken into considerations to achieve such “high” concentrations. However, the difference in mean total antimony concentrations from week 0 to 12 for the six brands had SPI register the highest difference (11.99) (**Table 4.5.6**). This was followed in decreasing order of difference in mean total antimony concentrations by VOL, ICP, VER, BQA and AQF. Bottled water brands VER, AQF, SPI and ICP had total antimony concentrations exceeding MCL Specified by EU and US EPA but below WHO MCL at the end of week 12. VOL and BQA however, had their total antimony concentrations exceeding WHO MCL at the end of week 12.

Comparing the difference in mean total antimony concentrations from week 0 to 12 for each brand of bottled water under the three selected storage conditions (**Table 4.5.6**) generated various migration rates (**Table 4.5.7**). Bottled water samples exposed to high air temperatures and sunlight outdoor had averagely higher migration rates compared to those stored in

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Table 4.5.6: Difference in mean total antimony of water samples under storage conditions

Bottled water	Difference in mean total antimony concentrations from week 0 to 12		
	Refrigerator	Indoor	Outdoor
AQF	1.16	2.15	6.87
BQA	2.67	2.19	7.97
ICP	1.44	2.57	8.94
SPI	1.94	3.78	11.99
VER	4.04	1.28	8.53
VOL	3.02	3.09	10.11

Table 4.5.7: Migration rates of antimony under the three storage conditions

Bottled water	Migration rates (µg/L/week)		
	Refrigerator	Indoor	Outdoor
AQF	0.097	0.179	0.573
BQA	0.222	0.183	0.664
ICP	0.120	0.214	0.745
SPI	0.162	0.315	0.999
VER	0.337	0.106	0.711
VOL	0.252	0.258	0.843

refrigerator and indoors. VER recorded the highest migration rate in refrigerator whilst SPI recorded the highest migration rate both in indoor and outdoor. Matching migration rates under the three storage conditions, SPI recorded the highest migration rate under outdoor conditions whilst AQF registered the least under refrigeratory conditions.

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4.5.2 Effect of storage conditions on antimony (III) species

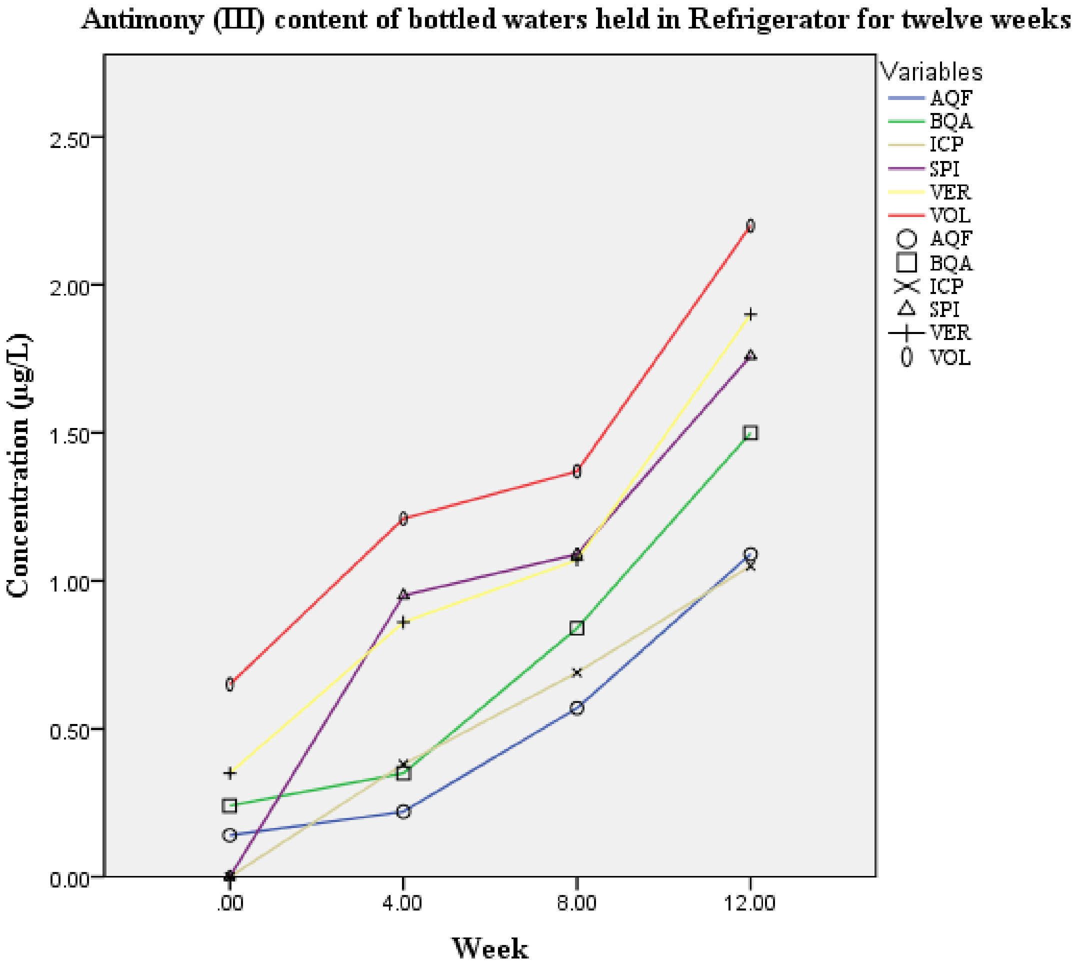

Figure 4.5.4: Antimony (III) concentrations of bottled water samples stored in a refrigerator for twelve weeks. *AQF – VOL represents coded names of the brands of bottled water.*

Figures 4.5.4 – **4.5.6** displays the determined antimony (III) concentrations of water samples for twelve weeks at intervals of four weeks under three selected storage conditions typical of bottled water usage. AQF, BQA, VER and VOL already had some amounts of antimony (III) present as at day one. No antimony (III) was detected for ICP and SPI on day one (week 0). The detected antimony (III) concentrations ranged from 0.14 to 0.65 µg/L with a median value of 0.29 µg/L. VOL recorded the highest antimony (III) concentration (0.65 µg/L) followed in decreasing order of concentration by VER (0.35 µg/L). AQF recorded the least detectable antimony (III) concentration (0.14 µg/L). All brands of bottled water observed

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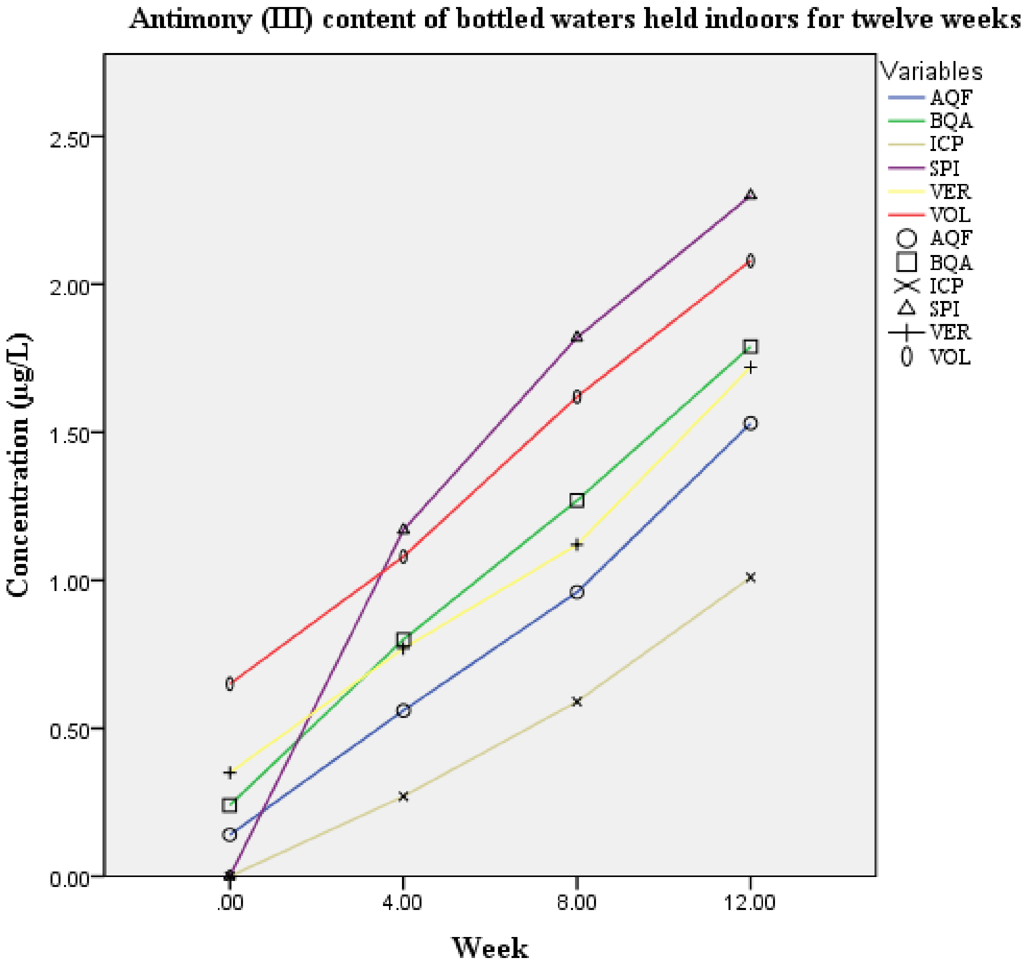

Figure 4.5.5: Antimony (III) concentrations of bottled water samples stored indoor for twelve weeks. *AQF – VOL represents coded names of the brands of bottled water.*

increase in antimony (III) concentrations from week 0 to 12 for all bottled water samples under the three storage conditions.

For bottled water samples stored in the refrigerator (**Figure 4.5.4**) in the period from week 0 to 4, the brands SPI, VER and VOL recorded difference in mean antimony (III) concentrations greater than 0.5 µg/L. Difference in mean antimony (III) concentrations for AQF, BQA and ICP were less than 0.5 µg/L. In the period from week 4 to 8, all brands of bottled water samples recorded difference in mean antimony (III) concentrations less than 0.5 µg/L. AQF, BQA, SPI, VER and VOL recorded a mean difference greater than 0.5 µg/L between week 8 and 12. Only ICP registered a difference in a mean concentration less than 0.5

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µg/L between week 8 and 12. VOL had the highest antimony (III) concentration (2.20 µg/L) at the end of week 12 in the refrigerator. This was followed in decreasing order of concentration by VER and ICP recording the least antimony (III) concentration at the end of the twelve weeks.

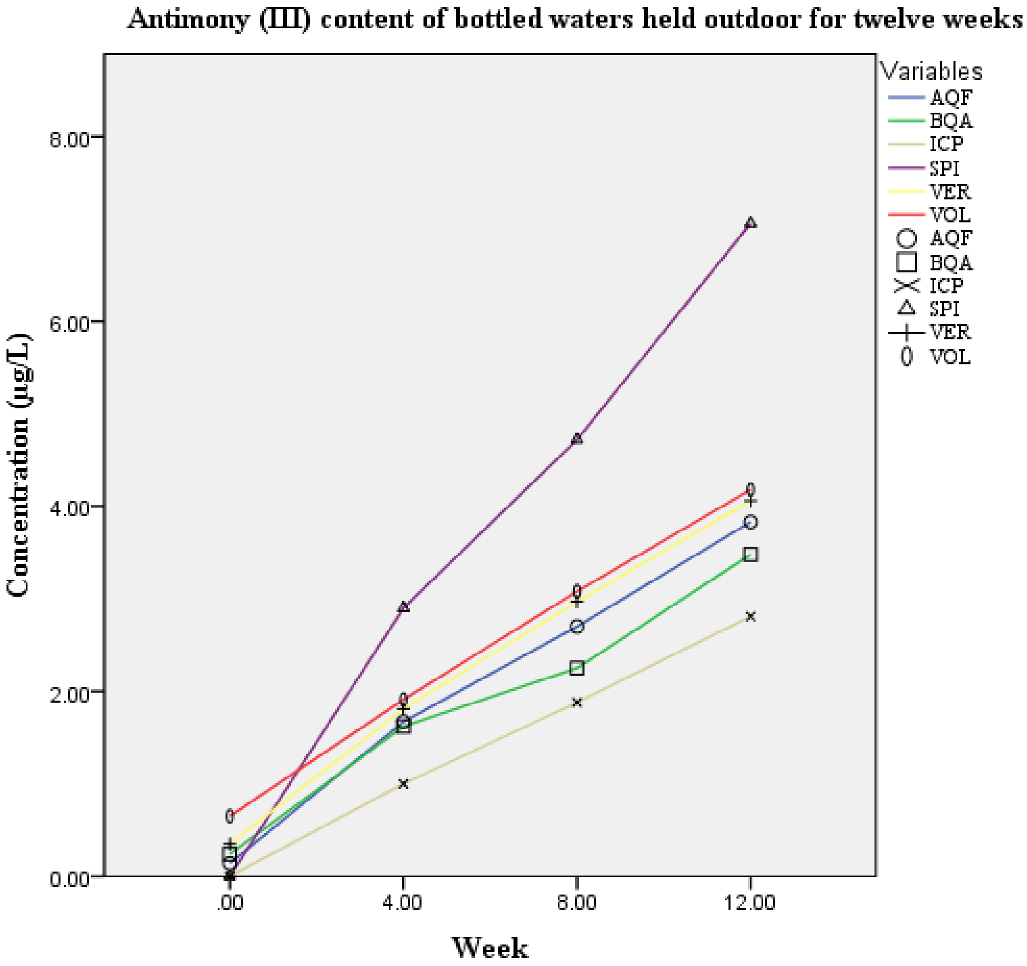

Figure 4.5.6: Antimony (III) concentrations of bottled water samples stored outdoor for twelve weeks. *AQF – VOL represents coded names of the brands of bottled water.*

Bottled water samples stored indoor saw increase in antimony (III) concentrations from week 0 to 12 (**Figure 4.5.5**). BQA and SPI had difference in mean antimony (III) concentrations greater than 0.5 µg/L between week 0 and 4. AQF, ICP, VER and VOL recorded a difference in mean concentrations less than 0.5 µg/L for the same period. For the period from week 4 to 8, the brands AQF, BQA, ICP and VER recorded a difference in mean concentrations

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less than 0.5 µg/L whilst SPI and VOL registered a difference in mean concentrations greater than 0.5 µg/L. Between week 8 and 12, bottled water brands ICP, SPI and VOL registered a difference in mean concentrations less than 0.5 µg/L whilst AQF, BQA and VER recorded a difference in mean concentrations greater 0.5 µg/L. SPI recorded the highest antimony (III) concentration (2.30 µg/L) at the end of the twelve weeks. This was followed by VOL (with antimony (III) concentration 2.08 µg/L) and ICP recording the least concentration (1.01 µg/L).

For bottled water samples stored outdoor in the open sun exposed to sunlight and high air temperatures, antimony (III) concentrations for all bottled water samples were observed to increase from week 0 to 12 (**Figure 4.5.6**). All brands of bottled water for periods between week 0 and 4, 4 and 8, and 8 and 12 had a difference in mean antimony (III) concentrations exceeding 0.5 µg/L. SPI recorded the highest antimony (III) concentration (7.06 µg/L) at the end of the twelve weeks. This was followed in decreasing order of concentration by VOL (4.18 µg/L) and ICP recording the minimum concentration (2.81 µg/L).

4.5.3 Effect of storage conditions antimony (V) species

Figures 4.5.7 – **4.5.9** shows antimony (V) concentrations of bottled water samples for the period of twelve weeks under the three selected storage conditions characteristic of bottled water usage. Antimony (V) concentrations increased for some brands whilst others witnessed decrements in between the four weeks' intervals for the twelve weeks' period. AQF, BQA, ICP, VER, and VOL already had some amounts of antimony (V) present as at day one (week 0). However, there was no antimony (V) present in SPI water samples as at day one. BQA had the highest antimony (V) concentration (14.42 µg/L) followed in decreasing order of concentration by VOL (13.12 µg/L). ICP recorded the least detectable antimony (V) concentration (1.11 µg/L) at day one.

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For bottled waters stored in refrigerator (**Figure 4.5.7**), the brands AQF, ICP and SPI registered mean difference in antimony (V) concentrations less than 0.5 µg/L whilst BQA, VER and VOL recorded differences in mean antimony (V) concentrations greater than 0.5 µg/L for the period between week 0 and 4. AQF, ICP, and SPI registered difference in mean antimony (V) concentration less than 0.5 µg/L whilst BQA, VER, and VOL recorded difference in mean antimony (V) concentration greater than 0.5 µg/L between week 4 and 8.All brands of bottled water recorded difference in antimony (V) concentrations less than 0.5 µg/L for the period between week 8 and 12. BQA had the highest antimony (V) concentration (15.82 µg/L)

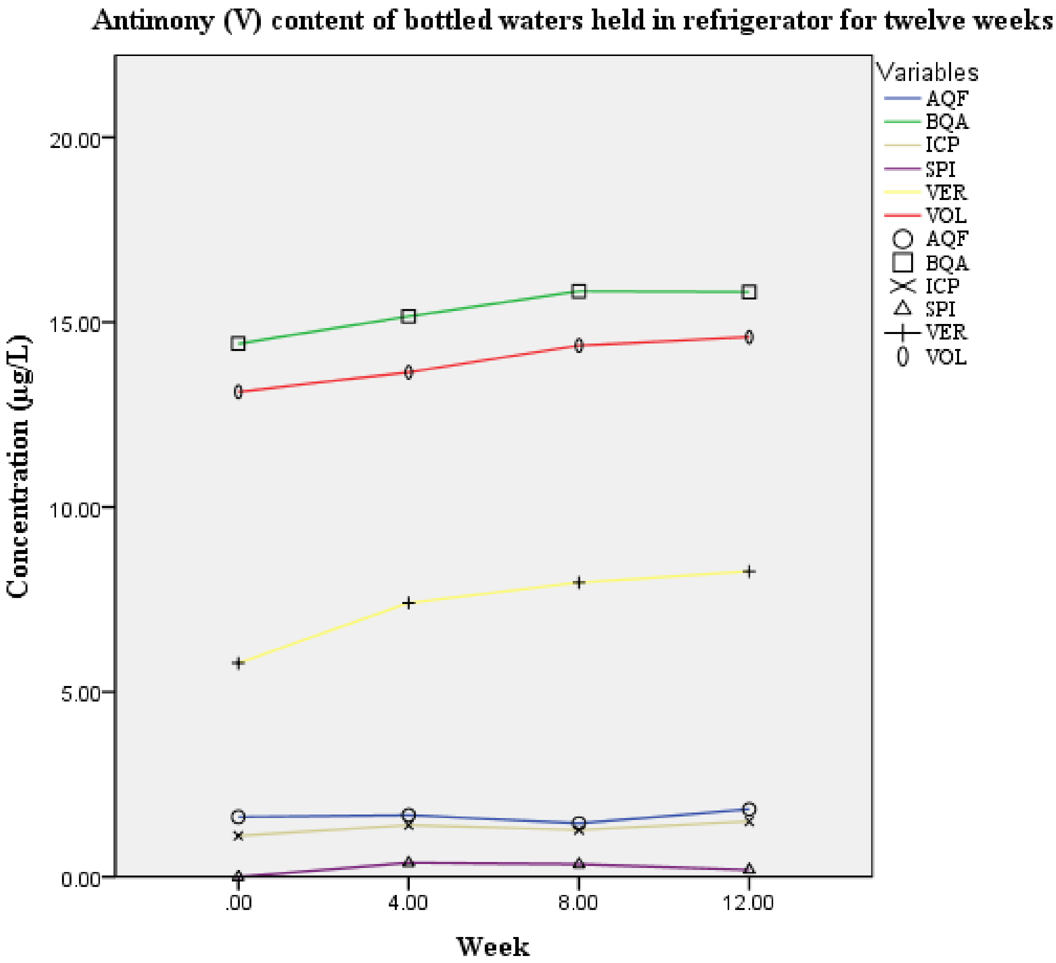

Figure 4.5.7: Antimony (V) concentrations of bottled water samples stored in a refrigerator for twelve weeks. *AQF – VOL represents coded names of the brands of bottled water.*

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followed by VOL (14.60 µg/L) at the end of the twelve weeks. SPI recorded the least antimony (V) concentration (0.19 µg/L) at the end of week 12.

Bottled water samples stored indoor witnessed increase or decrease in their antimony (V) concentrations depending on the bottled water brand type from week 0 to 12 (**Figure 4.5.8**). AQF, ICP, and SPI registered differences in mean antimony (V) concentrations greater than 0.5 µg/L whilst BQA, VER, and VOL recorded difference in a mean antimony (V) concentration less than 0.5 µg/L between week 0 and 8. For the period between week 4 and 8, the brands AQF, BQA, SPI, VER, and VOL recorded difference in mean antimony (V) concentration less than 0.5 µg/L whilst only ICP registered a difference in a mean concentration

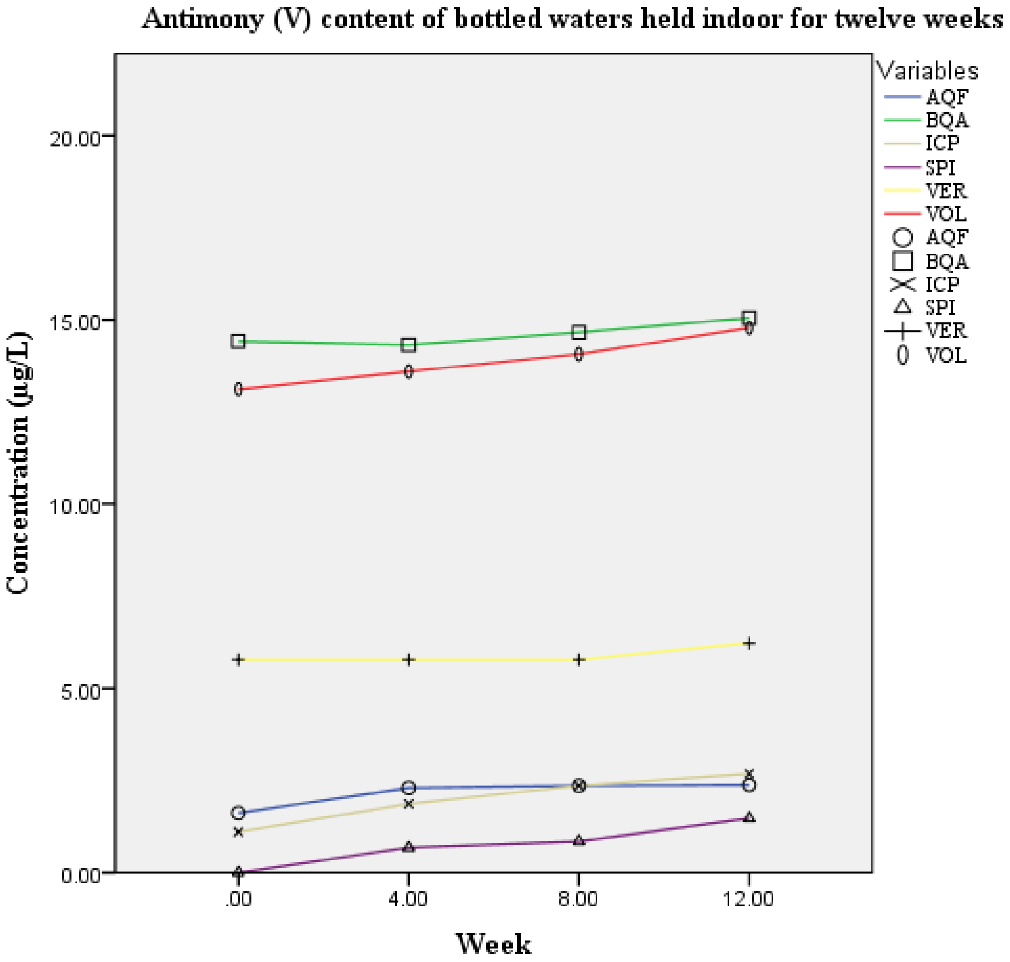

Figure 4.5.8: Antimony (V) concentrations of bottled water samples stored indoor for twelve weeks. *AQF – VOL represents coded names of the brands of bottled water.*

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greater than 0.5 µg/L. Bottled water brands SPI and VOL registered difference in mean antimony (V) concentrations greater than 0.5 µg/L whilst AQF, BQA, ICP, and VER recorded mean difference in antimony (V) concentration less than 0.5 µg/L for the period between week 8 and 12. BQA recorded the highest antimony (V) concentration followed by VOL at the end of the twelve weeks. BQA recorded the highest antimony (V) concentration (15.05 µg/L) at the end of week 12. This was closely followed in decreasing order of concentration by VOL (14.78 µg/L) with SPI recording the least antimony (V) concentration (1.48 µg/L).

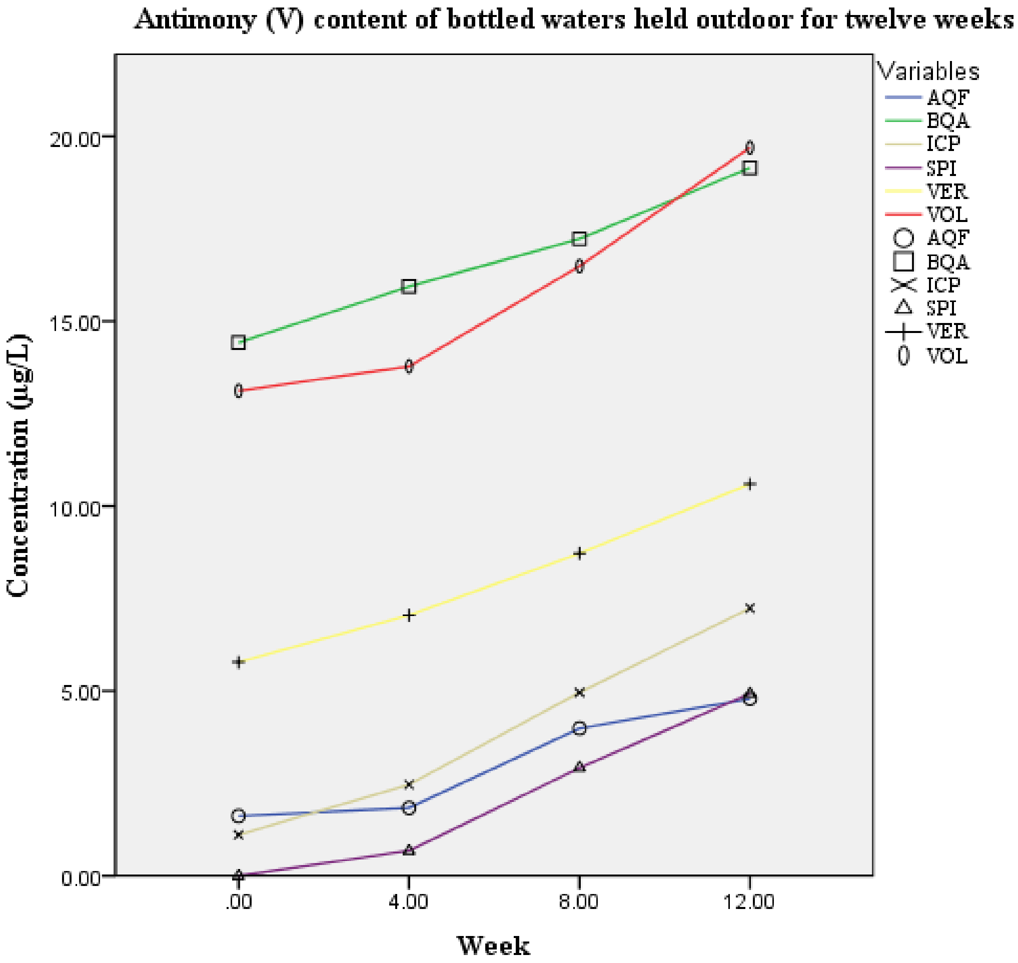

Figure 4.5.9: Antimony (V) concentrations of bottled water samples stored outdoor for twelve weeks. *AQF – VOL represents coded names of the brands of bottled water*.

For bottled water samples stored outdoor in the sun (**Figure 4.5.9**), the brands BQA, ICP, SPI, VER, and VOL registered difference in mean antimony (V) concentration greater than 0.5

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µg/L for the period between week 0 and 4. All brand samples of bottled water had difference in mean antimony (V) concentration exceeding 0.5 µg/L for the periods between week 4 and 8, and 8 and 12. VOL recorded the highest antimony (V) concentration (19.70 µg/L) at the end of the twelve weeks. This was followed closely by BQA (19.15 µg/L) with AQF registering the minimum antimony (V) concentration (4.79 µg/L).

4.6 Effect of storage time on total antimony concentrations

Waters packaged in PET bottles tend to have increments in total antimony concentrations over time (Hureiki & Mouneimne, 2012; Keresztes *et al.*, 2009; Shotyk *et al.*, 2006; Westerhoff *et al.*, 2008). The same phenomenon was observed for the six brands of plastic bottled water used in this study. **Appendix C** displays the linear regression equations for bottled waters stored under the three conditions characteristic of bottled water usage for twelve weeks. The linear regression was undertaken at a statistical significance of 0.05.

Taking bottled water AQF under refrigeratory conditions for twelve weeks, the correlation coefficient R^2 (the statistical measure of how close the data are to the fitted regression line) value (0.786) indicates a relatively strong positive correlation (closeness to the fitted regression line) between total antimony concentration and time. Comparing the significance levels, the significance value for bottled water stored in the refrigerator for twelve weeks $P = 0.114 > 0.05$ indicating that there is no supported relationship between concentration and time or there is no correlation between concentration and time. In other words, the correlation is statistically insignificant. This means that time does not statistically affect total antimony concentrations for the AQF bottled water samples stored in the refrigerator for twelve weeks. Nonetheless, using the regression equation, it will take approximately 38, 49 and 204 weeks for AQF bottled water samples stored under refrigeratory conditions to reach MCLs specified by EU, US EPA, and WHO respectively. AQF bottled water stored indoors for twelve weeks had correlation coefficient $R^2 = 0.962$. This is a strong positive correlation

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between total antimony concentrations and time. Comparing the significance levels, the significance value $P = 0.019 < 0.05$, indicating that, there exist a significant correlation between concentration and time. Hence, time statistically affects total antimony concentrations of water samples stored indoors at the 0.05 level. Using the linear regression equation for AQF bottled water samples stored indoor, total antimony concentrations will reach MCLs stipulated by EU, US EPA, and WHO after approximately 18, 24 and 104 weeks respectively. AQF bottled water samples outdoor exposed to sunlight and high air temperatures had correlation coefficient $R^2 = 0.987$, signifying a strong positive correlation between concentration and time. Comparing the significance levels, the significance value $P = 0.006 < 0.05$ suggesting that, time statistically affects concentration at the 0.05 level. Using the linear regression equation for AQF bottled water stored outdoor, total antimony concentrations are expected to reach MCLs specified by EU, US EPA and WHO after approximately 6, 7 and 31 weeks respectively.

BQA bottled water samples under refrigeration conditions for twelve weeks yielded a correlation coefficient $R^2 = 0.990$ which indicates a strong positive correlation between total antimony concentration and time. Comparing significance levels, the significance values $P = 0.005 < 0.05$. Hence, time statistically affects total antimony concentrations of water samples stored in the refrigerator at the 0.05 level. Using the linear regression equation, it will take approximately 23 weeks for total antimony concentrations to reach MCL specified by WHO. The correlation coefficient for BQA bottled water samples stored indoor produced correlation coefficient $R^2 = 0.981$ showing a strong positive correlation between concentration and time. The significance value $P = 0.010 < 0.05$ pointing that, time statistically affects total antimony concentrations at the 0.05 level. Using the linear regression equation for BQA bottled water samples stored indoor, it will take approximately 30 weeks to reach the MCL specified by WHO. For BQA bottled water samples exposed to sunlight and high air temperatures for twelve weeks gave a correlation coefficient $R^2 = 0.992$. This shows a strong positive correlation

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between concentration and time. The significance value $P = 0.004 < 0.05$ suggesting that time affects total antimony concentrations statistically at the 0.05 level. Using the linear regression equation accordingly, it will take approximately 8 weeks to for total antimony concentrations to reach MCL specified by WHO.

Bottled water ICP under refrigeration conditions generated a linear regression equation with correlation coefficient $R^2 = 0.963$. This is close to 1 suggesting a very strong positive correlation between concentration and time. Comparing the significance levels, the significance value $P = 0.019 < 0.05$. This shows that time statistically affects total antimony concentration at the 0.05 level. Using the linear regression equation for ICP bottled water samples held under refrigeratory conditions, total antimony concentrations are expected to reach MCLs specified by EU, US EPA, and WHO after approximately 34, 43 and 167 weeks respectively. In indoor conditions, ICP bottled water samples generated a linear regression equation with a correlation coefficient $R^2 = 0.994$. This is close to 1 indicating a very strong positive correlation between concentration and time. The significance value, $P = 0.003 < 0.005$ suggesting that time statistically affects concentration at the 0.05 level. Using the linear regression equation, it is expected that, total antimony concentrations will increase and reach MCLs specified by EU, US EPA, and WHO after approximately 18, 23 and 88 weeks respectively. In outdoor conditions exposed to sunlight and high air temperatures, the linear regression equation produced a correlation coefficient $R^2 = 0.995$. This shows a very strong positive correlation between concentration and time data points for ICP water samples stored outdoor in the sun for twelve weeks. Comparing the significance levels, the significance value $P = 0.003 < 0.05$ indicating time statistically affects total antimony concentration at the 0.05 level. Using the linear regression equation accordingly, total antimony concentrations are expected to reach MCLs specified by EU, US EPA, and WHO after 6, 7 and 25 weeks respectively.

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SPI under refrigerator conditions generated a linear regression equation with a correlation coefficient R^2 = 0.853. Compared to the correlation coefficients of bottled water BQA and ICP for water samples stored in refrigeratory conditions, this is a relatively weak positive correlation. The significance value, $P = 0.077 > 0.05$ suggesting that time does not statistically affect total antimony concentration at the 0.05 level. Notwithstanding that, total antimony concentrations are expected to reach MCLs specified by EU, US EPA, and WHO after 32, 39 and 133 weeks respectively. The linear regression equation for water samples of SPI stored indoor yielded a correlation coefficient R^2 = 0.971. This indicates a very strong positive correlation between concentration and time data points. The significance value, $P = 0.015 < 0.05$ shows that, time statistically affects total antimony concentration at the 0.05 significance level. Using the linear regression equation, total antimony concentrations are expected to reach MCLs specified by EU, US EPA, and WHO after approximately 16, 19 and 65 weeks respectively. The linear regression equation for water samples exposed to sunlight and high air temperatures generated a correlation coefficient R^2 = 0.998. This suggests a strong positive correlation between time and concentration. Comparing the significance levels, the significance value $P = 0.001 < 0.05$ indicating that, time statistically affects total antimony concentrations at the 0.05 significance level. Using the linear regression equation, we anticipate total antimony levels to reach MCLs of EU, US EPA, and WHO after approximately 5, 6 and 20 weeks respectively.

The linear regression equation for VER bottled waters under refrigeratory conditions for twelve weeks produced a correlation coefficient R^2 = 0.952. This is close to 1 indicating a very strong positive correlation between concentration and time. The significance value, $P = 0.024 < 0.05$ suggesting that time statistically affect total antimony concentration at the 0.05 level. Using the regression equation, total antimony concentrations are expected to reach MCL stipulated by WHO after 42 weeks. For VER bottled water samples stored indoor, the

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regression equation yielded correlation coefficient $R^2 = 0.932$ indicating a strong correlation between total antimony concentration and time. The significance value $P = 0.034 < 0.05$ suggesting that time statistically affects total antimony concentration at the 0.05 significance level. Therefore, under similar conditions, total antimony concentrations are projected to reach MCL specified by WHO after approximately 96 weeks. VER bottled water exposed to sunlight and high air temperatures outdoor generated a linear regression equation with a correlation coefficient $R^2 = 1.000$. This means a perfect positive correlation between concentration and time. The significance value, $P = 0.0005 < 0.05$ signifying that time totally statistically affect total antimony concentration at the 0.05 level. The total antimony concentration under likewise conditions is projected to reach MCL stipulated by WHO after approximately 20 weeks.

Bottled water samples of VOL stored under refrigeration conditions yielded a regression equation with correlation coefficient $R^2 = 0.999$. This means a nearly perfect positive correlation between concentration and time. The significance value $P = 0.001 < 0.05$ proposing that, time statistically affects total antimony concentration at the 0.05 significance level. Using the linear regression equation, it is therefore expected that total antimony concentrations will reach MCL specified by WHO after approximately 25 weeks. For VOL bottled water samples stored indoor, the linear regression equation yielded a correlation coefficient $R^2 = 0.971$ indicating a strong positive correlation between concentration and time. The significance value $P = 0.001 < 0.05$ suggesting that time statistically affect total antimony concentration at the 0.05 level. Hence, total antimony concentrations are predicted to hit 20 µg/L (WHO MCL) in approximately 24 weeks using the linear regression equation. The regression equation for VOL water samples stored outdoor exposed to sunlight and high air temperatures yielded a correlation coefficient $R^2 = 0.974$. The significance value $P = 0.013 < 0.05$ suggesting that time statistically affects total antimony concentration at the 0.05 significance level. Using the

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regression equation, it is anticipated that, total antimony concentrations will reach WHO MCL after approximately 8 weeks.

In summary, plastic bottled waters subjected to high air temperatures and sunlight took fewer weeks to reach stipulated MCLs compared to bottled waters held under indoor and refrigeratory conditions.

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CHAPTER FIVE

5.0 DISCUSSION

Quality assurance steps comprised blanks, replicate analyses, certified reference material, recoveries and calibrations. Reproducibility was calculated as percentage relative standard deviation (percentage coefficient of variation (CoV (%)) from four measurements of independent standard solutions of antimony (III) and antimony (V). Method validation for total antimony in the water samples was undertaken using certified reference material (CRM) (GEMS water standard) Spike and recovery were used to validate the determination procedures for antimony (III) in the waters contained in the PET containers and total antimony in the PET containers themselves.

Sample selection criterion was based on literature from previous studies (Bach *et al.*, 2013, 2014; Hureiki & Mouneimne, 2012; Keresztes *et al.*, 2009; Shotyk *et al.*, 2006; Westerhoff *et al.*, 2008). It was realised that the variability in the number of samples used was mainly dependent on the set objectives. Part of the study was to assess the effect of typical storage conditions on the migration of antimony from the plastic container into the water stored in it. Hence, the need to specify a difference between concentrations of the water samples between the storage regimes and time intervals that will reflect chemical or scientific significance. Using the sample number estimation procedure adopted from (Gardiner, 1997), a sample number of four was arrived at. This was based on a *two-tailed* test of equal sample size with a sample power of 80%, 0.05 significance, 0.25 standard deviation and difference of means ≥ 0.5 µg/L. A difference of concentration means ≥ 0.5 µg/L will, therefore, be an indication of chemical migration.

The plastic bottled water samples of the six brands were obtained at source in order to preserve their integrity before analysis. Moreover, the contact time between the water and PET

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plastic container was found to be critical when it comes to the migration of the metalloid (antimony) into water (Keresztes *et al.*, 2009). One size container (volume) was chosen for all the six brands because leaching rate has been found to be proportional to the contact surface area to volume ratio of the bottles. Small bottles have a larger surface to volume ratio and as such, will have higher antimony concentrations in water for similar contact time compared with larger bottles (Hureiki & Mouneimne, 2012).

The presence of "substantial" amounts of antimony in some of the brands of bottled water samples (**Figure 4.5.1** – **4.5.3**) determined on the day the waters were packaged were not likely to have originated from the PET plastic containers, as the contact time between the water and PET plastic container was too minimal (less than 12 hours) to contribute to such "significant" amounts of antimony in brands BQA, VER, and VOL. This, therefore, puts the focus on the origin of the waters before bottling and the surrounding environment. Typical concentrations of dissolved antimony are usually very low, less than 1 µg/L but in areas that are close to anthropogenic sources, concentrations can reach up to 100 times the natural levels (Dodd *et al.*, 1996; Zheng, Ohata, & Furuta, 2000). Moreover, in precipitates from hot springs, boreholes and in geothermal waters, antimony concentrations ranging 500 mg/L up to 10 wt. % have been reported (Filella *et al.*, 2002; Shotyk *et al.*, 2006). Although the bottled water companies happen to be in the same region (**Figure 3.2.1**), the source of water for bottling differ from one company to another. Furthermore, the surrounding environment and treatment processes for the waters before bottling also varies. The manufacturers of VOL, AQF, ICP, VER and SPI use water sourced deep underneath the ground rich in ions (aquifers) whilst producers of BQA use municipal water from Kpone (Belaqua.com.gh, 2015; Twellium industrial company, 2015; Volticghana.com, 2015). Slow moving ground water in contact with buried ore deposits may dissolve and transport trace elements like antimony forming aqueous dispersions (Grimes, Ficklin, Meier, & Mchugh, 1995). Treated waters from sources like these are bound to have

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more amounts of the metalloid (antimony) dissolved. This is because most of the purification steps are focused on the elimination of bacteria and particulate matter but not heavy metal contaminants like antimony. Thus, the origin of the water could have accounted for the presence of "substantial" amounts of antimony in AQF, BQA, ICP, VER and VOL water samples. No antimony was detected in SPI water samples on the first day. There is, therefore, a high possibility that, the rock from which the water is sourced from does not contain antimony minerals. AQF bottling plant is located in an industrial area whilst BQA bottling plant is in a semi-industrial area. Bottling plants of VOL, ICP, VER and SPI are located in areas that are considered to be relatively free from human activities (**Figure 3.2.1**). Generated airborne antimony compounds, especially in areas that have industrial activities ongoing can find their way into water sources, thereby increasing dissolved concentrations (Cavallo *et al.*, 2002). Thus, although manufacturers of BQA did not use water sourced from underground for production, the semi-industrial surrounding conditions can contribute to the level of antimony that was measured on the first day. In summary, the origin of the water for bottling and surroundings of bottling plants could have contributed to the "large" amounts of antimony already present before bottling.

Water samples stored under the three selected conditions typical of bottled water usage evidently showed differences in concentration patterns. At least four brands out of the six brands of bottled waters for all the three storage conditions saw a difference in mean total antimony concentrations exceeding 0.5 µg/L from day one to week 12. Moreover, this difference in mean total concentrations was not uniform. Between the four weeks' intervals of the twelve weeks' period, the difference in mean concentrations was below 0.5 µg/L for one interval and sometimes above 0.5 µg/L for the next interval. This difference of scientific significance undoubtedly reveals that: foremost, antimony was employed as the catalyst (in the form of Sb_2O_3) in the manufacture of the plastic bottles. Determined total antimony

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concentrations in plastic bottles confirmed the preceding assertion (**Figure 4.4.1**). The presence of antimony can be attributed to its use as a catalyst in the manufacture of PET plastics. It is added as the glycolate or in the trioxide form (Sb_2O_3). When added in the trioxide form, it readily converts to glycolate and at the end of the manufacturing process, it remains bound in the polymer chain as glycolate complexes (Carneado *et al.*, 2015). Proceeding, there is an indication that the residual antimony in the PET plastic container is slowly dissolving (solubility of 5.8×10^{-5} kmol/m^3 at 298K (Casas, Crisóstomo, & Cifuentes, 2004)) from the plastic bottles into the water contained inside and destabilising the equilibrium system. Thus, the equilibrium readjustments resulting in the non-uniformity of differences in mean total concentrations between time intervals.

Comparing the migration rates of antimony for the six brands of bottled water under the simulated storage conditions revealed that, SPI recorded the highest rate under outdoor conditions, having a value of approximately 1.00 µg/L per week (**Table 4.5.7**). AQF recorded the least migration rate of 0.10 µg/L per week under refrigeratory conditions (**Table 4.5.7**). This shows that the state in which the plastic bottled water is conditioned in for a particular period of time, affects the antimony migration process into the water. Water samples stored outdoor exposed to high air temperatures and sunlight had higher migration rates compared to those stored in the refrigerator and indoors. This migration phenomenon was observed by Bach *et al.* (2014) who saw an increase in antimony migration between 0 and 2 days on exposing ultrapure water in PET bottles to natural sunlight. It was however realised in a previous study by the same group (Bach *et al.*, 2013) that, antimony migration is less affected by exposure to sunlight but rather, temperature and carbon dioxide contributed considerably to migration. In a study by Carneado *et al.* (2014), bottled waters stored at temperatures 4ºC and 20ºC were not subject to antimony migration whilst those stored at 40ºC and 60ºC saw a substantial increase in antimony concentrations. In contrast to that our study saw significant increments (≥ 0.50

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µg/L difference after ten weeks) in total antimony concentrations for bottled water samples stored under refrigeratory, indoor and outdoor conditions. This indicates that, there exist differences in the quality of PET plastics used in packaging the waters (Y. Y. Fan *et al.*, 2014). High-quality plastics tend to have low migration trends for embedded chemical constituents like antimony. Thus, package material of AQF can be said to be of highest quality among the six brands under the selected conditions, as it recorded the least migration rates under the selected storage conditions (**Table 4.5.7**). As observed by researchers of previous studies, high temperatures accelerate the dissolution process of antimony from the PET plastic container resulting in high amounts in the water. This is likely as, at high temperatures, degradation of the polymer material can occur through thermo-oxidative and -mechanical means, leading to the faster release of chemical constituents like antimony which dissolve in the water (Bach *et al.*, 2014; Carneado *et al.*, 2015). Considering that antimony release is mainly caused by degradation as in Fan *et al.* (2014), the PET plastic container of SPI will be regarded as least in terms of quality, since it had the highest migration rate (*ca.* 1.00 µg/L per week) on exposure to high air temperatures and sunlight outdoor. Thus, it degraded very fast on exposure to high temperatures and sunlight compared to PET plastic containers of the other brands.

Four out of the six brands of bottled water recorded some amounts of antimony (III) and antimony (V) on the day the samples were acquired (week 0). Comparing the concentrations of the two species on the first day revealed antimony (V) as the predominant form (**Table 4.5.1**). This goes to confirm postulations by other researchers that, antimony (V) is the dominant form of the species in unpolluted oxygenated waters (Feng *et al.*, 1999; Kubota *et al.*, 2001; Zheng *et al.*, 2000). Some works have attributed this predominance to the unstable nature of the antimony (III) species, which is easily oxidised to antimony (V) (Michalski, Szopa, Jablonska, & Lyko, 2012). The presence of little amounts of antimony (III) can also be an indication of the existence of micro-organisms at the source who through biologically

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mediated reduction processes reduce antimony (V) to antimony (III) (Apte & Howard, 1986). The three selected storage conditions affected the antimony species in the bottled waters differently. Increments and decrements were observed for water samples in between the four weeks' intervals for the twelve weeks' period. Both species witnessed increments over time for some brands whilst others saw increments of one species and decrement for the other within the four weeks' intervals for the twelve weeks' period. Antimony (V) concentrations were not expected to increase over time. In contrast, antimony (V) concentrations increased and were even higher compared to antimony (III) concentrations. This likely indicates that species transformation was taking place in the water samples over time. The main source of antimony in the water is from the PET plastic container (as antimony (III) from the catalyst Sb_2O_3). This migrates into the water over time under the prevailing conditions. The slightly pervious nature of the PET plastic container (allowing oxygen to cross), pH of the water samples (in the range 6.70 – 7.50) and the lower concentrations of antimony (in µg/L) makes it favourable for the transformation (oxidation) of Sb(III) to Sb(V), resulting in the observed phenomenon (Ferreira *et al.*, 2014). This oxidation process tends to be slow and thus accounts for the presence of "little" amounts of antimony (III) in the water samples still present.

The physicochemical properties of the waters in the plastic containers can potentially affect the migration of antimony into the plastic bottled waters (Hureiki & Mouneimne, 2012). Solution pH was found not to have any statistically significant effect on total antimony and antimony (V) concentrations. Thus, pH does not affect the changing levels of total antimony and antimony (V) in the water samples. Few literatures have come to the same conclusion for total antimony (Hureiki & Mouneimne, 2012; Westerhoff *et al.*, 2008). On the other hand, pH of the water samples was found to affect antimony (III) concentration positively, implying that, high pH may accelerate the release of antimony (III) from the PET plastic container. The calcium content of the water samples was found to have no effect on total antimony, antimony

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(III) and antimony (V) concentrations. This implied that the calcium content may not affect the migration of antimony from the PET plastic container. Studies by Hureiki and Mouneimne, (2012) and Keresztes *et al.*, (2009) however revealed calcium had an effect on total antimony. This difference may be due to the lower calcium concentrations obtained in this study. Thus, there is the likelihood that, calcium concentrations beyond certain limits will begin to affect total antimony concentrations. Total antimony, antimony (III) and antimony (V) concentrations of the water samples were found to be unaffected by magnesium ion concentrations. Similar findings were obtained by Hureiki and Mouneimne, (2012). This will mean that magnesium ion concentration does not affect the migration of antimony from the PET plastic container. The bicarbonate ion content of the water samples was found not statistically affecting the levels of antimony species, implying that, migration of antimony from the plastic material is unaffected. Hureiki and Mouneimne observed a similar effect. Total dissolved solids (TDS) refers to the inorganic salts and small amounts of organic matter present in solution in water. The principal constituents comprise of calcium, magnesium, sodium, and potassium cations, and carbonate, hydrogen carbonate, chloride, sulphate, and nitrate anions (WHO, 1996). The TDS content was found not affecting total antimony, antimony (III) and antimony (V) concentrations. This will imply that TDS does not affect the migration of antimony from the packaging material. Contrary to that, Hureiki and Mouneimne, (2012) and Westerhoff *et al.*, (2012) found that higher TDS content resulted in higher total antimony in the water samples. A notice must, however, be taken of the fact that, the ionic composition of the water samples used in the study by Westerhoff *et al.*, (2012) comprised the summation of the divalent ions, calcium and magnesium. That of Hureiki and Mouneimne (2012), used ionic composition of the water samples specified by the manufacturers of the bottled waters.

Total antimony concentrations of the six brands of bottled waters varied with storage time under the simulated storage conditions. Within the same time period of twelve weeks, at

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least four out of the six brands of bottled water under refrigeratory, indoor and outdoor conditions had time affecting total antimony concentrations of the water samples. This implied that the contact time between the PET plastic container and the water was critical to the migration process of the metalloid (antimony). The longer the contact or storage time, the higher the total antimony concentration (Y. Y. Fan *et al.*, 2014). Similar occurrences were observed by Hureiki and Mouneimne (2012) and Keresztes *et al.*, (2009). Prevailing environmental factors like temperature and sunlight cannot be left out when looking at the time period samples were stored. Water samples held under refrigeratory conditions were maintained at 4ºC amidst intermittent power outages in the country at that time of the year. The results showed some effects that can be attributed to disruption of power supply. We anticipated for the period of twelve weeks, water samples held under refrigeratory conditions would have antimony concentrations to be a little less compared to indoor water samples. The opposite was however observed. This is unlikely and as such may have been caused by the power crisis situation during that time. Comparing the three simulated storage conditions for a period of one year, water samples held outdoor exposed to sunlight and high air temperatures (average temperatures: 23.0ºC in the morning and 39.5ºC in the afternoon) recorded the highest total antimony concentrations. Similar results were obtained by Bach *et al.*, (2013), Carneado et al, (2014), and Fan *et al.*, (2014). They observed that an increase in storage temperature accelerates the migration of antimony from the PET plastic container into the water. Furthermore, natural sunlight has been found to contribute to the migration of antimony from the PET plastic container into the water (Bach *et al.*, 2014). Thus, these factors go to add up explaining why bottled water samples exposed to sunlight and high air temperatures recorded high total antimony concentrations than samples held under indoor and refrigeratory conditions.

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Total antimony concentrations of the plastic bottled water samples changed with time under the simulated storage conditions. This change was chiefly caused by the migration of antimony from the PET plastic containers into the water samples. Concentrations of antimony can build up and depending on surrounding conditions can exceed MCLs. For the six brands of plastic bottled water used in this study, the limited time period before expiry specified was one year (52 weeks) after the production date. Putting the time period of 52 weeks into the linear regression equations (**Appendix C**), AQF bottled water samples held under refrigeratory and indoor conditions will not be safe for consumption according to EU and US EPA specifications. This is because, by comparison, after 18, 24, 38 and 49 weeks, total antimony concentrations will reach EU and US EPA MCLs respectively for indoor and refrigeratory bottled water samples. However, under WHO specifications for antimony MCLs, it will be safe because the times required for total antimony concentrations to reach the threshold are 204 and 104 weeks. Under outdoor conditions and using 52 weeks' time, total antimony levels are far above EU, US EPA and WHO MCLs specifications. For BQA bottled water samples, total antimony concentrations are all above MCLs specified by EU, US EPA and WHO for all the three storage conditions in 52 weeks' time. ICP bottled water samples stored under refrigeratory and indoor conditions will have total antimony concentrations above MCLs specified by EU and US EPA in 52 weeks' time. Nonetheless, total antimony concentrations are calculated to be below MCL specified by WHO for the same storage conditions and time. ICP bottled water samples held outdoor will have total antimony concentrations surpassing all the three specified MCLs in 52 weeks' time. SPI bottled water samples in 52 weeks' time will have total antimony concentrations exceeding MCLs specified by EU and US EPA but will be below WHO MCL for indoor and refrigeratory conditions. Outdoor bottled water samples of SPI will have total antimony concentrations exceeding all the three specified MCLs in 52 weeks' time. VER bottled water samples will have total antimony concentrations exceeding all

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the three specified MCLs for outdoor and refrigeratory conditions in 52 weeks' time. Indoor bottled water samples of VER will have total antimony concentrations exceeding EU and US EPA MCL but not WHO MCL. VOL bottled water samples will have total antimony levels exceeding all the three MCLs for all the three storage conditions in 52 weeks' time.

In summary, three (AQF, ICP and SPI) out of the six brands of plastic bottled water under the three selected storage conditions for the limited one-year time period of expiry have total antimony concentrations not reaching WHO MCL. Furthermore, AQF bottled water samples recorded lowest total antimony concentrations for water samples under the three storage conditions for the stipulated times and as such, can be considered to be the best for consumers. For the other three brands (VOL, BQA and VER), MCLs were surpassed in a comparatively shorter times because of major contributions from source. Thus, contamination via migration only will be improbable within the one-year limited time of expiry for bottled water samples for these brands.

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CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

Speciation analysis of antimony in polyethylene terephthalate (PET) bottled water marketed in Greater Accra was the primary objective of this work. Statistical methods (correlation analysis and linear regression) amongst others were used to evaluate the results obtained from analysing brand samples leading to objective inferences. This chapter presents the conclusions and the recommendations arrived at.

6.1 Conclusions

The study showed that antimony was already present in some of the water samples before they were packaged into their plastic containers. This goes to support the notion that, some of the natural sources of water for bottling may contain “substantial” amounts of antimony.

Total antimony concentrations of the waters stored in the plastic containers were found to increase with holding time under the three simulated storage conditions. This supports the view that, the majority of the PET plastic manufacturers use antimony trioxide as a catalyst and subsequently its migration into beverages stored with them.

Differences in the rate of migration of antimony were observed for the different kinds of PET plastics. This supports previous findings that, differences exist in the quality of the PET plastics used in packaging.

Increments were observed for total antimony, antimony (III) and antimony (V) for the majority of the brand samples stored under refrigeratory, indoor and outdoor conditions with the outdoor samples registering the highest concentrations in their water samples. This corroborates the view that, exposure to harsh conditions of the weather outdoor like sunlight and high air temperatures degraded the plastic polymer material (PET) more rapidly and accelerated the migration process for the metalloid (antimony).

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Both antimony (III) and antimony (V) species increased with storage time with the latter being the dominant form in solution. This most likely suggests that antimony is migrating into solution as antimony (III) (apparently from the catalyst used: Sb_2O_3) but is slowly being transformed (oxidised) into antimony (V) under the prevailing conditions.

Correlation analysis revealed that the physicochemical properties (calcium ion concentration, magnesium ion concentration, bicarbonate ion concentration and TDS) do not affect the migration process of antimony. Thus, these properties possibly do not affect the migration of antimony from the packaging material (PET) into solution. pH, on the other hand, did significantly correlate positively to antimony (III), suggesting that, high pH might accelerate the migration process of antimony.

Regression analysis showed that total antimony concentrations increased with storage time linearly for the period under study, for at least four of the brands used under the simulated storage conditions. This almost certainly suggests that the contact time between the PET plastic container and water is crucial to the migration of the metalloid (antimony). Longer contact times are usually associated with high antimony levels in the bottled water samples.

In conclusion, the null hypothesis of the study is rejected and the alternative hypothesis accepted. Thus, PET plastic bottled waters marketed in Greater Accra are not contaminated with antimony leaching from their PET plastic containers within the limited time of expiry under WHO MCL specification.

There is, however, evidence showing that, with time and the type of condition in which the bottled water is stored in, antimony release is likely to be accelerated leading to contamination in a shorter time and subsequently harm to consumers. The main anthropogenic source of antimony in PET bottled waters is from the catalyst (Sb_2O_3) used in the manufacture

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of the PET plastic container. Nonetheless, contributions from natural sources like aquifers used in production can contribute to significant amounts in the finished product (bottled water).

6.2 Recommendations

The period of storage used in this study was three months. Considering the expiration dates specified by bottled water manufacturers in Ghana, future studies should consider prolonging the storage time to about one or two years.

Research should be extended to other foods and drinks packaged in PET plastics such as milk, fruit juices, coffee, and beverages alike. These drinks have complex matrices and may contain constituents that may induce antimony migration.

Bottled water manufacturers should consider using PET plastics produced from titanium- or germanium-based catalyst or switch to other types of plastics entirely.

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APPENDICES

APPENDIX A

Pearson correlation between selected physicochemical properties and antimony content

Physicochemical property		Total antimony	Antimony (III)	Antimony (V)
pH	Pearson Correlation	0.752	0.819*	0.742
	Sig. (2-tailed)	0.085	0.046	0.091
	N	6	6	6
TDS	Pearson Correlation	0.522	0.545	0.516
	Sig. (2-tailed)	0.288	0.264	0.295
	N	6	6	6
Ca^{2+}	Pearson Correlation	0.616	0.786	0.603
	Sig. (2-tailed)	0.193	0.064	0.205
	N	6	6	6
Mg^{2+}	Pearson Correlation	0.384	-0.197	0.403
	Sig. (2-tailed)	0.453	0.708	0.429
	N	6	6	6
HCO_3^-	Pearson Correlation	0.472	0.505	0.466
	Sig. (2-tailed)	0.344	0.307	0.351
	N	6	6	6

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

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APPENDIX B

B1: Paired samples Test for GEMS standard reference material

		Paired Differences							
					95% Confidence Interval of the Difference				
		Mean	Std. Dev.	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)
Pair 1	Certified_values Measured_values	0.51	1.96	0.98	-2.61	3.63	0.52	3	0.639

B2: Paired samples Test for Spike and Recovery (Antimony (III) determination)

		Paired Differences							
					95% Confidence Interval of the Difference				
		Mean	Std. Dev.	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)
Pair 1	Certified_values Measured_values	0.03	0.24	0.12	-0.36	0.41	0.23	3	0.834

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B3: Paired samples Test for Spike and Recovery (Total Sb in PET plastic container samples)

		Paired Differences							
					95% Confidence Interval of the Difference				
		Mean	Std. Dev.	Std. Error Mean	Lower	Upper	t	df	Sig. (2-tailed)
Pair 1	Certified_values Measured_values	0.02	0.12	0.06	-0.17	0.21	0.34	3	0.755

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APPENDIX C

Linear regression equations for bottled waters stored under three specific conditions for twelve weeks using their total antimony concentrations.

Bottled Water	*W3*/RF	*W3*/IN	*W3*/SN	R^2(*W3*/RF)	R^2(*W3*/IN)	R^2(*W3*/SN)	Sig.(*W3*/RF)	Sig.(*W3*/IN)	Sig.(*W3*/SN)
AQF	C = 1.606 + 0.09W	C = 1.925 + 0.173W	C = 1.579 + 0.595W	0.786	0.962	0.987	0.114	0.019	0.006
BQA	C = 14.662 + 0.229W	C = 14.524 + 0.185W	C = 14.703 + 0.646W	0.990	0.981	0.992	0.005	0.010	0.004
ICP	C = 1.171 + 0.113W	C = 1.192 + 0.213W	C = 0.838 + 0.755W	0.963	0.994	0.995	0.019	0.003	0.003
SPI	C = 0.287 + 0.148W	C = 0.252 + 0.304W	C = -0.207 + 1.001W	0.853	0.971	0.998	0.077	0.015	0.001
VER	C = 6.463 + 0.322W	C = 6.010 + 0.145W	C = 6.067 + 0.711W	0.952	0.932	1.000	0.024	0.034	0.0005
VOL	C = 13.800 + 0.249W	C = 13.713 + 0.257W	C = 13.096 + 0.855W	0.999	0.917	0.974	0.001	0.001	0.013

C: Concentration, W: Weeks, W0: Day one, W1/RF: Four weeks in refrigerator, W1/IN: Four weeks indoor, W1/SN: Four weeks outdoor in the sun, W2/RF: Eight weeks in refrigerator, W2/IN: Eight weeks indoor, W2/SN: Eight weeks outdoor in sun, W3/RF: Twelve weeks in refrigerator, W3/IN: Twelve weeks indoor, W3/SN: Twelve weeks outdoor in sun.

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APPENDIX D

D1: Temperatures taken at week intervals for twelve weeks for outdoor water samples

Week	Morning (ºC)	Afternoon (ºC)
1	23.2	39.6
2	25.5	37.4
3	22.6	39.7
4	21.4	37.4
5	25.2	42.5
6	23.7	38.3
7	20.3	38.2
8	21.5	39.8
9	24.4	40.2
10	23.6	37.4
11	21.3	41.1
12	23.2	42.4

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D2: Temperatures taken at week intervals for twelve weeks for indoor water samples

Week	Morning (ºC)	Afternoon (ºC)
1	20.2	24.7
2	21.6	26.4
3	20.6	25.2
4	21.3	24.9
5	19.7	28.6
6	18.7	23.4
7	20.3	26.1
8	21.5	25.4
9	20.2	25.7
10	21.4	26.4
11	19.4	22.9
12	20.1	24.3

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APPENDIX E

E1: PHYSICOCHEMICAL PROPERTIES OF AQF WATER SAMPLES

Physicochemical Property	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
pH	6.70	6.85	6.80	6.78	6.78	0.06	0.92	0.10
TDS	41.50	41.06	41.17	41.14	41.22	0.19	0.47	0.31
Ca^{2+}	3.50	3.45	3.52	3.48	3.49	0.03	0.86	0.05
Mg^{2+}	3.00	2.96	2.90	2.98	2.96	0.04	1.46	0.07
HCO_3^-	35.00	34.65	34.75	34.68	34.77	0.16	0.46	0.25

E2: PHYSICOCHEMICAL PROPERTIES OF BQA WATER SAMPLES

Physicochemical Property	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
pH	7.20	7.25	7.15	7.22	7.21	0.04	0.58	0.07
TDS	39.40	40.29	39.68	39.89	39.82	0.37	0.94	0.60
Ca^{2+}	4.00	4.08	4.05	4.12	4.06	0.05	1.25	0.08
Mg^{2+}	4.90	5.01	4.98	4.93	4.96	0.05	1.00	0.08
HCO_3^-	30.50	31.20	30.65	30.84	30.80	0.30	0.98	0.48

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E3: PHYSICOCHEMICAL PROPERTIES OF ICP WATER SAMPLES

Physicochemical Property	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
pH	6.98	7.02	7.08	7.00	7.02	0.04	0.62	0.07
TDS	31.95	30.89	33.93	32.77	32.39	1.29	3.97	2.05
Ca^{2+}	2.15	2.65	2.43	2.37	2.40	0.21	8.57	0.33
Mg^{2+}	3.24	3.18	3.34	3.28	3.26	0.07	2.07	0.11
HCO_3^-	26.56	25.06	28.16	27.12	26.73	1.29	4.84	2.06

E4: PHYSICOCHEMICAL PROPERTIES OF SPI WATER SAMPLES

Physicochemical Property	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
pH	6.82	6.97	6.90	6.95	6.91	0.07	0.97	0.11
TDS	26.14	28.42	27.20	26.43	27.05	1.02	3.77	1.62
Ca^{2+}	3.20	3.26	3.32	3.18	3.24	0.06	1.95	0.10
Mg^{2+}	2.40	2.49	2.45	2.36	2.43	0.06	2.34	0.09
HCO_3^-	20.54	22.67	21.43	20.89	21.38	0.93	4.36	1.48

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E5: PHYSICOCHEMICAL PROPERTIES OF VER WATER SAMPLES

Physicochemical Property	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
pH	7.28	7.39	7.48	7.35	7.38	0.08	1.13	0.13
TDS	8.60	8.84	8.87	8.80	8.78	0.12	1.39	0.19
Ca^{2+}	1.60	1.52	1.68	1.62	1.61	0.07	4.12	0.11
Mg^{2+}	0.90	1.09	1.02	0.98	1.00	0.08	7.95	0.13
HCO_3^-	6.10	6.23	6.17	6.20	6.18	0.06	0.90	0.09

E6: PHYSICOCHEMICAL PROPERTIES OF VOL WATER SAMPLES

Physicochemical Property	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
pH	7.28	7.46	7.62	7.35	7.43	0.15	2.00	0.24
TDS	70.00	70.52	70.29	70.78	70.40	0.33	0.47	0.53
Ca^{2+}	12.40	12.32	12.46	12.38	12.39	0.06	0.47	0.09
Mg^{2+}	2.60	2.53	2.67	2.58	2.60	0.06	2.24	0.09
HCO_3^-	55.00	55.67	55.16	55.82	55.41	0.39	0.71	0.63

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APPENDIX F

TOTAL ANTIMONY CONCENTRATIONS OF PET PACKAGING MATERIAL

Bottled water	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
AQF	120.47	118.56	120.66	119.45	119.79	0.97	0.81	1.55
BQA	130.54	134.46	132.46	132.43	132.47	1.60	1.21	2.55
ICP	125.65	127.45	128.46	126.34	126.98	1.24	0.97	1.97
SPI	122.64	121.46	122.45	123.46	122.50	0.82	0.67	1.31
VER	145.67	146.47	145.46	146.45	146.01	0.52	0.36	0.83
VOL	140.56	139.65	140.64	142.46	140.83	1.18	0.84	1.87

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APPENDIX G

G1: TOTAL ANTIMONY CONCENTRATIONS OF AQF WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.87	1.65	1.72	1.78	1.76	0.09	5.31	0.15
4	1.92	1.85	1.90	1.88	1.89	0.03	1.58	0.05
8	1.95	2.05	1.99	2.08	2.02	0.06	2.90	0.09
12	2.82	2.95	3.01	2.88	2.92	0.08	2.84	0.13

G2: TOTAL ANTIMONY CONCENTRAIONS OF BQA WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	14.49	14.82	14.62	14.68	14.65	0.14	0.93	0.22
4	15.53	15.89	14.98	15.65	15.51	0.39	2.48	0.61
8	16.43	16.87	16.34	17.05	16.67	0.34	2.05	0.54
12	17.22	17.45	17.34	17.26	17.32	0.10	0.59	0.16

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G3: TOTAL ANTIMONY CONCENTRATIONS OF ICP WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.14	1.13	1.05	1.10	1.11	0.04	3.66	0.06
4	1.82	1.87	1.67	1.72	1.77	0.09	5.16	0.15
8	1.92	1.95	1.99	1.98	1.96	0.03	1.61	0.05
12	2.72	2.55	2.67	2.27	2.55	0.20	7.89	0.32

G4: TOTAL ANTIMONY CONCENTRATIONS OF SPI WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	1.24	1.35	1.45	1.27	1.33	0.09	7.08	0.15
8	1.38	1.48	1.42	1.44	1.43	0.04	2.91	0.07
12	1.92	1.95	1.99	1.90	1.94	0.04	2.02	0.06

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G5: TOTAL ANTIMONY CONCENTRATIONS OF VER WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	5.48	6.31	6.12	6.58	6.12	0.47	7.65	0.74
4	7.76	8.24	8.62	8.45	8.27	0.37	4.50	0.59
8	8.98	9.08	9.06	8.99	9.03	0.05	0.55	0.08
12	10.22	10.15	10.09	10.17	10.16	0.05	0.53	0.09

G6: TOTAL ANTIMONY CONCENTRATIONS OF VOL WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	13.77	13.62	13.94	13.75	13.77	0.13	0.95	0.21
4	14.76	15.34	14.46	14.87	14.86	0.37	2.46	0.58
8	15.45	15.74	15.87	15.92	15.75	0.21	1.34	0.34
12	16.78	16.82	16.85	16.72	16.79	0.06	0.33	0.09

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G7: TOTAL ANTIMONY CONCENTRATIONS OF AQF WATER SAMPLES HELD INDOORS AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.87	1.65	1.72	1.78	1.76	0.09	5.31	0.15
4	2.90	2.98	2.67	2.88	2.86	0.13	4.63	0.21
8	3.20	3.45	3.27	3.33	3.31	0.11	3.20	0.17
12	3.90	3.93	3.99	3.82	3.91	0.07	1.81	0.11

G8: TOTAL ANTIMONY CONCENTRATIONS OF BQA WATER SAMPLES HELD INDOORS AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	14.49	14.82	14.62	14.68	14.65	0.14	0.93	0.22
4	15.02	15.15	15.07	15.20	15.11	0.08	0.53	0.13
8	15.92	15.97	16.02	15.82	15.93	0.09	0.54	0.14
12	16.78	16.82	16.92	16.85	16.84	0.06	0.35	0.09

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G9: TOTAL ANTIMONY CONCENTRATIONS OF ICP WATER SAMPLES HELD INDOORS AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.14	1.13	1.05	1.10	1.11	0.04	3.66	0.06
4	2.07	2.15	2.22	2.11	2.14	0.06	2.99	0.10
8	2.92	2.98	3.02	2.87	2.95	0.07	2.24	0.11
12	3.54	3.75	3.82	3.62	3.68	0.13	3.42	0.20

G10: TOTAL ANTIMONY CONCENTRATIONS OF SPI WATER SAMPLES HELD INDOORS AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	1.82	1.78	1.88	1.92	1.85	0.06	3.36	0.10
8	2.65	2.72	2.78	2.55	2.68	0.10	3.69	0.16
12	3.78	3.82	3.88	3.62	3.78	0.11	2.95	0.18

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G11: TOTAL ANTIMONY CONCENTRATIONS OF VER WATER SAMPLES HELD INDOORS AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	5.48	6.31	6.12	6.58	6.12	0.47	7.65	0.74
4	6.57	6.45	6.62	6.58	6.56	0.07	1.12	0.12
8	6.98	6.82	6.87	6.92	6.90	0.07	0.99	0.11
12	7.87	7.92	8.02	7.95	7.94	0.06	0.79	0.10

G12: TOTAL ANTIMONY CONCENTRATIONS OF VOL WATER SAMPLES HELD INDOORS AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	13.77	13.62	13.94	13.75	13.77	0.13	0.95	0.21
4	14.72	14.67	14.58	14.77	14.69	0.08	0.55	0.13
8	15.55	15.69	15.72	15.82	15.70	0.11	0.71	0.18
12	16.78	16.84	16.92	16.88	16.86	0.06	0.35	0.10

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G13: TOTAL ANTIMONY CONCENTRATIONS OF AQF WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.87	1.65	1.72	1.78	1.76	0.09	5.31	0.15
4	3.25	3.56	3.78	3.46	3.51	0.22	6.27	0.35
8	6.45	6.88	6.67	6.75	6.69	0.18	2.70	0.29
12	8.42	8.67	8.54	8.87	8.63	0.19	2.23	0.31

G14: TOTAL ANTIMONY CONCENTRATIONS OF BQA WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	14.49	14.82	14.62	14.68	14.65	0.14	0.93	0.22
4	17.46	17.56	17.88	17.35	17.56	0.23	1.30	0.36
8	19.45	19.87	19.34	19.26	19.48	0.27	1.39	0.43
12	22.78	22.67	22.56	22.47	22.62	0.13	0.59	0.21

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G15: TOTAL ANTIMONY CONCENTRATIONS OF ICP WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.14	1.13	1.05	1.10	1.11	0.04	3.66	0.06
4	3.76	3.45	3.32	3.34	3.47	0.20	5.86	0.32
8	6.98	6.87	6.46	7.02	6.83	0.26	3.75	0.41
12	9.98	10.14	9.89	10.20	10.05	0.14	1.42	0.23

G16: TOTAL ANTIMONY CONCENTRATIONS OF SPI WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	3.67	3.32	3.43	3.87	3.57	0.25	6.90	0.39
8	7.34	7.78	7.87	7.54	7.63	0.24	3.14	0.38
12	11.78	11.89	12.06	12.21	11.99	0.19	1.58	0.30

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G17: TOTAL ANTIMONY CONCENTRATIONS OF VER WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	5.48	6.31	6.12	6.58	6.12	0.47	7.65	0.74
4	8.98	8.78	8.65	9.01	8.86	0.17	1.93	0.27
8	11.56	11.87	11.98	11.34	11.69	0.29	2.50	0.46
12	14.67	14.82	14.34	14.78	14.65	0.22	1.49	0.35

G18: TOTAL ANTIMONY CONCENTRATIONS OF VOL WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	13.77	13.62	13.94	13.75	13.77	0.13	0.95	0.21
4	15.43	15.98	15.72	15.62	15.69	0.23	1.46	0.36
8	19.22	19.78	19.92	19.34	19.57	0.34	1.73	0.54
12	23.87	24.05	23.67	23.92	23.88	0.16	0.66	0.25

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APPENDIX H

H1: ANTIMONY (III) CONCENTRATIONS OF AQF WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.15	0.13	0.14	0.12	0.14	0.01	9.56	0.02
4	0.23	0.21	0.22	0.20	0.22	0.01	6.00	0.02
8	0.55	0.52	0.57	0.62	0.57	0.04	7.44	0.07
12	1.02	1.15	1.07	1.12	1.09	0.06	5.24	0.09

H2: ANTIMONY (III) CONCENTRATIONS OF BQA WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.23	0.25	0.24	0.22	0.24	0.01	5.49	0.02
4	0.35	0.37	0.36	0.33	0.35	0.02	4.84	0.03
8	0.87	0.92	0.74	0.82	0.84	0.08	9.17	0.12
12	1.55	1.45	1.52	1.49	1.50	0.04	2.84	0.07

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H3: ANTIMONY (III) CONCENTRATIONS OF ICP WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	0.34	0.42	0.38	0.36	0.38	0.03	9.11	0.05
8	0.66	0.75	0.72	0.62	0.69	0.06	8.51	0.09
12	1.02	0.99	1.12	1.08	1.05	0.06	5.56	0.09

H4: ANTIMONY (III) CONCENTRATIONS OF SPI WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	0.97	0.87	0.92	1.02	0.95	0.06	6.83	0.10
8	1.12	1.02	1.15	1.06	1.09	0.06	5.38	0.09
12	1.72	1.83	1.69	1.78	1.76	0.06	3.56	0.10

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H5: ANTIMONY (III) CONCENTRATIONS OF VER WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.34	0.32	0.37	0.35	0.35	0.02	6.03	0.03
4	0.92	0.86	0.78	0.87	0.86	0.06	6.76	0.09
8	1.03	1.08	1.05	1.12	1.07	0.04	3.66	0.06
12	1.92	1.87	1.95	1.85	1.90	0.05	2.41	0.07

H6: ANTIMONY (III) CONCENTRATIONS OF VOL WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.62	0.73	0.56	0.68	0.65	0.07	11.38	0.12
4	1.12	1.25	1.29	1.17	1.21	0.08	6.36	0.12
8	1.32	1.39	1.36	1.42	1.37	0.04	3.11	0.07
12	2.15	2.22	2.17	2.25	2.20	0.05	2.08	0.07

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H7: ANTIMONY (III) CONCENTRATIONS OF AQF WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.15	0.13	0.14	0.12	0.14	0.01	9.56	0.02
4	0.54	0.58	0.49	0.62	0.56	0.06	9.97	0.09
8	0.92	0.96	1.05	0.89	0.96	0.07	7.28	0.11
12	1.52	1.48	1.57	1.55	1.53	0.04	2.56	0.06

H8: ANTIMONY (III) CONCENTRATIONS OF BQA WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.23	0.25	0.24	0.22	0.24	0.01	5.49	0.02
4	0.72	0.83	0.78	0.85	0.80	0.06	7.30	0.09
8	1.23	1.29	1.25	1.32	1.27	0.04	3.17	0.06
12	1.74	1.81	1.78	1.84	1.79	0.04	2.38	0.07

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H9: ANTIMONY (III) CONCENTRATIONS OF ICP WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	0.23	0.29	0.25	0.31	0.27	0.04	13.52	0.06
8	0.54	0.62	0.58	0.60	0.59	0.03	5.84	0.05
12	0.98	1.04	0.92	1.08	1.01	0.07	6.97	0.11

H10: ANTIMONY (III) CONCENTRATIONS OF SPI WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	1.12	1.24	1.17	1.15	1.17	0.05	4.36	0.08
8	1.78	1.84	1.87	1.80	1.82	0.04	2.21	0.06
12	2.25	2.33	2.29	2.31	2.30	0.03	1.49	0.05

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H11: ANTIMONY (III) CONCENTRATIONS OF VER WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.34	0.32	0.37	0.35	0.35	0.02	6.03	0.03
4	0.72	0.78	0.84	0.75	0.77	0.05	6.63	0.08
8	1.08	1.13	1.10	1.15	1.12	0.03	2.79	0.05
12	1.78	1.67	1.74	1.69	1.72	0.05	2.89	0.08

H12: ANTIMONY (III) CONCENTRATIONS OF VOL WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.62	0.73	0.56	0.68	0.65	0.07	11.38	0.12
4	1.04	1.09	1.07	1.13	1.08	0.04	3.49	0.06
8	1.57	1.64	1.60	1.68	1.62	0.05	2.95	0.08
12	2.02	2.13	2.07	2.09	2.08	0.05	2.20	0.07

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H13: ANTIMONY (III) CONCENTRATIONS OF AQF WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.15	0.13	0.14	0.12	0.14	0.01	9.56	0.02
4	1.62	1.68	1.74	1.65	1.67	0.05	3.06	0.08
8	2.64	2.73	2.69	2.75	2.70	0.05	1.80	0.08
12	3.79	3.87	3.85	3.82	3.83	0.04	0.91	0.06

H14: ANTIMONY (III) CONCENTRATIONS OF BQA WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.23	0.25	0.24	0.22	0.24	0.01	5.49	0.02
4	1.56	1.63	1.71	1.59	1.62	0.06	4.01	0.10
8	2.19	2.27	2.24	2.31	2.25	0.05	2.25	0.08
12	3.43	3.49	3.45	3.53	3.48	0.04	1.28	0.07

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H15: ANTIMONY (III) CONCENTRATIONS OF ICP WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	0.94	1.03	0.97	1.05	1.00	0.05	5.14	0.08
8	1.83	1.89	1.93	1.85	1.88	0.04	2.37	0.07
12	2.75	2.83	2.79	2.87	2.81	0.05	1.84	0.08

H16: ANTIMONY (III) CONCENTRATIONS OF SPI WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	2.87	2.92	2.83	2.96	2.90	0.06	1.96	0.09
8	4.65	4.73	4.69	4.79	4.72	0.06	1.27	0.10
12	6.98	7.09	7.04	7.12	7.06	0.06	0.87	0.10

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H17: ANTIMONY (III) CONCENTRATIONS OF VER WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.34	0.32	0.37	0.35	0.35	0.02	6.03	0.03
4	1.76	1.82	1.78	1.87	1.81	0.05	2.69	0.08
8	2.89	2.95	2.99	3.05	2.97	0.07	2.27	0.11
12	3.99	4.07	4.04	4.13	4.06	0.06	1.44	0.09

H18: ANTIMONY (III) CONCENTRATIONS OF VOL WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	0.62	0.73	0.56	0.68	0.65	0.07	11.38	0.12
4	1.85	1.93	1.89	1.97	1.91	0.05	2.70	0.08
8	2.97	3.05	3.17	3.12	3.08	0.09	2.82	0.14
12	4.13	4.19	4.23	4.17	4.18	0.04	1.00	0.07

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APPENDIX I

I1: ANTIMONY (V) CONCENTRATIONS OF AQF WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.72	1.52	1.58	1.66	1.62	0.09	5.81	0.15
4	1.69	1.64	1.68	1.68	1.67	0.02	1.33	0.04
8	1.40	1.53	1.42	1.46	1.45	0.06	3.95	0.09
12	1.80	1.80	1.94	1.76	1.83	0.08	4.33	0.13

I2: ANTIMONY (V) CONCENTRATIONS OF BQA WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	14.26	14.57	14.38	14.46	14.42	0.14	0.95	0.22
4	15.18	15.52	14.62	15.32	15.16	0.39	2.55	0.61
8	15.56	15.95	15.60	16.23	15.84	0.32	2.00	0.50
12	15.67	16.00	15.82	15.77	15.82	0.14	0.87	0.22

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I3: ANTIMONY (V) CONCENTRATIONS OF ICP WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.14	1.13	1.05	1.10	1.11	0.04	3.66	0.06
4	1.48	1.45	1.29	1.36	1.40	0.09	6.21	0.14
8	1.26	1.20	1.27	1.36	1.27	0.07	5.19	0.11
12	1.70	1.56	1.55	1.19	1.50	0.22	14.51	0.35

I4: ANTIMONY (V) CONCENTRATIONS OF SPI WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	0.27	0.48	0.53	0.25	0.38	0.14	37.42	0.23
8	0.26	0.46	0.27	0.38	0.34	0.10	27.84	0.15
12	0.20	0.12	0.30	0.12	0.19	0.09	46.18	0.14

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I5: ANTIMONY (V) CONCENTRATIONS OF VER WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	5.14	5.99	5.75	6.23	5.78	0.47	8.11	0.75
4	6.84	7.38	7.84	7.58	7.41	0.42	5.72	0.67
8	7.95	8.00	8.01	7.87	7.96	0.06	0.80	0.10
12	8.30	8.28	8.14	8.32	8.26	0.08	0.99	0.13

I6: ANTIMONY (V) CONCENTRATIONS OF VOL WATER SAMPLES HELD IN REFRIGERATOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	13.15	12.89	13.38	13.07	13.12	0.15	1.15	0.24
4	13.64	14.09	13.17	13.70	13.65	0.38	2.76	0.60
8	14.13	14.35	14.51	14.50	14.37	0.18	1.23	0.28
12	14.63	14.60	14.68	14.47	14.60	0.09	0.61	0.14

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I7: ANTIMONY (V) CONCENTRATIONS OF BQA WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.72	1.52	1.58	1.66	1.62	0.09	5.81	0.15
4	2.36	2.40	2.18	2.26	2.30	0.10	4.32	0.16
8	2.28	2.49	2.22	2.44	2.36	0.13	5.44	0.20
12	2.38	2.45	2.42	2.27	2.38	0.08	3.31	0.13

I8: ANTIMONY (V) CONCENTRATIONS OF BQA WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	14.26	14.57	14.38	14.46	14.42	0.14	0.95	0.22
4	14.30	14.32	14.29	14.35	14.32	0.03	0.18	0.04
8	14.69	14.68	14.77	14.50	14.66	0.11	0.78	0.18
12	15.04	15.01	15.14	15.01	15.05	0.06	0.41	0.10

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I9: ANTIMONY (V) CONCENTRATIONS OF ICP WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.14	1.13	1.05	1.10	1.11	0.04	3.66	0.06
4	1.84	1.86	1.97	1.80	1.87	0.07	3.90	0.12
8	2.38	2.36	2.44	2.27	2.36	0.07	2.98	0.11
12	2.56	2.71	2.90	2.54	2.68	0.17	6.22	0.27

I10: ANTIMONY (V) CONCENTRATIONS OF SPI WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	0.70	0.54	0.71	0.77	0.68	0.10	14.46	0.16
8	0.87	0.88	0.91	0.75	0.85	0.07	8.26	0.11
12	1.53	1.49	1.59	1.31	1.48	0.12	8.15	0.19

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I11: ANTIMONY (V) CONCENTRATIONS OF VER WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	5.14	5.99	5.75	6.23	5.78	0.47	8.11	0.75
4	5.85	5.67	5.78	5.83	5.78	0.08	1.39	0.13
8	5.90	5.69	5.77	5.77	5.78	0.09	1.50	0.14
12	6.09	6.25	6.28	6.26	6.22	0.09	1.41	0.14

I12: ANTIMONY (V) CONCENTRATIONS OF VOL WATER SAMPLES HELD INDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	13.15	12.89	13.38	13.07	13.12	0.15	1.15	0.24
4	13.68	13.58	13.51	13.64	13.60	0.07	0.54	0.12
8	13.98	14.05	14.12	14.14	14.07	0.07	0.52	0.12
12	14.76	14.71	14.85	14.79	14.78	0.06	0.40	0.09

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I13: ANTIMONY (V) CONCENTRATIONS OF AQF WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.72	1.52	1.58	1.66	1.62	0.09	5.81	0.15
4	1.63	1.88	2.04	1.81	1.84	0.17	9.23	0.27
8	3.81	4.15	3.98	4.00	3.99	0.14	3.49	0.22
12	4.63	4.80	4.69	5.05	4.79	0.19	3.87	0.30

I14: ANTIMONY (V) CONCENTRATIONS OF BQA WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	14.26	14.57	14.38	14.46	14.42	0.14	0.95	0.22
4	15.90	15.93	16.17	15.76	15.94	0.17	1.07	0.27
8	17.26	17.60	17.10	16.95	17.23	0.28	1.62	0.44
12	19.35	19.18	19.11	18.94	19.15	0.17	0.89	0.27

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I15: ANTIMONY (V) CONCENTRATIONS OF ICP WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	1.14	1.13	1.05	1.10	1.11	0.04	3.66	0.06
4	2.82	2.42	2.35	2.29	2.47	0.24	9.69	0.38
8	5.15	4.98	4.53	5.17	4.96	0.30	6.00	0.47
12	7.23	7.31	7.10	7.33	7.24	0.10	1.44	0.17

I16: ANTIMONY (V) CONCENTRATIONS OF SPI WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	-	-	-	-	-	-	-	-
4	0.80	0.40	0.60	0.91	0.68	0.23	33.23	0.36
8	2.69	3.05	3.18	2.75	2.92	0.24	8.07	0.37
12	4.80	4.80	5.02	5.09	4.93	0.15	3.04	0.24

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I17: ANTIMONY (V) CONCENTRATIONS OF VER WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	5.14	5.99	5.75	6.23	5.78	0.47	8.11	0.75
4	7.22	6.96	6.87	7.14	7.05	0.16	2.28	0.26
8	8.67	8.92	8.99	8.29	8.72	0.32	3.63	0.50
12	10.68	10.75	10.30	10.65	10.60	0.20	1.90	0.32

I18: ANTIMONY (V) CONCENTRATIONS OF VOL WATER SAMPLES HELD OUTDOOR AT INTERVALS OF FOUR WEEKS FOR TWELVE WEEKS.

Week	1	2	3	4	Mean	Std. Dev.	CoV (%)	CI (95%)
0	13.15	12.89	13.38	13.07	13.12	0.15	1.15	0.24
4	13.58	14.05	13.83	13.65	13.78	0.21	1.52	0.33
8	16.25	16.73	16.75	16.22	16.49	0.29	1.77	0.46
12	19.74	19.86	19.44	19.75	19.70	0.18	0.91	0.29