

Migration of Inorganic Antimony into Polyethylene Terephthalate Bottled Water Marketed in the Greater Accra Region of Ghana

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Abstract

The migration of inorganic antimony from polyethylene terephthalate plastic bottles into waters stored in them was investigated using hydride generation atomic absorption spectrophotometry. Six popular brands of bottled water marketed in the greater Accra region of Ghana were used. These were held under various storage conditions and their dissolved Sb monitored over a period. In addition, the Sb in the plastic containers and some physicochemical properties of the waters were determined. The determined Sb in the plastic containers revealed amounts ranging from 123.46 to 146.45mg/kg. The determined physicochemical properties were pH (6.78-7.43); Ca²⁺ (1.61-12.39mg/L); Mg²⁺ (1.00-4.96mg/L); HCO₃⁻ (6.18-55.41mg/L); and total dissolved solids (8.70-70.40mg/L). Differences in the residual amounts of Sb showed dissimilarities existed in the quality of the plastics used in packaging. The physicochemical properties were seen to have no effect on migration. Sb levels in the water stored in the plastic containers were observed to increase with time under all the storage conditions for all the brands of plastic bottled water. The plastic bottled waters were, however, found not to have Sb exceeding the world health organisation maximum contaminant level within the period taking into consideration the specified limited time of expiry.

Keywords: Migration; physicochemical properties; plastic bottles; spectrophotometry; storage conditions.

1. Introduction

The global bottled water market has witnessed a tremendous annual growth for the past fifteen years, reaching a total value of about €66 billion in the year 2010. The United Kingdom alone 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). China turned into the biggest marketplace in the intake of bottled water at 40 million tonnes in the year 2011 alone (Fan *et al.*, 2014; Rani, Maheshwari, Garg, & Prasad, 2012). 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, an indication that, bottled water in a few years to come will most likely be the sole drinking water worldwide.

In Ghana, the majority of the public consume drinking water that is packaged in “sachets” or plastic bottles. These “sachet” and plastic bottled waters are generally perceived to be clean, convenient, healthy and safer compared to tap water (Fan *et al.*, 2014; Grant & Yankson, 2003; Osei, Newman, Mingle, Ayeh-Kumi, & Kwasi, 2013; Westerhoff, Prapaipong, Shock, & Hillaireau, 2008). Therefore, to satisfy domestic Ghanaian demand for “sachet” and plastic bottled water, there has been a proliferation in the number of manufacturers on the market, most of whom are suspected not to have permits. This leads to difficulty in determining the exact number of “sachet” and bottled water manufacturers in the country. Nonetheless, there are leading brands of bottled water which are taken most by the public and thus, can represent a greater portion of consumers.

The plastic material for packaging drinking water differ from country to country, but the common package material used is polyethylene terephthalate (PET) (Keresztes *et al.*, 2009). This is due to its excellent material properties like unbreakability, good barrier properties towards moisture, high clarity, low migration trends for residual constituents and very low weight of the bottles compared with glass bottles of the same filling capacity (Fan *et al.*, 2014; Sanchez-Martinez, Perez-Corona, Camara, & Madrid, 2013; Welle, 2011; Westerhoff *et al.*, 2008). It is made from the polymerization of petroleum monomers of terephthalic acid and ethylene glycol using antimony-, titanium-, or germanium-based catalysts (Westerhoff *et al.*, 2008). Over 90% of globally manufactured PET utilize antimony-based catalysts, predominantly antimony trioxide (Sb₂O₃) 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, Hernandez-Nataren, Lopez-Sanchez, & Sahuquillo, 2015; Shotyk, Krachler, & Chen, 2006; Welle, 2011; Westerhoff *et al.*, 2008). An estimated 150 billion plastic bottles are produced from PET resins annually (Shotyk *et al.*, 2006). Commercialised PET resins produced from the use of Sb₂O₃ catalysts ordinarily have residual Sb ranging between 150-300mg/kg (Carneado *et al.*, 2015; Hureiki & Mouneimne, 2012; Keresztes *et al.*, 2009). These residual antimony amounts are very high and raise concerns, considering earlier

findings that, antimony was found to migrate into water and beverages stored in PET plastic containers over time (Carneado *et al.*, 2015; Fan *et al.*, 2014; Keresztes *et al.*, 2009).

Sb itself is a regulated drinking water contaminant and a non-essential element for plants and animals and has no known biological or physiological function and on a long-term exposure has been suspected to be carcinogenic (Carneado *et al.*, 2015; Keresztes *et al.*, 2009; Roberts & Orisakwe, 2011; Sanchez-Martinez *et al.*, 2013; Sayago, Beltrán, & Gómez-Ariza, 2000; Shotyk *et al.*, 2006; Tostar, Stenvall, Boldizar, & Foreman, 2013; Westerhoff *et al.*, 2008). In cases of acute intoxication, symptoms 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 long-term exposure to this metalloid include pneumonitis, fibrosis, bone marrow damage and carcinomas (Sayago *et al.*, 2000).

Several environmental factors have been found to 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 (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 in our part of the world are very different and more severe with variations in seasons. Moreover, the source of water for bottling and the packing material differs from one manufacturing company to another. Thus, it is imperative that PET bottled water stored under prevailing conditions be studied to ascertain whether migration rates are high leading to contamination.

2. Materials and Methods

2.1 Samples

PET plastic bottled water samples of six popular brands (displayed in Figure 2.1.1) distributed in the Greater Accra region were selected and purchased at source on the day of bottling. Bottling plants locations are geographically mapped out in Figure 2.1.2. All samples of a particular brand originate from the same batch of bottled water produced at that time of the day. All brands of bottled waters also had a transparent layer of PET material used in packaging and the waters stored in them had different degrees of mineral composition. The container volume chosen was 0.5L for all the six brands of plastic bottled water samples. Bottled water samples were not of the same bottling date but were all package in the range of two weeks. The bottled water samples remained sealed in their unique containers until analyses and antimony analyses for each brand (water samples and PET plastic containers) were carried out in quadruplicate (n=4). Thus, the obtained results corresponded to a mean of four independent measurements for both water samples and plastic package material originating from bottled water samples of the same batch.



Figure 2.1.1: The six brands of bottled water. From left, bottled water coded names are: VOL, AQF, VER, ICP, BQA and SPI respectively

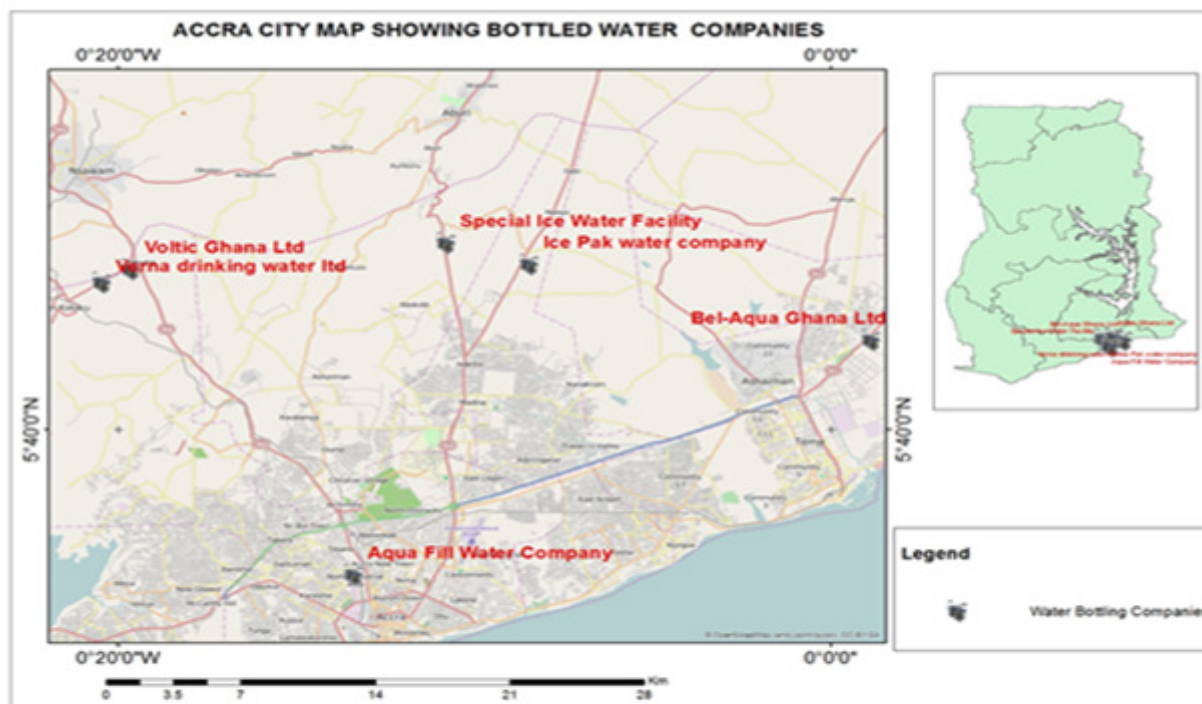


Figure 2.1.2: Geographical map showing locations of the bottled water companies in Greater Accra region. Inset at the top right corner displays the map of Ghana

2.2 Reagents and standards

The standards and reagents used in this study were prepared with ultrapure water ($8\text{-}10\text{M}\Omega\cdot\text{cm}^{-1}$ at 24.5°C) obtained from a Milli-Q water purification system. The 1mg/mL stock standard antimony(V) solution was prepared by dissolving 0.216g of potassium hexahydroxyantimonate (Sigma-Aldrich, 99%) in 100mL of 2.4M HCl. Antimony stock solutions were stored in polyethylene plastic bottles in refrigerator at 4°C and working solutions were prepared daily by dilution. The sodium borohydride solution used was prepared from dissolving 0.700g 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 dissolving 0.400g NaOH pellets (Merck, 99%). In the microwave digestion of the plastic container samples, concentrated HNO_3 (Panreac, hyper-pure reagent grade, 69%) and H_2O_2 (Merck, 96%) were used. The 1M L-Cysteine solution used to reduce antimony(V) in the total antimony determination was prepared by dissolving 1.212g of L-Cysteine (97%, Sigma-Aldrich) in 10mL of HCl (2.4M).

2.3 Instrumentation and operating conditions

Agilent 240 FS AA spectrophotometer with an antimony cathode lamp was used in the determination of trace inorganic antimony. Background absorption was corrected using a deuterium lamp. The operating conditions of the spectrophotometer during the determination were the wavelength, 217.6nm ; bandpass, 0.7nm ; lamp current, 14mA ; flame, 11.5L/min air and 3.6L/min acetylene. Background absorption was corrected using a deuterium lamp. Microwave digestion of the PET plastic container samples was performed using a Milestone ETHOS digester instrument.

2.4 Sample preparation

Before analysis, water samples were allowed to stand for an hour before treatment. This is to enable all the water samples held under the different storage conditions to acclimatise to the same experimental conditions before treatment and subsequent analysis. Also, before digestion, the PET plastic containers were cut into approximately $5\times 5\text{mm}^2$ pieces using a ceramic blade. Each cut-out replicate of the PET plastic container weighed approximately 0.250g .

2.5 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 in them, bottled water samples were assigned into three storage groupings, each group comprising bottled waters from the six different brands. Each group (excluding bottled water samples for analysis on the day of acquiring sample - day one) was further divided into three subgroups.

The three subgroupings (consisting of 4 bottled water samples for each brand) represented four weeks, eight weeks and twelve weeks under a specified storage condition. One group was stored in a refrigerator at 4°C; the second group exposed to high air temperatures and sunlight outdoor, and the third group in a closed cabinet away from sunlight indoor. The bottled water samples were held under these conditions for 12 weeks and antimony levels monitored at four weeks' intervals. The temperatures of the bottled waters kept outside and indoors were monitored on a weekly basis using a mercury bulb thermometer and those in the refrigerator maintained at 4°C. To establish the antimony levels in the source waters before bottling, determinations were made on some of the bottled water samples for each brand on the day of acquisition – within 12 hours of filling. The rest of the bottled water samples were then stored according to the group they were assigned into for the rest of the experimental period.

2.6 Analytical procedure

The analytical procedure used in the total inorganic antimony determination was adapted from the works of Apte and Howard (1986) and Feng, Narasaki, Chen, and Tian (1999). The pH of water samples (10mL) was adjusted to 2 by adding 10mL of 8M HCl, after which 5mL of 1M L-cysteine was added and allowed to stand 15 minutes to reduce all the antimony(V) to antimony(III). Solutions were then placed 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 1M L-cysteine) working standards of antimony(V) prepared by serial dilutions of a stock antimony(V) standard. Blanks were also prepared and used to correct interferences originating from the matrices of the solutions.

With regards to the total antimony determination in the PET containers, each cut-out replicate of the plastic package material was mixed with 10mL of concentrated HNO₃ and 2mL of concentrated H₂O₂ and digested in Teflon closed vessels using the Milestone ETHOS digester instrument. The maximum temperature and pressure were 180°C and ~250 psi respectively for 15-minutes using 50% of the digestion system's maximum power of 1000W. After digestion, 5mL of 1M 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 25mL 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 HNO₃ and H₂O₂ were added and digested as in the determination of the unknown. Antimony(V) in these solutions are 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 originating from the matrices of the solutions.

The pH of the water samples of the six brands of bottled water was taken using the basic benchtop pH meter. The meter was first calibrated with buffers at pH 4.70 and 10.01 at ambient temperature (24°C). The probe of the meter was then inserted into specific volumes (10mL) of the water samples and readings taken from the screen. For validation purposes, the pH of 1M KCl solution was similarly determined (ASTM International, 2012).

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, 2003). The total dissolved solids of the water samples were measured using the conductivity/TDS meter which was calibrated at ambient temperature (24°C) using HANNA standards. The probe of the meter was inserted into specific volumes (20mL) of the water samples. Total dissolved solids readings are then taken from the screen (ASTM International, 2010).

The calcium content of the water samples was determined spectrophotometrically at 422.7nm by atomic absorption. Aliquots of the water samples were first mixed with lanthanum chloride (LaCl₃) solution and then aspirated into an air-acetylene flame. The absorbance was then measured and compared to identically-prepared standard and blank solutions from which the concentration was obtained (ASTM International, 2014).

The magnesium concentration was determined by atomic absorption spectrophotometry (AAS) – direct aspiration. Aliquots (10mL) of water samples were mixed with 5 mL of 1M lanthanum chloride (LaCl₃) solution and aspirated into an air-acetylene reducing flame. The absorbance was measured spectrophotometrically at 285.2nm and compared to identically-prepared standard and blank solutions. From the absorbance, concentration is then obtained (ASTM international, 2014).

Bicarbonate ion concentration was determined by titration. Aliquots (10mL) of bottled water samples were titrated with 0.5M 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 (ASTM international, 2015).

3. Results and Discussion

3.1 Quality assurance and quality control

Quality assurance and control steps comprised blanks, replicate analyses, certified reference material and

calibrations. Reproducibility was calculated as %RSD of 4 measurements and this was <10% for 90% of measurements. Method validation for Sb in the water was undertaken using a certified reference material (CRM) - global environment monitoring systems (GEMS) water standard. The certified Sb content in the GEMS material used in validating the Sb determination procedure was $100\mu\text{gSb/kg}\pm 2\%$. This standard reference material was analysed in quadruplicate ($n=4$) in order to validate the precision of the measurement. The quantified Sb concentration was in agreement with the certified value taking into consideration the associated uncertainty, reaching a value of $99.49\mu\text{gSb/kg}\pm 2\%$. Spike and recovery were used to validate the determination procedure for Sb in the PET container cut-out samples. Spiked cut-out polyethylene container samples in the determination of Sb in the PET plastic containers had uncertainty within acceptable limits and recovery >95%.

3.2 Effect of different plastic types on migration

Figure 3.2.1 displays the total Sb in the plastic containers the waters were stored in. Differences were clearly shown in the residual Sb present in the PET containers. The antimony content ranged from 123.5mg/kg to 146.5mg/kg. VER had the highest Sb (146.5mg/kg) and AQF had the least (123.5mg/kg). These were lower compared to those of PET bottles obtained in some previous studies (Carneado *et al.*, 2015; Keresztes *et al.*, 2009; Tukur, Sharp, Stern, Tizaoui, & Benkreira, 2012). On the other hand, the amounts obtained were within the range (104-166mg/kg) obtained by Fan *et al.* (2014). Sanchez-Martinez *et al.* (2013) recorded higher Sb in the PET plastic containers used in their study.

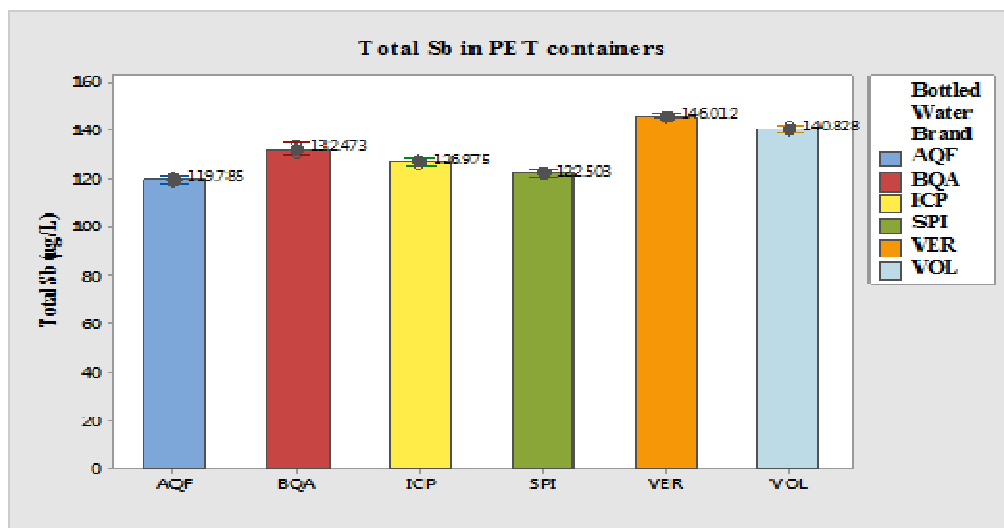


Figure 3.2.1: Total antimony amounts in the PET containers. Sb – antimony; PET – polyethylene terephthalate; mean values are shown on top of bars.

The presence of Sb in the plastic containers can be attributed to its likely use as a catalyst in the manufacturing process of the 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 stays attached to the polymer chain as glycolate complexes (Carneado *et al.*, 2015). The Sb glycolate complexes then slowly dissolve – solubility of $5.8\times 10^{-5}\text{kmol/m}^3$ at 298K (Casas, Crisóstomo, & Cifuentes, 2008) from the plastic bottles into the water contained inside. Thus, this goes to support the view that the technology used in the manufacturing the PET plastics differ and as such variances can be observed in the final product.

3.3 Effect of physicochemical properties on Sb migration

Figure 3.3.1 displays the matrix plot of dissolved Sb in bottled water versus the physicochemical properties of the water. The properties considered were pH, bicarbonate ion concentration, calcium ion (Ca^{2+}) concentration, magnesium ion (Mg^{2+}) concentration, and total dissolved solids (TDS). These were measured at the end of week 12. 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 varying between 6.78 and 7.43. pH statistically registered insignificant positive correlations ($P=0.066, 0.091 > 0.05, 0.01$) to Sb under indoor and outdoor conditions but not under refrigeratory conditions ($P=0.049 < 0.05 > 0.01$). This suggests that pH does not statistically affect Sb at the 0.05 and 0.01 significance level. Few literature have come to the same conclusion for Sb (Hureiki & Mouneimne, 2012; Westerhoff *et al.*, 2008).

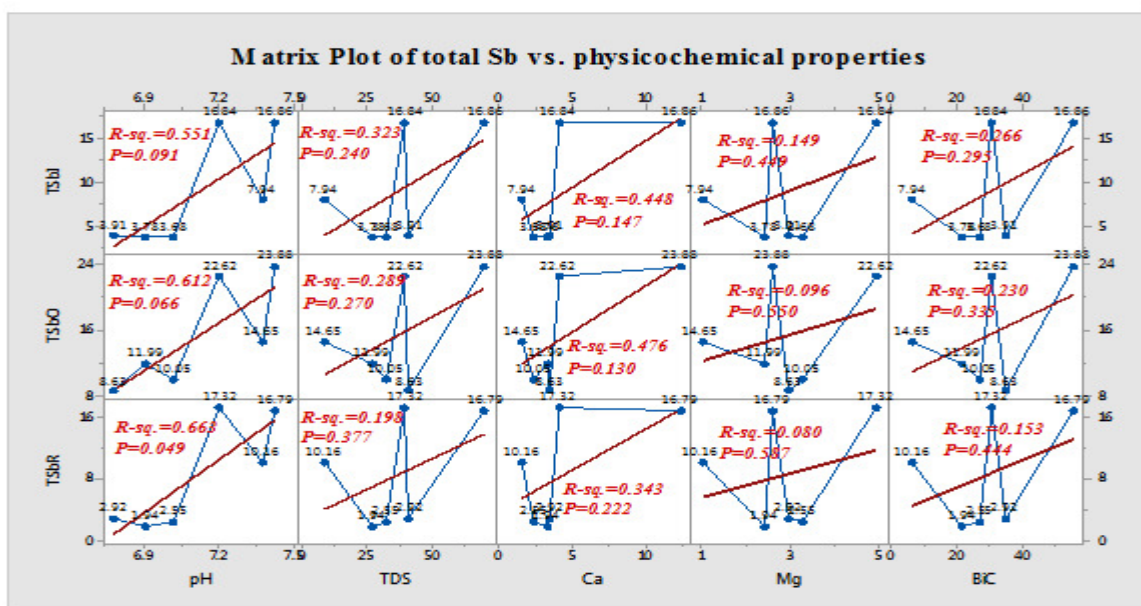


Figure 3.3.1: Matrix plot of Antimony versus Physicochemical Properties. TSbR – total antimony of bottled water stored in refrigerator; TSbI – total antimony of bottled water stored indoor; TSbO – total antimony of bottled water stored outdoor; TDS – total dissolved solids; BiC – bicarbonate ion concentration; Ca – calcium ion concentration; Mg – magnesium ion concentration; pH – (-log) hydrogen ion concentration; R-sq. – coefficient of determination; P – probability value.

The bicarbonate ion levels of the waters ranged from 6.18-55.41mg/L. This range is lower compared with those obtained by Hureiki and Mouneimne (2012) and Keresztes *et al.* (2009). The bicarbonate ion levels positively correlated Sb in the water under the three storage conditions. The correlations were, however, insignificant ($P=0.444, 0.335, 0.295 > 0.05, 0.01$) suggesting that, the bicarbonate levels statistically have no relationship with Sb content in the stored water. Hureiki and Mouneimne (2012) arrived at the same conclusion.

The calcium content of the water ranged from 1.61mg/L to 12.39mg/L with a mean and median value of 4.53mg/L and 3.36mg/L respectively. These were lower compared with those obtained by Hureiki and Mouneimne (2012) and Keresztes *et al.* (2009). The calcium content registered statistically insignificant positive correlation to Sb ($P=0.222, 0.130, 0.147 > 0.05, 0.01$) at 0.05 and 0.01 significance level. Thus, the calcium content does not appear to affect the changing levels of the Sb content in the stored water. Studies by Hureiki and Mouneimne (2012) and Keresztes *et al.* (2009) however revealed calcium had an effect on Sb. This difference may be due to the lower calcium levels obtained in this study. Thus, there is the likelihood calcium beyond certain limits will begin to induce Sb migration.

The magnesium levels for the six brands of bottled waters ranged from 1.00mg/L to 4.96mg/L with a mean and median value of 2.87mg/L and 2.78mg/L respectively. This range is lower compared with those obtained in a study by Hureiki and Mouneimne (2012) and Keresztes *et al.* (2009). The magnesium levels statistically correlated Sb positively under the three storage conditions. The correlations were however insignificant ($P=0.587, 0.550, 0.449 > 0.05, 0.01$). Therefore, the magnesium levels did not statistically affect Sb in the waters at the respective significance levels. Similar findings were obtained by Hureiki and Mouneimne (2012).

The TDS for the six brands of bottled water ranged from 8.78mg/L to 70.40mg/L with a mean a median of 36.61mg/L and 36.10mg/L respectively. This range is lower compared to that obtained by Hureiki and Mouneimne (2012) and Keresztes *et al.* (2009). TDS was found to be positively correlated to Sb under the three storage conditions. The correlations were however found to be insignificant ($P=0.377, 0.270, 0.240 > 0.05, 0.01$) suggesting that TDS does not statistically affect Sb in the waters at the respective significance levels. Contrary to that, Hureiki and Mouneimne (2012) and Westerhoff *et al.* (2008) found that higher TDS content accompanied in higher Sb in the bottled water. Cognisance must, however, be given to the fact that, the ionic composition of the water used in the study by Westerhoff *et al.* (2008) comprised the summation of the divalent ions, calcium and magnesium. That of Hureiki and Mouneimne (2012) used ionic composition of the water specified by the manufacturers of the bottled waters. The TDSs of the bottled water were not experimentally determined.

3.4 Effect of storage duration and type on Sb migration

Figure 3.4.1a and Figure 3.4.1b display the dissolved Sb of the water brands determined for twelve weeks at intervals of four weeks under the three selected storage conditions for the six brands of bottled water. The three

selected storage conditions (in a refrigerator [R] at 4°C; indoor [I] at room temperature; and outdoor [O] exposed to direct sunlight and high air temperatures) were specific and typical of bottled water usage in Ghana. Five (AQF, BQA, ICP, VER and VOL) out the six brands of bottled water had some amounts of dissolved Sb present in them on the day they were acquired - week 0. The dissolved Sb levels ranged below the detection limit (0.05µg/L) for SPI to 13.77µg/L for VOL. BQA, VER, and VOL registered dissolved Sb greater than the MCL specified by US EPA and EU but lower than the maximum contaminant level specified by WHO for week 0. The detection of dissolved Sb in the water before storage was not strange. Some previous studies have published accounts of this phenomenon. For instance, in a study of ‘the influence of storage time and temperature on Sb migration from PET bottles into mineral water’, Carneado *et al.* (2015) detected dissolved Sb in all tested water samples before storage. The detected dissolved Sb ranged from 0.3µg/L to 0.7µg/L. In another study by Tukur *et al.* (2012), levels ranging between 0.03µg/L and 6.61µg/L have been obtained for 47 freshly purchased British bottled contents. Westerhoff *et al.* (2008) in studying Sb leaching from PET plastics used for bottled drinking water equally discovered that, at the beginning of the study, the nine bottled water samples used contained some amounts of dissolved Sb (average dissolved Sb of the nine bottled waters 0.195±0.116ppb).

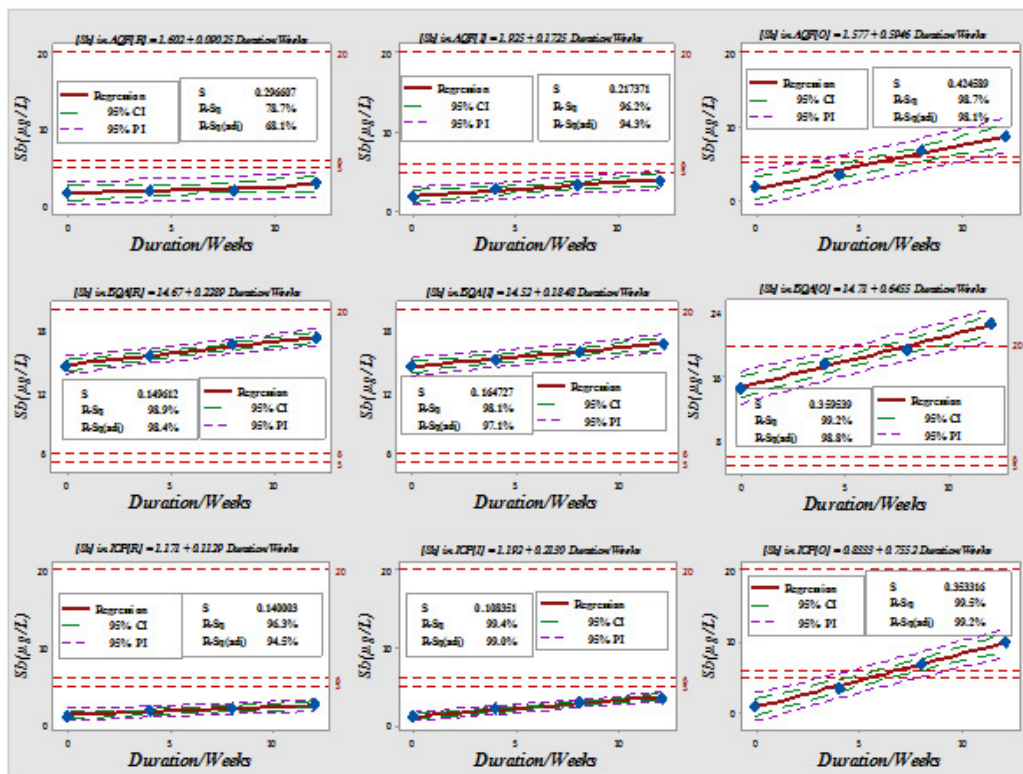


Figure 3.4.1a: Antimony amounts in PET bottled waters stored under selected conditions. Sb – antimony; CI – confidence interval; PI – prediction interval; S – standard error; R-sq. – coefficient of determination; R-sq.(adj) – adjusted coefficient of determination; [I] – bottled water stored indoor; [O] – bottled water stored outdoor; [R] – bottled water stored in refrigerator.

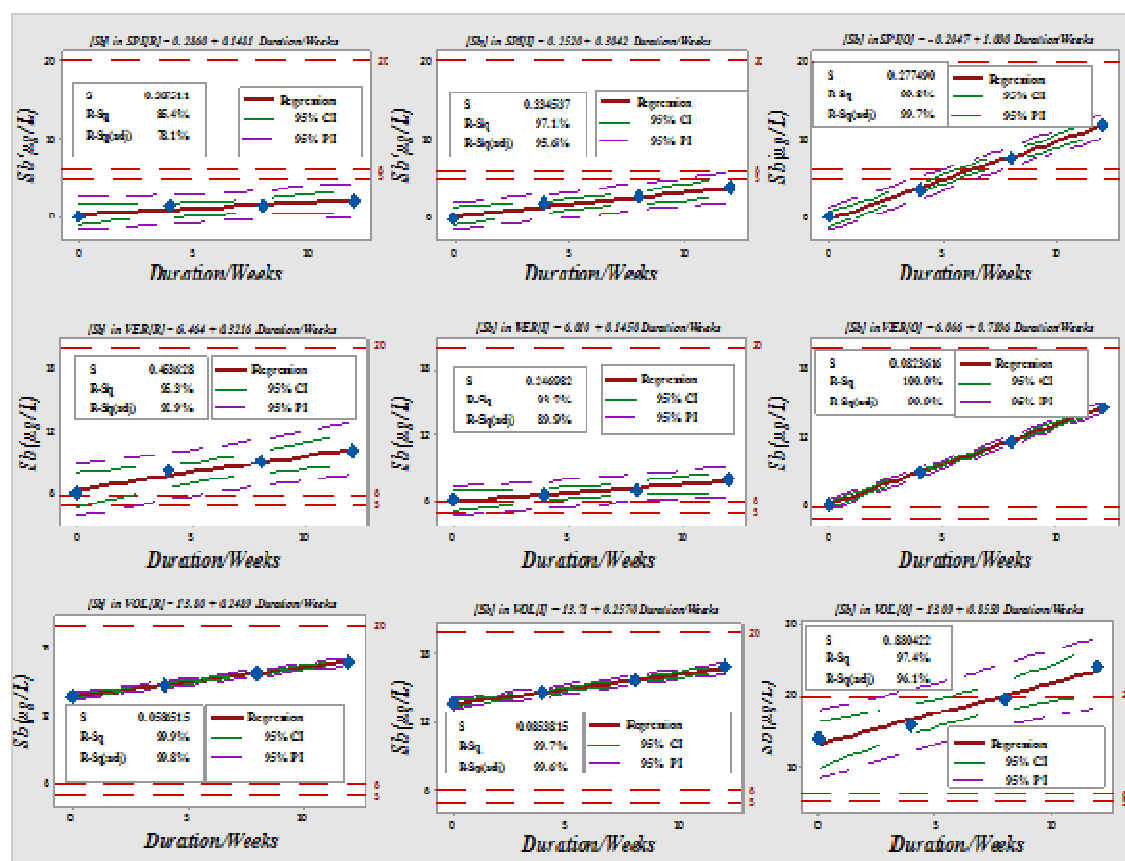


Figure 3.4.1b: Antimony amounts in PET bottled waters stored under selected conditions. Sb – antimony; CI – confidence interval; PI – prediction interval; S – standard error; R-sq. – coefficient of determination; R-sq.(adj) – adjusted coefficient of determination; [I] – bottled water stored indoor; [O] – bottled water stored outdoor; [R] – bottled water stored in refrigerator.

The presence of “substantial” amounts of dissolved Sb in some of the brands of bottled water samples determined on the day the waters were acquired was not likely to have originated from the PET plastic containers as, the contact time between the water and PET plastic containers was too minimal (less than 12 hours) to contribute to such “significant” amounts of dissolved Sb in brands BQA, VER, and VOL. This, therefore, places focus on the origin of the waters before bottling and the surrounding environment.

The bottled water companies are in the same region (Figure 2.1.2) but the source of water for bottling differ from one company to another. A visit to the production facilities revealed 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 Kpong.

In precipitates from hot springs, boreholes and in geothermal waters, Sb levels ranging 500mg/L up to 10wt.% have been recorded (Filella, Belzile, & Chen, 2002; Shotyky *et al.*, 2006). Slow moving groundwater in contact with buried ore deposits dissolves and transport trace elements like Sb forming aqueous dispersions (Grimes, Ficklin, Meier, & McHugh, 1995). Treated waters from sources like these are bound to have more amounts of the metalloid dissolved. This is because most of the purification steps are focused on the elimination of bacteria and particulate matter but not dissolved heavy metal contaminants like Sb. Thus, the origin of the water could have accounted for the presence of the “substantial” amounts of Sb in AQF, BQA, ICP, VER and VOL water samples. No Sb was detected in SPI water samples on week 0. There is, therefore, a high possibility that the rock from which the water was sourced does not contain Sb minerals.

The surrounding environment and treatment processes for the waters before bottling varies. Typical concentrations of dissolved Sb are usually very low – less than 1µg/L but in areas that are close to anthropogenic roots, levels can extend up to 100 times the natural levels (Dodd *et al.*, 1996; Zheng, Ohata, & Furuta, 2000). AQF bottling plant is located in an industrial area whilst BQA bottling plant is in a semi-industrial environment. Bottling plants of VOL, ICP, VER and SPI are located in areas that are considered to be relatively free from industrial activities (Figure 2.1.2). Generated airborne Sb compounds, especially in areas that have industrial

activities ongoing can find their way into water sources, thereby increasing dissolved amounts (Cavallo *et al.*, 2002). Thus, although manufacturers of BQA did not use water sourced from underground for production, the semi-industrial surrounding conditions could have contributed to the amounts of dissolved Sb determined in week 0.

Water samples stored under the three selected conditions typical of bottled water usage evidently showed differences in time series linear graphical patterns (Figure 3.4.1a and Figure 3.4.1b). Those stored in the refrigerator witnessed an increase in Sb from week 0 to week 12 for all brands of bottled water. BQA recorded the highest Sb at the end of week 12 under refrigeratory conditions. This was reached because of a major contribution from Sb determined on week 0. Despite the increments observed, none of the brands of bottled water had dissolved Sb exceeding the MCL specified by WHO at week 12 under refrigeratory conditions. Water samples stored indoor saw increase in Sb from week 0 to 12 for all the six brands of bottled water. VOL recorded the highest Sb (16.86µg/L) indoors at week 12. The major contribution of Sb was from Sb determined on week 0. Bottled water brands BQA, VER and VOL had Sb greater than the MCL defined by EU and US EPA but less than WHO MCL at week 12. Sb of water samples stored outdoor exposed to sunlight and high air temperatures increased from week 0 to 12 for all brands of bottled water. At week 12, VOL recorded the highest Sb (23.88 µg/L) followed by BQA. AQF recorded the least Sb (8.63µg/L) at the end of week 12. Sb obtained on week 0 were taken into considerations to realise such high amounts. Bottled water brands VER, AQF, SPI and ICP had Sb exceeding MCL Specified by EU and US EPA but below WHO MCL at of week 12. VOL and BQA, however, had Sb exceeding WHO MCL at week 12.

At least four out of the six brands of bottled waters under the three storage conditions saw a difference in means Sb exceeding 0.5µg/L from week 0 to 12. Moreover, this difference in mean was not uniform. Between the four weeks' intervals of the twelve weeks' period, the difference in means was below 0.5µg/L for one interval and sometimes above 0.5µg/L for the next interval. This difference of scientific significance undoubtedly reveals foremost: Sb may have been employed as the catalyst in the manufacture of the plastic bottles. Determined Sb in plastic bottles confirmed the preceding assertion (Figure 3.2.1). It is normally added as the glycolate or in the trioxide form. When added in the trioxide form, it readily converts to glycolate and at the end of the manufacturing process, it stays on attached to the polymer chain as glycolate complexes (Carneado *et al.*, 2015). Secondly, there is an indication that the residual Sb in the PET plastic containers is slowly dissolving – solubility of $5.8 \times 10^{-5} \text{ kmol/m}^3$ at 298K (Casas *et al.*, 2008) 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 Sb realised between time intervals.

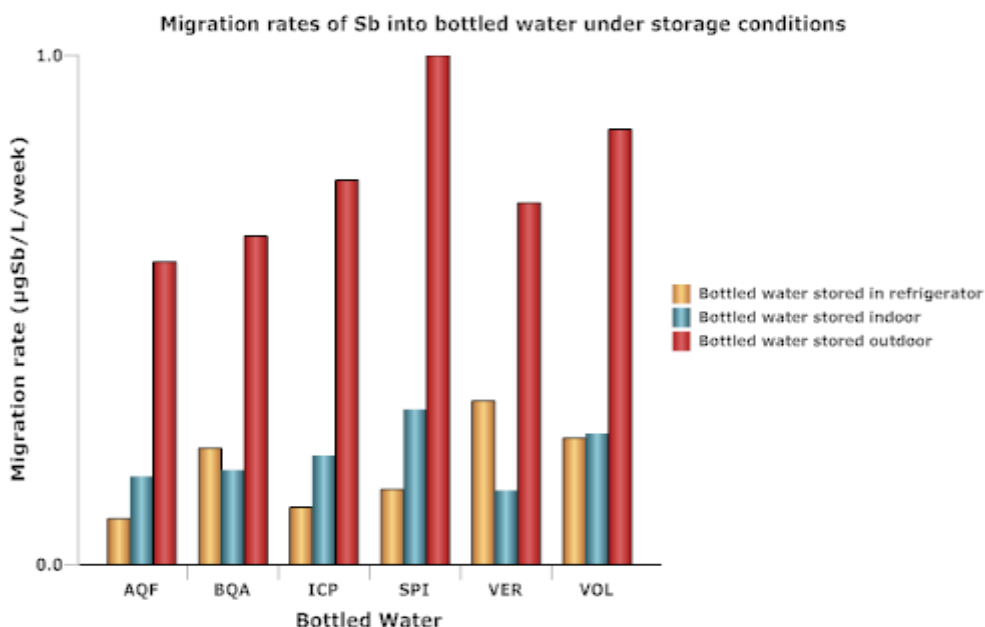


Figure 3.4.2: Migration rates antimony into bottled water under storage conditions. Bars represent migration rates

The various migration rates of Sb into the bottled water during the period are represented by the slopes of the linear equations (Figure 3.4.1a and Figure 3.4.1b). Bottled water samples exposed to high air temperatures and sunlight outdoor had averagely higher migration rates compared to those stored in the refrigerator and

indoors (Figure 3.4.2). VER recorded the highest migration rate in the refrigerator and AQF the least. SPI recorded the highest migration rate both in indoor and outdoor. A similar migration phenomenon was observed by Bach *et al.* (2014) who saw an increase in Sb 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, Sb migration is less affected by exposure to sunlight but rather, temperature and carbon dioxide contributed considerably to migration. As observed by researchers of previous studies, high temperatures accelerated the dissolution process of Sb from the PET plastic container resulting in high amounts of dissolved Sb 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 Sb which dissolve in the water (Bach *et al.*, 2014; Carneado *et al.*, 2015) In another study by Carneado *et al.* (2015), bottled waters stored at temperatures 4°C and 20°C were not subject to Sb migration whilst those stored at 40°C and 60°C saw a substantial increase in Sb. In contrast to that, our study saw significant increments ($\geq 0.50\mu\text{g/L}$ difference after 10 weeks) in Sb for bottled water samples stored under refrigeratory, indoor and outdoor conditions.

Waters packaged in PET bottles tend to have increments in Sb over time (Hureiki & Mouneimne, 2012; Keresztes *et al.*, 2009; Shotyk *et al.*, 2006; Westerhoff *et al.*, 2008). A comparable occurrence was observed for the six brands of plastic bottled water used in this study.

Dissolved Sb 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 least four out of the six brands of bottled water under refrigeratory, indoor and outdoor conditions had time affecting dissolved Sb of the water. This implied that the contact time between the PET plastic containers and the water was critical to the migration process of the metalloid (Fleeger, Carman, & Nisbet, 2003). The longer the contact or storage time, the higher the dissolved Sb (Fan *et al.*, 2014). A similar occurrence was 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 bottled waters were stored. Comparing the three simulated storage conditions for a period of one year using the time series linear equations to extrapolate (Figure 3.4.1a and Figure 3.4.1b), water held outdoor exposed to sunlight and high air temperatures (average temperatures: 23.0°C in the morning and 39.5°C in the afternoon) took shorter times to reach stipulated maximum contaminant levels (Table 3.4.1). Similar results were obtained by Bach *et al.* (2013), Carneado *et al.* (2015) and Fan *et al.* (2014). They observed that an increase in storage temperature accelerates the migration of Sb from the PET plastic container into the water. Furthermore, natural sunlight was found to contribute to the migration of Sb from the PET plastic container into the water (Bach *et al.*, 2014). Thus, these factors add up explaining why bottled water exposed to sunlight and high air temperatures recorded high Sb than their counterparts held under indoor and refrigeratory conditions.

Table 3.4.1: Duration for dissolved antimony to reach stipulated maximum contaminant levels (MCLs)

Storage Condition	Bottled Water	Weeks for TSb to reach EU MCL	Weeks for TSb to reach US EPA MCL	Weeks for TSb to reach WHO MCL
Refrigeratory	AQF	38	49	204
	BQA	**	**	23
	ICP	34	43	167
	SPI	32	39	133
	VER	**	**	42
	VOL	**	**	25
Indoor	AQF	18	24	104
	BQA	**	**	30
	ICP	18	23	88
	SPI	16	19	65
	VER	**	**	96
	VOL	**	**	24
Outdoor	AQF	6	7	31
	BQA	**	**	8
	ICP	6	7	25
	SPI	5	6	20
	VER	**	**	20
	VOL	**	**	8

** : cannot be defined by the linear equation; TSb: Total dissolved antimony; MCL: maximum contaminant level.

In summary, using the limited time before expiry (52 weeks for all the brands) quoted on the bottled water will render three (AQF, ICP and SPI) out of the six brands under the three selected storage conditions to have Sb not reaching the WHO MCL. For the other three brands (VOL, BQA and VER), MCLs were surpassed in comparatively shorter times because of major contributions from the sources. Thus, contamination via migration only will be improbable using the one-year limited time of expiry for the bottled water of these brands.

4. Conclusion

The study showed antimony was already present in some of the water before they were packaged in their plastic containers. This goes to support the notion that, some of the natural sources of water for bottling may contain “substantial” amounts of Sb. Differences in the rate of migration of Sb 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. 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 suggests that the contact time between the PET plastic container and water is critical to the migration of the metalloid. Longer contact times are usually associated with high antimony levels in the bottled water. The studied PET plastic bottled waters were found not to be exclusively contaminated with antimony leaching from their PET plastic containers within the limited time of expiry under WHO MCL specification. There is, however, evidence suggesting that, with time and the type of condition in which the bottled water is stored, Sb release is likely to be accelerated leading to contamination in a shorter time and subsequently harm to consumers.

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