University of Alberta

DETERMINATION OF ANTIMONY IN WATER, BEVERAGES, AND FRUITS

by

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ABSTRACT

Antimony is naturally occurring in the environment. The assessment of human exposure to environmental antimony is limited. This research focuses on the determination of antimony in water, beverages, and fruit.

First, we explored whether there is a correlation between arsenic and antimony in water samples with a wide range of arsenic and antimony concentrations. The results showed absent correlation.

Second, we determined antimony concentrations in bottled beverages including bottled water, soft drinks, juices and alcoholic drinks from Canada. The results showed that the antimony in most of these samples were below the Health Canada Guideline (6 μg/L) for drinking water except one alcoholic drink which contains 7 μg/L antimony.

Further analysis of lemons and oranges using high performance liquid chromatography (HPLC) separation and inductively coupled plasma mass spectrometry (ICP-MS) detection demonstrated the presence of antimony–citrate species in these fruits, which has not been reported in literature.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

As	Arsenic
Sb	Antimony
PHP	Potassium Hydrogen Pthalate
HPLC	High performance liquid chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
ESI-MS	Electrospray ionization mass spectrometry

Chapter 1. Introduction

1.1 Antimony in the Environment

Antimony (Sb) is a semi-metal element, atomic number 51 and atomic weight 121.75, found in Group 15 of the Periodic Table together with nitrogen (N), phosphorus (P), arsenic (As), and bismuth (Bi). Antimony is mainly found in the form of relatively insoluble sulfide compounds on the surface of the earth. The abundance of Sb in crustal rocks (0.3 μg/g) is lower than that of As (1.5 μg/g) [1]. The distribution and speciation of antimony in the environment have been poorly documented until quite recently, partly because it was difficult and expensive to analyze antimony with a sufficiently low detection limit. Recent studies have shown that the natural abundance of Sb in uncontaminated groundwater may be very low. The total concentration of antimony in unpolluted fresh water are normally below 1 μg/L. For example, in ground waters from southern Ontario, Canada, the average Sb concentration was only 2.2 ± 1.2 ng/L (n = 34) [2]. In oceans, the concentrations of Sb are about 0.2 μg/L. Concentrations of antimony in non-polluted soils and sediments, are about a few μg/g [3]. The antimony concentration in water has been extensively studied [4-22]. Industrial sources of antimony in the environment include fossil fuel combustion, mining and smelting

activities, and vehicle emissions [23].

1.2 Human Exposure to Antimony

The environmental levels of antimony can be affected by mining activity, burning of fossil fuels, smelting of ores, and the use of antimony in the manufacture of flame retardants, batteries, and ceramics. Contact with antimony occurs in a variety of ways.

1.2.1 Occupational exposure to antimony

The greatest exposure to antimony compounds over the long term has occurred in antimony processing workers. While the working environment of the antimony industry in Tyneside in the Northeast of England was being improved over 60 years, the effects of antimony exposure on the workers has been studied since the late 1940s. Over the last 60 years, exposure to antimony compounds, usually the ore stibnite (Sb_2S_3) or the oxide (Sb_2O_3), has occurred at high levels in workers processing the imported ore [24].

Occupational exposure to Sb can lead to “Sb spots” on the skin. Antimony process workers are excessively exposed to dirty working conditions, and controlling the dustiness of the process is necessary to reduce health risks from inhalation. Some Sb processing workers also suffered occasionally from headache, abdominal pain, constipation, and irritation of the inhalation system. Other health

effects were also observed, including heart disease and lung cancer. An excess of lung cancer was found in Sb processing workers, which brings antimony compounds under suspicion as carcinogens.

1.2.2 Antimony exposure of the general populations

From about 1988 on, Sb compounds were used as fire-retardants to meet the requirements of legislation designed to reduce the fire risk of furniture and furnishings. Fabric to which antimony compounds have been added smolder but do not burst into flames, thus restraining the spread of fire. Antimony was implicated in the cause of cot deaths, or Sudden Infant Death Syndrome (SIDS), in 1990 by Richardson [25]. A SIDS diagnosis is one of exclusion, and a cot death comes into that category when no other better defined diagnosis can be applied. Richardson suggested that antimony compounds used to fireproof cot furnishings (together with other additives) was primarily responsible for SIDS due to the action of a fungus (*Scopulariopsis brevicaulis*) growing on PVC cot mattress covers. In vitro experiments appeared to demonstrate the release of antimony species, from fire retardant and phosphorus plasticizers from polyvinyl chloride mattress covers which had been treated with these chemicals; the conclusion drawn from this work was that their toxicity had caused deaths [24]. People can also be exposed to Sb from breathing air, drinking water, and eating foods that contain Sb.

1.3 Toxicity of Sb(III) and Sb(V)

It is generally accepted that trivalent antimony compounds are more toxic than the pentavalent forms and a small number of results suggest that organoantimony compounds are less toxic than the inorganic forms [26]. All this information emphasizes the importance of identifying and quantifying the chemical forms of antimony to provide comprehensive information about its toxicity and environmental relevance.

Chemical speciation of elements in biological and environmental samples is important for the understanding of toxicity, metabolism, and transport properties of elements. Elemental Sb is more toxic than its salts and generally trivalent Sb compounds exert an acute toxicity 10 times higher than pentavalent Sb species [27] . Also, Sb(III) shows a high affinity for red blood cells and sulfhydryl groups of cell constituents, while red blood cells are almost impermeable to Sb(V) [28]. The International Agency for Research on Cancer (IARC) has assigned antimony trioxide to the group of substances which are suspected of being carcinogenic in humans (IARC) [29].

1.4 Detection of Antimony

The most common techniques for determining the total antimony concentrations include inductively coupled plasma mass spectrometry (ICP-MS),

graphite furnace atomic absorption spectrometry (GFAAS), and hydride generation (HG) coupled to an element-specific detector, such as atomic absorption spectroscopy (AAS) or atomic fluorescence spectrometry (AFS) [30]. However, the reality is that many natural water systems contain antimony concentrations close to the detection limit of these techniques (> 1 μg/L for AAS and 0.8 for AFS, 0.02 μg/L for ICP-MS). Shotyk et al. showed that use of inductively coupled plasma–sector field mass spectrometry (ICP-SMS) and clean laboratory methods are required for determining antimony not only in polar snow and ice but also in pristine groundwaters [2] Moreover, at such extremely low concentrations (<0.1 μg/L), not only is the detection limit of the analytical instrument a challenge, but contamination during sample collection, processing, and analysis is also a serious concern. It is also important to mention that the sample matrix may interfere the signal or cause peak shift, especially when determining Sb in complex organic matrices[31-34]. Finally, hydride generation techniques may not give 100% recovery when non-hydride-forming species are present in the sample because non-hydride-froming species can not be detected [35]. Antimony speciation has also been a challenging topic for many years. However, several reliable methods have been established using LC-MS as a platform [36-40]. In this thesis, we mainly used ICP-MS for the total analysis of Sb and HPLC-ICP-MS for Sb speciation because of the very low detection limit (0.02 μg/L for total concentration analysis, 1 μg/L level for speciation) and

relatively low interference for these methods.

1.5 Arsenic and Antimony

Because arsenic and antimony are in the same group of the periodic table, they have some similar chemical properties. Although antimony and arsenic could co-exist in nature, there is little information on the correlation or lack of correlation between these two elements in the environment. The occurrence of arsenic in water has been extensively studied, and many analytical techniques have been developed for arsenic detection [41-51]. Several groundwater aquifers throughout the world have been shown to have extreme high As concentrations, but similar locations are not reported for Sb [64-68]. It has been studied that in the uptake process of arsenic and antimony in cells of *Escherichia coli*, these two elements can influence the transportation behavior of each other, meaning that the toxicity of these two elements are related to each other [62]. The biomethylation of arsenic and antimony by fungus of *Scopulariopsis brevicaulis* are also associated. It's reported the methylation of antimony can be increased in the presence of arsenic. On the contrary, arsenic methylation will be inhibited with the presence of antimony [63].

1.6 Arsenic Distribution in Environmental Waters

In recent years, studies concerning high concentrations of As in groundwater in several regions across the world have been published [64-68]. Worldwide reported arsenic concentrations in natural water range from 20 ng/L to more than 5 mg/L. Chronic exposure to As in groundwater at concentrations over 500 μg/L may cause death in humans at a rate of 1 in 10 adults [64-66]. Arsenic presents naturally in two main oxidation states, arsenite As(III) and arsenate As(V), while As(III) is considerably more toxic than As(V)[67].

In several regions of Southeast Asia, where an estimated more than 100 million people are exposed to As in groundwater at concentrations greater than 10 μg/L, the As contamination of groundwater has been considered the most important environmental health problem [68]. About 60 million people in Southeast Asia are at risk of disease related to As, according to a study undertaken by World Bank. Other researchers have studied As contamination of soil and crops due to the use of groundwater contaminated with As being used for agricultural purposes, and the consequent risk to human health from ingestion of As-contaminated crops [70]. Arsenic exists worldwide in groundwater due to natural geological formations. Under certain environmental conditions, As can accumulate in both crops and fodder. Thus, ingestion of contaminated crops and vegetables, meat from animals ingesting contaminated fodder, as well as contaminated water could possibly lead

to risk of human health.

In Canada, arsenic is produced mainly as arsenic trioxide through arsenic gold ores[70] and is used mainly in metallurgical applications and in the manufacture of wood preservatives [71]. Arsenic is released naturally from rocks and soils into water through erosion, but human activities, such as mining processing, and the use of As pesticides and wood preservatives, as well as the disposal of waste materials, can also result in As contamination of water. High levels of arsenic, up to 1570 mg/L, have been reported in surface water and groundwater in Yellowknife [72]. The general Canadian population is exposed to arsenic from food and drinking water.

The concentration of arsenic in unpolluted surface water and groundwater in Canada usually ranges from 0.001 to 0.002 mg/L, and the levels of arsenic in drinking water are generally less than 0.005 mg/L [70]. There is a report, however, that in the town of Virden, Manitoba, arsenic levels ranged from 0.065 to 0.07 mg/L in the town's untreated source water, which originated as groundwater from an aquifer [72]. High arsenic concentrations have been reported in water near the vicinity of gold mining or ore roasting operations [73]. Other areas in Canada have also been reported to have high As levels; for example, concentrations up to 0.556 mg/L (averaging 0.0175 mg/L) were found in streams in British Columbia [74]. The As concentrations of the suspended particulates from Gegogan Lake, Nova Scotia, near an abandoned gold mine, ranged from 1500 to 5000 mg/kg, and

the arsenic content in filtered stream water ranged from 0.03 to 0.23 mg/L [77]. In the vicinity of Yellowknife, As concentrations in lake water ranged from 0.7 to 5.5 mg/L [75]. The surface water of Kam Lake, near Yellowknife, was estimated to contain up to 1570 mg/L of As [76]. However, little information was reported of As toxicity in people living near these areas.

Because arsenic and antimony are in the same group of the periodic table and they have some similar chemical properties, we reasoned that arsenic and antimony could co-exist in nature. Data on Sb is rarely obtained from these areas high in As, but highly As contaminated regions of the world could possibly be affected by Sb as well. To better understand the effects on human health caused by arsenic and antimony, it is necessary to study both arsenic and antimony concentrations in the environment. We hypothesize that in the environment there is a correlation between arsenic concentration and antimony concentration in water. The toxicity of these elements could be influenced by each other.

Studies have investigated the relationship between As and Sb in water. In this thesis (Chapter 2), we decided to determine the concentrations of both As and Sb in several natural water sources including samples collected from water plants across Canada, well water from northern Alberta, and river water from Xikuangshan mining site in Hunan China. These sets of water sample contain various of geochemical conditions and covered a wide range of concentrations of As and Sb in water samples. We hypothesize that a correlation could exist

between concentrations of As and Sb.

1.7 Regulations on Antimony

The importance of Sb determination is reflected by the fact that the U.S. Environmental Protection Agency (USEPA) considers it a priority pollutant. Antimony is regulated as a drinking water contaminant by, for instance, the USEPA, the Ontario Ministry of Environment, and Health Canada in municipal drinking water at a maximum contaminant level of 6 μg/L. The German Federal Ministry of Environment (5 μg/L), the European Union (5 μg/L), Japanese Ministry of Health, Labor and Welfare (2 μg/L), and the World Health Organization (20 μg/L) also have drinking water standards for antimony. The IARC has not classified antimony as a human carcinogen in water due to lack of studies. However, limited research shows that Sb has similar toxicity to As, a proven carcinogen [73].

1.8 Antimony in the Plastic Processing Industry

Antimony trioxide is the most important catalyst used in the manufacture of polyethylene terephthalate (PET). Bottles made using PET typically contain hundreds of mg/kg Sb in the plastic [76]. PET is produced by the polymerization of the petroleum monomers, terephthalic acid and ethylene glycol, using

antimony-, titanium- or germanium-based catalysts. Titanium catalysts may allow PET resin to be formed at higher temperatures, and no regulatory guidelines exist for titanium in drinking water [77]. No regulatory guidelines exist for germanium in drinking water either, and the metal has been used in some dietary supplements, although its overall human health effects have not been determined. But since germanium-based catalysts are more expensive than antimony-based catalysts, the latter account for more than 90% of the PET manufactured worldwide [76]. Both industry and municipal water agencies prefer to use PET plastics for bottled water because they are visibly clear. The consumers' preference for clear plastics is perhaps due to the perception of clear plastic being " visible clear."

1.9 Leaching of Antimony from PET Plastic to Drinking Water

Very low concentrations of Sb are detected in pristine groundwater, most published studies of Sb in bottled water report much higher values. A recent study of Sb in bottled water from Canada and Europe has shown that the water became contaminated during storage from Sb leaching from PET. Bottled water typically contains several hundred ng/L Sb, with much of this Sb stated to be due to leaching from PET [2]. In a study of bottled waters from Canada, Dabeka et al. found that 42 mineral waters averaged 320 ng/L Sb and 102 spring waters

averaged 300 ng/L [78]; these average values are more than 100 times greater than the average abundance of Sb found in pristine groundwater from southern Ontario, Canada (2.2 ± 1.2 ng/L) [2]. In a study of 56 bottled waters from Europe, the median Sb concentration was 165 ng/L which is high compared to its abundance in groundwater from Norway in which values are typically on the order of 30 ng/L but often less than 2 ng/L [79]. A study of Sb in bottled waters from Japan reported Sb above the limit of detection (500 ng/L) in 16 out of 55 brands [80]. A complicating factor is the widespread use of Sb in the manufacture of plastics; the lid of a plastic urine collection jar, for example, contained more than 100 mg/kg Sb. Moreover, a plastic dispenser commonly used to handle acids in the lab created a profound Sb contamination problem, with several μg/L Sb found in the dispensed HCl, compared with tens of ng/L Sb in the acid itself [2]. As a result, it is unclear at present whether the reported values for Sb in bottled waters are accurate reflections of the abundance of Sb originally present in the fluid, or whether the measured Sb concentrations represent a contamination level. The release of Sb from plastics into fluids might have wider implications for the study of environmental and health aspects of antimony. Public safety perceptions and convenience trends have led to greater use of bottled water instead of tap water. Another study looked into bottled waters from the United States, in which observed antimony concentrations ranged from <0.005 to >0.5 μg/L, and increased over time during storage [77]. This study compared the antimony

content of several bottled waters purchased in the southwestern U.S. and described the effects of storage temperature and exposure to sunlight on antimony release from PET plastic bottles into water; an accelerating effect on Sb leaching when exposed to temperature as high as 40°C was found.

Most commercially available bottled waters are sold in PET containers, as are other beverages, such as fruit juices. The findings of Shotyk et al., together with the fact that citric acid, a major constituent of citrus juices, has been reported to efficiently extract and preserve the oxidation state of Sb species present in solid materials [31], motivated us to study the Sb content of citrus fruit juices with regard to the total Sb concentrations and Sb speciation (Chapter 3).

1.10 Antimony in Fruit

In Chapter 4, we focused mainly on another possible source of Sb contamination in bottled juice—fruit. This is the first study of Sb compounds in fruit. Based on the results from Chapter 3, the Sb leaching behavior is quite different in various kind of fruit. Pergantis et al. also studied a broad range of commercially available orange and lemon fruit juices contained in PET bottles [82]. They found higher concentrations of Sb in juice than those in the bottled water studied by Shotyk et al. These results are consistent with ours (Chapter 3).

A previous study has shown that plants growing around Sb mining sites contain

higher Sb in their leaves and shoots than plants growing far from Sb mines [81]. We hypothesize that Sb in the bottled juice originates from the fruit. To test this hypothesis, we measured Sb concentrations in a range of fruit and characterized the antimony species in fruit. (Chapter 4).

1.11 Summary

The first objective was to determine and compare antimony and arsenic concentrations in drinking water samples in an attempt to explore whether there is a correlation between arsenic and antimony concentrations. While high concentrations of arsenic in drinking water affect millions of people around the world, little is known about the concentrations of antimony in drinking water. Our analyse of water samples contains a wide range of arsenic and antimony.

The second objective was to determine antimony concentrations in bottled beverages. Because antimony trioxide is a common catalyst used in the manufacture of polyethylene terephthalate (PET plastic), we hypothesize that the leaching of antimony from plastic bottles can result in elevated concentrations of antimony in beverages stored in PET plastic bottles. Further analysis of lemons and oranges is to demonstrate the presence of antimony in fruits. And the existing antimony in bottled juice could be the result of leaching from PET plastic and originally from the fruits.

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Chapter 2. Determination of Arsenic and Antimony in Natural Water

Introduction

Arsenic and antimony are in the same chemical group and therefore they exhibit some similarities in their behavior in the environment [30]. Both arsenic and antimony have high affinities for forming complexes with sulfide. In addition, both undergo conversions between their oxidized and reduced forms in response to changes in redox conditions and pH, and can be immobilized and mobilized by analogous processes in aquatic systems. Therefore, arsenic and antimony may occur in groundwater. However, considering their average crustal abundances, 1.5 μg/g for arsenic and 0.3 μg/g for antimony [31], arsenic might be expected to occur in water at substantially higher concentrations than antimony.

Exposure to high levels of arsenic is known to be associated with increased risk of skin, lung, and bladder cancer [1-10]. It is estimated that more than 100 million people around the world are exposed to arsenic in drinking water at concentrations exceeding the Health Canada Guideline (10 μg/L) [11-14]. The occurrence of arsenic in water has been extensively studied [15-19], but much less attention has been paid to antimony. Limited studies have shown that antimony species are as potentially toxic as arsenic species [20-22]. Therefore, it is important to determine

antimony species in water.

Another reason that motivated us to study the arsenic and antimony correlation is that during the uptake process of arsenic and antimony into cells, these two elements can influence the transport behavior of each other, meaning that the toxicity of these two elements are related to each other [23]. The biomethylation of arsenic and antimony by fungus are also associated. It's reported the methylation of antimony can be increased in the presence of arsenic. On the contrary, arsenic methylation was inhibited with the presence of antimony [24]. We hypothesize that in the environment there is a correlation between arsenic concentration and antimony concentration in water. This chapter describes the experiments to test this hypothesis and the results obtained. Groundwater and surface water samples were analyzed for both As and Sb to reveal any correlations between As and Sb. Water samples were collected from wells, Xikuangshan antimony mine site in Hunan, China, and tap water originating from rivers and lakes across Canada. This study is the first attempt to discover whether there is any correlation between As and Sb. These sets of water sample contain various of geochemical conditions and covered a wide range of concentrations of As and Sb in water samples.

2.1 Reagents, Instrumentation, and Methods

2.1.1 Antimony standards and other reagents

Antimony (III) (Sb(III)) and antimony (V) (Sb(V)) solutions were made by dissolving <10 mg of antimony(III)-oxide (Sigma Aldrich, Oakville, ON, Canada) or potassium hexahydroxo-antimonate into 1 L of water. The solutions were stirred overnight at room temperature, after which, they were decanted off, calibrated, and speciated. It is important to note that only glass containers were used to store both the standards and the solutions used to dilute them. This was because some of the small plastic containers were found to leach small amounts of Sb(V) into the solutions that they held in our experiments.

Solutions of the antimony species were calibrated against a multi-element calibration standard (Agilent, USA), which contained 10 µg/L Sb. The calibrations were verified using the NIST 1640 natural water standard from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Calibrations were developed by our group using flow injection ICP-MS, with 20 µL injection volumes, a 1% nitric acid mobile phase, and a flow rate of 1 ml/min. All reagents were of analytical grade quality or better. All water used was distilled and deionized.

2.1.2 Instrumentation

ICP-MS

The total Sb concentration was directly detected using an Elan 6100 DRC^{plus} ICP-MS (PE Sciex, Concord, ON, Canada), with Turbochrom Workstation v.6.1.2 software (PE Instruments) for data processing. The instrument was operated in standard mode. Antimony was monitored using both the ^{121}Sb (57.25%) and ^{123}Sb (42.75%). For quantification, external calibration was used, and minimal drift was seen. For total antimony analysis, ICP-MS was used, with 1 mL/min 1% HNO_3 as the carrier solution and 20 μL injections. External calibration was done and verified using the NIST 1640 natural water standard sample.

Statistical Analysis

All the results are reported in mean value ± standard deviation. To evaluate the correlation between arsenic and antimony concentrations in water samples Pearson's r was used to measure the linear correlation among concentrations variables. The correlation coefficient (R^2) was used to measure whether the variables are linearly related. The P value for correlation coefficient was calculated. A P value less than 0.05 was regarded as significantly different from control values.

2.1.3 Determination of arsenic species in water samples

The quantification of arsenic species in water samples was carried out using ion-pair chromatographic separation and inductively coupled plasma mass spectrometry (ICP-MS) detection. A Perkin-Elmer 200-series liquid chromatograph, equipped with an autosampler, quaternary pump, and column temperature compartment, was coupled to a Perkin-Elmer 6100 DRC^{plus} ICP-MS. Chromatographic separation of inorganic As(III) and As(V) was achieved on a reversed-phase C18 column (Phenomenex, 30 × 4.6 mm, 3-µm particle size) maintained at 50^{o}C. A mobile phase contained 5 mM tetrabutylammonium hydroxide, 3 mM malonic acid, and 5% methanol at pH 5.70. The ICP-MS was operated with the oxygen mode (to reduce isobaric interference); and arsenic oxide at m/z 91 was monitored. The NIST standard reference material 1640 Trace Elements in Natural Water was used for quality control. The method detection limits for both As(III) and As(V) were 0.1 µg/L.

2.1.4 Quantification of arsenic species in water from Health Canada using HPLC-ICP-MS

Arsenic species in water samples were quantified using high performance liquid chromatography (HPLC) separation with inductively coupled plasma mass spectrometry (ICP-MS) detection. An Agilent 1100 series HPLC system was

coupled with Agilent 7500cs octopole ICP-MS system (Agilent Technologies, Tokyo, Japan). The ICP was operated at a radio frequency power of 1550 W, and the argon carrier gas flow rate was 0.9–1.0 L/min. The ICP-MS was operated with helium mode, and helium (3.5 mL/min) was introduced to the octopole reaction cell to reduce isobaric and polyatomic interferences. Arsenic was monitored at m/z 75.

Chromatographic separation of inorganic arsenite As(III) and arsenate As(V) was achieved on a reversed-phase ODS-3 column (Phenomenex, 30×4.6 mm, 3-μm particle size) with an ODS guard cartridge (4×3 mm). The column was placed inside a column temperature compartment, which was maintained at 50 °C. The aqueous mobile phase contained 5 mM tetrabutylammonium hydroxide, 5% methanol, and 3 mM malonic acid (pH 5.65), and its flow rate was 1.2 mL/min. Aliquots of 50 μL water samples were injected for analysis. The effluent from the HPLC column was directly introduced into the nebulizer of the ICP-MS system using a PEEK tubing. Chromatograms from HPLC separation and ICP-MS detection were recorded and processed using the ChemStation software (Agilent Technologies, Santa Clara, CA).

A standard reference material SRM1640, Trace Elements in Natural Water (NIST), was used for quality control. The method detection limits for both As(III) and As(V) were 0.1 μg/L.

2.1.5 Determination of total antimony in water samples

The concentration of total antimony in water was determined using a Perkin-Elmer 6100 DRC ^{plus} ICP-MS, operated in standard mode. A 20-µL sample was injected into a 1% nitric acid carrier stream at a flow rate of 1 mL/min. Isotopes of Sb, ^{121}Sb, and ^{123}Sb were monitored for quantification. The detection limit of Sb was 0.02 µg/L.

2.1.6 Water sample collection

Water samples were collected from three sources. The first set comprising 121 water samples was from 36 sampling sites from rivers, wells, and lakes across Canada collected by Health Canada (Table 2-1). The initial intention was to evaluate the level of As and to compare the As concentrations with the Health Canada Guideline for drinking water. In the meantime, we were also interested in determination of Sb concentration in these samples. We also include blank samples from the sampling field to insure minimum of contamination was involved. Duplicate water samples were collected from the field to avoid error sampling. The samples were sealed in brown glass vials during the transportation, and were stored in 4℃ once they arrived at our lab.

The second set of samples comprised 239 water samples collected by Alberta Health and Wellness from northern Alberta. The government of Alberta was

interested in the As concentrations in wells on which the locals rely, and also wanted to monitor the efficiency of the filters used by local families. Therefore, some of the samples were collected directly from the wells, while others were collected after the water passed through the residence filtration facilities. This set of samples was ideal for us to examine the correlation of Sb and As from natural water sources in Alberta.

We also had another set of water samples (n=16) collected from an antimony mining sites in Xikuangshan, Hunan China. The Sb concentration was expected to be much higher than its average concentrations in water samples.

2.2 Results and Discussion

In the total 121 water samples collected by Health Canada, the mean value of As concentration was 0.52 μg/L with a range of 0.01 μg/L to 4.8 μg/L. The concentrations of Sb, however, are much lower: the mean value is 0.13 μg/L within a range of 0.01 μg/L to 0.80 μg/L. These concentrations of both As and Sb are the lowest of these three sets of samples. The results are shown in Figure 2-1.

In the total 239 samples from Alberta Health, the mean value of As concentration is 9.6 μg/L, with a very large range from non-detectable(<0.02 μg/L) to 44.7 μg/L, and the concentrations of Sb are still much lower than As, as shown in Figure 2-2.

The As concentrations in the water samples from Health Canada and Alberta Health are the sum of As(III) and As(V) concentrations, which were determined using HPLC-ICP-MS by one of our colleagues, Dr. Baowei Chen.

In 16 samples from an antimony mining site in China, the concentrations of both As and Sb are the highest among these three sets of samples; and the concentration of Sb is much higher than that of As (Fig.2-3). The mean value of As concentration is 0.59 μg/L within variation range from 0.19 μg/L to 1.83 μg/L. The mean value of Sb concentration is 4.9 μg/L within a range from 0.33 μg/L to 11.4 g/L.

The detection limits for arsenic species using an HPLC-ICP-MS method have been reported to be between 0.2–1.0 μg/L [25-27]. The detection limits for antimony species using an ICP-MS method have been reported to be 0.04 μg/L [28,29]. In our study, HPLC-ICP-MS was able to separate and detect As(III) and As(V) at levels as low as 0.1 μg/L. Antimony was detected at levels as low as 0.05 μg/L using ICP-MS.

In the published literature, arsenic and antimony have been shown to exist in several groundwater aquifers throughout the world [33-45]. Only a few studies have documented the presence of both arsenic and antimony species in the same area. In Bangladesh, where arsenic concentrations are known to be elevated, no published studies have reported on the potential correlation of arsenic and antimony. Frisbie et al. [32] surveyed 112 wells throughout Bangladesh and across

a variety of geochemical conditions, and reported that Sb concentrations ranged from 0.0015 to 1.8 μg/L, and that no correlation between As and Sb concentrations was found. In 2004, McCarty et al. measured 245 well water concentrations of arsenic and antimony in the Pabna region of Bangladesh. The arsenic concentrations ranged from < 1 μg/L to 747 μg/L and all water samples had antimony concentrations < 1 μg/L. McCarty et al. confirmed that no significant correlation between arsenic and antimony was found in well water in Pabna, Bangladesh. This result was also consistent with the study prepared by the British Geological Survey [33]. In the Xikuangshan antimony mine area in Hunan, China, high levels of antimony and moderate levels of arsenic are reported to be present in the aquatic environment. The antimony concentrations ranged from 8.66 μg/L to 156 μg/L, and the arsenic concentrations from 0.56 μg/L to 11.3 μg/L. The ratio of Sb/As was 2.99 to 48.7; indicating poor correlation [34]. In another investigation on arsenic and antimony concentrations in the Xikuangshan antimony mining site, significant correlation was found between the concentrations of arsenic and antimony in human hair samples from the local residents [35]. Landrum et al. measured arsenic, antimony, and other heavy metal elements in aqueous, mineral, and biological reservoirs from the El Tatio Geyser Field, Chile. The results suggest no correlation between arsenic and antimony [36]. The same results were found in Ghana [37], Greece [38], New South Wales, Australia [39], Poland [40-44], and Texas, USA [45].

This study aims to determine any correlation between As and Sb in natural water sources from Canada and a Chinese mining site. The measured water samples from rivers, lakes, and wells across Canada are low in both As and Sb: the As is below 5 μg/L and the Sb is below 0.8 μg/L. The antimony concentrations ranged from non-detectable to 0.80 μg/L whereas the arsenic concentrations varied significantly from non-detectable to 4.8 μg/L. These results are within the range of As as the background in surface water in Canada. The large variation in the arsenic concentration could possibly be due to population of aquatic organism in different aquifers. Fu et al. [34] indicated that antimony can accumulate in fish at much lower levels than arsenic; thus, arsenic concentration would be affected by aquatic organisms more than antimony. The correlation coefficient result (R^2 = 0.2421) reveals no correlation between the concentrations of antimony and arsenic. While the Pearson's r value ($r = 0.492$, $p < 0.05$) suggests there are median ($0.3 < r < 0.5$ is considered as medium correlation) correlation between arsenic and antimony levels.

The well water collected from northern Alberta is the major source of water for the local residents. The results reveal that the concentrations of As and Sb in these well water samples are higher than in the first set of surface water samples (i.e. from rivers, lakes ad wells across Canada).

The Sb concentration is expected to be high in the water samples collected around the antimony mining site in China. The antimony concentrations are

within the range of values reported by other authors examining mine-contaminated waters (several mg/L) [46] while the arsenic concentrations are much higher. The statistical results shows no significant correlation between arsenic and antimony concentrations in water samples from northern Alberta (R^2 = 0.137, r = 0.117, p > 0.05) and Chinese mine (R^2 = 0.0185, r = - 0.136, p > 0.05). We have to admit that the concentration of As and Sb in the water can only reflect how much chemical is dissolved into the water, while the actual amount of As and Sb in the soil and rocks around the water source could be different.

Arsenic and antimony are individually considered to be potentially toxic to human health on different levels, and each is regulated in drinking water by the USEPA. The concentrations of arsenic and antimony in water were compared with the USEPA and Health Canada guidelines for drinking water (As 10 μg/L, Sb 6 μg/L) because water is a major source of human exposure to arsenic and antimony. The concentrations of antimony in the well water samples collected by Alberta Health and Wellness and Health Canada are lower than the Health Canada guideline for drinking water. Some of the water samples collected around the antimony mining site exceeded the Health Canada antimony level guideline. The arsenic concentrations in surface water samples collected by Health Canada were well below the Health Canada guideline, but some of the samples from well water in northern Alberta and from Chinese mining site exceeded the guideline. The exposure of local residence to As and Sb need to be evaluate for further

assessment of health risks.

Arsenic and antimony may impact human health if exposures are high enough. Further research is required to reveal the behavior of As and Sb correlations in humans.

2.3 Conclusion

The first objective was to determine and compare antimony and arsenic concentrations in drinking water samples in an attempt to explore whether there is a correlation between arsenic and antimony concentrations. While high concentrations of arsenic in drinking water affect millions of people around the world, little is known about the concentrations of antimony in drinking water. Our analyses of water samples contains a wide range of arsenic and antimony. Our results showed lack of correlation between As and Sb concentrations in water samples.

Table 2-1. Health Canada water sample collection sites.

1. Capital region District (BC) – river, chlorination, chloramination, UV
2. Repentigny (QC) – river, chlorination, ozonation, pharma study
3. Montreal–Atwater (QC) – river, chlorination, ozonation
4. Quebec (QC) – river, chlorination, ozonation
5. Prince George (BC) – river, chloramination, fluoridation
6. Mannheim (ON) – river, chloramination, ozoanation, UV
7. TBD (Nun) – river, chlorination
8. Metro Vancouver (BC) – river/well, ozonation
9. Swift Current (SK) – river, chlorination
10. Erickson Creek (BC) – river, UV, membrane filtration
11. Trenton (ON) – river, chlorination,
12. Lavaltrie (QC) – river, chlorination, UV, pharma study
13. Lindsay (ON) – river, chlorination
14. Fort Nelson, Muskwa (BC) – river, chlorination, silt
15. St. George's Dribble Brook (NL) – river, chlorination, low pH
16. Hearst (ON) – river, chlorination
17. Alexandria (prov?) – river, chlorination
18. Port Harding (BC) – river, chlorination
19. TBD (Nun) – melt water, chlorination
20. St. J. Windsor Lake (NL) – lake, chloramination, UV
21. F. J. Horgan (ON) – lake, chloramination
22. St. John. Bay Bulls (NL) – lake, ozonation
23. Prince Albert (SK) – lake, chlorination
24. Iqualuit (Nun) – lake, chlorination
25. Ameliasburgh (ON) – lake, chlorination
26. Granby (QC) – lake, chlorination,
27. Courtenay/Comox (BC) – lake, chlorination
28. Caramat (ON) – lake, chlorination, NDMA detected
29. Oka (QC) – lake, chlorination
30. Saskatoon (SK) – well, chlorination
31. Whistler (BC) – well, chlorination
32. Stephenville (NL) – well, chlorination
33. Charlottetown (PEI) – well, chlorination
34. Souris (PEI) – well, chlorination
35. Princeville (QC) – well, chlorination
36. Georgetown (PEI) – well, not chlorinated

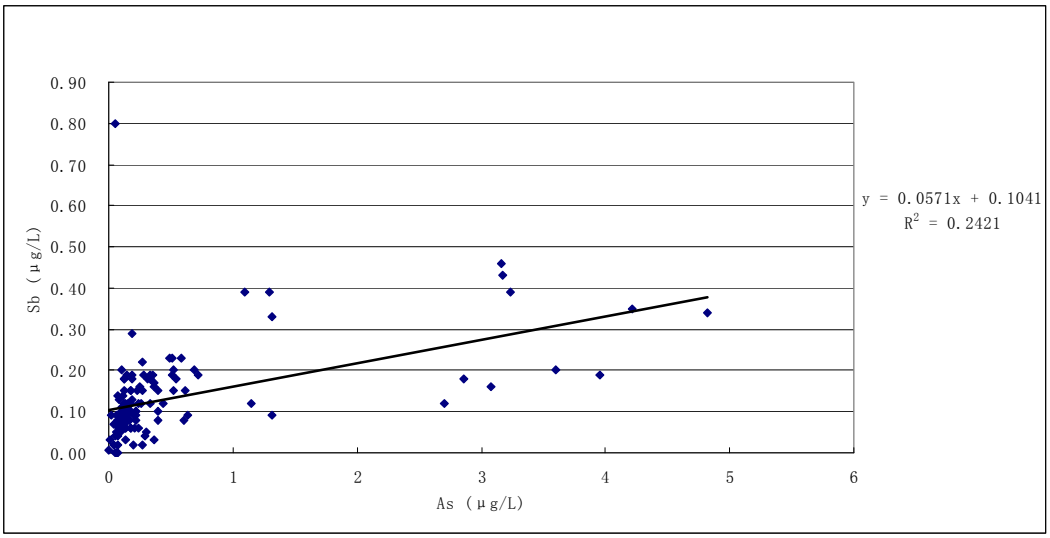

Figure 2-1. Concentrations As and Sb in water samples from Health Canada. n=121, r=0.492, $p<0.05$

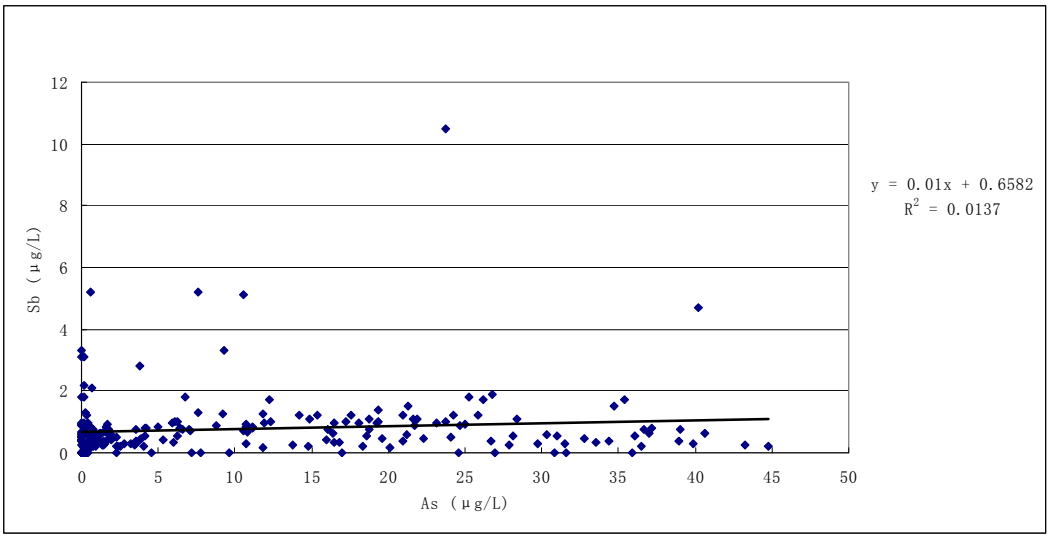

Figure 2-2. Concentrations of As and Sb in water samples from Alberta Health, n=239, r=0.117, p>0.05

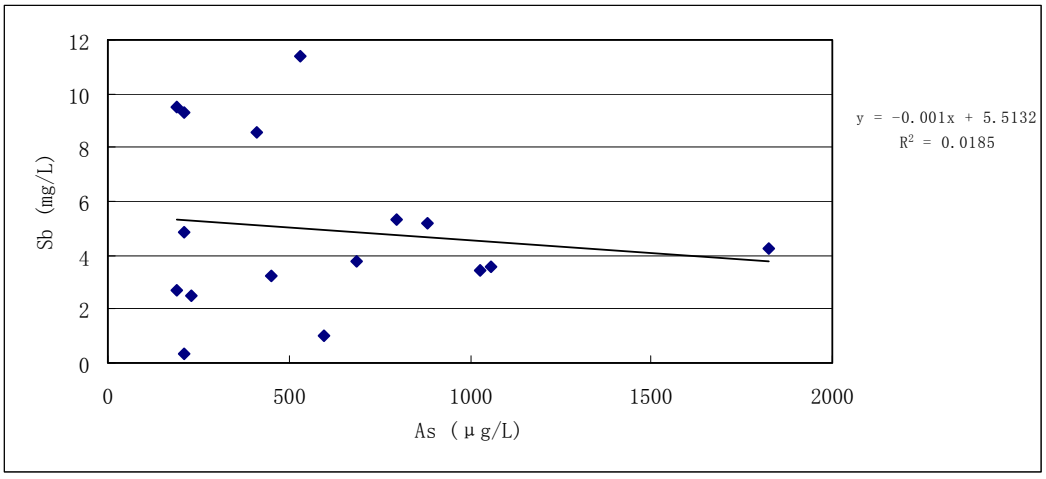

Figure 2-3. Concentrations As and Sb in water samples from Xikuangshan, Hunan China mining site. n=16, r=-0.136, p>0.05

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Chapter 3. Determination of Antimony in Beverages

Introduction

Antimony is a potentially toxic trace element [1-12]. It is found in very low concentration in unpolluted natural water [13, 14] as well as tap water [15-20]. The greatest exposure to antimony compounds has occurred in antimony processing workers with inhalation [21, 22]. Much less attention has been paid to antimony exposure in the general population [23]. Both industry and municipal water agencies prefer to use PET plastics for bottled water because they are visibly clear. The consumers' preference for clear plastics is perhaps due to the perception of clear plastic being "visible clear." In recent years, antimony was found in low concentrations in commercial bottled waters [13, 24-26]. Most commercially available drink bottles are made of polyethylene terephthalate (PET) plastic, which uses Sb as the catalyst in production. Shotyk et al. [13, 24, 25] has shown that Sb could leach into water from plastic bottles. However, the antimony concentration is lower than the USEPA and Health Canada Guideline for drinking water (6 μg/L) [27]. This research, together with the possibility that citric acid could extract Sb species from solid materials [28], motivated us to study the Sb content of citrus fruit juices stored in PET bottles for 6 months apart. We also

tested the possibilities of the other chemical compositions that commonly present in beverages (Vitamin C, Calcium, Magnesium, Potassium, Iron, and Citric acid) can leach Sb.

3.1 Experimental Methods

The reagents and analytical instrumentation were the same as described in Chapter 2. All the results are reported in mean value ± standard deviation. P value from t-test was calculated to evaluate the significance of difference between two sets of data.

3.1.1 Sampling of the beverages

Thirty-two tap water samples were collected from across Canada as comparison with beverages. They were sealed and transported in brown glass bottles and were stored at 4 ^{o}C once they arrived at our laboratory. We obtained ten types of bottled water in plastic bottles, twelve types of soft drinks, and thirty types of fruit juice from local grocery stores in Edmonton, Canada. Twenty-eight types of alcoholic drinks were collected from local liquor stores in Edmonton, Canada, and another six types were collected from Vancouver, Canada, by Dr. William R. Cullen's group in Chemistry Department at the University of British Columbia. The alcoholic drinks from UBC were collected without storage in plastic bottles originally, and then measured with storage in plastic bottles in six-month apart.

All plastic bottles were labeled as “PET plastic.” We collected three 10-μL samples from each type of beverage, transferring the samples into glass vials for further testing, and kept the remainder of each beverage in its original bottle for the six-month duration study. All of the samples were stored at room temperature and were not directly exposed to sunlight but instead to light from artificial sources.

3.1.2 Sample preparation

All of the beverage samples described here were measured for Sb in December 2008 for the first time and in May 2009 for the second time. An Elan 6100 DRC^{plus} ICP-MS (PE Sciex, Concord, ON, Canada) was used for the quantification of Sb in all samples. For analysis of juices and alcoholic drinks, samples were diluted ten times to reduce the concentration of sugar and ethanol as well as the viscosity which could lead to clogging of the instrument cones. All samples were filtered through a 0.45 μm filter and transferred to pre-washed glass vials. Analytical accuracy and precision for the measurements were determined by analyses of water standard reference materials NIST 1640; precisions were within 3%. Measured and certified values for standards were within the quoted errors. The limit of detection was below 0.02 μg/L.

3.1.3 Effect of pH on Sb leaching

Several experiments were launched to study factors that could potentially affect Sb leaching from PET bottles. Fruit juices contain a lot of acid which makes the juices in a wide range of pH values. We hypothesized that the pH value can affect Sb leaching from PET plastic. DASANI-brand PET plastic bottles originally containing bottled water were emptied and the bottles were then filled with nitric acid adjusted solutions. The pH range was 2 to 7, which covers the pH values of drinking water, soft drinks, and juices. The bottles were stored at room temperature overnight. All water samples were shaken before testing.

3.1.4 Effect of vitamin C, Ca^{2+}, Mg^{2+}, K^{+}, Fe^{3+}, and citric acid on Sb leaching

Besides examining the effect of pH on Sb leaching, we also considered the effect of other chemical content found in fruit juice. Vitamin C, $CaCl_2$, $MgCl_2$, KCl, $FeCl_3$, and citric acid were chosen for the study according to the chemical compositions listed on juice bottles. The concentrations for these chemicals in water solution were: vitamin C (0.5 mg/mL), Ca^{2+} (0.1 mg/mL), Mg^{2+} (0.03 mg/mL), K^{+} (0.05 mg/mL), Fe^{3+}(0.01 mg/mL) and citric acid (0.3 mol/L). The concentrations were according to the ingredients list of commercial beverage, and the mean values were chosen for this experiment. DASANI-brand PET plastic

bottles were emptied of their original contents (commercial bottled water) and filled with solutions mentioned above. These solutions were stored at room temperature for four weeks. At the beginning of each week, we removed 1 mL of these solutions for analysis using ICP-MS. All samples were shaken before testing.

3.1.5 Effect of citric acid concentrations on Sb leaching

The concentration of citric acid is an important factor with an effect on Sb leaching. We emptied the DASANI-brand PET plastic bottles of their original contents (commercial bottled water) and filled them with dilute citric acid with concentrations ranging from 0.1 to 0.5 mol/L, because citric acid exists naturally in citrus fruit juice at a concentration around 0.3 mol/L [32]. We stored these solutions for four weeks at room temperature and each week we removed 1 mL of each solution for analysis. All samples were shaken before testing.

3.2 Results and Discussion

3.2.1 Antimony in PET plastic

Plastic packaging is classified in seven groups according to its composition. Each group of plastic polymers can be identified by its Plastic Identification Code (PIC) [30]. For instance, polyethylene terephthalate can be identified by the

number 01 and/or the letters “PET.” The PIC usually appears on the bottom of plastic bottles.

PET plastic is one of the most popular plastic materials in food packaging. The production of PET bottles comprises 30% of the global demand of bottle production [31]. The bottled beverages examined in this study were contained in PET plastic bottles. Antimony is often used in the production of PET as a catalyst. After manufacturing, residual antimony remains within the material itself.

3.2.2 Comparison of Sb concentrations in different beverages

All tap water samples investigated were collected from across Canada and placed in glass containers. The 32 tap water samples in this study had a consistent Sb level, 0.2 ± 0.1 μg/L. The results of the analyses of bottled water in PET plastic bottles reveal that the bottled water samples (0.4 ± 0.2 μg/L, n = 10) contained Sb concentrations slightly higher than the tap water samples (0.2 ± 0.1 μg/L, n = 12). The p values from the t-test were: bottled water vs. tap water, 0.012; soft drinks vs. tap water, below 0.001. This result is consistent with previously reported data [13, 15-20, 24, 25].

In contrast to these data, samples of juices and alcoholic drinks contained in PET plastic bottles yielded much more Sb: juices contained Sb ranging from 0.5 to 2.6 μg/L with a mean concentration of 1.4 μg/L (n = 30) and alcoholic drinks contained Sb from 0.03 to 6.9 μg/L with a median concentration of 2.5 μg/L (n =

28). The p value from the t-tests between drinking water and juice is below 0.0001; between drinking water and alcoholic drinks, it is 0.0016 (Figure 3-1).

We note that, except for one alcoholic drink, other beverages (including bottled water) contain Sb in concentrations below the maximum allowable guideline for drinking water in Canada, which is 6 μg/L.

3.2.3 Sb leaching from PET bottles into juices and alcoholic drinks upon storage

Bottled drinking water has been reported to leach Sb during long term storage [13]. There is no published study, however, examining the amount of Sb leaching into juices and alcoholic drinks contained in PET plastic bottles.

Here we measured the Sb concentrations of PET bottled juices and alcoholic drinks at the beginning and end of the six-month study period (Figures 3-2, 3-3 and 3-4). The first 13 different juices examined were apple (3 brands), strawberry (4 brands), mango (2 brands), peach (2 brands), and pineapple (2 brands) juices, which contain low levels of citric acid. The next 17 different juices examined were orange (11 brands) and lemon (6 brands) juices, which are rich in citric acid. Over the six-month storage at 18°C , there were no significant difference in the Sb concentrations in the low citric acid juices, but Sb concentrations increased in the citric acid rich juices. In four citrus juices, the Sb concentration increased by 25% in average after 6 months storage. However, after storage, all samples contained

Sb levels below the Health Canada Guideline for drinking water of 6 μg/L. The production time and storage period of each beverage before it arrived at our lab was not clear. Some of them may have been stored for longer time than others.

We noticed that not only juices in PET bottles contained Sb, but also juices in glass bottles. Six replicates of lemon and orange juices stored in glass bottles showed no detectable increase of Sb in 6 months apart (Table 3-1). Therefore, the natural abundance of Sb in plastic bottled juice could be obtained from both the PET bottles and the fruit.

Figure 3-3 is the result of 6 alcoholic drinks and one control sample collected and analyzed by UBC. The alcoholic drinks were collected and analyzed before they were stored in plastic bottles. Then the Sb concentrations were measured again in six-month storage in PET bottles. The initial concentration of Sb of the UBC samples were low compared with the alcoholic drinks analyzed by our group (Figure 3-4) of which the production time and storage period are not clear. The leaching of Sb in alcoholic drinks samples did not have a clear trend. However, we did see Sb concentrations increasing in most of the alcoholic drinks stored in PET plastic bottles after six months of storage. This indicates that alcoholic drinks can also enhence Sb leaching from PET plastic.

3.2.4 Study of factors on Sb leaching

Studies have reported that drinking water stored in PET plastic bottles can leach

Sb [13, 24, 25]. Our results demonstrated that the juices and alcohol contained in PET bottles yield much more Sb than bottled water and soft drinks. We suspect there must be some potential factors promoting this leaching process.

Several experiments were conducted to study the factors that could potentially affect Sb leaching from PET bottles into juices. Fruit acid, Vitamin C, trace elements are investigated in this experiment. Figure 3-5 summarizes the results of control tests using PET bottles filled with pH-adjusted deionized water. Nitric acid was used to adjust the pH value. The pH value of the solutions were measured every week before Sb determination. No significant change was observed in pH values. The increasing of pH had little effect on Sb leaching over the range studied, suggesting that Sb leaching observed in juices is not due to low pH of the juice.

We also tested other factors that could potentially affect Sb leaching from PET bottles, including vitamin C, calcium, magnesium, potassium, iron, and citric acid. Figure 3-6 shows the results of the effect of these chemical components on Sb leaching from PET plastic. Vitamin C, calcium, potassium, and iron did not affect Sb leaching while magnesium had a small effect on Sb leaching over the four-week study. In contrast to other chemical components, citric acid increased Sb leaching. The concentration of Sb increased from 0 to 1.2 μg/L during the four-week study in the presence of 0.3 mol/L citric acid. We also noticed that in the long-term storage, the juices with higher citric acid content (Fig. 3-2) [32]

tended to release more Sb from the PET bottles in the same period of time.

In order to study the effect of the concentration of citric acid on Sb leaching, we prepared a set of citric acid solutions. The concentration of citric acid in citrus fruit ranges from 0.10 mol/L in oranges and grapefruit to 0.30 mol/L in lemons and limes. Therefore, three replicates of each concentration of citric acid (0.10, 0.20, 0.30, 0.40, and 0.50 mol/L) were applied to adjust deionized water, and filled into PET plastic bottles. At the end of four weeks of storage, the Sb concentrations ranged from 0.36 ± 0.08 μg/L to 1.42 ± 0.17 μg/L. These results suggest that the citric acid in fruit juice (0.1 mol/L to 0.5 mol/L) can enhance Sb leaching (Figure 3-7).

3.3 Conclusion

We evaluated the Sb content PET bottled beverages and found that Sb is able to leach from plastic bottles into juices and alcoholic drinks during a six-month storage period. Citric acid was found to be an important factor promoting the Sb leaching process in citrus fruit juices. The Sb content in all tap water and beverages, bottled water, soft drink, juices, and alcoholic drinks was below the Health Canada Guideline recommended for drinking water (6 μg/L). The use of PET plastic in food packaging is emerging in recent years, the Sb release from this type of plastic should be evaluate when assess the safety of PET plastic.

Table 3-1. Concentration of antimony in lemon and orange juices (n=6) stored in glass bottles.

	first measurement (μg/L)	six months later (μg/L)
Orange juice	1.21 ± 0.05	1.23 ± 0.06
Lemon juice	1.13 ± 0.03	1.11 ± 0.05

Table 3-2. Citric acid content in orange and lemon fruit juice and in some of the commercial citrus fruit juices (n=3). [32]

Product	Type of product	Citric acid concentration (mol/L)
Orange juice	Fresh, from fruit	0.047 ± 0.010
Lemon juice	Fresh, from fruit	0.25 ± 0.02
Lemon juice Realemon	Juice concentrate	0.18
Orange juice Tropicana	Ready-to-consume	0.088
Lemon juice Tropicana	Ready-to-consume	0.025 ± 0.003
Lemon juice Minutemaid	Ready-to-consume	0.038

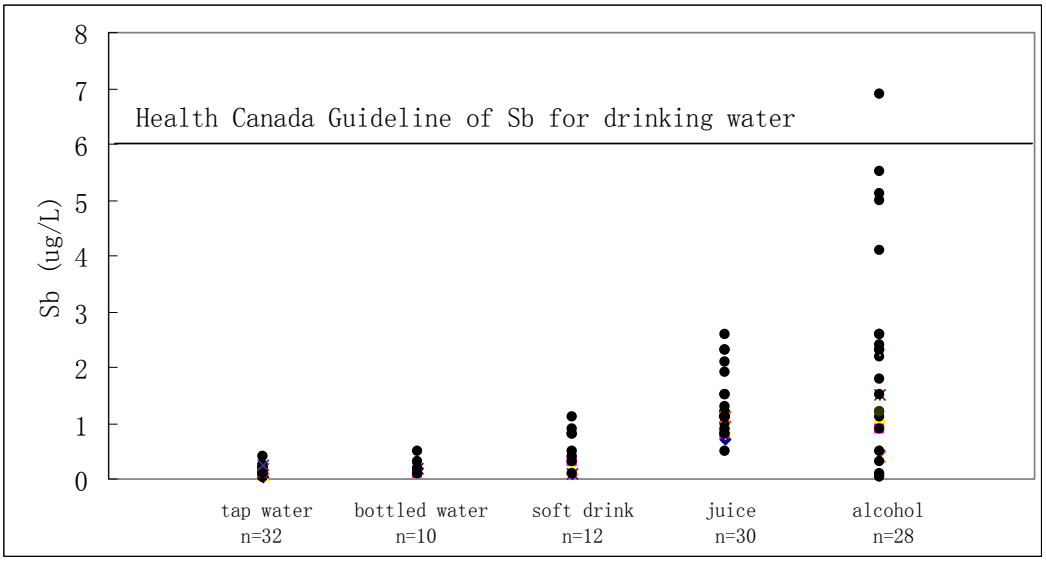

Figure 3-1. Overall concentrations of Sb in tap water (n=32) from across Canada, plastic bottled water (n=10), soft drinks (n=12), juices (n=30), and alcoholic drinks (n=28) from local grocery stores in Edmonton, Canada. Symbols are measured data of mean value. Error bars are smaller than the symbol that they cannot be shown in the figure. Beverages are stored in PET bottles. P (tap water, bottled water) = 0.012, P (tap water, soft drink) < 0.001, P (tap water, juice) < 0.0001, P (tap water, alcoholic drink) = 0.0016

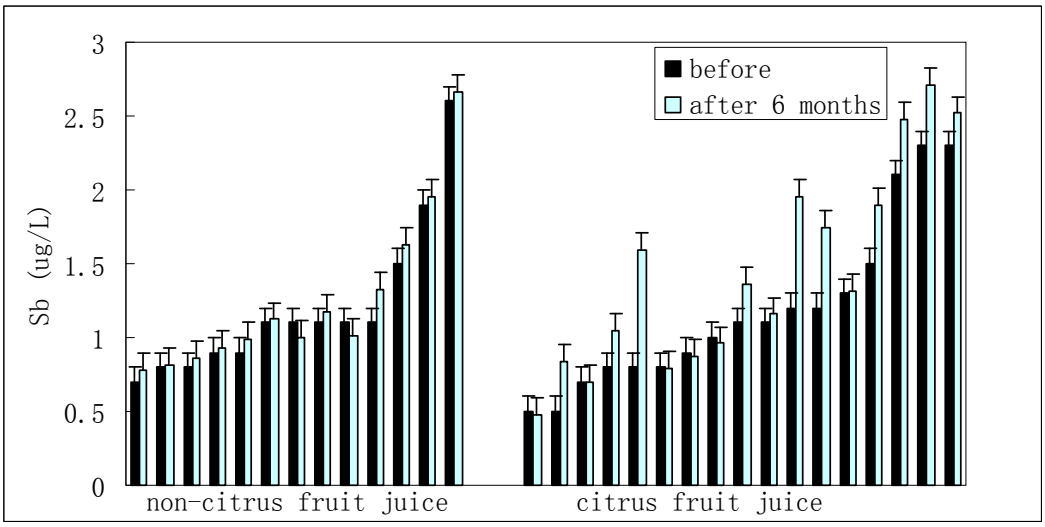

Figure 3-2. Sb concentrations in purchased bottled juice over a six-month holding period at room temperature. Averages of three bottles are shown; error bars represent the standard deviation from Sb analyses in the three juice bottles. The first group are juices with little citric acid (n=13). The second group are citrus fruit juices (n=17).

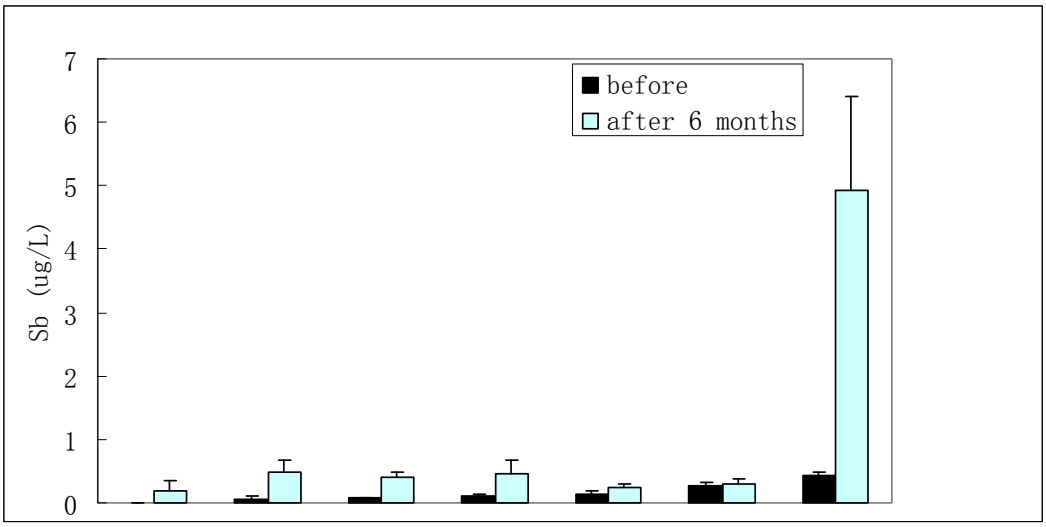

Figure 3-3. Sb concentrations in bottled alcoholic drinks (n=6) over a six-month holding period at room temperature conducted by UBC research group. Averages of three bottles are shown; error bars represent the standard deviation from Sb analyses in the three plastic bottles. The first pair of bars represent Sb concentration in a plastic bottle filled with 40% ethanol.

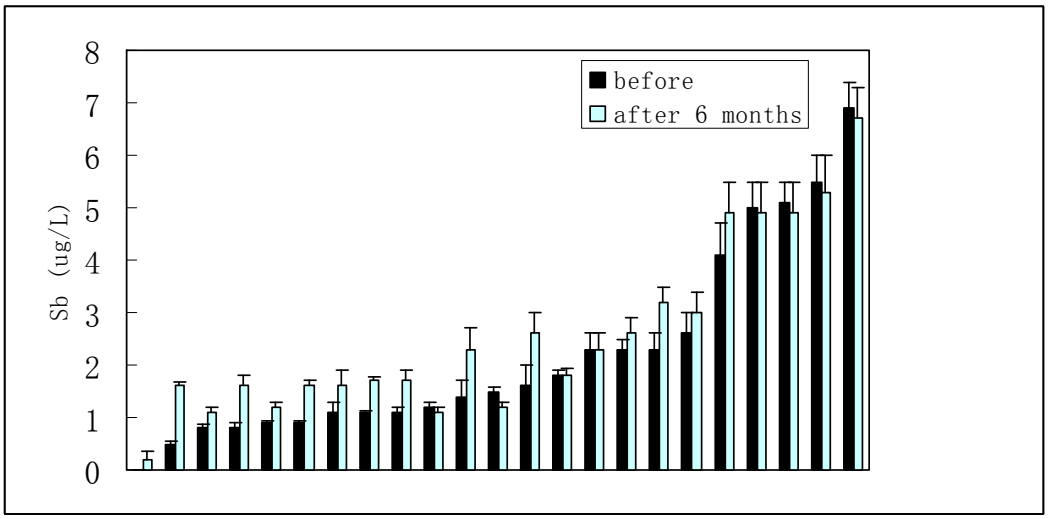

Figure 3-4. Sb concentrations in purchased bottled alcoholic drinks (n=22) over a six-month holding period at room temperature conducted by our group. Averages of three bottles are shown; error bars represent the standard deviation from Sb analyses in the three plastic bottles. The first pair of bars represent Sb concentration in a plastic bottle filled with 40% ethanol.

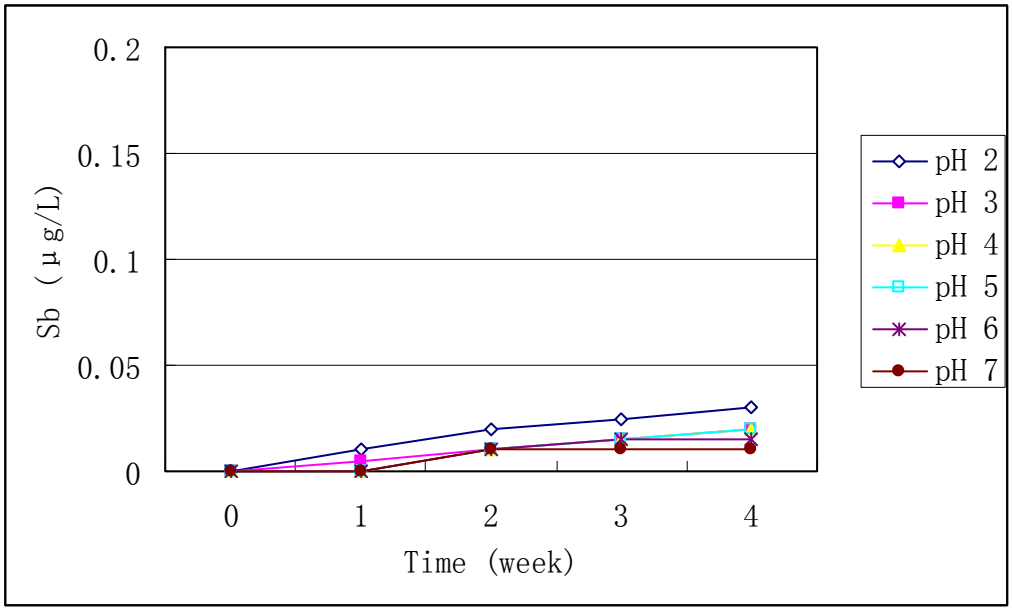

Figure 3-5. Effect of pH value on Sb leaching into water from plastic bottles. Nitric acid was used to adjust the pH value. Symbols are measured data. Error bars are smaller than the symbol that they cannot be shown in the figure.

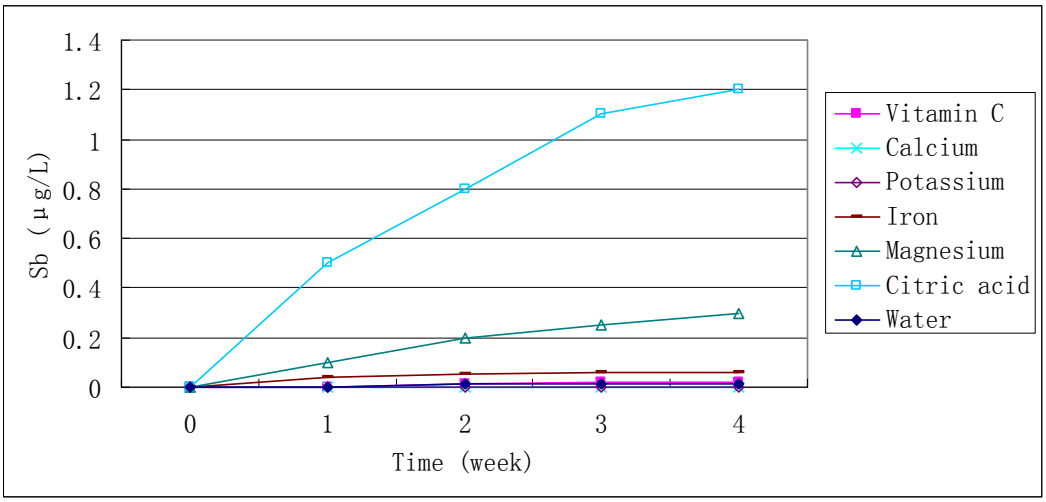

Figure 3-6. Effect of a set of chemicals on Sb leaching into water from plastic bottles. Symbols are measured data. Error bars are smaller than the symbol that they cannot be shown in the figure. Concentrations: vitamin C (0.5 mg/mL), Ca^{2+} (0.1 mg/mL), Mg^{2+} (0.03 mg/mL), K^{+} (0.05 mg/mL), Fe^{3+}(0.01 mg/mL), and citric acid (0.3 mol/L).

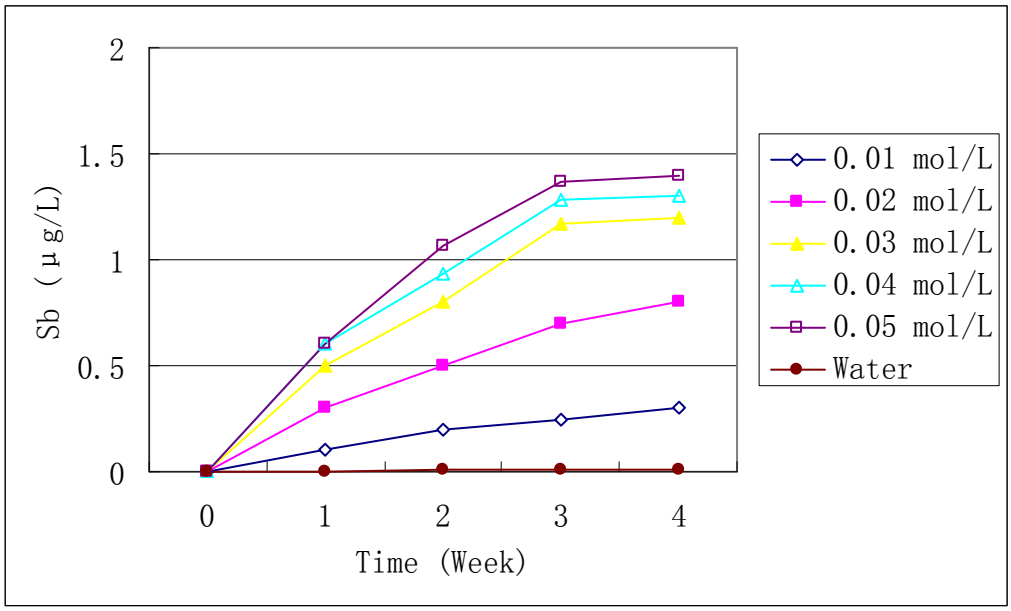

Figure 3-7. Effect of citric acid concentration on Sb leaching into water from plastic bottles. Symbols are measured data. Error bars are smaller than the symbol that they cannot be shown in the figure.

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Chapter 4. Determination of Antimony in Fruit

Introduction

Antimony occurs in the environment due to both natural and anthropogenic processes including mining activity, burning of fossil fuels, smelting of ores, and the use of antimony in the manufacture of flame retardants, batteries, and ceramics. [1-15]. It has an estimated abundance of 0.2-0.3 mg/kg in the earth crust and background concentrations in soils of < 0.3-8.4 mg/kg, but it tends to concentrate in the surface soils. Important anthropogenic source of antimony in soil are vehicle emissions and emissions of smelters [16-20]. In recent years, it has been found in bottled water and juice [21-26]. Antimony is believed to leach from the PET plastic bottles.

In Chapter 3, we also discussed the possibility of Sb leaching from PET bottles into beverages, especially fruit juices. Since we already found Sb in some of the juices at around 1.5–2.0 μg/L before we stored them for long-term observation, we suspected that some of the measured Sb could originate from the fruit. The literature on antimony in fruit is limited. In this chapter, we focused on determination of Sb concentration in a range of fruit.

4.1 Experimental Methods

4.1.1 Instrumentation

HPLC-ICP-MS

A Perkin-Elmer 200 series HPLC system (PE Instruments, Shelton, CT, USA) was used. For speciation of the standards and for verification of the method, a Hamilton PRP-X100 5µm anion-exchange column (4.1 x 150 mm) was used. Chromatographic separation on this column was done using an established method with isocratic elution and a mobile phase of 20 mM EDTA and 2 mM Potassium Hydrogen Pthalate (PHP) (pH 4.5).

The effluent coming from the HPLC was directly detected using an Elan 6100 DRC^{plus} ICP-MS (PE Sciex, Concord, ON, Canada), with Turbochrom Workstation v.6.1.2 software (PE instruments) for data processing. The instrument was operated in standard mode. Antimony was monitored using both the ^{121}Sb (57.25%) and ^{123}Sb (42.75%) isotopes. For quantification, external calibration was used, and minimal drift was seen.

HPLC-ICP-MS methods. For antimony speciation analysis, HPLC-ICP MS was used, with 1 mL/min of mobile phase of 20 mM EDTA and 2 mM PHP (pH 4.5). External calibration was done and verified using the NIST 1640 natural water standard.

4.1.2 Sampling of the fruit

Thirteen kinds of fruit comprising 33 brands were obtained from different stores in Edmonton, Canada (Table 4-1). Most of the fruit originated in north America, while the rest were from south America and China.

We collected at least three samples for each brand of fruit. The fruit was washed with tap water and then rinsed with deionized water. The water was used as sample blank.

4.1.3 Fresh juice squeezed from fruit

For orange, lemon, grapefruit, apple, pear, and grape, the juice was squeezed from the fruit with or without peel, and the antimony concentrations in the juice were compared. For strawberry, blackberry, and cherry, the juice was squeezed from the whole fruit because it is difficult to define which part is peel or flesh. For mango, kiwi, and pineapple, the juice was squeezed only from the flesh because common sense says that people do not eat the peel of these kinds of fruit. Each squeezed juice was placed in a 12 mL glass vial, and then filtered with a 0.45 μm filter. The juice was diluted 10 times before analysis to reduce the concentration of sugar. The process control blank was made of 1% nitric acid which also went through a 0.45 μm filter and was stored in a 12 mL glass vial prior to analysis.

4.1.4 Digestion of the fruit

For orange, lemon, grapefruit, apple, pear, and grape, we studied the peel and flesh separately. For each fruit, approximately 1 g of peel and flesh was weighed and digested with 40 mL mixed acid comprising HNO_3 (70%) and H_2SO_4 in a 1:3 ratio and kept overnight. The samples were then heated to 300°C for total digestion (3h). The digestion was complete when the acid evaporated until only 0.5 mL acid was left. Following the digestion, the solutions were diluted 20 times for further analysis.

4.1.5 Sb complexation with citric acid

Sb(V) and Sb(III) were mixed with citric acid to study their interaction with it. In the final solution, the concentrations of Sb(V) and Sb(III) were 2 μg/L, and the concentrations of citric acid varied from 0 to 0.1 μmol/L. We kept the samples overnight to complete the reaction (Chromatograms signal became stable). In the second day, we analyzed the samples with a PRP-X100 column and ICP-MS.

4.2 Results and Discussion

4.2.1 Sb concentration in fruit

Sb has not been previously reported to be present in fruit. In this work, we chose apple, grape, mango, strawberry, blueberry, blackberry, grapefruit,

pineapple, pear, kiwi, orange, and lemon because these are the most common fruit in North American grocery stores. In the previous study (Chapter 3), we found commercial bottled fruit juice to contain around 2 μg/L Sb, which led us to consider whether Sb comes from the bottles or from the fruit themselves. Figure 4-1 summarizes Sb concentration in a set of fruit juices squeezed from fresh fruit. The overall Sb concentration in fruit juice ranged from 0.23 ± 0.03 μg/L to 2.1 ± 0.4 μg/L. Apple contained the highest concentration of Sb of all the fruit examined, while kiwi contained a very low concentration of Sb.

Figure 4-2 summarizes the concentration of Sb in digested fruit flesh. The overall Sb concentration in fruit flesh ranged from 0.30 ± 0.02 μg/kg to 2.1 ± 0.2 μg/kg. The flesh of orange and lemon contained the highest concentration of Sb based on wet weight.

It is interesting that compared with other fruit, the Sb concentration in apple was much lower in the digestion study than in the fruit juice study. The free water content in apple is typically 40% – 50% in weight [27], while orange and lemon contain about 80% free water. When normalized to Sb concentrations in dry weight (corrected from water content), it's reasonable that Sb concentration in apple appears less concentrated than other fruit. So the apparent Sb concentration in apple on the wet weight basis appears lower than those in orange and lemon (Figure 4-2).

The Sb concentrations in orange and lemon flesh are within the same order of

magnitude compared to those in the orange and lemon juice. Due to different sample location and variation in the juice processing method, the concentration could not be perfectly matched. However, the amount of Sb in fruit and in bottled juice are of the same order of magnitude. Though the fruit are from different locations in the world (Table 4-1), our results do not reveal significant variations in Sb concentrations in the fruit from different locations.

The Health Canada Guideline for Sb in drinking water is set as 6 μg/L. The concentrations of Sb in fruit juice and the fruit tested are much lower than that in the drinking water. For most adults, the consumption of oranges and lemons is also less than the consumption of water. Thus, the levels of Sb in fruit is probably not a health risk for humans.

4.2.2 Comparing Sb in fruit flesh with peel

We focused our study on citrus fruit because they were found to contain the highest levels of Sb in this survey. The Sb concentration in flesh and peel of fruit other than orange and lemon after digestion are also studied as for comparison with orange and lemon. An interesting observation is that Sb concentration in citrus fruit juice when the fruit were squeezed with the peel was higher than when the peel was removed (Figure 4-3). The concentrations were 1.4 ± 0.4 μg/L in juice from the flesh and 2.0 ± 0.5 μg/L in juice from the flesh with the peel. To test whether more Sb stayed in the fruit peel, we analyzed the peel and flesh

separately. Figure 4-4a shows the digestion study of orange and lemon flesh compared with their peel. Indeed, the concentration (in wet weight) of Sb in the peel was higher than in the flesh. We also analyzed "organic" oranges from the USA. The results have the same trend, that peel contained more Sb (Figure 4-5), suggesting that the source of Sb could be the fruit itself rather than from pesticides. The water content in orange flesh is typically 75-80% and it was found that the peel fractions only contained only about 10% less moisture than flesh fractions [28,29]. Figure 4-4b is the result of normalization of Sb concentrations in orange flesh and peel in dry weight by taking into account of the differences in water content. The result still suggests Sb in peel are higher than that in flesh in orange and lemon.

Again, the consumption of fruit peel is much less than of fruit flesh, so this level of Sb in fruit peel is not likely a health concern for humans.

4.2.3 Speciation of Sb in fruit juice

We studied the speciation of three Sb species: inorganic Sb(III), inorganic Sb(V), and Sb-citrate. Chromatography analysis (Figure 4-6) shows that inorganic Sb(V) and inorganic Sb(III) apear first at 1.4 min and 2.2 min while Sb-citrate apears later at 4.1 min. In our analysis of orange juice samples, Sb apears at the same time as Sb-citrate. When we spiked the samples with 2 μg/L Sb-citrate, the peak increased about two times in peak area, confirming that the Sb species in the

orange juice samples is Sb-citrate (Figure 4-6). If Sb-citrate is the main species in fruit, we can understand why citrus fruit, which are very rich in citric acid, contain more Sb than other fruit. Plants are reported to be able to take up antimony from soil[30-36], so the origin of antimony in the fruit could be from the soil.

4.2.4 Sb reaction with citric acid

Recently, Ulrich et al. [37] reported the complexation of Sb(III) with citric acid based on the observation of changes in chromatographic retention times; no Sb(V) complex was observed through this approach. In contrast, Guy et al. [38] demonstrated the complexation between Sb(V) and citric acid, while no complexation between Sb(III) and citric acid was observed.

In this work, we examined the complexation of Sb compounds with citric acid using HPLC-ICP-MS. Stock solutions of Sb(III) and Sb(V) were mixed with citric acid according to the procedure described in the experimental section, to give a concentration of 2 μg/L Sb(III) and Sb(V) with a range of concentrations of citric acid. These solutions were kept overnight to complete the reaction prior to the HPLC-ICP MS measurement. Figure 4-7 shows the chromatograph obtained with different concentrations of citric acid. The first graph (a) shows that in the presence of low concentration of citric acid, Sb(V) and Sb(III) were slightly reduced and Sb-citrate increased. The second graph (b) shows that when the ratio of Sb to citric acid was 1:8, Sb(V) was diminished and we can still see a small

peak of Sb(III). The third graph (c) shows that Sb(III) diminished after the ratio of Sb to citric acid was increased to 1:10. Therefore the chromatograms shown in Figure 4-7 clearly indicate the complexation of Sb(V) and Sb(III) with citric acid.

The antimony and citric acid complexation effect was observed before this study using electrospray mass spectrometry (ES-MS) [26, 39]. Sb(III) species are easily oxidized to Sb(V) species. The Sb-citric acid complex is quite stable in 1% HCl, which is similar to the conditions of the human stomach [26].

4.3 Conclusion

A range of fruit was tested for Sb concentration, including fruit flesh and fruit peel. Orange and lemon contain higher levels of Sb than other fruit in both flesh and peel. Sb concentrations were around 2 μg/kg in the fruit flesh and 5 μg/kg in fruit peel in wet weight. The main species present in orange and lemon is Sb-citrate. These concentrations are below the Health Canada Guideline values recommended for drinking water in Canada. As the daily consumption of orange and lemon is far less than consumption of water by weight, the exposure to Sb from fruit is not likely to be considered a health concern.

Table 4-1. Fruit samples obtained from grocery stores in Edmonton, Canada.

Fruit	Number of Brands	Origin
Orange	4	USA
Lemon	3	USA
Grapefruit	2	USA
Apple	4	USA, Canada
Pear	4	USA, Canada, China
Grape	2	Canada
Strawberry	2	Canada
Blueberry	2	Canada
Blackberry	2	Canada
Cherry	1	Canada
Mango	3	Mexico
Kiwi	2	Canada, Peru
Pineapple	2	Canada

Table 4-2. Sb concentration in flesh and peel of fruit other than orange and lemon after digestion with nitric acid and sulfuric acid in 1:3 ratio (n=3)

	Flesh (µg/kg)	Peel (µg/kg)
Apple	0.77 ± 0.12	0.15 ± 0.03
Grape	1.72 ± 0.20	1.42 ± 0.19
Mango	1.71 ± 0.28	-
Strawberry	1.30 ± 0.22	-
Blueberry	1.11 ± 0.16	-
Blackberry	0.93 ± 0.11	-
Grapefruit	1.80 ± 0.14	2.32 ± 0.5
Pineapple	0.87 ± 0.13	-
Pear	0.81 ± 0.10	
Cherry	0.72 ± 0.12	-
Kiwi	0.23 ± 0.03	-

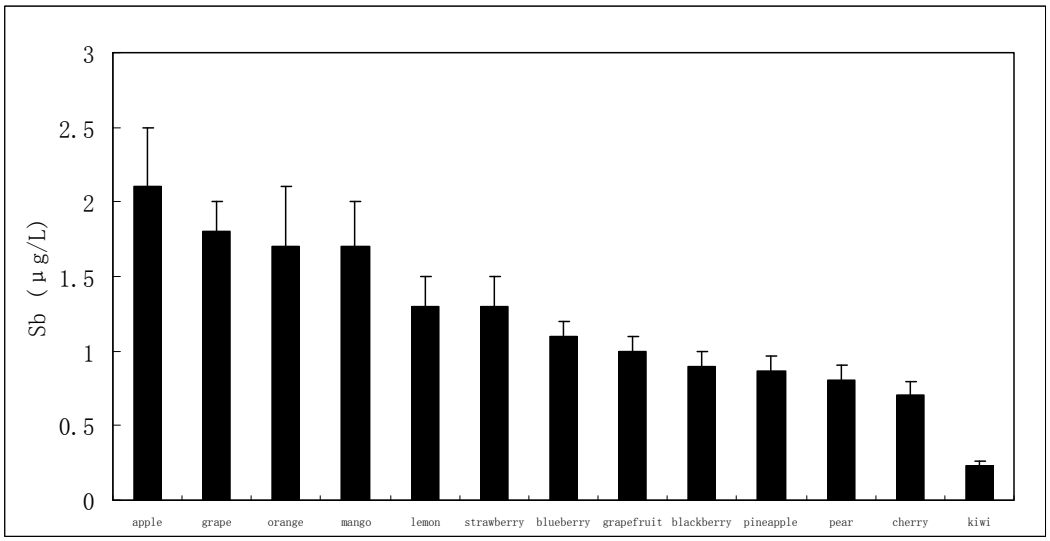


Figure 4-1. Sb concentration in fruit juice squeezed from fruit flesh (n=3). Data represents the mean value ± SD. Error bars represent standard deviation from triplicate analyses of three fruit samples.

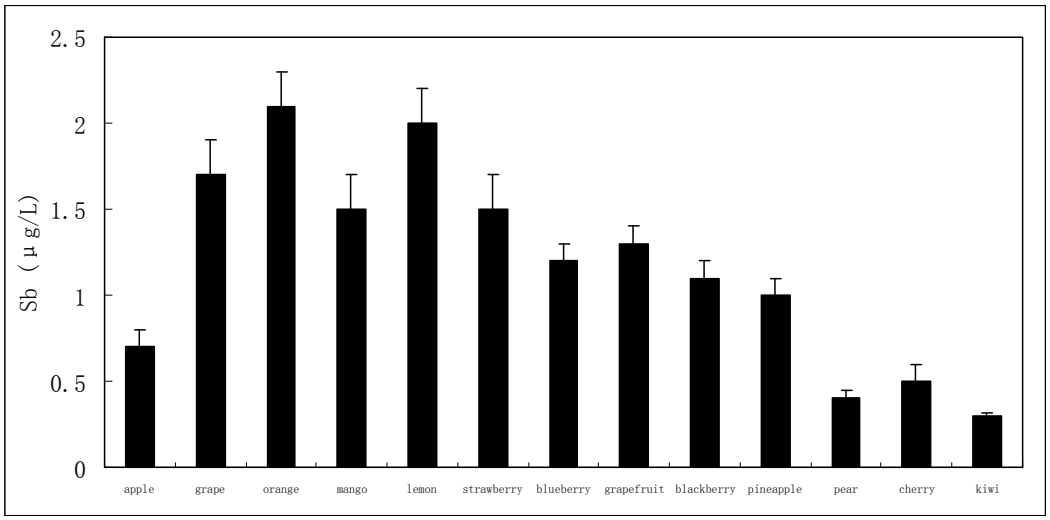


Figure 4-2. Sb concentration in fruit flesh after digestion with nitric acid and sulfuric acid in 1:3 ratio (n=3). Data represents the mean value ± SD. Error bars represent standard deviation from triplicate analyses of three fruit samples.

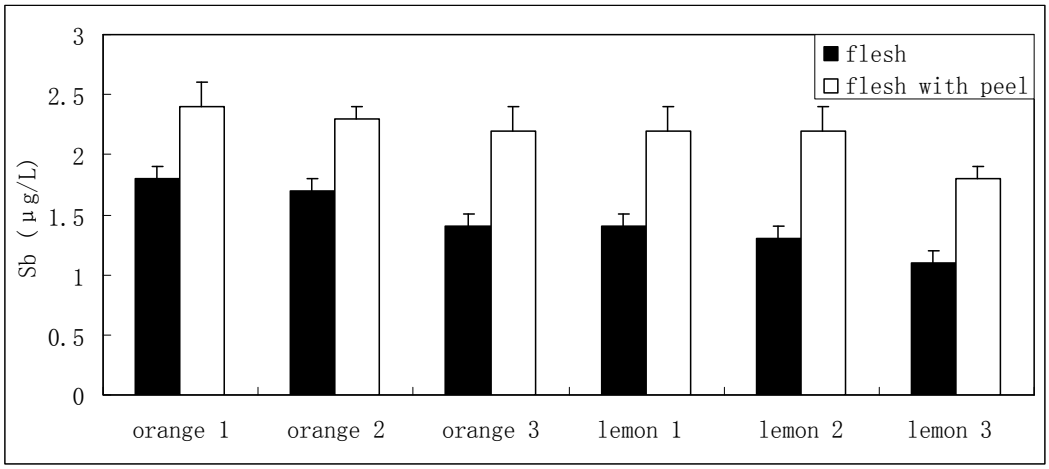


Figure 4-3. Sb concentration in orange and lemon juice squeezed from fruit flesh with and without peel (n=3). Data represents the mean value ± SD. Error bars represent standard deviation from triplicate analyses of three fruit samples.

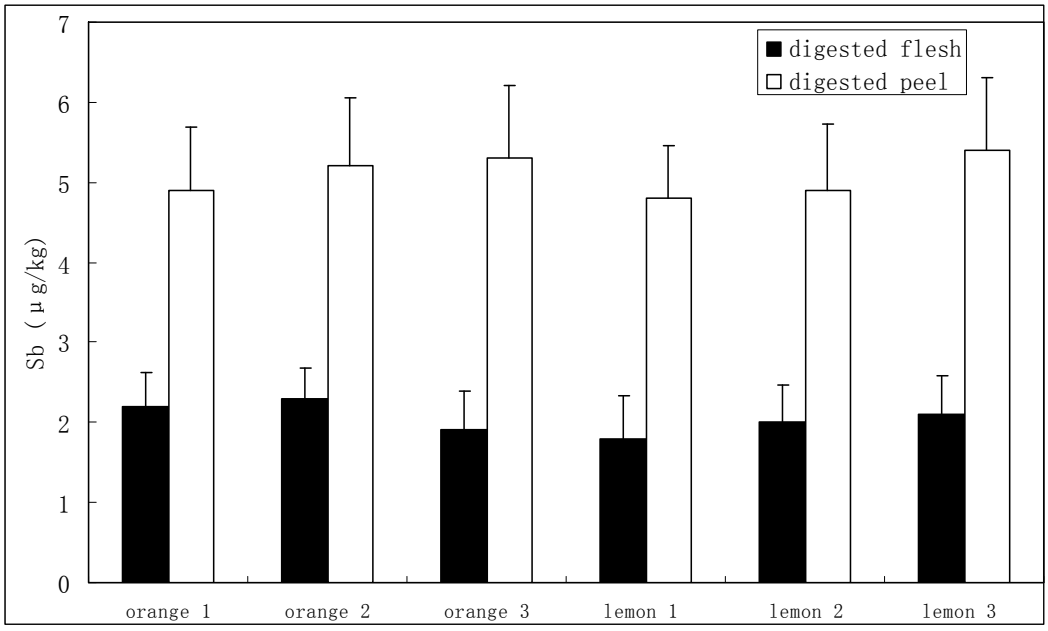


Figure 4-4a. Sb concentration in the flesh and peel of orange and lemon (n=3, wet weight) after digestion with nitric acid and sulfuric acid in 1:3 ratio. Data represents the mean value ± SD.

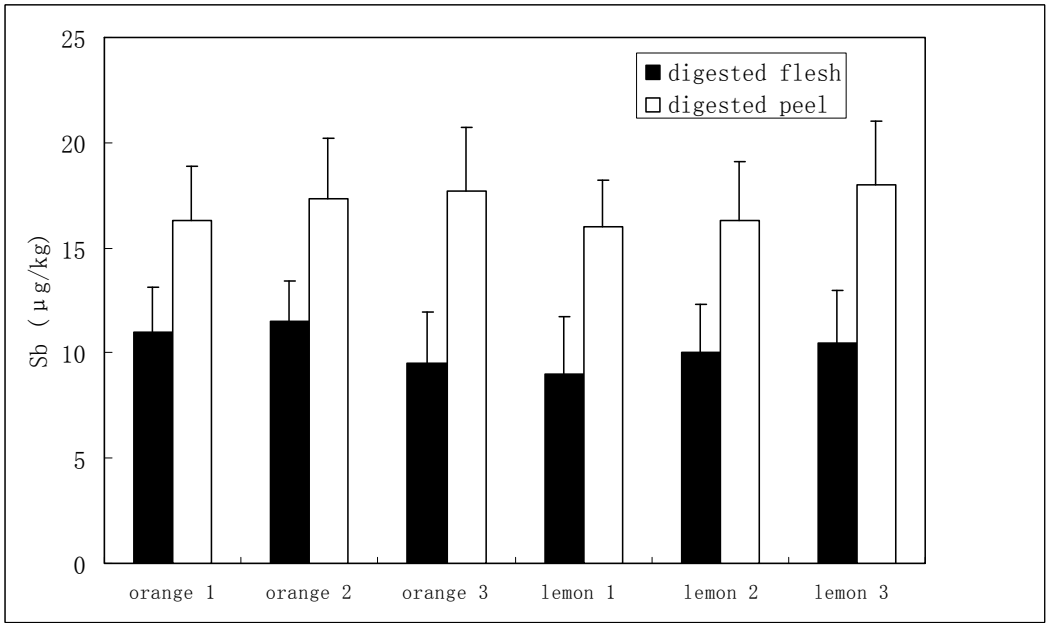


Figure 4-4b. Normalized of Sb concentration in the flesh and peel of orange and lemon in dry weight. The flesh and peel (n=3) were separately digested with nitric acid and sulfuric acid in 1:3 ratio (n=3). The values of water content used for the normalization were 80% for orange and lemon flesh, 70% for orange and lemon peel. Data represents the mean value ± SD.

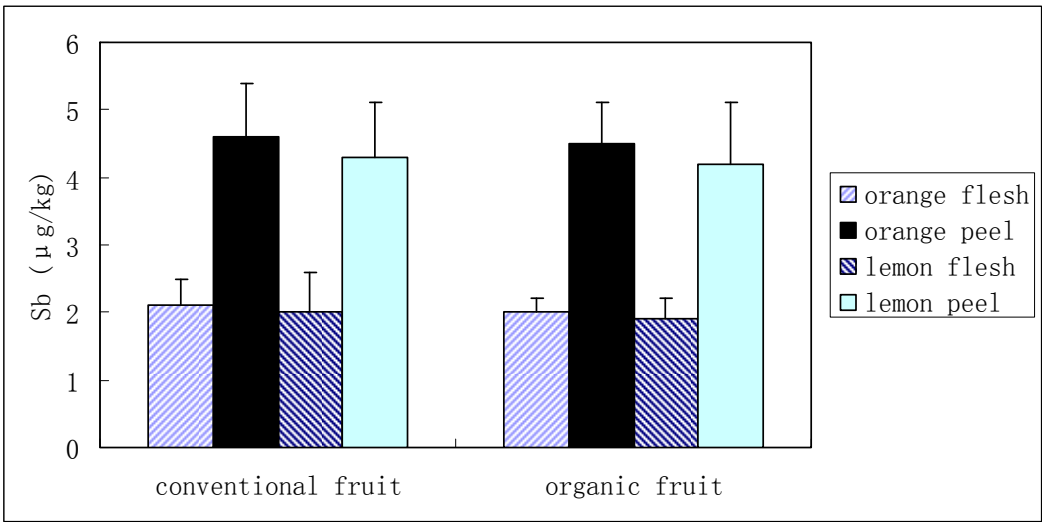
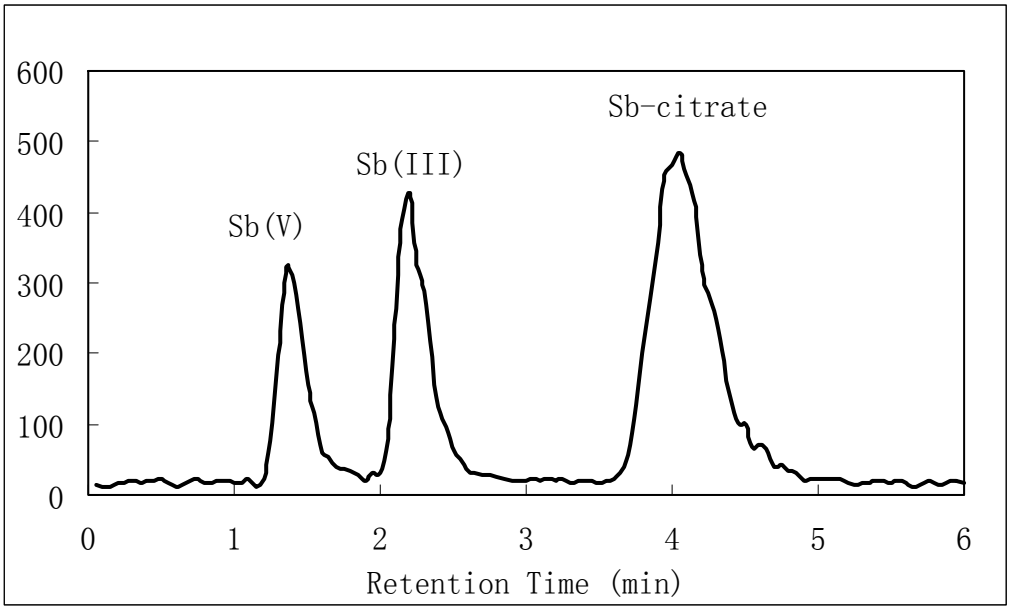
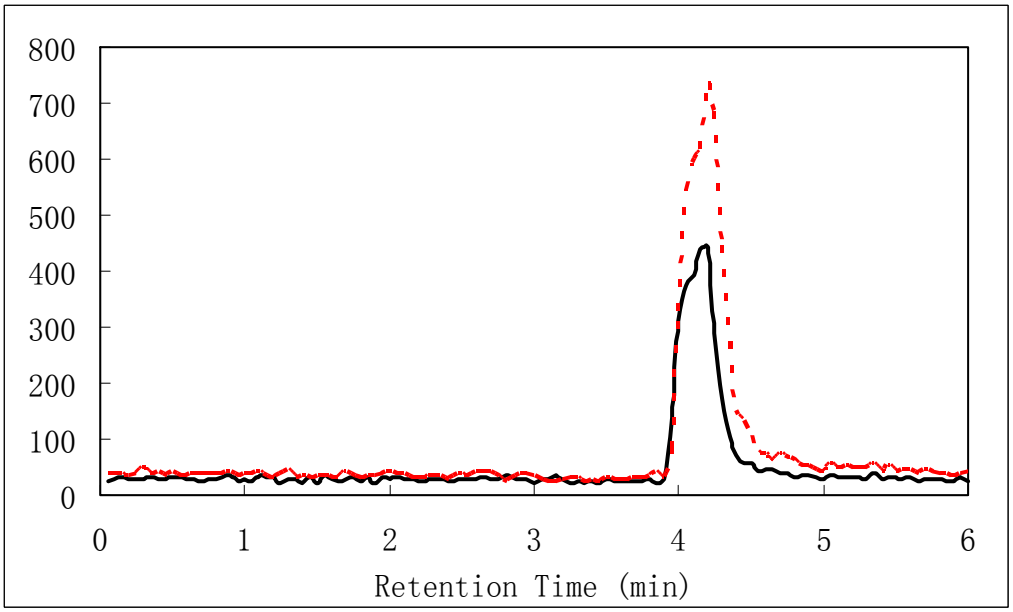


Figure 4-5. Sb concentration in the flesh and peel of conventional orange and lemon versus organic orange and lemon (n=3). Error bars represent standard deviation from triplicate analyses of three fruit samples. Data represents the mean value ± SD.

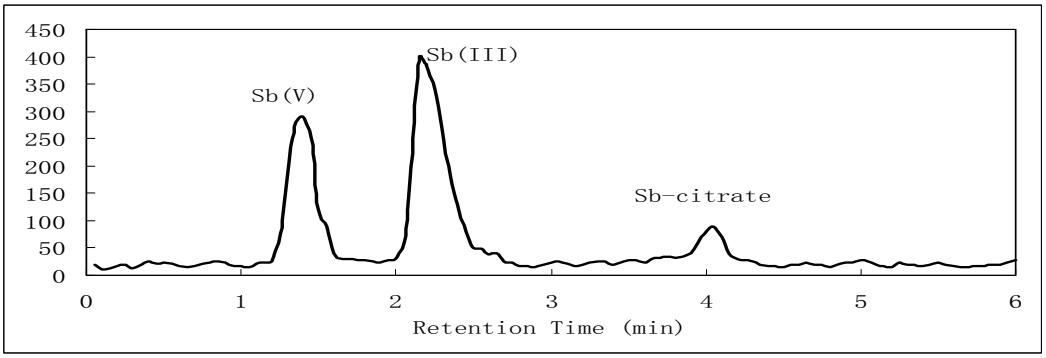


(a)

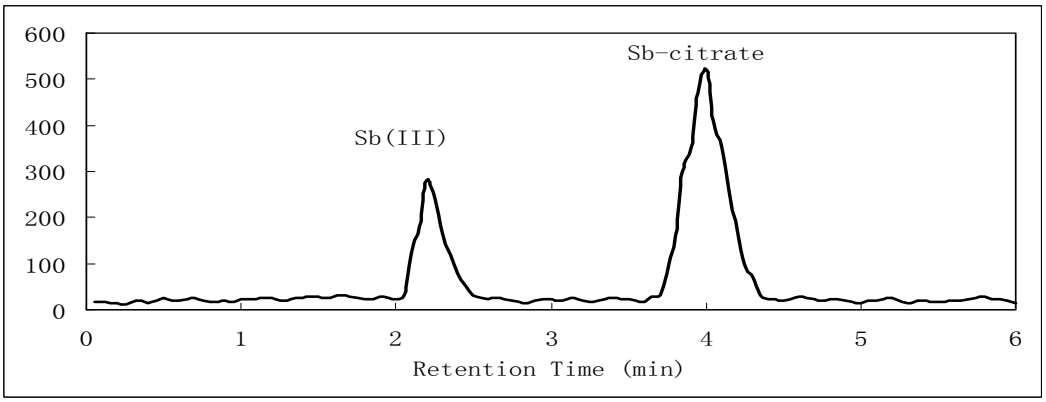


(b)

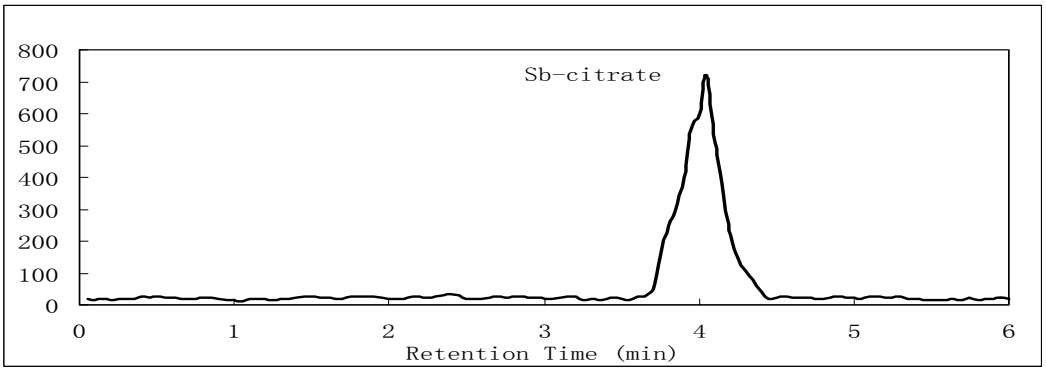
Figure 4-6. (a) chromatogram of Sb(V), Sb(III), and Sb-citrate standards. (b) chromatograms of orange juice sample alone (solid line) and orange juice sample spiked with 2 µg/L Sb-citrate (dotted line).



(a)



(b)



(c)

Figure 4-7. Chromatograms showing reaction mixtures containing Sb(V) (1.4 min), Sb (III) (2.2 min) and Sb-Citrate (4.1 min). Sb(V), Sb(III) and citric acid were incubated at room temperature overnight: (a) starting concentrations of Sb(V), Sb(III), and citric acid ratio was 1:1:2; (b) starting concentrations of Sb(V), Sb(III), and citric acid ratio was 1:1:8; (c) starting concentrations of Sb(V), Sb(III), and citric acid ratio was 1:1:10.

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Chapter 5. General Discussion and Conclusions

5.1 Review of Thesis Objectives

The objective of this thesis was to determine antimony concentrations in natural water, beverages, and fruit. The hypothesis of this work was that a correlation between arsenic and antimony concentration exists in natural water and that antimony in fruit juice occurs both due to leaching from the plastic material during six months storage and in the presence of citric acid and also due to concentrations naturally present in fresh fruit. Water samples were collected from rivers and lakes across Canada and wells in northern Alberta, as well as from an antimony mining site in China to study the correlation between antimony and arsenic (Chapter 2). The correlation was found to be weak. As an extension to this study, we also investigated antimony concentrations in beverages including bottled water, soft drinks, bottled juice, and alcoholic drinks (Chapter 3). To further confirm the origin of antimony in bottled juice, we analysed the concentration and species of antimony in fresh fruit (Chapter 4).

5.2 Summary of Results

This survey has shown a weak correlation between arsenic and antimony in natural water. The lowest concentrations of arsenic and antimony were found in surface water samples while the groundwater samples contained higher arsenic and antimony concentrations. The highest concentrations of arsenic and antimony were found in water samples from the antimony mining site. No correlation between concentrations of Sb and As are observed in these three sets of water samples.

The content and leaching behavior of antimony in bottled water, alcohol, and fruit juices are discussed in this study. Based on the Health Canada Guideline for antimony in drinking water (6 μg/L), the levels of antimony in the surveyed beverages are considered to be acceptable for human consumption. The leaching of antimony from the PET plastic bottles into water, alcohol, and juice was confirmed, especially when citric acid is present. Antimony can combine with citric acid to form an antimony-citrate complex, which could be the reason that higher antimony concentration was observed in fruit juices high in citric acid.

Antimony–citrate was also found in oranges and lemons. The concentration of antimony in fresh fruit is of the same order of magnitude as that in bottled juice, which suggests that the antimony found in bottled juice may not be present solely as a result of leaching from the PET plastic bottles but may also come directly

from the fruit.

5.3 Relevance to Environmental Toxicology

The arsenic and antimony study has contributed to the understanding of arsenic and antimony exposure to humans. This study reveals that water from some of the wells in northern Alberta containing antimony and arsenic at concentrations higher than the Health Canada Guideline and could pose a concern for local residents.

In addition, prior to this study, research had shown that antimony could leach from plastic bottles to the water contained within them [1-3], but only one report had been published on antimony species present in bottled juice [4]. However, the factors that affect antimony leaching are not well understood. This study monitored long-term storage of bottled juice, which happens in daily life, and which could affect the concentration of antimony in bottled juice. Fruit juice components such as citric acid can also promote the leaching process of antimony. This is the first study to show that many fruits surveyed contain antimony, and that the highest concentration occurs in oranges and lemons. The most important origin of antimony in bottled juice may be the fruit, and represents a possible exposure route of antimony for humans.

5.4 Limitation of Research

While the arsenic and antimony concentration survey did not reveal a strong correlation between them, further work is required to study if high antimony concentration may be present in water from arsenic affected areas. Significant correlations between the concentrations of arsenic and antimony have been reported in the human body [5], but the mechanism of accumulation process in human is unknown.

HPLC-ICP-MS is a useful technique for the speciation and determination of inorganic antimony with very good sensitivity and resolution. This technique is insufficient to confirm molecular information because the identification of certain species has to rely on matching the retention time with standard chemical. Applying techniques such as HPLC-ESI-MS in antimony speciation to provide structural information for further confirmation would be useful, especially in the analysis of organo-antimony compounds.

5.5 Future Work

There is a need for further evaluation of human exposure to environmental antimony because of the lack of information. The impact to human of exposure to low level of antimony is unknown.

The study of antimony in fruit could be interesting; the mechanism by which

antimony accumulates in fruit is still undiscovered. The accumulation of antimony in plants has been studied. Adriano [6] and Sauerbeck [7] have demonstrated that antimony can be transported through the roots into the upper parts of plants (leaves, shoots); there is a barrier, however, at the generative parts (grain, fruit). As a consequence, antimony levels in grain and fruit are less than in leaves and shoots.

This is the first time that antimony–citrate was found in oranges and lemons, and information about this complexation has rarely been published before.

Exposure to antimony is not only occurring in isolated areas. The exposure depends on the environmental chemistry of contaminants with human activities, management practices, and the subsequent toxicological consequences. To establish an antimony risk assessment is worthwhile due to the large environmental variation of antimony concentrations in different regions in the world and in numerous different exposure routes. Risk assessment is a process of estimating the potential harmful effects of antimony exposure to the population in a specific area. Developing a risk assessment model is a process that links antimony contamination levels, exposure routes with toxicity and harmful effects to general populations and determine the best approach for protecting humans and the environment [8-10].

5.6 References

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APPENDIX

Table A-1. Supplementary Data to Figure 2-1. Original data of As and Sb concentrations in water samples from Health Canada, n=121.

	As (μg/L)	Sb (μg/L)
CMP-09-W-ARE-T	0.11	0.10
CMP-09-W-ARE-R	0.00	0.01
CMP-09-W-AMO-T	0.69	0.20
CMP-09-W-AMO-R	0.12	0.06
CMP-09-W-OAK-T	0.08	0.08
CMP-09-W-MGE-R	2.86	0.18
CMP-09-W-MSO-T	3.08	0.16
CMP-09-W-MSO-R	2.71	0.12
CMP-09-W-BAM-T	0.19	0.02
CMP-09-W-BAM-R	0.36	0.03
CMP-09-W-MCH-T	0.63	0.09
CMP-09-W-MCH-R	0.61	0.08
CMP-09-W-HVA-T	0.14	0.08
CMP-09-W-HVA-R	0.08	0.06
CMP-09-W-ALA-T	0.14	0.19
CMP-09-W-ALA-R	0.18	0.06
CMP-09-W-APR-T	0.05	0.80
CMP-09-W-APR-R	0.10	0.11
CMP-09-W-AGR-T	0.35	0.19
CMP-09-W-AGR-R	0.34	0.18
CMP-09-W-HPR-T	0.40	0.15
CMP-09-W-HPR-R	0.01	0.03
CMP-09-W-HCO-T	0.12	0.18
CMP-09-W-HCO-R	0.16	0.12
CMP-09-W-HCA-T	0.11	0.08
CMP-09-W-HCA-R	0.10	0.09
CMP-09-W-HPO-T	0.12	0.15
CMP-09-W-HPO-R	0.08	0.14
CMP-09-W-HFO-T	0.08	0.02
CMP-09-W-HFO-R	0.22	0.10
CMP-09-W-HWH-T	0.11	0.20
CMP-09-W-HWH-R	0.10	0.10

CMP-09-W-BTR-R	0.13	0.08
CMP-09-W-BTR-T	0.05	0.02
CMP-09-W-BLI-R	0.13	0.12
CMP-09-W-BLI-T	0.09	0.06
CMP-09-W-BTO-R	0.72	0.19
CMP-09-W-BTO-T	0.58	0.23
CMP-09-W-AQU-R	0.23	0.15
CMP-09-W-AQU-T	0.28	0.19
CMP-09-W-BKI-R	0.19	0.29
CMP-09-W-BKI-T	0.06	0.05
CMP-09-W-BAL-R	0.04	0.07
CMP-09-W-BAL-T	0.02	0.09
CMP-09-W-IST-R	0.17	0.12
CMP-09-W-IST-T	0.22	0.08
CMP-09-W-IDR-R	0.13	0.07
CMP-09-W-IDR-T	0.14	0.09
CMP-09-W-IWI-R	0.06	0.09
CMP-09-W-IWI-T	0.05	0.07
CMP-09-W-IBA-R	0.14	0.06
CMP-09-W-IBA-T	0.14	0.03
CMP-09-W-EPR-R	0.37	0.16
CMP-09-W-EPR-T	0.17	0.15
CMP-09-W-ESA-R	1.09	0.39
CMP-09-W-ESA-T	0.18	0.18
CMP-09-W-EES-R	4.82	0.34
CMP-09-W-EES-T	3.96	0.19
CMP-09-W-EYO-R	1.31	0.09
CMP-09-W-EYO-T	1.15	0.12
CMP-09-W-BBR-R	0.30	0.05
CMP-09-W-BBR-T	0.29	0.04
CMP-09-W-BLE-R	0.33	0.12
CMP-09-W-BLE-T	0.37	0.17
CMP-09-W-BLE-T	0.44	0.12
CMP-09-W-BLE-R	0.32	0.18
CMP-09-W-BBR-R	0.27	0.22
CMP-09-W-BBR-T	0.34	0.19
CMP-09-W-IBA-T	0.13	0.18
CMP-09-W-IBA-R	0.16	0.12
CMP-09-W-IWI-R	0.11	0.14
CMP-09-W-IWI-T	0.07	0.08
CMP-09-S-AQU-T	0.24	0.06

CMP-09-S-AQU-R	0.40	0.08
CMP-09-S-ALA-R	0.27	0.02
CMP-09-S-ALA-T	0.17	0.06
CMP-09-S-ARE-R	0.11	0.10
CMP-09-S-ARE-T	0.07	0.04
CMP-09-S-AMO-R	0.61	0.15
CMP-09-S-AMO-T	0.52	0.23
CMP-09-S-AGR-R	0.40	0.10
CMP-09-S-AGR-T	0.22	0.09
CMP-09-S-AOK-R	0.21	0.06
CMP-09-S-AOK-T	0.15	0.08
CMP-09-S-EPR-R	0.52	0.20
CMP-09-S-EPR-T	0.08	0.13
CMP-09-S-ESA-R	0.51	0.19
CMP-09-S-ESA-T	0.15	0.08
CMP-09-S-EES-R	4.22	0.35
CMP-09-S-EES-T	3.60	0.20
CMP-09-S-EYO-R	1.32	0.33
CMP-09-S-EYO-T	1.30	0.39
CMP-09-S-MSO-T	3.18	0.43
CMP-09-S-MSO-R	3.16	0.46
CMP-09-S-MGE-R	3.23	0.39
CMP-09-S-MCH-R	0.54	0.18
CMP-09-S-MCH-T	0.52	0.15
CMP-09-S-IST-R	0.20	0.09
CMP-09-S-IST-T	0.22	0.10
CMP-09-S-IDR-R	0.15	0.11
CMP-09-S-IDR-T	0.19	0.13
CMP-09-S-HCA-R	0.06	0.07
CMP-09-S-HCA-T	0.05	0.04
CMP-09-W-HCO-R	0.16	0.08
CMP-09-W-HCO-T	0.13	0.06
CMP-09-W-HPO-R	0.07	0.08
CMP-09-W-HPO-T	0.13	0.12
CMP-09-W-HFO-R	0.18	0.15
CMP-09-W-HFO-T	0.11	0.09
CMP-09-W-HPR-R	0.11	0.07
CMP-09-W-HPR-T	0.24	0.12
CMP-09-W-HWH-R	0.05	0.00
CMP-09-W-HWH-T	0.07	0.00
CMP-09-W-HVA-R	0.11	0.06

CMP-09-W-HVA-T	0.09	0.05
CMP-09-W-BTR-R	0.26	0.12
CMP-09-W-BTR-T	0.18	0.10
CMP-09-W-BAM-R	0.49	0.23
CMP-09-W-BAM-T	0.27	0.15
CMP-09-W-BLI-R	0.25	0.16
CMP-09-W-BLI-T	0.18	0.19

Table A-2. Supplementary Data to Figure 2-2. Original data of As and Sb concentrations in water samples from Alberta Health, n=239.

	As (μg/L)	Sb (μg/L)
1	0.15	0.18 ± 0.00
2	18.72	1.10 ± 0.01
2t	18.05	0.97 ± 0.01
3	0.22	0.23 ± 0.00
4	26.18	1.70 ± 0.02
4t	26.78	1.90 ± 0.02
5	15.41	1.20 ± 0.01
5t	19.38	1.40 ± 0.01
6	24.24	1.20 ± 0.01
6t	21.89	1.10 ± 0.01
7	1.09	0.56 ± 0.01
7t	1.15	0.62 ± 0.01
8	2.24	0.49 ± 0.00
8t	1.96	0.41 ± 0.00
9	28.42	1.10 ± 0.01
9t	0.41	0.30 ± 0.00
12	25.26	1.80 ± 0.01
13	5.94	0.97 ± 0.01
13t	0.65	0.52 ± 0.00
14	2.29	0.22 ± 0.00
14t	0.00	0.00 ± 0.00
15	0.13	0.14 ± 0.00
15t	0.00	0.25 ± 0.00
16	6.41	0.80 ± 0.01
17	0.13	0.10 ± 0.00
18	0.17	0.26 ± 0.00
20	21.60	1.10 ± 0.01
20t	19.32	1.00 ± 0.01
21	19.25	0.95 ± 0.01
21t	21.69	0.89 ± 0.01
22	1.41	0.68 ± 0.00
22t	0.00	0.00 ± 0.00
23	17.57	1.20 ± 0.01
23t	0.00	0.00 ± 0.00
25	10.57	0.73 ± 0.01
25t	6.29	0.55 ± 0.00

26	3.21	0.29 ± 0.00
26t	3.56	0.37 ± 0.00
27	12.32	0.99 ± 0.01
27t	0.03	0.00 ± 0.00
29	12.21	1.70 ± 0.01
30t	1.74	0.59 ± 0.00
31	0.96	0.53 ± 0.00
32	1.44	0.39 ± 0.00
32t	0.92	0.19 ± 0.00
35	8.75	0.87 ± 0.01
35t	3.87	0.45 ± 0.00
36	0.45	0.15 ± 0.00
36t	0.37	0.00 ± 0.00
37	0.99	0.35 ± 0.00
37t	1.64	0.39 ± 0.00
38	11.95	0.98 ± 0.01
38t	0.10	0.00 ± 0.00
39	1.98	0.57 ± 0.00
40	14.16	1.20 ± 0.01
40t	6.46	0.78 ± 0.01
41	6.08	1.00 ± 0.01
42	21.32	1.50 ± 0.02
42t	20.96	1.20 ± 0.01
43	17.22	0.99 ± 0.01
43t	7.08	0.72 ± 0.01
45	4.15	0.53 ± 0.00
45t	0.28	0.19 ± 0.00
46t	0.30	0.18 ± 0.00
48	0.19	0.00 ± 0.00
49	14.85	1.10 ± 0.01
49t	6.56	0.74 ± 0.01
50	0.14	0.00 ± 0.00
50t	0.13	0.00 ± 0.00
51	25.86	1.20 ± 0.01
51t	24.65	0.88 ± 0.01
54	0.43	0.21 ± 0.00
57	0.16	0.00 ± 0.00
58	1.77	0.76 ± 0.02
58t	0.43	0.35 ± 0.00
60	2.82	0.28 ± 0.00
61	1.30	0.37 ± 0.01

61t	0.80	0.19 ± 0.00
62	0.63	0.15 ± 0.00
62t	0.27	0.22 ± 0.00
63	0.38	0.13 ± 0.00
63t	0.26	0.19 ± 0.00
64	1.32	0.27 ± 0.00
64t	0.24	0.00 ± 0.00
65	0.51	0.50 ± 0.00
66	10.72	0.92 ± 0.01
66t	11.12	0.78 ± 0.01
67	16.51	0.96 ± 0.01
67t	5.33	0.44 ± 0.00
68	11.79	1.25 ± 0.01
68t	7.59	1.29 ± 0.01
69	0.17	0.00 ± 0.00
69t	0.16	0.00 ± 0.00
70	0.54	0.24 ± 0.00
71	0.10	0.00 ± 0.00
71t	0.11	0.00 ± 0.00
72	35.40	1.70 ± 0.01
72t	34.72	1.50 ± 0.01
73	1.24	0.62 ± 0.01
73t	0.66	0.37 ± 0.00
74	5.99	0.33 ± 0.00
74t	3.51	0.31 ± 0.00
75	29.73	0.29 ± 0.00
75t	27.88	0.26 ± 0.00
76	0.62	0.54 ± 0.00
76t	24.07	0.52 ± 0.00
77	1.34	0.29 ± 0.00
78	19.61	0.46 ± 0.00
79	37.03	0.62 ± 0.00
79t	23.74	1.05 ± 0.01
80	0.25	0.85 ± 0.01
81	0.00	0.43 ± 0.00
81t	0.00	0.49 ± 0.00
82	25.04	0.92 ± 0.01
83	2.50	0.23 ± 0.00
83t	0.00	0.16 ± 0.00
84	18.58	0.56 ± 0.00
84t	0.21	0.69 ± 0.00

85	3.77	0.41 ± 0.00
86	20.93	0.36 ± 0.00
86t	0.12	0.21 ± 0.00
87	0.59	0.56 ± 0.00
87t	0.10	0.63 ± 0.00
88	0.13	0.86 ± 0.00
88t	0.14	0.93 ± 0.01
89	0.66	0.31 ± 0.00
89t	0.58	5.20 ± 0.05
90	1.42	0.26 ± 0.00
91	30.32	0.59 ± 0.00
92	3.52	0.74 ± 0.00
92t	4.99	0.84 ± 0.01
93	31.59	0.00 ± 0.00
93t	0.49	0.21 ± 0.00
94	16.44	0.33 ± 0.00
94t	16.82	0.35 ± 0.00
95	26.70	0.39 ± 0.00
95t	9.32	3.30 ± 0.03
96	22.25	0.47 ± 0.00
96t	1.13	0.56 ± 0.00
97	36.04	0.54 ± 0.00
97t	1.18	0.39 ± 0.00
98	16.36	0.64 ± 0.00
98t	4.21	0.78 ± 0.01
99t	2.27	0.00 ± 0.00
100	0.10	0.92 ± 0.01
100t	0.00	0.56 ± 0.00
101	0.00	0.30 ± 0.00
101t	0.00	0.10 ± 0.00
102	0.00	0.59 ± 0.00
102t	0.00	0.22 ± 0.00
103	32.80	0.47 ± 0.00
103t	31.00	0.56 ± 0.00
104	4.16	0.79 ± 0.01
104t	3.78	2.82 ± 0.03
105	1.53	0.29 ± 0.00
105t	0.00	0.36 ± 0.00
107	7.78	0.00 ± 0.00
107t	4.60	0.00 ± 0.00
108	16.04	0.74 ± 0.01

108t	0.82	0.62 ± 0.00
109	0.39	0.98 ± 0.01
109t	0.41	0.65 ± 0.00
110	4.02	0.21 ± 0.00
110t	2.32	0.19 ± 0.00
111	34.40	0.39 ± 0.00
111t	33.54	0.33 ± 0.00
112	0.00	0.42 ± 0.00
112t	0.00	0.29 ± 0.00
114	35.93	0.00 ± 0.00
114t	17.01	0.00 ± 0.00
115	7.00	0.74 ± 0.01
115t	0.00	0.89 ± 0.01
116	14.77	0.21 ± 0.00
116t	3.50	0.25 ± 0.00
117	38.90	0.36 ± 0.00
117t	39.88	0.31 ± 0.00
118	36.45	0.19 ± 0.00
118t	10.53	5.10 ± 0.05
119	0.00	0.32 ± 0.00
119t	0.00	0.13 ± 0.00
120	6.28	1.00 ± 0.01
120t	0.55	0.86 ± 0.01
121	0.00	0.00 ± 0.00
122	0.56	0.36 ± 0.00
122t	0.00	0.28 ± 0.00
123	1.59	0.85 ± 0.01
123t	1.70	0.92 ± 0.01
124	40.19	4.70 ± 0.05
124t	39.02	0.75 ± 0.01
125	36.64	0.77 ± 0.01
125t	37.17	0.79 ± 0.01
126	18.35	0.23 ± 0.00
126t	16.00	0.42 ± 0.00
127	0.00	0.12 ± 0.00
127t	0.00	0.16 ± 0.00
128	23.13	0.98 ± 0.01
129	0.63	0.79 ± 0.01
130	24.60	0.00 ± 0.00
131	18.74	0.74 ± 0.01
132	7.17	0.00 ± 0.00

133	21.21	0.59 ± 0.00
134	31.49	0.29 ± 0.00
135	20.13	0.17 ± 0.00
135t	0.16	3.10 ± 0.03
136	0.17	1.80 ± 0.02
136t	0.00	1.00 ± 0.01
137	13.80	0.25 ± 0.00
137t	0.65	2.10 ± 0.02
138	30.79	0.00 ± 0.00
138t	26.95	0.00 ± 0.00
139	9.24	1.25 ± 0.01
139t	6.79	1.79 ± 0.02
140	0.91	0.56 ± 0.00
140t	0.20	2.20 ± 0.02
141	11.12	0.86 ± 0.01
141t	10.78	0.69 ± 0.01
142	0.30	0.21 ± 0.00
142t	0.44	0.33 ± 0.00
143	10.75	0.84 ± 0.01
143t	10.70	0.29 ± 0.00
144	7.57	5.20 ± 0.05
144t	0.38	0.00 ± 0.00
145	9.61	0.00 ± 0.00
145t	0.75	0.77 ± 0.01
146	40.60	0.62 ± 0.00
146t	28.10	0.54 ± 0.00
147	23.73	1.02 ± 0.01
148	0.22	1.30 ± 0.01
148t	0.33	1.20 ± 0.01
149	0.34	0.59 ± 0.00
150	44.73	0.22 ± 0.00
150t	43.24	0.27 ± 0.00
151	0.12	0.96 ± 0.01
152	0.74	0.65 ± 0.00
152t	0.18	0.35 ± 0.00
153	0.22	0.29 ± 0.00
154	0.18	0.85 ± 0.01
154t	0.16	0.62 ± 0.00
155t	11.80	0.17 ± 0.00

Table A-3. Supplementary Data to Figure 2-3. Original data of As and Sb concentrations in water samples from China's mining sites, n=16.

	Sb (mg/L)	As (μg/L)
BK1-W-1	5.31 ± 0.05	796 ± 8
YKD-W-1	4.23 ± 0.03	1827 ± 18
SC2-W-0	9.53 ± 0.09	189 ± 2
SC2-W-1	3.47 ± 0.02	1027 ± 10
SC2-W-2	3.55 ± 0.04	1058 ± 10
SC3-W-2	3.80 ± 0.01	686 ± 6
WS-W-1	0.33 ± 0.01	212 ± 2
WS-W-2	8.57 ± 0.05	409 ± 3
WSB-W-1	3.21 ± 0.03	452 ± 4
WSB-W-2	2.70 ± 0.01	190 ± 1
WSB-W-3	2.50 ± 0.02	232 ± 2
NK-W-1	5.21 ± 0.04	882 ± 7
NK-W-2	9.30 ± 0.08	213 ± 2
NK-W-3	11.40 ± 0.03	531 ± 5
NK-W-4	4.88 ± 0.04	210 ± 2
NK-W-5	1.04 ± 0.01	598 ± 4

Table A-4. Supplementary Data to Figure 3-1. Original data of overall concentrations of Sb in beverages (μg/L).

Tap Water		Bottled Water		Soft Drink	
1	0.02	Western Family	0.22	Coca-Cola	0.11
2	0.10	Dasani	0.11	Coca-Cola	0.32
3	0.05	Whistler	0.21	Coca-Cola	0.21
4	0.20	Fiji	0.54	Pepsi	0.40
5	0.18	Real Canadian	0.22	Pepsi	0.14
6	0.06	Aquafina	0.34	Pepsi	0.51
7	0.02	Ice Mountain	0.11	Canada Dry	0.32
8	0.19	Naya	0.20	Canada Dry	0.10
9	0.20	Sierra	0.14	Canada Dry	0.80
10	0.02	President's choice	0.10	President's choice	0.81
11	0.06			President's choice	0.92
12	0.09			President's choice	1.10
13	0.13				
14	0.08				
15	0.12				
16	0.15				
17	0.08				
18	0.09				
19	0.11				
20	0.02				
21	0.07				
22	0.20				
23	0.10				
24	0.15				
25	0.03				
26	0.18				
27	0.24				
28	0.12				
29	0.08				
30	0.09				
31	0.25				
32	0.39				

Juice			Alcoholic Drink	
SUN-RYPE	Apple	0.72	Baja Rosa	0.51
Tropicana	Apple	0.87	Parrot Bay	0.92
Naked	Strawberry	0.94	Gibson's	1.12
V8	Strawberry	1.12	Claude val	1.20
Orchard Fresh	Mango	1.13	Malibu	2.32
Minut Maid	Orange	1.33	Minis	2.37
Tropicana	Lemon	2.12	Seagram's VO	2.69
Tropicana	Orange	2.35	Wiser's	5.11
Minut Maid	Orange	2.36	Captain Morgan	5.56
Tropicana	Lemon	1.55	Bacardi	6.91
Kang shi fu	Peach	1.15	Jack daniel's	5.06
Tropicana	Mango	1.10	Southern comfort	4.10
Western Classics	Orange	1.00	Kahlua	0.80
Tao Ti	Lemon	0.86	Smirnoff	0.13
Hong Food Tong	Lemon	0.89	Sky Vodka	1.10
SunnyD	Orange	0.51	Crown royal	2.35
Tropicana	Orange	1.11	Silent Sam	1.85
Kang shi fu	Pineapple	1.95	Red label	1.42
One	Pineapple	2.61	Baileys	1.14
SUN-RYPE	Peach	1.56	Goldschlager	0.98
Safeway	Orange	1.22	AS beer	0.43
Tropicana	Orange	1.27	Tia Maria	0.80
One	Lemon	0.97	Potter’s Vodka	0.12
Organics	Strawberry	0.91	Silent Sam	0.07
Real Time	Lemon	0.83	Alberta Pure	0.06
Qoo	Apple	0.82	Polar Ice	0.28
Minut Maid	Orange	1.10	Stone cellars	1.57
SUN-RYPE	Orange	0.53		
SunnyD	Orange	0.73		

Table A-5. Supplementary Data to Figure 3-2, Figure 3-3 and Figure 3-4**.** Original data of Sb concentrations in purchased bottled juice and bottled alcoholic drinks over a six-month holding period at room temperature (μg/L).

	Low Citric Acid Juice		
brand	type	first measure	six months later
SUN-RYPE	Apple	0.72 ± 0.08	0.76 ± 0.07
Tropicana	Apple	0.87 ± 0.06	0.81 ± 0.07
Qoo	Apple	0.82 ± 0.09	0.86 ± 0.09
Naked	Strawberry	0.94 ± 0.08	0.93 ± 0.07
Organics	Strawberry	0.91 ± 0.06	0.98 ± 0.06
V8	Strawberry	1.12 ± 0.09	1.12 ± 0.09
Western Classics	Strawberry	1.12 ± 0.09	1.00 ± 0.09
Orchard Fresh	Mango	1.13 ± 0.08	1.17 ± 0.09
Tropicana	Mango	1.10 ± 0.08	1.00 ± 0.08
Kang shi fu	Peach	1.15 ± 0.13	1.32 ± 0.12
SUN-RYPE	Peach	1.56 ± 0.10	1.62 ± 0.13
Kang shi fu	Pineapple	1.95 ± 0.13	1.95 ± 0.15
One	Pineapple	2.61 ± 0.21	2.66 ± 0.23
	Citric Acid Juice		
brand	type	first measure	six months later
SunnyD	Orange	0.51 ± 0.05	0.47 ± 0.03
SUN-RYPE	Orange	0.53 ± 0.04	0.83 ± 0.06
SunnyD	Orange	0.73 ± 0.07	0.70 ± 0.05
Tao Ti	Lemon	0.86 ± 0.05	1.04 ± 0.08
Hong Food Tong	Lemon	0.89 ± 0.07	1.59 ± 0.12
Real Time	Lemon	0.83 ± 0.07	0.79 ± 0.07
One	Lemon	0.97 ± 0.06	0.87 ± 0.09
Western Classics	Orange	1.00 ± 0.09	0.96 ± 0.10
Minut Maid	Orange	1.10 ± 0.09	1.35 ± 0.13
Tropicana	Orange	1.11 ± 0.05	1.15 ± 0.08
Safeway	Orange	1.22 ± 0.11	1.95 ± 0.15
Tropicana	Orange	1.27 ± 0.10	1.74 ± 0.13
Minut Maid	Orange	1.33 ± 0.12	1.31 ± 0.15
Tropicana	Lemon	1.55 ± 0.10	1.89 ± 0.15
Tropicana	Lemon	2.12 ± 0.16	2.47 ± 0.26

Tropicana	Orange	2.35 ± 0.17	2.71 ± 0.19
Minut Maid	Orange	2.36 ± 0.19	2.51 ± 0.22

Alcoholic Drink

brand	first measure	six months later
EtOH40%	0	0.20 ± 0.14
Alberta Pure	0.06 ± 0.04	0.48 ± 0.19
Silent Sam	0.07 ± 0.01	0.40 ± 0.09
Potter’s Vodka	0.12 ± 0.02	0.46 ± 0.22
Smirnoff	0.13 ± 0.05	0.23 ± 0.07
Polar Ice	0.28 ± 0.03	0.29 ± 0.10
AS beer	0.43 ± 0.06	4.92 ± 1.48
Baja Rosa	0.51 ± 0.04	1.60 ± 0.07
Kahlua	0.80 ± 0.06	1.10 ± 0.10
Tia Maria	0.80 ± 0.10	1.61 ± 0.20
Parrot Bay	0.92 ± 0.04	1.21 ± 0.09
Goldschlager	0.98 ± 0.05	1.60 ± 0.10
Gibson's	1.12 ± 0.20	1.67 ± 0.30
Baileys	1.14 ± 0.03	1.78 ± 0.08
Sky Vodka	1.10 ± 0.10	1.71 ± 0.20
Claude val	1.20 ± 0.09	1.15 ± 0.10
Red label	1.42 ± 0.30	2.34 ± 0.40
Stone cellars	1.57 ± 0.09	1.21 ± 0.10
Polar ice	1.61 ± 0.40	2.60 ± 0.40
Silent Sam	1.85 ± 0.10	1.88 ± 0.15
Malibu	2.32 ± 0.30	2.39 ± 0.30
Minis	2.37 ± 0.20	2.65 ± 0.30
Crown royal	2.35 ± 0.30	3.21 ± 0.30
Seagram's VO	2.69 ± 0.40	3.11 ± 0.40
Southern comfort	4.10 ± 0.60	4.92 ± 0.60
Jack daniel's	5.06 ± 0.50	4.90 ± 0.60
Wiser's	5.11 ± 0.40	4.97 ± 0.60
Captain Morgan	5.56 ± 0.50	5.35 ± 0.70
Bacardi	6.91 ± 0.50	6.78 ± 0.60

Table A-6. Supplementary Data to Figure 4-1 and Figure 4-2. Sb concentration in fruit juice squeezed from fruit flesh and after digestion (n=3) with nitric acid and sulfuric acid.

	Squeeze (μg/L)	Digest (μg/mg)
Apple	2.10 ± 0.40	0.71 ± 0.10
Grape	1.82 ± 0.20	1.71 ± 0.20
Orange	1.70 ± 0.40	2.10 ± 0.20
Mango	1.73 ± 0.30	1.50 ± 0.20
Lemon	1.30 ± 0.20	2.05 ± 0.20
Strawberry	1.30 ± 0.20	1.50 ± 0.20
Blueberry	1.10 ± 0.10	1.20 ± 0.10
Grapefruit	1.05 ± 0.10	1.30 ± 0.10
Blackberry	0.90 ± 0.10	1.10 ± 0.10
Pineapple	0.87 ± 0.10	1.00 ± 0.10
Pear	0.81 ± 0.10	1.06 ± 0.10
Cherry	0.70 ± 0.10	0.50 ± 0.10
Kiwi	0.23 ± 0.03	0.30 ± 0.02