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Leaching of metals and metalloids from highway marking glass beads and the potential environmental impact

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ABSTRACT

LEACHING OF METALS AND METALLOIDS FROM HIGHWAY MARKING GLASS BEADS AND THE POTENTIAL ENVIRONMENTAL IMPACT

by
Nimrat Kaur Sandhu

Glass beads are embedded in pavement markings to obtain retroreflectivity which plays a crucial role in the lighting-up effect needed for safe driving. Elevated metal and metalloid concentrations of As, Sb, and Pb have recently been observed in imported glass beads. The main objective of this research was to assess the environmental impact associated with applying these imported glass beads in highway markings. To achieve this objective, total metal concentrations were measured using two techniques: hydrofluoric acid digestion followed by inductively coupled plasma mass spectroscopy (HF/ICP-MS), and field portable x-ray fluorescence (FP-XRF) spectroscopy. A number of leaching studies were conducted and included two standard United States Environmental Protection Agency (U.S. EPA) methods: the toxicity characteristic leaching procedure (TCLP) and the synthetic precipitation leaching procedure (SPLP). In addition, a factorial study was conducted to determine the impact of environmentally relevant factors such as pH, chemicals applied on roadways, particle size, and time on metal and metalloid leaching. To compare results among the three types of studies (TCLP, SPLP, and factorial study), a select batch of glass beads with elevated concentrations was used. FP-XRF was observed to be as reliable a tool for measuring total metal and metalloid concentrations and is recommended over the use of HF/ICP-MS. Results demonstrated that the most important factors affecting leaching were pH and time. For anions such as $HAsO_4^{2-}$ and SbO_3^-, leaching increased with increasing pH, while for cations including Pb^{2+}, it increased as pH decreased. Sequential extraction was conducted as well to better understand the form of metals and metalloids associated with the glass beads. While 3% were extracted in the exchangeable (As, Mn, and Ba) and the oxidizable forms (Pb), greater than 97% of metals and metalloids were associated with the glass matrix. Further studies to assess leaching as a function of total concentration in the imported batch were conducted for 30 days. Non-parametric statistics were applied to test concentrations that resulted in excess of the groundwater quality criteria. Results demonstrated that the New Jersey Default Leachate Groundwater limits for As were exceeded for 98% of the samples tested. In case of Pb, these limits were exceeded for 58% of the samples and with Sb 15%. These results suggest a potential environmental impact to groundwater used as a drinking water source when either storing glass beads in bulk or disposing of the roadway marking material in bulk.

LEACHING OF METALS AND METALLOIDS FROM HIGHWAY MARKING GLASS BEADS AND THE POTENTIAL ENVIRONMENTAL IMPACT

by
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LEACHING OF METALS AND METALLOIDS FROM HIGHWAY MARKING GLASS BEADS AND THE POTENTIAL ENVIRONMENTAL IMPACT

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Sandhu, N. K., Ndiba, P. K., Axe, L., Jahan, K., Ramanujachary, K. V., Magdaleno, T. F. Leaching of heavy metals from highway marking beads. *96th American*

Association of State Highway and Transportation Officials (AASHTO) Sub Committee on Materials. August 8-12, 2010, Madison, Wisconsin.

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Sandhu, N. K., Ndiba, P. K., Axe, L., Jahan, K., Ramanujachary, K. V. Groundwater pollution from metals/metalloids present in highway marking glass beads. *96th Annual Conference on New Jersey Water Environment Association.* May 10-14, 2011, Atlantic City, NJ.

Sandhu, N. K., Ndiba, P. K., Axe, L., Jahan, K., Ramanujachary, K. V., Magdaleno, T. F. Heavy metal contamination in highway marking glass beads. *91st Annual Meeting of Transportation Research Board.* January 22-26, 2012, Washington DC.

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To my parents, for their unconditional love and support and unwavering trust in me.

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CHAPTER 1

INTRODUCTION

Currently, there is concern and evidence that glass beads used on roadways and highways have elevated metal and metalloid concentrations, which may be leachable. The transportation industry is one of the largest users of glass beads for highway marking. These markings are among the most efficient and economical means to safely guide traffic. Glass beads are embedded on pavement markings to provide *retroreflectivity* which is an optical phenomenon that plays a crucial role in maintaining the guiding function of the highway striping to ensure safe driving. The glass beads embedded in the marking material allow a vehicle's headlight beam to be returned to the driver's eye, resulting in a "light-up" effect of the striping. Integrating glass beads of good optical quality are essential to ensure clear visibility at night.

Glass beads used by the transportation sector in the U.S. for highway marking are required to meet the American Association of State Highway and Transportation Officials (AASHTO) MT 247-08 Specifications (Table 1.1; Appendix A). The specification details physical and optical properties of the glass beads. Using the U.S. Environmental Protection Agency (U.S. EPA) Method 1311, the toxicity characteristic leaching procedure (TCLP) (U.S. EPA 1991b), the classification of a waste is regulated through the Resource, Conservation and Recovery Act (RCRA) (Table 1.2) (U.S. EPA 1999). In addition to the AASHTO specifications, a number of states have adopted levels, for example, Louisiana developed a regulation for As, California promulgated regulations for As and Pb, while others have implemented further specifications (Table 1.3).

Table 1.1 Summary of AASHTO MT 247-08 Specifications

	Properties
Physical Properties	• Transparent, clean, colorless, smooth, and spherical • Free from milkiness, pits, and air bubbles • Minimum of 70% true spheres with 90% of the beads being able to float in xylene • Dry and free of lumps and clusters
Optical Properties	A refractive index of 1.50-1.55
Heavy Metal Content	The glass beads must not exhibit a characteristic of toxicity, relative to heavy metals, when tested in accordance with EPA 40 CFR 261.24.

Source: AASHTO MT 247-08 Specifications (Appendix A)

Table 1.2 RCRA Limits for Heavy Metals

Element	RCRA Limit (mg L^{-1})
As	5.0
Ba	100
Cd	1.0
Cr	5.0
Pb	5.0
Hg	0.2
Se	1.0
Ag	5.0

Table 1.3 Specifications and Regulations on Total Metal Content Proposed

Element	NJ, KS, OR, GA, IA (ppm)	TX (ppm)	WA (ppm)	CO, AZ (ppm)	CA** (ppm)	LA** (ppm)	ISO 4802-1 Container Glass (ppm)
As	200	75	20	75	75	75	100
Pb	200	100	50	100	100	-	100
Sb	200	-	-	75	-	-	100
Ba	-	-	100	-	-	-	-
Cd	-	-	1.0	-	-	-	-
Cr	-	-	5.0	-	-	-	-
Se	-	-	1.0	-	-	-	-
Ag	-	-	5.0	-	-	-	-
Hg	-	-	0.2	-	-	-	-

* All other states not listed here require the glass beads to exhibit toxicity levels less than those listed under RCRA (U.S. EPA 1999)

** This is a regulation and not a specification.

At the onset of this research based on a literature review, no study existed that addressed the leachable metal and metalloid concentrations in glass beads. Should metals or metalloids leach into the environment, the consequent environmental impact needs to be addressed. While National Institute of Standards and Technology (NIST) (NIST 1999) has issued regulations for metal concentrations in commercial glass manufacturing, other countries may not enforce these. Therefore, glass bead imports may exhibit elevated metal or metalloid concentrations.

The glass used for manufacturing highway marking glass beads is a soda-lime silica glass (Marini 2003). A typical soda-lime glass is composed primarily of 71 – 75% silica (SiO_2) derived mainly from sand, 12 – 16% sodium oxide (Na_2O) produced from soda ash (Na_2CO_3), and 10 – 15% calcium oxide (also known as lime from limestone – $CaCO_3$) (Table 1.4). A number of other minerals of lower concentrations are needed to impart specific properties to the glass (Table 1.5). Soda-lime glass is used by industries for jars, everyday tableware, and window glass. The widespread use of soda-lime glass results from its chemical and physical properties. Among the most important of these properties is the ability of soda-lime glass to transmit light, hence it is used in flat glass and transparent articles. The smooth, nonporous surface is also nonreactive under most applications with acceptable tensile and thermal properties. Furthermore, raw materials are comparatively cheap and economical to melt.

Typically, glass beads used in highway marking exhibit RCRA metal and metalloid concentrations less than 50 ppm (Sentruk 2008; van de Griend 2009). Specifically, As, Sb, and Pb are three elements that have been measured by a number of users of glass beads (Sentruk 2008; van de Griend 2009; Flint Trading 2008). These elements are used to improve the physical and optical properties of glass. For example, refining agents such as As_2O_3 and Sb_2O_3 are used for removing entrapped CO_2 gas formed during heating. Inorganic arsenic also acts as a decolorizer by controlling the oxidation state of iron in the glass. PbO is introduced as a stabilizer and modifier, improving the physical and chemical durability of glass. However, these improved properties can be achieved by using other non-toxic additives such as small amounts of tungsten, titanium, zirconium, and barium (Hayden 2004); obsolete methods, involving the use of regulated metals and metalloids for enhancing glass properties may still be practiced in developing countries. As such, glass beads produced and imported from China to the U.S. may have trace metal and metalloid concentrations.

Table 1.4 Major Raw Materials and their Function in the Formation of Glass

Raw Material	Function
Sand (SiO_2) 71-75%	Principal ingredient
Soda ash (Na_2CO_3) 12-16% Potassium carbonate (K_2CO_3)	Fluxing agents
Sodium sulfate (Na_2SO_4)	Refining and oxidizing agent
Calcium carbonate ($CaCO_3$) 10-15% Magnesium carbonate ($MgCO_3$)	Improve the hardness and chemical resistance
Aluminum oxide (Al_2O_3)	Improve chemical resistance and increase viscosity at lower temperatures.
Lead oxides (PbO and Pb_3O_4)	Increase the refractive index
Boron trioxide (B_2O_3)	Reduces glass expansion coefficient
Glass cullet	Requires less energy to melt than virgin raw materials, and every 1 ton of cullet replaces approximately 1.2 tons of virgin material.

Background arsenic concentrations in the environment vary from 1 - 10 µg L^{-1}; in freshwater, the range may be as low as 0.15 - 0.45 µg L^{-1} (Bissen and Frimmel 2003a, 2003b). On the other hand, in systems with arsenic-bearing minerals, concentrations ranging from 1 - 48,000 µg L^{-1} have been reported in the Western U.S. (Bissen and Frimmel 2003b). Typical concentrations of dissolved antimony in uncontaminated systems are less than 1 µg L^{-1}. However, in the presence of anthropogenic sources, concentrations may be more than 100 times natural levels with reports as great as 910 µg L^{-1} (Fillela et al. 2002; Rossmann and Barres 1988; Narasaki 1986). Lead is rarely found

Table 1.5 Raw Materials for Glass Making

Glass Forming Materials	Intermediate and Modifying Materials	Coloring/Decoloring Agents
Silica process cullet post-consumer cullet	Soda ash (Na_2CO_3), limestone ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$), feldspar ($KAlSi_3O_8$ - $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$), nepheline syenite ($(Na, K)AlSiO_4$), potassium carbonate (K_2CO_3), fluorspar (CaF_2), alumina (Al_2O_3), zinc oxide (ZnO), lead oxide (PbO), barium carbonate ($BaCO_3$), anhydrous sodium sulphate (Na_2SO_4), calcium sulphate ($CaSO_4$) gypsum ($CaSO_4 \cdot 2H_2O$), barium sulphate ($BaSO_4$), sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), borax ($Na_2B_4O_7 \cdot 10H_2O$), colemanite ($CaB_3O_4(OH)_3 \cdot H_2O$), boric acid (H_3BO_3), antimony oxide (Sb_2O_3), arsenic trioxide (As_2O_3), blast furnace slag (mixed calcium, aluminum, magnesium silicate and iron sulphide)	Iron chromite ($Fe_2O_3.Cr_2O_3$), iron oxide (Fe_2O_3), cobalt oxide (CoO, Co_2O_3, Co_3O_4) selenium/zinc selenide ($ZnSe$)

in source water, but enters tap water through corrosion of plumbing materials (ATSDR 1997).

In North America, approximately 500 million lbs per year of glass beads are used in pavement markings (Sentruk 2008; van de Griend 2009), which are increasingly being imported. As a result, metals and metalloids associated with these glass beads may be applied on the highways (Sentruk 2008). Because of their effectiveness in optimizing properties, As, Pb, and Sb are three elements that have been observed by a number of users of glass beads (Flint Trading 2008; van de Griend 2009). At the same time, concern has arisen because of their hazardous and toxic nature. Arsenic occurs naturally in soils and minerals and is a known carcinogen through both inhalation and oral routes of exposure (ATSDR 2007). Lead is a toxic metal that was used for many years in paint and gasoline for example; therefore, it has been found throughout the environment. Even at low levels, lead may cause a range of health effects including neurological ones in infants (ATSDR 1997). Antimony is found in the earth's crust but used in various industrial applications such as metal alloys, semi-conductors, coatings, pigments, and lead acid batteries. Oral exposure to antimony may result in gastrointestinal effects (ATSDR 1992). On the other hand, inhalation of antimony can cause pulmonary toxicity and chronic interstitial inflammation (U.S. EPA 1999).

Arsenic, antimony, and lead are the primary contaminants observed at elevated concentrations in imported glass beads; therefore, these contaminants are the focus of this study. The overall objective is to address the potential for leaching in the environment from the use of these glass beads. This dissertation includes a literature review that addresses the background on glass bead properties, soda-lime silica glass bead manufacturing process, composition and structure of soda-lime silica glass, its solubility, and leaching of metals and metalloids from silica systems (Chapter 2). Subsequently, objectives and hypotheses are stated (Chapter 3) and methodology described (Chapter 4). Results of total metal concentrations in glass beads (Chapter 5), leaching experiments (Chapter 6), and sequential extraction (Chapter 7) are presented and discussed. Finally, conclusions are drawn (Chapter 8) and future research described (Chapter 9).

CHAPTER 2

LITERATURE REVIEW

This chapter reviews glass bead properties, soda-lime silica glass bead manufacturing process, composition and structure of soda-lime silica glass, its solubility, and leaching of metals and metalloids from silica systems.

2.1 Glass Beads and Their Properties

Glass beads have been used for enhancing night-time reflectivity in pavements since the 1930s. This application of glass beads requires they exhibit a number of properties with respect to refractive index, roundness, gradation, and floatation to meet the AASHTO MT 247-08 specifications (Table 1.1 and Appendix A).

2.1.1 Retroreflectivity

When light strikes a glass bead it is both reflected and refracted. Refraction is the bending of light as it enters from one medium to another. When the light from a vehicle is transmitted to pavement markings, the light is refracted downward (Figure 2.1). The addition of glass beads to highway marking paint incorporates *retroreflectivit*y to the markings. Spherical glass beads reflect light directly to the source of the light. This phenomenon is termed *retroreflectivity* (Figure 2.2). The degree of light refracted is a characteristic of the glass material and is known as the refractive index (RI) of the glass bead. Typically glass beads used in the pavement industry have RI values ranging from 1.5 to 1.9; the higher end of this range is expensive and typically used in airport runways. The difference in pavement markings with and without reflective glass beads determines

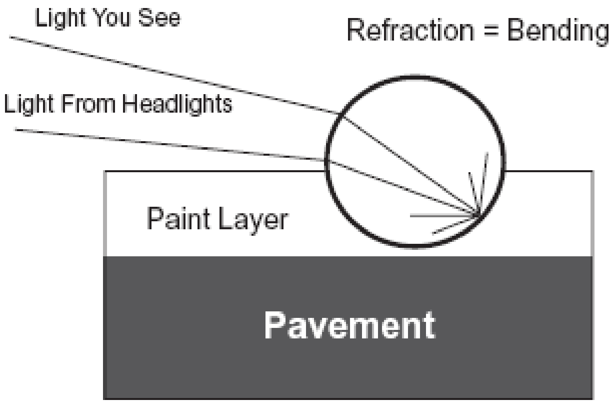


Figure 2.1 A glass bead exhibiting retroreflection of light.
Source: VADOT 2010

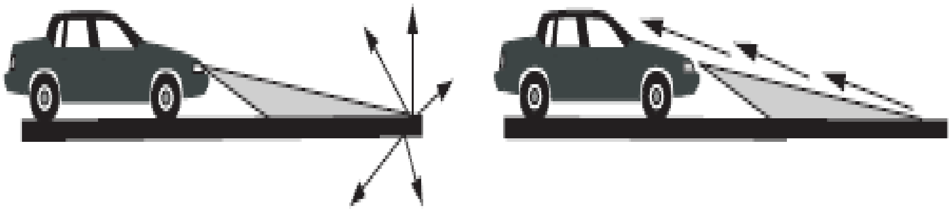


Figure 2.2 **(a)** Roadway with unbeaded markings **(b)** Roadway with beaded markings.
Source: VADOT 2010

Figure 2.3 **(a)** Pavement markings with reflective beads. **(b)** Pavement markings without reflective beads.
Source: VADOT 2010

the visibility for night-time driving (Figure 2.3). The refractive index (RI) is determined by

$$n = \frac{c}{v} \tag{2.1}$$

where *n* is the RI of the material, *c* is the velocity of light in vacuum, and *v* is the velocity of light in the material (Flinn and Trojan 1975). The RI of a glass depends on its composition and density (Figure 2.4). The density of soda-lime silica glass typically ranges between 1.9 and 2.5 g cm^{-3}. For this range of density, the refractive index for SiO_2-Na_2O glass varies from 1.48 to 1.52 (Shelby 2005).

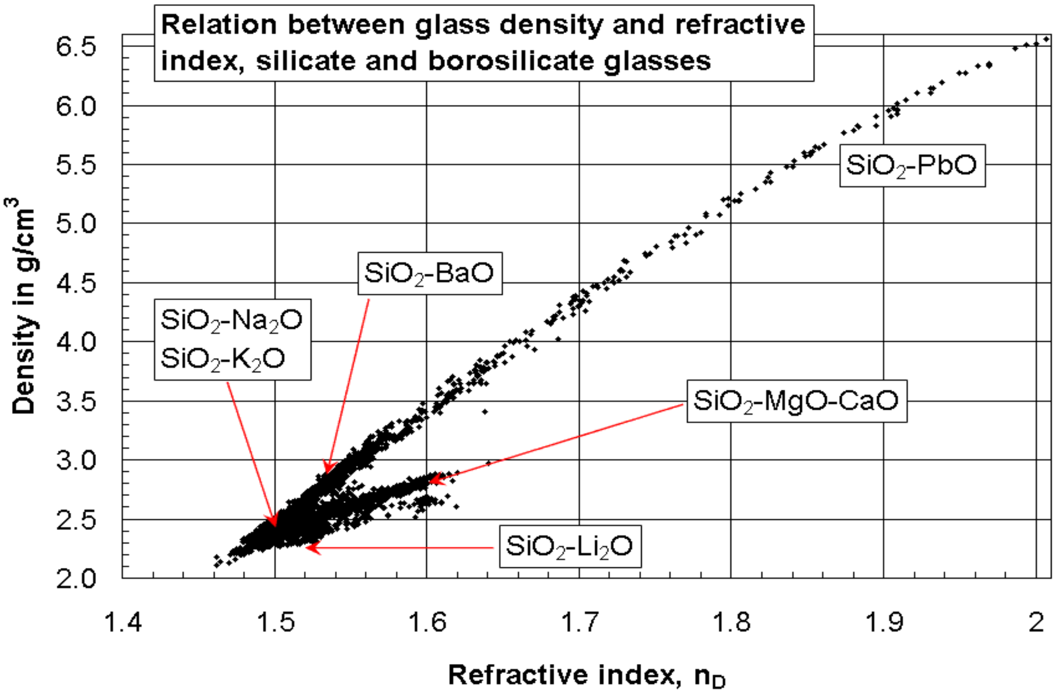


Figure 2.4 The relationship between density of glasses and their refractive indices (n_D). Source: Shelby 2005.

Retroreflectivity is dependent upon the embedment depth of the glass bead in the pavement marking epoxy/paint. Optimum embedment depth of glass beads is 50 to 60% assuring optimum reflectivity (VADOT 2010).

2.1.2 Roundness

The New Jersey Department of Transportation (NJDOT) requires greater than 80% of the glass beads to be “true spheres” (NJDOT 2008). Roundness of the glass beads is assessed using American Society of Testing Methods (ASTM) D 1155 (ASTM 2010). Roundness is critical to the application on roadways as it affects the optimum embedment into the paint. For optimum retroreflectivity and durability, a bead should be embedded at 50 to 60% of its diameter (Sheehy 2012; VADOT 2010).

2.1.3 Gradation

The gradation of glass beads is an important factor to be considered in their application. NJDOT (NJDOT 2008) requires 24 lbs of glass beads per gallon of epoxy in roadway application. Of these, 12 lbs of the glass beads (termed as small glass beads) should conform to AASHTO M 247 Type I specification requiring 100% to pass through 1.18 mm standard sieve (U.S. Mesh No. 16), 95-100% to pass through size 0.85 mm standard sieve (U.S. Mesh No. 18), and 75-95% to pass through 0.60 mm standard sieve (U.S. Mesh No. 30) (Figure 2.5). The remaining 12 lbs are termed large beads with 100% passing through the 2 mm standard sieve (U.S. Mesh No. 10), 95-100% passing through 1.7 mm standard sieve (U.S. Mesh No. 12), and 80-95% passing through 1.4 mm standard sieve (U.S. Mesh No. 14) (Figure 2.5). ASTM D 1214 (ASTM 2010) is used to assess the required gradation of the glass beads. Gradation is important because the size of glass beads will determine how deep they will embed into the paint. Optimum embedment depth is at 50-60% of the glass bead diameter. Not all glass beads will be at the optimum embedment depth; some are buried in the paint and others are embedded at depths less than 50-60%. As a result, the mix of large and small beads is applied to

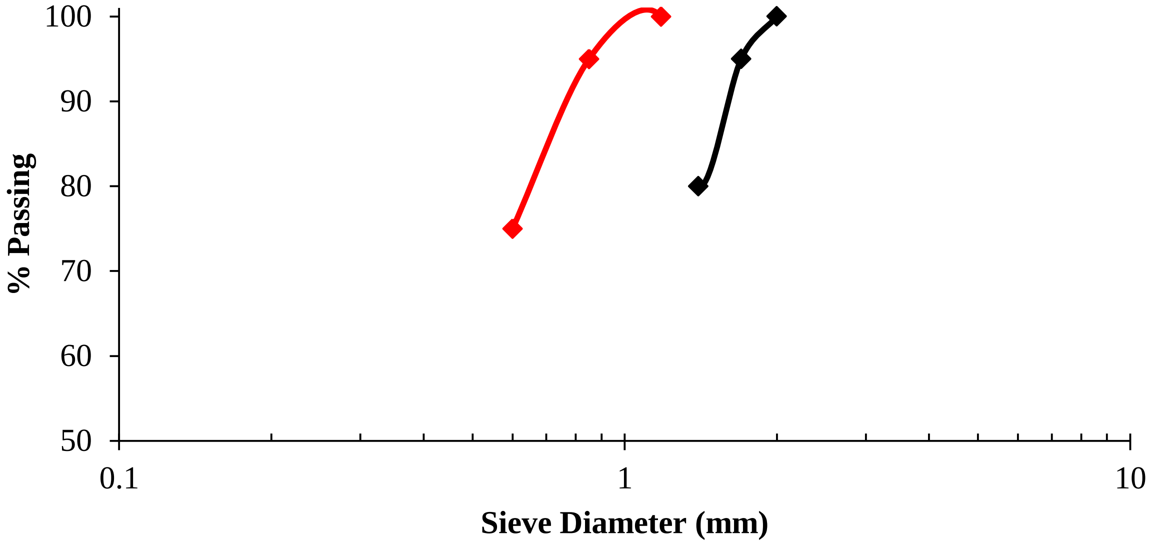
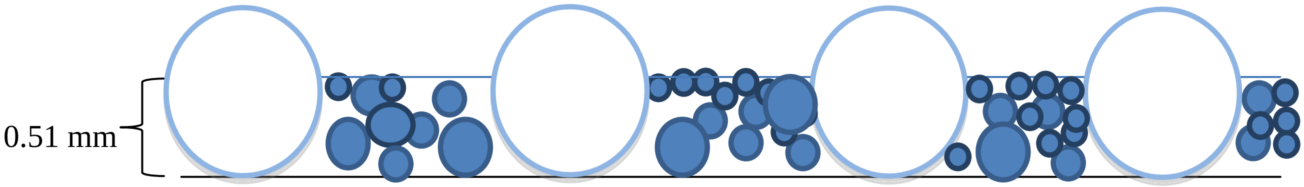


Figure 2.5 Gradation curve for glass beads as specified by NJDOT (NJDOT 2008).

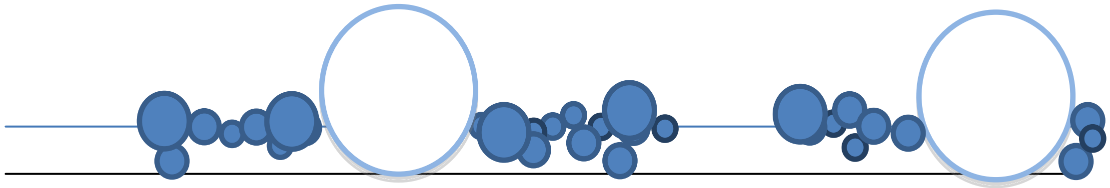
achieve optimum retroreflection from the smaller glass beads once larger glass beads have been abraded from traffic and erosion (Figure 2.6) (Sheehy 2012; VADOT 2010).

2.1.4 Floatation

For the glass beads to be embedded to the optimum depth that enables retroreflectivity, they are coated with a non-toxic organo-titanium derivative. This coating imparts buoyancy to the glass beads and causes them to float in the paint. The effectiveness of the coating is tested with xylene to ensure its oleophobic (oil-repelling) nature. Thirty milliliters of xylene is introduced in a petri dish containing a monolayer of glass beads (1 gm). The floating glass beads are then drawn off by suction and the remaining beads are oven dried and weighed to obtain the fraction removed. NJDOT requires a minimum of 90% of the beads to pass the xylene test (NJDOT 2008). As a result of the coating, beads



(a) Freshly Painted Road Surface with the Glass Beads.



(b) Road Surface after Abrasion and Wear & Tear

Figure 2.6 Effect of gradation on retroreflectivity of a highway.

are maintained at the surface enabling retroreflectivity (Sheehy 2012).

2.1.5 Glass Bead Application

In New Jersey, highway marking lanes are repainted every 3 years with reapplication of glass beads. Every 6 years marking lanes are ground up and new lanes painted. NJDOT uses 0.02 inches as the standard paint thickness applied on highway (Sheehy 2012). Glass beads are also applied simultaneously with the use of a hopper installed onto the paint applying equipment. This hopper mechanically distributes a mixture of large and small glass beads at the desired glass bead application rate (24 lbs/gallon of paint). Initially up to 70% of the glass beads sink in the wet paint and as it dries, beads float to the surface embedment depth of 50-60% (Sheehy 2012; VADOT 2010).In addition to the above requirements, glass beads should be moisture-free and non-toxic. While a number of states (Table 1.3) have adopted specifications and even regulations to address metal and metalloid concentrations in glass beads, federal regulations have not yet been promulgated. However, through the U.S. AASHTO MT 247-08, specifications are met (Table 2.1).

2.2 Glass Manufacturing

The following review on manufacturing of glass beads is from a report out of the Virginia DOT (VADOT 2010). Producing soda-lime silica glass involves heating raw materials to a molten condition. The temperature necessary for melting and refining the glass depends on the composition, and typically ranges between 1300°C and 1550°C. Because of the low thermal conductivity of the batch materials, the melting process is initially slow. Specifically, moisture evaporates, raw materials begin to decompose, and the gases trapped in the raw materials escape. The first reaction (decarburization) occurs at approximately 500°C. The raw materials melt between 750°C and 1200°C and silica begins to dissolve under the influence of the fluxing agents. Silica then combines with the sodium oxide from the soda ash along with other compounds to form silicates. At the same time, large amounts of gases escape through the decomposition of the hydrates, carbonates, nitrates, and sulfates, giving off water, carbon dioxide, and oxides of nitrogen and sulfur. The glass melt becomes transparent and the melting phase is completed. The phase is about 35 - 50% of the initial volume of batch materials due to the loss of gases and elimination of interstitial spaces. Two methods are used to produce the glass beads:

Table 2.1 Specifications Followed by all the States for Highway Marking Glass Beads

Serial No.	State	Specification Followed
1	Alabama	AASHTO M 247 Type I
2	Alaska	AASHTO M 247 Type I
3	Arizona	AASHTO M 247 Type I, Table 1.3
4	Arkansas	AASHTO M 247 Type I
5	California	AASHTO M 247 Type I, Table 1.3
6	Colorado	AASHTO M 247 Type I, Table 1.3
7	Connecticut	AASHTO M 247 Type I
8	Delaware	AASHTO M 247 Type I
9	Florida	AASHTO M 247 Type I, FP, 96
10	Georgia	AASHTO M 247 Type I, Table 1.3
11	Hawaii	AASHTO M 247 Type I
12	Idaho	AASHTO M 247 Type I
13	Illinois	AASHTO M 247 Type I
14	Indiana	AASHTO M 247 Type I
15	Iowa	AASHTO M 247 Type I
16	Kansas	AASHTO M 247 Type I, Table 1.3
17	Kentucky	AASHTO M 247 Type I
18	Louisiana	AASHTO M 247 Type I, Table 1.3
19	Maine	AASHTO M 247 Type I
20	Maryland	AASHTO M 247 Type I
21	Massachusetts	AASHTO M 247 Type I
22	Michigan	AASHTO M 247 Type I
23	Minnesota	AASHTO M 247 Type I
24	Mississippi	AASHTO M 247 Type I
25	Missouri	AASHTO M 247 Type I
26	Montana	State Requirements
27	Nebraska	AASHTO M 247 Type I
28	Nevada	AASHTO M 247 Type I
29	New Hampshire	AASHTO M 247 Type I
30	New Jersey	AASHTO M 247 Type I, Table 1.3
31	New Mexico	AASHTO M 247 Type I
32	New York	AASHTO M 247 Type I
33	North Carolina	AASHTO M 247 Type I, only North American cullet to be used
34	North Dakota	AASHTO M 247 Type I
35	Ohio	AASHTO M 247 Type I
36	Oklahoma	AASHTO M 247 Type I
37	Oregon	AASHTO M 247 Type I, Table 1.3
38	Pennsylvania	AASHTO M 247 Type I
39	Rhode Island	AASHTO M 247 Type I
40	South Carolina	AASHTO M 247 Type I
41	South Dakota	AASHTO M 247 Type I
42	Tennessee	AASHTO M 247 Type I
43	Texas	AASHTO M 247 Type I, Table 1.3
44	Utah	AASHTO M 247 Type I
45	Vermont	AASHTO M 247 Type I
46	Virginia	AASHTO M 247 Type I
47	Washington	AAHTO M 247 Type I, Table 1.3
48	West Virginia	AASHTO M 247 Type I
49	Wisconsin	AASHTO M 247 Type I
50	Wyoming	AASHTO M 247 Type I

the direct method and the indirect method (VADOT 2010). In the direct method, liquefied (molten) glass is sprayed and atomized into spheres similar to the formation of water droplets from a garden hose. As the molten glass is sprayed or forced out of the reactor, it is suspended as spherical droplets, which are cooled, collected, and then sifted through grading screens. This method can be tailored to glass requiring a RI between 1.65 and 1.90 where the rheology changes from a molten state to a hardened bead.

The indirect method is the most commonly employed process for RI values of 1.50-1.55. In this method, a selected material (either new or reclaimed cullet) is pulverized into glass powder. This powder is then poured, sprayed, or spread into a large three- to four-story furnace (Figure 2.7). The individual particles are blown through several flames until they soften and take the shape of spheres. These spherical droplets are cooled in the top half of the furnace and are then collected and sifted through grading screens. While glass manufacturing processes are proprietary, personal communication with Weissker Manufacturing Inc. (Wade 2012) revealed that the size of the glass beads produced is directly proportional to the size of the input cullet. Material from either method can be mixed to provide the necessary gradations to meet desired specifications. After manufacturing, these highway beads are bagged and stocked for shipment.

2.3 Glass Composition and Structure

Glass beads are comprised of soda-lime silica glass: 70-75% SiO_2, 11-15% Na_2O, 2-4% MgO, 6-10% CaO, and 1-2% Al_2O_3 (Martini 2003). They are produced from virgin materials and as much as 90% recycled glass commonly known as cullet. Use of cullet lowers the melt temperature reducing both use of virgin materials and costs of waste glass disposal. Historically, traces of As_2O_3 and Sb_2O_3 have been used in the manufacturing of

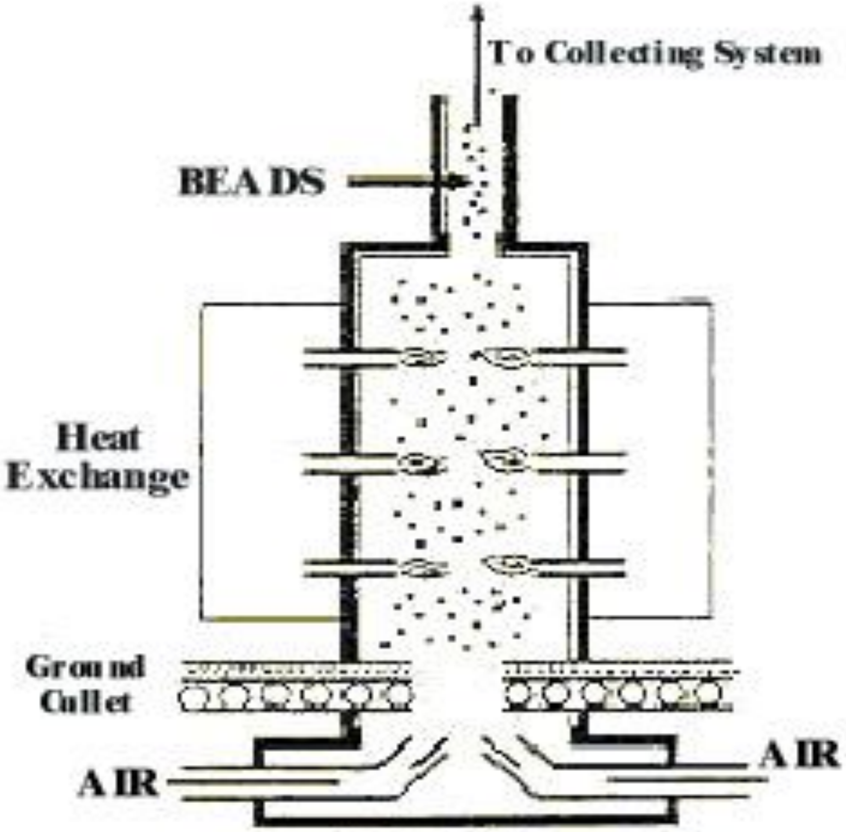


Figure 2.7 Typical glass beads manufacturing process.
Source: VADOT 2010

glass as fining agents and as decolorizers (Hynes and Jonson 1997). PbO is introduced as a stabilizer and modifier, and improves the physical and chemical durability of glass; it is also added to increase the brilliance of glass. However, although other non-harmful additives are available today (Hayden 2004), which are capable of producing the same effects, manufacturers of the imported glass beads are using technology involving the use of metals and metalloids (van de Griend et al. 2009).

The soda-lime silica glasses are Si-O networks in which the SiO_4 tetrahedral are joined together by the oxygen atoms located at the vertices. These tetrahedral connections become modified by the incorporation of the Na, Ca, Mg, Fe, K, and Al ions (Suszynska et al. 2010). The basic unit is a trigonal antiprism in which Na is coordinated to three O atoms at a distance of 2.3 Å with another three O atoms at non-bonding distances of approximately 3 Å (Greaves 1985). The bonding is random and hence, a random three-dimensional network is obtained. The configuration does not repeat itself at regular intervals, which makes the glass non-crystalline (Warren 1934). When alkali and alkaline earth metals such as Na, Ca, K, Mg, and Al are introduced in the glass structure, they form ionic (non-bridging) with the oxygen atoms (Figure 2.8). This results in the formation of a more open glass network which favors the dissolution of the glass structure under the influence of a chemical attack (Carmona et al. 2005; Clark et al. 1979; Sinton and LaCourse 2001).

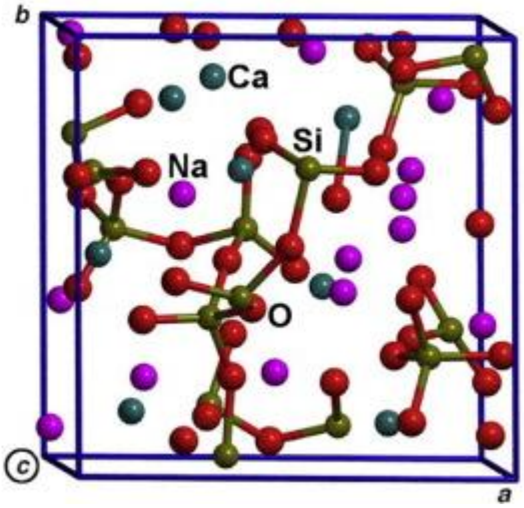


Figure 2.8 A modified random network for glass.
Source: Corno and Pedone 2009.

2.4 Problems of Metals and Metalloids

Analysis of glass beads from Australia, North America, and Europe were found to contain only background concentrations of trace metals, which were consistent with 'naturally occurring' minerals used in the manufacture of soda-lime silica glass. Australia and New Zealand recommend a maximum of 50 ppm for As, Sb, and Pb, and 10 ppm as a maximum for Cd, Hg, and Cr (DR 06734 2009). On the other hand, Austrian, Swedish, and Finnish authorities have set a maximum of 200 ppm (mg/kg) for each of the following As, Pb, and Sb (CEN 2008).

As glass beads are essentially manufactured from cullet, the source of cullet directly effects the concentration of metals and metalloids in the glass beads. Pavement markings in North America today use 500 million lbs of glass beads per year which are increasingly being imported. As a result, metals and metalloids associated with these glass beads may end up on the highways (Ufuk 2008). Glass bead manufacturers have made efforts to inform transportation agencies about the potential environmental impact of metals in glass beads used for highways (Flint Trading 2008; Ufuk 2008). Duty (2006) reported that of the nine imported and ten domestic glass bead samples, concentrations ranged as high as 880 mg kg^{-1} for As, 1,070 mg kg^{-1} for Pb, and 670 mg kg^{-1} for Sb in the foreign beads, while the majority of the North American beads did not exhibit detectable concentrations. Another study reported As concentrations of 1,000 mg kg^{-1} for beads imported from China, compared to the less than 15 mg kg^{-1} for those produced in North America (van De Griend et al. 2009). An environmental impact assessment conducted by the Swedish Environmental Research Institute (SERI) revealed concentrations in glass beads as great as 151 mg kg^{-1} of lead and 790 mg kg^{-1} of arsenic (Andersson and Woldegeorgis 2007). The presence of metals and metalloids at elevated concentrations requires further assessment for potential leaching under environmentally relevant factors.

2.5 Solubility of Silica

Glass is defined by the American Society for Testing and Materials (ASTM) as an inorganic product of fusion which has cooled to a rigid condition without crystallizing. One of the most studied properties of glasses is its durability. Solubility is a dominant factor controlling the chemical durability of glasses in aqueous solutions. During dissolution of glass in the aqueous phase, surface conditions change and leaching occurs. In the simplest case, the rate limiting reaction is

$$SiO_2 + H_2O \leftrightarrow H_2SiO_3$$

and the corrosion of glass has been observed to occur in two stages (Walker 1977; Clark et al. 1979; Carmona et al. 2005). First is the ion exchange process of cations (Na, Ca, B, Mg, K) in the glass with hydrogen ions from solution where the surface area may increase:

$$\equiv Si\text{-}O^{-}Na^{+} + (H^{+} + OH^{-}) \rightarrow \equiv Si\text{-}OH + Na^{+} + OH^{-}$$

This selective dissolution process results in the formation of a silica-rich modifier-depleted surface layer on the glass. In addition, hydroxyl ions may directly attack the silicate structure of the glass, resulting in network dissolution:

$$\equiv Si\text{-}O\text{-}Si \equiv + OH^{-} \rightarrow \equiv Si\text{-}OH + {}^{-}O\text{-}Si \equiv$$

The Si-O-Si bonds breakdown and generate silanol groups ($\equiv Si\text{-}OH$) and non-bridging oxygen groups ($\equiv Si\text{-}O^{-}$). Breakdown of the silica structure takes place at $pH > 9$ for soda-lime silica glasses. In acidic, neutral, and weakly alkaline solutions, the activity of $\equiv Si\text{-}OH$ groups is much greater than the activity of $\equiv Si\text{-}O^{-}$ groups. Increasing the hydroxyl ion activity would result in increased formation of $\equiv Si\text{-}O^{-}$ groups. Thus, at higher pH conditions the silica structure begins to break down. In multi-component glasses (i.e., glass beads), some of the bonds in the glass structure are non-bridging due to the presence of Na_2O, CaO, K_2O, and MgO; this structure results in an increased dissolution rate. As dissolution proceeds, ($\equiv$ Si-O$^-$) groups may react:

$$\equiv \text{Si-O}^- + (\text{H}^+ + \text{OH}^-) \rightarrow \equiv \text{Si-OH} + \text{OH}^-$$

giving rise to more silanol groups and hydroxyl ions which result in the aqueous medium becoming increasingly basic. The pH of the solution increases rapidly because of the high concentration of OH^- ions and attack becomes more aggressive in a basic medium (Figure 2.9). The solution pH is important as it determines the surface charge of the beads, and the degree of ionization and speciation of the elements in solution. The interactions between the charged ions in solution and the surface of beads contribute to the release or adsorption of species. Imported glass beads have recently been observed to exhibit the presence of metals and metalloids. The concern with applying these glass beads is the potential environmental impact from subsequent leaching. In the next section, leaching from silica related substrates is reviewed.

2.6 Leaching from Silica Based Matrices

Silica is a chemically stable phase at room temperatures. SiO_2 is a primary substrate for many products as well as a major substrate found in many wastes. Soils, fly ash, air-pollution-control residues, sludges, and sediments are examples of silica based matrices where their contribution is often as great as 60%. In this section, the leaching characteristics of silica matrices are reviewed which include studies on glasses, soils, sediments, fly ash, and coal combustion products (CCP).

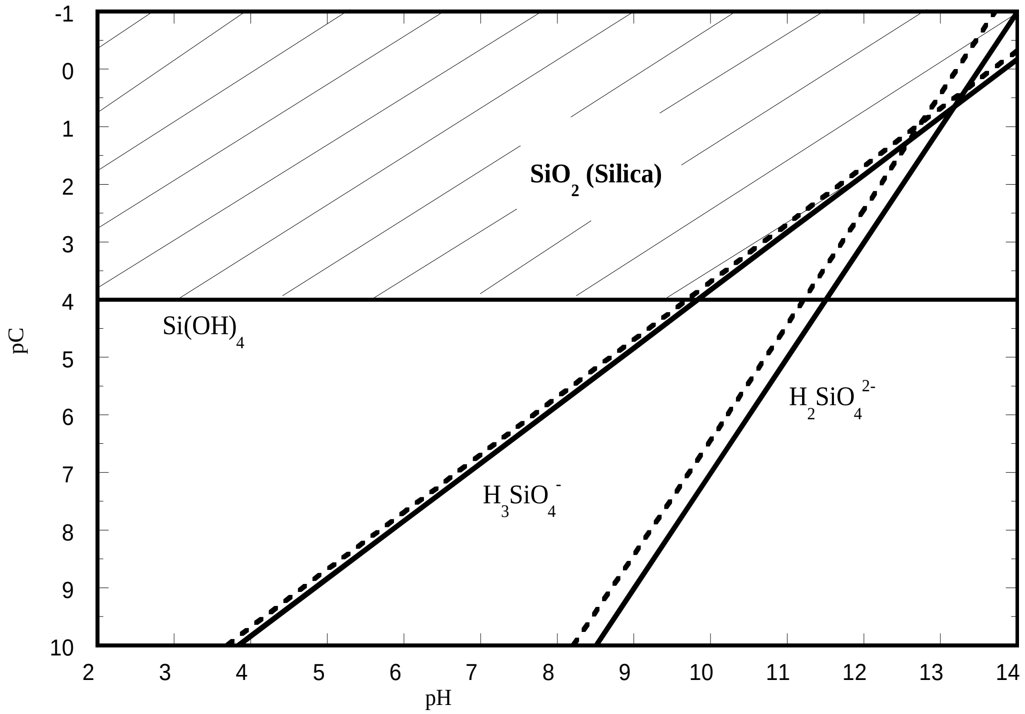


Figure 2.9 Silica solubility diagram for ionic strength 10^{-4} M (solid lines) and 5 ×10^{-1} M (dashed lines) showing increased solubility with pH and ionic strength; computed using MINEQL+ (MINEQL+ 1998).

Glasses: Glass has been a utilitarian and aesthetic item in all periods of history. The mechanisms involving dissolution of glass and leaching of its components have been studied in immense detail (Lombardo et al. 2005; Speirings and Van Dijk 1987; Cailleteau et al. 2008; Gitari et al. 2009; Chopinet et al. 2008). Cailleteau et al. (2008) studied the dissolution of three different glasses, borosilicate glass, aluminosilicate, and lead silicate, as a function of temperature and pH. Dissolution of borosilicate glass was evaluated at 90 ºC and pH 8.5 in a solution of HCl and trihydroxymethyl-aminomethane, while aluminosilicate and lead silicate were studied at 37 ºC and pH 4.6 in tribasic ammonium citrate and 60 ºC and pH 3-4 in acetic acid solution, respectively. In each of the glass families, results showed that dissolution of the glass structure increased with the increase in soluble oxides such as Na_2O and K_2O due to the increase in the number of non-bridging bonds in the silicate structure. Chopinet et al. (2008) found similar results with freshly prepared glass containers and powdered glass.

In another study on leaching of Pb and Cd from dinnerware, Sinha et al. (2007) used five organic acids: acetic acid, tartaric acid, citric acid, lactic acid, and ascorbic acid, at concentrations of 2%, 4%, and 8% for a period of 1 to 24 hours. Results demonstrated that leaching increased with increasing contact time, although maximum leaching of Pb and Cd occurred in the first two hours in 4% acetic acid solutions. Durability of commercial and experimental soda-lime silica glass was studied by Sinton and LaCourse (2001). Glass samples were milled to a size of 300-500 µm and leached in 98ºC de-ionized water for 1 h. Na was observed to leach preferentially over K. While Al_2O_3 increased durability, Na_2O and K_2O decreased durability.

Weathering of glass has been studied as well (Lombardo et al. 2005). Glass samples were placed in a pedestrian area for 2 years using two exposure modes: sheltered and unsheltered from the rain. Analyses revealed formation of leached layers on both types of samples though unsheltered samples were more weathered. The thickness of the leached Na layer was observed to grow with the square root of time, suggesting diffusion (rate) limited process. Carmona et al. (2005) observed that the attack can be more rapid for less resistant glasses which include potash-lime silicate glass (47% SiO_2, 19 % K_2O, 23% CaO, 3% P_2O_5, 3% MgO, 3% Al_2O_3, ~ 1% Na_2O) as compared to more resistant glasses such as lead crystal (59% SiO_2, 16% K_2O, 0.13% CaO, 24% PbO, 0.2% Al_2O_3, 0.1% Na_2O). The effect of time shows that when leached or alteration layers are formed, leaching of ions from the glass reduces and not until the layer breaks down, leaching resumes.

Soils and Sediments: Bioavailable metals and metalloids in soil, sediment, groundwater, and surface water pose a potential risk to human health and the environment. Anthropogenic sources are often deposited in roadside soils, where subsequent leaching has potential impacts on groundwater. A number of studies have examined leaching of heavy metals from soils (Dijkstra et al. 2004; Cappuyns and Swennen 2008; Ghosh et al. 2004). Dijkstra et al. (2004) studied leaching from contaminated soils over a wide range of pH (0.4-12). The susceptibility of metal cation release into water and the resulting transport depends on speciation and affinity to bind to reactive surfaces in the soil matrix. A batch leaching procedure with a pH-static system was used in combination with selective extraction to determine leaching of Pb, Zn, Cu, Cd, and Ni. Dijkstra et al. (2004) showed that leached concentrations made up a small fraction (approximately 2 to 10%) of the total metal present in the soils. They also found that leaching was a function of pH. In another study, Cappuyns and Swennen (2008) applied three approaches to investigate leaching from three different sediments: a column leaching test (NEN 7343 1995a), a cascade leaching experiment (NEN 7349 1995b), and a pH-static test (Table 2.2). In the column leaching studies, an increase in pH resulted in increasing redox potential as well as dissolved organic carbon (DOC) concentration, which enhanced mobilization of As, Cu, and Ni. As an anion, arsenic leaching was the most significant at higher pH, while Cd was the least. In the pH-static experiments, cations leached to a greater extent than anions with decreasing pH. The cascade leaching test was applied in another study as well where Zn was the most labile and Pb the least of metal cations from dredged sediments. Ghosh et al. (2004) used five experiments to study the degree of leaching from arsenic adsorbed on activated alumina and granular ferric

Table 2.2 List of Commonly used Leaching Tests Around the World

Test	Conditions	Time
TCLP, U.S. EPA Method 1311	Extraction fluid selected on the basis of an initial testing of pH of the waste 1. Extraction fluid # 1: Mixture of CH_3CH_2OOH and NaOH in Millipore-Q water at an initial pH of 4.93 ± 0.05. 2. Extraction Fluid # 2: Mixture of CH_3CH_2OOH and Millipore-Q water at an initial pH of 2.88 ± 0.05.	18 h
SPLP, U.S. EPA Method 1312	Extraction fluid selected on the basis of an initial testing of pH of the waste 1. Extraction fluid # 1: Solution of 60/40 by wt %mixture of H_2SO_4/HNO_3 in Millipore-Q water at an initial pH of 4.20 ± 0.05. 2. Extraction fluid # 2: Solution of 60/40 by wt % mixture of H_2SO_4/HNO_3 in Millipore-Q water at an initial pH of 5.00 ± 0.05.	18 h
Column Leaching Test	Millipore Super-Q water, acidified to pH 4 with HNO_3, L/S ratios of 0.1, 0.2, 0.5, 1, 2, 5, and 10	Variable
Cascade Leaching Test	Millipore Super-Q water, acidified to pH 4 with HNO_3, L/S ratio ranging from 20:1 to 100:1	22 h
German Standard Leaching Test (DIN-S4)	Extraction with Millipore Super-Q at a preset pH value (4-11), L/S ratios of 10:1.	24 h
European Union Leaching Test	Extraction with Millipore Super-Q at a L/S ratio of 10:1.	24 h
Sequential Extraction	1. 0.11 M CH_3COOH, L/S ratio 20:1, 30 rpm 2. 0.1 M $NH_2OH.HCl$; L/S ratio 20:1, pH 2 with HNO_3, 30 rpm 3. (a) 30 % H_2O_2, 85 ºC, L/S ratio 5:1 (b) 1 M CH_3COONH_4; L/S ratio 20:1, pH 2 with HNO_3	16 h 16 h 2 h 16 h
Modified Sequential Extraction	1. 0.11 M CH_3COOH, L/S ratio 20:1, 30 rpm 2. 0.5 M $NH_2OH.HCl$; L/S ratio 20:1, pH 2 with HNO_3, 30 rpm 3. (a) 30 % H_2O_2, 85 ºC, L/S ratio 5:1 (b) 1 M CH_3COONH_4; L/S ratio 20:1, pH 2 with HNO_3	16 h 16 h 2 h 16 h
pH static test	Batch experiment auto-titration with a pH electrode, L/S is variable	Variable
California Waste Extraction Test (WET)	Extraction with 0.2 M sodium citrate solution (prepared by titrating citric acid in Millipore Super-Q water with 4 N NaOH) at pH 5.0 ± 0.1, L/S ratio of 10:1	48 h

hydroxide sorbents. The TCLP (U.S. EPA 1991), the California Waste Extraction Test (WET) (CCR 1985), actual landfill leachate (LL), and two synthetic landfill leachates (SL1 and SL2) were used. While the TCLP and other leaching simulations with LL, SL1, and SL2 were conducted for 18 hours, the WET experiment was run for 48 hours. Interestingly, the WET study extracted eight times more As than the TCLP. Furthermore, leaching was observed to increase with time where up to a 10% increase in leaching was observed when solutions were allowed to equilibrate for 6 weeks.

Roadside soils and sediments are often repositories for heavy metal contamination. The levels of heavy metals in Nigerian roadside top soils were found to decrease rapidly with distance from the road and at about 50 m the concentrations leveled off to background ones (Fakayode and Olu-Owolabi 2003). Sources of metals observed in roadside soils included leaded gasoline until 1996, Zn from tires and crash barriers, Cu from brake linings, and Cd from tires and lubricating oils. Batch studies conducted showed that leaching increased with the addition of complexing ligands. Sequential extraction revealed that Zn was the most labile as it was associated with the exchangeable fraction, while Cd was the least as it was associated with non-extractable forms such as oxides and occluded in Al or Fe oxides.

Wang et al. (2007) used a simple bioavailability extraction test (SBET) to address incidental soil ingestion by children. Synthetic stomach fluid was prepared applying glycine and de-ionized water with a pH of 1.5 using HCl. Results showed that after 1 hour of leaching Pb and Zn were the most bioavailable (71% and 59%, respectively) with the following trend: Pb > Zn > Cu > As > Co > Ni > Cr. Consistently, bioavailability of cations increased with decreasing pH. Saeedi et al. (2009) used TCLP to better understand metal mobility on twenty seven roadside soil samples in Iran. The leached concentrations of Pb (4.91 mg L^{-1}) were close to that of the U.S. EPA RCRA limits (5 mg L^{-1}), which classify a waste as hazardous. In another study, Chen et al. (2010) applied column experiments to evaluate heavy metal mobility under simulated rainfall conditions. To prevent pollution of soil or groundwater by heavy metals from compost, many countries such as Belgium, Holland, and Germany have established standards for heavy metals in compost. For example, in Holland, maximum allowable concentrations of Zn, Cu, Pb, and Cd are 75, 25, 65, and 0.7 mg kg^{-1}, respectively, while in Germany they are 400, 100, 150, and 1.5 mg kg^{-1}, respectively. As observed with other studies, Chen et al. (2010) showed that leaching of Zn was greater than that for Cu, and Cu unlike Zn formed stable organic-Cu complexes on soil surfaces.

Norrström and Jacks (1998) studied the leaching of heavy metals from roadside sediments in Sweden under the effect of applied de-icing salts. Sequential extraction showed that a significant fraction of Pb, Cu, and Zn is susceptible to leaching when NaCl is used. The presence of Cl decreased metal adsorption through increasing chloride complexation in the leachate. The effect of salt on leaching of metals from roadside soils was studied recently by Nelson et al. (2009). Specifically, the effect of NaCl and $MgCl_2$ on heavy metal mobility was evaluated using soil columns. Cu was shown to be more mobile than Pb. While chloride increased Pb leaching through complexation, the presence of magnesium promoted flocculation and therefore reduced metal mobility.

Metal leaching from soils and sediments is dependent on a number of environmentally relevant factors including pH, the presence of complexing ligands and competing co-ions, organic matter, ionic strength, mineralogy, temperature, and time.

Soils and sediments are comprised of a number of surfaces among which silica, clays, iron oxides, manganese oxides, aluminum oxides, and solid organic matter are some of the more important surfaces. These surfaces and coatings are found in other systems as well including fly ashes where metals are also observed.

Fly ash/Air pollution control residues: Fly ash is a by-product of municipal solid waste (MSW) incineration and coal combustion processes. Typically, fly ash consists of 48-60% SiO_2, 20-30% Al_2O_3, 0.1-2% Na_2O, 1-8% Fe_2O_3, 3-11% CaO, and traces of heavy metals (Medina et al. 2010; Sheng et al. 2003; Zhang et al. 2010). The leaching from fly ash similar to that of soils and sediments depends strongly on the mineralogy, morphology, water chemistry, and the time scale of the leaching reactions. The pH of the extractant is important in the leaching as it influences adsorption/desorption, dissolution, and leaching of species from fly ash. Fly ash is also used as fill material in a variety of engineering applications potentially increasing risk from contaminant leaching. In a study conducted on municipal solid waste (MSW) fly ash, Zhang et al. (2010) applied sequential extraction to evaluate phases controlling contaminant mobility. Cd was found to be associated with the acid soluble, exchangeable, and water soluble phases; Pb was observed to be in the acid soluble phase; and, Zn and As were bound with organics and acid soluble phases. The influence of pH on air pollution control (APC) residues from MSW incinerator was studied with pH-static experiments (Astrup et al. 2001). As observed in other studies, Pb and Zn were observed to behave amphoterically with increased solubility at lower and higher pH conditions. Cd, Ni, and Cu leached to a greater extent as pH decreased in contrast to the reduced leaching as the pH increased.

The acid neutralizing capacity (alkaline pH) of APC residues led to lower releases of Cd as compared to Pb. At a pH greater than 8, $Pb(OH)_{2(s)}$ was the controlling phase, below pH 8 $Pb_5(PO_4)_3Cl$ was projected to dominate. Studies have shown that fly ash and air pollution control residues are likely to result in alkaline pH conditions for extended periods of time, up to thousands of years; thus, these surfaces can potentially serve as a source for leaching (Johnson and Furrer 2002; Crawford et al. 1997).

Glass and glass ceramics produced from fly ash were evaluated for their leaching characteristics using acidic (pH 3) and alkaline solutions (pH 10) (Park and Heo 2004). While leached concentrations of Cd, Cr, and Pb were found to be greatest at pH 3 and below the detection at pH 10, glass dissolution was most significant at pH 10. Interestingly, Song et al. (2004) found that leaching increased with decreasing silica concentrations: fly ash with 17% versus bottom ash with 53%. Vítková et al. (2009) investigated the pH dependent leaching behavior of metals from smelter ashes. Leachability was assessed for the fly ash before and after washing to remove readily soluble salts. As expected, metals associated with the washed fly ash leached less than those with the unwashed ash. Again, as observed in other studies, cations such as Pb and Zn were observed to leach as the pH decreased.

Zeolites found in fly ash produced during the combustion of powdered coal were evaluated for leaching of metals using column experiments (Steenbruggen and Hollman 1998). Results indicated rapid release of anions (As and Se) and very little release of cations (Cu, Pb, Zn) possibly due to the precipitation as hydroxides or due to structural bonding within the zeolite framework. In another study, Popovic et al. (2001) examined the leaching behavior from coal ash derived from a power plant in Yugoslavia using a modified sequential extraction procedure. Leaching was found to be most significant for Cr followed by Zn and then Ni.

Sheng et al. (2003) studied glass produced from vitrification of coal fly ash in China where SiO_2 and Al_2O_3 (main glass network formers) dominate and are used in fabricating composite materials. Results indicated that addition of ~10% by weight of Na_2O increased the compressive strength to ~60 MPa, which is comparable to the strength of commercial glasses. The vitrified glass was further tested with TCLP where leached concentrations ranged from 6 $\mu g\ L^{-1}$ to 117 $\mu g\ L^{-1}$ for Pb and 170 $\mu g\ L^{-1}$ to 1,076 $\mu g\ L^{-1}$ for Zn. In another study with coal fly ash in Mexico, the European Union leaching test (EN 12457) was applied where leaching was greater with oxalic acid as compared to deionized water and acetic acid (Medina et al. 2010). Gitari et al. (2009) investigated the leaching characteristics of coal fly ash from two locations in South Africa using the German Standard leaching test (DIN-S4) and acid neutralizing capacity (ANC). Significant concentrations of Na, Ca, and Ba were leached as these are found on the surface of the fly ash as well as in the glass associated fractions. Pb, Ni, and Cu were observed to be associated Mn and Fe oxides and leached as these phases dissolved. As, on the other hand, was controlled by the precipitation of $Ca_3(AsO_4)_2$ due to the high concentration of Ca present in the fly ash. Dudas (1981) studied the long term leachability of Na, Ca, Mg, and Al, along with other anions from fly ash collected from a power plant. Samples were leached in de-ionized water over a 2 year period. Because fly ash is highly alkaline in nature (pH 11-13), the solution pH increased from 8 to 9 by the end of the study. Boron exhibited greatest leachability due to its presence as an admixed borate salt of moderate solubility. On the other hand, Pb and phosphate were not detected at measurable concentrations and are likely sequestered within the silicate matrix through precipitation or adsorption. Na and K dissolved entirely suggesting initiation of the fly ash dissolution. Querol et al. (2000) studied 14 fly ashes from CCP. While lime and $Ca(OH)_2$ dissolved from the ash and raised the alkalinity of the solutions, the leachability of Pb and Cd was considerably reduced due to the elevated solution pH.

As demonstrated in studies with soils, sludges, sediments, fly ash, and coal combustion products, leaching of metals and metalloids from these matrices is a function of pH, composition, the presence of complexing ligands, and contact time with the leaching solution. One hypothesis in working with soda-lime glass is that the availability of metal contaminants on the surface of the particles may be associated with soluble substrates increasing the leachability of these species. Because glass is similar in structure to soils, sand, and fly ash, the leaching behavior from glass beads is likely comparable.

2.7 Summary

This chapter provided an overview on glass bead properties, their usage in the transportation industry, the manufacturing process, and the composition and structure of soda-lime silica glass. The review continued with the use of metals and metalloids in glass beads and their potential leachability. This chapter reviewed the solubility of glass and potential leaching mechanisms. As there are few studies on leaching from glass beads, the chapter concluded with a literature review on leaching from similar matrices which is function of pH, composition of the matrix, redox potential, contact time, ionic strength, and presence of other competing ligands.

CHAPTER 3

OBJECTIVES AND HYPOTHESES

Recently, imported glass beads used in highway marking have been observed to contain elevated metals or metalloid concentrations. Specifically, As, Sb, and Pb are the three elements found in glass beads. This research was developed to address the potential environmental impact of their presence. **The objectives of this research are to**:

1. Evaluate analytical techniques for total metal and metalloid concentrations in glass beads;

2. Conduct batch experiments utilizing glass beads to determine the impact of environmentally relevant factors such as salinity, pH, and time on metal leaching or dissolution. Studying leaching or dissolution from commercial glass beads will provide the degree to which the potential contaminated run-off impacts neighboring surface waters as well as groundwater through infiltration; and,

3. Assess metal and metalloid speciation to better understand and predict potential leaching for the glass beads.

Current regulations require leachable heavy metal or metalloid concentrations to be measured by U.S.EPA Method 1311 which is the TCLP. Results are compared against the metal limits set by RCRA that classify whether a waste is hazardous. While TCLP simulates leaching under low pH landfill conditions, U.S. EPA Method 1312 synthetic precipitation leaching procedure (SPLP) simulates leaching under acid rain conditions and the subsequent impact of leaching on groundwater. However, given their limited conditions, these standard methods may be inadequate in evaluating leaching behavior. Furthermore, complete dissolution of silica requires the use of hydrofluoric acid, which is hazardous to work with in the lab. As such, a rapid, nondestructive method is needed for assessing total metal concentration. Based on the objectives and literature review, the following hypotheses are tested in this research:

1. Field portable x-ray fluorescence spectroscopy (FP-XRF) is as reliable a technique for measuring the total metal and metalloid concentrations as is hydrofluoric acid digestion followed by inductively coupled plasma mass spectroscopy (ICP-MS).

2. The standard U.S EPA methods TCLP and SPLP are inefficient to predict the long-term leaching of metals and metalloids from glass beads.

3. The metals and metalloids associated with alkali oxides in the soda-lime silica glass beads are labile and leach under environmentally relevant conditions.

In the next chapter, methods are presented to address the objectives and test the hypotheses.

CHAPTER 4

EXPERIMENTAL METHODS

This chapter presents in detail the laboratory methods and experiments used in this research. The chapter begins with general quality assurance/quality control procedures, continues with the evaluation of total metals and metalloids, reviews the leaching experiments, and concludes with sequential extraction studies. This research involved procuring 18 batches of glass beads from NJDOT and their vendors, where 10 lb samples were collected from the original 2 ton source. Six of these batches were manufactured in the U.S.; the remaining twelve were imported and were the focus of the studies.

4.1 General Laboratory Quality Assurance/Quality Control (QA/QC)

Laboratory procedures followed Standard Methods for the Examination of Water and Wastewater (Greenburg et al. 1998). All sample containers were pre-washed with detergent and Millipore-Q water before use. The plastic and glass containers were soaked in 10% nitric acid for 24 hours and 48 hours, respectively; rinsed with Millipore-Q water; and, dried and stored in particle free environment before use. In general, the containers used were high density polyethylene (HDPE) Nalgene® 250 ml bottles. Chemicals of American Chemical Society (ACS) grade were applied.

4.2 Sampling Methodology

Samples were manually split into duplicates or triplicates throughout the study. This manual approach was evaluated against the use of a Riffle Splitter, which is a sampling device used by laboratories to mechanically split samples (Ingamells and Pitard 1986). Six samples from Batch 15 were split with the aid of the NJDOT Riffle Splitter. These mechanically split samples were analyzed with Niton® XL3t 600 Series FP-XRF and concentrations were compared to those split manually. Results demonstrated equivalent concentrations given the errors (Figure 4.1). Therefore, the manual approach used in this work to split samples was determined to be adequate and sampling was conducted manually throughout the study.

4.3 Total Metal Concentrations in the Glass Beads

Average composition of the domestic and imported glass beads was analyzed using bench scale PW 2400 x-ray fluorescence spectroscopy (XRF) spectrometer under helium gas conditions and analyzed quantitatively with SuperQ+ software. The Philips® PW 2400 (Serial #: DY 825) XRF is capable of measuring all elements from beryllium (atomic number 4) to uranium (atomic number 92) at trace levels to as low as 1 ppm. The accuracy of this analysis is reported at 0.01-0.1%. NIST standards 611, 613, 615, and 617 with concentrations of trace metals, 0.2, 1, 50, and 500 mg kg^{-1}, respectively, were applied for calibration in quantitative analysis of trace metals in the glass matrix (NIST 1999). The evaluation of metals and metalloids in complex matrices such as soils, sediments, and glass containing oxides, silicates, and organic substances, requires the measurement of total concentration.

To validate the FP-XRF approach as a tool for quantifying metal concentrations, more than a screening approach, two methods were used to determine total concentrations in the glass beads: Hydrofluoric acid digestion followed by ICP-MS (HF/ICP-MS) (ASTM 2005; U.S. EPA 1994) and FP-XRF (U.S. EPA 1996). HF acid

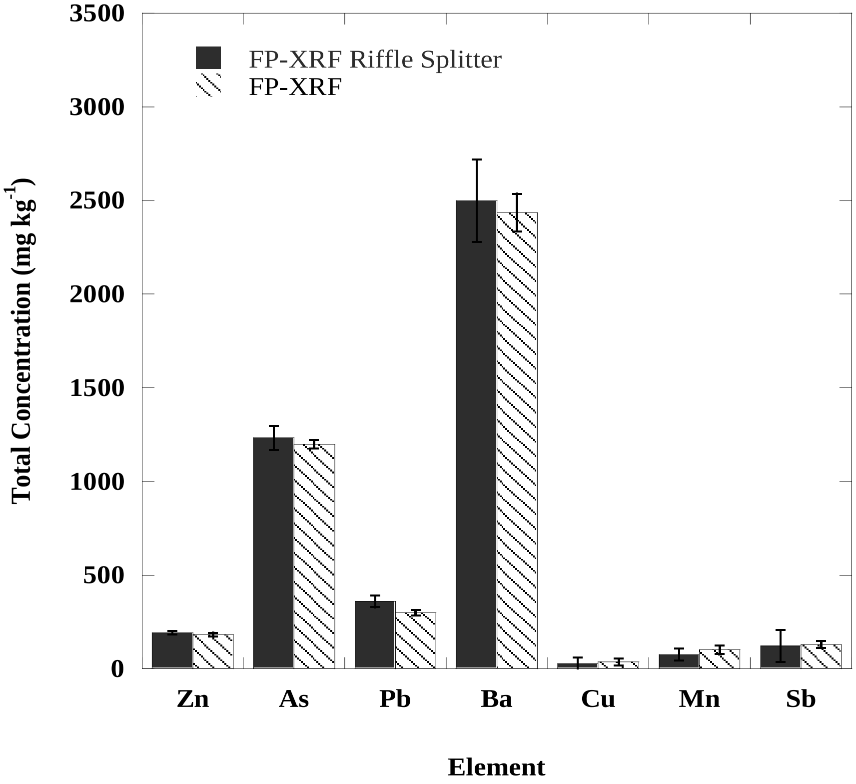


Figure 4.1 A comparison of average metal concentrations for each metal with and without using the Riffle Splitter. Error bars indicate 2 × S.E. based on six samples collected from adjacent locations in Batch 15.

digestion is the recommended medium for dissolving glass matrices. However, HF attacks parts of the ICP-MS instrument: the borosilicate glass nebulizer, spray chamber, and the quartz torch. Using HF requires either installation of an inert nebulizer or further treatment of the digest with $HClO_4$, H_3BO_3, or $AlCl_3$ (Mills 1986). Furthermore, HF is a highly reactive acid and when used requires unique safety plans and handling procedures. Niton® XL3t 600 Series FP-XRF with a 50 kV miniature x-ray tube and multiple primary filters was applied in this work as a tool that is rapid and non-destructive, providing elemental composition. An objective in this research was to assess the accuracy and precision of the FP-XRF as a tool for routinely evaluating batches of glass beads used on roadways. The analytical variability or error for each method, HF/ICP-MS and FP-XRF, was assessed based on the sensitivity as well as from the calibration of the instrument. The error associated with HF/ICP-MS was ±15 percent. The detection limits and associated error in using FP-XRF vary with element and matrix (U.S. EPA, 1996) (Table 4.1). Analytical error for FP-XRF is instrument-dependent and was measured by collecting duplicate samples from each batch. FP-XRF analytical errors ranged from 1-15% for As, 3-27% for Pb, and 2-28% for Sb.

Triplicate samples from 15 batches were collected at random and examined for total metal and metalloid concentrations using the two methods. Once samples were analyzed with FP-XRF, they underwent digestion with HF using the ASTM C169 Method (ASTM 2005) for chemical analysis of soda- lime and borosilicate glass. HF digestion (U.S. EPA 1996) was carried out for 7 days using 50% HF and 50% HNO_3 at 150 °C in a fume hood equipped with a filter for HF gas. Subsequently, HNO_3 was added to drive off HF in the form of SiF_6 to reduce the aggressiveness of the solution on the ICP-MS instrumentation (Mills 1986). Samples were then analyzed using an Agilent 7500a ICP-MS for measuring concentrations of As, Pb, Sb, Ag, Ba, Be, Co, Cu, Cr, Mn, and Ni.

For measuring the total metal and metalloid concentrations in the glass beads, a field portable Niton® XL3t 600 Series XRF analyzer (Thermo Scientific, Billerìca, Massachusetts) was used. Ten samples were collected from each of the 18 batches along with 10% replicates and 10% duplicates, thereby resulting in a total of 216 samples. The effective measurement area of FP-XRF was $1 \times 2\ cm^2$. XL3t is a self- calibrating instrument and involves a “Fundamental Parameters” (FP) approach to pre-determine

Table 4.1 Detection Limits of HF Digestion and FP-XRF

Element	Detection Limit (mg kg^{-1})	
	HF Digestion	FP-XRF
As	0.463	9
Pb	0.936	8
Sb	0.189	30
Zn	0.879	15
Ba	0.079	90
Ni	0.162	50
Cu	0.670	25
Co	0.098	40
Cr	0.112	65
Mn	0.012	55
Ag	0.63	10

inter-element matrix effects combined with pure element or known standard intensity responses in developing a quantitative algorithm for a specific sample type (Kalnicky and Singhvi 2001). FP methods provide multi-site capabilities by eliminating the requirement for site-specific standards. Each sample was analyzed for 180 s with errors ranging from 0.3 to 30%. The analyzer provides quantitative measurements of elements with an atomic number greater than 14. The tool is internally calibrated and has reported limits of detection for elements (As - 9 mg kg^{-1}, Pb - 8 mg kg^{-1}, and Sb - 30 mg kg^{-1}) with errors ranging from 1-15% for As, 3-27% for Pb, and 2-28% for Sb. Total concentrations measured were statistically analyzed to assess the sampling distribution using Minitab®. Variability within each of the 18 batches was also studied. Twenty samples, collected at periodic intervals within Batches 12, 13, and 14, were evaluated for assessing variability of total concentrations of As, Pb, and Sb.

Because an objective of this study was to address whether metal and metalloid concentrations were statistically different among the batches as well as between domestic and imported glass beads, an additional analysis was conducted. Concentrations in the imported batches were statistically compared to domestic batches using the Welch's *t* – test. The Welch's *t* - test is a variation of student *t* – test; it is used for unpaired samples with unequal variances. To apply this test, samples are assumed to come from a Gaussian distribution. Ten samples were collected from each batch obtained and analyzed for statistically significant differences in average concentrations.

4.4 Leaching Studies

Three types of experiments were conducted to analyze leaching from the glass beads: a fractional factorial study (Anderson 1974), the TCLP (U.S. EPA 1991b), and the SPLP (U.S. EPA 1994). One batch with representative elevated concentrations (Batch 15) was then used for the leaching studies to compare results. Environmentally relevant factors that influence the degree of leaching were evaluated through a fractional factorial method using the Latin Square design (Anderson 1974), which makes it possible to reduce the number of studies and at the same time isolate effects. Factors investigated included pH, salt, ionic strength, and time (Table 4.2). Assessment of main effects was carried out by analyzing metal and metalloid leachate concentrations and assessing the mean sum of squares (MSS) using analysis of variance (ANOVA). Each condition in the factorial study was conducted in triplicate using 250 ml HDPE Nalgene® bottles. A liquid to solid ratio of 10:1 was used, which is within the 10 – 40:1 range commonly applied in leaching studies (U.S. EPA 1994; Scott et al. 2005). The sample bottles were placed on a C1

Table 4.2 Fractional Factorial Design for Glass Beads of Particle Size > 100 µm

Experimental Run	Treatments*		
	Chemical	pH	IS (M)
Main Effects Tests			
1	NaCl	4	10^{-2}
2	NaCl	7	10^{-1}
3	NaCl	10	5
4	$CaCl_2$	4	5
5	$CaCl_2$	7	10^{-2}
6	CaCl2	10	10^{-1}
7	KAc	4	10^{-1}
8	KAc	7	5
9	KAc	10	10^{-2}
10	KCl	4	10^{-2}
11	KCl	7	10^{-1}
12	KCl	10	3

pH and IS Interaction Tests

Experimental Run	Treatments		
	Chemical	pH	IS (M)
13	KCl	4	5
14	KCl	10	10^{-2}

platform shaker and the contents mixed continuously at 65 rpm at room temperature of 25 ± 2 ºC for the entire study period.

The factorial study was conducted on glass beads as received, 98% of which were observed to be greater than 100 µm using Beckman and Coulter Particle Size Analyzer (Table 4.3). Filtrate obtained using a 0.22 µm Millex® GP filter was collected at 10, 20,

Table 4.3 Particle Size Distribution of Glass Beads using the Beckman Particle Size Analyzer in the gas phase

Diameter (μm)	%
111	0.0016
121.8	0.037
133.7	0.21
146.8	0.57
161.2	1.06
176.9	1.58
194.2	2.06
213.2	2.47
234	2.96
256.9	3.7
282.1	4.87
309.6	6.52
339.9	8.47
373.1	10.3
409.6	11.5
449.7	11.7
493.6	10.6
541.9	8.61
594.8	6.11
653	3.74
716.8	1.91
786.9	0.76
863.9	0.17
948.3	0.01

30, 60, 90, and 160 days. The salts applied in the study included ones commonly used to reduce the freezing temperature of water: NaCl, $CaCl_2 \cdot 2H_2O$, KCl, and KCH_3COO (KAc) (Joutti et al. 2003). Concentrations were determined based on applications practiced in NJ prior to snow storm events. Snowfall typically ranges between 0.0025 m and 0.7 m with an average of 0.12 m per storm (NJSC 2008) for a freshly fallen snow density of 0.05 to 0.2 g cm^{-3} (Ward and Trimble 2003). Based on a salt application of 99 kg km^{-1} $lane^{-1}$ (159 kg $lane^{-1}$ $mile^{-1}$) on a 3.6 m wide lane (Personal Communication 12/2007), ionic strength conditions were considered from 10^{-2} to 10^{-1}. A pH range of 4 to

10 was studied, which includes acid rain (pH 4.2) that has been observed in NJ (USGS 2001) as well as possible basic conditions (Paul 1977; USGS 2001). The pH of the leaching solution is inarguably the most important factor in the extraction of metals and metalloids from glass (Sinton and LaCourse 2001; Shotyk and Krachler 2007; Reimann et al. 2010; Dijkstra et al. 2004; Pérez et al. 2008). The release of cations from leached glasses affects the pH of non-buffered solutions further modifying the dissolution properties (Cailleteau et al. 2008). For this reason, the pH of all the samples was measured with a Thermo Scientific Orion 3 Star bench pH meter and maintained by addition of 10^{-2} M NaOH and 10^{-2} M HNO_3 solutions. All studies and pH measurements were conducted at room temperature, to an accuracy of ± 0.1 pH units. Filtered samples were acidified with 1% HNO_3 to a pH less than 2 (Greenburg et al. 1998) and analyzed for metals and metalloids using an Agilent 7500a ICP-MS.

To account for the effect of weathering and wear and tear of roads, experiments were conducted on smaller size ranges of glass beads including less than 37 µm and 37-100 µm. Using a Spex 8000M milling tool, 5 to 10 grams of glass beads all greater than 100 µm (as received) were ground for 4 to 8 minutes based in a preliminary assessment of time required. After grinding, the beads were separated into the two size ranges of less than 37 µm and 37-100 µm using Standard Sieve No. 140 and Sieve No. 450, respectively. Based on results from the factorial study, the experimental conditions for the leaching of smaller beads were selected. This study was carried out for 120 days where samples were collected at 10, 20, 30, 45, 60, 90, and 120 day intervals. In this second set of studies, only the main effects identified in the factorial experiments were selected and used (Table 4.4). A randomized block design was not applied in this latter study.

Results from the factorial study were compared to the two standard U.S. EPA leaching methods, the TCLP (U.S. EPA 1991b) and SPLP (U.S. EPA 1994). The TCLP is used to determine whether the beads should be classified as a hazardous waste or non-hazardous waste in determining its ultimate disposal. TCLP uses two types of extraction fluids: extraction Fluid 1 and extraction Fluid 2. Fluid 1 is prepared by adding 5.7 mL of glacial acetic acid (CH_3CH_2OOH) to 64.3 mL of 1 N NaOH and bringing the mixture up to 1000 mL with deionized water resulting in an initial pH of 4.93 ± 0.05. Extraction Fluid 2 is prepared by diluting 5.7 mL of CH_3CH_2OOH with deionized water to make the volume up to 1000 mL with an initial pH of 2.88 ± 0.05. The choice of the extraction fluid depends on the type of waste. A preliminary analysis is conducted on the waste to determine which extraction fluid should be used for the actual TCLP. In the case of glass beads (100% solid), 5 grams of glass beads were placed in Erlenmeyer flask and 96.5 mL of deionized water were added. This solution was mixed with a magnetic stirrer for 5 minutes and the pH was found to be greater than 5.0. Therefore, 3.5 mL of 1 N HCl were added to the solution and heated at 50 °C for 10 minutes. The final pH after cooling was observed to be less than 5.0 and thus extraction Fluid 1 was used. Extractions were carried out with 20:1 liquid to solid ratio in 2 L HDPE bottles.

The SPLP (U.S. EPA 1994) is used to assess the risk of groundwater contamination posed by the land application of granular solid wastes. Theoretically, the SPLP simulates contaminant leaching by acid rain through extraction with an HNO_3 /H_2SO_4 solution at an initial pH of 4.20 and a L/S ratio of 20:1. The extract is interpreted

Table 4.4 Experimental set up for leaching from <37 µm and 37-100 µm

Size Range (µm)	Salt	pH	Ionic Strength (M)
100 - 37	NaCl	4	10^{-2}
100 - 37	NaCl	10	10^{-1}
100 - 37	$CaCl_2$	7	10^{-2}
100 - 37	$CaCl_2$	10	10^{-2}
100 - 37	KAc	10	10^{-2}
100 - 37	KCl	4	10^{-2}
< 37	NaCl	4	10^{-2}
< 37	NaCl	10	10^{-1}
< 37	$CaCl_2$	7	10^{-2}
< 37	$CaCl_2$	10	10^{-2}
< 37	KAc	7	10^{-1}
< 37	KCl	4	10^{-2}

to represent the leachate from-land application of the material and is gauged against criteria for assessing risk to groundwater used as a drinking water source. These criteria are derived from state based groundwater quality limits (GQL) that, in some cases, are the U.S. EPA maximum contaminant levels (MCL) for drinking water, multiplied by dilution attenuation factors (DAF) to account for dilution in an aquifer. The New Jersey Department of Environmental Protection (NJDEP) develops remediation standards on a site-by-site basis; without such, applies a default DAF of 13 based on their hydrogeological studies (NJDEP 2008). While SPLP is an approach used to evaluate leaching due to acid rain, it does not provide a mechanistic basis and therefore a magnitude of leaching as a function of environmental conditions especially pH (Ndiba and Axe 2010). As New Jersey is located east of Mississippi River, the extraction fluid was prepared by mixing H_2SO_4 and HNO_3 at 60/40 by weight ratio to achieve an initial pH of 4.20 ± 0.05. Both the TCLP and SPLP tests were conducted in triplicate in an end-over-end tumbler rotated at 30 rpm for 18 hours after which the pH was measured, the samples were filtered with 0.7 µM borosilicate filter, acidified to less than pH 2, and stored for analysis in closed Nalgene® bottles under refrigeration at 4 ºC (Greenburg et al. 1998). Metals in the extract were analyzed with ICP-MS.

4.5 Potential Impact to Groundwater Studies

Experiments were conducted on eight imported batches, as four of the twelve imported batches did not have sufficient sample required to carry out the studies. In these experiments, based on the factorial study, the conditions under which leaching was most significant were applied to consider the affect of the initial concentration on leaching. Domestic batches were not studied as metal and metalloid concentrations were one to two orders of magnitude lower (a number of batches had concentrations less than the detection limit) than those in imported batches. Samples studied in the leaching experiments were first analyzed with FP-XRF for total concentrations. Leaching from these glass bead samples was then examined under environmentally relevant conditions where leaching was most significant for As, Pb, and Sb based on results from our previous studies (Table 4.5). Specifically for anions As and Sb, maximum leaching was observed at pH values of 7 and 10 with 10^{-2} M $CaCl_2 \cdot 2H_2O$. On the other hand, the most significant leaching for Pb, present as a cation, was found at pH 4 with 10^{-2} M NaCl. Three samples from each batch were studied and run in triplicate, resulting in 72 samples. Of these samples, 48 were analyzed for leaching of As and Sb while 24 were examined under the conditions for the leaching of Pb. This study was conducted for a period of 30 days as this represented approximately 80% of the maximum leaching observed over the 160 days studied. After 30 days, filtered samples were acidified with 1% HNO_3 to a pH

Table 4.5 Summary of Leaching Studies.

Leaching Studies	Conditions	No. of Samples	Time
TCLP U.S EPA Method 1311	Diluted solution of CH_3CH_2OOH and NaOH at an initial pH of 4.93 ± 0.05. **Conducted on Batch 15.**	6	18 hrs.
SPLP U.S. EPA Method 1312	Diluted solution of 60/40 by weight percent mixture of H_2SO_4/HNO_3 at an initial pH of 4.20 ± 0.05. **Conducted on Batch 15.**	6	18 hrs.
Factorial Study	**Conducted on Batch 15**	88	160 Days
• pH	• 4, 7, and 10		
• Salt	• NaCl, KCl, KCH_3CHOO, and $CaCl_2.2H_2O$		
• Particle size	• > 100 µm, 37-100 µm, and < 37 µm		
• Ionic Strength	• 10^{-2} and 10^{-1} M		
Potential Impact Studies	**Conducted on Batches 9, 10, 11, 12, 13, 14, 16, and 18**		30 Days
• As	• pH 7 & 10, 10^{-2} M $CaCl_2\cdot 2H_2O$, > 100 µm	48	
• Pb	• pH 4, 10^{-2} M NaCl, > 100 µm	24	
• Sb	• pH 7 & 10, 10^{-2} M $CaCl_2\cdot 2H_2O$, > 100 µm	48	

less than 2 (Greenburg et al. 1998) and analyzed for metals and metalloids using ICP-MS (U.S. EPA 1994).

4.6 Sequential Extraction Procedure

To determine the phases that metal and metalloids are associated with in the soda-lime-silica glass, sequential extraction was carried out on six samples collected from one of the imported batches. The extractions were conducted with the modified three-step sequential extraction procedure proposed by the Commission of the European Communities Bureau of Reference (BCR) of the Standards, Measurements and Testing (SM&T) Programme

(Rauret et al. 1999). Extractions were performed in 40 mL borosilicate glass centrifuge bottles with an end-over-end shaker rotated at 30 rpm. Between successive extractions, the extract was separated from the residue by centrifugation at 3,000 g for 20 minutes.

The supernatant was decanted into high density polyethylene (HDPE) Nalgene® bottles, acidified to pH less than 2, and refrigerated until analysis with ICP-MS (U.S. EPA 1994). The residue was washed with 20 mL of deionized water, centrifuged for 20 min, and the supernatant discarded. In the first step, exchangeable and carbonate forms were extracted with 0.11 M acetic acid solution (CH_3COOH). The fraction of metals and metalloids observed to leach are hypothesized to be associated with alkali oxides which form non-bridging bonds with the silicate structure (Carmona et al. 2005) and are considered soluble; this fraction would therefore be associated with the exchangeable fraction. In the second step sorption to iron and manganese phases are extracted with 0.5 M hydroxylammonium chloride ($NH_2OH{\cdot}HCl$) and 0.05 M HNO_3 solution; this contribution is not expected to be significant with the soda-lime glass. In the third step, remaining residue is treated at 85 ± 2 ^{o}C with two sequential 10-mL portions of 30% H_2O_2 adjusted to pH 2 with HNO_3, and then extracted at pH 2.0 ± 0.1 with 1.0 M ammonium acetate (CH_3COONH_4) solution for the organics and sulfide fractions. Step 4, which employs HCl and HNO_3 (aqua regia) digestion to measure total metals remaining, was not carried out as glass dissolution is not achieved with aqua regia (Davutluoglu et al. 2010; Kilbride et al. 2006). Based on the mass balance, the difference between initial and leached concentrations from the first three steps of sequential extraction provides an estimate of the metals associated with oxide fraction, while the residue remaining for the fourth step provides the fraction associated with the silicate structure, considered immobile.

4.7 X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)

X-ray diffraction (XRD) for both domestic and imported bead samples revealed that silica dominated the diffractograms. The LEO 1530 field emission scanning electron microscopy (FE-SEM) equipped with an energy dispersive X-ray micro analyzer (EDX) Inca series 200 was utilized to study the surface morphology of domestic, imported, and extracted beads. For the FE-SEM, samples were coated under high vacuum with a layer of carbon using an Edward’s 12E6/1266 coating unit.

In the following chapters, results are discussed: Chapter 5, Total Metal and Metalloid Concentrations; Chapter 6, Leaching of Metals and Metalloids from Highway Marking Glass Beads; and Chapter 7, Environmental Impact of Leaching of Metals and Metalloids from Highway Marking Glass Beads.

CHAPTER 5

TOTAL METAL CONCENTRATIONS

This chapter first presents the results from evaluating total metal and metalloid concentrations in glass bead batches obtained for this study. Total As, Pb, and Sb concentrations in the domestic and imported batches are compared, variability is assessed, and is followed by regression analysis of the data from using the two methods, HF/ICP-MS and FP-XRF. The chapter concludes with a study on distribution of As, Pb, and Sb in the glass bead batches.

5.1 North American Beads vs. Imported Beads

The results demonstrate differences in composition between the U.S. manufactured glass beads and those imported from China. The average composition measured using the XRF spectrometer on domestic beads and imported beads clearly indicate the presence of metallic oxides in the latter (Table 5.1). While concentrations of the silica and dominant oxides were comparable, the absence of CuO, As_2O_3, PbO, and Sb_2O_3 in domestic batches and their presence in the imported batches highlights the production differences. The domestically manufactured glass beads showed on average 0.02% of BaO and 0.01% of ZnO, and on the other hand, the concentrations of both were relatively greater in the imported glass beads: 0.3% BaO and 0.05% ZnO. More significantly, for the domestic batches PbO, CuO, As_2O_3, and Sb_2O_3 were not observed; in contrast for the imported beads, they ranged between 0.005 and 0.13%. It is important to note that oxides of Pb, Cu, As, Sb, Ba, and Zn are assumed in quantifying concentrations through the XRF analysis; the speciation has not been assessed. A number of product recalls have involved

Table 5.1 Average % Composition of Major Oxides in Domestic and Imported Beads

Oxide	Domestic (%) (Batches 1-6)	Imported (%) (Batches 7-18)	Difference (%)
SiO_2	76.4 ± 0.9	76 ± 0.5	-0.4
CaO	10.7 ± 0.5	10 ± 0.5	-0.7
Na_2O	9.1 ± 1.4	8 ± 0.7	-1.1
Al_2O_3	0.6 ± 0.1	2 ± 0.4	1.4
MgO	2.3 ± 0.1	2 ± 0.7	-0.3
K_2O	0.1 ± 0.02	0.7 ± 0.2	0.6
P_2O_5	0.04 ± 0.03	0.06 ± 0.04	0.02
Fe_2O_3	0.4 ± 0.3	0.25 ± 0.05	-0.15
TiO_2	0.03 ± 0.03	0.04 ± 0.02	0.01
CuO	*ND*[*]	*0.005 ± 0.005*	*0.005*
ZnO	*0.01 ± 0.00*	*0.05 ± 0.09*	*0.04*
MnO	*0.02 ± 0.03*	*0.01 ± 0.006*	*-0.01*
As_2O_3	*ND*[*]	*0.13 ± 0.08*	*0.13*
Sb_2O_3	*ND*[*]	*0.013 ± 0.013*	*0.013*
BaO	*0.02 ± 0.01*	*0.30 ± 0.31*	*0.28*
PbO	*ND*[*]	*0.025 ± 0.02*	*0.025*

*ND: Non Detected

imported and namely Chinese-made goods. In 2007, the toy company Mattel recalled 1 million Chinese-produced toys found with lead-based paint exceeding 180 ppm (O'Donnell 2007). In their analysis, Berman and Swani (2010) reported that although minimizing the production cost plays a role, poor enforcement of safety standards in

China is one of the main reasons of such failures. In the case of glass beads, outdated technology is at fault (van de Griend et al. 2009). Manufacturers in China may be using obsolete technology involving metals and metalloids to enhance optical properties of glass beads, whereas advanced technology without the use of such metals is currently available (van de Griend et al. 2009; Hayden 2004).

5.2 Total Concentrations and Variability

In an effort to apply the FP-XRF as a tool for quantifying accurate metal and metalloid concentrations, two methods, HF/ICP-MS and FP-XRF, were compared. Results from HF/ICP-MS showed peak concentrations of 518 mg kg^{-1} for As, 230 mg kg^{-1} for Pb, and 190 mg kg^{-1} for Sb. The most elevated concentrations of As were observed in Batches 12-15. Measurable As concentrations ranged between 0.4 and 2 mg kg^{-1} in Batches 1-6 (i.e., the domestic batches), and 0.3 and 518 mg kg^{-1} in the imported Batches 7-15 (Figure 5.1). Pb concentrations revealed similar trends ranging from 1.4 to 86 mg kg^{-1} in Batches 1-6, and varying between 1.1 and 230 mg kg^{-1} in Batches 7-15. Detectable concentrations of Sb lay between 2.5 and 21 mg kg^{-1} in the U.S. produced batches, peaking at 190 mg kg^{-1} in the imported batches. While microwave assisted digestion is the standard method for siliceous matrices and provides accurate results, there are a number of disadvantages associated with combinations of complex acids. Because HF etches glassware, boric acid is employed to react with fluoride in solution, which can result in negative matrix effects; spiked concentrations of some elements and non-detection of others. Furthermore, during HF digestion, evaporation of the solution and loss of trace metals has been observed as the temperature rises to 350^{o}F (ASTM 2005; Nascimento et al. 2005). Furthermore, at the

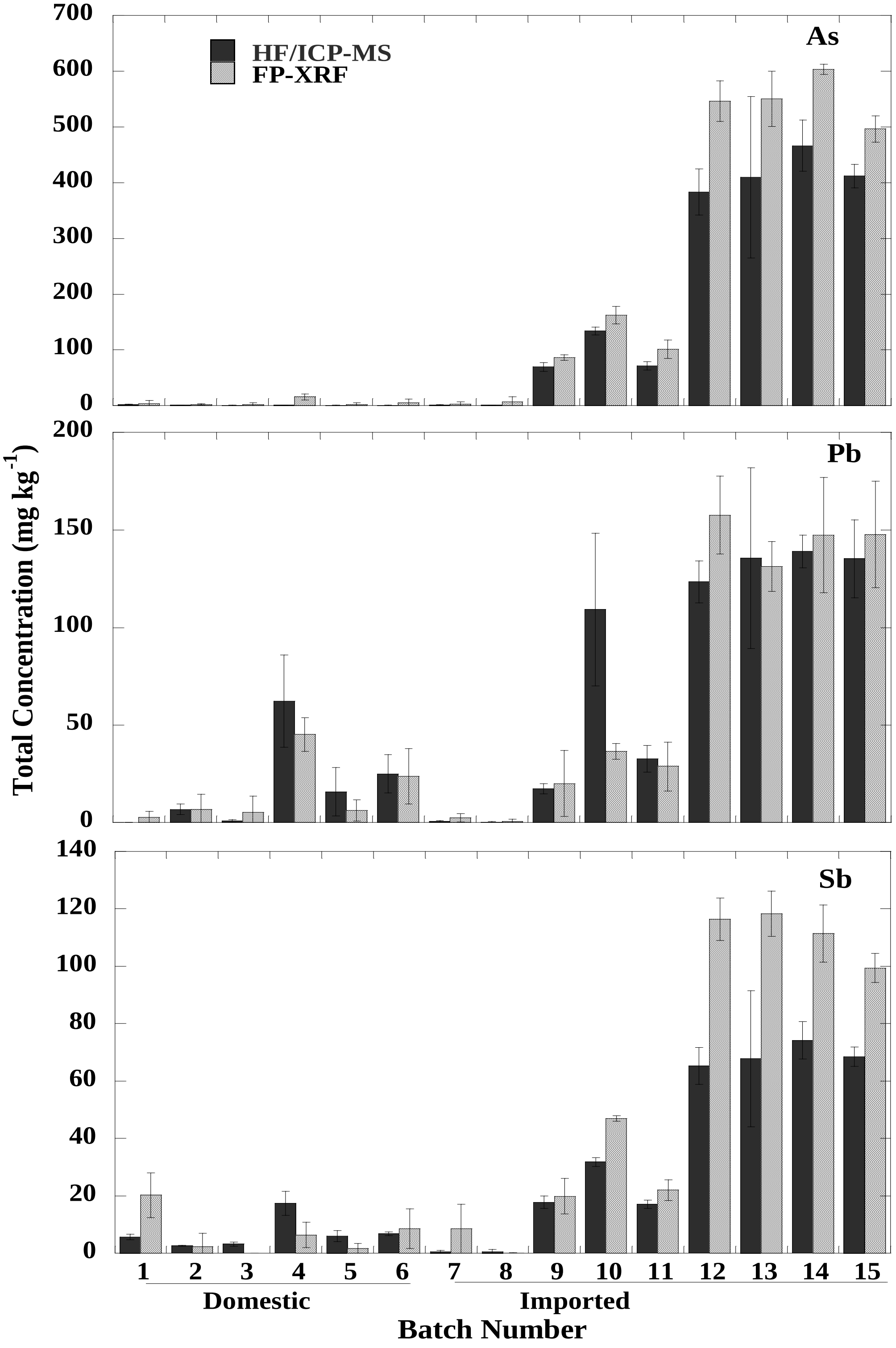


Figure 5.1 Total average metal concentrations measured with HF/ICP-MS and FP-XRF based on triplicate samples collected from Batches 1-15 (45 samples). Error bars represent standard error based on 2 × S.D.

elevated temperature, metals or metalloids such as As (III) and Sb (V) may volatilize (Bajo 1978). This loss of metals may reduce the effectiveness of quantifying concentrations from glass dissolution.

Using FP-XRF, peak concentrations in the imported batches were observed at 612, 171, and 126 mg kg^{-1} for As, Pb, and Sb, respectively. FP-XRF results demonstrated the presence of As ranging from 1 to 21 mg kg^{-1} in Batches 1-6 and 3 to 612 mg kg^{-1} in Batches 7-15 (Figure 5.1). Similarly, Pb concentrations in domestic batches were observed between 1 and 50 mg kg^{-1} while imported batches exhibited comparatively greater concentrations from 0.6 to 171 mg kg^{-1}. Sb results revealed the greatest concentrations in Batches 12-15 ranging from 95 to 126 mg kg^{-1} with significantly lower concentrations in Batches 1-6: 2 to 27 mg kg^{-1} (Figure 5.1). Concentrations measured with the two methods demonstrated strong correlations (R^2 = 0.99 for As, R^2 = 0.87 for Pb, and R^2 = 0.96 for Sb) (Figure 5.2). These results are comparable with results published by other authors (Radu and Diamond 2009; Binstock et al. 2009; Kilbride et al. 2006; Hürkamp et al. 2009). While concentrations of As and Pb measured with the two methods were comparable in all batches, results of Sb concentrations were observed to be greater with FP-XRF than with HF/ICP-MS. Increased digestion periods with HF/ICP-MS can result in the formation of colloidal silica gels which may initiate co-precipitation and loss of trace elements (Hödrejärv and Vaarman 1999). Glass is difficult to dissolve and even after 7 days, incomplete digestion was observed in this work. Moreover, loss of metals and metalloids during extraction due to volatilization may also explain the lower concentrations of Sb found with HF/ICP-MS (Savio et al. 2010; Bajo 1978). As a result, Sb associated with the residual glass matrix goes undetected by ICP-MS but is quantified

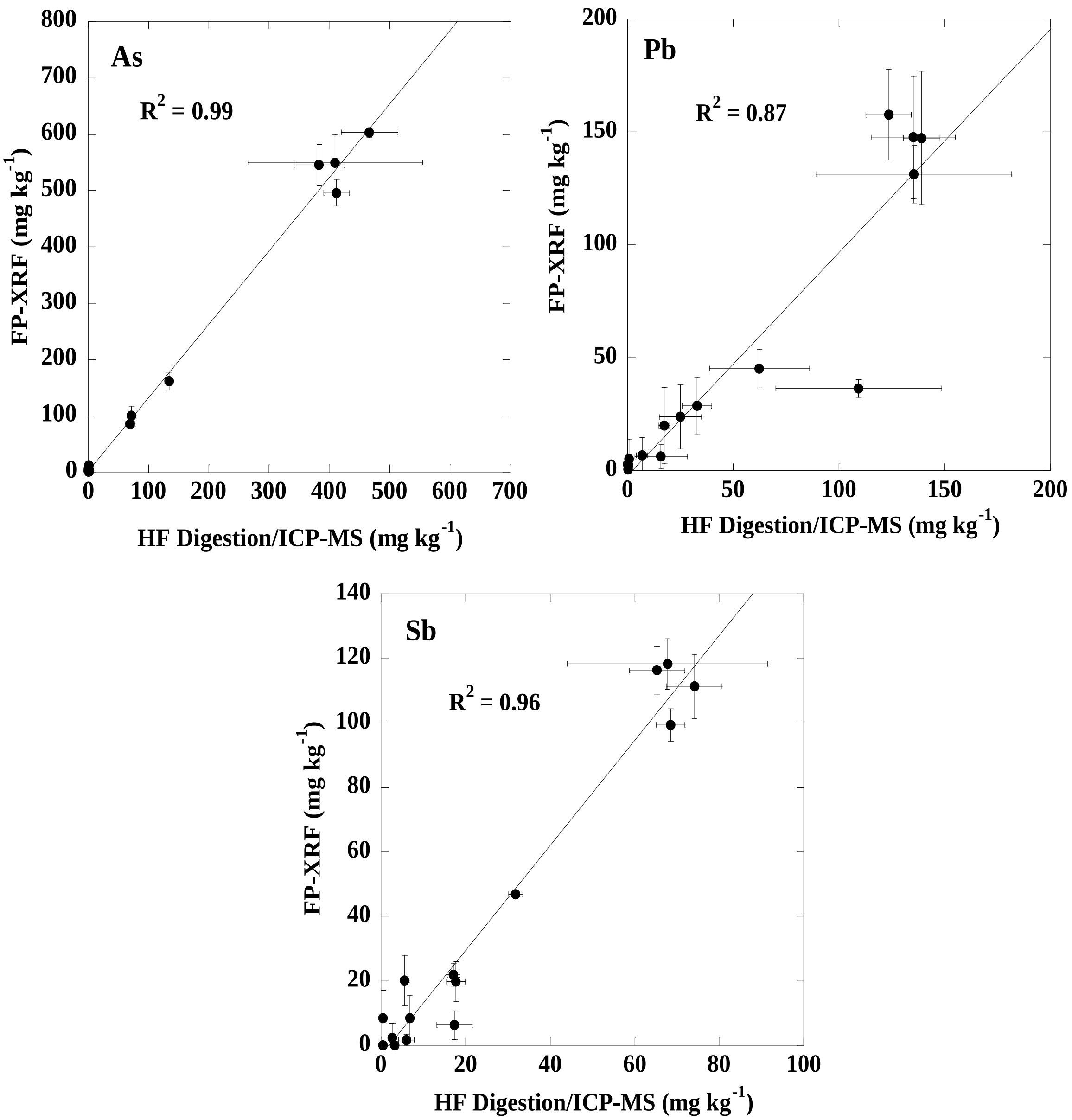


Figure 5.2 Total metal concentrations as measured with HF Digestion/ICP-MS and FP-XRF for Batches 1-15 based on triplicate samples from each batch.

with FP-XRF. Overall, based on the coefficients of determination between the two methods, FP-XRF is a viable, nondestructive, and rapid alternative to the HF/ICP-MS procedure. Therefore, further measurements were carried out with FP-XRF.

Concentrations in domestic batches measured with FP-XRF were observed to range from non-detectable levels (NDL) to 8 mg kg^{-1} for As, NDL to 23 mg kg^{-1} for Pb, and from 34 to 55 mg kg^{-1} for Sb (Figure 5.3). Peak concentrations were as great as 22 mg kg^{-1} for As, 98 mg kg^{-1} for Pb, and 74 mg kg^{-1} for Sb. Among the domestic batches, Batches 4 and 6 were observed to have statistically greater concentrations of As, Pb, and Sb as compared to the other Batches 1, 2, 3, and 5 (Figure 5.3). Results of the imported batches revealed much greater concentrations of As, Pb, and Sb; peak concentrations were found at 876 mg kg^{-1} for As, 691 mg kg^{-1} for Pb, and 198 mg kg^{-1} for Sb. Concentrations ranged between 1 and 846 mg kg^{-1} for As, NDL and 188 mg kg^{-1} for Pb, and 34 and 185 mg kg^{-1} for Sb. For the imported glass beads, Batches 7-11 exhibited concentrations statistically lower than Batches 12-18 (Figure 5.3). Variability was significant for the imported batches where three (12-14) batches were assessed with 20 samples: Pb (50-83%), As (18-22%), and Sb (16-18%) (Figure 5.4). Results suggest that the glass cullet used in manufacturing the beads appear to exhibit non-uniform concentrations in the trace metal composition.

Manufacturing of glass beads involves crushing glass (recycled or virgin) and heating it to a semi-molten state in a furnace. The semi-molten glass particles then become spheres in the processing and are collected upon cooling (VADOT 2010). Because of the physical state of the glass, a non-uniform distribution of metals results as observed in batch variability.

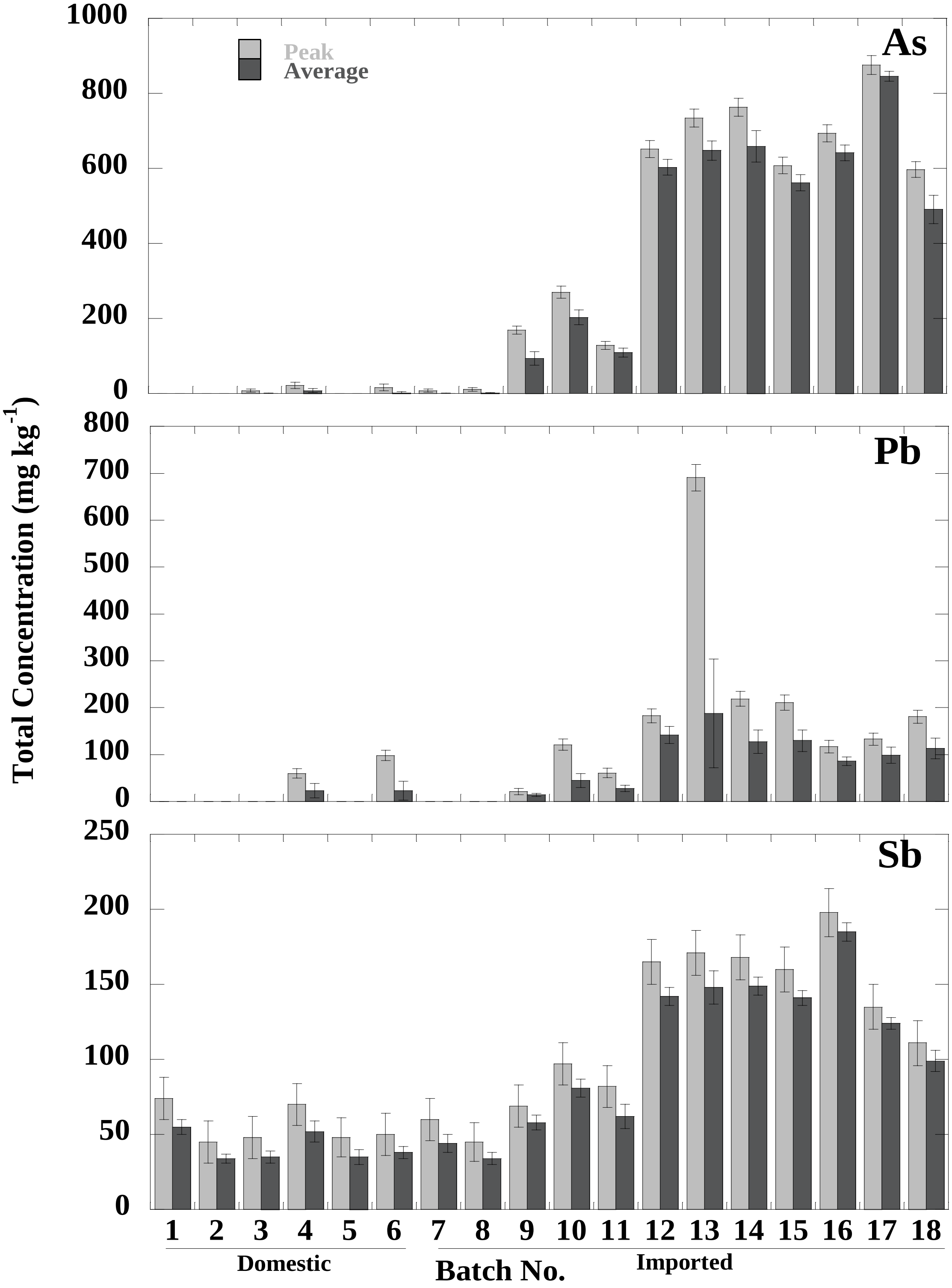


Figure 5.3 Peak and average total metal concentrations measured with FP-XRF based on 10 samples collected from Batches 1-18. Error bars represent standard error based on 2 × S.D.

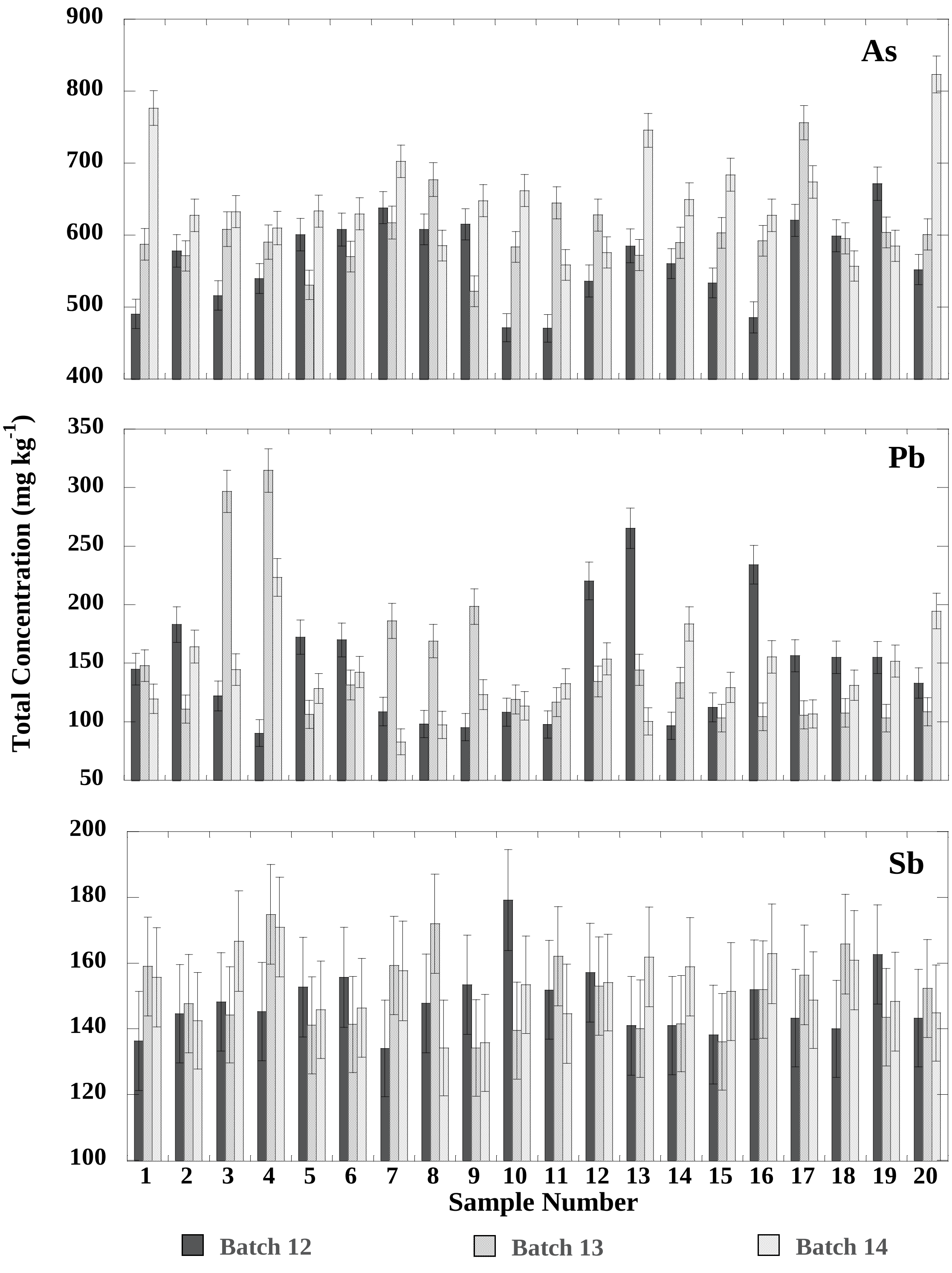
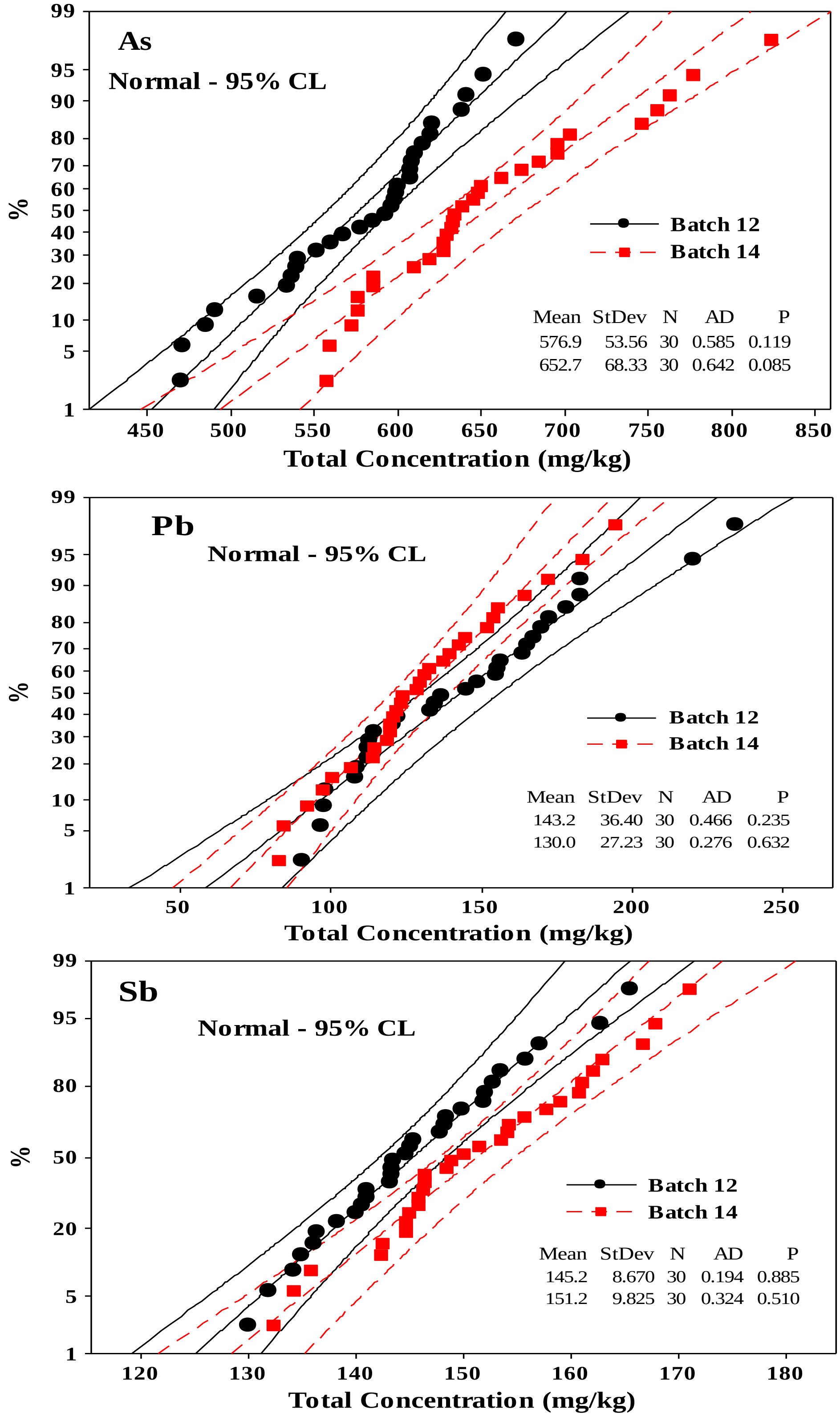


Figure 5.4 Analysis of batch variability for As, Pb, and Sb based on 20 samples from each batch shown. Variability ranged from 17-22% for As, 50-83% for Pb, and 13-16% for Sb.

5.3 Distribution of Total Concentrations

Total metal concentrations in domestic and imported batches were observed to follow Gaussian distributions; additional moments were not needed for skewing or broadening of the tails. To illustrate the sampling distribution, results from studying Batches 12 and 14 are reviewed (Figure 5.5). Total As, Pb, and Sb concentrations from Batches 12 and 14 were measured using FP-XRF. The fit of the distribution was examined with the Anderson-Darling (AD) test statistic, which measures how well the data follow a particular distribution. When the p-value for the Anderson-Darling test is greater than the chosen significance level (usually 0.05), the fit is considered significant. The probability plot for As concentrations in Batches 12 and 14 reveals p-values of 0.118 and 0.085, respectively; both greater than the α of 0.05 (95% confidence level). Testing the null hypothesis that metal concentrations follow a Gaussian distribution versus the alternative that they do not, results show that the null hypothesis cannot be rejected. Similarly, the sampling distribution for Pb concentrations was consistent with Gaussian distributions (p-values of 0.235 and 0.632, respectively). For Sb (Figure 5.5), results show p-values of 0.885 and 0.510 (>0.05), demonstrating the strength of the Gaussian distributions.

To address whether concentrations were significantly different between batches, the Welch's t - test was applied. Testing was carried out with the null hypothesis that there is no difference between mean concentrations in two select batches ($|\mu_1 - \mu_2| = 0$) against the alternative hypothesis that the means are different ($|\mu_1 - \mu_2| \neq 0$) at a 95% confidence level. For a *p*-value greater than the significance level (i.e., 0.05), the null hypothesis cannot be rejected; alternatively for *p*-values less than or equal to 0.05, the null hypothesis can be rejected. In general, metal and metalloid concentrations in



Mean	StDev	N	AD	P
576.9	53.56	30	0.585	0.119
652.7	68.33	30	0.642	0.085

Mean	StDev	N	AD	P
143.2	36.40	30	0.466	0.235
130.0	27.23	30	0.276	0.632

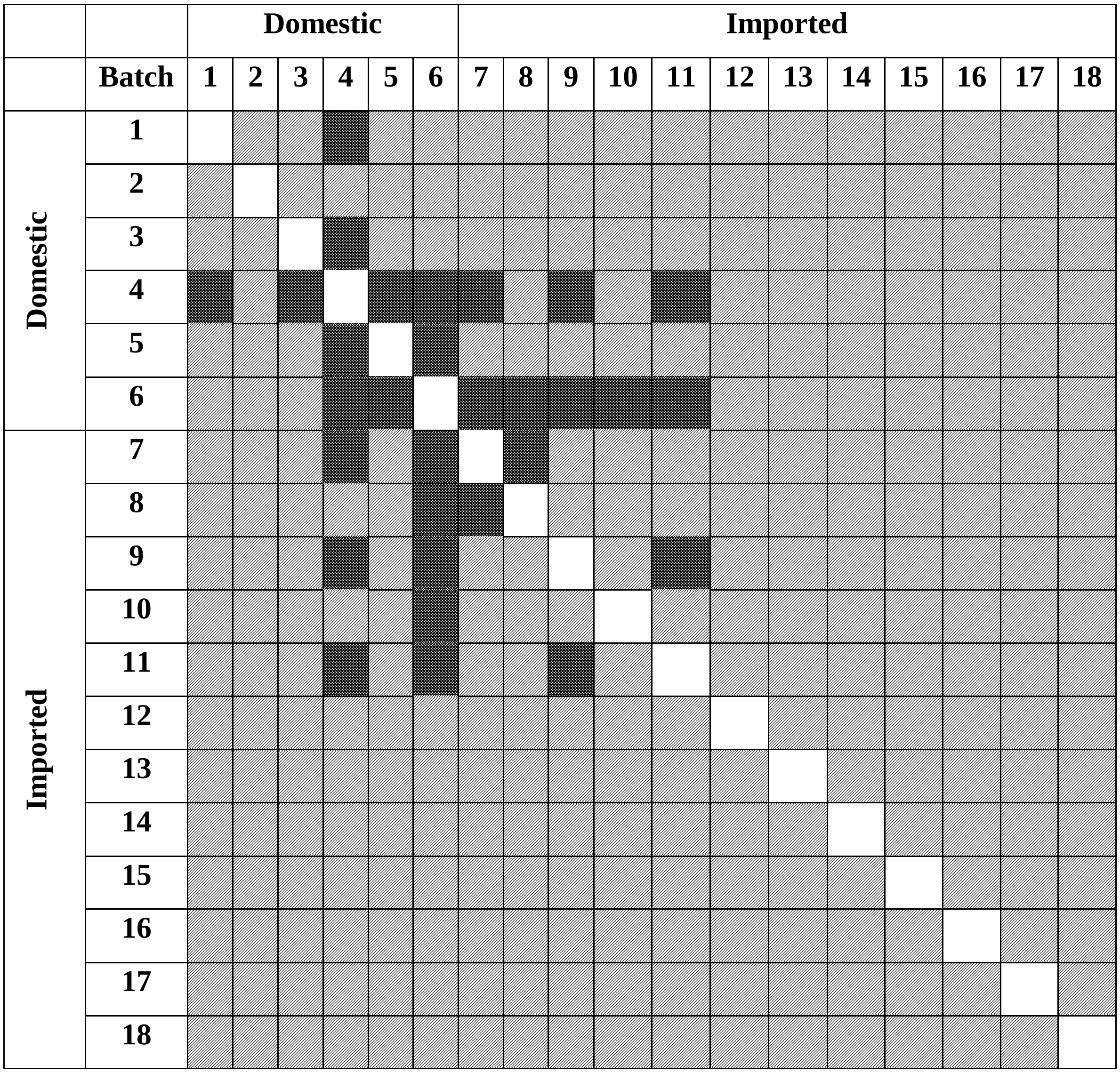
Mean	StDev	N	AD	P
145.2	8.670	30	0.194	0.885
151.2	9.825	30	0.324	0.510

Figure 5.5 Assessment of the confidence levels for the data following a Gaussian distribution based on 30 samples. Batches 12 and 14 are illustrated for As, Pb, and Sb.

domestic batches were an order of magnitude lower than concentrations observed in the imported batches. Apart from a few exceptions, results of the Welch's t-test for domestic versus imported batches indicate that the null hypothesis can be rejected (*p*-value <0.05) (Figure 5.6); thereby signifying differences in mean concentrations. However, anomalies were observed within test samples. The test showed that the null hypothesis cannot be rejected for average metal concentrations in domestic Batches 4 and 6 compared to those in imported Batches 7-11 (Figure 5.6). Within the domestic batches, Batches 4 and 6 were observed to have greater concentrations as compared to Batches 1, 2, 3, and 5. Among the imported batches, Batches 7-11 were found with lower metal concentrations as compared to Batches 12-18, indicating that the null hypothesis can be rejected (Figure 5.6). Nonetheless, concentrations of metals and metalloids in imported batches are statistically different from the domestic based on this testing (Figure 5.6). The elevated concentrations require further study to address the potential impact from applying the glass beads on roadways.

5.4 Summary

The results revealed the presence of elevated concentrations of As, Pb, and Sb in the glass beads. However, concentrations in domestic batches were less than those observed in imported batches. While HF digestion followed by ICP-MS is the standard (ASTM 2005) method for evaluating total metal and metalloid concentrations in glass beads, the applicability of FP-XRF versus HF digestion/ICP-MS was studied. FP-XRF was demonstrated to be accurate and reliable providing a rapid analysis of glass beads. This approach offers distinct advantages over the conventional HF-acid digestion method such



		Domestic						Imported											
	Batch	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
Domestic	**1**		▨	▨	■	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	2	▨		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	3	▨	▨		■	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	4	■	▨	■		■	■	■	▨	■	▨	■	▨	▨	▨	▨	▨	▨	▨
	5	▨	▨	▨	■		■	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	6	▨	▨	▨	■	■		■	■	■	■	■	▨	▨	▨	▨	▨	▨	▨
Imported	**7**	▨	▨	▨	■	▨	■		■	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	8	▨	▨	▨	▨	▨	■	■		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	9	▨	▨	▨	■	▨	■	▨	▨		▨	■	▨	▨	▨	▨	▨	▨	▨
	10	▨	▨	▨	▨	▨	■	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨	▨
	11	▨	▨	▨	■	▨	■	▨	▨	■	▨		▨	▨	▨	▨	▨	▨	▨
	12	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨
	13	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨
	14	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨
	15	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨
	16	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨
	17	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨
	18	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	

▨ Null hypothesis can be rejected; *p*-values ≤ 0.05

■ Null hypothesis cannot be rejected; *p*-values > 0.05

Figure 5.6 Results of the Welch's *t*-test between batches at a 95% confidence level with the H_o: $|\mu_1\text{-}\mu_2| = 0$ versus H_1: $|\mu_1\text{-}\mu_2| \neq 0$.

as portability, increased sample analysis, rapid analysis, minimal sample preparation, and non-destructive. Variability within the batches was observed to be significant and should be accounted for when randomly sampling batches. Samples from the batches showed that total concentrations were consistent with Gaussian distributions. Furthermore, based on the Welch t- test, differences between the domestic and imported concentrations was statistically significant. The metal and metalloid concentrations observed in the highway marking beads raises the question of whether leaching may be an important process in the long-term use of these glass beads. Therefore, an understanding of leaching characteristics is needed over a range of relevant environmental conditions: namely, pH, deicing salts and their concentrations, abrasion, and leaching time. In the next chapter, results of leaching studies on one selected batch (Batch 15) are presented and discussed.

CHAPTER 6

LEACHING OF METALS AND METALLOIDS FROM GLASS BEADS

This chapter presents results of leaching from soda-lime-silica glass beads based on environmentally relevant factors. Specifically, leaching is investigated as a function of pH, salt application, ionic strength, particle size, and time. Because of the large number of factors involved in leaching, a fractional factorial study was applied to address these environmental conditions as well as simulate wear and tear on roads. The results are important in providing insight on the potential impact of applying soda-lime silica beads.

6.1 Fractional Factorial Study

The leaching study was based on a fractional factorial design of experiments wherein 14 tests were conducted on a select batch that was among those exhibiting elevated metal concentrations, consistent with other imported batches. The intent in using one batch was to allow for comparison of results between experiments. Each test condition was evaluated in triplicate while five reagent blanks were included for the control, resulting in a total of 47 samples.

6.1.1. Total Metal Concentrations

Results from using the FP-XRF were found to be consistent with those obtained from following standard methods as discussed in Chapter 5 for digestion of lime-soda glass (ASTM 2005) using HF/ICP-MS (U.S. EPA 1994). Prior to conducting the leaching tests, the total metal and metalloid concentrations and associated variability in the selected batch were measured using FP-XRF (Figure 6.1). Arsenic was observed at concentrations

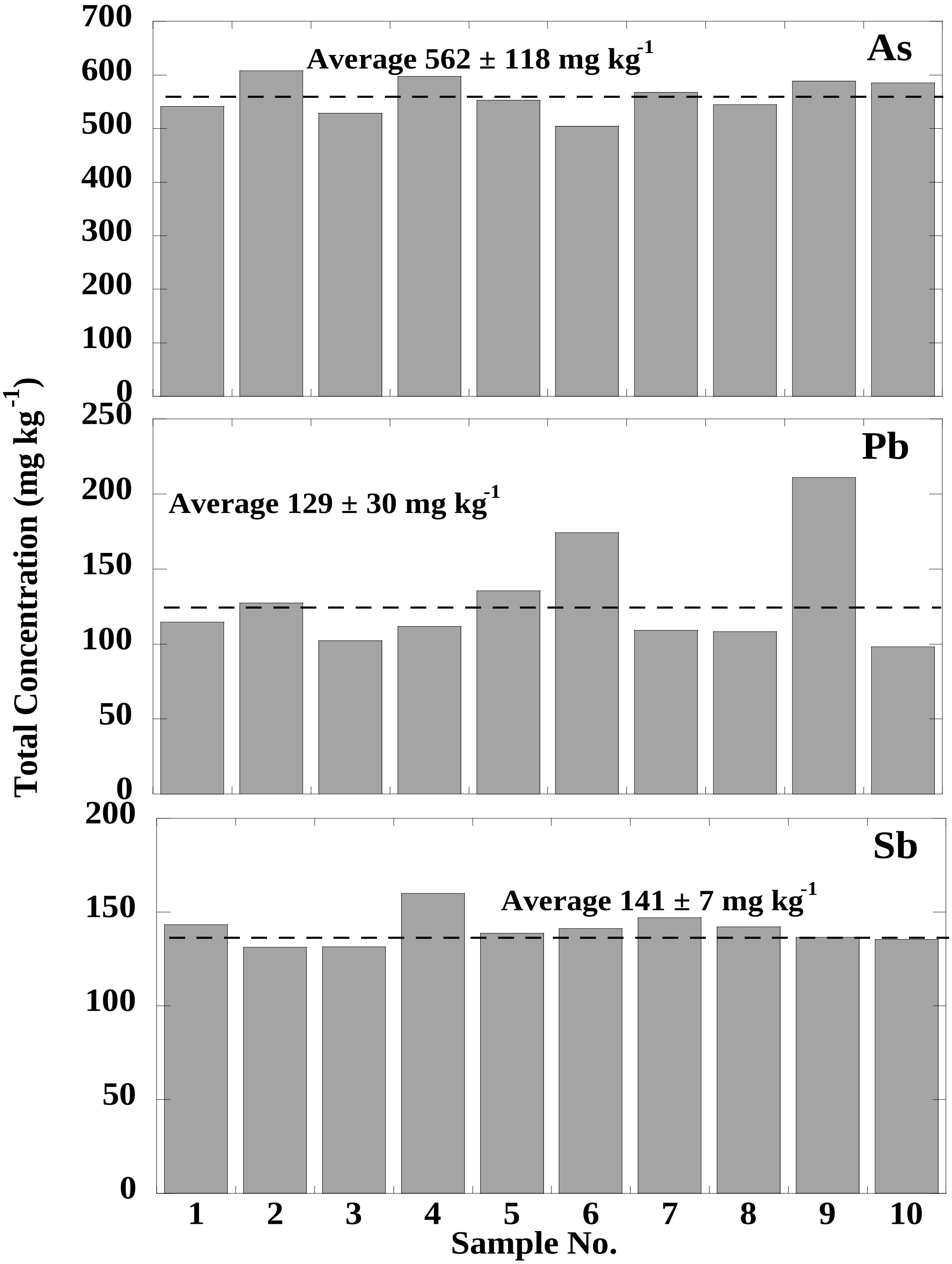


Figure 6.1 Total concentrations of As, Pb, and Sb in glass bead samples collected from ten sampling locations within the batch and measured with FP-XRF. The standard errors for As, Pb, and Sb were observed to be 21%, 23%, and 5%, respectively.

ranging from 504 – 608 mg kg^{-1}, Pb from 98 – 211 mg kg^{-1}, and Sb from 131 – 160 mg kg^{-1}. Average concentrations involved 562 mg kg^{-1} for As, 129 mg kg^{-1} for Pb, and 141 mg kg^{-1} for Sb. The metal and metalloid concentrations were observed to be highly variable with an error of ±23% for Pb, ±21% for As, and ±5% for Sb. This variability in the initial metal concentrations results in variable leached concentrations.

6.1.2. Leaching of Metals and Metalloids

Results of the factorial study revealed that approximately 2-3% of the total metal concentration associated with the glass beads leached after 160 days. Nevertheless, the greatest concentration leached was 6,213 µg L^{-1} for As, 520 µg L^{-1} for Pb, and 110 µg L^{-1} for Sb over the period of the experiment (Table 6.1).

Effect of pH: As reported in a number of studies (Clark and Hench 1983; Bunker and Arnold 1983; Clark et al. 1979), corrosion of glass occurs in two stages. The first stage involves an ion exchange process where cations (e.g., Na, Ca, B, Mg, and K) in the glass exchange with hydrogen ions from solution during which the surface area may increase. This selective dissolution results in the formation of a silica-rich modifier-depleted surface layer on the glass. At pH < 9, $Si(OH)_4^0$ is the dominant species (Figure 2.9). As hydroxyl ions attack the silicate structure at a pH > 9 for soda-lime silica glasses (El Shamy et al. 1972), the $H_3SiO_4^-$ species dominates. At pH greater than 12, $H_2SiO_4^{2-}$ is the major form found in solution. In multi-component glasses such as those used in glass beads, some of the bonds in the glass structure are non-bridging due to the presence of alkali oxides such as Na_2O, CaO, K_2O, and MgO. Speirings and Van Dijk (1987) studied the effect of temperature and composition on the dissolution of Na_2O-MgO-CaO-SiO_2

Table 6.1 Comparison of Water Quality Criterion and Metal Concentration in the leachate

Contaminant	Default Leachate Criteria For Groundwater (μg L^{-1})	RCRA Regulatory Level (μg L^{-1})	EPA Aquatic Life Criteria		Maximum Contaminant Levels		Maximum Concentration after 160 days leaching (μg L^{-1})	SPLP Results (μg L^{-1})	TCLP Results (μg L^{-1})
			Freshwater (μg L^{-1})	Saltwater (μg L^{-1})	NJ (μg L^{-1})	EPA (μg L^{-1})			
As	3	5,000	340	69	5	10	6,213	77	64
Pb	65	5,000	65	210	15*	15*	520	LD	LD
Sb	78	NA	NA	NA	6	6	133	LD	LD
Ba	78,000	100,000	NA	NA	2,000	2,000	14,287	7	148
Zn	26,000	NA	120	90	5,000	5,000	15,337	32	104
Be	13	NA	NA	NA	4	4	12	LD	LD
Cd	52	1,000	2	40	5	5	23	0.5	0.9
Co	NA	NA	NA	NA	NA	NA	9	LD	LD
Cu	16,900	NA	13	4.8	13,000*	13,000*	796	LD	34
Cr	NA	5,000	570	NA	100	100	110	1.7	1.9
Mn	650	NA	NA	NA	50	50	22.8	LD	LD
Hg	26	200	1.4	1.8	2	2	NA	LD	LD
Ni	1,300	NA	470	74	NA	NA	20	LD	LD

LD: less than the detection limit
*Action Level

glass using HF, and observed an increased dissolution rate as compared to vitreous SiO_2.

In this study, pH was observed to be the most important factor resulting in leaching (Appendix B). As the pH determines the surface charge of the beads as well as the speciation, interactions between the ions in solution and the surface contribute to the release or adsorption of species. The leached concentrations (Figures 6.2 - 6.4) of all metals and metalloids show strong pH dependence. Under ambient conditions, As(V) and Sb(V) dominate (Sharma et al. 2009; Villaescusa and Bollinger 2008; Fillela et al. 2002) as such leaching increased with increasing pH (Figure 6.2). Specifically for As with 13% AsO_4^{3-} and 87% $HAsO_4^{2-}$ (Schecher and McAvoy 1998) (Figure 6.5 (a)) maximum leaching was observed at pH 10 and 10^{-2} M $CaCl_2·2H_2O$. The *p*-value of 0.036 and 0.006 between pH 4 and pH 10 at 10 and 20 days of leaching, respectively, demonstrates a significant effect, while there was no significant difference between pH 7 and pH 10. At 160 days, the effect of pH was not significant and equivalent concentrations of As were leached at all pHs (Figure 6.2). For Sb which exists as SbO^-_3 (99.5%) (Figure 6.5 (c)), maximum leaching occurred at a pH of 7 with 10^{-2} M $CaCl_2·2H_2O$. As an anion, there was minimal leaching at pH 4 and leaching increased due to the formation of soluble anionic hydroxyl complexes at higher pH conditions (Figure 6.3). Although there was no significant difference between leaching at pH 4, 7, and 10 (*p*-value = 0.075, 0.385, and 0.397 at 10, 60, and 160 days respectively), the effect of increasing pH was nonetheless visible.

A reverse trend was observed for the cation Pb where leaching increased with a decrease in pH. The zero point of charge for silica is 2.85 ± 0.31 (Xu and Axe 2005). As the pH increases, the surface becomes more negatively charged and cation adsorption

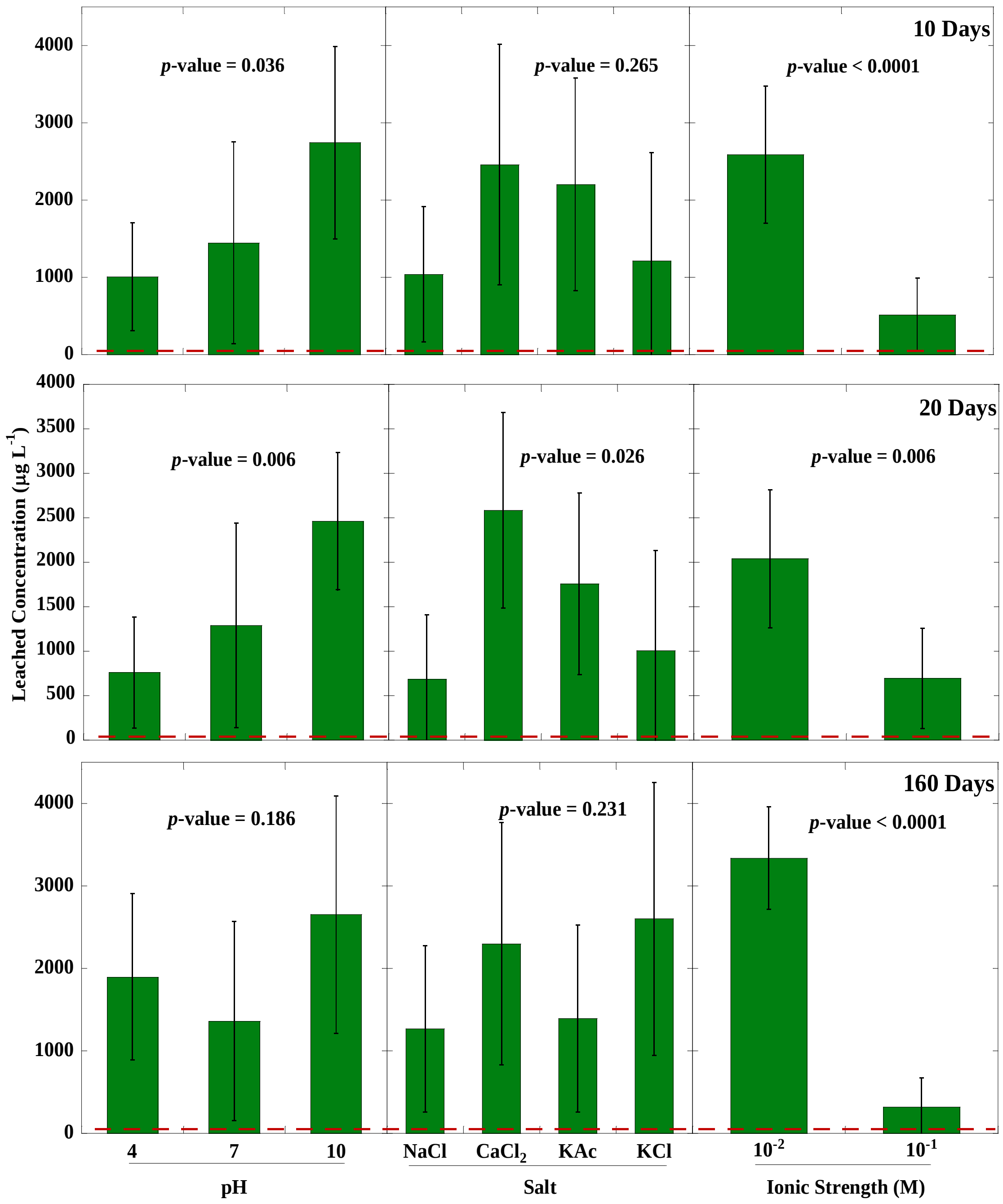


Figure 6.2 Leaching of As depending upon pH, salt, ionic strength, and time for glass beads > 100 µm. Error bars indicate standard error based on 2 × S.D. The New Jersey Ground Water Leachate Criteria for As is 3 µg/L and is shown by a red line.

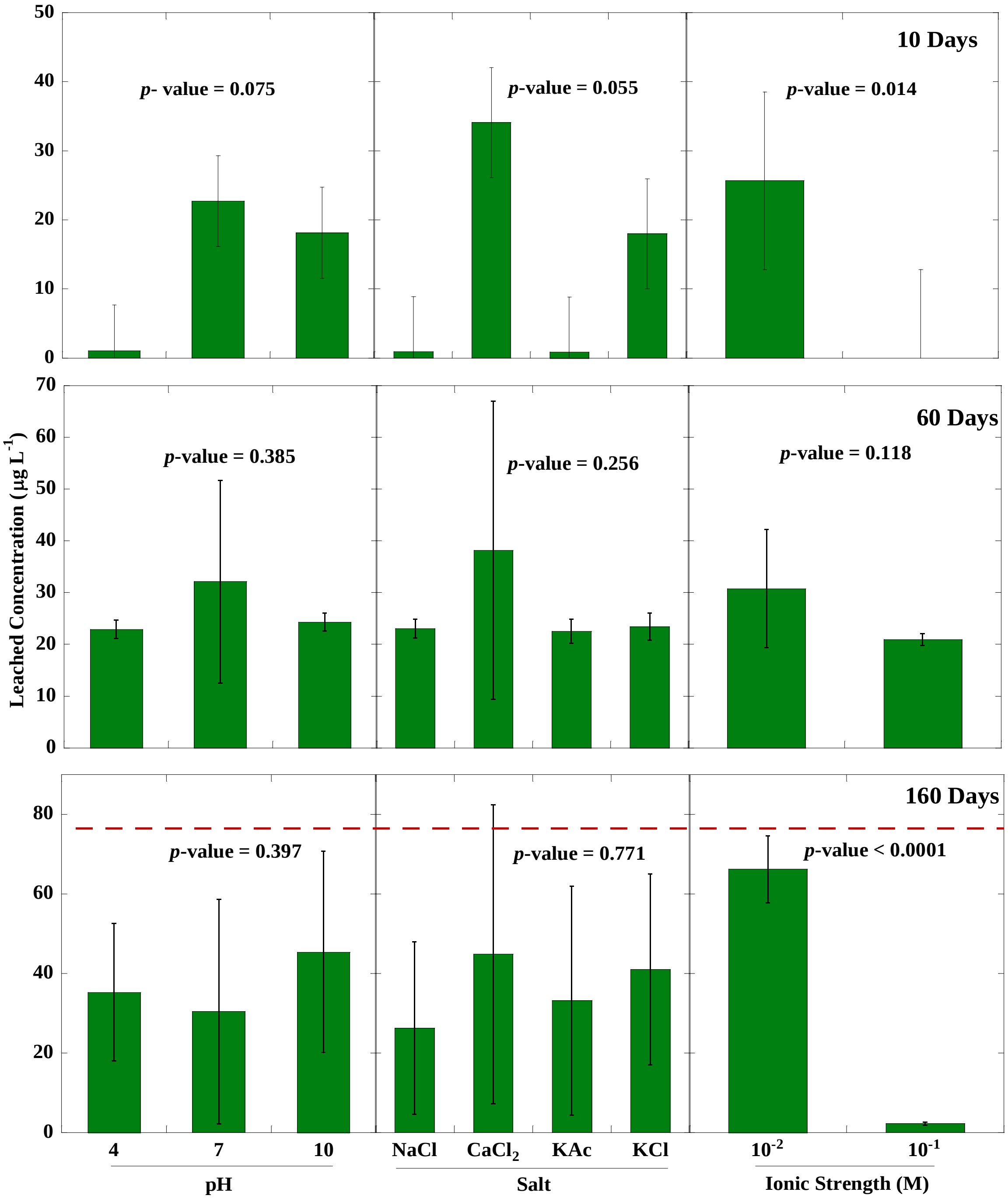


Figure 6.3 Leaching of Sb depending upon pH, salt, ionic strength, and time for glass beads > 100 µm. Error bars indicate standard error based on 2 × S.D. The New Jersey Ground Water Leachate Criteria for Sb is 78 µg/L and was not exceeded.

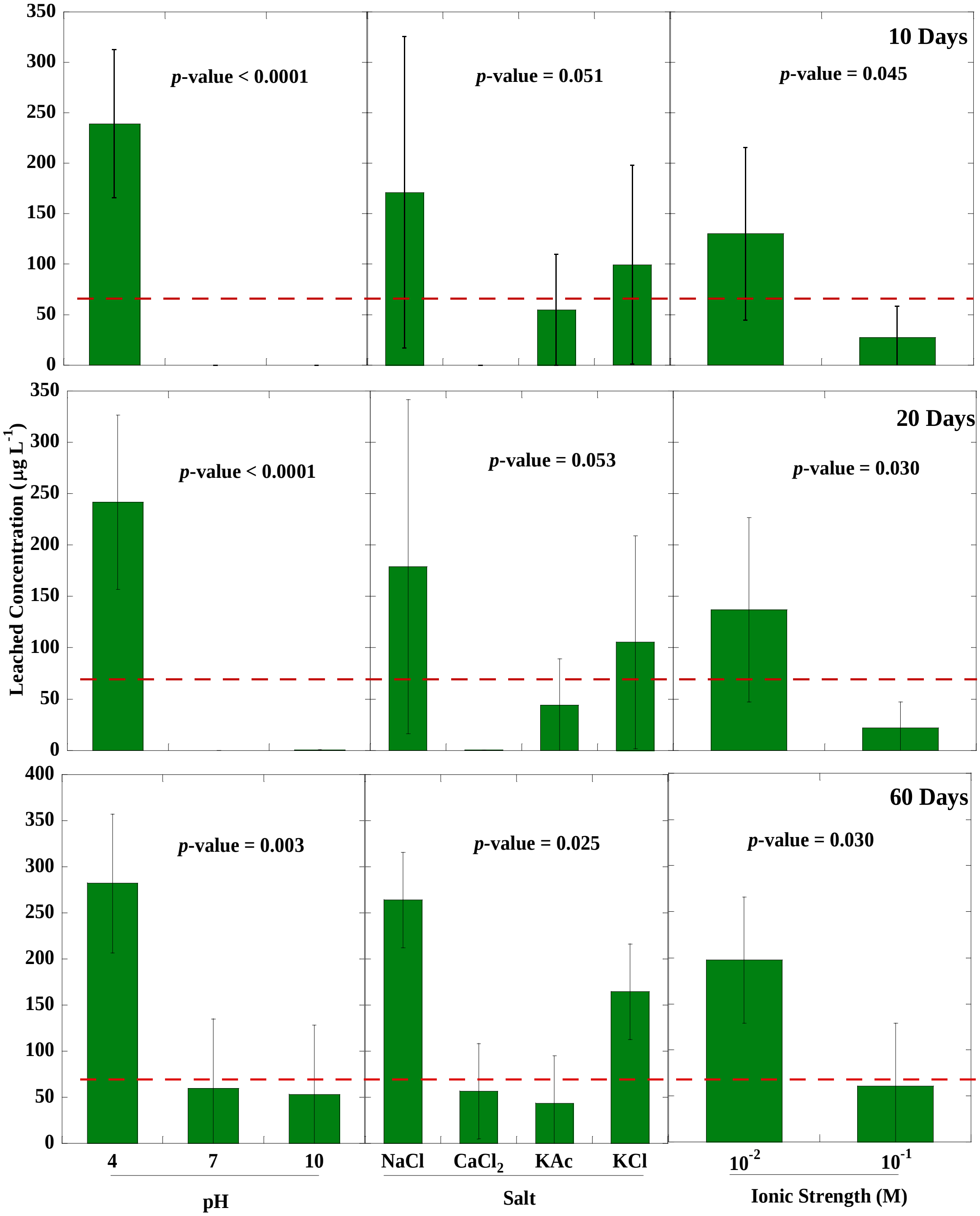


Figure 6.4 Leaching of Pb depending upon pH, salt, ionic strength, and time for glass beads > 100 µm. Error bars indicate standard error based on 2 × S.D. The New Jersey Ground Water Leachate Criteria for Pb is 65 µg/L and is shown by a red line.

increases.

Several leaching studies (Dijkstra et al. 2004; Quina et al. 2009; Rigol et al. 2009) of matrices similar to glass such as soils, fly ash, and air pollution control residues have shown that at higher pH, the surfaces of particles are negatively charged. The extent of leaching for Pb was greatest at pH 4 (Figure 6.4) (p-value < 0.0001 at 10 and 20 days, and p-value$=0.003$ at 60 days into the leaching), one to two orders of magnitude greater than concentrations observed at pH 7 and pH 10. At pH 4 and 10^{-2} M NaCl, the dominant species are 80% Pb^{2+} and 19% $PbCl^{+}$ (Figure 6.5 (b)). Park and Heo (2004) studied leaching of Pb and Cd from ground specimens, 75 to 150 µm, of vitrified fly ash over 15 days where leaching was the most significant at pH 3. This trend has been observed for Pb in other wastes as well including wood, tires, and fly ash (Carmona et al. 2005). Another important factor contributing to leaching is solubility of the species which for cations generally decreases as pH increases. Under alkaline conditions, lead precipitates for example, as $PbCO_3$ or $Pb(OH)_2$ (Baes et al. 1976). A decrease in the leached concentrations of Pb is observed as pH increases due to either adsorption or precipitation of $Pb(OH)_2$ (Van Herck et al. 2005; Zhang et al. 2008a).

Overall, concentrations of As reduced over an order of magnitude between pH 10 and pH 4 and those of Sb decreased up to one order of magnitude between pH 7 and pH 4. In contrast, those of Pb increased over an order of magnitude between pH 10 and pH 4 (Figures 6.2 - 6.4). While pH was one of the most important factors affecting leaching, other factors such as ionic strength and salt demonstrated significant effects as well.

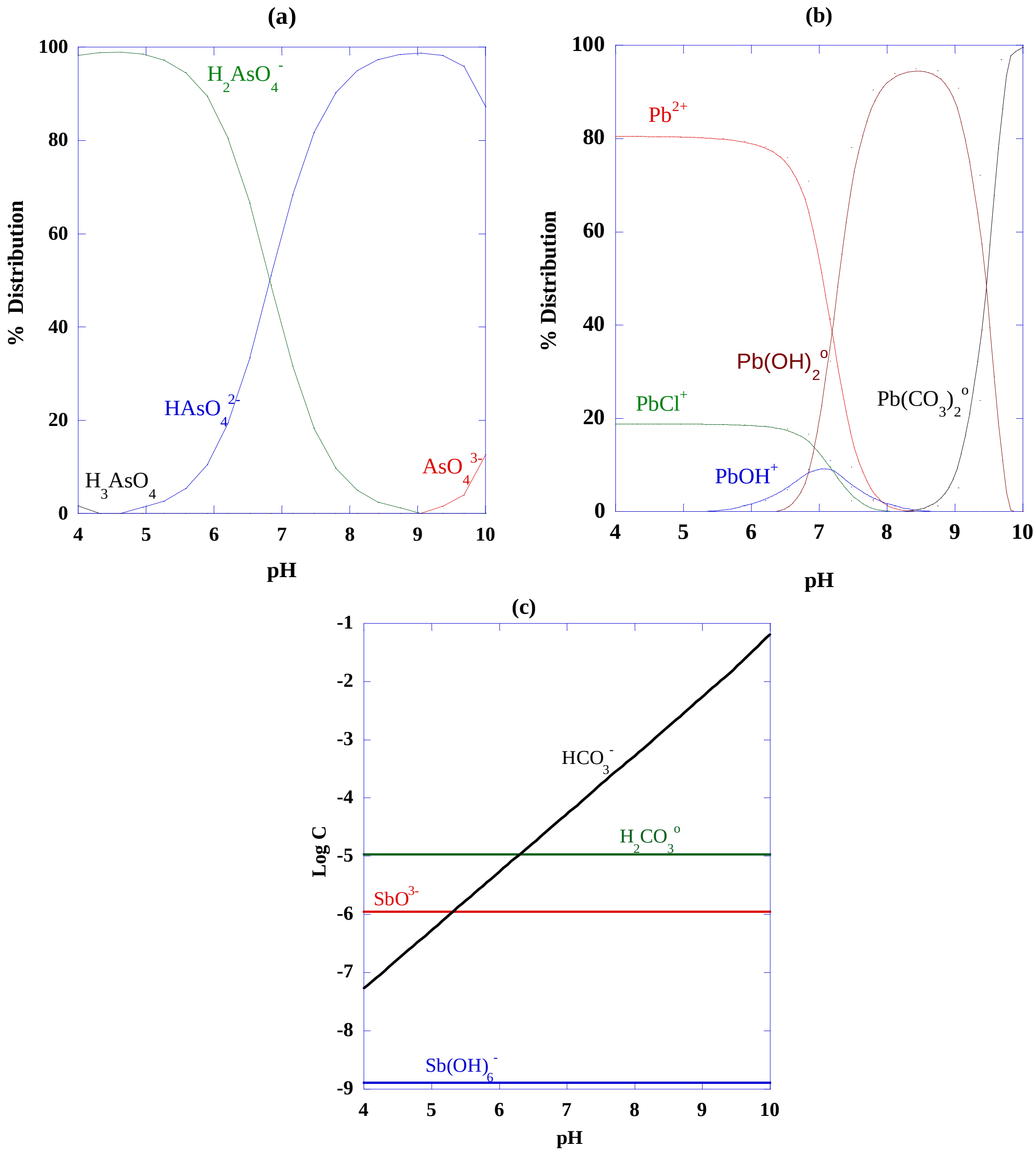


Figure 6.5 (a) Arsenate speciation with 10^{-2} M KCH_3COO, 298 K, $pCO_2 = 10^{-3.5}$ and a total concentration of 1.11 × 10^{-6} M, (b) Pb speciation with 10^{-2} M NaCl, 298 K, $pCO_2 = 10^{-3.5}$ and a total concentration of 2.51 × 10^{-6} M, (c) Sb speciation with 10^{-2} M KCl, 298 K, $pCO_2 = 10^{-3.5}$ and a total concentration of 1.092 × 10^{-6} M.

Effect of ionic strength and salt: All metals and metalloids studied showed that leaching increased with decreasing ionic strength from 10^{-1} to 10^{-2} (Figures 6.2 - 6.4). Studies (Jantzen and Ramsay 1990; Feng and Pegg 1994) considering leaching from glass used to encapsulate nuclear waste reveals rates decreased as the ionic strength increased. Greater leaching rates were observed in de-ionized water (lowest ionic strength studied) than in salt solutions with concentrations as great as 0.1 M. In contrast, Elzinga and Sparks (2002) observed that Pb sorption to amorphous silica increased with decreasing ionic strength. The glass beads used in this study exhibited elevated concentrations of metals and metalloids which we hypothesize to be associated with oxides in the soda-lime-silica. As, Pb, and Sb leaching was significantly greater at the lower ionic strength of 10^{-2} (p-values < 0.05) (Figures 6.2 - 6.4). The type of salt also had a considerable effect on leaching as well. While Pb showed maximum leaching with NaCl and KCl due to the formation of chloro complexes (p-value = 0.025), As leached more with $CaCl_2 \cdot 2H_2O$ and KAc (p-value = 0.026). Norrström and Jacks (1998) studied roadside soils for the presence of Pb, Cd, Zn, and Cu and their mobility based on sequential extraction. Results showed that these cations were vulnerable to leaching when exposed to high NaCl concentrations where it was used as a de-icing salt. The type of salt however did not have a significant impact on leaching of Sb (p-values > 0.05) (Figure 6.3). During use on roadways, the surface of glass beads would likely be impacted from abrasion resulting in a reduced particle size of the glass beads. The increased surface area in contact with environmental conditions such as the de-icing salt solutions will affect the degree of leaching of metals and metalloids.

Effect of particle size: Leaching increased with a decrease in size due to an increase in surface area (Paul 1977, Appendices C and D). Approximately a two to three fold increase in Pb and Sb leaching was observed as the glass bead size was reduced from its original size, > 100 µm, to < 37 µm (Figure 6.6). Specifically, Pb concentrations increased by 138% with a decrease in the glass bead size as compared to the original. An increase in leaching was also observed for Sb by as much as 267%. However, for As leaching was observed to decrease by 38% from >100 µm size. This effect may be attributed to the non-uniform concentrations in the 10 lb batch of glass beads studied (Figure 6.1). The average concentration of As in this batch was 562 mg kg^{-1} with an error of 118 mg kg^{-1} based on FP-XRF analysis. However, variabilities as great as 50-83% were observed in similar batches of glass beads (Sandhu et al. 2012a). Therefore, the initial concentrations of As were likely much greater with > 100 µm as compared to that of the smaller particle size studies. In addition to particle size, time has been observed to be an important variable in the leaching process (Shotyk and Krachler 2007; Reimann et al. 2010; Paul 1977).

Effect of time: One of the most significant factors affecting leaching was time; typically, plateaus were observed at approximately 90 days (Figure 6.6). For As, an increase in leaching was observed from 3,870 µg L^{-1} at 20 d to 5,881 µg L^{-1} at 160 d. Similarly for Pb and Sb, leaching began to level off at 60 d with concentrations approaching 520 µg L^{-1} and 110 µg L^{-1}, respectively. Leaching has been observed to increase with time (Shotyk and Krachler 2007; Reimann et al. 2010; Paul 1977) in other work as well where Shotyk and Krachler (2007) and Reimann et al. (2010) found that the leaching of trace metals

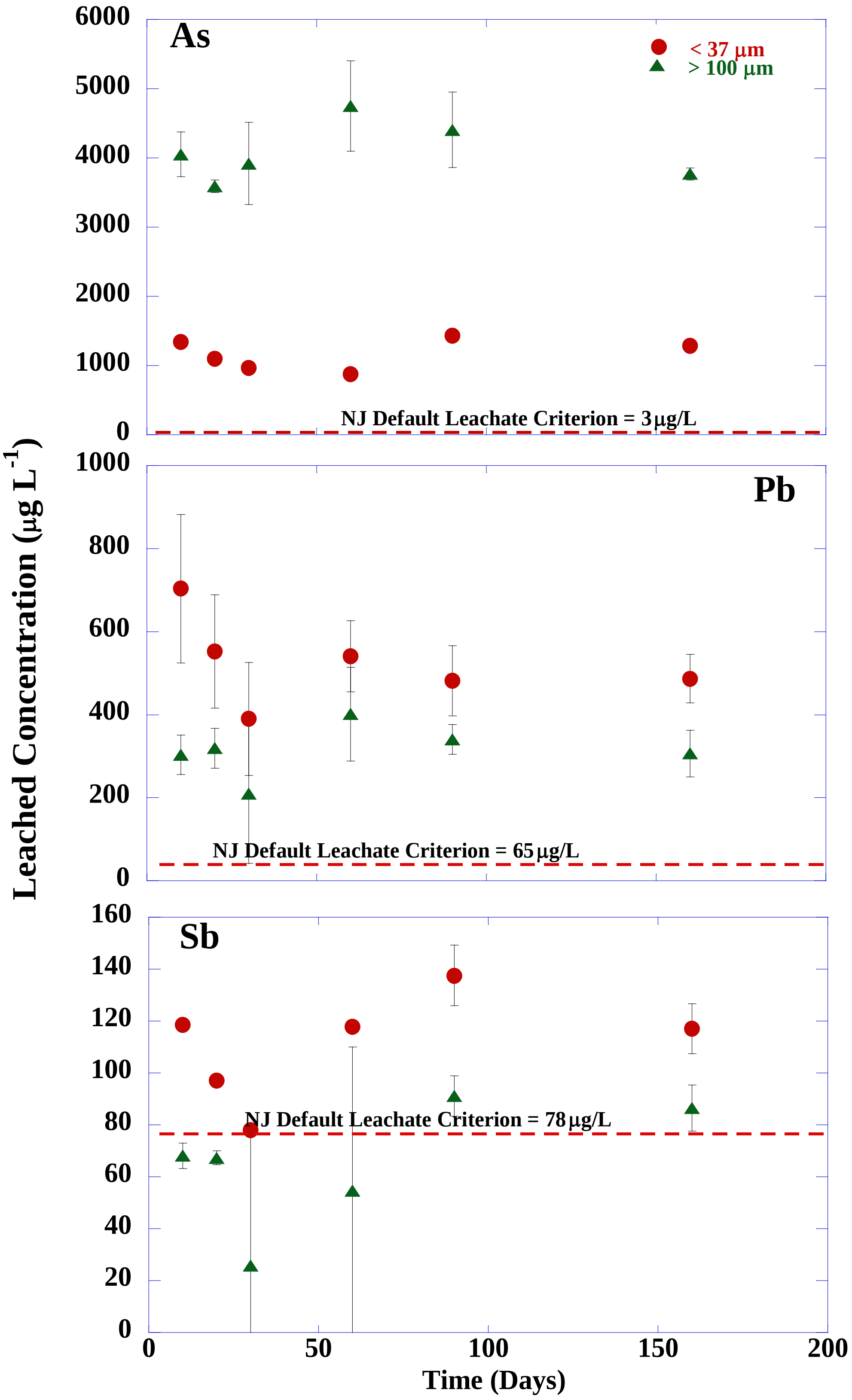


Figure 6.6 Effect of particle size on leaching of As, Pb, and Sb over the period of study.

and metalloids from contaminated bottles increased with the duration of storage. Carmona et al. (2005) reported that the attack can be more rapid for less resistant glasses which typically involve potash-lime silicate glass (with 47% SiO_2, 19 % K_2O, 23% CaO, 3% P_2O_5, 3% MgO, 3% Al_2O_3, and ~ 1% Na_2O) as compared to more resistant glasses such as lead crystal (i.e., 59% SiO_2, 16% K_2O, 0.13% CaO, 24% PbO, 0.2% Al_2O_3, 0.1% Na_2O). Leaching of Pb and Sb decreased from 10 to 60 days. Studies (Clark and Hench 1983; Bunker and Arnold 1983; Clark et al. 1979) have found that when glass is subjected to chemical attack, alkali ions leach from the silicate structure and are replaced by H ions. Lombardo et al. (2005) found that the depletion of Na and Ca from the surface of glass resulted in simultaneous H and Si enrichment and subsequent formation of leached layers (hydroxides and carbonates). Carmona et al. (2005) observed that as these leached layers are formed, subsequent leaching from the glass reduces until the layer undergoes further dissolution. In this study, initially the oxides dissolved resulting in leaching of Pb and Sb. Other mechanisms soon took place such as adsorption to the silica structure. Further dissolution of the oxides in the silica pore structure facilitated desorption and therefore metal leaching. Overall, in the factorial study, leaching was observed to increase with time, leveling off at approximately 90 days and remaining relatively constant through the duration of the 160 day study. This effect is most significant when comparing results to the 18 hour TCLP and SPLP results.

6.2 TCLP and SPLP Studies

The effect of time on leaching is demonstrated for the TCLP and SPLP results. As these tests are conducted for a period of 18 hrs, the concentrations leached were observed to be much lower than those from the factorial study. Leaching for 18 hrs with the TCLP and

SPLP revealed As concentrations of 64 and 77 μg L^{-1}, respectively, which is two orders of magnitude less than the maximum leaching observed after 160 days. Similarly, Sb and Pb leached 55 μg L^{-1} and 402 μg L^{-1}, respectively, after 60 days in the factorial study whereas they were below detection levels in TCLP and SPLP leachates. However, for TCLP and SPLP tests, the pH is not maintained constant and does increase from the initial conditions in both the experiments, most likely due to oxide dissolution from the glass. The increase was slightly greater with the SPLP as in the case of the TCLP test the solution is buffered. Although the initial pH of the SPLP solution was 4.2, the final pH after 18 hrs varied from 7.5 to 10.3. Solubility of cations generally decreases in this pH range (van der Sloot 1977). While TCLP and SPLP tests are the standard ones used by U.S. EPA, they failed to provide an accurate assessment of the leaching potential from glass beads. For rate limited leaching processes, the TCLP does not accurately estimate metal release. Moreover, leaching is addressed at only one pH condition. Therefore, the TCLP and SPLP cannot capture long-term implications of using glass beads on roadways.

The leached concentrations observed were less than the Toxicity Characteristic Limits (Table 6.1) (U.S. EPA 1999). However, based on SPLP results, concentrations of As and Pb exceeded the New Jersey Default Leachate Criteria for Ground Water (NJDEP 2006), which is derived from multiplying the state based groundwater quality limits (GQL), that in some cases are the U.S. EPA maximum contaminants levels (MCL) from the Safe Drinking Water Act, by a default dilution attenuation factor (DAF) (13 for NJ) (NJDEP 2008). The SPLP extract is interpreted to represent the leachate leaving the applied material and is gauged against criteria for assessing risk to groundwater. Several states including New Jersey, Florida, and Wisconsin use SPLP as an assessment of risk (NJDEP 2008; FDEP 2005; WAC 2008). Florida and Wisconsin consider the SPLP leachate to have an inherent 20:1 dilution and compare it directly to GQL, i.e. a DAF of 1. These criteria can aid in addressing the potential site-specific impact to groundwater that is considered a drinking water source (U.S. EPA 1999). The concentrations observed in the factorial study also exceeded the U.S. EPA Chronic and Acute Aquatic Life Criteria for surface salt waters as well as freshwaters (U.S. EPA 2002).

6.3 Summary

These leaching studies have demonstrated the potential bioavailability of metals and metalloids from the glass beads. The 18 hour period used for the TCLP and SPLP tests proved to be insufficient as compared to the 160 day factorial studies where leached concentrations were one to two orders of magnitude greater. Although equilibrium appeared to be obtained during the study, less than 2% of the total metal or metalloid concentration leached from the glass beads. Results demonstrate that glass beads may leach As, Sb, and Pb under environmentally relevant conditions typical of those considered in this work. The metal and metalloid species associated with the alkali oxides and the silica surface offer the most plausible explanation for the observed leached concentrations.

In the next chapter, relationship between total concentrations and leached concentrations will be assessed. The form and phase of metals and metalloids will also be discussed.

CHAPTER 7

ENVIRONMENTAL IMPACT OF METAL AND METALLOID LEACHING FROM HIGHWAY MARKING GLASS BEADS

Based on initial studies, environmentally relevant conditions under which leaching was most significant were applied to better understand the relationship between the total and leached concentrations. Moreover, the mobility of metal and metalloids from the soda-lime silica glass beads may be controlled by the oxides present. Therefore, sequential extraction was used to better evaluate the forms within which the metals are bound.

7.1 Sequential Extraction Procedure

The soda-lime silica glasses are Si-O networks in which the SiO_4 tetrahedral are joined together by the oxygen atoms located at the vertices. These tetrahedral connections become modified by the incorporation of the Na, Ca, Mg, Fe, K, and Al ions (Suszynska et al. 2010). The basic unit is a trigonal antiprism in which Na is coordinated to three O atoms at a distance of 2.3 Å with another three O atoms at non-bonding distances of approximately 3 Å (Greaves 1985). The degree of a chemical attack on glasses increases with increasing concentration of alkali oxides due to formation of a more open glass network (Carmona et al. 2005; Clark et al. 1979; Sinton and LaCourse 2001). EDX microanalysis on soda lime glass exposed to chemical attack with simulated marine water showed loss of Na_2O and SiO_2 with respect to the original glass (Carmona et al. 2005). Corrosion of glass occurs primarily by two mechanisms (a) leaching (or dealkalization) and (b) network dissolution (Clark and Hench 1983; El-Batal et al. 2010). The first stage involves an ion exchange process where cations (e.g., Na, Ca, B, Mg, and K) in the glass structure exchange with hydrogen ions from solution during which the surface area may increase. This selective dissolution results in the formation of a silica-rich alkali-depleted surface layer on the glass. The attacking acidic solution is progressively neutralized by continuous liberation of alkali ions. At a pH > 9 for soda-lime silica glasses (El Shamy et al. 1972; El-Batal et al. 2010), the corrosion mechanism changes from selective leaching to uniform dissolution of all the glass structure. Dubrovo and Shmidt (1955) observed that with glasses of high silica content ($SiO_2 > 65\%$), the dominant process involves Na_2O dissolution from the glass. Depletion of alkali oxides under simulated marine conditions has been observed to follow the trend: $Na_2O > K_2O > CaO > MgO > Al_2O_3$ (Carmona et al. 2005; Sinton and LaCourse 2001). The hypothesis in this study is that metals are associated with alkali and alkaline earth metal oxides (such as Na_2O, K_2O, CaO, and MgO) that undergo the corrosion and dissolution process in the aqueous phase.

To test this hypothesis, the modified BCR sequential extraction procedure was conducted. This approach makes use of several reagents consecutively to extract operationally defined phases (Jamali et al. 2009; Álvarez-Valero et al. 2009; Ndiba and Axe 2009). The recoveries of fractions from sequential extraction were computed based on the total metal concentrations initially present as determined by FP-XRF. The first step in sequential extraction (pH 2) revealed 0.04 to 0.23% (5 to 35 $\mu g\ L^{-1}$) of As, 0.46 to 0.76% (16 to 30 $\mu g\ L^{-1}$) of Pb, 0.76 to 1.66% (82 to 221 $\mu g\ L^{-1}$) of Ba, and 0.46 to 0.60% (9 to13 $\mu g\ L^{-1}$) of Mn (Figure 7.1). This phase represents metals and metalloids that are exchangeable and weakly bound. During the leaching experiments, this form is expected to be released in the aqueous phase. In the manufacturing of glasses, As is introduced in the form of As_2O_3 in the glass melt. As a fining agent it is converted to As_2O_5, then back

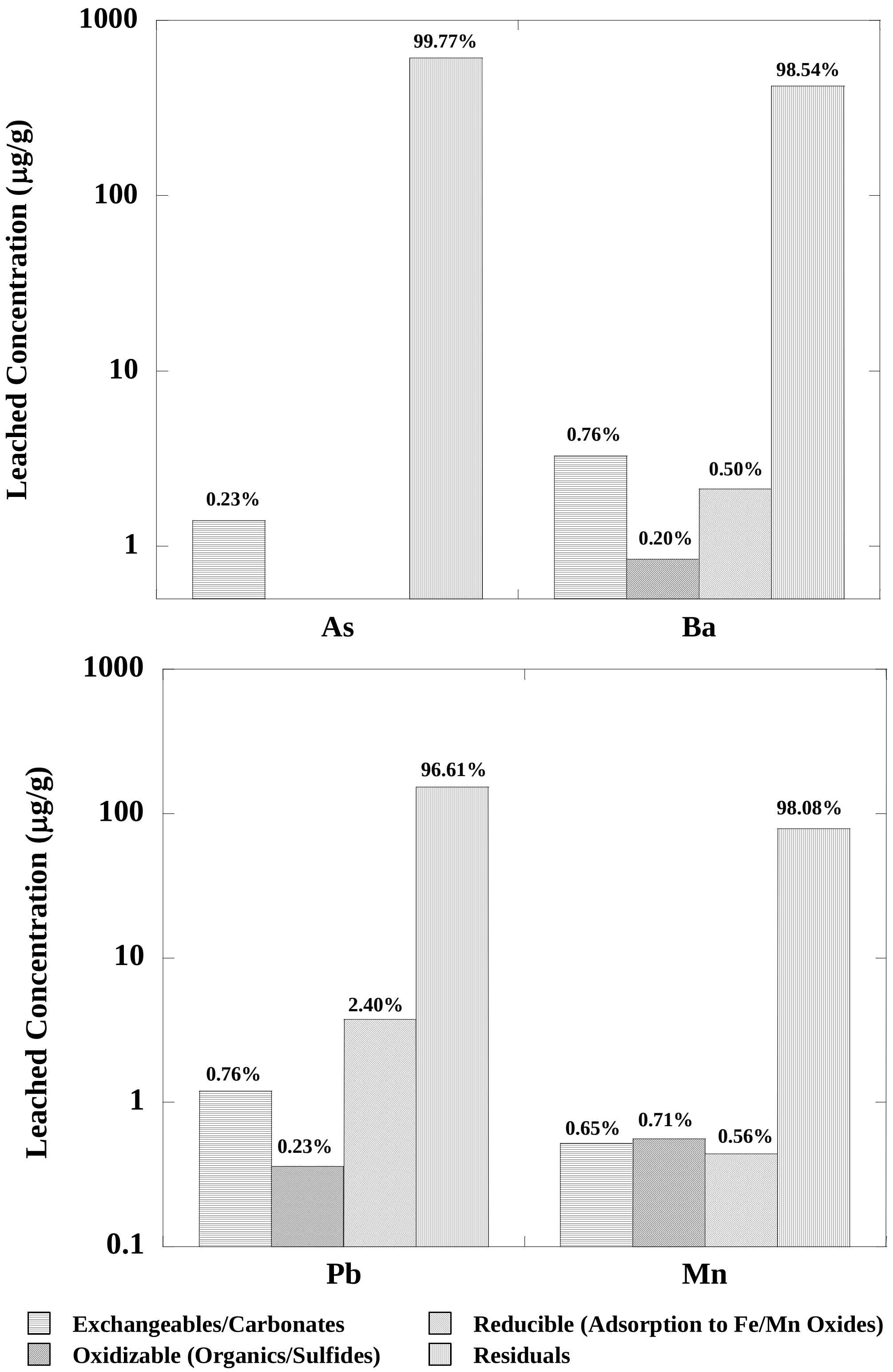


Figure 7.1 Mass balances of selective sequential extraction fractions for As, Ba, Pb, and Mn.

again to As_2O_3 at higher melt temperatures, and may be present as As (III) or As (V) in the final glass product (Nascimento et al. 2005; Shelby 1997; Del Barrio et al. 1993). However, studies of matrices similar to glass (soils, sediments, and fly ash) have revealed that the dominant form is As(V) present was calcium arsenate (pharmacolite, $Ca_3(AsO_4)_2$, pK_{so} = 14.40 at 20°C) with calcium pyroarsenate, a sparingly soluble form ($Ca_2As_2O_7$), observed to a lesser extent (Bolanz et al. 2012; Jackson and Miller 1999; Huggins et al. 2007; Luo et al. 2011). These structures may also be found in glass (Luo et al. 2011). Past studies have reported that arsenic vapor is captured by lime and calcium silicates (Jadhav and Fan 2001; Sterling and Helble 2003). As the glass beads are subjected to an aqueous solution of 0.11 M acetic acid at a pH of 2 (pK_a = 4.76 at 20°C), sodium and calcium ions are preferentially extracted from the glass bead surface due to dissolution (CaO, pK_{so} = 3.34 at 20°C); thereby releasing associated metals and metalloids. Pb, Ba, and Mn are also present in the structure of the glass and are associated with alkali oxides, silica, or non-bridging oxygens. Using x-ray photoelectron spectroscopy (XPS) and XRD, PbO, Pb_2SiO_4, BaO, and $MgMnSi_2O_6$ were observed in fly ash samples (Eighmy et al. 1994); of these, the two oxides are ones are most likely to undergo dissolution in the extraction and leaching experiments (Del Barrio et al. 1993; Eighmy et al. 1994).

The second step of the extraction (pH 3 and 0.5 M) resulted in the leaching of 0.23 to 0.26% (9 to 34 μg L^{-1}) of Pb, 0.05 to 0.20% (7 to 21 μg L^{-1}) of Ba, and 0.57 to 0.63% (11 to 14 μg L^{-1}) of Mn (Figure 7.1). Because hydroxylamine hydrochloride is applied to dissolve Mn/Fe oxides and hydroxides, strong scavengers for trace metals (Post 1999), this extraction did not result in significant concentrations. The third extractant, hydrogen peroxide followed by ammonium acetate (pH 2) resulted in 1.2 to

2.43% (41 to 94 μg L^{-1}) of Pb, 0.17 to 0.51% (22 to 53 μg L^{-1}) of Ba, and 0.46 to 0.50% (9 to 11 μg L^{-1}) of Mn (Figure 7.1). In this study the dominant phase that Pb was observed to be associated with was the oxidizable fraction, similar to results observed by others (Álvarez-Valero et al. 2009; Hürkamp et al. 2009; Norström and Jacks 1998). The third stage is used to extract organic and oxidizable sulfides leading to the release of associated metals. The observed increase in Pb associated with organics suggests that the oleophobic coating on the glass beads may provide a sink for the Pb ions. Glass beads are coated with non-toxic organo-titanium derivatives to support their ability to float in the paint marking process. This application allows for their exposure on the surface providing retroreflectivity (Brown 1968; Sheehy 2012). During successive extractions, redistribution of metals is likely (Hass and Fine 2010) which may explain the association of Pb with this surface.

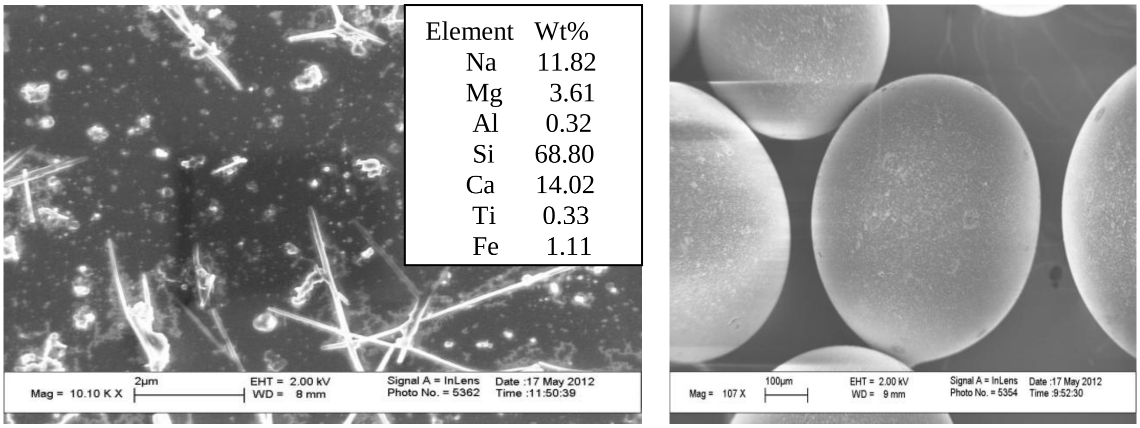
The residual fraction consists of metals embedded in the lattice structure and is considered the immobilized fraction. In this study, sequential extraction was applied to better understand the phases that As, Sb, and Pb may be associated with and because silica dissolution requires the use of hydrofluoric acid (Young et al. 2006; U.S. EPA 1996), the final step of the extraction involving aqua regia digestion was not conducted. Although Sb was not extracted, leached concentrations of Sb were consistently lower than As and Pb. Using a mass balance, approximately 99% of As, 98% of Ba, 98% of Mn, and 97% of Pb were associated with the residual fraction. The degree of mobilization observed in this extraction followed the trend of Pb > Ba ≈ Mn > As.

7.2 FE-SEM Results

FE-SEM with EDX analysis of extracted beads indicates As and Ba concentrations on the surface at 0.41 and 1.38% by weight, respectively (Figure 7.2). While analysis of domestic as well as imported beads (before extraction) did not reveal the presence of these metal and metalloids on the surface, the imported beads which underwent sequential extraction were observed to exhibit detectable concentrations of As and Ba on their surfaces (Figure 7.2). The hypothesis in this study was that the metals and metalloids are associated with the alkali and alkaline earth oxides present in the silica structure of the glass beads. Based on the results of sequential extraction, Pb is observed to be associated with the exchangeable and organic fractions on the surface of the glass beads. However, the silica structure is the sink for over 95% of the metals and metalloids present, which is consistent with results found by others (Davutluoglu et al. 2010; Iavazzo et al. 2012) where more than 60% of Pb, Mn, Cr, Cu, Zn, and Ni was associated with the residual fraction.

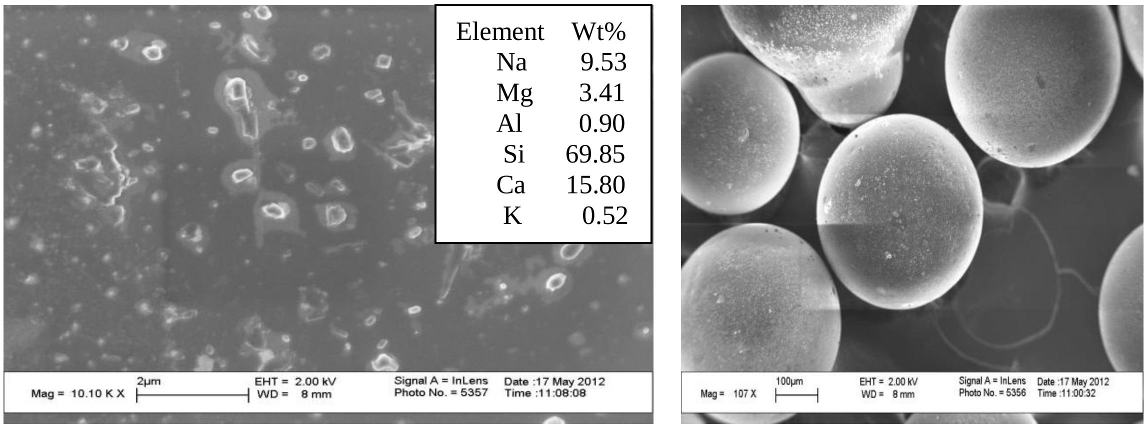
7.3 Potential Impact on Groundwater Used as Drinking Water

Results from using FP-XRF revealed that average total concentrations for the imported batches of glass beads ranged from 103 to 683 mg kg^{-1} for As, 62 to 187 mg kg^{-1} for Sb, 23 to 179 mg kg^{-1} for Pb (Figure 7.3). Variability was significant with the average error for each batch ranging from 10 to 42% for As, 30 to 89% for Pb, and 9 to 24% for Sb consistent with previous studies discussed in Chapter 5. Leached concentrations were as great as 538 μg L^{-1} for As, 1,092 μg L^{-1} for Pb, and 160 μg L^{-1} for Sb (Figure 7.4). Similar concentrations of As and Sb have been observed in the previous studies. While the peak concentration for Pb reached 1,092 μg L^{-1}, this degree of leaching is plausible



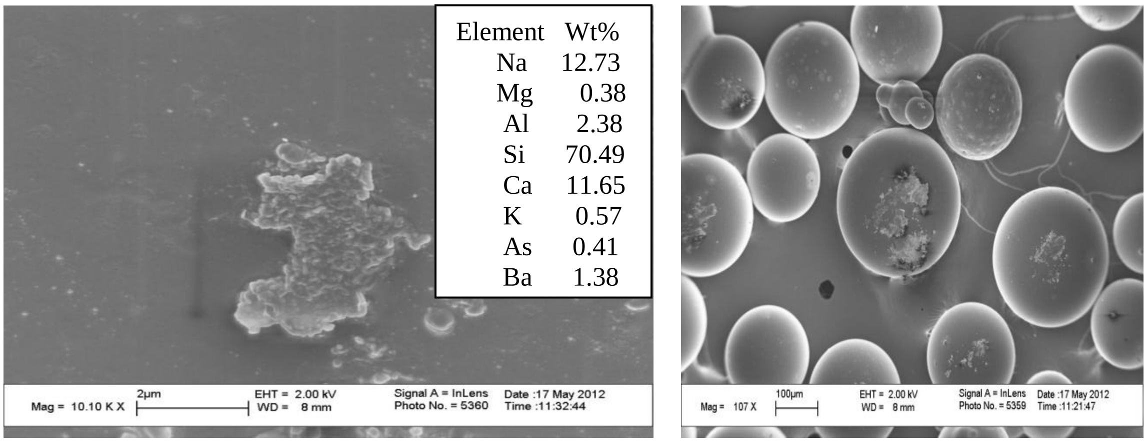
Element	Wt%
Na	11.82
Mg	3.61
Al	0.32
Si	68.80
Ca	14.02
Ti	0.33
Fe	1.11

(a) Domestic Glass Bead Surface



Element	Wt%
Na	9.53
Mg	3.41
Al	0.90
Si	69.85
Ca	15.80
K	0.52

(b) Imported Glass Bead Surface



Element	Wt%
Na	12.73
Mg	0.38
Al	2.38
Si	70.49
Ca	11.65
K	0.57
As	0.41
Ba	1.38

(c) Sequentially Extracted Surface from Imported Glass Bead

Figure 7.2 FE-SEM micrographs of(a) domestic, (b) imported, and (c) leached glass bead surfaces at 2 μm and 100 μm, respectively. EDX analysis is shown in inserts.

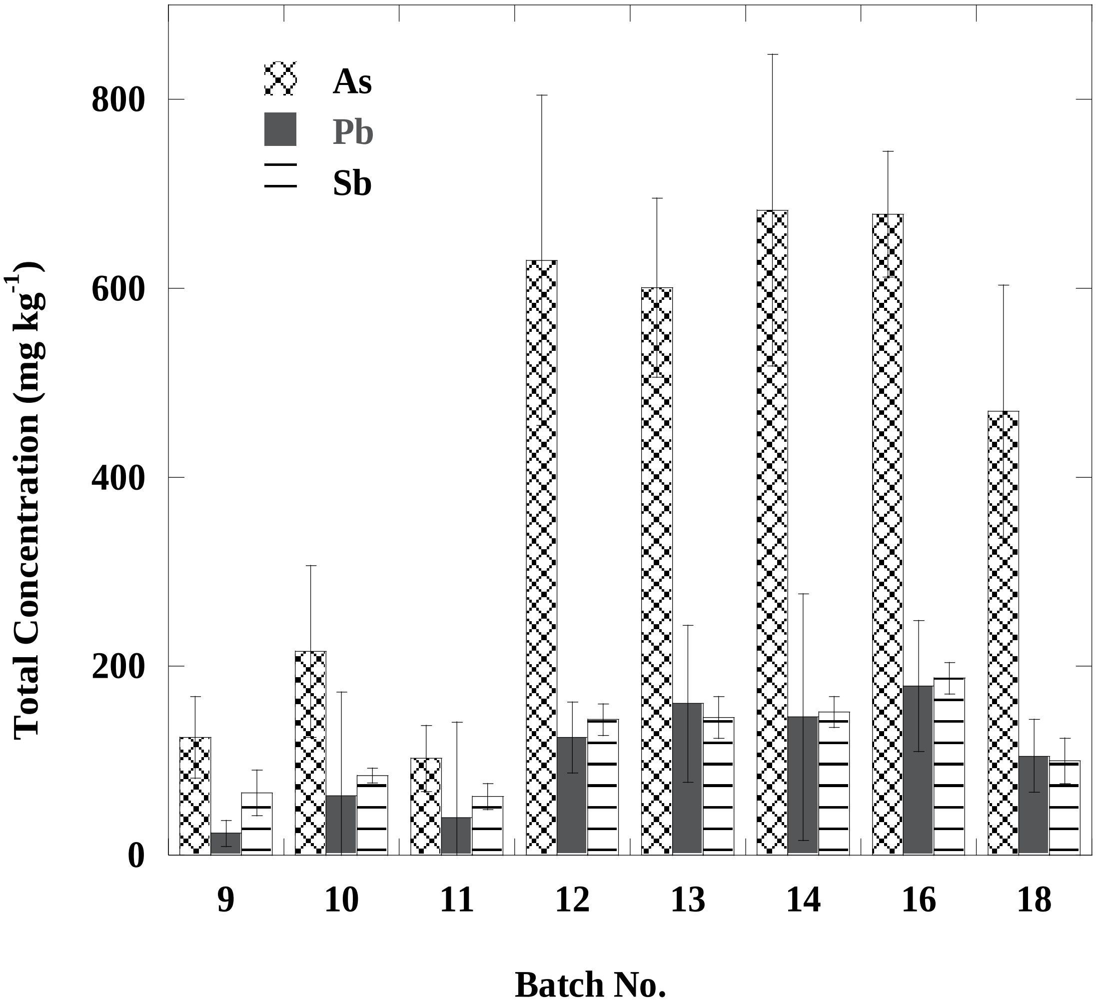


Figure 7.3 Total average concentrations of As, Pb, and Sb measured using FP-XRF based on triplicate samples from Batches 9, 10, 11, 12, 13, 14, 16, and 18. Variability of concentrations was observed to range from 10-42% for As, 30-89% for Pb, and 9-24% for Sb, respectively.

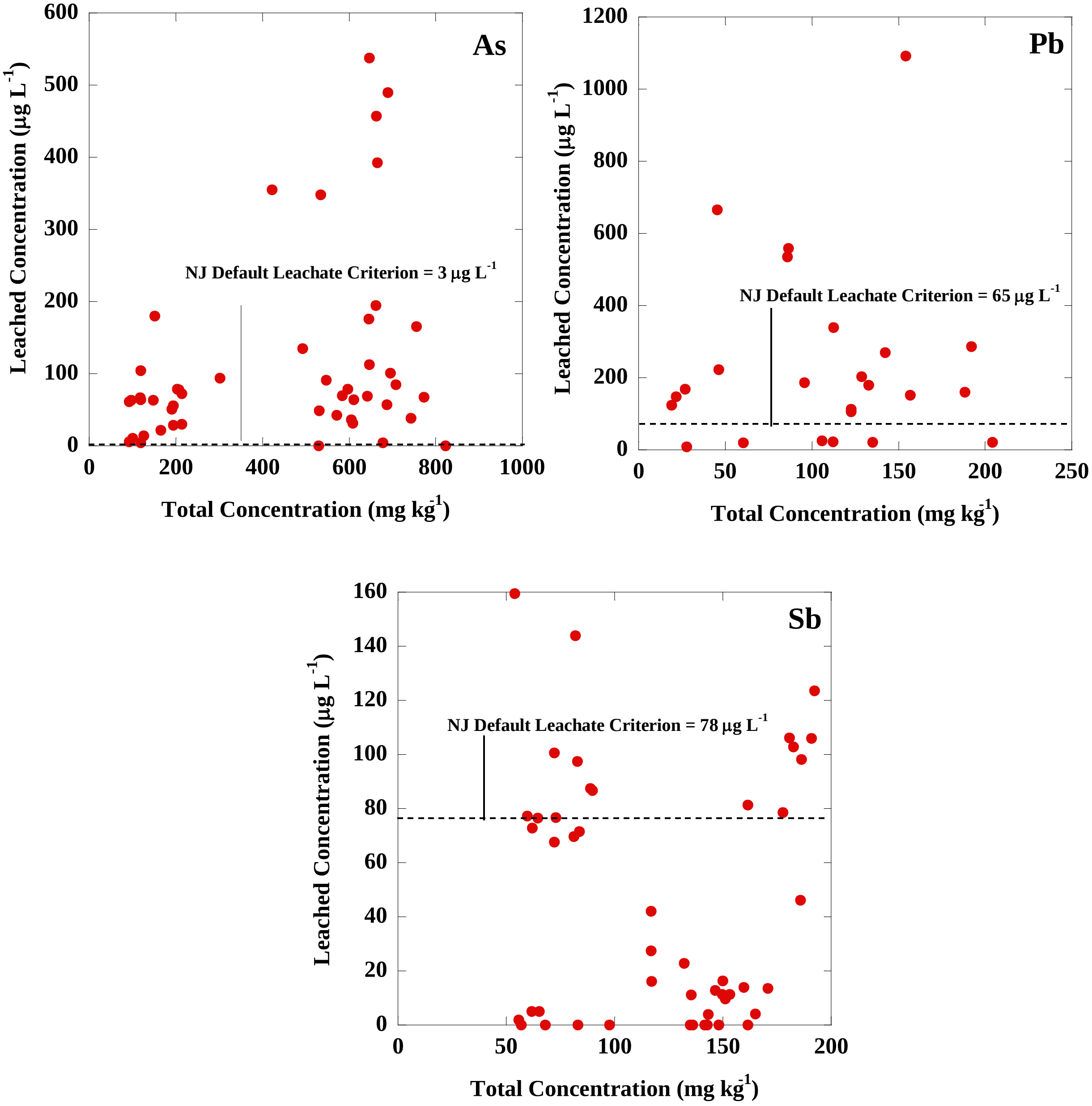


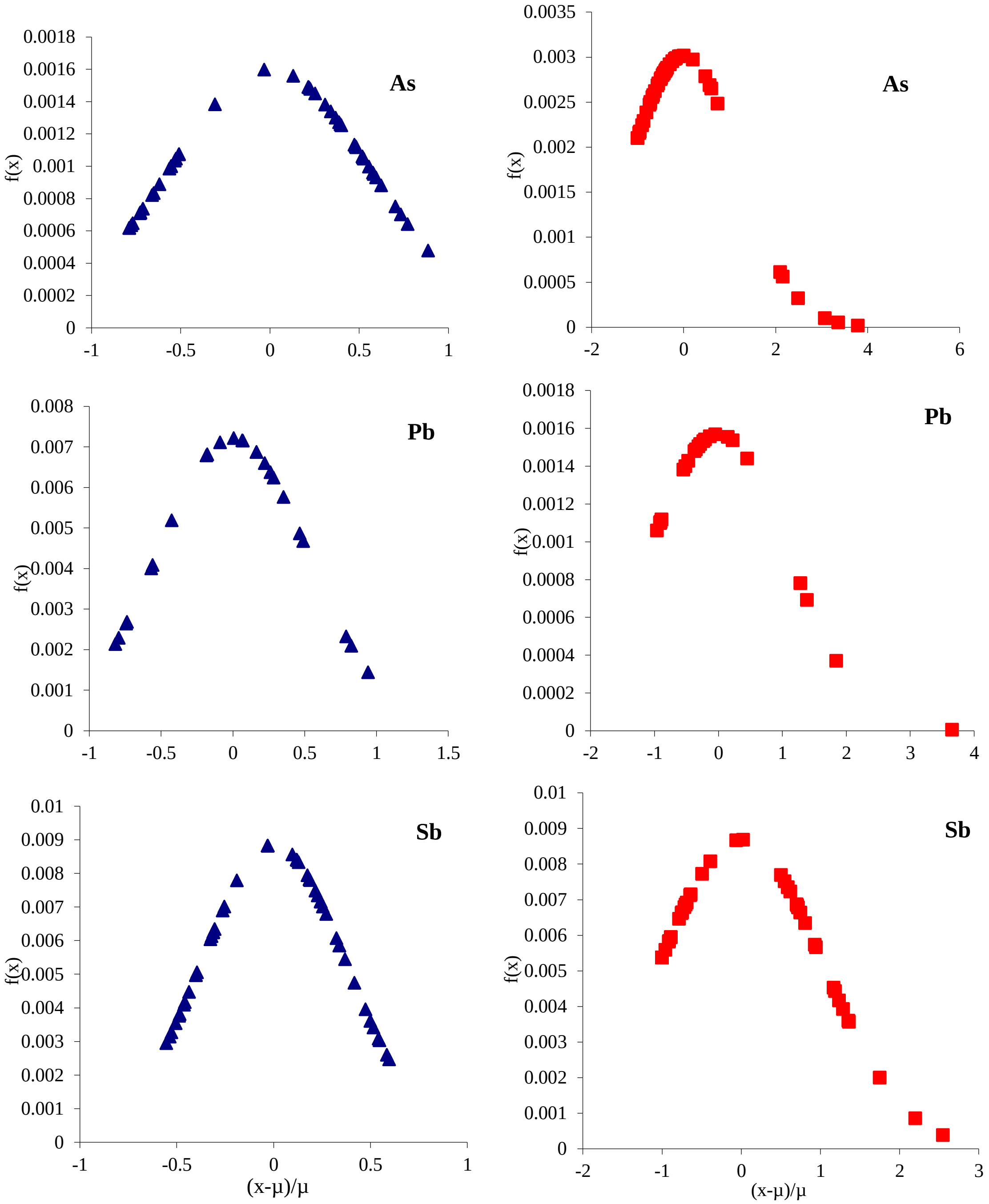
Figure 7.4 Leached concentrations versus the total concentrations for As, Pb, and Sb. NJ Default Leachate Criteria is shown by dashed lines. Florida and Wisconsin both use a Default Leachate Criteria of 10 µg L^{-1} and 15 µg L^{-1} for As and Pb, respectively. For Sb, FL limit is 14 µg L^{-1}and WI uses 6 µg L^{-1}.

given the significant variability observed (30-89%).

Although a relationship between the leached and initial total concentrations was not discernible, the potential impact associated with glass bead application, use, and management is considered. One impact would be whether the glass beads are considered a hazardous waste. TCLP results indicated that glass beads are non-hazardous in nature. However, leaching under environmentally relevant conditions reveals elevated concentrations for As, Pb, and Sb which would have a potential impact when disposed as a bulk solid waste. For bulk storage on a surface or subsurface and in considering a worst case scenario, leached concentrations can diffuse through the surrounding soils and impact groundwater (used as a drinking water source). Estimating pore water concentrations can be challenging (Townsend et al. 2006). As noted earlier, several states including New Jersey, Florida, and Wisconsin require an assessment of risk through application of the U.S. EPA Method 1312 SPLP test (U. S. EPA 1994; FDEP 2005; NJDEP 2008; WAC 2008). The SPLP extract represents the leachate and is gauged against criteria for assessing potential risk to groundwater. However, the SPLP approach may under-predict leaching from glass beads as concentrations were two orders of magnitude smaller than those observed in other batch studies using environmentally relevant conditions. A better understanding of contaminant speciation and behavior may involve several types of studies, such as extractable concentrations, SPLP, and leaching as a function of pH, time, salt, and ionic strength.

In this study, the NJ Default Leachate Criteria with a DAF of 13 was applied to consider the potential impact using a conservative condition of leaching from bulk glass beads (i.e., a storage or solid waste condition) into groundwater (used as a drinking water source) (Figure 7.4). For As, 96% of the leached concentrations observed exceeded the NJ Default Leachate Criterion of 3 µg L^{-1} where the initial As concentration in the beads ranged from 92 to 823 mg kg^{-1} (Figure 7.4). Although the GQL for As is set at 0.02 µg L^{-1} (NJDEP 2006), NJDEP specifies a default criterion of 3 µg L^{-1} based on the practical quantitation limit. For Pb, 75% of leached concentrations exceeded the criterion of 65 µg L^{-1} with initial Pb concentrations ranging between 19 mg kg^{-1} and 204 mg kg^{-1} (Figure 7.4). Leached concentrations of Sb exceeded the threshold limit of 78 µg L^{-1} for 27% of the samples where the initial concentration varied between 54 mg kg^{-1} and 192 mg kg^{-1} (Figure 7.4). Leached concentrations of As, Pb, and Sb also exceeded the Florida and Wisconsin groundwater quality criteria (Figure 7.4). With regard to other potential impacts, surface water quality limits (340 µg L^{-1} for As and 65 µg L^{-1} for Pb in freshwater; 69 µg L^{-1} for As and 210 µg L^{-1} for Pb in saltwater) set by the U.S. EPA (U.S. EPA 2002) as well as NJDEP (NJDEP 2006) for aquatic life were also exceeded for As and Pb.

The distribution of leached concentrations was not normal (Figure 7.5). Specifically, for As 2.1% of leached concentrations lied outside the ($\mu \pm 3\sigma$) limit, where broadening of the tails suggest the need for additional moments to describe the distribution. For Pb, 4.2% of the leached concentrations fell outside the $\mu \pm 3\sigma$ limits. On the other hand, samples from measuring total concentrations revealed Gaussian distributions for As (99.7%) and Pb (99%). For Sb both the total and leached concentrations measured were normally distributed. Based on these distributions, non-parametric statistics were applied to further evaluate leached concentrations. These methods use relative ranks of the sample observations rather than their actual numerical



(a) Total Concentrations

(b) Leached Concentrations

Figure 7.5 Gaussian plots of (a) total vs. (b) leached concentrations for As, Pb, and Sb.

values.

The Wilcoxon Signed Rank test was applied (Mendenhall and Sincich 1988) and is stronger than the simple Sign Test (Conover 1999). This test has been frequently used in environmental studies to compare water quality characteristics as a function of seasonal changes (Elzinga and Sparks 2002), metal concentrations in contaminated sediments (Zhang and O'Connor 2005), and lead concentrations in workplace air samples (Morley et al. 1999). The sample differences from a test median (M) were ranked and statistically evaluated. The test median (M) in this study was assumed to be the NJ Default Leachate Criterion for each metal and metalloid (3 µg L^{-1} for As, 65 µg L^{-1} for Pb, and 78 µg L^{-1} for Sb). The following hypothesis was tested:

> H_o: When the initial metal concentration is less than X mg kg^{-1}, the median of the leached concentrations (M_Y) is less than the NJ Default Leachate Criteria (3 µg L^{-1} for As, 65 µg L^{-1} for Pb, and 78 µg L^{-1} Sb), that is $M_Y < 3$ µg L^{-1} (for As), $M_Y < 65$ µg L^{-1} (for Pb), $M_Y < 78$ µg L^{-1} (for Sb).
>
> H_1: When the initial metal concentration is greater than or equal to X mg kg^{-1}, the median of the leached concentrations (M_Y) is greater than or equal to the NJ Default Leachate Criteria (3 µg L^{-1} for As, 65 µg L^{-1} for Pb, and 78 µg L^{-1} for Sb), that is $M_Y \geq 3$ µg L^{-1} (for As), $M_Y \geq 65$ µg L^{-1} (for Pb), $M_Y \geq 78$ µg L^{-1} (for Sb).

A survey conducted across the U.S. indicates that the present allowable total metal concentrations in glass beads set by various states (NJ, GA, LA, CA, TX, CO, AZ, WA, OR, and KS) range between 50 to 200 mg kg^{-1} for As, Pb, and Sb (Jahan et al.

2011). The hypothesis was tested down to the lowest detectable total metal concentration observed. In the case of As, the analysis was applied at 100, 150, and 200 mg kg^{-1}. For Pb and Sb, the lowest metal concentrations were approximately 20 and 50 mg kg^{-1}, respectively. The analysis for Pb was applied at X = 20, 50, 75, and 100 mg kg^{-1} and for Sb at X = 50, 75, 100, 150, and 175 mg kg^{-1} as total concentrations of Sb did not exceed 200 mg kg^{-1}. The minimum total concentration resulting in a leached concentration exceeding the NJ Default Leachate Criterion and for which the results of the non-parametric test applied was observed to be statistically significant is identified as the concentration that may potentially pose a risk to groundwater used as a drinking water source (Appendix C). This analysis (illustrated for Pb with initial concentrations exceeding 100 mg kg^{-1} in Table 7.1) implies that as the total concentrations of As, Pb, and Sb in the glass beads exceed these thresholds, there is a potential risk based on this approach (U.S. EPA 2002; NJDEP 2008).

The Wilcoxon Signed Rank Test entails the following steps: Considering initial total metal concentrations greater than or equal to X in mg kg^{-1}, along with the corresponding leached concentrations.

1. Subtracting the test median (as defined by the hypothesis; 3 µg L^{-1} for As, 65 µg L^{-1} for Pb, and 78 µg L^{-1} for Sb) from the leached concentrations. This difference provides both positive and negative numbers. If H_o is true, then the subtracted numbers are symmetrically distributed about median.
2. Applying the modulus for the difference calculated in Step 2.
3. Ranking the differences observed in Step 3. Average ranks must be assigned in case of ties.

Table 7.1 Wilcoxon Signed Rank Test applied on Pb with initial metal concentrations exceeding 100 mg kg^{-1}; 65 µg L^{-1} represents the test median for Pb (NJ Default Leachate Criteria)

Total (mg kg^{-1})	Leached (µg L^{-1}) (Y)	Y - 65	Sign	Modulus or Absolute $\lvert Y - 65 \rvert$	Rank (R)	Sign*Rank	R^2
142	269	204	+	204	11	11	121
188	161	96	+	96	8	8	64
129	203	138	+	138	10	10	100
113	340	275	+	275	13	13	169
135	21	-44	-	44	4.5	-4.5	20.25
157	152	87	+	87	7	7	49
123	106	41	+	41	2	2	4
192	287	222	+	222	12	12	144
112	22	-43	-	43	3	-3	9
204	21	-44	-	44	4.5	-4.5	20.25
106	25	-40	-	40	1	-1	1
154	1092	1027	+	1027	14	14	196
133	179	114	+	114	9	9	81
123	113	48	+	48	6	6	36

Sum of positive ranks (R^+) = 92
Sum of negative ranks (R^-) = 13
Sum of R^2 = 1014.5

Using Eq. (7.1),

$$Z = \frac{(92 - 13)}{\sqrt{1014.5}}, \quad Z = 2.480$$

p-value = 0.006 for $Z \geq 2.480$

4. Multiplying the ranks by the original sign of the differences determined in Step 2, resulting in positive and negative ranks.
5. Identifying the Wilcoxon test statistic for
    - The sum of positive signed ranks, R^+.
    - The sum of negative signed ranks, R^-.
6. Defining an upper-tailed test as H_o: $M_Y < 3$ for As, $M_Y < 65$ for Pb, $M_Y < 78$ for Sb with H_1: $M_Y \geq 3$ for As, $M_Y \geq 65$ for Pb, $M_Y \geq 78$ for Sb), the p-value is calculated as$^{(119)}$:

$$\text{p-value} = P\left(Z \geq \frac{\sum_{i=1}^{n} R_i - 1}{\sqrt{\sum_{i=1}^{n} R_i^2}} \right) \qquad \text{Equation 7.1}$$

where R_i is the difference in the sums of R^+ and R^-. If the p-value is less than the selected level of confidence, then H_o can be rejected and the test is termed as statistically significant.

Following these steps for As, when the total concentration was greater than or equal to 100 mg kg^{-1}, the leached concentrations exceeded the NJ Default Leachate Criterion of 3 µg L^{-1} at a 99% confidence level (Table 7.2). Similarly, in the case of Sb, total concentrations greater than or equal to 175 mg kg^{-1} resulted in leachates exceeding the criterion at the 90% confidence level. The NJ Default Leachate Criterion of 65 µg L^{-1} for Pb was exceeded at total concentrations greater than 20 mg kg^{-1} with the Wilcoxon Signed Rank test. The maximum concentration for lead allowable in food (glass) containers is regulated at 100 ppm (ISO 2010). This limit was established by testing the

Table 7.2 Results of Wilcoxon Signed Rank test. A *p*-value less than the selected level of confidence, results in the rejection of H_o and indicates a statistically significant result

Element	Total Concentration (X) (mg kg^{-1})	Calculated z - value	*P*- value	Significance		
				90% (α=0.1)	95% (α=0.05)	99% (α=0.01)
As	***100***	***5.710***	***10^{-5}***	***Yes***	***Yes***	***Yes***
	150	5.300	10^{-5}	Yes	Yes	Yes
	200	4.920	10^{-5}	Yes	Yes	Yes
Pb	20	3.450	10^{-5}	Yes	Yes	Yes
	50	2.896	0.002	Yes	Yes	Yes
	75	3.006	0.001	Yes	Yes	Yes
	100	***2.480***	***0.007***	***Yes***	***Yes***	***Yes***
	150	1.753	0.040	Yes	No	No
Sb	50	-3.892	1.000	No	No	No
	75	-3.744	1.000	No	No	No
	100	-3.945	1.000	No	No	No
	150	-2.017	0.978	No	No	No
	175	***1.355***	***0.088***	***Yes***	***No***	***No***

hydrolytic/corrosion resistance of glass food containers with hydrochloric acid. Food containers, as a virtue of their function, come in contact with a variety of acidic chemicals (*e.g.* vinegar). To address corrosion resistance, a standard hydrolytic resistance test is carried out on all food containers made from glass. In processing glass beads, more than 90% of the melt is from recycled glass. If source concentrations of 100 mg kg^{-1} are assumed to be representative in manufacturing, then leachates may exceed the criterion at the 99% confidence level.

7.4 Summary

This chapter demonstrated leaching of As, Sb, and Pb from imported batches of glass beads under environmentally relevant conditions. The average total concentrations for the imported batches of glass beads ranged from 103 to 683 mg kg^{-1} for As, 62 to 187 mg kg^{-1} for Sb, 23 to 179 mg kg^{-1} for Pb. Leached concentrations were as great as 538 µg L^{-1} for As, 1,092 µg L^{-1} for Pb, and 160 µg L^{-1} for Sb. Sequential extraction revealed that of these, As and Pb were extractable: for As the exchangeable fraction is consistent with its association with the alkali and alkaline earth oxides in the glass beads. Extractable Pb is expected to be associated with the exchangeable and organic fractions on the surface of the glass beads. Sb was not extracted. A relationship was not observed between total metal and leached concentrations under environmentally relevant conditions. This result may be attributed to the heterogeneity of metals and metalloids associated with the glass beads. Results of the Wilcoxon Signed Rank test suggest a potential environmental impact to groundwater used as a drinking water source when either storing glass beads in bulk or disposing of the roadway marking material in bulk when concentrations of As and Pb exceed 100 mg kg^{-1}, and those of Sb exceed 175 mg kg^{-1}. While the leached concentrations observed are associated with the exchangeable fraction, greater than 97% is associated with the residual fraction, the silica structure. The labile fraction is nonetheless significant and may impact groundwater used as a drinking water source. Considering the highway as a line source, an analysis was conducted to examine leaching of metals and metalloids under a control volume. Based on the average annual precipitation in NJ as well as the lowest and the highest annual average precipitation over the last 117 years, results indicated that the leached concentrations exceeded the NJ Default leachate criterion for As (Appendix E).

CHAPTER 8

CONCLUSIONS

Glass beads are embedded on pavement markings to provide retroreflectivity, an optical phenomenon that plays a crucial role in maintaining the guiding function of highway striping to ensure safe driving. The presence of metals and metalloids in the glass beads is of environmental concern due to their potential for leaching under environmentally relevant conditions.

Based on this work, the results revealed the presence of elevated concentrations of As, Pb, and Sb in the glass beads. Furthermore, based on the Welch t- test, differences between the domestic and imported concentrations was statistically significant. Elevated concentrations of metals and metalloids have been observed in the glass beads with significant variability: 50-83% for Pb, 17-22% for As, and 13-16% for Sb. FP-XRF proved to be a viable technique as it correlated well with the standard approach involving HF digestion followed by ICP-MS. Currently, FP-XRF is considered a screening tool and typically used in conjunction with other laboratory analytical methods such as ICP-MS and AAS. However, correlations (>86%) observed between concentrations measured with ICP-MS and those with FP-XRF show that FP-XRF is a reliable and a rapid approach to assess glass beads for metal and metalloid concentrations.

The rigorous factorial study (to assess the leaching potential of the glass beads) conducted with glass bead samples demonstrated the potential bioavailability of metals and metalloids, specifically, As, Sb, and Pb. TCLP and SPLP tests were not adequate in assessing concentrations leached as in these 18 hour studies less than 2% of As and non-detectable concentrations of Pb and Sb leached as compared to the 160 day studies. Results demonstrate that glass beads may leach under environmentally relevant conditions, where pH, salt, particle size, ionic strength, and time were considered. Of these factors, pH and time, showed the most significant impact on leaching.

The form and phase of metals and metalloids were assessed using sequential extraction procedure. The results revealed that As and Pb were extractable: for As the exchangeable fraction is consistent with its association with the alkali and alkaline earth oxides in the glass beads. Extractable Pb is expected to be associated with the exchangeable and organic fractions on the surface of the glass beads. Sb was not extracted. The degree of mobilization observed in this extraction followed the trend of Pb > Ba ≈ Mn > As. While the leached concentrations observed are associated with the exchangeable fraction, greater than 97% is associated with the residual fraction, the silica structure. The labile fraction is nonetheless significant and may impact groundwater used as a drinking water source.

A relationship was not observed between total metal and leached concentrations under environmentally relevant conditions. This result may be attributed to the heterogeneity of metals and metalloids associated with the glass beads. Based on non-parametric statistical analysis, the initial metal concentrations which resulted in leached concentrations exceeding the NJ Default Leachate Criteria and for which the results of the Wilcoxon Signed Rank test were observed to be statistically significant indicated potential impact to groundwater used as a drinking water source when glass beads are stored in bulk; these concentrations were observed to be 100 mg kg^{-1} for As, 100 mg kg^{-1} for Pb, and 175 mg kg^{-1} for Sb.

CHAPTER 9

FUTURE WORK

This research demonstrated that leaching of As, Pb, and Sb from the glass beads is significant under environmentally relevant conditions. TCLP and SPLP tests were not adequate to address the potential environmental impact posed by the glass beads. For this research, further work in understanding speciation could benefit from advanced tools such as x-ray absorption spectroscopy (XAS), which probes the local coordination environment as well as the oxidation state. One limitation of this advanced analysis is that results are based on a bulk average and with glass beads; greater than 90% of the metal or metalloid concentration is associated with the residual phase.

Additionally, further insight on glass bead transport over its life-time is needed and should be addressed based using on-site conditions. Therefore, future work associated with this research may include life cycle assessment of glass beads and continuous monitoring of metals and metalloids in applied glass beads over the lifetime of the pavement marking. Glass beads samples from the roadways should be collected and assessed for degree of abrasion and morphological properties as well.

Understanding relationships between glass matrix, metal forms, and dissolution is important in predicting leaching. The feasibility of setting up a control volume on a highway may be investigated. Likely hurdles include: separation of abraded glass beads from the surrounding soils which have almost the same chemical composition, precipitation contact time, and predicting a line source of leached metal concentrations through the soil. Leaching of metals from glass beads embedded on the paint and the fraction of glass beads abraded needs to be studied in detail. Future studies addressing particle size distribution due to the gradation specifications of the glass beads should be conducted. In this study the effect of particle size was studied by milling/grinding the glass beads to a smaller size. Future studies involving glass beads produced in the size range of < 37 μm to 100 μm may assist in our understanding of the effect of size on the leaching mechanisms.

APPENDIX A

AASHTO SPECIFICATIONS

This appendix highlights the specification set forth by AASHTO.

Standard Specification for

Glass Beads Used in Traffic Paints

AASHTO Designation: M 247-08

1. SCOPE

1.1. This specification covers glass beads to be dropped or sprayed upon pavement markings so as to produce a reflectorized pavement marking.

1.2. *Types*:

1.2.1. *Type I* - shall be known as a standard gradation.

1.2.2. *Type IM* - shall be known as modified gradation.

1.2.3. *Type II* - shall be known as a uniform gradation.

1.3. *Coatings:*

1.3.1. *Flotation* - Any of the above gradation types may be obtained with oleophobic properties at the request of the purchaser (Note 1).

1.3.2. *Moisture Resistance* - Any of the above types may be obtained with hydrophobic properties if so specified by the purchaser.

1.3.3. *Adherence* - Any of the above types may be obtained with an adhesion coating is so specified by the purchase.

Note 1- Any of the above types of beads may be specified with a combination of two of the above coatings. Dual coated beads must test positive for the presence of both specified properties.

1.4. The values stated in SI units are to be regarded as the standard.

2. REFERENCED DOCUMENTS

2.1. *ASTM Standards:*

- D 75, Standard Practice for Sampling Aggregates
- D 1214, Test Method of Sieve Analysis of Glass Spheres
- D 1155, Test Method for Roundness of Glass Spheres
- D 1213, Test Method for Crushing Resistance of Glass Spheres
- E 105, Standard Practice for Probability Sampling of Materials
- E 1617, Standard Practice for Reporting Particle Size Characterization Data
- E 1994, Standard Practice for Use of Process Oriented AOQL and LTPD Sampling Plans

2.2. Federal Standards:

- Federal Standard No. 40, CFR 261.24, Table 1 Maximum Concentration of Contaminants for the Toxicity Characteristic

2.3. Other Standards:

- ANSI/ASQ Z.4 and Z1.9, Sampling Procedure and Tables for Inspection by Attributes

3. GENERAL REQUIREMENTS

3.1. The beads shall be transparent, clean, colorless glass, smooth and spherically shaped, free from milkiness, pits, or excessive air bubbles and conform to the following specific requirements.

3.2. The glass beads must not exhibit a characteristic of toxicity, relative to heavy metals, when tested in accordance with EPA 40 CFR 261.24.

4. SPECIFIC PROPERTIES

4.1. *Gradation* - The beads shall meet the gradation requirements for type as given in Table 1.

Table 1 - Gradation of Glass Beads

Sieve Designation		Mass Percent Passing		
Standard, mm	Alternate No.	Type I	Type IM	Type II
1.18	16	100	100	—
0.850	20	95-100	90-100	—
0.600	30	75–95	50-75	100
0.425	40	—	15-45	90–100
0.300	50	15–35	0-15	50–75
0.180	80	—	0-5	0–5
0.150	100	0–5	—	—

4.2. *Roundness* - The glass beads shall have a minimum of 70 percent true spheres.

4.3. *Refractive Index* - The glass beads shall have a refractive index of 1.50–1.55.

4.4. *Coatings*: Flotation, Moisture Resistance, and Adherence - When tested in accordance with Section 5.3, the presence of the purchaser specified coatings will be unambiguous.

4.5. The beads shall be dry and free of lumps and clusters.

5. METHODS OF SAMPLING AND TESTING

5.1. *The sampling shall be random in the following ratios*—45 kg (100 lb) of sample (in full bags) per 4535 kg (10000 lb) shipped. Upon arrival material shall be reduced in a sample splitter to a size of approximately 1 kg. Alternatively, Statistical Process Control Methods following ASTM E 105 and E 1994, and D 75 or ANSI/ASQ Z1.4 and Z1.9 may be used to monitor the quality of the product so that it meets the requirement of the applicable detail specification. The supplier shall state in a Declaration of Conformity the sampling plans and test methods used.

5.2. The following requirements shall be tested with the following test methods:

5.2.1. *Gradation* - ASTM D 1214. Alternatively a mechanical, optical or instrumental method with traceable standards is acceptable provided that it correlates to acceptable results obtained using ASTM D 1214, or documentation showing correlation to the referee method referenced in ASTM D 1214, and follows ASTM E 1617. In the event of nonconformity ASTM D 1214 “Hand Sieve” will be the referee method.

5.2.2. *Roundness* - ASTM D 1155. Alternatively a mechanical, optical, or instrumental method with traceable standards is acceptable provided that it correlates to acceptable results obtained using ASTM D 1155, or documentation showing correlation to the referee method referenced in ASTM D 1155, and follows ASTM E 1617. In the event of nonconformity ASTM D 1155, Procedure B, will be the referee method.

5.2.3. *Refractive Index* shall be tested by a liquid immersion method (Becke Line Method or equal) at a temperature of 25 ± 5°C (77 ± 9°F).

5.3. *Coatings Tests:*

5.3.1. *Flow Characteristics Test* - Referee Method

5.3.1.1. A 100 g sample of beads is placed in a Corning 3140 crystallizing dish (or equivalent), 100-mm diameter by 50-mm depth. Place the dish in a Corning 3080 Desiccator (or equivalent) 250-mm inside diameter by 330-mm overall height and 130-mm chamber depth, which shall be filled with a sulfuric acid-water solution having a specific gravity of 1.10 (approximately 94 percent humidity) to a point 25.4 mm below the top of a size 5 Coors 60003 Desiccator Plate (or equivalent). The sample shall remain in the covered Desiccator at 25 ± 5°C for four hours. Remove the sample from the Desiccator and transfer the beads to a metal pan. The beads shall flow without stoppage when poured slowly through a standard glass funnel (Corning 6120 or equivalent), 127-mm diameter, 102-mm stem length, and 11-mm stem inside diameter (Note 2).

Note 2 - The test operations should be performed immediately on removal of the beads from the Desiccator.

5.3.2. *Moisture Proof Coating Test* - Referee Method

5.3.2.1. A 100-g sample of beads is placed in a 600-mL beaker. With the beaker held at about a 45 degree angle, 100 mL of distilled water is slowly added to the beaker. The water is carefully poured down the side of the tilted beaker. The beads are to remain undisturbed. The beaker is allowed to stand, undisturbed, for five minutes. At the end of the standing time, the water is carefully poured from the beaker. It may be necessary to slightly rotate the beaker to avoid trapping pockets of water. Holding the beaker at the “pour angle,” the beads are transferred to a clean, dry 600-mL beaker. A thin, even layer of beads may coat the inside of the original beaker. The second beaker is allowed to stand, undisturbed, for five minutes. At the end of the standing time, the beads are slowly poured into a standard glass funnel (Corning 6120 or equivalent), 127 mm in diameter, 102-mm stem length and 11-mm stem inside diameter. The beads should flow through the funnel stem without stopping. Slight initial agitation to start the flow of beads through the funnel is permissible.

5.3.3. *Flotation Test* - Referee Method

5.3.3.1. Determine the mass of approximately 1 g to the nearest 0.0005 g, evenly distribute beads into a clean standard 100-mm glass Petri dish previously weighed to the nearest 0.0005 g. The dish is vibrated slightly to attain as near as possible a monolayer of beads. Xylene, C.P. Grade, is introduced at one side of the dish at a rate of 10 to 15 mL per minute from a burette until 30 mL has been added. The floating beads are then carefully drawn off by suction through a suitably constricted delivery tube connected to a receiving flask. Excess xylene is drawn off so that no remaining beads are lost and the dish dried in an oven at 110 ± 5ºC. The dish is weighed and the percentage of floating beads calculated.

5.3.4. *Adherence Coating Oven Test* - Referee Method

5.3.4.1. Prepare a solution by weighing 0.2 grams of dansyl chloride and dissolving in 25 ml of acetone. (See note 3). This solution can be used for several tests during the day, but must be kept refrigerated in a closed dark container between uses. Make a fresh solution daily. DANSYL CHLORIDE IS HAZARDOUS. DO NOT ALLOW SKIN CONTACT OR TOUCH THE BEADS AFTER TESTING.

Note 3 - Dansyl chloride tests for the presence of amino functional groups which are present in most common adhesion coatings. If the supplier is using alternate adhesion chemistry, a comparable simple test must be supplied. Dansyl chloride will oxidize on prolonged contact with air and light. Solutions should be stored in a dark, brown glass jar. Fresh solutions are a pale, yellow green. Unusable stale solutions are yellow brown.

5.3.4.2. Weigh 10 grams of beads and place in aluminum trays. Saturate the glass bead sample with the dansyl chloride solution using an eyedropper. Dry the beads in an oven at 60°C (140°F) for 15 minutes. Beads will be yellow and agglomerated. Rinse the beads by placing them in the funnel containing new filter paper and pouring 100 ml of acetone over them. Use suction during the step. Remove the beads from the funnel, and again place in aluminum trays. Dry the beads in the oven until free flowing. Place the beads on glass filter paper and inspect them under ultra-violet light. Inspection must be in a dark room. A yellow green fluorescence will be observed if adherence coating present. (See notes 3 and 4). If all beads have a yellow green fluorescence with the oven test, the beads are properly coated with adherence coating. If some or no beads have a yellow green fluorescence then this is cause for rejection.

Note 4 - Fluorescence is proportional to the intensity of the incident UV light. Longwave UV lamps designed for quality control, industrial inspection, and nondestructive testing are typically 100W. Portable lamps with 6W or 8W bulbs will show much less fluorescence on the same samples. Longwave UV bulbs emit at 365 nm wavelength. Shortwave UV lamps, 254 or 302 nm, and low-watt penlight lamps are not sufficient for this test.

5.3.5. *Alternative Flotation Test* - As Permitted by Purchasing Agency

5.3.5.1. A 15-20 g sample of beads is placed in a 60 mL (2 oz.) aluminum weighing dish, 57-mm inside diameter by 16-mm depth. The filled dish should be placed on a flat surface and shaken lightly so that the beads present a flat surface. Carefully place small drops of hexadecane [approximately 5 mm (0.187 in.) in diameter or 0.05 mL volume] on the test beads in three locations so that the drops are not touching. The dish should be left flat and the drops should be put in the center of the dish. Do not touch the beads with the dropper tip. A positive test for the presence of coating occurs if all three drops applied show clear well rounded appearance with high contact angle, i.e. the test liquid beads up. A negative test for coating shows the loss of contact angle of the drop, i.e. if wetting of the beads as evidenced by a darkening of the surface or sinking of the drop into the surface or bead interface occurs within 2 min ± 10 s.

5.3.6. *Alternative Moisture Resistance Test* - As Permitted by Purchasing Agency

5.3.6.1. The above Alternative Flotation test in Section 5.3.6 is performed with three distilled water drops instead of hexadecane.

5.3.7. *Alternative Adherence Test* - As Permitted by Purchasing Agency

5.3.7.1. The above test in 5.3.4 is performed with one eyedropper full (1.0ml) of 0.02 wt % dansyl chloride (5-dimethylaminonaphthalene-1-sulfonyl chloride) solution in acetone with the following exceptions.

5.3.7.2. The entire amount of liquid is dropped around the center. Do not disturb or mix the beads after wetting. After 30 minutes a positive test for the presence of coating occurs if the wetting area shows clear fluorescence, a bright green to blue glow, under strong long UV light (365 nm) against a dark background in a darkened room or stray light-free enclosure. A negative test for coating occurs if the wetted surface of the beads shows no fluorescence. The reaction may be speeded by heating the tested sample to 60 ± 5°C (140°F ± 9°F) for 5 min. It is best practice to use heat and simultaneously test the sample alongside beads known to have no adhesion coating. A positive presence of coating should be unambiguous.

6. PACKAGING AND MARKING

6.1. Glass beads shall be furnished in kilogram (pound) lots as specified by the purchaser and packaged in moisture-proofed bags. Containers are to be guaranteed to furnish dry and undamaged beads. Each package shall contain the following information: name and address of manufacturer, shipping point, trademark or name, the wording “glass beads,” the specification number, number of kilograms (pounds), the lot or batch number and the month and year of manufacture.

APPENDIX B

FACTORIAL STUDY RESULTS

Figures B. 1 to B. 6 show leaching of As, Pb, and Sb throughout the period of study for glass beads > 100 μm.

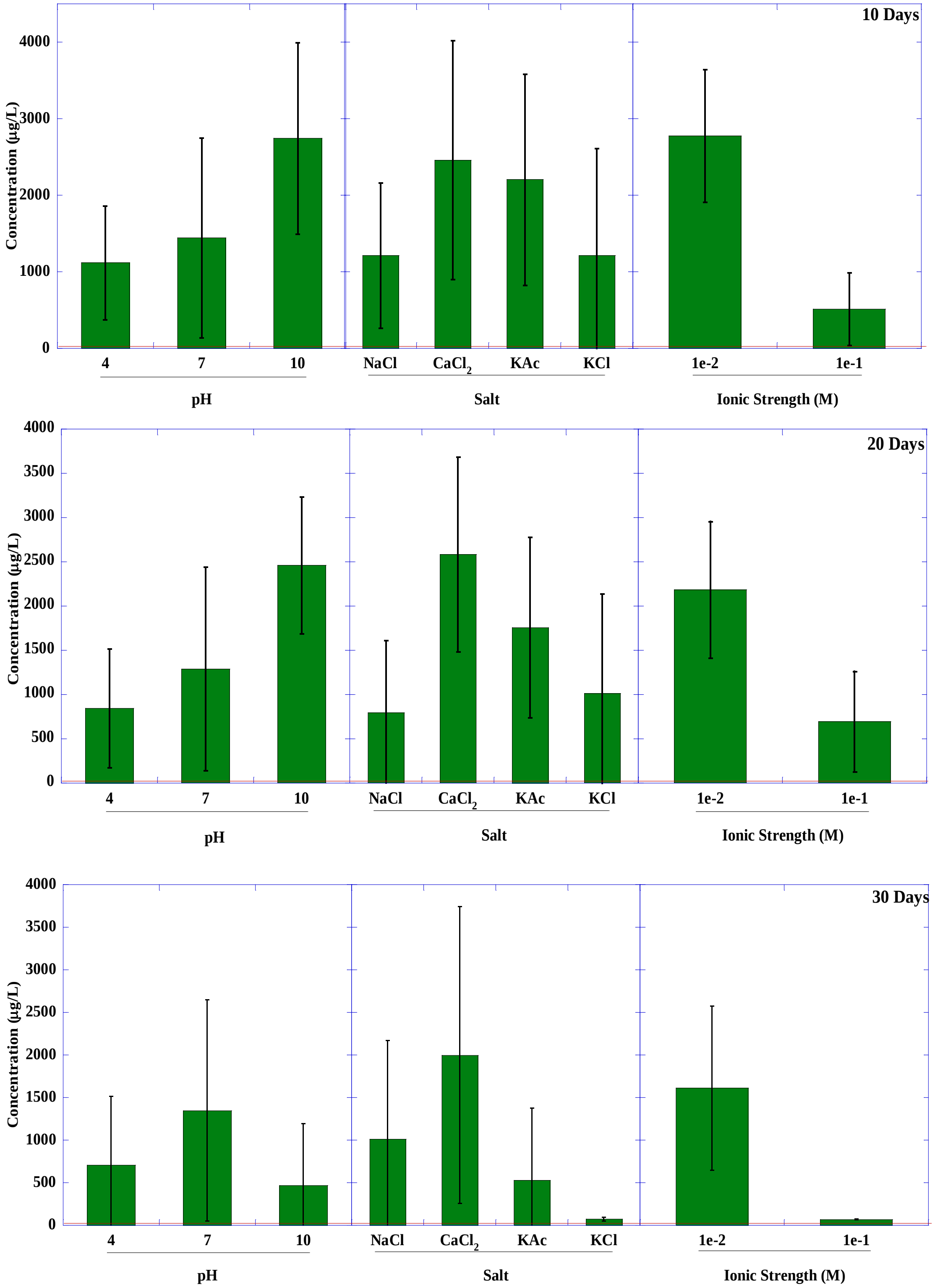


Figure B. 1 Leaching of As according to the factorial design depending upon pH, salt, ionic strength, and time for glass beads > 100 µm. Error bars indicate 2 × S.E. The New Jersey Ground Water Leachate Criteria for As is 3 µg/L and is shown by a red line.

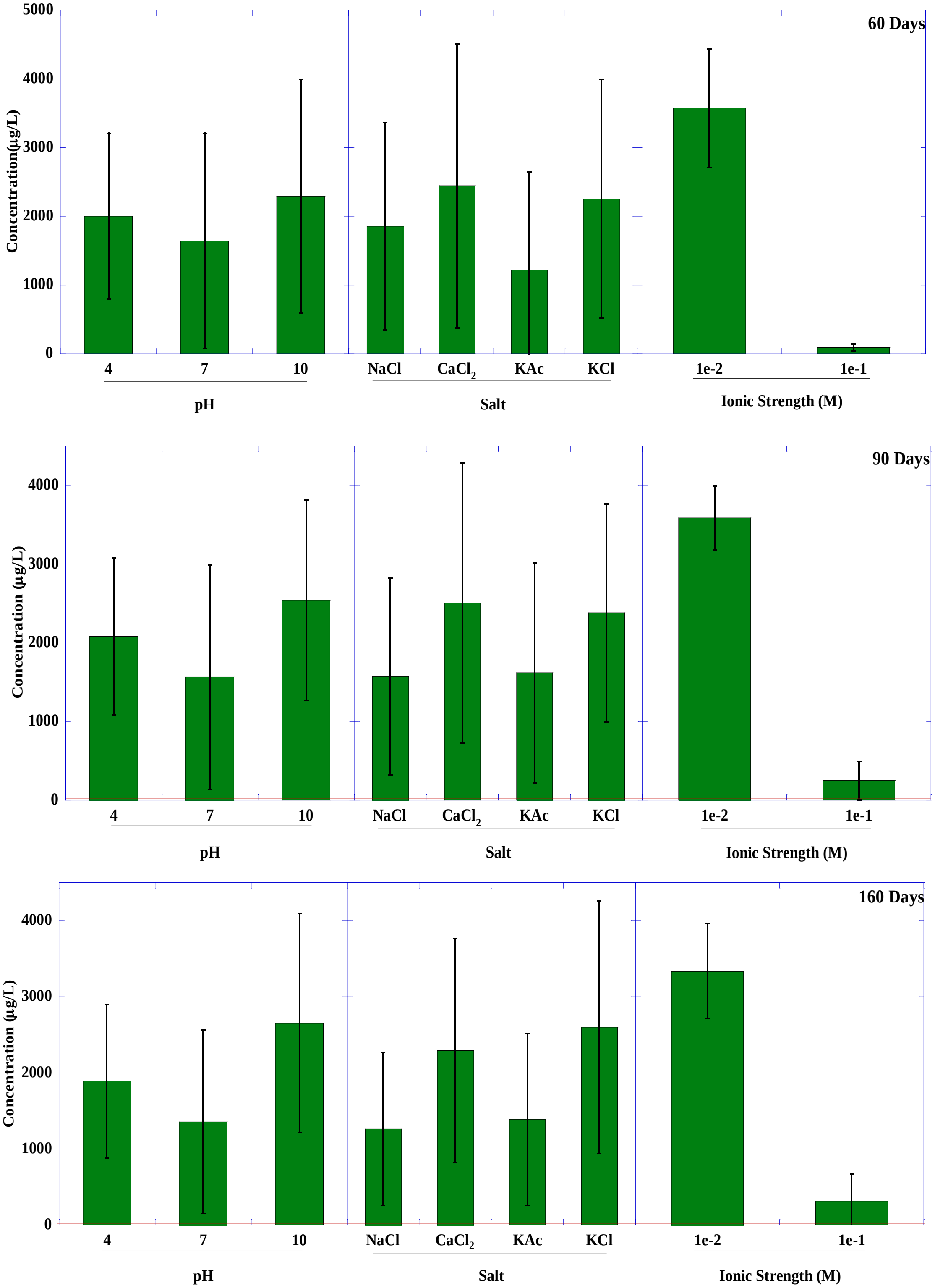


Figure B. 2 Leaching of As according to the factorial design depending upon pH, salt, ionic strength, and time for glass beads > 100 μm. Error bars indicate 2 × S.E. The New Jersey Ground Water Leachate Criteria for As is 3 μg/L and is shown by a red line.

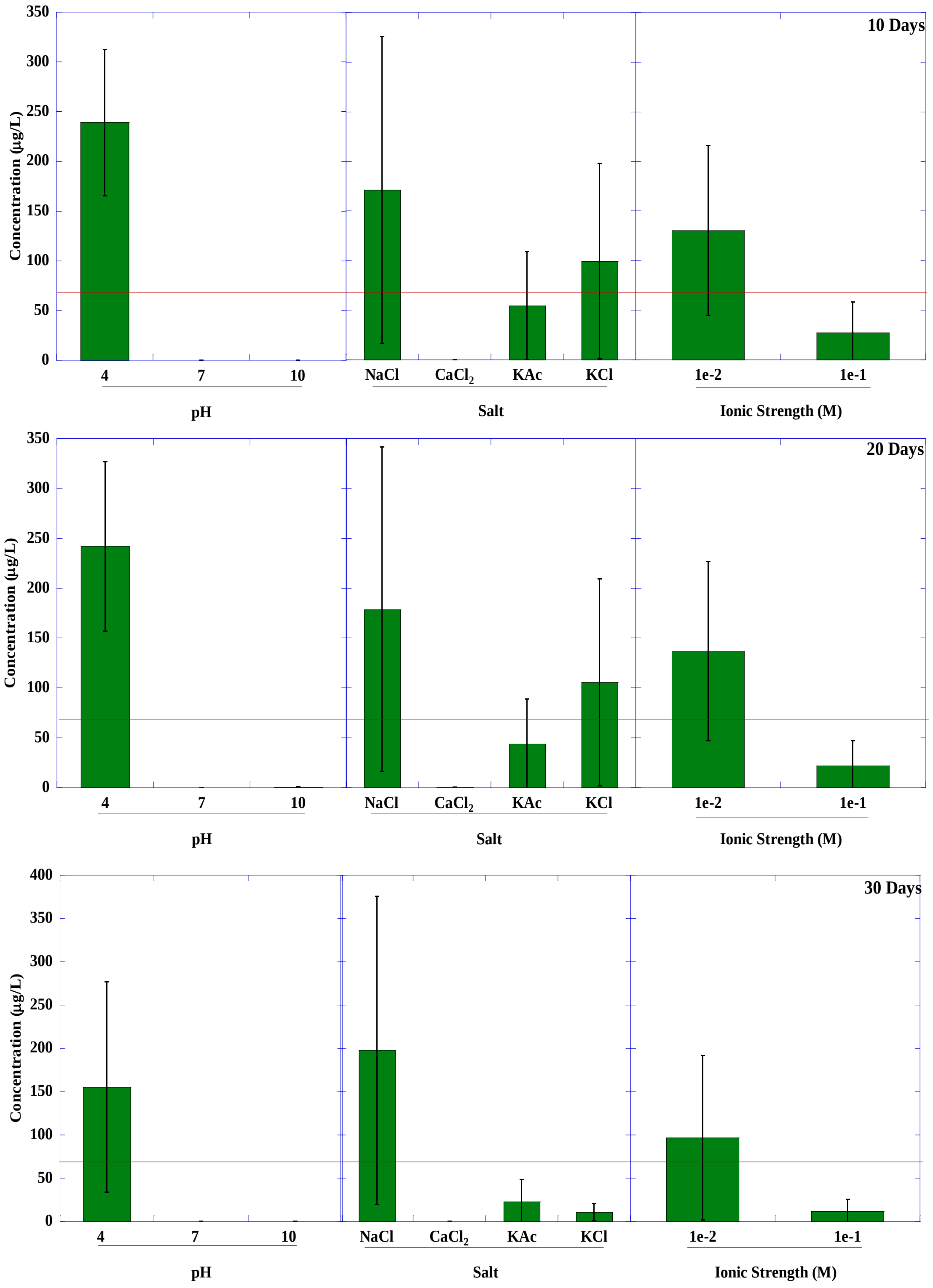


Figure B. 3 Leaching of Pb according to the factorial design depending upon pH, salt, ionic strength, and time for glass beads > 100 µm. Error bars indicate 2 × S.E. The New Jersey Ground Water Leachate Criteria for Pb is 65 µg/L and is shown by a red line.

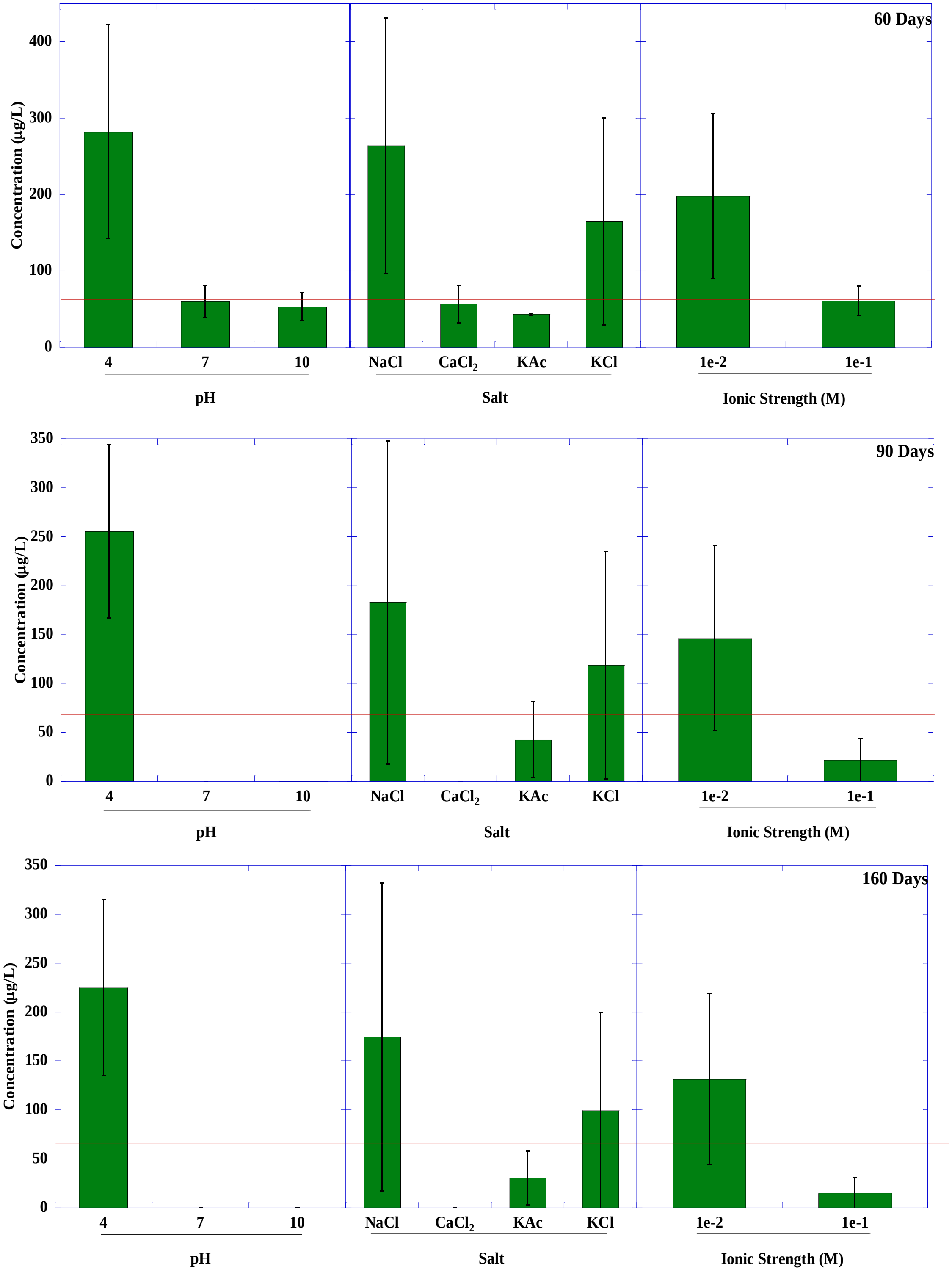


Figure B. 4 Leaching of Pb according to the factorial design depending upon pH, salt, ionic strength, and time for glass beads > 100 µm. Error bars indicate 2 × S.E. The New Jersey Ground Water Leachate Criteria for Pb is 65 µg/L and is shown by a red line.

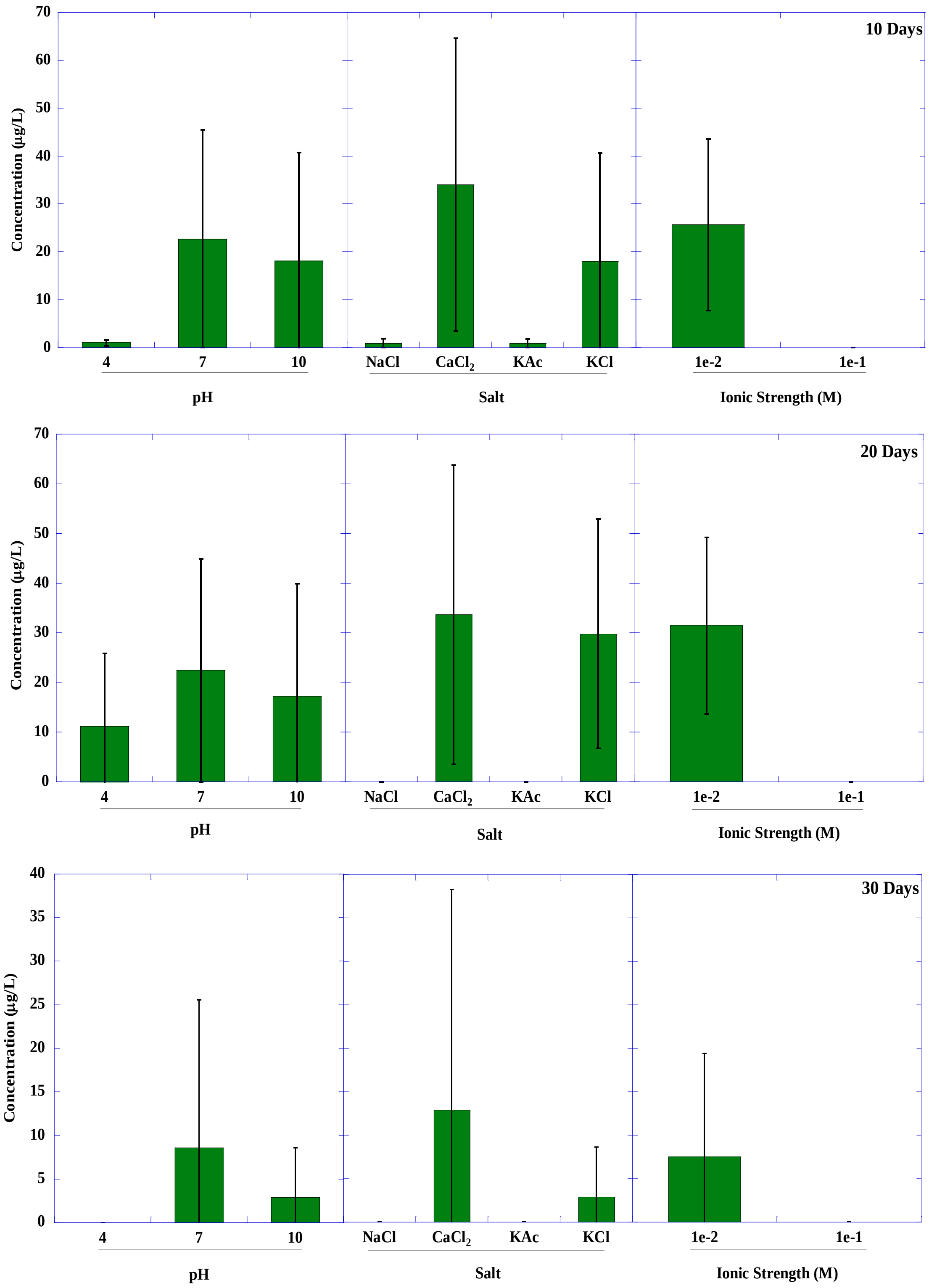


Figure B. 5 Leaching of Sb according to the factorial design depending upon pH, salt, ionic strength, and time for glass beads > 100 µm. Error bars indicate 2 × S.E. The New Jersey Ground Water Leachate Criteria for Sb is 78 µg/L.

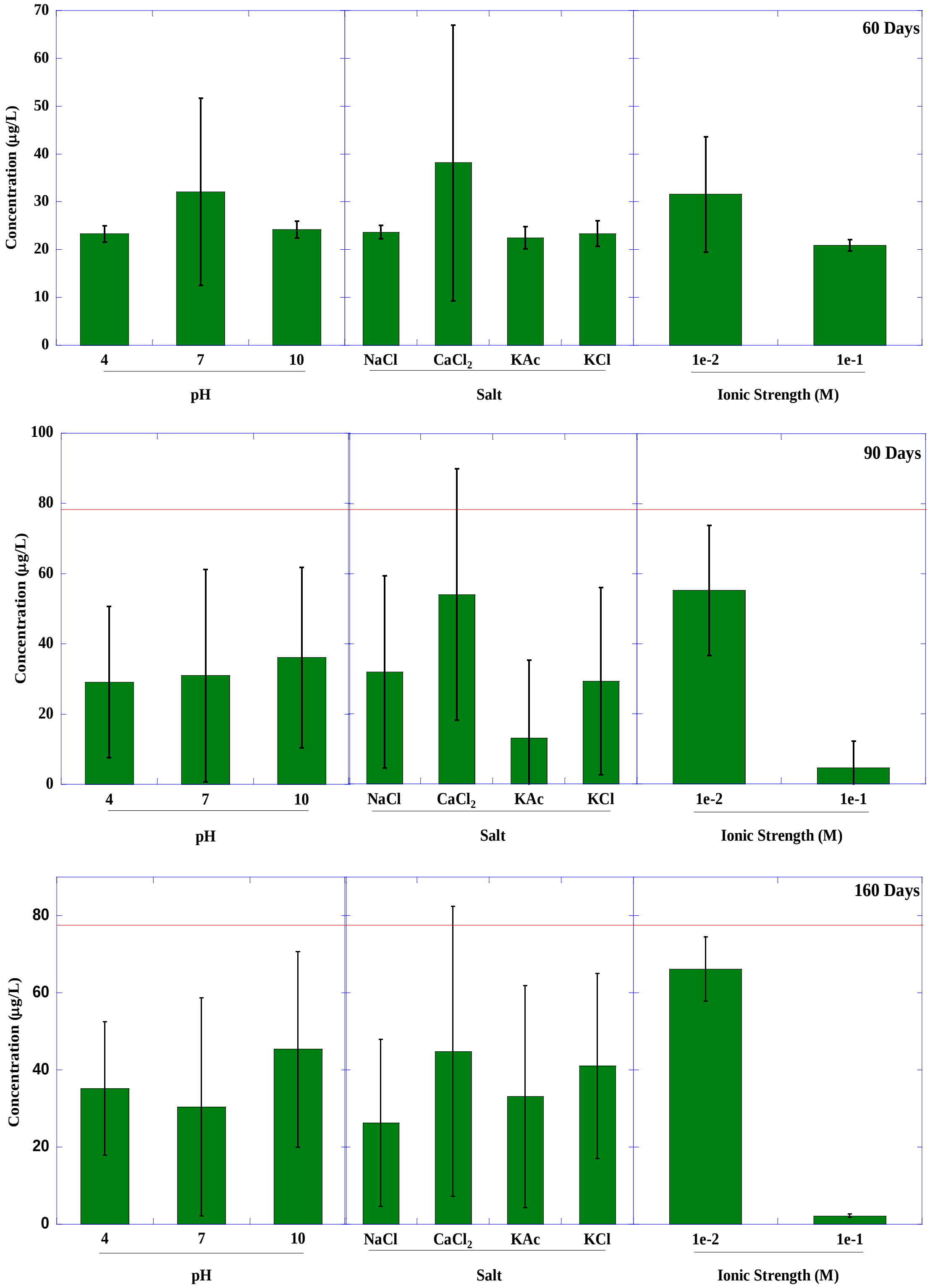


Figure B. 6 Leaching of Sb according to the factorial design depending upon pH, salt, ionic strength, and time for glass beads > 100 µm. Error bars indicate 2 × S.E. The New Jersey Ground Water Leachate Criteria for Sb is 78 µg/L and is shown by a red line.

APPENDIX C

LEACHING RESULTS FROM SMALL SIZES

Figures C. 1 to C. 12 show leaching of As, Pb, and Sb throughout the period of the study from glass beads of size 37 – 100 μm and < 37 μm.

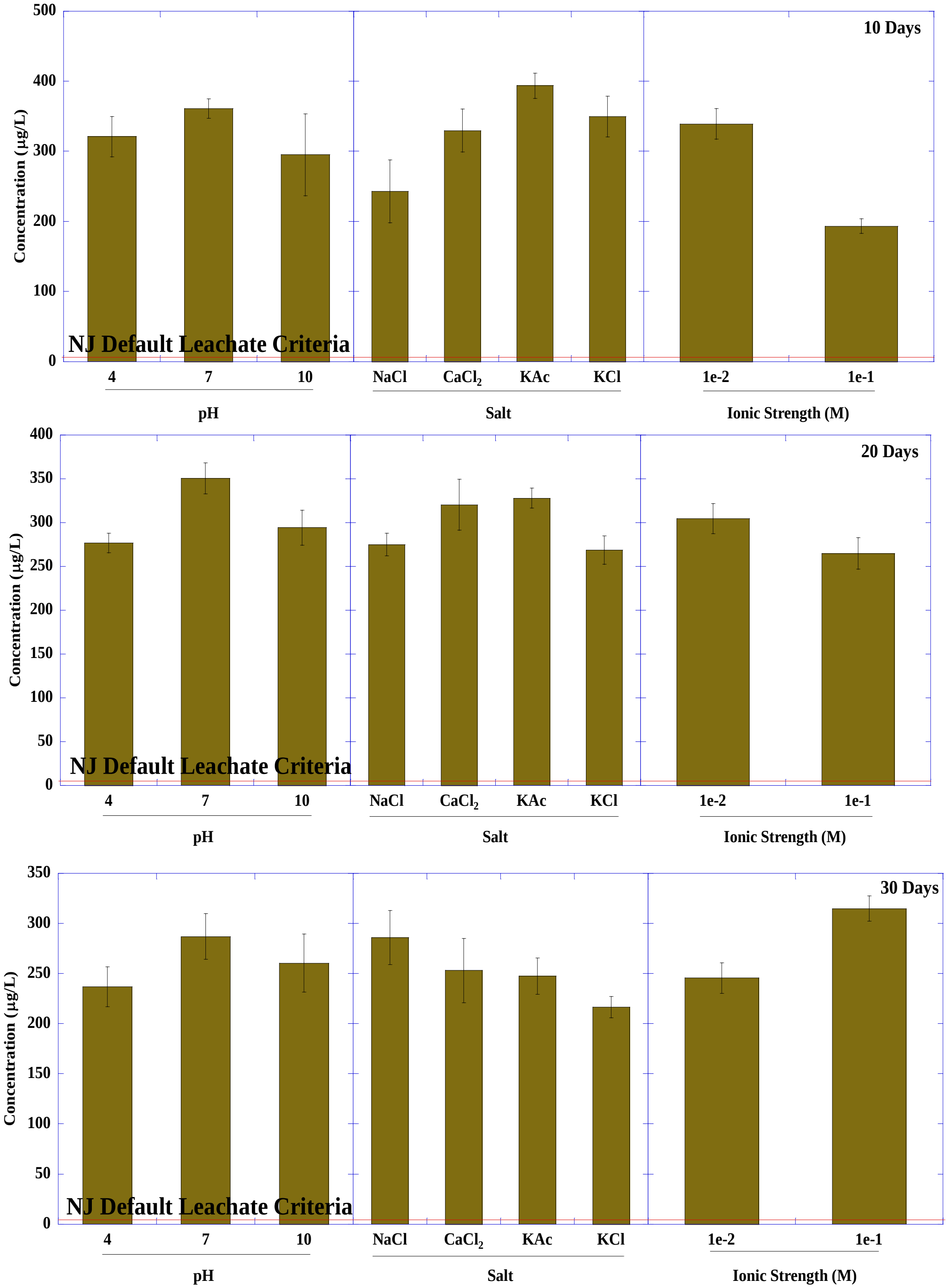


Figure C. 1 Leaching of As according to the factorial design depending upon pH, salt and ionic strength for particle size 37-100 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 111 and 147 µg/L, respectively. TCLP regulatory level for As is 5,000 µg/L.

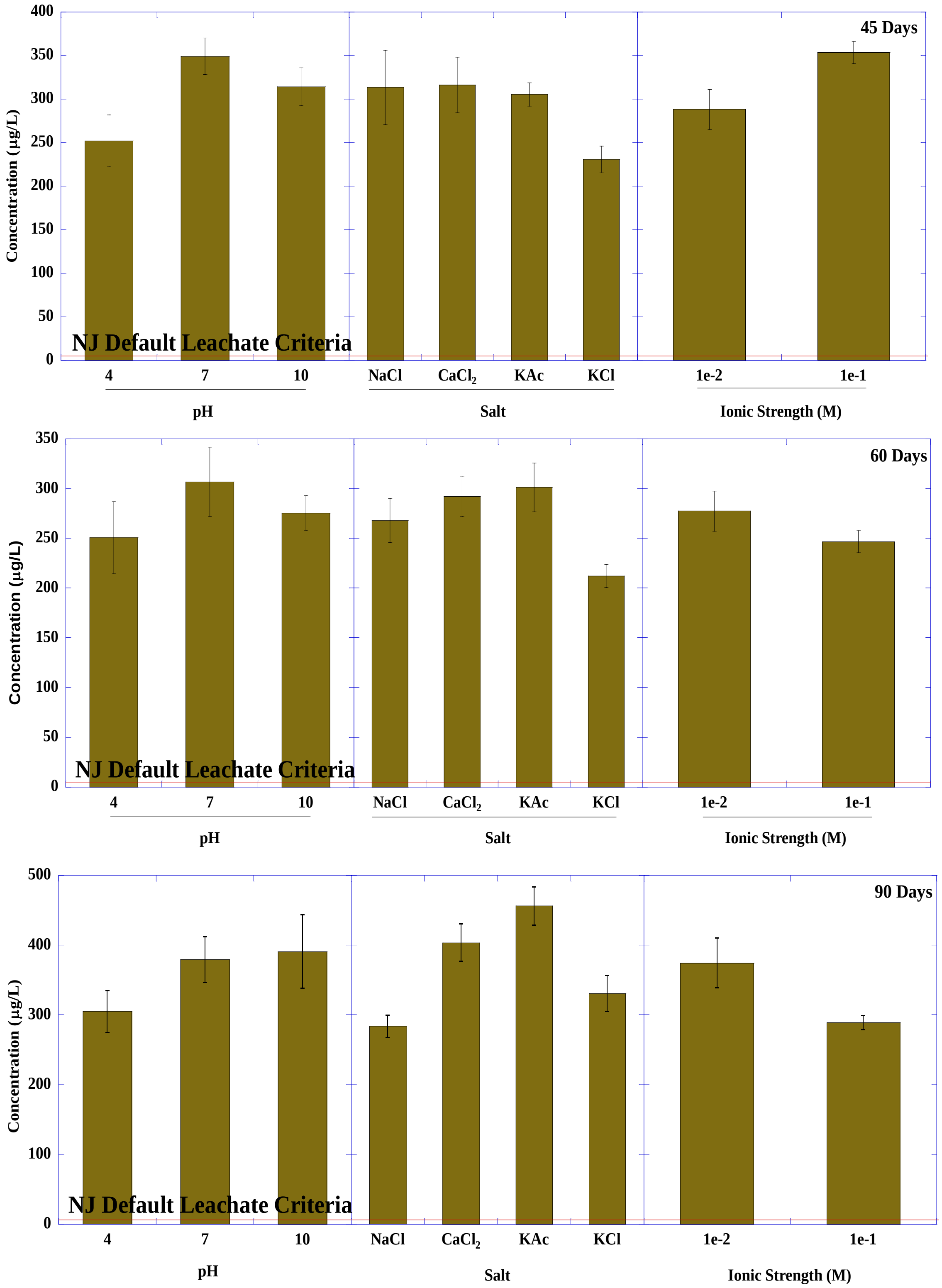


Figure C. 2 Leaching of As according to the factorial design depending upon pH, salt and ionic strength for particle size 37-100 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 111 and 147 µg/L, respectively. TCLP regulatory level for As is 5,000 µg/L.

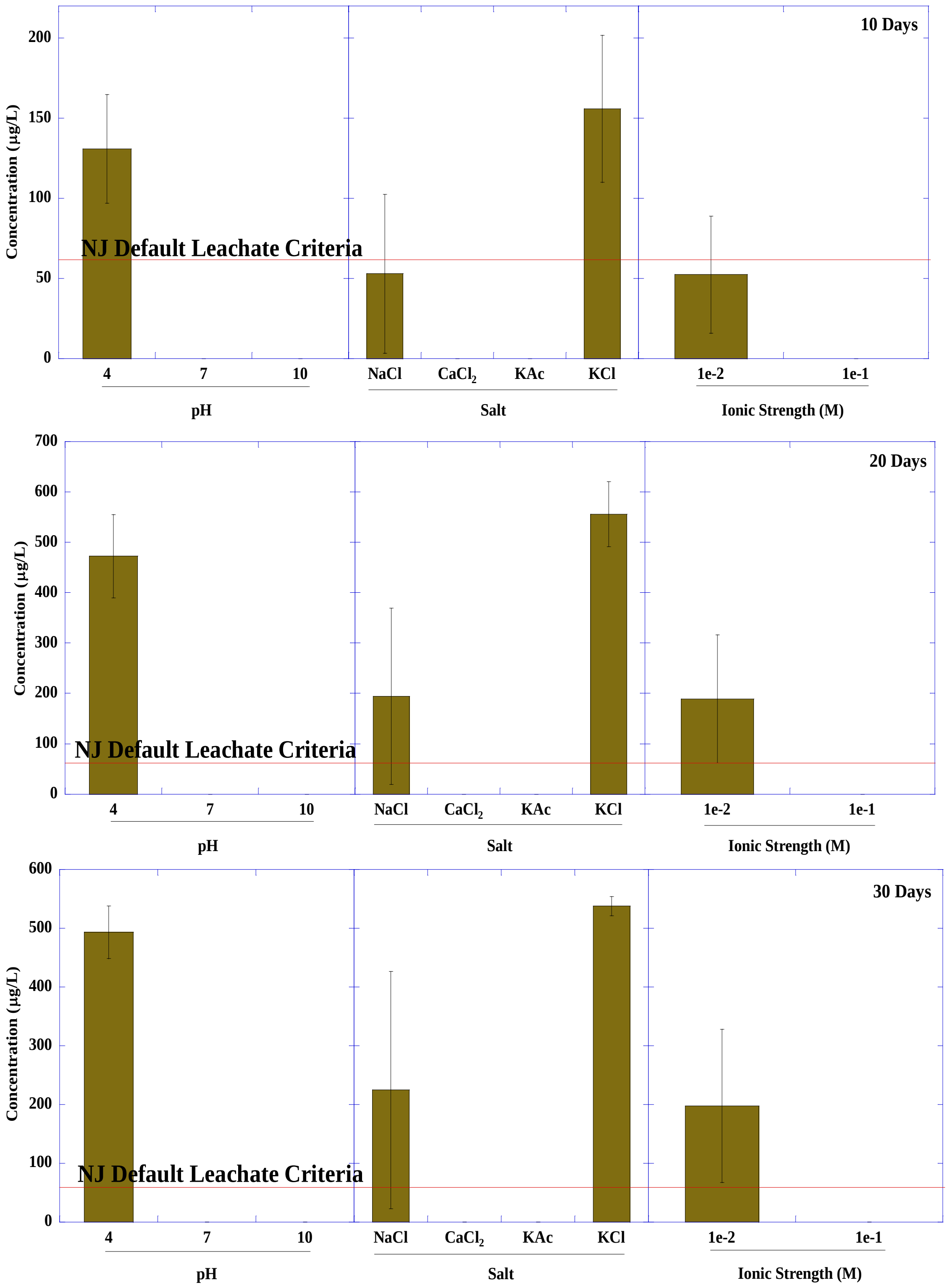


Figure C. 3 Leaching of Pb according to the factorial design depending upon pH, salt and ionic strength for particle size 37-100 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 795 and 0 µg/L, respectively. TCLP regulatory level for Pb is 5,000 µg/L.

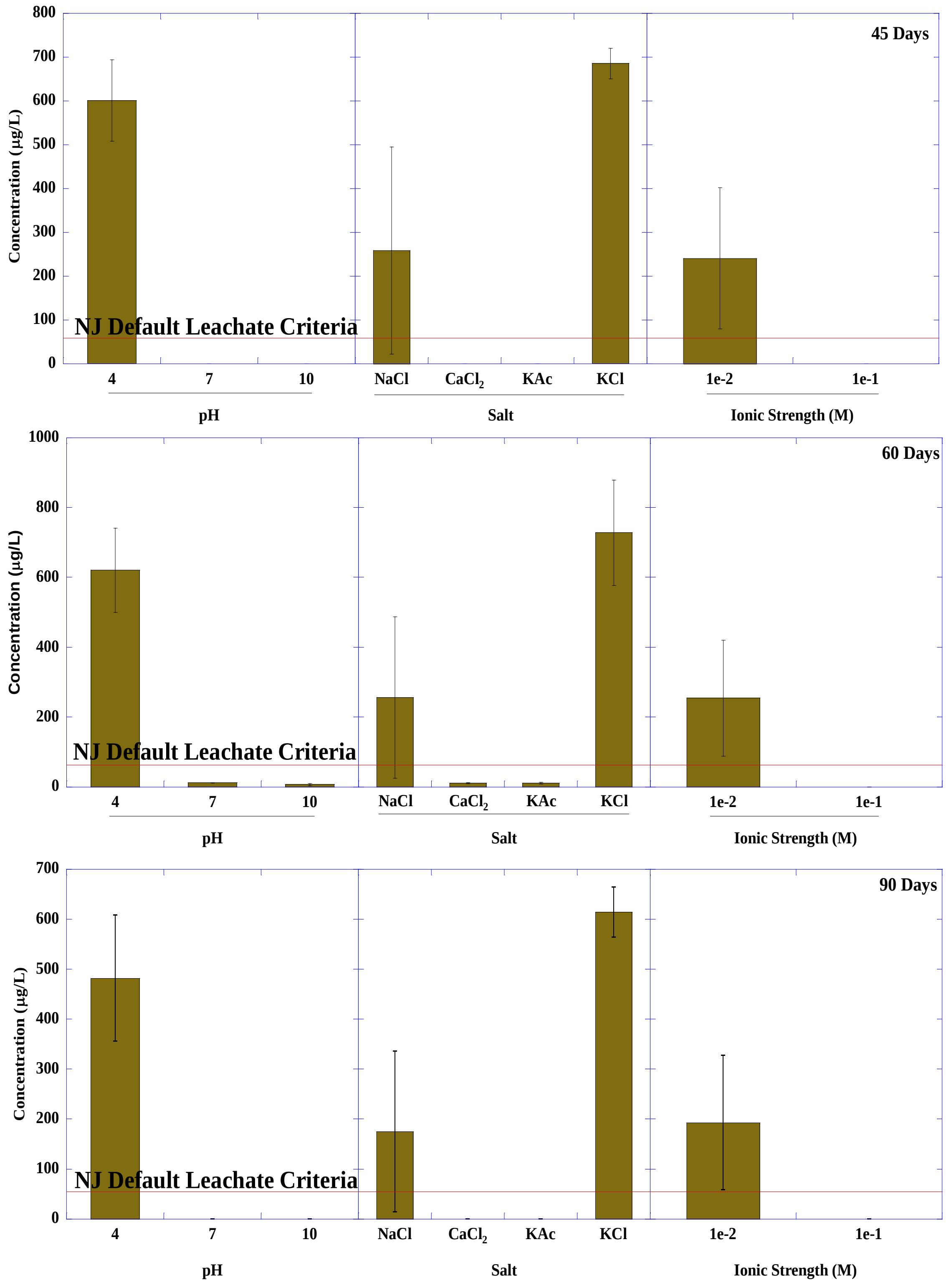


Figure C. 4 Leaching of Pb according to the factorial design depending upon pH, salt and ionic strength for particle size 37-100 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 795 and 0 µg/L, respectively. TCLP regulatory level for Pb is 5,000 µg/L.

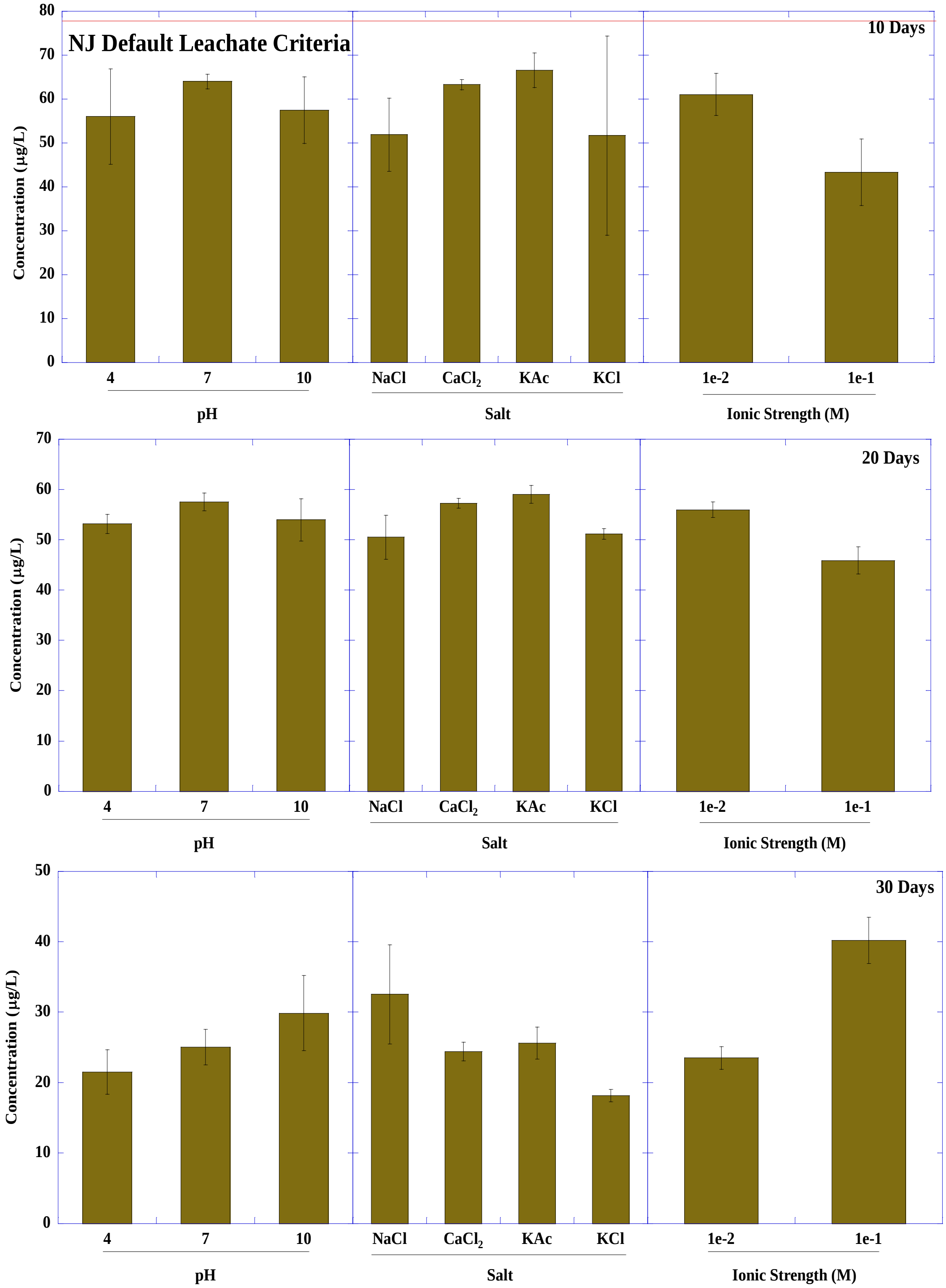


Figure C. 5 Leaching of Sb according to the factorial design depending upon pH, salt and ionic strength for particle size 37-100 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 10 and 30 µg/L, respectively. TCLP regulatory level for Sb is not available.

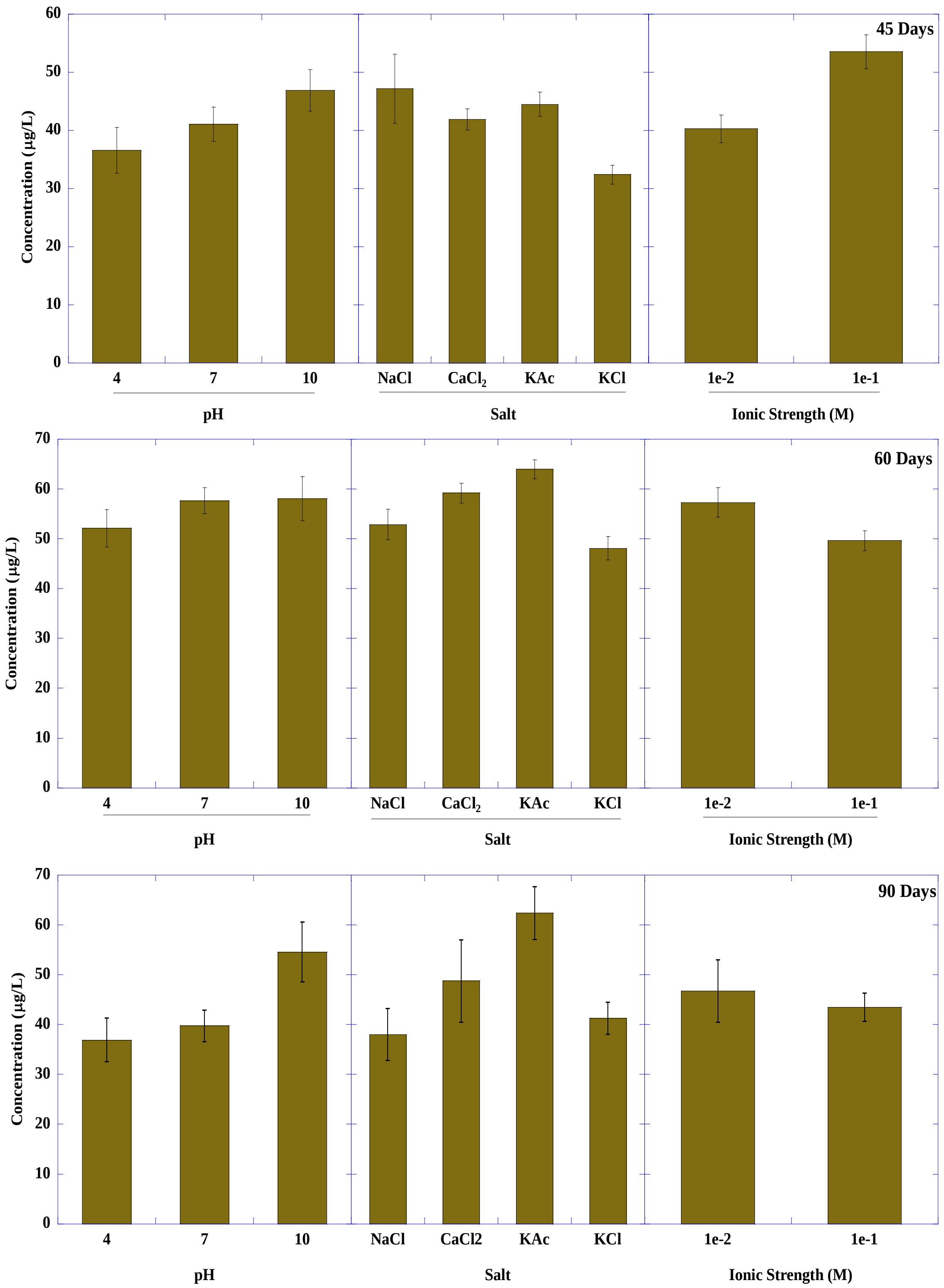


Figure C. 6 Leaching of Sb according to the factorial design depending upon pH, salt and ionic strength for particle size 37-100 μm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 10 and 30 μg/L, respectively. TCLP regulatory level for Sb is not available.

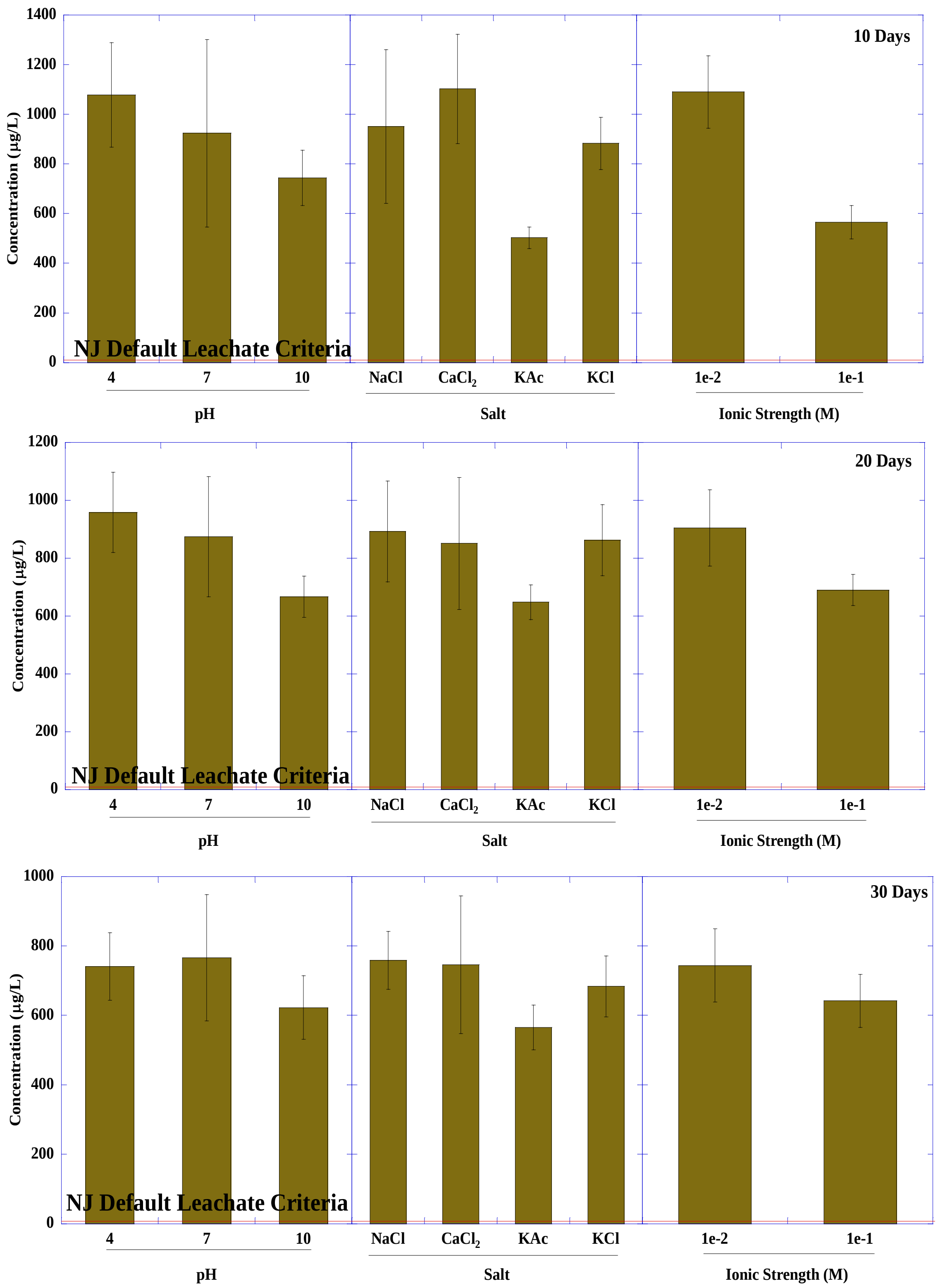


Figure C. 7 Leaching of As according to the factorial design depending upon pH, salt and ionic strength for particle size <37 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 322 and 288 µg/L, respectively. TCLP regulatory level for As is 5,000 µg/L.

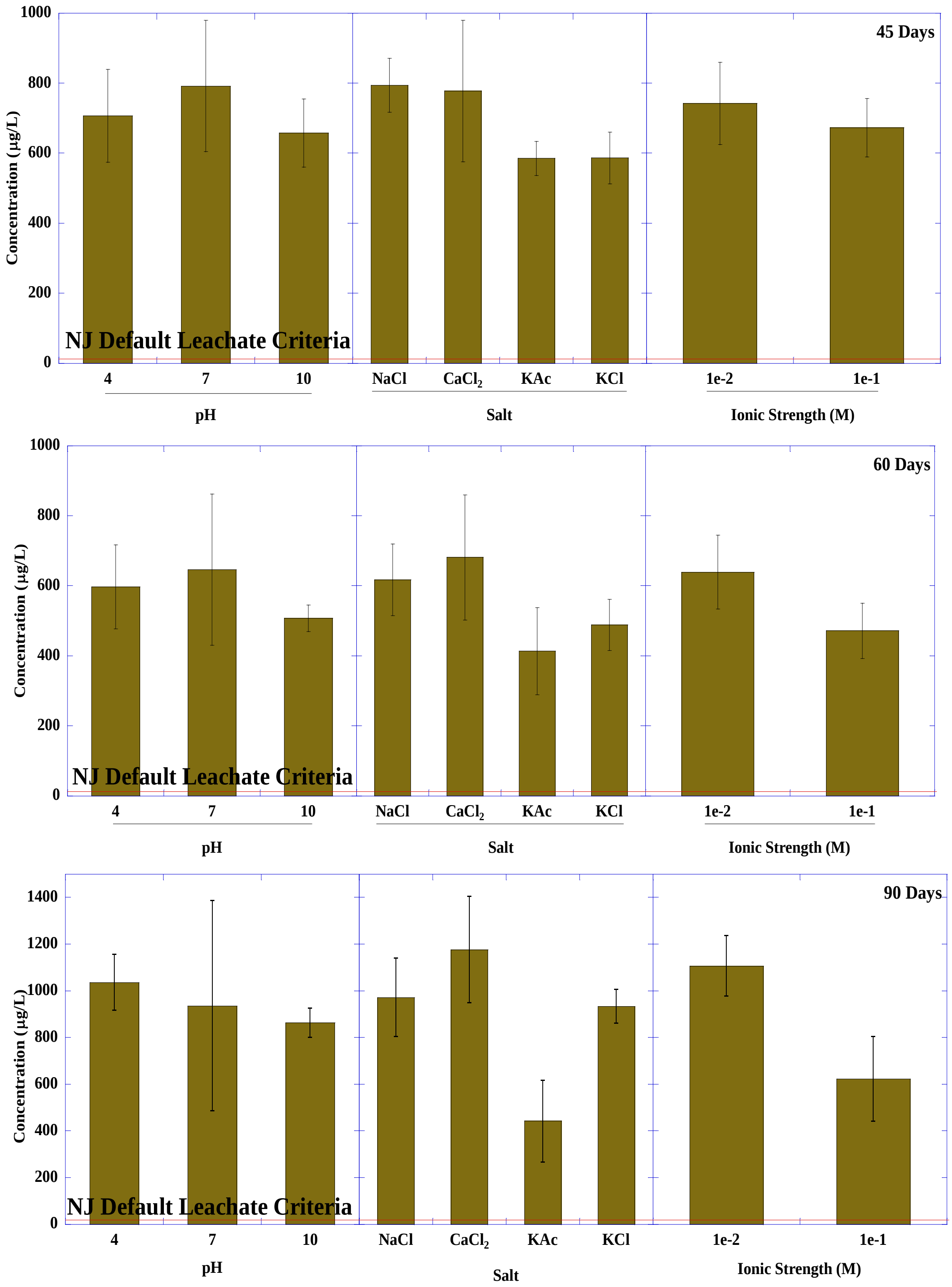


Figure C. 8 Leaching of As according to the factorial design depending upon pH, salt and ionic strength for particle size <37 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 322 and 288 µg/L, respectively. TCLP regulatory level for As is 5,000 µg/L.

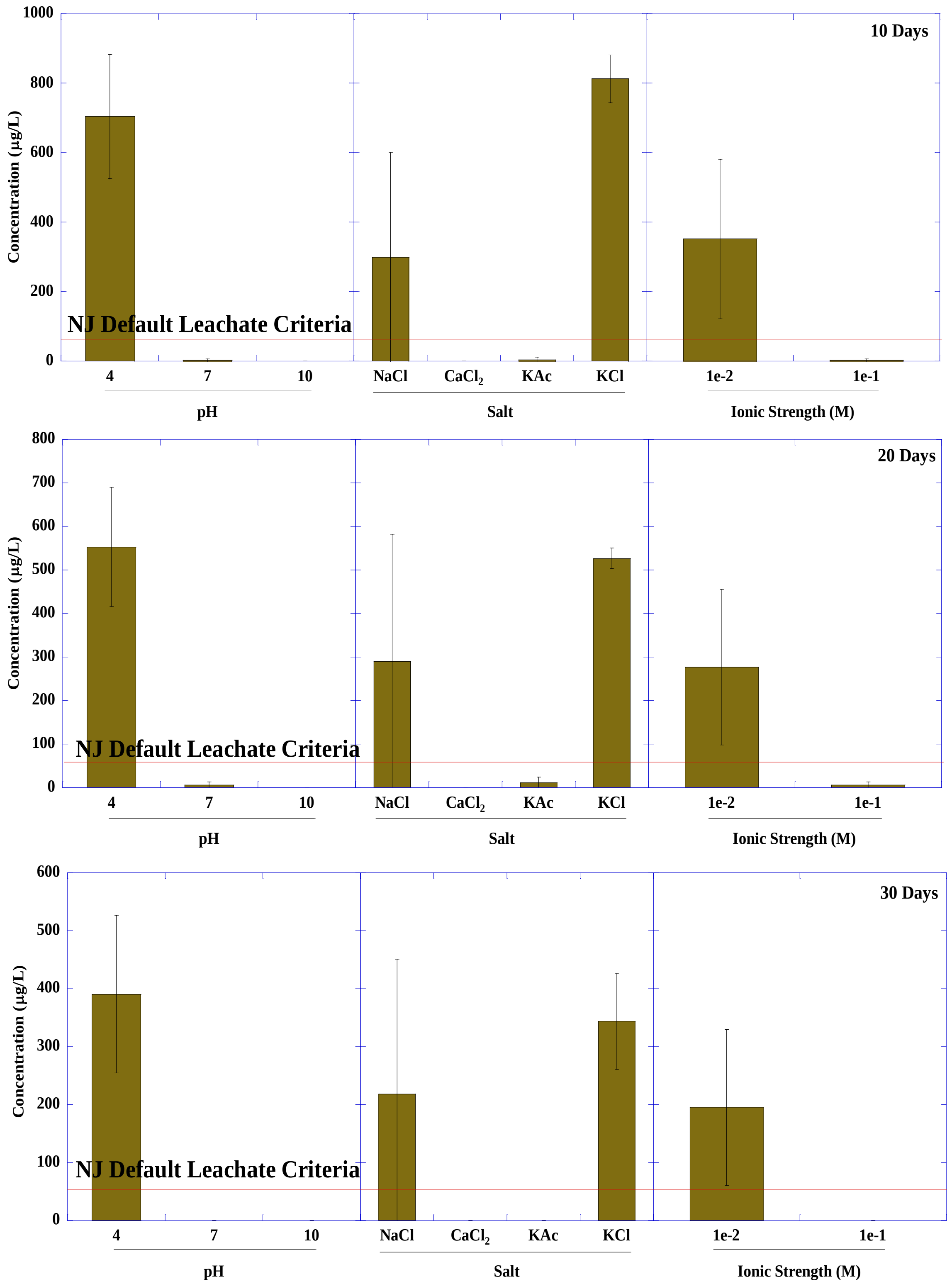


Figure C. 9 Leaching of Pb according to the factorial design depending upon pH, salt and ionic strength for particle size <37 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 1,009 and 0 µg/L, respectively. TCLP regulatory level for Pb is 5,000 µg/L.

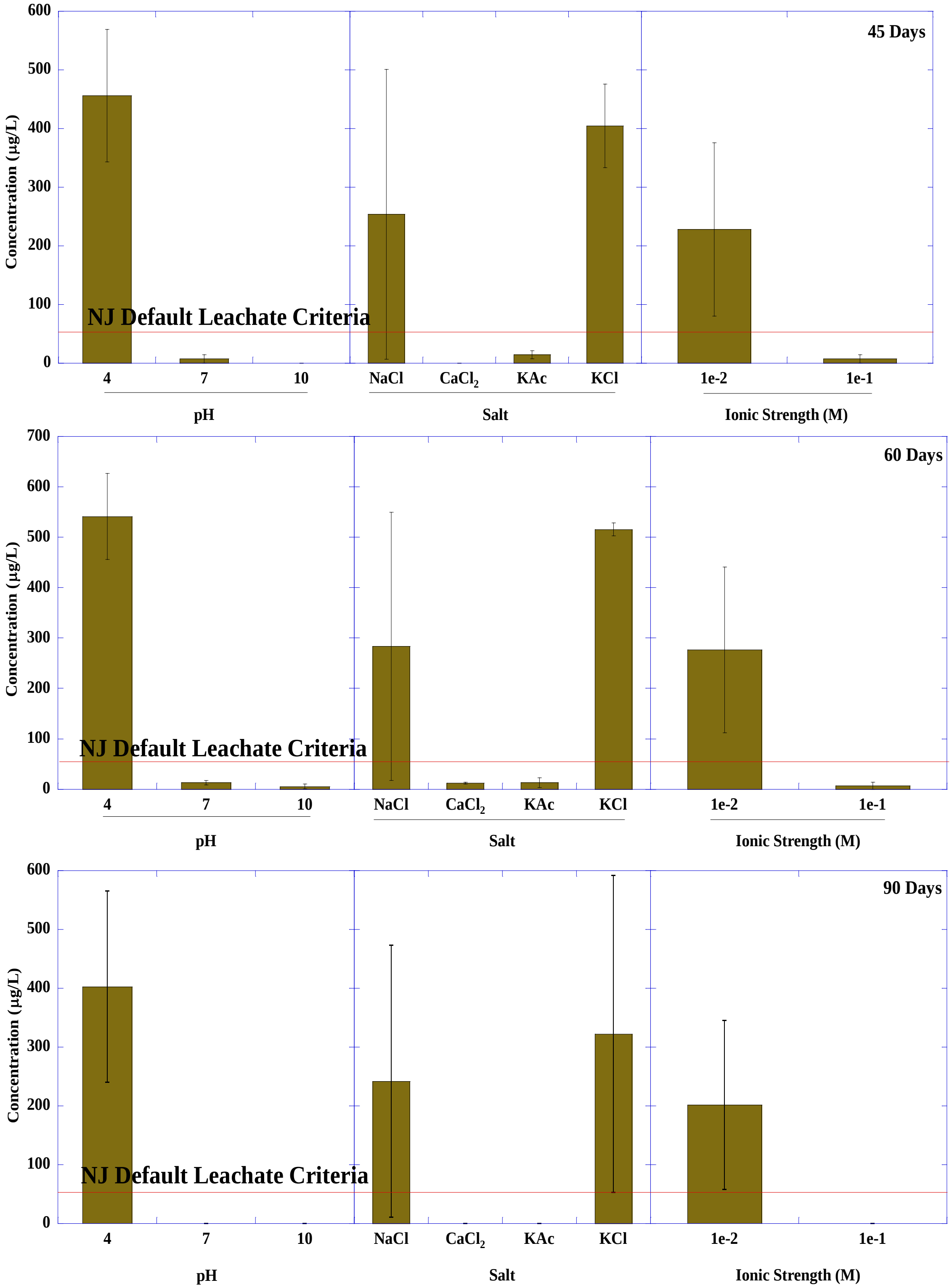


Figure C. 10 Leaching of Pb according to the factorial design depending upon pH, salt and ionic strength for particle size <37 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 1,009 and 0 µg/L, respectively. TCLP regulatory level for Pb is 5,000 µg/L.

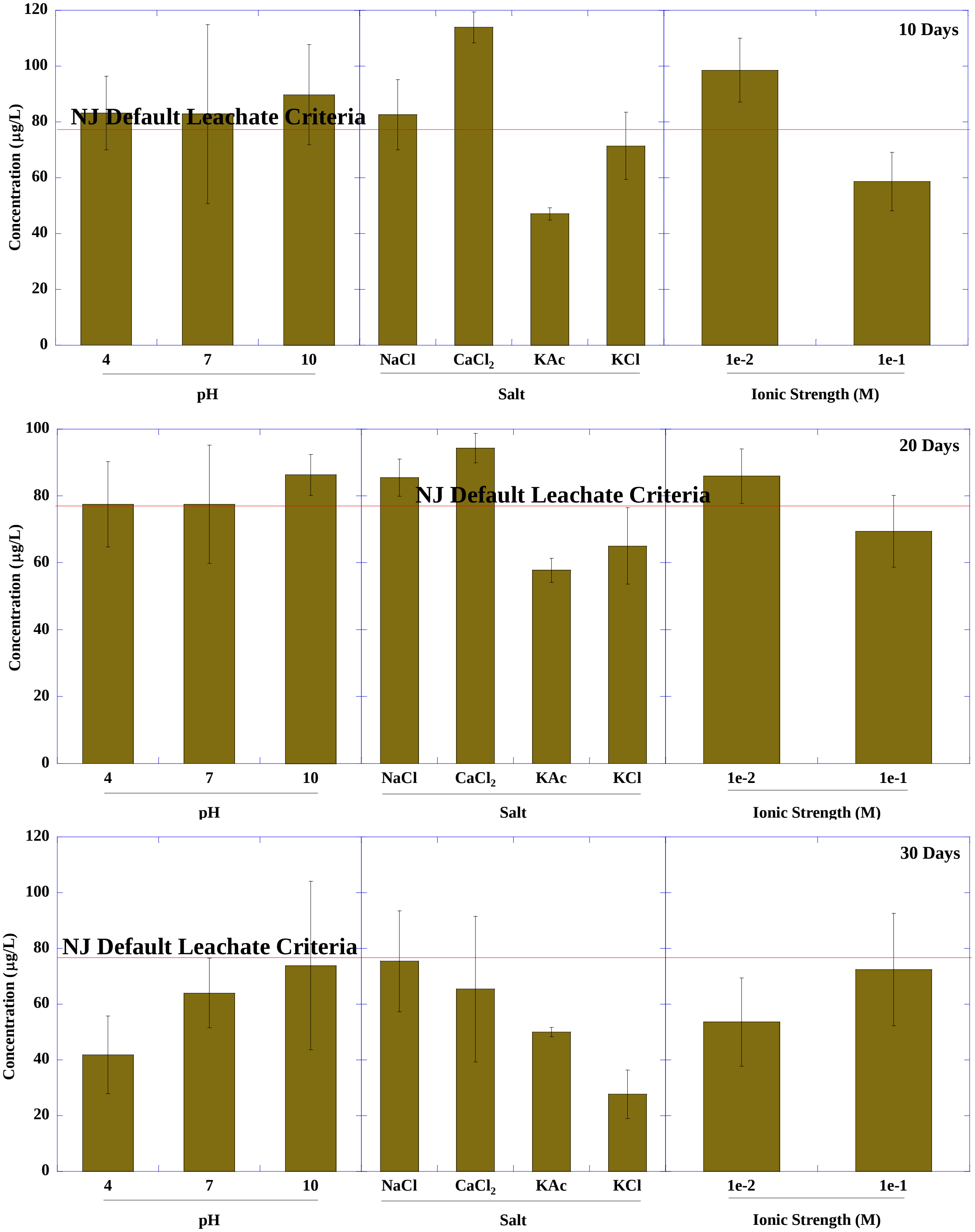


Figure C. 11 Leaching of Sb according to the factorial design depending upon pH, salt and ionic strength for particle size <37 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 19 and 68 µg/L, respectively. TCLP regulatory level for Sb is not available.

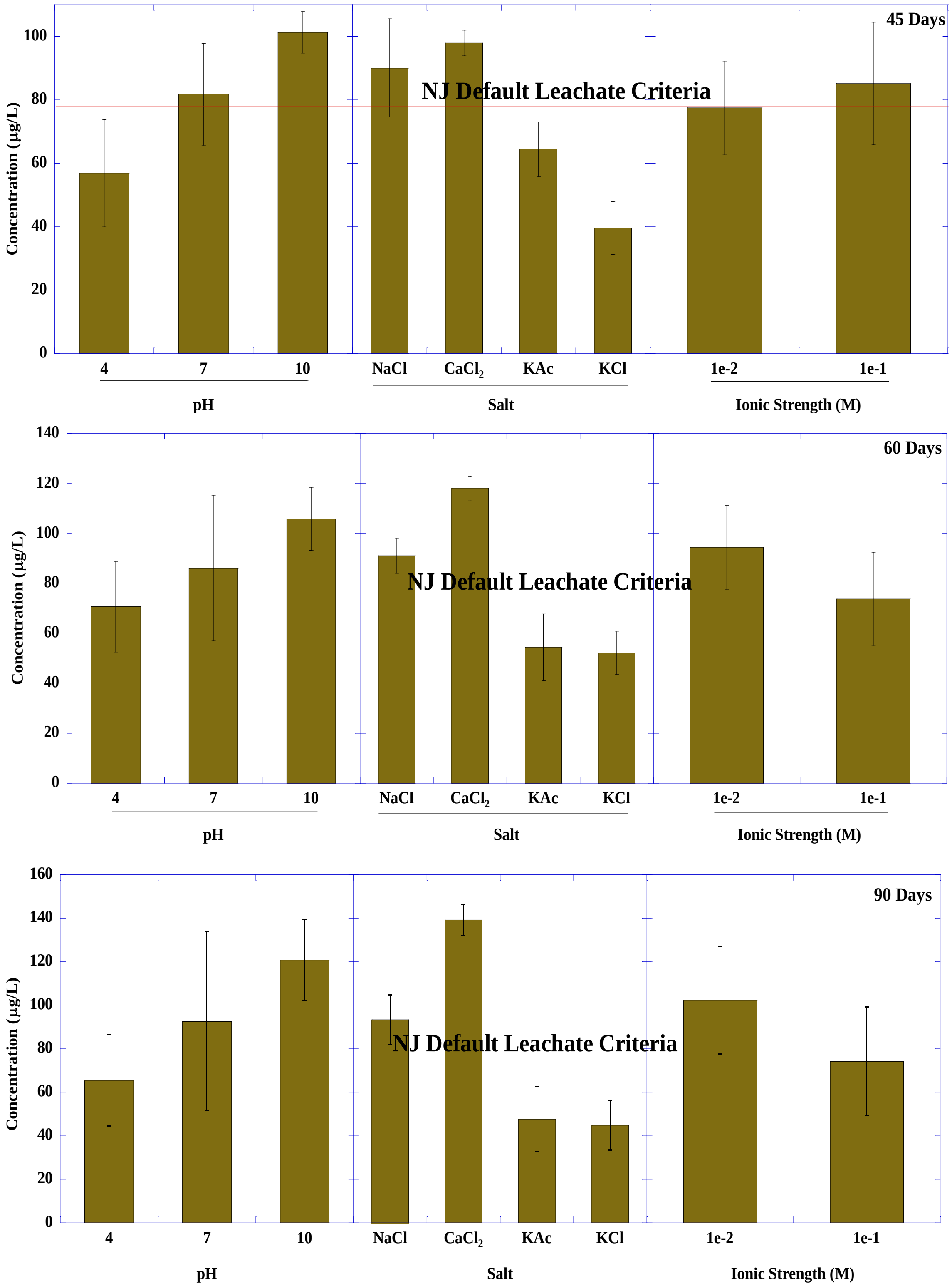


Figure C. 12 Leaching of Sb according to the factorial design depending upon pH, salt and ionic strength for particle size <37 µm. Error bars indicate 2 × S.E. TCLP and SPLP concentrations were found to be 19 and 68 µg/L, respectively. TCLP regulatory level for Sb is not available.

APPENDIX D

WILCOXON SIGNED RANK TEST RESULTS

This appendix shows the results of the Wilcoxon Signed Rank Test.

ARSENIC

If X>100 mg/kg

Total	Leached Conc. (Y)	Y - 3	Sign	|Y - 3|	Rank	Sign*Rank	Rank^2
166	22	19	Positive	19	6.00	6.00	36
194	29	26	Positive	26	7.00	7.00	49
214	30	27	Positive	27	8.00	8.00	64
101	11	8	Positive	8	4.00	4.00	16
611	64	61	Positive	61	19.50	19.50	380
647	112	109	Positive	109	34.00	34.00	1156
645	176	173	Positive	173	37.00	37.00	1369
647	538	535	Positive	535	45.00	45.00	2025
535	348	345	Positive	345	40.00	40.00	1600
195	56	53	Positive	53	15.00	15.00	225
126	14	11	Positive	11	5.00	5.00	25
597	78	75	Positive	75	27.00	27.00	729
695	101	98	Positive	98	32.00	32.00	1024
756	165	162	Positive	162	36.00	36.00	1296
690	490	487	Positive	487	44.00	44.00	1936
493	135	132	Positive	132	35.00	35.00	1225
119	64	61	Positive	61	19.50	19.50	380
204	78	75	Positive	75	27.00	27.00	729
585	70	67	Positive	67	24.00	24.00	576
571	42	39	Positive	39	12.00	12.00	144
708	85	82	Positive	82	29.00	29.00	841
666	392	389	Positive	389	42.00	42.00	1764
148	63	60	Positive	60	17.00	17.00	289
213	72	69	Positive	69	25.00	25.00	625
120	4	1	Positive	1	1.50	1.50	2
532	48	45	Positive	45	13.00	13.00	169
608	31	28	Positive	28	9.00	9.00	81
643	69	66	Positive	66	23.00	23.00	529
664	457	454	Positive	454	43.00	43.00	1849
152	180	177	Positive	177	38.00	38.00	1444
207	78	75	Positive	75	27.00	27.00	729
773	68	65	Positive	65	22.00	22.00	484
678	4	1	Positive	1	1.50	1.50	2
823	0	-3	Negative	3	3.50	-3.50	12
662	195	192	Positive	192	39.00	39.00	1521
530	0	-3	Negative	3	3.50	-3.50	12
120	104	101	Positive	101	33.00	33.00	1089
302	94	91	Positive	91	31.00	31.00	961
118	67	64	Positive	64	21.00	21.00	441
605	36	33	Positive	33	10.00	10.00	100
547	91	88	Positive	88	30.00	30.00	900
688	57	54	Positive	54	16.00	16.00	256
743	38	35	Positive	35	11.00	11.00	121
422	355	352	Positive	352	41.00	41.00	1681

191	51	48	Positive	48	14.00	14.00	196

Sum of (+) ranks	1014	
Sum of (-) ranks	-7	
Sum of squared ranks		31084

Z =(1014-7)/(31084)^0.5 Z = 5.71 and p-value for Z ≥ 5.71 = 1.0E-5

As the p-value is less than α-values of 0.01, 0.05, and 0.1 at 99%, 95% and 90% levels of confidence respectively, so the test is significant at all these levels.

If X>150 mg/kg

Total	Leached Conc. (Y)	Y-3	Sign	│Y - 3│	Rank	Sign*Rank	Rank^2
166	22	19	Positive	19	4.00	4.00	16
194	29	26	Positive	26	5.00	5.00	25
214	30	27	Positive	27	6.00	6.00	36
611	64	61	Positive	61	15.00	15.00	225
647	112	109	Positive	109	27.00	27.00	729
645	176	173	Positive	173	30.00	30.00	900
647	538	535	Positive	535	38.00	38.00	1444
535	348	345	Positive	345	33.00	33.00	1089
195	56	53	Positive	53	13.00	13.00	169
597	78	75	Positive	75	21.00	21.00	441
695	101	98	Positive	98	26.00	26.00	676
756	165	162	Positive	162	29.00	29.00	841
690	490	487	Positive	487	37.00	37.00	1369
493	135	132	Positive	132	28.00	28.00	784
204	78	75	Positive	75	21.00	21.00	441
585	70	67	Positive	67	18.00	18.00	324
571	42	39	Positive	39	10.00	10.00	100
708	85	82	Positive	82	23.00	23.00	529
666	392	389	Positive	389	35.00	35.00	1225
213	72	69	Positive	69	19.00	19.00	361
532	48	45	Positive	45	11.00	11.00	121
608	31	28	Positive	28	7.00	7.00	49
643	69	66	Positive	66	17.00	17.00	289
664	457	454	Positive	454	36.00	36.00	1296
152	180	177	Positive	177	31.00	31.00	961
207	78	75	Positive	75	21.00	21.00	441
773	68	65	Positive	65	16.00	16.00	256
678	4	1	Positive	1	1.00	1.00	1
823	0	-3	Negative	3	2.50	-2.50	6
662	195	192	Positive	192	32.00	32.00	1024
530	0	-3	Negative	3	2.50	-2.50	6
302	94	91	Positive	91	25.00	25.00	625
605	36	33	Positive	33	8.00	8.00	64
547	91	88	Positive	88	24.00	24.00	576
688	57	54	Positive	54	14.00	14.00	196
743	38	35	Positive	35	9.00	9.00	81
422	355	352	Positive	352	34.00	34.00	1156
191	51	48	Positive	48	12.00	12.00	144

Sum of (+) ranks	736	
Sum of (-) ranks	-5	
Sum of squared		19017

ranks

$Z = (736-5)/(19017)^{0.5}$	$Z = 5.30$	and p-value for $Z \geq 5.30 = 1.0E-5$

As the p-value is less than α-values of 0.01, 0.05, and 0.1 at 99%, 95% and 90% levels of confidence respectively, so the test is significant at all these levels.

If X>200 mg/kg

Total	Leached Conc. (Y)	Y - 3	Sign	$\lvert Y - 3 \rvert$	Rank	Sign*Rank	Rank^2
214	30	27	Positive	27	4.00	4.00	16
611	64	61	Positive	61	11.00	11.00	121
647	112	109	Positive	109	23.00	23.00	529
645	176	173	Positive	173	26.00	26.00	676
647	538	535	Positive	535	33.00	33.00	1089
535	348	345	Positive	345	28.00	28.00	784
597	78	75	Positive	75	17.00	17.00	289
695	101	98	Positive	98	22.00	22.00	484
756	165	162	Positive	162	25.00	25.00	625
690	490	487	Positive	487	32.00	32.00	1024
493	135	132	Positive	132	24.00	24.00	576
204	78	75	Positive	75	17.00	17.00	289
585	70	67	Positive	67	14.00	14.00	196
571	42	39	Positive	39	8.00	8.00	64
708	85	82	Positive	82	19.00	19.00	361
666	392	389	Positive	389	30.00	30.00	900
213	72	69	Positive	69	15.00	15.00	225
532	48	45	Positive	45	9.00	9.00	81
608	31	28	Positive	28	5.00	5.00	25
643	69	66	Positive	66	13.00	13.00	169
664	457	454	Positive	454	31.00	31.00	961
207	78	75	Positive	75	17.00	17.00	289
773	68	65	Positive	65	12.00	12.00	144
678	4	1	Positive	1	1.00	1.00	1
823	0	-3	Negative	3	2.50	-2.50	6
662	195	192	Positive	192	27.00	27.00	729
530	0	-3	Negative	3	2.50	-2.50	6
302	94	91	Positive	91	21.00	21.00	441
605	36	33	Positive	33	6.00	6.00	36
547	91	88	Positive	88	20.00	20.00	400
688	57	54	Positive	54	10.00	10.00	100
743	38	35	Positive	35	7.00	7.00	49
422	355	352	Positive	352	29.00	29.00	841

Sum of (+) ranks	556	
Sum of (-) ranks	-5	
Sum of squared ranks		12527

Z =(556-5)/(12527)^0.5 Z = 4.92 and p-value for Z ≥ 4.92 = 1.0E5

As the p-value is less than α-values of 0.01, 0.05, and 0.1 at 99%, 95% and 90% levels of confidence, respectively, so the test is significant at all levels.

LEAD

If X>20 mg/kg

Total	**Leached Conc. (Y)**	**Y-65**	**Sign**	**│Y - 65│**	**Rank**	**Sign*Rank**	**Rank^2**
45	666	601	Positive	601	23	23	529
28	9	-56	Negative	56	8	-8	64
142	269	204	Positive	204	18	18	324
188	161	96	Positive	96	12	12	144
129	203	138	Positive	138	16	16	256
86	535	470	Positive	470	21	21	441
113	340	275	Positive	275	20	20	400
22	147	82	Positive	82	10	10	100
87	559	494	Positive	494	22	22	484
60	20	-45	Negative	45	6	-6	36
135	21	-44	Negative	44	4.5	-4.5	20.25
157	152	87	Positive	87	11	11	121
123	106	41	Positive	41	2	2	4
192	287	222	Positive	222	19	19	361
27	168	103	Positive	103	13	13	169
46	223	158	Positive	158	17	17	289
20	124	59	Positive	59	9	9	81
112	22	-43	Negative	43	3	-3	9
204	21	-44	Negative	44	4.5	-4.5	20.25
106	25	-40	Negative	40	1	-1	1
154	1092	1027	Positive	1027	24	24	576
96	186	121	Positive	121	15	15	225
133	179	114	Positive	114	14	14	196
123	113	48	Positive	48	7	7	49

Sum of (+) ranks	268.5	
Sum of (-) ranks	-27	
Sum of squared ranks		4899.5

Z =(268.5-27)/(4899.5)^0.5 Z = 3.45 and p-value for Z ≥ 3.45 = 1.0E-5

As the p-value is less than α-values of 0.01, 0.05, and 0.1 at 99%, 95% and 90% levels of confidence respectively, so the test is significant at all these levels.

If X >50 mg/kg

Total	Leached conc. (Y)	Y - 65	Sign	⎮Y - 65⎮	Rank	Sign*Rank	Rank^2
142	269	204	Positive	204	13	13	169
188	161	96	Positive	96	9	9	81
129	203	138	Positive	138	12	12	144
86	535	470	Positive	470	16	16	256
113	340	275	Positive	275	15	15	225
87	559	494	Positive	494	17	17	289
60	20	-45	Negative	45	6	-6	36
135	21	-44	Negative	44	4.5	-4.5	20.25
157	152	87	Positive	87	8	8	64
123	106	41	Positive	41	2	2	4
192	287	222	Positive	222	14	14	196
112	22	-43	Negative	43	3	-3	9
204	21	-44	Negative	44	4.5	-4.5	20.25
106	25	-40	Negative	40	1	-1	1
154	1092	1027	Positive	1027	18	18	324
96	186	121	Positive	121	11	11	121
133	179	114	Positive	114	10	10	100
123	113	48	Positive	48	7	7	49

Sum of (+) ranks	152	
Sum of (-) ranks	-19	
Sum of squared ranks		2108.5

Z =(152-19)/(2108.5)^0.5 Z = 2.896 and p-value for Z ≥ 2.896 = 0.002

As the p-value is less than α-values of 0.01, 0.05, and 0.1 at 99%, 95% and 90% levels of confidence respectively, so the test is significant at all these levels

If X >75 mg/kg

Total	Leached conc. (Y)	Y - 65	Sign	|Y - 65|	Rank	Sign*Rank	Rank^2
142	269	204	Positive	204	12	12	144
188	161	96	Positive	96	8	8	64
129	203	138	Positive	138	11	11	121
86	535	470	Positive	470	15	15	225
113	340	275	Positive	275	14	14	196
87	559	494	Positive	494	16	16	256
135	21	-44	Negative	44	4.5	-4.5	20.25
157	152	87	Positive	87	7	7	49
123	106	41	Positive	41	2	2	4
192	287	222	Positive	222	13	13	169
112	22	-43	Negative	43	3	-3	9
204	21	-44	Negative	44	4.5	-4.5	20.25
106	25	-40	Negative	40	1	-1	1
154	1092	1027	Positive	1027	17	17	289
96	186	121	Positive	121	10	10	100
133	179	114	Positive	114	9	9	81
123	113	48	Positive	48	6	6	36

Sum of (+) ranks	140	
Sum of (-) ranks	-13	
Sum of squared ranks		1784.5

Z =(140-13)/(1784.5)^0.5 Z = 3.006 and p-value for Z ≥ 3.006= 0.001

As the p-value is less than α-values of 0.01, 0.05, and 0.1 at 99%, 95% and 90% levels of confidence respectively, so the test is significant at all these levels.

If X >100 mg/kg

Total	Leached (Y)	Y - 65	Sign	│Y - 65│	Rank	Sign*Rank	Rank^2
142	269	204	Positive	204	11	11	121
188	161	96	Positive	96	8	8	64
129	203	138	Positive	138	10	10	100
113	340	275	Positive	275	13	13	169
135	21	-44	Negative	44	4.5	-4.5	20.25
157	152	87	Positive	87	7	7	49
123	106	41	Positive	41	2	2	4
192	287	222	Positive	222	12	12	144
112	22	-43	Negative	43	3	-3	9
204	21	-44	Negative	44	4.5	-4.5	20.25
106	25	-40	Negative	40	1	-1	1
154	1092	1027	Positive	1027	14	14	196
133	179	114	Positive	114	9	9	81
123	113	48	Positive	48	6	6	36

Sum of (+) ranks	92	
Sum of (-) ranks	-13	
Sum of squared ranks		1014.5

Z =(92-13)/(1014.5)^0.5 Z = 2.480 and p-value for Z≥2.480= 0.006

As the p-value is less than α-values of 0.01, 0.05, and 0.1 at 99%, 95% and 90% levels of confidence respectively, so the test is significant at all these levels.

If X >150 mg/kg

Total	Leached (Y)	Y - 65	Sign	⎮Y - 65⎮	Rank	Sign*Rank	Rank^2
188	161	96	Positive	96	3	3	9
157	152	87	Positive	87	2	2	4
192	287	222	Positive	222	4	4	16
204	21	-44	Negative	44	1	-1	1
154	1092	1027	Positive	1027	5	5	25

Sum of (+) ranks	14	
Sum of (-) ranks	-1	
Sum of squared ranks		55

	Z =	and p-value for Z ≥ 1.753=
Z =(14-1)/(55)^0.5	1.753	0.040

As the p-value is less than α-values of 0.05 and 0.1 at 95% and 90% levels of confidence respectively, so the test is significant at all these levels.

ANTIMONY

If X>50 mg/kg

Total	Leached Conc. (Y)	Y - 78	Sign	⎮Y - 78⎮	Rank	Sign*Rank	Rank^2
83	0	-78	Negative	78	42.5	-42.5	1806.25
68	0	-78	Negative	78	42.5	-42.5	1806.25
135	0	-78	Negative	78	42.5	-42.5	1806.25
165	4	-74	Negative	74	35.5	-35.5	1260.25
150	16	-62	Negative	62	23.5	-23.5	552.25
181	106	28	Positive	28	16.5	16.5	272.25
117	28	-50	Negative	50	21	-21	441
62	5	-73	Negative	73	33.5	-33.5	1122.25
57	0	-78	Negative	78	42.5	-42.5	1806.25
143	4	-74	Negative	74	35.5	-35.5	1260.25
171	13	-65	Negative	65	26.5	-26.5	702.25
132	23	-55	Negative	55	22	-22	484
192	124	46	Positive	46	20	20	400
117	16	-62	Negative	62	23.5	-23.5	552.25
62	73	-5	Negative	5	6	-6	36
84	72	-6	Negative	6	7	-7	49
56	2	-76	Negative	76	37	-37	1369
150	11	-67	Negative	67	30	-30	900
151	10	-68	Negative	68	32	-32	1024
160	14	-64	Negative	64	25	-25	625
183	103	25	Positive	25	15	15	225
72	68	-10	Negative	10	11	-11	121
81	70	-8	Negative	8	8	-8	64
65	5	-73	Negative	73	33.5	-33.5	1122.25
153	11	-67	Negative	67	30	-30	900
135	11	-67	Negative	67	30	-30	900
147	13	-65	Negative	65	26.5	-26.5	702.25
186	98	20	Positive	20	13	13	169
54	160	82	Positive	82	48	48	2304
90	87	9	Positive	9	9.5	9.5	90.25
73	77	-1	Negative	1	2	-2	4
161	81	3	Positive	3	5	5	25
136	0	-78	Negative	78	42.5	-42.5	1806.25
162	0	-78	Negative	78	42.5	-42.5	1806.25
186	46	-32	Negative	32	18	-18	324
98	0	-78	Negative	78	42.5	-42.5	1806.25
72	101	23	Positive	23	14	14	196
89	87	9	Positive	9	9.5	9.5	90.25
60	77	-1	Negative	1	2	-2	4
148	0	-78	Negative	78	42.5	-42.5	1806.25
142	0	-78	Negative	78	42.5	-42.5	1806.25
143	0	-78	Negative	78	42.5	-42.5	1806.25
191	106	28	Positive	28	16.5	16.5	272.25
117	42	-36	Negative	36	19	-19	361
83	97	19	Positive	19	12	12	144
82	144	66	Positive	66	28	28	784

65	76	-2	Negative	2	4	-4	16
178	79	1	Positive	1	2	2	4

Sum of (+) ranks	209	
Sum of (-) ranks	-967	
Sum of squared ranks		37934.5

$Z = (-967+209)/(37934.5)^{0.5}$ $Z = -3.892$ and p-value for $Z \geq -3.892 = 1$

As it is more than the α-vales of 0.01, 0.05, and 0.1 corresponding to confidence levels 99%, 95%, and 90%, respectively so the test is not significant.

If X>75 mg/kg

Total	Leached Conc. (Y)	Y - 78	Sign	$\lvert Y - 78 \rvert$	Rank	Sign*Rank	Rank^2
83	0	-78	Negative	78	32.5	-32.5	1056.25
135	0	-78	Negative	78	32.5	-32.5	1056.25
165	4	-74	Negative	74	27.5	-27.5	756.25
150	16	-62	Negative	62	17.5	-17.5	306.25
181	106	28	Positive	28	10.5	10.5	110.25
117	28	-50	Negative	50	15	-15	225
143	4	-74	Negative	74	27.5	-27.5	756.25
171	13	-65	Negative	65	20.5	-20.5	420.25
132	23	-55	Negative	55	16	-16	256
192	124	46	Positive	46	14	14	196
117	16	-62	Negative	62	17.5	-17.5	306.25
84	72	-6	Negative	6	3	-3	9
150	11	-67	Negative	67	24	-24	576
151	10	-68	Negative	68	26	-26	676
160	14	-64	Negative	64	19	-19	361
183	103	25	Positive	25	9	9	81
81	70	-8	Negative	8	4	-4	16
153	11	-67	Negative	67	24	-24	576
135	11	-67	Negative	67	24	-24	576
147	13	-65	Negative	65	20.5	-20.5	420.25
186	98	20	Positive	20	8	8	64
90	87	9	Positive	9	5.5	5.5	30.25
161	81	3	Positive	3	2	2	4
136	0	-78	Negative	78	32.5	-32.5	1056.25
162	0	-78	Negative	78	32.5	-32.5	1056.25
186	46	-32	Negative	32	12	-12	144
98	0	-78	Negative	78	32.5	-32.5	1056.25
89	87	9	Positive	9	5.5	5.5	30.25
148	0	-78	Negative	78	32.5	-32.5	1056.25
142	0	-78	Negative	78	32.5	-32.5	1056.25
143	0	-78	Negative	78	32.5	-32.5	1056.25
191	106	28	Positive	28	10.5	10.5	110.25
117	42	-36	Negative	36	13	-13	169
83	97	19	Positive	19	7	7	49
82	144	66	Positive	66	22	22	484
178	79	1	Positive	1	1	1	1

Sum of (+) ranks	95	
Sum of (-) ranks	-571	
Sum of squared ranks		16159.5

Z =(-571+95)/(16159.5)^0.5 Z = -3.744 and p-value for Z ≥ -3.744 = 1

As it is more than the α-vales of 0.01, 0.05, and 0.1 corresponding to confidence levels 99%, 95%, and 90%,respectively so the test is not significant.

If X>100 mg/kg

Total	Leached (Y)	Y - 78	Sign	$\lvert Y - 78 \rvert$	Rank	Sign*Rank	Rank^2
135	0	-78	Negative	78	25.5	-25.5	650.25
165	4	-74	Negative	74	21.5	-21.5	462.25
150	16	-62	Negative	62	12.5	-12.5	156.25
181	106	28	Positive	28	5.5	5.5	30.25
117	28	-50	Negative	50	10	-10	100
143	4	-74	Negative	74	21.5	-21.5	462.25
171	13	-65	Negative	65	15.5	-15.5	240.25
132	23	-55	Negative	55	11	-11	121
192	124	46	Positive	46	9	9	81
117	16	-62	Negative	62	12.5	-12.5	156.25
150	11	-67	Negative	67	18	-18	324
151	10	-68	Negative	68	20	-20	400
160	14	-64	Negative	64	14	-14	196
183	103	25	Positive	25	4	4	16
153	11	-67	Negative	67	18	-18	324
135	11	-67	Negative	67	18	-18	324
147	13	-65	Negative	65	15.5	-15.5	240.25
186	98	20	Positive	20	3	3	9
161	81	3	Positive	3	2	2	4
136	0	-78	Negative	78	25.5	-25.5	650.25
162	0	-78	Negative	78	25.5	-25.5	650.25
186	46	-32	Negative	32	7	-7	49
148	0	-78	Negative	78	25.5	-25.5	650.25
142	0	-78	Negative	78	25.5	-25.5	650.25
143	0	-78	Negative	78	25.5	-25.5	650.25
191	106	28	Positive	28	5.5	5.5	30.25
117	42	-36	Negative	36	8	-8	64
178	79	1	Positive	1	1	1	1

Sum of (+) ranks	30	
Sum of (-) ranks	-376	
Sum of squared ranks		7692.5

Z =(-376+30)/(7692.5)^0.5   Z = -3.945   and p-value for Z ≥ -3.945 = 1

As it is more than the α-vales of 0.01, 0.05, and 0.1 corresponding to confidence levels 99%, 95%, and 90%, respectively so the test is not significant.

If X>150 mg/kg

Total	Leached (Y)	Y - 78	Sign	│Y - 78│	Rank	Sign*Rank	Rank^2
165	4	-74	Negative	74	15	-15	225
150	16	-62	Negative	62	9	-9	81
181	106	28	Positive	28	5.5	5.5	30.25
171	13	-65	Negative	65	11	-11	121
192	124	46	Positive	46	8	8	64
150	11	-67	Negative	67	12.5	-12.5	156.25
151	10	-68	Negative	68	14	-14	196
160	14	-64	Negative	64	10	-10	100
183	103	25	Positive	25	4	4	16
153	11	-67	Negative	67	12.5	-12.5	156.25
186	98	20	Positive	20	3	3	9
161	81	3	Positive	3	2	2	4
162	0	-78	Negative	78	16	-16	256
186	46	-32	Negative	32	7	-7	49
191	106	28	Positive	28	5.5	5.5	30.25
178	79	1	Positive	1	1	1	1

Sum of (+) ranks	29	
Sum of (-) ranks	-107	
Sum of squared ranks		1495

Z =(-107+29)/(1495)^0.5 Z = -2.017 and p-value for Z ≥ -2.017 = 0.978

As it is more than the α-vales of 0.01, 0.05, and 0.1 corresponding to confidence levels 99%, 95%, and 90%, respectively so the test is not significant.

If X>175 mg/kg

Total	Leached Conc. (Y)	Y - 78	Sign	|Y - 78|	Rank	Sign*Rank	Rank^2
181	106	28	Positive	28	4.5	4.5	20.25
192	124	46	Positive	46	7	7	49
183	103	25	Positive	25	3	3	9
186	98	20	Positive	20	2	2	4
186	46	-32	Negative	32	6	-6	36
191	106	28	Positive	28	4.5	4.5	20.25
178	79	1	Positive	1	1	1	1

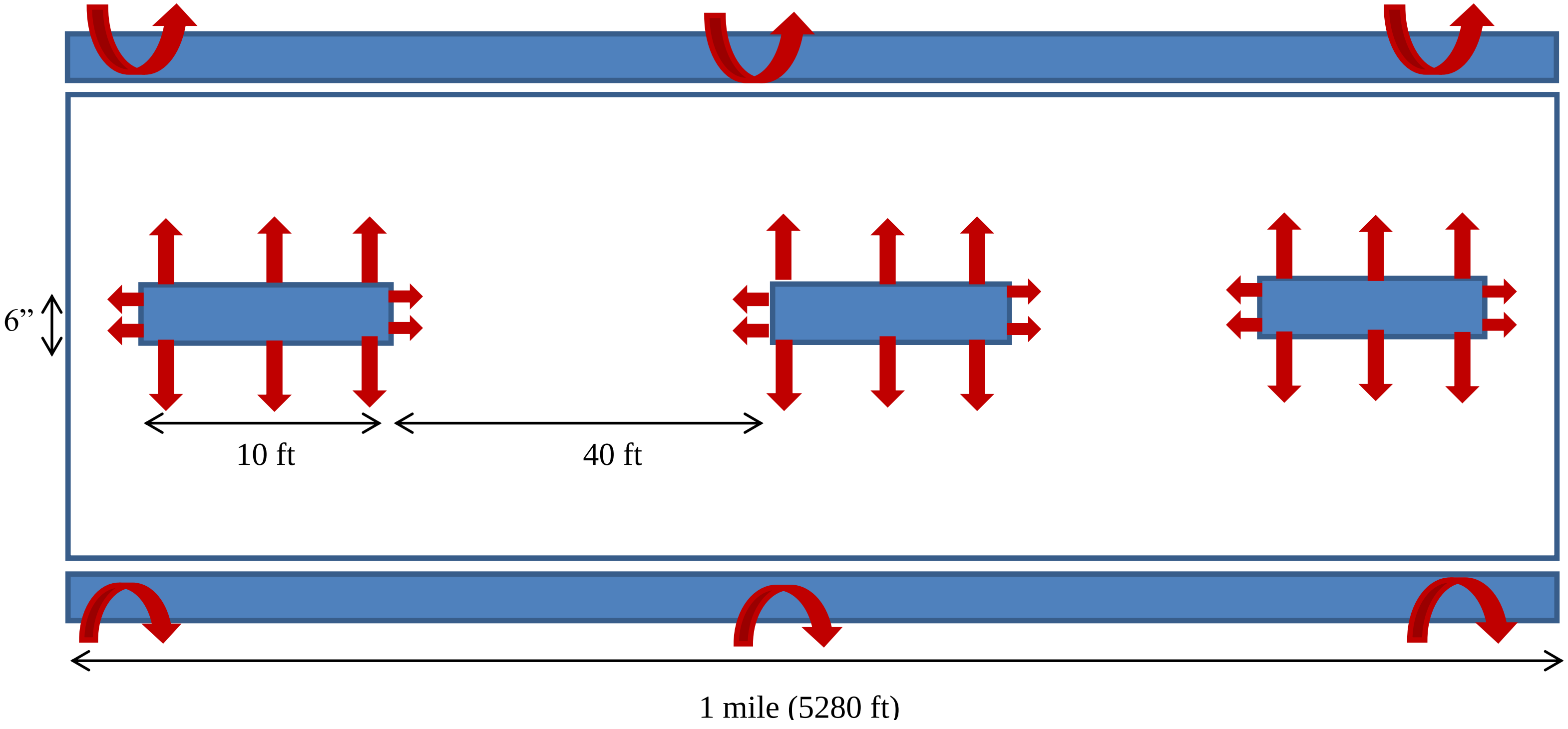
Sum of (+) ranks	22	
Sum of (-) ranks	-6	
Sum of squared ranks		139.5

Z =(22-6)/(139.5)^0.5 Z = 1.355 and p-value for Z≥1.355 = 0.088

As it is less than 0.1 (ie. 90% level of confidence), so the test is significant at 90%. However, it is not significant at 95% and 99% levels of confidence as the value is more than the α-values of 0.05 and 0.01, respectively.

APPENDIX E

LEACHING ASSESSMENT CONSIDERING THE HIGHWAY AS A LINE SOURCE



ASSUMPTIONS

1. Average annual rainfall is NJ is 40” (ie. 40” in 365 days). Based on fractional factorial study, leached concentrations plateaued at 90 days. Assuming 90 days as the worst case scenario, effective rainfall can be taken as $\frac{40''}{4}$ = 10”.
2. Assume all precipitation contacts the glass beads.
3. Assume a 2-lane, 24’ wide highway that drains equally on both sides.

CONSTANTS

1. ***Paint thickness*** = 20 mil = 0.02 inches

2. ***Volume of paint used/mile*** = $\frac{6''}{12''} \times 5280\ ft \times 2\ side\ lanes \times 0.02'' \times \frac{1ft}{12''} + \frac{6''}{12''} \times 10\ ft \times 0.02'' \times \frac{1ft}{12''} \times 106\ center\ strips/mile =$

   9.683 ft^3 = $9.683\ ft^3 \times \frac{7.48\ gallons}{1ft^3}$ = 72.43 gallons/mile

3. ***Volume of rainfall***

   Volume of rain on a typical NJ 2-lane highway, 24' wide and 5280' long = $10'' \times \frac{1'}{12''} \times 24' \times 5280'$

   $= 105600\ ft^3 \times \frac{28.32\ L}{1ft^3} \times \frac{10^3\ mL}{1\ L} = \mathbf{3 \times 10^9\ mL}$

4. ***Glass beads application rate***

   24 lbs of glass beads are used/gallon of paint; in 1 mile 72.43 gallons of paint are used. Therefore, 1738 lbs of beads or 790 kg of beads/mile. Assuming optimum embedment at 50% of the glass bead, 395 kg of glass beads/mile are exposed to the environment i.e. $\frac{395\ Kg\ of\ glass\ beads/mile}{3 \times 10^9\ mL\ of\ rainfall} \times \frac{10^3\ g}{1\ Kg} = \mathbf{1.32 \times 10^{-4}\ \frac{g\ of\ beads}{mL\ of\ rainfall\ .\ mile}}$

MAXIMUM OBSERVED LEACHING

1. Maximum leaching for As was observed to be **6,213 $\frac{\mu g}{L}$** from a solution containing $\frac{25\text{ g of glass beads}}{250\text{ mL of water}}$ $i.e.\left(\frac{0.1\ g\ beads}{mL\ of\ water}\right)$

   $\frac{0.1\ g\ beads}{mL\ of\ water}$ resulted in a leached concentration of **6,213 $\frac{\mu g}{L}$ of As**

   $\mathbf{1.32\times10^{-4}}\ \frac{g\ of\ beads}{mL\ of\ rainfall\ .\ mile}$ will result in a leached concentration of **6,213 $\frac{\mu g}{L}$** $\times\ \frac{1}{\frac{0.1\ g\ beads}{mL\ of\ water}}\times\mathbf{1.32\times10^{-4}}\ \frac{g\ of\ beads}{mL\ of\ rainfall\ .\ mile}$

   = 8.20 $\frac{\mu g}{L\ .mile}$ > NJ Default Leachate Criteria for As (3 µg L^{-1})

2. Maximum leaching for Pb was observed to be **520 $\frac{\mu g}{L}$** from a solution containing $\frac{25\text{ g of glass beads}}{250\text{ mL of water}}$ $i.e.\left(\frac{0.1\ g\ beads}{mL\ of\ water}\right)$

   $\frac{0.1\ g\ beads}{mL\ of\ water}$ resulted in a leached concentration of **520 $\frac{\mu g}{L}$ of Pb**

   $\mathbf{1.32\times10^{-4}}\ \frac{g\ of\ beads}{mL\ of\ rainfall\ .\ mile}$ will result in a leached concentration of **520 $\frac{\mu g}{L}$** $\times\ \frac{1}{\frac{0.1\ g\ beads}{mL\ of\ water}}\times\mathbf{1.32\times10^{-4}}\ \frac{g\ of\ beads}{mL\ of\ rainfall\ .\ mile}$

   = 0.70 $\frac{\mu g}{L\ .mile}$ < NJ Default Leachate Criteria for Pb (65 µg L^{-1})

3. Maximum leaching for Sb was observed to be **110 $\frac{\mu g}{L}$** from a solution containing $\frac{25\text{ g of glass beads}}{250\text{ mL of water}}$ $i.e.\left(\frac{0.1\ g\ beads}{mL\ of\ water}\right)$

   $\frac{0.1\ g\ beads}{mL\ of\ water}$ resulted in a leached concentration of **110 $\frac{\mu g}{L}$ of Sb**

$\mathbf{1.32 \times 10^{-4}}\ \frac{\boldsymbol{g\ of\ beads}}{\boldsymbol{mL\ of\ rainfall\ .\ mile}}$ will result in a leached concentration of $\mathbf{110}\ \frac{\mathbf{\mu g}}{\mathbf{L}} \times \frac{\mathbf{1}}{\frac{\boldsymbol{0.1\ g\ beads}}{\boldsymbol{mL\ of\ water}}} \times \mathbf{1.32 \times 10^{-4}}\ \frac{\boldsymbol{g\ of\ beads}}{\boldsymbol{mL\ of\ rainfall\ .\ mile}}$

$= 0.15\ \frac{\mu g}{L\ .mile}$ < NJ Default Leachate Criteria for Pb (78 µg L^{-1})

Lowest Average Annual Rainfall Observed in New Jersey (29.36" in 1965)

Element	Volume of paint used (gallons.mile^{-1})	Volume of Rainfall over 1 mile (mL)	Maximum leaching in 160 days (µg L^{-1})	Glass beads application rate (g of beads mL rainfall^{-1} mile^{-1})	Expected Leaching (µg L^{-1} mile^{-1})	NJ Default Leachate Criterion (µg L^{-1})
As	72.43	4.84×10^9	6, 213	8.16×10^{-5}	***5.07***	***3***
Pb	72.43	4.84×10^9	520	8.16×10^{-5}	0.42	65
Sb	72.43	4.84×10^9	110	8.16×10^{-5}	0.09	78

Highest Average Annual Rainfall Observed in New Jersey (64.78" in 2011)

Element	Volume of paint used (gallons.mile^{-1})	Volume of Rainfall over 1 mile (mL)	Maximum leaching in 160 days (µg L^{-1})	Glass beads application rate (g of beads mL rainfall^{-1} mile^{-1})	Expected Leaching (µg L^{-1} mile^{-1})	NJ Default Leachate Criterion (µg L^{-1})
As	72.43	2.2×10^9	6, 213	1.80×10^{-4}	***11.20***	***3***
Pb	72.43	2.2×10^9	520	1.80×10^{-4}	0.94	65
Sb	72.43	2.2×10^9	110	1.80×10^{-4}	0.20	78

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