HEAVY METALS IN ROAD DEPOSITED SEDIMENT IN TOWN OF OYSTER BAY, LONG ISLAND, NEW YORK

MASTER'S THESIS

(Final Draft)

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Abstract

This paper discusses a novel approach to road deposited sediment (RDS) characterization building on the street sweeping policy survey conducted between 2014 and 2015 on Long Island. This study focuses on the heavy metal content of RDS collected by street sweepers from roadways in the unincorporated hamlets of Town of Oyster Bay (TOB), New York. The TOB study site includes impaired bays and waterways polluted with pathogens, nitrogen, and low dissolved oxygen. Urban runoff is a known contributor to surface water pollution in the study site. Among the contaminants found in urban runoff in RDS are elevated levels of heavy metals, nutrients, bacteria, and organic pollutants. These pollutants often come from personal vehicle component corrosion, partially combusted fossil fuels, lawn waste, pet and animal waste, vehicle engine oil and lubricants, and atmospheric deposition. An x-ray analysis of heavy elements on TOB RDS was conducted. Elevated levels of chromium (58.3+/-2.10 parts per million [ppm]), copper (217+/-17.7 ppm), zirconium (426+/-14.1ppm), cobalt (88.12+/-24.27ppm), arsenic (14.11+/-3.42ppm), nickel (38.54+/-11.81ppm), vanadium (126+/-4.17ppm) and zinc (323+/-19.2ppm) were found. A novel method for calculating total annual heavy metal loading was developed to calculate an estimate of total remaining RDS heavy metal loading on roadways. This research may be used to inform street sweeping policy, including storage and uses of RDS and future RDS research.

1 Introduction

1.1 Rationale for Research

This RDS characterization study is a continuation of the street sweeping survey between 2014 and 2015 across several Long Island municipalities. A survey was conducted by faculty and undergraduate students at Hofstra University of local governments about their street sweeping policies that culminated in a presentation at the annual Geological Society of America conference in Baltimore, Maryland in November 2015 (Brinkmann et al. 2015). Road deposited sediment is a major input to urban stormwater and runoff. However, there has been little research on the content of RDS on Long Island. This is the first time that RDS on Long Island has been characterized.

1.2 Stormwater Pollution

The complex process of sediment and contaminant transport in an urban river basin has been mapped in diagrams and discussed in detail in Taylor and Owens (2009), including upstream discharges and site characteristics. The suspected sources of contaminants often found in urban rivers are discussed, including those reaches both upstream and downstream of the urban centers.

Brown and Peake (2006) conducted an analysis to determine the source of water pollution using water quality results in a watershed that traced the contents of nearby RDS to the study site in New Zealand. During this experiment, components of RDS were compared to pollutants found in urban runoff at outfalls in an urban watershed. The concentrations of metal contaminants found in RDS were used to “fingerprint” the source of pollutants found in the urban watershed. The contaminants found in suspended solids from local bodies of water were tracked back to urban sediment, suggesting that urban runoff was indeed responsible for the pollution.

Suspended solids can affect the growth of plant life by limiting sunlight. It can also cause the migration or death of invertebrates by interfering with feeding mechanisms. The concentration, duration of exposure, chemical composition, and particle size distribution of suspended solids contribute to the impact of suspended solids on aquatic life (Bilotta and Brazier 2008). Suspended solids are made up of only sediment and detrital organic matter. The focus of this paper is on RDS, which can be managed with many different best management practices (BMPs), meaning pollution controls.

1.3 Stormwater Management Solutions

Extensive work has been done by public officials and community organizations to coordinate stormwater management in Nassau County. Public involvement has been explored as its own subject and as part of the process of stormwater management (Shah-Gavnoudias 2009). Several community and non-profit organizations that specialize in water-related issues are partners to the stormwater management plan. Best management practices are generally mandated. Storm water outfalls have been mapped and characterized by size. A list of ongoing infrastructure improvement projects is regularly maintained. Illicit discharge is acknowledged and a strategy to combat such sources of pollution has been put forward. Household best management practices are included in this report as both a study of non-RDS sources of stormwater pollution and a summary of what is being done to prevent it.

1.4 Household Best Management Practices (BMPs)

The education and involvement of the community is a high priority for stormwater BMPs because much of the stormwater pollution comes from households and can be prevented through information campaigns. Household hazardous waste pose a serious threat of groundwater contamination. Dumping waste into a storm drain has the same result as dumping the materials directly into a water body.

Washing your car and degreasing auto parts at home can send detergents and other contaminants through the storm sewer system. Use a commercial car wash that treats or recycles its wastewater or wash your car on your yard so the water infiltrates into the ground. Repair leaks and dispose of used auto fluids and batteries at designated drop-off or recycling locations.

If you own a water well, have your water tested yearly. Also test if there is a change in the odor, taste, or smell. Having your water tested may cost money, but it could provide you with potentially lifesaving information.

Pet waste can be a major source of bacteria and excess nutrients in local waters. When walking your pet, remember to pick up the waste and dispose of it properly. Flushing pet waste is the best disposal method. This measure costs you nothing except time, the benefit will be cleaner streets and waterways

Rain barrels collect rainwater from rooftops in mosquito-proof containers. The water can later be used on lawn or garden areas. Initial cost will be from the installation of the rain barrel, but as water collects and is used in place of tap water, it can save you money on your water bill.

1.4.1 Septic Systems

Septic systems release nutrients and pathogens that can be picked up by stormwater and discharged into nearby waterways. Inspect your system every 3 years and pump your tank as necessary every 3 to 5 years. Don’t dispose of household hazardous waste in sinks or toilets. It may cost you a few hundred dollars to get it inspected, but it provides you with the benefit of knowing that you’re not polluting the ground beneath you.

1.4.2 Lawn Care and Garden Care

Excess fertilizers and pesticides applied to lawns and gardens wash off and cause pollution - use fertilizers and pesticides sparingly; use organic mulch or integrated pest management; avoid application if the forecast calls for rain; use slow watering devices such as trickle irrigation or soaker hoses, which reduce runoff and are 20 percent more effective than sprinklers; water lawn only once every other day in the cool part of the day, before 10 am or after 4 pm, because water will evaporate less quickly at these times; don’t leave yard waste in the street or sweep it into storm drains. Not only will using these tips help you tend to your lawn or garden, but they will also save you money.

1.4.3 Hazardous Waste

Programs for the proper disposal of insecticides, pesticides, paint, solvents, used motor oil and other auto fluids reduce contaminants at the source. Use low phosphate or phosphate free detergents; use water-based products when possible; do not pour household hazardous wastes into sinks, toilets, the ground, or storm drains. Managing hazardous waste usually will only cost you time, but you can be sure that you're doing your part to protect the environment. Electronic waste has low biodegradability and contains materials that are highly toxic when released into the environment. Try to recycle E-waste if you are able to. Some stores have recycling receptacles for items such as batteries or used ink cartridges.

1.4.4 Green Infrastructure

One of the solutions coming from research on land use planning and construction is the additional provision of green infrastructure. There are many kinds of green infrastructure projects with varying costs and benefits to improved stormwater sanitation. Examples of green infrastructure include green roofs, grassed swales, porous pavement, rain gardens, and properly designed catch basins. These design instruments can be integrated into a development as part of development plan or as post hoc construction.

Land use planning is a highly effective stormwater BMP that uses known sensitive areas and areas of planned development to anticipate stormwater challenges and develop strategies to implement stormwater management. Specially designed areas planted with native plants can provide natural places for rainwater to collect and soak into the ground. Rain from rooftop areas or paved areas can be diverted into these areas rather than into storm drains. Rain gardens are usually placed in areas where the pooling of water is apparent. By installing a rain garden, plants will help absorb this rainwater and prevent pooling. Initially the cost for installing a rain garden or grassy swale is high, but over time, it can filter thousands of gallons of water and aid in groundwater intrusion, which prevents flooding and erosion, as well as sewage overflow.

One of the solutions coming from research on land use planning and construction is the additional provision of green infrastructure. There are many kinds of green infrastructure projects with varying costs and benefits to improved stormwater sanitation. Examples of green infrastructure include green roofs, grassed swales, porous pavement, rain gardens, and properly designed catch basins. Vegetated Filter Strips are areas of native grass or plants created along roadways or streams. They trap the pollutants stormwater picks up as it flows across driveways and streets. These significantly reduce the amount of pollution introduced to waterways after a storm. These design instruments can be integrated into a development as part of a development plan or post hoc construction.

While stormwater management plans are commonplace in municipalities across the United States, the BMPs for stormwater pollution prevention are not universally implemented or even applied in the same way among states and municipalities. Lists and guides of BMPs are maintained in part for the industries that would use them. The U.S. Environmental Protection Agency (2000) and New York State Department of Environmental Conservation (2002) keep guides to stormwater BMPs for public information.

1.5 Street Sweeping Technology

Road deposited sediment is removed through the practice of street sweeping. This paper examines the historical and current practice of street sweeping, and developments in the technology used for street sweeping. To date, these improvements have essentially been those which utilize a suction device in addition to the mechanical sweeper, for trapping the RDS particulate.

The scientific literature on street sweeping technology is limited (Brinkmann and Tobin 2001) and the role of street sweeping has changed over time. It has gone from being a practice mostly of aesthetic value, meaning of clearing streets of litter and large debris, to an environmental BMP, which adds an element of pollution control. Contaminants are found to be highly concentrated in fine sediments. There is no agreed upon frequency or type of street sweeper to use for best results. However, a schedule of weekly street sweeping after spring thaw is generally recommended as a starting point for street sweeping policy.

The efficiency of current street sweeping technology has been evaluated (James 1996). Street sweeping literature on the ability of street sweepers to remove contaminants including those found in fine sediment had largely found low rates (<50%) of efficiency (EPA 1983). James used the most recent information available at the time to update the academic view about the role of street sweepers in picking up fine sediment. Developments in street sweeping technology have improved the ability of street sweepers to pick up coarse and fine sediments. It was found that a combination of mechanical and regenerative air street sweepers increased the efficiency by more than 80% of fine sediment removal compared to either technology alone.

1.6 Road Deposited Sediment

Road deposited sediment has been found to be enriched with anthropogenic contaminants in many studies (Li et al. 2015; Bian and Zhu 2008; Sutherland et al. 2012). These may come from vehicle exhaust, tires and body wear, brake-lining, construction debris, road salt, road paint and pedestrian debris, or natural sources such as soil material, yard litter, and atmospheric deposition (Loganathan et al. 2013). The presence of heavy metals in RDS is of concern to researchers and community stakeholders.

The contaminants often found in cities as well as urban areas impact human health and ecosystem health. In grain-size fractionated RDS and urban runoff analyzed for heavy metal content it was determined that most the metal loading on RDS was found in the small grain size (<250µm), about 80% (Zhao et al. 2010). Research that split the RDS into six categories of sediment by grain size shows that lead is found to be present in higher concentrations in the fine grain-size fractions (<1000µm) of RDS (Sutherland 2003). Not much difference was found between concentrations in the grain-size fractions of sediment below 1000µm. This study builds on these findings to present a novel method for calculating the total loading of heavy metals in the study site.

Impervious roads at three urban land use types with varying road-surface conditions were studied in a study site in a district of Beijing (Zhao et al. 2010). Most of the metal loading on RDS was found in the small grain size (<250µm), about 80%. This is the grain size RDS that is more difficult for street sweepers to pick up. The metal concentration was found to exceed lowest screening effect levels and severe screening effect levels, indicating a moderate to severe impact on ecosystem health.

2 STUDY SITE

2.1 WATER QUALITY ON LONG ISLAND

The impaired waterways of the Atlantic Ocean and Long Island Sound Basin on Long Island have been examined in detail (Myers 2011). For the purposes of this study, the subwatersheds of Oyster Bay/Huntington Bay and South Oyster Bay/Jones Inlet are examined in further detail. This project focuses on street sweeping litter in the South Oyster Bay, Oyster Bay Harbor and Mill Neck Creek watersheds (**Figure 1**). **Table 1** lists the unincorporated hamlets and incorporated villages in these watersheds.

Figure 1. Town of Oyster Bay and Selected Intersecting Watersheds. This map shows the major watersheds associated with the Town of Oyster Bay boundaries. The Glen Cove Creek subwatershed in the Hempstead Harbor/Manhasset Bay Watershed had not been assessed at the time of this study.

2.1.1 Oyster Bay/Huntington Bay Watershed

On the north shore, the Oyster Bay/Huntington Bay watersheds within the study area are Mill Neck Creek, Oyster Bay Harbor, and tributaries and smaller waterbodies including Mill Pond, and Beaver Lake. The Mill Neck Creek and Oyster Bay Harbor have similar pollutants. These include pathogens, biological oxygen demand (BOD), and elevated nitrogen. Myers details how appropriate uses of waterways are impaired, how severely they are impaired, and by what pollutants, including urban runoff. Emphasis is on categorizing the severity of waterway impairment and describing the uses that are impaired.

2.1.1.1 Mill Neck Creek

About 93 percent of Mill Neck Creek is shut down year-round. Beaches are closed more than ten days a year. Fish and shellfish consumption should be limited in these areas due to water quality and presumed PCB accumulation in migratory fish species.

There are 10 municipalities in the study area including Glen Cove, Lattingtown, Glen Head, Bayville, Locust Valley, Matinecock, Brookville, Old Brookville, Upper Brookville, and Mill Neck. According to the recent Waterbody Inventory/Priority Waterbodies List, Mill Neck Creek faces water quality stress from the presence of pathogens, nitrogen, low dissolved oxygen, and possibly poly-chlorinated biphenyls (PCBs).

The sources of the pollutants are urban stormwater runoff and septic systems. Note that samples collected from the TOB Highway Department include RDS from unincorporated hamlets only (see **Table 1**). Some of the municipalities in the Mill Neck Creek subwatershed are unincorporated and therefore served by the TOB Highway Department.

2.1.1.2 Oyster Bay Harbor

The municipalities in the study site that intersect with the Oyster Bay Harbor watershed include Oyster Bay, Centre Island, East Norwich, Muttontown, Oyster Bay Cove, Syosset, Woodbury, Laurel Hollow, Cove Neck, and Lloyd Harbor. Oyster Bay Harbor is categorized as an impaired waterway. The pollutants responsible for the water quality issues are the presence of pathogens, nitrogen, low dissolved oxygen, and possibly poly-chlorinated biphenyls (PCBs). The sources of the pollutants are municipal discharge, migratory species, urban stormwater runoff, and septic systems (NYS DEC 2016).

Mill Pond is in the Oyster Bay Harbor watershed. It is considered impaired from phosphorous pollution, suspected to be from urban and stormwater runoff. The focus of this project exclusively looks at street sediment, which is a principal contributor to stormwater pollution.

The water quality issues discussed above impact shellfishing, public bathing, recreation, aquatic life, and fish consumption. These economic and public uses are curtailed by current water quality, which translates into direct economic losses. Beach advisories and closures are sometimes called more than ten times a year. Shellfishing is restricted to certain parts of the Bay only at specified times of year. Aquatic life is limited by low dissolved oxygen. Fish consumption is restricted to one meal per week.

2.1.2 South Oyster Bay/Jones Inlet

The South Oyster Bay watershed includes municipalities in the Town of Oyster Bay including North Massapequa, East Massapequa, Massapequa Park, Massapequa, Bethpage, Plainedge, Seaford. It is classified for shellfishing, public bathing, recreation, aquatic life, and fish consumption. It is listed as an impaired waterbody by the New York State Department of Environmental Conservation (NYSDEC). There is known shellfishing and fish consumption impairment due to pathogens from urban stromwater and runoff and possibly PCB levels. Public bathing and aquatic life are fully supported uses of South Oyster Bay. However, recreation is considered threatened due to the shellfish and fish consumption restrictions.

The tidal tributaries to South Oyster Bay include Massapequa Creek, Amityville Creek, Narraskutuck Creek, Carmans Creek, and Jones Creek. These waterbodies are classified for recreation, aquatic life, and fish consumption. The recreation and fish consumption uses are restricted due to pathogens and possibly algae growth due to urban stormwater and runoff. The recreation uses of these tributaries are considered stress due to restrictions on fish consumption. The Massapequa Creek subwatershed includes the municipalities of Farmingdale, South Farmingdale, Old Bethpage, Woodbury, Syosset, and Plainview. It is polluted by phosphorous and pathogens from urban runoff and non-permitted or illicit discharges. Note that the TOB Highway Department dump site ("the dump site") is in Syosset, which is in this subwatershed.

2.1.3 East Bay

East Bay is classified as an impaired waterbody. It has been assessed for shellfishing, bathing, recreation, and fish consumption use. While shellfishing is known to be impaired, it is suspsected that bathing, recreation and fish consumption are stressed by pathogens and possibly PCBs. The known source of pollutants is urban stormwater and runoff.

Table 1. Unincorpoated Hamlets and Incorporated Villages in TOB. This table shows which municipalities are unincorporated, and therefore possibly included in the study, and those that are incorporated, who manage their own street sweeping.

Unincorporated Hamlets (included in study)	Incorporated Villages
Bethpage	Bayville
East Massapequa	Brookville
East Norwich	Centre Island
Glen Head	Cove Neck
Glenwood Landing	East Norwich
Greenvale	Farmingdale
Hicksville	Glen Head
Jericho	Lattingtown
Locust Valley	Laurel Hollow
Massapequa	Massapequa Park
North Massapequa	Matinecock
Old Bethpage	Mill Neck
Plainedge	Muttontown
Plainview	Old Brookville
South Farmingdale	Oyster Bay
Syosset	Oyster Bay Cove
Syosset	Roslyn Harbor
Woodbury	Upper Brookville

2.2 Streetsweeping in Town of Oyster Bay

Streetsweeping is conducted on a scheduled basis for five days a week during certain weeks and on an as needed basis on larger roads. The streetsweepers use mechanical brushes as the primary mechanism of removal. A water spray is employed to reduce the ejection of fines into the air during streetsweeping. In general, the machines carry about a hundred gallons of water, which is enough to spray water for about half of a working day. There used to be vacuums on the machines, however it was decided that the vacuums would not be used because it could not be determined whether they were better at picking up wet sand and fines.

3 METHODS

3.1 DISCOVERY

This paper presents original research based on a novel approach to sampling RDS from a street sweeper litter dump site. Other studies have used methods of extraction from the street or site where the source of the sediment is (Brinkmann 2001). However, in this study, the sediment is collected from a storage site. This makes the step of collecting samples much easier.

The early stages of this project included discovery about the feasibility of the study and would determine the method used to collect the soil sediment. Contact was made with representatives of these municipal governments, and additionally representatives from Hempstead Harbor, Oyster Bay/Coldspring Harbor, and Lattingtown. In incorporated villages information about the presence of a street sweeping program or lack of street sweeping and parties involved was not readily available. It was determined that hamlets in TOB, if they were unincorporated, had their streets swept by TOB.

Upon contacting the director of the Town of Oyster Bay Highway Department (TOBHD) and explaining the needs of this project, it was discovered that TOBHD building was also a dump site for all the street sweeper litter for unincorporated hamlets. Thus, the decision to make the TOBHD building the site for sample collection was one of convenience. So, sample collection was conducted rather than collecting street sweeper litter directly from specific villages. To collect these samples, contact was made with the commissioner of the TOB Highway Department for three reasons:

1. To establish contact and a line of communication;
2. To introduce the current project; and,
3. To gain permission to collect sediment samples.

When permission had been granted, the next step of the process was to schedule a time and place to collect the samples. The street sweeping program generally begins in May. It is collected at intervals. In May, one container was obtained from the street sweeping material. The next sample was taken in September. Then, four 5-gallon food-grade buckets from Home Depot were partially filled with sediment from one main dump site. The sampling plan is pictured below (add picture). The next samples were taken in November, from a different part of the dump site.

Once the samples were acquired, they were transported and stored. The standard procedure for the non-volatile components that will be analyzed, being heavy metals, is to store the samples in a refrigerator. However, for the purposes of this study, the samples were stored at room temperature in a laboratory. These methods should adhere to the standard method and provisions for metals and nutrients (US EPA 1994).

3.2 Sample Bias

The samples were collected from various locations on the surface of the dump site behind the Highway Department building. The dump site contains RDS from across the unincorporated hamlets of TOB. So, there is no information about where a sample specifically came from.

The samples are representative of the sediment that is collected by street sweepers and present on the streets pre-sweeping. This means that the samples collected have been removed from the roads, and therefore are not necessarily flushed to the bays and waterways. Furthermore, the samples do not represent the RDS that is not removed by street sweepers. Typically, street sweepers remove a higher proportion of coarse sediments, leaving behind more fines.

Current street sweeping technology can collect a broad range of particle sizes and is therefore assumed to pick up at least some of the fine-sized grains. It is assumed that the remaining sediment will have a higher proportion of fine-sized grains than the roads pre-sweeping.

3.3 Sample Preparation

The sample preparation involved the sieving separation, fine-sieving, and finally encapsulation of the samples in x-ray transparent tubes. First, the bucket samples were rough sieved using 5000 µm sieves. Leaves and twigs and other larger debris was discarded at this stage. Then, the sediment was separated into three sub-samples. These sub-samples were each sieved using a full set of sieves between -1.0 and 4.0 phi on the Krumbein phi scale on a table shaker.

In addition, a simplified sieving procedure was used for the purposes of this study. Instead of a full set of sieves, three sieves including 2000µm, 354µm, and 63µm were used to sieve the samples to <63 micrometers. This process was repeated for three sub-samples in each of eight buckets. Then, the super-fines were spooned into x-ray transparent capsules for analysis. An analysis of the grain size fractionation is included in the results. In total, 41 readings were taken on 25 samples.

3.4 Sample Analysis

Hofstra University has on-site capacity for measuring heavy metals. A Portable X-Ray Fluourescence machine (pXRF) was used to analyze the heavy elements. In general, pXRF works by bombarding a dry sample with a single-wavelength electromagnetic radiation. Heavy elements reflect specific spectra of electromagnetic radiation when its electrons are excited. The machine can store the energy of the reflected spectra as data that are identifiable as a concentration of individual elements (“What is” 2016).

The portable x-ray fluorescence ray gun shoots x-rays through a window located on the bottom of the stand at a single capsule of soil. The x-rays excite electrons on the valence shells of heavy elements to jump out of their shells, which a detector then sends to a processor to analyze the presence of heavy elements. These results were recorded in a spreadsheet. One sample from each triplicate of sample buckets was analyzed three times. So, three random samples from each bucket were individually sieved and characterized using the pXRF.

3.5 Data Analysis

3.5.1 Statistical Analysis

Common statistical analyses for this type of data analysis include averages and 90 percent confidence intervals or error bars equal to sample standard deviation. Non-parametric statistical tests will be used to determine the differences in variance between buckets and between the months the samples were collected. A Mann-Whitney summed rank test is a non-parametric test used to test two groups of continuous data to identify differences in variance. A Kruskal-Wallis test is related to a Mann-Whitney summed rank test and is used when there are more than two groups of continuous data.

3.5.1.1 Censored Data

Censored data is a common issue in environmental data. For variables with missing data, substitution with the mean or a proportion of the limit of detection (LOD) is not a sufficient method of analysis. The reporting of variables with missing values requires special methods. For the purposes of this report, a maximum likelihood estimator made specifically to work with the type of left-censored data found in this report was used.

R is an open source statistical software program. It has tools to analyze censored environmental data. One of these tools is a package called NADA. This package was used to create boxplots for analytes with censored or missing data using the uncensored data and LODs, and determine the mean and standard deviation for cobalt and nickel (Helsel 2012).

3.5.2 Environmental Quality Standards for Soil

Urban soils are associated with public health, ecological, and groundwater risks. These risks are calculated based on potential exposures to a chemical, mode of ingestion, toxicity of the chemical, carcinogenicity, and other site-specific and chemical-specific factors. For the purposes of this study, various national and state soil quality standards were compiled to compare to the concentrations of heavy metals to identify heavy metals of concern for future research (**Table 2**).

Table 2. Summary of Selected Actionable Thresholds. The collected soil quality standards from nations and states representing concentration thresholds for several of the tested analytes.

Analyte	EPA Regional Screening Levels (RSL) (mg/kg)[1]	Target Substances and Standards (Japan) (mg/kg)[1]	Soil and Groundwater Intervention Values (Netherlands) (mg/kg)[1]	Soil Quality Guidelines (Canada) (mg/kg)[1]	Assessment Levels for Soil (Australia) (mg/kg)[1]	Soil Guideline Values (UK) (mg/kg)[1]	NYS DEC Public Health Soil Cleanup Objectives (mg/kg)[1]
Antimony	31		22	20	31		
Arsenic	39	150	76	12	100	32	16
Barium	15000			500	15,000		350
Cadmium	71	150	13	10	20	10	0.86
Calcium							
Cesium							
Chromium	230			64			22
Cobalt	23		190	50	100		
Copper	3100		190	63	1000		270
Gold							
Iron	55000						
Lead	400	150	530	140	300		400
Manganese	1800				1500		2000
Mercury	11	15		6.6	15	1	0.81
Molybdinum	390		190	10	390		
Nickel	1500		100	50	600	130	140
Palladium							
Potassium							
Rubidium							
Scandium							
Selenium	390		100	1		350	36
Silver	390		15	20			36
Strontium	47000						
Sulfur							

Analyte	EPA Regional Screening Levels (RSL) (mg/kg)[1]	Target Substances and Standards (Japan) (mg/kg)[1]	Soil and Groundwater Intervention Values (Netherlands) (mg/kg)[1]	Soil Quality Guidelines (Canada) (mg/kg)[1]	Assessment Levels for Soil (Australia) (mg/kg)[1]	Soil Guideline Values (UK) (mg/kg)[1]	NYS DEC Public Health Soil Cleanup Objectives (mg/kg)[1]
Tellurium			600				
Thorium							
Tin	47000		900	50	47000		
Titanium							
Tungsten	63						
Uranium	230			23			
Vanadium	390		250	130	550		
Zinc	23000		720	200	7000		2200
Zirconium	6.3						

[1]mg/kg = milligrams per kilogram

3.6 Loading

A novel approach to calculating metal loading was developed to determine the ecological impact of RDS in the study site. The equation uses a value of 80 percent for the assumed total loading in the fine sediments (<354µm) in accordance with background information found. For the purposes of this baseline study, the first to characterize Long Island RDS, the loading is equal to the concentration of a heavy element divided by the proportion of fines (<354µm) to total sediment (<2000µm) not including the largest sediment (<5000µm) and discarded sediment (>5000µm) divided by the proportion of total loading found in the fine sediments times the weight of RDS removed annually from the TOB roadways. In other words,

$$Total\ Loading = \frac{Concentration\left(\frac{mg}{kg}\right)}{80\%}\ x\ RDS(kg)\ x\,\frac{Fines}{Total}\,(\frac{g}{g})$$

Note that in the denominator, Very Fines/Fines Total corrects the concentration assuming an equal even distribution of heavy metals in the fines (<354µm) and the very fines (<63µm). This method can be used because the concentration of heavy metals is assumed to be equally evenly distributed through the fines.

Furthermore, the 80 percent figure, as discussed above, is used to correct for the loading factor on the fines compared to the total sediment (<2000µm) as found in the literature. This is not a correction for weight, but of the loading. Therefore, the concentrations are not necessarily the same. Instead the assumption is that we find 80 percent of the loading in the sediments we measured (with corrections for fine sediments (<354µm). Therefore, the correction factors on load, not on sample weight.

The amount of annual RDS is based on a volume that was provided by the commissioner of the TOB Highway Department to the nest of their knowledge. The amount of RDS is known because the waste hauler weighs the trucks of street sweeper litter to tabulate the cost of disposal.

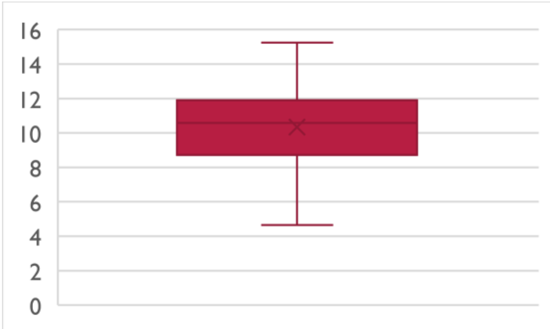
The volume is used to determine the cost of disposal of the sediment rather than a weight because of the change in density of wet sand to dry sand. The density of the sample was measured to calculate the dry weight of the sand. The RDS collected by the street sweeping program is landfilled at intervals.

The amount of sediment with heavy metal loading contained in the annual RDS is unknown. The RDS that is removed from roads includes leaves, twigs, litter, pebbles, and other types of sediment that may or may not have heavy motel contamination associated with them. So, it is unknown how much of the RDS that is collected may impact the heavy metal exposure of waterbodies and groundwater. Furthermore, the distribution of grain size fraction is expected to be different after street sweeping because the RDS that is removed tends to be larger grained fractions.

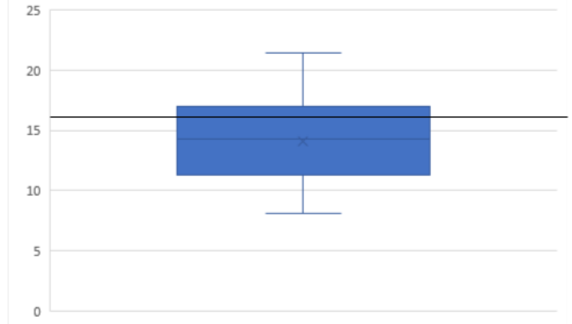
4 RESULTS

The pXRF tested the following thirty-three heavy metal components: Antimony, Arsenic, Barium, Cadmium, Calcium, Cesium, Chromium, Cobalt, Copper, Gold, Iron, Lead, Manganese, Mercury, Molybdenum, Nickel, Palladium, Potassium, Rubidium, Scandium, Selenium, Silver, Strontium, Sulfur, Tellurium, Thorium, Tin, Titanium, Tungsten, Uranium, Vanadium, Zinc, and Zirconium. Where heavy metals were detected, they were compared to environmental quality standards for soil from the National EPA (NEPA) and NYSDEC. The loading on waterways by RDS was calculated with available estimates of annual RDS removal.

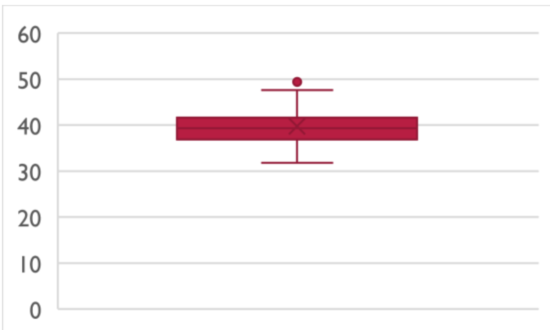
Descriptive statistics were used to analyze the data collected from the grain-size fractionation and x-ray analysis. This included graphing the averages of grain-size partitions (**Figures 3, 4, and 5**) and boxplots of heavy metal concentrations (**Figures 2 and 6**).



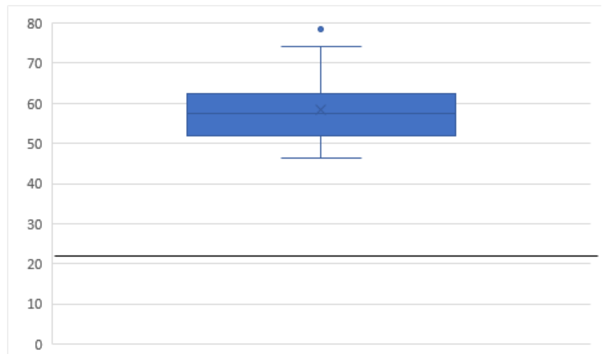
Thorium



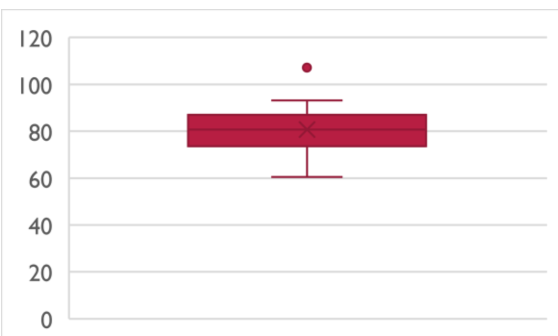
Arsenic[1]



Rubidium



Chromium[1]



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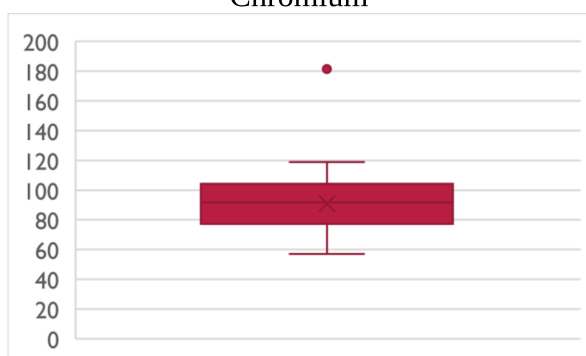
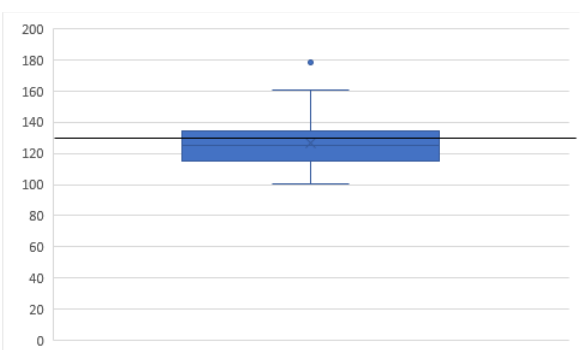
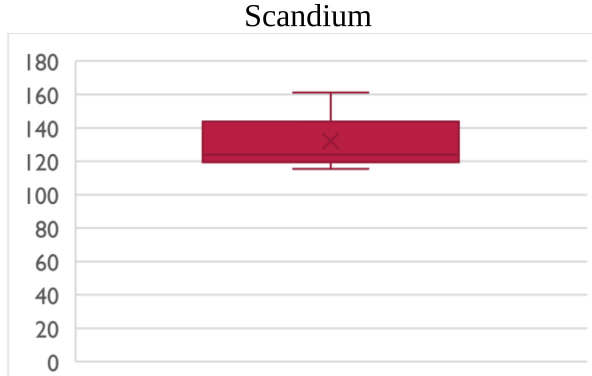


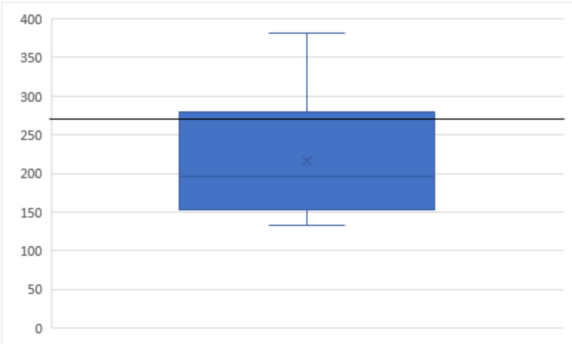
Scandium



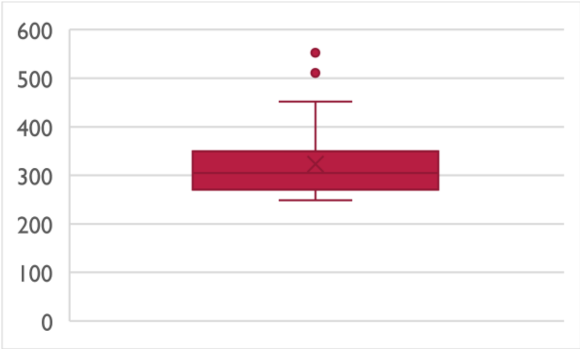
Vanadium[2]



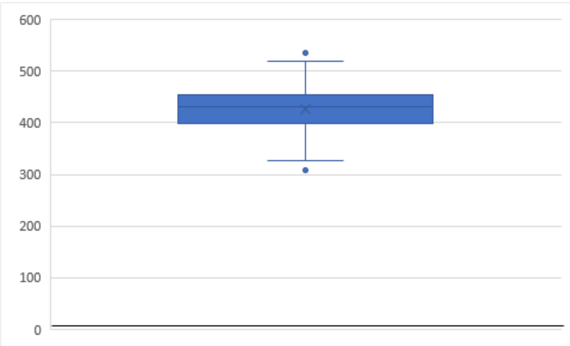
Strontium



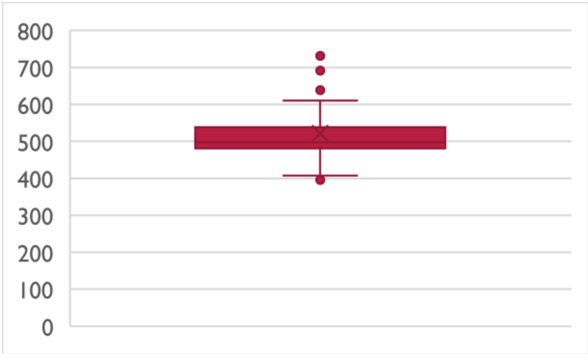
Copper[1]



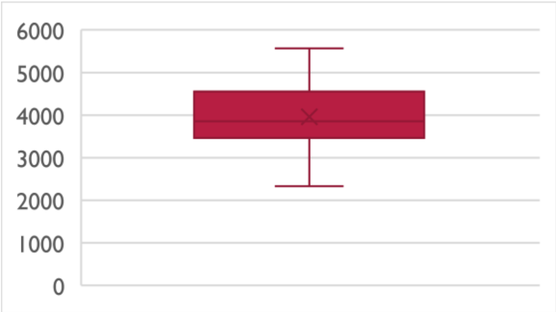
Zinc



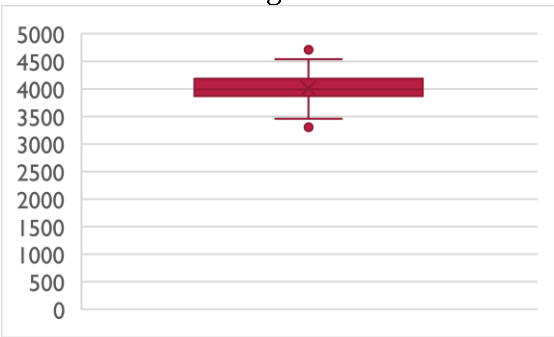
Zirconium[3]



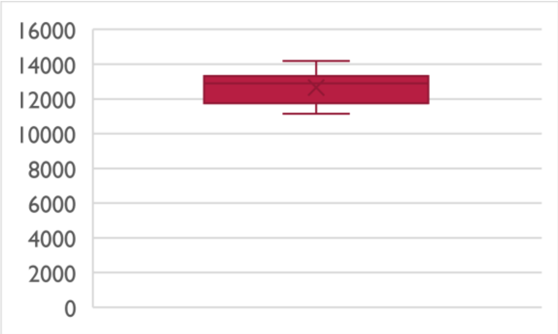
Manganese



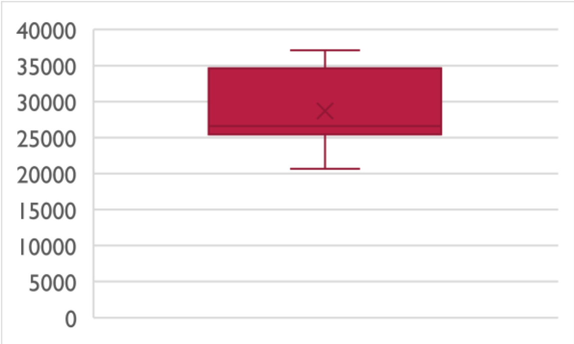
Sulfur



Titanium



Potassium



Iron

Calcium

[1]New York State Department of Environmental Conservation Soil Cleanup Objective
[2]Canadian Soil Quality Guideline
[3]United States National Environmental Protection Agency Regional Screening Level

Figure 2. Boxplots of Analytes with Selected Soil Quality Standards. These boxplots represent the distributions of concentrations of elements. Where shown, the respective SQS is labelled on the graph. This data shows an element's quantile relative to a relevant action threshold.

4.1 Soil Quality Standards Analysis

This section describes the elements that were found to exceed a threshold for soil quality standards (SQSs). The United States National Environmental Protection Agency Regional Screening Levels (NEPA RSLs), New York State Department of Environmental Conservation Soil Cleanup Objectives, Canadian Soil Quality Guidelines, and Dutch Soil and Groundwater Intervention Values are included in this section.

4.1.1 NEPA Regional Screening Level (RSL)

The levels of zirconium exceed National EPA Regional Screening Levels (EPA RSLs) by more than an order of magnitude. Levels of cobalt exceeded the EPA Regional Screening Levels. One bucket sample showed consistently elevated levels of zinc compared to EPA RSLs.

4.1.2 NYSDEC Soil Cleanup Objectives (SCOs)

Measured levels of chromium exceed SCOs. Five out of eight bucket samples had one or more sub-samples exceeding the New York SCOs for arsenic; four of eight buckets had one or more sub-samples exceeding SCOs for copper; and, one reading showed elevated levels of Barium.

4.1.3 Soil Quality Guidelines (Canada)

Copper, zinc, cobalt; more than half of readings of arsenic, vanadium; and half or fewer readings of nickel and chromium exceed the Canadian Soil Quality Guidelines. One reading of molybdenum was above the Canadian guideline. Note that Canada has the stricter levels of the SQSs found during this report for almost all the standards that it includes.

4.1.4 Soil and Groundwater Intervention Values (Netherlands)

More than half of copper readings represented values above the threshold for Dutch Intervention Values (Rijkswaterstaat 2013). Even though not all readings of copper were above NYSDEC SCOs, many were above Dutch soil intervention values and all were above Canadian soil quality guidelines. This suggests that it may be of interest to future research.

4.2 Grain-Size Fractionation Analysis

A grain size fraction shows that the largest grain size fraction was found in 2000-5000μm region (**Figure 5**). This suggests a large portion of the RDS collected by street sweepers is larger than that that is believed to bear significant loading. Unlike previous studies that sampled RDS from roadways, this is a sampling of RDS collected by street sweepers. The grain size fractionation suggests that vacuum sweeper technology may be a useful tool for removing higher amounts of fine particulates.

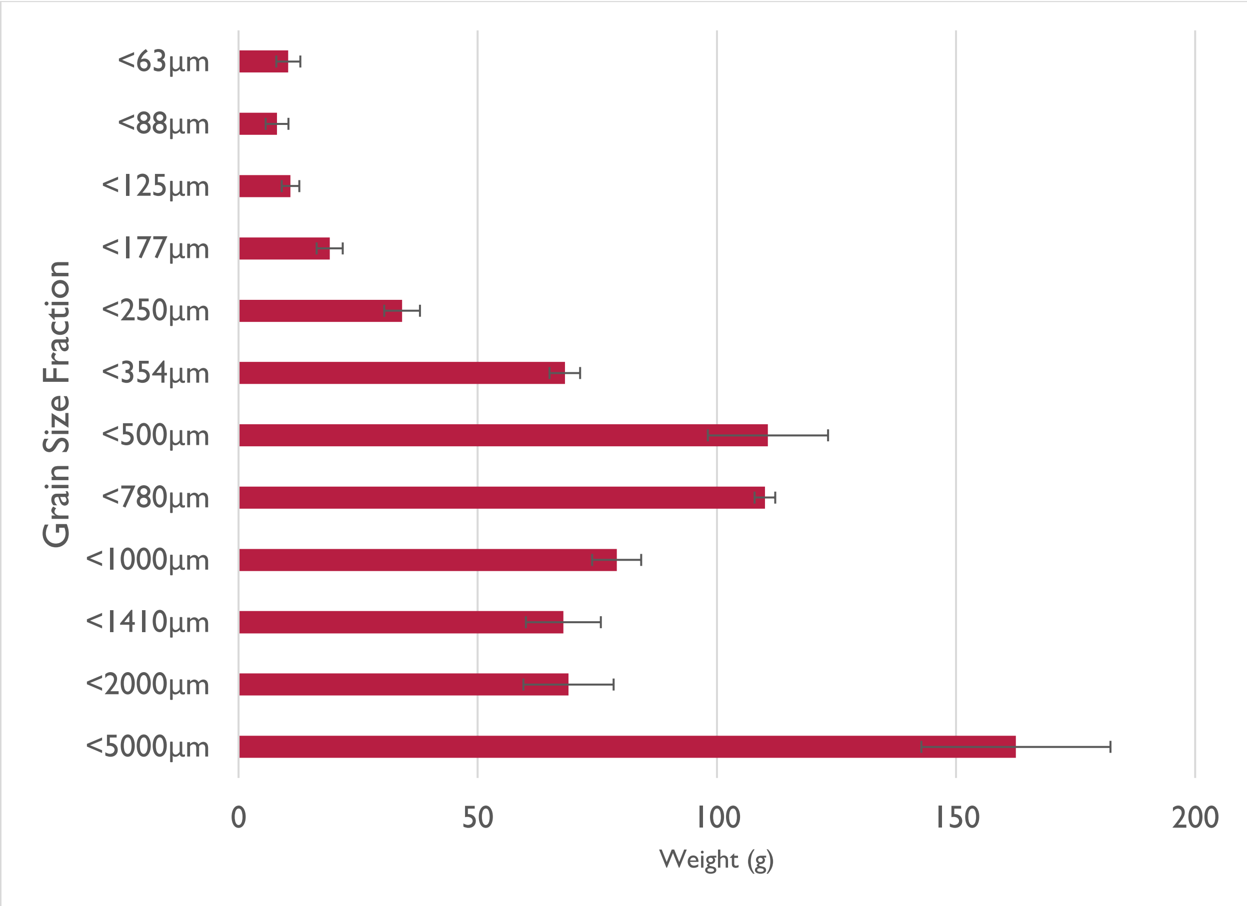


Figure 3. Grain Size Fractionation. This figure shows the weight distribution of phi levels and mid-phi levels on the Krumbein phi scale. The sediment above 5000µm was discarded.

An analysis of the grain size fractionation using a full set of sieves compared to the simplified sieving process showed no difference in the amounts of sediment collected across particle sizes by weight, meaning that the sum of the samples sieved into smaller fractions was equal to the fractions that were sieved using fewer sieves (**Figure 4**).

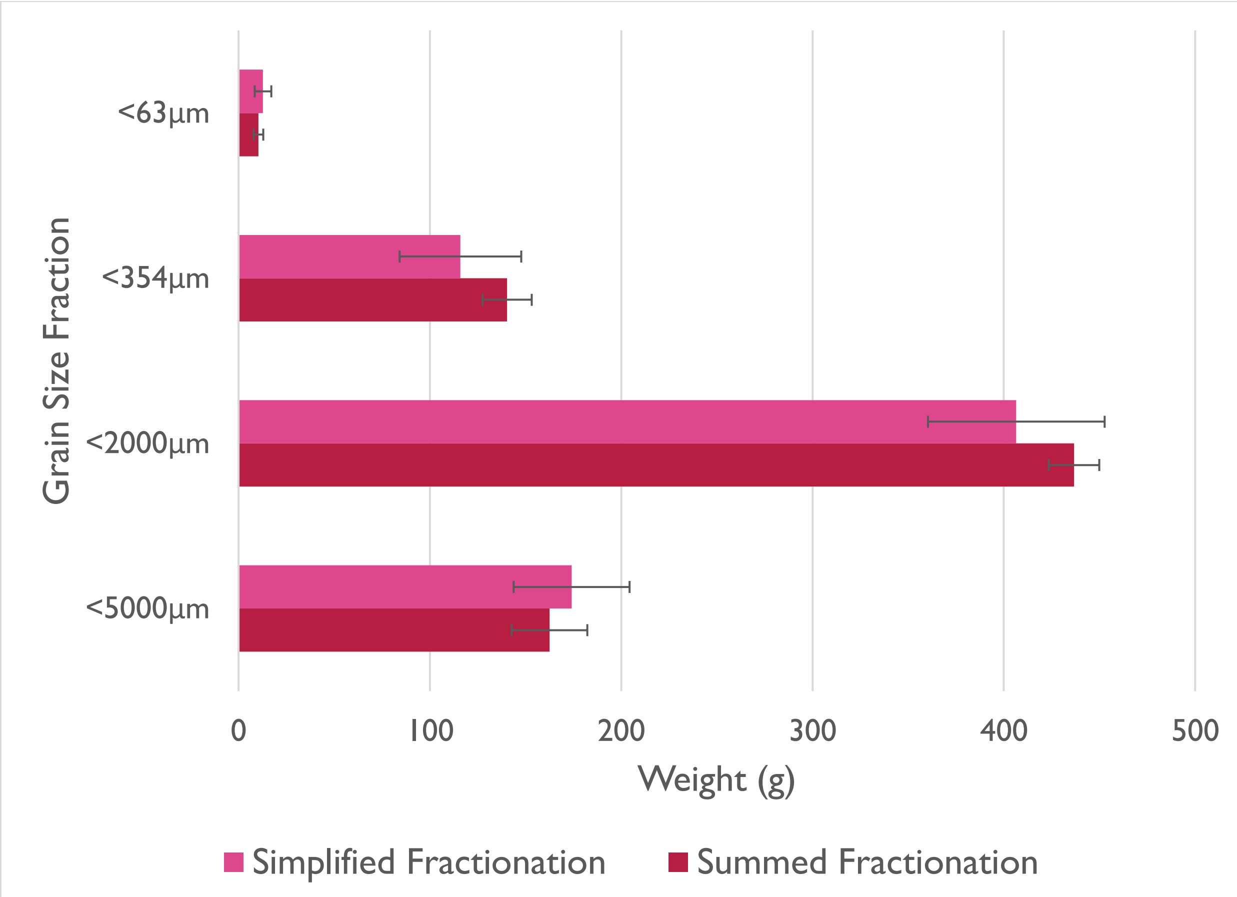


Figure 4. Grain Size Fraction Methods Comparison. Side-by-side comparison of the sums of the equivalent grain size fractionation of the simplified method of three sieves.

This is evidence that the sieving procedure was appropriate and did not alter the weights of sediment collected by diameter. The fine grain size sediment was found to be approximately 18 percent of the total sediment collected (**Figure 5**).

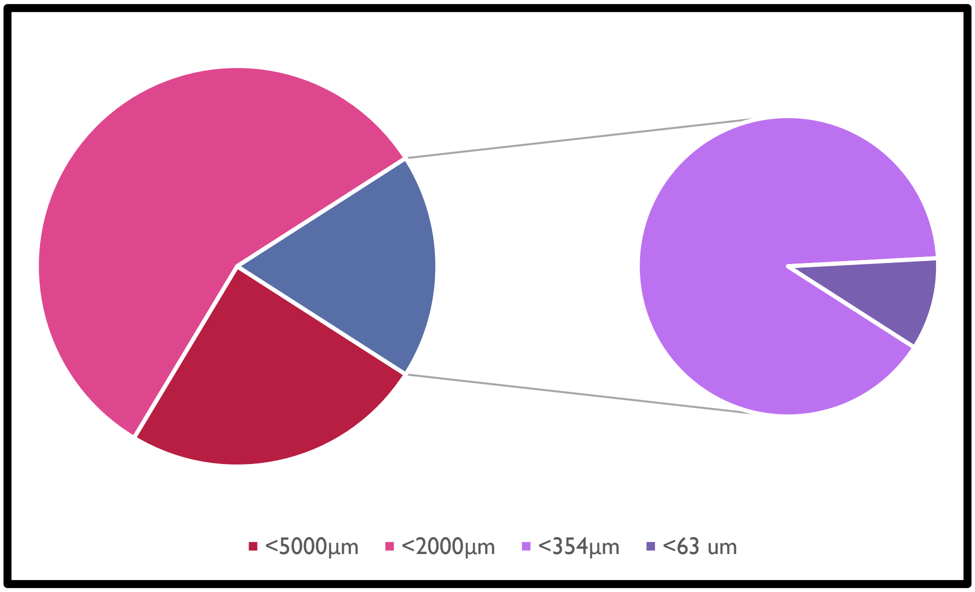


Figure 5. The Average Contribution of Grain Size Fractions by Weight. The very fines (<63µm) make up less than 2 percent of the total sediment measured. Of the total fines (<354µm), the very fines make up about 10 percent.

4.3 Data Analysis

4.3.1 Variability

A Kruskall-Wallis test was preformed to determine whether the concentration of an element was affected by bucket. This test is related to a Mann-Whitney ranked sum test and is used to test variance when there are more than two groups of data, such as the buckets. There was a statistically significant difference between the distributions of readings of specific elements between buckets and between months collected. Essentially, the variances of several elements are different between at least two buckets.

A Mann-Whitney ranked sum test was performed to determine whether the concentrations of an element was affected by the collection month. There was a statistically significant difference between the distributions of readings of specific elements between collection months. This suggests that variances of several elements are different between months.

4.3.2 Outliers

The calculation of outliers can be an indicator that some batches had anomalous values for some values, which might require further investigation. Five out of eight buckets had samples with readings that were outliers in at least one heavy metal concentration. There were 15 subsamples that had readings with minor outliers for at least one element. Seven samples had values that were outliers for at least two elements.

There were outliers found in at least one reading for the following 11 elements: Zirconium, Rubidium, Lead, Zinc, Tungsten, Manganese, Chromium (total), Titanium, Cobalt, Tin, and Selenium. And, there were three or more minor outliers for the following four elements: Zirconium, Zinc, Manganese, and Titanium. This suggests that these elements were particularly prone to outlier data for some reason.

4.4 Loading

The loading is calculated based on the findings of previous studies of the street sweepings that remain on the roads after a street sweeper collects the RDS (**Table 3**). In those studies, there was a large fraction of the loading on RDS found in the fines (<250µm). About 80 percent of loading was found in this fraction, with little or no difference in the concentrations of heavy metals. Based on this information, the loading of heavy metals on roadways can be calculated using the equation above.

Table 3. Loading Calculation Values. This table shows the values used to calculate loading of heavy metals on TOB roadways. The RDS remaining on the roads more closely resembles the distribution of that of previous research, with about 80 percent of loading on the fines (<354μm). The sand (<2000μm) accounts for about 80 percent of the total sediment (<5000μm). Density was measured to be 1224 kg/m^3 to estimate the weight of annual RDS. The rightmost column details the amount of heavy metal loading removed each year from roadways.

Analyte	**Concentration (mg/kg)**	**Annual Volume RDS (yd3)**	**Estimated Annual RDS (kg)**	**Percent Loading**	**Percent Fines**	**Adjusted Loading (kg)**
Mo[1]	5.04	1500	1.4E+06	80%	25%	2.21
Zr	426.48	1500	1.4E+06	80%	25%	187.08
Sr	132.15	1500	1.4E+06	80%	25%	57.97
U[1]	6.59	1500	1.4E+06	80%	25%	2.89
Rb	39.76	1500	1.4E+06	80%	25%	17.44
Th	10.34	1500	1.4E+06	80%	25%	4.53
Pb	80.65	1500	1.4E+06	80%	25%	35.38
As	14.11	1500	1.4E+06	80%	25%	6.19
Zn	323.08	1500	1.4E+06	80%	25%	141.73
W[1]	39.22	1500	1.4E+06	80%	25%	17.20
Cu	216.89	1500	1.4E+06	80%	25%	95.14
Ni[1]	38.54	1500	1.4E+06	80%	25%	16.91
Co[1]	88.12	1500	1.4E+06	80%	25%	38.66
Fe	28700.81	1500	1.4E+06	80%	25%	12590.00
Mn	522.24	1500	1.4E+06	80%	25%	229.09
Cr	58.30	1500	1.4E+06	80%	25%	25.57
V	126.47	1500	1.4E+06	80%	25%	55.48
Ti	4007.21	1500	1.4E+06	80%	25%	1757.82
Sc	90.89	1500	1.4E+06	80%	25%	39.87
Ca	44976.63	1500	1.4E+06	80%	25%	19729.60
K	12658.70	1500	1.4E+06	80%	25%	5552.91
S	3963.54	1500	1.4E+06	80%	25%	1738.66
Ba[1]	236.83	1500	1.4E+06	80%	25%	103.89
Cs[1]	14.29	1500	1.4E+06	80%	25%	6.27
Te[1]	21.82	1500	1.4E+06	80%	25%	9.57
Sb[1]	10.30	1500	1.4E+06	80%	25%	4.52
Sn[1]	9.39	1500	1.4E+06	80%	25%	4.12

[1]Calculated using a maximum likelihood estimator

4.5 CENSORED DATA

The following section details elements that had censored values below the limit of detection (LOD). The pXRF user manual details the LOD to be equal to three times the standard deviation of the concentration of the analyte. An element concentration will be uncensored if it is equal to 1.5 times the precision, which is defined as two times the standard deviation. These values are dependent on the composition of the sample and the other elements in the analysis. **Table 4** details the percent of censored data by analyte. **Figure 6** is a group of boxplots of the censored values with a horizontal line representing the highest LOD.

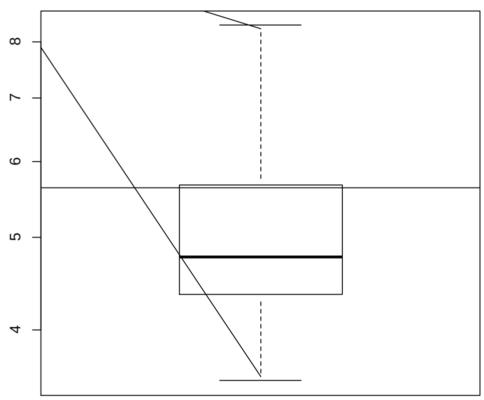
Table 4. Percent Censored Data.

Analyte	Percent Censored (%)
Cobalt	2.439024
Nickel	12.19512
Barium	12.19512
Cesium	12.19512
Molybdenum	26.82927
Tin	48.78049
Uranium	51.21951
Tellurium	60.97561
Antimony	65.85366
Tungsten	90.2439
Mercury	97.56098
Cadmium	97.56098
Gold	100
Selenium	100
Silver	100
Palladium	100

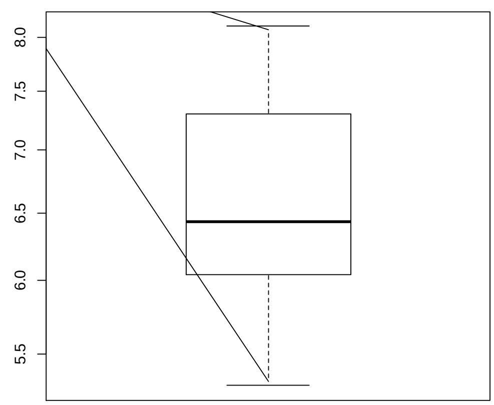
Gold, selenium, silver and palladium were not reported above the LOD. Their highest LODs were 8.60 ppm, 5.45 ppm, 8.64 ppm, and 9.93 ppm, respectively. Instead of doing statistics on the LODs, it is more accurate to report that the values are between zero and the highest respective LOD.

The following heavy elements were detected in only one sample batch: mercury and cadmium. Their levels were 13.2 ppm and 8.16 ppm, respectively. The highest LODs for mercury and cadmium were above the highest uncensored data, at 16.53 ppm and 12.27, respectively. This means that the uncensored readings should be considered invalid. However, the mercury anomaly is above the EPA regional screening levels of 11 ppm. The cadmium anomaly exceeds the NYSDEC target value for Public Health in a residential area of 0.86 ppm.

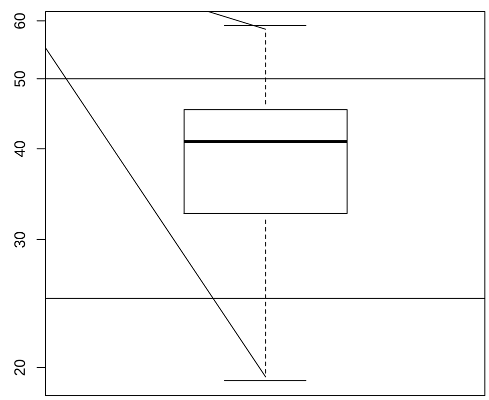
Tungsten was found in four samples. Over 90 percent of data for tungsten were censored. The highest LOD for tungsten exceeded the highest uncensored data point, being 55.47 ppm and 48.00 ppm, respectively. So, the readings for tungsten should be considered invalid.



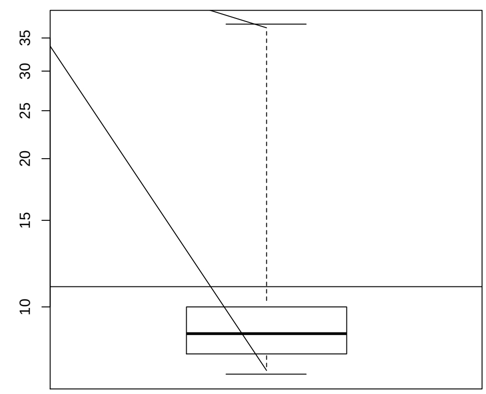
Molybdenum



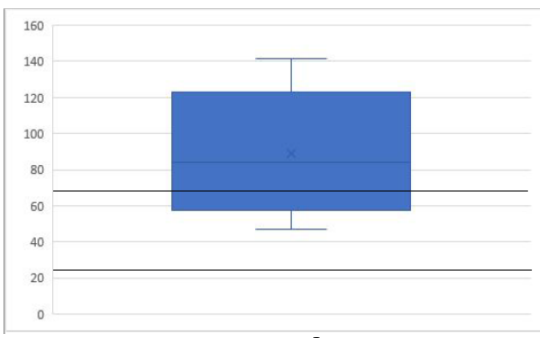
Uranium



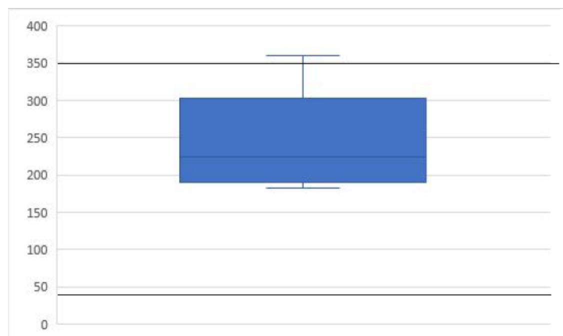
Nickel[1]



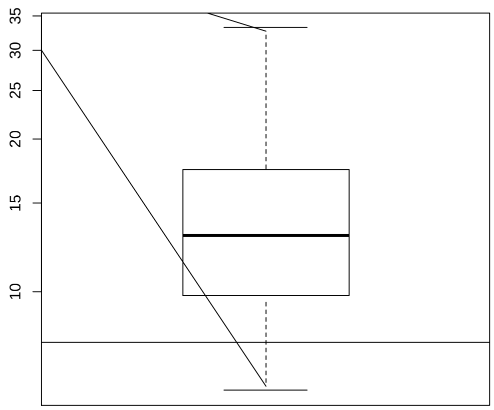
Tin



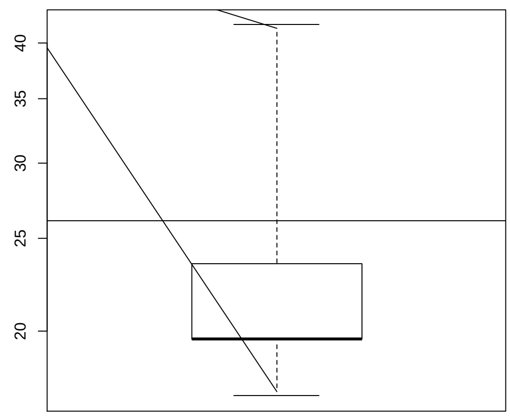
Cobalt[3]



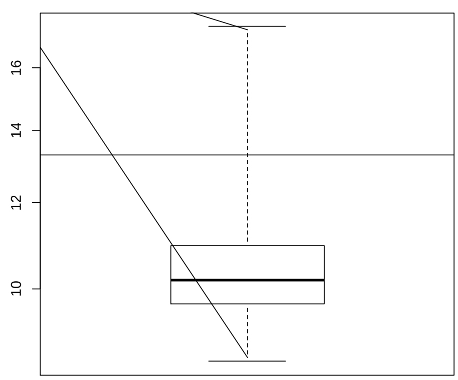
Barium[2]



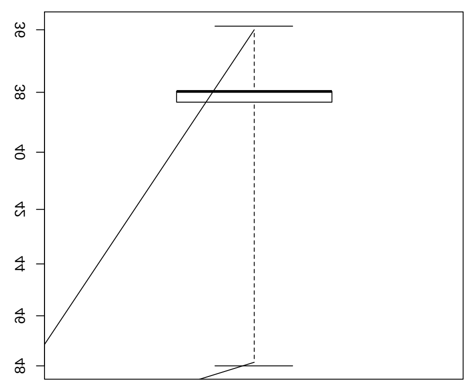
Cesium



Tellurium



Antimony



Tungsten

[1]Shows the Canadian action threshold for nickel at 50 ppm above its highest limit of detection.
[2]This quantile was calculated using a regression on ordered statistics. It shows the NYSDEC action threshold for barium at 350 ppm. The highest LOD is 36.975 ppm.
[3]This quantile was calculated using a regression on ordered statistics. It shows the NEPA action threshold for cobalt at 23 ppm, and the highest LOD of 68.55 ppm.

Figure 6. **Boxplots for Analytes with Censored Data.** The horizontal lines represent the highest LODs for each analyte. Some LODs were higher than the highest uncensored data point, and were omitted from the graph. The vertical axes on all graphs are in parts per million. Cadmium and mercury were not included because they only had one uncensored value that were below the highest limit of detection, and therefore should be considered invalid. Analytes with 100 percent censored data were not included. So, what is noticeable from these graphs is that the highest LODs sometimes exceed the majority of uncensored data. Any data below this threshold should

be viewed as invalid. This includes all of the tungsten and uranium data. On the other hand, all of the barium concentrations are valid, including one above the NYSDEC SCO of 350 ppm. Of note in this group of graphs is that although cobalt has an LOD that exceeds about a quarter of reported values, much of the uncensored data is above the reporting limit and the NEPA RSL of 23 ppm. This value is not shown because it is below the range of the chart.

5 Discussion

Road deposited sediment is a form of urban soil that is characterized by high levels of contamination from various human activities. The study of RDS can solve policy and environmental quality research questions: geographic hotspots of high levels of contaminants found in roadways, how to store street sweeper litter, how often to sweep streets, and ecological and human health risks. This paper challenges to assess with broad strokes the contents of RDS on Long Island and compares them to available environmental quality standards.

5.1 Heavy Metals In Road Deposited Sediment In Town of Oyster Bay

The RDS on Long Island does contain significant amounts of heavy metals. However, most of the heavy metals tested are below the soil quality standards found during this research, or did not have soil quality standards associated with them. Five contaminants did appear to breach the threshold for health safety according to the EPA or NYSDEC, including zirconium, cobalt, chromium, copper, and arsenic, although arsenic had half or fewer readings above its NYSDEC soil cleanup objective (SCO).

a) According to the Canadian Soil Quality Guidelines, about 68 percent of arsenic readings exceeded the guideline. In addition, about 24 percent of readings were above the NYSDEC SCO for arsenic.

b) Chromium exceeded the SCO for hexavalent and trivalent chromium. While the measured chromium levels represent total chromium, the effective total chromium SCO is considered the stricter of the hexavalent and trivalent oxidation states or 22 ppm. All readings of all sub-samples were more than twice that threshold.

c) Copper exceeded the Canadian Soil Quality Guidelines; 54 percent of readings breached the Dutch threshold for Soil Intervention Values; and, 32 percent of readings were above the SCO for copper.

d) The levels of levels of cobalt consistently achieved the threshold for RSL in all but one sample that was below the measurement detection for the pXRF. All positive readings were more than twice the screening level of 23 ppm, with the lowest reading being equal to 47.03 ppm.

e) The largest breach of a soil quality standard was by zirconium. Levels of zirconium exceeded the NEPA RSLs by almost two magnitudes of order. While the RSL was 6.3 ppm, the readings had a mean of 426.5 ppm with a standard deviation of 55.0 ppm.

f) Zinc, vanadium and nickel exceeded the Canadian Soil Quality Guidelines and no other SQSs.

g) Molybdenum and barium had one reading that exceeded their respective minimum SQS.

5.2 Loading

The weights of heavy metals that are collected in the column labeled "Adjusted Loading" in **Table 2** are estimates of the annual heavy metals remaining on roadways. Although, the amount of sediment remaining after street sweeping is unknown, the loading can be estimated based on three values:

a) the concentrations of heavy metals on the very fine sediments (<63 μ m);

b) the total annual weight of RDS; and,

c) the proportion of fines (<354 μ m) to sand (<2000 μ m).

Previous studies have determined the loading found on street sweepings are found mostly in the small grain size fractions (<250μm). Although the street sweepers remove much of these sweepings, the assumption of loading is still useful, since the loading on the remaining RDS is found in this same fraction. So, the distribution of the remaining sediment is not necessary to determine the loading. On the other hand, the amount of remaining sediment and its grain size distribution is unknown. This is a best estimate based on the available information.

5.3 Statistical Analysis

The results of statistical tests showed that the variances of some samples were different. This means that at least two buckets contained materials that had different levels of variability for certain elements. So, the distribution of heavy metal concentrations was different across buckets. The differences in variability can be attributed to the heterogeneity of solid samples, and spatial variations in materials collected at the dump site. To find out which buckets had different amounts of variability, further pairwise statistical tests are needed.

Despite statistically significant differences in variability between buckets and between months of collection, the 90 percent confidence intervals reveal that the data has relatively low distribution. Even though there were outliers in many sub-sample readings and heavy metal levels, the outliers were minor outliers, except for two readings of manganese that came from the same bucket sample. This is in part because the very fine particles (<63μm) tend to have lower variability, possibly because of the high surface area to volume ratio.

Overall, the variability of the samples is relatively low, which indicates that mixing took place during the collection and processing of samples for analysis. The sediment was transported by street sweeper basin to behind the highway department building and released at a dump site, allowing sediment from across the unincorporated hamlets to mix during transport and release of the sediment.

6 LIMITATIONS

These samples are sediment from roads before it has been transported by stormwater into the bays and surface waters being studied. So, the generalizability of these results to determine the contents of loading on waterways is limited.

It's not clear whether the soil standards for unrestricted use, residential, industrial, or commercial soils should be applied to road deposited sediment, since the roads are swept across TOB. The roadways in the study area include residential, industrial, and commercial soils since the RDS was removed from across TOB.

It has been shown that metals adsorb to fine-sized particles in higher concentrations than those adsorbed to large-sized particles. This study assumed that the sediment <354μm in diameter had equally evenly distributed concentrations of heavy metals to the <63μm portion and that accounted for 80 percent of the total metal loading on RDS.

7 FURTHER RESEARCH

Previous studies have shown that heavy metals tend to be found in higher concentrations in fine sediments of RDS. Furthermore, heavy metals tend to be disproportionately loaded on fines. This study assumes that the concentrations of heavy metals are the same throughout the fines and uses a finding from a previous study that shows that the fines contain approximately 80 percent of the total loading of heavy metals. These assumptions are useful for determining the loading of heavy metals on bays and waterways affected by RDS. By analyzing the larger grain size fractions, the results could be made more robust.

Since modern methods of street sweeping have been estimated to remove approximately 80 percent of RDS on swept roads, a method could be conceived to determine the amount of remaining RDS and loading associated with it. Furthermore, the leachability of RDS into groundwater is of interest at the dump site, considering the potential for groundwater contamination. To determine the leachability of the metals and nutrients, the synthetic precipitation leaching procedure (SPLP) may be used. This is a standard procedure for preparing soils to simulate how likely it is for metals, nutrients, and other chemicals will become mobile during rainfall. There may be further preparations depending on the metal or nutrient being tested that is not included in the SPLP (United States EPA 1994).

There are methods of analysis for nutrients. A CHN analyzer could reveal information about nitrogen loading, a subject of interest for north shore bays on Long Island, which suffer from nitrogen contamination in part from urban and stormwater runoff.

It was assumed that the brass sieves used to conduct the sieving procedure did not affect the concentrations of elements found in the x-ray analysis. An analysis could be conducted of wet-sieved in a non-brass sieve to determine potential brass sieve impact.

The use of the TOBHD dump site makes the origin of the sediment unknown. It is therefore challenging to geographically pinpoint high concentrations of individual samples. A geospatial analysis is limited to the dump site and its contents regarding the storage of RDS in a hydrological system. So, a hydrologic analysis would yield information about the movement of heavy metals in groundwater on Long Island. The mobility and bioavailability of heavy metals and the leachability of soil samples would yield information about the risks associated with the dump site.

There is an environmental risk assessment presented in Zhu et al. 2008 based on an earlier study. This assessment uses heavy metal risk factors and the concentrations of varying grain size fractions to determine an environmental risk factor. The background levels of heavy metals were used to in these calculations.

A novel index that takes elements of traditional analysis of RDS and information about sediment mobility has been developed to characterize environmental risk (Zhao and Li 2013). Characteristics of RDS including mobility and grain size are considered in the metal risk assessment. The study analyzed the data using different methods of risk assessment. These risk assessments were all dependent on grain size, so in the novel risk assessment grain size was used. The metal risks for each grain size were accounted for in the ecological risk index for RDS.

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