Evaluation of Contaminated Suspended Sediment in the Exposure Pathway

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Thesis in the Field of Sustainability and Environmental Management

In Partial Fulfillment of the Requirements

For a Master of Liberal Arts (ALM) Degree in Extension Studies

Harvard University Extension School

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Evaluation of Contaminated Suspended Sediment in the Exposure Pathway

Summary

The pollution of surface water in the United States is a significant environmental concern. Pollution from regulated or non-regulated physical, chemical, or microbial contaminants from a wide variety of origins, naturally occurring or manufactured, can significantly impair the quality of surface water.

Water quality investigations have historically focused on dissolved-phase concentrations of contaminants alone, though there has been an increasing amount of work done to sample and analyze settled (bed) sediments in recent years. Although some work on examining the release of dissolved contaminants during resuspension has been done, direct investigation of suspended sediment (SS), however, has not been very well incorporated into water quality investigations. The sampling and analysis of SS as a potential exposure source may have increasing importance with regards to the investigation and monitoring of ubiquitous, low-concentration contaminants (metals) or contaminants of emerging concern, such as pesticides, pharmaceutical and personal care products (PPCPs), nanoparticles (engineered or other), and their respective chemical breakdown products. Of even more recent concern is the possibility that nanoparticles (NPs), particles having a size less than 0.1 micron, could be new contaminants of concern.

This study is a qualitative evaluation of whether SS sampling and analysis should be included in the performance of environmental investigations. Specifically, this study considered the metals copper (Cu), iron (Fe), lead (Pb), titanium (Ti), and zinc (Zn). The use of an emerging analytical technique for sub-micron particulates in water, single particle Inductively
Coupled Plasma Mass Spectrometry (spICP-MS) was also examined for its relevance in environmental investigations. The key research questions and associated hypotheses follow:

Does measuring the concentration of chemical contaminants in SS provide increased information with regards to analyzing water quality? I hypothesized that due to their limited solubility, the concentrations of Cu, Fe, Pb, and Ti present as SS, would be greater than the concentrations of those metals in the dissolved fraction. The concentration of Zn in the dissolved fraction would be greater than the concentration of Zn in the solids fraction as a result of Zn’s higher solubility. The first task of this study was to perform a comparative analysis of new and existing chemical concentration data to examine these relationships in surface water.

Are the aqueous concentrations of contaminants associated with NPs a significant source of the overall contaminant picture, despite their small mass contribution? I hypothesized that the nanoparticle portion of the contaminant concentration would provide a small contribution to the total concentration (milligrams per liter [mg/L]) of the contaminant in the water phase despite having a much higher concentration of the contaminant of potential concern (COPC) per mass of particle than a coarser particle (milligrams per kilogram [mg/kg]). The second task of this study was to describe the nanoparticles and report how much mass concentration of the COPC that they contained.

Data collection included the secondary evaluation of existing water chemistry data sets (which included both total and dissolved chemical concentration results) and a small effort of collection and analysis of field samples from Colorado. Field samples were collected using a grab sample collection method and were analyzed through a series of settling or filtration steps followed by analysis by spICP-MS for the selected chemical contaminants.
The outcomes of this study are a series of comparative analyses demonstrating potential benefits of including SS data in the evaluation of water quality. The broader goals of this work are to encourage environmental practitioners to include SS as a medium of concern in their sampling program design and to encourage the study of NPs in surface water.
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Definition of Terms

CEC  Contaminants of Emerging Concern
COPC Contaminant of Potential Concern
Cu  Copper
CWA  Clean Water Act
ENM  Engineered nanomaterial
Fe  Iron
mg/kg  milligrams per kilogram
mg/L  milligrams per liter
nm  nanometer
NP  nanoparticle
Pb  Lead
ppb  parts per billion
PPCP  Pharmaceutical and Personal Care Products
spICP-MS  single particle Inductively Coupled Plasma Mass Spectrometry
SS  Suspended Sediment
Ti  Titanium
Zn  Zinc
μm  micron or micrometer
Introduction

Chemical pollution of surface water is a significant environmental concern. It results from the transport of pollutants in the environment by direct or indirect discharge. Direct discharge is from a point source, and results from known release points such as industrial or wastewater treatment plant discharge. Diffuse or nonpoint source discharges result from non-discrete locations such as storm water, surface water, groundwater, aerial deposition, infrastructure seepage, and other modes; it can be generated by single or multiple sources (USEPA, 2017a). Chemical pollution may include regulated or non-regulated physical, chemical, or microbial pollutants from a wide variety of naturally occurring or manufactured origins (WQA, 2017).

The importance in investigating and analyzing chemical contaminants in the environment entails considerations of risk associated with hazardous exposure. In order for exposure to occur, the chemical contaminant must be both present and existing in sufficient concentration to cause harm to a receptor. A receptor is a human or other organism which may contact the contaminant. The second part of the exposure scenario is that in order for exposure to occur, a receptor must be present. Hazard is a measure of the amount of harm that exposure will cause to the receptor. The combination of exposure likelihood and hazard leads to the level of risk. The focus of this study is on the exposure portion of the risk scenario; this study does not address the issue of harm.

Chemical contaminants in the aquatic environment are present in the dissolved phase and the suspended solid phase. Contaminants can be attached to particles/sediment surface through adsorption or may be present as a component of the solid. Sediments containing contaminants
are present as either settled (bed sediment) or suspended (water column sediment). Suspended sediment (SS) is comprised of particulate matter which has not settled or which has become resuspended as a result of disturbance.

In order to manage chemical pollution of surface water and sediments, it is important to have sufficient representative data upon which to base decisions. Environmental investigations generally include sampling and analysis of water and settled sediment. SS is often overlooked because it represents a relatively small mass fraction of the overall water column, is typically discounted by traditional sampling and analysis methods, and can be logistically difficult to evaluate. By discounting the sampling and analysis of SS, investigators are missing an important portion of the exposure pathway for contaminants of potential concern (COPC), particularly with regards to ubiquitous low-concentration contaminants such as metals, pesticides, pharmaceutical and personal care products (PPCPs), nanoparticles (engineered or other), and their respective chemical breakdown products.

Research Significance and Objectives

My research examined whether the concentration of contaminants in SS should be considered in environmental investigations. SS loading of a water body is an episodic event. Due to the possible presence of chemical contaminants in SS, there is a potential chance of exposure, which should be measured especially because of the non-constant nature of this loading. Short term events may result in greater consequences than long-term exposure to baseline conditions.

The objectives of this study were to:
1. Evaluate whether collecting chemical concentration data associated with SS is beneficial to evaluating water quality.
2. Evaluate the implications of particle size, especially nanoparticles (NPs), with regards to chemical concentration.
3. Encourage environmental practitioners to consider the implications of contaminants present in SS when designing and implementing sampling and analysis programs.
4. Encourage researchers and environmental practitioners to perform additional investigation on NPs in surface water.

**Background**

In the United States in the early 1970s, there was an increasing awareness of the potential impacts of pollution in the nation’s waters. In 1972, the Clean Water Act (CWA) was implemented with the goals of minimizing the inputs of contaminants into the environment and to assessing the presence of contaminants in the environment. The act relies heavily on the term “water quality”, a phrase used to describe the chemical, biological, and physical characteristics of water (USGS, 2018), and the subsequent need for water quality criteria, which are a set of standards that define the suitability of a water source for a given use based on those parameters (CWA of 1972, 2002). Subsequent to the CWA, and in the spirit of environmental stewardship, there have been thousands of studies performed on various bodies of water to determine what chemical contaminants may be present. Over time, the level of quality of those data has increased with increased understanding of sampling design and implementation. In order to be useful in the decision-making process, data must be of suitable quality for the level of inquiry.
Designing an appropriate sampling program involves incorporating both chemical and physical factors which may affect the nature of chemical contaminants in the environment. A major focus of sampling design should be analysis of the fate and transport of chemical contaminants in the environment. This can be performed in a general sense for the purpose of advancing our overall knowledge of contaminant behavior. It should be performed on a site-specific and/or chemical-specific basis when being implemented on individual sampling projects.

Chemical Considerations

Contaminants are present in the dissolved phase (in water), the adsorbed phase (in sediment), and as solid particulates (in sediment). All of these fractions are present to some degree in the water column. Data suggest that there is variability between the concentrations of contaminants detected in water versus the concentrations of contaminants detected in sediment (Wilkinson, Hooda, Barker, Barton, & Swindon, 2017a). Water, sediment, and fish tissue samples analyzed from an urban California waterway showed the concentrations of some COPCs to be near project action limits (threshold values assigned for the project at which some decision would be made) in water while the concentrations of different COPCs were near project action limits in sediment (Maruya et al., 2015). Similarly, evaluation of 60 paired water and sediment samples analyzed for 15 contaminants of emerging concern (CECs) in another sampling location showed the presence of analyzed contaminants in both water and sediment, but not necessarily in the paired samples (Fairbairn et al., 2015). The study also found that seasonality affected the concentrations of CECs in water but not in sediment. A study which examined the concentrations of metals in surface water downstream from both mining and urban sites found that distribution of metals between the different fractions depended on the setting (Gagnon,
The partitioning of metals in surface water was affected by parameters such as iron and carbonate content and the reactivity of the metals released. Studies performed on the Upper Arkansas River, which is heavily impacted by historic mining operations, have shown that the formation of colloids has an impact on the metals transport in the water column (Kimball, Callender, Axtmann, 1995). The highest concentrations of metals occurred closest to the mining-impacted inflow, with a measurable decrease of metals being transported downstream in the water column within a short distance of the mixing zone due to sedimentation of the aggregated colloids. Iron and copper concentrations in the bed sediment in this stretch of water closely mirrored the iron and copper concentrations in the colloids collected from the water column. Colloids rich in iron and aluminum contribute to the transport of other metals such as copper, lead, and zinc (Schemel, Kimball, and Bencala, 2000).

Theoretically, the concentration of chemicals should reach equilibrium, a state at which the sum of the contaminant concentration in each phase equals the total concentration. Due to variability in the environment and difficulty in obtaining complete sampling data, however, chemical equilibrium calculations have shown to be inaccurate in predicting contaminant loading (Inostroza, Massei, Wild, Krauss, & Brack, 2017). This is further complicated by the fact that flowing water systems may not always be considered at equilibrium (Fairbairn et al., 2015).

Factors such as dilution, degradation, mixing with other chemicals in the water, and partitioning (presence of chemicals in multiple phases) should be part of the fate and transport evaluation for chemical contaminants. A controlled experiment performed by introducing the pesticides metolachlor and atrazine to both sediment and sediment-free water columns found that the presence of sediment in the water column can have significant effect on the fate of pesticides, affecting dissipation through sorption and degradation rates (Rice, Anderson, & Coats, 2004).
The resulting presence of degradation products in the water columns varied between pesticides, indicating that the potential environmental impact of the two pesticides in the same environment would be different. Polychlorinated biphenols have been shown to be transported in the adsorbed phase in low-energy environments and the dissolved phase in high-energy environments (Gdaniec-Pietryka, Mechlińska, Wolska, Gałuszka, & Namieśnik, 2013).

While there is a large amount of data available for settled sediments, there is a significantly smaller amount of data available for disturbed sediments (Quesada et al., 2014). Studies performed in Spain (Silva et al., 2011), China (Nie et al., 2015; Zheng, Wang, Lei, & Nan, 2016), and England (Wilkinson, Hooda, Swinden, Barker, & Barton, 2017b) support the idea that the concentration of chemical contaminants in SS may be critical to accurately quantifying water quality. In these studies, the results showed COPC concentrations in SS to be both different than the concentrations of COPCs in settled sediments and to be significant with regards to COPC concentrations when compared against water or sediment samples. With the relative lack of information about the activity of chemical contaminants in SS, additional investigation is warranted (Rugner, Schwientek, Egner, & Grathwohl, 2014; Quesada et al., 2014; Roberts, 2012; Eggleton & Thomas, 2004).

Physical Considerations

The physical characteristics of water (such as flowrate, depth, temperature, pH, oxygen reduction potential, salinity, turbidity, etc.) can influence the fate and transport of contaminants. For example, the distribution of glyphosate, a commonly used pesticide, can be greatly influenced by stream characteristics. Application of glyphosate to a water-sediment system will result in a rapid initial decrease in the aqueous phase concentration of glyphosate in the water
due to adsorption on to SS followed by a slower degradation due to microbial activity (Zaranyika & Nyandoro, 1993). During both phases of this degradation process, the chemical is moving in the environment. If the stream is turbid, the adsorbed chemicals will stay suspended and move further downstream. Similarly, if the water is moving quickly, the dissolved phase chemical will also move further downstream while it undergoes the slower degradation process.

Consideration must be given to whether the water is moving or still, whether there is current or prior sedimentation, and whether there are conditions suitable for sediment resuspension activity. Sediments may be present as either settled or suspended. SS may be from recent introduction to the water body from the surrounding watershed (for example erosion or active runoff from a paved surface) or from resuspension of benthic materials.

The presence of chemical contaminants in road dust can be a major contributor to the chemical composition of surface water in urban areas. Trace metals, such as copper, lead, platinum, and zinc, are released from vehicle tires, brakes, and mechanical operation to the road surface and subsequently washed in to surface water by rain water or snow melt (Hwang, Fiala, Park, and Wade, 2016). Although regulations such as those which resulted in the removal of lead from gasoline and the anticipated reduction of copper content in brake pads have been shown to have a pollution-reducing effect on road dust composition, there is still a significant impact to surface water from these materials.

Sediments may be resuspended as a result of disturbance. Review of existing studies showed that the fate of contaminants in disturbed sediment was poorly understood, particularly with regards to chemical release resulting in toxicity or bioavailability to the water column following the resuspension (Eggleton & Thomas, 2004). Ecological impacts and sub-lethal exposures have been observed from resuspension events, confirming the importance of analyzing
sediments which may have been resuspended as a result of natural or anthropogenic events (Roberts, 2011).

The stable state, where sediments are predominantly settled, should not be considered as the typical condition for sediments in surface water. Events such as tidal activities, precipitation events, storm events, water releases, and anthropogenic intrusions should be considered normal or typical in a water body. These actions will result in the resuspension of sediments along with any adsorbed chemical contaminants, thus changing the potential for environmental exposure (Roberts, 2012).

Reservoir sluicing, the rapid release of water from a reservoir through a dam, is an extreme example of a disturbance event which would cause the resuspension of particulates from both the reservoir and the receiving waters. An investigation of this activity showed that the sluicing activity significantly altered the water parameters, especially the water to solids ratio, the redox potential, and the pH (Fremion et al., 2016). During the sluicing action, there was an increase in the concentration of metals in the dissolved phase despite the significant quantity of solids loading.

An increase in solids loading, or resuspension, is seen in less dramatic disturbance events as well. Variable wind experiments performed at Taihu Lake in China found that as the wind forces and duration increased, both resuspension of solids and the total concentration of metals in the water increased (Zheng, Wang, Wang, Hou, and Quain, 2016). Physicochemical factors such as pH, dissolved oxygen, and suspended particulate matter had a close relationship to the total metals concentrations. There was a large increase in the metals concentration in the suspended particulate matter, though there was not much variation in the concentration of metals in the dissolved phase.
The physical characteristics of sediments (such as carbon content, grain size, etc.) complicate the assessment as to whether the sediment sample accurately reflects the water quality at the location from which it was collected. Sediment is “supplied, transported, and stored by nonlinear and episodic processes at different temporal and spatial scales than water” (Wohl et al, 2015). Contaminants in sediment may be from recent or historical deposition. A survey of benthic sediment contaminants in the Columbia River Estuary conducted in 2014 identified differing concentrations of contaminants in sediments with different characteristics such as grain size and status (stable, deposited, eroded, etc.) (Counihan et al., 2014).

Metals in the Environment

Metals occur in the environment from natural, agricultural, industrial, mining, and urban sources. In most cases, industrial inputs are from a point source discharge. Mining discharges may also be considered point sources in some instances, however historic mining practices have resulted in widespread mining contamination which discharges to surface waters in a number of ways (Luoma & Rainbow, 2008). Natural occurrence (including atmospheric deposition from geologic events), agricultural, and urban inputs (except discharges from wastewater treatment plants) are considered non-point source discharges. Sources of metals in urban inputs include automobiles, building products, leaded gasoline, PPCPs, and engineered nanomaterials (ENM).

Nanomaterials

A nanomaterial is a material which has any external dimension in the nanoscale (length from one to 100 nanometers [nm]) (ISO/TS 80004-1:2015). This definition is broad in order to include materials of varying shapes (including spherical particles, very thin plate structures, long
tubes, crystalline shapes, etc.) into the classification (NNI, 2019). Materials in the nanoscale exhibit properties differently than larger materials (NNI, 2019). At the nanoscale, material properties such as melting point, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity change as a function of particle size. Nanomaterials also have increased surface area. As the surface area per mass increases, there is a greater amount of contact with surrounding materials, thus affecting reactivity. Since nanomaterials are highly reactive, it is likely that their status will change over time in the environment (Montano et al., 2014).

Nanomaterials can be either naturally occurring or engineered (ENM). Common naturally occurring nanomaterials include the clay fraction, iron and aluminum oxides, metal sulfides, and humic substances (Montano et al., 2014). These materials can exist in relatively high concentrations in environmental water samples, ranging from one to 1,000 parts per million in surface waters (Buffle, J and Leewen, HP in Montano et al., 2014). Naturally occurring nanomaterials can complicate the sampling and analysis of ENMs in environmental samples.

An ENM is any nanomaterial which has been engineered for a specific purpose or function (NNI, 2019). Manufacture of ENMs began in the 1980’s following the discovery of the Buckyball (Klaine et al., 2008). The number of applications for nanomaterials is vast, ranging from “everyday” products such as anti-microbial socks to complex healthcare and energy applications. ENMs are grouped into five major classes: zerovalent metals (gold, silver, and iron), metal oxides (silicon dioxide, titanium dioxide, zinc oxide, and cerium dioxide), semiconductors (cadmium selenide, cadmium telluride), carbonaceous materials (carbon nanotubes, fullerenes), and dendrimers (multi-functional polymers) (Montano et al., 2014). The following is a brief summary of these classes (Klaine et al., 2008). Zerovalent metals have been developed and used to remediate contaminated soil and water. Metal oxides, including both
individual and binary oxides, are relatively easy to synthesize and manufacture. They are used widely for their photocatalytic properties. Semiconductors, nanocrystals or quantum dots, are used in medical applications, photovoltaics, specialty inks, and other applications. Carbon nanotubes are used as additives to a large number of materials used in the plastics, electronics, aerospace, and automotive industries. Dendrimers are multifunctional polymers used in biologic and material science applications.

ENMs are released to the environment intentionally, as in remediation applications, and unintentionally, as in atmospheric emissions, degradation from ENM containing products, and as solid or liquid waste (Klaine et al., 2008). Once released into the environment, ENMs will be transported to surface water.

The fate of nanomaterials in water is dependent on the solubility of the material and the various chemical, biological, or physical reactions between the nanomaterial and the surrounding environment (EPA Whitepaper). Nanomaterials may remain in suspension as individual particles or may adsorb on to sediment particles. The aggregation of nanomaterials with larger particles impacts their sedimentation rate and transport in water (Krysanov et al., 2010). Historically, nanomaterials have been operationally considered part of the dissolved phase in aqueous solutions since they can pass through a 0.45 micron (µm) filter (Montano et al., 2014). This operational definition is inherently flawed, however, because very small particles and colloids have different characteristics and different bioavailability than truly soluble species (Klaine et al., 2008).

This flawed definition may result in the improper assessment of the quality of the water sample. This potential source of error could have significant impacts to the output of risk assessment calculations, particularly for sensitive receptors.
One reason fine particles have not historically been considered is the lack of technology to detect and quantify the concentration of particulate COPCs in the nanoscale. Measuring nanomaterials in bulk samples (non-homogenous solutions) is difficult due to technology limitations, the intrinsic nature of the nanomaterials, the small size of nanomaterials, and the low concentration of nanomaterials relative to the surrounding sample (Montano et al., 2014).

Analyzing Water Samples for NPs

Research has been conducted on numerous methods to effectively analyze NPs. Examples of these include scanning electron microscopy, transmission electron microscopy, atomic force microscopy, and separation techniques such as differential centrifugation (Wilbur, Yamanaka, and Sannac, 2017). Single particle Inductively Coupled Plasma Mass Spectrometry (spICP-MS) has emerged as advantageous over these other methods because it is relatively fast, requires less sample preparation, and provides multiple data points as outputs (for example, particle size, intensity, and number). spICP-MS has been shown to provide accurate NP number concentrations (Montaño et al., 2016). As an emerging analytical technique, there are challenges to be overcome and additional experimentation to be done, however this technology has shown significant promise as the most effective method to analyze NPs in environmental samples.

Research Questions, Hypothesis and Specific Aims

This study is a qualitative and quantitative evaluation of whether SS sampling and analysis should be included in the performance of environmental investigations. The key research questions are as follows:
1. Does measuring the concentration of chemical contaminants in SS provide increased information with regards to analyzing water quality? I hypothesize that due to their limited solubility, the concentrations of Cu, Fe, Pb, and Ti, present as SS, will be greater than the concentrations of those metals in the dissolved fraction, however the concentration of Zn in the dissolved fraction will be greater than the concentration of Zn in the solids fraction as a result of Zn’s higher solubility.

2. Are the aqueous concentrations of contaminants associated with NPs a significant source of the overall contaminant picture, despite their small mass contribution? I hypothesize that the nanoparticle portion of the contaminant concentration will provide a small contribution to the total concentration of the contaminant in the water phase despite having a much higher concentration of the COPC per mass of particle size than a coarser particle. The second task of this study is to describe the nanoparticles and report how much mass concentration of the COPC that they contain.

Specific Aims

The specific aims for this study are as follows:

1. Collate sets of data which contain chemical concentration data for total, solid, and dissolved phases (or any combination thereof).

2. Compile concentration data into tables and develop graphical representations of the data as appropriate.

3. Analyze the compiled data with respect to the project research questions.
4. Evaluate the concentration of chemical contaminants in aqueous solutions as a function of particle size.

5. Illustrate the function of spICP-MS in the analysis of SS in surface water.

Methods

This study included the analysis of data from existing data sets and the collection of limited environmental samples for analysis by spICP-MS. COPC concentration data were generated from literature, data sets obtained from other investigators, and as part of ongoing research activities for nanometals in the urban watershed of Denver, Colorado. The COPCs examined during this study were Cu, Fe, Pb, Ti, and Zn. These COPCs were selected based on the following criteria: ubiquitous in the surface water environment (especially in mining-impacted and urban settings), commonly analyzed, potentially used in engineered nanoparticle processes, and known to have varying solubility or reactive responses in aqueous solutions.

There were two goals to the data collection: gather a significantly large body of analytical data containing chemical concentration data for the COPCs in the total and “dissolved” states to perform a comparative analysis of COPC concentration in the suspended solid fraction versus the dissolved fraction and gather chemical concentration data for COPCs in the adsorbed fractions (coarse and fine particulates) and dissolved fraction to analyze the potential inputs of chemical contaminants in the various fractions.

For the first set of analyses, the term dissolved followed the industry standard definition of any material that passes through a 0.45 µm filter. For the second set of analyses, coarse particulates, including particles and settleable particles are defined as having an approximate size of 5 µm or greater, fine particulates were defined as ranging from 5 µm to 0.02 µm, and the
dissolved fraction was defined as particulates smaller than 0.02 µm and completely dissolved materials.

Analysis of Existing Data

The data analysis task included compilation and evaluation of the data collected from existing data sets and sampling activities. Existing COPC concentration data was generated from four sources: the Water Quality Portal (NWQMC, 2019), the River Watch of Colorado database (River Watch of Colorado, 2019), publicly available data from the Gold King Mine spill (CDPHE, 2019), and two unpublished research studies performed in coordination with the Colorado School of Mines including a study of a mining-impacted stream (Meyer et al. 2018) and a nanoparticle study of Denver urban streams. The applicable data from these two sources was tabulated in Excel sheets. The first of these studies included samples collected under “normal” hydrologic conditions; the Gold King Mine data was collected during an active release of sediments from a mine tailings pond to the Las Animas River which occurred on August 5, 2015 when the tailings pond was ruptured by a construction contractor during remediation work.

Tabulated COPC concentration data were used to generate graphs which show the relative concentrations of COPCs in the dissolved phase and the particulate phase. The primary purpose of these are for visual representation and ease of reviewing data. Data and graphs were used to perform a comparative analysis of COPC concentrations across each fraction in the water column.

New Sample Collection
Primary data were generated for the size analysis by collecting raw water samples (water and suspended sediment collected simultaneously in the same sampling device), performing laboratory analysis for selected COPCs, and evaluating the analytical results. The sampling program is summarized herein.

The sample population for the study consisted of the raw water from streams that could potentially be impacted by COPCs. The sample collection locations were selected to be representative of surface water flowing into and out of the Denver metro area.

Grab samples were collected from a logistically available location within the flowing channel at each location. Eleven grab samples, collected by inserting a sampling device (adjustable handle water sample dipper) into the water to collect a water sample and then transferring the water to a dedicated sample bottle, were considered sufficiently representative of the water bodies sampled for the purpose of this study. The temporal boundary for the sampling consisted of the duration of each of the individual sampling events performed during the study. The study did not include the periods of time which are between or beyond the duration of each sampling event because contaminant deposition is likely ongoing; however, the sampling program was not designed to perform continuous monitoring.

Field parameter information during the sampling was limited to the visual observations made by the sample collection personnel. Additional meteorological data from regional weather stations available online was used to provide supplemental information about the surface water conditions at the time of sampling.

Water samples were collected with a sample collection device made of material compatible and non-reactive with the study COPCs. The collected sample volume was placed in individual plastic (polyethylene, polycarbonate, or polypropylene) sample bottles for
laboratory preparation and analysis. The sample bottle volume was variable as samples from some locations were collected for additional analysis outside the scope of this project. Samples were stored in cool conditions until they could be transferred to a laboratory refrigerator or freezer.

Sample Preparation and Analysis

Water samples were prepared and analyzed at the Colorado School of Mines Chemistry Department. Samples were prepared as follows: the whole sample was agitated by vigorously shaking the sample bottle. A subsample of the water and suspended particles were allowed to settle. Finally, a subsample was filtered using a 0.02 µm filter. All three sample types were analyzed using a PerkinElmer NexION 350D ICP-MS operating in single particle mode. In this mode, the ICP-MS is able to detect and quantify the number and masses of the particulates in the aqueous solution. This result is used to determine the mass concentration (mg/L) and number concentration (particle #/L) of the particulate for each COPC in the solution. The particulate mass concentration comprises the quantity of fine particulates present in the sample. The concentration of the COPC in each fraction (coarse, fine, and dissolved) was then calculated.

Analysis of New Nanoparticle Data

Twenty-one samples were collected from the urban Denver area. The sampling locations were selected to be representative of the major inflows and outflows of surface water for the city. Zinc was selected as the COPC for analysis because it is commonly present in urban surface water and may pose human and ecological risk in the environment.
Sample preparation included processing each whole sample into multiple subsamples for analysis. The subsamples for this analysis included raw water, settled, and filtered samples. Raw water is the whole sample; it includes nearly everything that was in the water that was extracted from the sampling location. It does not include large particles which do not remain in suspension or which could damage the analytical instrument. The large particles were avoided by keeping the ICP-MS sampling tube well above the bottom of the sample container. The second subsample was the settled fraction. Stokes Law was used to determine that, in general, particles larger than 5 µm will sediment out of solution after a short settling period (approximately 70 minutes was used for this analysis). The third subsample was the filtered fraction. A 0.02 µm filter was used to filter the settled water fraction to generate this fraction which contains very fine particles (particles which are smaller than the size of the filtration media plus any additional particles which are trapped due to limitations in the sample preparation capability) and dissolved metals.

Each sample was analyzed by the spICP-MS method to gather data on the size and amount (number and mass of particles) of zinc in each water sample. The data output from the ICP-MS software is an ICP pulse graph. An example of this output is shown in Figure 1. The output provides information on the size of the particles detected, the intensity of the signal, and the number of particle generated peaks detected. This output can be used to generate data for the COPC which can be used in the evaluation of the water sample.
The ICP pulse graph shows a series of peaks and a baseline. The peaks represent the nanoparticles. The baseline represents the concentration of particles too small to be resolved as individual peaks plus the dissolved phase concentration. Integration of these data provides mass concentration of the COPC for that sample. The nanoparticle concentration of the COPC in the sample can be calculated using the measured mass and the known composition of the COPC. For example, 10 mg/l Zn would represent 12.5 mg/L ZnO. This concentration represents the fine particulate concentration containing the COPC or interest of each sample.

Analysis of different subsamples provides additional information about the size distribution and concentration of the COPC in the sample. Figure 2 shows the ICP pulse graph for both a filtered subsample (where the filtered sample represents the concentration which is as close to only containing dissolved metals as possible by the analytical method) and a raw water subsample. The software is capable of differentiating the raw water sample data into two categories, resolved particles and background (termed dissolved by the software). Large pulses
that can easily be seen to be above background are termed “resolved particles”. The background signal for the raw sample contains both small particles and dissolved species. The concentration of unresolved NPs (NPs for which the size and number of counts cannot be determined) is calculated by subtracting the mass concentration of the dissolved metals from the mass concentration of the raw water sample background.

![Figure 2. Comparison of Output Signals. Example output from the ICP-MS for a raw water sample and a filtered sample which allows for the evaluation of resolved vs. unresolved nanoparticles (Ranville, 2019).](image)

After analysis, six concentration values were known for each sample location: total particle concentration, resolved particle concentration (particles larger than 5 µm in the raw water sample), non-resolved (fine) particle concentration (particles smaller than 5 µm and larger than 0.02 µm), dissolved phase concentration (includes particles smaller than 0.02 µm and dissolved phase), resolved NP concentration remaining after settling, and unresolved particle concentration remaining after settling. The concentration data, combined with the particle size data, are used to evaluate the impact of zinc NP in the water sample overall.
Results

This study included evaluation of suspended sediments in aqueous samples in two different ways: review/comparison of existing data and analysis of new NP data.

Evaluation of Existing Data

Surface water chemistry data from the Water Quality Portal (NWQMC, 2019), the River Watch of Colorado database (River Watch of Colorado, 2019), publicly available data from the Gold King Mine spill (CDPHE, 2019), and research on a mining impacted stream performed in coordination with the Colorado School of Mines (Meyer et al. 2018) was tabulated for evaluation. Data were included from a variety of locations that represented rural/agricultural sites, mining impacted sites, and urban sites.

The analytical results are presented as total metals and dissolved metals concentrations. The suspended solids metal concentrations were calculated by subtracting the dissolved concentrations from the total concentrations. An initial review of the data quality was performed to eliminate obvious sampling errors such as holding-time violations and other results errors. The data was determined to be of sufficient precision to serve the purpose of this phase of the study which was to provide a broad overview of the available data and discern trends.

A total of 1,478 sample results were included in the analysis. This included 405 copper results, 379 iron results, 303 lead results, 376 zinc results, and 15 titanium results. There were 1,084 detections of the COPCs in the suspended solid phase and 921 detections of the COPCs in the dissolved phase. Although there were individual sampling results which did not contain
metals in both phases, both the solid and dissolved phase were present in every COPC for each location type. A summary of the data is shown in Table 1.
Table 1. Compiled Sample Results Data. Summary of analytical data collected from literature and other publicly available sources used to evaluate the potential for COPCs in the solid and dissolved fractions of aqueous samples.

<table>
<thead>
<tr>
<th>Location Type</th>
<th>Metal</th>
<th>No. of Samples</th>
<th>No. Solids Detections</th>
<th>% of Time Solids Present</th>
<th>Concentration of Solids Greater than Concentration Dissolved</th>
<th>Median % Solids</th>
<th>No. Dissolved Detections</th>
<th>% of Time Dissolved Present</th>
<th>Concentration of Dissolved Greater than Concentration of Solids</th>
<th>Median % Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural/Agricultural</td>
<td>Cu</td>
<td>123</td>
<td>73</td>
<td>59%</td>
<td>82%</td>
<td>63-100</td>
<td>40</td>
<td>33%</td>
<td>18%</td>
<td>0-37</td>
</tr>
<tr>
<td>Mining Impacted</td>
<td>Cu</td>
<td>145</td>
<td>96</td>
<td>66%</td>
<td>50%</td>
<td>0-62</td>
<td>101</td>
<td>70%</td>
<td>50%</td>
<td>0-100</td>
</tr>
<tr>
<td>Urban</td>
<td>Cu</td>
<td>137</td>
<td>135</td>
<td>99%</td>
<td>23%</td>
<td>23-39</td>
<td>124</td>
<td>91%</td>
<td>77%</td>
<td>61-77</td>
</tr>
<tr>
<td>Overall Copper</td>
<td>Cu</td>
<td>405</td>
<td>304</td>
<td>75%</td>
<td>46%</td>
<td>0-100</td>
<td>265</td>
<td>65%</td>
<td>54%</td>
<td>0-100</td>
</tr>
<tr>
<td>Rural/Agricultural</td>
<td>Fe</td>
<td>123</td>
<td>119</td>
<td>97%</td>
<td>95%</td>
<td>88-100</td>
<td>81</td>
<td>66%</td>
<td>5%</td>
<td>0-25</td>
</tr>
<tr>
<td>Mining Impacted</td>
<td>Fe</td>
<td>115</td>
<td>109</td>
<td>95%</td>
<td>90%</td>
<td>74-96</td>
<td>109</td>
<td>95%</td>
<td>10%</td>
<td>4-26</td>
</tr>
<tr>
<td>Urban</td>
<td>Fe</td>
<td>141</td>
<td>141</td>
<td>100%</td>
<td>85%</td>
<td>73-88</td>
<td>111</td>
<td>79%</td>
<td>15%</td>
<td>12-26</td>
</tr>
<tr>
<td>Overall Iron</td>
<td>Fe</td>
<td>379</td>
<td>369</td>
<td>97%</td>
<td>90%</td>
<td>73-100</td>
<td>301</td>
<td>79%</td>
<td>10%</td>
<td>4-26</td>
</tr>
<tr>
<td>Rural/Agricultural</td>
<td>Pb</td>
<td>123</td>
<td>49</td>
<td>40%</td>
<td>68%</td>
<td>2-100</td>
<td>18</td>
<td>15%</td>
<td>32%</td>
<td>0-80</td>
</tr>
<tr>
<td>Mining Impacted</td>
<td>Pb</td>
<td>31</td>
<td>25</td>
<td>81%</td>
<td>72%</td>
<td>50-96</td>
<td>29</td>
<td>94%</td>
<td>28%</td>
<td>1-50</td>
</tr>
<tr>
<td>Urban</td>
<td>Pb</td>
<td>149</td>
<td>32</td>
<td>21%</td>
<td>79%</td>
<td>0</td>
<td>8</td>
<td>5%</td>
<td>21%</td>
<td>0</td>
</tr>
<tr>
<td>Overall Lead</td>
<td>Pb</td>
<td>303</td>
<td>106</td>
<td>35%</td>
<td>73%</td>
<td>0-100</td>
<td>55</td>
<td>18%</td>
<td>27%</td>
<td>0-80</td>
</tr>
<tr>
<td>Rural/Agricultural</td>
<td>Zn</td>
<td>117</td>
<td>72</td>
<td>62%</td>
<td>72%</td>
<td>39-100</td>
<td>42</td>
<td>36%</td>
<td>28%</td>
<td>0-61</td>
</tr>
<tr>
<td>Mining Impacted</td>
<td>Zn</td>
<td>142</td>
<td>105</td>
<td>74%</td>
<td>5%</td>
<td>2-49</td>
<td>139</td>
<td>98%</td>
<td>95%</td>
<td>51-100</td>
</tr>
<tr>
<td>Urban</td>
<td>Zn</td>
<td>117</td>
<td>113</td>
<td>97%</td>
<td>22%</td>
<td>16-37</td>
<td>106</td>
<td>91%</td>
<td>78%</td>
<td>63-84</td>
</tr>
<tr>
<td>Overall Zinc</td>
<td>Zn</td>
<td>376</td>
<td>290</td>
<td>77%</td>
<td>26%</td>
<td>2-100</td>
<td>287</td>
<td>76%</td>
<td>74%</td>
<td>0-84</td>
</tr>
<tr>
<td>Overall Titanium</td>
<td>Ti</td>
<td>15</td>
<td>15</td>
<td>100%</td>
<td>73%</td>
<td>55-100</td>
<td>13</td>
<td>87%</td>
<td>13%</td>
<td>0-45</td>
</tr>
<tr>
<td>Results (only mining impacted)</td>
<td>Ti</td>
<td>15</td>
<td>15</td>
<td>100%</td>
<td>73%</td>
<td>55-100</td>
<td>13</td>
<td>87%</td>
<td>13%</td>
<td>0-45</td>
</tr>
</tbody>
</table>
**Frequency of Detection**

When examining all samples, suspended solid metals were present 75% of the time in copper results, 97% of the time in iron results, 35% of the time in lead results, 77% of the time in zinc results, and 100% of the time in titanium results. Across the different location types, copper was present in the solid phase for at least 59% of the time (rural/agricultural), with the highest percentage of detections occurring in the urban location type. Iron was present in the solid phase at least 95% of the time (mining impacted), with the highest percentage occurring in the urban locations. Lead was present in the solid phase between 21% to 81% of the time, with the highest percentage of results in the mining impacted location type. The number of detections of lead in any phase (dissolved or solid) was low with only 303 (53%) samples having measurable concentrations of lead above the analytical detection limit. Zinc was present in the solid phase between 62% and 97% of the times, with the highest percentages of detections occurring in the urban location type. Titanium results were only available for the mining impacted location type. Titanium was detected in 100% of the samples in the mining impacted location type.

Across all samples, dissolved metals were present 65% of the time in copper results, 79% of the time in iron results, 18% of the time in lead results, 76% of the time in zinc results, and 87% of the time in titanium results. Copper was present in the dissolved phase 33% to 91% of the time, with the highest percentage of detections occurring in the urban location type. Iron was present in the dissolved phase 66% to 95% of the time, with the highest percentage occurring in the mining-impacted location type. Lead was
present in the dissolved phase ranging from 5% to 94% of the time, with the highest percentage of results in the mining impacted location type. Zinc was present in the dissolved phase between 36% and 98% of the time, with the highest percentages of detections occurring in the mining-impacted location type. Titanium results were only available for the mining impacted location type. Titanium was detected in 87% of the samples in the mining impacted location type.

Relative Concentrations of Solid and Dissolved Phases

An “if/then” statement was used to count the number of times the solid metal concentration was greater than the dissolved metal concentration. This value was then converted into a percentage of the number of samples and reported in the table. The percentage of the time that the solids concentration was greater than the dissolved concentration was 46% for copper, 90% for iron, 73% for lead, 26% for zinc, and 73% for titanium. The same analysis was also performed in reverse. The percentage of the time that the dissolved concentration was greater than the solids concentration was 54% for copper, 10% for iron, 27% for lead, 74% for zinc, and 13% for titanium.

The relative concentrations of copper in the solid and dissolved phases were similar overall, but there were significant differences in the concentrations of each phase by location type. The concentration of the copper solids was greater than the concentration of dissolved copper 82% of the time in the rural/agricultural samples, 50% of the time in the mining impacted samples, and 23% of the time in the urban samples. Thus the concentration of dissolved copper was greater than the concentration of copper solids 18% of the time in rural/agricultural samples, 50% of the time in mining impacted samples, and 77% of the time in urban samples. The relative concentration analysis for
copper suggests that the location type has significance with regards to which phase has the greater portion of the total concentration in the water sample.

The relative concentrations of iron in the solid and dissolved phase were generally consistent across location types. The concentration of iron solids was greater than the concentration of dissolved iron 85% to 93% of the time. The concentration of dissolved iron was greater than the concentration of iron solids 5% to 15% of the time. The relative concentration analysis for iron indicates that the solids concentration is the dominant fraction of the total concentration in every location type examined.

The relative concentrations of lead in the solid and dissolved phases were similar overall, however there were significant differences by location type. In general, the concentration of lead solids was greater than the concentration of dissolved lead roughly twice as often as the concentration of dissolved lead was higher than the concentration of lead solids. The concentration of lead solids was greater than the concentration of dissolved lead 72% of the time in mining impacted sites. The concentration of dissolved lead was greater than the concentration of lead solids 28% of the time in mining impacted sites.

The relative concentrations of zinc in the solid and dissolved phases were relatively consistent, with the concentration of dissolved zinc being greater than the concentration of zinc solids a majority of the time. This trend was true in both mining and urban sites; however, it was not true in the rural/agricultural sites where the zinc solids concentrations were greater than the dissolved zinc concentrations 72% of the time compared to the opposite finding at 28% of the time.
Based on the limited data set available, the relative concentrations of titanium in the solids phase were greater than the concentrations of titanium in the dissolved phase 73% of the time. The concentrations of titanium in the dissolved phase were greater than the concentration of titanium in the solids phase 13% of the time.

**Median Percentages by Phase**

The median percent solids and the median percent dissolved were calculated for each COPC. The range of median percentages of solids for each COPC overall were 0 to 100 for copper, 73 to 100 for iron, 0 to 100 for lead, 2 to 100 for zinc, and 55 to 100 for titanium. The range of median percentages of dissolved for each COPC overall were 0 to 100 for copper, 4 to 26 for iron, 0 to 80 for lead, 0 to 84 for zinc, and 0 to 45 for titanium.

The distributions of median percent copper solids and median percent dissolved copper when summarized across the three location types are shown in Figure 3. There is a relatively even distribution of the copper concentration between the solid and dissolved phases in water samples. Forty percent of the time, the concentration of copper in the solid phase was greater than 50% of the total concentration of copper detected in the water sample. Forty-eight percent of the time, the concentration of copper in the dissolved phase was greater than 50 percent of the total concentration of copper detected in the water sample.
The distribution of copper between the solid and dissolved phases is different for different location types. Figure 4 shows the median percentage distributions for copper solids and dissolved phase by location type. The concentration of copper in the solid phase makes up a much greater percentage of the total copper concentration in the water samples in the rural location type than it does in either the mining or the urban location types. The percentage of the copper concentration is the most evenly distributed between the solid and dissolved phases in the mining location type samples. The concentration of copper in the urban sample location type is mostly distributed to the dissolved phase.
Figure 4. Median Percent Copper in Water Samples by Location Type. Median percent of copper in solid and dissolved fractions by location type. The percentages indicate how many of the results for the samples were in that percentage of the sample.
The distributions of median percent iron solids and median percent dissolved iron summarized across the three location types are shown in Figure 5. The concentration of iron in water samples primarily occurs in the solid phase. Eighty-two percent of the time, the concentration of iron in the solid phase was 76 to 100 percent of the total concentration of iron detected in the water sample. Eighty-six percent of the time, the concentration of iron in the dissolved phase was 0 to 25 percent of the total concentration of the iron detected in the water sample.

![Figure 5. Median Percent Iron in Water Samples. Summarized sample result data were used to determine the median percent of iron in the water samples in both the solid and dissolved fractions. The percentages indicate how many of the results for the samples were in that percentage of the sample.](image)

The distribution of iron between the solid and dissolved phases is not significantly different for different location types. Figure 6 shows the median percentage distributions for iron solids and dissolved phase by location type. The concentration of iron is the greatest in the solid phase for each of the three location types.
Figure 6. Median Percent Iron in Water Samples by Location Type. Median percent of iron in solid and dissolved fractions by location type. The percentages indicate how many of the results for the samples were in that percentage of the sample.
The distributions of median percent lead solids and median percent dissolved lead summarized across the three location types are shown in Figure 7. A greater percentage of the overall concentration of lead is present in the solid phase than the dissolved phase. Fifty percent of the time, the concentration of lead in the solid phase was greater than 50 percent of the total concentration of the lead detected in the water sample. Seventy-eight percent of the time, the concentration of lead in the dissolved phase was 0 to 25 percent of the total concentration of the lead detected in the water sample.

Figure 7. Median Percent Lead in Water Samples. Summarized sample result data were used to determine the median percent of lead in the water samples in both the solid and dissolved fractions. The percentages indicate how many of the results for the samples were in that percentage of the sample.

The distribution of lead between the solid and dissolved phases does not vary significantly between the rural and mining location types, however the urban location type is different. In the rural and mining location types, the higher percentage of lead concentration is found in the solid phase. In the urban location type, the dissolved phase
of lead predominates. Figure 8 shows the median percentage distributions for lead solids and dissolved phase by location type.
Figure 8. Median Percent Lead in Water Samples by Location Type. Median percent of lead in solid and dissolved fractions by location type. The percentages indicate how many of the results for the samples were in that percentage of the sample.
The distributions of median percent zinc solids and median percent dissolved zinc summarized across the three location types are shown in Figure 9. A greater percentage of the overall concentration of zinc is present in the dissolved phase than the solid phase. Fifty-two percent of the time, the concentration of zinc in the solid phase was between 0 and 25% of the overall concentration of zinc in the water sample. Eighty percent of the time, the concentration of zinc in the dissolved phase was greater than 50 percent of the total concentration of zinc detected in the water sample.

Figure 9. Median Percent Zinc in Water Samples. Summarized sample result data were used to determine the median percent of zinc in the water samples in both the solid and dissolved fractions. The percentages indicate how many of the results for the samples were in that percentage of the sample.

The distribution of zinc between the solid and dissolved phases does not vary significantly between the mining and urban location types, however the rural location type is different. In the mining and urban location types, the higher percentage of zinc
concentration is found in the dissolved phase. In the rural location type, the higher percentage of the zinc concentration is observed in the solid phase. Figure 10 shows the median percentage distributions for zinc solids and dissolved phase by location type.
Figure 10. Median Percent Zinc in Water Samples by Location Type. Median percent of zinc in solid and dissolved fractions by location type. The percentages indicate how many of the results for the samples were in that percentage of the sample.
The distributions of median percent titanium solids and median percent dissolved titanium summarized across the three location types are shown in Figure 11. Although the number of samples analyzed for titanium is not statistically significant, the results preliminarily indicate that the overall concentration of titanium in water samples is greater in the solid phase. Of the four samples evaluated, the concentration of titanium in the solid phase was greater than 50 percent of the overall titanium concentration in the water sample. The concentration of titanium in the dissolved phase was less than 50 percent of the total concentration in the four samples evaluated. Due to lack of available data, only one location type was evaluated for titanium.

![Figure 11. Median Percent Titanium in Water Samples. Summarized sample result data were used to determine the median percent of titanium in the water samples in both the solid and dissolved fractions. The percentages indicate how many of the results for the samples were in that percentage of the sample.](image-url)
Evaluation of New NP Data

Samples collected from the Denver urban area (Figure 12) were analyzed using the spICP-MS method by the Colorado School of Mines. The samples were analyzed for a single COPC, zinc. Three groups of results from this NP analysis are included in this thesis: size distribution, resolved vs. unresolved concentrations, and zinc concentrations in particles vs. dissolved zinc concentrations.

Figure 12. Sample Locations. Approximate sampling locations for aqueous samples collected for analysis of zinc by spICP-MS. (Source: Google Earth 2018)
Size Distribution

The particle size for NPs containing zinc was calculated assuming the zinc was present as ZnO. The mean NP size for each sample was calculated from this data, tabulated in Table 2, and shown graphically in Figure 13. The size reported for the dissolved samples represents the size detection limit and particles are likely smaller than this value in this fraction.

Table 2. Mean Nanoparticle Size. Nanoparticle size data for zinc in grab samples collected from urban Denver surface water.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Location</th>
<th>Mean Nanoparticle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn_SPAWWTP_7.16.18</td>
<td>South Platte above WWTP</td>
<td>98 85 54</td>
</tr>
<tr>
<td>Zn_SPBWWTP_7.16.18</td>
<td>South Platte below WWTP</td>
<td>96 91 58</td>
</tr>
<tr>
<td>Zn_Cherry_7.17.18</td>
<td>Cherry Creek</td>
<td>63 62 57</td>
</tr>
<tr>
<td>Zn_ECC_7.16.18</td>
<td>East Clear Creek</td>
<td>1141 101 57</td>
</tr>
<tr>
<td>Zn_ECC_7.17.18</td>
<td>East Clear Creek</td>
<td>94 90 58</td>
</tr>
<tr>
<td>Zn_ESC_7.17.18</td>
<td>East Sand Creek</td>
<td>117 106 57</td>
</tr>
<tr>
<td>Zn_NSP_7.16.18</td>
<td>North South Platte</td>
<td>66 96 58</td>
</tr>
<tr>
<td>Zn_NSP_7.17.18</td>
<td>North South Platte</td>
<td>105 95 66</td>
</tr>
<tr>
<td>Zn_Sand_7.16.18</td>
<td>Sand Creek</td>
<td>123 95 56</td>
</tr>
<tr>
<td>Zn_SSP_7.17.18</td>
<td>South South Platte</td>
<td>73 65 53</td>
</tr>
<tr>
<td>Zn_WCC_7.17.18</td>
<td>West Clear Creek</td>
<td>134 131 51</td>
</tr>
</tbody>
</table>
The largest NP are contained in the raw water samples, with NP ranging from 63 nm to 134 nm. With the exception of the Zn_NSP_7.16.18 sample, the mean NP size in the settled samples is 2 to 23% smaller than the NP size in the raw water samples, with NPs ranging from 62 to 131 nm. The mean particle size in the settled sample from Zn_NSP_7.16.18 is 45% larger than the mean NP size in the raw water sample from Zn_NSP_7.16.18. This discrepancy may be the result of sample preparation error, the presence of an anomalous large particle which did not settle, or the presence of zinc within a particle which was not homogenous (contained more than zinc oxide). This result is considered an outlier for this sample set.

Figure 13. Nanoparticle Size Distribution. Size of the nanoparticles containing zinc in each sample. Histogram shows the sizes in each of the fractions (raw water, settled, and dissolved).
The mean NP size in the dissolved sample (samples filtered using 0.02 µm [20 nm] filter media) were 8 to 61% smaller than the mean NP sizes measured in the settled samples and 12 to 62% smaller than the raw water samples. Although the dissolved samples were filtered to 20 nm, the mean NP size measured in the samples was between 51 and 66 nm. The difference between the theoretical filtration size and the size measured is due to limits of the analytical method. For this reason, the detection limit for zinc during this analysis would be considered 55 nm. At the detection limit, defined as three standard deviations above background, there is a 99% chance of stating that the result is positive (detection), there is a 1% chance that there is a false positive result (ALS Environmental, 2019). This “gray area” is a function of the sensitivity of the analytical method. Although a Limit of Detection, a “factor of safety” analysis which identifies the point at which high confidence in an accurate result is indicated, has not been calculated for this sample set, there is good consistency shown in the results and there is high confidence that the results are of sufficient quality for the purposes of this study. The results suggest that to avoid artifacts a size cut-off value somewhat greater than 55 nm should be used when presenting the size results for the raw and settled samples. Raising the size cutoff to 5 standard deviations about background would provide this safety factor.

Resolved vs. Unresolved Concentrations

The resolved concentration represents the portion of the NPs in the aqueous sample which can be directly quantified by spICP-MS. These are the peaks that are greater than 3 standard deviations above the background in the raw sample (Figure 2).
The unresolved concentration represents the NPs in the aqueous sample which are known to be particles, but for which specific size and count information cannot be determined.

The unresolved concentration is determined by subtracting the “dissolved” concentration (< 0.02 micron) of the COPC from the “background” concentration in the raw water sample. The resolved and unresolved concentrations for each sample collected during this study are tabulated in Table 3.

Table 3. Resolved vs. Unresolved Particles. Concentration of zinc in the resolved and unresolved fractions after analysis by spICP-MS.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Zinc Concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Resolved</td>
</tr>
<tr>
<td>Zn SPAWWTP 7.16.18</td>
<td>0.55</td>
</tr>
<tr>
<td>Zn SPBWWTP 7.16.18</td>
<td>0.48</td>
</tr>
<tr>
<td>Zn Cherry 7.17.18</td>
<td>-0.22</td>
</tr>
<tr>
<td>Zn ECC 7.16.18</td>
<td>1.47</td>
</tr>
<tr>
<td>Zn ECC 7.17.18</td>
<td>-10.48</td>
</tr>
<tr>
<td>Zn ESC 7.17.18</td>
<td>2.28</td>
</tr>
<tr>
<td>Zn NSP 7.16.18</td>
<td>-0.64</td>
</tr>
<tr>
<td>Zn NSP 7.17.18</td>
<td>0.39</td>
</tr>
<tr>
<td>Zn Sand 7.16.18</td>
<td>2.73</td>
</tr>
<tr>
<td>Zn SSP 7.17.18</td>
<td>0.31</td>
</tr>
<tr>
<td>Zn WCC 7.17.18</td>
<td>1.04</td>
</tr>
</tbody>
</table>

The mass zinc concentration in the resolved fraction is small compared to the mass zinc concentration in the unresolved fraction. The mass zinc concentration in the resolved fraction ranges from 0.31 parts per billion (ppb) to 2.73 ppb. The negative numbers shown in the table are artifacts of the limitations of the analytical method. The mass of the zinc concentration in the unresolved fraction ranges from 1.51 ppb to 27.70 ppb.
Zinc Concentrations in Particles vs. Dissolved Zinc Concentrations

The concentrations of zinc in each of the aqueous samples (including total and subsamples) is shown in Table 4. Analysis of both the raw water and settled subsamples allows for some analysis of the form of zinc present in the aqueous sample. The mass concentration of zinc in the raw water and settled subsamples would be approximately equal if zinc was consistently present in the same form. Since the raw water and settled subsamples have different concentrations, this may indicate that zinc is present in other forms (such as adhered to a larger particle not composed solely of zinc).

Table 4. Zinc Concentrations. The concentration of zinc (in ppb) for each sample collected from urban Denver surface water. The dissolved concentration has been subtracted from the raw water and settled concentrations.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Zinc Concentration (ppb)</th>
<th>Total</th>
<th>Raw Water Background</th>
<th>Settled Background</th>
<th>Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn SPAWWTP 7.16.18</td>
<td>6.67</td>
<td>5.37</td>
<td>3.44</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Zn SPBWWT 7.16.18</td>
<td>10.61</td>
<td>4.74</td>
<td>3.42</td>
<td>5.39</td>
<td></td>
</tr>
<tr>
<td>Zn Cherry 7.17.18</td>
<td>-0.39</td>
<td>0.89</td>
<td>0.40</td>
<td>-1.07</td>
<td></td>
</tr>
<tr>
<td>Zn ECC 7.16.18</td>
<td>16.20</td>
<td>10.99</td>
<td>7.50</td>
<td>3.74</td>
<td></td>
</tr>
<tr>
<td>Zn ECC 7.17.18</td>
<td>-1.55</td>
<td>3.50</td>
<td>1.32</td>
<td>5.43</td>
<td></td>
</tr>
<tr>
<td>Zn ESC 7.17.18</td>
<td>25.22</td>
<td>24.12</td>
<td>16.11</td>
<td>-1.17</td>
<td></td>
</tr>
<tr>
<td>Zn NSP 7.16.18</td>
<td>13.26</td>
<td>10.29</td>
<td>5.33</td>
<td>3.60</td>
<td></td>
</tr>
<tr>
<td>Zn NSP 7.17.18</td>
<td>19.82</td>
<td>5.54</td>
<td>-5.56</td>
<td>13.90</td>
<td></td>
</tr>
<tr>
<td>Zn Sand 7.16.18</td>
<td>17.03</td>
<td>14.69</td>
<td>7.17</td>
<td>-0.39</td>
<td></td>
</tr>
<tr>
<td>Zn SSP 7.17.18</td>
<td>0.51</td>
<td>1.51</td>
<td>-0.07</td>
<td>-1.32</td>
<td></td>
</tr>
<tr>
<td>Zn WCC 7.17.18</td>
<td>29.74</td>
<td>27.70</td>
<td>21.92</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

The raw water mass concentration of zinc was subtracted from the total mass concentration of zinc to determine the mass concentration of zinc which was present in the fine particulate fraction. The dissolved concentration of zinc was subtracted from the
raw water mass concentration of zinc to determine the mass concentration of zinc which was present in the nanoparticle fraction. The negative numbers shown in the table are artifacts of the limitations of the analytical method. The negative values are reported for completeness, but are disregarded for data evaluation. Each of the three fraction concentrations was then divided by the total mass concentration of zinc to calculate the percentage of zinc present in each fraction. The mass concentrations by fraction and the percentage of the mass concentration of zinc in each fraction are shown in Table 5.
Table 5. Sample Concentrations. Mass concentration of zinc in each fraction of the aqueous samples collected from urban Denver surface water.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Zinc Concentration (ppb)</th>
<th>Percentage of Zinc Concentration by Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fine Particles</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>Zn_SPAWWTP_7.16.18</td>
<td>0.55</td>
<td>5.37</td>
</tr>
<tr>
<td>Zn_SPBWWTP_7.16.18</td>
<td>0.48</td>
<td>4.74</td>
</tr>
<tr>
<td>Zn_Cherry_7.17.18</td>
<td>-0.22</td>
<td>0.89</td>
</tr>
<tr>
<td>Zn_ECC_7.16.18</td>
<td>1.47</td>
<td>10.99</td>
</tr>
<tr>
<td>Zn_ECC_7.17.18</td>
<td>-10.48</td>
<td>3.50</td>
</tr>
<tr>
<td>Zn_ESC_7.17.18</td>
<td>2.28</td>
<td>24.12</td>
</tr>
<tr>
<td>Zn_NSP_7.16.18</td>
<td>-0.64</td>
<td>10.29</td>
</tr>
<tr>
<td>Zn_NSP_7.17.18</td>
<td>0.39</td>
<td>5.54</td>
</tr>
<tr>
<td>Zn_Sand_7.16.18</td>
<td>2.73</td>
<td>14.69</td>
</tr>
<tr>
<td>Zn_SSP_7.17.18</td>
<td>0.31</td>
<td>1.51</td>
</tr>
<tr>
<td>Zn_WCC_7.17.18</td>
<td>1.04</td>
<td>27.70</td>
</tr>
</tbody>
</table>

The percentage of zinc in the fine particles fraction ranges from 2 to 62 percent. The percentage of zinc in the nanoparticle fraction ranges from 28 to 96 percent. The dissolved concentration ranges from 3 to 70 percent. In these samples, a majority of the mass concentration of zinc was present in the nanoparticle fraction. The Zn_Cherry_7.17.18, Zn_ESC_7.17.18, Zn_NSP_7.16.18, and Zn_SSP_7.17.18 samples have negative mass concentrations in at least one fraction. This is due to limitations of the analytical method. These results are reported for completeness, but are disregarded from the data evaluation.

**Discussion**

The prime objective of this study was to evaluate whether measuring the concentration of contaminants in SS would provide increased information with regards to water quality. To do this, a significantly large body of analytical data containing
chemical concentration results for select COPCs was examined. These data were used to perform a comparative analysis of COPC concentrations in the suspended solid fraction versus the dissolved fraction. The analytical data were examined in three ways: percentage of times COPCs in SS were present, relative concentrations of COPC in SS and dissolved fractions, and median percentages by fraction.

Frequency of Detection

The first evaluation method, percentage of times present, was used to report whether COPCs as solids were present in water samples. The results indicated that out of 1,478 sample results, solids containing measurable concentrations of the subject COPCs were present in water samples a significant percent of the time for every COPC examined. Solids concentrations were present greater than 75% of the time for every COPC except lead. The low frequency of lead solids detections can be explained by the high level of regulation and remediation that limit environmental lead concentrations in general. The results of this evaluation confirm that SS is present in whole water samples and that there are frequently measurable concentrations of COPCs in the solid phase in water samples.

Relative Concentrations of Solid and Dissolved Phases

The second evaluation method, relative concentrations of solid and dissolved phases, was used to examine whether the concentrations of some COPCs were greater in the solid fraction than the dissolved fraction. A hypothesis of this study stated that the concentrations of Cu, Fe, Pb, and Ti in the solid fraction would be greater than the
concentrations of those metals in the dissolved fraction. The concentration of Zn in the dissolved fraction would be greater than the concentration of Zn in the solids fraction. The analysis showed that this hypothesis was too broad and attempted to overly simplify a complex question. The second evaluation method confirmed that there is considerable variation in the speciation of metals in the water column and that measuring both the solid and dissolved phase concentrations of COPCs is critical to assessing the characteristics of the water sample.

The concentrations of copper in the solid phase were greater than the concentrations of copper in the dissolved phase 32% of the time overall: 50% of the time for rural location types, 34% of the time for mining impacted location types, and 23% of the time for urban location types. The concentrations of copper in the dissolved phase were greater than the concentration of copper in the solids phase 39% of the time: 11% of the time for rural location types, 35% of the time for mining impacted sites, and 77% of the time for urban sites. If a sampling study were to be performed on just a rural site, then the stated hypothesis would be supported. If the study were performed on an urban site, then the hypothesis would not be supported. A study performed on a mining site may prove the hypothesis either true or false, the results of the analysis are too similar to differentiate. The speciation of copper is dependent on the pH, particulate loading, organic content, iron oxide content, and carbonate content of the water (Gagnon, Turcotte, Vigneault 2009; Grassi, Shi, and Allen 2000). Since the different location types are likely to have differing characteristics with regards to these factors, the concentration of copper in the solid versus the dissolved phase is anticipated to be similarly variable. This suggests that a review of site-specific characteristics is
particularly important in the design of sampling programs with regards to copper in water. Complete site-specific data should be evaluated multiple ways to examine the relationships of contaminants in water to best assess fate and transport of these materials. This will also be important to analyzing other remediation or environmental risk factors.

The concentrations of iron in the solid phase were greater than the concentrations of iron in the dissolved phase 87% of the time overall: 93% of the time for rural sites, 85% of the time for mining impacted sites, and 85% of the time for urban sites. The concentrations of iron in the dissolved phase were 10% overall: 5% in rural location types, 10% in mining-impacted location types, and 15% in urban location types. The hypothesis is true for every location type for iron. Since iron has low solubility in water (Hem and Cropper, 1959), this result is as anticipated. Higher concentrations of dissolved iron are only likely in highly acidic or highly alkaline waters (Hem and Cropper, 1959). High concentrations of iron in the solid phase are likely to contribute to the speciation of other constituents in the water.

The concentrations of lead in the solid phase were greater than the concentrations of lead in the dissolved phase 25% of the time overall: 26% of the time for rural location types, 58% of the time for mining-impacted location types, and 18% of the time for urban location types. The concentration of lead in the dissolved phase was greater than the concentration of lead in the solid phase 27% of the time overall: 12% of the time for rural location types, 23% of the time for mining-impacted location types, and 5% of the time for urban location types. The hypothesis is supported for lead for every location type, despite the overall results appearing to demonstrate the opposite. The different result is a mathematic relic due to the way each number is calculated and is not relevant
to the discussion. Historically, significant sources of lead in the environment included atmospheric deposition from leaded gasoline and point sources such as mining and industrial facilities (Prosi, 1989). With the near-elimination of tetraethyl lead from gasoline in 1996 (EPA, 1996) and regulation of lead discharges under the CWA and other regulations, the sources of lead in surface water have been greatly reduced, particularly in urban areas. These efforts are reflected in the data from this study which shows very low incidence of lead at detection limits in water samples in both the dissolved and solid phases. Mining impacted location types continue to show elevated concentrations of lead, particularly in the solid phase. This result is consistent with historic evidence that lead is released from mining sites in the inorganic form which is largely insoluble due to its precipitation as lead carbonate (USGS, 1995).

The concentrations of zinc in the solid phase were greater than the concentration of zinc in the dissolved phase 23% of the time overall: 45% of the time for rural location types, 5% of the time for mining-impacted location types, and 24% of the time for urban location types. The concentration of zinc in the dissolved phase was greater than the concentration of zinc in the solid phase 60% of the time overall: 18% of the time for rural location types, 93% of the time for mining-impacted location types, and 83% of the time for urban location types. The hypothesis is supported for the mining-impacted and urban location types, but it is contradicted by the available data for the rural location types. The speciation of zinc in the various location types is a function of both the metal source and the chemistry of the receiving water. Zinc is insoluble in water, but soluble in acids and bases (Lenntech, 2019). The high percentage of zinc in the mining-impacted location types may be at least partly due to the elevated acidity of water associated with
mining-impacted sites. The properties of the zinc particulates released from mining sites may also be in a more reactive form than the zinc released from urban sources (Gagnon, Turcotte, and Vigneault, 2009). This would also affect the partitioning and transport of the metal in the surface water.

The concentrations of titanium in the solid phase were greater than the concentration of titanium in the dissolved phase 73% of the time overall (mining-impacted location type). The concentration of titanium in the dissolved phase were greater than the concentrations of titanium in the solids phase 13% of the time overall (mining impacted location type). The hypothesis is supported for titanium in a mining-impacted location type.

Median Percentages by Phase

The third evaluation method, median percentages by phase, was used to examine what percentage of each COPC was present in either the solid or dissolved phase. The results of the median percentages by phase analysis are generally similar to the results of the relative concentrations by phase analysis. The results indicate that some COPCs are more evenly distributed between the solid and dissolved phases than others, and that the location type may significantly impact the partitioning of difference COPCs.

In addition, this evaluation is also useful because it provides information about what the consequence of not analyzing the solid phase of the COPCs in water samples may be. Extrapolation from these results can also be used to make some assessment about which phase (solid or dissolved) of the COPC contains the more significant concentration of the COPC.
For example, in the copper results, the median percent solids were the highest in rural samples, lowest in urban samples, and in between for the mining-impacted samples. This indicates that the solids phase concentration of copper is probably the predominant fraction for the copper concentration in the rural samples, but it may not predominate for copper concentrations in the urban samples. The median percent dissolved copper was higher than the median percent copper solids in the urban samples, which also supports this statement.

The site model designed for the sampling and analysis of environmental sites should incorporate these differences. In areas where the sampling and analysis is an ongoing effort, these evaluations can be used to optimize the sampling program. In areas where there is limited preliminary data available, a broader set of samples and analyses should be incorporated in order to better develop the site model.

Nanoparticle Analysis by spICP-MS

In the samples collected, the percentage of zinc in the nanoparticle fraction was generally greater than the percentage of zinc in the fine particle fraction and the dissolved fraction. This indicates that the concentration of zinc in the nanoparticle fraction was a significant source of the overall contaminant picture, despite the small mass contribution.

The size distribution of the NPs in the aqueous samples was generally as expected, the largest NPs were in the raw water samples and the smallest NPs were in the dissolved fraction. The mass concentration of the resolved particles was much lower than the mass concentration of the unresolved particles. When particles cannot be resolved, there is less information available about those particles. The data show that the
unresolved particles are present within a certain size distribution, but it is not possible to
determine where in the distribution they actually occur. If it is important to the outcome
of a study to know where in the NP range (less than 100 nm) a particle falls, then this
would be a source of error which would require additional analysis. A second potential
source of error is in the “dissolved” phase result. In the results for the dissolved fraction,
this study should not have measured particles which were larger than 20 nm, yet particles
in the range of 50 nm were observed. This indicates that what is referred to in the results
as “dissolved” is actually dissolved phase zinc and very small particles of zinc. These
potential sources of error may be important to consider as the technology to analyze for
NPs in environmental samples continues to improve. For the purposes of this study,
however, these unknowns are germane only for the purposes of discussion.

Conclusions

In this study, I examined a variety of data pertaining to the solid and dissolved
fractions of COPCs in aqueous samples. The results of this study indicate that there is
sufficient evidence to indicate that the concentration of contaminants in SS should be
considered in environmental investigations. The evaluation of existing chemical
concentration data showed that COPCs were commonly present in both the solid and
dissolved phases. The detections of COPCs in the solid phase indicate that the COPCs
are present in the water as suspended solids. The evaluation of the new NP data also
supports the idea that COPCs are present as solids suspended in aqueous samples.

Although no risk assessment work was conducted as part of this study, the results
indicate that there is sufficient mass of the chemical contaminants present in SS to
warrant analysis during site characterization work. The COPCs examined in this study were metals which are ubiquitous in the surface waters of the world. Since different receptors (human, ecological, etc.) have a different response to different forms of exposures (for instance a particulate vs. a dissolved phase contaminant), the analysis of the chemical concentrations present in the SS is warranted.

The assessment of “water quality” is an evolving science. As new materials are brought to the market, new research shows additional information about environmental effects, and new health studies are performed, the science of environmental investigation must continue to improve. This improvement needs to come in the form of additional site modelling, comprehensive sampling and analysis planning, and the use of innovative analytical methods.
References


Ranville, James. (2019). Making newly-developed nanoanalysis tools (spICP-MS, FFF-ICP-MS) more readily utilized for exposure studies. Presented at QEEN II Characterization Discussion


