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Brief Report

Comprehensive Examination of Cu, Pb, Zn, Fe, Mn and Cd in Lackawanna County Waters, Northeastern Pennsylvania: A Brief Report

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Abstract: Lackawanna, a US county seat in Northeastern Pennsylvania has an estimated population of 216,000 in 2020. Over the years, it has been reported that several bodies of water found within the county have been contaminated with various metals. However, a comprehensive examination of the presence of these metals has not been conducted. The goal of this brief report was to perform a preliminary quantitative determination of the concentration of various metals found in Lackawanna County water sources. The sources analyzed included Lake Scranton, the Lackawanna River, the Griffin Reservoir, and Keyser Creek. Samples were taken from each source and analyses of copper, lead, zinc, iron, manganese, and cadmium using atomic absorption spectroscopy were performed. A copper concentration of 0.100 ppm was found in the Griffin Reservoir, and 0.380 ppm of iron was found in the Lackawanna River. The concentration of copper and iron in the Griffin Reservoir and Lackawanna River, respectively, were determined to be within safe levels according to guidelines set by the US Environmental Protection Agency.

Keywords: atomic absorption spectroscopy; Lackawanna County; metal analysis; Lake Scranton

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1. Introduction

The Lackawanna River is a 40-mile long river in Northeastern Pennsylvania which originates from the Bone Pond and Wayne County and flows 53.8 miles to its confluence with the Susquehanna River near Pittston, Luzerne County [1,2]. It drains an area of 348 square miles with the Leggetts Creek, Spring Brook, and Roaring Brook as its major tributaries [2]. The river's watershed is 350 square miles hitting regions of Susquehanna, Luzerne, Wayne, and Lackawanna counties in Northeastern Pennsylvania [1]. In total, it serves over 250,000 people in these counties [3]. The Lackawanna River is considered to be the largest point source of pollution in the Chesapeake Bay and has been severely polluted over the years with microplastics, heavy metals, sulfides, and sediment from thousands of acres of abandoned mine spoil piles [4–7]. Several pollutants of concern in the river include hexavalent chromium, lead, mercury, manganese, sulfate, zinc, cyanide, arsenic, and cadmium among others [2]. The aim of this brief report was to provide an assessment of the concentrations of various metals including copper, lead, zinc, iron, manganese, and cadmium in various water bodies within the Lackawanna County.

Copper presents a major source of contamination in drinking water, and while its ingestion can be safe in instances of low intake, overexposure to concentrations over 1.300 ppm can result in chronic effects, such as diarrhea, headaches, and, in severe cases, kidney failure [8,9]. In the case of lead, on the other hand, exposure to this metal in children was found to have negative effects in neurological development. According to a study by Rodrigues et al., it was found that children in areas with higher exposure to lead scored lower on neurological tests such as the Bayley Scales of Infant and Toddler Development Tests [10]. For adults, exposure to lead was found to lead to more colds and influenza. This was seen in adults with blood lead levels of more than 0.100 ppm [11]. Further, lead was determined to be a probable human carcinogen [11]. It was found to inhibit DNA repair in vitro and acts with other mutagens causing kidney, brain, and lung cancer [12]. Ingestion of more than 5 ppm of zinc, on the other hand, may have several short-term effects such as stomach cramps, nausea, and vomiting. Ingestion of this metal over several months may have more dangerous effects, such as anemia, pancreas damage, and decreased levels of high-density lipoprotein cholesterol [13]. The US Environmental Protection Agency (US EPA) guidelines state that drinking water with a zinc concentration greater than 0.5 ppm is considered unsafe [13].

Manganese is another analyte of concern in this research. Since manganese naturally exists in rocks and soil, it is common to find it in water sources. An exposure of more than 0.100 ppm of this metal in water, however, can lead to memory, attention, and motor skills problems. For babies under one year old, learning and behavioral issues may develop [14]. In addition to manganese, iron is another metal of concern in this study. While low levels of iron in water can be considered safe, concentrations higher than 0.300 ppm may have adverse health effects such as stomach issues, diabetes, hemochromatosis, and nausea [15]. Lastly, cadmium, a by-product of copper, lead, and zinc ores, is known to be prevalent where most of those elements may be refined or naturally present. To add on to all of the other element's health hazards, cadmium has its own hazards. If more than 0.005 ppm is present, health effects such as kidney, liver, bone, and blood damage from long-term exposure may occur [16]. Due to the health risks posed by these metals, it is important to assess their concentrations in water sources.

The selected sites for this study included Lake Scranton, Lackawanna River, the Griffin Reservoir, and the Keyser Creek (Figure 1). Several criteria were considered in the selection of the analyzed sites. Lake Scranton was chosen due to its use as a major water supply to the greater Scranton area. Lake Scranton holds approximately 2.5 billion gallons of water and provides drinking water to more than 16,000 people in the surrounding area [17]. Another key factor in choosing Lake Scranton as a sampling site is that it is distantly connected to the Lackawanna River through the Spring Brook, Stafford Meadow Brook, and the Rocky Glen Pond. The drainage basins of the Spring Brook and Stafford Meadow Brook are designated as a Coldwater and Migratory fishery, and the Spring Brook is considered to be Class A Wild Trout Waters for brook and brown trout fishes [18,19]. The Rocky Glen Pond, on the other hand, features many fish, such as bluegill, bass, muskie, sucker, and crappie [20]. The Lackawanna River was selected because of its length that spans throughout the Lackawanna County. The Griffin Reservoir and Keyser Creek were selected since they are tributaries either flowing into or out of the Lackawanna River. The Griffin Reservoir is a major watershed for Leggett's Creek, a tributary to the Lackawanna River [21]. The Keyser Creek, on the other hand, directly flows into the Lackawanna River. These sites were also chosen because of their proximity to the US EPA "superfund sites." Superfund sites are areas that have been contaminated due to hazardous wastes, like heavy metals or large organic compounds, being dumped, left out in the open, or otherwise improperly managed [22]. To determine the optimal collection locations at each site, a topographical map of the area surrounding the superfund site was observed. Then, the samples were collected from water sources that were downhill from the aforementioned sites. The Keyser Creek sample was used because of its proximity to the superfund site labeled as "Lackawanna Refuse", which was a mining area that was active from the late 1800s until the 1950s. It was featured on the National Priorities List until 1999 but continues to be monitored because of the presence of contaminated materials, such as heavy metals, large and small organic compounds, and acidic and basic compounds [23]. The Griffin Reservoir was used because of its proximity to the "Aladdin Plating" superfund site, which was the location of an electroplating business from 1947 to 1982. Operators at this site disposed of contaminated rinse water and sludge, which caused the site to appear on the National Priorities List until 2001. The US EPA still collects groundwater samples both on-site and off-site to ensure the safety of the site [24]. This preliminary study is the first to comprehensively examine the presence of copper, lead, zinc, iron, manganese, and cadmium in the abovementioned sites. No published studies have yet assessed the levels of the aforementioned metals in these sites.

Figure 1. Map showing all water sampling sites as indicated by the red circles.

2. Materials and Methods

Several considerations were taken into consideration in selecting metals for analysis in the various abovementioned sites. For Lake Scranton, the Environmental Working Group (EWG) has a list of metals and other contaminants listed on their website [25]. After reviewing the EWG website, cadmium and manganese were chosen for analysis in this lake. The metals in the Lackawanna River, on the other hand, were decided based on the Pennsylvania Department of Environmental Protection's Lackawanna River Watershed Total Maximum Daily Load [26]. As such, iron and manganese were chosen for analysis in this area. Finally, for Keyser Creek and the Griffin Reservoir, the US EPA has a list of contaminants on each superfund site. Copper, lead, and zinc were selected for analysis in Keyser Creek, while copper and lead were only selected for analysis in the Griffin Reservoir. In this experiment, water was collected from different sources. Each sample was obtained in accordance with the Arkansas Water Resources Center procedure for collection of water samples [27]. Water samples were obtained using a clean 0.5-L bottle. The bottle was then rinsed three times, before the water was collected by submerging the bottle 0.5–1.0 feet deep below the surface of the water at a spot several feet away from the edge of the water source [27]. The geographical latitudes and longitudes as well as the elevation of each collection site are tabulated in Table 1.

Table 1. Geographical coordinates and elevations for each collection site.

Collection Site	Geographical Coordinates	Elevation (Feet)
Lake Scranton	41°23′50″ N 75°37′32″ W	1280
Griffin Reservoir	41°29′48″ N 75°39′48″ W	1350
Keyser Creek	41°23′34″ N 75°42′10″ W	680
Lackawanna River	41°24′57″ N 75°39′50″ W	690

After the samples were collected, they were then stored in a cooler at approximately 2.22 °C. This temperature was deemed to be the optimum temperature for storage of substances used in the communal lab space. Once the samples were ready for preparation, the US EPA's Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by Flame Atomic Absorption procedures [28] was followed. Briefly, 100 mL of a well-mixed sample was prepared and put in a beaker. Then, 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl were added to the solution. The solution was then heated to 95 °C and boiled lightly until the total volume reduced to 15–20 mL. To induce reflux, a ribbed watch glass was placed on top of the beaker. Once the solution was reduced and cooled, the final volume was adjusted to 100 mL with reverse osmosis water. The prepared solutions were then analyzed using an AAS (Perkin Elmer AAnalyst 300).

In the establishment of the calibration curves, three sets of absorbance values were automatically obtained from the instrument at each known concentration. Additionally, the mean and standard deviation of each triplicate were calculated and automatically provided by the instrument. For each unknown water sample, nine absorbance values were obtained. The average absorbance value of each sample was manually calculated from the dataset obtained.

3. Results

3.1. Development of Calibration Curves

Using the absorbance values obtained from the AAS for each standard solution, calibration curves were created for copper, lead, zinc, manganese, iron, and cadmium (Figures S2–S7). In addition to the equation of the line of best fit, the correlation coefficient of each trendline, represented by R^2, is displayed on each graph. These correlation coefficients generated values of 0.9867, 0.9991, 0.9992, 1.0, 0.9986 and 0.9706 for the copper, lead, zinc, manganese, iron, and cadmium calibration curves, respectively (Figures S2–S7).

3.2. Analysis of Water Samples

There were two metals that contained quantifiable data (Table 2 and Figure 2). The copper concentration in the Griffin Reservoir was found to be at 0.100 ppm. This amount is below the hazardous level of 1.300 ppm according to the US EPA guidelines [29]. Table 2 also shows an iron concentration of 0.380 ppm in the Lackawanna River. This value is near the accepted value of 0.300 ppm that is deemed safe by the US EPA [30], as well as various state and local government agencies [31].

Table 2. Calculated concentrations in Griffin Reservoir, Keyser Creek, and Lackawanna River samples. "NA" implies that the metal was not tested for that specific sample site.

Sample	[Cu] (ppm)	[Fe] (ppm)
Griffin Reservoir	0.100	NA
Lackawanna River	NA	0.380

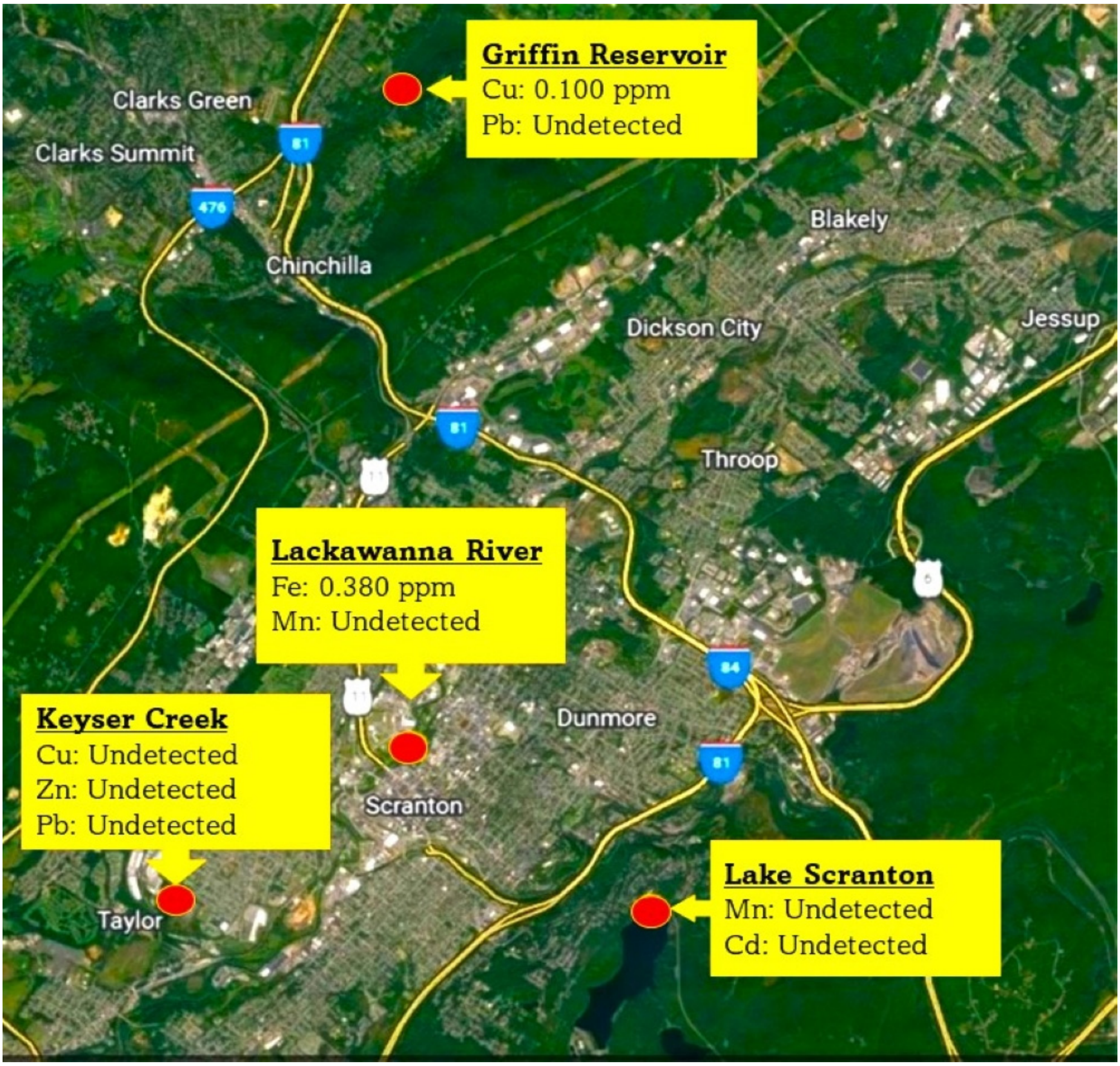

Figure 2. Map showing the concentrations of analyzed metals at each sampling site, which are indicated by the red circles.

4. Discussion

The Lackawanna River is a major tributary of the North Branch of the Susquehanna River. Large increases in metal concentrations were reported in the section of the Susquehanna River that receives the Lackawanna River [32]. However, no recent studies have investigated the levels of copper, lead, zinc, iron, manganese, and cadmium in Lackawanna River and other specific bodies of water within the county. This is the first study to assess the levels of the abovementioned metals in the area.

Undetectable concentrations of lead, zinc, manganese, and cadmium in some of the water sources within the county including that of the Lackawanna River may be attributed to several factors. The US EPA's webpage for the Lackawanna Refuse and Aladdin Plating superfund sites were recently removed from the National Priority List [33] as the hazardous contaminants at the sites as they are now deemed to be at safer levels than they used to be. Specifically, the Lackawanna Refuse site was removed from the list in 1999 because of actions taken to clean up the site, such as removal and disposal of drums, highly contaminated municipal refuse, dried paint, as well as contaminated soil. It is also set to be reviewed again in 2024 [23]. The Aladdin Plating site, on the other hand, was removed in 2001, after efforts to remove soil and groundwater that were contaminated by chromium and other metals performed at the site [24]. Beyond this, one limitation of the study is the restricted detection limit of the AAS instrument, which can only detect metal concentrations greater than 50 ppb. Some of the observed metals may exist in insufficient levels to allow AAS detection. In order to circumvent this limitation, an Inductively Coupled Plasma Mass Spectrometry may be used in future studies. Several routes can be taken to further expand this research. One major route is to analyze various areas of the Lackawanna River and its tributaries for levels of iron similar to a study performed by Byman et al., which assessed the effects of sewage treatment plants on the chemistry of the water at different coordinates on the aforementioned river [32]. Performing such an experiment, however, may require samples to be taken within one-mile increments to assess how iron concentration compares among different sampling coordinates. Such experiments may also be repeated multiples times throughout the year to account for differences in sampling seasonality.

It is the intent of this research to also analyze metals in soil or sediments near water sources. Copper, a metal of major interest in this study, can be found in high concentrations in sediment and soils around water sources [34]. Lead, on the other hand, may be found in river surface water between 3–30 ppm [35] as well as in soils [36]. Manganese, another metal of interest, may be found mainly in groundwater and rarely in river water [37]. As such, this may explain the undetectable concentration of manganese in the river water.

As noted in this research, iron was found to have a relatively higher concentration than other metals. Iron can be found naturally in groundwater, river water, and lakes which may explain its abundance [38]. Further the Lackawanna River watershed is impaired by high concentration of iron in 2005 [21], although no iron analysis has been scientifically published in recent years. It has been known that remnants of iron in the river can be attributed to the discharge of mine water into the river via the Old Forge borehole (Figure 3). The borehole was established to relieve the water pressure that caused flooded basements and yards in the area. Once iron oxide interacts with the river water, the metal compounds precipitate out of the solution forming a bright yellow or orange sludge that colors the rocks and the riverbed, which was seen in small amounts in the water sampling process [39]. It should be noted that while iron in this analysis is within safe levels according to the US EPA guidelines, co-exposure of iron with microplastics could aggravate the cognitive impairment by disturbing brain iron homeostasis, and further inducing ferroptosis in cognitive-related brain areas [40]. This is particularly important since microplastics have recently been identified in Lackawanna River and in 52 other Pennsylvania waterways [5]. Microplastics are considered ubiquitous pollutants that efficiently adsorb persistent organic pollutants from the surrounding environment. Further, due their small size, they are easily available for ingestion at all trophic levels inducing mechanical damage, various cellular responses, and inducing mechanical damage [41]. While the focus of this brief report is not in microplastics, it is, imperative to consider the analysis of these pollutants in Lackawanna River and other bodies of water within the county due to the negative consequence of co-exposure of iron with microplastics as mentioned earlier.

Addressing heavy metal pollution is a serious issue and requires multiple avenues to address contamination. A detailed understanding of the metal-induced mechanisms is important in devising an effective remediation plan for heavy metal removal. Such remediation methods may include extraction, physical separation, immobilization, toxicity reduction, and isolation [42]. It is, indeed, apparent, that anthropogenic activities may have contributed to the heavy metal contamination in this study. Therefore, strict monitoring of these activities is a suggested solution to mitigate this issue [42]. For more than six decades now, there has been an uncontrolled release of polluted mine water into the Lackawanna River from an outlet near Scranton, Pennsylvania. The river is just upstream from where it flows into the Susquehanna River. Acid levels may have declined to normal levels, but some outlets may still be dumping significant amount of iron into the river daily [43]. Beyond the analysis of metals, other parameters need to be assessed to determine the overall health of various bodies of water in Lackawanna County. As such, carbon oxygen demand, ammonium, phosphorus, microplastic levels, and antibiotics concentrations will also need to be considered.

Figure 3. Map Showing the Location of the Old Forge Borehole (purple) in relation to the previous sites mentioned (red).

5. Conclusions

In this research, the AAS method was used to quantitatively analyze the concentrations of metals found in different water sources throughout Lackawanna County. Water samples were obtained from Lake Scranton, the Lackawanna River, Keyser Creek, and the Griffin Reservoir. The metals analyzed were copper, lead, zinc, manganese, iron, and cadmium. Ultimately, two of these samples were determined to contain metal contaminants. The Griffin Reservoir sample was determined to possess 0.100 ppm of copper and the Lackawanna River possessed 0.380 ppm of iron. These concentrations are relatively safe for these two metals. The acquisition of data in a preliminary study like this may offer a pivotal step towards assessing the status of all metals in Lackawanna River and its various tributaries and runoff areas.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/analytica3030021/s1, Figure S1: Water collection sites at (**a**) Lake Scranton; (**b**) Griffin Reservoir; (**c**) Keyser Creek; (**d**) Lackawanna River; Figure S2: Calibration curve for copper; Figure S3: Calibration curve for lead; Figure S4: Calibration curve for zinc; Figure S5: Calibration curve for manganese; Figure S6: Calibration curve for iron; Figure S7: Calibration curve for cadmium.

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