A Study on Arsenic in the Geo-Environment: Soil through Natural Hydrogeological Mechanisms

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Abstract

Arsenic, a pervasive element, is widely distributed in the atmosphere, soils, rocks, natural waters, and various organisms. Its prevalence is further amplified by mining operations, the combustion of fossil fuels, and the utilization of arsenical pesticides, herbicides, and crop desiccants. Additionally, the inclusion of arsenic in livestock feed, particularly for poultry, contributes to its status as a common trace constituent in most soils. Arsenic accumulations are evident in soil, sediments, surface water, and groundwater. Its presence in soils and groundwater is a global phenomenon, impacting numerous countries such as Bangladesh, the Czech Republic, China, Argentina, Pakistan, India, Cambodia, Ethiopia, the United States, and Mexico. The widespread distribution of arsenic is exacerbated by changes in environmental land use patterns, extensive mineral mining, resource overexploitation, and unplanned human activities. These factors collectively intensify the toxic risk associated with arsenic. Arsenic concentrations in soil, influenced by both natural processes and human activities, pose a substantial threat to the environment, microbial communities, and human populations worldwide.

Keywords: Arsenic; Geochemistry; Heavy metals; USEPA; Soils; Groundwater; GIS.

Introduction

Arsenic, a hazardous element, is naturally present in soil with concentrations ranging from 10 mg/kg to 10,000 mg/kg. The weathering of bedrock containing arsenic-bearing minerals facilitates the migration of arsenic from bedrock to soil, eventually reaching groundwater, the food chain, plants, and animals. Elevated concentrations of inorganic arsenic in groundwater have been reported across diverse regions. The concentration and migration of arsenic are intricately linked to soil properties, including clay, silt, sand, ionic charges, and various minerals in different soil forms. Arsenic adsorption and desorption processes are influenced by soil physiochemical characteristics, exhibiting variations between soil types. Sandy soils, with lower levels of Fe and Al oxides and clay minerals, tend to have higher arsenic availability, posing increased toxicities to humans, plants, animals, and groundwater [1].

The complex behavior of arsenic in soil involves strong reactions

with soil solid constituents through time-dependent retention and release processes. While arsenic is generally considered relatively immobile, redox conditions can enhance its mobility through reductive dissolution of arsenic-bearing inorganic mineral oxides and the reduction of arsenate to arsenite. Flooding and the development of anaerobic conditions can lead to the release of arsenic from soils below the redox boundary. Most environmental arsenic issues result from mobilization under natural hydrogeologic conditions.

Arsenic and heavy metals have adverse effects on human health, leading to classifications as human carcinogens by the EPA, the

International Agency for Research on Cancer (IARC), and the National Toxicology Program (NTP). Ingestion and inhalation exposure to inorganic arsenic increase the risk of various cancers, including lung, skin, bladder, kidney, and liver cancers. The long-term health effects associated with non-fatal doses include vascular diseases [2-5].

Elevated arsenic levels in some public water systems in New England were discovered through required testing after state and federal regulations were imposed. Investigations into the causes of elevated arsenic levels in New England groundwater pointed to potential geologic sources. This paper presents a detailed study of one geographic area in New England, specifically Worcester County in Central Massachusetts, where high arsenic concentrations were frequently reported during environmental site assessments. The study aims to comprehend the current status of arsenic and heavy metals at different depths in soil and explore correlations with underlying bedrock geochemistry. The main objectives include evaluating arsenic concentrations in soils and bedrock under different conditions, assessing relationships with other heavy metals, and determining correlations with underlying bedrock geochemistry.

The increasing concern for human health risks drives the study of the biogeochemical cycling of arsenic in the environment.

Materials and Methods

Geologic Features of the Study Area

The investigation focused on Worcester and surrounding towns in central Massachusetts. Worcester, situated on the eastern edge of the central Massachusetts uplands, exhibits a topography dominated by small highland areas known as drumlins. These hills trend in a north-south direction and are interconnected by lower-lying highlands, forming a plateau dissected by erosion. The lowlands between the hills contain surface waters like wetlands, brooks, and ponds flowing southerly (Figure 1).

The region encompasses two significant drainage basins, the northeast-flowing Nashua River and the northwest-flowing Assabet River. The primary aquifers in this basin consist of unconsolidated glaciofluvial deposits of sand and gravel, capable of yielding substantial water for various needs [6-8].

Most of the bedrock belongs to the Merrimack terrane, a Gondwana terrane extending to the coast across northeastern Massachusetts. The Clinton-Newbury fault forms its eastern border, and the terrane includes a mix of metamorphosed sedimentary, volcanic, and plutonic rocks. In Worcester, the bedrock consists of foliated schist, gneiss, and granite, with variations in rock types.

Environmental Databases and Arsenic Data Compilation

Existing environmental databases and reports, particularly those containing soil and groundwater analytical data for arsenic, were accessed. The data were compiled from selected sites within central Massachusetts, confirming widespread reports of arsenic levels above regulatory "background" levels in soil (Figure 2).

Bedrock Geologic Map: A map illustrating the type of bedrock in the study area was generated, providing insights into the geological composition.

Arsenic Concentrations in Soil: Maximum arsenic concentrations in soil per town were mapped, highlighting areas with elevated arsenic levels.
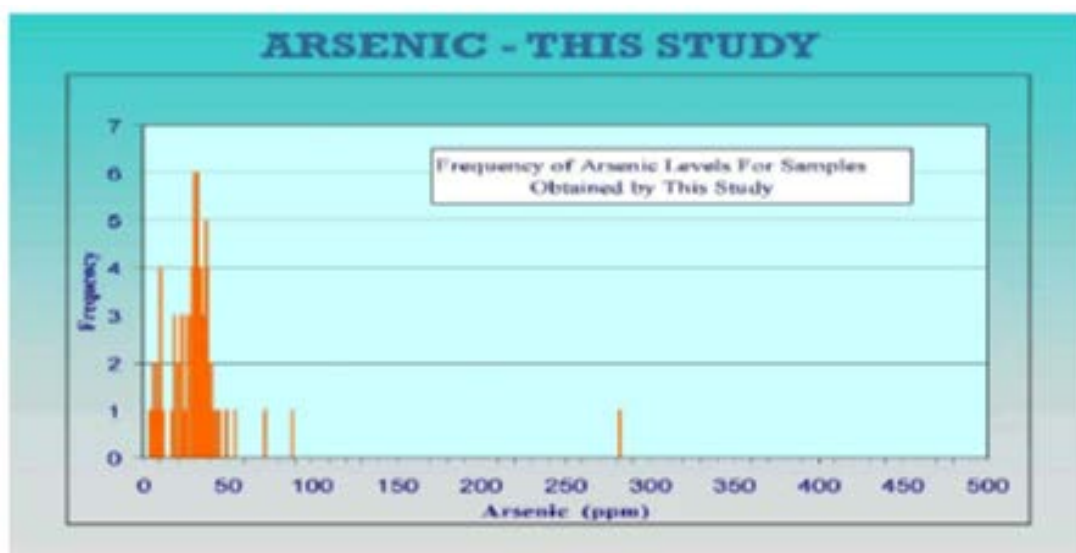

Figure 1: Arsenic concentration (ppm) frequency in overburden soils in the study site.
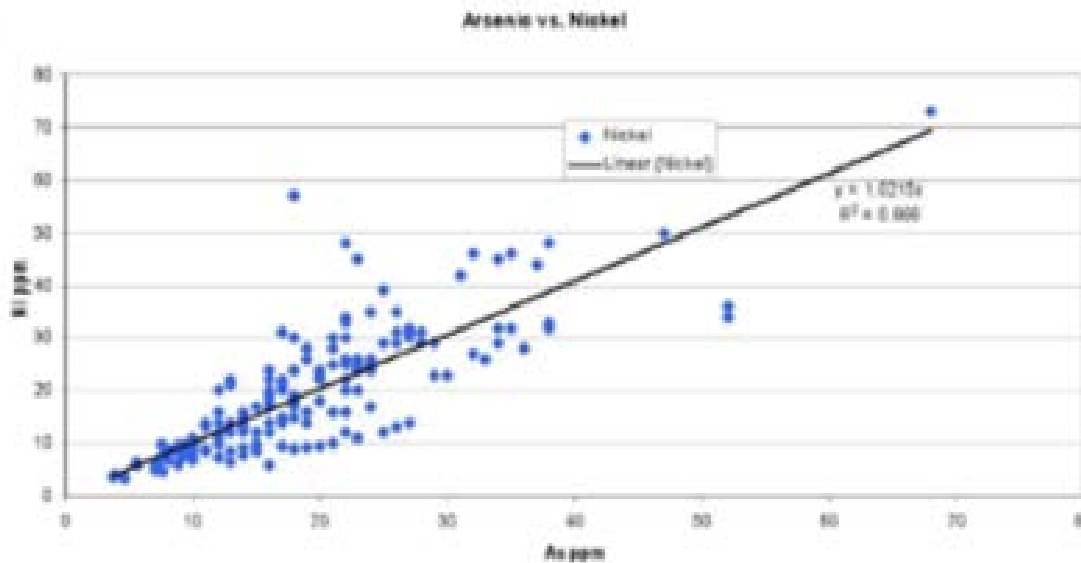
Figure 2: Relationship of Arsenic concentration (ppm) with Nickel in the study site.
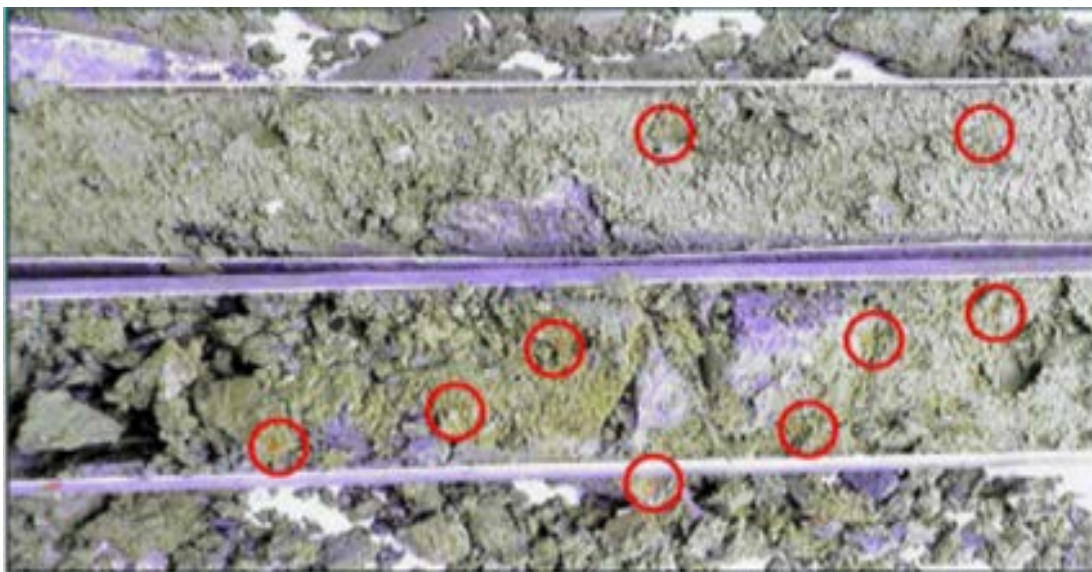

Figure 3: Soil core samples with sulfide rock fragments. Note: Soil cores with lighter orange/yellow colored particles (arsenic sulfides) are noted in the red circles.

Soil Sampling and Analysis

Hillside and Valley Sites: A table categorized sites based on environmental deposition (hillside, lake, river, wetland) and displayed arsenic concentrations at various depths below the land surface.

Hillside Soil Sampling Study: A detailed analysis of arsenic distribution was conducted atop Green Hill, with continuous soil cores collected to a depth of 30 feet below the ground surface. The study confirmed elevated arsenic concentrations in hillside areas.

Statistical Analysis and Correlation

Database Compilation: A database of 283 soil sample locations from near the ground surface up to a depth of 30 feet below the ground surface was analyzed. Soil samples from hillside sites exhibited an average arsenic content of 31 ppm, while samples from valley or flat-lying areas had an average of 71 ppm.

Frequency Histogram: The compiled data were presented in a frequency histogram, visually representing the distribution of arsenic concentrations in hillside and valley/flat-lying areas.

The statistical analysis and correlation aimed to understand the

spatial distribution of arsenic in relation to geographic features and soil composition within the study area.

Results and Discussion

Arsenic Distribution in Soil

The frequency distribution curves for arsenic concentrations in soil revealed two distinct subsets: 20 ppm to 50 ppm and 50 ppm to 800 ppm. The most common concentrations ranged from 25 ppm to 40 ppm, with 82% of soil samples exceeding 17 ppm. Statistical analysis and correlation with heavy metals showed a strong relationship between arsenic and cobalt (R2=99), followed by iron (R2=98), chromium (R2=89), and nickel (R2=66). The correlation graph demonstrated a linear relationship between arsenic and nickel concentrations [9-15].

Vertical Distribution and Soil Types

The vertical distribution of heavy metal concentrations was influenced by soil texture and horizon types (A, E, B, C). Loam clay soil contained double the heavy metal content compared to sand and silt. Sandy soil showed lower metal concentrations in the upper layer and higher concentrations in lower horizons. Soil cores revealed lighter orange/yellow particles (arsenic sulfides) in specific areas (Figure 3).

Bedrock Analysis

Bedrock analysis confirmed the presence of pyrites (FeS2) and cobaltites (CoAsS) through electron microprobe analysis. The arsenic percentages in cobaltites ranged from 40% to 47%. Researchers reported a strong relationship between cobalt and arsenic, with cobalt bonding strongly with iron and nickel. Sulfide bonding with cobalt, nickel, and arsenic was observed.

Biogeochemical Migration of Arsenic

The oxidation form and speciation of arsenic played a crucial role in its biogeochemical migration. Geochemical processes, such as redox potential and pH, influenced the movement of metallic elements in the solid-aqueous environment. The arsenic movement involved both releasing it from parent materials and retaining it in deep horizons. The presence of arsenic sulfides in soil cores indicated potential mechanisms of migration and precipitation.

Spatial Distribution and Arsenic Migration

Elevated arsenic concentrations (30 to 800 ppm) in soils of central Massachusetts exhibited a pattern of higher concentrations at lower elevations and lower concentrations at higher elevations. The arsenic levels returned to background levels (<20 ppm) at each end of the traverse. The average arsenic concentrations at hillside sites were 50% lower than sites in valleys, suggesting arsenic migration along the direction of groundwater flow. Groundwater recharge at higher elevations dissolved arsenic, which precipitated in flat-lying aquifers before discharge to the surface drainage system.

Relationship with Bedrock Geochemistry

The study emphasized that the derivation of soils from local bedrock formations, including occasional sulfide incorporation, explained elevated arsenic concentrations. Knowledge of underlying bedrock geochemistry aided in predicting elevated arsenic levels in overburden soils. The central Massachusetts "arsenic province" correlated with the geochemistry of the bedrock.

Conclusion

The study identified the redistribution of arsenic in soils by natural hydrogeologic processes, emphasizing specific geographic areas. Environmental factors during soil deposition correlated with varying arsenic concentrations. Bedrock analysis indicated the presence of arsenic-bearing minerals, especially cobaltite (CoAsS), suggesting a potential correlation between high arsenic in groundwater and soils. The study proposed broader applicability of these principles to predict areas with elevated arsenic in soils across the U.S. Geographic Information Systems (GIS) could leverage existing databases to estimate arsenic concentrations nationally. Legislative mandates, public awareness, and proactive measures were highlighted as crucial factors to prevent exposure to this environmental toxin.

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