

Geochemical and Mineralogical Investigation of Elevated Arsenic and Trace Elements in Soils and Sediments of New Jersey Inner Coastal Plain

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Executive Summary

Soil cores were collected in 2018 at four locations in the Burlington-Bordentown-Hamilton region of central New Jersey to examine occurrences of elevated concentrations of arsenic (As), vanadium (V), and other metals at various depths in this region. Chemical analyses by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and by portable X-ray fluorescence (pXRF), and mineralogical studies by X-ray diffraction (XRD) and scanning-electron microscopy (SEM) were performed on collected soil samples to evaluate geologic factors that may control the distribution of the high As and V zones in soils.

The comparable results between pXRF and chemical analysis by ICP AES suggested that the pXRF method can provide a fast and useful tool for initial assessment of metals in soil in the field and in field-lab conditions. In general, concentrations of As, iron (Fe), and V increased with depth at all core sites. The mean and median values of As and V in the soil samples exceeded New Jersey Department Environmental Protection (NJDEP) Site Remediation Standards (SRS) (As = 19 mg/kg, V = 78 mg/kg). The major minerals observed in selected core samples by the XRD analysis were quartz and phyllosilicates, including biotite and various clay minerals (glaucanite and kaolinite). The XRD and SEM analyses indicated that primary minerals likely associated with As and V in soils are glaucanite, pyrite, and other As-bearing minerals such as goethite and scorodite, which are mostly products of soil weathering processes. Positive relations between V and primary elements such as potassium (K) and aluminum (Al) that form the phyllosilicate glaucanite indicated that glaucanite is a likely source of elevated V in soils. Arsenic and V are predominantly associated with amorphous and crystalline forms of Fe and Al oxides that occur as coatings on mineral grains. Arsenic and V bound to these amorphous and crystallized hydrous oxides of Fe and Al fractions can be highly labile, and may be mobilized by changing geochemical (soil) conditions such as pH or redox potential (Eh), potentially resulting from changes in soil saturation driven by irrigation and seasonal water-table fluctuation.

Based on the limited data collected in this study, elevated concentrations of some metal(oids) in undeveloped soils of this region are likely to be naturally occurring and should be further examined. Many elements are enriched in the iron hydroxides, along with As, making 'fingerprinting' of arsenic sources difficult.

This summary report supplements a jointly-funded study between USGS NJ Water Science Center and NJDEP DSR titled "Geochemical and mineralogic investigation of elevated arsenic and trace element concentrations in glaucanitic soils and sediments of the New Jersey Inner Coastal Plain". This research supports the efforts of the NJ DEP Contaminated Site Remediation & Redevelopment program. The full data release can be found at <https://doi.org/10.5066/P922Q288>.

1. Background

Elevated levels of arsenic and vanadium (As, V) have been detected in soil and sediment samples at multiple locations along the Route 130 corridor in the Burlington – Bordentown – Hamilton – East Windsor- Cranbury region (Schick, 2013) with no associated industrial discharge or agricultural arsenical pesticide/fungicide usage (Figure 1a). The maximum values identified in soils of these locations were 899 mg/kg and 1,320 mg/kg for As and V, respectively, which greatly exceeded the 19 mg/kg and 78 mg/kg residential direct contact (RDC) SRS (NJAC, 2012). The concentrations of As, V increased with depth below land surface and were associated with the occurrence of dark green/black clay in the subsurface. The concentrations at these depths (mostly at depths 5 ft and greater) were higher than the previously defined natural baseline concentrations for As/V and other trace elements associated with shallow (mostly less than 5 ft) glauconitic soils (Figure 1b) in the area (Dooley, 2001; Sanders, 2003).

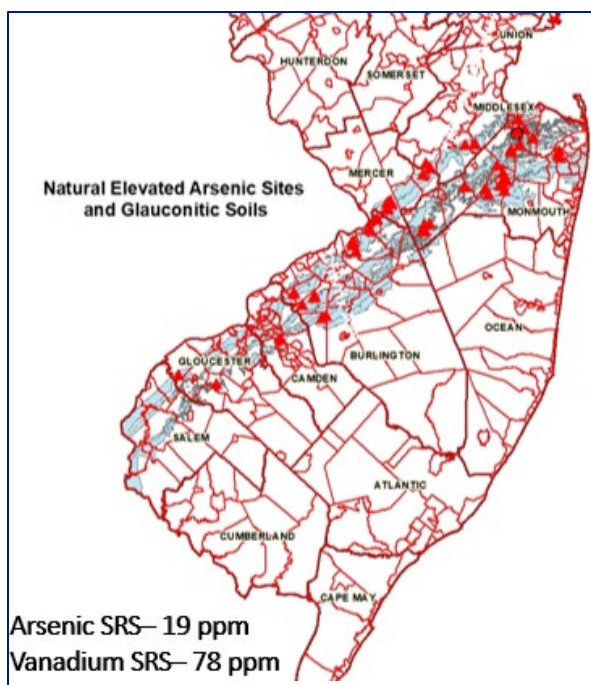


Figure 1a

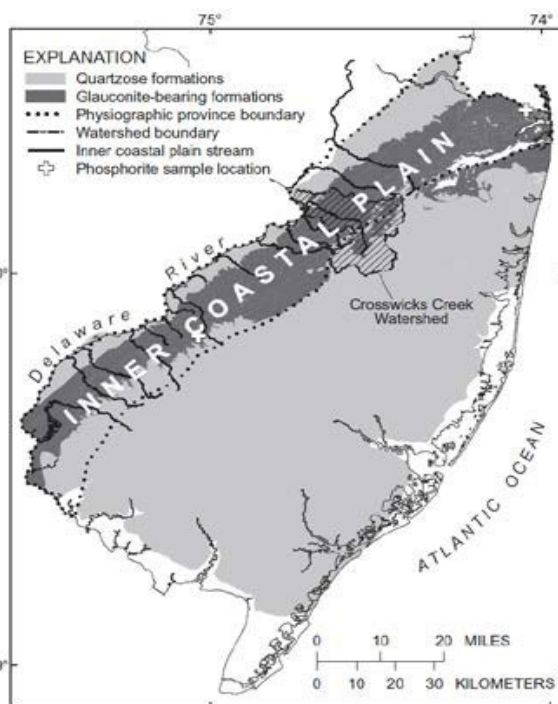


Figure 1b

Figure 1a. Map of remedial investigation locations in NJ with elevated concentrations of arsenic in soils (Map provided by Kevin Schick, NJDEP, 2018, written communication). Red triangles are remedial investigation site locations. The blue shaded area defines the NJ Inner Coastal Plain (Watson and Schopp, 2009). **Figure 1b.** Generalized geology of the New Jersey Coastal Plain showing the outcrop extent of glauconite-bearing formations and major westward draining streams of the Inner Coastal Plain in central New Jersey (sub-province extent from Watson and Schopp, 2009).

These multiple occurrences of elevated trace element concentrations in soil demonstrate that this geochemical feature or phenomenon may be more common than previously expected. Therefore, it was considered beneficial to re-characterize the natural background range for metals in the soils and sediments of this region that contains extensive glauconitic soils (Figure 1b) as it is important consideration in soil standard and remediation implementation efforts (Zhou et al., 2017).

The review of previous investigations, reports, and data suggest that some of the highest concentrations of the trace elements are at sites underlain by black glauconitic formations and occur at depths near the water table. The NJDEP, in cooperation with the US Geological Survey (USGS), conducted a pilot study (Reilly et al., 2023) to examine the occurrences of As and V at various depths in this region by assessing the geologic factors and sediment properties associated with As and V enriched soils. The study attempted to determine if certain minerals or soils, such as glauconite, contribute to the exceedance of NJDEP SRS, as suggested by previous studies. The study also evaluated the use of multiple tools to further investigate sediment properties associated with SRS exceedances.

This summary report supplements a jointly-funded study between USGS NJ Water Science Center and NJDEP DSR titled “Geochemical and mineralogic investigation of elevated arsenic and trace element concentrations in glauconitic soils and sediments of the New Jersey Inner Coastal Plain”. This research supports the efforts of the NJ Contaminated Site Remediation & Redevelopment program. The full data release can be found at <https://doi.org/10.5066/P922Q288>.

2. Geologic setting

Many of the sites with elevated As/V fall within the Inner Coastal Plain of New Jersey, where glauconitic sediments crop out in a series of bands that trend NE–SW, generally paralleling the lower reaches of the Delaware River (Fig. 1). The underlying geologic formations found to be most inclusive of glauconite are the Manasquan, Hornerstown, Navesink, Marshalltown, Merchantville, and the Woodbury Formations (Barringer et al., 2011). The glauconitic sediments are far from uniform, ranging from nearly black clay to light gray sand, and layers of phosphorite deposits (Sugarman, 1999; dePaul and Szabo, 2007). Dooley (2001) and Barringer et al. (2001, 2011, and 2013) have shown that these glauconitic sediments are most likely the geologic source of arsenic (As), beryllium (Be), iron (Fe), vanadium (V), and chromium (Cr) when found elevated in the region. Barringer et al. (2001) showed that a few of the glauconitic sediments contained higher concentrations of arsenic (about 50 mg/kg) than soils derived from adjacent sandy geological materials, even though arsenical pesticides had historically been used on the orchards that tended to be situated on the well-drained sandy soils (Murphy and Aucott, 1998). The baseline range of concentrations for As, V, Be, and Cr for shallow soils in the area derived from the glauconitic sediments were defined by Dooley (2001) from hand-augered sediment samples collected from undeveloped areas (non-agricultural, non-industrial). However, later investigations (Schick, 2013; Barringer et al., 2001, 2011, 2013) have identified concentrations much higher than those Dooley (2001) reported, as discussed in the previous section.

3. Methods

A two-phase study was carried out to investigate geologic factors that may influence the extent of the high As and V occurrences in soils. This two-phase approach was designed (i) to obtain existing soil analytical information (data) to evaluate the relationship between As and V distributions and geology and stratigraphy and (ii) to collect new soil samples to determine sediment chemistry and mineralogy in glauconitic strata in the areas with the elevated As and V.

Phase i: A review of the geology and stratigraphy was conducted to determine whether the elevated As and trace element concentrations were restricted to a specific geological formation, stratigraphic unit, lithology or texture type, or a specific depth horizon. Geologic and stratigraphic factors were evaluated by compiling existing digital information such as trace soil metal concentration data collected during remedial investigations (RI) and lithologic descriptions of borehole samples (Schick, 2013). This data was integrated with digitized geological and soil properties (NRCS, 2018; NJDEP, 2019), using ArcGIS to determine if there are naturally enriched zones of trace metals within sediments.

Phase ii: Chemical and mineralogical investigations of soils at sites with elevated trace elements can help verify whether the enriched zones of As, V, and select other trace elements occur in secondary “sediment redox zones” near or at the water table (Stuckey et al., 2016; Meng et al., 2017; Schaefer et al., 2016) or in specific sediments with specific characteristics (distinctive chemistry or mineralogy) that represent primary deposits with possible zones of post-depositional diagenetic enrichment. Mineral composition can be identified using standard X-ray diffraction (XRD) techniques (Peppe et al., 2001) and scanning-electron microscopy (SEM) (Goldstein et al., 1981 & 2017).

In Phase ii, this study also evaluated the effectiveness of portable X-ray fluorescence (pXRF) analysis in determining sediment chemistry (metals) compared to the standard laboratory-based method using ICP-AES to determine whether the As-rich zones can be preliminarily identified in the

field.

3.1. Data Compilation and GIS analysis

Several reports and summaries for RI investigations by NJDEP (Dooley, 2001; Sanders, 2003; Schick, 2013) were reviewed to obtain data for phase i. As an initial part of this project, relevant digital RI information was compiled into a geodatabase to examine baseline concentration exceedances at a spatial scale to select additional sampling locations. A spatial analysis of sample trend was conducted with regards to topography, geology, land use, hydrology, proximity to other elevated-level trace-element sites, and depths of the elevated-level trace- element samples to select new sample locations.

3.2. Soil/Sediment Sample collection

Four sample locations (Figure 2a) were located within the Inner Coastal Plain (as defined by Watson and Schopp, 2009, and Owens et al., 1999), and focused on areas of minimal development (such as forests, wetlands, and parks). Site selection was targeted toward outcrops of geological formations known to have geologically enriched trace element concentrations with known NJDEP SRS exceedances for As and V (Dooley, 2001). Factors considered in site selection included accessibility and safety of the sites, underlying surficial and bedrock geology, historic land use, and documented soil characteristics (NJDEP, 2019 and NRCS, 2018). The primary goal for the site selection was to capture the spatial and vertical variability of trace elements in minimally weathered geologic formations (background) as opposed to soils altered by human activity.

In 2018, the following soil cores (Figure 2a) were collected to a depth of approximately 20 ft below land surface at each location:

- BFR & KUS Cores:
 - Near historic agricultural area and known NJDEP SRS exceedances for sites in Hamilton Township
 - Represents Merchantville Formation

- BUD core:
 - Historically forested area (natural geologic setting), but near historic agricultural area and orchard with known NJDEP SRS exceedances for As in Florence Township
 - Represents Merchantville Formation

- BURL core:
 - Historically forested area in Burlington Township to represent a natural geologic setting
 - Represent Woodbury Formation
 - Previously sampled location (Dooley, 2001)

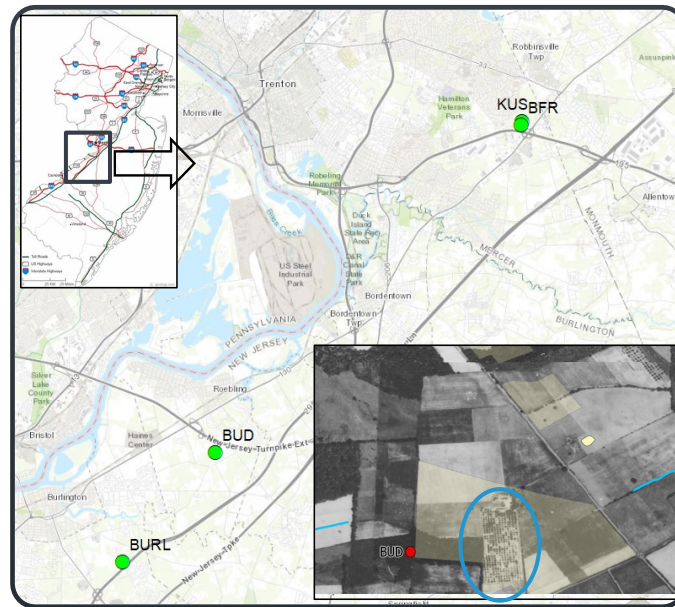


Figure 2a.



Figure 2b



Figure 2c

Figure 2a. Map of NJ and subset map showing the core sample locations (green circles). Lower Aerial photo shows historic land use (1930) near the BUD core. Yellow shaded areas have NJDEP SRS soil exceedances for arsenic and the blue circle shows historic orchards in the vicinity of the core sample. **Figure 2b.** Soil core collection with a Geoprobe® Macro-Core Soil Sampler. **Figure 2c.** Soil cores collected at the KUS site using a Geoprobe® Macro-Core Soil Sampler.

Soil core collection and sampling were conducted in accordance with USGS and NJDEP guidances (Radtke, 2005; NJDEP, 2022). A Geoprobe direct-push drill rig (Figure 2b) was used to advance a pre-cleaned stainless-steel Macro-Core Soil Sampler to collect continuous-core samples from the surface to the bottom of the borehole (roughly from 0-20 feet below land surface). The stainless-steel corer was lined with disposable pre-cleaned acid-rinsed (5%hydrochloric acid (HCl) solution) butyl acetate liners to prevent cross contamination of the samples. At each site, the cores were collected in liners of 48 inches in length by 1.25 inches in diameter to a depth of about 20 feet below land surface (Figure 2c). The core tubes were securely capped, labeled, and chilled at 4°C. The cores were then transported to the laboratory at USGS New Jersey Water Science Center (NJWSC) and stored at 4°C.

Later, soil cores were photographed and soil characteristics were documented in a field logbook. Each core was split into multiple containers (every six inches of core or by lithologic feature) following visual evaluation. Using a pre-cleaned, acid-rinsed (5% HCl solution) plastic trowel, samples were placed into acid-rinsed polyethylene containers and stored at 4°C at the USGS NJWSC for chemical and mineralogical analyses.

3.3. Analysis of Soils

A pXRF analyzer was used as a screening tool to qualitatively measure the concentrations of As, V, and other trace elements in the core. The core soils selected for additional chemical and mineralogical analysis were based on site lithology, geology, and highest trace element concentrations as determined by the pXRF. One split sample at each selected core depth was dried, homogenized, and sent to a NJDEP contract laboratory to determine trace element and ancillary sediment chemistry. For a subset of samples, a second unprocessed split sample was sent to for mineralogy analysis using XRD and SEM to identify trace metal(loid) bearing minerals in the study area.

3.3.1. Qualitative Analysis with X-ray fluorescence (pXRF) Analyzer

A portable hand-held Niton XL3t GOLDD+ X-ray fluorescence (pXRF) analyzer was used as a screening tool to qualitatively measure the concentrations of As, V, and other trace elements in the USGS NJWSC laboratory. Unhomogenized core samples were placed in an pXRF cup using an a pre-cleaned, acid-rinsed (5% HCl solution) plastic trowel. The pXRF cup was covered with 7-micron thick Mylar film. National Institute of Standards and Technology (NIST) soil standards were used to verify pXRF factory calibration before each use. Data acquisition was performed for 120 seconds in “SOILS” mode to limit inter-element peak interference effects (ThermoScientific, 2010). Measurements were made on 196 samples (171 samples and 25 duplicate samples) over the course of the study. However, only the elements of interest (As, V, and Pb) are presented in this report. The routine Quality Assurance and Quality Check (QA/QC) included silica (SiO₂) blank samples, NIST soils standards run after every twenty (20) samples, duplicate samples analysis, and replicate analysis on same sample performed to determine variability in the pXRF analysis method.

3.3.2. Chemical (Quantitative) Analysis of Soils

Thirty-two (32) split samples (BUR = 7, BUD = 9, BFR = 7, and KUS = 9) for chemical analysis were dried (110°C for 12 hours) in the USGS NJWSC laboratory and then homogenized using a 5-percent HCl pre-cleaned agate mortar and pestle to ensure homogenous sediment samples prior to shipment to a NJDEP contract laboratory (TestAmerica Environmental Services LLC). The EPA CLP Method ISM02.4, which is based on EPA methods SW-846 6010D and 200.7 (EPA, 2016) was used for analyzing 22 trace elements in soil and water (blank sample). The method uses a hydrochloric acid digestion of the sediment samples followed by analysis with an ICP-AES instrument. The QA/QC of analytical procedure included equipment blank (water) sample, duplicate (3) samples, matrix spike (3) samples, and double blind samples (2 samples of geochemical reference material with known concentrations of elements). The NJDEP Office of Quality Assurance performed data validation after receiving the analytical data from the contract laboratory.

3.3.3. Mineralogical Analysis of Soils

Ten (10) selected splits of the soil samples with the highest pXRF As and V concentrations were taken directly from the core sub sample (unhomogenized and shipped unrefrigerated) and analyzed for semi-quantitative (with clay) whole rock mineralogy by XRD at the USGS Geology, Geophysics, and Geochemistry Science Center Laboratory in Denver, Colorado. A small number of samples (n=5) were also analyzed using a SEM equipped with energy dispersive x-ray spectrometer (EDS) for semi-quantitative detection of elements to identify distinct As and/or V enriched mineral phases or zones within mineral grains. Details on the methodology and QA/QC are available in USGS ScienceBase metadata release (Reilly et al., 2023).

4. Results and Discussion

Qualitative, chemical, and mineralogical analysis results are discussed in terms of the applicability of the qualitative (pXRF) method, depth distribution of selected metals, and their sources/sinks in the sediments.

4.1. Applicability of pXRF Analysis

The pXRF analysis overestimated concentrations of trace metals by ~10% compared to chemical analysis done by ICP AES (Figure 3), thus the method can provide a fast and useful tool for an initial assessment of metals in soil. The fact that the pXRF estimates the total concentration of targeted metal, whereas the analytical method measures the recoverable portion of metal in soils, could explain the observed discrepancy in concentrations between the two methods. The other factors that affect the pXRF detection are water content, soil organic matter content, and soil particle size (Chen et al., 2021). Also, the effect of sample (chemical samples) homogenization may contribute to the said discrepancy in concentrations. It is also important to note that not exactly the same aliquots were used for the two different analyses, as the ICP-AES method used a subsample of the aliquot contained within the pXRF cup for any given sample. Nevertheless, the pXRF can be used as a qualitative or quantitative screening tool (Figure 4) for sample analysis decisions depending on the analyte of interest (as defined by Parsons et al., 2013)

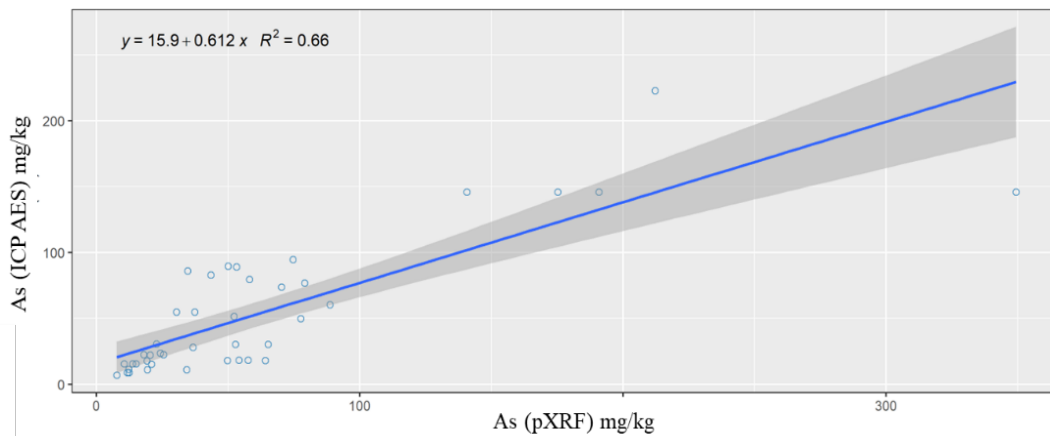


Figure 3 - Plots of Chemical (ICP AES) vs pXRF As analyses from the four NJ soil cores. The KUS 129-133 sample was removed as an outlier. Parsons et al., 2013, have shown that a pXRF can be used as a quantitative or qualitative screening tool.

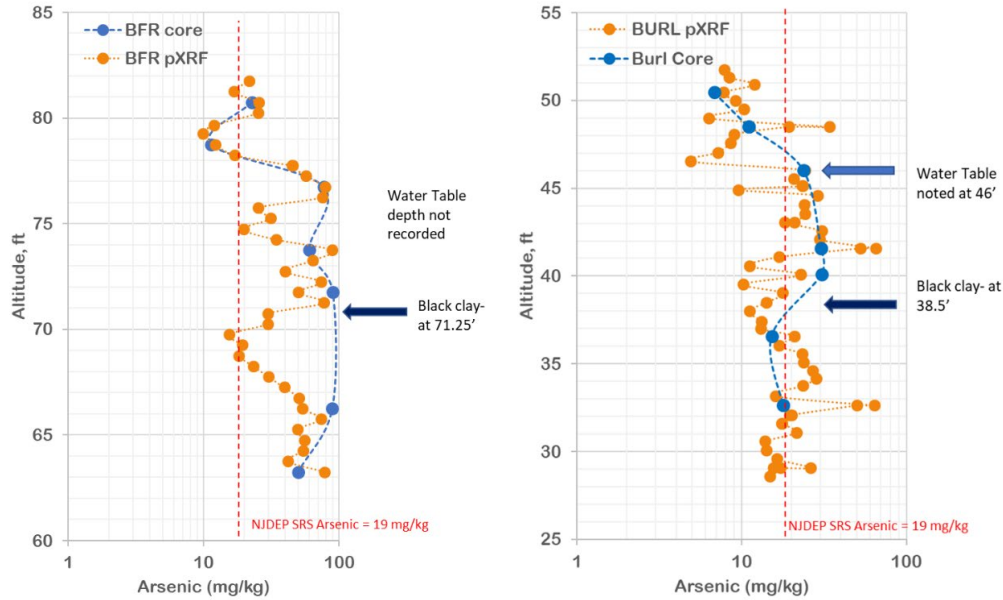


Figure 4 – Comparison of As concentration determined by pXRF (orange) and analytical method (blue) at BFR and BURL core sites.

4.2. Depth Distribution of Metals

As, Cd, Fe, Pb, and V were detected above the reporting limits. However, only As and V exceeded the NJDEP SRS values of 19 mg/kg and 78 mg/kg respectively (Exceedances: As = 23 of 32 samples and V = 17 of 32 samples) (Table 1). Relatively high concentrations of these metals were observed at the BUD core site, while the lowest concentrations were observed at the BURL core site (Figure 5). Although, concentrations seemed scattered with depth, average increase in concentrations of As, Fe, and V with depth was observed at all four core sites (Figure 5). Dooley (2001) reported the As concentrations in soils ranged between 3 and 131 mg/kg with a median concentration of 29.5 mg/kg, which is lower than the observed range (6.8-223 mg/kg) and median (40.2 mg/kg) of As concentrations in this study. It should be noted that soil samples were collected at deeper depths and targeted (based on pXRF screening) towards soil zones with high As for this study.

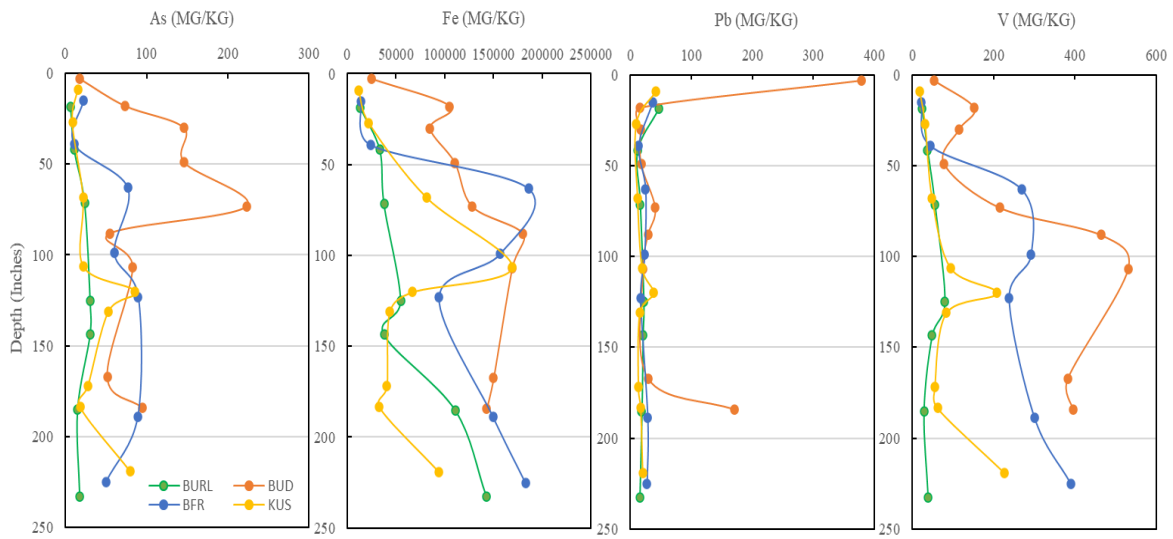


Figure 5 – Depth profiles of selected metals (Fe, Pb, As, and V) determined by chemical analysis (ICP AES) at four NJ soil core sites.

Table 1 – Summary of chemical analysis results (n = 32, in mg/kg) for selected metals detected above the reporting limit.

	Arsenic	Iron	Lead	Vanadium
Mean	55.0	90481	38.3	158.6
Median	40.2	89400	20.4	81.6
Std deviation	48.0	58039	67.1	146.0
Min	6.8	11300	9.4	17.3
Max	223.0	186000	379.0	531.0
# > NJDEP SRS ¹	23	-	0	17
% > NJDEP SRS	71.9	-	0	53.1
¹ SRS = Soil remediation standard. Pb = 400 mg/kg for dermal contact. SRS is not available for iron.				

A high Pb:As ratio (>4:1) was observed at BUD and BUR core sites; As concentrations were below NJDEP SRS (19 mg/kg) in these samples (Figure 5). Pb (379.0 mg/kg) and As (17.7 mg/kg) were detected at the near surface soil (0-6”) of the BUD site, which is located adjacent to a farm field. The other high Pb:As ratio (Pb 46.1 mg/kg and As 6.8 mg/kg) was detected at a slightly greater depth (16-21”) at the BURL site, which is located in a historically forested area and adjacent to a highway. Dooley (2001) suggested that the increasing trend in Pb in the BURL core (Holmdel soil series) was associated with natural sources. However, the high Pb observed at the BUD site might be associated with the historical application of pesticides (residue pesticides) in the area. High Pb, As, V, and Cd were also observed at relatively greater depth (181-187.5”) in the BUD core sample.

4.3. Mineralogy and Source/Sink of Metals

The major minerals observed in selected core samples by the XRD analyses were quartz and phyllosilicates, including biotite and clay minerals (glaucanite and kaolinite). The primary natural sources of As and V in soils are minerals like glaucanite, pyrite, and other less-common As bearing minerals. The images in Figure 6 show grains of glaucanitic composites in the BUD 46-52” core sample. The soil cores also contain a considerable percentage of goethite (iron mineral FeO(OH)). Pyrite was identified by SEM in many samples and may be associated with glaucanite as embedded grains or in voids, which are common modes of occurrence as described by Rabenhorst and Fanning (1989). For example, the small discrete euhedral pyrite crystals are associated with glaucanite in the BUD 181-187.5” sample (Figure 7). A high concentration of V (395 mg/kg) was observed in the BUD 181-187.5” soil sample with a high weight percentage (20.5%) of glaucanite mineral. Positive relations between V and primary elements such as potassium and aluminum that form the phyllosilicate glaucanite indicated that glaucanite is likely to be rich in V (Figure 8).

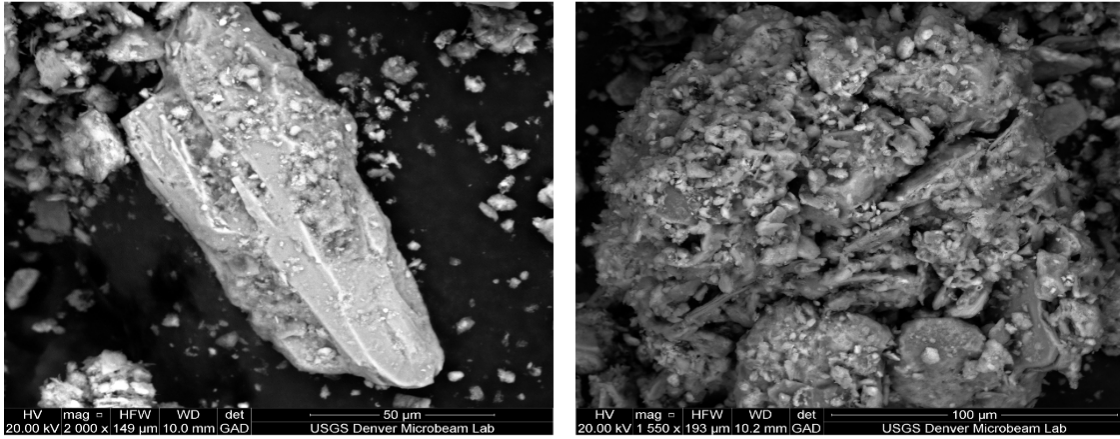


Figure 6 - The images show glauconite in the BUD 46-52” core sample. The grains have the chemical composition of glauconite (left), while the image on the right may represent a glauconite pellet.

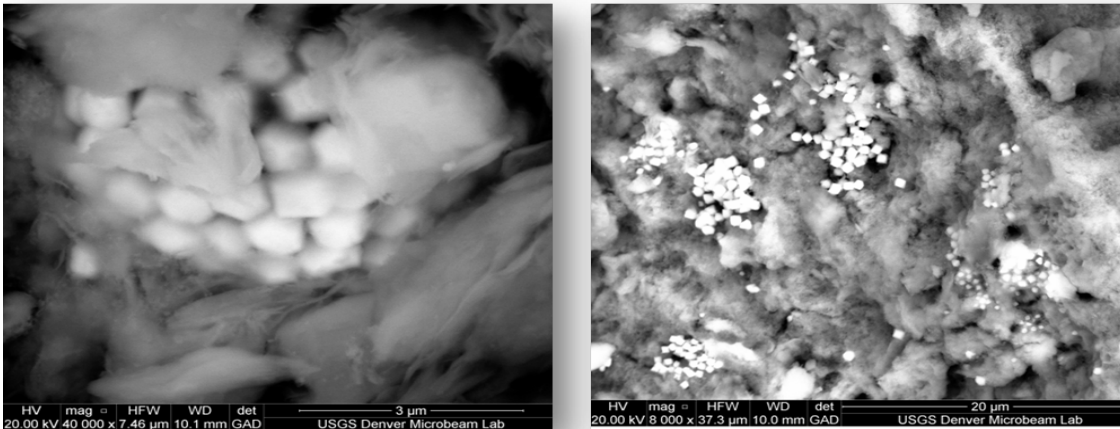


Figure 7 - SEM images of small euhedral pyrite crystals in the BUD 181-187.5” sample.

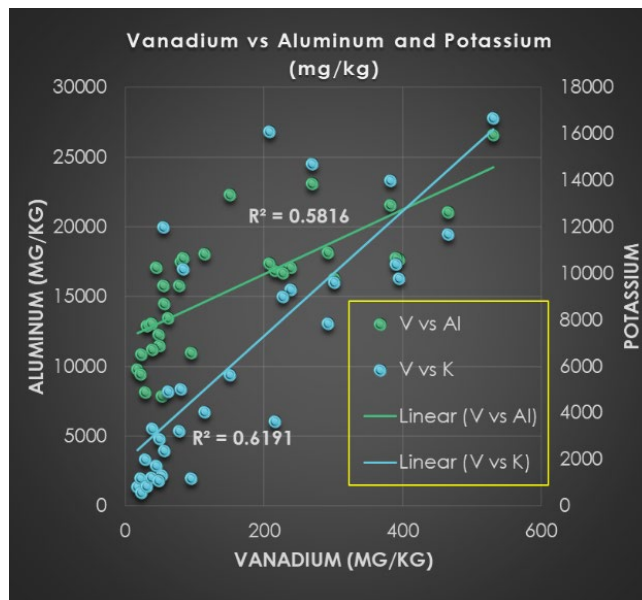


Figure 8 - The relation of vanadium to the primary elements that make up the phyllosilicate glauconite (Potassium and Aluminum).

In general, As is predominantly associated with amorphous and crystalline forms of Fe and Al oxides, as suggested by some studies (Gerdeldani et al., 2021, Pedersen et al., 2006). Amorphous Iron oxides (AIO) were identified by the SEM analysis in the sample BUD 70-76" where the highest As concentration of 223 mg/kg was measured by chemical analysis. The AIO occurs primarily as non-crystalline forms and coatings on larger grains, which contain As and V in this core sample (Figure 9). As and V bound to these amorphous and crystallized hydrous oxides of Fe and Al fractions can be highly labile (potential source), which could be mobilized by changing geochemical (soil) conditions such as pH or redox potential (Eh) due to changes in soil saturation driven by irrigation and seasonal water table fluctuation (Gerdeldani et al., 2021; Meng et al., 2017; Schaefer et al., 2016; Shaheen et al., 2016; Stuckey et al., 2016).

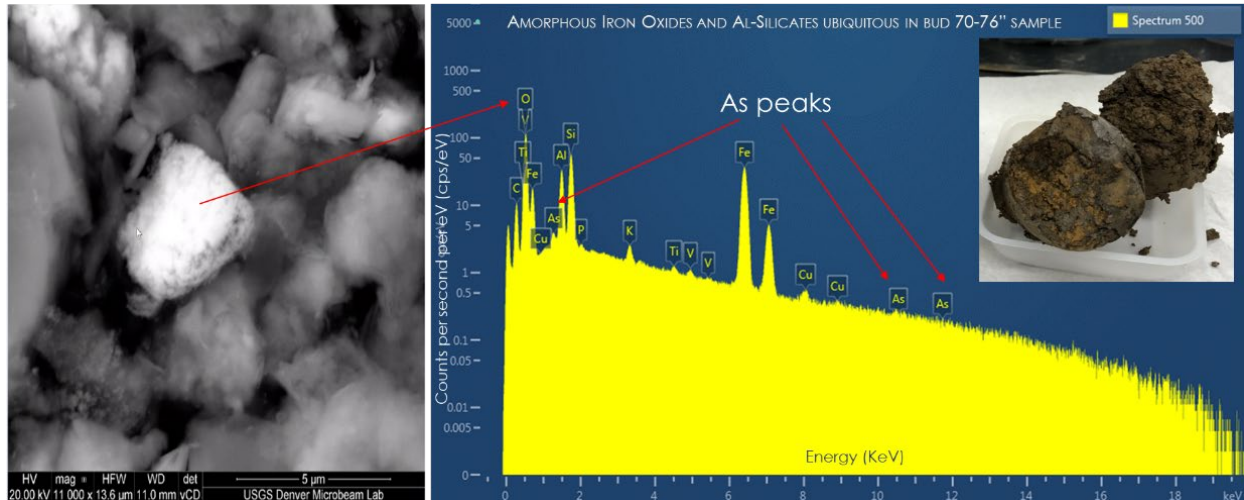


Figure 9 - Amorphous Iron Oxides coating on grains (left panel) observed in BUD 70-76" core sample (inset photo on right). The grain coatings contain As and V (right panel).

Arsenic mobility and release from soils is highly dependent on oxidation state (redox) which could be indicated by lithologic evidence such as redoximorphic features (RMFs) and lithochromatic mottles (LCMs) present in soils. RMFs are formed by oxidation/reduction of iron and/or manganese coupled with their removal, translocation, or accumulation in soils (Lindbo et al., 2010). The LCMs, which occurred as deposits of gray clay with iron stainings were observed in cores collected for the study (Figure 10).



KUS Core 65-72"

KUS Core 117-123"

Figure 10 - Color variations and LCMs in the KUS core.

Goethite ($\text{FeO}(\text{OH})$) was abundant in the upper weathered section of cores, which could be from the weathering of glauconite (Dooley, 2001). Glauconite and possibly Scorodite were identified in the KUS129-133” sample using SEM (Figure 11). Scorodite is a hydrous iron arsenate mineral ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), which is a relatively common secondary mineral resulting from the oxidation and weathering of arsenic-bearing mineral species such as arsenopyrite. Pyrite (1.4 wt%) and Glauconite (38.6 wt%) were observed in the deeper sample (KUS 169-175”). However, As concentration was not quantifiable in pyrite clusters and framboids by SEM because of the relatively high detection limit of ~ 200 mg/kg As.

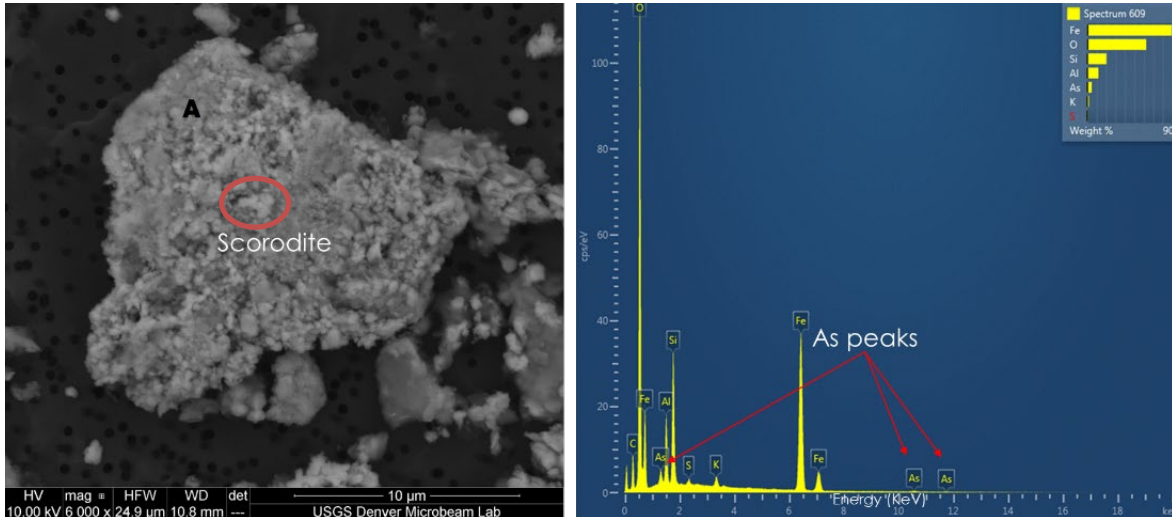


Figure 11 - SEM Image and EDS graph with semi-quantitative detection of As mineral (Scorodite, shown by red circle) in KUS 129-133”.

Iron accumulation and LCMs, as seen in the sample KUS 129-133” (Figure 12), may also indicate areas of As enrichment by the formation of secondary As bearing mineral such as scorodite, or other iron oxide minerals. Soil saturation (from water level fluctuation) can produce reducing conditions that promote reductive dissolution of As-bearing mineral oxides and reduction of arsenate and potential As mobilization and ongoing enrichment (Frohne et al., 2011; Shaheen et al., 2016; Schaefer et al., 2016; LeMonte et al., 2017; Meng et al., 2017).

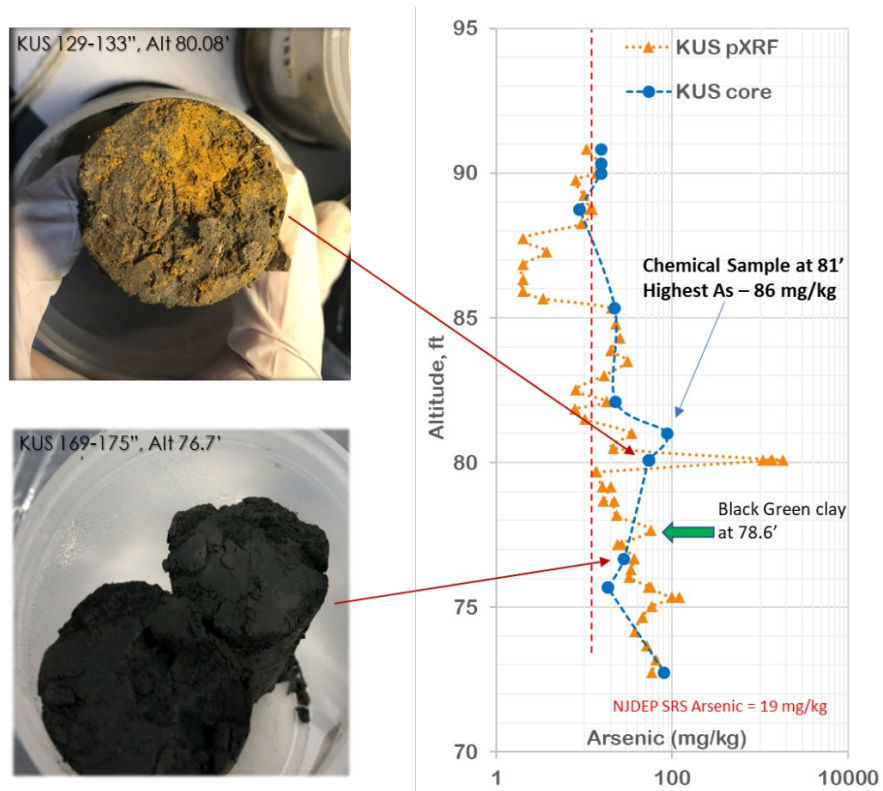


Figure 12 - Glauconite and possibly Scorodite (Hydrous Iron Arsenate: $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) were identified in the KUS129-133". Deeper sample KUS 169-175" contained Glauconite and Pyrite.

5. Conclusions

Chemical and mineralogical analyses and detailed lithology indicated that glauconite, scorodite, pyrite, and other As-bearing minerals, as well as amorphous grain coatings may be natural sources for As and V observed in the cores collected at these sites. Redoximorphic features and lithochromatic mottles may be indicative of arsenic mobilization through soils and secondary arsenic enrichment. The pXRF method can provide a fast and useful tool for initial assessment of metals in soil. However, differences between pXRF values and chemical concentrations indicated that matrix effects and homogenization of samples can affect the analysis results.

The analysis of collected samples indicated that elevated concentrations of metals in these areas are likely to be naturally occurring and should be further examined. Moreover, many elements are enriched in iron hydroxides, along with arsenic, making "fingerprinting" of arsenic sources difficult.

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