

Soil Profile Concentration Distributions of Antimony and Bismuth across Southeastern Missouri (USA)

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Abstract

Recent research has suggested that increased industrial and technological utilization of antimony and bismuth necessitates greater research to determine the soil and water chemistry and the environmental risks associated with these elements. The near-total soil profile concentrations of antimony and bismuth were determined for key soil series across southeastern Missouri. The antimony concentrations ranged from 0.65 to 0.08 mg kg⁻¹, whereas the bismuth soil profile concentrations ranged from 0.92 to 0.03 mg kg⁻¹. Most pedons showed antimony concentrations ranging from 20 to 30 mg kg⁻¹, whereas bismuth concentrations were commonly 10 to 20 mg kg⁻¹. For soils having argillic horizons, antimony and bismuth concentrations were greater for the illuvial horizons than the eluvial horizons, whereas Entisols, Inceptisols, and one Vertisol showed rather uniform antimony and bismuth concentrations, features paralleling the soil texture distribution. Both antimony and bismuth showed significant correlations with iron.

Keywords

Trace Elements, Antimony, Bismuth, Soils, Group 15

1. Introduction

Group 15 of the Periodic Table consists of the elements nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). In this manuscript, the emphasis will focus on antimony and bismuth. Previously, Aide *et al.* [1] published soil profile distributions involving arsenic across southeastern Missouri.

1.1. Introduction to Antimony

The ground state electronic configuration for Sb is [Kr] $4d^{10}5s^2p^3$ and the cova-

lent radius is 0.141 nm [2]. Filella *et al.* [3] noted that the primary Sb valence states are Sb⁺⁵, Sb⁺³, and Sb⁻³, with Sb⁵⁺ as the more commonly occurring oxidation state. Stability constants and other selected thermodynamic data are limited. Antimony compounds are considered priority pollutants in the United States and European Union and elevated antimony soil and sediment concentrations are primarily related to anthropogenic sources or high arsenic bearing sulfide ores. Stable anionic thiocomplexes include SbS₂²⁻ and SbS₄³⁻ [3]. Antimony has a wide range of uses including the manufacture of semiconductors, diodes, flame-proof retardants, lead hardeners, batteries, small arms, tracer bullets, automobile brake linings, and pigments [3].

In a detailed survey of the literature, Kabata-Pendias [4] reported the crustal average Sb concentrations are approximately 0.2 mg kg⁻¹, with argillaceous sediments showing slightly larger average concentrations of up to 4 mg kg⁻¹. Hou *et al.* [5] reported that the average Sb concentration ranges in Japanese soils were 0.83 ± 0.32 mg kg⁻¹. Stibnite (Sb₂S₃) is the most important antimony ore, followed by valentinite (Sb₂O₃). Other sulfide minerals include pyrargyrite, zinkenite, jamesonite, and boulangerite.

Filella *et al.* [3] reported an ordering for antimony species toxicity, which is antimonites $(Sb^{3+}) >$ antimonates $(Sb^{5+}) >$ organoantimonials. Kolesnikov *et al.* [6] evaluated the ecotoxicity of 23 metals, metalloids, and nonmetals in a Haplic Chernozem and proposed three hazard classes with Sb in class II (intermediate hazard class). Antimony was determined to be bound to relatively immobile Fe and Al oxihydroxides and to a lesser degree as antimony-organic substances [7].

Antimony (III) and (V) ions undergo hydrolysis readily in aqueous solutions. In oxic water and soil conditions, the Sb(V) species are the major species [8]. Antimonic acid has been represented as H[Sb(OH)₆], Sb(OH)₅, or HSbO₃ and frequently forms polymers as the pH increases. Antimonous acid [Sb(III)] is frequently represented as SbO⁺, Sb(OH)₂⁺ in acidic media and as Sb(OH)₄⁻ or hydrated SbO₂⁻ in basic media. Antimony(III) chloride will form successive chlorocomplexes [8]. Under reducing conditions and in the presence of sulfur, the mineral stibnite (Sb₂S₃) will crystalize in acid soils, whereas in alkaline pH levels the mineral SbS₂ replaces stibnite.

Sb(III) prefers sulfur as a ligand; however, Sb³⁺ will form stable complexes with ligands such as citric, lactic, mandelic, and tartaric acids Antimony(V) forms complexes with polyhydric alcohols, polyhydric phenols, and citric, malic, and lactic acids. Antimonic acid (Sb₂O₅.nH₂O or H₃O₄Sb) forms complexes with low molecular weight acids that have oxygen-containing functional groups, including humic compounds. Pilarski *et al.* [9] investigated the adsorption of Sb(III) and Sb(V) with humic acid, demonstrating adsorption was effectively described using Langmuir isotherms. Bagherifam *et al.* [10] investigated high organic matter soils incubated with antimony and documented that humic substances were responsible for 63% of the extractable Sb. In the humic acid fraction, antimony was largely associated with the low molecular weight fulvic acids and correlated with total organic carbon and nitrogen contents [9]. Thanabalasingam *et al.* [11] investigated antimony adsorption onto hydrous oxides of Mn, Fe, and Al. Capacity values decreased along the sequence MnOOH > $Al(OH)_3$ > FeOOH and adsorption on each substrate decreased gradually at pH values greater than pH 6. Factors influencing Sb sorption included substrate surface charge, chemical form of Sb and surface interactions. In oxic soil conditions antimony is present as Sb(OH)₆ and in anoxic soil conditions Sb(OH).

Tang *et al.* [12] and Vidya *et al.* [13] noted that mine waste leaching, the weathering of sulfide ores and shooting ranges using Sb adulterated lead-based ammunition are major Sb pathways for impacting soils and aquatic environments. Tang *et al.* [12] also documented that Sb toxicity in plants reduces i) root and shoot growth, ii) seed germination, and iii) yield potential. Furthermore, antimony induces chlorosis, reduces photosynthetic efficiency, membrane stability, and nutrient uptake, and increases reactive oxygen species. Vidya *et al.* [13] reported that the majority of plant uptake of Sb is confined to root tissues; however, some of the metalloid is translocated to the shoot. Inhibition of photosynthesis, modified root and leaf patterns, activation of antioxidant systems, and plant membrane disruption are some of the deleterious effects of antimony on plant growth and development. Bowen [14] documented that terrestrial plant uptake of antimony may result in a plant tissue concentration of approximately 60 μ g kg⁻¹.

1.2. Introduction to Bismuth

The ground state electronic configuration Bi is [Xe] $4f^{14}5d^{10}6s^2p^3$ [2]. The covalent radius for Bi is 0.152 nm [2]. In a detailed survey of literature, Kabata-Pendias [4] noted the crustal average Bi concentrations are approximately 0.2 mg kg⁻¹, with argillaceous sediments showing slightly larger concentrations up to 4 mg kg⁻¹. In the United States, Govindaraju [15] reported that soil Bi averages range from 0.03 to 0.69 mg kg⁻¹. Hou *et al.* [5] reported average Bi concentration ranges in Japanese soils were 0.32 ± 0.12 mg kg⁻¹. Hou *et al.* [5] reported that average Bi distributions among the more dominant chemical fractions were noncrystalline (26%), peroxide extractable organic (26%) and metal organic (19%), residual (17%) and crystalline iron (12%). In Japan, Manaka [16] documented that Sb, and Bi were positively correlated with the amorphous Fe₂O₃.

Murata [17] investigated Bi solubility as influenced by pH and the presence of EDTA, citric acid, tartaric acid, L-cysteine, soil humic acids, and dissolved organic matter. Solution pH and the presence of citric acid, tartaric acid, L-cysteine, and soil humic acids influenced bismuth solubility. Kleja *et al.* [18] investigated the binding of Bi3+ to organic soil materials and noted that Bi3+ formed organic soil complexes, forming a dimeric Bi3+ complex.

The objectives of this investigation are: i) to estimate the soil abundances of antimony and bismuth across southeastern Missouri, and ii) to determine their potential soil profile distribution because of eluviation-illuviation and iron oxide abundances.

2. Materials and Methods

2.1. Study Area

The study area in Missouri is located between the Mississippi River and the St. Francois River. The northern section consists of thin to thick loess mantles overlying primarily Precambrian igneous and Ordovician carbonate rocks. The southern portion is in the Mississippi River embayment and consists of flood-plains and terraces that have coarse to fine sediments.

The climate is continental humid. The average daily January temperatures are 2 to $4^{\circ}C$ (35 to 39°F), whereas the average summer temperatures are 25 to 26°C (77 to 79°F). The rainfall is reasonably well distributed, with the total annual precipitation averaging 1.20 m. The remnants of tropical storms from the Gulf of Mexico provide periodic intense rainfall events [19] [20] [21].

2.2. Methods

Soils were selected from the following soil orders: i) Mollisols, ii) Alfisols, iii) Ultisols, iv) Entisols, v) Inceptisols, and vi) Vertisols. In total, 27 soil series were selected, many with multiple pedons. The soils used in this investigation were routinely characterized: i) to verify that the pedon was a member of the soil series, and ii) to provide routine soil chemical characterization. Laboratory analysis was performed only on the fine earth fraction, that is material finer than 2 mm. Standard routine methods included pH in water, exchangeable cations, total neutralizable acidity, and organic matter content by loss on ignition. These methods were performed by the soil testing laboratory at the University Missouri-Columbia Fisher Delta Center (Portageville, MO). Soil taxonomic classifications were from the United States Department of Agriculture official soil series descriptions [22].

An aqua regia digestion was employed to obtain a near total estimation of elemental abundance associated with all but the most recalcitrant soil chemical environments. Homogenized samples (0.75 g) were equilibrated with 0.01 liter of aqua-regia (3 mole nitric acid: 1 mole hydrochloric acid) in a 35°C incubator for 24 hours. Samples were shaken, centrifuged, and filtered (0.45 µm), with a known aliquot volume analyzed using inductively coupled plasma emission mass spectrometry. Selected samples were duplicated and known reference materials were employed to guarantee analytical accuracy. A water extraction was performed to recover only the most labile or potentially labile fractions. A hot water extraction involved equilibrating 0.5 g samples in 0.02 L distilled-deionized water at 80°C for one hour followed by 0.45 µm filtering and elemental determination using inductively coupled plasma emission - mass spectrometry. For the water extraction, selected samples were duplicated, and reference materials were employed to guarantee analytical precession. Simple statistics included mean, standard deviation (STD), coefficient of variation, and linear regression analysis were each performed using Excel.

3. Soil Series Characterization

Twenty-seven soil series were characterized, involving ten series from the Alfisol order, five series from the Ultisol order, five series from the Entisol order, three series from the Inceptisol order, three series from the Mollisol order and one series from the Vertisol order. Most of the soil series were deep to very deep, whereas a few soil series were shallow to moderately deep. Soil profiles ranged from excessively well-drained to poorly-drained. The soil classifications for the 27-soil series are listed in **Appendix 1**.

4. Antimony and Bismuth Soil Profile Concentrations

The mean soil profile antimony concentrations range from 0.65 mg kg⁻¹ for the Foley pedon to 0.08 mg kg⁻¹ for the Killarney pedon, which are within the typical soil concentration ranges reported by the cited literature. The Irondale (0.53 mg kg⁻¹) and Taumsauk (0.5 mg kg⁻¹) pedon are adjacent to each other and are composed of mass-wasting loess mixed with rhyolite residuum on steep sides-lopes, whereas the Knobtop (0.08 mg kg⁻¹) resides on summit positions and has a comparatively thick loess mantle discretely overlying rhyolite (**Table 1**). Thus, the stark differences are likely attributed to parent material inheritance.

The mean soil profile bismuth concentrations range from 0.92 mg kg⁻¹ for the Wakeland pedon and 0.53 mg kg⁻¹ for the Haymond pedon to 0.03 mg kg⁻¹ for the Malden pedon and 0.05 mg kg⁻¹ for the Clana pedon. Interesting the Wakeland and Haymond are adjacent pedons in a silty-textured floodplain, whereas the adjacent Malden and Clana pedons reside on coarse-textured terrace positions. The Sb and Bi mean and standard deviations for all soil series are in **Table 1**.

The mean and standard deviations for Sb resulting from a hot water extraction was intended to estimate the quantity of antimony that is biologically available. Bi concentrations from the hot water extraction were typically below detection limit (0.8 μ g kg⁻¹). The Sb hot water extraction values range from 0.27 μ g kg⁻¹ for the Lilbourn soil series to 5.94 μ m kg⁻¹ for the Calhoun soil series (**Table** 2). The mean soil profile aqua regia digestion concentration for the Calhoun soil series was 0.24 mg kg⁻¹, whereas the hot water extraction was 0.0059 mg kg⁻¹, or 2.5% of the total antimony concentration.

The coefficient of variation for antimony and bismuth may be easily calculated (standard deviation * 100 / mean) for each soil series. The mean and standard deviation of the Sb and Bi coefficients of variation were determined for those soil series having argillic horizons and lacking argillic horizons. Argillic horizons are defined as mineral soil horizons that are characterized by the illuvial accumulation of layer-lattice silicate clays, which is soil horizons having accumulated translocated clay from superimposed soil horizons. The mean and standard deviation for the coefficients of variation for antimony and bismuth for soil series having and lacking argillic horizons are displayed in **Table 3**. Application of t-test for mean separation demonstrates that antimony means are significantly different between soils having and lacking argillic horizons ($\alpha = 0.015$), whereas bismuth means are not significantly different between soils having and lacking argillic horizons ($\alpha = 0.13$).

The implication is that the greater antimony coefficient of variations for soils having argillic horizons is attributed to the greater antimony concentrations of the clay-enriched illuvial soil horizons. The greater clay contents, with their associated Fe-oxyhydroxides, provide a more intense antimony adsorption capacity. In this manuscript, Entisols, Inceptisols and the Vertisol samples have rather uniform soil profile textures and correspondingly rather uniform adsorption capacities, thus antimony soil profile concentration distributions have smaller variances.

	Antimony (mg / kg)		Bismuth (mg / kg)	
Soil	Mean	Standard dev	Mean	Standard dev
Alred	0.47	0.18	0.15	0.08
Amagon	0.26	0.13	0.09	0.04
Broseley	0.20	0.05	0.07	0.03
Calhoun	0.24	0.08	0.07	0.04
Clana	0.28	0.06	0.05	0.02
Commerce	0.33	0.06	0.17	0.05
Dubbs	0.30	0.09	0.13	0.03
Foley	0.65	0.22	0.22	0.05
Frenchmill	0.10	0.02	0.17	0.03
Haymond	0.19	0.03	0.53	0.30
Hildebrecht	0.21	0.05	0.18	0.07
Irondale	0.53	0.15	0.20	0.02
Kaintuck	0.24	0.02	0.13	0.01
Killarney	0.09	0.02	0.11	0.01
Knobtop	0.08	0.03	0.16	0.04
Lilbourn	0.26	0.09	0.10	0.09
Malden	0.25	0.05	0.03	0.01
Menfro	0.38	0.10	0.20	0.05
Overcup	0.44	0.26	0.20	0.03
Portageville	0.38	0.06	0.35	0.01
Reelfoot	0.39	0.07	0.17	0.03
Rueter	0.32	0.08	0.10	0.04
Sharkey	0.39	0.05	0.34	0.04

Table 1. Mean and standard deviation for antimony and bismuth in soils.

Continued				
Taumsauk	0.50	0.17	0.19	0.04
Tiptonville	0.41	0.08	0.16	0.04
Wakeland	0.16	0.03	0.92	0.51
Wilbur	0.39	0.09	0.13	0.04

Table 2. Mean and standard deviation for antimony water extract.

	Antimony (µg / kg)		
Soil	Mean	Mean Standard Deviation	
Amagon	3.43	0.96	
Calhoun	5.94	6.22	
Irondale	4.56	3.66	
Kaintuck	1.98	0.36	
Lilbourn	0.27	0.10	
Wilbur	4.27	1.31	

Table 3. The mean and standard deviation for the coefficients of variation for Sb and Bi for soil series having and lacking argillic horizons.

Statistic	Soils Having Argillic Horizons		Soils Lacking Argillic Horizons	
	Sb	Bi	Sb	Bi
Mean	30	27	19	39
Standard Dev.	11	15	7	25

Standard Dev is standard deviation.

5. Relationship of Antimony and Bismuth with Iron

The antimony and bismuth concentrations for the Alred and Rueter pedons were pooled given their profile similarities and their adjacent geographic locations. The antimony and bismuth concentrations show positive linear relationships with respect to iron (Figure 1 and Figure 2). Similarly, the Menfro pedons show positive antimony and bismuth linear relationships with respect to iron (Figure 3 and Figure 4). Two features are prominent: i) the iron concentration variance is predicated on greater Fe concentrations associated with the phyllosilicate enriched argillic horizons, and ii) antimony and bismuth concentrations are correlated with iron.

The soil profile distribution of antimony and bismuth in the Menfro pedons (Figure 5 and Figure 6) illustrate the importance of the argillic horizon's antimony and bismuth adsorption capacity. Similarly, the antimony soil profile distribution demonstrates greater concentrations for the illuvial horizons (Figure 7); however, the portageville pedon demonstrates rather uniform antimony and bismuth concentrations (Figure 8 and Figure 9).





Figure 1. The relationship of antimony and iron for the pooled Alred and Rueter pedons.

















Antimony (ppm) two Menfro pedons

Figure 5. Antimony concentration distribution by soil horizon for the two Menfro pedons.



Bismuth (ppm) for two Menfro Pedons



0.3





Figure 7. Antimony concentration distribution by soil horizon for the Amagon pedon.

Figure 8. Antimony concentration distribution by soil horizon for the Portageville pedon.





6. Discussion

6.1. Assessment of Antimony and Bismuth Soil Concentrations across Southeastern Missouri

The antimony concentrations ranged from very low concentrations to 0.65 mg kg⁻¹, whereas the bismuth soil profile concentrations ranged from very low concentrations to 0.92 mg kg⁻¹. For the Alfisols and Ultisols, the antimony soil profile distributions show greater concentrations in the illuvial horizons than the eluvial horizons, whereas for the antimony soil profile distributions for the majority of the Entisols, Inceptisols, Mollisols and the solitary Vertisol show rather uniform concentrations. Zhao *et al.* [23] noted that adsorption was an important phenomenon influencing antimony accumulation, with clay and iron oxyhydroxides important soil substrates.

The magnitude of the antimony and bismuth concentrations are within the concentration ranges documented for pristine, non-impacted (geogenic) soils [4] [23] [24] [25] [26]. In their review, Bolan *et al.* [24] did report that background and average antimony concentration values were 0.3 to 8.6 mg kg⁻¹. Thus, the sampled soils across southeastern Missouri are not inferred to be impacted by mining or other anthropogenic activities.

6.2. Potential Environmental Risks Associated with Antimony and Bismuth across Southeastern Missouri Are Presently Extremely Limited

Tang *et al.* [26] recently described sources of soil antimony pollution and its environmental impact, and proposed remediation techniques, noting use of ferrous sulfate, phosphate amendments, clay minerals and biochar for adsorption, selected bacterial communities, and phytoremediation. Antimony pollution sources include mining, pharmaceutical manufacturing, vehicle emissions, plastic waste leaching, shooting ranges, and others [23] [25] [26]. The maximum concentration of antimony for drinking water is 6 ppb by the United States Environmental Protection Agency and 20 ppb by World Health Organization [26]. Vidya *et al.* [13] reviewed the influence of antimony on plant growth and development, including i) stunted growth, ii) reduced photosynthesis and accumulation biomass, iii) generation of reactive oxygen species, and lipid peroxidation. However, the literature addressing antimony and bismuth as environmental risks is a relatively recent activity.

Bolan *et al.* [24] noted that no definitive review of the biogeochemistry of antimony has completely described antimony mobilization, bioavailability, toxicity, and threats to environmental and human health. Bolin *et al.* [24] significantly reviewed recent literature of the biogeochemical processes influencing soil antimony, noting that clay minerals and the oxyhydroxides of Mn, Al and Fe were implemental in regulating antimony soil chemistry.

7. Conclusion

The soil profile concentrations of antimony and bismuth were determined for

key soil series across southeastern Missouri. The antimony concentrations ranged from 0.65 to 0.08 mg kg⁻¹, whereas the bismuth soil profile concentrations ranged from 0.92 to 0.03 mg kg⁻¹. For soils having argillic horizons, antimony and bismuth concentrations were greater for the illuvial horizons than the eluvial horizons. Both elements show significant correlations with iron.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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Soil Series	Classification		
Alfisols			
Alred	Loamy-skeletal over clayey, siliceous, semiactive, mesic Typic Paleu- dalfs		
Amagon	Fine-silty, mixed, active, thermic Typic Endoaqualfs		
Broseley	Loamy, mixed, superactive, thermic Arenic Hapludalfs		
Calhoun	Fine-silty, mixed, active, thermic Typic Glossaqualfs		
Dubbs	Fine-silty, mixed, active, thermic Typic Hapludalfs		
Foley	Fine-silty, mixed, active, thermic Albic Glossic Natraqualfs,		
Hildebrecht	Fine-silty, mixed, active, mesic Oxyaquic Fragiudalfs		
Menfro	Fine-silty, mixed, superactive, mesic Typic Hapludalfs		
Overcup	Fine, smectitic, thermic Vertic Albaqualfs		
Rueter	Loamy-skeletal, siliceous, active, mesic Typic Paleudalfs		
Ultisols			
Frenchmill	Loamy-skeletal, mixed, active, mesic Typic Paleudults		
Irondale	Loamy-skeletal, mixed, active, mesic Typic Hapludults		
Killarney	Loamy-skeletal, mixed, active, mesic Typic Fragiudults		
Knobtop	Fine-silty, mixed, active, mesic Aquic Hapludults		
Taumsauk	Loamy-skeletal, mixed, active, mesic Lithic Hapludults		
	Entisols		
Clana	Mixed, thermic Aquic Udipsamments		
Kaintuck	Coarse-loamy, siliceous, superactive, nonacid, mesic Typic Udifluvents		
Lilbourn	Coarse-loamy, mixed, superactive, nonacid, thermic Aeric Fluvaquents		
Malden	Mixed, thermic Typic Udipsamments		
Wakeland	Coarse-silty, mixed, superactive, nonacid, mesic Aeric Fluvaquents		
Inceptisols			
Commerce	Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoa- quepts		
Haymond	Coarse-silty, mixed, superactive, mesic Dystric Fluventic Eutrudepts		
Wilbur	Coarse-silty, mixed, superactive, mesic Fluvaquentic Eutrudepts		
	Mollisols		
Portageville	Fine, smectitic, calcareous, thermic Vertic Endoaquolls		
Reelfoot	Fine-silty, mixed, superactive, thermic Aquic Argiudolls		
Tiptonville	Fine-silty, mixed, superactive, thermic Oxyaquic Argiudolls		
	Vertisols		
Sharkey	Very-fine, smectitic, thermic Chromic Epiaquerts		

Appendix 1. Soil Series Characterization