

Soil Profile Concentration Distributions of Aluminum, Gallium, Indium and Thallium across Southeastern Missouri

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Abstract

The soil chemistry of gallium, indium, and thallium is not well defined, particularly with emerging evidence that these elements have toxic properties and may influence food safety. The purpose of this investigation was to estimate the soil concentrations of gallium, indium, and thallium and determine if these elements have a soil chemistry like aluminum and therefore demonstrate significant concentration correlations with aluminum. Twenty-seven soil series were selected, and the elemental concentrations were determined using aqua regia digestion with analytical determination performed using inductively coupled plasma emission-mass spectroscopy. The concentrations of gallium, indium, and thallium generally compared with the known literature. Aluminum-gallium and aluminum-thallium exhibited significant concentration correlations across the soil horizons of the sampled soils. Aluminum, gallium, and thallium did demonstrate concentration increases in soil horizons having illuviation of phyllosilicates, implying these phyllosilicates have adsorption and isomorphic substitution behaviors involving these elements.

Keywords

Trace Elements, Gallium, Indium, Thallium, Soils, Aluminum

1. Introduction

Group 13 of the Periodic Table consists of the elements boron (B), aluminum (Al), gallium (Ga), indium (In) and thallium (Tl). In this manuscript the emphasis will focus on aluminum, gallium, indium, and thallium, given that boron is essentially a non-metal which primarily forms covalent bonds. Aluminum is the most metallic of the group 13 elements, with Ga, In and Tl exhibiting reduced

electropositive behavior because of poor d electron shielding. Lee (1991) discusses atomic number, ground state electronic designations and the ionic radius for the monovalent (I) and trivalent (III) oxidation states (Table 1). The electron descriptions are for the electron ground state configuration. The trivalent oxidation state for Al, Ga, and In is the dominant oxidation state, whereas the monovalent oxidation state is more dominant for Tl.

Aluminum is approximately 8.2% of the earth's crust and is considered a Lewis acid. Common aluminum bearing minerals include boehmite (γ -AlOOH), diasporite (α -AlOOH), corundum (Al_2O_3), and gibbsite (γ -Al(OH)₃). An immense literature reference exists for aluminum across geology, soil science and other disciplines (Aide, 2022).

The typical earth crust concentration range for gallium is 15 - 19 mg·kg⁻¹ (Pendias, 2011). Gallium is frequently associated with feldspars, amphiboles, micas, and phyllosilicates (Pendias, 2011). In the United States (California) the gallium soil concentration ranges from 16 to 35 (Wilson et al., 1994). In the United States the soil indium concentration ranges from less than 0.2 to 0.5 mg·kg⁻¹ (Wilson et al., 1994), whereas the earth crust indium concentration ranges from 0.11 to 0.25 mg·kg⁻¹ (Pendias, 2011). In the United States the soil thallium concentration ranges from 0.02 to 2.8 mg·kg⁻¹ (Smith & Carson, 1977). In Taiwan region, Liu et al. (2021) examined gallium, indium, and thallium as emerging soil contaminants and estimated the soil profile distributions for total elemental abundance and EDTA available concentrations in highly-weathered soils. The total element content varied from 2.3 to 9.5 mg·kg⁻¹ for Ga, 4.8 - 37.1 $\mu\text{g}\cdot\text{kg}^{-1}$ for In, and 56 to 206 $\mu\text{g}\cdot\text{kg}^{-1}$ for Tl. The median content of EDTA-extracted Ga, In, and Tl accounted for 24, 8.7, and 5.1% of the total elemental abundance, respectively.

The literature review of gallium consists largely of region-specific soil and plant Ga abundances (Pendias, 2011); however, more recent literature citations involving impacted sites concentrate on gallium as an environmental risk. Investigating gallium contaminated soil, Chen et al. (2022) determined the Ga speciation in soils and its accumulation in rice (*Oryza sativa*). Coarse-textured, acidic soils exhibited the highest soil Ga availability. Gallium uptake by rice roots showed a limited transference from roots to grain.

Indium is frequently associated with Fe-bearing minerals and sulfides of ZnS, PbS and CuFeS₂ (Pendias, 2011), thus indium is commonly associated with lead and zinc mining (Aide et al., 2019). Chang et al. (2020) investigated indium uptake

Table 1. Chemical description of periodic table group 13.

Element	Atomic Number	Electronic Configuration	Ionic Radius trivalent (nm)	Ionic Radius Monovalent (nm)
Al	13	[Ne] 3s ² 3p ¹	0.0535	--
Ga	31	[Ar] 3d ¹⁰ 4s ² 4p ¹	0.0620	0.12
In	49	[Kr]4d ¹⁰ 5s ² 5p ¹	0.0800	0.14
Tl	81	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	0.0885	0.05

and accumulation in rice (*Oryza sativa*) and wheat (*Triticum aestivum*) and evaluated potential risks associated with human consumption. Soil indium was associated with iron hydroxides and indium precipitation resulted in reduced indium plant availability. Indium translocation from soil to root and root to grain reduces the risk to human consumption; however, further studies are required for authentication. [Chang et al. \(2023\)](#) focused on indium speciation and fractionation in continuous submerged rice soils. Indium was primarily associated with Fe-oxyhydroxides and indium phosphates. During continuous submergence, anoxic soil conditions support Fe-oxyhydroxide dissolution and indium release; however, rhizosphere re-adsorption reactions limited indium root uptake. Investigating Canadian Humic Andosols, Eutric Fluvisols, and Mollic Gleysols, [Asami et al. \(1990\)](#) determined the indium mean (0.037 mg/kg) and range (0.016 - 0.078 mg/kg) concentrations. In heavy metal impacted soils greater indium concentrations were associated with cadmium, zinc, and lead.

Naturally occurring sources of thallium include feldspars and micas, given the isomorphic substitution of Tl^+ with K^+ . [Karbowska \(2016\)](#) noted the primary sources of thallium involved in soil pollution include smelting and coal mining/combustion. Thallium is also frequently associated with Hg and As rich weathering products, including coal ash, sulfide minerals (pyrite, sphalerite, and marcasite) and cement production. Thallium is commonly associated with Mn/Fe oxides and with soil organic matter under reducing conditions ([Aide, 2022](#)). Thallium is very toxic at low concentrations, a feature attributed to its solubility in water, bioavailability, and bioaccumulation potential ([Karbowska, 2016](#)). The USA Environmental Agency maximum concentration for drinking water is $2 \mu\text{g}\cdot\text{L}^{-1}$ ([United States Environmental Protection Agency, 2015](#)). Thallium (Tl^+) may substitute for K^+ in various metabolic processes, leading to stomach/intestinal ulcers, polyneuropathy, paralysis, loss of body mass, internal bleeding, and myocardial injury ([Karbowska, 2016](#)).

In Spain, [Garcia et al. \(2004\)](#) investigated thallium concentrations and chemical speciation at 91 sites contaminated by pyrite mine tailings. Thallium speciation was largely as unweathered mineral particles adsorbed onto crystalline oxyhydroxides. Some of the thallium was associated with noncrystalline oxyhydroxides. In acidic soils, thallium adsorption was primarily with iron oxyhydroxides, whereas in neutral-alkaline soils thallium adsorption was primarily with aluminum oxyhydroxides. In France, [Rose et al. \(2023\)](#) reported that thallium is primarily associated with sulfide rich deposits. Upon weathering they observed that sulfuric acid production supported the formation of Tl-jarosite ($(K,Tl)Fe_3(SO_4)_2(OH)_6$) and dorallcharite ($TlFe_3(SO_4)_2(OH)_6$).

[Lin et al. \(2021\)](#) determined the adsorption and desorption of Tl^+ in six soils. The X-ray absorption near-edge structure spectroscopy revealed that illite, vermiculite, and smectite were the dominant soil adsorbents; however, adsorption was reversible at low Tl^{+1} adsorption loadings. The Tl^{+1} adsorption release requires further examination before estimating environmental risk. In a microcosm study, [Svetlana et al. \(2017\)](#) noted the impact of the oxidation-reduction

status on thallium release. Increased oxidizing conditions increased soluble thallium concentrations. Thallium mobilization was related to the gradual oxidation of Tl-bearing sulfides, reductive dissolution of Fe-Mn oxides and desorption from minerals. Although not a focus of this manuscript, the emerging literature is also focusing on Tl plant uptake, especially for estimating risks in food safety (Espinosa et al., 2023).

Soil research involving gallium, indium and thallium is mostly non-existent, other than the characterization of their geochemical abundances in various lithologies. The novelty of this manuscript lies in the opportunity to assess if the group 13 elements share sufficient soil chemical behavior that congruent weathering of primary minerals preserves the elemental transfers to phyllosilicate minerals.

The objectives of this investigation are: 1) to estimate the soil abundances of gallium, indium, and thallium across southeastern Missouri, 2) to determine their potential soil profile distribution because of eluviation-illuviation and 3) to assess if these elements are strongly correlated to aluminum.

2. Materials and Methods

2.1. Study Area

The study area is located between the Mississippi River and the St. Francois River in southeastern Missouri. The northern section consists of thin to thick loess mantles overlying igneous and sedimentary rocks. The southern portion is in the Mississippi River embayment and consists of floodplains and terraces.

The climate is continental humid. The average daily January temperatures are 2°C to 4°C (35 to 39°F), whereas the average summer temperatures are 25°C to 26°C (77 to 79°F). The soils are frozen only at the surface and only for brief periods of time. The rainfall is reasonably well distributed, with the total annual precipitation averaging 1.14 to 1.27 m. The remnants of tropical storms from the Gulf of Mexico may provide more than 0.25 m of rainfall during major rainfall events (Festervand, 1981; Brown & Childress, 1985; Festervand, 1986).

2.2. Methods

Soils were selected from the following soil orders: 1) Mollisols, 2) Alfisols, 3) Ultisols, 4) Entisols, 5) Inceptisols, and 6) Vertisols. In total, 27 soil series were selected, many with multiple pedons. The soils used in this investigation were routinely characterized: 1) to verify that the pedon was a member of the soil series, and 2) to provide routine soil chemical characterization. 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). The clay, silt and sand fractions were separated by Na-saturation of the exchange complex, washing with water-methanol mixtures, dispersion in Na₂CO₃ (pH 9.2), followed by centrifuge fractionation for the clay

separate and wet sieving for the silt and sand separates (Carter, 1993). Soil taxonomic classifications were from the United States Department of Agriculture official soil series descriptions (USDA Official Series Descriptions, 2023).

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.

Simple soil statistics included mean, standard deviation (STD), and linear regression analysis using Excel.

3. Soil Series Characterization

Ten soil series were Alfisols ((1) Alred, Loamy-skeletal over clayey, siliceous, semiactive, mesic Typic Paleudalfs; (2) Amagon, Fine-silty, mixed, active, thermic Typic Endoaqualfs; (3) Broseley, Loamy, mixed, superactive, thermic Arenic Hapludalfs; (4) Calhoun, Fine-silty, mixed, active, thermic Typic Glosaqualfs; (5) Dubbs, Fine-silty, mixed, active, thermic Typic Hapludalfs; (6) Foley, Fine-silty, mixed, active, thermic Albic Glossic Natraqualfs, (7) Hildebrecht, Fine-silty, mixed, active, mesic Oxyaquic Fragiudalfs, (8) Menfro, Fine-silty, mixed, superactive, mesic Typic Hapludalfs; (9) Overcup, Fine, smectitic, thermic Vertic Albaqualfs; (10) Rueter, Loamy-skeletal, siliceous, active, mesic Typic Paleudalfs). Five soil series were Ultisols ((1) Frenchmill, Loamy-skeletal, mixed, active, mesic Typic Paleudults; (2) Irondale, Loamy-skeletal, mixed, active, mesic Typic Hapludults; (3) Killarney, Loamy-skeletal, mixed, active, mesic Typic Fragiudults; (4) Knobtop, Fine-silty, mixed, active, mesic Aquic Hapludults; (5) Taumsauk, Loamy-skeletal, mixed, active, mesic Lithic Hapludults). Five soil series were Entisols ((1) Clana, Mixed, thermic Aquic Udipsamments; (2) Kaintuck, Coarse-loamy, siliceous, superactive, nonacid, mesic Typic Udifluvents; (3) Lilbourn, Coarse-loamy, mixed, superactive, nonacid, thermic Aeric Fluvaquents, (4) Malden, Mixed, thermic Typic Udipsamments; (5) Wakeland Coarse-silty, mixed, superactive, nonacid, mesic Aeric Fluvaquents). Three soil series were Inceptisols ((1) Commerce, Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts; (2) Haymond, Coarse-silty, mixed, superactive, mesic Dystric Fluventic Eutrudepts; (3) Wilbur, Coarse-silty, mixed, superactive, mesic Fluvaquentic Eutrudepts). Three soil series were Mollisols ((1) Portageville, Fine, smectitic, calcareous, thermic Vertic Endoaquolls; (2) Reelfoot, Fine-silty, mixed, superactive, thermic Aquic Argiudolls; (3) Tiptonville, Fine-silty, mixed, superactive, thermic Oxyaquic Argiudolls). One soil series was a Vertisol (Sharkey, Very-fine, smectitic, thermic Chromic Epiaquerts). Most of the soil series were very deep to deep, whereas a few soil series were moderately

deep and shallow. Pedons ranged from excessively well-drained to poorly-drained. Parent materials in the northern portion of the study area were loess, limestone, and igneous rock residuum, whereas the parent materials in the southern portion of the study area exhibited alluvial parent materials with variable textures.

To facilitate manuscript clarity and augment the number of observations for the linear regression evaluation, the data fields of selected soil series were pooled, and subsequently labeled as “pooled”. The “pooled” soil series are: 1) Irondale pooled having data fields from the Irondale and Taumsauk pedons, 2) Killarney pooled having data fields from the Killarney and Frenchmill pedons, 3) Wakeland pooled having data fields from the Wakeland and Haymond pedons, 4) Calhoun pooled having data fields from the Calhoun and Amagon pedons, 5) Dubbs pooled having data fields from the Dubbs, Portageville and Tiptonville pedons, and 6) Clana pooled having data fields from the Clana and Malden pedons. Soil pedons were only pooled if the soil series were closely located and possessed shared soil boundaries.

4. Results and Discussion

4.1. Relationships Involving Aluminum and Gallium Concentrations

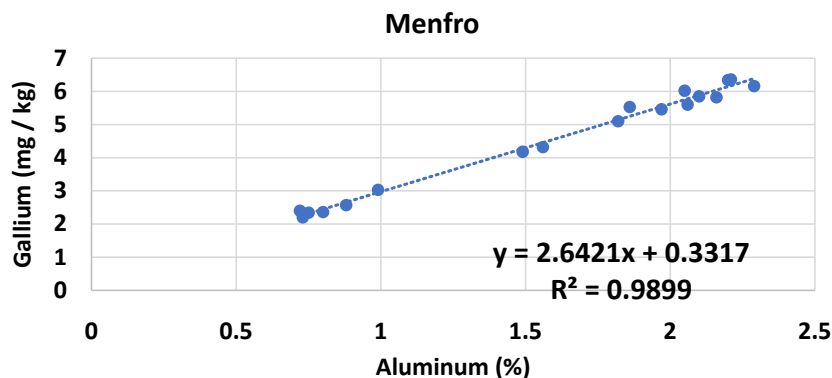
Gallium and aluminum aqua regia digestion concentrations demonstrate highly significant linear relationships for almost all soils (**Table 2**). The Kaintuck soil series has a very low clay content and the corresponding gallium concentrations are near the detection limit. The mean aluminum contents for the coarse-textured Clana-Malden, Kaintuck and Lilbourn pedons are less than 1.3%, whereas the Alred, the pooled Dubbs pedons and the Sharkey pedons have aluminum contents greater than 2.7%. Soils with argillic horizons have substantially greater aluminum and gallium concentrations in the illuvial horizons than the corresponding eluvial horizons, a feature represented by greater soil profile standard deviations involving both aluminum and gallium (**Table 2**).

The Menfro series are soils of the Alfisol order having an ochric-argillic (A-E-Bt-C (loess) horizon sequence with a mixed mineralogy composed mainly of primarily of smectite, illite and kaolinite. The phyllosilicates are likely the main Al and Ga bearing minerals in the soils. The silt loam eluvial horizons and the silty clay loam illuvial horizons demonstrate discrete Al-Ga concentration domains that retain similar Al/Ga concentration ratios (**Figure 1**). The Calhoun-Amagon pedons are soils of the Alfisol order having A-E-Bt-Btg-C horizons, a feature attributed to fluctuating (seasonal) water-tables within the solum. The eluvial and illuvial horizons exhibit similar Al-Ga characteristics as the Menfro pedons (**Figure 2**). The Dubbs, Overcup, Tiptonville and Portageville soils are Alfisols and Mollisols that have different soil textures and soil water drainage that ranges from well-drained to poorly-drained; however, the aluminum-gallium concentrations are similar (**Figure 3**).

Table 2. Aluminum and gallium aqua regia digestion soil profile distributions.

Soil	Aluminum (%)		Gallium (mg/kg)		R ²
	Mean	STD	Mean	STD	
Alred	2.75	1.75	7.60	4.30	0.99
Broseley	0.97	0.52	2.92	1.26	0.99
Calhoun pooled	1.74	0.56	4.57	1.39	0.99
Clana pooled	1.02	0.33	3.09	0.88	0.96
Commerce	2.04	0.52	5.38	1.24	0.99
Dubbs pooled	2.65	1.33	7.03	3.54	0.99
Foley	2.35	0.67	7.10	1.79	0.96
Hildebrecht	1.70	0.81	5.82	3.67	0.99
Irondale pooled	2.43	1.44	6.50	4.10	0.94
Kaintuck	1.23	0.06	0.17	0.28	NS
Killarney pooled	2.07	1.07	6.0	2.20	0.98
Knobtop	2.53	1.18	7.8	2.90	0.99
Lilbourn	1.21	0.20	2.91	0.48	0.80
Menfro	1.59	0.60	4.53	1.61	0.99
Overcup	2.75	0.71	5.25	1.64	0.97
Reelfoot	1.95	0.60	5.94	1.70	0.99
Rueter	1.36	0.66	4.20	1.80	0.98
Sharkey	3.65	0.83	9.06	2.37	0.91
Wakeland pooled	1.50	0.40	4.60	0.22	0.94
Wilbur	1.88	0.30	4.86	0.73	0.95

STD is standard deviation; NS indicates regression involving Al and Ga is insignificant; R² is coefficient of determination.

**Figure 1.** Relationship between gallium and aluminum from two-pooled Menfro pedons.

The exceptionally coherent correlation of gallium with aluminum strongly implies that the soil chemistry of these elements is remarkably similar. Considering that the regression's coefficients of determination for Ga and Al are always greater

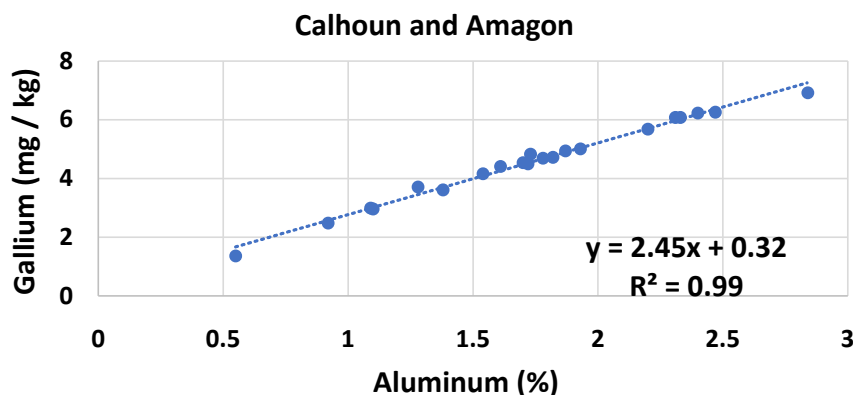


Figure 2. Relationship between gallium and aluminum for pooled Calhoun and Amagon pedons.

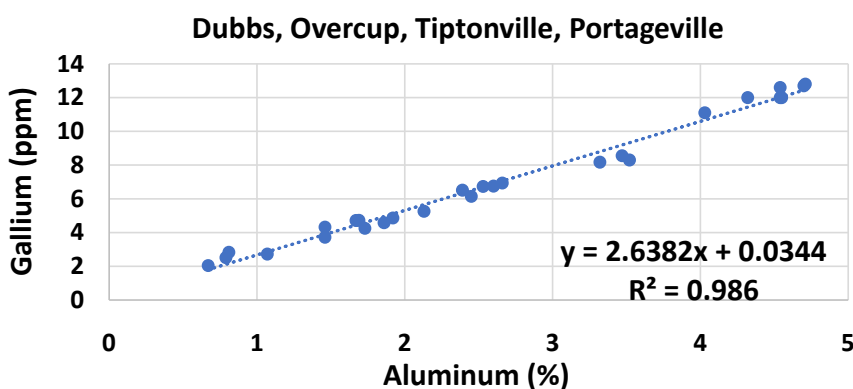


Figure 3. Relationship between gallium and aluminum for pooled Dubbs, Overcup, Tiptonville, and Portageville pedons.

than 0.90 and considering that the abundance of aluminum is primarily determined by clay content, suggests that gallium is similarly associated with aluminum in phyllosilicate lattice structures. Thus, clay formation appears to preserve the initial aluminum and gallium abundances.

4.2. Relationships Involving Soil Profile Aluminum, Indium, and Thallium Concentrations

The relationships between aluminum and indium do not exhibit significant linear relationships, that is the concentration relationship of indium to aluminum is random. Several features in the data fields reduce the aluminum-indium coefficient of determination: 1) the mean indium concentrations are only slightly greater than the detection limit and 2) they exhibit little variance (**Table 3**). The indium concentrations range from less than 0.01 to 0.05 mg·kg⁻¹. The elevated indium concentrations of 0.25 mg·kg⁻¹ for the pooled Irondale pedons and 0.21 mg·kg⁻¹ for the Kaintuck pedons are impacted by lead (Pb) mining activities with co-contamination involving zinc (Zn), cadmium (Cd) and indium. The relationships between aluminum and thallium do exhibit linear relationships (**Table 3**). The mean soil thallium concentrations range from 0.10 to 0.44 mg·kg⁻¹.

Table 3. Indium and thallium aqua regia digestion soil profile distributions.

Soil	Indium (mg/kg)		Thallium (mg/kg)		R ²
	Mean	STD	Mean	STD	
Alred	0.05	0.12	0.23	0.12	0.98
Broseley	ND	0.05	0.10	0.05	NS
Calhoun pooled	0.02	0.05	0.24	0.05	NS
Clana pooled	Not Detected	0.03	0.10	0.03	0.66
Commerce	0.01	0.08	0.32	0.08	0.99
Dubbs pooled	ND	0.05	0.25	0.05	0.91
Foley	0.03	1.12	0.41	1.12	0.97
Hildebrecht	0.03	0.07	0.21	0.07	0.85
Irondale pooled	0.25	0.07	0.27	0.07	0.94
Kaintuck	0.21	0.01	0.16	0.01	NS
Killarney pooled	0.03	0.09	0.23	0.09	0.87
Knobtop	0.04	0.14	0.15	0.14	0.99
Lilbourn	Not Detected	0.01	0.10	0.01	NS
Menfro	Not Detected	0.08	0.29	0.08	0.89
Overcup	Not Detected	0.05	0.29	0.05	0.99
Reelfoot	0.01	0.06	0.23	0.06	0.66
Rueter	0.03	0.32	0.15	0.32	0.93
Sharkey	0.03	0.11	0.44	0.11	0.85
Wakeland pooled	0.02	0.05	0.22	0.05	0.86
Wilbur	0.01	0.04	0.20	0.04	0.84

STD is standard deviation; NS indicates regression involving Al and Tl is insignificant; R² is coefficient of determination.

The Alred and Rueter highly significant aluminum and thallium linear relationship implies that the aluminum and thallium relationship is invariant, especially when considering that the eluvial and illuvial horizons exhibited discretely different mean aluminum and thallium concentrations (**Figure 4**). Similarly, the Dubbs, Overcup, Tiptonville and Portageville pedons conform to a significant aluminum and thallium relationship, especially when considering the different soil drainages, contrasting soil textures, and intensity of the eluviation-illuviation process (**Figure 5**).

Nathan (1985) reviewed previous mineralogy citations using the cation to anion ratio to estimate the likelihood for trigonal, tetrahedral, octahedral, or cubic coordination. For octahedral coordination the following geometric relationship is indicated:

$$0.414 < \rho < 0.732,$$

where ρ is the cation to anion ionic ratio. Aluminum coordination with oxygen may have either tetrahedral or octahedral coordination, whereas gallium, indium,

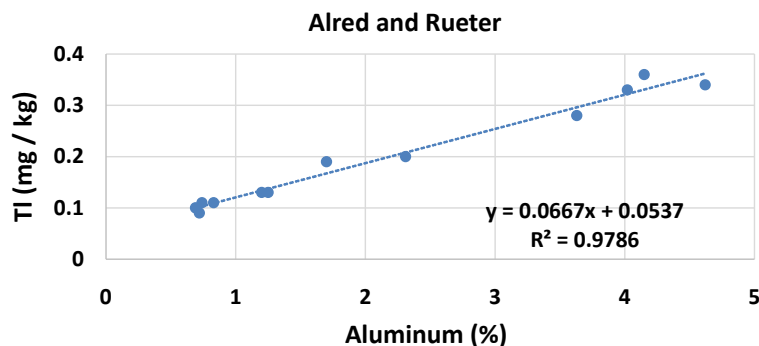


Figure 4. Relationship between thallium and aluminum from pooled Alred and Rueter pedons.

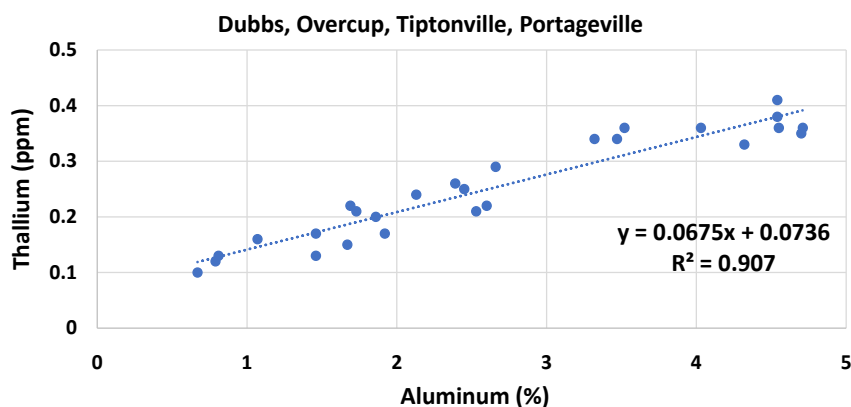


Figure 5. Relationship between thallium and aluminum from soil horizons of the Dubbs, Overcup, Tiptonville, and Portageville pedons.

and thallium (III) prefer octahedral coordination with oxygen. Thallium (I) will assume cubic coordination with oxygen. Phyllosilicates will present aluminum in octahedral coordination (kaolinite, smectites), or tetrahedral and octahedral coordination (vermiculite and illite). Gallium and thallium (III) likely present as octahedral lattice constituents in phyllosilicates, whereas thallium (I) may have isomorphic substitution relationships with potassium in feldspars, micas, vermiculite and illite. It is also probable that Ga and Tl are present as exchangeable cations.

The correlation of thallium with aluminum implies that the soil chemistry of these elements is similar. Considering that the regression's coefficients of determination for Tl and Al are always greater than 0.80 and considering that the abundance of aluminum is primarily determined by clay content, suggests that thallium is associated with aluminum in phyllosilicate lattice structures. However, thallium with its monovalent oxidation state and cubic coordination with oxygen suggests that thallium may occupy both octahedral cubic coordination position.

4.3. Aluminum and Gallium Concentration Relationships for Whole Soil Comparison

Previous discussions focused on linear Al-Ga relationships within the soil profile,

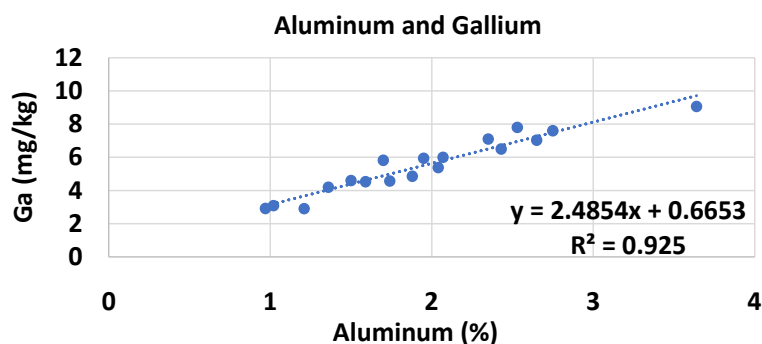


Figure 6. Relationship between the mean values for gallium and aluminum from 18 soil series.

whereas this section addresses Al-Ga linear relationships involving coefficient of determination for mean soil profiles across 18 soil series (Figure 6). The positive and significant linear relationship involving Al-Ga indicates that regional similarities in selected soil forming factors converge to preserve the correlation of Al and Ga across soil series. The diversity of parent materials (alluvium, loess, residuum) and selected soil processes (illuviation-illuviation) do not appear to exert sufficient influence to alter the Al-Ga relationship across different soil series. The climatic, organismal and time of soil formation influences also do not significantly alter the Al-Ga ratio. Topographic differences are more the result of fluvial processes that result in elevated terraces and depressional backswamp environments. The resulting textural differences do influence the aluminum concentration; however, the Al-Ga relationships remain evident. The aluminum and thallium relations for whole soil comparison were not significant.

The significant coefficient of determination of gallium and aluminum in this study are independent of soil series; however, the coefficient of determination of thallium and aluminum is not significant across soil series. Phyllosilicates and micaceous minerals that have potassium in cubic coordination likely provided sufficient thallium coordination diversity to reduce the coefficient of determination across soil series.

5. Conclusions and Future Research Needs

The aluminum, gallium, indium, and thallium concentrations were determined for 27 soil series, some with multiple pedons, and spanning across six soil orders. The research was conducted in southeastern Missouri and involved landscapes having 1) loess mantles overlying sedimental and igneous materials, and 2) fluvial sediments associated with the current and ancestral Mississippi and Ohio Rivers.

For most of the soil series aluminum and gallium concentrations formed linear regression trendlines with highly significant coefficients of determination. Similarly, aluminum and thallium concentrations formed linear regression trendlines with highly significant coefficients of determination. Conversely, indium did not for significant relationships with aluminum. Whole soil concentrations

of aluminum, gallium, and thallium were primarily a function of clay content.

Further understanding of the soil chemistry of gallium, indium, and thallium requires a greater emphasis on the thermodynamics of these elements, particularly their hydrolysis, complexation, and oxidation-reduction behavior. Additionally, evaluating crystal lattices of phyllosilicates for isomorphic substitution of gallium and thallium will provide an opportunity to separate gallium and thallium inclusion in lattice structures from gallium and thallium derived from unintended anthropogenic impacts.

Conflicts of Interest

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

References

- Aide, M. (2022). Aluminum Soil Chemistry: Influence on Soil Health and Forest Ecosystem Productivity. *Agricultural Sciences*, *13*, 917-935. <https://doi.org/10.4236/as.2022.138057>
- Aide, M. T., Aide, C., Braden, I. S., & Necas, K. (2019). Lead Immobilization Using Triple Superphosphate in Impacted Floodplain Soils in East-Central Missouri (USA). *The International Journal of Applied Agricultural Research*, *14*, 93-105.
- Asami, T., Yoshino, A., Kubota, M., & Gotoh, S. (1990). Background Level of Indium and Gallium in Soil with Special Reference to the Pollution of the Soils from Zinc and Lead Smelters. *Journal of Plant Nutrition and Soil Science*, *153*, 257-259. <https://doi.org/10.1002/jpln.19901530411>
- Brown, B. C., & Childress, J. D. (1985). *Soil Survey of Ste. Genevieve County, Missouri*. Produced in Cooperation with the United States Department of Agriculture, United States Forest Service, and the University Missouri-Columbia. Printed Washington DC.
- Carter, M. R. (1993). *Soil Sampling and Methods of Analysis*. Lewis Publ.
- Chang, H.-F., Yang, P.-T., Hashimoto, Y., Yeh, K.-C., & Wang, S.-L. (2023). Temporal Transformation of Indium Speciation in Rice Paddy Soils and Spatial Distribution of Indium in Rice Rhizosphere. *Environmental Pollution*, *326*, Article 121473. <https://doi.org/10.1016/j.envpol.2023.121473>
- Chang, H.-F., Yang, P.-T., Lin, H.-W., Yeh, K.-C., Chen, M.-N., & Wang, S.-L. (2020). Indium Uptake and Accumulation by Rice and Wheat and Health Risk Associated with Their Consumption. *Environmental Science & Technology*, *54*, 14946-14954. <https://doi.org/10.1021/acs.est.0c02676>
- Chen, K. Y., Yang, P. T., Chang, H. F., Yeh, K. C., & Wang, S. L. (2022). Soil Gallium Speciation and Resulting Gallium Uptake by Rice Plants. *Journal of Hazardous Materials*, *424*, Article 127582. <https://doi.org/10.1016/j.jhazmat.2021.127582>
- Espinosa, F., Ortega, A., Espinosa-Vellarino, F. L., & Garrido, I. (2023). Effect of Thallium(I) on Growth, Nutrient Absorption, Photosynthetic Pigments, and Antioxidant Response of Dittrichia Plants. *Antioxidants*, *12*, Article 678. <https://doi.org/10.3390/antiox12030678>
- Festervand, D. F. (1981). *Soil Survey of Cape Girardeau, Scott and Mississippi Counties, Missouri*. Produced in cooperation with the United States Department of Agriculture, United States Forest Service, and the University Missouri-Columbia. Printed Washington DC.

- Festervand, D. F. (1986). *Soil Survey of Perry County, Missouri*. Produced in cooperation with the United States Department of Agriculture, United States Forest Service, and the University Missouri-Columbia. Printed Washington DC.
- Garcia, M. F., Dorransoro, C., Simon, M., Aguilar, J., Ortiz, I., Fernandez, E., & Fernandez, J. (2004). Thallium Behavior in Soils Polluted by Pyrite Tailings (Aznalcóllar, Spain). *Soil and Sediment Contamination: An International Journal*, 13, 25-36.
<https://doi.org/10.1080/10588330490269769>
- Karbowska, B. (2016). Presence of Thallium in the Environment: Sources of Contaminations, Distribution and Monitoring Methods. *Environmental Monitoring and Assessment*, 188, Article No. 640. <https://doi.org/10.1007/s10661-016-5647-y>
- Lee, J. D. (1991). *Concise Inorganic Chemistry*. Chapman Hall.
- Lin, H.-Y., Chuang, T.-J., Yang, P.-T., Guo, L.-Y., & Wang, S.-L. (2021). Adsorption and Desorption of Thallium(I) in Soils: The Predominant Contribution by Clay Minerals. *Applied Clay Science*, 205, Article 106063. <https://doi.org/10.1016/j.clay.2021.106063>
- Liu, Y.-H., Shaheen, S. M., Rinklebe, J., & Hseu, Z.-Y. (2021). Pedogeochemical Distribution of Gallium, Indium and Thallium, Their Potential Availability and Associated Risk in Highly-Weathered Soil Profiles of Taiwan Region. *Environmental Research*, 197, Article 110994. <https://doi.org/10.1016/j.envres.2021.110994>
- Nathan, L. C. (1985). Predictions of Crystal Structure Based on Radius Ratio: How Reliable Are They? *Journal of Chemical Education*, 62, 215.
<https://doi.org/10.1021/ed062p215>
- Pendias, K. (2011). *Trace Elements in Soils and Plants*. CRC Press.
- Rose, J., Chaurand, P., Dentant, C., Angeletti, B., Borschneck, D., Kieffer, I., Proux, O., Bonet, R., Auffan, M., Levard, C., Fehlauer, T., Collin, B., & Doelsch, E. (2023). Thallium Long-Term Fate from Rock-Deposit to Soil: The Jas Roux Sulfosalt Natural Analogue. *ACS Earth and Space Chemistry*, 7, 1848-1857.
<https://doi.org/10.1021/acsearthspacechem.3c00021>
- Smith, I. C., & Carson, B. L. (1977). *Trace Metals in the Environment Vol. 1*. Scientific Publications.
- Svetlana, A. M., Frohne, T., Kresović, M., Stärk, H. J., Savić, D., Ličina, V., & Rinklebe, J. (2017). Redox-Controlled Release Dynamics of Thallium in Periodically Flooded Arable Soil. *Chemosphere*, 178, 268-276.
<https://doi.org/10.1016/j.chemosphere.2017.03.060>
- United States Environmental Protection Agency (USEPA) (2015). *Regulation Development for Drinking Water Contaminants*.
<https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#Inorganic>
- USDA Official Series Descriptions (2023).
<https://www.nrcs.usda.gov/resources/data-and-reports/official-soil-series-descriptions-osd>
- Wilson, S. A., Briggs, P. K., Mee, J. S., & Siems, D. F. (1994). Determination of Thirty-Two Major and Trace Elements in Three NIST Soil SRMs Using ICP-AES and WDXRF. *Geostandards Newsletter*, 18, 85-89.
<https://doi.org/10.1111/j.1751-908X.1994.tb00506.x>