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Aluminum and Gallium Concentrations in Southeastern Missouri Mississippi River Floodplain Soil Profile

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Abstract

The aluminum and gallium soil chemistry interaction is not well defined. The purpose of this investigation was to determine the aluminum (Al) and gallium (Ga) soil profile concentrations in floodplain soils along the Mississippi River and estimate the concentration correlations of these elements. Two soil series were selected, each having two sampled pedons. The gallium soil concentrations were comparatively small compared to the research literature. Gallium and aluminum concentrations across soil associations were significantly correlated, even though the selected soil series were quite different in clay content. Assessment of the Na-acetate recovery of exchangeable gallium was a small proportion of the total gallium content; thus, the gallium mobility and plant uptake potential was perceived as minimal. There exists continued research to determine gallium adsorption and isomorphic substitution behaviors and soil organic complexation reactions to provide clarity on potential environmental impacts because of mining and manufacturing.

Keywords

Trace Elements, Gallium, Soil Pollution, Aluminum, Isomorphic Substitution

1. Introduction

1.1. Basic Chemistry of Aluminum and Gallium

In this manuscript aluminum (Al) and gallium (Ga) will be evaluated to determine the similarity of their soil chemistries and to determine the likelihood that they may be used to infer aspects of soil genesis. Aluminum is the most metallic of the group 13 elements and is considered a Lewis acid, with aluminum having an earth crustal average of 8.2% (Lee, 1991). Montmorillonite typically has an aluminum content of 7% to 11%, with differences attributed to the degree of magnesium isomorphic substitution and the extent of Al-intercalation. Common aluminum bearing minerals include boehmite (γ-AlOOH), diaspore (α-AlOOH) and gibbsite (γ-$Al(OH)_3$). An immense literature database exists for aluminum soil chemistry and the influence of aluminum in soil fertility and plant nutrition (Hsu, 1989).

Aluminum (atomic number 13) has a ground state electronic designation of [Ne] $3s^23p1$ and an ionic radius of 53.5 pm for tetrahedral coordination and 67.5 pm for octahedral coordination. Aluminum (Al^{3+}) hydrolysis initiates near pH 4 and yields $Al(OH)^{2+}$ ($4 < pH < 5$), $Al(OH)_2^+$ ($5.5 < pH < 7$), and $Al(OH)_4^-$ at pH levels greater than pH 7. The tridecameric species ($AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$) is a primary proposed polynuclear aluminum species, which presents one tetrahedral Al surrounded by 12 octahedral Al.

Compared to aluminum, Ga exhibits reduced electropositive behavior because of poor d electron shielding (Lee, 1991). Gallium (atomic number 31) has a ground state electronic designation of [Ar] $3d^{10}4s^24p^1$ and an ionic radius of 62 pm for Ga^{3+}. Gallium has two predominant isotopes, (^{69}Ga (60.11%) and ^{71}Ga (39.89%)).

1.2. Typical Earth Crust and Soil Gallium Concentrations

The earth's gallium crust concentration ranges from 15 to 19 mg·kg^{-1} (Pendias, 2011). Gallium is largely considered an isomorphic substitution element in felsic rocks and phyllosilicates, with typical United States gallium soil concentrations ranging from 16 to 39 mg·kg^{-1} (Pendias, 2011). Aide (2024) investigated 20 soil series across southeastern Missouri and the mean aluminum concentrations ranged from 0.97% to 3.65%, whereas the mean gallium concentrations ranged from 0.22 to 4.30 mg·kg^{-1}. Chen et al. (2022) determined the Ga speciation in selected soils, noting that coarse-textured, acidic soils exhibited the highest soil Ga availability. Liu et al. (2021) surveyed gallium's total elemental abundance in highly-weathered soils (2.3 to 9.5 mg·kg^{-1}). Liu et al. (2021) also determined that the median EDTA-extracted Ga content accounted for 24% of the total elemental abundance. The average abundance of gallium in Earth's crust is generally less than 19 mg·kg^{-1} (Yuan et al., 2021; Foley et al., 2017). The Al:Ga ratio varies widely in river water owing to differences in the mobility of gallium and aluminum in aqueous solutions (Yuan et al., 2021).

1.3. Gallium Thermodynamic Properties, Hydrolysis and Complexation Reactions

Baes and Mesmer (1976) and Brown and Ekberg (2016) provide thermodynamic data for gallium hydrolysis. Yuan et al. (2021) reviewed gallium hydrolysis and provided Bjerrum plots (at 25˚C and low ionic strengths) showing that Ga^{3+} is the predominant species at pH levels less than pH 3.2, $Ga(OH)^{2+}$ from pH 3.2 to pH 4.3, $Ga(OH)_2^+$ is a minor species at pH 4.3, and $Ga(OH)_4^-$ is the dominant species at pH levels greater than pH 4.3. Yuan et al. (2021) proposed that the strong binding of Ga^{3+} with normal organic matter increases Ga solubility and inhibits further inorganic hydrolysis. At typical environmental concentrations, Ga^{3+} forms stable, mononuclear organic complexes inhibiting the formation of inorganic Ga^{3+} hydroxides. Ga^{3+} forms strong complexes with hard ligands, such as fluoride, hydroxide, phosphate, and sulfate (Yuan et al., 2021), thus altering is solubility and mobility. Benedicto et al. (2014) reported that gallium sorption on montmorillonite and illite at less than pH 4.5 was by simple cation exchange, whereas at higher pH levels sorption was dominated by surface complexation.

Hagvall et al. (2014) noted that gallium formed stable complexes with organic ligands and suppressed hydrolysis. Hieronymus et al. (2001) documented that soil gallium-aluminum correlations were retained during moderate soil weathering; however, gallium and aluminum showed different mobilities under intense weathering. Using soils impacted by mining activities, Chen et al. (2022) noted that the coarse-textured soils had a greater gallium bioavailability.

1.4. Gallium Associations with Phyllosilicates and Oxyhydroxides

Octahedral coordination is likely if the following geometric relationship is $0.414 <$ cation to anion ratio < 0.732 is observed (Nathan, 1985). Gallium exhibits a chemical similarity to Al^{3+} (ionic radius of about 54 pm), Fe^{3+} (ionic radius of about 69 pm) and Zn^{2+} (ionic radius of about 72 pm) and can substitute for these elements in the common rock-forming minerals (Yuan et al., 2021). Mg-beidellite synthesis permitted isomorphic substitution of gallium into octahedral positions, replacing aluminum in the clay lattice (Brandt & Kydd, 1998). X-ray diffractograms reveals that gallium will form synthetic Al-Ga pillered clays with considerable hydrothermal stability (Gonzalez et al., 1992). In Poland, Poledniok (2008) employed a Tessler sequential extraction and documented that gallium speciation sequence was exchangeable > organic > Fe-Mn oxide for agricultural soils.

1.5. Gallium Resource Areas

Presently, the global Ga supply comes from bauxite and lead-zinc deposits. Gallium is frequently associated with Mississippi Valley Lead-Zinc Type Carbonate deposits, substituting preferentially with sphalerite, which may contain gallium from 0.02 $mg \cdot kg^{-1}$ to more than 500 $mg \cdot kg^{-1}$, with a mean of 58 $mg \cdot kg^{-1}$ (Foley et al., 2017; Yuan et al., 2021). The Mississippi Valley Lead-Zinc Type Carbonate deposits in Missouri have an ancestral mining history that has impacted some soils with elevated lead, cadmium and zinc concentrations (Aide & Aide, 2025).

The purpose of this investigation was to determine the total aluminum (Al) and gallium (Ga) soil profile concentrations in Missouri floodplain soils along the Mississippi River and estimate the concentration correlation of these elements. A secondary aspect of this investigation was to determine the cation exchangeability of gallium to estimate availability.

2. Materials and Methods

2.1. Study Area

The study area is located on floodplains along the Mississippi River in Cape Girardeau County, Missouri. The climate is continental humid. The average daily January temperatures are 2˚C to 4˚C, whereas the average summer temperatures are 25˚C to 26˚C. Rainfall is reasonably well distributed, with the typical annual precipitation averaging 1.14 to 1.27 m. The remnants of tropical storms from the Gulf of Mexico may provide additional rainfall (Festervand, 1981).

Two soil series were selected to represent a fine-textured and coarse-textured sediment depositional areas. The soil series were sampled in spring 2025. Two soil pedons on the Commerce soil series (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts) are deep, somewhat poorly drained, moderately slowly permeable soils that formed in loamy to fine textured alluvial sediments. The soil sequence consists of an Ochric Epipedon (A horizon) overlying a Cambic horizon featuring Bw and Bssg horizons. Two pedons of the Caruthersville soil series (Coarse-silty, mixed, superactive, calcareous, thermic Typic Udifluvents) consist of deep, moderately well drained, moderately permeable soils formed in coarse-textured to loamy textured alluvium. The soil horizon sequence consists of an A horizon overlying C horizons with an irregular sequence of soil textures.

2.2. Experimental Protocols

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 and were analyzed at the soil testing laboratory at the University Missouri-Columbia.

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 liters of aqua-regia 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. For the Na-acetate leach, a 0.75 g soil sample of passing a 60-mesh sieve was leached with a sodium acetate matrix at 30˚C for one hour. The Na-Acetate leach was selected because Na^+ is less likely to exchange with Ga^{3+} than Ca^{2+}, Mg^{2+}, NH_4^+, thus recovering Ga^{3+} that is the most available. The Na-Acetate leach is understood to be an operational fraction rather than a total available gallium estimate. Soil analysis for the aqua regia digestion and Na-acetate extraction were performed by Activation Laboratories (Ancaster, Ontario). For both the aqua regia digestions and the Na-Acetate leach, Activation Laboratories included two reference samples and duplicate sampling for quality assurance. The solutions are analyzed using inductively coupled plasma-mass spectrometry. The detection limit for the Na-Acetate leach was 5 mg·kg^{-1} for aluminum and 10 µg·kg^{-1} for gallium, both well below the actual reported concentrations. Simple soil statistics included mean, standard deviation, and linear regression analysis using Excel.

3. Results and Discussion

3.1. Routine Soil Characterization

The Caruthersville pedons exhibit silt loam to sandy loam horizons, slightly alkaline pH levels and soil organic matter contents ranging from 0.4% to 1.3% (Table 1). Both A horizons have 1.1% organic matter contents, with organic matter contents in the deeper horizons irregularly alternating from 0.4% to 1.3%. The Commerce pedons exhibit silty clay to clay-textured horizons, having slightly alkaline pH levels and organic matter contents of 3.4% in both A horizons and the deeper soil horizons range from 2.2% to 3.1%. The cation exchange capacity of the Caruthersville pedons varies from 10 to 23.3 cmol·kg^{-1}, whereas the cation exchange capacity of the Commerce pedons varies from 23.6 to 40.4 cmol·kg^{-1}.

Table 1. Soil pH, soil organic matter and cation exchange capacity for two soil series.

	pH		Organic Matter (%)		Cation Exchange Capacity (cmol/kg)	
Horizon	Pedon #1	Pedon #2	Pedon #1	Pedon #2	Pedon #1	Pedon #2
Caruthersville Soil Series						
A	7.7	8.1	1.1	1.1	16.9	16.6
C1	7.9	8.1	0.6	0.8	19.8	15.5
C2	8.0	8.1	0.6	0.6	17.8	14.0
C3	7.9	8.1	1.6	0.6	23.3	13.5
C4	8.0	7.9	0.8	1.3	14.4	14.2
C5	8.1	8.1	1.0	0.4	16.5	10.0
Commerce Soil Series						
A	7.8	7.9	3.4	3.4	34.8	24.2
Bw1	7.8	7.9	2.6	3.1	26.3	28.0
Bw2	7.9	7.9	2.3	2.3	27.5	38.6
Bw3	7.9	7.8	2.5	2.2	23.6	40.4
Bw4	7.6	7.7	2.9	2.2	29.0	29.4

3.2. Soil Aluminum and Gallium Concentrations

The gallium concentrations within a soil series do not substantially vary with respect to soil depth and across pedons. The mean gallium concentrations of the Commerce soil series (5.9 mg·kg^{-1}) were substantially greater than the mean gallium concentrations of the Caruthersville soil series (2.2 mg·kg^{-1}) (Table 2). The soils of the Commerce series are Inceptisols and the soils of the Caruthersville series are Entisols, implying that the soil horizons lack eluviation and illuviation activities and within each soil series the soil horizons are likely to be similar in their gallium, aluminum and iron concentrations. The gallium concentrations of these soils are smaller than the typical gallium concentration range reported by Pendias (2011) and Yuan et al. (2021); however, these concentration range were within the gallium concentration range reported by Aide (2024). Gallium concentrations do not suggest that gallium accumulation has occurred, and the present environmental threat appears to be minimal.

Table 2. The total concentration, standard deviation, number of observations and range for aluminum, iron, and gallium by soil series.

Element and Series	Mean	Standard Deviation	Observation	Range
Commerce-Al	1.77%	0.20%	10	0.66%
Commerce -Ga	5.86 ppm	0.81 ppm	10	2.76 ppm
Commerce-Fe	2.29%	0.21%	10	0.69%
Caruthersville-Al	0.56%	0.13%	12	0.38%
Caruthersville-Ga	2.24 ppm	0.39 ppm	12	1.11 ppm
Caruthersville-Fe	0.80%	0.11%	12	0.35%

3.3. Soil Relationships Involving Aluminum and Gallium Concentrations

The regression equation for aluminum (%) as the independent variable and gallium ($mg\cdot kg^{-1}$) as the dependent variable is [Ga] = 2.99 [Al] + 0.55 with $r^2 = 0.987$ (**Figure 1**). The gallium and aluminum correlations were pooled for both soil series to show that the Ga/Al ratio for these two distinctively different morphologies were very similar. The pooled Commerce and Caruthersville data set suggests that the gallium-aluminum correlation is similar across both soil series, even though the soil series aluminum concentrations are distinctively different. The inference is that the sediment-clay contents of the two soils are derived from a similar source area; however, the possibility that similar clay mineralogy and oxide contents of the sediments simply predispose adsorption reactions to yield comparable gallium to aluminum ratios. Further research is desired to evaluate the hypothesis that Ga:Al ratios may indicate source area similarity is warranted.

The regression equation for the pooled Commerce and Caruthersville soil series involving gallium concentration and cation exchange capacity is [Ga] = 0.194 [CEC] − 0.462 with $r^2 = 0.72$, where CEC is the cation exchange capacity (**Figure 2**). Given that the scientific classification of both soil series are “superactive” implies that the sediment has an exchange capacity greater than 0.6 cmol charge kg-clay^{-1} (implying that the clay separate is smectite enriched). Sionneau et al. (2008) supports the premise that the study area sediment is smectite (montmorillonite) enriched. Thus, the likelihood that montmorillonite is the dominant phyllosilicate indicates that the CEC may be used as a proxy for clay content.

Gallium may be present soil because of isomorphic substitutions involving: 1) phyllosilicates, 2) the formation of aluminum interlayers, and 3) iron oxides. In a review, Schwertmann and Taylor (1989) reported that virtually all iron oxides and oxyhydroxides have a degree of aluminum attributed to isomorphic substitution. Gallium may also be present in the soil as an exchangeable cation and complexed with soil organic matter.

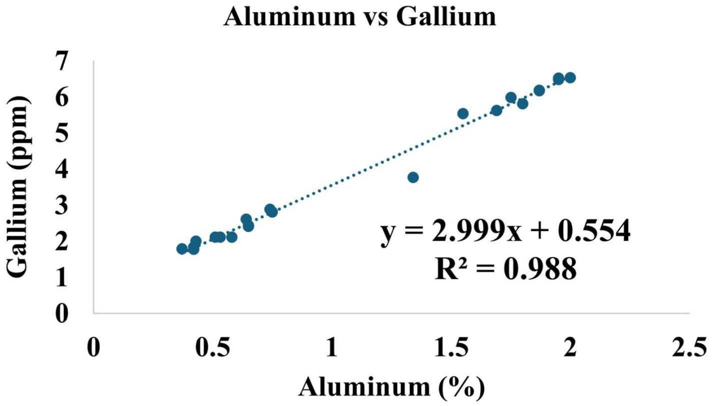


Figure 1. The regression equation for aluminum (%) as the independent Variable and gallium (ppm) as the dependent variable for the pooled Commerce and Caruthersville soil series.

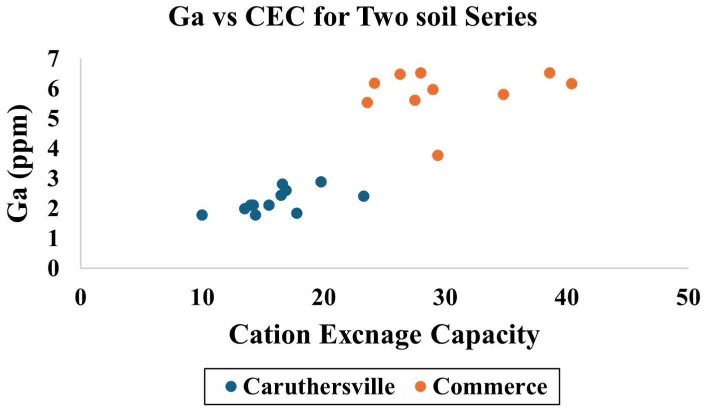
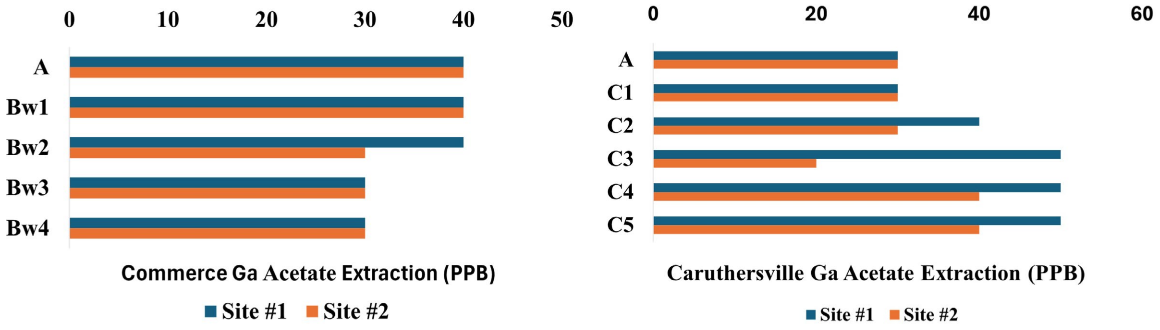


Figure 2. The scatterplot of the gallium concentrations with respect to the cation exchange capacity (cmol·kg^{-1}) for two soil series.

3.4. Relationships Involving Na-Acetate Extractable Gallium for the Commerce and Caruthersville Soil Series

The Na-acetate leach (extractable) gallium concentrations for the Commerce soil series are 30 to 40 μg·kg^{-1}, whereas the Caruthersville soil series gallium concentrations are 25 to 45 μg·kg^{-1} (**Figure 3(a)** and **Figure 3(b)**). The ratio of the mean gallium Na-acetate concentrations to the mean total gallium concentrations is 0.59% for the Commerce soil series and 1.79% for the Caruthersville soil series. These ratios do indicate that the overall perceived soil gallium mobility and availability is minimal. The gallium availability is greater in the coarse-textured Caruthersville soil series. Chen et al. (2022) noted that the coarse-textured soils frequently had greater gallium bioavailability.



(a)

(b)

Figure 3. (a) The soil profile distribution of Na-acetate leaching of gallium for the Commerce soil series (Units are μg·kg^{-1}); (b) The soil profile distribution of Na-acetate leaching of gallium for the Caruthersville soil series (Units are μg·kg^{-1}).

4. Summary

The study estimates the presence of gallium in selected floodplain soils along the Mississippi River. Within the study area, gallium has comparatively low soil concentrations when compared to reported gallium concentrations in the literature. The selected floodplain soils are Entisols and Inceptisols, thus within the sampled pedons the soil horizons lack textural differences attributed to eluviation or illuviation. Textural differences between the soil series are attributed to differences in alluvium deposition (backswamp versus natural levees). The aluminum and gallium concentrations demonstrate similar correlation, both among the soil horizons of individual pedons and between soil series. The nature of the soil profiles and the differences in soil texture suggests that the alluvium in these soil series is derived from the sediment source areas, rather than accumulation from the Mississippi River post-deposition. The gallium exchangeable concentrations indicate that gallium mobility and plant uptake potential remains minimal.

5. The Perspective and Importance for Assessing Gallium in Soil

Gallium is primarily used in the manufacture of semiconductors, light-emitting diodes, smartphone components, medical imaging instruments, high-temperature thermometers, alloys and solar cells (Foley et al., 2017). In medical studies, gallium compounds have displayed anti-inflammatory and immunosuppressive activity in animal models (Chitambar, 2010).

With increased industrial demand for gallium, the incidence of soil contamination is expected to increase and plant damage will likely ensue. In a medium culture involving *Arabidopsis thaliana* with factorial gallium concentrations, Chang et al. (2017) reported that gallium plant uptake could cause increased production of malondialdehyde. Gallium hydroxide was precipitated in the root intercellular spaces, likely causing *Arabidopsis thaliana* to immobilize gallium and reduce the oxidative stress. Increased root secretions of citrate and malate were proposed to improve plant resistance in response to elevated gallium root uptake.

Gallium and its soil chemistry, like many other elements that are increasingly used in industry and manufacturing, are active research areas because of potential environmental impacts. Important research questions include: 1) understanding the basic soil chemistry influencing biological availability and mobility, 2) understanding plant uptake and their influence on plant physiology, 3) pathways into animal and human food chains, 4) soil and plant culture protocols for limiting their environmental threat, 5) characterizing the criteria to assess the degree of soil degradation, and 6) methods of soil reclamation.

Conflicts of Interest

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

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