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Selenium Concentrations in Southeastern Missouri Soils and Its Impact on Livestock Nutrition

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Abstract

Selenium is a trace element in animal nutrition provided through forage. Vegetation should accumulate adequate levels to meet this livestock requirement. This study assessed southeastern Missouri soils for their selenium concentrations. Multiple sites across southeastern Missouri were sampled, from which a total of twenty-six soils were collected. Parent materials ranged from coarse to fine-textured alluvium and terrace deposits, colluvium, loess, limestone residuum and rhyolite residuum from poor to well-drained soils. The mean whole soil selenium contents ranged from less than 0.1 mg Se kg^{-1} for the Kaintuck pedons to 1.0, 2.2, and 2.4 mg Se kg^{-1} for the Irondale, Killarney, and Frenchmill pedons. For individual soils, Menfro pedons were deep, well-drained soils developed in loess. Paired Menfro pedons having similar soil morphology and having A-E-BE-Bt-C horizon sequences were selected and the greatest selenium concentrations were in the argillic horizons. Soils having fine textures (clayey) had moderate selenium concentrations, whereas soils having coarse textures (sandy) revealed minimal selenium concentrations. A wide soil selenium concentration variation was shown; however, no toxic selenium levels were measured. Therefore, soil selenium toxicity is not a regional issue. Noting that soil selenium concentrations in medium to fine-textured soils are appropriate for providing selenium to livestock, the need to artificially soil incorporate selenium or add selenium into the livestock ration remains critical for coarse-textured soils.

Keywords

Selenite, Selenide, Animal Nutrition, Soil, Forages, Animal Health, Selenomethionine

1. Introduction

Selenium is an element with atomic number 34 and is considered a chalcogen. The ground state electronic configuration is [Ar] $3d^{10}$ $4s^2$ $4p^4$. Selenium has four primary valence states [−2], [0], [+4], and [+6]. The selenium [+6] valence state is difficult to reach, requiring an exceptionally electronegative element, such as fluorine [1]. The ionic radius changes with oxidation state, ranging from 0.198 nm for [−2] to 0.042 nm for [+6]. Other atomic and physical properties are available in Lee [1] and Perrone *et al.* [2].

Selenium ionic species typically are: 1) selenate or SeO_4^{2-}, 2) Selenite or SeO_3^{2-}, 3) elemental selenium or Se^0, and 4) reduced selenide or Se^{2-}. Argillaceous sediments typically have 0.3 to 0.6 mg Se kg^{-1}, whereas sandstone and limestones range from 0.01 to 0.1 mg Se kg^{-1}. Typically soils between 0.05 to 1.5 mg Se kg^{-1}, with a mean of 0.44 mg Se kg^{-1} [3] Selenium occurs mostly as a secondary constituent of heavy metal sulfides, such as Ag, Cu, Pb, Hg, and Ni [4]. Bacterial derived Se methylation may occur, forming $(CH_3)_2Se$. Manure may sometimes be a significant selenium source.

Selenium is frequently associated with phyllosilicate minerals and Fe-oxyhydroxides, whose adsorption potential may limit plant availability [4] [5] [6]. Selenate and selenite adsorb onto Fe-oxyhydroxides, with maximal adsorption from pH 3 to pH 5. Thus, with increasing pH levels above pH 5 selenium generally shows more mobility. In more oxic environments ferric selenite ($Fe_2(OH)_4SeO_3$) forms and in anoxic environments iron selenide (FeSe) may precipitate [5]. Selenite is stable in the most oxic soil environments, whereas selenide (HSe^-) is stable in the most anoxic soil environments [4] [5] [6]. H_2Se is considered extremely toxic, whereas Se^0 is relatively nontoxic and is considered an essential element in animal nutrition. Selenium will oxidize to selenate in soils that experience drainage [4] [5].

Selenium content frequently decreases with increased soil depth, given the affinity of Se for soil organic matter interaction. Conversely, many soils exhibit greater Se content in illuvial horizons that have increased clay and Fe-oxyhydroxide contents [4]. In more oxic soil environments, selenate and selenite bind preferentially with aluminum-octahedral sheets associated with the margins of phyllosilicates, a feature frequently associated with greater Se concentrations in argillic horizons [4] [5].

Selenium binds strongly to fulvic acid. In a review, Manojlovic [4] described how selenium concentrations frequently dimmish with increasing soil profile depth, a feature attributed to selenium's tendency to bind to proteins, fulvic acids, and other N-containing compounds. Zhang *et al.* [7] in a study with rice (*Oryza sativa*) seedlings documented that fulvic acid amendments negated the growth stimulation potential of selenium. These authors suggested that selenite uptake was inhibited.

Using thermodynamic data from Essington [5] authors of this manuscript constructed a pH − pe activity diagram, where the activity of soluble Se species was standardized to 10^{-6} and the water activity was unity (**Figure 1**). The acid dissociation reactions were: 1) $H_2SeO_3 = HSeO_3^- + H^+$ with log Ka = −2.58, 2) $HSeO_3^- = SeO_3^{2-} + H^+$ with log Ka = −7.29, and 3) $H_2Se = HSe^- + H^+$ with log Ka = −3.81 [5]. No provision was permitted for adsorption or complexation with fulvic acid, H_2Se volatilization or methylation. SeO_4^{2-} and $HSeO_3^-$ and SeO_3^{2-} are present in oxic and suboxic soil environments, with $HSeO_3^-$ transitioning to SeO_3^{2-} at pH 7.5. HSe^- was present in anoxic soil environments. Selenite typically is less abundant than selenate in well-drained soils having a neutral to alkaline pH than in well-drained acidic soils. Given selenite adsorption, the bioavailability for plant uptake is at a minimum below pH 5.

Peak and Sparks [8] investigated selenate adsorption on hematite, goethite, and hydrous ferric oxide. Extended X-ray adsorption fine structure spectroscopy suggests selenate forms inner-sphere complexes on hematite, whereas selenate forms both inner-sphere and outer-sphere complexes on goethite and hydrous ferric oxide. Mathematical models for soil movement of selenate, selenite and selenomethionide based on 1) oxidation reduction, 2) adsorption-desorption, 3) volatilization and Se speciation show respectable predictive capabilities [9] [10]. Hu *et al.* [11] developed a selenium field trial with rice (Oryza sativa), showing that selenium amended soils reduced plant uptake of lead (Pb) and cadmium (Cd).

2. Selenium and Grain-Oilseed Production

Selenium uptake by forage, grain and oil seed crops supports animal and human nutrition. Song *et al.* [12] observed that selenium uptake in rice (*Oryza sativa*) is greater than for soybean (*Glycine max*) and corn (*Zea mays*); however, soybeans exhibited greater seed transfer factors. Rice selenium concentrations were 0.20 mg·kg^{-1} (root), 0.18 mg·kg^{-1} (leaf), 0.12 mg·kg^{-1} (stem), and 0.04 mg·kg^{-1} (grain),

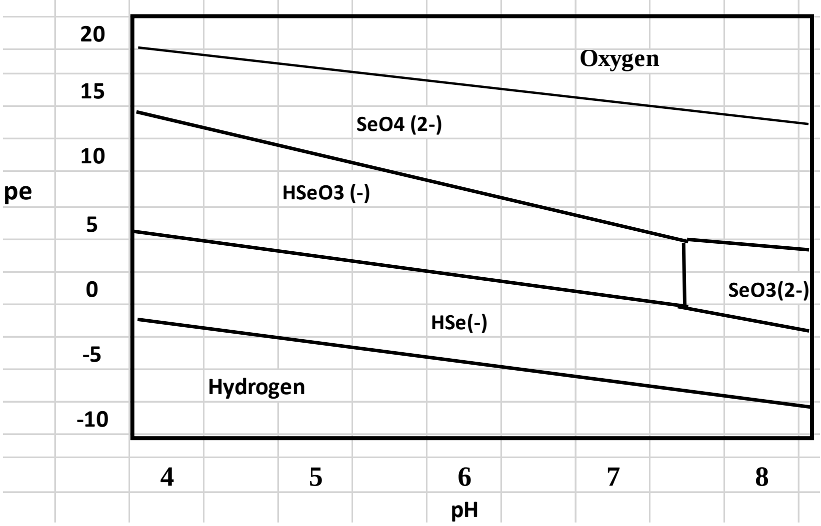

Figure 1. pe and pH diagram of selenium from pH 4 to 8. No solid species were involved in the equilibrium depiction (developed by the authors of this manuscript).

respectively. Bitterli *et al.* [13] observed that across different plant species Se accumulations vary widely, even with specified soil Se concentrations. Transfer of Se from soil into plants results primarily from the Se species solubility and selenium transfer factors were between 0.01 and 100 with few exceptions. Where selenium was soil incorporated, the selenium transfer factors were one or more orders of magnitude higher than selenium transfer factors derived for "native" selenium.

Wang *et al.* [14] selected soils having similar concentrations of total Se, bio-available selenium and related soil parameters and cultivated wheat (*Triticum aestivum*), rice (*Oryza sativa*) and canola (*Brassica napus*). The plant selenium concentrations differed significantly between crop species. Wheat seeds exhibited significantly higher Se concentration than rice seeds and canola seeds; however, wheat stem and root selenium concentrations were smaller than those from canola and rice. Yang *et al.* [15] confirmed that sodium selenite and Se-enriched mixed fertilizer amendments supported improved selenium contents in soybeans (*Glycine max*). Foliar selenium applications provided greater soybean selenium contents than the soil amendments. Soybean cultivars exhibited different selenium accumulations, demonstrating cultivar differences. In China, Fang *et al.* [16] analyzed rice (*Oryza sativa*) samples from different locations and noted that Se levels varied considerably. The mean content of Se was 0.02 $mg \cdot kg^{-1}$. In a subsequent field trial involving rice the Se content of rice could be significantly increased by 194%.

Selenium competes with sulfur and is transported by the sulfate transporter. Selenium hyperaccumulator plants typically accumulate more than 1,000 mg Se kg^{-1}, whereas non-accumulators accumulate less than 100 mg Se kg^{-1} [17]. Plants that generally accumulate between 100 and 1000 mg Se kg^{-1} are termed secondary accumulator. Grasses and field crops are typically non-accumulators, whereas brassica, broccoli (*Brassica oleracea*) and aster are secondary-accumulators. Selenomethionine (SeMet), Se-MeSeCys (Se-Methylselenocysteine), selenite and selenate are the primary selenium species in plant materials [17].

3. Selenium and Pasture-Forage Management

Soil is the major source of Se for vegetation, including pastures and forage [18]. Plants absorb selenium in the form of selenate or selenite; however, the distribution of available and unavailable forms of selenium influence plant uptake patterns. Soil management therefore plays a significant role in optimizing selenium uptake and subsequent plant growth. The usage of inorganic fertilizers with sulfur, over application of acidic fertilizers and soil compaction decrease selenium plant availability. Management practices that increase soil acidity and decrease aeration promote insoluble complexes between selenium and other substrates. Selenium soil deficiency is usually addressed by applying selenium containing fertilizers or selenium in feed additives to livestock.

The intensity of selenium uptake in plants is largely determined by plant genetics, with significant influences conferred by rainfall, soil pH, soil redox status, abundance of Fe-oxyhydroxides, clay content, and microbial activity [4]. Phosphorus has been shown to synergically augment selenium uptake [4]. Plant uptake of selenium results in the metabolic formation of selenoamino acids, with a particular abundance of selenomethionine (SeMet), selenocysteine, Se-methyl selenomethionine and Se-methyl-selenocysteine. SeMet is a main constituent of cereals ranging from 46% - 82%, 55% - 87%, 50% - 81% and 63% - 72% of the plant selenium in corn, rice, wheat, and soybean [19] [20]. Surai [21] demonstrated that cereals adapted to selenomethionine become an important selenium source for livestock. Selenomethionine has been shown to have higher concentrations in the seeds and roots compared to culms (stems) and leaves [22].

Crush *et al.* [23] investigated foliar micronutrient (B, Co, Cu, Fe, Mn, Mo, Se, and Zn) concentrations applied to eight perennial ryegrass (*Lolium perenne*) cultivars cultured across various regions in New Zealand. Selenium perennial ryegrass concentrations ranged from 0.026 to 0.036 mg Se kg^{-1}, 0.007 to 0.009 mg Se kg^{-1}, 0.017 to 0.026 mg Se kg^{-1}, and 0.070 to 0.109 mg Se kg^{-1} across four New Zealand regions. The concentration differences were attributed to cultivar, site, seasonality, and nitrogen amendment rates. Wu *et al.* [24] investigated selenium uptake and accumulation in tall fescue (*Festuca arundinacea*) and white clover (*Trifolium repens*). Selenium tolerance appeared to be related to selenium plant uptake exclusion. The assimilation of selenium into proteins is correlated with selenium toxicity. Owusu-Sekyere *et al.* [25] used nutrient solution cultures to demonstrate that alfalfa (*Medicago sativa*) exhibited increased soluble sugars and starch contents at various selenium concentrations and the plant tissue selenium concentrations were nitrogen dependent. Selenium accumulation may have increased nodulation.

4. Selenium in Livestock Nutrition

Edens and Sefton [26] showed that selenium is a key trace element in animal nutrition, whereas Mayland [27] demonstrated that animals require diets containing 0.1 - 0.3 $mg\cdot kg^{-1}$ selenium for adequate growth and development. Forage and grain crops are the major dietary source of Se. Beef cattle requirement is 0.1 mg Se kg^{-1} in the livestock diet to meet daily requirements [28]. Soils with potentially high levels of sulfur may lower forage selenium contents [17] [28]. When soils are selenium deficient, producers supplement selenium in livestock diets to alleviate white muscle disease and improve calf disease immunity [28]. Timmerman and Omaye [29] provided a substantial review of selenium essentiality in livestock and biochemical pathways for selenomethionine and selenocysteine to produce selenoproteins.

Selenium plays a substantial role in antioxidative enzymatic systems, including the synthesis of glutathione peroxidase. Glutathione peroxidase is a key enzyme that reduces adverse oxidation reactions and improves immunity [4]. Selenium was shown to have a complementary role to Vitamin E, preventing dietary hepatic necrosis and exudative diathesis in rats and chicks [30]. More recently, Lyons *et al.* [17] documented that selenium increased the quality and efficiency of egg, meat, and milk production.

Optimal levels of selenium are required in feed rations; however, there is a small concentration range between deficiency and toxicity. Doucha *et al.* [31] detailed various conditions and health issues associated with low and high levels of selenium in humans, livestock, fish, and birds. Selenium deficiency is reported to increase susceptibility to various diseases in animals. Symptoms of selenium deficiency in livestock are reduced appetite, infertility, and muscle weakness [28] [32]. Feed rations with either organic or inorganic selenite and selenate are provided to poultry, pigs, and cattle to minimize deficiencies and to improve reproductive performance and growth. [31].

Plants will either have low, adequate, or high levels of selenium depending on the soil type. Plants could be deficient in selenium when growing on soils having unavailable forms of selenium, such as selenium-iron complexes. These not readily available soil complexes may be either inorganic (SeO_4, SeO_3, Se^0) or organic (selenomethionine) [33]. Soils with concentrations above 3 - 15 $mg \cdot kg^{-1}$ generally have plants that are toxic to livestock. Incorporating these toxic selenium plants in livestock diets frequently results in health defects and death. Selenium toxicity is characterized by hair and hoof loss, impaired vision, embryonic deformities, and infertility [27]. Séboussi *et al.* [34] supported the usage of selenium fertilized forage to improve the performance of lactating dairy cows. de Abreu Faria *et al.* [35] observed tropical pastures and their potential for improved animal performance with selenium soil amendments.

Pfister *et al.* [36] studied if sheep and cattle could discriminate between forages and feeds with different selenium concentrations. The selenium concentrations ranged from 0.8 to 50 $mg \cdot kg^{-1}$ in wheatgrass (*Thinopyrum intermedium*), 1.4 to 275 $mg \cdot kg^{-1}$ in alfalfa (*Medicago sativa*), and 4 to 4455 $mg \cdot kg^{-1}$ in western aster (*Symphyotrichum ascendens*). Selenium concentrations exhibited no influence on sheep or cattle preference. When given selenium containing pellets, initially cattle and sheep responses were variable, but they subsequently adjusted their intake to avoid excessive intake of Se. Juszczak-Czasnojć and Tomza-Marciniak [37] noted that beef cattle from conventional farms had significantly ($p < 0.05$) higher serum Se concentration than those on organic farms.

Mehdi and Dufrasne [38] noted selenium is an antioxidant and the nutritional requirements of selenium in cattle are estimated at 100 $\mu g \cdot kg^{-1}$ DM (dry matter) for beef cattle and at 300 $\mu g \cdot kg^{-1}$ DM for dairy cows. Rations high in fermentable carbohydrates, nitrates, sulfates, calcium, or hydrogen cyanide negatively influence the use of dietary selenium. Selenium supplementation may reduce the incidence of metritis and ovarian cysts during the postpartum period. The addition of selenium yeasts in the foodstuffs of cows significantly increases the Se content and the percentage of polyunsaturated fatty acids in milk compared to the addition of sodium selenite. Enrichment of selenium in the diet did not significantly affect the slaughter weight and carcass yield of bulls. The impact and results of selenium supplementation in cattle depend on physiological stage, selenium status of animals, type and content of selenium and types of selenium administration [28] [38].

5. Materials and Methods

5.1. Study Area

Multiple sites across southeastern Missouri were sampled from which a total of twenty-six soils were collected (**Table 1**). The regional climate is continental and humid. Summers are hot and humid with a mean July temperature of 26˚C and winter temperatures are mild with a mean January temperature of 2˚C. The mean annual precipitation of 1.19 m is relatively evenly distributed, with slightly greater rainfall in Spring. In the southern portion of the study area the pre-settlement vegetation was a mixed hardwood forest generally classified as "bottomland forests," "swamp forests," and "hardwood forests" communities within Braun's Southeastern Evergreen Forest Region, as described by Dyer [39]. Canopy dominants included sweetgum (*Liquidambar styraciflua*), white oak (*Quercus alba*), southern red oak (*Quercus falcata*), yellow poplar (*Liriodendron tulipifera*) and baldcypress (*Taxodium distichum*). Currently, most of the region has been artificially drained by a series of extensive canals and the forests cleared for row-crop agriculture. In the northern portion of the study area, the dominant pre-settlement vegetation was Oak-Hickory featuring white oak (*Quercus alba*), northern red oak (*Quercus rubra*), southern red oak (*Quercus falcata*), and several species of maple (*Acer*).

5.2. Field and Laboratory Protocols

Pedons were located, described, and sampled according to Soil Survey Division Staff [40], with most sites using excavated pits. Samples of soil horizons from each pedon were oven dried, lightly crushed, and sieved to remove materials larger than 2 mm. Soil pH using equal volumes of soil and water, the NH_4-acetate (pH 7.0) extraction of exchangeable cations, the total acidity by slow titration to pH 8.2, and soil organic matter contents by loss on ignition were performed [40]. The particle size distribution (mechanical analysis) was determined by Na-saturation of the exchange complex, dispersion in Na_2CO_3 (pH 9.0) and centrifuge fractionated to remove clay followed by wet sieving of the silt and sand separates [41].

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. Aqua-regia does not appreciably degrade quartz, albite, orthoclase, anatase, barite, monazite, sphene, chromite, ilmenite, rutile and cassiterite, whereas aqua-regia partially degrades anorthite and phyllosilicates [42]. Homogenized

Table 1. Selected Missouri soils and their taxonomic classification.

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

samples (0.75 g) were equilibrated with 0.01 liter of aqua-regia (3 volumes HNO_3 to 1 volume HCl) in a 35˚C incubator for 24 hours. Duplicated samples were shaken, centrifuged, and filtered (0.45 µm), with a known aliquot volume analyzed using inductively coupled plasma mass spectrometry. Reference samples with known elemental concentrations were employed for quality control [42]. 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 mass spectrometry. Selected samples were duplicated, and reference materials were employed to guarantee analytical precession.

6. Selenium Content in Selected Missouri Soils

6.1. Soil Taxonomy and Selenium Soil Concentrations

The soil taxonomic classification of 26 soil series selected for this manuscript are listed in Table 1. Soil orders include Alfisols, Entisols, Inceptisols, Mollisols, Vertisols, and Ultisols.

Parent materials ranged from coarse to fine-textured alluvium and terrace deposits, colluvium, loess, limestone residuum and rhyolite residuum (Table 2).

Soil drainage ranged from very poorly-drained to well-drained (Table 3).

The mean whole soil profile selenium contents ranged from less than 0.1 mg Se kg^{-1} for the Kaintuck pedons to 1.0, 2.2 and 2.4 mg Se kg^{-1} for the Irondale,

Table 2. Selected Missouri soils and their parent materials.

Soil	Description
Alred	Cherty hillslope sediments and the underlying clayey residuum.
Amagon	Loamy alluvium
Broseley	Sandy alluvium
Calhoun	Loess-like material with low sand content
Clana	Sandy alluvium on old natural levees and terraces.
Commerce	Loamy alluvial sediments.
Dubbs	Loamy alluvium
Foley	Silty material high in sodium
Frenchmill	Colluvial materials weathered from acid igneous rocks
Haymond	Silty alluvium
Hildebrecht	Loess over residuum weathered from dolomite
Irondale	Residuum from fine grained igneous rock
Kaintuck	Loamy alluvium on flood plains
Killarney	Slope alluvium with loess and the underlying rhyolite residuum
Knobtop	Loess and the underlying igneous rock residuum
Lilbourn	Loamy alluvium over buried alluvium
Malden	Sandy alluvium on natural levees and terraces
Menfro	Loess
Overcup	Silty alluvium.
Portageville	Clayey alluvium
Reelfoot	Fine silty alluvium
Rueter	Colluvium and residuum from cherty limestone
Sharkey	Clayey alluvium
Tiptonville	Silty alluvium
Wakeland	Silty alluvium
Wilbur	Silty alluvium on flood plains

Table 3. Drainage classification of selected Missouri soils.

Alred	Very deep, well drained soils
Amagon	Very deep, poorly drained
Broseley	Deep, well and somewhat excessively drained
Calhoun	Very deep, poorly drained
Clana	Very deep, moderately well drained
Commerce	Deep, somewhat poorly drained
Dubbs	Very deep, well drained
Foley	Very deep, poorly drained
Frenchmill	Very deep, well drained
Haymond	Very deep, well drained
Hildebrecht	Very deep, moderately well-drained
Irondale	Moderately deep, well drained
Kaintuck	Very deep, well drained
Killarney	Very deep, moderately well-drained
Knobtop	Moderately deep, moderately well drained soils
Lilbourn	Very deep, somewhat poorly drained
Malden	Very deep, excessively drained
Menfro	Very deep, well drained
Overcup	Very deep, poorly drained
Portageville	Very deep, poorly drained
Reelfoot	Very deep, somewhat poorly drained
Rueter	Very deep, somewhat excessively drained
Sharkey	Very deep, poorly, and very poorly drained
Tiptonville	Very deep, moderately well drained
Wakeland	Very deep, somewhat poorly drained
Wilbur	Very deep, moderately well drained

Killarney and Frenchmill pedons, respectively (Table 4). The Irondale, Killarney and Frenchmill pedons are unique in that the parent materials are largely rhyolite colluvium and residuum, whereas the other pedons have sedimentary parent materials, including limestone derived materials, loess and alluvium. If the Irondale, Killarney and Frenchmill pedons were omitted, then the soil pedons with the greatest whole soil profile selenium concentrations are the Portageville and Sharkey clayey-textured pedons. The Kaintuck pedons are coarse-textured to loamy-textured pedons on floodplains. Other coarse-textured pedons include the Broseley, Clana, and Malden pedons with 0.3 mg Se kg^{-1} or smaller selenium concentrations.

Table 4. Soil profile total selenium mean and coefficient variation concentrations.

Soil	Mean ($\text{mg}\cdot\text{kg}^{-1}$)	Coefficient Variation (%)	Comments
Alred	0.5	45	Eluvial horizons below detection
Amagon	0.5	49	No significant soil profile variation
Broseley	0.3	29	No significant soil profile variation
Calhoun	0.6	13	No significant soil profile variation
Clana	0.3	22	No significant soil profile variation
Commerce	0.4	53	Slightly greater in eluvial horizons
Dubbs	0.4	35	Slightly greater in eluvial horizons
Foley	0.9	18	Slightly greater in eluvial horizons
Frenchmill	2.4	35	Irregular distribution
Haymond	0.7	65	Greater in eluvial horizons
Hildebrecht	0.5	39	Slightly greater in argillic horizon
Irondale	1.0	23	No significant soil profile variation
Kaintuck	<0.1	--	All horizons below detection limit
Killarney	2.2	54	Irregular distribution
Knobtop	0.6	26	No significant soil profile variation
Lilbourn	0.4	32	No significant soil profile variation
Malden	0.2	23	No significant soil profile variation
Menfro	0.4	38	No significant soil profile variation
Overcup	0.7	36	Slightly greater in deeper argillic horizons
Portageville	1.0	28	Slightly greater in eluvial horizons
Reelfoot	0.6	20	No significant soil profile variation
Rueter	0.2	39	No significant soil profile variation
Sharkey	1.0	38	No significant soil profile variation
Tiptonville	0.5	33	Slightly greater in eluvial horizons
Wakeland	0.7	32	No significant soil profile variation
Wilbur	0.5	67	No significant soil profile variation

Detection limit was 0.1 $\text{mg}\cdot\text{kg}^{-1}$.

6.2. Examples of Selenium in Individual Soils

The Menfro pedons are deep, well-drained soils developed in loess (**Table 5**). Paired pedons having similar soil morphology and having A-E-BE-Bt-C horizon sequences were selected. In general, the greatest selenium concentrations were in the argillic horizons; however, the A and E horizons did exhibit nearly comparable Se concentrations. Clay-selenium adsorption is important in influencing the greater selenium concentrations in the argillic horizons and selenium organic matter interactions and biocycling are likely important in elevating the selenium concentrations in the eluvial horizons.

Selenium in the Overcup pedons was assessed from the sand (2 to 0.05 mm), silt (0.05 to 0.002 mm) and clay (less than 0.002 mm) separates. The Overcup series is an Albaqualf, in which a fluctuating seasonal water table fostered the synthesis of Fe- and Mn-concretions, particularly in the argillic and deeper soil horizons. The sand separates showed the greatest selenium concentration (**Table 6**). The sand separate contained fine quartz minerals and glabules (concretions composed of Fe-Mn minerals that formed because of alternating oxic and anoxic

Table 5. Selenium content (mg·kg^{-1}) of paired Menfro pedons.

Horizon	Pedon 1	Pedon 2
A	0.4	0.5
E	0.4	0.5
BE	0.2	0.5
Bt1	0.1	0.4
Bt2	0.6	0.4
Bt3	0.6	0.6
Bt4	0.2	0.4
Bt5	0.4	0.3
BC	0.5	0.4

Table 6. Selenium content (mg·kg^{-1}) of the Overcup soil series partitioned by texture separates across soil horizons.

Horizon	Clay	Silt	Sand
Ap	0.4	0.4	1.1
E	0.4	0.3	1.9
BE	0.5	0.2	2.6
Btg1	0.4	0.3	7.8
Btg2	0.4	0.2	4.1
Btg3	0.9	0.5	6.5
Btg4	0.5	<0.1	2.3

Detection limit is 0.1 mg·kg^{-1}.

Table 7. Selected soils comparing selenium aqua regia digestion with water extraction.

Soil	Texture	--------Aqua Regia--------		------Water Extraction------	
		Mean (mg·kg^{-1})	CV (%)	Mean (μg·kg^{-1})	CV (%)
Clana	Sand	0.3	22	8	54
Malden	Sand	0.2	41	8	49
Sharkey	Clay	0.5	37	34	20
Kaintuck	Sandy loam	Largely undetected	--	13	21
Wilbur	Silt loam	0.4	35	10	70

CV is coefficient variation.

soil conditions). Thus, the unique presence of an abundance of Mn and Fe-oxyhydroxides in the sand separate was instrumental in partitioning selenium preferentially in the sand and clay separates. The Foley pedon (data not displayed) was like the Overcup pedon in that the argillic (Btg) horizons presented selenium-bearing sand-sized glabules.

A selenium water extraction approximates labile selenium; that is, selenium that potentially will become involved in root uptake (**Table 7**). For five soils the water extractable selenium concentrations range from 8 to 34 μg·kg^{-1}, concentrations that are approximately two orders of magnitude smaller than the aqua regia digestion concentrations. The selenium water extract concentrations were greatest for the clay-textured Sharkey pedon.

7. Conclusions

Selenium is an important nutrient, protecting plants as an antioxidant. In Missouri, selenium is a soil nutrient that is frequently deficient, especially in beef cattle (*Bos taurus*) production. Therefore, there is a need for selenium in livestock rations.

The greatest selenium concentrations in soils are derived from felsic materials (rhyolite). All other soils possessed parent materials derived from limestone residuum, loess, and alluvium. Soil having fine textures (clayey) had significant selenium concentrations, whereas soils having coarse textures (sandy) exhibited the smallest selenium concentrations. Selenium was associated with Fe-oxyhydroxides, typically Fe-oxyhydroxides associated with the clay separate.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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