Long-term impacts of biosolids on Florida sandy soils: assessing legacy phosphorus and heavy metals 14 years post-application

JoAnn B. Donald[1], Robert G. Hatfield[2], Rex Ellis[3], Todd Z. Osborne[1, 4], Allan R. Bacon[1], Yang Lin[1, *]

[1] Department of Soil, Water, and Ecosystem Sciences, University of Florida, Gainesville, FL 32611

[2] Department of Geological Sciences, University of Florida, Gainesville, FL 32611

[3] St. Johns River Water Management District, Palatka, FL 32178

[4] The Whitney laboratory for Marine Biosciences, University of Florida, St. Augustine, FL 32080

[*] Corresponding author, ylin2@ufl.edu

This is an accepted version of the following:

Donald, J. B., Hatfield, R. G., Ellis, R., Osborne, T. Z., Bacon, A. R., & Lin, Y. (2025). Biosolids-derived phosphorus persists in Florida sandy soils. *Geoderma Regional*, *41*, e00961. https://doi.org/10.1016/j.geodrs.2025.e00961

Abstract

Biosolids, the solid byproduct from sewage treatment plants, are utilized as soil conditioners and fertilizers due to their rich organic matter and nutrient content. However, there are concerns about heavy metals and high levels of phosphorus (P) in biosolids which can lead to environmental issues such as increased biotoxicity and eutrophication of water bodies. This study examines the effects of historical biosolid applications on sandy soils at a former ranch in Seminole County, Florida, focusing on the persistence of legacy P and heavy metals 14-years post-application. Soil samples were analyzed using magnetic susceptibility (MS), X-ray fluorescence (XRF), and the Ignition Total Phosphorus (ITP) protocol. The analysis showed that concentrations of heavy metals such as chromium, copper, nickel, lead, and zinc in the top 15 cm of soil were well below EPA and EU recommended limits, indicating no significant long-term accumulation. In contrast, P levels were notably higher in biosolid-treated soils compared to untreated samples, demonstrating the persistence of legacy P and raising concerns about potential eutrophication in water bodies. Examination of the vertical movement of biosolid-derived materials revealed elevated P and calcium (Ca) levels in both topsoil and subsoil horizons, suggesting that P is moving with Ca. These findings highlight the persistent residual effects of legacy P, evident even in well-drained, leachable soils 14 years post-application, suggesting that legacy P may have a longer half-life than currently assumed and that its role in long-term biosolid application projects could be underestimated.

Keywords

Biosolids, Legacy Phosphorus, Heavy metals, Sandy soils, Eutrophication

Highlights

- Long-term effects of biosolids applications were studied 14 years post-treatment on Florida sandy soils.
- Heavy metal concentrations in biosolid-treated soils remain below EPA and EU recommended limits.
- Phosphorus from biosolids persists in the soil, raising concerns about eutrophication risks.
- Vertical movement of P and calcium was observed, potentially affecting deeper soil horizons.
- Legacy P from biosolids exhibits long-term persistence even in highly leachable soils, suggesting its role in biosolid applications may be underestimated.

1. Introduction

Approximately 34 billion gallons of wastewater are treated daily in the United States to remove contaminants from domestic, industrial, and stormwater sources (EPA, 2023). Following the Clean Water Act of 1972, treatment facilities remove pollutants from wastewater before releasing treated effluent into natural water bodies (Brown et al., 2020; EPA, 2023). The residual by-product, known as sewage sludge, can be incinerated, landfilled, or treated to produce biosolids through stabilization processes that reduce pathogens, heavy metals, and other contaminants (Pi et al., 2018). Due to their nutrient-rich organic matter, biosolids are widely used as fertilizers and soil conditioners in agriculture, pasture grazing, and land reclamation (Gianico et al., 2021; Florida DEP, 2022). Biosolids enhance soil fertility and structure, improving aggregate stability, water retention, and microbial communities (Lu et al., 2012; Pi et al., 2018). They can reduce reliance on synthetic fertilizers, mitigating environmental impacts such as water contamination from fertilizer production and nutrient runoff (Marchuk et al., 2023). However, the overapplication of biosolids, similar to chemical fertilizers, can contribute to eutrophication and harmful algal blooms, posing risks to water quality and ecosystem health (Chislock et al., 2013; Zhidkova et al., 2020).

While biosolids typically contain lower nutrient concentrations than synthetic fertilizers, they provide essential macro and micronutrients, including nitrogen (N), phosphorus (P), copper (Cu), zinc (Zn), calcium (Ca), iron (Fe), and magnesium (Mg), which support crop growth (Lu et al., 2012). However, they also contain heavy metals such as cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), and zinc (Zn), which can accumulate in soils, potentially leading to bioaccumulation in livestock, phytotoxicity in plants, and leaching into ground and surface waters (Marchuk et al., 2023; Sharma et al., 2017). The bioavailability and mobility of these metals are influenced by soil properties; sandy soils with low pH, such as those common in

Florida, present higher risks for heavy metal leaching compared to clay-rich or high organic matter soils (McLaughlin et al., 2000; EPA, 2018). Florida’s sandy soils, warm climate, and high rainfall also increase the risk of P leaching, posing a persistent threat to water quality (McBride, 2022). Phosphorus can persist in soils for long periods, and biosolids applications can lead to an excess amount of P accumulation in the soils (Liang et al., 2022; Sharpley et al., 1994). When biosolids or other fertilizers are applied in quantities that exceed plant P requirements, the surplus P accumulates in the soil. Repeated applications over time result in increasing amounts of stored P, creating a "legacy" effect (Haygarth et al., 2013). This legacy P, which can persist in soils for decades even after fertilizer use has ceased, represents a significant source of P that can slowly release into the environment, contributing to eutrophication (Sharpley et al., 2013).

Since 2019, Florida has produced around 340,000 dry tons of biosolids annually, with approximately two-thirds used in land applications (Frick, 2019). Florida's unique geologic conditions require careful management of biosolids use due to increased risks of leaching. The state’s numerous shallow water tables and interconnected water bodies make legacy P and heavy metals of particular concern, as they may leach into both groundwater and surface water, potentially affecting the Floridan aquifer system, a major source of drinking water for the state. While the Florida Department of Environmental Protection (DEP) regulates biosolid P content and imposes limits to minimize contamination risks, public concern over heavy metal contamination persists (Silveira et al., 2017; Florida DEP, 2022). The regulation of biosolids use remains controversial, with some speculating that biosolid applications have contributed to harmful algal blooms in South Florida lakes, leading to increased biosolid shipments to North and North Central Florida. These regions also report concerns that biosolids are elevating P levels, leading to eutrophication and algal blooms in local water bodies (Canion et al., 2022). Extensive research has investigated the safety of biosolids (Ippolito & Barbarick et al., 2022; Marchuk et al., 2023; Sharma et al., 2017), yet significant knowledge gaps remain, particularly concerning the long-term fate of P and heavy metals in soils after biosolids applications have ceased.

In this study, we investigated the long-term environmental impacts of biosolids application on sandy soils on a former ranch in Florida. We chose Florida soils as they are typically some of the most organic and nutrient poor well drained sandy soils, they can be considered endmember behavior for heavy metal and legacy P retention and mobility. We used X-ray fluorescence (XRF), Ignition Total Phosphorus (ITP), and magnetic susceptibility (MS), to assess heavy metal contamination, P enrichment, and soil properties as indicators of past biosolids applications. Specifically, we examined concentrations of heavy metals (i.e., Cr, Cu, Ni, Pb, and Zn) in biosolids-treated soils compared to untreated soils and evaluated the potential for accumulation of these metals in deeper horizons, given their risks of bioaccumulation and leaching. The persistence of P in soils 14 years post-application was also assessed, considering its potential to cause environmental issues like algal blooms. We explored whether changes in organic matter, pH, MS, and elements like Ca can serve as reliable markers of historical biosolids applications. In addition, we investigated the vertical movement of biosolid-derived materials, including organic matter, Ca, metals, and P, to evaluate the potential for deeper soil contamination and groundwater risk. Overall, this research aims to determine the environmental legacy of biosolids in well-drained, sandy soil endmembers that given their lack of OM we would expect to perform the most poorly in terms of legacy P and heavy metal retention.

2. Materials and methods

2.1. Study site, sample collection and soil description

The study site is located in Seminole County, Florida, within the Charles E. Bronson Wildlife Refuge. Formerly known as Lee Ranch, this area functioned as a cattle ranch where biosolids were applied between 2001 and 2008. The site comprises 17 fields with varying biosolids application rates, of which this research focused on 11 fields covering approximately 2 square miles. The biosolids application rates for each field were obtained from records maintained by the Florida DEP, based on data reported by the contractors responsible for supplying biosolids. The predominant soils of the site are Basinger and Myakka series, with some Smyrna and EauGallie fine sands, classified as sandy, siliceous, hyperthermic Aeric Alaquods, and siliceous, hyperthermic Spodic Psammaquents (Soil Survey Staff). The setting consists of depressions and flatlands on marine terraces.

Soil samples were collected from the top 15 cm using soil cores, and subsoil samples were obtained using an auger to a depth of 150 cm. Sampling followed a grid pattern, with select fields subjected to stratified sampling based on accessibility, and GPS coordinates were recorded for each location (Fig. 1). A total of 186 surface soil samples were collected at an average density of 80-100 samples per square mile, along with six control samples from adjacent areas, including three subsoil controls and subsoil samples from seven field locations. All samples were air-dried, homogenized using a 2 mm stainless-steel sieve, and sub-sampled for analysis.

2.2. Magnetic measurements

Magnetic susceptibility is strongly sensitive to the concentration of Fe-oxides in the soil which can originate from geological (primary) and/or anthropogenic (secondary) sources. In organic poor, quartz dominated, sandy soils like those in this study, the geological component is likely to be low or negative. As Fe-oxide concentrations often co-occur with heavy metals then we can potentially use MS as a proxy for heavy metals and legacy P accumulation if a co-occurring relationship can be established. This technique offers a rapid and non-destructive approach for assessing the spatial distribution of iron oxides and associated heavy metals in soil, making it a valuable tool for large-scale studies (Paradelo et al., 2009).

Magnetic susceptibility measurements were conducted using an AGICO KLY-3 Kappabridge in the Dept. of Geological Sciences at the University of Florida. Plastic cubes with a volume of 8 cm^3 were weighed, filled with soil samples to the top, capped, and then re-weighed. The weight of the empty cube was subtracted from the total weight to determine the weight of the soil. Each soil-filled cube was then measured for volumetric magnetic susceptibility five times, and the results were averaged to obtain a single value for each sample.To account for the magnetic susceptibility of the plastic cubes themselves, five empty plastic cubes were measured five times each, and their average magnetic susceptibility was calculated. This average value was subtracted from the soil sample measurements to correct for the diamagnetic influence of the plastic cube. To normalize the cube-corrected MS measurements for variations in soil mass, the following mass normalization formula was applied:

$$X\mathrm{lf} = k/\mathrm{p} \tag{1}$$

Where Xlf is the low frequency (lf; 300 A/m at 875 Hz) mass specific susceptibility (m^3 kg^{-1}), k is the (corrected) volume susceptibility, and p is the sample bulk density (kg m^{-3}) (Dearing, 1994).

2.3. Loss on ignition

Loss on ignition (LOI) was performed to determine the organic matter content and prepare soils for XRF and P analysis. Ten grams of each soil sample were oven-dried at 105°C for 3 hours, then ashed at 550°C for 4.5 hours. The organic matter content was calculated by the weight difference before and after ashing.

2.4. X-ray fluorescence (XRF)

Elemental analysis of soil samples was performed using a SHIMADZU EDX Fluorescence Spectrometer to quantify heavy metals via X-ray fluorescence (XRF). XRF is a non-destructive and cost-effective method for evaluating trace elements in soils with the ability to detect a wide range of heavy metals including arsenic (As), Cr, Cu, Ni, Pb, V, and Zn, making it an excellent tool for analyzing soils with previous biosolids applications (Ene et al., 2010).

The XRF chamber was purged with helium to reduce atmospheric interference, enhancing the detection of light elements. Instrument calibration was verified using a standard metal, and NIST Standard Reference soils were used to generate calibration curves.

Six NIST reference soils were diluted with pure silica powder to concentrations of 75%, 50%, 25%, and 10%, creating 30 standard samples, including undiluted (100%) samples. These standards were ashed to remove organic content and then were analyzed alongside pure silica powder to establish baseline readings and correct for matrix effects. Calibration curves were developed by plotting known element concentrations of the standards against XRF responses, validated using linear regression and R-squared analysis.

Soil samples were prepared by pouring approximately 1 cm of soil into Mylar cups, for a total of 274 samples, including 15 duplicates for consistency checks. Data were exported as Excel CSV files containing z-scores, raw and normalized frequencies, and overlaps for standards and samples. The following formula was used to convert the ka frequency (raw spectra) of the soil samples into a concentration:

$$\text{Element (ppm)} = \frac{\text{raw ka frequency} - \text{standard curve intercept}}{\text{standard curve slope}} \tag{2}$$

By applying this formula, the raw spectral data were converted to elemental concentrations in ppm, providing a quantitative measure of an element’s presence in each soil sample.

2.5. Ignition total phosphorus (ITP)

Soil total P was quantified using the Ignition Total Phosphorus (ITP) protocol, as described by Saunders and Williams (1955), utilizing LOI to release P embedded in the mineral matrix of the soil, followed by acid extraction and colorimetric estimation of P. LOI-treated soil samples (0.8000 g) were placed in 50 mL centrifuge tubes and extracted with 40 mL of 1 M H_2SO_4. The samples were shaken for 16 hours, centrifuged at 4000 rpm for 3 minutes, and the supernatant was filtered through Whatman #42 filters prior to colorimetric determination of P following Murphy and Riley (1962).

2.6. Statistical analysis

Pearson's correlation coefficient was calculated to assess the relationship between the magnetic susceptibility and the concentrations of heavy metals and P in soil samples. Additionally, correlations and ANOVAs were examined between the reported rate of biosolids application across different fields and control sites. The application rates were grouped into four categories: 200-400 (n=32), 401-600 (n=25), 601-800 (n=55), and 801-1166 (n=74) kg of total P per hectare. These groupings were based on the range of application rates reported across the fields, allowing for a more structured comparison of P accumulation and its potential effects across different treatment levels. Linear regressions were conducted to further explore the associations with P concentration. Descriptive statistics were also performed to summarize the data. All statistical analyses were conducted using R (Posit Team 2024).

3. Results and discussion

3.1. Heavy metal contaminants in biosolids

XRF results showed the levels of heavy metals in the top 15 cm of soil samples were below phytotoxicity thresholds and below concentrations harmful to the environment and humans (Table 1). All metals that were analyzed were well below the EPA (garden soils) and EU (agricultural soils) recommended upper limits (Kinuthia et al., 2020; Martin & Griswold et al., 2009), with the exception of one sample that had Ni slightly above these thresholds (Fig. 2). Analyzed metals included Cr, Ni, Cu, Zn, and Pb, while As was below the detection limit. There was also no significant difference found between the concentrations of heavy metals in the biosolids-impacted soil samples and those in the control soil samples. These findings suggest that biosolids applications between 2001 and 2008 have not resulted in significant heavy metal accumulation, even 14 years post-application. This outcome may be attributed to stringent biosolid regulations and natural attenuation processes over time.

Subsoil analysis from selected fields indicated no significant accumulation of heavy metals below 15 cm. Concentrations decreased within the E horizons and slightly increased in the Bh horizons, a trend also observed in the control samples (Table 2). These results are consistent with other studies showing minimal heavy metal buildup from biosolids in British Columbia rangelands and Colorado semi-arid grasslands years after application (Avery et al., 2018; Ippolito et al., 2010).

Unregulated metals titanium (Ti) and zirconium (Zr) were also analyzed, with Ti exhibiting a median concentration of 1340 ppm and Zr 157 ppm in the top 15 cm of soil (Table 1). Titanium naturally occurs in the environment as minerals such as rutile and ilmenite, but it can also be found as titanium dioxide nanoparticles used globally in various industries such as cosmetics, food, and plastics (Lyu et al., 2017). Despite its widespread presence in modern environments, including biosolids, it is unlikely its occurrence here originated from biosolids. Instead, a strong correlation between Ti and Zr concentrations suggests a geological origin rather than an anthropogenic one (Fig.2). These elements are likely derived from the natural composition of the Pamlico relict beach ridge at the study site. The coastal area of the prehistoric

Pamlico Sea is known for its heavy mineral deposits in sands and sediments, which could contribute to the observed concentrations of these elements (MacNeil, 1949). Titanium and zircon are both mined in Florida soils with zircon being used in the ceramics industry and Ti from ilmenite and rutile used for titanium dioxide pigments (Florida DEP, 2023). To definitively determine the origin, transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) would need to be performed on samples to identify the mineral composition of these elements and establish if they exist as nanoparticles.

Iron levels in the top 15 cm of soil were generally very low, with most samples falling below the limit of detection (LOD) of approximately 300 ppm, while higher concentrations were observed in the subsoil samples of the Bh, Bw, Btg, Eg, and E' horizons (Table 1). In contrast, aluminum (Al) levels were high in the top 15 cm and showed a significant increase in the same subsoil horizons with elevated Fe levels. This pattern is consistent with the characteristics of spodosols, where Fe and Al accumulate in the subsoil layers (McKeague et al, 1983).

3.2. Phosphorus enrichment in soil

Total P analysis using the ignition method showed elevated P levels in the top 15 cm of soil from biosolid-applied fields ($n = 186$), with concentrations ranging from 471 to 3,504 ppm and a median of 1,096 ppm (Table 1). In contrast, control samples from nearby wooded areas had significantly lower P levels, ranging from 462 to 748 ppm, with a median of 520.5 ppm, approximately half the median of the biosolids fields. ANOVA results indicated a significant difference in P concentrations when compared to sites historical biosolids application rates and control samples ($p < 0.001$) (Fig. 3A). The P concentrations highlight the persistence of P in the environment. Even after 14 years without biosolids applications, legacy P remains prevalent in the soil. These findings suggest that P persists in the soil long after biosolids applications have ceased, raising concerns about its potential impact on eutrophication in connected water bodies.

3.3. Remaining P stock

A back-of-the-envelope estimate of the remaining P stock 14 years after biosolids application was calculated by subtracting the median P concentration (ppm) in the control samples from that in the median of the biosolids-amended fields to find the remaining P amount. This was combined with the biosolids application rate (kg ha-1) and the estimated soil mass (kg/ha) to determine the concentration rate and the percentage of P remaining in the soil. Overall, using median rates for the entire study site, approximately 73% of the applied P still remains in the soil 14 years after application.

3.4. Calcium concentration in soil

Calcium concentrations in the top 15 cm of soil samples from the biosolid-applied fields were notably high, ranging from 3,999 to 55,804 ppm, with a median of 15,989 ppm, while the control samples exhibited lower Ca levels, ranging from 504 to 14,498 ppm with a median of 3,714 ppm (Table 1). This elevated Ca concentration may be partly attributed to small shell fragments less than 2 mm in size found in the soil samples. According to the Florida Geological Survey, the sediment at the study site dates to the Quaternary period and consists of undifferentiated sands with variable amounts of clay and some shelly sands from lagoonal deposits (Scott, 1993). While some Ca is naturally occurring, biosolids also contribute significantly to the Ca content due to lime treatments (Ca oxide or hydroxide) to raise their pH and reduce pathogen levels (Obreza & O'Connor et al., 2003; Smith et al., 1998). Statistical analysis revealed a significant difference in Ca levels depending on the rate of biosolids application ($p < 0.001$) (Fig. 3B), indicating that past biosolids applications have contributed to the increased Ca content in the soil. This suggests that the Ca levels are due to past biosolids applications (Brown et al., 1997).

3.5. Soil pH levels

The soils at the study site are naturally acidic. Although lime-stabilized biosolids can temporarily increase soil pH levels, the pH of the top 15 cm at the study site ranged from 4.73 to 7.33, with a mean of 6.13, indicating that the soil remains slightly acidic (Table 3). Studies, such as those by Dickens et al. (2020), have shown a slight increase in soil pH even 10 years after biosolids application. While the application of biosolids may have initially raised soil pH, it has since returned to slightly acidic levels. This is due to the high rainfall and warm, humid climate of the area, combined with the considerable time elapsed since biosolids were last applied. However, since there were no pH measurements taken before the biosolids treatments, it is possible that the current pH is slightly higher than it was prior to the applications. According to the Soil Web Survey, the soils in this area typically have a pH range of about 5.1 to 5.5, indicating that the current pH levels are now slightly above this typical range (Table 3).

3.6. Loss on ignition and organic matter content of soil samples

The loss on ignition analysis revealed that the organic matter content in the top 15 cm of soil ranged from 2.4% to 8.7%, with an average of 5.17%. There was no significant difference in organic matter content across different biosolids application rates in the various fields. This suggests that any initial differences in organic matter due to biosolids application rates may have diminished in the top 15 cm over the 14-year period since the last application. In comparison, the six control samples taken from wooded areas outside the fields had an average organic matter content of 5.55%. Although this value is not significantly higher, the presence of observable pine needles in the samples before ashing—too small to remove due to fragmentation—might have contributed to the content of organic matter.

3.7. Mass-specific magnetic susceptibility analysis

Mass-specific magnetic susceptibility values ranged from -2.660 × 10^{-9} m^3 kg^{-1} to 11.4 × 10^{-9} m^3 kg^{-1}, with a median of -0.4 × 10^{-9} m^3 kg^{-1} and a mean of 0.129 × 10^{-9} m^3 kg^{-1}. The negative susceptibility is primarily attributed to diamagnetic content of quartz which is the dominant constituent of the soil. The low magnetic susceptibility values indicate that the soils have very low concentrations of ferrimagnetic minerals (e.g. magnetite, titanomagnetite, maghemite) and/or are dominated by paramagnetic phases (e.g. ilmenite). Further analysis is required to determine the exact nature of the magnetic mineral carriers in these samples, however, the correlation coefficient with Ti ($r = 0.15$) and Zr is relatively low ($r = 0.21$) suggesting that geological sources are likely not the dominant driver of MS.

Magnetic susceptibility has been employed as a proxy to detect heavy metal pollution in soils (Morton-Bermea et al., 2009). However, in the soil samples from the study site, heavy metal and Fe concentrations were generally low, with many measurements falling below the limit of detection. This limited the strength of the correlations between magnetic susceptibility and heavy metals, although some significant relationships were still observed for certain metals. Pearson's moment correlation coefficient was conducted to explore the relationships between various elements, including heavy metals to magnetic susceptibility (Table 4). Of these the elements that had a significant p value ($p < 0.05$) were Fe, P, Al, Ca, Cu, Zn, and Ti (Table 4).

Phosphorus, despite being diamagnetic, can adsorb onto or precipitate as inorganic phosphates associated with Al and Fe oxides (Achat et al., 2016). This association with Fe oxides suggests that magnetic susceptibility measurements could potentially serve as a proxy for P in soil (Poggere et al., 2020; Jordanova, 2016).

3.8. Pearson correlation analysis of soil enrichment from previous biosolids applications

Correlation analysis revealed significant positive relationships between P and several soil variables, including pH, Ca, Al, Cu, Zn, and magnetic susceptibility ($p < 0.01$ for all). These results indicate that P enrichment in biosolid-treated soils is closely linked to other soil characteristics, highlighting complex interactions that affect P availability and mobility. Notably, the strong positive correlation between P and Ca ($r = 0.66$, $n = 192$, $R^2 = 0.45$, $p < 0.001$) suggests that Ca may play a role in regulating P availability, potentially through the formation of calcium-phosphate complexes (Fig. 4A). This relationship underscores the persistent high levels of both P and Ca in the soil, which reflect the long-term impact of biosolids applications on soil chemistry.

In addition, a significant positive correlation was observed between P and soil pH ($r = 0.64$, $R^2 = 0.41$, $p < 0.001$) (Fig. 4B), indicating that higher P concentrations are associated with increased soil pH. This is most likely due to the liming effect of biosolids, which can raise soil pH and further influence P dynamics. Similarly, Ca and pH also exhibited a strong positive relationship ($r = 0.65$, $R^2 = 0.42$, $p < 0.001$), further confirming the influence of biosolids on soil alkalinity. Finally, P was positively correlated with magnetic susceptibility ($r = 0.55$, $R^2 = 0.31$, $p < 0.001$) (Fig. 4C), even in soils with low iron (Fe) concentrations, suggesting that magnetic susceptibility could serve as a useful proxy for P in biosolid-affected soils.

3.9. Vertical movement of biosolids-derived materials

The distribution of organic matter, P, Ca, Al, and magnetic susceptibility was assessed in three core samples—two from field 7 and one from field 8—and three control cores (Fig. 5A-E). Four cores extended to a depth of 150 cm, while one core from field 8 reached 84 cm and one control core extended to 92 cm. The fields previously treated with biosolids showed slightly higher organic matter content and significantly elevated concentrations of P and Ca in the top 15 cm compared to the control cores (Fig. 5A-C). This was followed by a decrease of all three in the E horizons, with levels of organic matter, P, and Ca rising again in the B horizons. In contrast, the control cores exhibited declines in the E horizons with no subsequent increases in the B horizons. The higher organic matter content observed in the B horizons of the biosolids-treated fields likely reflects the accumulation from previous biosolids applications. The distinct distribution patterns of P and Ca in the biosolids-treated cores highlight the influence of biosolids applications within the soil profile. Previous studies have demonstrated that in lime-treated biosolids, P tends to associate more with Ca than with Fe and Al (Penn & Sims et al., 2002). This suggests that P and organic matter could be vertically transported along with Ca oxides and hydroxides, as well as Fe and Al.

Figures 5D and 5E show depth-related trends in Al concentrations and magnetic susceptibility, respectively. Al concentrations increased consistently in subsoil horizons of both control and biosolids-treated cores between 40 to 100 cm, corresponding to the Bh horizons of spodosols. The ubiquitous accumulation of Al in subsoils suggests that the Al primarily originates from natural soil processes rather than the addition of biosolids. Similarly, magnetic susceptibility followed a typical spodosol profile, with higher values in the A horizon, a decrease in the E horizon, and a subsequent rise in the Bh horizons, reflecting the accumulation of Fe in these deeper layers (Fig. 5E). Due to their high P sorption capacity, the accumulation of Al and Fe minerals helped to retain the P and Ca derived from biosolids in Bh horizons. These findings indicate that while biosolids have influenced the distribution of elements like P and Ca, the natural properties of spodosols continue to play a significant role in shaping the soil composition at depth.

4. Environmental Implications

This study provides important insights into the environmental impacts of historical biosolid applications on soils, particularly in areas with sandy soils. Analysis showed that historical biosolids applications have not led to harmful heavy metal accumulation, likely due to regulatory controls and natural attenuation. The absence of significant heavy metal accumulation in subsoil horizons further supports this conclusion. While the heavy metal concentrations in biosolid-treated soils remained well below recommended regulatory thresholds, indicating minimal long-term contamination, P levels tell a different story.

The significantly higher P concentrations in the biosolids-amended soil 14 years post-application is approximately double those of untreated soil samples, highlighting the persistence of P in the environment. These elevated P levels pose potential risks for eutrophication in connected water bodies, emphasizing the need for monitoring and management to mitigate environmental impacts such as harmful algal blooms. The findings align with previous studies documenting long-term alterations in soil composition following biosolids applications (Avery et al., 2018; Ippolito et al., 2010; Dickens et al., 2020).

Potential indicators of past biosolids applications were identified, including changes in soil pH and magnetic susceptibility. While soils remained slightly acidic, mean pH levels were slightly elevated, possibly due to lime-stabilized biosolids. Magnetic susceptibility, despite low Fe concentrations, correlated significantly with P, suggesting it could serve as a proxy for detecting biosolids impact and assessing long-term soil changes.

The primary markers of previous biosolids applications were elevated levels of P and Ca. Vertical movement of biosolids-derived materials revealed higher P and Ca concentrations in the top 15 cm of biosolid-treated soils with distinct patterns across different horizons. These findings indicate the potential for vertical transport of biosolids-derived materials, which may influence deeper soil layers and groundwater quality.

Overall, while biosolids can enhance soil fertility in agricultural contexts, they may pose risks to sensitive ecosystems, such as areas transitioning to conservation or wetland restoration where elevated P can degrade water quality. Therefore, understanding the residual impacts of biosolids is critical for informed land management and environmental protection.

5. Conclusion

This study demonstrated that historical biosolids applications at a ranch in Seminole County, Florida, have not led to significant heavy metal contamination but have resulted in persistent phosphorus enrichment of the soil, posing potential environmental risks. The vertical movement of biosolid-derived phosphorus and Ca was also evident in soil profiles. The results underscore the importance of monitoring and managing legacy phosphorus in soils to prevent negative ecological impacts, particularly in regions vulnerable to nutrient pollution.

Acknowledgments

This work was supported by the St. Johns River Water Management District, the USDA National Needs Fellowship Grant 2021-38420-34936, and USDA Hatch Grant SWS-006103. We extend our gratitude to Angelique Bochnak for her invaluable assistance with the XRF analysis. Additional thanks to Swarnali Mahmood and Me’Keila Lightfoot for their contributions to laboratory work. We also appreciate the Whitney Laboratory for Marine Biosciences for providing access to the soil samples utilized in this study.

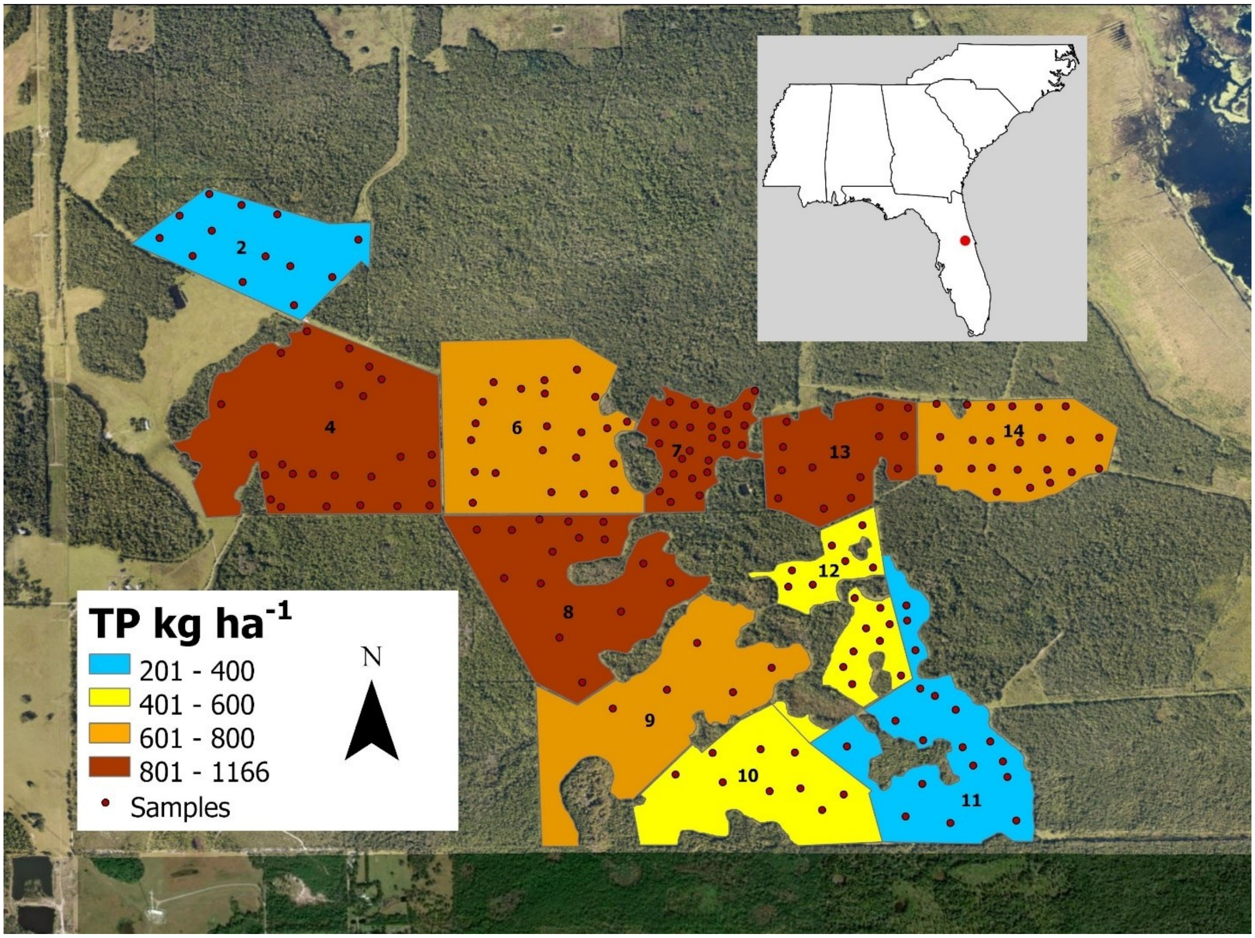

Fig. 1. Map of the study site in Seminole County Fl, showing the rate of total phosphorus applied as biosolids in kg ha^{-1} for different fields and location of samples taken.

Table 1. Descriptive statistics for XRF elemental analysis in the top 15 cm of historical biosolids amended soil samples and samples from control sites.

Historical biosolids amended soil samples, top 15 cm

Element	Min	1st Qu.	Median	Mean	3rd Qu.	Max	n =
Al	311	4,254	6,557	7818	10,090	32,833	186
P	471	891	1,096	1180	1,364	3,504	186
S	889	2,555	3,250	3462	4013	13,280	186
K	4	119	239	290	388	4,107	162
Ca	3,999	11,933	15,989	18,432	22,656	55,804	186
Ti	368	1,022	1,340	1485	1,825	4,048	186
V	0	12	23	26	35	92	170
Cr	0	2	5	6.6	8	22	14
Mn	0	6	12	14.8	21	54	89
Fe	309	497	926	1764	2,385	6,783	9
Ni	0	6	16	19.8	25	101	61
Cu	0	14	27	28.4	39	91	176
Zn	0	7	16	17.4	23	58	133
Zr	51	115	157	180	233	440	186
Mo	0	5	10	10.4	15	24	108
Pb	0	7	11	11	15	29	178

Control site soil samples, top 15 cm

Element	Min	1st Qu.	Median	Mean	3rd Qu.	Max	n =
Al	2500	3491	6274	7632	8468	18,981	6
P	462	481	520.5	551	568	748	6
S	473	836	2695	3337	3891	9654	6
K	26	221	471	670	562	2218	5
Ca	504	1192	3714	5988	10,785	14,498	6
Ti	676	848	927	2145	3436	5248	6
V	2	4	11	42	75	129	6
Cr	ND	ND	ND	ND	ND	ND	0
Mn	42	42	42	42	42	42	1
Fe	ND	ND	ND	ND	ND	ND	0
Ni	20	20	20	20	20	20	1
Cu	10	10	38	41	69	79	4
Zn	5	8	11	11	13	16	2
Zr	103	114	184	222	339	379	6
Mo	7	10	13	11	13.5	14	3
Pb	7	9	11	11.4	12	18	5

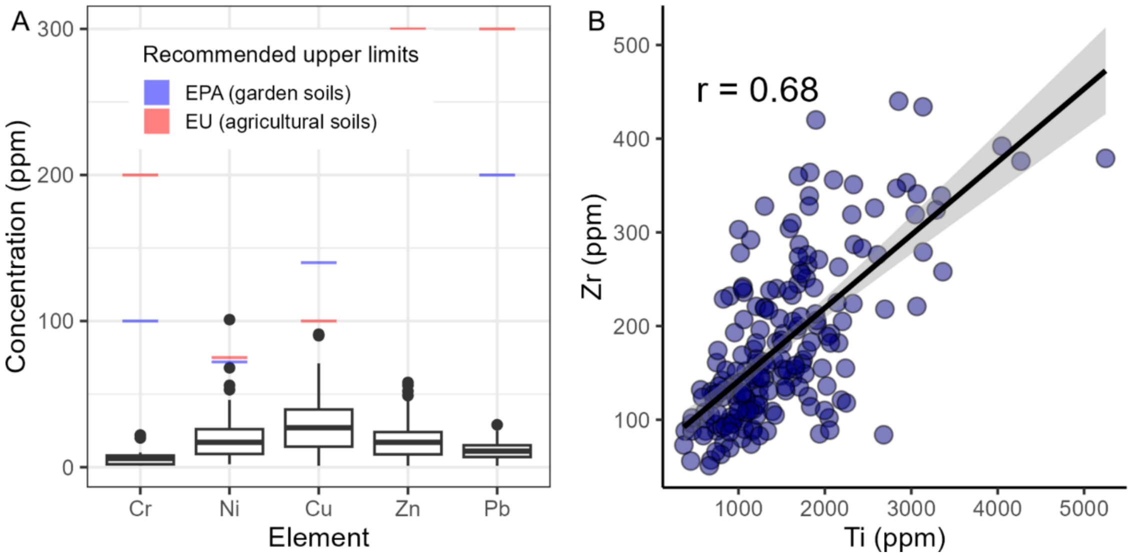

Fig. 2. (A) Heavy metals from XRF analysis in the top 15 cm of soil samples compared to the EPA (garden soils) and EU (agricultural soils) upper recommended limits. Dashed lines represent the recommended limits for safe levels. (B) Pearson correlation analysis between titanium and zirconium in top 15 cm of soil samples. There is a high correlation between titanium and zirconium, R = 0.68.

Table 2. Elemental concentrations (ppm) at depth for the 3 control samples.

Control	**Depth (cm)**	**Al**	**P**	**Ca**	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**Mo**	**Pb**
1	0-14	6805	462	504	ND	ND	ND	10	ND	ND	18
1	14-37	273	405	65	ND	ND	ND	4	ND	10	6
1	37-62	5367	426	54	ND	ND	ND	ND	ND	18	2
1	62-100	19591	410	491	ND	ND	ND	1	ND	ND	ND
1	100-120	51632	416	1075	ND	620	ND	ND	ND	4	6
1	120-200	57041	411	1263	ND	52	1	8	ND	ND	10
Control	**Depth (cm)**	**Al**	**P**	**Ca**	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**Mo**	**Pb**
2	0-8	9023	605	12971	ND	ND	ND	ND	ND	ND	11
2	8-15	9289	551	3473	ND	ND	ND	ND	ND	17	2
2	15-40	35030	738	8559	ND	ND	ND	ND	ND	ND	6
2	40-56	14163	443	1856	ND	ND	ND	ND	ND	ND	6
2	56-92	48128	429	1079	ND	1234	28	ND	2	1	8
Control	**Depth (cm)**	**Al**	**P**	**Ca**	**Cr**	**Fe**	**Ni**	**Cu**	**Zn**	**Mo**	**Pb**
3	0-10	5742	474	523	ND	ND	ND	ND	ND	ND	7
3	10-30	855	414	91	ND	ND	60	2	ND	17	16
3	30-50	1592	407	10	4	ND	ND	ND	ND	8	16
3	50-70	10403	400	113	ND	ND	ND	8	ND	ND	22
3	70-90	47115	427	1134	ND	3889	ND	ND	ND	8	7
3	90-110	83139	430	1808	7	3864	ND	ND	ND	ND	14
3	110-130	63853	437	1903	ND	2942	ND	ND	ND	ND	19
3	130-150	41887	424	1080	2	758	34	ND	ND	20	7

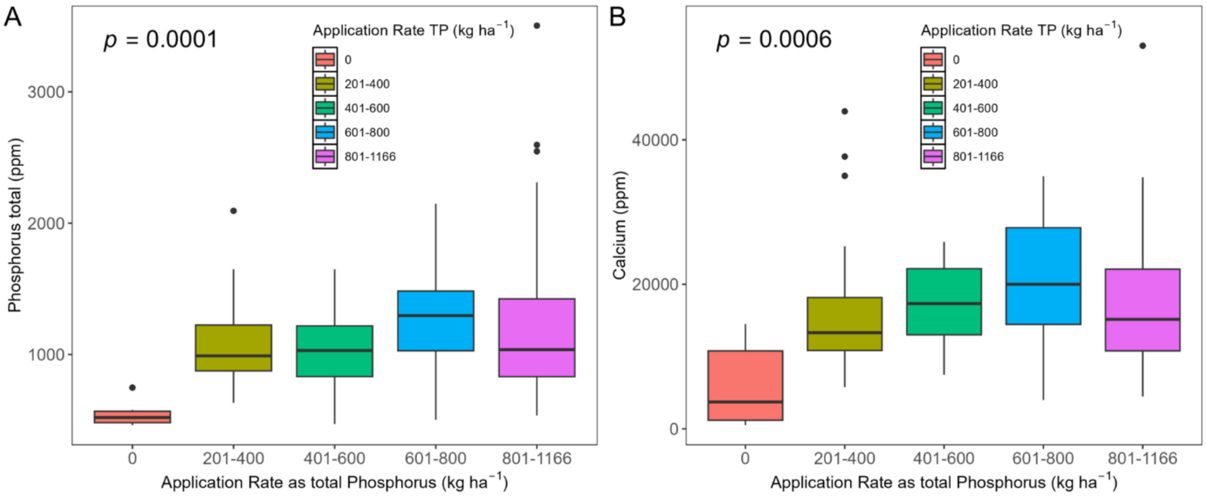

Fig. 3. (A) Phosphorus (ppm) compared to the different biosolids application rates and the control samples with a highly significant p value = 0.0001. (B) Calcium (ppm) compared to the different biosolids application rates and the control samples with a highly significant p value = 0.0006. (Application rates: 0, n=6; 201-400, n=32; 401-600, n=25; 601-800, n=55; 801-1166, n=74)

Table 3. Summary statistics for pH levels of top 15 cm of soil samples.

Field	**Min pH**	**1st Qu pH**	**Median pH**	**Mean pH**	**3rd Qu pH**	**Max pH**
2	5.48	6.09	6.48	6.35	6.66	7.13
4	4.73	5.58	6.09	6.19	7.03	7.33
6	5.15	5.59	5.92	5.93	6.26	6.83
7	5.09	5.53	5.69	5.78	5.91	7.16
8	4.92	5.28	5.90	5.65	5.99	6.38
9	5.22	5.82	5.84	6.11	6.69	6.99
10	5.34	5.67	5.82	5.94	6.06	7.02
11	5.42	5.96	6.13	6.14	6.31	6.71
12	5.50	5.85	5.96	5.96	6.06	6.72
13	5.40	6.13	6.67	6.45	6.76	7.15
14	5.25	6.67	7.01	6.84	7.14	7.24

Table 4. Pearson coefficients and p values between MS and elements

Element	**Pearson Coefficient with Magnetic Susceptibility (MS)**	**P-value**
Fe	0.68	**0.045**
P	0.55	**<0.001**
Al	0.33	**<0.001**
Ca	0.24	**<0.001**
Cu	0.24	**0.001**
Zn	0.22	**0.009**
Zr	0.21	**0.003**
Ti	0.15	**0.041**
Ni	-0.01	0.915
Pb	-0.04	0.587
Cr	-0.19	0.513

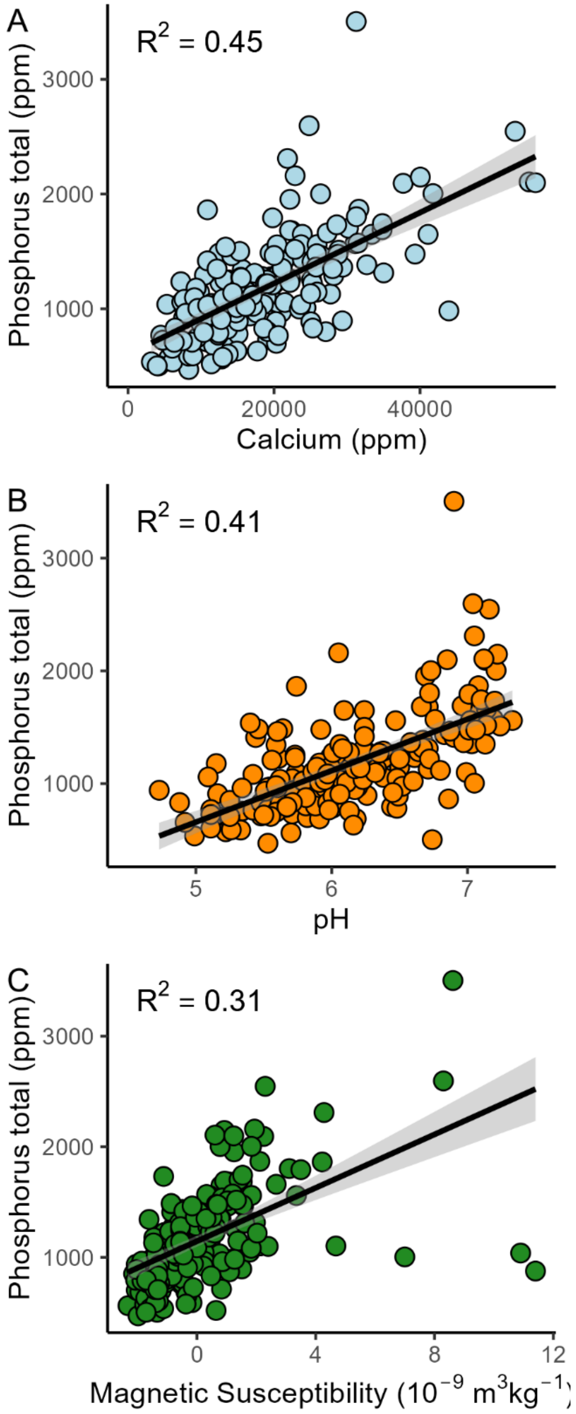

Fig. 4. Positive linear relationship between (A) calcium and phosphorus ($r = 0.66$, $p < 0.001$), (B) pH and phosphorus ($r = 0.64$, $p < 0.001$), (C) magnetic susceptibility and phosphorus ($r = 0.55$, $p < 0.0001$). $n = 186$

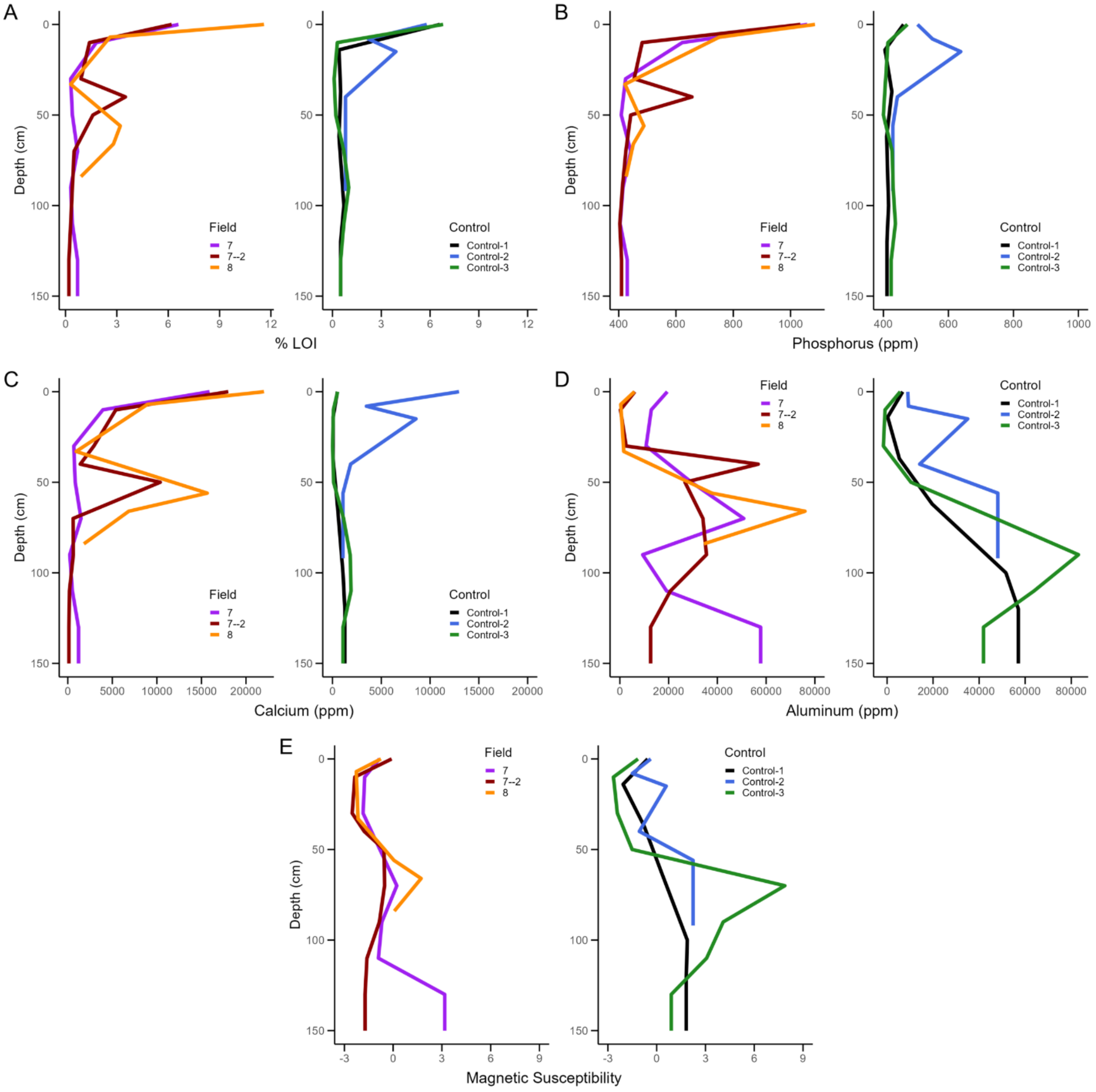

Fig. 5. Core comparisons to a depth of 150 cm for cores from three biosolids fields and three control sites of (A) organic matter % from loss on ignition, (B) phosphorus (ppm), (C) calcium (ppm), (D) aluminum (ppm), (E) mass-specific magnetic susceptibility (10^{-9} m^3 kg^{-1}).

References

Achat, D. L., Pousse, N., Nicolas, M., Brédoire, F., & Augusto, L. (2016). Soil properties controlling inorganic phosphorus availability: general results from a national forest network and a global compilation of the literature. *Biogeochemistry, 127*, 255-272.

Avery, E., Krzic, M., Wallace, B., Newman, R. F., Smukler, S., & Bradfield, G. (2018). One-time application of biosolids to ungrazed semiarid rangelands: 14 yr soil responses. *Canadian Journal of Soil Science, 98*(4), 696-708.

Brown, S., Ippolito, J. A., Hundal, L. S., & Basta, N. T. (2020). Municipal biosolids—A resource for sustainable communities. *Current Opinion in Environmental Science & Health*, *14*, 56-62.

Brown, S., Chaney, R., & Angle, J. S. (1997). Subsurface liming and metal movement in soils amended with lime-stabilized biosolids (Vol. 26, No. 3, pp. 724-732). American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America.

Canion, A., V. Hoge, J. Hendrickson, T. Jobes, and D. Dobberfuhl. (2022). Trends in phosphorus fluxes are driven by intensification of biosolids applications in the Upper St. Johns River Basin (Florida, United States). Lake and Reservoir Management 38:215–227.

Chislock, M. F., Doster, E., Zitomer, R. A. & Wilson, A. E. (2013) Eutrophication: Causes, Consequences, and Controls in Aquatic Ecosystems. Nature Education Knowledge 4(4):10

Dearing, J. A. (1994). *Environmental magnetic susceptibility: using the Bartington MS2 system*. Chi Pub.

Dickens, E. D., Clabo, D., & Moorhead, D. J. (2020). Effect of lime stabilized biosolids and inorganic fertilizer applications on soil and foliar nutrient status, growth, pine straw production, and economics in a thinned longleaf pine stand–ten-year results. WSFNR-20-33A. University of Georgia Warnell School of Forestry and Natural Resources, Athens, GA.

Ene, A., Bosneaga, A., & Georgescu, L. (2010). Determination of heavy metals in soils using XRF technique. *Romanian Journal of Physics, 55*(7-8), 815-820.

EPA (Environmental Protection Agency). (2023, January 18). Basic information about biosolids. Retrieved from https://www.epa.gov/biosolids/basic-information-about-biosolids#basics

EPA Office of Inspector General. (2018, November 15). EPA unable to assess the impact of hundreds of unregulated pollutants in land-applied biosolids on human health and the environment. Report No. 19-P-0002. Retrieved from https://www.epa.gov/sites/default/files/2018-11/documents/_epaoig_20181115-19-p-0002.pdf

Evans, M., & Heller, F. (2003). *Environmental magnetism: principles and applications of enviromagnetics* (Vol. 86). Academic Press.

Florida DEP (Florida Department of Environmental Protection). (2023, August 16). Heavy minerals. *Florida Department of Environmental Protection*. Retrieved from https://floridadep.gov/water/mining-mitigation/content/heavy-minerals

Florida DEP (Florida Department of Environmental Protection). (2022, April 20). Domestic wastewater biosolids. Retrieved from https://floridadep.gov/water/domestic-wastewater/content/domestic-wastewater-biosolids

Frick, T. (2019, June). Biosolids in Florida. [PowerPoint slides] Division of Environmental Assessment and Restoration. Retrieved from https://www.florida-stormwater.org/assets/MemberServices/Conference/AC19/02%20-%20Frick%20Tom.pdf

Gianico, A., Braguglia, C. M., Gallipoli, A., Montecchio, D., & Mininni, G. (2021). Land application of biosolids in Europe: possibilities, constraints, and future perspectives. *Water, 13*(1), 103.

Haygarth, P. M., Jarvie, H. P., Powers, S. M., Sharpley, A. N., Elser, J. J., Shen, J., ... & Liu, X. (2014). Sustainable phosphorus management and the need for a long-term perspective: The legacy hypothesis.

Ippolito, J. A., & Barbarick, K. A. (2022). The Clean Water Act and biosolids: A 45-year chronological review of biosolids land application research in Colorado. *Journal of Environmental Quality, 51*(5), 780-796.

Ippolito, J. A., Barbarick, K. A., Paschke, M. W., & Brobst, R. B. (2010). Infrequent composted biosolids applications affect semi-arid grassland soils and vegetation. *Journal of Environmental Management, 91*(5), 1123-1130. doi:10.1016/j.jenvman.2010.01.00

Jordanova, N., Mokreva, A., Jordanova, D., Tcherkezova, E., & Stoyanova, V. (2024). Mineral magnetic properties of urban forest soils tailored to soil quality indicator. *Catena*, *234*, 107569.

Jordanova, N. (2016). *Soil magnetism: Applications in pedology, environmental science and agriculture*. Academic press.

Kinuthia, G. K., Ngure, V., Beti, D., Lugalia, R., Wangila, A., & Kamau, L. (2020). Levels of heavy metals in wastewater and soil samples from open drainage channels in Nairobi, Kenya: community health implication. *Scientific Reports, 10*(1), 8434.

Liang, H., Wang, C., Lu, X., Sai, C., & Liang, Y. (2022). Dynamic changes in soil phosphorus accumulation and bioavailability in phosphorus-contaminated protected fields. *International Journal of Environmental Research and Public Health*, *19*(19), 12262.

Lu, Q., He, Z. L., & Stoffella, P. J. (2012). Land application of biosolids in the USA: a review. *Applied and Environmental Soil Science, 2012*.

Lyu, S., Wei, X., Chen, J., Wang, C., Wang, X., & Pan, D. (2017). Titanium as a beneficial element for crop production. *Frontiers in Plant Science, 8*, 237149.

MacNeil, F. (1949). Pleistocene shore lines in Florida and Georgia: US Geol. Survey Prof. Paper, 221.

Marchuk, S., Tait, S., Sinha, P., Harris, P., Antille, D. L., & McCabe, B. K. (2023). Biosolids-derived fertilizers: A review of challenges and opportunities. *Science of The Total Environment, 162555.*

Martin, S., & Griswold, W. (2009). Human health effects of heavy metals. *Environmental Science and Technology briefs for citizens, 15*(5).

McBride, M. B. (2022). Long-Term Biosolids Application on Land: Beneficial Recycling of Nutrients or Eutrophication of Agroecosystems?. *Soil Systems*, *6*(1), 9.

McKeague, J. A., DeConinck, F., & Franzmeier, D. P. (1983). Spodosols. In *Developments in Soil Science* (Vol. 11, pp. 217-252). Elsevier.

McLaughlin, M. J., Hamon, R. E., McLaren, R. G., Speir, T. W., & Rogers, S. L. (2000). A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Soil Research, 38*, 1037–1086.

Morton-Bermea, O., Hernandez, E., Martinez-Pichardo, E., Soler-Arechalde, A. M., Santa-Cruz, R. L., Gonzalez-Hernandez, G., ... & Urrutia-Fucugauchi, J. (2009). Mexico City topsoils: Heavy metals vs. magnetic susceptibility. *Geoderma*, *151*(3-4), 121-125.

Murphy, J., & Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta, 27, 31–36. https://doi.org/10.1016/S0003-2670(00)88444-5

Obreza, T. A., & O'Connor, G. A. (2003). The basics of biosolids application to land in Florida. University of Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, EDIS.

Paradelo, R., Moldes, A. B., Barral, M. T., & Moldes, A. B. (2009). Magnetic susceptibility as an indicator of heavy metal contamination in compost. *Waste Management & Research, 27*(1), 46-51.

Penn, C. J., & Sims, J. T. (2002). Phosphorus forms in biosolids-amended soils and losses in runoff: Effects of wastewater treatment process. *Journal of Environmental Quality*, 31(4), 1349-1361.

Pi, H., Sharratt, B., Schillinger, W. F., Bary, A. I., & Cogger, C. G. (2018). Wind erosion potential of a winter wheat–summer fallow rotation after land application of biosolids. *Aeolian research*, *32*, 53-59.

Poggere, G. C., Barrón, V., Inda, A. V., Barbosa, J. Z., Brito, A. D. B., & Curi, N. (2020). Linking phosphorus sorption and magnetic susceptibility in clays and tropical soils. *Soil Research, 58*(5), 430-440.

Posit Team. (2024). *RStudio: Integrated Development Environment for R* (Version 2024.4.1.748) [Computer software]. Posit Software, PBC. http://www.posit.co/

Saunders, W. M. H., & Williams, E. G. (1955). Observations on the determination of total organic phosphorus in soils. *Journal of Soil Science, 6*(2), 254-267.

Scott, T. (1993). Geologic map of Seminole County, Florida (FGS: Open file map series 43) [Map]. Tallahassee, FL: Florida Geological Survey. Retrieved from http://ufdc.ufl.edu/UF00094364/00001

Sharma, B., Sarkar, A., Singh, P., & Singh, R. P. (2017). Agricultural utilization of biosolids: A review on potential effects on soil and plant grown. *Waste Management (New York, N.Y.), 64*, 117–132.

Sharpley, A. N., Chapra, S. C., Wedepohl, R., Sims, J. T., Daniel, T. C., & Reddy, K. R. (1994). Managing agricultural phosphorus for protection of surface waters: Issues and options. *Journal of environmental quality*, *23*(3), 437-451.

Silveira, M. L., O'Connor, G. A., & Vendramini, J. M. B. (2017). Utilization of biosolids in forage production systems in Florida. *EDIS, 2017*(2), 4. https://doi.org/10.32473/edis-ss658-2017

Smith, K. A., Goins, L. E., & Logan, T. J. (1998). Effect of calcium oxide dose on thermal reactions, lime speciation, and physical properties of alkaline stabilized biosolids. *Water Environment Research, 70*(2), 224-230.

Soil Survey Staff. (n.d.). Web Soil Survey [dataset]. online.

Zhidkova, A. Y., Podberesnij, V. V., Zarubina, R. V., & Kononova, O. A. (2020). The effect of eutrophication on human health on the example of the Gulf of Taganrog of the Sea of Azov. In *IOP Conference Series: Earth and Environmental Science* (Vol. 548, No. 5, p. 052053). IOP Publishing.