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Metal and nanoparticle occurrence in biosolid-amended soils



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HIGHLIGHTS

- Biosolid land application increased the unregulated metal contents in surface soil.
- Metals (e.g., Ag) associated with ENMs show accumulation and low mobility in soils.
- Titanium-containing nanoparticle (50 nm in diameter) was identified in the soils.

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ABSTRACT

Metals can accumulate in soils amended with biosolids in which metals have been concentrated during wastewater treatment. The goal of this study is to inspect agricultural sites with long-term biosolid application for a suite of regulated and unregulated metals, including some potentially present as commonly used engineered nanomaterials (ENMs). Sampling occurred in fields at a municipal and a privately operated biosolid recycling facilities in Texas. Depth profiles of various metals were developed for control soils without biosolid amendment and soils with different rates of biosolid application (6.6 to 74 dry tons per hectare per year) over 5 to 25 years. Regulated metals of known toxicity, including chromium, copper, cadmium, lead, and zinc, had higher concentrations in the upper layer of biosolid-amended soils (top 0–30 cm or 0–15 cm) than in control soils. The depth profiles of unregulated metals (antimony, hafnium, molybdenum, niobium, gold, silver, tantalum, tin, tungsten, and zirconium) indicate higher concentrations in the 0–30 cm soil increment than in the 70–100 cm soil increment, indicating low vertical mobility after entering the soils. Titanium-containing particles between 50 nm and 250 nm in diameter were identified in soil by transmission electron microscopy (TEM) coupled with energy dispersive x-ray spectroscopy (EDX) analysis. In conjunction with other studies, this research shows the potential for nanomaterials used in society that enter the sewer system to be removed at municipal biological wastewater treatment plants and accumulate in agricultural fields. The metal concentrations observed herein could be used as representative exposure levels for eco-toxicological studies in these soils.

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1. Introduction

Roughly 40% of the 7 million dry tons of biosolids (i.e., sewage sludge) produced each year are land applied as supplemental fertilizer or landfill cover in United States (U.S. EPA, 1999). The long-term land application of biosolids has led to concerns about the potential accumulation and ecotoxicity of metals in biosolid-amended soils (Illera et al., 2000; Sloan et al., 1997). The land application of biosolids is currently subject to several metal concentration limits according to the U.S. EPA Part 503 Biosolids Rule, including those for arsenic (As), cadmium

(Cd), copper (Cu), lead (Pb), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (Se), and zinc (Zn) (U.S. EPA, 1995). However, despite their widespread use in industry, less information exists on classically unregulated metals (e.g., minor metals, MMs) or rare earth elements (REEs), and metals associated with nanomaterials (Chang et al., 1984; Graedel and Van Der Voet, 2010; Han et al., 2000; Jorg et al., 1999; Tourinho et al., 2012). Engineered nanomaterials (ENMs) that are discharged to sewers and accumulate in biosolids could eventually end up in soils amended with those biosolids (de la Rosa et al., 2011; Judy et al., 2012; Kim et al., 2012). Concerns about ENMs include soil eco-toxicological risks to soil microbial and invertebrate communities, soil runoff, and uptake of nano- and micron-scale metals and metal oxides by plants (de la Rosa et al., 2011; Ge et al., 2011; Judy et al.,

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2012), the consumption of which leads to possible accumulation in other organisms. This paper explores the presence of a wide range of metals in biosolid-amended soils and prospects for nano- to micron-sized metal materials, potentially of an engineered origin, to be transferred to the soils via wastewater biosolids.

Diverse sources of nanomaterials may lead to ENM accumulation in biosolid-amended soils. Nanosilver and copper in products can be released or sorbed to wastewater biomass (Benn and Westerhoff, 2008; Glover et al., 2011). The estimated concentrations in sludge-treated soils of nano-TiO₂ and nano-silver are 42 µg/kg and 662 ng/kg per year, respectively (Gottschalk et al., 2009). Ecological concerns increase due to the antimicrobial/toxic effects of nano-silver and TiO₂ (Choi et al., 2010; Yang et al., 2012a,b), which could inhibit a wide range of microorganisms in the soil environment (Ge et al., 2011; U.S. EPA, 2010; Yang et al., 2013). Determination of the presence of nano-scale metals expected to occur in soils after biosolid application is critical to closing the mass balance of materials from largely anthropogenic sources.

Many factors, including sludge resources, application rate, pH and other soil properties, organic matter content, and redox potential, affect the accumulation of regulated metals in biosolid-amended soils (Hue and Ranjith, 1994; Singh and Agrawal, 2008; Smith, 2009). However, information on MMs, REEs and/or platinum group elements (PGEs), and ENMs in soils is limited (Gottschalk et al., 2009; Kim et al., 2012; Nowack and Bucheli, 2007). For example, experiments with ENMs demonstrated the presence of TiO₂ nanoparticles in biosolids only recently (Kim et al., 2012). Therefore, this study aims to address the following objective-directed questions: (1) what is the extent of metal accumulation in biosolid-amended soils; (2) what are the depth migration patterns of these metals; and (3) do some of the metals manifest as ENMs? To answer these questions, we tested soil samples from two large-scale field sites where biosolids have been applied at different rates and for different periods of time. The samples were processed via a microwave-assisted acid digestion, after which the metal concentration was determined by inductively coupled plasma-mass spectrometry (ICP-MS). The concentrations of regulated, trace, and precious metals were investigated. Transmission electron microscopy (TEM) equipped with energy dispersive x-ray spectroscopy (EDX) was employed to determine the presence of and characterize any metallic ENMs in undigested samples.

2. Methodology

2.1. Study areas and sample collection

The biosolid-amended soils evaluated in this study were collected at two biosolid land application sites in Texas with permission (Fig. S1).

Site 1 is a 486 hectare (ha), municipally operated biosolid recycling facility in Travis County (Jin et al., 2011). Site 2 is a 243 ha, privately operated biosolid recycling facility in Bell County. Both sites are maintained as continuous, no-tillage forage production systems consisting of coastal Bermuda grass (*Cynodon dactylon* L.). Forage is harvested three to five times per season depending on rainfall and resultant biomass production. No topsoil is removed during harvest at either site. Biosolids were applied to fields of varying size for a total life-time application area of 220 ha at site 1 and 149 ha at site 2 at the time of sampling, respectively (Table 1).

Site 1 soils are classified as fine-silty, mixed, superactive, thermic Cumulic Haplustolls (Bergstrom silt loams and silty clay loams). Soils are very deep (>2 m to groundwater) and well drained, with slopes generally <1% (Jin et al., 2011). The 30-year mean annual temperature at site 1 is 19.6 °C, and the 30-year mean annual precipitation is 817 mm (1981–2010, National Climate Data Center, <http://www.ncdc.noaa.gov/>). Volatile solid content for soils at site 1 ranged from 3.6% to 4.4% of total dry mass, which were determined from 48 soil samples using standard methods (APHA et al., 2005). At site 1, three subsites have received biosolids at the state-approved application rates of 25, 49, and 74 dry tons biosolids per hectare per year (dry tons/ha/y) for 8 years prior to soil sampling; these are named site 1-1, 1-2, and 1-3 in this paper for simplicity (Table 1). Hereafter, treatments are described using these rates, although only 85% to 95% of the maximum rates are applied in practice. In addition, a long-term application field (30 ac) (named site 1-4) received biosolids at a rate of 25 dry tons/ha/y for 20 years (1985–2005), followed by a reduced application rate of 6.6 dry tons/ha/y every other year in compliance with the facility's current nutrient management plan. Prior to soil sampling, only one application at this lower rate occurred in the long-term field (on year 2007). Control soil was sampled from a 12-ha field without any biosolid application, which was named site 1-control. Samples of the biosolids applied to site 1 (Class B biosolids) were obtained as a random grab sample from a biosolid stockpile on Oct 20th, 2011. This material was the untreated, belt-pressed biosolids which was being stockpiled prior to land application. The material sampled was relatively new (1–2 days old) due to the grab sample coming from the outer surface of the stockpile, the age of which varied from weeks to months depending on time of year and application schedule. Samples of the biosolids were used for metal concentration comparison among control soil, biosolid-amended soil, and biosolids. Biosolid samples from previous years were not available to evaluate metal concentrations over time. Although temporal variation in biosolid metal concentrations can occur (U.S. EPA, 1999), the biosolid grab-sample in this study provides an approximation of potential metal loading concentration for evaluating metal accumulation in biosolid-amended soils.

Table 1
Descriptions of biosolid-applied areas at sites used in this study prior to soil sampling.

Site location	Sub-site specified	Biosolid application description			
		Area applied (hectare)	History (year)	Rate (dry tons/ha/y)	Waste type
Site 1 – Travis County	Site 1-control	2	Control	0	No applications
	Site 1-1	20	2002–2009	25	Class B biosolids
	Site 1-2	36	2002–2009	49	Class B biosolids
	Site 1-3	49	2002–2009	74	Class B biosolids
	Site 1-4	^a 12	1985–2005 2007	25 6.6	Class B biosolids Class B biosolids
Site 2 – Bell County	Site 2-A31	13	2007–2010	6.6	Class B biosolids
	Site 2-I30	12	2003–2010	6.6	Class B biosolids
	Site 2-F16	6	2003–2010	6.6	Class B biosolids
	Site 2-J22	9	2000–2005	6.6	Domestic septage
	Site 2-D32	^b 13	1978–1992 1993–2010	6.6 6.6	Domestic septage Class B biosolids

^a Field was applied with 25 dry tons/ha/y (1985–2005), then 6.6 dry tons/ha/y (2007 only).

^b Field was applied with domestic septage (1978–1992), then Class B biosolids (1992–2010).

Site 2 soils are classified as a fine-silty, mixed, active, thermic Udic Calciustoll (Lewisville silty clay) and a fine-loamy, mixed, thermic Udic Calciustoll (Venus clay loam). Soils are calcareous (up to 40% carbonate by weight) and well drained, with slopes of 1–3% (USDA-NRCS, 2007). The 30-year MAT at site 2 is 18.9 °C, and the 30-year mean annual precipitation is 840 mm (1981–2010, National Climate Data Center, <http://www.ncdc.noaa.gov/>). Mean volatile solid content for soil samples at site 2 ranged from 6% to 10% of total dry mass analyzed using standard methods (APHA et al., 2005). Waste type and application histories varied, ranging from 4 to 33 years of application (Table 1). The state-approved maximum application rate for biosolids or domestic septage at site 2 was 6.6 dry tons/ha/y. In addition to forage production, site 2 also implemented rotational cattle grazing in all biosolid-applied fields following the required no-entry period of 30 days immediately post-application. Treatment fields from site 2 were historically given IDs of site 2-A31, site 2-I30, site 2-F16, site 2-J22, and site 2-D32 (Table 1). We only presented the metal concentration in site 2-D32 with the longest application time of 32 years, and in site 2-F16 with the shortest application time of 8 years, since metal concentrations in the rest of the subsites were within concentration ranges of site 2-F16 to site 2-D32. We did not obtain any control soil or biosolid samples for site 2. Thus, the metal analysis results from site 2 include only metal abundance and depth profiles.

Sampling depth intervals at site 1 generally matched the generic horizon designations (0–30 cm, 30–70 cm, and 70–100 cm). Sampling intervals at site 2 corresponded with standard soil testing intervals (0–15 cm and 15–60 cm) (Franzen and Cihacek, 1998), as the objective of sampling this site was to provide management recommendations to this private stakeholder who had historical records for nutrients using these soil depth intervals. Soil cores (6.35 cm diameter) were collected using a truck-mounted hydraulic soil-sampling rig (Giddings Machine Co., Windsor, CO, U.S.). No biosolids had been applied at any sampling location for at least 90 days prior to sampling. Along a transect spanning the center of each treatment field, paired soil cores were collected and composited by depth increment at 15 m to 50 m intervals, depending on the size of the field ($n = 4$ composited pairs per treatment for site 1, $n = 3$ composited pairs per treatment for site 2). No cores were taken within 20 m of the field edge due to possible edge effects (i.e., increased soil compaction due to higher equipment traffic). Visible biosolids and plant material were removed from the soil surface prior to sampling. At site 1, soils from biosolid-applied fields were sampled at 0–30, 30–70, and 70–100 cm depth increments in September 2009. Control soils were sampled similarly in March 2009. At site 2, soils were sampled at 0–15 and 15–60 cm depth increments in June 2010. For each paired set, soils were composited by depth, passed through 2 mm sieve, and stored in acid-washed glass jars with clear Teflon-lined screw caps. Samples were stored in the dark in a temperature-controlled sample archival room until subsampled for further chemical analysis.

2.2. Chemical analysis

To determine the metal content in soil, samples were microwave digested according to the standard method 3030 G and then analyzed by ICP-MS (APHA et al., 2005). Air-dried soil and biosolid samples of approximately 0.5 g were added to a 55 mL microwave digestion vessel separately, along with 8 mL of 70% nitric acid (ULTREX® II Ultrapure Reagent, J.T. Baker, Avantor Materials, PA, U.S.), 4 mL of hydrochloric acid (33%–36% w/w, ULTREX® II Ultrapure Reagent, J.T. Baker, Avantor Materials, PA, U.S.), and 2 mL of hydrofluoric acid (47–51% w/w, ULTREX® II Ultrapure Reagent, J.T. Baker, Avantor Materials, PA, USA). The samples in vessels were digested in a Microwave Assisted Reaction System (MARS) Express instrument (MARS 6, CEM, NC, U.S.). After cooling down to room temperature, the vessels were rinsed 3 times using a total of 20 mL of a 2% nitric acid solution into a Teflon® beaker. An aliquot of 2 mL of 30% hydrogen peroxide (BAKER ANALYZED® A.C.S.

Reagent, Avantor Materials, PA, U.S.) was added to each beaker to digest any remaining organics. The beaker was then heated on a hot plate at 180 °C until between 1 and 5 mL of solution remained. The beakers were removed from the hot plate and allowed to cool to room temperature. The beakers were rinsed 3 times with 5% nitric acid solution into a 100 mL volumetric flask before being stored for analysis. XSERIE-2 ICP-MS (Thermo Scientific, U.S.) was used for metal content analysis.

Analyzed metals include regulated metals, precious metals, and MMs as follows: antimony (Sb), As, beryllium (Be), Cd, cerium (Ce), chromium (Cr), cobalt (Co), gold (Au), hafnium (Hf), iridium (Ir), lithium (Li), Mo, niobium (Nb), platinum (Pt), palladium (Pd), rhenium (Re), rhodium (Rh), ruthenium (Ru), Se, silver (Ag), tantalum (Ta), tellurium (Te), Ti, tungsten (W), vanadium (V), zirconium (Zr), and Zn (alphabetical order). In the soil samples Ru, Rh, Pd, and V were below the detection limit (1 ppb); thus, they are not presented in the results.

2.3. Ratio of surface-to-subsurface soil metal concentrations

To show the vertical profile of all assayed metals at site 1, metal concentrations in soil samples from the 0–30 cm surface layer were normalized to those in soil samples from the deepest layer of 70–100 cm. The normalization was conducted for each soil core. In the same way, metal concentrations in soil samples from the 0–15 cm layer were normalized to those in soil samples from the 15–60 cm layer for site 2. A normalized ratio greater than one indicates a higher concentration of metals in near-surface soil relative to the deep soil layer, suggesting low potential for vertical mobility. Additionally, to obtain a more detailed vertical profile of the enrichment of each metal via biosolid application, illustrative vertical profiles were constructed for site 1 only because it contained control soil samples as base line for justifying metal accumulation by biosolid application.

2.4. Characterization of ENMs by TEM

Biosolids for site 1 and soil samples from both sites were dried and ground to powder in a mortar and pestle. An aliquot of 0.5 g of each sample was suspended in 5 mL of DI water. After sonication in a water bath for 1 h, 1 mL of slurry was diluted with 25 mL of methanol. One or two drops of this suspension were applied to a specimen stub for electron microscopy. High-resolution TEM coupled with EDX (Philips CM200 FEG TEM/STEM, U.S.) was used to characterize the nanoparticles visually and to determine their chemical composition.

2.5. Statistical analysis

Statistical analysis was conducted by the software SPSS 11.5 for Windows (SPSS Inc., Chicago, IL). The difference of metal concentrations in each soil depth between site 1 (site 1: 1-1, 1-2, 1-3, and 1-4) and site 1-control was analyzed with one-way analyses of variance (ANOVA) to test for the effects of biosolid application (i.e., biosolid-amended soil verse control soil). The difference of averaged metal concentrations in each subsite and metal concentrations in each layer of subsites (e.g., metal from 0 to 30 cm layer in site 1-1 vs. metal from 0 to 30 cm layer in site 1-2) from a different application rate/time was analyzed by one-way ANOVA as well. The normality of replicate data on metal concentrations was examined when necessary upon Shapiro–Wilk's W test by SPSS 11.5 ($p > 0.05$).

3. Results

3.1. Metal levels in biosolid-amended soil

Fig. 1 shows the concentrations of metals in soils, computed as an average overall sample at each site from multiple individual locations, based on averaging 12 samples for each subsite at site 1 (e.g., 12 samples for site 1-1) or 8 samples for each subsite at site 2 (e.g., 8 samples for site

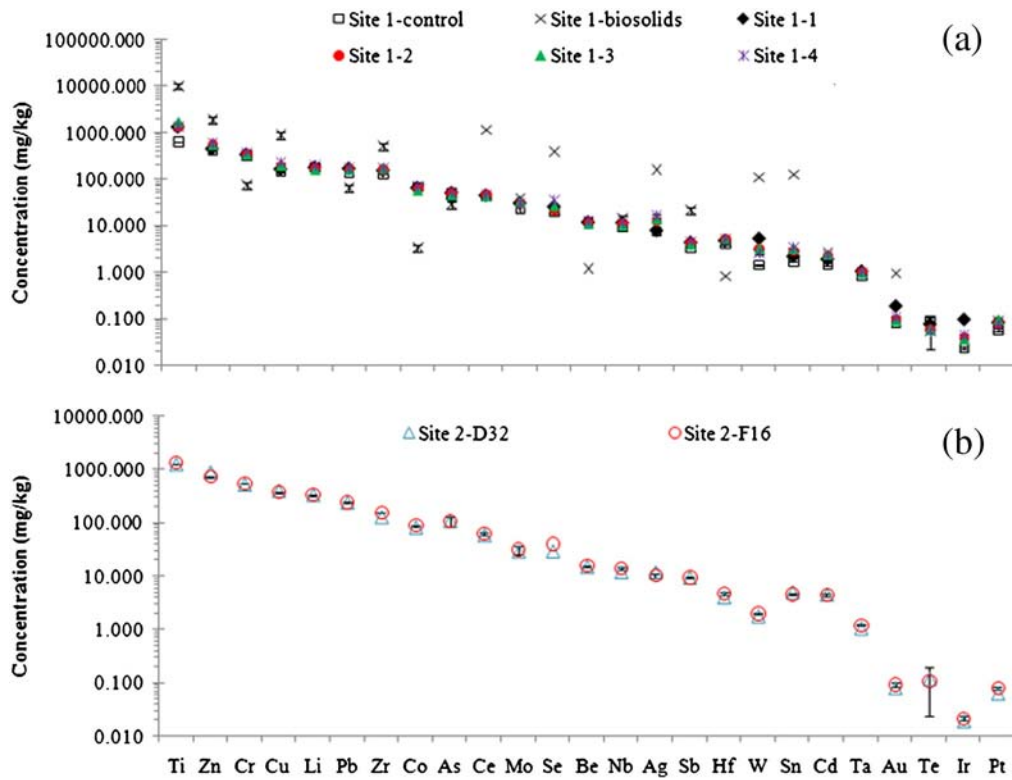


Fig. 1. The concentrations of selected metals (mg metal/kg dry soil), averaged by depth, found in soils at site 1 (a) and site 2 (b), respectively. Cr, Cu, Zn, Pb, As, Se, Mo, and Cd are currently regulated in biosolids. Error bars represent one standard deviation of 8 or 12 replicate samples.

2-D32) regardless of the depth of the soil layers. In terms of this averaged concentration of metals, the higher application rate of biosolids in site 1-3 did not lead to higher metal concentration compared to other subsites in site 1 ($p > 0.05$). At both sites, the concentrations of Au, Te, Ir, and Pt were ≤ 1 mg/kg, whereas Cr, Cu, Li, Pb, Ti, Zr, and Zn exhibited concentrations > 100 mg/kg. The other elements had intermediate concentrations between 1 and 100 mg/kg. The differences in metal concentrations among control soils, biosolid-amended soils, and

biosolids were examined for site 1. Higher concentrations of As, Be, Cr, Co, Hf, and Pb in the biosolid-amended soils than in the biosolids were indicative of accumulation. In contrast, the concentrations of Ag, Au, Cu, Ce, Se, Sb, Sn, Ti, W, Zr, and Zn were lower in the biosolid-amended soils than in the biosolids, which indicated a lower original metal concentration in biosolid-amended soils than in biosolids, given the fact that all visible biosolids were removed prior to soil sampling. However, since biosolid samples were just from one year and related metal

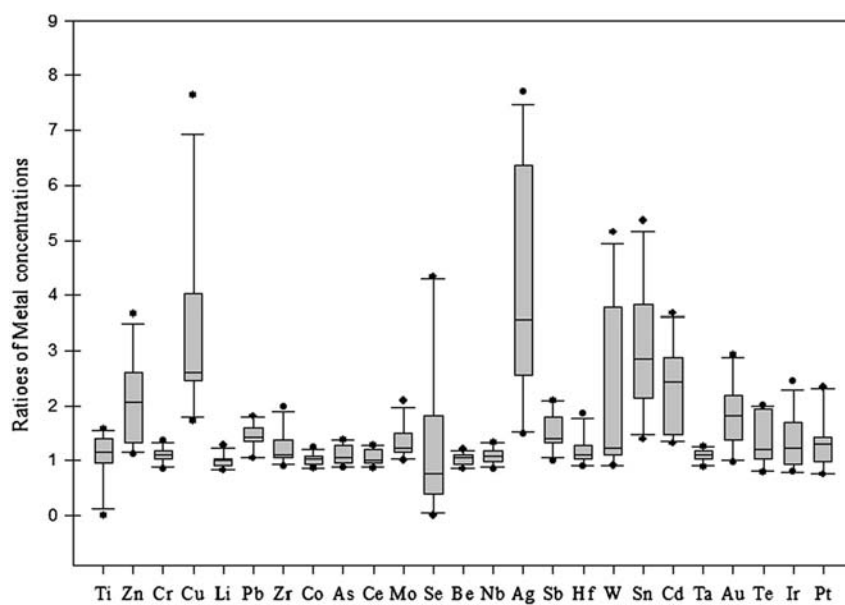


Fig. 2. Box-and-whisker plot of enrichment factors for selected metal abundance in the near-surface layer (0–30 cm for site 1 and 0–15 cm for site 2) normalized to their deepest sampling horizons (70–100 cm for site 1 and 15–60 cm for site 2). Each box describes ratios from 30 soil samples. Top and bottom of box = 75th and 25th percentiles, respectively. Top and bottom of whiskers = 90th and 10th percentiles, respectively. Line across inside of box = median (50th percentile). Points beyond whiskers = outliers.

concentration fluctuated in past years, the actual accumulation of metals would be ruled out upon comparison of metal concentrations in control soils and biosolid-amended soils.

Soil samples had a similar concentration range to each other within all the subsites of site 2 for the metals present, possibly due to the same application rate. Therefore, Fig. 1 presents metal concentrations for site 2-D32, which had the longest application time (32 years, including application of class B biosolids for only 18 years); site 2-F16, which had the shortest application time (8 years). Metal concentrations in the rest of the subsites were within concentration ranges of site 2-F16 to site 2-D32 and thus are not presented here. Since U.S. EPA Part 503 Risk Assessment guidelines for calculating acceptable soil concentrations need background soil concentrations (only available for site 1) (U.S. EPA, 1995), the limit levels of the regulated metals Cu, Cd, Pb, Se, and Zn were calculated for a 0–100 cm layer of soils in site 1, which were 257.9 mg/kg for Cu, 4.4 mg/kg for Cd, 162.1 mg/kg for Pb, 28.3 mg/kg for Se, and 634.2 mg/kg for Zn for site 1. Therefore, concentrations of all the regulated elements in site 1 were below the regulated levels.

3.2. Metal profiles at different soil depths

Regulated metals (Cr, Cu, Cd, Pb, Zn) and other metals (Ag, Au, Hf, Mo, Nb, Sn, Sb, Ta, W, and Zr) were enriched in the surface layer of soils sampled at both site 1 and site 2 (Fig. 2, Table 1). The enrichment of regulated metals at both sites was consistent with previous findings that showed the accumulation of Cd, Cr, Cu, Ni, Pb, and Zn in the

0–15 cm depth of soil following sludge application to a different type of soil (Chang et al., 1984). A similar accumulation of Cd, and Cu was found in soils fertilized with poultry litter (Gupta and Charles, 1999). Au and Ag are retained in soils under long-term application of biosolids (McBride et al., 1997). To our knowledge, the accumulation in surface soil of some metals analyzed in this test (i.e., Mo, Sn, Sb, Nb, Hf, Ta, W, and Zr) has not been addressed in previous literature.

Illustrative vertical profiles were constructed for representative metals at site 1 only, including one regulated metal (Zn), two non-regulated metals potentially associated with ENMs (Ag, Ti), one MM (Ce), and one PGE (Pt) (Fig. 3). The profiles of the remaining metals assayed at site 1 are listed in the supporting information (Figs. S2–S4). Ag and Zn had similar vertical profiles with higher concentrations near the surface (0–30 cm) than in deeper soil layers (30–70 cm and 70–100 cm, Fig. 3). In the near-surface layers, Ag and Zn concentrations were significantly higher in biosolid-amended soils than in the control ($p < 0.05$, Table S1). In deeper soil layers (30–70 cm and 70–100 cm), there were no significant differences in Ag and Zn contents between biosolid-amended soils and control soils ($p > 0.05$, specific values are listed in Table S1). Specifically, the concentrations of Ag in the surface layers of soils were 15 ± 1.0 , 27 ± 0.2 , 32 ± 1.6 , and 39 ± 1.8 mg/kg, at site 1-1 to site 1-4, respectively, which were much higher than the Ag concentrations in the rest of the soil depths, which averaged 5 mg/kg. The concentration of Zn was in the range of 612–910 mg/kg in the near surface soil layer of the sampling core, whereas in the other layers and the control the concentrations were approximately 401 ± 44 mg/kg. The

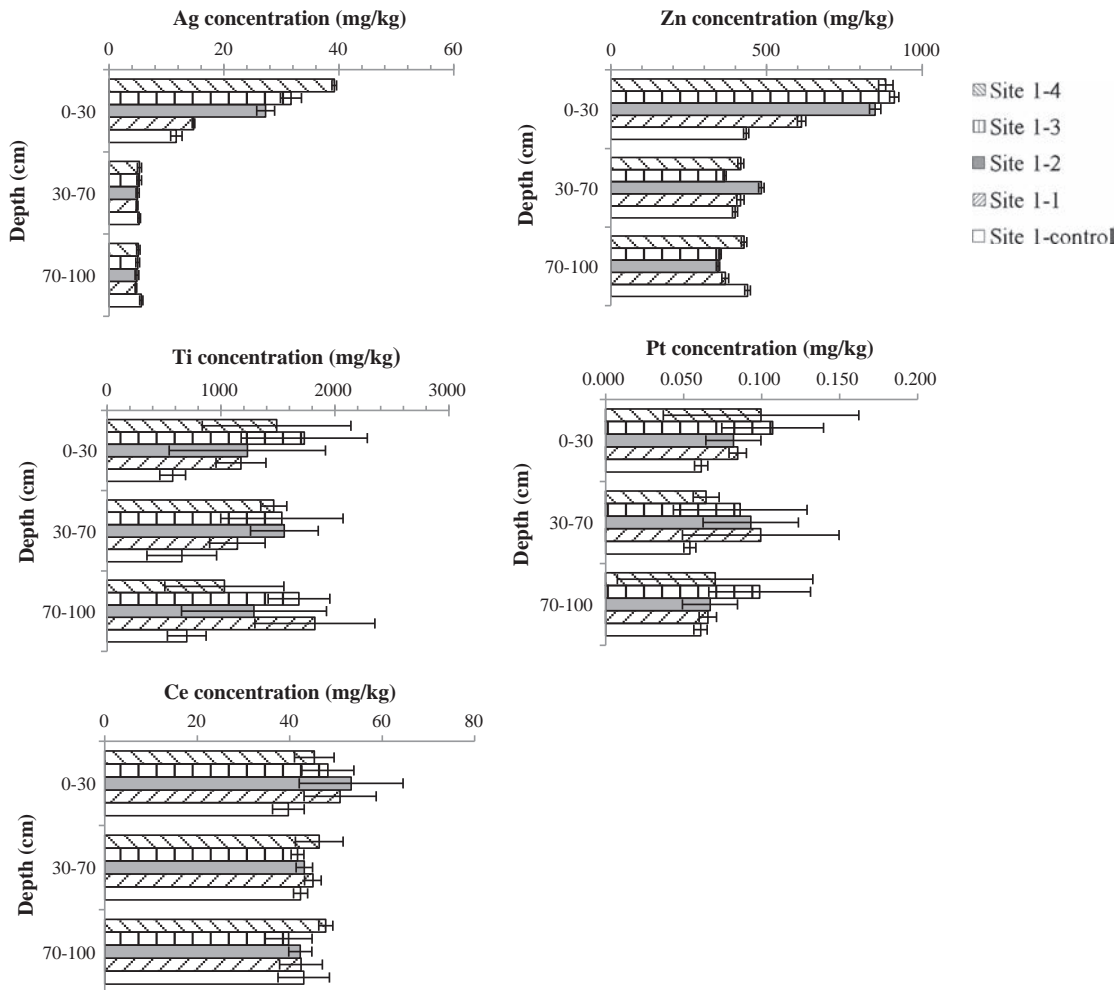


Fig. 3. Concentrations (mg/kg) of silver, titanium (a metal potentially associated with ENMs), zinc (a typical heavy metal), cerium (a minor metal), and platinum (precious metal) from biosolid application plants at three soil depths (below ground surface) at site 1-1, site 1-2, site 1-3, and site 1-4. Error bars represent one standard deviation.

accumulation of Zn was observed only in the near-surface layer (0–30 cm) of biosolid-amended soils. Other metals, including Cu, Cd, Mo, Pb, Sb, Sn, and W, exhibited profiles similar to those of Ag and Zn, with higher concentrations in biosolid-amended soils than in the control, a diminishing vertical concentration gradient, and the highest concentrations in near-surface soil (Table S1).

Ti did not exhibit a vertical concentration gradient like that of Ag or Zn (Fig. 3), as it had an average concentration of 1428 ± 253 mg/kg in biosolid-amended soils across all three depths ($p < 0.05$). In the control soil samples Ti had a background value of 643 ± 62 mg/kg, which is lower than the typical reported range of 1000 to 9000 mg/kg in upper continental crust (Kabata-Pendias and Pendias, 2001). The profiles of Au, Cr, Hf, Nb, Ta, and Zr exhibited significant biosolid-application impacts, including higher metal concentrations in biosolid-amended soils than in control

soils and similar to Ti profile (p values are listed in Table S1). Cerium and platinum had similar concentrations in control and biosolid-amended soils. The abundances of As, Be, Co, Ir, Li, Se, and Te did not differ significantly across the soil profile, suggesting that these metals did not accumulate in soils after long-term biosolid application.

3.3. Presence and characterization of nano-TiO₂ in biosolids and soils

Both micron- and nano-size Ti-containing particles were identified in soil samples. Fig. 4 shows Ti-based colloids approximately 50 nm in diameter in a sample from 0 to 30 cm layer of site 1-3. From the EDX spectrum (Fig. 4b), the atomic ratio of O to Ti is 5.5, which is much higher than the ratio of 2 found in TiO₂. The presence of Al, Fe, Ca, and K in the spectrum was also observed. Spectral analysis suggests that

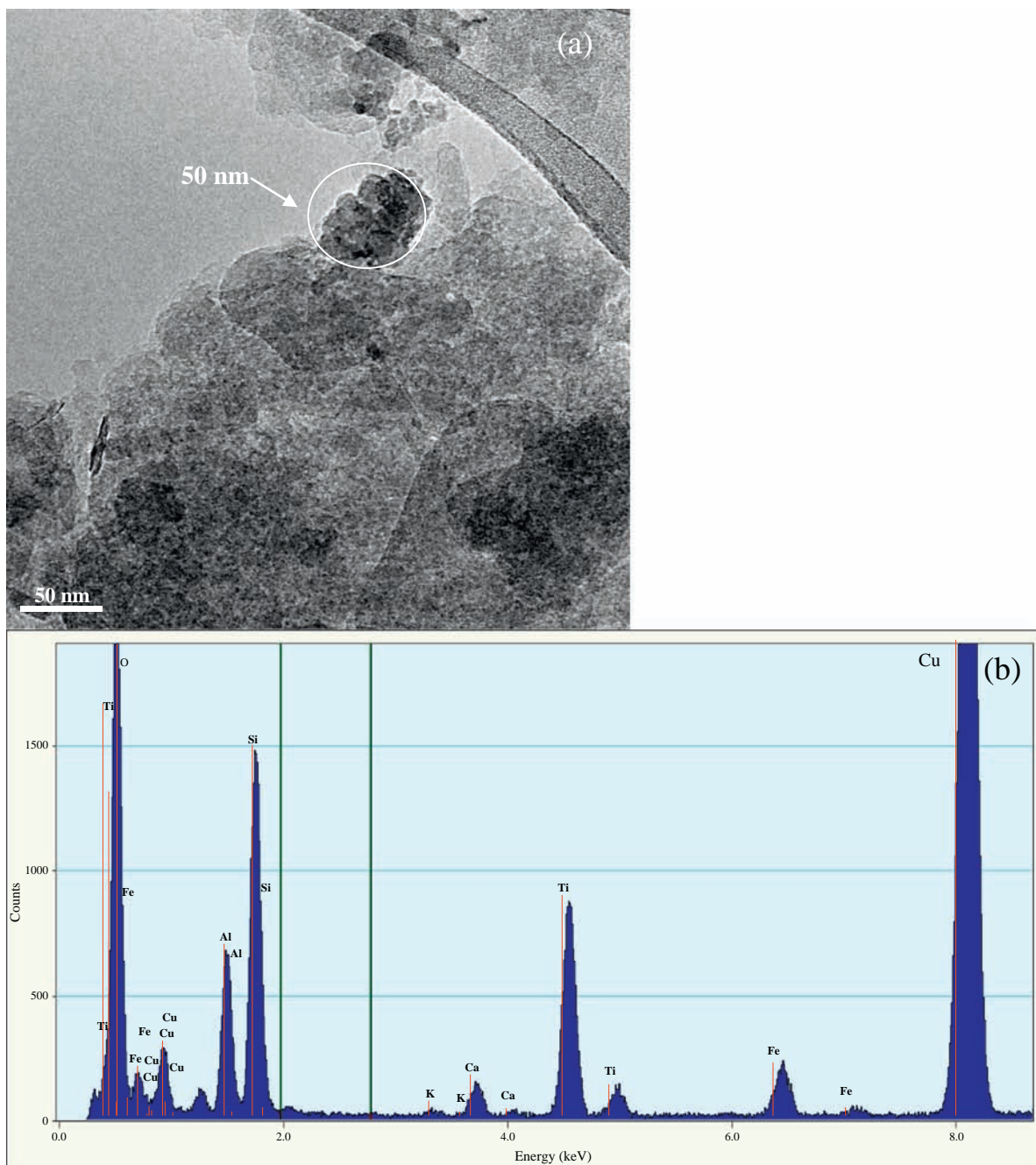


Fig. 4. Transmission electron microscopy (TEM) images and energy dispersive x-ray spectroscopy (EDX) of titanium dioxide nanoparticles embedded in soil samples: (a) TEM images of Ti-containing nanoparticles and (b) EDX of Ti-containing nanoparticles. Samples were from 0 to 30 cm layer of site 1-3.

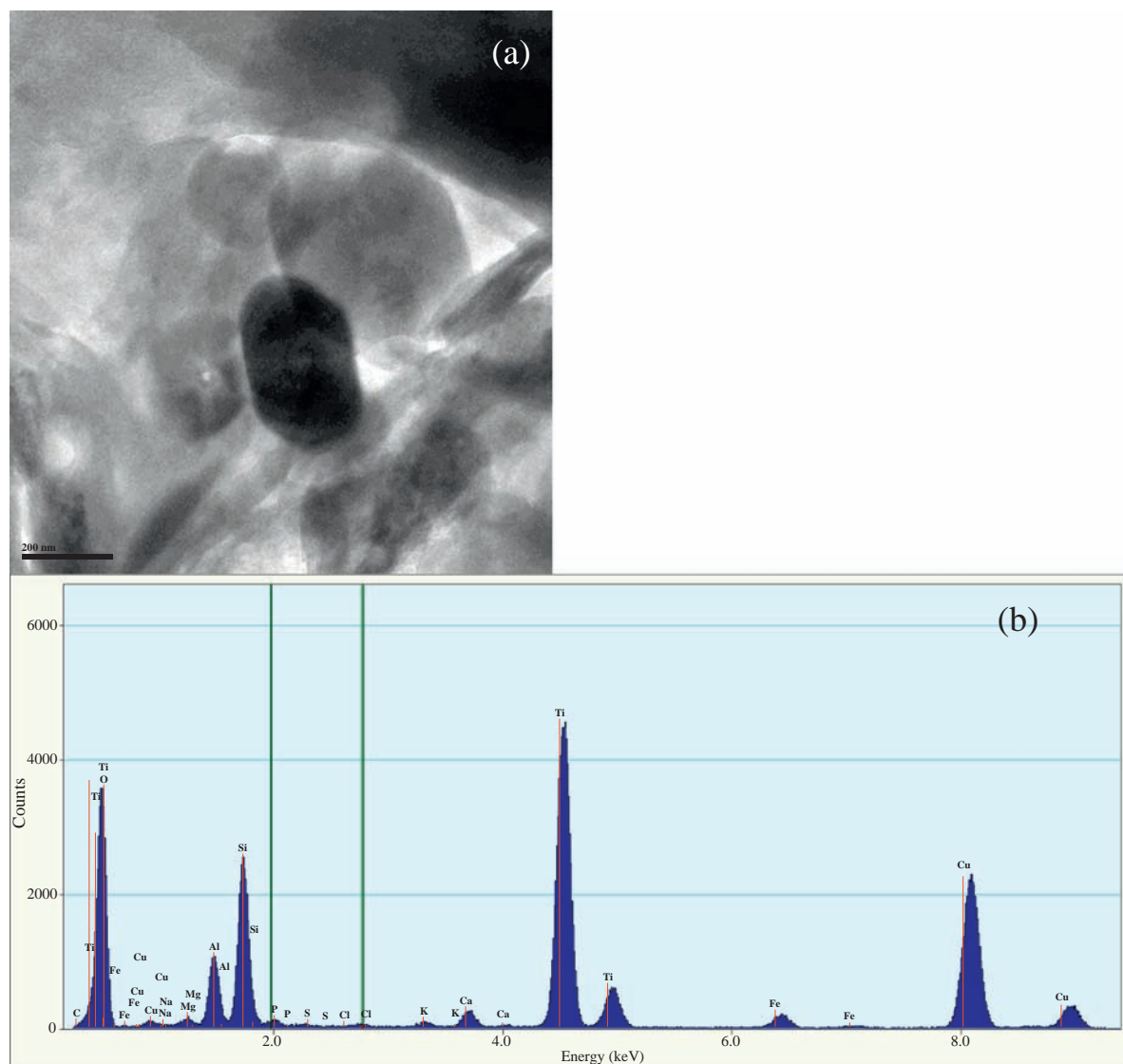


Fig. 5. Transmission electron microscopy (TEM) images and energy dispersive x-ray spectroscopy (EDX) of titanium dioxide particles embedded in soil samples: (a) TEM images of TiO₂ particles and (b) EDX of TiO₂ particles. Samples were from 0 to 30 cm layer of site 1-3.

this Ti-containing nanoparticle is most likely a composite of nano-TiO₂ (or titanate) and Fe/Al oxide, which was mixed with or embedded in the surrounding organic material, resulting in a higher O/Ti ratio.

Micron-size TiO₂ particles were frequently observed in TEM images of soil samples in both sites. Fig. 5 shows a TiO₂ particle with a diameter of 250 nm and an atomic ratio of O to Ti of 2.2 in a sample from 0–30 cm layer of site 1-3. Additional TEM images (Figs. S5–S7) indicate that TiO₂ particles were aggregated or attached on the surface of silicate particles. In these TEM images, most of the TiO₂ particles present are micron size.

3.4. Characterization of other metallic particles in soils

Despite the soils containing up to 16.5 mg/kg of Ag, particles composed of Ag (e.g., Ag nanoparticle) were not observed in any samples. It is not surprising that Ag concentrations in soil were about 100 times less than Ti concentrations. None of the EDX analyses showed any silver response. This does not mean that they are not present, but, given their estimated mass concentration and particle density, the likelihood of locating a nano-silver particle in a biosolid by TEM was less than 0.001% of that of nano-TiO₂ (Westerhoff, 2014).

Significant effort was made (16 TEM samples) to identify other metallic objects that were <100 nm in size in soil samples; however,

we were unable to detect any other ENMs in these soils. However, large particles containing Al, Fe, Ca, and Si were detected in nearly all the soil samples. Most of them were present as oxide or silica-oxides, and frequently contained multiple elements (e.g., Si, Al, O, C). These particles were often in the 0.5 μm to 10 μm range in diameter.

4. Discussion

4.1. Accumulation and distribution of metals in biosolid-amended soils

The enrichment of regulated metals in near-surface soil following biosolid application, relative to deeper soil depths, has been reported in various types of soils (Chang et al., 1984; McBride et al., 1997). Our data showed that at site 1 all the regulated metals except As and Se have similar vertical distribution profiles with a decreasing gradient from near-surface soils (0–30 cm) to deeper soils (30–70 cm, 70–100 cm) (Fig. 3). Soils with high clay content could preferentially retain regulated metals, which may explain the accumulation of regulated metals in surface soils (Cabrera et al., 1999; Han et al., 2000). Anions such as chloride and sulfide, which can complex or associate with metal ions, reduced the metal solubility and mobility (Singh and Agrawal, 2008). Metals that could form complexes or precipitates with

anions were more resistant to leaching and thus were retained in the near-surface layer after entering into the soils. For instance, Ag ions can form precipitates with several anions (e.g. S^{2-} , Cl^{-} , OH^{-}) with low solubility (Stumm and Morgan, 1996), which might lead to the lower mobility of silver and thus showed higher concentration in surface soils than in deeper soils.

At site 1, comparison of control soils and biosolid-amended soils indicated that Ce, Pt, and many other metals (As, Be, Co, Ir, Li, Se, and Te) did not accumulate in biosolid-amended soils. The measured Ce concentration in soils was (45 ± 4 mg/L) consistent with values previously reported by USGS, namely, an average Ce concentration of 75 mg/kg and a maximum concentration of 300 mg/kg, based on a survey of soil samples from more than 21 US states (Shacklette and Boerngen, 1984). Because water can easily desorb Ce from soils (Wen et al., 2002), the even distribution of Ce in soils could be expected in an area with a mean annual precipitation of 817 mm though other reason could not be excluded (e.g. the historical concentrations of Ce in biosolids might be extremely low). Concentrations of other elements, including As, Be, Co, Ir, Li, Se, Te, and Ti did not exhibit a metal accumulation to biosolid application; these elements may be more mobile in soils. Elements including Au, Cr, Hf, Nb, Ta, Ti, and Zr had higher concentrations in the near-surface layer (0–30 cm) in biosolid-amended soils than in control soils.

The length of the biosolid application period and the application rate contribute to the final content of some metals in soils. The long-term (20+ years) application field at site 1–4 had the highest Cu concentration in surface soil. Sn concentrations were statistically the same at site 1–4 and site 1–3 ($p > 0.05$) but higher than at site 1–1 and site 1–2, which had lower biosolid application rates. Metals that behave more similarly to Ti did not exhibit this trend, likely due to their higher mobility in soils. Therefore, the biosolid application rate and duration may have more impact on the accumulation of metals with lower mobility in soils than of metals with higher mobility, particularly in areas like those assayed where erosion rates are low. Further research focused on the exact mechanisms of metal transport in biosolid-amended soils is needed, which would discuss more about the effects of climatology, hydrology, and solubility/partitioning of metals in soils.

4.2. The ratio of nano TiO_2 relative to the bulk TiO_2 in biosolid-amended soils

The ratio of nano- TiO_2 particles relative to the bulk TiO_2 (total amount) could be estimated upon determined Ti concentration and published nano- TiO_2 concentration in biosolid-amended soils. Assuming that all Ti analyzed was in the form of TiO_2 though the existence of other Ti containing salts/materials was not excluded, the concentrations of TiO_2 ranged from 91 to 230 mg/kg per year at site 1 (TiO_2 concentrations divided by application years). Following the estimated concentration of nano- TiO_2 in biosolid-amended soils is 170 $\mu\text{g}/\text{kg}$ per year (Gottschalk et al., 2009), the nano- TiO_2 in our analyzed samples accounts for roughly 0.07%–0.2% of the total Ti. Therefore, only one Ti-containing nanoparticle was observed in biosolid-amended soils (Fig. 4), whereas most of the Ti-containing particles were of micron size. Whether this particle came from an anthropogenic source or occurred naturally in soils is not clear; more research is needed to track the sources of nanomaterials in biosolid treatment facilities.

5. Conclusions

The land application of biosolids poses potential ecotoxicity concerns with regard to enriched metals. A survey of metal concentrations in Texas biosolid treatment facilities indicated that the land application of biosolids may lead to the accumulation of regulated metals (e.g., Cr) and ENM-related metals (e.g., Ti). Specifically, regulated metals (Cr, Cu, Cd, Pb, Zn), plus various other metals (Ag, Au, Hf, Mo, Nb, Sn, Sb, Ta, W, and Zr) accumulated in near-surface soils. This research provides

the first baseline for potential nano-metal forms in soils. Profiles of major ENM-related metals (Ag, Ti, and Zn) reveal their accumulation and indicate their low mobility after entering the soils. A major ENM, a Ti-containing nanomaterial (approximately 50 nm in diameter, and sometimes ~250 nm), was identified by TEM in a soil sample. Therefore, ecotoxicity tests need to be conducted on biosolid-amended soils in situ as a result of the regulated metal accumulation and the existence of ENMs.

Conflict of interest

The authors declare no potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, the work.

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Appendix A. Supplementary data

Additional details covered by this paper 419 include additional TEM micrographs of TiO_2 420 particles in soils and vertical profiles of metals at different depths of the soil samples from 421 site 1. Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.03.122>.

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Metal and Nanoparticle Occurrence in Biosolid Amended Soils

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Table S1. The significant difference (p value) in metal content between biosolids-amended soils and control soil at site 1

Metals	Site 1-1			Site 1-2			Site 1-3			Site 1-4		
	0-30 cm	30-70 cm	70-100 cm	0-30 cm	30-70 cm	70-100 cm	0-30 cm	30-70 cm	70-100 cm	0-30 cm	30-70 cm	70-100 cm
Cr	0.004	0.005	0.617	0.088	0.173	0.880	0.052	0.567	0.959	0.015	0.177	0.032
Cu	0.000	0.099	0.083	0.034	0.880	0.247	0.000	0.129	0.040	0.000	0.258	0.628
Zn	0.032	0.353	0.140	0.052	0.307	0.354	0.019	0.126	0.094	0.012	0.613	0.885
Pb	0.071	0.057	0.326	0.008	0.065	0.479	0.001	0.636	0.221	0.001	0.264	0.889
As	0.008	0.079	0.044	0.001	0.125	0.008	0.559	0.322	0.178	0.341	0.194	0.027
Se	0.838	0.085	0.480	0.498	0.084	0.908	0.632	0.298	0.448	0.829	0.081	0.121
Mo	0.000	0.024	0.141	0.003	0.001	0.211	0.000	0.000	0.135	0.000	0.003	0.039
Cd	0.006	0.416	0.212	0.011	0.410	0.436	0.000	0.774	0.113	0.000	0.458	0.351
Li	0.383	0.016	0.096	0.028	0.108	0.683	0.003	0.036	0.836	0.043	0.410	0.004
Zr	0.016	0.004	0.095	0.003	0.005	0.154	0.000	0.001	0.097	0.001	0.006	0.010
Nb	0.003	0.003	0.019	0.045	0.003	0.335	0.619	0.034	0.238	0.053	0.033	0.005
Co	0.731	0.744	0.694	0.015	0.063	0.614	0.002	0.011	0.319	0.099	0.787	0.061
Be	0.254	0.800	0.630	0.408	0.213	0.438	0.030	0.265	0.551	0.441	0.918	0.126
Ce	0.137	0.170	0.480	0.136	0.581	0.706	0.164	0.787	0.990	0.437	0.255	0.062
Sn	0.000	0.046	0.156	0.019	0.194	0.399	0.000	0.195	0.109	0.000	0.180	0.439
Sb	0.011	0.004	0.093	0.023	0.014	0.882	0.000	0.328	0.618	0.000	0.052	0.052
Hf	0.020	0.002	0.151	0.011	0.004	0.103	0.000	0.000	0.082	0.006	0.008	0.005
Ta	0.002	0.028	0.005	0.036	0.019	0.251	0.003	0.176	0.193	0.032	0.046	0.004
W	0.000	0.007	0.256	0.007	0.003	0.468	0.000	0.264	0.516	0.000	0.156	0.332
Te	0.000	0.000	0.014	0.009	0.001	0.000	0.000	0.010	0.000	0.000	0.000	0.007
Ir	0.001	0.094	0.113	0.064	0.192	0.010	0.222	0.139	0.035	0.098	0.095	0.178
Pt	0.004	0.186	0.509	0.063	0.093	0.443	0.031	0.191	0.251	0.263	0.104	0.086
Au	0.000	0.591	0.139	0.000	0.472	0.068	0.003	0.559	0.400	0.003	0.831	0.229
Ag	0.001	0.351	0.016	0.010	0.574	0.243	0.000	0.982	0.022	0.001	0.903	0.046
Ti	0.004	0.047	0.005	0.108	0.001	0.123	0.003	0.040	0.086	0.030	0.040	0.275

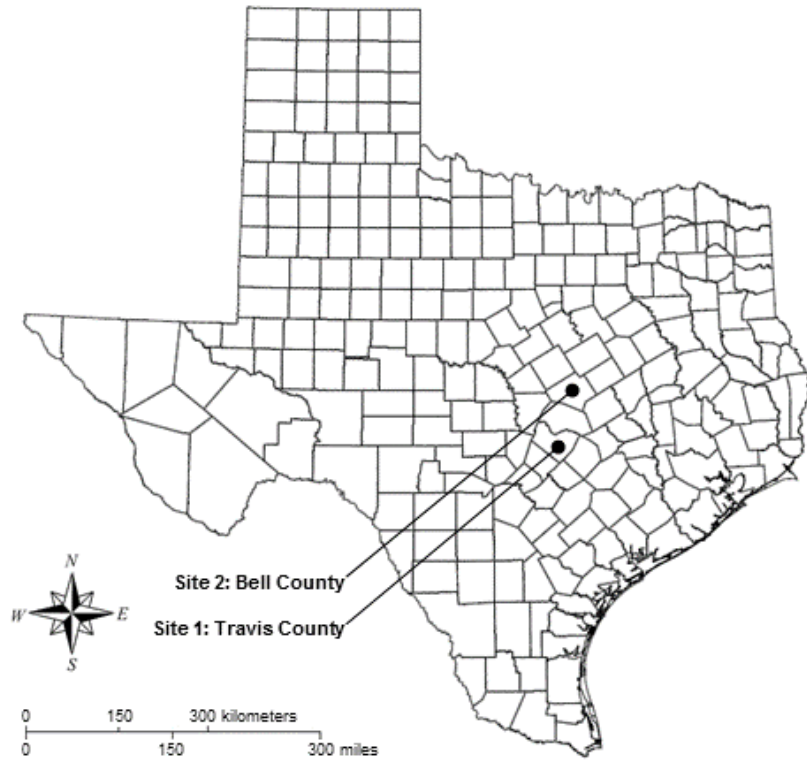


Fig.S1. Study site locations in Texas (map source: Texas Parks and Wildlife).

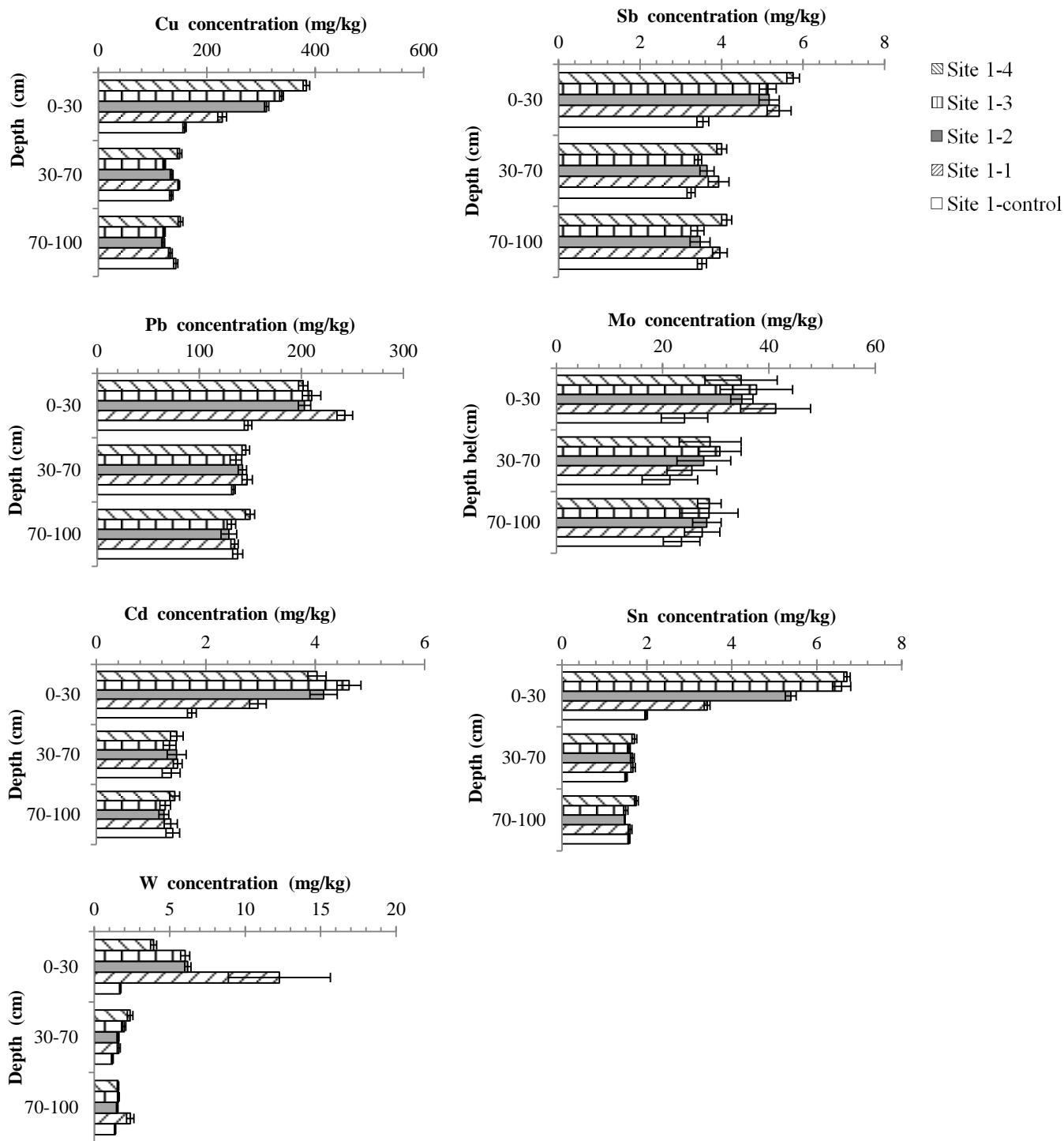


Fig. S2. Concentrations (mg/kg) of metals (Cu, Sb, Pb, Mo, Cd, Sn, and W) at site 1-1, site 1-2, site 1-3, and site 1-4 at three depths of soils amended by biosolids. Error bars represent one standard deviation of measured samples. The metals exhibit trends similar to those of Ag and Zn.

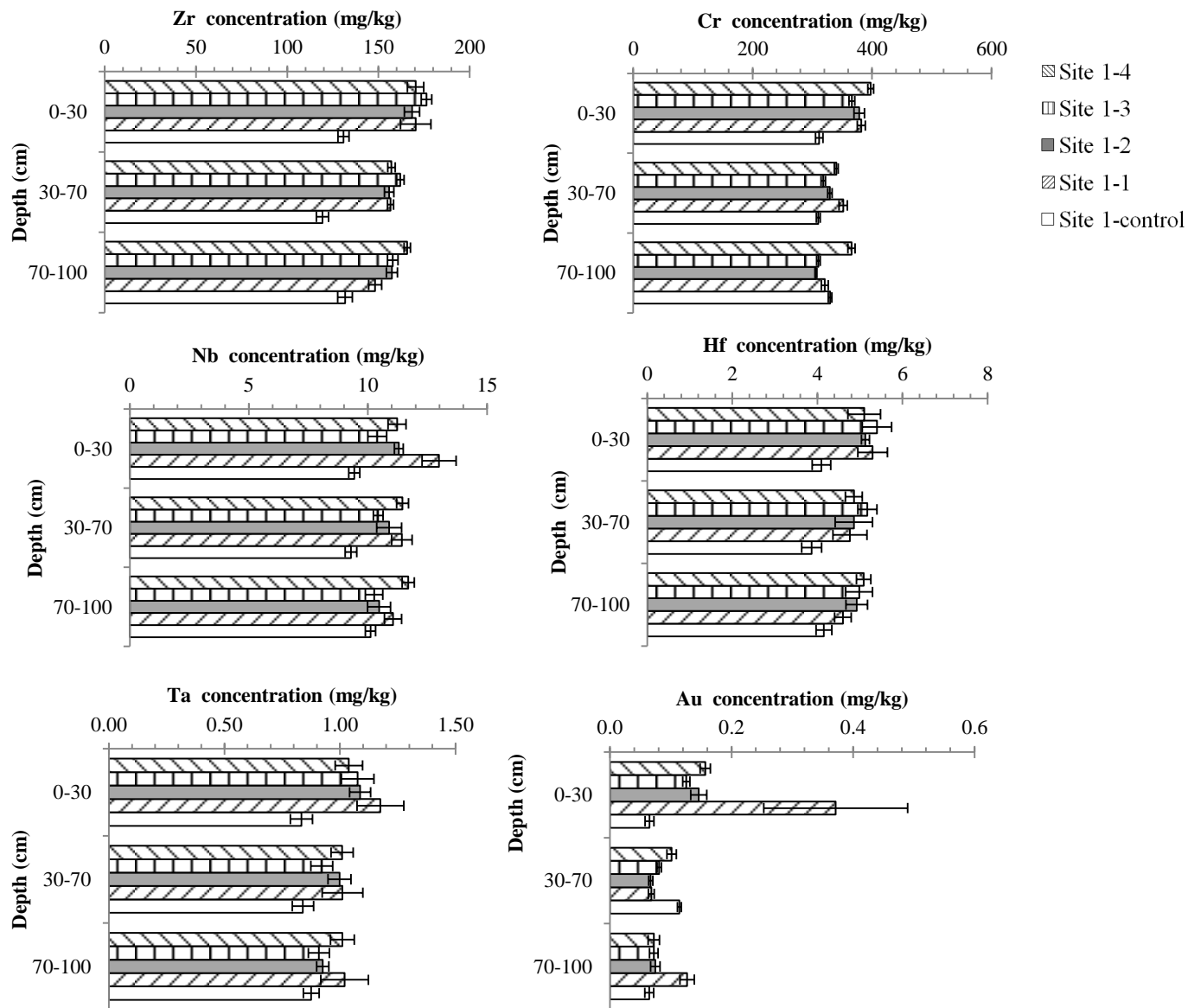


Fig. S3. Concentrations (mg/kg) of metals (Zr, Cr, Nb, Hf, Ta, and Au) at site 1-1, site 1-2, site 1-3, and site 1-4 at three depths of soils amended by biosolids. Error bars represent one standard deviation of measured samples. The metals exhibit trends similar to that of Ti.

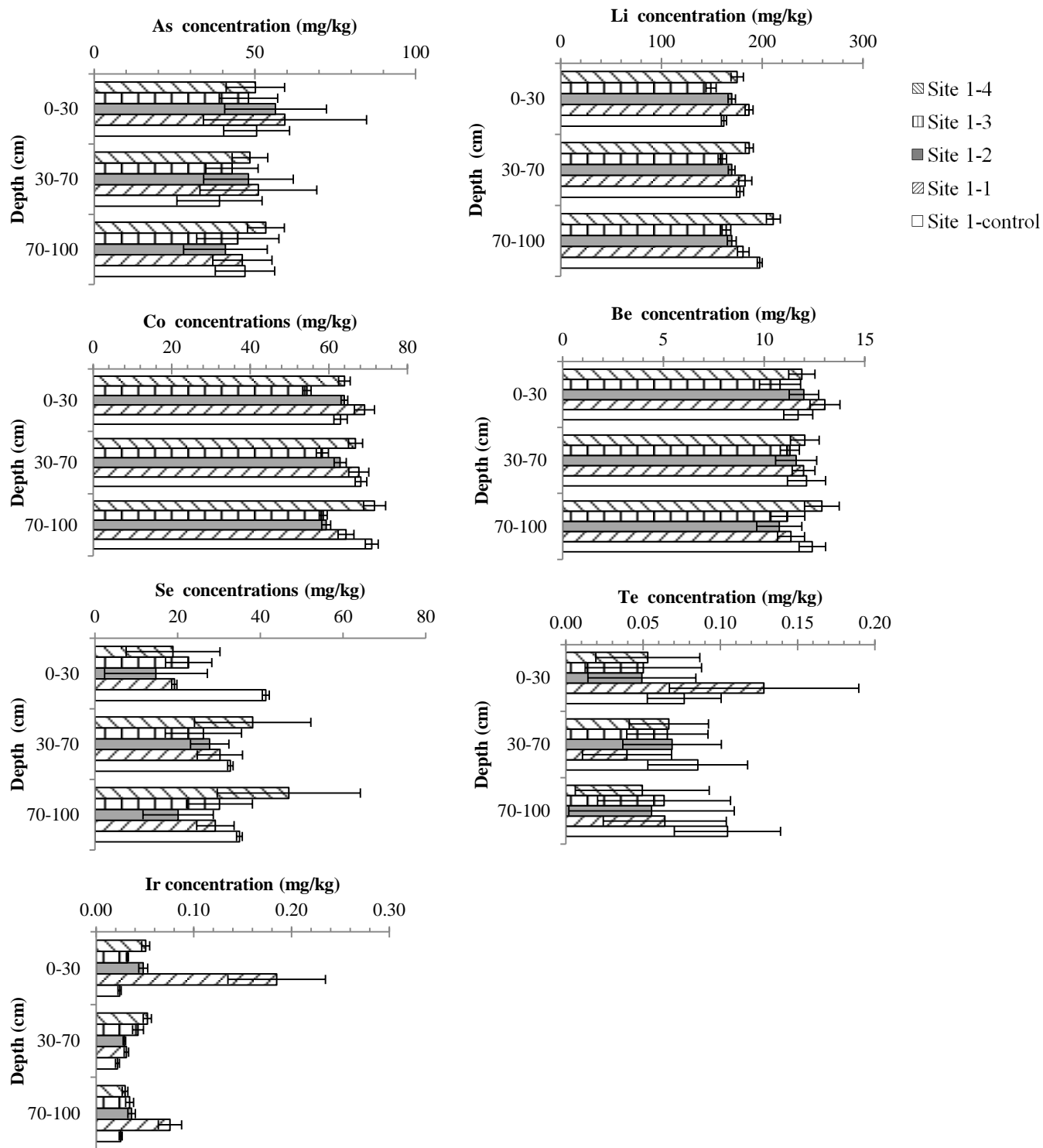


Fig. S4. Concentrations (mg/kg) of metals (As, Li, Co, Be, Se, Te, and Ir) at site 1-1, site 1-2, site 1-3, and site 1-4 at three depths of soils amended by biosolids. Error bars represent one standard deviation of measured samples. The metals exhibit trends similar to those of Pt and Ce.

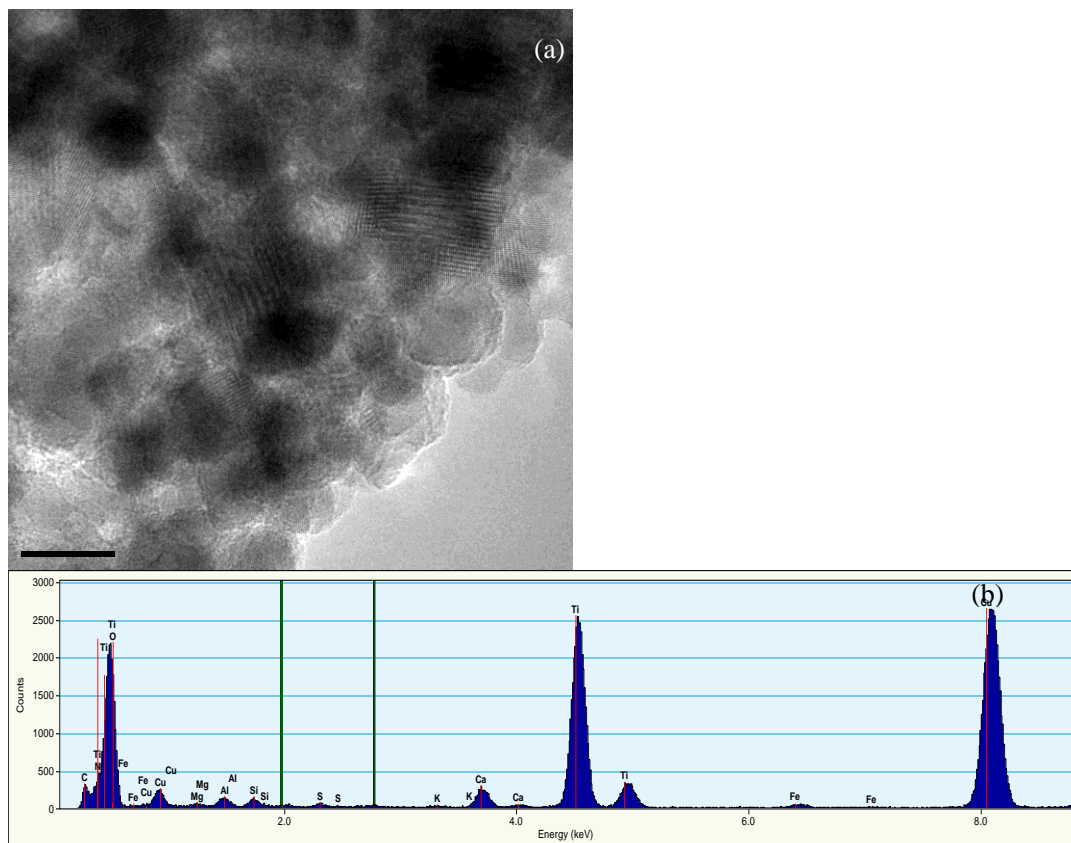


Fig.S5. (a)Transmission electron microscopy (TEM) image and (b) energy dispersive x-ray spectroscopy (EDX) of titanium dioxide particles embedded in soil (0–15 cm, Field D32, Belton, TX).

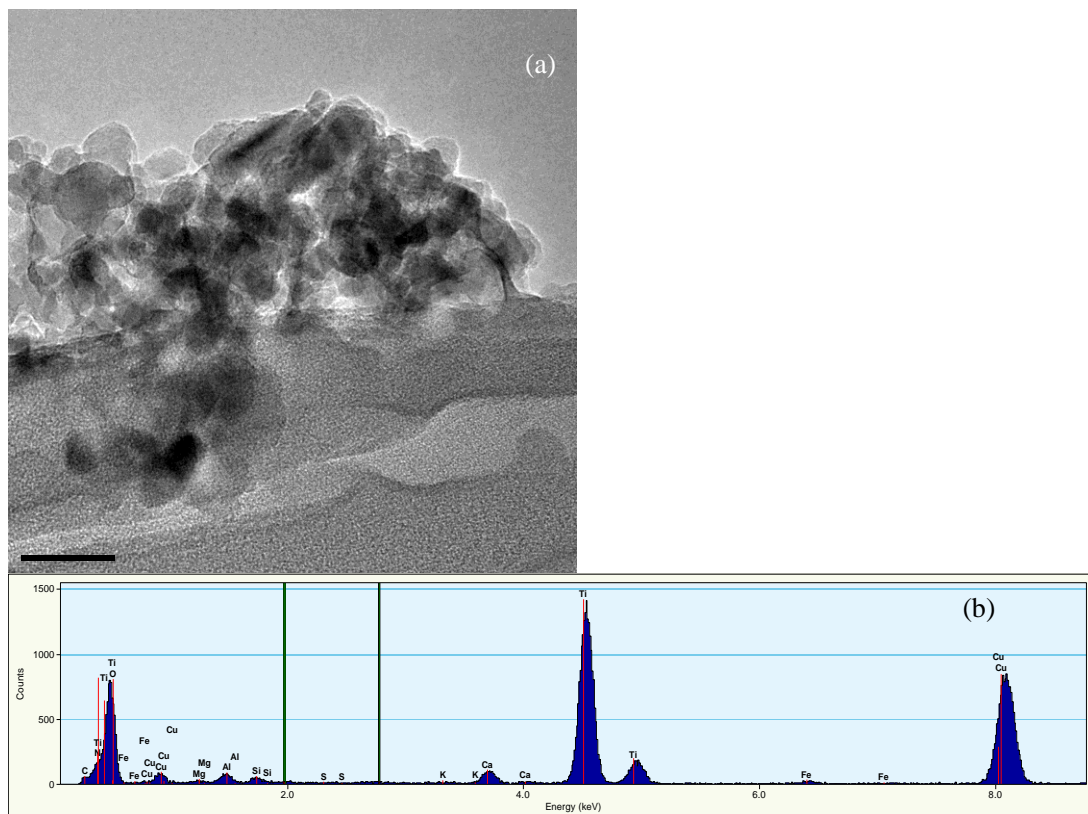


Fig.S6. (a) Transmission electron microscopy (TEM) image and (b) energy dispersive x-ray spectroscopy (EDX) of titanium dioxide particles embedded in soil (0–15 cm, Field D32, Belton, TX).

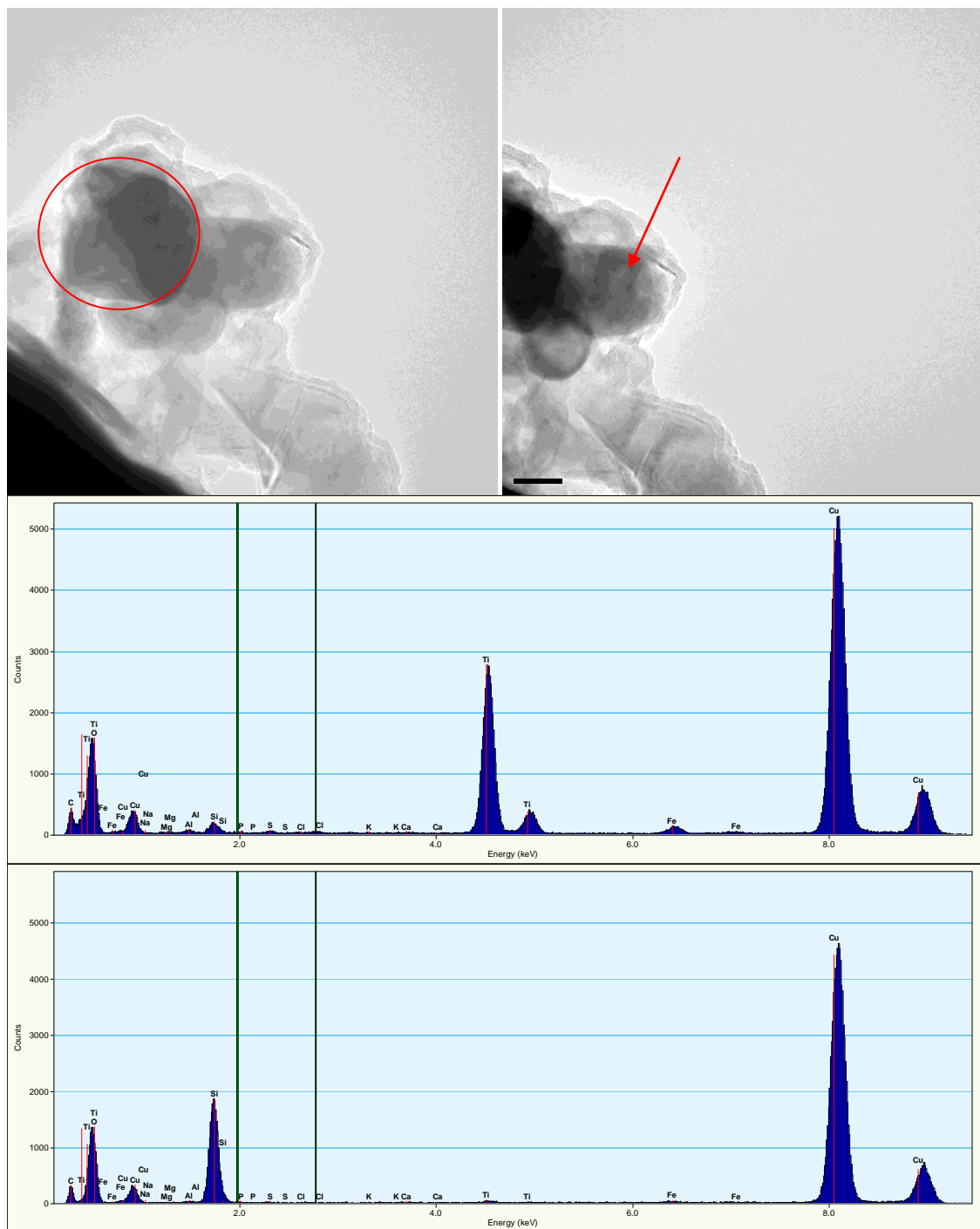


Fig.S7.Transmission electron microscopy (TEM) images and energy dispersive x-ray spectroscopy(EDX) of titanium dioxide particles and silicate particles embedded in soil.(a) TEM image of TiO₂ particles, (b) TEM image of SiO₂ particles, (c) EDX of TiO₂ particles, and (d) EDX of SiO₂ particles. Samples were from 0-30 cm layer of site 1-3.