



# Phosphate recycled as struvite immobilizes bioaccessible soil lead while minimizing environmental risk

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## Abstract

Phosphorus (P) usage and water quality concerns are associated with using phosphate-based amendments to remediate lead (Pb) contaminated soils in urban areas. Struvite has gained increasing attention in the last decade to recover P from point sources while being used as a novel P fertilizer with reduced P loss risk, but its potential for serving as a P amendment for Pb immobilization has not yet been evaluated. This study evaluated the potential of using struvite to maximize Pb immobilization in alkaline urban soils while minimizing P loss risk by comparing the influences of three P amendments (triple superphosphate [TSP], struvite, phosphate rock [PR]) and two particle sizes (0.5 vs 2–4 mm) on Pb immobilization efficacy (relative change in Pb concentrations of *in vitro* physiologically based extraction test [PBET] test,  $P_{PBET}$ ), P loss risk (water extractable P,  $P_w$ ) and the translocation of Pb from soil to plant. The P amendments were added to two Pb-contaminated soils under urban agricultural use with contrasting clay contents (280 mg kg<sup>-1</sup> with 4% clay versus 727 mg kg<sup>-1</sup> with 14% clay) at a rate commonly used for Pb immobilization based on the soil elemental molar ratio of 4:1 (P/[Cd + Zn + Pb]). Greater immobilization efficacy of Pb (up to 19%) occurred for granular (2–4 mm diameter) than ground (<0.5 mm) struvite. For a given particle size, Pb immobilization and plant tissue Pb decreased in the order of PR ≥ struvite > TSP, but the order reversed for P loss risk, with up to 177-fold greater  $P_w$  for TSP than PR and struvite. Greater immobilization for granular PR and struvite could be caused by lower dissolution rates which may better synchronize P dissolution and desorption of Pb. In addition to avoiding secondary contamination compared to conventional P amendments (e.g., Cd content), granular struvite can optimize trade-offs among soil Pb immobilization, crop Pb health risk, and P loss risk.

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## 1. Introduction

Lead (Pb) contamination of soils in urban areas is widespread due to the historic use of Pb-containing products (e.g., paint, gasoline) (Hung et al., 2018). Soil Pb contamination is a serious public health hazard because elevated levels of blood Pb can cause irreversible neurological and physical developmental harm to children, and kidney damage and cancer in adults (Henry et al., 2015). Due to these deleterious health effects, the United States Centers for Disease Control and Prevention (CDC) deems no blood Pb concentration to be safe for children (CDC, 2012). Though direct ingestion of Pb-contaminated soil via hand to mouth contact is the dominant Pb

exposure pathway in urban areas (Ruby and Lowney, 2012), consumption of plants grown in such soils can be an appreciable exposure pathway, accounting for up to 25% of child exposure (Clark et al., 2006). With up to 15% of the local to regional demand for perishable produce being met from peri-urban agriculture in the U.S. (Attanayake et al., 2014; USDA, 2012), this exposure pathway is significant but relatively undervalued for leafy crops (Brown et al., 2016). In the U.S., mean soil Pb concentrations in major urban regions have been found to exceed 150 mg kg<sup>-1</sup> (Brown et al., 2016; Henry et al., 2015), well above the (arithmetic) geogenic soil mean of 19 mg kg<sup>-1</sup> (Holmgren et al., 1993; Shacklette and Boerngen, 1984). Consequently, there is a need to remediate urban soils with low Pb concentrations to decrease both direct (e.g., ingestion of soil) and indirect (e.g., phytoaccumulation and human consumption of plants) Pb exposure risks.

The conventional approach to mitigate Pb exposure risk in urban soils is excavation and removal, though this is neither practical nor feasible in many areas (Henry et al., 2015). *In situ* mitigation is

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better strategy for soils with low Pb concentrations (Hettiarachchi and Pierzynski, 2004). To decrease Pb exposure risk to humans (i.e., Pb absorption in gut), phosphate is often added to soils to decrease Pb solubility and thereby minimize Pb bioaccessibility (Plunkett et al., 2018). Phosphorus (P) amendments are demonstrated amendments for *in situ* soil Pb mitigation (Melamed et al., 2003) because the major reaction product of P and Pb, pyromorphite, is the most thermodynamically stable soil Pb species across a wide pH range (3–9) (Plunkett et al., 2018). However, using P amendments to immobilize soil Pb presents a multifactorial trade-off because P is a valuable resource with limited global supply (Chowdhury et al., 2017) and because high application rates of P (e.g., triple superphosphate [TSP];  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ) can contribute to eutrophication (Brown et al., 2004; Kumpiene et al., 2019). Moreover, commonly utilized P amendments may not balance the benefits and risks for many urban soils, which often are neutral or alkaline due to generation and/or deposition of carbonate- and (hydr)oxide-rich construction and waste materials (e.g., cement). Urban soils can be alkaline (Asabere et al., 2018) even when non-urban soils in the region are acidic (Biasioli et al., 2006; Jim, 1998). The low desorption and/or dissolution of soil Pb in neutral or alkaline soils necessitates acidification of soil prior to applying P amendments for Pb immobilization (Kumpiene et al., 2019; Zhu et al., 2004), but this is often cost-prohibitive (Laidlaw et al., 2017).

Due to these limitations, lowly soluble and thus ‘slow-release’ P amendments have been proposed as a promising soil Pb mitigation strategy (Freeman, 2012; Sneddon et al., 2008). Many such alternative P amendments are waste products or recovered from waste streams by virtue of their low water solubility, and thereby offer locally available and/or inexpensive forms of P (Deydier et al., 2007). For example, calcium phosphate-rich waste products such as fish bone and bone meal (poorly crystalline hydroxyapatite, 6.3–8.7% P) can immobilize Pb while minimizing P loss risk (Deydier et al., 2007; Freeman, 2012; Hodson et al., 2000). However, application of alternative P amendments may engender new considerations, such as carbon-rich bone meal potentially mobilizing Pb or the co-addition of trace elements of human health concern such as cadmium (Cd) (Cao et al., 2003; Rijkenberg and Depree, 2010; Sneddon et al., 2008).

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), recovered from diverse types of municipal and industrial waste streams (Soobhany, 2019) has high potential for use as an amendment for soil Pb immobilization that has yet to be evaluated. Though dissolution of struvite is low in water (<5%) (Ahmed et al., 2016) it can be markedly enhanced by organic acids exuded by roots and the presence of P concentration gradients (Ahmed et al., 2016). Because struvite can be dissolved in alkaline conditions (Wang et al., 2016), it is gaining increasing traction as a slow-release P fertilizer in moderately acidic to moderately alkaline soils (Margenot et al., 2019; Massey et al., 2007, 2009). Additionally, struvite contains orders of magnitude lower concentrations of trace elements of potential human health concern, in particular Cd (<0.9 mg Cd  $\text{kg}^{-1}$  P) (Ronteltap et al., 2007), compared to phosphate rock-based P amendments such as PR or TSP (3–110 mg Cd  $\text{kg}^{-1}$  P) (McLaughlin et al., 1996; Soler and Rovira, 1996). The high rates of P used to immobilize Pb using traditional P sources risk secondary contamination of soils with Cd (Pizzol et al., 2014), or may exceed maximum permissible limits of Cd loading or total soil Cd content (McLaughlin et al., 1996; Ulrich, 2019). Struvite is therefore a low-Cd source of P that could immobilize soil Pb in alkaline soils.

The interaction of P amendment particle size and major soil properties such as clay content and organic matter influence the dissolution of P and Pb species and hence impact the overall efficacy of Pb immobilization (Henry et al., 2015; Hettiarachchi et al., 2000). For example, reducing particle size of PR and struvite by

1-fold entailed up to 4-fold greater dissolution rates in soils (Degryse et al., 2017; Kirk and Nye, 1986). Consequently, comparisons of soil types with contrasting clay and organic matter content, though clay and organic matter are often co-correlated (Rasmussen et al., 2018), are useful to evaluate hypothesized soil-specific efficacy of struvite for Pb immobilization relative to conventional P amendments.

This study evaluated struvite as a novel P amendment that may balance the objectives of maximizing Pb immobilization in alkaline soils while minimizing P loss risk. Specific objectives were: (1) to compare the Pb immobilization efficacy of amendments in alkaline soils; (2) to examine the influences of particle size of TSP, struvite, and PR on Pb immobilization efficacy; (3) to evaluate the P loss risk potential of amendments; (4) to quantify effects of amendments on Pb uptake by a leafy green vegetable. The hypotheses are (1) smaller particle size of P sources will result in greater immobilization of Pb, but may raise P loss risk by increasing soluble P in soil; (2) for a given particle size, Pb immobilization will decrease in the order of TSP > struvite > PR; (3) for a given particle size, P loss risk will decrease in the order of TSP > struvite > PR; (4) Pb in plant tissues will decrease in the order of TSP > struvite > PR.

## 2. Materials and methods

### 2.1. Materials and characterization

Soils were collected from two urban agriculture sites in southern Chicago, Illinois with high and low levels of Pb contamination and clay contents, abbreviated using HC (high clay) and LC (low clay) soils (Table 1). The median concentration of soil Pb in Chicago is 198 mg  $\text{kg}^{-1}$ , a 13-fold enrichment compared to regional (non-urban north central U.S.) concentrations (Cannon and Horton, 2009). Sources of soil Pb contamination in Chicago are most likely historical due to combustion of leaded paint and gasoline, with highways serving as a conduit for transportation and re-deposition of airborne Pb-sediments (Cannon and Horton, 2009). Historical mean annual precipitation is 96.5 cm and mean annual temperature is 11.0 °C. Surface soils (0–15 cm depth) were air-dried and sieved (<4 mm) prior to greenhouse experiments and soil analyses. Soil pH was determined in a 1:5 soil/water mixture. Soil texture was measured by hydrometer (Beretta et al., 2014), and water holding capacity (WHC) was determined gravimetrically (Basso et al., 2013). Total concentrations of trace metal elements in soils were quantified using U.S. EPA Method 3050B in triplicate with a relative standard deviations of <10% (Table 1). In brief,  $1.00 \pm 0.01$  g dry soil was digested with nitric acid ( $\text{HNO}_3$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The obtained supernatants were further digested

**Table 1**  
Properties of the soils used to assess phosphorus amendments for immobilization of soil lead (Pb). Soils (0–15 cm depth) were harvested from contaminated sites being used for urban agriculture in southern Chicago, Illinois, USA. HC soil: high clay soil; LC soil: low clay soil. The detection limits for Pb, chromium, cadmium, and zinc were 3.0, 2.2, 2.6 and 17.0  $\mu\text{g kg}^{-1}$ , respectively. Standard deviations of properties indicated in parentheses (n = 3).

	LC soil	HC soil
pH	7.8 (0.0)	7.4 (0.0)
Water holding capacity (%)	30.8 (0.1)	35.6 (0.1)
Textural class (USDA)	Sand	Sandy loam
Clay (%)	4.2 (1.5)	13.7 (1.4)
Organic matter (%)	3.68 (0.33)	6.45 (0.45)
Nitrogen (%)	0.23 (0.04)	0.29 (0.02)
Lead (mg $\text{kg}^{-1}$ )	279.8 (14.5)	726.8 (37.1)
Chromium (mg $\text{kg}^{-1}$ )	26.9 (1.3)	46.7 (3.0)
Cadmium (mg $\text{kg}^{-1}$ )	0.35 (0.04)	1.97 (0.54)
Zinc (mg $\text{kg}^{-1}$ )	161.0 (16.6)	334.9 (5.4)

by concentrated HCl and refluxed. The final digestate was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Three P immobilization amendments were evaluated: TSP, struvite and PR, sourced from Bonide Products Inc., Ostara Nutrient Recovery Technologies Inc., and Peaceful Valley Farm Supply Inc., respectively (Table 2). The water solubility of these amendments decreases in the order of TSP (>90%) (IPNI, 2014), struvite (0.4–4.4%) (Le Corre et al., 2009; Meyer et al., 2018) and PR (~0.8%) (Ghani et al., 1994). Amendments were homogenized by hand mixing, followed by grinding to sequentially pass <4 mm, 2 mm, and 0.5 mm sieves to obtain amendment of two particle size classes of <0.5 mm and 2–4 mm. The Ca, Mg and P concentrations in the amendments were determined by 1 M HCl digestion and ICP-OES. Together with the measurement of the concentrations of trace elements in the soils, concentrations of other trace elements (e.g., Pb, Cd) in the amendments were measured using the same protocols as for the soils at the Brookside Laboratories Inc., New Bremen, OH, USA. Prior to digestion, the amendments were finely ground (<0.15 mm diameter) to further ensure homogeneity.

## 2.2. Experimental design

A full factorial greenhouse experiment was conducted using three amendments, two amendment particle sizes, and two soil types to test Pb immobilization and crop Pb bioaccumulation. Each treatment was replicated four times for a total of 48 experimental units. Kale (*Brassica oleracea* var. *sabellica* Cv. Lacinto) was surface seeded in 0.500 kg soils in a 750 mL polypropylene plastic pot. Kale was selected as a model crop because this leafy vegetable is common in U.S. urban agriculture, including in Chicago (Taylor and Lovell, 2015), and because Pb accumulation in leafy vegetables is a common health concern (Nabulo et al., 2010). To avoid potential fertility limitations to kale growth, for all treatments soils were fertilized with N (as  $\text{NH}_4\text{NO}_3$ ) and K (as KCl) at an equivalent field-rate of 40 kg  $\text{ha}^{-1}$  of N and K, assuming a depth of incorporation of 0–15 cm and using recommended rates for kale (Wang and Huang, 2008). Rates of P amendments were calculated using a soil elemental molar ratio of 4:1 (P/[Cd + Zn + Pb]). This ratio was chosen because Zn and Cd can also precipitate with P and because employing a slightly higher ratio than the evaluated ratio (3:1) in Basta et al. (2001) ensures the formation of pyromorphite (Basta et al., 2001; Melamed et al., 2003). Assuming a 0–15 cm depth of incorporation and given the bulk density of 1.3 g  $\text{cm}^{-3}$  to which soil was packed in pots, P amendment rates for LC and HC soils were

equivalent to a field-scale application rate of 923 and 2091 kg  $\text{P ha}^{-1}$ , respectively. Differences in Ca, Mg and N among P amendment treatments were controlled by adding appropriate amounts of  $\text{NH}_4\text{Cl}$ ,  $\text{MgCl}_2$  and  $\text{CaCl}_2$ . Though this translates to relatively high rates of application of  $\text{Cl}^-$ , this is an inevitable trade-off of controlling for cations added across different P amendment treatments. Cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ) may interfere with the Pb–P immobilization more than anions presumably because  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can compete with  $\text{Pb}^{2+}$  for P to form precipitates, and  $\text{NH}_4^+$  is a nutrient ion that can influence plant growth and thus amount of Pb uptake by biomass dilution. In contrast,  $\text{Cl}^-$  does not form inner-sphere complexes with cations on mineral surfaces or precipitate with cations and is readily leached (Sparks, 2003). Moreover, no visual symptoms of Cl toxicity were observed in any of the plants at the end of the experiment. Chemicals were thoroughly mixed throughout the entirety of the soil in each pot. Control soils with no amendment application were included in quadruplicate. Soil moisture was initially maintained at 70% WHC using 18.2 M $\Omega$ ·cm water until germination and emergence of first true leaves, then adjusted to 60%. Seedlings were thinned to one per pot in the second week post-germination. Plants were grown under all treatments at 18.3 °C for 73 days with 12–12 h light-dark cycle under a randomized design with four blocks.

## 2.3. Sample collection

Soil samples were collected, air-dried and sieved (<2 mm). Kale in each pot was harvested as two biomass fractions: belowground biomass (root) and aboveground biomass (shoot). The biomass of the two fractions were sequentially rinsed by reverse-osmosis water, 0.01 M sodium EDTA [ $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\text{Na}_4$ ] solution, and finally 18.2 M $\Omega$ ·cm water to remove potential surface-bound Pb in a slight modification of Azcue (1996). Both roots and shoot biomass were dried in a forced-air oven at 75 °C for 48 h to determine dry biomass.

## 2.4. Chemical analysis

Soil pH was analyzed in 1:5 soil/water mixture. Phosphorus phytoavailability and loss risk were evaluated using the agronomic test of Olsen (Olsen et al., 1954), in which soil is extracted with a solution:solid ratio of 1:20 in 0.5 M  $\text{NaHCO}_3$  solution (pH 8.5) by shaking for 30 min. This test is recommended for soils with pH > 6.5 to estimate plant P needs, and recent evidence indicates Pb extracted by Olsen is bioaccessible (Plunkett et al., 2018; Sims,

**Table 2**

Concentrations of major and trace elements in phosphate rock (PR), struvite and triple superphosphate (TSP) determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), with standard deviation of triplicate analyses (n = 3) indicated in parentheses. Measured together with the soil samples, the relative standard deviations for the trace elements in these amendments were likely smaller than these in the soils (<10%) because the amendments were finely ground (<0.15 mm) and because the heterogeneity of the soils is greater than the amendments. N.A.: not applicable; N.D.: not detected.

	PR	Struvite	TSP	Detection limit
pH	7.24 (0.04)	8.21 (0.04)	2.63 (0.01)	N.A.
Phosphorus (%)	8.29 (0.36)	12.44 (0.17)	20.67 (0.23)	N.A.
Magnesium (%)	0.18 (0.03)	10.09 (0.20)	0.46 (0.02)	N.A.
Calcium (%)	18.36 (0.9)	0.14 (0.05)	17.38 (0.46)	N.A.
Arsenic (mg $\text{kg}^{-1}$ )	4.6	N.D.	5.4	1.6
Cadmium (mg $\text{kg}^{-1}$ )	2.8	N.D.	18.5	0.4
Chromium (mg $\text{kg}^{-1}$ )	79.9	N.D.	110.9	0.8
Copper (mg $\text{kg}^{-1}$ )	9.7	N.D.	27.9	0.8
Lead (mg $\text{kg}^{-1}$ )	45.8	N.D.	N.D.	3.9
Mercury (mg $\text{kg}^{-1}$ )	N.D.	N.D.	N.D.	0.04
Molybdenum (mg $\text{kg}^{-1}$ )	N.D.	N.D.	14.6	3.9
Nickel (mg $\text{kg}^{-1}$ )	26.1	N.D.	47.5	0.8
Selenium (mg $\text{kg}^{-1}$ )	N.D.	N.D.	8.9	1.6
Zinc (mg $\text{kg}^{-1}$ )	45.3	N.D.	471.9	2.4

2000). Though originally developed as an agronomic soil test, Olsen P can be additionally used to identify soil P concentrations that are strongly correlated with off-field P losses (Watson et al., 2007). Since water-extractable P ( $P_w$ ) is most consistently well-correlated with dissolved reactive P concentrations in surface runoff (Wang et al., 2015),  $P_w$  offers an additional and potentially more direct indicator of P loss risk (Anderson and Xia, 2001). Thus,  $P_w$  was determined using water:solid ratio of 1:10 for evaluation of P loss risk (Murphy and Stevens, 2010).

Inorganic P extracted by 18.2 MΩ·cm water was quantified by molybdate colorimetry (Murphy and Riley, 1962), and Pb concentrations in the extracts of Olsen test were measured by ICP-OES. As the standard protocol for evaluation of soil Pb bioaccessibility, In vitro physiologically based extraction test (PBET) was conducted using U.S. EPA method 1340 at a modified pH of 2.5 (Attanayake et al., 2014; Obrycki et al., 2017). The concentrations of Pb in aboveground and belowground biomass were also quantified to evaluate the impacts of P amendments on crop Pb risk, with a detection limit of 0.1 mg kg<sup>-1</sup>. A subset of 10% of soils were analyzed in triplicate for  $P_w$ , Olsen P and Pb concentrations, which confirmed that relative standard deviations were <5%. The detection limit for Olsen Pb was 1.00 mg kg<sup>-1</sup>.

The changes of  $P_w$  and PBET Pb ( $Pb_{PBET}$ ) concentration relative to control for given P amendment were calculated to indicate the P loss risk and Pb immobilization, respectively, using the following the equation:

$$\text{Relative change(\%)} = \frac{C_t - C_c}{C_c} \times 100\%$$

In which  $C_t$  represents the concentrations of P or Pb for the amended soils, and  $C_c$  represents the concentrations of P or Pb for the control soils.

### 2.5. Statistical analyses

The statistical differences among treatments were examined by analysis of variance (ANOVA) followed by Duncan's post-hoc test ( $p = 0.05$ ) using SPSS version 25 (SPSS Inc., Chicago, IL, US). Prior to ANOVA test, the Levene test for homoscedasticity test was conducted and data transformation (natural log) was performed for  $Pb_{PBET}$  to ensure assumptions were met.

## 3. Results

### 3.1. Soil pH changes

After 73 days incubation, compared to pH of the un-incubated soil (Table 1), soil pH for both HC and LC control soils was elevated (Fig. 1). Compared to controls, soil pH decreased significantly across treatments likely due to the addition of P amendments. Irrespective of particle size, the TSP treatments entailed significantly greater soil pH decreases compared to PR and struvite.

### 3.2. PBET test for Pb immobilization

Decreases in Pb immobilization among P amendments differed by amendment type and particle size (Fig. 2A). For LC soil, finely ground TSP mobilized Pb whereas finely ground PR and struvite immobilized Pb. In contrast, when P amendments were used in granular form (2–4 mm diameter), struvite and PR induced similar Pb immobilization (~18%) while TSP was less efficient (~10%). For HC soil, PR and struvite achieved similarly greater Pb immobilization (~18%) than TSP (~1%) in granular form. However, for finely ground amendments, in HC soil the Pb immobilization efficacy of

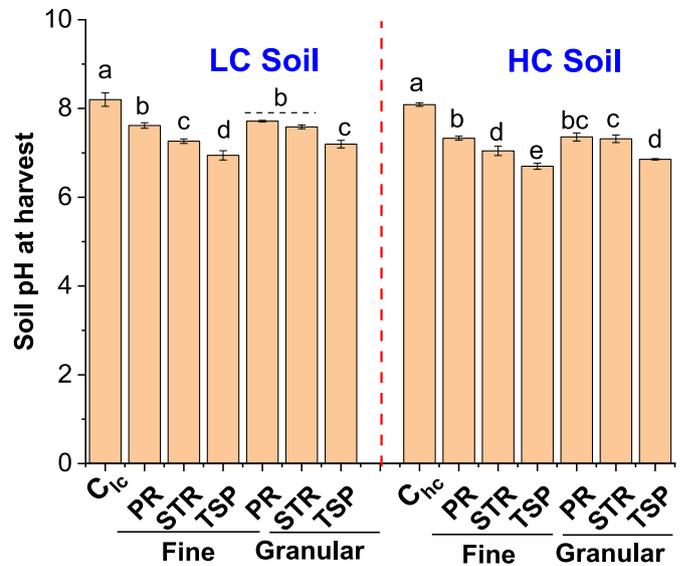


Fig. 1. Soil pH after different treatments for 73-day greenhouse evaluations of phosphorus amendments for immobilization of lead in Chicago soils. Standard deviation was indicated by the variance bar ( $n = 4$ ). The amendments were evaluated for particle size effects (fine: <0.5 mm and granular: 2–4 mm). Lowercase letters denote the statistical significance ( $p < 0.05$ ) of the differences in soil pH among treatments in the low clay (LC) or high clay (HC) soil group. C<sub>1c</sub>: control LC soil; C<sub>1c</sub>: control HC soil; PR: phosphate rock; STR: struvite; TSP: triple superphosphate.

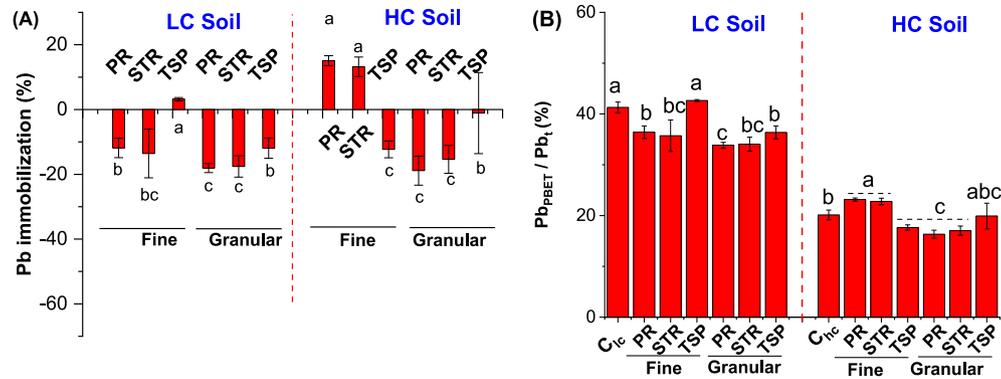
struvite and PR treatments were positive, indicating net increase of Pb bioaccessibility. Overall, among all the combinations of P amendments and particle size for both HC and LC soils, granular struvite induced comparable Pb immobilization efficacy compared to PR, and greater immobilization efficacy than TSP.

The ratio of  $Pb_{PBET}$  to soil total Pb ( $Pb_t$ ) differed by soil and particle size of P amendments to some degree (Fig. 2B). The ratio of  $Pb_{PBET}$  to  $Pb_t$  was 83–130% higher for LC soil than for HC soil for all treatments (Fig. 2B). Compared to the unamended control, the ratio decreased for granular amendments in both HC and LC soils and were comparable or increased for finely ground struvite and TSP except the finely ground TSP in HC soil (Fig. 2B), consistent with changes in Pb immobilization.

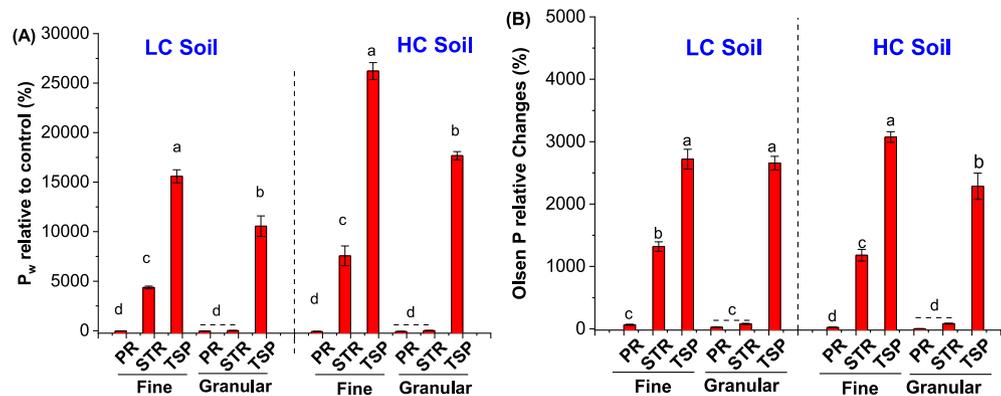
### 3.3. Phosphorus concentrations in water and Olsen test extracts for P loss risk and availability

Phosphorus loss risk as assessed by  $P_w$  and Olsen P generally differed by P amendments and amendment particle size, and absolute changes in these were soil specific (Fig. 3A). The change of  $P_w$  relative to the unamended control decreased in the order of TSP, struvite and PR by three orders of magnitude. Soils amended with finely ground struvite exhibited at least 50-fold higher  $P_w$  than unamended control soils. The finely ground struvite treatments displayed 1.5-fold greater  $P_w$  relative changes for HC soil than LC soil. Consequently, granular struvite produced the minimum P loss risk ( $P_w$ ) but comparable Pb immobilization as PR. These results reflected the relative water-solubility of the amendments and the particle size impacts on solubility, i.e., for granular size, TSP > struvite ≈ PR, and for the finely ground size, TSP >> struvite >> PR.

Irrespective of particle size and soil, Olsen P concentrations decreased in the order of TSP > struvite > PR > controls (Table S1). Treatments with finely ground PR and TSP had slightly higher Olsen P than those with granular size of PR and TSP for both soils. In contrast, Olsen P for soils treated with finely ground struvite was



**Fig. 2.** Lead (Pb) immobilization (%) defined as the relative change in Pb concentrations of *in vitro* physiologically based extraction test [PBET] (A), and the ratio of extractable Pb concentrations by PBET ( $Pb_{PBET}$ ) to total soil Pb ( $Pb_t$ , B) for soils after different treatments of 73-day greenhouse experiments compared to control (soil only). The amendments were evaluated for particle size effects (fine: <0.5 mm and granular: 2–4 mm). Lowercase letters denote the statistical significance ( $p < 0.05$ ) of the differences in response variables among treatments in low clay (LC) or high clay (HC) soil group.  $C_{LC}$ : control LC soil;  $C_{HC}$ : control HC soil; PR: phosphate rock; STR: struvite; TSP: triple superphosphate.



**Fig. 3.** Change (%) in phosphorus (P,  $mg\ kg^{-1}$ ) extracted by water (A,  $P_w$ ) and Olsen test (B, 0.5 M  $NaHCO_3$ , pH 8.5), after different treatments in soils after different treatments of 73-day greenhouse experiments compared to control (soil only). The amendments were evaluated for particle size effects (fine: <0.5 mm and granular: 2–4 mm). Lowercase letters denote the statistical significance ( $p < 0.05$ ) of the differences in response variables among treatments in the low clay (LC) or high clay (HC) soil group. PR: phosphate rock; STR: struvite; TSP: triple superphosphate.

about 7-fold greater than for granular struvite for both HC and LC soils, indicating a dominant impact of particle size on P availability.

### 3.4. Lead concentrations in biomass

More Pb accumulated in kale roots than shoots, and was below the detection limit in shoots ( $<0.1\ mg\ kg^{-1}$ ) (Fig. 4). Root Pb concentrations ranged from 29.9 to 89.9  $mg\ kg^{-1}$ . Though not significant for some cases, mean concentrations of root Pb generally decreased in the order of PR > struvite > TSP, with the exception that granular TSP of LC soil yielded similar root Pb concentrations as for struvite.

### 3.5. Lead concentrations in Olsen test extracts

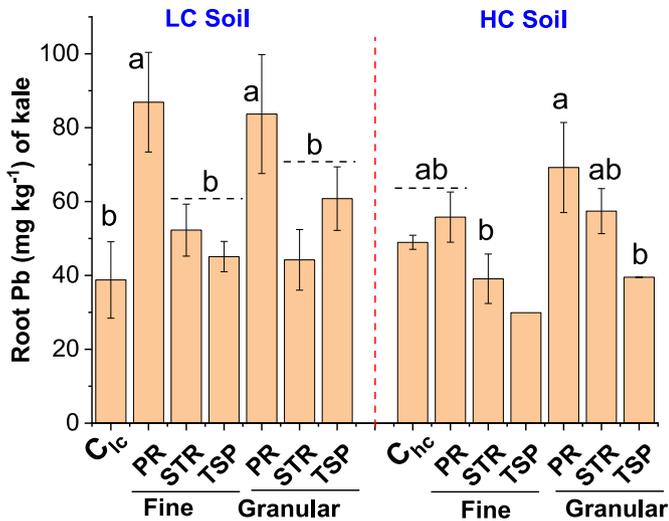
Changes in Olsen Pb concentrations relative to the Olsen Pb in the control did not show consistent trends with treatments and were highly soil-specific (Fig. 5A). Olsen Pb was below the detection limit ( $<1.00\ mg\ kg^{-1}$ ) for all HC soil treatments and LC soils amended with TSP. Olsen Pb for LC soil treatments did not differ for the granular P amendments but showed a 2.6-fold difference for the finely ground P of PR and struvite, and was not detectable for the TSP treatments. In contrast, soils amended with lowly soluble P amendments of struvite and PR were detectable, and Olsen Pb was higher for soils amended with struvite relative to PR. Olsen Pb and  $Pb_{PBET}$  concentrations were not related (Fig. 5B).

## 4. Discussion

Struvite has gained attraction in the last decade as a means to recover P from point sources for re-use as a novel P fertilizer (Hertzberger et al., 2020). This study demonstrates for the first time the potential of struvite as a P amendment to balance the trade-offs among human and plant bioaccessibility and environmental quality. Granular (2–4 mm diameter) struvite can optimize immobilization of Pb while mitigating P loss risk. Struvite can achieve similar efficacy of Pb immobilization compared to PR while mitigating plant Pb uptake on a magnitude comparable to TSP, but with lower P loss risk comparable to PR. In addition, struvite contained markedly lower trace elements of human health concern, in particular Cd, than TSP and PR. Thus, granular struvite optimized Pb immobilization, P loss risk and crop health risk, with the least secondary contamination of soils by Cd.

### 4.1. Pb immobilization in urban (alkaline) soils

Lead contamination of urban soils that tend to be alkaline (Asabere et al., 2018; Biasioli et al., 2006; Jim, 1998) requires economically feasible mitigation practices to reduce Pb health risk via direct exposure (human ingestion of soil) or indirect exposure (consumption of vegetable tissues) (Weber et al., 2015). However, previous evaluations of Pb immobilization by P amendments have focused on acidic soils and/or pre-acidified alkaline soils (Cao et al.,



**Fig. 4.** Root lead (Pb) concentrations ( $\text{mg kg}^{-1}$ ) of kale (*Brassica oleracea* var. *acephala* Cv. Lacinto) grown in Pb-contaminated Chicago soils treated with different phosphate amendments for 73-day greenhouse experiments. The amendments were evaluated for particle size effects (fine:  $<0.5$  mm and granular: 2–4 mm). Lowercase letters denote the statistical significance ( $p < 0.05$ ) of the differences in root Pb concentrations among treatments in the low clay (LC) or high clay (HC) soil group. Finely ground ("Fine") triple superphosphate (TSP) in HC soil was not included in the analysis of variance (ANOVA) analysis because only one replicate plant was viable. C<sub>lc</sub>: control LC soil; C<sub>hc</sub>: control HC soil; PR: phosphate rock; STR: struvite.

2002). In many urban regions in which circumneutral or alkaline soils are used for agriculture, such as Chicago, it is not feasible to pre-acidify soils to facilitate Pb immobilization. Although high soil pH limits Pb solubility and high calcium likely competed with Pb for phosphate (Obrycki et al., 2017), the appreciable immobilization Pb efficacy of struvite in the two studied alkaline soils were likely caused by the root exudates that accelerated struvite dissolution (Massey et al., 2007).

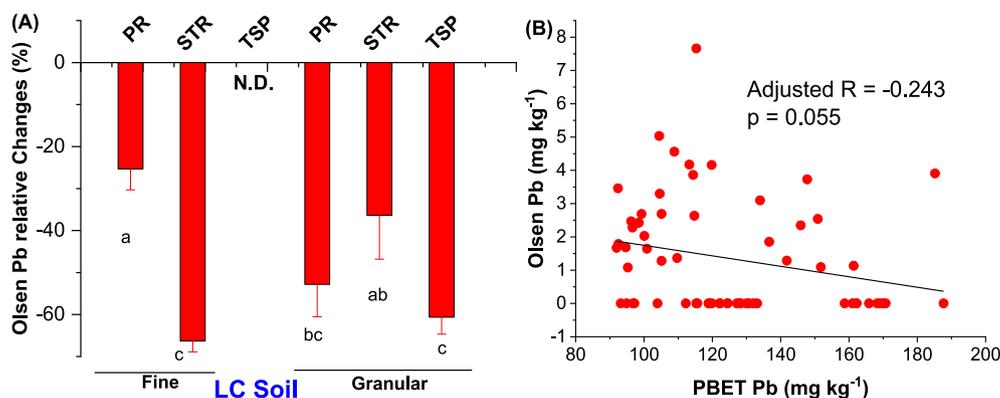
Soil properties may have influenced P-induced Pb immobilization in a more complex way than anticipated. Pre-acidification has been proposed to be necessary to improve Pb immobilization by P amendments (Cao et al., 2002). However, this study suggests that pH may not necessarily be critical because Pb immobilization efficiency was least in TSP treatments, despite these having the lowest pH (Figs. 1 and 2). The lower pH in TSP treatments than in others could be caused by the much lower pH of TSP (2.63) than PR and struvite (7.24, 8.21, respectively; Table 2), consistent with the TSP-

induced pH decrease in treated soils (Weber et al., 2015). Differences in Pb mobilization in HC soil but not the LC soil by finely ground PR and struvite may be caused by the distinct pattern of phosphate dissolution and fixation under conditions of contrasting clay contents (Gu et al., 2019), such as stronger adsorption and weaker desorption of certain common anions including P in HC soils (Gu et al., 2016, 2020). Elucidating how clay minerals influence Pb immobilization under same P treatments merits further study. Likely mechanisms for the observed decrease in Pb<sub>PBET</sub> include the formation of lowly soluble and bioaccessible hydroxypyromorphite [ $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ ] and Pb adsorption on mineral surfaces favored under alkaline condition for Pb immobilization in alkaline soils (Scheckel and Ryan, 2003; Wang et al., 2016). Enhanced Pb immobilization by the granular forms of P amendments could be due to the slower dissolution rate of larger particles and hence greater synchronization of phosphate release and Pb dissolution and/or desorption over time.

Recently, it has been shown that Pb concentrations extracted by agronomic tests such as Mehlich-3 or Olsen in acidic soils ( $\text{pH } 6.4 \pm 0.2$ ) provided comparable information on relative Pb bioaccessibility as measured by the standard PBET protocol of U.S. EPA 1340 and characterized by extended X-ray absorption fine structure spectroscopy, respectively (Plunkett et al., 2018). As standard agronomic tests for acidic and alkaline soils, Mehlich-3 and Olsen were developed to predict crop yield response and thus P fertilization rates, and are often used as a proxy of bioavailable (crop) phosphate in soil. Analogous to the ability of Mehlich-3 Pb to predict Pb<sub>PBET</sub> in acidic soils (Plunkett et al., 2018), it was hypothesized that Olsen Pb should predict Pb<sub>PBET</sub> in alkaline soils. However, for the alkaline soils from Chicago in this study (Havlin et al., 2013), Olsen Pb was not correlated to Pb<sub>PBET</sub>. Differences in prediction of Pb<sub>PBET</sub> using Mehlich-3 and Olsen tests may be due to the similar low pH conditions ( $\text{pH } 2.5$ ) of the Mehlich-3 and PBET extractants that likely favor the extraction of strongly bound Pb, whereas the Olsen extraction solution may be limited to exchangeable surface-bound Pb via bicarbonate.

#### 4.2. P loss risk using P-based amendments

Phosphate-based mitigation of soil Pb bioaccessibility was developed in arid climates of the Western U.S. (Hettiarachchi et al., 2001), in which the water-borne pathway of phosphate loss to surface waters poses a lower risk to environmental quality. However, in more humid climates, high rates of P used to immobilize Pb (e.g.,  $>15,768 \text{ kg P ha}^{-1}$ ; Weber et al., 2015) poses a water quality



**Fig. 5.** The relative change of lead (Pb) concentrations in the Olsen extracts (A) of soils after different treatments for a 73-day greenhouse experiment compared to control (soil only) and the correlation between Olsen Pb and extractable Pb concentrations by *in vitro* physiologically based extraction test (PBET Pb) (B). Lowercase letters denote the statistical significance ( $p < 0.05$ ) of the differences in the relative changes of Olsen Pb among treatments in the low clay (LC) soils (Olsen Pb was not detected in high clay [HC] soils). N.D.: not detected.

risk, as reflected by extremely high values for agronomic Olsen test and  $P_w$  obtained for amended soils in this study (Horta and Torrent, 2007; Wang et al., 2012). The greater Olsen P in soils treated with finely ground struvite (~7-fold) than granular struvite for both HC and LC soils indicates a dominant impact of particle size on P availability, in line with the much lower dissolution rate of granular than ground struvite (Degryse et al., 2017) and consistent with the relative changes of Olsen P (Fig. 3B). Despite the strong correlation between Olsen P and  $P_w$  for the two urban soils evaluated (Fig. S1), Olsen P was not as sensitive to P amendment type and particle size as  $P_w$  (Fig. 3). Additionally, there may not be as well-defined thresholds of P loss risk based on Olsen P compared to  $P_w$ . Previous studies have shown the ability to use Olsen P to predict P loss can be site-specific. For example, there was no threshold Olsen P concentration at which P losses increased in grassland soils (Watson et al., 2007) whereas elsewhere a threshold of 22 mg L<sup>-1</sup> air-dried soil (14.6 mg kg<sup>-1</sup> soil assuming 1.3 g cm<sup>-3</sup> bulk density) was identified (Jordan et al., 2000), yet others have identified higher thresholds of 20, and 50 mg kg<sup>-1</sup> soil for acidic and alkaline soils, respectively (Horta and Torrent, 2007). The environmental threshold of  $P_w$  has been found to range between 5 and 10 mg kg<sup>-1</sup>, above which there is an appreciable P loss risk to surface waters (Khiari et al., 2000; Pöthig et al., 2010; Wang et al., 2012). In this study,  $P_w$  was orders of magnitude higher with TSP and finely ground struvite, indicating the advantage of maintaining struvite in granular form to minimize P loss risk.

#### 4.3. Crop Pb risk

Though there was no detectable Pb in kale shoots regardless of P amendment treatments and given that kale is a leafy vegetable, using kale root Pb as a proxy for general crop translocation of Pb from soil demonstrates the advantage of struvite over TSP and PR for mitigating crop Pb uptake. Additionally, this study demonstrates relatively low Pb risk entailed in the consumption of leafy vegetable in soils that represent above-median values of soil Pb contamination in Chicago of 198 mg kg<sup>-1</sup>, a 13-fold enrichment over the geogenic background (Cannon and Horton, 2009; USGS). Maximum levels of Pb concentrations in vegetables have been established by the WHO FAO to mitigate Pb exposure (Commission, 2016). For example, a Chicago field survey on Pb accumulation in leafy vegetables revealed appreciable accumulation in the edible shoots of cilantro, coriander and mint, but not in cabbage (Finster et al., 2004). Since maximum permissible Pb concentrations are 0.3 mg kg<sup>-1</sup> for leafy vegetables (Commission, 2016), results demonstrated that kale, consumed as a leafy vegetable, could be safe even when grown in soils conditions where  $P_b$  and  $P_{PBET}$  concentrations are an order of magnitude above geogenic background for the Chicago region (26 mg kg<sup>-1</sup>) (Cannon and Horton, 2009) reflective of U.S. soil geogenic concentrations of 19 mg kg<sup>-1</sup> (Grossman, 2004). Lower Pb accumulation in kale shoots in this study (<0.1 mg kg<sup>-1</sup>) compared to other leafy vegetables such as cilantro have been found to be caused by plant-specific absorption of dust Pb on tissue surfaces (Attanayake et al., 2014; Finster et al., 2004). However, since the kale shoot surfaces in this study were carefully washed with EDTA solution to remove potential Pb-bearing dust, the findings on the safety of kale shoot consumption is based on intra-tissue Pb, as opposed to unwashed kale shoots that may contain Pb-bearing dust (Finster et al., 2004). Lead is likely accumulated in root xylem of kale as demonstrated for other crop species such as carrot, radish, red beet and turnip (Brown et al., 2016). Given the similarity in the biomass of roots and shoots (Table S2), the difference in root Pb among treatments suggests that shared trends of root Pb and  $P_{PBET}$  (PR>struvite>TSP) could reflect similar mechanisms of decreased

$P_{PBET}$  and Pb phytoavailability, which differed by P amendments and soil.

#### 4.4. Additional considerations for struvite as a clean and renewable P amendment

In addition to optimizing trade-offs for human health risk and water quality, struvite offers additional advantages over PR and TSP. Unlike phosphate rock-based fertilizers, including PR itself and TSP, struvite has orders of magnitude lower Cd concentrations (as low as < 0.9 mg Cd kg<sup>-1</sup> P) due to its synthesis via precipitation (McLaughlin et al., 1996; Münch and Barr, 2001; Ronteltap et al., 2007). With proposed regulation in the European Union (EU) and some U.S. states such as California on maximum permissible Cd content of P fertilizers of 8.7 mg Cd kg<sup>-1</sup> P (Ulrich, 2019), many P amendments would not be useable (e.g., median of 63.7 mg Cd kg<sup>-1</sup> P for n = 196 conventional fertilizers [e.g., PR and TSP] in the EU) (Nziguheba and Smolders, 2008). Soil Cd loading entailed by the high P rates used to immobilize Pb would also be a concern (Pizzol et al., 2014) and would likely exceed regulatory limits. For example, even at the relatively low (for Pb immobilization) rate of 2091 kg P ha<sup>-1</sup> used in this study a P fertilizer with a median Cd content of 63.7 mg Cd kg<sup>-1</sup> P (Nziguheba and Smolders, 2008) would translate to 133.2 g Cd ha<sup>-1</sup> in a single application event, 48% greater than the maximum permissible Cd loading rate in Canada and the U.S. state of Washington of 88.9 g Cd ha<sup>-1</sup> yr<sup>-1</sup> (Roberts, 2014). Thus, struvite offers a low-Cd P amendment (Ulrich, 2019).

More broadly, struvite offers re-use of P already in the human trophic chain, as opposed to using P amendments directly derived from geographically limited PR reserves. Recycling P from waste streams in forms such as struvite increases P use efficiency across the agricultural production chain, which globally lags behind other major crop nutrient inputs such as nitrogen (Schneider et al., 2019). While forecasts of “peak phosphorus” within the coming decades are often proposed as a rationale for recycling P in forms such as struvite (Cordell et al., 2009), evidence suggests such forecasts are simplistic and that PR reserves do not risk depletion for at least several centuries (Koppelaar and Weikard, 2013; Scholz and Wellmer, 2013; Ulrich and Frossard, 2014; Vaccari and Strigul, 2011). Increasing reliability of access to P amendments may still provide a benefit of decoupling P amendments from potential volatilities of global P markets. Struvite produced as a by-product of wastewater treatment is a locally available P resource that dovetails with improvements in human sanitation systems (Trimmer and Guest, 2018; Trimmer et al., 2019) and/or could be incentivized as a cost recovery mechanism for P point source mitigation (Margenot et al., 2019). Moreover, struvite supports comparable crop growth as concentrated P fertilizers (e.g., TSP, monoammonium phosphate) (Ahmed et al., 2018; Huygens and Saveyn, 2018), especially at high rates such as those used to immobilize Pb (Hertzberger et al., 2020). The crop availability of P added as struvite is notably higher than PR, particularly for alkaline soils common in urban regions such as the Chicago soils in this study (Meyer et al., 2018). Thus, in the context of urban agriculture, struvite may offer yet another advantage relative to TSP and PR of providing an adequate P source of low loss risk.

## 5. Conclusions

Effective and environmentally sound remediation of contaminated soils in urban regions is a grand challenge of the Anthropocene. Contamination of urban soils with Pb is a well-recognized and widespread risk to human health, in particular with increasing production of food in periurban regions. Traditional approaches to reduce soil Pb risk to humans employ P amendments to immobilize

Pb, but pose high risk to surface waters and/or risk secondary contamination due to relatively high Cd contents of conventional P amendments. We tested the potential of struvite as both amendment and fertilizer for Pb immobilization in alkaline soils and kale growth while decreasing P loss risk. Using Pb-contaminated soils from Chicago under urban agricultural use, this study demonstrates that granular struvite immobilizes Pb as efficiently as PR with minimal P loss risk and entails less Pb accumulation than PR in kale biomass. Lower dissolution rate of granular struvite could better synchronize phosphate release with the dissolution and/or desorption of Pb compounds from soil colloids, leading to greater Pb immobilization. Additionally, the significantly lower Cd content of struvite compared to the conventional P amendments offers a significant and overlooked advantage given the high P rates used to immobilize soil Pb. Thus, struvite is a cleaner and recyclable P amendment compared to conventional P amendments that optimizes trade-offs among soil Pb immobilization, Pb crop uptake risk, and P loss risk. Evaluating struvite for Pb immobilization across greater edaphic variability (e.g., soil pH) and at the field scale is a next step to inform its usage as a cleaner Pb abatement technology to improve environmental quality.

### CRedit authorship contribution statement

**Chunhao Gu:** Data curation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Brianne A. Gates:** Investigation, Writing - review & editing. **Andrew J. Margenot:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Methodology, Writing - original draft, Writing - review & editing, Supervision.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

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