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Determination of Phosphorus Fertilizer Soil Reactions by Raman and Synchrotron Infrared Microspectroscopy

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The reaction mechanisms of phosphate-bearing mineral phases from sewage sludge ash-based fertilizers in soil were determined by Raman and synchrotron infrared microspectroscopy. Different reaction mechanisms in wet soil were found for calcium and magnesium (pyro-) phosphates. Calcium orthophosphates were converted over time to hydroxyapatite. Conversely, different magnesium phosphates were transformed to trimagnesium phosphate. Since the magnesium phosphates are unable to form an apatite structure, the plant-available phosphorus remains in the soil, leading to better growth results observed in agricultural pot experiments. The pyrophosphates also reacted very differently. Calcium pyrophosphate is unreactive in soil. In contrast, magnesium pyrophosphate quickly formed plant-available dimagnesium phosphate.

Index Headings: Fertilizer; Soil; Sewage sludge ash; Phosphate-bearing mineral phases; Raman microspectroscopy; Synchrotron infrared microspectroscopy.

INTRODUCTION

Phosphorus is an essential element for all forms of life. It is necessary for the metabolism process (ADP/ATP), an integral part of the DNA molecule and the cell membrane. For this reason, phosphorus is termed a macronutrient and must be applied in agricultural crop production in the form of phosphorus fertilizers. In general, mineral phosphates from external sources (phosphate rock) are used for fertilizer production. With decreasing phosphate resources¹ and increasing phosphate rock prices, alternative sources of P fertilizers, such as sewage sludge, become of increasing importance as vital phosphate sources.

The separation of organic and inorganic pollutants from sewage sludge is a two-step process that was developed in the sixth and seventh EU framework projects Sustainable and Safe Re-use of Municipal Sewage Sludge for Nutrient Recovery (SUSAN)² and Sustainable Symbiotic Phosphorus Fertilizer Production from Two Renewable Raw Materials (SUSYPHOS). In the first step, the sewage sludge is mono-incinerated to destroy the organic pollutants. In the second step, the heavy metals are separated by thermochemical treatment of the sewage sludge ash (SSA) with Cl-donors [CaCl₂ (3), MgCl₂, HCl (4)] in a rotary kiln at approx. 1000 °C. During this

thermochemical treatment, new P-bearing mineral phases are also formed.³

The SSA-based fertilizers, which were prepared with CaCl₂ or HCl, respectively, contain chlorapatite [Ca₅(PO₄)₃Cl] as the major P phase, whereas thermochemical treatment with MgCl₂ results in formation of chlorapatite and trimagnesium phosphate [Mg₃(PO₄)₂]. The plant availability of these fertilizers was tested in agricultural pot experiments^{5,6} with the result that the SSA-based fertilizers, which contain trimagnesium phosphate, consistently gave the highest grain yields. Calcium and magnesium are in the same group of the periodic table, and the properties of their phosphates should not strongly diverge. Although there has been much research on calcium phosphates in the context of agriculture, there has not been much research on magnesium phosphates in agricultural investigations. Mondrzak-Rosenberg and Hagin⁷ showed that magnesium phosphates [Mg₃(PO₄)₂ and Mg₂PO₄F] have only a slightly lower effectiveness than the commercial fertilizer monocalcium phosphate [Ca(H₂PO₄)₂·H₂O].

The chemical form of soil phosphorus has been analyzed by many different spectroscopic techniques (XANES, P-NMR, infrared and Raman spectroscopy) in the past.⁸ All these methods have distinct advantages and disadvantages. The first infrared study in this area by Beaton et al.⁹ used a dispersive infrared spectrometer to identify fertilizer-soil reactions of water-soluble P fertilizers. X-ray absorption near edge structure spectroscopy has a significant advantage in that it is unaffected by the host matrix (i.e., soil or other fertilizer components), but if there is more than one compound of an element in a sample, it is difficult to determine the chemical state.

Previously, we successfully used mid- and far-infrared spectroscopy¹⁰ and Raman microspectroscopy,¹¹ respectively, for the determination of phosphate phases in SSA-based fertilizers. More recently, we applied both Raman microspectroscopy and synchrotron infrared microspectroscopy to visualize the P fertilizer soil reactions on a microscale. These latter techniques have the advantage that they have a lateral resolution down to the diffraction limit (~300 nm with a 514 nm Raman excitation laser and ~5–10 μm with synchrotron radiation infrared spectroscopy), allowing for the detection and characterization of small phosphate particles. In this paper, we report the microspectroscopic analysis of P fertilizer soil reactions of SSA-based fertilizers and related reference phosphates to clarify possible differences in the reaction mechanisms of calcium and magnesium (pyro-) phosphates.

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FIG. 1. Raman chemical images ($80\ \mu\text{m} \times 65\ \mu\text{m}$; blue: low concentration; red/orange: high concentration) and (a) extracted spectra for different compounds of soil + SSA-Mg after 28 days of wetting, and (b) related reference spectra.

FIG. 2. Normalized Raman spectra of pure chlor- (black) and hydroxyapatite (blue) and chlorapatite wetted for 28 days (red) and 56 days (green) with soil.

MATERIALS AND INSTRUMENTATION

The SSA used in this work was sourced from an incineration plant in the Netherlands and originated from wastewater treatment plants (WWTPs) primarily using Fe salts for phosphate precipitation. Thermochemical treatments of SSA with calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; extra pure, Merck, Darmstadt, Germany) and magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; cryst., Merck, Darmstadt, Germany), respectively, were carried out in a rotary corundum furnace (Thermal Technology, RT1700, Bayreuth, Germany) for approx. 30 min at $950\ ^\circ\text{C}$ (hereafter, the products of this treatment are referred to as SSA-

FIG. 3. Raman chemical images ($80\ \mu\text{m} \times 105\ \mu\text{m}$; blue: low concentration; red/orange: high concentration) and (a) extracted spectra for different compounds of SSA-Mg + H_2SO_4 and (b) related reference spectra.

FIG. 4. Visible image, infrared chemical images (left, $65\ \mu\text{m} \times 30\ \mu\text{m}$, blue: low concentration; red/orange: high concentration), and extracted spectra (middle, integrated areas are red shaded) for different compounds of soil + SSA-Mg + H_2SO_4 after 28 days of wetting and related reference spectra (right).

Ca and SSA-Mg, respectively). Sewage sludge ash treated with calcium chloride and SSA-Mg was also post-treated with 20% H_3PO_4 and H_2SO_4 solution, respectively, to form more plant-available phosphate phases. Upon entry to Australia, all SSA samples were subjected to ^{60}Co gamma irradiation, as required by customs. After irradiation, calcium and magnesium pyrophosphates were found in some samples.¹¹ Other mineral phases were not modified. Furthermore, a commercial fertilizer, triple super phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] and the following reference phosphates were used: $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_3(\text{PO}_4)_2$, $\text{Mg}_3(\text{PO}_4)_2$ (all three: p.a., Sigma-Aldrich, Germany), $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (both: p.a. Alfa-Aesar, Karlsruhe, Germany). Hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$] was precipitated from aqueous solutions of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$. The pH was adjusted to 9 with concentrated

NH_4OH solution. Calcium and magnesium pyrophosphates were precipitated from aqueous solutions of sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 99%, AnalaR, England) with calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, p.a., Sigma-Aldrich, Australia) and magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, p.a., Merck, Australia). After precipitation the solid material was filtered and dried at $200\ ^\circ\text{C}$ in a drying oven. Chlorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$] was thermally prepared from $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CaNO}_3 \cdot 4\text{H}_2\text{O}$, respectively, in a platinum crucible at $1000\ ^\circ\text{C}$ (all chemicals: p.a., Sigma-Aldrich, Germany).

Soil [30 g; $\text{pH}(\text{H}_2\text{O}) = 7.97$; $\text{pH}(\text{CaCl}_2) = 7.12$] was mixed with 5 g of fertilizer and 10 g of water and stored in plastic boxes at $20\ ^\circ\text{C}$ for 4–56 days. After different reaction times, parts of the samples were dried in a fume cupboard at $20\ ^\circ\text{C}$ and analyzed by Raman and infrared microspectroscopy. For

FIG. 5. (a) Visible image, infrared chemical images (95 $\mu\text{m} \times 65 \mu\text{m}$; blue: low concentration; red/orange: high concentration), and extracted spectrum of soil + TSP after 28 days of wetting (integrated area is red shaded), and (b) infrared spectra of pure TSP.

clarification of the P fertilizer soil reactions of SSA-based fertilizer mixtures of reference phosphates with soil were also analyzed under the same experimental procedure.

Furthermore, the mineral phases of an Australian sandy soil and an alluvial soil from an area periodically exposed to river floods were analyzed by synchrotron infrared microspectroscopy.

Raman images and spectra were collected with a Renishaw InVia confocal micro-Raman system with an Ar ion laser (514 nm, approx. 300 mW) with the line focus fast-map option. The system was operated with the software WIRE 2.0. The samples were mapped without further sample preparation with a lateral step of 5 μm and a nominal line focus width of 1 μm . The spectral resolution of the obtained spectra was 1 cm^{-1} . Raman chemical images were constructed by color-coding the intensities of the major bands in the spectra to the background at 800 cm^{-1} (blue: low concentration; red/orange: high concentration). Four representative areas of approx. 80 $\mu\text{m} \times 70 \mu\text{m}$ were mapped for each sample.

Synchrotron infrared chemical images were collected with a Bruker Hyperion 2000 microscope (36 $\times$ objective) coupled to a Bruker Vertex 80v spectrometer at the infrared microspectroscopy beamline of the Australian Synchrotron. The samples were mapped in transmission mode after compression between two diamond windows (spectral resolution 4 cm^{-1} ; 64 scans were co-added per spectrum). An aperture of 5 $\times$ 5 μm^2 and a step size of 5 μm were used for mapping. Infrared chemical images were constructed by color-coding the integrated area of selected bands, which do not overlap with bands of other compounds, in the spectra (blue: low concentration; red/orange: high concentration). Again, four representative areas of approx. 80 $\times$ 60 μm^2 were mapped for each sample.

From the point with the highest intensity (red dot or area) of the Raman and the infrared chemical images, a single spectrum was extracted and displayed next to the chemical image.

RESULTS AND DISCUSSION

Figure 1 shows the Raman chemical images, extracted spectra, and reference spectra of the dried mixture of soil + SSA-Mg after 28 days of wetting. Sewage sludge ash treated with magnesium chloride contained the P-phase trimagnesium phosphate and hydroxy/chlorapatite before wetting.¹¹ After wetting, trimagnesium phosphate, quartz (SiO_2), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and hydroxy/chlorapatite were detected. Quartz and gypsum in the soil were identified and imaged using their major Raman bands at 460 cm^{-1} and 1008 cm^{-1} , respectively. The trimagnesium phosphate (Raman band at 978 cm^{-1}) of the SSA-based fertilizers did not show any changes in chemical structure even after a long period of wetting. Furthermore, a mixed hydroxy/chlorapatite phase was determined in the mixture. As reported in a previous paper,¹¹ SSA-

FIG. 6. Schematic of determined reactions of calcium and magnesium (pyro-) phosphates on a slightly alkaline soil.

FIG. 7. Visible image, infrared chemical images ($85\ \mu\text{m} \times 75\ \mu\text{m}$; blue: low concentration; red/orange: high concentration), and extracted spectra for different compounds of a sandy soil (integrated areas are red shaded).

based fertilizers contain a hydroxy/chlorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH/Cl}$], which is substituted with traces of different elements, resulting in defects of the lattice and the observed broad range of resultant Raman bands ($950\text{--}963\ \text{cm}^{-1}$). Raman spectroscopic analysis of wetted mixtures of pure chlorapatite and hydroxyapatite with soil showed that chlorapatite converted almost to hydroxyapatite after 56 days, as evidenced by a shift of Raman band from 960 to $963\ \text{cm}^{-1}$ (see Fig. 2), whereas for hydroxyapatite no reaction was detectable.

Figure 3 shows the Raman chemical images, extracted spectra, and reference spectra of the fertilizer SSA-Mg + H_2SO_4 . The fertilizer contains gypsum, $(\text{Na,K})\text{AlSi}_3\text{O}_8$,¹² magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), and hydroxy/chlorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH/Cl}$]. The extracted spectra of $(\text{Na,K})\text{AlSi}_3\text{O}_8$, $\text{Mg}_2\text{P}_2\text{O}_7$, and $\text{Ca}_5(\text{PO}_4)_3\text{OH/Cl}$ also contain Raman bands of gypsum.

In Fig. 4, the visible image, infrared chemical images, extracted spectra, and reference spectra of soil + SSA-Mg + H_2SO_4 after 28 days of wetting are displayed. The red areas in the extracted spectra show the bands for which the integrated absorption areas were used to construct each infrared chemical image. After 28 days of wetting, dimagnesium phosphate ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), hydroxy/chlorapatite, Ca/MgSO_4 , and quartz were detected. Calcium and magnesium sulfates

developed from the chemical post-treatment of the fertilizer with sulfuric acid. Magnesium pyrophosphate converted to the readily plant-available dimagnesium phosphate. Conversely, the calcium pyrophosphate of the other samples did not show any reaction even after 56 days. Hossner and Melton¹² have also reported that calcium pyrophosphate does not hydrolyze in soil. In contrast, ammonium pyrophosphate¹³ and sodium pyrophosphate¹⁴ quickly form orthophosphates during wetting in soils. Thus, $\text{Mg}_2\text{P}_2\text{O}_7$ in contrast to $\text{Ca}_2\text{P}_2\text{O}_7$ is a reactive pyrophosphate that forms plant-available P phases.

Figure 5a shows the visible image, infrared chemical image, and related extracted spectrum of soil + triple super phosphate [TSP; $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] after 28 days of wetting. For comparison, in Fig. 5b, an infrared spectrum of pure TSP is displayed. After wetting, all monocalcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] converted to dicalcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). Lindsay et al.¹⁵ and Sample et al.¹⁶ also showed by x-ray diffraction analysis that dicalcium phosphate is the major product after a short period of wetting of TSP/monocalcium phosphate in soils.

For clarification of the P fertilizer soil reactions of SSA-based fertilizer, the same experimental procedures but with mixtures of reference phosphates with soil were carried out. Figure 6 shows the reactions of the calcium and magnesium

FIG. 8. Visible image, infrared chemical images ($75\ \mu\text{m} \times 50\ \mu\text{m}$; blue: low concentration; red/orange: high concentration), and extracted spectra for different compounds of an alluvial soil (integrated areas are red shaded).

(pyro-) phosphates that were determined. The calcium and magnesium phosphates react differently. As outlined above, calcium pyrophosphate did not react in soils, whereas magnesium pyrophosphate forms dimagnesium phosphate. The plant availability of the displayed phosphates in Fig. 6 decreases from left to right. Monocalcium phosphate initially reacted to give dicalcium phosphate, and after a longer time, further reaction produced tricalcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ and finally the resultant hydroxyapatite, the phosphate with the lowest plant availability. Also, chlorapatite reacted during wetting to produce hydroxyapatite in soils. Dimagnesium phosphate, however, only changes over time to trimagnesium phosphate. Klement¹⁷ reported that magnesium phosphates cannot form an apatite structure; thus, the advantage of the magnesium phosphates is that the end product in soil is trimagnesium phosphate, which still is plant available. Conversely, after a long period, all calcium orthophosphates convert to the non-plant-available hydroxyapatite.

Additionally, we tried to detect P phases in pure soil by Raman and synchrotron infrared microspectroscopy. Raman microspectroscopy measurements (with 413, 532, 633, and 785 nm lasers) of soils were impossible due to high fluorescence, so the only information comes from synchrotron FT-IR with its limited lateral resolution. Figures 7 and 8 show the visible image, infrared chemical images, and extracted spectra of a sandy and an alluvial soil, respectively. In the sandy soil, two mineral phases were detected: quartz (darker area) and the aluminosilicate kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$, brighter area]. The alluvial soil contains calcium carbonate (CaCO_3), quartz, and montmorillonite $[(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$.¹⁸ In the extracted spectra of CaCO_3 , also quartz and montmorillonite are visible. Due to the low mass fraction of phosphorus in the soil (<0.5%) no P-phases were detectable. The greater lateral resolution of Raman microspectroscopy would probably solve this problem, but a 1064 nm-based system of the type now becoming available would be required to overcome the fluorescent background.

CONCLUSIONS

The differences in fertilizer-soil reactions of calcium and magnesium (pyro-) phosphates, respectively, were successfully determined by Raman and synchrotron infrared microspectroscopy. All calcium orthophosphates convert to hydroxyapatite in soil over time. On the other hand, magnesium orthophosphates react only as far as trimagnesium phosphate because of their inability to form an apatite structure. Thus, for the magnesium-based compound, phosphorus remains in a plant-available form. Also, the pyrophosphates of calcium and magnesium react very differently. Calcium pyrophosphate did not react in soil, whereas magnesium pyrophosphate quickly forms dimagnesium phosphate. However, P phases in soil were not detectable with this technique due to the low mass fraction of <0.5% phosphorus. Furthermore, mineral phases of soils were detectable by infrared microspectroscopy.

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