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Effects of Long-Term Wastewater Application on Chemical Properties and Phosphorus Adsorption Capacity in Soils of a Wastewater Land Treatment System

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The buildup of phosphorus (P) in the soil is a major factor limiting the operating life of a wastewater land treatment system. In this study, we evaluated changes of chemical properties, P profiles, and adsorption isotherms in the soils of a Muskegon wastewater land treatment system, which has received wastewater for ~30 years. It was found that the pH in the 15-cm topsoil increased from ~5–6 in 1973 to ~7.4–7.8 in 2003; a large amount of salt (e.g., Ca, Mg) in wastewater was adsorbed by the soil; the soil Al content (either exchangeable or oxalate extractable) decreased, while the oxalate-extractable Fe content remained at the same level. Ca-bound P accounted for $\geq 70\%$ of the total P adsorbed in the soil. The soil P adsorption capacity increased and was positively correlated with the concentration of exchangeable Ca in the soil. A higher concentration of exchangeable Ca was found in the 15-cm topsoil, where a higher total organic carbon was present. More P was accumulated in the upper soil than in the deeper soil. The adsorption of Ca in wastewater by the soil may extend the life expectancy of the Muskegon land treatment system.

Introduction

Land disposal of municipal and industrial wastewater (with or without secondary treatment) has been applied effectively in the United States for decades. Land treatment systems can satisfactorily remove nutrients (e.g., phosphorus and nitrogen) that otherwise are difficult to degrade by biological treatment systems. On the basis of long-term observation, wastewater applications are usually limited by nitrogen or hydraulic considerations on a short-term basis, but phosphorus (P) application may be a limiting factor over the life of a land treatment system (1). In land treatment systems, P is removed from wastewater effluents primarily by sorption (including precipitation, adsorption and absorption) in the soil. The soil capacity reacting with applied P and the buildup of P in the soil are the two critical parameters for predicting the life expectancy of a land treatment system.

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In the past, many researchers developed several kinetic models (2–4) that are very useful for design and operation of a land treatment system. However, these models and previous studies did not focus on the prediction of the life expectancy of a land treatment system. To estimate the life expectancy of a land treatment system, the key issue is to elucidate when P movement is likely to occur and when/how this can be predicted. In fact, this issue has puzzled both environmental and agricultural engineers for a long time. While some recent studies have focused on P transfer to subsurface flow (5, 6), no consensus has been reached on issues related to P leaching. Hesketh and Brookes (7) found that the dissolved P concentration in tile drainage water increased dramatically (from 0.15 to 2.75 mg/L) when the critical soil test P (STP) value in the plow layer was above 60 mg/kg Olsen P (termed the *change point*) for a silt loam. Schoumans and Groenendijk (8) reported that when the P concentration of the leachate of the topsoil (0–20 cm) needs to be ≤ 0.1 mg P/L, the P_w (water-soluble P) values must be reduced to 5–7 mg/kg (low soil P fertility). Sinaj et al. (9) pointed out the risks associated with assessing potential P losses on the basis of P mobility in the topsoil alone. McDowell et al. (10) recommended that the P sorption strength derived from the monolayer Langmuir equation be used to estimate the potential for P loss in subsurface flow when the simpler STP is unclear or unsuitable.

For both modeling and prediction of P leaching from soil, the maximum P sorption capacity of the soil (P_{max}) may be one of the most critical parameters. The P_{max} depends on the texture, oxides of Al, Fe, Ca, and Mg compounds, and the pH of the soil (3, 11). In the literature, P_{max} is assumed to be constant for soil at a certain location and would not change with time. This assumption could be wrong for a land treatment system, where soil properties will change with the application of wastewater. Will these changes greatly affect the P_{max} ? How does the P_{max} change with time? Very limited information is available on these issues.

The objectives of this study were to evaluate (1) the effects of long-term wastewater application on major chemical properties and P sorption capacity of the soil of a wastewater land treatment system at Muskegon County, MI and (2) the possible relationships among several profiles, that is, different P forms, exchangeable Ca, and 1-day P_{max} along the depth of the Muskegon soils. In addition, we further evaluated effects of changes in major soil properties on soil P leaching potential and the life expectancy of the Muskegon system.

Material and Methods

Sites Description. The Muskegon County wastewater land treatment system has been operating since 1974 (Table 1). The facility is located on 4452 ha of sandy, unproductive soil with 53 circular fields (total area = 2104 ha farmland) on the site (12–14). The system consists of collection, transmission, aeration, storage, irrigation, soil, crop, and drainage components. The facility currently treats 98410 m³/d (26 MGD) of wastewater. About 50% of the wastewater comes from a paper mill, ~25% from other industries, and ~25% from domestic wastewater. Before it is sprayed on the soil, wastewater is pretreated in full-mixing basins and aerating-settling basins, and then stored in two storage lagoons (345 ha each). The pretreatment processes remove >90% of the original organic compounds and ~30% of P in the wastewater (Tables 1 and 3) (14).

The major soil types of the site are categorized as Rubicon, Roscommon, Au Gres, and Granby sands (Tables 1 and 2). Originally, these soils were very friable and strongly acidic

TABLE 1. Some Design and Operational Parameters of the Muskegon System (1, 13, 14)

| | |
|--------------------------------------|--|
| av wastewater (WW) flow | $Q = 98\,410\text{ m}^3/\text{d}$ (26 MGD) in 2004 (design capacity = $158\,970\text{ m}^3/\text{d}$, 42 MGD) |
| WW applied in 1974–2001 (cm) | Rubicon soil = 12 055; Roscommon = 8666; AuGres = 9601 |
| P loading (kg/m^2) | Rubicon soil = 0.12; Roscommon = 0.03; AuGres = 0.09 |
| crop type | corn, soybean, and alfalfa, rotated yearly in each irrigation field |
| irrigation systems | sprinkler (center pivot), time on/off varies; usually, the sprinkler will rotate one circle per day |
| WW application rate | Rubicon soil (best) and Roscommon (2nd best) = 2.5 cm/d for ~180 d; AuGres = 0.8–1.5 cm/d for 180 d; whole site av weekly rate = 7.6 cm for ~180 d |
| annual precipitation/evaporation | av rainfall in 1974–2001 = 85.1 cm; annual evaporation = 76.2 cm |

TABLE 2. Topsoil Physical Properties in 1973 (13)

| soil type | composition | hydraulic conductivity (cm/h) | bulk density (g/cm^3) | volumetric water content (%) |
|-----------|--------------------------------|-------------------------------|---|------------------------------|
| Rubicon | medium, fine sand ^a | 32 | 1.4 | 19 |
| AuGres | medium, fine sand | 38 | 1.2 | 25 |
| Roscommon | medium, fine sand | 34 | 1.2 | 30 |
| Granby | medium, fine sand + 1% clay | 16 | 1.4 | 25 |

^a Sand diameter ranging from 100 to 500 μm .

TABLE 3. Wastewater Characteristics in Influent and Effluent of the Muskegon System^a

| parameter | plant influent | influent of each field | plant effluent |
|----------------------------|-----------------|------------------------|-----------------|
| BOD (mg/L) | 257 ± 3.5 | 5.15 ± 4.5 | <2 |
| pH | 7.08 ± 0.24 | 8.5 ± 0.34 | 7.5 ± 0.31 |
| total P (mg/L) | 3.06 ± 0.22 | 1.88 ± 0.18 | 0.03 ± 0.01 |
| SO_4^{2-} (mg/L) | 267 ± 7.68 | 337 ± 11.68 | 184 ± 8.35 |
| NH_3 (mg/L) | 7.24 ± 0.85 | 1.32 ± 0.17 | 0.09 ± 0.03 |
| Ca^{2+} (mg/L) | NM | 123 ± 8.2 | 119 ± 11.5 |
| Mg^{2+} (mg/L) | NM | 20 ± 2.8 | 28 ± 3.3 |
| $\text{Fe}^{2+/3+}$ (mg/L) | NM | <0.5 | <0.5 |
| Al^{3+} (mg/L) | NM | <0.01 | <0.01 |

^a Plant influent: wastewater before any pretreatment. Influent of each field: the Muskegon plant uses the sample taken from the transient ditch between the lagoon outlet and the pump station as the influent of each field. Plant effluent is sampled from the final outfall of the plant. The BOD, pH, total P, SO_4^{2-} , and NH_3 values are the monthly averages \pm standard deviations that were obtained from a routine Muskegon report to the state of Michigan (September 2003). Ca^{2+} , Mg^{2+} , $\text{Fe}^{2+/3+}$, and Al^{3+} are measured results of a composite sample of three grab samples taken in this study. NM = not measured.

(pH 3–5), except the Granby, which is neutral at the top and slightly acidic at the subsoil (13). The soil distribution of the sites is very uniform (12). The mechanical composition, soil water characteristics, bulk density, and hydraulic conductivity are remarkably similar among different samples taken from different fields of the same type of soil (12, 13). We tested variations of the concentrations of exchangeable Na, K, Mg, and Ca, Bray-1 P, and total organic carbon (TOC) in the top 60 cm soils sampled from fields 5, 6, 8, 9, 17, 18, 28, 29, and 34. We found that each type of soil also has very similar chemical properties, even though they may be sampled from different fields, which allows use of only a few samples to obtain the information with negligible error.

Soil Sampling and Preparation. Soil samples were taken from fields 6 (Rubicon), 29 (Roscommon), and 17 (AuGres) using a $5 \times 15\text{ cm}$ ($2 \times 6\text{ in.}$) soil sampling kit (AMS Inc, ID). No soil samples were taken from fields of the Granby soil, because little wastewater was applied on them due to their low hydraulic conductivity. At each field, we selected three locations along the line toward the center of the field that were 20 m away from each other; we then took soil core samples along the depth of the soil. Soil samples were divided into 15-cm depth increments from the surface (0 cm) to the groundwater table (about 244–274 cm). In addition, the

Muskegon plant provided some of the original soil sampled in 1973, 1976, and 1977. These soil samples were taken using a hydraulic-powered soil-sampling machine; once in the laboratory, they were separated according to their depth and then dried, sieved, and stored in glass bottles in a dark room at the Muskegon plant.

Once in the laboratory, each of these soil samples was dried at room temperature, passed through a 2-mm sieve, and stored in a glass jar (bottle) with a cap. In this study, one composite soil sample was made for each increment by mixing the same quantity of the three sieved soil samples that were taken at the same depth.

P Adsorption Isotherms. P sorption isotherms were obtained by continuously agitating batch reactors for 24 h (15). Each batch reactor was a 50-mL equilibration tube containing 25 mL of 0.01 M CaCl_2 solution, 2 g of air-dried soil, and a specified P concentration of 0.5, 1, 2, 5, 7, or 10 mg/L, respectively. For a long-term sorption test, two sets of the initial P concentration in the batch reactors (tubes) were 0.5, 1, 2, 5, 7, 10 mg/L and 5, 7, 10, 20, 30, 40 mg/L. For each P concentration, multiple batch reactors were prepared; at each predetermined time interval, one reactor was removed from the rotating box (with a 30 rpm rotating speed) and sacrificed for sample analysis. The predetermined time intervals were 2, 3, 24, 48, and 100 h for the first set of the test and 300, 1000, and 2000 h for the second set.

Chemicals and Analytical Methods. Unless otherwise indicated, all aqueous solutions were prepared with deionized water (DI) with resistivity between 15 and 18 M Ω cm (Barnstead Nanopure series 550, Barnstead/Thermolyne Co., Dubuque, IA). All commercially available chemicals were from VWR Scientific and were ACS (American Chemistry Society) or high-performance liquid chromatography (HPLC) grade and used as received. All tests and analyses were conducted at room temperature ($24 \pm 1\text{ }^\circ\text{C}$). In this study, the average of the triplicates ($n = 3$) of a composite soil (sampled at three locations) at each depth is reported.

We define 1 M NH_4Cl -extractable P as easily removable or labile P (16), NaOH-extractable P as Fe-/Al-associated P, and HCl-extractable P as Ca-/Mg-associated P (17). A 2-g air-dried soil sample was sequentially extracted with 20 mL of 1 M NH_4Cl (adjusted to pH 7.0) with 2 h of shaking, 0.1 M NaOH with 17 h of shaking, and 0.5 M HCl with 24 h of shaking. After each extraction, the contents were centrifuged for 15 min at 3620g and filtered through a 0.45- μm filter (Pall Gelman Lab., Ann Arbor, MI). The inorganic P in the aforementioned soil extracts was determined colorimetrically

TABLE 4. Changes in Chemical Properties of 15-cm Topsoils^a

| soil type | properties for 1973 vs 2003 (\pm standard deviation) | | | | | | | | |
|-----------|---|-----------------|-----------------|--------------------|----------------|--------------------|------------------|----------------|-------------------------------|
| | pH | Fe ^b | Al ^c | ex-Ca ^d | total Ca | ex-Mg ^e | TOC ^f | Bray-1 P | P _{max} ^g |
| Rubicon | 5.0 | 850 | 360 | 82 | 1800 | 8 | 0.93 | 26 | 160 |
| | 7.8 \pm 0.34 | 784 \pm 20 | <DL | 1205 \pm 45 | 2800 \pm 79 | 72.5 \pm 15 | 1.74 \pm 0.11 | 33 \pm 3.2 | 420 \pm 24 |
| AuGres | 5.5 | 1189 | 872 | 310 | 1800 | 49 | 1.14 | 11.5 | 115 |
| | 7.4 \pm 0.26 | 1300 \pm 47 | <DL | 1159 \pm 36 | 2700 \pm 90 | 76.5 \pm 11 | 1.84 \pm 0.15 | 17.5 \pm 1.1 | 454 \pm 20 |
| Roscommon | 5.6 | 720 | 560 | 420 | 2700 | 78 | 1.48 | 9.6 | 137 |
| | 7.8 \pm 0.22 | 673 \pm 23 | <DL | 1359 \pm 47 | 4180 \pm 110 | 98.5 \pm 17 | 2.68 \pm 0.14 | 13.8 \pm 1.1 | 312 \pm 17 |

^a All units are mg/kg of soil, except pH (unitless). Data on top are for 1973 and those on the bottom are for 2003 (\pm standard deviation). pH, Ca, Mg, P, and P_{max} values for 1973 are from an U.S. EPA report (13). Other data (Fe, Al, TOC) for 1973 were measured in this study with the original soil sampled during 1973 (provided by the Muskegon plant). All data for 2003 were obtained from this study. ^b Oxalate-extracted Fe. ^c Oxalate-extracted Al; <DL = lower than the detection limit. ^d Exchangeable Ca. ^e Exchangeable Mg. ^f Total organic carbon. ^g One-day maximum P sorption capacity.

using the ascorbic acid reduction method (18). Total P was determined by the perchloric acid digestion method (19).

Soil pH was determined by measuring the pH of a 1:2 soil and water suspension with an ORION semimicro pH probe (20). Oxalate-extractable Al (Ox-Al), Fe (Ox-Fe), and P (Ox-P) were determined by extracting soil with 0.2 M oxalic acid + 0.2 M ammonium oxalate (pH 3.0) (21); the suspension was equilibrated for 4 h in the dark with continuous shaking, centrifuged, filtered through a 0.45- μ m filter, and analyzed for Al, Fe, and P. Exchangeable-Al was extracted with 1 N KCl with 2 h of shaking (22). Al (Ox- and exchangeable-Al) was determined using a spectrophotometer (Hach DR/2000). Fe was analyzed with an atomic adsorption spectrometer (Model 3110, Perkin-Elmer) at a wavelength of 248.3 nm. P was measured with a spectrophotometer (Spectronic 21, Milton Roy) at a wavelength of 882 nm.

Exchangeable Ca and Mg were measured by an HPLC system (Dionex DX-500, Dionex Co., Sunnyvale, CA). To prepare samples, 5 g of soil was mixed with 1 M ammonium acetate (pH 7). The mixture was shaken end-over-end for 5 min (23) and then filtered with a 0.45- μ m filter. The filtrate was then used for HPLC analysis. To measure Ca²⁺ and Mg²⁺, a conductivity detector (CD 20) and a self-regenerating suppressor (SRS, CSRS-II 4-mm) with a 100-mA current were used. An IonPac CG12A 4 \times 50 mm precolumn and a 4 \times 250 mm separation column were used with 22 mM H₂SO₄ eluent at a flow rate of 1.2 mL/min. Total organic matter was estimated by the loss-on-ignition method (24). The CaCO₃ content of the soil samples was determined as per the standard procedure (25).

Results and Discussion

Changes in Soil Chemical Properties. As shown in Tables 3 and 4, the chemical properties of the Muskegon soils have changed, probably due to the long-term application of the wastewater with a high pH (~8.5) and a high salt content (Ca, Mg, etc.). The soil pH increased from 4 to 6 in 1973 to >7 in 2003 (Table 4), indicating that the soil might have adsorbed some OH⁻ ions or that H⁺ ions in the soils might have been replaced by other cations, such as Na, K, Ca, Mg, in the wastewater.

The concentration of oxalate-extracted Fe in both 1973 and 2003 is the same order of magnitude (Table 4). Since the concentration of Fe in both influent and effluent is <0.5 mg/L (Table 3), it is possible that the Fe precipitates still remain in the soil. Unlike Fe ions, the concentration of oxalate-extracted Al in 2003 is lower than the detection limit (Table 4). Additional measurements at different depths of the soils indicate that there is no measurable exchangeable Al in the deeper soils in 2003. Therefore, the extractable Al was lost through the drainage water. The difference between the Fe and Al accumulation at the Muskegon site may be due to the different effects of the soil pH on their activity, which

is maintained by their oxides and hydroxides, and will decrease ~1000-fold for each unit increase in pH (26). When the pH is above 7, the activity of Al³⁺ is below 10⁻¹⁰ M and Fe³⁺ is below 10⁻¹⁶ M (26). Most of the Fe ions form some insoluble minerals, while the Al ions, besides forming some insoluble minerals, become soluble as Al(OH)₄⁻ and Al(OH)₅²⁻ (26), which will leach out in the drainage water.

In this study, the exchangeable Ca and Mg were selected as the parameters to represent the Ca and Mg adsorbed in the soil. This kind of Ca and Mg is water soluble and rapidly exchangeable, so they are ready to react with phosphate (27, 28). As shown in Table 4, the exchangeable Ca concentrations in 2003 are almost 10 times higher than those in 1973; the exchangeable Mg in the soils also increased, especially in Rubicon soil. The total Ca concentration did not increase as much as exchangeable Ca. It seems that the soils have reached their maximum Ca or Mg adsorption capacity because the Ca or Mg concentrations in influent and effluent are almost the same (Table 3). In addition, we found that the exchangeable Ca adsorbed in the 15-cm topsoil of Rubicon (field 6) was 82, 895, 1070, and 1205 mg/kg of soil for soils sampled in 1973, 1976, 1977, and 2003, respectively. Therefore, the soil at the site can achieve its equilibrium for Ca adsorption after just a few years of wastewater application.

Although the Ca adsorption capacity of sandy soil is quite low, the Muskegon soil can accumulate >1300 mg/kg exchangeable Ca in the 15-cm topsoil. This may be because the increase in the soils' pH and TOC results in a great increase in the soils' Ca adsorption capacity by promoting some chemical reactions of Ca within the soils (29). In addition, ~45% [(337-184)/337, Table 3] of the sulfate in wastewater was removed by the system, which could increase the soil surface charge and thereby facilitate the Ca adsorption (1, 27-30).

Due to the complexity of the soil environment, however, the above analyses may not be correct. For example, the adsorbed sulfate may be reduced to sulfide by sulfate-reducing bacteria, which would change the cation exchange capacity of the soil. Also, it is not known how the soil P adsorption capacity or the cation exchange capacity changes as a function of the soil TOC. Further studies are needed to evaluate why Ca accumulates at the Muskegon site and whether this Ca accumulation phenomenon exists in other less sandy soils as well.

Profiles of Different Forms of P, Exchangeable Ca, and P_{max}. The concentration of labile P is very low in the Muskegon soils (Table 5). There is no measurable labile P at the depth of 137-213 cm in AuGres soil. The statistical analyses indicate that the labile P distribution is not correlated with that of the total P or Fe-bound P, or Ca-bound and/or Mg-bound P (Ca/Mg-bound P) at the Muskegon site (data not shown). This is particularly true for Roscommon soil (field 29), where the labile P in the deeper soil is higher than that in the topsoil,

TABLE 5. Profiles of Different Forms of P (mg/kg ± SD) in Muskegon Soils^a

| depth, cm | labile P | Fe-bound P | Ca-/Mg-bound P | total P |
|------------------|------------------|--------------|----------------|---------------|
| Rubicon | | | | |
| 0–15 | 6.23 ± 0.36 | 9.82 ± 1.52 | 276.71 ± 1.81 | 305.91 ± 5.78 |
| 15–31 | 2.68 ± 0.19 | 15.42 ± 2.91 | 287.24 ± 3.90 | 321.09 ± 4.10 |
| 31–46 | 2.13 ± 0.12 | 12.22 ± 1.58 | 213.53 ± 2.07 | 241.50 ± 4.94 |
| 46–61 | 1.71 ± 0.07 | 17.56 ± 1.85 | 199.77 ± 4.56 | 231.15 ± 1.20 |
| 61–91 | 1.43 ± 0.01 | 11.76 ± 2.19 | 128.20 ± 2.54 | 154.73 ± 3.20 |
| 107–122 | 0.9 ± 0.01 | 6.97 ± 1.22 | 58.75 ± 3.17 | 75.06 ± 4.15 |
| 137–152 | 0.96 ± 0.01 | 7.12 ± 1.36 | 53.94 ± 1.49 | 64.43 ± 2.21 |
| 168–183 | 0.78 ± 0.05 | 6.23 ± 1.12 | 61.66 ± 4.72 | 71.27 ± 3.86 |
| 198–213 | 0.75 ± 0.07 | 6.54 ± 1.25 | 59.88 ± 1.17 | 66.60 ± 3.38 |
| AuGres | | | | |
| 0–15 | 3.12 ± 0.12 | 23.92 ± 2.77 | 257.87 ± 0.38 | 301.29 ± 1.83 |
| 15–31 | 1.2 ± 0.11 | 28.06 ± 2.87 | 167.41 ± 0.41 | 201.51 ± 2.13 |
| 31–46 | 1.05 ± 0.04 | 44.62 ± 4.68 | 73.39 ± 1.13 | 130.80 ± 0.27 |
| 46–61 | 0.93 ± 0.01 | 28.06 ± 5.69 | 62.01 ± 1.41 | 101.73 ± 2.44 |
| 61–91 | 0.67 ± 0.01 | 14.94 ± 0.74 | 78.65 ± 1.66 | 92.70 ± 2.41 |
| 107–122 | 0.66 ± 0.01 | 19.89 ± 0.07 | 52.04 ± 0.67 | 70.04 ± 0.06 |
| 137–152 | <DL ^b | 5.66 ± 0.90 | 28.32 ± 1.18 | 35.84 ± 0.21 |
| 168–183 | <DL | 4.10 ± 0.56 | 24.46 ± 0.38 | 28.70 ± 1.07 |
| 198–213 | <DL | 3.68 ± 0.44 | 14.08 ± 1.35 | 18.4 ± 0.79 |
| Roscommon | | | | |
| 0–15 | 0.67 ± 0.03 | 13.14 ± 1.20 | 96.12 ± 2.65 | 117.14 ± 0.42 |
| 15–31 | 0.59 ± 0.02 | 11.98 ± 1.43 | 56.59 ± 4.81 | 77.98 ± 2.25 |
| 31–46 | 0.73 ± 0.02 | 1.69 ± 0.43 | 21.80 ± 1.68 | 30.69 ± 0.64 |
| 46–61 | 0.66 ± 0.02 | 5.59 ± 1.27 | 38.53 ± 2.07 | 51.59 ± 1.04 |
| 61–91 | 1.32 ± 0.02 | 1.84 ± 0.64 | 33.25 ± 2.46 | 42.84 ± 0.23 |
| 107–122 | 1.04 ± 0.08 | 3.27 ± 1.03 | 27.86 ± 3.01 | 39.27 ± 0.38 |
| 137–152 | 1.12 ± 0.11 | 4.51 ± 0.68 | 28.14 ± 2.62 | 40.51 ± 0.15 |
| 168–183 | 1.14 ± 0.22 | 3.52 ± 0.67 | 27.94 ± 2.90 | 39.52 ± 2.10 |
| 198–213 | 1.73 ± 0.32 | 4.59 ± 0.57 | 32.67 ± 3.28 | 45.59 ± 3.55 |

^a All data are the average of triplicates of the composite sample at each depth. The Al content is so low that no procedure was done to separate the Al-bound P from others. ^b <DL = lower than the detection limit.

even though more P accumulated in the topsoil (Table 5).

The concentration of Fe-bound P in AuGres is the highest among the three soils. The Roscommon has a similar level of Fe-bound P with Rubicon, even in the topsoil. The Fe-bound P may not be related to the different loading rates of P application because the P mass loading in AuGres is 0.090 kg/m² from 1973 to 2001 (Table 1), which is lower than that in Rubicon (0.12 kg/m²) but higher than that in Roscommon (0.03 kg/m²). It has been reported that Fe oxides are the most active sorbents in the calcareous soils (30, 31). We found that the CaCO₃ content in the top 60-cm soil are all below 2%, indicating that the original sandy, acidic soils have not changed to calcareous soils, even though they received a large amount of Ca. Therefore, we believe that, after the soil pH rose to 7, considering the low activity of Fe³⁺, the applied P should mainly react with Ca and Mg ions in Muskegon soils.

As shown in Figure 1, the exchangeable Ca, Ca-bound P, and P_{max} for the three soils decrease with depth. Most of Ca is accumulated in the 15-cm topsoil, where a higher TOC was present (Figure 1). For the soil, where the organic matter forms the major variable-charge component, Ca²⁺ is probably adsorbed by complex formation through electrostatic attraction of Ca²⁺ onto the carboxyl and phenolic hydroxyl groups (29, 32). In all three soils, the concentration of exchangeable Ca reduces very quickly in the first 60 cm near the top and reduces gradually after that, except for AuGres soil.

In general, Rubicon has the highest concentration of Ca- and Mg-bound P at different depths, followed by AuGres and Roscommon. The Ca- and Mg-bound P are the major forms of P adsorbed in the soils, accounting for >70% of the total P adsorbed in the soils (Table 5). On the basis of the P

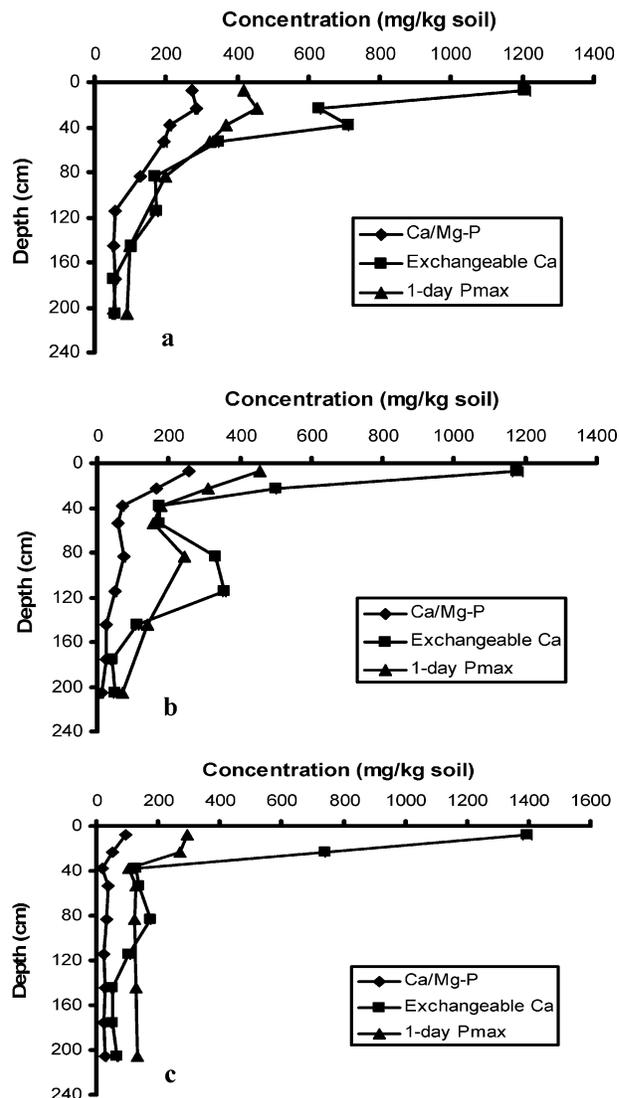


FIGURE 1. Profiles of exchangeable Ca, Ca-/Mg-bound P, and 1-d P_{max} in (a) Rubicon, (b) AuGres, and (c) Roscommon soils sampled at 2003. Values and error bars (buried in the marks) represent the average ± 1 standard deviation, respectively, from triplicates of a composite sample at each depth for Ca-/Mg-bound P and Exchangeable Ca.

loading (Table 1), the difference in the total P concentration adsorbed in the different soils may be related to the different P (mass) loading rates.

Both Ca-bound P and exchangeable Ca decrease with depth. For Rubicon, the concentration of Ca-bound P increases from 275 mg/kg at the depth of 0–15 cm to 284 mg/kg at the depth of 15–30 cm, but the concentration of the exchangeable Ca decreases sharply from 1205 to 631 mg/kg in the corresponding depth (Figure 1a). For Roscommon, the Ca-bound P concentration does not change much after the 30-cm depth, but the corresponding Ca concentration reduces from 170 to 50 mg/kg. Therefore, the trend of the Ca-bound P profiles does not match that of the exchangeable Ca profiles very well, indicating that P might not have saturated the Ca adsorbed in the Muskegon soils.

The 1-day P_{max} of the topsoils has increased by ~3 times since 1973 (Table 4). While the 1-day P_{max} decreases along the depth (Figure 1), a larger 1-day P_{max} corresponds to a higher concentration of exchangeable Ca (Figures 1 and 2); the 1-day P_{max} could be significantly influenced by the quantity of exchangeable Ca adsorbed in the soil (Figure 2).

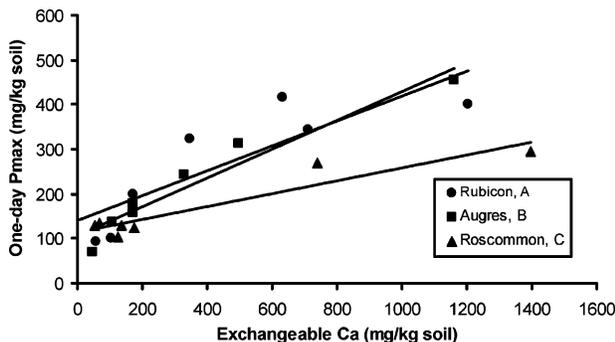


FIGURE 2. Relationship between exchangeable Ca and maximum P sorption capacity of Muskegon soils (data from profiles in Figure 1). The straight lines can be represented by $Y = aX + b$, where $Y = 1\text{-d } P_{\max}$, $X = \text{exchangeable Ca}$, $a = \text{the slope}$, and $b = \text{the interception}$. For Rubicon, $a = 0.2811$, $b = 140.39$, $R^2 = 0.71$, $t \text{ value} = 3.1932$ at $p < 0.025$; for Augres, $a = 0.3282$, $b = 108.03$, $R^2 = 0.93$, $t \text{ value} = 35.3891$ at $p < 0.005$; for Roscommon, $a = 0.1463$, $b = 113.6$, $R^2 = 0.88$, $t \text{ value} = 6.3327$ at $p < 0.005$.

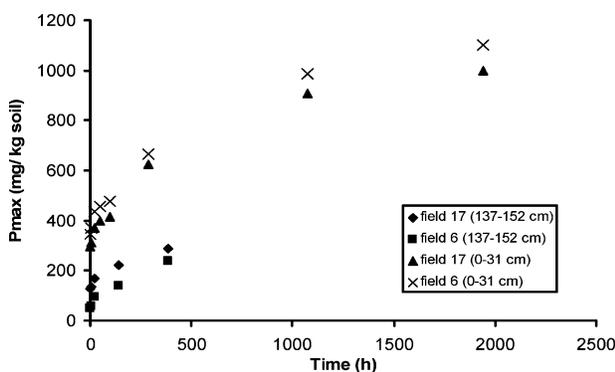


FIGURE 3. Time-dependent P_{\max} data from P sorption isotherms batch tests. Soils at the depth of 0–30 cm (0–12 in.) contained 917 and 830 mg/kg exchangeable Ca and at 137–152 cm (54–60 in.) contained 102 and 106 mg/kg exchangeable Ca for Rubicon and Augres, respectively.

The exchangeable Ca may be a useful parameter for predicting the 1-day P_{\max} of the soils.

Although we evaluated the 1-day P_{\max} of the soils, still we know neither the exact P_{\max} of the soils at the Muskegon site nor how and why the Ca ions adsorbed in the soils affect the 1-day P_{\max} . It has been reported that the real P adsorption capacity in the field is about 3–5 times higher than that of the estimated 1-day P_{\max} (1, 33). Results of our long-term P adsorption tests show that the P_{\max} increases with adsorption time during the batch tests (Figure 3). The P_{\max} did not approach its maximum value even after 390- and 2000-h adsorption for the soils at two different depths. It should be noted, however, that these P_{\max} tests appear to be a highly artificial measurement, as high P and Ca doses are added; in the real situation with lower concentrations this P_{\max} may never be reached anyway. Nevertheless, the results of the P_{\max} tests indicate that it is possible for the soil to continuously adsorb P, and it is difficult to obtain an absolute P_{\max} with isotherm tests within a reasonably short period.

Implications. For the Muskegon County wastewater land treatment system, changes in soil pH and the amount of Ca adsorbed by the soil are significant and have not been reported in the past. As a result of these changes, the major inorganic P form in the soil is Ca-bound P. Results indicate that the amount of Ca adsorbed in the soil also affects the P adsorption capability of the soil. Our results are strongly related to evaluation of (1) P accumulation and (2) P leaching potential in a land wastewater treatment system, as elaborated below.

(1) Currently, the exact mechanisms of P adsorption onto the soil with a large amount of Ca are not known. While most of the applied P has been accumulated in the topsoil at the Muskegon site, we did identify different forms of P in deeper soils. Considering the higher P loading rate of Rubicon (0.12 kg/m²) and the 1-d P_{\max} of Rubicon being much less than its saturation value (Figure 3) at the topsoil (0–15 cm), it is possible that some of the P in wastewater is not adsorbed or precipitated quickly enough in the topsoil and thereby, moves down with the wastewater. This inference seems to be supported by the two-stage theory for the reaction of P with Ca (34). The initial adsorption (as the first stage) is thought to occur at certain sites where lateral interaction between phosphate ions produces surface clusters that then act as nuclei for subsequent crystal growth (the second stage). The second stage is much slower than the first stage (34). On the basis of this two-stage theory, it can be deduced that P buildup is from the topsoil and moves down deeper and deeper, and any P moving downward through the soil should eventually react with Ca ions. Therefore, the Ca sorption capacity of the soil becomes an important parameter for predicting the P leaching potential and, furthermore, the life expectancy of a land treatment system.

(2) Labile P distribution is not correlated with that of total P, nor Fe-bound P, nor Ca/Mg-bound P and, thus, may not be a good indicator for predicating P leaching in a wastewater land treatment system. On the basis of the 10-year soil test data (data not shown) of the Muskegon soils, the Bray-1 P (35) is not suitable for the predicting purpose, because the Bray-P fluctuated in these years, instead of increasing with the accumulation of the total P. Recent studies suggest using the DPS (degree of phosphorus saturation) to evaluate the soil P release potential. Our results indicate that the exchangeable Ca has a good relationship with the 1-day P maximum adsorption capacity of the soil. In addition, we found that the major forms of P in the Muskegon soils are Ca- and Fe-bound P. Therefore, it may be possible to develop an index that is similar to the DPS and accounts for the effects of Ca adsorption and Ca-bound P on P leaching potential in soils of a land treatment system.

Results of this study challenge the current knowledge on P fate and transport in soils of land treatment systems. Currently, we do not have the answers for several important questions, such as, how will the wastewater properties affect the adsorption of Ca and, thereby, P in the soil? How are the wastewater application rate and the soil adsorption capacity for Ca and P linked with P leaching from the land treatment system and, thus, the life expectancy of the system? An extended question would be whether the phenomenon of the Ca and P accumulation capacity increasing with long-term wastewater application also occurs in other wastewater land treatment systems. Further studies are needed to answer these questions.

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