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Physicochemical Properties Related to Long-Term Phosphorus Retention by Drinking-Water Treatment Residuals

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Drinking-water treatment residuals (WTRs) are nonhazardous materials that can be obtained free-of-charge from drinking-water treatment plants to reduce soluble phosphorus (P) concentrations in poorly P sorbing soils. Phosphorus sorption capacities of WTRs can vary 1–2 orders of magnitude, on the basis of short-term equilibration times (up to 7 d), but studies dealing with long-term (weeks to months) P retention by WTRs are lacking. Properties that most affect long-term P sorption capacities are pertinent to the efficacy of WTRs as amendments to stabilize P in soils. This research addressed the long-term (up to 80 d) P sorption/desorption characteristics and kinetics for seven WTRs, including the influence of specific surface area (SSA), porosity, and total C content on the overall magnitude of P sorption by seven WTRs. The data confirm a strong but variable affinity for P by WTRs. Aluminum-based WTRs tended to have higher P sorption capacity than Fe-based WTRs. Phosphorus sorption with time was biphasic in nature for most samples and best fit to a second-order rate model. The P sorption rate dependency was strongly correlated with a hysteretic P desorption, consistent with kinetic limitations on P desorption from micropores. Oxalate-extractable Al + Fe concentrations of the WTRs did not effectively explain long-term (80 d) P sorption capacities of the WTRs. Micropore (CO₂-based) SSAs were greater than BET-N₂ SSAs for most WTRs, except those with the lowest (<80 g kg⁻¹) total C content. There was a significant negative linear correlation between the total C content and the CO₂/N₂ SSA ratio. The data suggest that C in WTRs increases microporosity, but reduces P sorption per unit pore volume or surface area. Hence, variability in C content confounds direct relations among SSA, porosity, and P sorption. Total C, N₂-based SSA, and CO₂-based SSAs explained 82% of the variability in the long-term P sorption

capacities of the WTRs. Prediction of long-term P sorption capacities for different WTRs may be achieved by taking into account the three proposed variables.

Introduction

Low phosphorus (P) sorption capacity of sandy soils often makes them vulnerable to P losses (1). Agricultural activities have resulted in elevated P inputs in soils and stimulated efforts to reduce P concentrations in surface runoff and leaching of soils. Drinking-water treatment residuals (WTRs) are cost-free amendments that reduce excess soluble P concentrations in systems high in P (2). Drinking-WTRs are a waste product of drinking-water purification. They are physical mixtures of either iron or aluminum hydr(oxides) or CaCO₃ that also contain sediment and small quantities of activated carbon and/or polymer (3). Most of the C in WTRs is associated with natural organic matter entrained in the raw water, since organic polymers used as coagulants are added at very low concentrations (0.15–0.20 mg L⁻¹). Addition of Fe, Al, or Ca salts to raw water removes colloids, color, sediment, and contaminants from surface and groundwater supplies intended for potable water use. These residuals are herein referred to as Al-WTRs (use of Al salt) or Fe-WTRs (Fe salt) (4). Reactions of Ca-WTRs (Ca salts) are not considered here.

Typically, WTRs are disposed of in landfills. Land application, as an alternative to land-filling, could function as a means both of WTR disposal and of immobilizing P in poorly P sorbing soils. The high amorphous [Al + Fe] content of the WTRs would be expected to increase a sandy soil's P sorption capacity (5). In the short term, WTRs can dramatically reduce soluble P in soils and runoff from areas amended with different P sources (6–8), but little is known about factors that influence the long-term P retention of WTRs and WTR-amended soils. The long-term stability of sorbed P by WTRs is an important issue in considering the merits of a WTR use as a soil amendment.

Drinking-water treatment plant facilities use different water sources and different coagulants/polyelectrolytes. Thus, they produce WTRs with variable elemental compositions and P sorption capacities. An Fe-WTR (total Fe 195 000 mg kg⁻¹) sorbed approximately 186 000 mg of P kg⁻¹ within 7 d (9). Ippolito et al. (10) found that the P sorption capacity of an Al-WTR (total Al 64 000 mg kg⁻¹) was 12 500 mg of P kg⁻¹ after a 1 d shaking equilibration time. Dayton et al. (11) reported a wide range in Langmuir-based P sorption capacities (300–5140 mg of P kg⁻¹) for 21 Al-WTRs shaken for 0.6 d. Runoff-soluble P was reduced in proportion to the P sorption capacities of the Al-WTRs (11).

Differences in P sorption capacities coupled with variable P sorption kinetics may influence the field performance of land-applied WTRs. It is necessary to determine the true long-term P sorption capacities of WTRs, if used to reduce soluble P in systems very high in P, such as in animal waste lagoons. Work in our laboratory showed that P sorption by a single Fe-WTR was explained by kinetically driven P diffusion into internal sorption sites (12). However, findings from a single WTR may not apply generally to using WTRs to reduce soluble P in sandy soils or animal waste lagoons over the long term.

The only study dealing with multiple WTRs ranging in physicochemical properties measured short-term (0.6 d) P sorption capacities of 20 Al-WTRs (11). Dayton et al. (11) attempted to relate ($r^2 = 0.69$, quadratic model) the maximum P sorption capacities (0.30–5.14 g P kg⁻¹) calculated from

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the Langmuir equation with the oxalate (200 mM)-extractable Al concentrations of the 20 Al-WTRs. Traditional measurements of oxalate-extractable P, Fe, and Al have been used to explain trends in runoff P (8, 11), and P leaching losses in soils amended with animal wastes and WTRs (2). The use of oxalate (200 mM)-extractable Fe + Al concentrations in the phosphorus saturation index (PSI) may prove useful to explain P leaching losses, but several limitations associated with the use of PSI of the materials to predict P availability have been noted (2).

The total surface area of the WTRs consists of mostly internal surfaces with an extensive network of porosity (13). We hypothesized that the porous nature and chemical composition of WTRs, rather than simply the oxalate-extractable Fe + Al concentrations, are the major factors influencing the kinetics and magnitude of P sorption. The objectives of this study were to (i) characterize the long-term (80 d) P sorption and desorption behavior and kinetics of seven WTRs differing in elemental composition and (ii) evaluate the influence of specific surface area, porosity, and total C content on the long-term P retention by these WTRs.

Materials and Methods

WTR Collection. Seven WTRs were used in this study: four were Al-based, and three were Fe-based.

The Al-WTRs were obtained from two water treatment plants in Florida (Bradenton and Melbourne), one in Holland, MI, and one in Lowell, AR. The Bradenton material was obtained from the Manatee County water treatment plant in Bradenton, FL. Additions of alum and a small amount of a copolymer of sodium acrylate and acrylamide produced the Al-WTR. The Melbourne material (Lake Washington water treatment plant near Melbourne, FL) was produced using alum combined with quicklime (CaO), acrylamide with sodium acrylate copolymer, and powdered activated carbon (PAC). The process produces ~15000 tons of WTR yr⁻¹ (14). The PAC content of the WTR was only a small fraction of the total WTR mass (3%) produced annually. The Melbourne material has been used in a large-scale (5265 ha) restoration effort of muck farmland to marsh habitat to reduce external P loading to Lake Apopka, FL (14). More than 60000 wet tons of WTR was hauled and applied to the site. Subsamples were transferred to our laboratory (in 2003) from the initial stockpile that was land-applied in 1997. Another Al-WTR was collected from the Holland, MI, water treatment plant. This material is produced by alum addition to raw water. The material was used in a field experiment at Holland, MI, to evaluate the long-term (5.5 yr) WTR effect on decreasing P availability in waste-amended soils high in soil test P levels (15). Archived subsamples from the initial stockpile that was land-applied in 1998 were transferred to our laboratory in 2001. The fourth Al-WTR was provided to us from the Beaver water treatment plant in Lowell, AR. Another batch of the same WTR was successfully used to reduce runoff P in rainfall simulation plots with excessively high soil test P levels (6).

All Fe-based WTRs were collected from Florida water treatment plants. The Hillsboro River water treatment plant in Tampa, FL, provided an Fe-WTR where Fe₂(SO₄)₃ is used as the coagulant. The process involves coagulation and subsequent flocculation of evolving iron hydroxides with natural organic matter in the raw water to produce Fe-WTR. The material is marketed as an Fe source (Fe-humate) by the Kemiron company. Another Fe-based WTR came from the Taylor Creek surface water treatment plant, Cocoa Beach, FL, where iron sulfate is coupled with PAC (100 tons) and polymer (7 tons) additions, annually. The Panama City surface water treatment plant in Florida provided an Fe-WTR where iron sulfate is used as the coagulant. WTRs were originally sampled from stockpiles that were formed within 1 yr of

production. All WTRs were allowed to air-dry, and were subsequently passed through a 2 mm sieve before analyses.

General Physicochemical Properties of WTRs. The pH and soluble reactive P concentrations of the WTRs were measured in a 0.01 M KCl solution at a 1:10 solid:solution ratio, after 40 d of reaction. Total C and N were determined by combustion at 1010 °C using a Carlo Erba NA-1500 CNS analyzer. Total recoverable P, Fe, and Al were determined by inductively coupled plasma atomic emissions spectroscopy (ICP-AES) following digestion according to EPA method 3050B (16). Oxalate-extractable P, Fe, and Al were determined by ICP after extraction at a 1:60 solid:solution ratio (g mL⁻¹), following the procedures of McKeague et al. (17). Oxalate-extractable Fe and Al represent noncrystalline and organically complexed Fe and Al present in the solid (17).

Preliminary experiments were conducted to determine the effect of filter size and centrifuge speed on soluble P concentrations. Colloidal material of the WTRs might contribute significantly to soluble P concentrations when using 0.45 μm filters (18). Use of 0.1 and 0.01 μm filters helped to test this hypothesis. We also investigated the potential effect of centrifuge speed (3000g, 6000g, and 12 000g) on the overall P sorption by WTRs. Results showed that 0.45 μm and 3000g did not deviate significantly from those of the other treatments, and hence, these protocols were used in this study.

Phosphorus Sorption and Desorption by WTRs. Phosphorus sorption maxima of the WTRs were determined in batch equilibration, based on the work of O'Connor and Elliott (19). Representative air-dried (<2 mm) samples of the WTRs were reacted with inorganic P in 1:10 [g of WTR (mL of P solution)⁻¹] solutions at P loads of 2500–10000 mg P kg⁻¹ for 1, 10, 20, 40, and 80 d to determine P sorption capacities and kinetics at 23 ± 2 °C. On the basis of earlier work on P sorption isotherms, a 0.01 M KCl supporting electrolyte solution was selected to control the solution ionic strength (4). No biological inhibitor was added to the suspensions. The selection of the above range of P loads was based on preliminary sorption experiments. Initial P loads exceeded those typically found in P-enriched soils, but were selected to account for cases where repeated annual P-source applications or systems very high in soluble P concentrations are encountered.

The pH was not controlled and suspensions were not shaken during the equilibration period. No mechanical energy (shaking) was applied, since shaking is not a field process and preliminary work revealed no significant difference in P sorption after 10 d between shaken and unshaken samples. We also wanted to avoid the possible generation of surfaces during shaking (due to abrasive forces), as increases in specific surface area (SSA) may influence the magnitude of P sorption. Following the contact period, suspensions were centrifuged (3000g), filtered (0.45 μm), and analyzed for P, Al, and Fe by ICP.

After sorption, the supernatant was removed and WTR-containing tubes were filled with a 5 mM oxalate (oxalic acid/ammonium oxalate) solution mixture in the dark (1:10 WTR:oxalate solution ratio) to test the ability of a common soil organic ligand to desorb P from the WTR (20). Suspensions were reacted in the dark for 1, 10, 20, 40, and 80 d, without shaking or pH control. The amount of P desorbed was calculated as the difference between P sorbed and P measured in solution after the desorption step, accounting for entrained solution P.

Surface Area and Porosity. Drinking-WTR samples from the 40 d P sorption experiment were selected for the SSA measurements. The 40 d treatment was selected to represent WTR sorption at the stage when the rate of sorption was changing very slowly. Phosphorus-treated (10 g kg⁻¹ initial P load) and untreated WTR particles were air-dried before being subjected to SSA analyses. SSA of the WTRs was

measured at 77 and 273 K using N₂ and CO₂, respectively, as adsorbates in a volumetric apparatus (Quantachrome Autosorb-1, Quantachrome Corp.), after outgassing at 70 °C for 4 h. Details of the SSA calculations are given elsewhere (12). In brief, BET-N₂ SSAs were calculated from the classic BET equation using the 0.03–0.3 relative pressure region. The Saito–Foley (SF) method (21) based on data from the N₂ gas sorption isotherms was used to calculate micropore volume distributions for the WTRs. The micropore volume of the WTRs was also calculated on the basis of CO₂ sorption using the Dubinin–Radushkevich (DR) model (22). Micropore monolayer SSA was calculated from the DRK equation, which is a special case of the DR model.

Results and Discussion

General Chemical Properties. All Al-based WTRs were acidic, except the Holland WTR (Table 1). The KCl-extractable P represented only a small fraction of total P, and ranged from 0.2% to 0.7%. The KCl-extractable P is considered the most available pool of P and varies among different P sources (poultry, dairy, swine animal wastes, or fertilizer P). The low amounts of KCl-P imply that Al-WTRs may be sinks for P immobilization in poorly P sorbing soils.

Total C varied significantly among the Al-WTRs (34–225 g kg⁻¹) (Table 1). Total C values agreed with the range of organic C found in 20 Al-WTRs (23–205 g kg⁻¹) (11). Total C determinations may overestimate organic C content since the combustion method measures both organic and inorganic C. However, organic C determination with the Walkley–Black method gave similar percentages of C (within experimental error, data not presented), suggesting minimal inorganic C.

Total P content was within the typical range for Al-WTRs (300–4000 mg of P kg⁻¹) (11). Total P in WTRs comes from the raw water purified in drinking-water treatment plants and becomes a part of the WTR structure. Total Al ranged from 37000 to 103000 mg of Al kg⁻¹ for the Al-WTRs and within the range for Al-WTRs (15000–177000 mg of Al kg⁻¹) (11). X-ray diffraction analysis (data not shown) revealed no crystalline aluminum hydr(oxide) components. Oxalate (200 mM)-extractable P, Fe, and Al are usually associated with the noncrystalline (amorphous) phase of metal oxides. Oxalate-extractable Al values were close to total Al concentrations (80–98% of total Al), consistent with an amorphous nature of the Al-WTRs.

The Fe-based WTRs were acidic (Table 1). As with the Al-WTRs, KCl-P represented a minor fraction of total P, and ranged from 0.2% to 2%. Total C values ranged from 94 to 206 g kg⁻¹. Total C in the Fe-WTRs also agreed with the range of organic C values measured in 21 WTRs (23–205 g kg⁻¹) (11). Total P concentrations of the Fe-WTRs ranged from 300 to 3200 mg of P kg⁻¹. Total Fe concentrations ranged from 242 000 to 311 000 mg of Fe kg⁻¹. Total Fe measurements were above typical values found for WTRs (50 000–150 000 mg kg⁻¹) (23). Large total Fe concentrations may not necessarily correlate well with elemental bioavailability, or increased P sorption capacities. Gallimore et al. (8) concluded that the amorphous, rather than the total, metal content of WTRs determines WTR effectiveness in reducing runoff P.

X-ray diffraction analysis (data not shown) suggested that amorphous iron (hydr)oxides dominated all Fe-WTRs, with no apparent crystalline iron (hydr)oxides. Traditional measurements of oxalate-extractable metal concentrations have been positively correlated with P sorption capacities of WTRs (9). Iron-based WTRs had lower oxalate (200 mM)-extractable Fe values as a percentage of total Fe (45–64%) compared with the Al-WTRs. This difference could suggest a lower P sorption capacity of Fe-WTRs compared with Al-WTRs on a metal-equivalent basis.

Phosphorus Sorption/Desorption. Phosphorus sorption/desorption isotherms showed that all four Al-based WTRs

TABLE 1. General Chemical Properties of Seven WTRs^a

source	form	pH	KCl-P (mg kg ⁻¹)	total					oxalate (200 mM)		
				C (g kg ⁻¹)	N (g kg ⁻¹)	P (g kg ⁻¹)	Al (g kg ⁻¹)	Fe (g kg ⁻¹)	P (g kg ⁻¹)	Al(g kg ⁻¹)	Fe(g kg ⁻¹)
Holland, MI	Al-based	7.4	5.62 ± 0.05	34 ± 0.2	3.0 ± 0.5	0.8 ± 0.02	37 ± 0.8	8.7 ± 0.2	0.57 ± 0.09	29 ± 4.01	2.3 ± 0.3
Lowell, AR	Al-based	6.8	5.26 ± 0.01	76 ± 2.0	7.0 ± 0.2	0.8 ± 0.05	103 ± 6.1	20.7 ± 1.9	0.5 ± 0.01	89 ± 1.4	5.8 ± 0.5
Bradenton, FL	Al-based	5.4	5.08 ± 0.04	162 ± 8.0	6.0 ± 0.2	3.1 ± 0.04	92 ± 0.04	6.2 ± 0.04	2.98 ± 0.0	91 ± 0.1	5.2 ± 0.2
Melbourne, FL	Al-based	5.7	2.20 ± 0.14	225 ± 6.0	10 ± 0.1	1.1 ± 0.06	87 ± 0.7	5.7 ± 0.4	0.6 ± 0.06	79.4 ± 0.2	3.6 ± 0.1
Tampa, FL	Fe-based	6.3	6.21 ± 0.8	141 ± 6.0	8.0 ± 0.4	3.2 ± 0.1	9.8 ± 0.1	251 ± 5.6	2.6 ± 0.05	6.0 ± 0.1	161 ± 8.0
Panama City, FL	Fe-based	5.6	6.31 ± 0.1	94 ± 1.0	5.0 ± 0.1	0.3 ± 0.01	1.5 ± 0.03	311 ± 14	0.2 ± 0.08	1.3 ± 0.1	195 ± 4.1
Cocoa Beach City, FL	Fe-based	3.9	6.25 ± 0.1	206 ± 2.0	11 ± 0.1	0.7 ± 0.02	2.2 ± 0.04	242 ± 3.5	0.14 ± 0.03	nd ^b	108 ± 2.98

^a Numbers are the mean of two replicates ± 1 standard deviation. ^b Not detected.

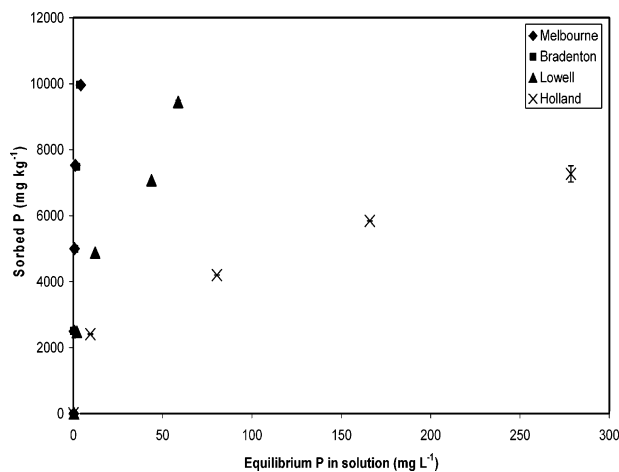


FIGURE 1. Phosphorus sorption isotherms (23 °C) of four Al-WTRs after 10 d. No shaking or pH control was applied. Error bars represent 1 standard deviation of the mean ($n = 2$).

had a high affinity for P (Figure 1). Most of the WTRs (both Al- and Fe-based) sorbed ~70–100% of the initial P loads after 10 d of reaction; thus, the 10 d reaction time data were selected for presentation. After 10 d of reaction with the highest initial P load (10 000 mg kg⁻¹), the Melbourne material sorbed the greatest amount of P (10 000 mg kg⁻¹), followed by Bradenton (~9700 mg kg⁻¹), Lowell (~9100 mg kg⁻¹), and Holland (~7500 mg kg⁻¹). Langmuir-based P sorption maxima were not determined since isotherms exhibited Freundlich behavior, without reaching an obvious plateau (Figure 1). Initial P load was the limiting factor in determining the true P sorption maxima of Al-WTRs. A P load of 10 000 mg of P kg⁻¹ is greater than P loads typical of soils.

The Tampa Fe-WTR had the highest affinity for P among the Fe-based WTRs, followed by Panama City > Cocoa Beach materials after 10 d of reaction (Figure 2). Given enough time (80 d), the Tampa material nearly sorbed all P from solution (92% of initial P load) (24). The Panama City WTR sorbed ~4500 mg P kg⁻¹ after 80 d (45% of initial P load). Another sample of the Panama City material had lower P sorption capacity (~3400 mg of P kg⁻¹) probably due to the shorter equilibration time (8 d) used (4). The Cocoa Beach material sorbed the least amount of P (~2500 mg of P kg⁻¹) of all WTRs, even after reaction for 80 d. Reaction time (either 10 or 80 d) had no effect on the amount of P sorbed by the Cocoa Beach material; P retained after 10 d (~2800 mg of P kg⁻¹) at the highest initial P load (10 000 g kg⁻¹) was not significantly different from the amount sorbed after 80 d.

Phosphorus sorption kinetic data for WTRs (Table 2) were best fit to a second-order reaction rate model (24, 25), except for the Cocoa Beach material, which fit neither a first- nor a second-order model due to limited P sorption. Phosphorus sorption by the WTRs was initially fast followed by a slow P sorption stage. The fast stage of P sorption presumably would encompass highly accessible surfaces (particle exteriors and macropores) (26), while the slower stage may be associated with diffusion in micropores (27).

The magnitude of the slow P sorption stage varied among WTRs (Table 2). The second-order reaction rate coefficients increased with the P sorption capacities of the materials. This is because samples with the highest P sorption generally showed significant time dependency up to 40 or 80 d, while samples with low P sorption did not. The Melbourne sample was an exception only because its capacity was high enough to completely deplete soluble P within 10 d. Apparently, samples with relatively low P sorption capacity did not have appreciable rate-limited P surface access (as in certain micropores) compared with samples with high P sorption

capacity. The same trend in rate limitation applies to desorption; in effect, the higher the second-order rate coefficient, the lower the proportion of desorbed P (Figure 3). Despite the large differences (4–5 orders of magnitude) in rate coefficients, a log-linear model explained differences in P desorption reasonably well. This is favorable behavior with respect to the stability of P sorbed to highly retentive WTRs. Second-order rate coefficients for Fe-based WTRs were generally smaller than those of Al-based WTRs, consistent with there being less P sorption for the second biphasic (longer term) sorption stage.

Potential particle dissolution, particularly under acidic conditions, is a concern with respect to WTR field applications in humid regions. Soluble Al concentrations were monitored during P sorption by the Al-WTRs. Aluminum concentrations of untreated (no P added) Al-WTR suspensions after 80 d were below the instrument's (ICP-AES) detection limit (0.03 mg of Al L⁻¹). This result suggests no particle dissolution in 0.01 M KCl solution after 80 d. Most P-treated (10 000 mg kg⁻¹ initial P load) Al-WTR suspensions released minor quantities of soluble Al (<10 mg kg⁻¹) during the 80 d P sorption experiment, except the Bradenton material (46 mg of Al kg⁻¹). The pH during P sorption was not controlled, and after 10 d, suspension pHs of P-treated Al-WTRs ranged from 5.8 for the Melbourne material to 8.3 for the Holland material.

Oxalate (5 mM)-extractable Fe after 160 d (80 d for P sorption and subsequent 80 d for P desorption) was minimal for the Cocoa Beach material, which was the most acidic (pH 3.9) of all WTRs. Oxalate (200 mM) extractions are commonly performed at pH 3, which dissolves significant amounts of noncrystalline Fe and Al components of the WTRs (17). However, such a large oxalate concentration (200 mM) is rarely encountered in natural systems, so 5 mM oxalate was used to more closely mimic soil solution (20). We have shown that 5 mM oxalate solution dissolves noncrystalline aluminum or iron hydroxides prepared in the laboratory (unpublished data). However, the 5 mM oxalate dissolving strength is reduced when compared with that of the 200 mM oxalate concentration. The Tampa Fe-WTRs released a small portion of oxalate (5 mM)-extractable Fe in solution (~1.0% of the 200 mM oxalate-extractable levels) in the absence of added P. The Panama City material did not release Fe to solution even after 80 d. Supernatants of the Panama City suspensions contained black-colored flocs, probably humic materials, on the water/air interface of the test tubes. Desorbed Fe from the untreated (no P added) Fe-WTRs was gradually removed from solution after P was added to the system. This implies a precipitation mechanism for P removal. No soluble Fe was found in supernatants of P-treated WTRs within 1 d. Iron that was desorbed from WTR surfaces after 20 or 40 d (in the absence of added P) apparently reacted with the added P, resulting in minimal soluble Fe concentrations (ICP instrumental detection limit 0.02 mg of Fe L⁻¹) at the highest initial P load (10 000 mg kg⁻¹) and a solid:solution ratio of 1:10 (g mL⁻¹).

Phosphorus desorption to a 5 mM oxalate solution from the WTRs also was monitored for different contact times. Phosphorus desorption from the Al-WTRs decreased with increasing desorption time, suggesting continuous P sorption (data not shown). This phenomenon was also observed in a long-term (211 d) P desorption experiment of an Al-WTR, where P desorption was minimal (0.2% of sorbed P) (10). Maximum percentages of oxalate (5 mM)-desorbable P (percent previously sorbed) were generally <0.2% for all Al-WTRs, except for the Holland material (1.5%). The percentages were observed for desorption experiments conducted for either 10 or 20 d (data not shown). As desorption time increased to 40 or 80 d, no soluble P concentrations (ICP instrument P detection limit 0.3 mg of P L⁻¹) were measured for any Al-WTR, suggesting continuous P sorption.

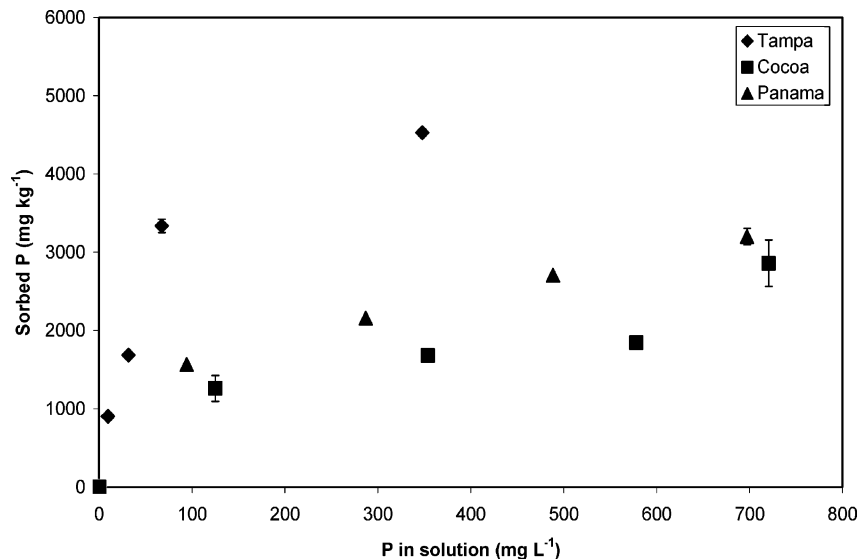


FIGURE 2. Phosphorus sorption isotherms (23 °C) of the three Fe-WTRs after 10 d. pH was not controlled, and samples were not shaken. Error bars represent 1 standard deviation of the mean ($n = 2$).

TABLE 2. Reaction Rate Constants in WTR Suspensions after a 1000 mg of P L⁻¹ Initial Pulse Input

source	form	first-order rate fit (r^2)	second-order rate fit (r^2)	second-order reaction rate k^a (L s ⁻¹ mg ⁻¹)
Holland, MI	Al-based	0.87	0.98	2×10^{-7}
Lowell, AR	Al-based	0.86	0.95	3.4×10^{-5}
Bradenton, FL	Al-based	0.84	0.94	1.3×10^{-4}
Melbourne, FL	Al-based	0.89	0.96	2.4×10^{-4}
Tampa, FL	Fe-based	0.80	0.97	1.07×10^{-7}
Panama City, FL	Fe-based	0.71	0.77	5.8×10^{-9}
Cocoa Beach City, FL	Fe-based	0.12	0.12	1.24×10^{-9}

^a Where the slope of a linear fit to an n th-order reaction equals $(n - 1)k_n C_0^{n-1}$.

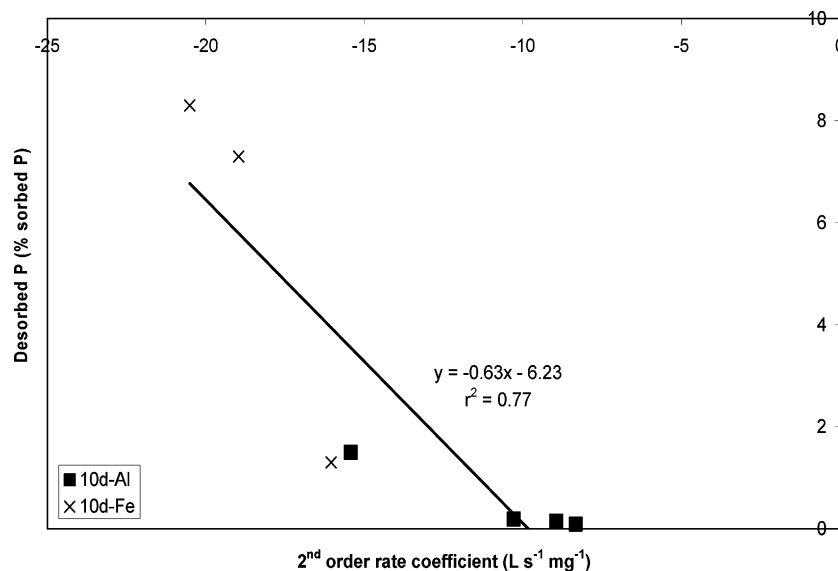


FIGURE 3. Semi (x-axis)-log-transformed plot of the second-order rate coefficient changes with the amount of P desorbed after 80 d of reaction for three Fe-WTRs (10 d Fe) and four Al-WTRs (10 d Al).

Residual P that was sorbed during desorption came from the entrained solution after sorption. Apparently, P sorbed by Al-WTRs is chemisorbed on WTR surfaces, and resists desorption to a 5 mM oxalate solution.

As with the Al-WTRs, the amount of P desorbed from Fe-WTRs by 5 mM oxalate decreased with increasing desorption time (from 10 to 80 d), implying a continuous nonequilibrium P sorption process. The Tampa WTR de-

sorbed the least amount of previously sorbed P (1.3%), followed by Panama City (7.3%), and Cocoa Beach (8.3%) (data not presented). There was an inverse trend in the percentage of sorbed and desorbed P. The Cocoa Beach material desorbed the greatest proportion of P, and also sorbed the least amount of P of all the WTRs.

At all reaction times, P sorption induced a steep sigmoidal type of pH increase with P load, suggesting exchange of

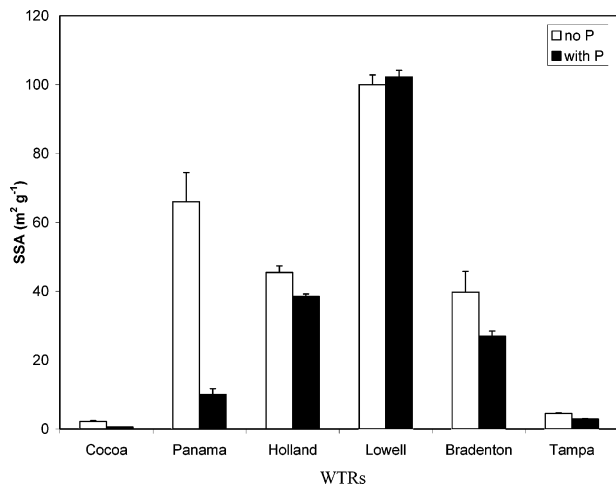


FIGURE 4. BET-N₂ SSA measurements for WTRs untreated and P-treated (10 g of P kg⁻¹ initial load) for 40 d. Error bars denote 1 standard deviation of two replicated runs.

phosphate molecules for structural hydroxyls (data not presented). An exception was the Bradenton material that exhibited a slow pH decrease with P load (from 5.4 down to 3.9), which induced minimal Al dissolution. After 20 d, no pH decrease was observed during P sorption by the Bradenton Al-WTR. However, the P-treated suspension pH started to decrease after 40 d, and Al dissolution was initiated. The total amount of soluble Al desorbed from the Bradenton material after 40 d was only 0.4% of the oxalate-extractable Al; the reason for the pH drift is unknown. Biological activity could be a factor in pH drift. However, the WTRs we used were air-dried for a few months before being used in the sorption experiments, such that significant microbial activity seems unlikely. Typical air-dried Fe- and Al-based WTR show minimal bacterial activity (<20 coliforms g⁻¹) due to air-drying, long-term storage, and chlorine addition during the drinking-water purification process (5).

The minimal desorption of P that is bound to WTRs is a favorable property in the consideration of their land application in areas of poorly P sorbing sandy soils. In the presence of oxalate (5 mM), a considerable amount of

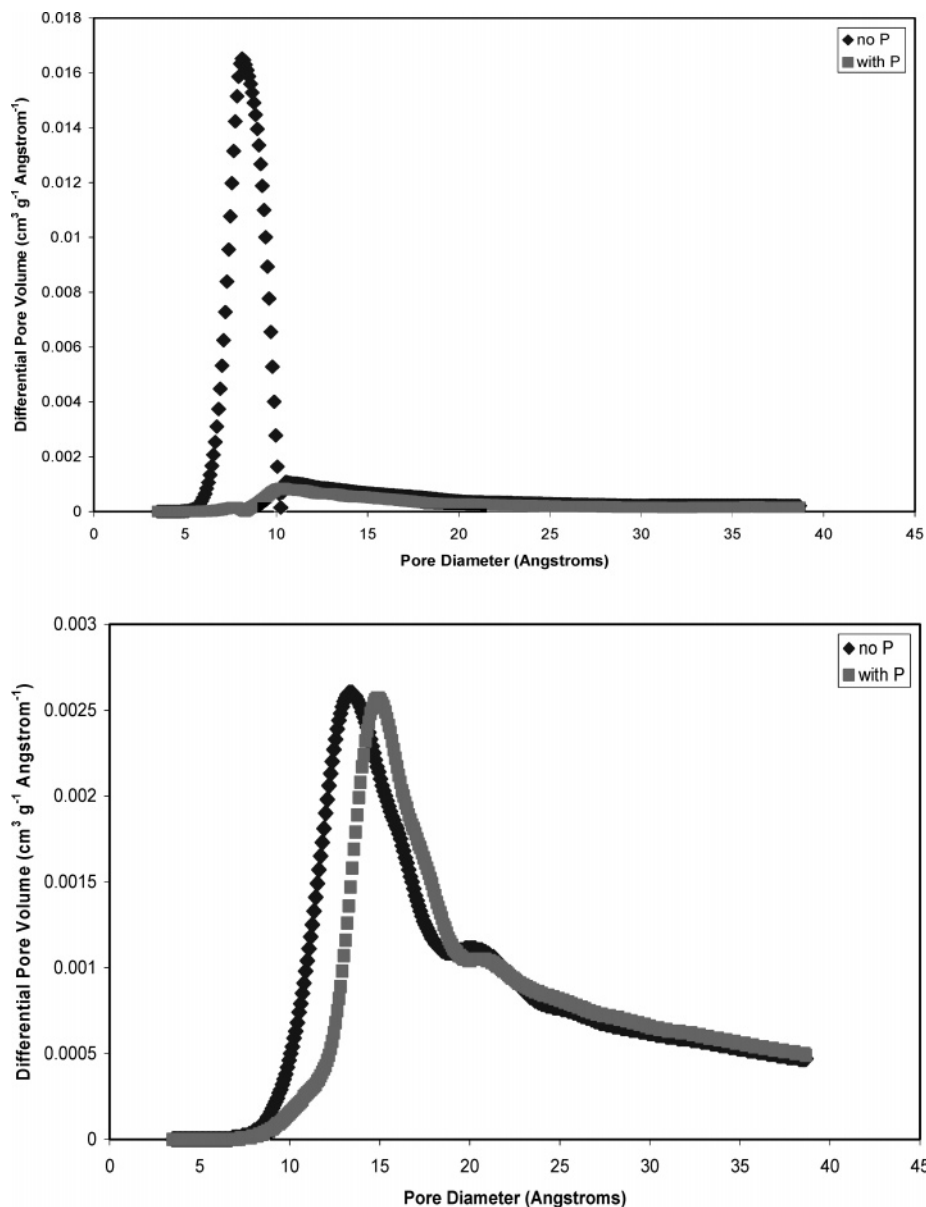


FIGURE 5. Dinitrogen-based (Saito-Foley method) micropore volume distributions for untreated and P-treated Lowell (bottom) and Bradenton (top) WTRs (10 g of P kg⁻¹ initial load) after 40 d.

TABLE 3. Micropore Volumes of Untreated WTRs Obtained from BET-N₂ Isotherms with the SF Method and Total Pore Volumes Obtained at 0.99 = P/P₀

WTR	micropore vol (cm ³ g ⁻¹)	total pore vol (cm ³ g ⁻¹)	micropore vol % of total
Melbourne	8 × 10 ⁻²	2.0 × 10 ⁻¹	40
Lowell	4.3 × 10 ⁻²	2.4 × 10 ⁻¹	18
Bradenton	4.2 × 10 ⁻²	9.2 × 10 ⁻²	46
Holland	1.05 × 10 ⁻²	1.2 × 10 ⁻¹	9
Tampa	1.45 × 10 ⁻³	4.3 × 10 ⁻³	34
Panama	1.4 × 10 ⁻³	1.2 × 10 ⁻²	12
Cocoa	1.2 × 10 ⁻³	7.5 × 10 ⁻³	16

phosphate was desorbed from Bh horizons of a nonamended Pomona sandy soil in Florida (28). Ligand exchange and dissolution of mineral surfaces were the mechanisms proposed as responsible for the observed P release. Phosphorus released was not allowed to reprecipitate with soluble Al or Fe due to formation of stable soluble oxalate–Al/Fe complexes. The difference in P desorption by oxalate (5 mM) between WTRs and soil material (e.g., Bh horizons) may suggest that oxalate access to WTR-P sites is partially restricted, and that significant P release from WTRs by oxalate requires particle dissolution. The resistance to P desorption from WTRs was explained on the basis of P intraparticle diffusion in the micropores of WTRs (27).

Butkus et al. (9) suggested that WTRs can act as P sources when total Fe (~190 000 mg kg⁻¹) is matched by sorbed P (~190 000 mg P kg⁻¹) on an Fe-WTR. Data from our desorption experiment do not support this idea, since minimal P was released from P-loaded Fe-WTRs where total Fe:total P mass ratios ranged from 27 to 80. Phosphorus loads that exceed a 1:1 stoichiometric P:metal molar ratio may transform WTRs from a sink to a P source. Such loads are not usually encountered, even in agricultural practices.

Oxalate (200 mM)-extractable Al concentrations have been used to explain differences in P sorption capacities of WTRs (11), but with limited success (*r*² = 0.69, quadratic model). We found no significant correlation between oxalate (200 mM)-extractable Fe + Al concentrations of the WTRs and long-term (80 d) P sorption capacities. Thus, a simple oxalate extraction may not be a reliable index of the long-term P sorption capacities for the WTRs. In addition, WTRs that

exhibit a slow P sorption stage may not reach equilibrium in 1–2 d, a contact time that has traditionally been used by researchers (2, 4, 11). Longer contact times may be needed to fully characterize true WTR-P sorption capacities. The WTRs used in the present study required significantly different times to sorb a specific amount of P.

Factors affecting the magnitude of the slow P sorption kinetics and P sorption capacities of WTRs remain unclear. Heil and Barbarick (29) argued that aging could reduce P sorption capacities of WTRs. The Melbourne and Holland materials were sampled from solid retention ponds in 1997 and 1998, respectively. Air-dried samples of both materials exhibited large P sorption capacities despite aging of the materials in the laboratory for ~5 yr (air-dried, room temperature). Aging under air-drying conditions did not influence the P sorption capacities of the two materials (13). Both materials sorbed essentially all P from solution (13). Thermogravimetric analysis showed that water is retained within the internal structure of air-dried WTRs (data not shown). Thus, the number of sorption sites and particle rigidity should have been maintained even under air-drying conditions at room temperature.

Surface Area and Porosity: Relations to P Sorption by WTRs. Traditional BET-N₂ measurements showed large differences in SSAs among the untreated (no P added) WTRs (Figure 4). The Lowell Al-WTR had the greatest BET-N₂ SSA of all WTRs tested (100 m² g⁻¹) followed by Panama > Bradenton > Holland > Tampa > Cocoa Beach. Phosphorus sorption by WTRs reduced N₂-based SSAs for all WTRs except for the Lowell and Holland materials. However, BET-N₂ SSAs did not correlate significantly with the P sorption capacities of the materials (maximum initial P load 10 g of P kg⁻¹). Correlation may have been confounded by underestimation of P sorption capacities because of the huge affinity for soluble P by the WTRs. Alternatively, or perhaps additionally, N₂ molecules may not have reached all sorption sites due to diffusional restrictions. De Jonge and Mittelmeijer-Hazeleger (30) showed that SSAs of three soil organic matter samples were underestimated on the basis of BET-N₂ measurements. The significant C contents of WTRs (34–210 g kg⁻¹) could affect BET-N₂ SSA measurements.

Micropore volume distributions by the Saito–Foley method increased with increasing N₂-based SSAs for all WTRs,

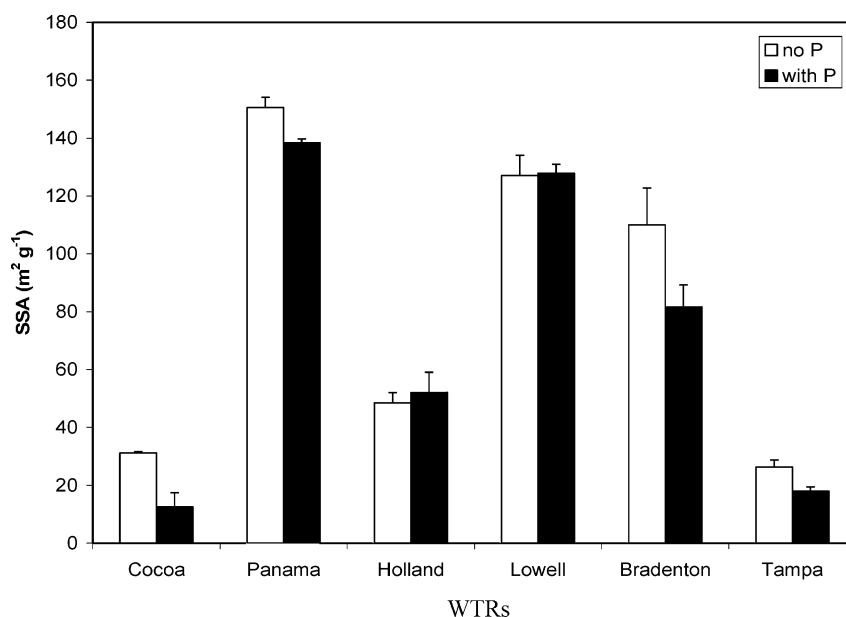


FIGURE 6. Micropore CO₂ SSA measurements for WTRs untreated and P-treated (10 g of P kg⁻¹ initial load) for 40 d. Micropore SSAs were calculated with the DRK method. Error bars denote 1 standard deviation of two replicated runs.

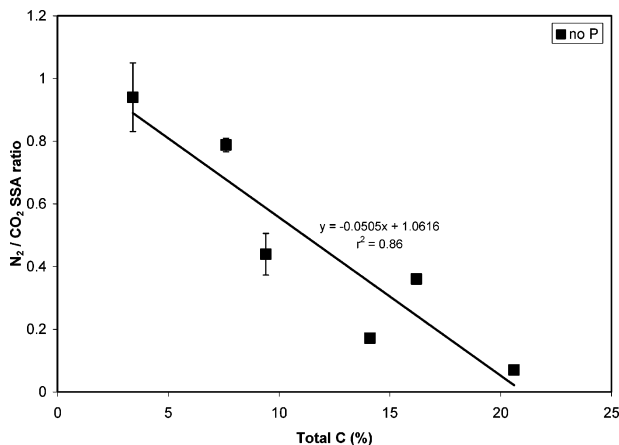


FIGURE 7. Correlation between the SSA ratio of BET-N₂ and CO₂ gas with total C of the untreated (no P) WTRs tested in this study. Error bars denote 1 standard deviation of two replicates.

but decreased when P was added, except for the two materials (Lowell and Holland) with the smallest C contents.

Representative micropore distributions (Figure 5) are presented here only for two materials: one from the group that showed micropore volume reduction when P was added (Bradenton), and one from the group that did not (Lowell). The reason for the contrasting behaviors may be related to the data in Table 3. The Lowell and Holland materials had the lowest micropore volume percent of the total pore volume (18% and 9%, respectively), whereas the Bradenton WTR had the highest (46%). Materials with large micropore volume contents showed significant pore volume reductions following P addition, whereas materials low in meso- and micropore volume content were unaffected by P addition. The data are consistent with restricted micropore access imposed by sorbed phosphate molecules.

We also hypothesized that variable-sized organic components could be trapped in the pore network of WTRs, regulating the diffusion of water and phosphate molecules. Thus, for gas molecules to diffuse through such small pores, greater activation energy is required (31). Using CO₂ instead of N₂ as the adsorbate at a higher sorption temperature (273 K) (33) enabled access to micropores of effective widths < 15 Å (Figure 6). The CO₂-based micropore SSAs of WTRs were

greater than the corresponding BET-N₂ SSAs, except for the Lowell and Holland materials. Lowell and Holland WTRs had the lowest total C content, suggesting little influence of organic C on the degree of accessibility of sorption sites, by either CO₂ or N₂. These two materials also had less micropore volume than the other Al-WTRs. No differences between CO₂-based and N₂-based SSAs were observed for P-treated samples of the Lowell and Holland materials. Phosphorus addition to the other materials significantly decreased micropore SSA, as measured with CO₂ (Figure 6), again suggesting micropore blockage by phosphates (27). Micropore widths on the order of 0.4–1 nm are comparable to the phosphate ionic diameter (around 0.4 nm). Phosphate sorption onto the pore opening could retard or restrict other solute movement. Micropore filling is another mechanism that would restrict solute movement into the micropore (32).

The CO₂ and N₂ SSA data suggest that organic compounds trapped in WTR micropores regulate the diffusion of gas molecules in and out of the micropores. A strong linear negative correlation ($r^2 = 0.86$) was observed between total C and the N₂:CO₂ SSA ratios (Figure 7). Materials with low total C content (Holland and Lowell) showed little difference in the amounts of N₂ and CO₂ sorbed (N₂:CO₂ SSA ratio close to 1). However, as the total C content of WTRs increased, so did the difference in SSAs measured by CO₂ and N₂ (CO₂ > N₂). Apparently, organic C restricted diffusion and sorption of N₂ to a much greater extent than for CO₂. Similar use of the N₂:CO₂ SSA ratio normalized to the C content was employed for native grassy or forest Chicago soils (33). They proposed using N₂:CO₂ SSA ratios to characterize and predict various soils' behavior in sequestration processes involving humic substances (33).

Data from SSA analyses for the two WTRs most extensively characterized (Tampa and Bradenton materials) showed that CO₂ SSA was better than N₂ SSA in estimating pores associated with P (27). Dinitrogen-based SSAs may exceed actual external surface areas because N₂ can also access some micropores. However, CO₂ molecules can access micropores in the lower size range (0.35–1.2 nm) where N₂ diffusion may be severely restricted. Thus, CO₂ molecules may access micropores accessible by phosphates, and/or ultramicropores (micropores smaller than 0.7 nm) (34) not accessible by phosphates. Ultramicropores may be associated with carbon structures indigenous to the WTR pore network. Thus, CO₂-

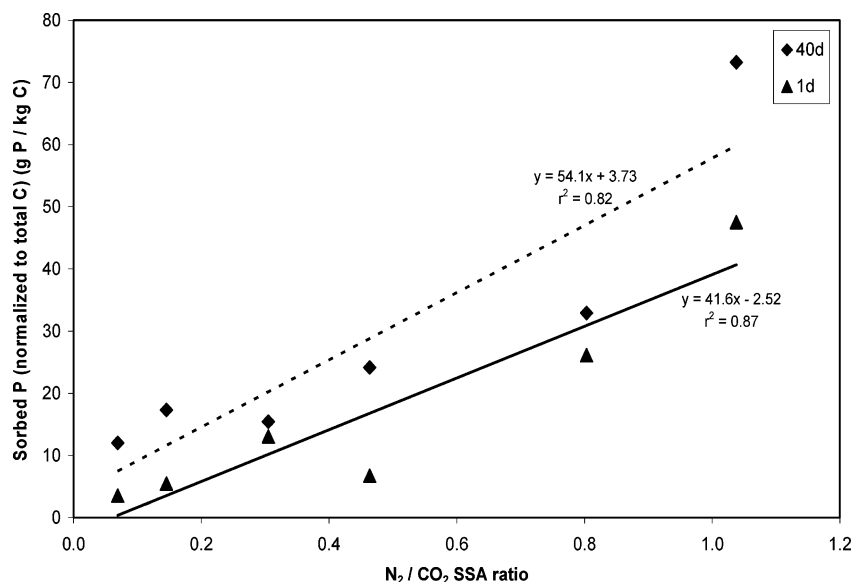


FIGURE 8. Correlation between the SSA ratio of BET-N₂ and CO₂ gas with long-term (40 d) P sorption capacities of WTRs. The initial P load was 2.5 g of P kg⁻¹. The 40 d treatment was selected as the long-term data used here. The 80 d treatment was avoided because most of the WTRs exhausted all added P from solution; thus, there were no differences in P sorption capacities among the WTRs.

based SSAs may overestimate the effective SSA that is actually accessed by phosphates.

Prediction of the long-term P sorption capacities of WTRs is not straightforward, and apparently relates to information collected from both N₂- and CO₂-based SSAs. Despite the fact that CO₂-based SSA data were better in explaining P sorption than N₂-based data, the relationship was not perfect. We used the N₂:CO₂ SSA ratios to predict the long-term capacities of the WTRs. The factor that best correlated with the N₂:CO₂ SSA ratios was total C content. The presence of organics probably retards P diffusion toward internal sites, rather than serving as significant sorption sites for phosphate molecules. Normalizing the P sorption capacity to the C content of WTRs shows the negative impact of organic C moieties on P sorption (Figure 8). This normalization does not likely reflect the amount of P sorbed by organic C (which is probably negligible), but rather the retarding effect (steric) of organic C moieties on phosphate migration toward micropores. There was a significant ($p < 0.001$) positive linear relationship between the amount of P sorbed, normalized to C, and the N₂:CO₂ SSA ratios of the WTRs (Figure 8) at the 2.5 g kg⁻¹ initial P load. There was no significant difference at the 95% confidence limit between the slopes of P sorption data obtained at 2.5 and 10 g kg⁻¹ initial P added load (Figure 8). The 2.5 g kg⁻¹ initial P load treatment was selected because it is a more realistic P load. Measuring three independent variables, i.e., total C, N₂, and CO₂ SSAs, we were able to explain 82% of the variability in the long-term measured P sorption capacities of the WTRs. The magnitude and rate of P sorption are related to WTR internal structure, i.e., pore size distribution and SSA, which in turn may be affected by organic C, a major but variable component of WTRs.

The data of this study have favorable implications for the long-term safety and efficacy of WTRs as soil amendments to mitigate P losses from sandy soils. A model that included C content along with CO₂ and N₂ SSA measurements enabled relatively accurate predictions of P sorption capacities for WTRs with different P sorption capacities. Obviously, "one size does not fit all" for WTRs that differ in physicochemical characteristics, and hence, they vary in P sorption capacities. High P sorption capacity of WTRs is favored by relatively high microporosity and SSA in conjunction with relatively low C content. Further documentation of the long-term stability of WTR particles themselves is needed.

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