

Colloidal Phosphorus in Surface Runoff and Water Extracts from Semiarid Soils of the Western United States

Benjamin L. Turner,* Mary A. Kay, and Dale T. Westermann

ABSTRACT

Colloidal particles in runoff may have an important role in P transfer from soils to waterbodies, but remain poorly understood. We investigated colloidal molybdate-reactive phosphorus (MRP) in surface runoff and water extracts of calcareous arable soils from the semiarid western United States. Colloidal MRP was determined by ultrafiltration and operationally defined as MRP associated with particles between 1 μm and 1 nm diameter, although a smaller pore-size filter (0.3 nm) was used to define the lower size limit of colloids in water extracts. In surface runoff from three calcareous soils generated by simulated sprinkler irrigation, colloidal MRP concentrations ranged between 0.16 and 3.07 μM , constituting between 11 and 56% of the MRP in the <1- μm fraction. Concentrations were strongly correlated with agronomic and environmental soil-test P concentrations for individual soils. Water extracts of a range of similar soils contained two size fractions of colloidal MRP: a larger fraction (1.0–0.2 μm) probably associated with fine clays, and a smaller fraction (3–0.3 nm) probably associated with Ca–phosphate minerals. Colloidal MRP was solubilized in the acidic medium of the colorimetric detection procedure, suggesting that a fraction of the filterable MRP in runoff from calcareous soils may not be as readily bioavailable as free phosphate in waterbodies. Our results suggest that colloidal MRP is an important but poorly understood component of P transfer in runoff from calcareous western U.S. soils and should be given greater consideration in mechanistic studies of the P transfer process.

PHOSPHORUS TRANSFER in runoff from agricultural soils to watercourses can contribute to blooms of toxin producing cyanobacteria (blue-green algae) and other water quality problems associated with eutrophication (Foy and Withers, 1995; Leinweber et al., 2002). As a result, a considerable research effort has aimed to quantify P transfer from agricultural land, and data now exist for a range of soils and agronomic management practices (for a recent review see Haygarth and Jarvis [1999]). Meaningful interpretation of such data requires a thorough understanding of P speciation and the analytical procedures involved in its determination.

Conventionally, it is considered desirable to know the concentration of free phosphate in runoff, because this is the form most readily available to algae in waterbodies (Reynolds, 1984). This is estimated by crude fractionation based on membrane filtration (typically 0.45- or 0.2- μm pore size) and reaction with molybdate (Murphy and Riley, 1962), but rarely provides an accurate value of the true dissolved phosphate concentration in envi-

ronmental samples, because a continuum of colloidal particles pass through the membrane filter. Phosphorus associated with such colloids can contribute to the MRP fraction following solubilization in the acidic medium of the reaction solution. Some acid-labile organic phosphates can also be hydrolyzed, but their contribution is negligible in the analysis of soil and soil solution (Bowman, 1989; Hens and Merckx, 2001).

Colloids are operationally defined as particles between 1 μm and 1 nm in size (Kretzschmar et al., 1999). This is somewhat arbitrary, but useful for defining particles with specific properties relating to contaminant transport in the environment. In particular, colloids have a large specific surface area, are mobile in the soil, and remain in solution for long periods of time, although sorption, flocculation, and deposition of colloids can also occur (Kretzschmar et al., 1999). The presence of colloids in runoff therefore has marked implications for understanding the P transfer process, because they facilitate the transport of contaminants such as P from the soil. They also have considerable implications for understanding the effect of P transfer on waterbodies. For example, Hudson et al. (2000) recently demonstrated that dissolved phosphate concentrations in large Canadian lakes were overestimated by orders of magnitude by molybdate colorimetry. This suggests the importance of colloidal P species in maintaining P availability to organisms and highlights the need for more detailed information on P speciation in runoff from terrestrial environments.

Colloidal P compounds can comprise a substantial component of the filterable MRP in soil solution (Shand et al., 2000; Hens and Merckx, 2002), soil water extracts (Sinaj et al., 1998), agricultural runoff, and river water (Haygarth et al., 1997). There is relatively little information on the nature of colloidal P compounds, but they can include primary and secondary P minerals, P occluded within mineral or organic compounds, P sorbed to soil particles or organic molecules, including clay–humic–metal complexes, and live bacterial cells (biocolloids) or cell fragments (Kretzschmar et al., 1999).

Most research into colloidal P in soil waters has focused on acidic and neutral soils with relatively high organic matter concentrations, in which colloidal P typically occurs as humic–metal–phosphate complexes (Gerke, 1992; Dolfing et al., 1999; Hens and Merckx, 2001). However, no information exists on colloidal P in runoff from irrigated soils of the semiarid western United States, which typically contain considerable amounts of CaCO_3 and relatively small concentrations of organic C (<10 g kg^{-1}). Such soils are agronomically important,

USDA-ARS, Northwest Irrigation and Soils Research Laboratory, 3793 N. 3600 E., Kimberly, ID 83341. B.L. Turner, current address: Soil and Water Science Department, University of Florida, 106 Newell Hall, P.O. Box 110510, Gainesville, FL 32611. Received 17 Sept. 2003.
*Corresponding author (bturner@ifas.ufl.edu).

Table 1. Site details and properties of soils used in sprinkler irrigation simulation experiments.†

	Portneuf	Warden	Greenleaf
Location	Kimberly, ID	Prosser, WA	Parma, ID
Texture	silt loam	very fine sandy loam	silt loam
Description	coarse-silty, mixed, superactive, mesic Durinodic Xeric Haplocalcids	coarse-silty, mixed, superactive, mesic Xeric Haplocambids	fine-silty, mixed, superactive, mesic Xeric Calcicargids
Mean annual temperature, °C	8.7	10.1	10.2
Mean annual rainfall, mm	275	209	260
Treatment	organic and mineral fertilizers	mineral fertilizer	mineral fertilizer
Olsen P, mg P kg ⁻¹ dry soil	34–145	11–101	4–8
	<u>Topsoil</u>	<u>Subsoil</u>	
Sand, g kg ⁻¹ dry soil	180	170	280
Silt, g kg ⁻¹ dry soil	570	660	490
Clay, g kg ⁻¹ dry soil	250	170	230
CaCO ₃ , g kg ⁻¹ dry soil	118	245	120
Organic C, g kg ⁻¹ dry soil	9.3	7.0	5.9
pH	8.0	8.1	7.7

† Soils were taken to 30 cm. Values for organic C, pH, and CaCO₃ in the Warden and Greenleaf soils are from Turner et al. (2003) (except for CaCO₃ in the Greenleaf soil, due to a specific difference in the field used for rainfall simulation experiments), while values for organic C and CaCO₃ for the Portneuf top- and subsoils are mean values of several plots (Westermann et al., 2001).

because irrigated agriculture produces nearly 40% of the total U.S. crop value from only 15% of the total cropped land (Bajwa et al., 1992). Much of this land is irrigated by sprinkler systems; for example, in the Pacific Northwest region about two-thirds of the irrigated land (1.7 million ha) is irrigated by sprinklers (USDA National Agricultural Statistics Service, 1999). The aim of this study was to quantify the importance of colloidal MRP in P transfer from calcareous arable soils of the western United States. To achieve this we used micro- and ultrafiltration to measure an operationally defined colloidal MRP fraction in surface runoff generated by simulated sprinkler irrigation, then investigated the influence of soil properties by determining colloidal MRP in water extracts of a range of western U.S. soils.

METHODS

Collection of Samples

Sprinkler Irrigation Experiments

Sprinkler irrigation experiments were conducted on soils where experimental plots with a range of soil-test P concentrations had been previously established (Table 1). Soils contained various concentrations of CaCO₃ (22–245 g kg⁻¹), <10 g kg⁻¹ organic C, and had slightly alkaline pH. The Portneuf and Greenleaf soils were silt loams, while the Warden soil was a fine sandy loam. The Portneuf soil included standard

topsoil plots, plus plots where the surface 30 cm of soil was removed to simulate the effect of erosion by long-term furrow irrigation exposing the highly calcareous subsoil (Robbins et al., 1999). The climate of the locations is semiarid, with hot, dry summers and cool, moist winters. All experiments were conducted on bare tilled soils between May and September 2002.

Sprinkler irrigation was generated using a standardized simulator and experimental protocol (Humphry et al., 2002). Briefly, the simulator was constructed from Al pipe with a single HH 50 WSQ nozzle (Spraying Systems, Wheaton, IL) 3 m above the center of the plot. Irrigation was applied onto adjacent duplicate subplots (1-m width × 2-m length) at 70 mm h⁻¹, which approximates a typical irrigation intensity from the outer ends of center-pivot sprinklers in southern Idaho. The subplots were isolated by steel frames inserted into the ground to 5 cm, leaving 5-cm borders above the surface. Surface runoff was channeled to a collection point after passing over a lip placed level with the soil surface at the down-slope end of the frame. Runoff was generated twice on each plot, first on soils at field moisture (moisture content 2–5%), then on the same plots after 24 h (moisture content 17–29%). Irrigation water was generated by reverse osmosis and supplied from a portable 1000-L tank. The water had an electrical conductivity of 7.0 μS cm⁻¹, with concentrations (mean ± standard deviation; *n* = 16) of elements (μM) being: Ca = 10.7 ± 3.5, Fe = 0.18 ± 0.14, K = 3.61 ± 1.69, Mg = 4.11 ± 1.60, Na = 51.4 ± 15.5, P = 0.06 ± 0.16, and Si = 13.1 ± 4.4.

Irrigation continued until 30 min of continuous runoff was

Table 2. Physical and chemical properties of 12 semiarid soils of the western United States, ranked in order of their organic C concentration.

Soil type†	Texture	Organic C	CaCO ₃	Clay	pH	Olsen P	Water P‡	CaCl ₂ P‡
		g kg ⁻¹ soil				mg P kg ⁻¹ soil		
Declo	loam	4.5	99	150	7.94	19.2	13.3	4.9
Portneuf subsoil (conventional)§	silt loam	5.5	234	150	8.11	30.1	15.4	5.6
Greenleaf	silt loam	5.9	29	230	7.74	13.4	11.9	3.2
Williams	loam	8.0	4	140	7.14	15.1	10.5	3.2
Portneuf subsoil (manure)§	silt loam	8.1	234	200	8.07	105.8	55.7	25.6
Portneuf (conventional)	silt loam	8.2	47	260	7.93	18.5	16.1	5.6
Roza	clay loam	8.8	2	220	6.86	22.3	18.6	5.6
Portneuf (manure)	silt loam	9.1	106	230	7.98	54.4	36.8	18.6
Millville	silt loam	10.4	480	150	8.05	6.5	4.6	1.4
Portneuf (native)	silt loam	13.4	3	150	6.70	31.4	30.7	13.3
Brinegar	loam	13.5	2	190	5.63	25.2	18.9	6.0
Palouse	silt loam	18.2	<1	240	5.16	30.5	22.1	4.6

† Conventionally managed soils received only mineral fertilizer, while manured soils received a large single application of dairy manure several years before sampling.

‡ Extracted in a 1:200 soil to solution ratio.

§ Sampled from experimental plots from which topsoil was removed to simulate the effect of erosion exposing highly calcareous subsoil (Robbins et al., 1999).

Table 3. Microfilter and ultrafilter membranes used in the study.

Membrane	Pore size μm	NMWL [†] Da	Samples filtered
Prefiltration			
Whatman GF/B	1.0 (approximate)	NA [‡]	all samples
Microfiltration			
Cyclopure Track Etch	1.0	NA	all samples
Cyclopure Track Etch	0.4	NA	water extracts
Cyclopure Track Etch	0.2	NA	water extracts
Cyclopure Track Etch	0.1	NA	water extracts
Ultrafiltration			
Amicon YM 100	0.03 (approximate)	100 000	water extracts
Amicon YM 10	0.003 (approximate)	10 000	water extracts
Amicon YM 3	0.001 (approximate)	3 000	runoff samples
Amicon YM 1	0.0003 (approximate)	1 000	water extracts

[†] Nominal molecular weight limit.

[‡] Not applicable.

collected. Total runoff was collected from each subplot in 12-L drums at 5-min intervals from the onset of runoff (determined as continuous flow of water from the collection points). Runoff samples for colloidal MRP analysis were collected in 60-mL plastic bottles and filtered immediately in the field through glass microfiber filters (GF/B; Whatman, Maidstone, UK) to remove suspended sediment. These filters have an approximate pore size of 1 μm , but preliminary tests showed that larger particles routinely passed through the filters. The filtered samples were returned to the laboratory on ice for further filtration and analysis (see below). In addition, parallel samples were filtered in the field through 0.45- μm cellulose-nitrate membranes (Millipore, Billerica, MA) for comparison with 1- μm filtered samples.

Runoff samples from the Portneuf soil were ultrafiltered and analyzed within 6 h of collection, while samples from the other soils were ultrafiltered within 6 h, stored at 4°C, and analyzed within 7 d. We considered this longer storage time acceptable given the high ionic strength in runoff from these calcareous soils, which minimizes changes associated with the determination of filterable MRP (Jarvie et al., 2002). However, the possibility that extended storage influenced colloids (e.g., aggregation, flocculation, sorption-desorption of P) cannot be ruled out. Samples for colloidal MRP determination were collected differently for the three soils. For the Portneuf soil, colloidal P was determined on samples from one subplot only, but all six 5-min samples were analyzed and reported values are flow-weighted means. For the Warden and Greenleaf soils,

colloidal P was determined on a single sample from each subplot after 30 min of runoff, and reported values are means of these two samples.

Six portions of soil were taken from the top 2 to 3 cm of each subplot before each rainfall simulation experiment and combined to produce a single bulked sample. These subplot samples were analyzed separately and the results averaged to produce a single value for each main plot. All soils were air-dried at 30°C for 7 d and stored at ambient laboratory temperature for 3 mo before analysis by four soil-test P procedures. Olsen P, an agronomic test for plant-available P, was determined by extraction with 0.5 M NaHCO₃ (adjusted to pH 8.5) for 30 min in a 1:20 soil to solution ratio (Olsen et al., 1954) and filtration through Whatman no. 42 filter papers before analysis. Water-extractable P was determined in two soil to solution ratios (1:10 and 1:200) using deionized water. Samples were shaken horizontally (160 min⁻¹) for 1 h and centrifuged at 3000 × g for 15 min. Calcium chloride-extractable P was determined by extraction with 0.01 M CaCl₂ for 1 h in a 1:10 soil to solution ratio. Both water and CaCl₂ extracts were filtered through 0.45- μm cellulose-acetate membranes (Nalgene, Rochester, NY) before analysis. In all procedures, extractions were conducted at 20°C and MRP was determined by the method of Murphy and Riley (1962). Soil pH was determined in a 1:2 soil to deionized water mixture, and moisture content was determined by drying a 100-g sample at 105°C for 24 h. Organic C concentrations were determined by

Table 4. Colloidal (1 μm –1 nm) and dissolved (<1 nm) molybdate-reactive phosphorus (MRP) and major cation concentrations in runoff generated by simulated sprinkler irrigation onto three semiarid arable soils.[†]

	Filter size	Portneuf	Warden	Greenleaf
MRP, % of MRP <1 μm	1 μm –1 nm	13–22 (18)	11–39 (24)	37–56 (45)
	<1 nm	78–87 (82)	61–89 (76)	44–63 (55)
		μM		
MRP	1 μm –1 nm	0.5–3.1 (1.4)	0.2–1.5 (0.5)	0.3–0.7 (0.5)
	<1 nm	2.1–16.6 (6.8)	0.5–5.8 (1.8)	0.4–0.8 (0.6)
Al	1 μm –1 nm	2.2–22.2 (9.3)	ND [‡] –4.5 (1.5)	1.1–7.8 (4.1)
	<1 nm	ND–0.7 (ND)	ND–3.0 (0.7)	ND–3.0 (1.1)
Ca	1 μm –1 nm	3.5–61.1 (31.7)	0.5–12.7 (7.2)	2.5–10.5 (8.2)
	<1 nm	62.1–156.2 (127.8)	2.3–15.0 (9.0)	53.2–68.9 (62.1)
Fe	1 μm –1 nm	0.7–5.4 (2.2)	ND–2.2 (0.7)	0.5–13.1 (4.5)
	<1 nm	ND–0.2 (ND)	ND–1.6 (0.4)	ND–0.2 (ND)
K	1 μm –1 nm	2.6–14.1 (6.1)	1.0–17.1 (7.4)	<0.3–1.5 (0.8)
	<1 nm	19.7–63.7 (35.6)	4.9–28.9 (16.9)	29.9–30.1 (38.1)
Mg	1 μm –1 nm	2.1–7.8 (5.4)	ND–3.7 (2.1)	3.3–7.8 (5.4)
	<1 nm	13.2–40.3 (27.6)	0.8–3.7 (2.5)	12.8–18.5 (15.6)
Si	1 μm –1 nm	5.0–59.5 (27.1)	0.7–14.2 (5.3)	4.6–22.1 (13.5)
	<1 nm	13.9–51.3 (35.6)	4.6–16.0 (8.2)	19.6–29.2 (24.6)

[†] Values are the range of concentrations from runoff generated on dry and wet soils, with the mean value in parentheses. Values for the Portneuf soil are flow-weighted means of six samples taken at 5-min intervals during 30 min of continuous runoff. Values for the Warden and Greenleaf soils are means of samples taken from each of two subplots after 30 min of continuous runoff.

[‡] Not detectable (less than the limit of detection).

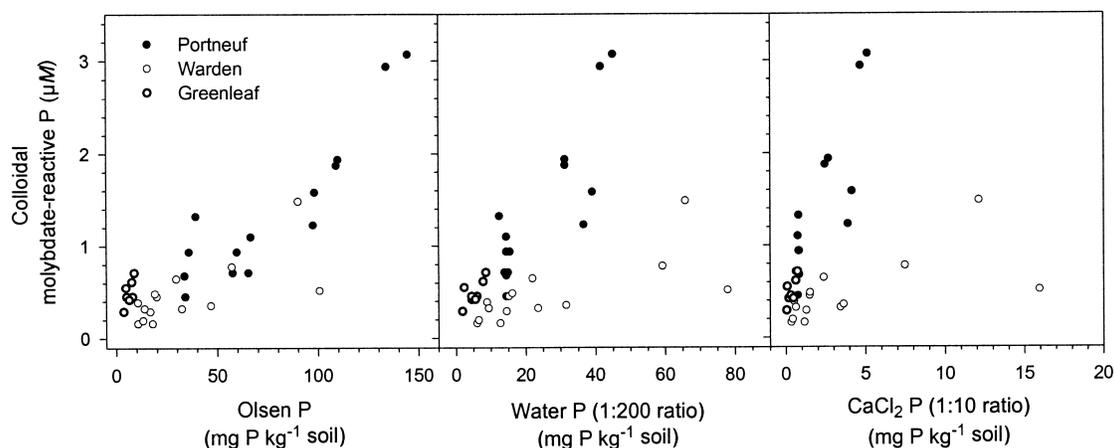


Fig. 1. Concentrations of colloidal molybdate-reactive phosphorus (MRP) (μM) in surface runoff and soil-test P (mg P kg^{-1}) for three calcareous arable soils from the semiarid western United States. Values are from sprinkler irrigation simulation experiments conducted on dry and wet soils.

dichromate digestion (Nelson and Sommers, 1982) and CaCO_3 concentrations by acid titration (Allison and Moodie, 1965).

Water Extracts of Western U.S. Soils

Twelve soils, selected to provide a range of properties typical of irrigated arable soils, were sampled to 30 cm from locations around the western United States during 2000 (Table 2). All soils were under irrigated arable cropping except the native Portneuf, which was under native (nonirrigated) sagebrush (*Artemisia tridentata* Nutt.). The sites were semiarid, with mean annual temperatures from 5.0°C at Fargo, ND, to 13.8°C at Amarillo, TX, and mean annual precipitation from 209 mm at Othello, WA, to 547 mm at Pullman, WA. The soils contained organic C concentrations between 4.5 and 18.2 g C kg⁻¹ dry soil, CaCO_3 concentrations between <1 and 480 g kg⁻¹ dry soil, and pH values between 5.16 and 8.11. The soils were air-dried (30°C), sieved (<2 mm), and stored at ambient laboratory temperature before analysis. Water- and CaCl_2 -extractable MRP were determined by mixing 5 g of soil and 1 L of solution (1:200 soil to solution ratio) in rotating drums (20 rpm) for 4 h. Samples were filtered through 0.2- μm cellulose-acetate membranes (Nalgene) and analyzed for MRP (see below).

The soils were also extracted with deionized water in a 1:100 soil to solution ratio for 4 h at 20°C to simulate surface runoff and associated colloidal P concentrations. The 4-h extraction time allowed P concentrations to equilibrate in solution. Extracts were centrifuged at 3000 \times g for 15 min, filtered through 47-mm-diameter GF/B glass microfiber filters, and stored overnight at 4°C before further filtration and chemical analysis within 24 h (see below).

Colloidal Molybdate-Reactive Phosphorus Analysis

After prefiltration, all samples (runoff and water extracts) were microfiltered through 1.0- μm Cyclopore Track Etched Membranes (Whatman) to define an upper size limit for colloidal MRP. These polycarbonate surface-capture membranes have precise cylindrical pores that provide a distinct particle size cut-off. Separations are therefore accurate and reproducible compared with those using standard membranes (e.g., cellulose-nitrate). All membranes were 47 mm in diameter, and sample loading (1–2 mL cm⁻²) was minimized to reduce clogging. As well as the 1.0- μm membranes, water extracts were also filtered through three other pore-size Cyclopore membranes to fractionate large colloidal particles (Table 3).

Ultrafiltration was performed using a 200-mL Amicon stirred ultrafiltration cell (Millipore) pressurized with N_2 (4.0 kg cm⁻³). Membranes were Amicon YM series regenerated cellulose (63.5-mm diameter), and four nominal molecular-weight limit (NMWL) membranes were used (Table 3). The membranes were initially washed in water to remove preservatives and stored in a 10% ethanol and water solution at 4°C. Before ultrafiltration, 1 mL of 5 M NaCl was added to 49 mL of sample to give a final NaCl concentration of 0.1 M. This was necessary to prevent electrostatic interaction between phosphate and the membrane surface (Shand et al., 2000), although it can also reduce the effective diameter of some colloids, particularly organic colloids, by changing their configuration. The suitability of this procedure was confirmed by the quantitative recovery of phosphate standards between 1 and 30 μM . Only half of each the sample was filtered (approximately 20 mL), which required about 15 min of filtration time.

Runoff samples (<1 μM) were ultrafiltered directly through a 3000-NMWL membrane to provide an operationally defined colloidal fraction (i.e., 1 μm –1 nm). Water extracts were micro- and ultrafiltered through a cascade of membranes to provide detailed information on colloidal size fractions (Table 3). Filtration was performed in parallel (i.e., aliquots of each water extract were filtered independently through a single membrane). All filtrates were analyzed for MRP, total P, and major cations. Total P and soluble cations (Al, Ca, Fe, K, Mg, Si) were determined by inductively coupled plasma–optical emission spectrometry (ICP–OES), with limits of detection (determined as the mean + 1.96 standard deviations of 23 blanks) being (μM): Al = 0.08, Ca = 0.25, Fe = 0.02, K = 0.26, Mg = 0.08, P = 0.06, and Si = 0.07. Molybdate-reactive P (limit of detection = 0.12 μM) was determined at 880 nm using a 1-cm cell and a 12-min reaction time (Murphy and Riley, 1962). Molybdate-unreactive P, which includes organic P, inorganic polyphosphates, and acid-resistant colloidal P, was calculated as the difference between total P and MRP, but concentrations were negligible in almost all samples and are not reported.

It is possible that Si interference may have influenced MRP determination in this study, but we consider this unlikely. In particular, interference is negligible in solutions with relatively low Si to P ratios similar to those analyzed here, and is also minimized when a short reaction time and a relatively strong H_2SO_4 concentration are used (as here) in the colorimetric procedure (Ciavatta et al., 1990).

Acidification of Water Extracts

Water extracts of three soils (Portneuf topsoil, Portneuf subsoil, Greenleaf) were further investigated by acidification before ultrafiltration. Filtered samples ($<1 \mu\text{m}$) were acidified with HCl to various pH values to pH 2. After 10 min the solutions were neutralized with NaOH (to avoid damage to ultrafiltration membranes) and colloidal MRP was determined by ultrafiltration through a 1-nm (3000-NMWL) membrane.

Statistical Analysis

Flow-weighted mean filterable MRP and sediment concentrations were calculated using concentration and flow volume data from 5-min samples. Statistical differences in regression models describing the relationship between the concentrations of soil-test P and colloidal MRP in runoff were determined using procedures described by Neter and Wasserman (1974) to indicate the significance of differences in gradients and intercepts. Data from dry and wet runs were pooled before analysis.

RESULTS

Colloidal Molybdate-Reactive Phosphorus in Surface Runoff

Colloidal MRP concentrations in surface runoff (MRP associated with particles between $1 \mu\text{m}$ and 1 nm in diameter) varied among soils, being greatest from the Portneuf soil ($0.45\text{--}3.07 \mu\text{M}$) and least from the Greenleaf soil ($0.29\text{--}0.71 \mu\text{M}$) (Table 4). Concentrations were proportionally greatest in runoff from the Greenleaf soil (37–56%) compared with the Portneuf (13–22%) and Warden soils (11–39%). Molybdate-reactive P concentrations in samples filtered through a $1.0\text{-}\mu\text{m}$ membrane were rarely different from those measured in parallel samples filtered through a $0.45\text{-}\mu\text{m}$ membrane (data not shown).

For individual soils, colloidal MRP concentrations in runoff were strongly correlated with soil-test P concentrations (Fig. 1; Portneuf, $r > 0.85$, $P < 0.001$; Warden, $r > 0.65$, $P < 0.01$; Greenleaf, $r > 0.68$, $P < 0.10$). However, there were statistically significant differences in gradients of the regression models among the three soils, with the Warden soil being significantly different from the Greenleaf and Portneuf soils for all soil P tests. The latter two soils were not significantly different for any soil P test (data not shown).

Most Al and Fe in surface runoff was colloidal (Table 4), with only small amounts passing through a 1-nm membrane. In contrast, only small proportions of Ca, K, Mg, and Si were colloidal. For example, in runoff from the Greenleaf soil, concentrations of colloidal Fe ranged between 0.54 and $13.07 \mu\text{M}$, with $<0.18 \mu\text{M}$ passing through a 1-nm membrane. In contrast, concentrations of colloidal K were $<1.53 \mu\text{M}$, with between 29.92 and $30.13 \mu\text{M}$ passing through a 1-nm membrane (Table 4). For the Portneuf and Greenleaf soils, colloidal MRP was significantly correlated with colloidal Ca ($P < 0.001$; Fig. 2), but no such correlations existed for other cations ($P > 0.05$). In contrast, colloidal MRP concentrations were significantly correlated with concentrations of col-

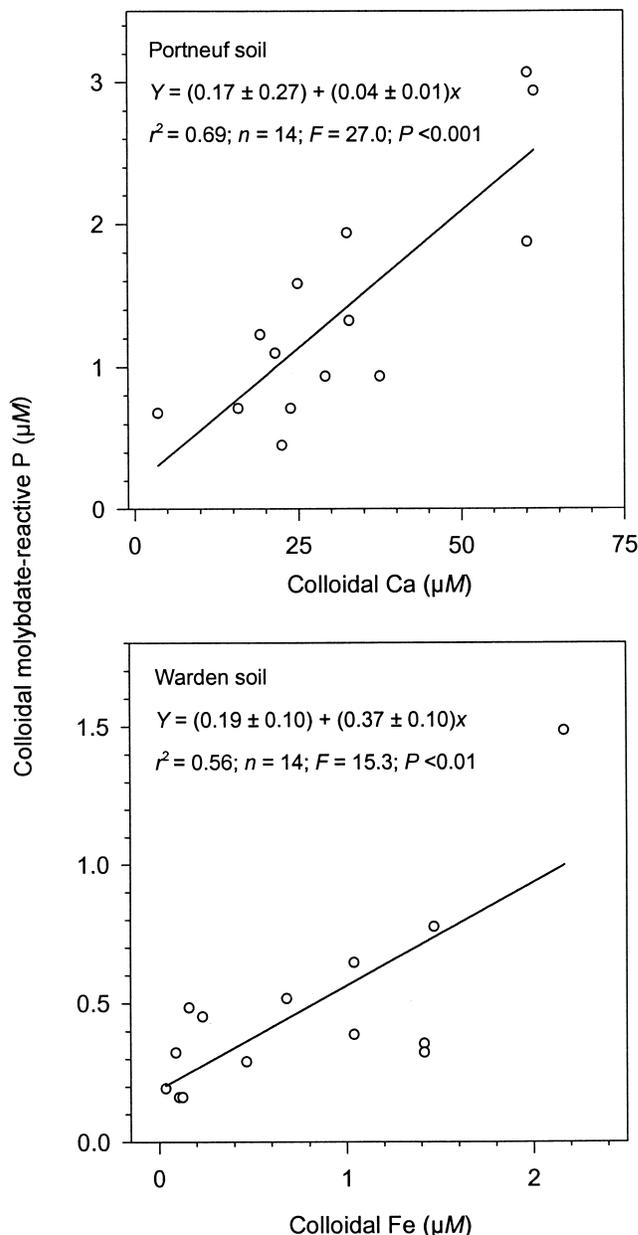


Fig. 2. Correlations between surface runoff concentrations of colloidal molybdate-reactive phosphorus (MRP) (μM) and colloidal Ca (μM) for the Portneuf soil (top), and colloidal Fe (μM) for the Warden soil (bottom). Runoff was generated by simulated sprinkler irrigation. Colloidal fractions were defined as particles between $1 \mu\text{m}$ and 1 nm in diameter.

loidal Al, Fe, and Si in runoff from the Warden soil ($P < 0.01$; e.g., for colloidal Fe, Fig. 2).

Colloidal Molybdate-Reactive Phosphorus in Water Extracts

Concentrations of colloidal MRP in water extracts (MRP associated with particles between $1 \mu\text{m}$ and 0.3 nm in diameter) ranged from $0.20 \mu\text{M}$ for the Williams loam to $2.88 \mu\text{M}$ for the manured Portneuf topsoil, being proportionally smallest for the native Portneuf and the Brinegar loam (21%) and greatest for the Millville silt

Table 5. Concentrations of elements and molybdate-reactive phosphorus (MRP) associated with particles between 1 μm and 0.3 nm in water extracts (1:100 soil to solution ratio) of 12 western U.S. soils.[†]

Soil type‡	Colloidal element concentration				
	MRP	Al	Ca	Fe	Mg
	μM				
Declo	0.8 \pm 0.3 (38)	10.8 \pm 5.6 (99)	50.1 \pm 21.1 (28)	3.1 \pm 1.6 (100)	11.3 \pm 2.2 (36)
Portneuf subsoil (conventional)	1.1 \pm 0.3 (42)	5.4 \pm 1.5 (92)	95.6 \pm 29.2 (41)	1.7 \pm 0.3 (100)	18.2 \pm 4.5 (30)
Greenleaf	1.2 \pm 0.1 (35)	15.7 \pm 0.4 (100)	21.5 \pm 6.4 (19)	6.0 \pm 0.2 (99)	8.9 \pm 0.7 (39)
Williams	0.2 \pm 0.1 (29)	28.4 \pm 4.0 (98)	9.4 \pm 2.0 (17)	9.5 \pm 1.2 (98)	10.0 \pm 0.6 (36)
Portneuf subsoil (manure)	2.6 \pm 0.9 (25)	4.3 \pm 1.3 (83)	51.1 \pm 24.4 (24)	1.3 \pm 0.3 (88)	16.0 \pm 4.8 (29)
Portneuf (conventional)	1.3 \pm 0.3 (29)	21.2 \pm 6.3 (99)	28.6 \pm 4.1 (20)	6.3 \pm 1.8 (99)	13.4 \pm 1.7 (34)
Roza	1.3 \pm 0.2 (24)	18.1 \pm 1.0 (100)	2.6 \pm 0.8 (21)	5.0 \pm 0.3 (99)	3.5 \pm 0.2 (44)
Portneuf (manure)	2.9 \pm 0.5 (30)	26.7 \pm 0.9 (99)	67.2 \pm 3.0 (35)	7.9 \pm 0.3 (100)	17.4 \pm 1.4 (35)
Millville	0.8 \pm 0.1 (51)	21.2 \pm 2.5 (99)	28.8 \pm 4.8 (20)	6.2 \pm 0.7 (99)	14.3 \pm 0.9 (41)
Portneuf (native)	1.8 \pm 0.5 (21)	21.1 \pm 3.2 (99)	2.0 \pm 4.2 (7)	6.2 \pm 0.9 (99)	6.5 \pm 1.4 (36)
Brinegar	1.2 \pm 0.2 (21)	32.4 \pm 6.9 (95)	3.7 \pm 3.1 (21)	10.7 \pm 2.1 (96)	6.3 \pm 2.4 (53)
Palouse	0.9 \pm 0.1 (18)	22.5 \pm 3.0 (99)	1.2 \pm 2.4 (10)	7.9 \pm 1.1 (100)	2.7 \pm 0.4 (45)

[†] Values are mean \pm standard deviation of three replicate extracts, with the proportion of the total (<1 μm) element concentration in parentheses.

[‡] Conventionally managed soils received only mineral fertilizer, while manured soils received a large single application of dairy manure several years before sampling.

loam (51%) (Table 5). The latter soil contains a large CaCO_3 concentration derived from dolomitic limestone. Most of the colloidal MRP occurred in the 1.0- to 0.4- μm and 3- to 0.3-nm fractions, with relatively little of intermediate size (Fig. 3).

Concentrations of colloidal Al and Fe in water extracts were smallest in the manured Portneuf subsoil (4.31 and 1.25 μM for Al and Fe, respectively), and greatest in the Brinegar loam (32.42 and 10.65 μM for Al and Fe, respectively). These concentrations represented >95% of the Al and Fe in the <1- μm fraction for all soils except the conventionally managed Portneuf subsoil (Table 5). Almost all colloidal Al (not shown) and Fe occurred in the 1.0- to 0.2- μm size range (Fig. 3).

Concentrations of colloidal Ca and Mg in water extracts were considerably greater in the more calcareous soils. For example, concentrations of colloidal Ca ranged from 1.18 μM in extracts of the acidic Palouse silt loam, to 95.63 μM in extracts of the highly calcareous conventionally managed Portneuf subsoil (Table 5). Colloidal Ca concentrations were proportionally smallest for the native Portneuf soil (7%) and greatest for the conventionally fertilized Portneuf subsoil (41%). Water extracts of the latter soil also contained the greatest concentration of colloidal Mg (18.24 μM). Proportions of colloidal Mg were smallest for the manured Portneuf subsoil (29%) and greatest for the Brinegar loam (53%). Most colloidal Ca occurred in the 1.0- to 0.4- μm and 3- to 0.3-nm fractions, whereas colloidal Mg was more evenly distributed across the whole colloidal size range (Fig. 3).

Colloidal MRP concentrations in water extracts were not significantly correlated with any of the colloidal elements, but were strongly positively correlated with soil-test P concentrations (Fig. 4). Indeed, similar relationships existed between soil-test P and colloidal MRP for both agronomic (Olsen P) and environmental (water and CaCl_2) soil-test P procedures. Proportions of colloidal MRP were greater in alkaline soils containing large concentrations of CaCO_3 and smaller concentrations of organic C (Fig. 4).

Acid Solubilization of Colloidal Molybdate-Reactive Phosphorus

Colloidal MRP concentrations in water extracts of three soils decreased markedly on acidification (Fig. 5). Most of the decrease occurred between pH 6 and 3, with relatively little change on further acidification to pH 2. Proportional decreases in colloidal MRP concentrations were between 64 and 69% for the three soils.

DISCUSSION

Up to 50% of the filterable (<1 μm) MRP in surface runoff from calcareous arable soils was associated with colloidal particles, representing an important component of P transfer from these soils, and a considerable error in the estimation of free phosphate by molybdate colorimetry. Furthermore, these values are probably underestimates, because ultrafiltration of water extracts through a finer membrane (0.3 nm) than that used to operationally define the colloidal fraction in surface runoff removed even more MRP from solution. Colloidal MRP concentrations were greatest in water extracts of alkaline soils with high CaCO_3 and low organic matter concentrations, and were positively correlated with both agronomic and environmental soil-test P procedures. As these correlations were derived from several different soils, this suggests a relatively consistent response of colloidal MRP to soil-test P irrespective of soil physical and chemical properties.

The importance of colloidal MRP in runoff from calcareous soils was unexpected, because colloidal MRP is conventionally perceived as being most important in neutral or acidic soils with relatively high organic matter concentrations, in which humic-metal-phosphate complexes predominate (e.g., Gerke, 1992; Hens and Merckx, 2001). For example, water extracts of three acidic soils rich in Al and Fe contained much greater proportions of colloidal MRP than an extract of a calcareous Xerochrept from Albania (Sinaj et al., 1998). In the current study, it is possible that the use of reverse-osmosis water in irrigation simulation experiments facilitated colloid detachment, because soil dispersion is favored by low-

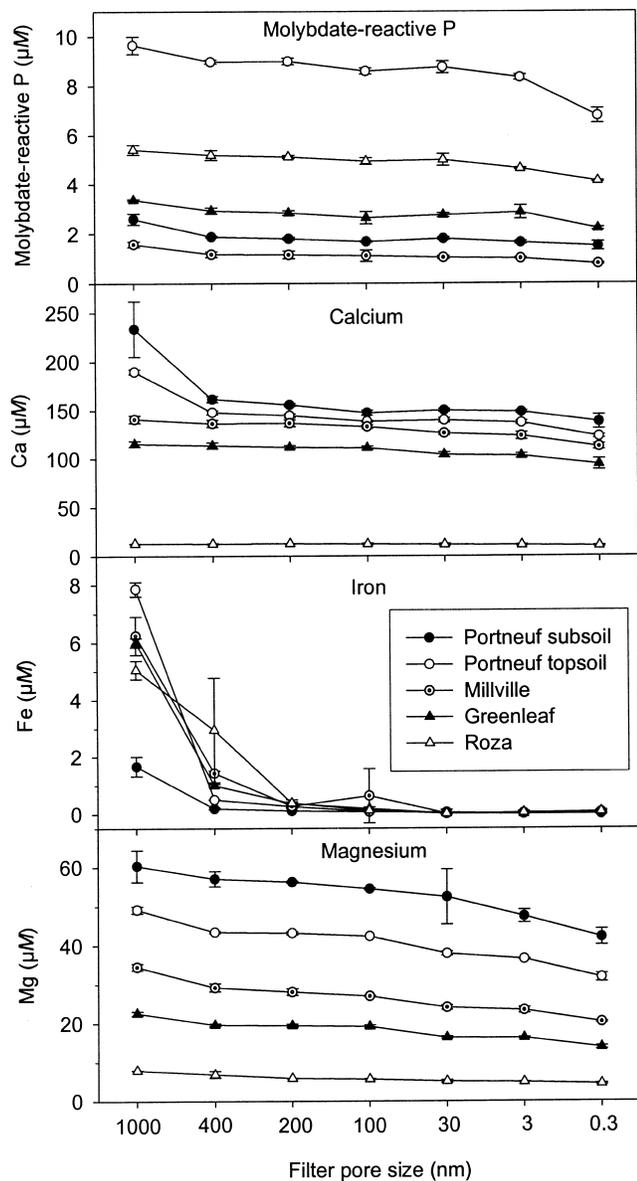


Fig. 3. Concentrations (μM) of molybdate-reactive phosphorus (MRP), Ca, Fe, and Mg in size fractions of water extracts of five representative semiarid arable soils of the western United States. Values for each filter pore size indicate the concentration passing through that filter.

ionic-strength water (Kretzschmar et al., 1999). This suggests that colloidal MRP might be quantitatively less important in runoff generated by the relatively high-ionic-strength irrigation water used in the western United States, the main source of runoff from farmland in this semiarid region.

Colloidal MRP was associated with two size fractions. The larger fraction (1.0–0.2 μm) was mainly associated with Al and Fe, so probably represented phosphate sorbed to clay-sized particles. This fraction was almost completely removed by filtration through a 0.2- μm membrane, and probably constituted the majority of the colloids in runoff from the Warden soil. A second smaller size fraction (3–0.3 nm) was associated with colloidal Ca and Mg, suggesting the presence of Ca-

and Mg-phosphate minerals. These smaller particles probably constituted the majority of the colloids in runoff from the more calcareous Greenleaf and Portneuf soils. Based on the mineralogy of these calcareous soils, it is probable that colloidal compounds included β -tricalcium phosphate, octocalcium phosphate, and possibly some hydroxyapatite (Robbins et al., 1999). It is unlikely that Mg-phosphates would contribute, because they are relatively soluble and only likely to occur ephemerally following phosphate fertilization (Lindsay et al., 1962). However, it is possible that Mg is associated with some of the Ca-phosphate minerals, which may explain the strong correlations between colloidal concentrations of MRP and Mg. Furthermore, it is interesting to note that Ca- and Mg-phosphate complexes can exist in solution between pH 7 and 9 if sufficient Ca and Mg ions are present (Lindsay, 1979). Molecular weights of such complexes are <1000, suggesting that at least some of the MRP that passed through the finest pore-size filter membrane (1000 NMWL, 0.3 nm) was not free phosphate. Confirmation of the contribution of Ca- and Mg-phosphates to the colloidal MRP fraction requires detailed investigation of colloidal particles by analytical techniques such as scanning electron microscopy.

The presence of large concentrations of colloidal P in surface runoff places an important limitation on our understanding of P transfer from western U.S. soils. For example, large concentrations of colloidal MRP suggest a greater mobility of MRP in the environment, because phosphate is readily removed from solution by sorption to soil and sediments, whereas colloids are much more mobile and can escape relatively easily to surface water systems (Kretzschmar et al., 1999). Such mobility can facilitate P leaching to depth in soils that would otherwise retain phosphate in the profile (Turner and Haygarth, 2000). In addition, evaluation of mechanisms involved in phosphate desorption is difficult when a large proportion of the filterable MRP is associated with colloidal particles and, therefore, not technically solubilized (Hamon and McLaughlin, 2002).

The presence of large concentrations of colloidal P in runoff also has important implications for the impact of P transfer on waterbodies. Free phosphate is considered to be readily bioavailable to aquatic microorganisms and, therefore, to pose the greatest threat to water quality (Reynolds, 1984; Haygarth and Jarvis, 1999). However, if much of the MRP in runoff from calcareous soils actually consists of mineral phosphates that become solubilized only at pH values unlikely to be encountered in the environment, then at least a fraction of the MRP cannot be considered readily bioavailable. This suggests that simple assumptions concerning the potential bioavailability of MRP in runoff from calcareous soils may be misleading, but does not preclude the possibility that aquatic microorganisms possess mechanisms to access colloidal P (e.g., by inducing local changes in pH), nor that phosphate may be released from colloids following changes in the carrying solution (e.g., sediment to solution ratio). Indeed, it is likely that the free phosphate concentration in solution fluctuates

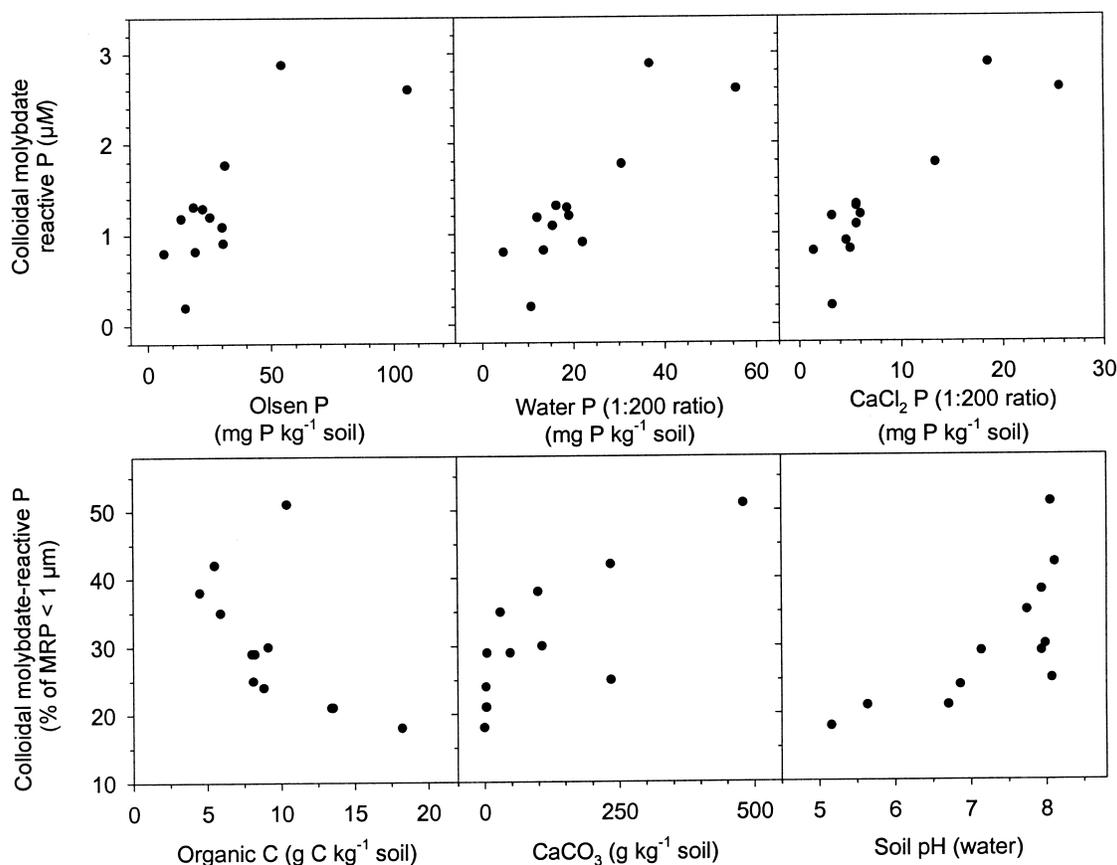


Fig. 4. Correlations between soil properties and concentrations of colloidal molybdate-reactive phosphorus (MRP) in water extracts of 12 semiarid arable soils of the western United States. Colloidal MRP concentrations are in μM (top row of figures) and as the proportion (%) of the filterable ($<1\ \mu\text{m}$) MRP (bottom row of figures). Colloidal MRP was defined as P associated with particles between $1\ \mu\text{m}$ and $0.3\ \text{nm}$ in diameter.

continuously in response to a range of physical, chemical, and biological processes during transport (Baldwin et al., 2002). It may be possible to estimate the potential bioavailability of the colloidal P fraction by adaptation of an anion-exchange resin procedure described recently for the particulate fraction (Uusitalo et al., 2003).

It seems difficult to overcome problems associated with the presence of colloidal P species in runoff, at least for routine analysis. Ion chromatography provides a much closer approximation of free phosphate in solution, but is relatively impractical for routine analysis of large numbers of samples, and phosphate sorption to colloidal particles can still interfere in the procedure (Sinaj et al., 1998). The use of 0.2- rather than 0.45- μm membrane filters will eliminate interference from fine clays (as often used by limnologists and recommended by Sinaj et al., 1998), but not the presence of the finer colloidal fraction. Ultrafiltration provides a more accurate measure of free phosphate, but lengthens analytical time to impractical levels for routine analysis. However, ultrafiltration or ion chromatography of a small number of representative samples will at least indicate the likely importance of colloidal MRP in the particular environment under investigation, and is recommended for future studies of MRP in runoff from agricultural land.

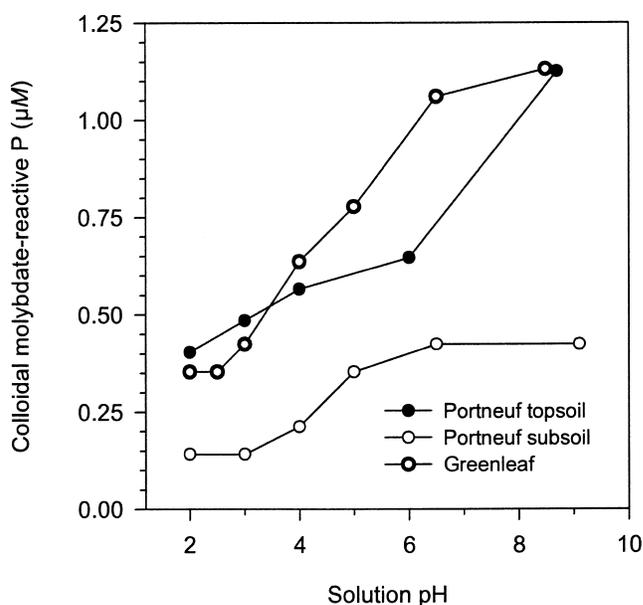


Fig. 5. Concentrations of colloidal molybdate-reactive phosphorus (MRP) (μM) in water extracts of three semiarid arable soils following acidification to different pH values with HCl. Colloidal MRP was defined as P associated with particles between $1\ \mu\text{m}$ and $0.3\ \text{nm}$ in diameter, and solutions were neutralized before filtration to prevent membrane damage.

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