Subsurface transport of orthophosphate in five agricultural watersheds, USA

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SUMMARY

Concentrations of dissolved orthophosphate (ortho P) in the unsaturated zone, groundwater, tile drains, and groundwater/stream water interfaces were assessed in five agricultural watersheds to determine the potential for subsurface transport. Concentrations of iron oxides were measured in the aquifer material and adsorption of ortho P on oxide surfaces was assessed by geochemical modeling. Attenuation of ortho P in these aquifers was attributed primarily to sorption onto iron oxides, and in one location onto clay minerals. Only one location showed a clear indication of phosphorus transport to a stream from ground-water discharge, although groundwater did contribute to the stream load elsewhere. Subsurface ortho P movement at a site in California resulted in a plume down gradient from orchards, which was attenuated by a 200 m thick riparian zone with natural vegetation. Iron oxides had an effect on phosphorus movement and concentrations at all locations, and groundwater chemistry, especially pH, exerted a major control on the amount of phosphorus adsorbed. Groundwater pH at a site in Maryland was below 5 and that resulted in complete sequestration of phosphorus and no movement toward the stream. Geochemical modeling indicated that as the surfaces approached saturation, groundwater concentrations of ortho P rise rapidly.

1. Introduction

Nutrient transport (nitrogen and phosphorus compounds) from agricultural fields to surface and groundwater is one of the most serious environmental problems throughout the world (Salvia-Castellvi et al., 2005; National Research Council, 2005; Diaz et al., 2004). Eutrophication, or excessive growth of algae, of surface water bodies impairs their use for recreation and domestic consumption and limits their use by native biota. Where surface water is chlorinated and used for drinking water, increased levels of algae contribute to the formation of trihalomethanes and haloacetic acids (Scully et al., 1988; Oliver and Shindler, 1980), which have been shown to be both carcinogenic and mutagenic in laboratory toxicity studies (Boorman, 1999). Recently, Sprague and Lorenz (2009) reported an increase in total phosphorus concentrations in streams in the central United States between 1993 and 2003. The increase in total phosphorus was significantly correlated with an increase in fertilizer use. No significant change in total phosphorus was found in streams in the western or eastern United States.

In natural systems, phosphorus is mainly cycled through a plant-soil dynamic. However in agricultural systems, phosphorus is removed at harvest and must be replenished with either mineral fertilizer or manure. Soils may be over applied with respect to phosphorus because many management programs are tied to nitrogen control or crop needs and phosphorus management is not always considered (Sharpley et al., 2003). This issue is common in areas using manure, which typically has a N:P ratio lower than needed by most crops. Application of manure to meet N requirements often results in the application of P exceeding crop demand. Surface water contamination with phosphorus due to runoff from manured fields (Klauser et al., 1976; Hergert et al., 1981; Allen and Mallarino, 2008) and agriculture in general (Baker et al., 1975; Burwell et al., 1977; Sharples and Syers, 1979; Vollenweider, 1968) is a well-studied topic.

It is known that phosphorus sorbs to soil particles. Phosphorus sorbs onto oxides of iron and aluminum (Hemwell, 1957; Zhang and Huang, 2007), clay minerals (Parfitt, 1978) and to calcium carbonate (Cole et al., 1953). It has been assumed that phosphorus transport to groundwater is negligible because of sorption and therefore earlier studies on phosphorus transport have been focused solely on surface water pathways (Baker et al., 1975; Burwell et al., 1977; Sharples and Syers, 1979; Vollenweider, 1968). Attenuation of phosphorus movement and plant availability by interactions onto soil particles has been recognized by previous research (Gunjigake and Wada, 1981; Anderegg and Naylor, 1988; Parfitt, 1978). More recent studies (Devau et al., 2009), for example, have...
Further refined understanding of various factors, such as soil pH, with respect to phosphorus mobility or plant availability and the importance of clay minerals, in addition to iron and aluminum oxides for controlling the distribution of phosphorus between soil and water.

It was hypothesized for this study that phosphorus movement in the unsaturated zone and along a groundwater flow path to a stream or tile drain would be different with location because of hydrological and chemical factors. Processes affecting the rate of water movement through the unsaturated zone are likely to be important for phosphorus transport as well as processes that affect sorption or dissolution. Chemical equilibrium may not be achieved in the unsaturated zone because of short residence times at some locations, if transport times are fast such as might occur because of preferential flow paths, and because of competition for sorption sites from competing ions. It was further hypothesized that groundwater processes affecting phosphorus would more likely be closer to equilibrium relative to the unsaturated zone as residence time increases and groundwater chemistry stabilizes allowing equilibrium conditions between the fluid and the solids. Groundwater/surface water interactions should also differ with location relative to the amount and direction of exchange of water across the streambed interface. Unsaturated zone, groundwater, and streambed materials and water chemistry are expected to affect the transport or immobilization of phosphorus. In a previous study at a set of five watersheds across a range of climatic and soil types in the United States, Domagalski et al. (2008a) showed that baseflow contributed more than 20% of the annual ortho P load in some of the streams of this study. Tesoriero et al. (2009) examined the baseflow index of some of the same streams, as this study, with a range of groundwater contributions to discharge. They found that the baseflow index was negatively correlated with in-stream ortho P concentrations at most sites. However, at sites dominated by baseflow or having favorable geochemical conditions (e.g., aquifers having low dissolved oxygen concentrations or lacking in iron and aluminum oxides, clay minerals, and calcium carbonate) groundwater contributions of ortho P to streams are important (Tesoriero et al., 2009). The purpose of this investigation was to examine the geochemical conditions and reactions affecting ortho P concentrations in the subsurface environmental compartments (unsaturated zone, groundwater, groundwater/surface water interface) of the five watersheds from the Domagalski et al. (2008a) and Tesoriero et al. (2009) studies. Geochemical modeling was used to determine the level of saturation of ortho P with respect to minerals and sorption onto iron oxides. The results of the modeling were used to interpret the subsurface ortho P concentrations and assess the potential for phosphorus transport along the groundwater flow paths.

2. Study areas

Five study areas were chosen in agricultural watersheds nested within larger basins that are being investigated by the US Geological Survey (USGS) NAWQA Program (US Geological Survey, 2010a) (Fig. 1). Specific characteristics of the aquifers, crop types, and phosphorus use for each study area are shown in Table 1. Study areas were chosen from a previous investigation that included important agricultural systems and to cover a range of hydrologic settings using the hydrologic landscape concept (Capel et al., 2008). The focus of the previous investigation was on nitrogen and pesticide transport. Transport of water, nitrogen, and pesticides had previously been examined within and across different hydrologic compartments including the atmosphere, the unsaturated zone, groundwater, and the stream/groundwater interface (Fisher and Healy, 2008; Green et al., 2008; Essaid et al., 2008; Puckett et al., 2008; Steele et al., 2008; Domagalski et al., 2008a, 2008b; Hancock et al., 2008). Watersheds selected were the DR2 Drain within the Yakima River Basin, Washington; the lower Merced River, within the San Joaquin-Tulare Basins, California; Maple Creek within the Central Nebraska Basins, Nebraska; the Leary Weber Ditch within the White River Basin, Indiana; and Morgan Creek within the Delmarva Peninsula, Maryland. Detailed site locations have been described previously (Capel et al., 2008).

The lower Merced River Basin is located in the eastern San Joaquin Valley of California and occupies 1323 km². The climate is semi-arid with most of the rainfall occurring in the winter. The major crops are orchards and vineyards with some row crops and pasture. Soils are mainly loams and sandy loams. There is a narrow strip of natural vegetation adjacent to the river. All agriculture requires irrigation and most of that water is transported from outside of the immediate study area. The groundwater flow in the immediate study area is towards the Merced River. The riverbed consists of coarse sand and gravel alluvial deposits. Recharge in the study area occurs primarily at the land surface with secondary contributions from subsurface inflow from upgradient areas. About two thirds of areal recharge is attributed to irrigation return flow, and the remainder to precipitation. Irrigation drives a downward gradient of recharge water in the agricultural fields and orchards (Domagalski et al., 2008b). About one third of the applied phosphorus is chemical and the remainder is manure (Gronberg and Kratzer, 2006).

The DR2 Drain is located in south-central Washington and occupies 5.5 km². The climate is arid to semi-arid, with very little or no rainfall occurring during the growing season, and crops include corn, other row crops, orchards, vineyards, and dairies. Most of the soils are well drained, are sandy to clayey in texture, and are very shallow to very deep. The upper 3–10 m of aquifer material is silty sands and clayey silts (Payne et al., 2007). Irrigation water is supplied from outside the DR2 basin from the Yakima River through a series of canals. Shallow subsurface flow in this area has been modified by an extensive system of buried drains (Capel et al., 2008). The shallow subsurface flow discharges to the DR2 Drain and contributes greatly to year-round flow (Capel et al., 2008). The bed of the DR2 Drain consists of silty sands and clayey silts similar to the aquifer material and, locally, has relatively high organic matter content. Phosphorus use data are not available for this watershed, but it is known that a combination of chemical fertilizer and manure is used, with considerable amounts of manure application.

Maple Creek is a tributary to the Elkhorn River in eastern Nebraska and occupies 956 km². Land use is predominately agriculture consisting mainly of corn, soybeans, and alfalfa. Glacial till and Quaternary-age loess mantles the hills and forms terraces over sand and gravel deposits that make up the primary aquifer materials. Soils are fine-textured aeolian sand, silt, and loess. The climate is humid continental and precipitation is supplemented with irrigation from groundwater to supply crop water needs. Groundwater discharge supports baseflow during the late growing season and winter; this discharge occurs where stream channels intersect the sand and gravel aquifer (Frederick et al., 2006; Puckett et al., 2008). Amounts of phosphorus from manure are not available.

The Leary Weber Ditch is a 7.5 km² watershed in Central Indiana, with the agriculture dominated by corn and soybeans. The climate is humid continental and precipitation supplies all crop water demand. The watershed is underlain by glacial till deposits, and soils are loams or silty loams. The till-derived soils have poor drainage, which necessitates the use of tile drains to prevent water logging of the soils (Baker et al., 2006). Most of the applied phosphorus is chemical, and manure use is minimal (Lathrop, 2006).

Morgan Creek is a 31 km² watershed in eastern Maryland within the Chester River Basin. Crops include corn, soybeans and grains.
The climate is humid subtropical (Hancock and Brayton, 2006) and precipitation supplies most of the crop water needs except during dry periods. Soils are mainly well to moderately well drained fine silt loams with some clay. The watershed is underlain by quartz sands and gravels (Owens and Denny, 1979; Owens and Minard, 1979). Within the study reach, the entire flood plain consists of a 1–2 m thick layer of heavy silt and clay. This impervious clay layer prevents direct movement of groundwater through the streambed; however groundwater discharges from seepage zones at the lateral margins of the flood plain. Both chemical fertilizer and manure are used (Hancock and Brayton, 2006).

3. Methods

3.1. Field methods

Unsaturated-zone monitoring locations were equipped with instrumentation to measure surficial soil temperature, soil heat flux, soil water matric potential and soil moisture at depth in order to estimate the flux of water out of the soil and the amount of water in the soil. Polyvinylchloride lysimeters with ceramic porous cups were installed at various depths to collect unsaturated zone water for chemical analysis by applied suction. The shallowest lysimeter was located just below the root zone and the deepest just above the water table. In all cases, lysimeters were always installed at the upper portion of the flow path location. Additional lysimeters were installed at other locations in order to obtain more information on recharge characteristics.

Details of the study design have been described previously (Carpel et al., 2008). In general, clusters of monitoring wells were installed at sites along a groundwater transect that was oriented in the general direction of groundwater flow. The direction of flow was determined by water levels and monitoring of hydraulic head. Wells were drilled at appropriate depths at each study site in order to capture the chemistry and hydrology of the recently recharged water and water of various ages along the flow path to the stream.

Table 1

Aquifer characteristics, crop types, and phosphorus use for each location.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Washington</th>
<th>California</th>
<th>Nebraska</th>
<th>Indiana</th>
<th>Maryland</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crop</strong></td>
<td>Corn/orchards</td>
<td>Almonds/Corn</td>
<td>Corn/soybeans</td>
<td>Corn/soybeans</td>
<td>Corn/soybeans</td>
</tr>
<tr>
<td><strong>Irrigation rate (yr, cm)</strong> (Fisher and Healy, 2008)</td>
<td>74.4</td>
<td>120</td>
<td>20.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Phosphorus use, 2004 (kg/ha)</strong></td>
<td>Not available</td>
<td>21 (Gronberg and Kratzer, 2006)</td>
<td>45 (Fredrick et al., 2006)</td>
<td>67 (Lathrop, 2006)</td>
<td>48 (Hancock and Brayton, 2006)</td>
</tr>
<tr>
<td><strong>Water table depths (m)</strong></td>
<td>4.8</td>
<td>7.2</td>
<td>4.4–21.8</td>
<td>1.0–1.8</td>
<td>4.4–11.1</td>
</tr>
<tr>
<td><strong>Soil texture</strong></td>
<td>Silty clay to fine sand</td>
<td>Fine to medium sand</td>
<td>Deep, well to poorly drained, silt and silty clay</td>
<td>Silty clay loam to silt loam</td>
<td>Fine sandy loam to medium sand</td>
</tr>
<tr>
<td><strong>Average weight (%) sand</strong></td>
<td>52.6</td>
<td>92.4</td>
<td>56</td>
<td>14</td>
<td>62.1</td>
</tr>
<tr>
<td><strong>Average weight (%) silt</strong></td>
<td>42.5</td>
<td>6.5</td>
<td>36</td>
<td>73.5</td>
<td>31.2</td>
</tr>
<tr>
<td><strong>Average weight (%) clay</strong></td>
<td>4.9</td>
<td>1.1</td>
<td>8</td>
<td>12.5</td>
<td>6.7</td>
</tr>
<tr>
<td><strong>Bulk mineralogy</strong></td>
<td>Quartz, plagioclase, feldspar, calcite</td>
<td>Quartz, plagioclase, feldspar</td>
<td>Quartz, plagioclase, feldspar</td>
<td>Quartz, dolomite, plagioclase, calcite</td>
<td>Quartz, clay, feldspar</td>
</tr>
<tr>
<td><strong>Organic matter, %</strong></td>
<td>2</td>
<td>0.4</td>
<td>4.4</td>
<td>3.6</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Because of the drainage pattern at the Indiana location, the study design was modified and tile drains were sampled. River transects, where appropriate, were established to gather information on the interaction of groundwater and surface water. Transects were established down gradient of the groundwater flow path. Wells were installed in the riverbed at 0.5 m and 2–3 m depth and equipped with pressure transducers and temperature loggers to measure direction of groundwater flow. Five sets of these well pairs were installed including a set on each bank and three pairs within the channel. To collect water samples, 4.5 cm stainless steel drive-point tips with 2-cm screens were co-located with each well set. Nylon tubing (6 mm) was attached to the drive-point tips and routed to a shelter on the bank for sampling access.

Recharge and water travel times from land surface to various depths within the unsaturated zone were estimated by means of a bromide tracer test conducted at each study site. Bromide was applied to a level of 12–15 g/m² to the surface of a 12 m² section of land overlying the lysimeter clusters. Water samples collected from the lysimeters over time were analyzed by ion chromatography to define bromide breakthrough curves. Analyses of these samples enabled calculation of a range of travel times, velocities, and specific water fluxes for each site. Travel time and velocity of water movement in the unsaturated zone was also estimated by a previously described piston-flow model (Fisher and Healy, 2008).

Water samples were collected by various methods depending on the environmental compartment. Samples were collected from the lysimeters, after 3–24 h of vacuum, through nylon tubing. The groundwater samples were collected with stainless steel pumps and Teflon tubing, and the surface water samples were collected in Teflon bottles and split into equivalent aliquots using a Teflon churn. Further details about sample collection methods are available from Capel et al. (2008). Methods for collection of surface water or overland flow samples are available from Capel et al. (2008), or Domagalski et al. (2008a).

3.2. Analytical methods

Water samples were processed by filtering through 0.45 μm filters for dissolved inorganic constituents (orthophosphate, major cations and anions, iron, manganese, and alkalinity). Dissolved orthophosphate (ortho P) was analyzed using US Environmental Protection Agency (US EPA) method 365.1 (US Environmental Protection Agency, 1993). The method detection limit for ortho P was 0.008 mg/L. Orthophosphate concentrations are expressed in this paper as mg/L, or mmol/L as P. Major ions (Na, Ca, K, Mg, Cl, and SO₄) were analyzed by the methods of Fishman (1993), Fishman and Friedman (1989), and the American Public Health Association (1998). The estimated age of groundwater samples was determined using measurements of sulfur hexafluoride (Busenberg and Plummer, 2000) and corrected for recharge temperature using measurements of dissolved nitrogen and argon in the groundwater samples (US Geological Survey, 2010b). Quality assurance consisted of the collection of routine field and equipment blanks and replicates. Analysis of the blanks indicated that samples were free of artifacts, cross-contamination, or carry-over, and the analysis of replicates indicated that reproducibility was consistent with the analytical method.

Selected samples of sediment from the unsaturated zone, groundwater flow path, and at the groundwater/surface water locations were analyzed for labile phosphorus concentrations using two methods. Samples were collected by either soil auger or through a hollow-stem auger from the drilling. The Olsen method (Olsen et al., 1954) utilizes a sodium bicarbonate solution at pH 8.5, and is thought to be most appropriate for alkaline or calcareous soils. The Mehlich-3 method (Mehlich, 1984) utilizes two acids (acetic and nitric), two salts (ammonium fluoride and ammonium nitrate) and a chelating agent (ethylenediaminetetraacetic acid). Neither method recovers total phosphorus, but only that loosely bound to the soil or sediment. A more thorough phosphorus digestion method of the US Environmental Protection Agency (US EPA 3051) was also used (US Environmental Protection Agency, 1995a, 1995b). Samples from drill cores were also analyzed for the apparent concentration of amorphous iron oxide by extraction with 0.5 M HCl plus hydroxylamine hydrochloride (Lovley and Phillips, 1987).

3.3. Geochemical modeling

Geochemical modeling was completed using the code PHREEQC (Parkhurst and Appelo, 1999). The PHREEQC model calculates chemical equilibria using a thermodynamic database, and performs other simulations with solutions and solid phases, including mixing and adsorption. In this analysis, PHREEQC was used to calculate the saturation state of various minerals containing phosphorus relative to phosphorus concentrations measured in water and also to calculate the equilibrium surface adsorption of phosphorus (PO₄³⁻, HPO₄²⁻, H₂PO₄⁻) and competing ions onto iron oxide surfaces. The default databases contain thermodynamic data for a surface named “Hfo” (Hydrous ferric oxide) that are derived from Dzombak and Morel (1990). Two sites are defined in the databases: a strong binding site, Hfo_s, and a weak binding site Hfo_w. Dzombak and Morel (1990) used 0.2 mol weak sites and 0.005 mol strong sites per mol Fe, a surface area of 53,300 m²/mol Fe, and a gram-formula weight of 89 g Hfo/mol Fe; to be consistent with their model, the relative number of strong and weak sites should remain constant as the total number of sites varies (Parkhurst and Appelo, 1999). Total amounts of iron oxide present were calculated from the hydroxylamine hydrochloride analysis as previously described. Water chemistry, as measured from each well, was used to calculate saturation indices and sorption competition, and to set oxidation-reduction levels. Complete details of the sorption calculation model are given by Parkhurst and Appelo (1999).

4. Results and discussion

4.1. Phosphorus concentrations and water chemistry

Concentrations of ortho P for each hydrological compartment (unsaturated zone, groundwater, groundwater/surface water interface, streams, and tile drains (Indiana site only) are shown in Fig. 2, along with the US EPA criteria for total phosphorus in specific ecoregions (US Environmental Protection Agency, 2010). Concentrations of ortho P in rainfall were below the laboratory-reporting limit of 0.008 mg/L. Therefore rain was not considered a source of phosphorus to the soil.

Concentrations of ortho P at each location were assessed among the hydrological compartments by a post hoc multiple comparison test (Simes, 1986; Hochberg, 1988) on the results of pairwise two-sample Wilcoxon rank sum tests. Statistical designations are given on Fig. 2 and show the hydrological compartments within a study area that have median ortho P concentrations which are similar or different at a level of significance of 0.05.

The highest concentrations of ortho P were measured in the unsaturated zone of the Washington site (concentration maximum: 4.5 mg/L). However, concentrations drop rapidly from the unsaturated zone to groundwater. Surface water concentrations were slightly higher than concentrations at the groundwater or groundwater/surface water sites suggesting an additional source of ortho P. Overland flow contributed up to the 19% of the discharge at the DR2 Drain (Domagalski et al., 2008a), and is a
possible source. However, the median concentration of ortho P in overland flow water was 0.009 mg/L as compared to the median concentration of ortho P in the DR2 Drain of 0.1 mg/L. Concentrations of ortho P in tile drains were even less. At the California location, a similar drop in concentrations from the unsaturated zone to groundwater occurs, but not to the extent as at the Washington site. The median concentration of ortho P in the unsaturated zone is different from all environmental compartments at the California site, with median concentrations decreasing from the unsaturated zone to the groundwater, to the groundwater/surface water interface, and to the stream.

In contrast to the California and Washington sites, the median concentration of ortho P of the unsaturated zone and groundwater is similar at the Nebraska site. Groundwater ortho P is similar to the stream, the unsaturated zone, and the groundwater/surface water interface. Both the groundwater and the groundwater/surface water interface are higher than the stream.

Concentrations of ortho P are uniformly low at all of the environmental compartments of the Indiana location. Tile drains largely control the discharge of the Leary Weber Ditch. In addition to tile drains, overland flow contributes to the Leary Weber Ditch discharge (Domagalski et al., 2008a). Concentrations of ortho P for the Leary Weber Ditch are similar to that for groundwater and tile drains. Some higher concentrations of ortho P were measured at the Leary Weber Ditch as indicated by the 75th and 90th percentile of the data range (Fig. 2). Median concentration of ortho P in overland flow was 0.29 mg/L and that for total P was 0.58 mg/L. Overland flow probably is the source of the higher ortho P concentrations in the stream. The unsaturated zone water is largely removed by tile drains at the Indiana site (Domagalski et al., 2008a) and therefore only minimally contributes to the flux of water to the aquifer where the drains are present.

Similar to Indiana, concentrations of ortho P at the Maryland site are uniformly low. Groundwater concentrations are statistically less than all of the other environmental compartments. The range of ortho P concentrations of the unsaturated zone is higher than the other hydrologic compartments. An impervious clay layer prevents direct movement of groundwater through the streambed; however, groundwater discharges from seepage zones at the lateral margins of the floodplain and then flows across the floodplain in small channels and as diffuse sheet flow to the creek. Some of those seeps may contribute ortho P to the stream if the concentrations are from shallow horizons with concentrations similar to the unsaturated zone.

Suggested criteria for total phosphorus in surface water for specific ecoregions, as specified by the US EPA (US Environmental Protection Agency, 2010) are shown in Fig. 2. Concentrations of ortho P in excess of the criterion are exceeded for the majority of measurements made at the Washington and Nebraska sites. The criterion is also exceeded for the unsaturated zone, groundwater and the groundwater/surface water interface at the California location, but the stream water is mostly within the established criteria. Most of the measurements taken at the Indiana site indicate that that location is within the recommended criterion, at least with regard to ortho P. The unsaturated zone concentrations at the Maryland location are generally higher than the total P criteria, as are some of the groundwater/surface water interface concentrations. About 25% of the measurements taken at the Maryland stream are above the recommended criterion, but the groundwater only contributes minimally to those concentrations. Groundwater may contribute to the exceedance of the recommended criterion at the Washington, California, and Nebraska sites, but not the Indiana and Maryland.

Domagalski et al. (2008a) calculated basin yields of ortho P and total phosphorus of the streams from these locations and provided estimates of the yearly load that was contributed by baseflow. In addition, Tesoriero et al. (2009) calculated base flow index (ratio of base flow to total flow volume) at three of these locations and the contribution of ortho P loading from base flow. At the Washington site, baseflow contributes about 41% of the discharge with introduced canal water contributing about 40% and overland flow the remainder (Domagalski et al., 2008a). About 25% of the annual load of ortho P was contributed to the stream by baseflow during the irrigation season. Tesoriero et al. (2009) calculated a baseflow index of 0.57 for the Washington site and that 32% of the annual ortho P load could be attributed to baseflow. The Washington site had the highest yield of ortho P of any of the study sites at 1 kg/ha (Domagalski et al., 2008a). At the Nebraska site (Maple Creek), about 20% of the annual load of ortho P was contributed by groundwater baseflow (Domagalski et al., 2008a). Tesoriero et al. (2009) calculated a baseflow index of 0.35 for the Nebraska site and that 30% of the annual ortho P load was from baseflow. The calculation method was different between the two studies and therefore there are differences in the calculated amounts of phosphorus contributed from baseflow.

Baseflow does contribute to the load of ortho P in some cases to the studied streams, and it was the intent of this study to determine the connection of the different hydrologic compartments to the transport of ortho P and the processes that result in ortho P transport. In other words, does application of phosphorus at the land surface result in some component of downward movement below the root zone and once the agriculturally-applied phosphorus is transported to the aquifer, can it move along a flow path to a stream interface. Alternatively, the phosphorus may be taken up by plant tissue, be sorbed onto mineral surfaces, or precipitated as a new phase either in the unsaturated zone or the groundwater. Concentrations measured in groundwater might then be the result of local chemical equilibrium, as opposed to advective movement.

Geochemical conditions, such as redox, pH, or major element chemistry, might change along the flow path and result in a different potential for adsorption, precipitation or, alternatively, dissolution. The connection between the hydrological compartments to one another was initially investigated by comparing the major element chemistry by using piper plots (Fig. 3). Major element chemistry varies widely at these locations and is controlled by a combination of water and sediment interactions, chemical equilibrium, types of agricultural chemicals applied, and direction of water movement. Mineralogical buffers and soil amendments influence the amounts of individual ions. At the Indiana location, dolomite and calcite exert a strong influence on the ion distribution resulting in waters dominated by Ca, Mg, and HCO3 in all environmental compartments. The cations and anions of the waters at the Nebraska site are also tightly clustered suggesting a similar source of water that is close to equilibrium with the aquifer sediments. At the other extreme is the Maryland location. The upper 3–5 m of the unsaturated zone is fluvial sand and gravel that are underlain by moderately weathered marine quartz and glauconitic sand and silt. The underlying aquifer material is composed mainly of marine quartz and glauconitic sand. The minerals at the Maryland site are very insoluble, and the water chemistry of the unsaturated zone and groundwater is influenced by agricultural soil amendments. The unsaturated zone water has a wide range of anions with sulfate dominant in several samples. In contrast to the unsaturated zone, most of the groundwater samples have a similar chemistry with calcium and chloride as the dominant ions, and little sulfate. Applications of fertilizers containing sulfate explain the elevated concentrations of sulfate. Ion composition at the groundwater/surface water interface is variable and suggests different sources of water. Puckett et al. (2008) found no evidence of significant exchange between groundwater and stream due to the clay layer. However, abundant seeps and upward head gradients along the margin of the floodplain allow groundwater discharge and con-
precipitation pH values below 4.5 (National Atmospheric Deposition Program, 2010) and the low buffering capacity of the sediments that make up the aquifer. The pH is close to the neutral range for the other areas with the highest pH generally found in the unsaturated zone, groundwater, and exchange across the groundwater/surface water interface. The unsaturated zone is slightly enriched in sulfate from agricultural amendments, while the groundwater is more enriched in bicarbonate from the dissolution of carbonate minerals present in small amounts in the aquifer. Water moves from the unsaturated zone to groundwater, and then along short flow paths to the stream (Domagalski et al., 2008a).

Therefore, the major element chemistry is tightly clustered and the stream chemistry plots between that of the other hydrological compartments. The water chemistry at the California site is variable and subject to wide variations depending on what types of agricultural chemicals were used, and the source of the water. Water movement can be in either direction across the streambed at the California site and therefore the chemistry might be similar to the adjacent groundwater system, or may be the result of river water from upstream sources (Domagalski et al., 2008b).

The pH of the waters in the unsaturated zone, groundwater and groundwater/surface water interfaces varies across these locations (Fig. 4). The pH of the Maryland location is the lowest for groundwater and the groundwater/surface water interface, because of precipitation pH values below 4.5 (National Atmospheric Deposition Program, 2010) and the low buffering capacity of the sediments that make up the aquifer. The pH is close to the neutral range for the other areas with the highest pH generally found in the Washington location. The water pH is not necessarily a good predictor of phosphorus mobility as low concentrations occur at both the Maryland site, with acidic groundwater and at the Indiana site with groundwater of alkaline pH. Ortho P concentrations, however, might be related to pH at the Maryland site since adsorption onto iron oxides is dependent on the pH of the solution. Sorption of anions increases with decreasing pH (Stumm, 1992). This occurs because the oxide surfaces become more positively charged and therefore have a greater capacity to adsorb anions, such as ortho-P.

4.2. Contents of phosphorus and iron in aquifer and unsaturated zone solids

Only a certain percentage of phosphorus in soil or on aquifer solids can be mobilized into solution or exchanged between solution and a solid. The portion of phosphorus that is reactive in this manner has sometimes been termed the environmentally available phosphorus (Devau et al., 2009). Estimates were made of the environmentally available phosphorus in aquifer or unsaturated zone solids by measuring the amount extracted by two methods: Olsen (Olsen et al., 1954) and Mehlich-3 (Mehlich, 1984) (Fig. 5). Both methods have long been used to determine levels of soil saturation with respect to phosphorus (Maquire and Sims, 2002; Sims et al., 2000; Thompson and McFarland, 2010; Heckrath et al., 1995). The Mehlich-3 method has been demonstrated to accurately predict the amount of water-soluble phosphorus and the amount that could be desorbed from iron oxides in soils of the mid-Atlantic region of the US (Sims et al., 2002). The Olsen test generally is recommended only for alkaline soils (Sims, 2009) whereas the Mehlich-3 provides reasonable estimates of exchangeable phosphorus in most soils (Sims, 2009). For the Washington, California, and Nebraska samples, the Mehlich-3 method results for the aquifer sediments are higher than the Olsen, but for the Maryland samples, they are similar. Given the fact that the Mehlich-3 utilizes a mix of extracting agents, it is not surprising that more phosphorus is mobilized relative to the Olsen method in some locations. For the Indiana location, contents of phosphorus in aquifer solids were less than the Mehlich-3 detection limit suggesting that little of the phosphorus was labile. The contents measured in the Washington and California aquifers were similar as were those measured in Nebraska, Indiana, and Maryland. In all cases, total phosphorus in sediment (Fig. 5) exceeds the amount considered labile. There is

Fig. 2. Boxplots of dissolved orthophosphate concentrations in hydrological compartments per study area and US Environmental Protection Agency total phosphorus ecoregion specific criteria for protection of surface water resources. Statistical groupings (A–C) indicate which groups of samples are statistically similar.
a wide range of total phosphorus in the aquifer material with the highest at the Washington site and the lowest at the Maryland site. This is likely attributable to different minerals with varying amounts of phosphorus. The content of total phosphorus in sedi-

![Image of Piper plots](image-url)

Fig. 3. Piper plots. (a) Washington, (b) California, (c) Nebraska, (d) Indiana and (e) Maryland.
ment has no relation to the concentrations of ortho P in groundwa-
ter. The Olsen or Mehlich-3 methods do not dissolve the mineral-
ogical forms of that phosphorus.

Contents of labile phosphorus were higher in the unsaturated
zone relative to the aquifers in all cases. The median contents of
phosphorus measured by the two methods are given in Fig. 5. In
all cases, the contents of phosphorus were higher near the surface
and decreased with depth in the unsaturated zone.

It is generally recognized that iron oxides and hydroxides are
the most important reservoirs of exchangeable phosphorus in most
soils (Hemwell, 1957; Zhang and Huang, 2007; Hingston et al.,
1974; Sigg and Stumm, 1980; Hawke et al., 1989; Parfitt, 1978),
although aluminum oxyhydroxides, certain clay minerals, and car-
bonate minerals may serve as the primary reservoir of exchange-
able phosphorus in some environments (Hemwell, 1957; Shariatmadari and Mermut, 1999; Parfitt, 1978). Iron can be pres-
ent in sediments in a variety of forms including crystalline phases
such as hematite or magnetite, or poorly crystalline phases includ-
ing goethite or limonite. It was assumed that the forms of iron
most likely to result in sorption of ortho P would be the poorly
crystalline phases, because they would likely have the highest sur-
face area, and that the concentration of those could be estimated
by selective extraction. Amounts of iron recovered by hydroxyl-
amine hydrochloride in the aquifers are shown in Fig. 6. The high-
est median content (1500 μg/g) was at the Washington location,
followed by the California location (765 μg/g). The Nebraska loca-
tion had the lowest amount (60 μg/g). Reducing conditions also oc-
cur in the Nebraska location, as indicated by the presence of
dissolved ferrous iron, and the lower relative amounts of iron oxides
might be partially attributable to ferric iron reduction. At the
other locations, some reducing conditions occur, but the lack of
elevated concentrations of dissolved ferrous iron suggests that
the oxides are stable.

4.3. Geochemical modeling

It was assumed that measured concentrations of ortho P in the
unsaturated zone and within the aquifer would be limited by equili-
librium with solids, either by precipitation or co-precipitation as
mineral phases, or by sorption onto iron oxides and other minerals,
and that those relationships could be examined by geochemical
modeling. Phosphorus concentrations might be limited, for exam-
ple, by precipitation of hydroxyapatite (Ca$_5$(PO$_4$)$_3$(OH)). However,
only a few instances of supersaturation with hydroxyapatite, as indi-
cated by the model, were found, such as the unsaturated zone at the
Washington, California, and Nebraska sites, because of high ortho P
and calcium concentrations. A few instances of supersaturation with
respect to hydroxyapatite in the groundwater of the California loca-
tion were also found. It has been reported previously that supersat-
uration with respect to hydroxyapatite has been observed in
groundwater plumes down gradient of septic systems but that pre-
cipitation is not an effective control on the transport of phosphorus
possibly because of slow kinetics (Robertson et al., 1998). In general,
precipitation of hydroxyapatite cannot be invoked as a primary
mechanism controlling the transport of phosphorus through the
flow paths of these agricultural systems since most measured con-
centrations were below the saturation index.

Since precipitation of hydroxyapatite may not be controlling
phosphorus concentrations, sorption onto iron oxides may be an
important factor. The observed concentrations of ortho P at the time
of sampling would then be the result of equilibrium with the sorbing
phase. It would be useful to know the degree of saturation of iron
oxides of the unsaturated zone or aquifer that result in the observed
ortho P concentrations. The level of saturation with respect to sorp-
tion will dictate whether or not the aquifers might be a source of
phosphorus to the stream. As the oxides become saturated, phos-
phorus transport would become more likely. In order to understand
that relationship, a geochemical model was utilized whereby con-
centrations of ortho P were changed to levels above and below the
actually observed to determine the relative levels of saturation with-
in the hydrological compartments along the flow path.

A plot of the modeled amount of sorbed phosphorus relative to
ortho P is shown in Fig. 7 for the unsaturated zone, aquifer, and
groundwater/stream interface for the Washington location.

In Fig. 7, it is apparent that dissolved concentrations of phos-
phorus are low until the iron oxides are saturated, if sorption onto
oxides is the primary factor limiting phosphorus transport in the
subsurface. Saturation, or near saturation of the oxides, is defined
in this discussion as that point in the plots where there is a rapid
increase in the concentration of ortho P with only minimal changes
in the amount of phosphorus adsorbed. The high concentrations of
ortho P measured in the Washington unsaturated zone (Fig. 2) are
the result of saturation or near saturation of the oxides with phos-
phorus. Use of manure as a fertilizer probably accounts for the high
concentrations in the unsaturated zone. The groundwater concen-
trations of phosphorus are much lower and the median concentra-
tion (0.0015 mmol/L) is close to the point where the oxides are
starting to become saturated. The highest concentration measured
in groundwater was 0.006 mmol/L. Phosphorus in the unsaturated
zone is therefore a source to the groundwater and it is likely that
the levels sorbed onto aquifer solids will increase under the cur-
rent management practices. Most of the ortho P concentrations
at the groundwater/surface water interface are slightly greater
than the recommended US EPA criteria for protection of surface
water. Therefore, groundwater discharge might contribute to the
load of phosphorus in the stream as well as concentrations above
the recommended criteria.

Competing ions for sorption sites on the iron oxide surfaces for
the Washington location include hydrogen ion, and magnesium.
The competing ions limit the potential sites for phosphorus sorp-
tion. At the condition of the median phosphorus concentration in
the unsaturated zone, hydrogen ions occupy about 41% of the
available sorption sites, while phosphorus occupies about 40%. Magnesium occupies about 16% of the available sorption surface.
Other cations or anions are not important with respect to sorption.
Although sulfate is present in relatively high concentration at
55 mg/L, very little sulfate sorbs to iron oxide surfaces under these
conditions. At the highest dissolved concentration of ortho P in the
unsaturated zone (0.146 mmol/L), representing a high level of
oxide saturation with respect to phosphorus, about 46% of the
available oxide surface is occupied by phosphorus while hydrogen
ions occupy about 35%. In contrast to the unsaturated zone, phos-
phorus occupies about 18% of the oxide surfaces in the saturated
zone. This is less than half of that for the unsaturated zone. As
was the case for the unsaturated zone, the main competing ions
in the saturated zone are hydrogen ions and magnesium.

The average annual rate of water movement through the unsat-
urated zone of the Washington location was the slowest of all
study units as estimated by a piston-flow model at 0.1 cm/day
(Fisher and Healy, 2008). This slow rate of water movement results
in an average unsaturated zone residence time of 8.1 years (Fisher
and Healy, 2008). However, during the summer irrigation season,
downward movement is much faster. Use of the bromide tracer
suggested a downward movement of 2.5–2.7 cm/d (Fisher and
Healy, 2008).

The predicted amount of phosphorus sorbed onto aquifer sedi-
ment at the Washington location, based on the median ortho P con-
centration in the groundwater, was about 0.275 mmol/kg
(8.5 mg/kg). This lies between the amount analyzed by the Meh-
litch-3 and Olsen methods. Therefore, the modeled amounts of
sorbed phosphorus are probably close to the potentially environ-
mentally available phosphorus.
A plot of modeled sorption of phosphorus onto iron oxides for the unsaturated zone, aquifer, and groundwater/stream water interface of the California location is shown in Fig. 8.

The unsaturated zone solids of the California location have the highest level of saturation with respect to phosphorus and the median groundwater phosphorus concentration indicates that those solids are approaching saturation. The groundwater/surface water interface has a lower level of oxide saturation. The amount of phosphorus predicted by the model as sorbed to iron oxides in the aquifer at the California location was 0.9 mmol/kg (28 mg/kg), based on the median ortho P concentration in groundwater. This is within the range of concentrations measured by the Mehlich-3 method. The model predicted that phosphorus covered about 50% of the available sorption sites within the aquifer at the
top of the flow path where ortho P concentrations were the highest. The major competing ion was hydrogen, which accounted for most of the remaining sorption sites.

A schematic of the flow system at the California location is shown in Fig. 9. At the California location, ortho P has migrated down into the aquifer, but does not appear to have been transported to the river interface.

There is an order of magnitude difference in ortho P concentrations between the wells of the middle portion of the flow path and those situated in the riparian zone. Since there is no fertilization in the riparian zone, ortho P concentrations are lower, probably close to natural levels. It is likely that agricultural use of fertilizers, either chemicals or manure have affected the aquifer at the top and middle portion of the flow path, and the downward gradients of groundwater flow from irrigation have allowed phosphorus to migrate below the root zone. Transport time of water in the unsaturated zone of the California location was one of the higher of these study areas. The rate of unsaturated zone water movement was estimated by a piston-flow model as 1.0 cm/day (Fisher and Healy, 2008). This translates to an unsaturated zone residence time of 3 years.

The predicted amount of phosphorus sorbed onto iron oxides for the Nebraska location, based on the median ortho P concentration in groundwater, was about 0.022 mmol/kg (0.7 mg/kg). This concentration is within the range of the amount of phosphorus extracted by the Olsen and Mehlich-3 methods. The model predicts that phosphorus sorption covers 37% of the available oxide surfaces while hydrogen ions cover 59%. Most of the remaining surface is occupied by magnesium. Therefore, the low amounts of iron oxides in the flow path allow for elevated concentrations of ortho P along the flow path and groundwater has become a significant source of phosphorus concentrations to the stream.

The modeled sorption plot for the Maryland location (Fig. 11) is different from the others showing that the sediments of the aquifer can sorb substantially more phosphorus than that of the unsaturated zone.

The difference between the sorption in the unsaturated zone and the aquifer for the Maryland location is the effect of pH, as the amount of iron oxides does not change. The sorption of phosphorus onto iron oxides increases with decreasing pH. There is a substantial decrease in pH from the unsaturated zone to the aquifer (Fig. 3). Rain in equilibrium with quartz and other insoluble minerals in the aquifer sediments recharge the aquifer water. Because of the lack of significant reactions with aquifer minerals, the pH reflects equilibrium with atmospheric CO₂ and the pH is low relative to the other sites. The unsaturated zone solids are actually close to saturation with respect to phosphorus sorption onto iron oxides, but the aquifer solids are very unsaturated. Although groundwater can contribute to the load of phosphorus in the stream, the concentrations are always less than the recommended criteria of the US EPA (Fig. 2). In fact, the stream concentrations are less than the criteria for most of the measurements taken.

The predicted amount of phosphorus sorbed by iron oxides in the aquifer at the Maryland site, based on the median concentration of ortho P in groundwater was 0.5 mmol/kg (15.5 mg/kg). This is similar to the range of concentrations measured by either the Mehlich-3 or Olsen methods. Phosphorus occupies about 21% of the available sorption sites within the aquifer while hydrogen ions occupy 68%. Because of the low pH of the Maryland groundwater,
the oxides are undersaturated with respect to phosphorus and groundwater is not currently a source of high concentrations of phosphorus to the stream. In contrast to the other sites, there is some sorption of sulfate. Sulfate occupies about 10% of the sorption sites. The annual average rate of water movement within the unsaturated zone is 0.4 cm/d with a residence time of 7.1 years (Fisher and Healy, 2008). Much of the recharge, however, occurs during the non-growing season. Active recharge occurs during about 70% of the year and yields an average rate of 0.57 cm/d and a residence time of 2–4 years. Given the high affinity of the aquifer solids for phosphorus, it is unlikely that groundwater transport will contribute significant concentrations of phosphorus to the stream under the given agricultural management.

Movement of water and associated chemicals is different at the Indiana location relative to the others because of the presence of tile drains, which were installed because of poor drainage. The presence of tile drains greatly reduces the amount of water recharged to the aquifer since water is rapidly transported out of the soil to the Ditch. Therefore, the movement of water and chemicals is primarily through the unsaturated zone to the drains and directly to the stream, except for an additional component of overland flow. Although the soils have poor drainage, preferential flow paths do exist (Stone and Wilson, 2006; Fisher and Healy, 2008). Evidence for preferential flow paths was obtained from the bromide tracer experiment as bromide was detected within a week after application at a depth of 1.5 m. Presumably, these preferential flow paths also allowed for the transport of agricultural chemicals, including phosphorus. However, bromide concentrations measured in lysimeters were steady for some time after application in lysimeters at depths of 0.9 and 1.2 m suggesting that water that was initially transported by preferential flow paths became trapped in the soil matrix (Fisher and Healy, 2008). Some soils are also more slowly drained because of their distance to the tiles. Concentrations of ortho P are always low in both the unsaturated...
Concentrations of ortho P are slightly higher in the stream water, but the unsaturated zone and the tile drains do not appear to be a major source of phosphorus to the stream. Most measurements of ortho P at the Indiana location are lower than the USEPA recommended criteria for protection of surface water. Higher concentrations in the stream, relative to the tile drains, are likely the result of overland runoff. Levels of labile phosphorus are low at the Indiana location. Most of the analyses for the Mehlich-3 method yielded results below the method detection limit. Modeling of the sorption of phosphorus onto iron oxides suggests undersaturation at the concentrations of ortho P of the unsaturated zone. The model predicts, based on a median concentration of ortho P in the unsaturated zone of 0.01 mg/L, about 0.08 mmol/kg (2.5 mg/kg) of phosphorus will be adsorbed onto iron oxides. This amount is higher than the levels analyzed by either the Mehlich-3 or the Olsen methods.

Because of the low amount of labile phosphorus in the unsaturated zone, the oxide surfaces are very undersaturated with respect to the ortho P concentration.
to phosphorus relative to the other study locations. Possible reasons for the low amount of oxide sorption at Indiana might be lower use of phosphorus for agriculture or a very low amount of phosphorus transport below the root zone. Sequestration in the root zone might be very effective at the Indiana location. Concentrations of near-surface soil phosphorus as measured by the Mehlich-3 method at a depth of 7.6–23 cm were between 54 and 100 mg/kg. Immediately below this horizon at a soil depth of 28–48 cm, the concentration of Mehlich-3 extractable P was down to 11 mg/kg, which then decreases down to 5 mg/kg immediately below. The Indiana location has the highest levels of silts and clays relative to the other four study areas, and movement of phosphorus past the clays of the root zone may be limited. In addition, the highest level of sedimentary calcium (total calcium) occurs at Indiana. The median level of total calcium at the Indiana site was 96,870 mg/kg, and the next highest was at the Washington site (14,870 mg/kg). Calcium in sediment was much lower at the other three sites because of the lack of carbonate minerals in the drainage basin. These higher levels of calcium at the Indiana location are because calcite and dolomite are abundant in the unsaturated zone and aquifer sediments due to the presence of carbonate outcrops. It has been suggested that carbonate minerals are an effective sink of phosphate in soils (Shariatmadari and Mermut, 1999; Freeman and Rowell, 1981; Avnimelech, 1980). The unsaturated zone water is slightly supersaturated with respect to calcite and the mineral probably undergoes both dissolution and precipitation thereby possibly providing a source of new surface for phosphate sorption or co-precipitation. However, other studies have suggested that carbonate minerals in soil are not an effective sink of phosphorus, but that sorption onto oxides and non-carbonate clay is more effective (Zhou and Li, 2001). The actual mechanism of phosphate sequestration in the root zone was beyond the scope of this study.

Apparent distribution coefficients, \( K_d \), were estimated for the aquifer and unsaturated zone of these locations using the median concentration as measured by the Mehlich-3 method and median concentrations of ortho P in either the unsaturated zone or the aquifer. These distribution coefficients were calculated as the logarithm of the concentration of phosphorus in soil or sediment measured by the Mehlich-3 method divided by the median water concentration (units = L/kg). The apparent \( K_d \) for the Washington aquifer was 2.3. The value for the California aquifer was 1.4. The value for the Nebraska aquifer was 1.3, and that for the Maryland aquifer was 6. Values of \( K_d \) for the unsaturated zone were sometimes similar to those for the aquifers, and in some cases different. The \( \log K_d \) for the Washington unsaturated zone was 1.1. That can be understood with respect to the high concentrations of ortho P in the unsaturated zone. The \( \log K_d \) for the unsaturated zone of California and Nebraska were each 1.5, similar to the aquifers. The \( \log K_d \) for the Indiana unsaturated zone was 3.0, which was the highest of any of the study sites. This can be attributed to the larger amount of clay and calcium carbonate in the soil. The \( \log K_d \) for the Maryland unsaturated zone was 2.5. These apparent \( K_d \) values can be understood in the context of the concentrations of the sorbent materials, water chemistry, and the agricultural practices. The Maryland aquifer has the highest \( K_d \) which is much higher than any other location, because of the effect of the low pH, which allows for increased sorption on iron oxides. In contrast, the Maryland unsaturated zone \( K_d \) is lower because of the higher pH. The apparent \( K_d \) for the California location was calculated for the part of the aquifer in the upper portion of the flow path where continuous fertilization has resulted in a net downward movement of phosphorus into the aquifer. Because of near saturation on the oxides, at a neutral pH, the apparent \( K_d \) is relatively low, and the soil is losing its capacity to adsorb additional phosphorus. The California unsaturated zone soil is also close to saturation with phosphorus and therefore, the \( K_d \) is close to that of the aquifer. Similarly, the Nebraska location has a low value of the apparent \( K_d \) because of low concentrations of iron oxide in either the aquifer or unsaturated zone that are also at or near saturation with respect to phosphorus. The Washington aquifer has a higher apparent \( K_d \) relative to California and Nebraska, because of higher concentrations of iron oxides in the aquifer material, but the unsaturated zone \( K_d \) is lower probably because of the high use of manure, which leads to high concentrations of ortho P in the unsaturated zone water. The \( K_d \) values obtained in this study were similar to those measured in other studies. For example, in a study of Nigerian soils (Egwu et al., 2010) measured P partition coefficients ranged from 1.29 to 4.06 (log values). The lowest value in that study was in a soil with the highest sand content (84%).

The modeling of phosphorus sorption onto iron oxides is compared among the five locations on Fig. 12. Concentrations of ortho

![Fig. 11. Plot of dissolved orthophosphate and modeled phosphorus concentrations sorbed onto iron oxides, Maryland location.](image-url)
P, at any location, will be low as a result of sorption until the available sites are saturated. The point of saturation is indicated by a break of slope (Fig. 12). The modeling results for the Maryland location plot closest to the y-axis as the oxides have the greatest affinity for phosphorus because of the effect of pH even though the concentration of oxides is less relative to California and Washington. Therefore, the relative amount of phosphorus on the oxide surfaces is much greater than that in equilibrium with the dissolved compared to the other locations. The plots for Washington, California, and Indiana are similar because of either similar levels of oxides or solution chemistry that results in a similar amount of sorption. A contrasting situation is for the Nebraska location where the break in slope occurs furthest to the left in the plot at a ratio of dissolved to sorbed P of about 0.1. Because of the low amount of available oxide surfaces due to low iron concentrations, phosphorus is not effectively sorbed and the sub-surface transport of phosphorus can occur to a much greater extent.

5. Summary and conclusion

Phosphorus can be transported below the root zone to the unsaturated zone and through an aquifer in agricultural settings. This study showed that under conditions where phosphorus is either not entirely taken up by plant tissue or where soil chemistry does not favor either precipitation or sorption, that sub-surface transport can result in elevated concentrations in groundwater or transport to the stream was demonstrated most clearly at the Nebraska location, although groundwater transport did contribute to the stream loads at other sites. A low concentration of iron oxides in the sand, silt, and loess soils at the Nebraska location resulted in low sorptive capacity. The median concentration of ortho P at the groundwater/stream interface was 0.2 mg/L at the Nebraska location. In some cases, agriculturally applied phosphorus will likely not be transported through the aquifer under current management practices. That was demonstrated most clearly at the Maryland location. Although oxides were close to saturation with respect to phosphorus in the unsaturated zone, the aquifer solids had high sorptive capacity because of the low groundwater pH (<5) within the aquifer. Under that condition, ortho P concentrations were low to undetectable in the aquifer and transport to the stream was not a concern. A similar situation occurred at Indiana although for different reasons. The apparent situation for phosphorus in Indiana was very low transport out of the root zone to the sub-surface. It was surmised that the clay and carbonate chemistry of the root zone effectively sequestered phosphorus and as a result oxides in the subsurface sorbed what little environmentally available phosphorus that was present.

In contrast to Indiana, transport of phosphorus out of the root zone to the unsaturated zone occurred to a greater extent at the Washington and California locations. High unsaturated zone concentrations in Washington were the result of the widespread use of manure. Phosphorus was also applied throughout the growing season at the California site and strong downward gradients of water, driven by irrigation, resulted in transport of phosphorus below the sandy root zone and into the unsaturated zone and aquifer. Phosphorus was effectively sorbed within the aquifer at the Washington location because of higher iron oxide contents, relative to the other study areas. It was demonstrated at the California location that the current agricultural management practices result in movement of phosphorus through the aquifer in the zone of groundwater that had been dated between 10 and 25 years. Phosphorus was not transported to the stream interface at the California location because of the presence of a riparian zone with natural vegetation with no external inputs of phosphorus.

This study also showed that concentrations of ortho P in the sub-surface that are close to or above the eco-region specific criteria for protection of surface water are probably the result of aquifer solids that are at or above saturation with respect to sorbed phosphorus. In those instances, agricultural management practices should consider methods to prevent plumes of sub-surface phosphorus from reaching discharge areas at stream interfaces.

Fig. 12. Ratio of modeled orthophosphate to sorbed phosphorus vs dissolved orthophosphate at five study locations. Best lines are drawn to show ratio of dissolved orthophosphate to sorbed phosphorus at saturation conditions.

**References**


