

Phosphorus Retention and Remobilization along Hydrological Pathways in Karst Terrain

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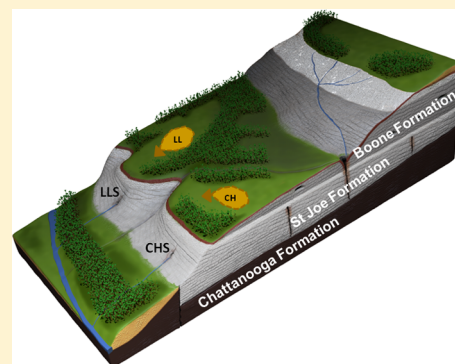
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Supporting Information

ABSTRACT: Karst landscapes are often perceived as highly vulnerable to agricultural phosphorus (P) loss, via solution-enlarged conduits that bypass P retention processes. Although attenuation of P concentrations has been widely reported within karst drainage, the extent to which this results from hydrological dilution, rather than P retention, is poorly understood. This is of strategic importance for understanding the resilience of karst landscapes to P inputs, given increasing pressures for intensified agricultural production. Here hydrochemical tracers were used to account for dilution of P, and to quantify net P retention, along transport pathways between agricultural fields and emergent springs, for the karst of the Ozark Plateau, midcontinent USA. Up to ~70% of the annual total P flux and ~90% of the annual soluble reactive P flux was retained, with preferential retention of the most bioavailable (soluble reactive) P fractions. Our results suggest that, in some cases, karst drainage may provide a greater P sink than previously considered. However, the subsequent remobilization and release of the retained P may become a long-term source of slowly released “legacy” P to surface waters.



INTRODUCTION

More than 25% of the world's population either lives on or obtains its drinking water from karst aquifers. Karst underlies 30% of the land area of China, 30% of Europe, and 20% of the United States.^{1,2} Karst aquifers exert an important control on the quality and ecology of surface waters in these areas.³ The complexity of subsurface drainage^{4,5} and the difficulties in deconvoluting flow pathways and groundwater contributing areas⁶ have been a significant barrier to detailed studies of nutrient transport and fate in karst systems.^{7,8} Nevertheless, it is widely assumed that karst drainage systems (formed by dissolution of carbonate rocks, mainly limestone) are highly vulnerable to phosphorus (P) impairment from agricultural sources.

This vulnerability is assumed to arise from the low nutrient buffering capacity of the thin cherty soils which overlie karst and the rapid transmission of surface runoff through conduits enlarged by dissolution,^{9,10} which is thought to bypass the zones where key processes of P retention occur.^{11–13} Nonetheless, highly intensive monitoring of Irish karst springs, in areas of livestock, demonstrated major P attenuation (reduction in P concentrations) relative to agricultural runoff,^{14,15} with low P concentrations in spring discharge, even during storm events

when agricultural P losses are expected to be highest. This attenuation was attributed to a combination of both hydrological dilution and P retention during infiltration and transmission of runoff along groundwater conduit pathways.

Crucially, we lack information on the extent to which P attenuation is controlled by P retention processes during transit along karst flow paths,¹⁴ or by hydrological dilution of agricultural runoff by cleaner groundwater sources.¹⁶ This is of strategic importance for understanding the P buffering capacity and wider resilience of karst landscapes to nutrient inputs.^{10,17,18} Many karst lands have traditionally been used for low-intensity livestock farming, owing to poor soils and their unsuitability for arable production.⁹ However, there is increasing pressure for intensive livestock production, as global demands for greater efficiency in food production intensify.^{19,20} Given the move toward more intensive livestock production systems, which accumulate P,^{21,22} and the perceived vulnerability of karst drainage systems to P loss, there is now a pressing and strategic

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Table 1. Summary of Concentrations of Soluble Reactive Phosphorus (SRP), Total Phosphorus (TP), Potassium (K), Rubidium (Rb), and Calcium (Ca) in Field Runoff and Spring-Water Samples

		field runoff ($\text{m}^3 \text{ha}^{-1}$) spring flow (L s^{-1})	SRP (mg L^{-1})	TP (mg L^{-1})	Rb ($\mu\text{g L}^{-1}$)	K (mg L^{-1})	Ca (mg L^{-1})
Langle Field (LL)	mean	38.0	2.21	2.57	6.97	10.4	5.12
	median	35.5	1.87	2.12	5.96	10.2	4.94
	range	3.4–91.5	0.59–5.02	0.8–5.53	0.93–20.6	2.04–26.3	2.11–9.87
Copperhead Field (CH)	mean	23.1	0.68	1.09	2.94	6.11	3.45
	median	14.6	0.57	1.03	2.52	5.11	3.43
	range	1.8–79.9	0.47–1.22	0.63–1.91	0.58–8.76	1.4–14.7	1.95–7.34
Langle Spring (LLS)	mean	13.1	0.029	0.057	1.06	1.54	37.5
	median	9.38	0.012	0.034	0.878	1.14	36.7
	range	1.24–59	0–0.403	0.002–0.608	0.195–3.57	0.534–4.92	12.2–65.9
Copperhead Spring (CHS)	mean	22.5	0.019	0.041	1.08	1.37	40.5
	median	2.62	0.017	0.032	1.1	1.4	42.9
	range	0.19–253	0.001–0.12	0–0.58	0.328–1.9	0.84–2.17	14.5–61.5

need for better understanding of the fate and transport of P in karst landscapes. Here this shortfall is addressed for karst terrain in south-central USA. Hydrochemical tracers and endmember mixing analysis^{23–26} were used to assess the vulnerability to P loss, by accounting for the hydrological dilution of agricultural runoff and directly quantifying net P retention, during infiltration through the soil, and along karst transport pathways, through to the emergent springs.

EXPERIMENTAL METHODS

Study Area. The study was undertaken at the University of Arkansas long-term Savoy Experimental Watershed (SEW), NW Arkansas, USA.²⁷ The SEW is located in the Illinois River Watershed, a mixed land-use watershed ($\sim 4330 \text{ km}^2$), which spans the states of Arkansas and Oklahoma.^{28,29} The SEW covers 1250 ha and is typical of the karst terrain of the Ozark Plateau of midcontinental USA (Figure SI-1a, Supporting Information). The soils of the SEW are predominantly silt loams (see Supporting Information). Around 70% of the land is native forest, with the remaining 30% rolling pasture grazed by beef cattle (~ 2 cows ha^{-1}). The SEW also supports poultry production, with the resulting poultry litter used to fertilize pastures. There are no septic tanks or settlements in the SEW, and agricultural runoff from pastures grazed by cattle provides the overwhelmingly dominant P source in the watershed.³⁰

The stratigraphy of the SEW^{30–32} (see Figure SI-1c, Supporting Information) includes (a) the limestone aquifer of the St. Joe Formation, (b) the Boone Formation, an impure limestone which mantles the St. Joe Formation and forms “epikarst”, and (c) a layer of regolith (vadose zone) which overlies the Boone Formation. Karst drainage has a major control on water quality in the Illinois River;^{29,33} 67% of annual river flow comes from karst springs, rising to 80% of flow in the summer and fall.³⁴

Sample Collection and Analysis. Surface runoff and spring-water chemistry and flow monitoring (Figure SI-1a and c, Supporting Information) were undertaken at the following: (1) two adjacent karst springs (Langle Spring, LLS, and Copperhead Spring, CHS), which flow continually from the St. Joe Formation (focused conduit flow) springs; (2) two surface runoff field plots (Langle, LL, 1.07 ha, and Copperhead, CH, 1.05 ha), which are located above and within the watershed (recharge zone) of the LLS and CHS springs. These runoff plots are located on Razort silt loams which make up most of the grazed pastures of the SEW. All pastures are treated similarly in terms of grazing

intensity and maintenance fertilizer applications (30 kg P ha^{-1} every two years as either poultry litter or diammonium phosphate).

Flows at the karst springs (LLS and CHS) were monitored on 15-min intervals (see Supporting Information). Karst spring water was sampled weekly, with stage-triggered, subdaily automated sampling using an ISCO sampler during storm events. Figure SI-2 (Supporting Information) shows the distribution of samples collected on the rising and falling stage of the storm hydrographs. The volume of surface runoff from both fields was automatically measured, and samples were collected on a flow-weighted basis by an ISCO autosampler. All water samples were filtered within 24 h of the water being sampled and were analyzed following EPA standard protocols, as described below (and in the Supporting Information). Filtered ($<0.45 \mu\text{m}$) samples were analyzed for soluble reactive phosphorus (SRP), by colorimetric analysis,³⁵ and for a full suite of major cations (including potassium, K, and calcium, Ca) and trace elements (including lanthanum, La, and rubidium, Rb) (see Supporting Information). Unfiltered samples were analyzed for total phosphorus (TP), after acid-persulfate digestion, by colorimetric analysis.^{35,36} These measurements are consistent with standard protocols for TP and SRP analysis.³⁷

Use of Conservative Tracers and Endmember Mixing Analysis. Conservative chemical tracers and endmember mixing models were used to apportion water sources, and to differentiate the effects of hydrological dilution from the biogeochemical processes, which retain and cycle P during transit through the karst drainage system. Chemical tracers have been widely used in watershed hydrology for tracing water sources and flow pathways,³⁸ owing to their conservative behavior (chemical inertness). Here we made use of chemical tracers already in the watershed to apportion water sources. Using the hydrochemical monitoring data, tracers were chosen which had elevated concentrations in either base flow groundwater or in agricultural runoff. First, two-component endmember mixing models^{23,39} were used to link the spring-water chemistry to sources within the watershed, by (a) quantifying the relative proportions of surface runoff and groundwater and (b) estimating the contribution of surface runoff from the agricultural grazed land. Second, comparing the mixing patterns of P in spring water with a conservative tracer of agricultural runoff allowed us to directly evaluate whether P was behaving nonconservatively (i.e., being taken up or released) along the hydrological pathways in the karst drainage system.

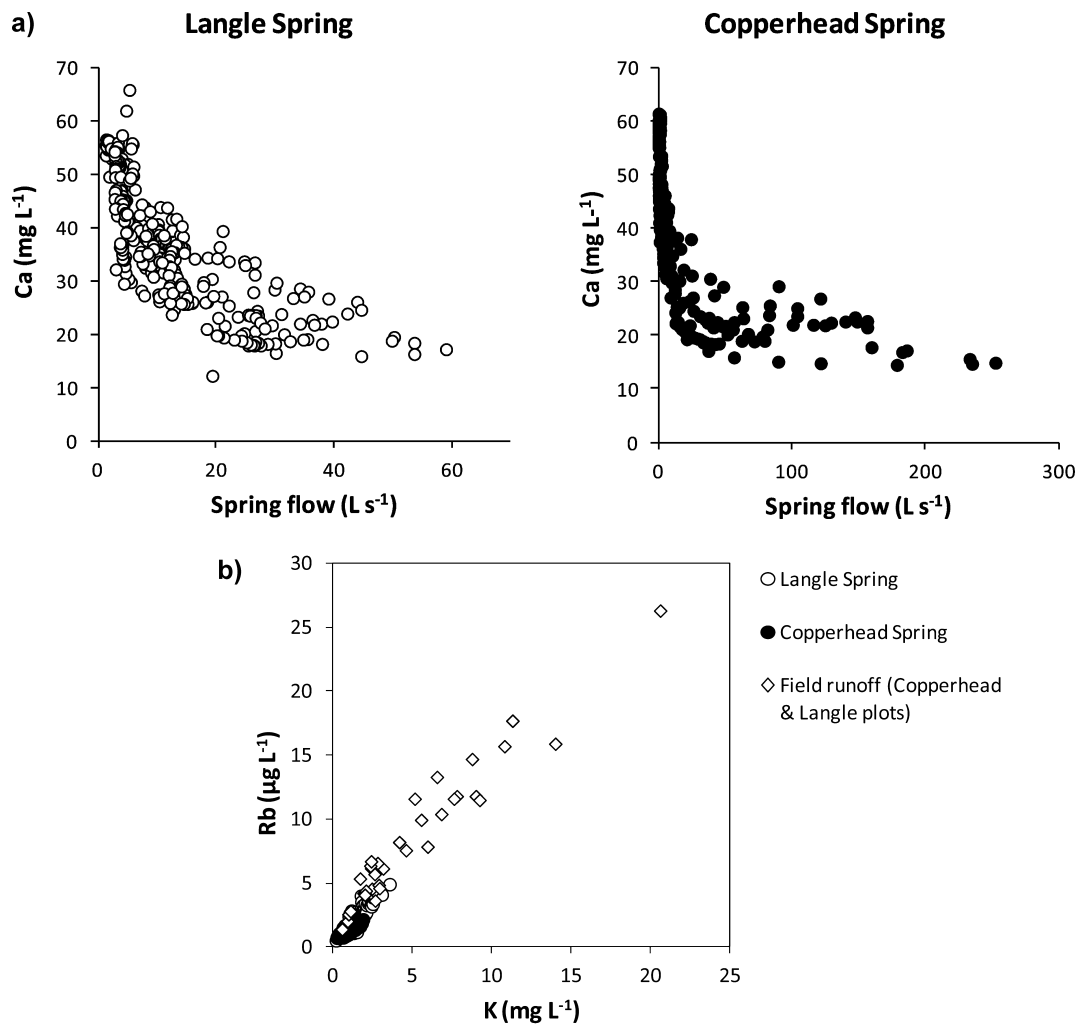


Figure 1. (a) Relationships between calcium (Ca) concentrations and flow at Langle and Copperhead springs. (b) Relationship between rubidium (Rb) and potassium (K) concentrations in field runoff and spring-water samples.

RESULTS AND DISCUSSION

Comparison of Agricultural Runoff and Spring-Water Chemistry. Concentrations of TP, SRP, K, and Rb were consistently highest in field runoff, relative to the springs (Table 1), and runoff from the grazed fields provides the greatest concentrations of P, K, and Rb within the SEW. In contrast, Ca concentrations were consistently highest in the springs, compared with runoff. This indicates a dominant base flow groundwater source of Ca, from dissolution of limestone, which is diluted by surface runoff (Figure 1a).

Concentrations of SRP, TP, K, and Rb were all higher in field runoff at LL compared with CH. This likely reflects higher cattle grazing density at LL (2.5 cows ha⁻¹) than at CH (1.0 cows ha⁻¹), as well as higher runoff per unit area that likely led to greater solute and particulate entrainment and transport capacity compared with CH. This may also reflect a larger hydrologically active area contributing runoff at LL, linked to greater soil compaction from more intensive cattle grazing.

For the springs, there was a greater variability in SRP, TP, K, and Rb concentrations at LLS than at CHS, despite a much lower variability in spring flow at LLS (Table 1). However, concentrations of TP, SRP, K, and Rb did not correlate with flow at either of the springs. For most storm events at LLS, concentrations of TP, SRP, K, and Rb increased dramatically

above base flow concentrations, especially on the rising stage of the storm hydrograph (Figure SI-2, Supporting Information). These high concentrations on the rising stage are likely due to upstream point recharge of surface runoff from pasture land into the underlying St. Joe aquifer in locations where the confining chert layer is breached. At CHS, the response of TP, SRP, K, and Rb to storm events was more mixed. Small initial increases in concentration occurred with the onset of higher flows, followed by marked reductions in concentration, reflecting substantial dilution by a water source with relatively low SRP, TP, K, and Rb concentrations, most likely from the nonagricultural (ungrazed and forested) parts of the watershed. Indeed, karst inventories have verified that this part of the flow regime reflects runoff from areas which are not grazed by livestock.^{30,31}

To evaluate the attenuation (i.e., the reductions in concentrations) of TP, SRP, K, and Rb during transit through the karst, the median concentrations in agricultural runoff were compared with the corresponding median concentrations in CHS and LLS springs (Table 1). The average attenuation of TP and SRP concentrations ranged from 96% to 99%. In contrast, the average attenuation of K and Rb concentrations was lower, at 56% to 89%. Correspondingly, under storm flow conditions, comparisons of average field runoff concentrations and the 90th percentile concentrations in spring water (which typically correspond with the rising stage of the storm hydrographs of

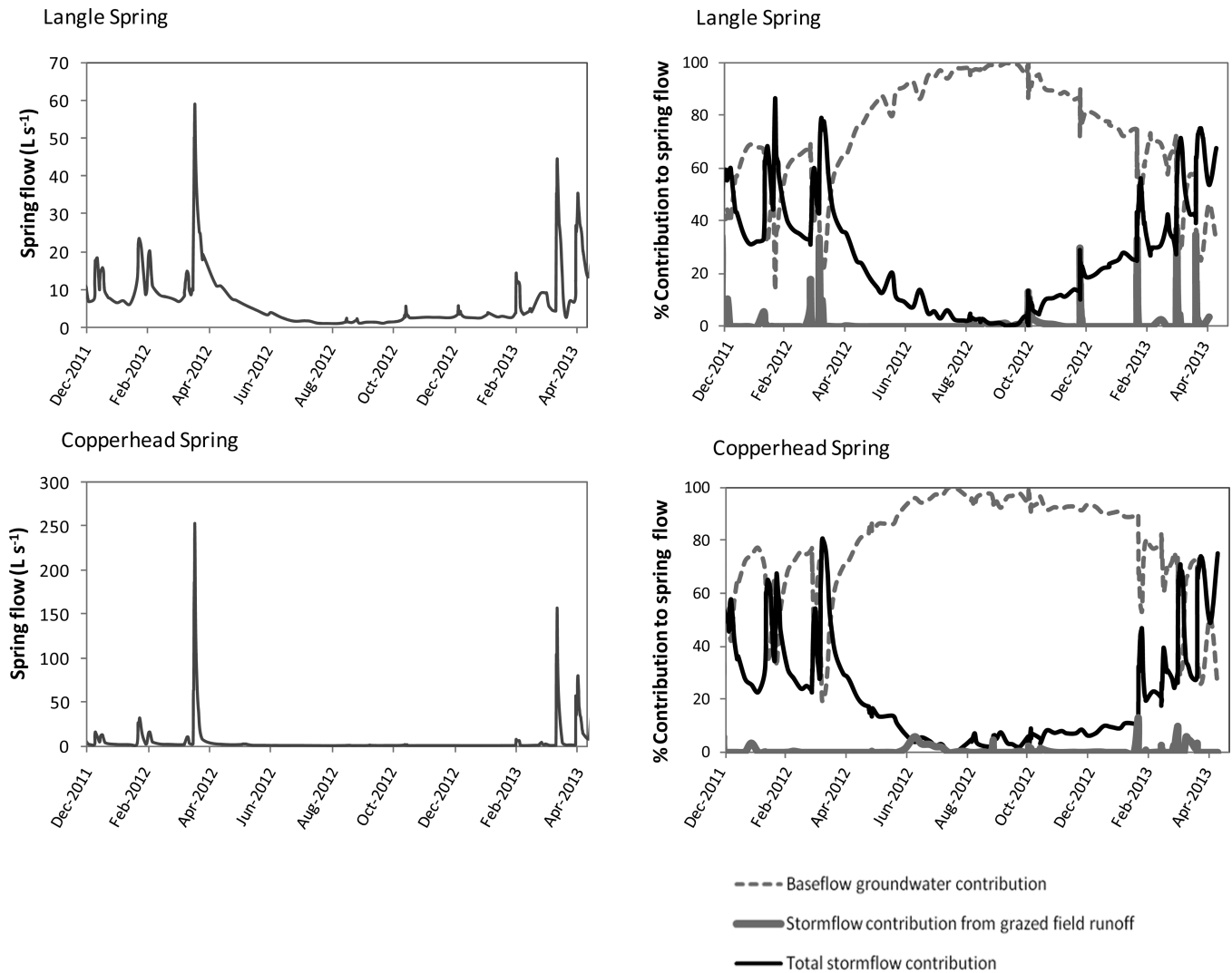


Figure 2. Hydrographs and water source apportionment for Langle and Copperhead springs.

the springs) revealed that storm flow attenuation of TP and SRP ranged from 93% to 96%, compared with 46% to 74% for K and Rb. Across all flow conditions, the higher rates of attenuation of P concentrations, relative to K and Rb, reflect the nonconservative behavior of P during transit through the karst.

K and Rb show high correlation (Figure 1b) due to their similar hydrogeochemistry (group 1a monovalent base cations of relatively small hydration size). Figure 1b shows a dominant two-component mixing series between a high concentration “endmember” (i.e., surface runoff from fertilizer and grazed pastures in runoff) and a low concentration spring-water “endmember” (i.e., runoff from nonagricultural and forested areas, which have no grazing or fertilizer inputs). Both K and Rb are highly soluble monovalent ions, and once transmitted into the karst drainage system, chemical interactions will be relatively small. Therefore, the attenuation of K and Rb during transport through the karst will be largely controlled by hydrological dilution, without retention mechanisms (with only possibly a small attenuation or release within the epikarst where there is a high proportion of clays^{31,40}). In contrast, P behaves non-conservatively, reflected by the higher rates of attenuation of P relative to K and Rb.

Spring Hydrology and Water-Source Apportionment. Comparing the hydrology of the two springs (Figure 2), base

flows at CHS were consistently lower than at LLS; the median flow at CHS was 2.62 L s^{-1} , compared with 13.1 L s^{-1} at LLS (Table 1). Further, CHS exhibited a more flashy flow regime than LLS, and storm flows were dramatically higher at CHS. For instance, the average of the highest 10% of flows was 139 L s^{-1} at CHS, compared with 40 L s^{-1} at LLS. This discrepancy reflects the following: (i) LLS being the “underflow” spring (3 cm lower than CHS), with a much larger groundwater drainage area under low-flow conditions than CHS, which accounts for the higher base flows at LLS; (ii) water capture (spring “piracy”) by CHS during storm events, which has been shown to result in a dramatic expansion in the watershed drainage area for CHS relative to LLS.^{32,33}

Contributions to spring water at LLS and CHS were apportioned by two-component endmember mixing analysis.^{23,41} Here Ca was used as a tracer of groundwater and K as a tracer of agricultural runoff, based on the observed dominant groundwater source of Ca and the dominant agricultural runoff source of K. For the mixing model, endmembers were defined as the following:

- (i) A base flow groundwater endmember with elevated Ca, and a storm flow endmember with low Ca concentrations.
- (ii) Runoff endmember from agricultural land with high K concentration, and a spring base flow low K endmember.

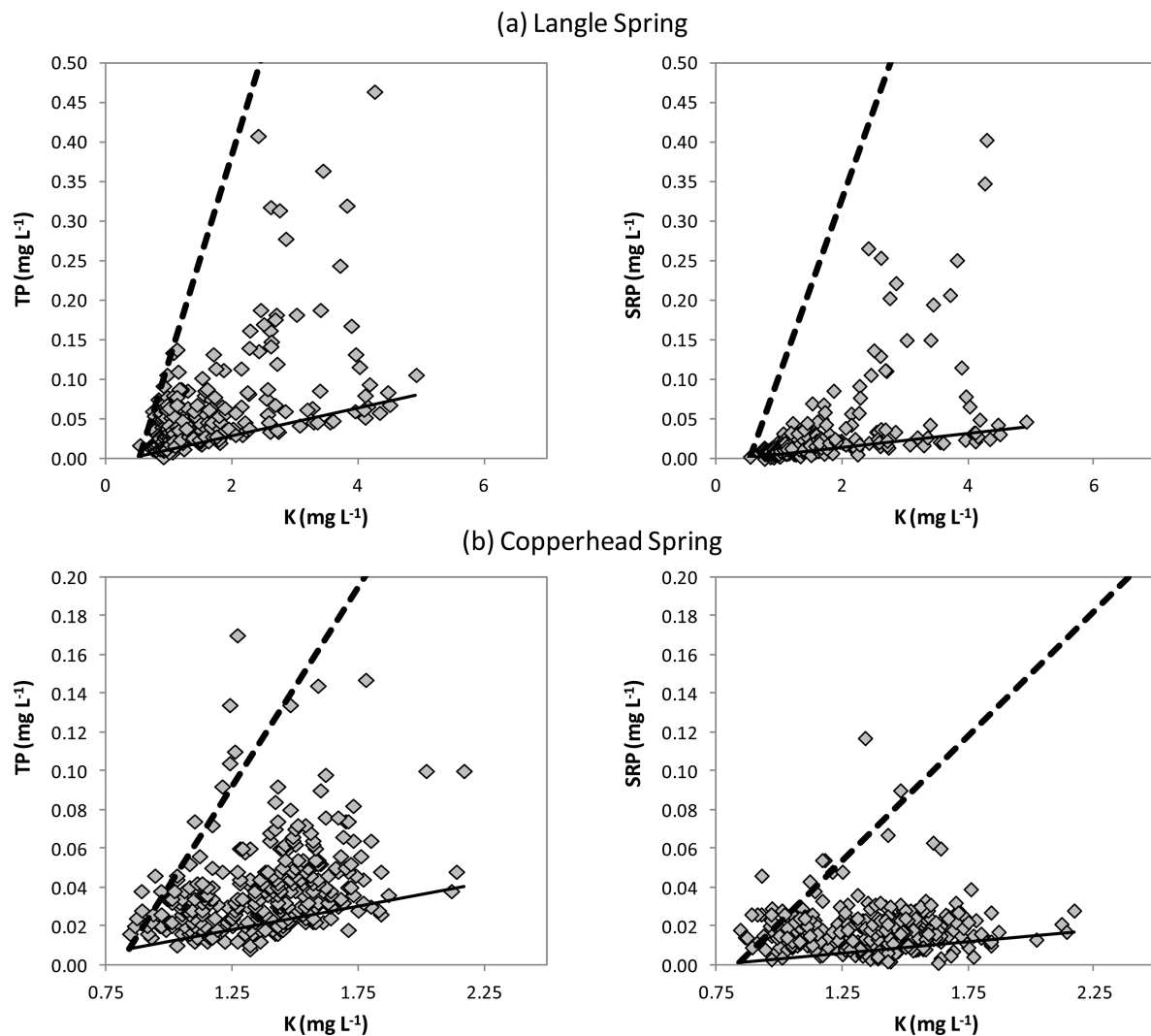


Figure 3. Relationships between total phosphorus (TP), soluble reactive phosphorus (SRP), and potassium (K) for (a) Langle Spring and (b) Copperhead Spring. The dashed line denotes the conservative mixing line, and the solid line denotes a line of maximum P retention (see text for explanation).

Applying a simple two-component mixing model^{23,41} (eq 1) and the endmembers identified above, Ca concentrations were used to partition the contributions to spring flow at LLS and CHS from base flow groundwater (the high concentration endmember) and from stormwater runoff (the low concentration endmember). Then a second two-component mixing model was used for K, to quantify the contributions from grazed pasture runoff (eq 2).

$$\begin{aligned} & \% \text{ total storm runoff} \\ & = 100 \times (Ca_{\text{gw}} - Ca_{\text{m}}) / (Ca_{\text{gw}} - Ca_{\text{ro}}) \end{aligned} \quad (1)$$

$$\begin{aligned} & \% \text{ agricultural runoff} \\ & = 100 \times (K_{\text{bf}} - K_{\text{m}}) / (K_{\text{bf}} - K_{\text{ag}}) \end{aligned} \quad (2)$$

where Ca_{gw} was the groundwater Ca concentration (high concentration base flow endmember), defined here as the average Ca concentration for the lowest 10% of flows sampled, Ca_{m} was the measured spring-water Ca concentration, Ca_{ro} was the stormwater (agricultural runoff) endmember, defined here as the average field runoff Ca concentration, K_{bf} was the base flow endmember (average K concentration for the lowest 10% of

spring flows sampled), K_{m} was the measured spring-water K concentration, and K_{ag} was the agricultural runoff endmember, defined here as the average field runoff K concentration. The values used to define the endmember concentrations at LLS and CHS are shown in Table SI-1, Supporting Information.

The water source apportionment for LLS and CHS (Figure 2) showed similar percentage contributions from base flow groundwater and total storm flow at LLS and CHS for most of the year and particularly during storm events. During winter and spring storm events, a much greater proportion of flow at LLS was derived from agricultural (grazed field) runoff (up to approximately a third of flow). This greater contribution of water from pastures than from nonagricultural land at LLS accounted for the higher storm-event concentrations of K and Rb at LLS. Agricultural runoff contributed a much lower proportion of winter and spring storm event flow at CHS (typically less than 10%). These results and the much higher storm flow discharges at CHS suggest that the water “piracy” at CHS, during storm events, captured water sources, which had a lower K and Rb concentration, from the nonagricultural (ungrazed and forested) areas.

Table 2. Measured and “Conservative” Annual Loads, and Mean Daily Base Flow and Storm Flow Loads, of Total Phosphorus (TP) and Soluble Reactive Phosphorus (SRP) in Langle and Copperhead Springs, with Net and Percentage TP and SRP Retention

		measured P load (kg y ⁻¹ or g d ⁻¹)	“conservative” P load (kg y ⁻¹ or g d ⁻¹)	net P retention (kg y ⁻¹ or g d ⁻¹)	% net P retention
Langle Spring (LLS)	annual TP load (kg y ⁻¹)	7.01	22.3	15.3	69
	annual SRP load (kg y ⁻¹)	1.85	19.0	17.2	90
Copperhead Spring (CHS)	annual TP load (kg y ⁻¹)	2.65	5.7	3.1	54
	annual SRP load (kg y ⁻¹)	0.98	3.3	2.3	70
Langle Spring (LLS)	avg base flow TP load (g d ⁻¹)	10.3	23.3	13.0	56
	avg base flow SRP load (g d ⁻¹)	2.21	19.8	17.6	89
Copperhead Spring (CHS)	avg base flow TP load (g d ⁻¹)	1.27	3.55	2.28	64
	avg base flow SRP load (g d ⁻¹)	0.45	2.14	1.69	79
Langle Spring (LLS)	avg storm flow TP load (g d ⁻¹)	112	1448	1336	92
	avg storm flow SRP load (g d ⁻¹)	51.4	1240	1189	96
Copperhead Spring (CHS)	avg storm flow TP load (g d ⁻¹)	445	971	527	54
	avg storm flow SRP load (g d ⁻¹)	175	567	392	69

Quantifying Net P Retention in Karst Drainage.

Endmember mixing analysis^{23–26} was applied using the “conservative” tracer, K, to explore the net P retention and release along karst hydrological pathways from infiltration through the soil, to spring discharge. First, concentrations of TP and SRP were plotted against K as the “conservative” tracer (Figure 3). Two dominant and distinct sources of spring water (both with different TP, SRP, and K concentrations) are hypothesized (Table SI-1, Supporting Information): (i) a high concentration agricultural endmember source (K_{ag} , TP_{ag} , SRP_{ag}), defined here as the average concentrations (of K, TP, and SRP) in agricultural field runoff at the LL and CH field plots, and (ii) a low concentration (nonagricultural) endmember (K_{na} , TP_{na} , SRP_{na}). As the source of this low concentration runoff could come from a wide range of nonagricultural sources (ungrazed and forest land) across the watershed, the most reliable means of capturing the integrated low-concentration endmember signal was to use the minimum measured spring-water K, TP, and SRP concentrations at LLS and CHS.

A theoretical linear two-component mixing series, i.e., a “conservative mixing line” between the high concentration and low concentration endmembers (Figure 3), would be observed if P behaved conservatively during mixing of the two endmember water sources during transport through the karst. In contrast, the observed relationships between TP and K, and SRP and K, in spring water were highly scattered at LLS and CHS (Figure 3). Most of the samples plot well below the conservative mixing line, showing predominantly net retention of TP and SRP relative to K. A few isolated samples plotted above the conservative mixing line, which are indicative of some sporadic net P release relative to the K tracer. The mixing patterns between TP, SRP, and K concentrations in Figure 3 had a well-defined lower boundary of samples with the lowest P concentrations relative to K (shown in Figure 3 as a “line of maximum P retention”). This line of maximum P retention probably represents a secondary endmember mixing line, between the same low concentration nonagricultural runoff endmember and a secondary agricultural

field runoff endmember, with high K but lower P concentrations as a result of P retention processes filtering out P. We posit that the majority of this P was “filtered” out during diffuse recharge of water as through the soil and the epikarst, into the karst aquifer. The spring-water samples which lie between the line of maximum retention and the conservative mixing series therefore likely reflect the *net* effects of P retention and remobilization processes for runoff water entering the karst drainage system via a mixture of diffuse and point recharge.

By comparing the observed spring-water TP and SRP versus K relationships with the theoretical linear conservative mixing series, the *net* effects of P retention and release can be directly quantified (Figure 3). By applying the theoretical conservative mixing series (TP versus K and SRP versus K) to the measured spring-water K concentrations at LLS and CHS, “conservative” TP and SRP concentration time series were derived (Figure SI-3a,b, Supporting Information) and converted to loads, using the corresponding spring flow data. By taking the difference between measured and “conservative” TP and SRP loads, we calculated net TP and net SRP retention on an annual basis, as well as for base flows (lowest 10% of flows) and storm flows (highest 10% of flows) (Table 2).

Annual net TP retention ranged from 69% at LLS to 54% at CHS. Net percentage P retention was consistently higher for SRP compared with TP, not only on an annual basis but also under storm and base flow conditions. This indicated preferential retention of more labile SRP fractions by sorption/uptake and greater mobility of TP organic and particulate P fractions. Similar patterns of soluble and particulate P retention have also been observed in other karst soils and drainage systems.^{7,11,13} Highest percentage net P retention occurred during storm events at LLS (92% TP retention and 96% SRP retention). However, the two springs showed very different patterns in P retention under storm and base flow conditions. At LLS, net P retention was greatest during storm flows than under base flow conditions, reflecting a high efficiency of P retention from agricultural runoff at LLS. In contrast, at CHS, a greater percentage of the P load was retained

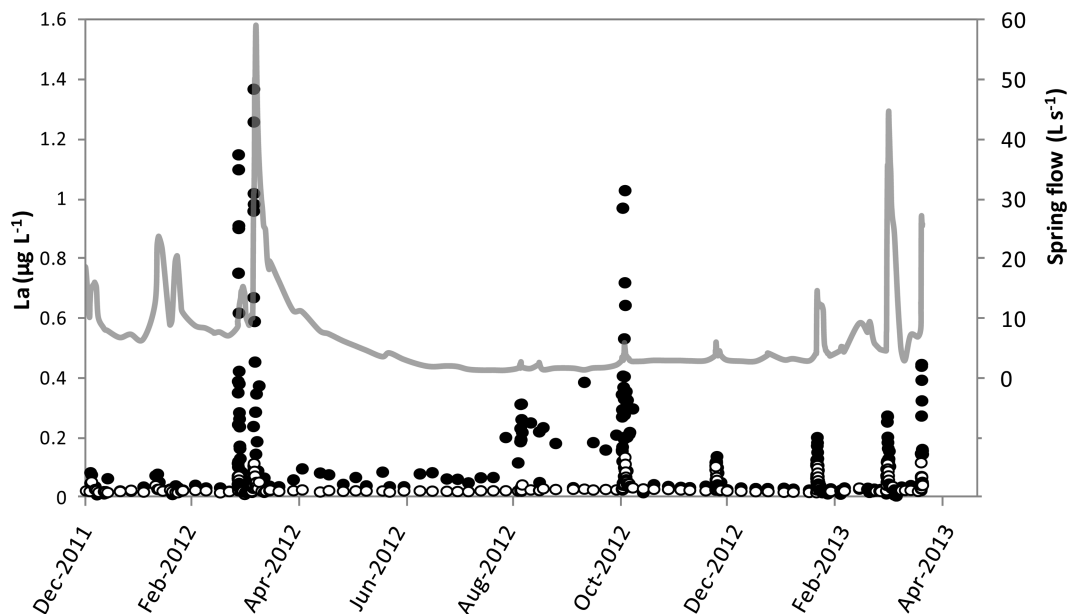


Figure 4. Time series of measured and “conservative” lanthanum (La) concentrations and flow at Langle spring. Measured La concentrations are denoted by solid circles; “conservative” La concentrations are denoted by open circles. See text for explanation of how “conservative” La concentrations were calculated.

under base flow than during storm flow. This reflects much lower base flows at CHS, which increase water residence time and promote particulate sedimentation and P retention, and higher storm flows linked to stream piracy, which provide greater flushing from nonagricultural areas, where flows have a low P concentration.

Contaminant Residence Times in Karst Drainage. While monitoring P relative to a conservative tracer provides us with valuable information on rates of annual and storm flow/base flow net retention, it provides no information about the residence times of P within the karst, or the time scales over which retention and remobilization may occur. This is of strategic concern in relation to the “legacy” of P within watersheds,^{42,43} whereby time-lags in release of retained P may mask the effects of conservation measures on receiving water quality. By measuring a full suite of trace elements using ICP-MS, a “serendipitous” observation was made, which may help provide clues about the wider contaminant residence times within the karst drainage. Concentrations of “dissolved” (<0.45 μm) lanthanum (La) in storm flow spring discharge at LLS were more than an order of magnitude higher than could be accounted for by the runoff sources measured within the SEW. Figure 4 shows the concentrations of La in the spring discharge at LLS and a “conservative” (maximum) concentration from runoff, which accounts for the dilution of agricultural runoff during transit through the karst drainage, using K as a tracer. The high storm flow La concentrations observed at LLS are likely a “legacy” signal from a past tracer experiment. In 2001, lanthanum-labeled montmorillonite clays were injected into a losing stream at SEW as part of a study to examine clay and bacterial transport.⁴⁴

While the La tracer was detected at LLS around 16 h after it was injected,⁴⁴ our monitoring suggests the La tracer was also retained within the karst drainage system and continues to be remobilized and released during storm events more than 10 years later. Unfortunately, it is impossible to perform a mass balance to quantify how much of the La applied in the tracer study remains within the karst drainage system and how long a La “legacy” might persist, as no La measurements were made in the

intervening 10 years between the tracer injection in 2001 and our monitoring which started in November 2011. Within the scope of this study, it was also not possible to determine whether the La concentrations measured were truly dissolved or a <0.45 μm colloidal/clay fraction or whether La geochemistry is sufficiently similar to be used as an indicator of P transport. However, these results indicate that La, a tracer expected to be flushed rapidly through the karst, was retained and continues to be remobilized and released during storm events, more than 10 years later. This indicates the potential for contaminant retention in the subsurface karst drainage system, where contaminant storage and gradual rerelease may occur over time scales of at least a decade.

Wider Implications. Hydrochemical tracers of agricultural runoff allowed us to directly evaluate the nonconservative behavior of P, within karst drainage, and quantify net P retention. Our results challenge the widely held assumption that karst landscapes are always highly vulnerable to P loss and suggest that, in some cases, karst drainage may provide a greater sink for P than previously considered. P from agricultural runoff was attenuated by hydrological dilution from cleaner (nonagricultural) sources during transport through karst drainage. However, there was also a high capacity for net P retention, especially for Langle Spring, which was subject to the highest agricultural P loadings. Here ~70% of the annual TP flux and ~90% of the annual SRP flux was retained. Moreover, the buffering within the soils and karst drainage not only retained a high proportion of incoming fluxes of P from agricultural runoff but preferentially retained the most bioavailable P fractions. For instance, much research has documented the capacity of soil to retain applied P in various inorganic (Al, Fe, Ca complexes) and organic forms of varying stability.^{45,46} The long-term accumulation of P in soil, however, can be released slowly to soil water.^{28,47}

The mechanisms of P retention were not investigated here but likely include varying combinations of processes including adsorption onto clays, coprecipitation of P with CaCO_3 , and binding with particulate humic substances^{11–13} in the soil, in epikarst, and within the fractures and conduits. These adsorption

products and precipitates will be physically retained as the water velocity slows and will be deposited as sediment along the base of the conduit flow paths. With the recurrence of high flow, these sediments are resuspended by turbulent flow and moved along the flow path, until redeposited, or eventually resurged at the base-level spring. Given the potential importance of CaCO_3 -P coprecipitation for P retention in karst terrain, and the possibility of reductions in the efficiency of this coprecipitation mechanism under higher P and dissolved organic carbon (DOC) concentrations,^{12,48,49} further work is needed to examine any unforeseen impacts of increasing agricultural intensification on this “self-cleansing” P retention mechanism. However, in this study, the site with the higher livestock intensity and with higher manure-enriched runoff actually demonstrated greater efficiency of P retention. This may indicate that critical P and DOC thresholds for inhibition of CaCO_3 precipitation were not reached or that other P retention process mechanisms were occurring.

The patterns in spring-water La concentrations suggest continued release of La from springs more than 10 years after a tracer injection and indicate the potential for long-term contaminant retention, storage, and subsequent release. Indeed, the complex nature of karst hydrological pathways can result in large distributions in water and contaminant residence times, and lag times for discharge to surface waters may be much longer than expected.^{50–52} Our findings indicate that retention of P within karst drainage may reduce the risk of acute episodic storm-driven losses of agricultural P. However, the potential buffering of P in the epikarst, and within the fracture and conduit drainage system, can provide a slow, but long-term, source of P released via springs to surface waters. Further work is needed to determine the ecological impacts of such patterns of P release to receiving streams and the ability of those streams to assimilate those inputs, compared with higher pulse inputs during storm flows.

■ ASSOCIATED CONTENT

● Supporting Information

Map of the SEW and the karst water flow system; time series of spring-water TP, SRP, K, and Rb concentrations; table of Ca, TP, and SRP endmember concentrations; soils and geology of the Savoy Experimental Watershed; experimental methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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