Jarvie, Helen P.; Sharpley, Andrew N.; Brahana, Van; Simmons, Tarra; Price, April; Neal, Colin; Lawlor, Alan J.; Sleep, Darren; Thacker, Sarah; Haggard, Brian E. 2014. **Phosphorus retention and remobilization along hydrological pathways in karst terrain**. *Environmental Science & Technology*, 48 (9). 4860-4868. 10.1021/es405585b

Phosphorus retention and remobilization along hydrological pathways in karst terrain

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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, mid-continent 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 percent 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 areas[6], 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 agriculture sources.

This vulnerability is assumed to arise from low nutrient buffering capacity of the thin cherty soils which overlie karst, and rapid transmission of surface runoff through conduits enlarged by dissolution[9, 10], which is thought to by-pass 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 either by P retention processes during transit along karst flow paths[14], or simply 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 towards 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 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, using hydrochemical tracers and endmember mixing analysis [23-26], 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 (~ 4330 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 mid-continental USA (Figure SI-1a). The soils of the SEW are predominantly silt loams (see SI). 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 SI and Figure SI-1c) 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-1) were undertaken at:

- Two adjacent karst springs (Langle Spring, LLS, and Copperhead Spring, CHS), which flow continually from the St Joe Formation (focused conduit-flow) springs;
- Two surface runoff field plots (Langle, LL, 1.07ha, and Copperhead, CH, 1.05 ha), which are located above, and within the watershed (recharge zone) of 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 fertiliser 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-minute intervals (see Supporting Information, SI). Karst spring water was sampled weekly, with stage-triggered, sub-daily automated sampling using an ISCO sampler during storm events. Figure SI-2 shows the distribution of samples collected on the rising and falling stage of the hydrograph. 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 hours of the water being sampled, and analyzed following EPA standard protocols, as described below (and in the SI). Filtered (<0.45µm) 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 SI). Unfiltered samples were analyzed for total phosphorus (TP), after acid-persulphate 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 behaviour (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 baseflow groundwater or in agricultural runoff. Firstly, 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. Secondly, 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.

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 baseflow groundwater source of Ca, from dissolution of limestone, which is diluted by surface runoff (Figure 1a).

<*Insert Figure 1 here*>

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 CH (1.0 cow 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 baseflow concentrations, especially on the rising stage of the storm hydrograph (Figure SI-2). 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].

<Insert Table 1 here>

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 stormflow 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 the springs) revealed that stormflow attenuation of TP and SRP ranged from 93-96%, compared with 46%-74% for K and Rb. Across all flow conditions, the higher rates of attenuation of P concentrations, relative to K and Rb, reflect the non-conservative behaviour 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 non agricultural 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, baseflows at CHS were consistently lower than LLS (Table 1; Figure SI-2); the median flow at CHS was 2.62 L s^{-1}, compared with 13.1 L s^{-1} at LLS. 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: (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 baseflows at LLS; and (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:

(i) A baseflow groundwater endmember with elevated Ca, and a stormflow endmember with low Ca concentrations.

(ii) Runoff endmember from agricultural land with high K concentration, and a spring baseflow low K endmember.

Applying a simple 2-component mixing model[23,41] (Equation 1) and the endmembers identified above, Ca concentrations were used to partition the contributions to spring flow at LLS and CHS from baseflow groundwater (the high concentration endmember) and from storm water runoff (the low concentration endmember). Then, a second 2-component mixing model was used for K, to quantify the contributions from grazed pasture runoff (Equation 2).

$$\%\ total\ storm\ runoff = 100 * (Ca_{gw} - Ca_{m})/(Ca_{gw} - Ca_{ro}) \qquad \textit{Equation 1}$$

$$\%\ agricultural\ runoff = 100 * (K_{bf} - K_{m})/(K_{bf} - K_{ag}) \qquad \textit{Equation 2}$$

Where Ca_{gw} was the groundwater Ca concentration (high concentration baseflow 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 baseflow endmember (average K concentration for the lowest 10% of spring flows sampled); K_{m} was the measured spring-water K concentration, 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.

<Insert Figure 2 here>

The water source apportionment for LLS and CHS (Figure 2) showed similar percentage contributions from baseflow groundwater and total stormflow 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 runoff (up to approximately a third of flow). This greater contribution of water from pastures than non-agricultural 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 stormflow 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 non-agricultural (ungrazed and forested) areas.

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. Firstly, 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): (i) a high concentration agricultural end-member 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 (non-agricultural) endmember (K_{na}, TP_{na}, SRP_{na}). As the source of this low concentration runoff could come from a wide range of non-agricultural 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..

<*Insert Figure 3 here*>

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 non-agricultural 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 of 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) 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 baseflows (lowest 10% of flows) and stormflows (highest 10% of flows) (Table 2).

<Insert table 2 here>

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 baseflow 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 baseflow conditions. At LLS, net P retention was greatest during stormflows than under baseflow 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 under baseflow than during stormflow. This reflects much lower baseflows at CHS, which increase water residence time, promote particulate sedimentation and P retention, and higher stormflows linked to stream piracy, which provide greater flushing from non-agricultural areas, where flows have a low P concentration.

Contaminant residence times in karst drainage.

Whilst monitoring P relative to a conservative tracer provides us with valuable information on rates of annual and stormflow/baseflow net retention, it provides no information about the residence times of P within the karst, or the timescales 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 um) lanthanum (La) in stormflow 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 stormflow

La concentrations observed at LLS are likely a 'legacy' signal from a past tracer experiment. In 2001, lanthanum-labelled montmorillonite clays were injected into a losing stream at SEW as part of a study to examine clay and bacterial transport[44].

<*Insert Figure 4 here*>

Whilst the La tracer was detected at LLS around 16 hours 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 this lanthanum 'legacy' will 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 ten years later. This indicates the potential for contaminant retention in the subsurface karst drainage system, where contaminant storage and gradual re-release may occur over timescales of at least a decade.

Wider implications

Hydrochemical tracers of agricultural runoff allowed us to directly evaluate the non-conservative behaviour 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 (non-agricultural 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, co-precipitation of P with $CaCO_3$, and binding with particulate humic substances[11-13] in the soil, 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 flowpaths. With the recurrence of high flow, these sediments are resuspended by turbulent flow and moved along the flowpath, until redeposited, or eventually resurged at the base-level spring. Given the potential importance of $CaCO_3$-P co-precipitation for P retention in karst terrain, and the possibility of reductions in the efficiency of this co-precipitation 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 lanthanum concentrations suggest continued released 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 to 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 Available

Map of the SEW and the karst water flow system; Time series of spring-water TP, SRP, K, 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.

■ ACKNOWLEDGMENTS

HPJ acknowledges funding and support from the UK Natural Environment Research Council, a Fulbright Distinguished Scholar Award, and an OECD Co-operative Research Programme Fellowship. We thank Chris Wardle (British Geological Survey) for help with the artwork, and Dr. Tiong Ee Ting for permission to reproduce tracer experiment results in the Supporting Information.

References

1. Panno, S. V. Karst aquifers: Can they be protected? *Ground Water* **2006,** *44*, (4), 494-494.; DOI 10.1111/j.1745-6584.2006.00164.x.

2. White, W. B.; Culver, D. C.; Herman, J. S.; Kane, T. C.; Mylroie, J. E., Karst lands. *American Scientist* **1995,** *83*, (5), 450-459.

3. Owen, M. R.; Pavlowsky, R. T., Base flow hydrology and water quality of an Ozarks spring and associated recharge area, southern Missouri, USA. *Environ. Earth Sci.* **2011,** *64*, (1), 169-183; DOI 10.1007/s12665-010-0836-4.

4. Baffaut, C.; Benson, V. W., Modeling flow and pollutant transport in a karst watershed with SWAT. *Trans. Asabe* **2009,** *52*, (2), 469-479.

5. Fournier, M.; Motelay-Massei, A.; Massei, N.; Aubert, M.; Bakalowicz, M.; Dupont, J. P., Investigation of transport processes inside karst aquifer by means of STATIS. *Ground Water* **2009,** *47*, (3), 391-400; DOI 10.1111/j.1745-6584.2008.00532.x.

6. Brahana, J. V., Rationale and methodology for approximating spring-basin boundaries in the mantled karst terrane of the Springfield Plateau, northwestern Arkansas. In *The engineering geology and hydrogeology of karst terranes*; Beck, B. F. ; Stephenson, B. F., Eds; A.A. Balkema: Rotterdam 1997; pp 77-82.

7. Kilroy, G.; Coxon, C., Temporal variability of phosphorus fractions in Irish karst springs. *Environ. Geol.* **2005,** *47*, (3), 421-430; DOI 10.1007/s00254-004-1171-4.

8. Lerch, R. N., Contaminant transport in two central Missouri karst recharge areas. *J. Cave Karst Stud.* **2011,** *73*, (2), 99-113; DOI 10.4311/jcks2010es0163.

9. Coxon, C., Agriculture and karst. *In Karst Management*, Beynen, P. E., Ed. Springer: Netherlands 2011; pp 103-138.

10. Kacaroglu, F., Review of groundwater pollution and protection in karst areas. *Wat. Air Soil Poll.* **1999,** *113*, (1-4), 337-356; DOI 10.1023/A:1005014532330.

11. Allousha, G. A.; Boyer, D. G.; Belesky, D. P.; Halvorson, J. J., Phosphorus mobility in a karst landscape under pasture grazing system. *Agron.* **2003,** *23*, (7), 593-600; DOI 10.1051/agro:2003033.

12. Neal, C.; Jarvie, H. P.; Williams, R. J.; Neal, M.; Wickham, H.; Hill, L., Phosphorus-calcium carbonate saturation relationships in a lowland chalk river impacted by sewage inputs and phosphorus remediation: an assessment of phosphorus self-cleansing mechanisms in natural waters. *Sci. Tot. Environ.* **2002,** *282*, 295-310.

13. von Wandruszka, R., Phosphorus retention in calcareous soils and the effect of organic matter on its mobility. *Geochem. Trans.* **2006,** *7*, 6; DOI 10.1186/1467-4866-7-6.

14. Mellander, P.-E.; Jordan, P.; Melland, A. R.; Murphy, P. N. C.; Wall, D. P.; Mechan, S.; Meehan, R.; Kelly, C.; Shine, O.; Shortle, G., Quantification of phosphorus transport from a karstic agricultural watershed to emerging spring water. *Environ. Sci. Technol.* **2013,** *47*, (12), 6111-6119; DOI 10.1021/es304909y.

15. Mellander, P.-E.; Jordan, P.; Wall, D. P.; Melland, A. R.; Meehan, R.; Kelly, C.; Shortle, G., Delivery and impact bypass in a karst aquifer with high phosphorus source and pathway potential. *Wat. Res.* **2012,** *46*, (7), 2225-2236; DOI 10.1016/j.watres.2012.01.048.

16. Stueber, A. M.; Criss, R. E., Origin and transport of dissolved chemicals in a karst watershed, southwestern Illinois. *J. Amer. Wat. Res. Assoc.* **2005,** *41*, (2), 267-290; DOI 10.1111/j.1752-1688.2005.tb03734.x.

17. Kleinman, P. J. A.; Sharpley, A. N.; McDowell, R. W.; Flaten, D. N.; Buda, A. R.; Tao, L.; Bergstrom, L.; Zhu, Q., Managing agricultural phosphorus for water quality protection: principles for progress. *Plant Soil* **2011,** *349*, (1-2), 169-182; DOI 10.1007/s11104-011-0832-9.

18. Sharpley, A. N.; Kleinman, P. J. A.; Flaten, D. N.; Buda, A. R., Critical source area management of agricultural phosphorus: experiences, challenges and opportunities. *Wat. Sci. Technol.* **2011,** *64*, (4), 945-952; DOI 10.2166/wst.2011.712.

19. Sharpley, A. N.; Jarvie, H. P. Agricultural management, water quality & ecology: Putting practice into policy. In *National Agricultural Biotechnology Council Report 24*; Eaglesham, A., Korth, K., Hardy, R. W. F., Eds.; Jacobs Press: Auburn, NY. 2012. pp 73-99.

20. Sims, J. T.; Ma, L.; Oenema, O.; Dou, Z.; Zhang, F. S., Advances and challenges for nutrient management in China in the 21st Century. *J. Environ. Qual.* **2013,** *42*, (4), 947-950; DOI 10.2134/jeq2013.05.0173.

21 Kellogg, R. L.; Lander, C. H.; Moffitt, D. C.; Gollehon, N., Manure nutrients relative to the capacity of cropland and pastureland to assimilate nutrients: Spatial and temporal trends for the United States. *Resource Assessment and Strategic Planning Working Paper 98-1*, USDA, Natural Resources Conservation Service and Economic Research Service, General Services Administration, National Forms and Publication Center, Fort Worth, TX. 140 pages. 2000, http://www.nrcs.usda.gov/technical/land/pubs/manntr.pdf

22. Maguire, R. O.; Rubæk, G. H.; Haggard, B. E.; Foy, B. H. Critical evaluation of the implementation of mitigation options for phosphorus from field to catchment scales *J. Environ. Qual.* **2009,** 38: 5: 1989-1997; DOI 10.2134/jeq2007.0659.

23. Christophersen, N.; Neal, C.; Hooper, R. P.; Vogt, R. D.; Andersen, S., Modeling streamwater chemistry as a mixture of soilwater end-members - A step towards 2nd-generation acidification models. *J. Hydrol.* **1990,** *116*, (1-4), 307-320; DOI 10.1016/0022-1694(90)90130-P.

24. Neal, C.; Jarvie, H. P.; Williams, R.; Love, A.; Neal, M.; Wickham, H.; Harman, S.; Armstrong, L., Declines in phosphorus concentration in the upper River Thames (UK): Links to sewage effluent cleanup and extended end-member mixing analysis. *Sci. Tot. Environ.* **2010,** *408*, (6), 1315-1330; DOI 10.1016/j.scitotenv.2009.10.055.

25. Jarvie, H. P.; Neal, C.; Withers, P. J. A.; Baker, D. B.; Richards, R. P.; Sharpley, A. N., Quantifying phosphorus retention and release in rivers and watersheds using extended end-member mixing analysis (E-EMMA). *J. Environ. Qual.* **2011,** *40*, (2), 492-504; DOI 10.2134/jeq2010.0298.

26. Jarvie, H. P.; Sharpley, A. N.; Scott, J. T.; Haggard, B. E.; Bowes, M. J.; Massey, L. B., Within-river phosphorus retention: Accounting for a missing piece in the watershed phosphorus puzzle. *Environ. Sci. Technol.* **2012,** *46*, (24), 13284-13292; DOI 10.1021/es303562y

27. Brahana, V., The Savoy Experimental Watershed—A long-term research site for karst hydrogeology: *In* Palmer, A.N. and Palmer, Margaret V., Caves and Karst of the USA, National

Speleological Society Guidebook for the International Congress of Speleology, section 5-Ozark Plateaus, **2009**, p. 179.

28. Sharpley, A.N.; Kleinman P.J.A.; Jordan, P.; Bergström, L.; and Allen, A.L., Evaluating the success of phosphorus management from field to watershed. *J. Environ. Qual.* **2009.** 38:1981-1988; DOI 10.2134/jeq2008.0056.

29. Scott, J. T.; Haggard, B. E.; Sharpley, A. N.; Romeis, J. J., Change point analysis of phosphorus trends in the Illinois River (Oklahoma) demonstrates the effects of watershed management. *J. Environ. Qual.* **2011,** *40*, (4), 1249-1256; DOI 10.2134/jeq2010.0476.

30. Brahana, J.V., Controlling influences on ground-water flow and transport in the shallow karst aquifer of northeastern Oklahoma and northwestern Arkansas: Proceedings Volume, Hydrologic Problems Along the Arkansas-Oklahoma Border, Arkansas Water Resources Center Publication No. MSC-168, **1995**, p. 25-30.33.

31. Brahana, J.V., Ting, T.; Al-Qinna, M.; Murdock, J.; Davis, R.K.; Lainz, J.; Killingbeck, J.J.; Szilvagyi, E.; Doheny-Skubic, M.; Chaubey, I.; Hays, P.D.; and Thoma, G., Quantification of hydrologic budget parameters for the vadose zone and epikarst in mantled karst. U.S. Geological Survey Karst Interest Group Proceedings, Rapid City, South Dakota, September 12-15, 2005, editor E.L. Kuniansky. U.S. Geological Survey, Scientific Investigations Report **2005**-5160, pp 144-152.

32. Leh, M. D.; Chaubey, I.; Murdoch, J.; Brahana, J. V.; Haggard, B. E., Delineating runoff processes and critical runoff source areas in a pasture hillslope of the Ozark Highlands. *Hydrol.Proc.* **2008,** *22*, (21), 4190-4204; DOI 10.1002/hyp.7021.

33. Haggard, B. E., Phosphorus concentrations, loads, and sources within the Illinois River drainage area, Northwest Arkansas, 1997-2008. *J. Environ. Qual.* **2010,** *39*, (6), 2113-2120; DOI 10.2134/jeq2010.0049.

34. Tortorelli, R.L.; Pickup, B.E., Phosphorus concentrations, loads, and yields in the Illinois River basin, Arkansas and Oklahoma, 2000–2004: U.S. Geological Survey Scientific Investigations Report 2006–5175, 38 p.

35. Murphy, J.; Riley, J. P., A modified single solution method for the determination of phosphate in natural-waters. *Anal. Chim. Acta* **1962***, 27,* 31–36.

36. Eisenreich, S.J.; Bannerman, R.T.; Armstrong, D.E. Simplified phosphorus analytical technique. *Environ. Lett.* **1975**, 9 (1), 43-53.

37. Jarvie H. P.; Withers P. J. A.; Neal C. Review of robust measurement of phosphorus in river water: sampling, storage, fractionation and sensitivity. *Hydrol. Earth Syst.Sci.* **2002**, 6, 113-131.

38. Divine, C. E.; McDonnell, J. J. The future of applied tracers in hydrogeology. *J. Hydrogeol.*, **2005**, 13, 255-258; DOI 10.1007/s10040-004-0416-3.

39. Burns, D. A.; McDonnell, J. J.; Hooper, R. P.; Peters, N. E.; Freer, J. E.; Kendall, C.; Beven, K. Quantifying contributions to storm runoff through endmember mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA). *Hydrol. Proc*. **2001**, 15, 1903-1924; DOI 10.1002/hyp.246.

40. Williams, P.W. The role of the epikarst in karst and cave hydrogeology: a review. *Int. J. Speleo.* **2008**, 31, 1-10.

41. Jarvie, H. P.; Neal, C.; Smart, R.; Owen, R.; Fraser, D.; Forbes, I.; Wade, A., Use of continuous water quality records for hydrograph separation and to assess short-term variability and extremes in acidity and dissolved carbon dioxide for the River Dee, Scotland. *Sci. Tot. Environ.* **2001,** *265*, (1-3), 85-98; DOI 10.1016/S0048-9697(00)00651-3

42. Jarvie, H. P.; Sharpley, A. N.; Spears, B.; Buda, A. R.; May, L.; Kleinman, P. J. A., Water quality remediation faces unprecedented challenges from "Legacy Phosphorus". *Environ. Sci. Technol.* **2013,** *47*, (16), 8997-8998; **DOI:** 10.1021/es403160a.

43. Sharpley, A.; Jarvie, H. P.; Buda, A.; May, L.; Spears, B.; Kleinman, P., Phosphorus Legacy: Overcoming the effects of past management practices to mitigate future water quality impairment. *J. Environ. Qual.* **2013,** *42*, (5), 1308-1326; DOI 10.2134/jeq2013.03.0098

44. Ting, T.E.E., Assessing bacterial transport, storage and viability in mantled karst of northwest Arkansas using clay and *Escherichia coli* labeled with lanthanide-series metals: Ph.D. Dissertation, University of Arkansas, 2005.

45. Sharpley, A. N.; Smith, S. J.; Bain, W. R., Nitrogen and phosphorus fate from long-term poultry litter applications to Oklahoma soils. *Soil Sci. Soc. Amer. J.* **1993,** *57*, (4), 1131-1137.

46. Frossard, E.; Condron L. M.; Oberson A.; Sinaj S.; Fardeau J. C., . Processes governing phosphorus availability in temperate soils. *J. Environ. Qual.* **2000**, *29*, (1), 15-23.

47. Cox, F. R.; Kamprath, E. J.; McCollum, R. E., A descriptive model of soil test nutrient levels following fertilization. *Soil Sci. Soc. Amer. J.* **1981,** *45*,(3), 529-532.

48. Inskeep, W. P.; Bloom, P. R., kinetics of calcite precipitation in the presence of water-soluble organic-ligands. *Soil Sci. Soc. Amer. J.* **1986,** *50*, (5), 1167-1172.

49. Dove, P. M.; Hochella, M. F., Calcite precipitation mechanisms and inhibition by orthophosphate - insitu observations by scanning force microscopy. *Geochim. Cosmochim. Acta* **1993,** *57*, (3), 705-714; DOI 10.1016/0016-7037(93)90381-6.

50. Kirchner, J. W.; Feng, X. H.; Neal, C., Fractal stream chemistry and its implications for contaminant transport in catchments. *Nature* **2000,** *403*, (6769), 524-527; DOI 10.1038/35000537.

51. Kirchner, J. W.; Neal, C., Universal fractal scaling in stream chemistry and its implications for solute transport and water quality trend detection. *Proc. Nat. Acad. Sci.* **2013,** *110*, (30), 12213-12218; DOI 10.1073/pnas.1304328110.

52. Neal, C., Catchment water quality: the inconvenient but necessary truth of fractal functioning. *Hydrol. Proc.* **2013,** *27*, (24), 3516-3520; DOI 10.1002/hyp.10052

		Field runoff (m^3 ha^{-1}) Spring flow (L s^{-1})	**SRP (mg L^{-1})**	**TP (mg L^{-1})**	**Rb (µg 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

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.

		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)	Av. baseflow TP load ($g\ d^{-1}$)	10.3	23.3	13.0	56
	Av.baseflow SRP load ($g\ d^{-1}$)	2.21	19.8	17.6	89
Copperhead Spring (CHS)	Av. baseflow TP load ($g\ d^{-1}$)	1.27	3.55	2.28	64
	Av. baseflow SRP load ($g\ d^{-1}$)	0.45	2.14	1.69	79
Langle Spring (LLS)	Av.stormflow TP load ($g\ d^{-1}$)	112	1448	1336	92
	Av. stormflow SRP load ($g\ d^{-1}$)	51.4	1240	1189	96
Copperhead Spring (CHS)	Av. stormflow TP load ($g\ d^{-1}$)	445	971	527	54
	Av.stormflow SRP load ($g\ d^{-1}$)	175	567	392	69

Table 2: Measured and 'conservative' annual loads, and mean daily baseflow and stormflow loads, of total phosphorus (TP) and dissolved phosphorus (SRP) in Langle and Copperhead springs, with net and percentage TP and SRP retention.

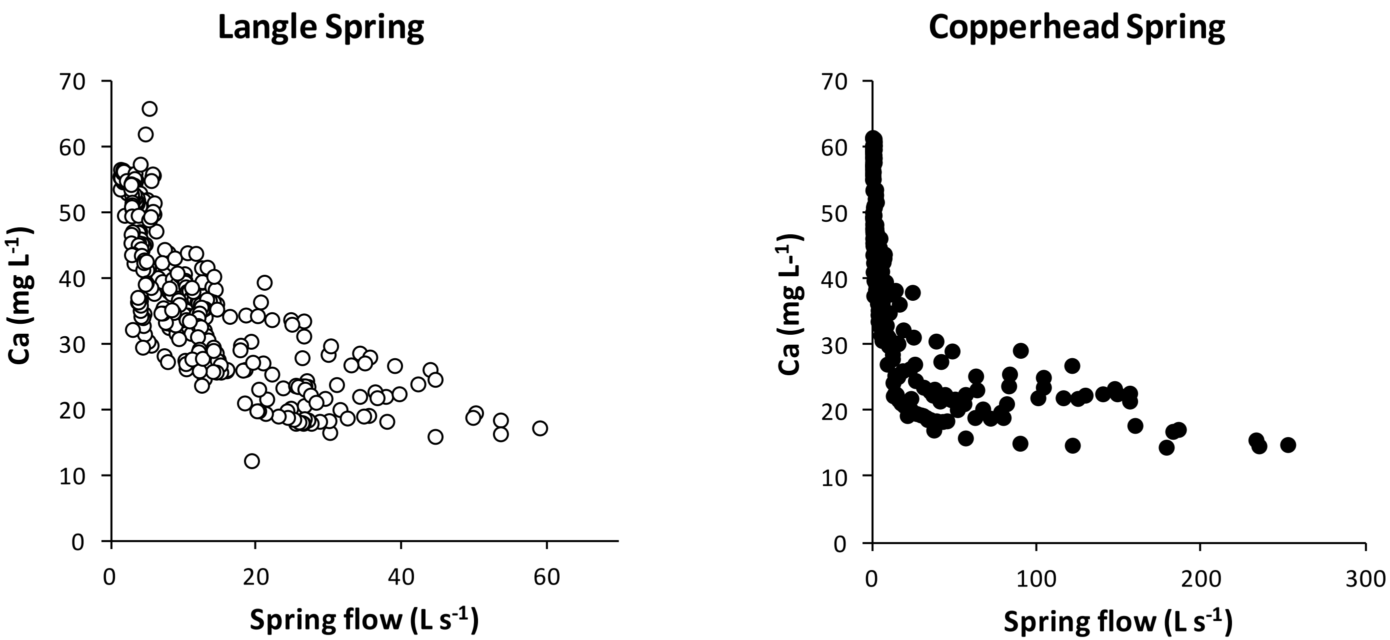

Fig 1a Relationships between calcium (Ca) concentrations and flow at Langle and Copperhead springs

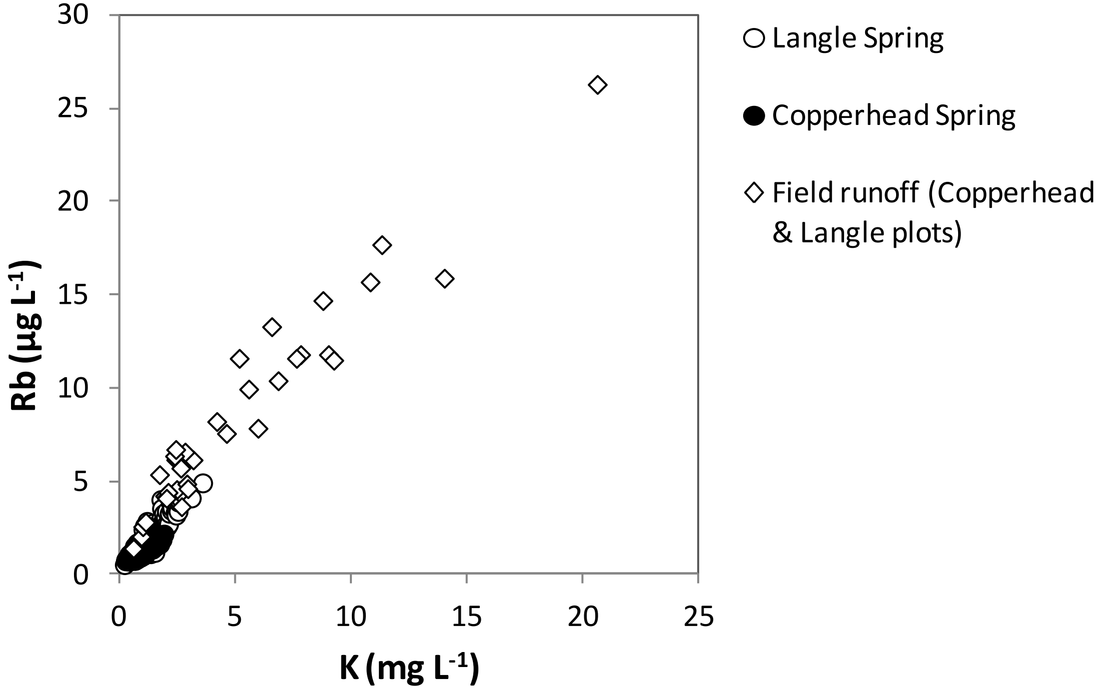

Fig 1b Relationship between rubidium (Rb) and potassium (K) concentrations in field runoff and spring water samples

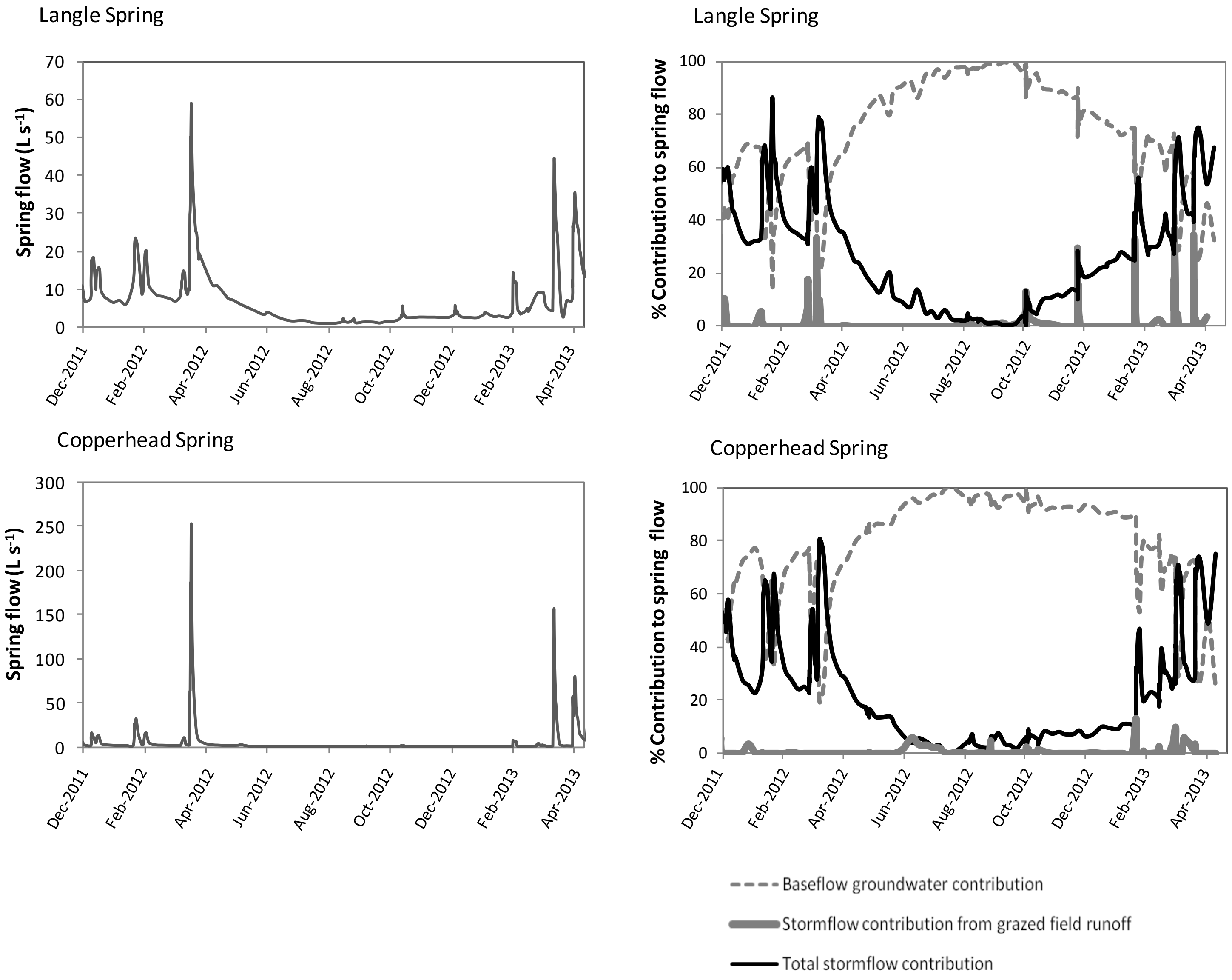

Fig 2 Hydrographs and water source apportionment for Langle and Copperhead springs

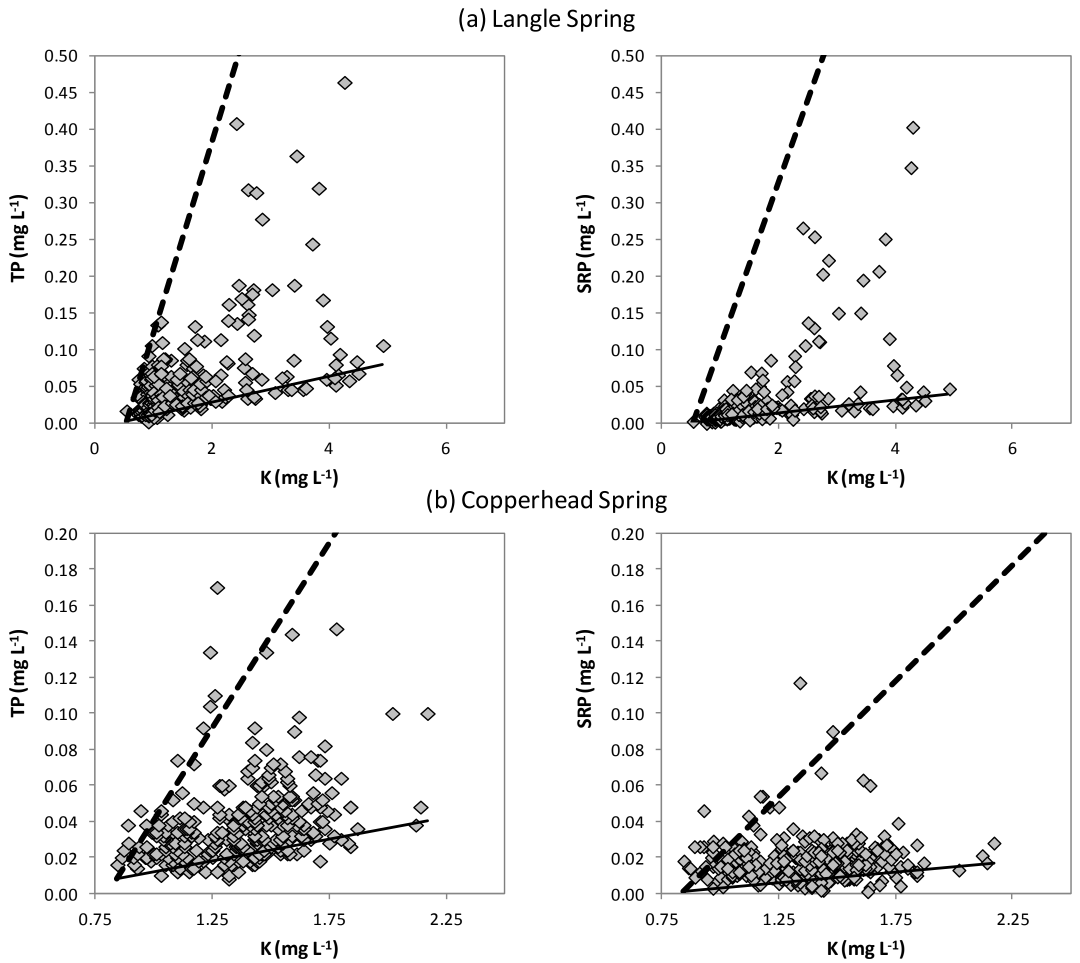

Fig 3 Relationships between total phosphorus (TP), soluble reactive phosphorus (SRP), and potassium (K) for (a) Langle spring and (b) Copperhead spring. The dashed line denotes the 'conservative' mixing line, and the solid line denotes a line of maximum P retention (see text for explanation)

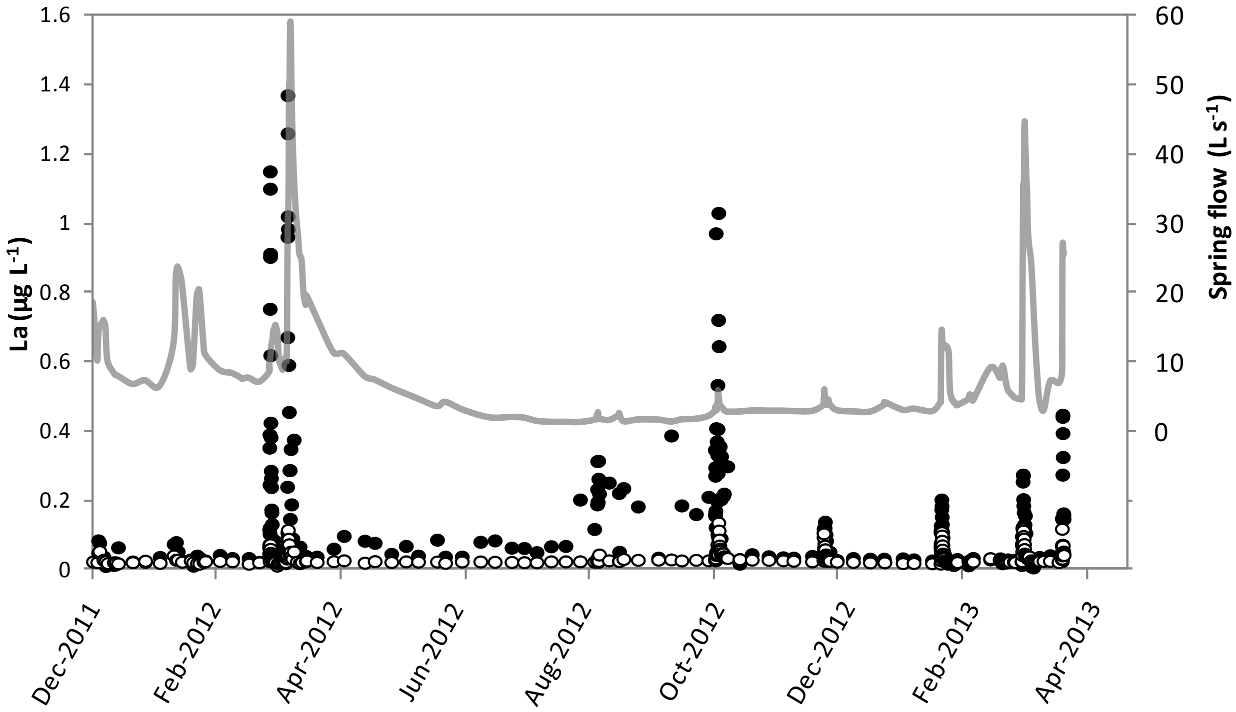

Figure 4 Timeseries of measured and ‘conservative’ lanthanum (La) concentrations and flow at Langle spring. Measured La concentrations are denoted by solid circles; ‘conservative’ La concentrations are denoted by open circles. See text for explanation of how ‘conservative’ La concentrations were calculated.

SUPPORTING INFORMATION

Journal: Environmental Science & Technology

Phosphorus retention and remobilization along hydrological pathways in karst terrain

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Number of pages: 11

Number of Figures: 3

Number of Tables: 1

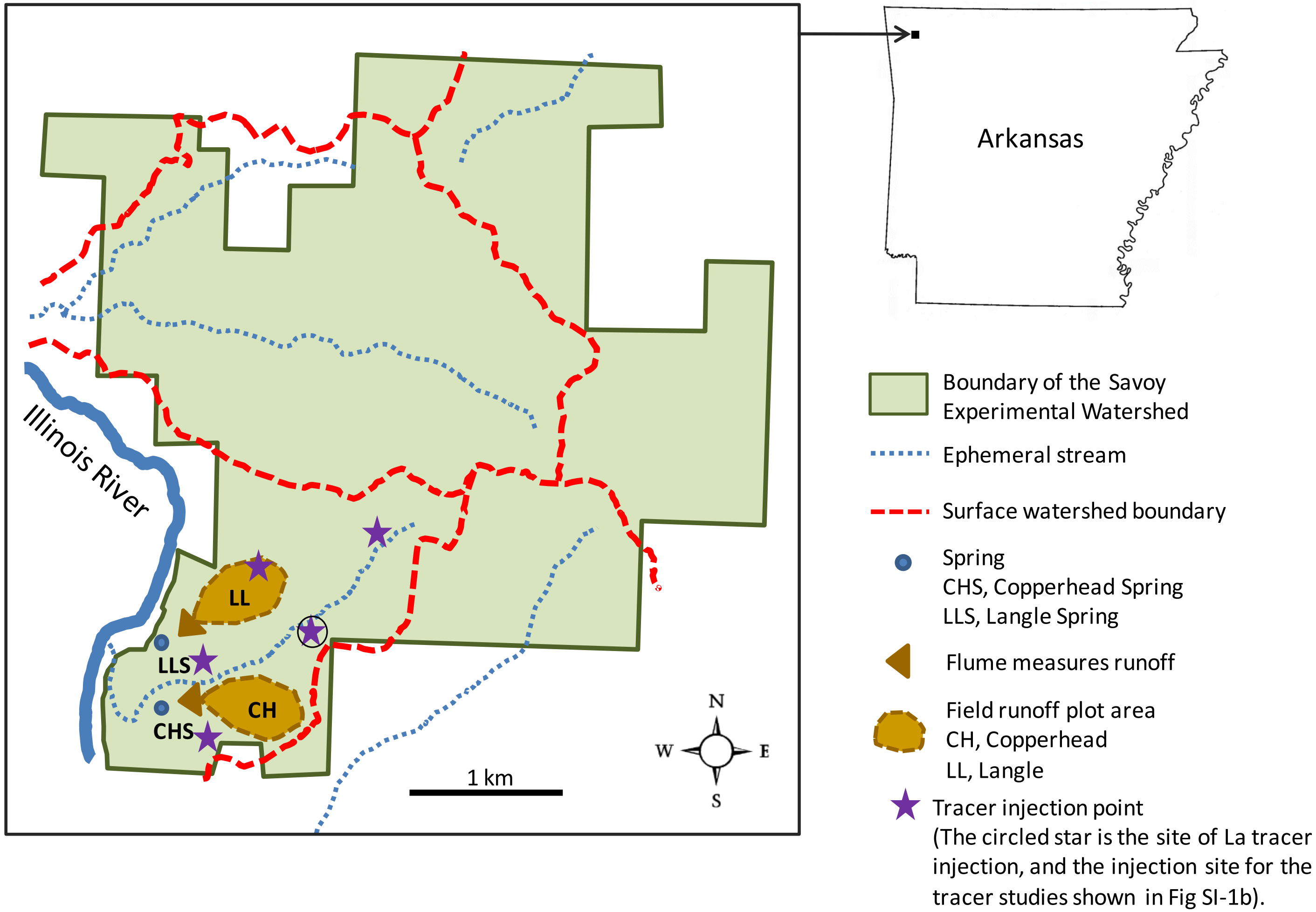

Fig SI-1a. Map of the Savoy Experimental Watershed, Arkansas, showing the location of the Langle and Copperhead springs and field runoff areas (adapted from Leh et al., 2008[1]).

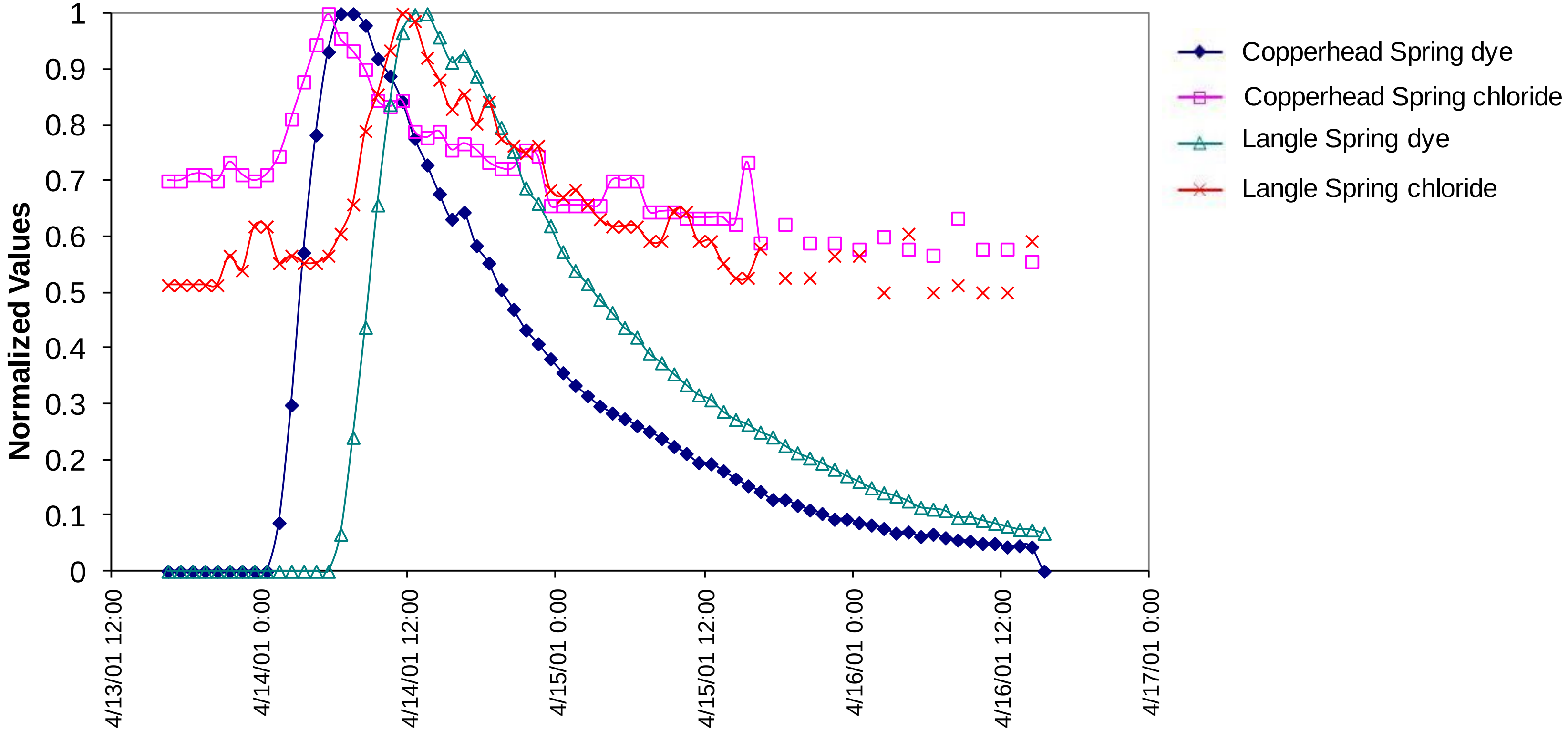

Fig SI-1b. Rhodamine WT (RWT) dye and chloride tracer results[2], showing tracer appearance at Copperhead and Langle Springs after injection at the location shown in Fig SI-1a. These results are presented to demonstrate the hydrological connectivity of both springs with the watershed surface. At Copperhead Spring, the first tracer appearance after injection was for RWT, 11.5 hours after injection, with a peak for RWT at 16.5 hours and C^{l-} at 15.5 hours after injection. At Langle Spring, the first tracer appearance was RWT, 16.5 hrs after injection, with a peak for RWT at 24.5 hours and Cl^- 21.5 hrs after injection. These data are reproduced by kind permission of Dr. Tiong Ee Ting.

Fig SI-1c Block diagram showing the structure of the karst drainage system at the Savoy Experimental Watershed, and the location of the monitored springs (Langle spring, LLS, and Copperhead spring, CHS), and field runoff plots (Langle plot, LL, and Copperhead plot, CH). Surface runoff enters the karst groundwater drainage system via diffuse and point recharge; karst groundwater follows the slight dip of the sedimentary beds, flowing westwards and discharging via a series of springs directly into the nearby Illinois River, which flows on top of the Chattanooga Formation.

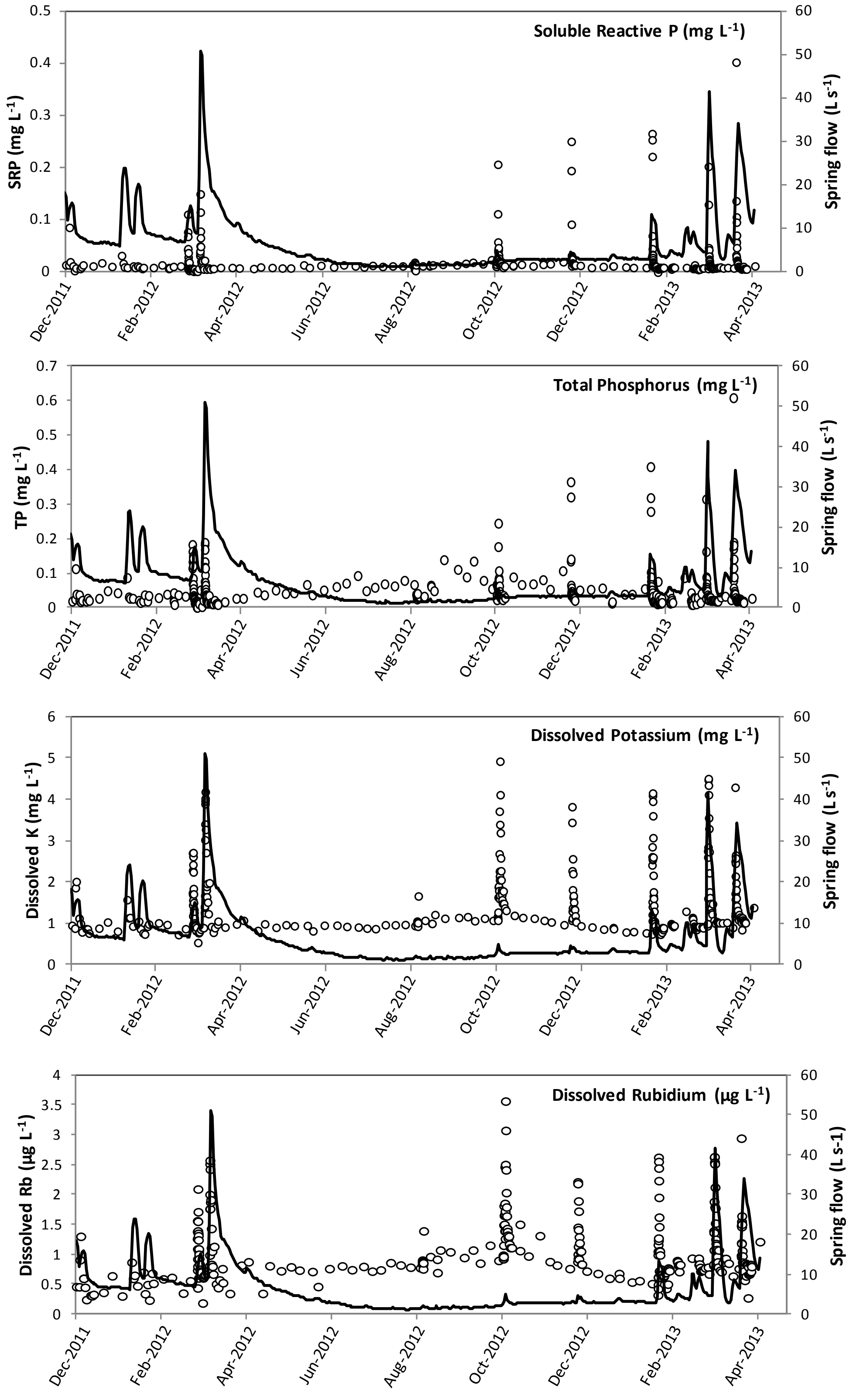

Figure SI-2a Timeseries of flow (solid line) and, soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved potassium (K) and dissolved rubidium (Rb) for Langle Spring.

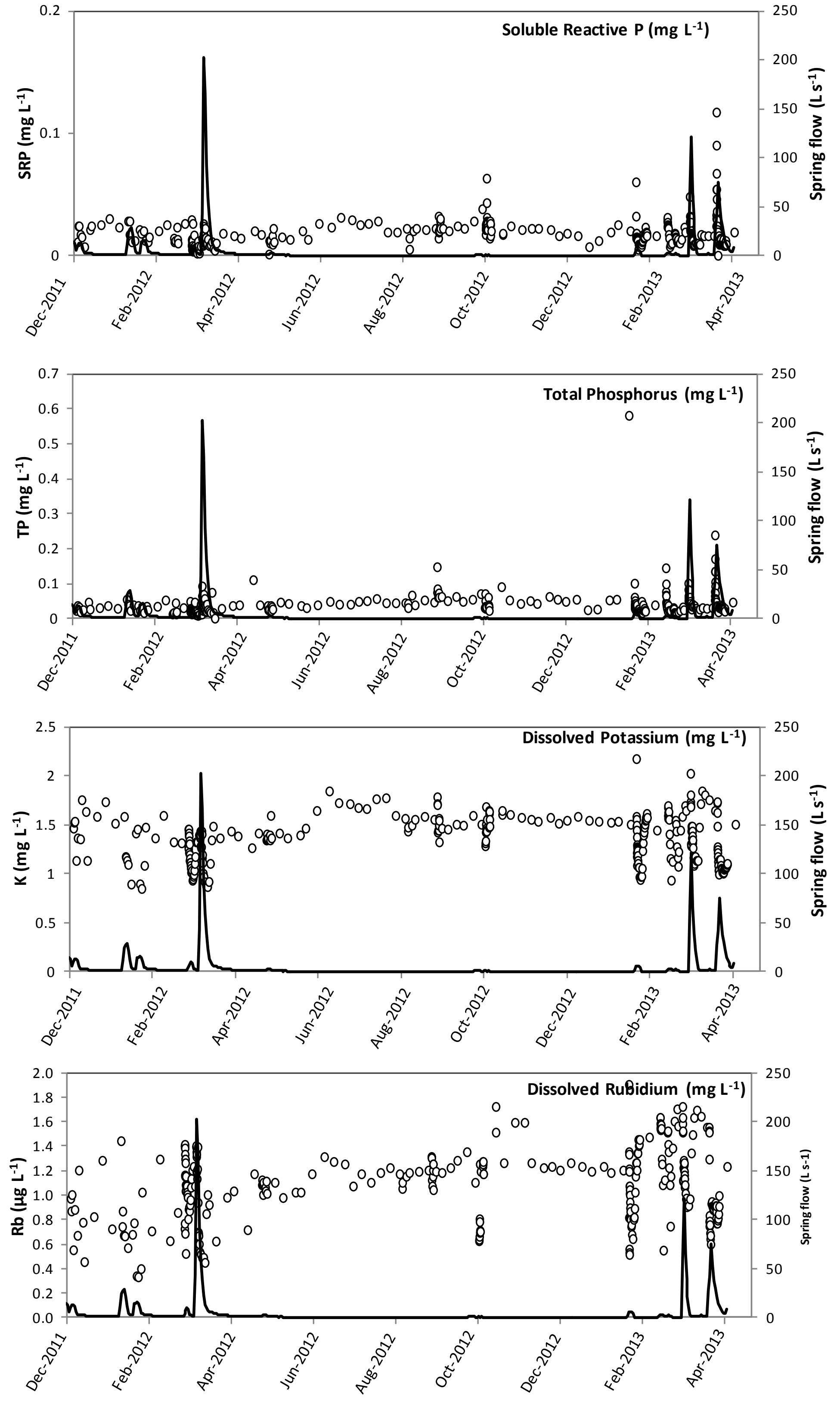

Figure SI-2b Timeseries of flow (solid line) and, soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved potassium (K) and dissolved rubidium (Rb) for Copperhead Spring

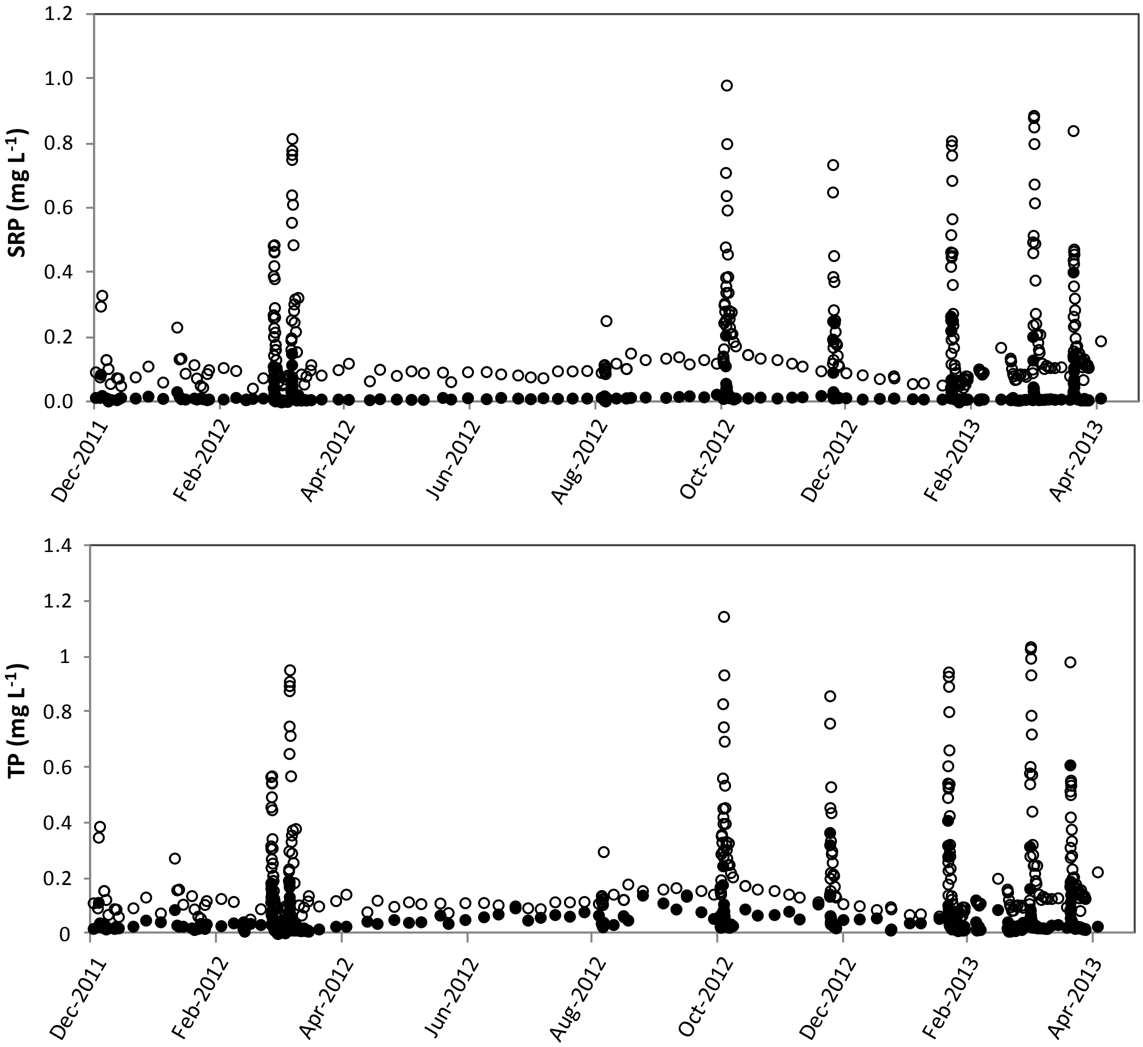

Figure SI-3a Timeseries of measured and 'conservative' soluble reactive phosphorus (SRP) and total phosphorus (TP) concentrations at Langle Spring. Measured P concentrations are denoted by solid circles; 'conservative' P concentrations are denoted by open circles

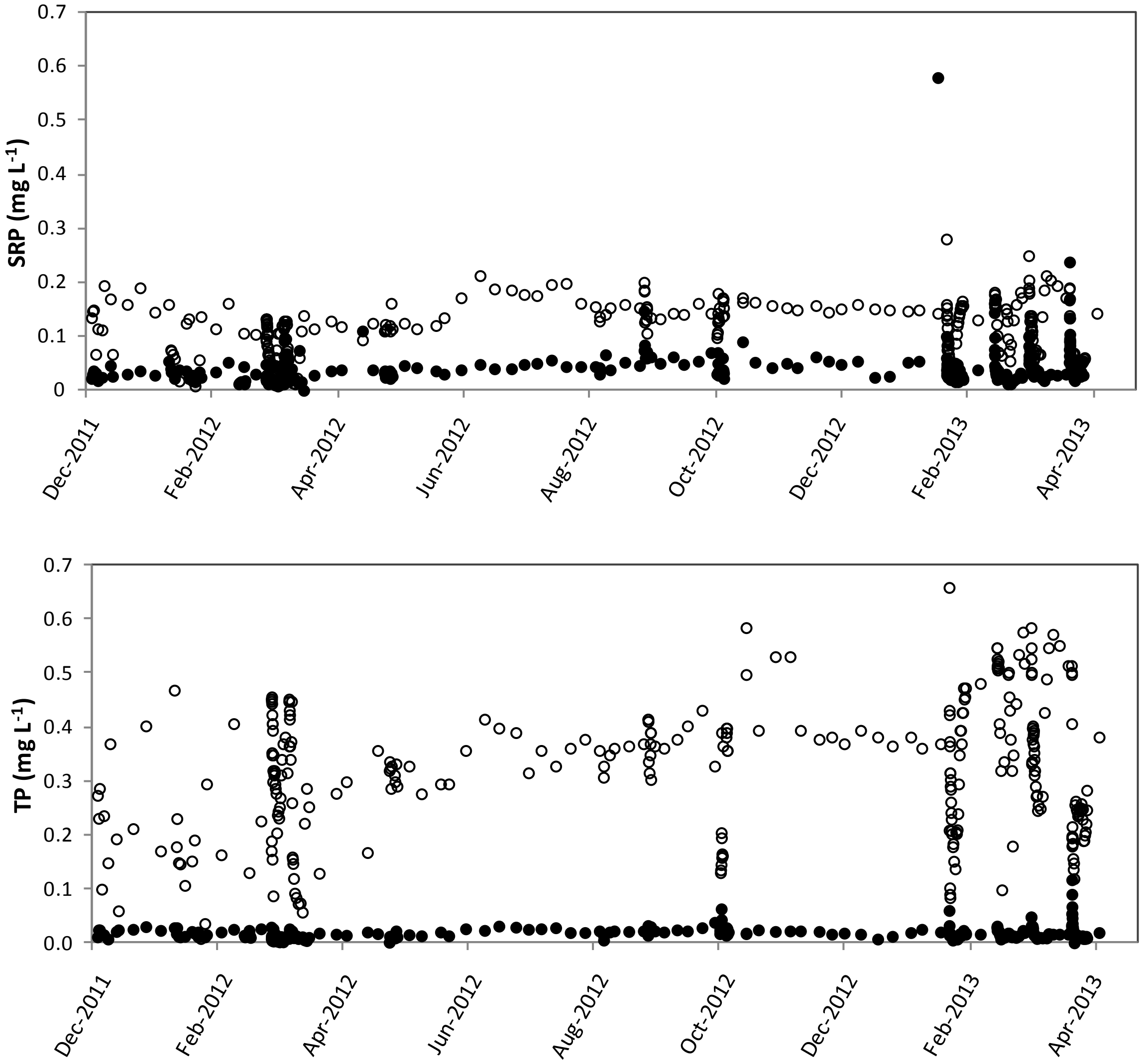

Figure SI-3b Timeseries of measured and 'conservative' soluble reactive phosphorus (SRP) and total phosphorus (TP) concentrations at Copperhead Spring. Measured P concentrations are denoted by solid circles; 'conservative' P concentrations are denoted by open circles.

		Endmember concentrations (mg L^{-1})	
Analyte	**Endmember**	**Langle**	**Copperhead**
Calcium	Ca_{ro}	5.12	3.45
	Ca_{gw}	56.6	61.5
Potassium	K_{ag}	10.4	6.11
	K_{bf}	1.04	1.57
	K_{na}	0.534	0.844
Total P	TP_{ag}	2.57	1.09
	TP_{na}	0.002	0.008
Soluble	SRP_{ag}	2.21	0.68
Reactive P	SRP_{na}	0	0.001

Table SI-1. Concentrations of calcium, potassium, total phosphorus and soluble reactive phosphorus, used to define the endmember concentrations at Langle and Copperhead springs.

Where: Ca_{gw} was the groundwater (high concentration baseflow endmember) concentration, defined here as the average Ca concentration for the lowest 10% of spring-water flows sampled; Ca_{ro} was the stormwater (agricultural runoff) endmember, defined here as the average field runoff Ca concentration; K_{na}, TP_{na} *and* SRP_{na} were the non-agricultural water source (low concentration) endmembers, defined here as the minimum measured spring-water K, TP and DP concentrations; K_{bf} was the baseflow K endmember, i.e., the average K concentration for the lowest 10% of spring-water flows sampled; K_{ag}, TP_{ag} *and* SRP_{ag} were the agricultural runoff endmembers, defined here as the average field runoff K, TP and SRP concentrations.

Soils and Geology of the Savoy Experimental Watershed

The soils of the Savoy Experimental Watershed (SEW) are predominantly Clarksville extremely gravelly silt loam (12 to 60% slopes and 34% of SEW by area); Razort loams and silt loams, which are occasionally flooded by the Illinois River (0 to 3% slopes and 24% of SEW soils by area); and Nixa very gravelly silt loams (3 to 8% slopes and 21% by area).

The stratigraphy of the SEW includes: (a) the limestone aquifer of the St Joe Formation, which is the predominant karst-forming unit with the main conduit flow zone, formed in pure carbonate lithology; (b) the Boone Formation, an impure limestone, with a high clay and chert content (up to 70%) which mantles the St Joe Formation and forms the main lateral perched flow zone or 'epikarst'; and (c) a layer of regolith, which overlies the Boone Formation. The regolith is a non-indurated vadose zone, forming the interface through which diffuse groundwater recharge occurs. Groundwater flow in the SEW is lithologically controlled, with the Chattanooga Formation, a shale, forming the underlying impermeable boundary.

Experimental Methods

1. Monitoring of runoff volume and water sample collection from the CH and LL field plots

Berms were constructed to direct surface runoff to a single collection point, where we installed a 1.5 foot H-fume to continuously measure flow volume and rate. The berms and flumes were positioned such that we captured runoff from 1.05 ha at the Copperhead (CH) site and 1.07 ha at the Langle (LL) site. ISCO automatic water samplers were installed at the CH and LL field plots to collect runoff.

2. Monitoring of spring flow and water sample collection at Langle and Copperhead springs

The primary measurement devices at both springs were compound weirs (Langle: 90° v-notch, 3 ft rectangular; Copperhead: 45° v-notch, 3 ft rectangular) to accommodate a wide range of flow. Level was measured using a pressure transducer and recorded on an ISCO autosampler. Discrete sampling was initiated by a rise in water level, with samples taken at timed intervals that increased over the duration of the storm response. In addition to automated samples, grab samples from storm events were taken when collecting field runoff. Baseflow grab samples were taken weekly and autosampler levels confirmed to ensure accuracy. Samples were processed according to EPA standard protocols and analysed for total phosphorus and soluble reactive phosphorus (see manuscript for details)[3-6]. A full suite of major cations (including potassium, K, and calcium, Ca), were assayed on a filtered water sample, using a Perkin Elmer DV7300 inductively coupled plasma optical emission spectroscopy, together with a wide suite of trace elements (including lanthanum, La, and rubidium, Rb) using Perkin Elmer Elan DRC 11 and Nexion 300D inductively coupled plasma mass spectrometers (ICP-MS).

[1] Leh, M. D.; Chaubey, I.; Murdoch, J.; Brahana, J. V.; Haggard, B. E., Delineating runoff processes and critical runoff source areas in a pasture hillslope of the Ozark Highlands. *Hydrol.Proc.* **2008,** *22*, (21), 4190-4204; DOI 10.1002/hyp.7021.

[2]Ting, T.E.E., Assessing bacterial transport, storage and viability in mantled karst of northwest Arkansas using clay and *Escherichia coli* labeled with lanthanide-series metals: Ph.D. Dissertation, University of Arkansas, 2005.

[3]Kovar J.L., and Pierzynski, G.M. Editors. 2009. Methods for Phosphorus Analysis for Soils, Sediments, Residuals, and Waters. Southern Cooperative Series Bulletin No. 408. http://www.sera17.ext.vt.edu/Documents/P_Methods2ndEdition2009.pdf

[4]Murphy, J.; Riley, J. P., A modified single solution method for the determination of phosphate in natural-waters. *Anal. Chim. Acta* **1962***, 27,* 31–36.

[5]Eisenreich, S.J.; Bannerman, R.T.; Armstrong, D.E. Simplified phosphorus analytical technique. *Environ. Lett.* **1975**, 9 (1), 43-53.

[6]Jarvie H. P.; Withers P. J. A.; Neal C. Review of robust measurement of phosphorus in river water: sampling, storage, fractionation and sensitivity. *Hydrol. Earth Syst.Sci.* **2002**, *6*, 113-131.