

The Role of Field-Scale Management on Soil and Surface Runoff C/N/P Stoichiometry

Douglas R. Smith,* Helen P. Jarvie, R. Daren Harmel, and Rick L. Haney

Abstract

Agricultural runoff is an important contributor to water quality impairment. This study was conducted to evaluate the potential role of field-scale management on carbon (C), nitrogen (N), and phosphorus (P) stoichiometry in soils and runoff from agricultural fields. Cultivated and pasture fields at the Riesel watersheds in central Texas were used for this analysis, and nutrients were transformed to evaluate relative to the Redfield ratio (106 C/16 N/1 P). Using the Redfield ratio, all soil samples were P depleted relative to C and N. The majority of stormflow and baseflow runoff samples contained 9 to 19% Redfield N relative to C and P. Shifting from inorganic fertilizer application to poultry litter as a fertilizer source resulted in increased absolute C, N, and P concentrations in stormflow and baseflow runoff. Increasing rates of poultry litter application increased the Redfield P relative to Redfield C, whereas Redfield N remained relatively constant at roughly 9 to 11% in stormflow runoff from cultivated fields. This study shows how land use and management can affect C/N/P stoichiometry in stormflow and baseflow runoff.

Core Ideas

- The C/N/P stoichiometry in soil and runoff samples from fields was compared.
- Soil samples were P depleted relative to N and C.
- Runoff samples were N depleted relative to P and C.
- Runoff from pastures had lower C and P concentrations than cultivated fields.
- High poultry litter rate increased runoff Redfield P while decreasing Redfield C.

WATER SECURITY is a global concern with increasing pressures as global population increases. One major challenge for water security is eutrophication (Jarvie et al., 2015), as we humans are deeply dependent on water for drinking sources, food (directly [fisheries] or indirectly [irrigation]), and recreation. While our very survival as a species depends on our water resources, human activities (e.g., urbanization or agriculture) may accelerate eutrophication. Agricultural producers must apply nitrogen (N) and phosphorus (P) to crops, as these are two of the macronutrients most limiting agronomic production (Dhital and Raun, 2016; Haegele et al., 2014). Unfortunately, since these fertilizers are applied to soils, which are inherently leaky systems, some losses of these nutrients to streams, rivers, and lakes impair water quality (Jarvie et al., 2017; Smith et al., 2015a; Woodley et al., 2018).

Algae respond to the levels of macronutrients P, N, and carbon (C) in surface waters (Redfield, 1958). When excessive levels of nutrients exist, algal proliferation can lead to hypoxia (Rabalais et al., 2001) or unsafe drinking water (Smith et al., 2015b). The Redfield ratio (106 C/16 N/1 P) is widely used as a reference “optimum” C/N/P ratio in water for primary producers (Redfield, 1958), although it is also recognized that the Redfield ratio does not represent a universal chemical optimum but rather an average of species-specific C/N/P ratios (Kolzau et al., 2014). Recently, land use, particularly in terms of population density or agriculture, in UK rivers and streams has been shown to result in stoichiometric shifts toward greater N and P, which could result in algal blooms (Jarvie et al., 2018). There is less knowledge about how specific agricultural management activities affect C/N/P stoichiometry in field runoff. Most research on the impacts of agricultural field management and water quality focuses on N and/or P concentrations or loads from fields. These are indeed important, but putting them in context of C/N/P stoichiometric ratios will provide useful information about the relative availability of these three macronutrients in runoff sources as they enter receiving waters. The objective of this study was to determine if the C/N/P stoichiometric ratios in runoff water were affected by field-scale agricultural land uses.

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*Corresponding author (douglas.r.smith@usda.gov).

D.R. Smith and R.L. Haney, USDA-ARS, Grassland, Soil and Water Research Lab., Temple, TX 76502; H.P. Jarvie, Centre for Ecology and Hydrology, Wallingford, Oxon OX10 8BB, UK; R.D. Harmel, USDA-ARS, Center for Agricultural Resources Research, 2150 Centre Ave., Ft. Collins, CO 80526. Assigned to Associate Editor Merrin Macrae.

Abbreviations: ICP–OES, inductively coupled plasma optical emission spectrometry; TDC, total dissolved carbon; TDN, total dissolved nitrogen; TDP, total dissolved phosphorus.

Materials and Methods

This study was conducted at the Riesel watersheds, a 430-ha experimental farm and ranch near Riesel, TX, in 2015 (Fig. 1). Six cultivated fields (4–8 ha), four pasture–grassland fields (1–8 ha), and three mixed use watersheds (19–69 ha) that drain multiple fields were monitored for runoff water quantity and quality (Table 1). Cultivated fields were fertilized with either

inorganic fertilizers or poultry litter from 4.5 to 13.5 Mg ha⁻¹. Pasture–grassland fields were unfertilized native grassland, pasture fertilized with inorganic fertilizers, grazed by cattle, or had 13.5 Mg ha⁻¹ poultry litter applied. Mixed-use runoff stations included grazed and cultivated land. Fertility management was constant for ~15 yr prior to this study. Soil samples (eight 0–15 cm deep by 10-cm-diam. soil cores) were collected from cultivated and pasture fields in winter of 2015. Samples were

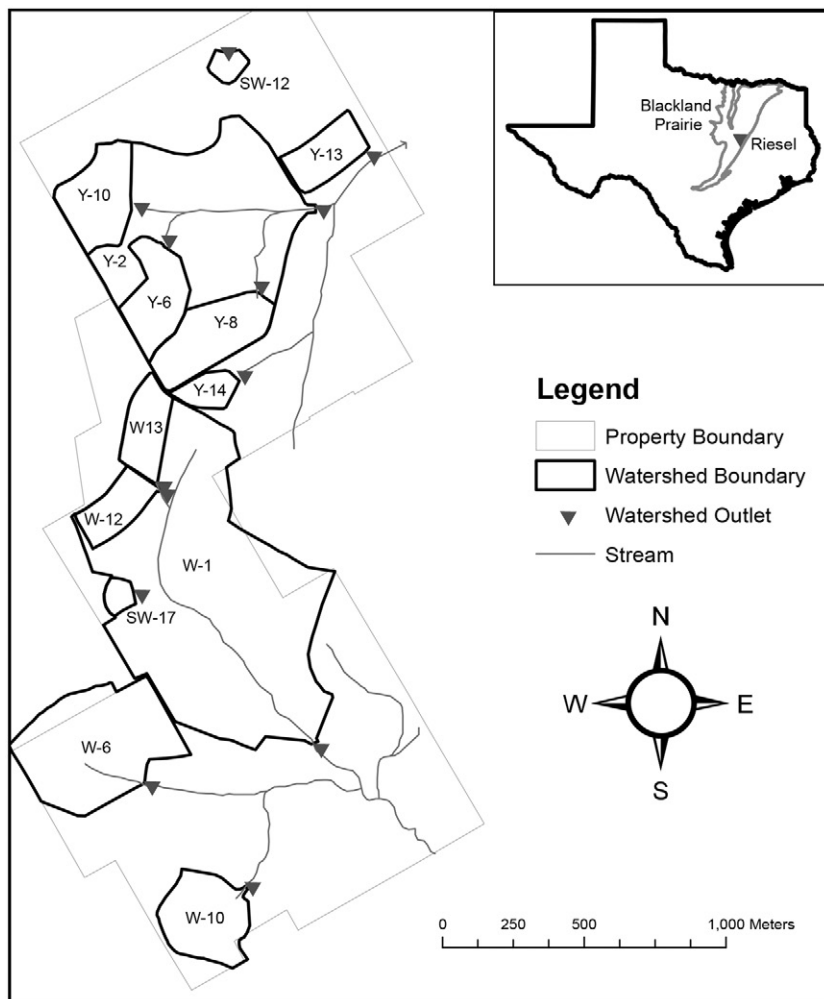


Fig. 1. Map of cultivated, pasture, and downstream and mixed-land-use sites monitored at Riesel, TX, for this study.

Table 1. Description of Riesel watersheds size, land use, and fertility treatments.

Runoff station	Size	Land use	Fertility	Includes nested runoff stations
	ha			
Y6	6.4	Cultivated	Inorganic fertilizer	
Y13	4.5	Cultivated	4.5 Mg ha ⁻¹ poultry litter	
Y10	7.3	Cultivated	6.7 Mg ha ⁻¹ poultry litter	
W12	4.0	Cultivated	9.0 Mg ha ⁻¹ poultry litter	
W13	4.6	Cultivated	11.2 Mg ha ⁻¹ poultry litter	
Y8	8.2	Cultivated	13.5 Mg ha ⁻¹ poultry litter	
SW12	1.2	Native Prairie	Unfertilized	
SW17	1.1	Pasture–hay	Mixed litter + inorganic	
W10	8.2	Pasture–grazed	Cattle grazing	
Y14	2.2	Pasture–hay	13.5 Mg ha ⁻¹ poultry litter	
Y2	52.7	Mixed	Mixed	Y6, Y8, Y10
W1	68.9	Mixed	Mixed	W12, W13, SW17
W6	19.1	Mixed	Mixed	No nested monitoring stations

dried at 60°C and ground to pass a 2-mm sieve. A 3-g soil sample was extracted with 30 mL of deionized water and analyzed for total dissolved C (TDC) and total dissolved N (TDN) using an Apollo C/N analyzer (Teledyne Tekmar). Another aliquot of this sample was analyzed via inductively coupled plasma optical emission spectrometry (ICP–OES) for total dissolved P (TDP).

Water quality samples were collected from each runoff event in 2015 using flow-paced sampling with ISCO Avalanche automated samplers using methods described in Harmel et al. (2006a, 2006b). Storm runoff samples were removed from the autosampler within 24 h of collection and taken to a laboratory onsite for preliminary processing. Baseflow water quality samples were collected manually from all sites at the end of storm events and each subsequent week as long as flow persisted. Samples were allowed to settle for 24 h and an aliquot was decanted for analysis, which was transported to the analytical laboratory in Temple, TX. Runoff TDC and TDN were analyzed on an Apollo C/N analyzer (Teledyne Tekmar). Runoff TDP was analyzed using ICP–OES.

To estimate the stoichiometric ratios, data were converted to a Redfield ratio C/N/P basis (see Smith et al., 2017). This was done by multiplying the molar concentration of TDN by 6.625 and TDP by 106. To plot the data, the Redfield ratio concentrations were summed, then each constituent was divided by the Redfield sum. Thus, ternary plots were created, whereby the sum of TDC, TDN, and TDP equal 100 for each sample.

Results and Discussion

Soils

In both cultivated and pasture soils, there was very little variation in soil Redfield stoichiometry, which was typically low in P relative to C and N (i.e., <20% Redfield P; Fig. 2). In cultivated soils, the primary shift was in the Redfield P percentages from <5% Redfield P in the Y6 inorganic fertilized field to >10% P in fields fertilized with poultry litter. The highest rates of poultry litter (9 [W12] and 13 Mg ha⁻¹ [Y8]) averaged about 20 and 19% Redfield P, respectively. Most of the soil samples from pasture fields (Fig. 2B) were below 5% Redfield P. Although all the soil samples clustered between 30 and 36% Redfield N, the primary shift resulted from poultry litter application to Y14, which increased Redfield P to ~9%.

It is unsurprising that C dominates these soils. These soils have 2 to 4% organic matter and are derived from limestone deposits (Templin et al., 1956). Thus, there is a tremendous amount of both organic and inorganic C available in the soils. The pastures, with their perennial grass cover, tend to have greater organic matter than the cultivated fields, resulting in all pasture soils having >55% Redfield C.

Land use has been shown to have a significant effect on soil C/N/P stoichiometry, even exhibiting “Redfield-like” ratios (Fazhu et al., 2015). Other studies have shown that land use has little impact on soil nutrient stoichiometry (Alvarez et al., 2018). Frossard et al. (2016) suggested that fertilizers applied to soils had little impact on C/N/P ratios, and that soil properties were generally of greater importance. Since the current study was restricted to one soil type, we could not test the role of inherent soil properties. Tillage and inorganic fertilizers have been

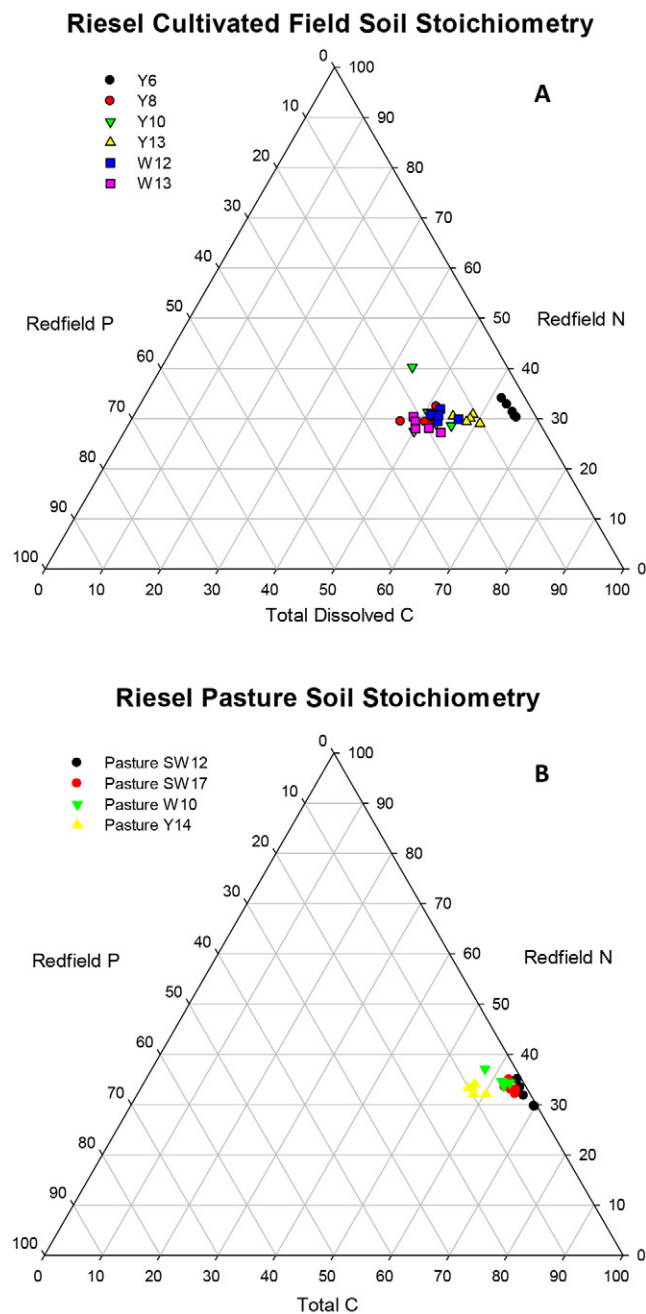


Fig. 2. Soil Redfield C/N/P stoichiometry for (A) cultivated and (B) pasture fields at Riesel, TX.

shown to decrease soil C levels (Khan et al., 2007; Poirier et al., 2009). However, we were able to determine shifts in soil nutrient stoichiometry with management. Whereas pasture soils were dominated by C and N (Fig. 2), there was a shift in soil nutrient stoichiometry from C- and N-dominated cultivated soils fertilized with inorganic fertilizers, toward the central Redfield zone with increasing poultry litter application rates that was associated with an increase in the relative Redfield P levels.

Runoff and Lateral Baseflow

Fields Y8 and W13 (which received the highest poultry litter application rates) resulted in the greatest concentrations of TDC, TDN, and TDP (56, 3.2, and 2.1 mg L⁻¹ and 45, 2.4, and 2.1 mg L⁻¹, respectively) in runoff compared with the other cultivated fields (Table 2), whereas Y6 resulted in the lowest concentrations

(29, 1.1, and 0.2 mg L⁻¹, respectively). Application of poultry litter to cultivated fields at all rates significantly increased the concentration of total dissolved P compared with the inorganic fertilizer applications. Only the 6.7-Mg ha⁻¹ poultry litter application rate (Y10) was not significantly different from the inorganic fertilized field (Y6) for TDC, whereas the 4.5- (Y13) and 6.7-Mg ha⁻¹ poultry litter rates were similar to the inorganic fertilized field for TDN concentration.

Although the soils were lower in P relative to C and N, almost all storm runoff samples showed N depletion relative to C and P along a relatively narrow range of Redfield N. The major transition occurred along an axis of increasing Redfield P and decreasing Redfield C (Fig. 3A). Nearly all the data points for stormflow runoff from cultivated fields were around 5 to 20% Redfield N, with the only exception being one value from Y6 (inorganic fertilizer) with 38% Redfield N. This would indicate that the primary shift in Redfield stoichiometric relationships was centered around C/P ratios. The inorganic fertilizer treatment (Y6) resulted in the lowest Redfield P and the highest Redfield C percentages in runoff (Table 2). The low poultry litter application rate (4.5 Mg ha⁻¹, Y13) produced the highest Redfield C percentage and the lowest Redfield P percentage of the poultry litter application treatments. Generally, as the poultry litter application rate increased, Redfield C decreased and Redfield P increased.

Taking into account the importance of P in the Redfield ratio (weighted 106 times for each C and 16 times for each N), this implies that the rate of increase in P concentrations far exceeds the corresponding Redfield ratio increases in N or C. Indeed, the P concentration increased roughly 800% between the inorganic fertilized field (Y6) and the highest rate of poultry litter (Y8), whereas C increased by roughly 100% and N increased by 180% from Y8 compared with Y6 (Table 2). Poultry litter applications have been shown to increase P losses while decreasing N losses relative to commercial fertilizer applications from fields (Harmel et al., 2009).

There were consistent patterns between baseflow and stormflow runoff stoichiometry for both cultivated fields and pasture fields. Baseflow Redfield C/N/P stoichiometric ratios also tended to be centered ~10% Redfield N (Fig. 3B). As with the stormflow samples, Y6 (inorganic fertilizer) resulted in the greatest Redfield C percentages in baseflow samples. Poultry litter applications tended to increase Redfield P at the expense of decreasing Redfield C in baseflow samples. In contrast with consistent results between stormflow and baseflow stoichiometry reported here, extremes in flow in an agricultural drainage ditch, within the western Lake Erie drainage basin, shifted from either relative N or P depletion at baseflow toward the central Redfield zone at high flow (Smith and Jarvie, 2018).

Stormflow runoff from pasture fields also exhibited relatively static Redfield N (Fig. 4A). The native pasture SW12 field tended to be dominated by TDC loss, accounting for >70% of the Redfield stoichiometric losses in all but three samples. Field SW17 is a hay pasture and tended to have more TDC than Redfield P. The highest Redfield P ratios from this land use were from Y14, which received high rates of poultry litter (13.5 Mg ha⁻¹). Poultry litter has been shown to increase P loss from pastures (Smith et al., 2004). The grazed pasture W10 ranged from about 19 to 75% Redfield P. As with runoff from cultivated fields, runoff from these grasslands was generally N depleted relative to C and P.

Sites larger than a single field also tended to have <30% Redfield N (Fig. 4B). The mixed-use site (W6), which aggregates runoff from a cultivated field, a small-grains (oat [*Avena sativa* L.]) grazed pasture and a grass-grazed pasture tended to have higher Redfield TDC than the other two aggregate sites. Site Y2 aggregates runoff from cultivated fields Y10, Y6, and Y8, whereas site W1 aggregates runoff from cultivated fields W12, W13, and SW17. The stoichiometric signatures of aggregated sites tended to be similar.

Table 2. Total dissolved C (TDC), total dissolved N (TDN), and total dissolved P (TDP) concentrations, as well as relative Redfield ternary C, N, and P contributions in runoff for cultivated, pasture, and downstream sites at Riesel, TX. Different letters within a column for a group of sites (cultivated, pasture, or downstream) indicates significant differences at $P < 0.05$.

Field	TDC	TDN	TDP	Ternary C	Ternary N	Ternary P
	mg L ⁻¹			%		
Cultivated fields						
Y6	28.9c	1.12c	0.223d	67.2a	13.3a	19.5d
Y13	44.3b	1.78bc	0.972c	44.9b	10.5b	44.6c
Y10	39.3bc	1.54bc	1.27bc	39.2bc	8.7b	52.1ab
W12	45.9ab	2.17b	1.54b	39.2bc	9.9b	50.9bc
W13	45.2ab	2.38ab	2.09a	31.3d	9.2b	59.5a
Y8	56.2a	3.16a	2.08a	35.4cd	10.8ab	53.8ab
P	<0.001	<0.001	<0.001	<0.001	<0.05	<0.001
Pasture fields						
SW12	36.5a	0.92	0.139d	74.8a	11.4	13.8d
SW17	23.7b	3.34	0.378c	52.3b	19.0	28.7c
W10	29.5ab	1.33	0.632b	48.3b	11.6	40.1b
Y14	23.7b	3.34	0.969a	34.6c	14.9	50.5a
P	<0.01	0.405	<0.001	<0.001	0.19	<0.001
Downstream and mixed-land-use sites						
Y2	40.0	1.77	0.740a	47.1b	12.1	40.8a
W1	35.3	1.92	0.780a	65.5a	16.2	18.3b
W6	35.1	1.47	0.229b	49.7b	12.4	37.9a
P	0.45	0.693	<0.001	<0.001	<0.1	<0.001

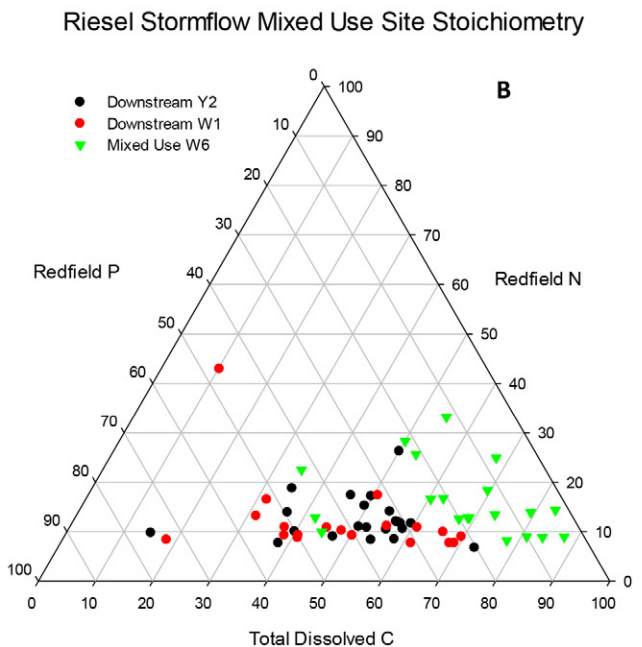
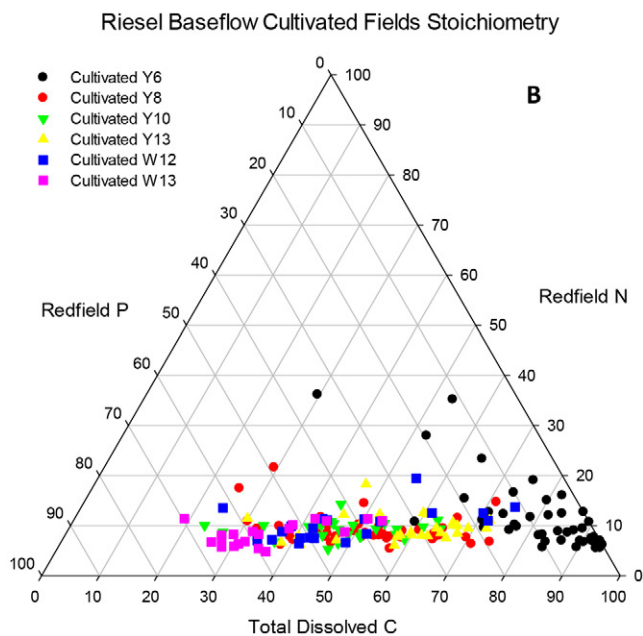
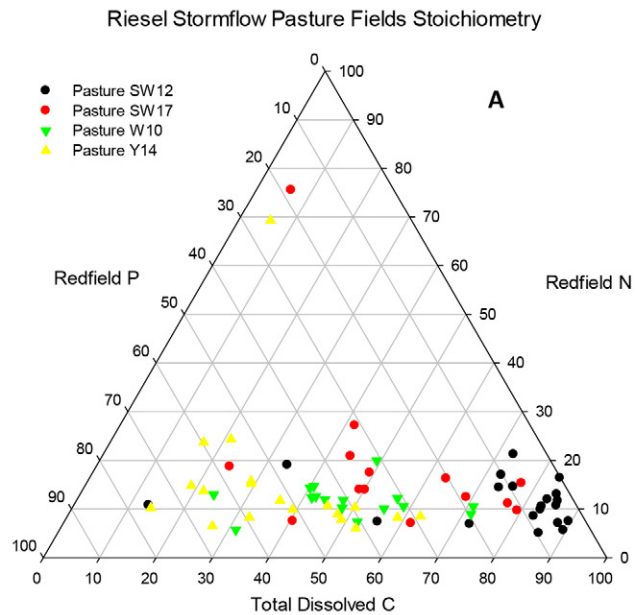
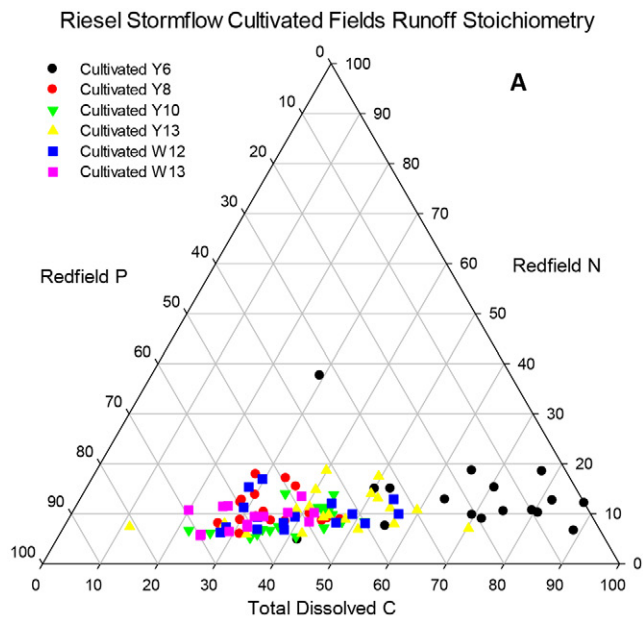


Fig. 3. Redfield C/N/P stoichiometry in (A) stormflow runoff and (B) baseflow runoff from cultivated fields at Riesel, TX.

Fig. 4. Stormflow Redfield stoichiometry in runoff from (A) pasture and (B) downstream and mixed-use ephemeral sites.

Runoff and baseflow from fields and small watersheds in this study appear to be N depleted relative to C and P based on the stoichiometric ratios. In rivers of the Thames catchment in the United Kingdom, it was observed that algal growth appeared to be limited when P accounted for <13% of the relative Redfield ratio (Smith et al., 2017). Although the climatic, hydrological, and biogeochemical setting of this study is different from the Thames catchment in the United Kingdom, it is apparent that both organic and inorganic C levels are sufficiently high in runoff from fields and streams that C depletion is unlikely (Jarvie et al., 2018).

Conclusions

This is one of the first studies to examine the role of agricultural management on the macronutrient stoichiometry of soils and runoff water quality at the field scale. When examining soil

stoichiometry using the Redfield ratio, which was developed for algal uptake in aquatic systems, these management systems seemed to indicate P depletion relative to C and N, although high rates of poultry litter applied to cultivated fields shifted these ratios toward the Redfield ratio. The stoichiometry of soil appeared to have little impact on runoff (stormflow or baseflow) stoichiometry. Runoff water from both stormflow and baseflow conditions indicated N depletion relative to C and P. Runoff from the native prairie was sufficiently enriched with TDC to result in relative Redfield N and P codepletion. For cultivated fields, nutrient concentrations increased with rate of poultry litter application; however, the weighting of P relative to C and N resulted in large increases in Redfield P and decreases in C relative to N, which remained static near 10% Redfield N. Stormflow runoff from grasslands also resulted in large shifts in the C and P relative to N. Poultry litter

applications had relatively little impact on soil stoichiometry but resulted in large changes in runoff stoichiometry shifts owing to increased TDP losses relative to TDC or TDN.

Conflict of Interest

The authors declare no conflict of interest.

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References

- Alvarez, R., A. Gimenez, M.M. Caffaro, F. Pagnamini, V. Recondo, C.D. Molina, et al. 2018. Land use affected nutrient mass with minor impact on stoichiometry ratios in Pampean soils. *Nutr. Cycl. Agroecosyst.* 110:257–276. doi:10.1007/s10705-017-9896-0
- Dhital, S., and W.R. Raun. 2016. Variability in optimum N rates for maize. *Agron. J.* 108:2165–2173. doi:10.2134/agronj2016.03.0139
- Fazhu, Z., S. Jiao, R. Chengjie, K. Di, D. Jian, H. Xinhui, et al. 2015. Land use change influences soil C, N and P stoichiometry under 'Grain-to-Green Program' in China. *Sci. Rep.* 5:10195. doi:10.1038/srep10195
- Frossard, E., N. Buchmann, E.K. Bunemann, D.I. Kiba, F. Lompo, A. Oberson, et al. 2016. Soil properties and not inputs control carbon/nitrogen/phosphorus ratios in cropped soils in the long term. *SOIL* 2:83–99. doi:10.5194/soil-2-83-2016
- Haegel, J.W., R.J. Becker, A.S. Henninger, and F.E. Below. 2014. Row arrangement, phosphorus fertility, and hybrid contributions to managing increased plant density of maize. *Agron. J.* 106:1838–1846. doi:10.2134/agronj2013.0382
- Harmel, R.D., R.J. Cooper, R.M. Slade, R.L. Haney, and J.G. Arnold. 2006a. Cumulative uncertainty in measured streamflow and water quality data for small watersheds. *Trans. ASABE* 49:689–701. doi:10.13031/2013.20488
- Harmel, R.D., K.W. King, B.E. Haggard, D.G. Wren, and J.M. Sheridan. 2006b. Practical guidance for discharge and water quality data collection on small watersheds. *Trans. ASABE* 49:937–948. doi:10.13031/2013.21745
- Harmel, R.D., D.R. Smith, R.L. Haney, and M.C. Dozier. 2009. Nitrogen and phosphorus runoff from cropland and pasture fields fertilized with poultry litter. *J. Soil Water Conserv.* 64:400–412. doi:10.2489/jswc.64.6.400
- Jarvie, H.P., L. Johnson, A.N. Sharpley, D.R. Smith, D. Baker, T. Bruulsema, and R. Confessor. 2017. Increased soluble phosphorus loads to Lake Erie: Unintended consequences of conservation practices? *J. Environ. Qual.* 46:123–132. doi:10.2134/jeq2016.07.0248
- Jarvie, H.P., A.N. Sharpley, D. Flaten, P.J.A. Kleinman, A. Jenkins, and T. Simmons. 2015. The pivotal role of P in a resilient water–energy–food security nexus. *J. Environ. Qual.* 44:1049–1062. doi:10.2134/jeq2015.01.0030
- Jarvie, H.P., D.R. Smith, L. Norton, F. Edwards, M. Bowes, S.M. King, et al. 2018. Phosphorus and nitrogen limitation and impairment of headwater streams relative to rivers: A national perspective for Great Britain. *Sci. Total Environ.* 621:849–862. doi:10.1016/j.scitotenv.2017.11.128
- Khan, S.A., R.L. Mulvaney, T.R. Ellsworth, and C.W. Boast. 2007. The myth of nitrogen fertilization for soil carbon sequestration. *J. Environ. Qual.* 36:1821–1832. doi:10.2134/jeq2007.0099
- Kolzau, S., C. Wiedner, J. Rucker, J. Kohler, A. Kohler, and A.M. Dolman. 2014. Seasonal patterns of nitrogen and phosphorus limitation in four German lakes and the predictability of limitation status from ambient nutrient concentrations. *PLoS One* 9:e96065. doi:10.1371/journal.pone.0096065
- Poirier, V., D.A. Angers, P. Rochette, M.H. Chantigny, N. Ziadi, G. Tremblay, and J. Fortin. 2009. Interactive effects of tillage and mineral fertilization on soil carbon profiles. *Soil Sci. Soc. Am. J.* 73:255–261. doi:10.2136/sssaj2008.0006
- Rabalais, N.N., R.E. Turner, and W.J. Wiseman. 2001. Hypoxia in the Gulf of Mexico. *J. Environ. Qual.* 30:320–329. doi:10.2134/jeq2001.302320x
- Redfield, A.C. 1958. The biological control of chemical factors in the environment. *Am. Sci.* 46:205–221.
- Smith, D.R., W. Francesconi, S.J. Livingston, and C. Huang. 2015a. Phosphorus loss from monitored fields with conservation practices in the Lake Erie Basin, USA. *Ambio* 44:S319–S331. doi:10.1007/s13280-014-0624-6
- Smith, D.R., and H.P. Jarvie. 2018. Carbon, nitrogen, and phosphorus stoichiometric response to hydrologic extremes in a tributary to Lake Erie, USA. *Agric. Environ. Lett.* 3:180043. doi:10.2134/aer2018.08.0043
- Smith, D.R., H.P. Jarvie, and M.J. Bowes. 2017. Carbon, nitrogen and phosphorus stoichiometry in River Thames tributaries, UK. *Agric. Environ. Lett.* 2:170020. doi:10.2134/aer2017.06.0020
- Smith, D.R., K.W. King, and M.R. Williams. 2015b. What is causing the harmful algal blooms in Lake Erie? *J. Soil Water Conserv.* 70:27A–29A. doi:10.2489/jswc.70.2.27A
- Smith, D.R., P.A. Moore, Jr., D.M. Miles, B.E. Haggard, and T.C. Daniel. 2004. Decreasing phosphorus runoff losses from land-applied poultry litter with dietary modifications and alum additions. *J. Environ. Qual.* 33:2210–2216. doi:10.2134/jeq2004.2210
- Templin, E.H., I.C. Mowery, and G.W. Kunze. 1956. Houston Black clay, the type Grumusol: 1. Field morphology and geography. *Soil Sci. Soc. Am. J.* 20:88–90. doi:10.2136/sssaj1956.03615995002000010022x
- Woodley, A.L., C.F. Drury, W.D. Reynolds, C.S. Tan, X.M. Yang, and T.O. Oloya. 2018. Long-term cropping effects on partitioning of water flow and nitrate loss between surface runoff and tile drainage. *J. Environ. Qual.* 47:820–829. doi:10.2134/jeq2017.07.0292