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Relative role of transport and source-limited controls for estrogen, TDP, and DOC export for two manure application methods

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ABSTRACT

Developing successful mitigation strategies for emerging contaminants can be difficult due to incomplete understanding of factors controlling their fate and transport. A variety of data analysis techniques can be used to assess the fate and transport behavior of pollutants in runoff water. Here, we use concentration-discharge, load-discharge, and coefficient of variation relationships to examine how two methods of dairy manure application (surface broadcast and shallow disk injection) affect the transport dynamics of estrogens, total dissolved phosphorus (TDP), and dissolved organic carbon (DOC). Nine surface runoff events were sampled from Oct 2014–June 2015 from 12 research plots (six with each application method) in Central Pennsylvania after fall application. The plots received inorganic fertilizer for 15 years, but only four manure applications since 2012. Both TDP and DOC exhibited similar transport behavior under both manure application methods that indicate transport-limited control of export, potentially due to legacy sources in soils. However, estrogen loads exhibited dilution responses, a sign of source-limited controls. The strength of the dilution response for estrogens was greater for surface applied manure relative to the injected manure, suggesting that manure application methods can be used to control the mobilization potential of estrogens. Additionally, results suggest the longer-term application history of inorganic fertilizer led to the transport-limited dynamics exhibited by TDP, while the short-term application history of manure caused estrogen transport to be source-limited. Our findings provide insight into how anthropogenic drivers (application type, method, and history) and natural drivers (hydrology, biogeochemistry) are interconnected in agricultural fields, and point to opportunities for protecting downstream water quality.

1. Introduction

The application of livestock manure to agricultural fields provides essential nutrients for crops and adds organic matter to soils. However, manure also introduces emerging contaminants to the environment, including the natural estrogens 17α-estradiol (17α-E2), 17β-estradiol (17β-E2), estrone (E1), and estriol (E3) (Hanselman et al., 2003; Kolodziej et al., 2004; Soto et al., 2004; Gall et al., 2011; Mansell et al., 2011; Shappell et al., 2016). Many factors influence the fate and transport of manure-borne constituents, including the type of manure applied, the rate and timing of application, the method and history of application, as well as natural drivers such as hydrologic processes and biogeochemical cycling.

In the Northeastern United States (U.S.), manure management is an area of active research, outreach, and extension. Adoption of manure injection remains relatively uncommon due to equipment costs and unfavorable soil characteristics (Duo et al., 2001; Johnson et al., 2011). On small dairy farms typical of the mid-Atlantic U.S., manure is most frequently applied in the spring and fall, but manure application may occur year round. Winter manure application regulations are inconsistent across states, ranging from complete bans during winter months for some states to restrictions based upon site conditions. Manure is generally applied to corn crops, although other crops also receive manure, including legumes. In Europe, slurry application is recommended in the spring, but fall application also occurs, especially if soil structure, costs, or time are a concern to the farmer (Berisso et al., 2012; de Toro and Hanson, 2004). There is variability for the closed periods of manure application across Europe; however, with few exceptions, the manure application period is closed between mid-November and the end of January, with many European countries also having closed periods in September, October, and early February (Webb et al., 2013).

The method of animal manure application can influence the availability of nutrients and estrogens to runoff water. Several studies have

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shown the potential benefits of shallow disk injection for reducing phosphorus and nitrate transport in surface runoff compared to surface broadcasting (Daverede et al., 2004; Maguire et al., 2011). Additionally, Mina et al. (2016) found significantly reduced estrogen transport in runoff from shallow disk injection plots relative to surface broadcast plots. However, the extent to which the dominant factors that control nutrients and hormones differ between application methods have not yet been explored.

When manure is applied to agricultural fields at rates sufficient to meet crop nitrogen (N) demand, the amount of phosphorus (P) in manure is typically much greater than the amounts taken up by crops. Excess P increases the risk of P loss from fields, which can lead to accelerated eutrophication of receiving water bodies. Dairy manure in the United States, Europe, Canada, and Japan has an N:P ratio of approximately 5.6:1–5.8:1 (Kleinman et al., 2005; Bouwman et al., 2017), approximately 7:1 in Australia (Gourley et al., 2011), and 4.4:1 in China (Chen et al., 2008), while most row crops require a higher N:P ratio (e.g., 8:1; Pote et al., 2011).

Application of manure also increases the presence of dissolved organic carbon (DOC), thus increasing DOC transport in surface runoff (Royer et al., 2007; Veum et al., 2009). While the DOC present in soil represents a small fraction of the total organic carbon pool, it is the most mobile fraction (Leenheer and Croue, 2003; Veum et al., 2009). DOC is known to facilitate transport of other pollutants, such as estrogens and pesticides, due to reduced sorption and mineralization in soils and sediments with higher DOC content (Briceno et al., 2008; Delgado-Moreno et al., 2010; Stumpe and Marschner, 2009; Dutta et al., 2012). Therefore, manure application methods that lead to increased presence of DOC in runoff may lead to increased transport of endocrine disrupting compounds and emerging contaminants.

Few studies compare transport dynamics of estrogens to the dynamics of more commonly measured water quality parameters. Shappell et al. (2016) evaluated estrogenic activity along with Ca^{2+} and Mg^{2+} transport following winter turkey and swine manure applications and found strong correlations between estradiol equivalence and nutrient concentrations in surface runoff. Gall et al. (2015) compared nutrient (nitrate and phosphate) behavior to estrogen fate and transport and found no strong relationships between estrogen and nutrient concentrations; however, hydrologic variability was identified as the dominant controlling factor for both estrogen and nutrient loads. In the research conducted by Shappell et al. (2016), manure applications had occurred for only three years, whereas applications in the Gall et al. (2015) study had occurred for nearly two decades. Differences between the results in these studies suggest that application frequency and history (i.e., number of years over which applications occurred) may influence the relationship between nutrient and estrogen export.

Since estrogen analysis is time-intensive and expensive, identifying relationships or similar transport mechanisms with routinely analyzed constituents has the potential to accelerate understanding of estrogen fate and transport. However, as previous research suggests, these relationships may be a function of manure type, application method, and the application history of the field. If a field has been under decades of agricultural management, studies have shown that nutrients exhibit low to moderate variability in their concentrations in discharge across scales as small as field tile drains and as large as the Mississippi River and Baltic Sea basins, with higher variability observed in forested landscapes (Basu et al., 2010, 2011; Guan et al., 2011; Thompson et al., 2011; Gall et al., 2013, 2015). The relatively low concentration variability may reflect a prevalence of “legacy sources” of nutrients that are able to buffer the natural biogeochemical variability observed in non-agricultural systems (Basu et al., 2010, 2011; Guan et al., 2011; Thompson et al., 2011). In the case of estrogens, low variability in runoff concentrations has been observed (Gall et al., 2015) and modeled (Gall et al., 2016) in an agroecosystem that received long-term (multi-decade) manure applications, with legacy sources of estrogens arising due to the long-term, repeated, and frequent applications of animal residuals.

Concentration-discharge (*C*-*Q*) and load-discharge (*L*-*Q*) relationships are often employed to better understand solute export dynamics and to classify the observed dynamics as source-limited or transport-limited. Concentration is often expressed as a function of flowrate using a power-law relationship, $C = aQ^b$, where a and b are empirical parameters (Anderson et al., 1997; Basu et al., 2010; Haygarth et al., 2004; Herndon et al., 2015; Vogel et al., 2005). Broadly, *C*-*Q* responses are generally classified as: (1) an accretion pattern, in which there is a positive relationship ($b > 0$) between solute concentrations and flowrates; (2) a dilution pattern, in which concentrations decrease ($b < 0$) with increasing flowrates; or (3) a chemostatic pattern, in which concentrations remain relatively constant ($b \approx 0$) across all ranges of flowrates. The results of such an analysis can be helpful in understanding the potential impact on sensitive aquatic organisms in receiving water bodies. For example, a chemostatic response would suggest that concentrations discharged from a field have low variability over the range of runoff rates and implies that exposure would be relatively consistent (i.e., chronic). Both an accretion and dilution response would be associated with acute exposure, as concentrations would vary widely over ranges of runoff rates. Given that most ecotoxicological studies have been conducted using acute exposure, the effects of chronic exposure to low-levels of endocrine disrupting compounds, such as estrogens, are not yet well understood (Christen et al., 2010; Vestel et al., 2016).

The overall goal of this study was to compare the transport behavior of estrogens, total dissolved phosphorus (TDP), and DOC in surface runoff to evaluate how the behavior changes as a function of dairy manure application method (surface broadcast vs. shallow disk injection). We used several metrics, including *C*-*Q* relationships, *L*-*Q* relationships, and a coefficient of variation ratio between concentration and discharge(CV_C/CV_Q) to classify the transport dynamics of estrogens, TDP, and DOC as transport or source-limited. A field study was conducted in Central Pennsylvania, United States, on a site that had received inorganic fertilizer from 1999 to 2012, and only four applications of dairy manure from 2012 to 2014. We used the results to understand the influence of site history and manure application methods on the export dynamics of estrogens, TDP, and DOC, and the important implications on the health of downstream aquatic ecosystems.

2. Materials and methods

2.1. Study site description and experimental design

This research took place at the Kepler Farm plots (Fig. 1), which are located at the Russell E. Larson Agricultural Research Center in Rock Springs, Pennsylvania near The Pennsylvania State University’s main campus. The site consists of 12 hydrologically isolated plots (27 m wide x 15 m long), with slopes that range from 7 to 15%. The dominant soil types are Hagerstown silt loam (fine, mixed, semiactive, mesic Typic Hapludalf) and Opequon silty clay loam (clayey, mixed, active, mesic Lithic Hapludaulf).

Surface runoff from each plot is collected via drains placed just upslope of an earthen berm along the bottom edge of each plot, and routed downslope through PVC pipes to huts near the plots (Fig. 1). The huts are equipped with tipping buckets that measure the surface runoff flowrate. The number of tips is recorded by a Campbell Scientific datalogger at five-minute intervals. Rainfall depths are also measured with a tipping bucket rain gauge at five-minute intervals (see **Table S1** for data).

All 12 plots were amended with dairy manure slurry on 2 October 2014, one week after corn was harvested. The manure was applied at a rate of approximately 55 Mg ha^{-1} (wet weight), providing a dry weight of 172 kg-N ha^{-1}, 29.5 kg-P ha^{-1}, and 145 kg-K ha^{-1}, based on the content of total N, total P, and total K in the manure slurry (Table 1). Six plots (2, 4, 5, 6, 9 and 11) received dairy manure via surface