READERS' FORUM

Commentary on "A possible trade-off between clean air and clean water" by Smith et al. (2017)

Wayne Robarge, Owen Duckworth, Deanna Osmond, Jot Smyth, and Mark River

uthors of the recent feature article by Smith et al., which was published in the A Section of the July/August 2017 issue of the Journal of Soil and Water Conservation (A Section articles are not peerreviewed while articles in the Research Section of the journal are peer-reviewed), have conducted water quality research in the Western Lake Erie Basin (WLEB) and demonstrated multiple potential causes of increased soluble phosphorous (SP) loading, including agricultural practice changes such as increased no-till, tile drainage, surface application of fall fertilizer, and weather. In their article, "A possible tradeoff between clean air and clean water," these authors propose an additional cause: the connection between the success of the Clean Air Act in improving air quality in the United States and increases in SP loading that have contributed to harmful algal blooms in the WLEB. Although we agree that scientists must always be vigilant for pernicious consequences of well-meaning actions, we believe that there are flaws in the study design and data interpretation that undermine the conclusion of article. Specifically, what we see as flaws in the interpretation of the data presented in table 1 and figures 2 and 3 are described below. Furthermore, the authors do not provide mechanisms for their observations, and their conjecture for the need for more similar studies avoids the obvious trends in rising carbon dioxide (CO₂) levels in the atmosphere and the increasing intensity in rainfall events as predicted as a consequence of impacts on climate from a failure to control CO2 emissions (Sinha et al. 2017). Mechanisms for enhancing phosphate (PO₄³⁻) mobility from agricultural soils and surrounding surface water bod-

Wayne Robarge is a professor, Owen Duckworth is an associate professor, Deanna Osmond is a professor, and Jot Smyth is a professor in the Department of Soil Sciences, North Carolina State University, Raleigh, North Carolina. Mark River is a PhD candidate in the Nicholas School of the Environment, Duke University, Durham, North Carolina.

ies as a result of intensity of rain events are well documented. Additionally, and specific to WLEB as well as other regions, hydrologic modifications (e.g., intensifying tile drainage) have occurred during this same time period, which has greatly increased connectivity. We are concerned that the Smith et al. (2017) article will be read as potential policy recommendations based on spurious results. As such, we believe it is important to discuss methodological concerns of this work.

TABLE 1

Data provided are the result of a fiveminute extraction with the two treatment (labeled 1990 and 2011) solutions formulated from the National Atmospheric Deposition Program data. Inspection of table 1 reveals the rather remarkable mobilization of not only aluminum (Al) and calcium (Ca), but iron (Fe) from the six soils used in the study by essentially dilute (low ionic strength) solutions. Typically, the kinetics of mineral dissolution of Fe and Al bearing minerals are significantly slower than would result in this concentration of dissolved species from this short contact time (Martin 2005; Dietzel and Bohme 2005). Based on the experimental procedure (filtration with a 0.45 µm [1.8 \times 10⁻⁵ in] filter followed by acidification), it is more likely that the unrealistically high concentrations of dissolved species are the result of colloidal material present in the filtered extracts, and thus predictably, values in table 1 result from postfiltration dissolution of this material by the subsequent acidification of the filtered extract. This explanation is consistent with previous studies which have shown elevated Fe, Al, and P in 0.45 µm filtrate, due to colloidal particles passing through the filter (Danielsson 1982; Horowitz et al. 1996). Colloidal particles tend to be enriched in Fe and P because of their high specific surface area and Fe oxide coatings (Massey and Jackson 1952; Sharpley 1980). Indeed, transmission electron microscopy (TEM) of particles in 0.45 µm filtrate from the Maumee River shows numerous types of particles rich in Fe, Al, and P. TEM and energy-dispersive X-ray spectra of nanoparticles from the Maumee River are shown in figure 1 here.

In addition, it is well known that the ion-coupled argon plasma torch in modern emission spectrometers readily breakdowns fine colloids in the injected sample stream. This explanation also readily explains the apparent correlation between SP and Al for soil OH4 in figure 2 and the apparent randomness in supposed positive correlations denoted in table 1 in Smith et al. (2017). It can also explain why only two soil extracts showed a decrease in P between 1990 and 2011 (OH1 and OH4), as each of these filtered extracts also had a decrease in Fe along with P. We also express concern over the overstatement of data precision in table 1, as our experience suggests that many of those numbers should be rounded to only two significant figures.

FIGURE 3

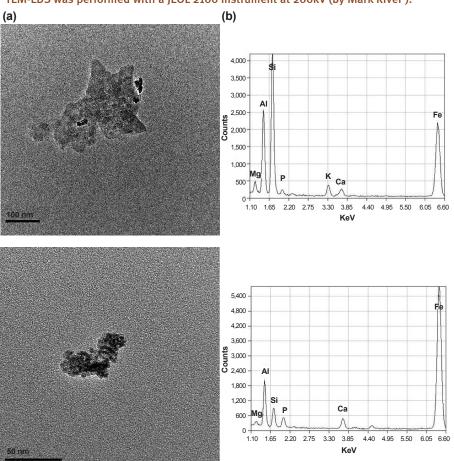
Data presented purportedly shows an increase in solubility between the two treatments (2011 > 1990). No proposed mechanism is provided to support an increase in P solubility due to changes in rainfall chemistry. In fact, this data is counterintuitive in that it contradicts chemical theory and the impact of ionic strength on solubility. Again, a simple explanation is increased dispersion of <0.45 μ m (<1.8 \times 10⁻⁵ in) colloids and failure to remove these fine particulates from the soil extracts.

CHANGES IN SOIL DISSOLVED ORGANIC CARBON

Care needs to be exercised in taking observations of recovery of soils in non-agricultural ecosystems and assuming similar processes in intensively managed agricultural systems. Calls for reductions in atmospheric deposition of nitrogen (N) and sulfur (S) were driven by essentially N and S saturation of nonagricultural low acid neutralization capacity ecosystems where the natural anions in soil solu-

Figure 1

(a) Transmission electron micrographs (TEM) and (b) energy-dispersive X-ray spectra (TEM-EDS) of nanoparticles in 0.45 µm filtrate of the Maumee River. Samples were prepared by depositing and wicking one drop of filtrate on a 200 mesh TEM grid. TEM-EDS was performed with a JEOL 2100 instrument at 200kV (by Mark River).



tion (dissolved organic C and bicarbonate [HCO₃-]) were displaced by the hard acid anions of nitrate (NO₂⁻) and sulfate (SO₄²⁻). The presence of NO₃⁻ and SO₄²⁻ enhances leaching of bases and especially acid cations, and subsequent transport of these cations from soils into nearby surface streams. The success of the Clean Air Act has been the beginning of the return of many of these impacted ecosystems to their natural internal cycling prior to impacts from acidic deposition. In this context, the Clean Air Act is not causing anything new, but has directed actions that are allowing natural ecosystems to return/ recover to the extent possible.

We are not opposed to any discovery of new processes that better enhance our understanding of the natural world, nor the potential unintended result (good or bad) of anthropogenic activities. However, hypotheses and subsequent data regarding the potential existence of such impacts must be consistent with current, well-documented, and peer-reviewed scientific theory. We are concerned that the article by Smith et al. (2017) does not meet these criteria.

REFERENCES

Danielsson, L.G. 1982. On the use of filters for distinguishing between dissolved and particulate fractions in natural waters. Water Research 16(2):179–82.

Dietzel, M., and G. Bohme. 2005. The dissolution rates of gibbsite in the presence of chloride, nitrate, silica, sulfate, and citrate in open and closed systems at 20°C. Geochimica et Cosmochimica Acta 69(5):1199-1211.

Horowitz, A.J., K.R. Lum, J.R. Garbarino, G.E.M. Hall, C. Lemieux, and C.R. Demas. 1996. Problems associated with using filtration to define dissolved trace element concentrations in natural water samples. Environmental Science & Technology 30(3):954–63.

Martin, S.T. 2005. Precipitation and dissolution of iron and manganese oxides. *In* Environmental Catalysis, ed. V.H. Grassian, 61–81. Boca Raton: Marcel-Dekker, CRC Press.

Massey, H.F., and M.L. Jackson. 1952. Selective erosion of soil fertility constituents. Soil Science Society of America Journal 16(4):353–356.

Sharpley, A.N. 1980. The enrichment of soil phosphorus in runoff sediments. Journal of Environmental Quality 9(3):521–526.

Sinha, E., A.M. Michalak, and V. Balaji. 2017. Eutrophication will increase during the 21st century as a result of precipitation change. Science 357:405-408, doi:10.1126/science.aan2409.

Smith, D.R., M. Stephensen, K.W. King, H.P. Jarvie, R. Haney, and M.R. Williams. 2017. A possible trade-off between clean air and clean water. Journal of Soil and Water Conservation 72(4):75A-79A, doi:10.2489/jswc.72.4.75A.