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Response of soil fertility to 25 years of experimental acidification in a temperate hardwood forest

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Abstract

The effects of enhanced acid deposition from the atmosphere, and associated elevated inputs of N, are widely evident, especially for forests where excess N has led to a variety of deleterious effects. These include declines in biodiversity, a response that will likely require considerable time for recovery. The purpose of this study was to determine responses of plant nutrient availability in surface mineral soil to 25 yr of experimental acidification and N addition in a central Appalachian hardwood forest ecosystem. We hypothesized that chronic additions of $(NH_4)_2SO_4$ will increase mineral N, decrease soil pH, P, and base cations, increase micronutrients (Mn^{2+} and Fe^{2+}), and increase levels of Al^{3+}. Results supported these predictions, although Mn^{2+} did not vary significantly. Earlier work on these plots found no response of any of the extractable nutrients to 3 yr of treatment, yet after 25 yr, our results suggest that impacts are apparent in the top 5 cm of the A horizon. We surmise that impacts in these soils may have lagged behind the onset of acidification treatments or that several years of treatment were required to overcome preexisting differences in soil ions. Generally, current findings confirm that $(NH_4)_2SO_4$ treatments have lowered the pH, enhanced levels of exchangeable Al^{3+}, and increased stream-water exports of NO_3^- and base cations—a process that further acidifies soil. The combination of these changes in surface soils, with their high proportion of fine roots, may contribute to the reduced growth and competitiveness of some hardwood species at the acidified site.

1 | INTRODUCTION

The efficacy of the Clean Air Act in the United States has led to notable declines in acidic deposition, including atmospheric deposition of nitrogen (N), although much of the latter is in the form of oxidized N, as reduced N has increased in some regions (Du, De Vries, Galloway, Hu, & Fang, 2014; Du, Fenn, De Vries, & OK, 2019; Gilliam et al., 2019). Deposition of N remains high in parts of the conterminous United States and beyond, with the biogeochemical signature of elevated N being evident even in remote areas of the Northern Hemisphere (Holtgrieve et al., 2011; Vet et al., 2014). For areas where chronic atmospheric deposition of N has led to N saturation, wherein the supply of available N exceeds plant and microbial demand for N (Aber et al., 1998; Stoddard, 1994), excess N still represents a chronic threat to ecosystem structure and function. This

Abbreviations: EC, electrical conductivity; FEF, Fernow Experimental Forest; PME, phosphomonoesterase; WAS, Watershed Acidification Study; WS, watershed.

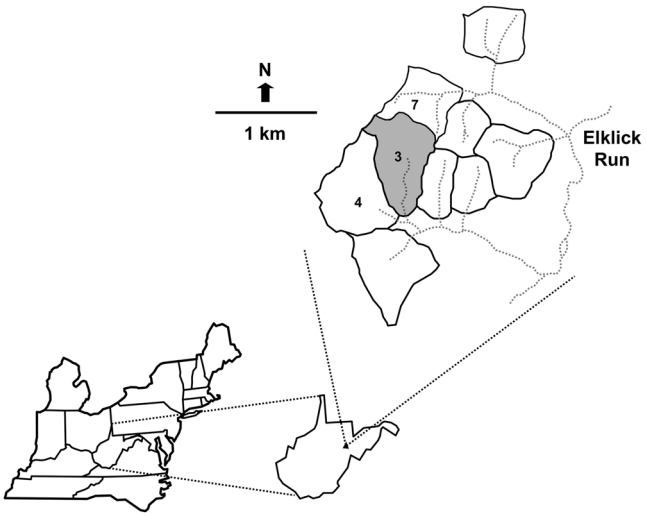

FIGURE 1 Study watersheds: WS3 (treatment), WS4 (reference), and WS7 (reference) at Fernow Experimental Forest, West Virginia

Core Ideas

- Excess acidification and N can alter surface soil fertility of forest ecosystems.
- Our earlier work found no effects after 3 yr of $(NH_4)_2SO_4$ addition on soil nutrients.
- This study found notable change in soil nutrients after 25 yr of acidification.
- Extractable N, Fe, and Al increased; pH and extractable base cations decreased.
- Results have implications for management of impacted forests.

has been especially the case for temperate forest ecosystems, with a high spatial coincidence of dense human populations and elevated levels of acid and N deposition (Holland & Lamarque, 1997; Gilliam, 2016). Critical loads for N in the United States are still widely exceeded for many ecosystem types, particularly forests (Pardo et al., 2011), leading to a variety of deleterious effects, including loss of biodiversity (Clark, Morefield, Gilliam, & Pardo, 2013; Clark, Simkin, et al., 2019; Simkin et al., 2016). Also, recovery of acidified and N-impacted sites may require extended periods of time (Gilliam et al., 2019; Schmitz et al., 2019, Stevens, 2016), especially in locations where base cations, such as calcium (Ca^{2+}), have been depleted by accelerated nitrate (NO_3^-) leaching (Likens, Driscoll, & Buso, 1996; Likens et al., 1998). Thus, understanding the potential biogeochemical responses of forest ecosystems to chronically elevated acidification and N inputs still remains essential.

In addition to evidence that symptoms of N saturation have developed on a long-term reference watershed in the Fernow Experimental Forest (FEF) in West Virginia (Peterjohn, Adams, & Gilliam, 1996), an ongoing experiment at this site—the Watershed Acidification Study (WAS; Adams, DeWalle, & Hom, 2006)—has examined the response of a small (35-ha) forested watershed to aerial applications of ammonium sulfate [$(NH_4)_2SO_4$] (Figure 1). To date, results have demonstrated numerous treatment-mediated changes in plant communities (Gilliam, Billmyer, Walter, & Peterjohn, 2016; Gilliam, Welch, et al., 2016; Gilliam, May, & Adams, 2018) and watershed biogeochemistry (Edwards, Williard, Wood, & Sharpe, 2006), but some of these changes have taken considerable time to emerge.

For example, based on permanent plots in the three watersheds that comprise the WAS, Gilliam, Turrill, Aulick, Evans, and Adams (1994) was unable to detect a response in the levels of exchangeable soil ions in 1991, after 3 yr of experimental additions of $(NH_4)_2SO_4$. This delay was unexpected considering that (a) treatment-mediated increases in stream NO_3 had already commenced, along with notable increases in stream concentrations of base cations, as well as similar results for soil solutions (Adams, DeWalle, Peterjohn, et al., 2006; Edwards et al., 2006), and (b) studies in other hardwood forests have shown relatively rapid responses to experimental manipulations such as ours (Moore & Houle, 2009, 2013).

Soils were sampled for nutrients in some of these watersheds in 1994 (Adams, DeWalle, Peterjohn, et al., 2006), 1995 (Tepp, 1995), 2000 (Odenwald, 2002), and 2002 (Adams, DeWalle, Peterjohn, et al., 2006). There are also a limited number of pretreatment data from soils collected in 1988. By the time the samples were collected for this study in 2015, Watershed 3 (WS3) had undergone treatment for 25 yr, or more than eight times longer than when the initial comparison was done in 1991. Although these studies differed in methodology and sampling locations, they suggest that patterns of change in the surface soils have been emerging as the experimental treatment continued, especially a decrease in soil pH and base cation availability (Figure 2).

To more conclusively assess whether detectable changes in soil fertility have emerged after 25 yr of whole-watershed acidification, in this study, we measured extractable ions in surface mineral soils collected from 7 of the 15 plots where soils were collected in 1991 (Gilliam et al., 1994). We also expanded on the earlier study by measuring extractable aluminum (Al) because of its potential influence on plant root dynamics, nutrient uptake, and forest health.

Changes in soil fertility, especially under deposition of excess acidity, often occur via leaching of inorganic

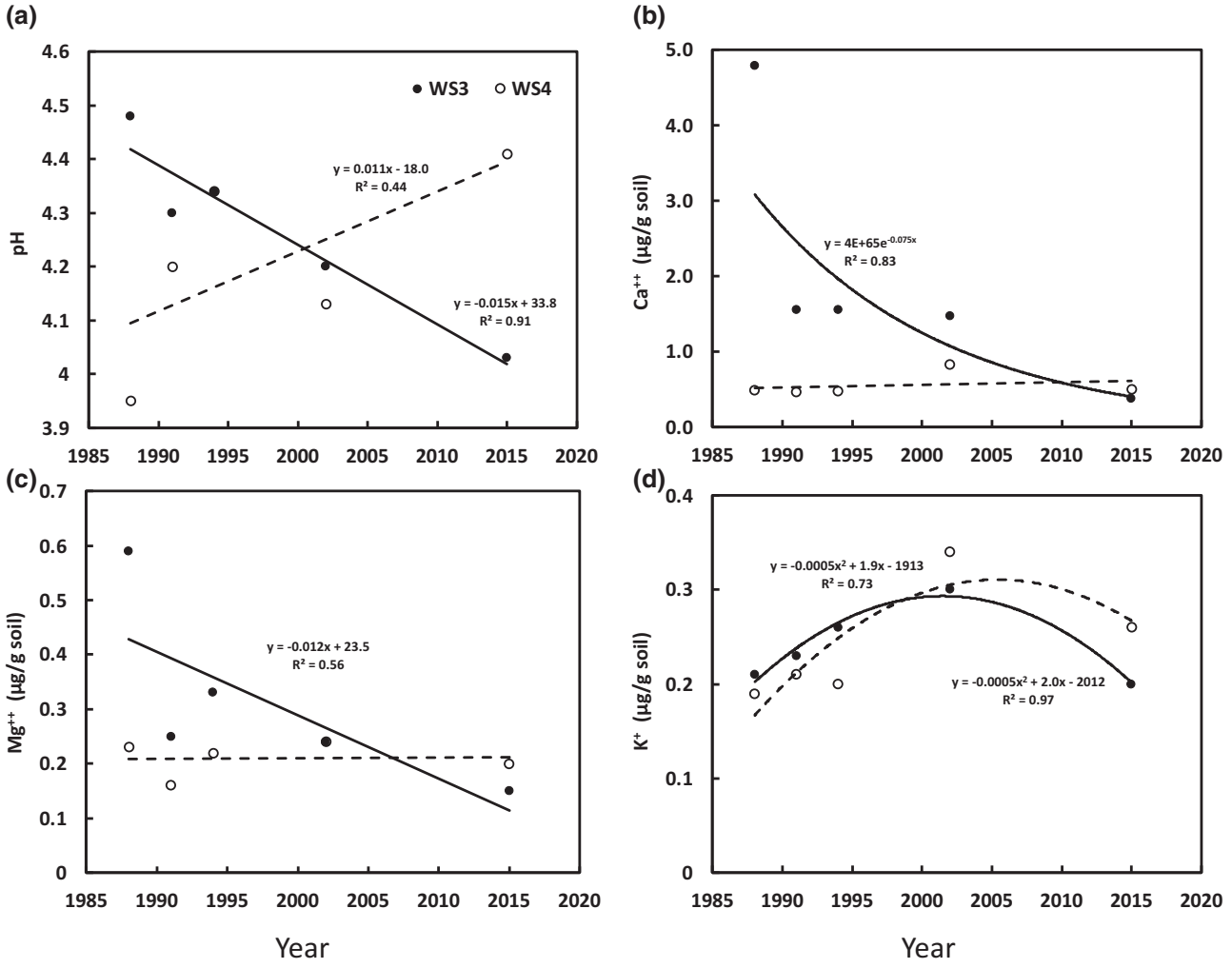

FIGURE 2 Previously and currently reported mean values for ions in the surface (0–10 cm or A horizon) mineral soils of the acidified (WS3) and reference (WS4) watersheds in the Fernow Experimental Forest: (a) pH, (b) Ca^{2+}, (c) Mg^{2+}, and (d) K^{+}. Change in pH or ion concentrations over time shown as linear and curvilinear relationships yielding the best fit per watershed (highest r^2). Dashed lines for WS4 in Graphs b and c are not significant at $P > .05$. Data sources: 1988 (pretreatment), Adams, DeWalle, Peterjohn, et al. (2006), and unpublished data (for K^{+}); 1991, Gilliam et al. (1994); 2002, Adams, DeWalle, Peterjohn, et al. (2006); 2015, this study

nutrients through the soil column and into streams. Thus, a continuous record of stream chemistry may help us assess, and deepen our understanding of, apparent temporal patterns inferred from periodic measurements of soil nutrients as they respond to chronic acid deposition. Accordingly, along with soil data from these sites, we also present a unique combination of nearly 30 yr of pH, electrical conductivity, and ionic concentrations in stream flow for the same treatment period.

We then used these measurements to test the following four hypotheses: 25 yr of acidification treatment will (a) increase pools of inorganic N (ammonium [NH_4^+] and NO_3^-), (b) decrease soil pH, phosphorus (P), and base cations (Ca^{2+}, magnesium [Mg^{2+}], and potassium [K^{+}]), (c) increase extractable micronutrients (manganese [Mn^{2+}] and iron [Fe^{2+}]), and (d) elevate levels of phytotoxic Al^{3+}. In addition, we were interested in determining how quickly changes in surface soils might be reflected in altered stream-water chemistry.

2 | MATERIALS AND METHODS

2.1 | Study site

This study comprises over a quarter century of ongoing research (the WAS, Adams, DeWalle, & Hom, 2006) that has focused on the response of a temperate hardwood forest ecosystem to experimental soil acidification at FEF, a ~1,900-ha research area in the Allegheny Mountain

TABLE 1 Means (±1 SE) of extractable soil analytes for experimental watersheds at Fernow Experimental Forest in West Virginia in 2015

Analyte	WS3	WS4	WS7
pH	**4.03 ± 0.09b**	**4.41 ± 0.05a**	**4.39 ± 0.05a**
Acidity, $cmol_c$ 100 g^{-1}	**7.9 ± 1.0a**	**6.5 ± 0.5ab**	**5.7 ± 0.4b**
NH_4^+, μg N g^{-1} soil	**6.7 ± 2.0a**	**3.1 ± 0.8b**	**2.3 ± 0.5b**
NO_3^-, μg N g^{-1} soil	**3.1 ± 0.8a**	**1.2 ± 0.5b**	**1.3 ± 0.6b**
Ca^{2+}, μg g^{-1} soil	**75.6 ± 8.5b**	**99.3 ± 16.4b**	**159.6 ± 36.3a**
K^+, μg g^{-1} soil	**80.3 ± 4.7b**	**99.6 ± 8.5ab**	**133.9 ± 36.0a**
Mg^{2+}, μg g^{-1} soil	**18.0 ± 0.8b**	**24.6 ± 2.3a**	**28.4 ± 3.1a**
P, μg g^{-1} soil	**1.6 ± 0.2b**	**1.8 ± 0.2ab**	**2.2 ± 0.2a**
Al^{3+}, μg g^{-1} soil	**513.4 ± 81.7a**	**398.0 ± 42.9ab**	**330.4 ± 35.9b**
Fe^{2+}, μg g^{-1} soil	**10.5 ± 4.3a**	**2.0 ± 0.6b**	**3.01 ± 1.1b**
Mn^{2+}, μg g^{-1} soil	134.1 ± 30.1a	133.0 ± 8.7a	120.6 ± 24.3a

Note. Watershed 3 (WS3) is the treatment watershed, and WS4 and WS7 are untreated reference watersheds. For a given analyte, means followed by the same letter are not significantly different at $P < .10$, and significant differences among watersheds are highlighted in bold.

section on the unglaciated Allegheny Plateau, and located in Tucker County, West Virginia (39°03′15″ N, 79°49′15″ W). Mean precipitation at this site is ~1,430 mm yr^{-1}, relatively evenly distributed seasonally (Kochenderfer, 2006), and increasing with higher elevation (Gilliam & Adams, 1996).

Consistent with the earlier study (Gilliam et al., 1994), three watersheds were used in this study: WS3, WS4, and WS7 (Figure 1). As the treatment watershed, WS3 has received aerial additions of $(NH_4)_2SO_4$ since 1989. WS4 and WS7 serve as unfertilized reference watersheds. Watershed soils are primarily Inceptisols of the Berks and Calvin series, both of which are loamy-skeletal, mixed, mesic Typic Dystrochrepts. These soils are derived from sandstone and shale and are mostly coarse-textured sandy loams that are well drained, ~1 m in depth, and are generally acidic (Table 1) and high in organic matter (Adams, DeWalle, & Hom, 2006).

Experimental additions of $(NH_4)_2SO_4$ to WS3 were made three times per year, administered by either rotary- or fixed-wing aircraft. March and November applications were of ~7 kg N ha^{-1}, whereas July applications were of ~21 kg N ha^{-1}. The total annual additions reflect a rate approximately twice the ambient rates of N and sulfur (S) deposited as throughfall on the watersheds in the early 1980s (Adams, DeWalle, & Hom, 2006). WS3 and WS7 support even-aged, 45-yr-old hardwood stands, with stand initiation on WS3 arising from clearcutting the watershed in 1969, and stand initiation on WS7 arising from release in 1969 from herbicide treatment after clearcutting between 1963 and 1967. WS4 supports an even-aged hardwood stand ~100 yr old (Kochenderfer, 2006).

Stands on all watersheds are dominated by mixed hardwood species, including sugar maple (*Acer saccharum* Marsh.), sweet birch (*Betula lenta* L.), American beech (*Fagus grandifolia* Ehrh.), yellow poplar (*Liriodendron tulipifera* L.), black cherry (*Prunus serotina* Ehrh.), and northern red oak (*Quercus rubra* L.) (Kochenderfer, 2006). Despite stand age and management differences, the composition of the herb layer community was initially similar between watersheds (Gilliam et al., 1994). Prominent species were *Viola* spp., *Rubus allegheniensis* Porter, mixed ferns, and seedlings of *Acer pensylvanicum* L. and *A. rubrum* L. During the course of the experiment, *R. alleghe-niensis* increased significantly on WS3 and WS4, but especially on treatment WS3, where it now represents ~50% of total herb-layer cover (Gilliam, Welch, et al., 2016).

2.2 | Field sampling and laboratory analyses

In July 2015, mineral soil was sampled to a depth of 5 cm by hand trowel at five points within each of seven circular 0.04-ha plots in each watershed. As this paper focuses on the response of plant-available nutrients to experimental treatments, we confined our sampling to surface mineral soils where fine roots (Jackson et al., 1996) and the availability of most nutrients (Jobbágy & Jackson, 2001) are typically most abundant. Also, these are the same depth and plot locations used in ongoing, long-term investigations into effects of acidification on soil N dynamics via in situ incubations (i.e., buried bags) (Gilliam, Walter, Adams, & Peterjohn, 2018). The five individual samples from each plot were combined and thoroughly mixed into a single composite sample, placed in a sterile polyethylene bag, and refrigerated immediately upon return to the laboratory.

Prior to sieving and air drying, subsamples of soil were extracted with 1 M potassium chloride (KCl) and analyzed for NH_4^+ and NO_3^- colorimetrically with an Auto

Analyzer III system in the Marshall University Weeds and Dirt Laboratory. All remaining soil material was sieved to pass a 1-mm mesh and air dried for shipment to the University of Maine Soil Testing Service and Analytical Laboratory for determination of pH (in distilled water [H_2O]), and ammonium chloride (NH_4Cl)-extractable macronutrients (P, Ca, Mg, and K), micronutrients (Fe and Mn), and Al (inductively coupled plasma optical emission spectrometry). Organic matter was measured by loss on ignition at 550 °C. Exchangeable acidity was extracted in KCl and measured by titration.

Each of the experimental watersheds used in this study is gauged with a V-notch weir and a water level recorder. Water samples collected at a fixed location upstream from the weir have been analyzed weekly since 1970 for a variety of analytes, including dissolved NO_3 concentrations (Edwards & Wood, 2011). These and other data are currently available at www.nrs.fs.fed.us/ef/locations/wv/fernow/data/ and www.as.wvu.edu/fernow/data.html.

2.3 | Data analysis

As this study is an example of simple pseudoreplication (Hurlbert, 1984), with replications represented as plots within single watersheds, interpretation of data should be made with that in mind. It is our contention, however, that effects reported are most appropriately interpreted as resulting from experimental treatment, rather than preexisting differences among watersheds, especially considering that the apparent changes are consistent with those commonly expected in acidified soils.

Means of all measured variables were compared for significant differences among watersheds using ANOVA and LSD tests. A priori significant differences were accepted for all statistical tests at $P < .10$ to accommodate naturally high spatial variability at the watershed scale (Zar, 2009).

3 | RESULTS AND DISCUSSION

Although Gilliam et al. (1994) were unable to detect a response in exchangeable soil nutrients after 3 yr of experimental acidification, continued treatment over an additional 22 yr has altered extractable ions in the surface mineral soils in ways that are largely consistent with both theoretical expectations and patterns suggested from findings of other research (Table 1, Figure 2). After 25 yr of $(NH4)_2SO_4$ additions, extractable concentrations of both NH_4^+ and NO_3^- were higher, whereas soil pH and extractable Ca^{2+}, Mg^{2+}, K^+, and P concentrations generally were lower in the treated watershed (WS3), relative to the reference watersheds (WS4 and WS7) (Table 1). Although concentrations of extractable Fe^{2+} and Al^{3+} were significantly greater in WS3, extractable Mn^{2+} did not vary significantly between treatment and reference watersheds, contrary to expectations. There were no detectable differences in soil organic matter among watersheds, which averaged ~12%. This was consistent with Gilliam et al. (1994), who also reported no differences in organic matter for soils collected in 1991 from the same watersheds, and with values reported for surface soils in WS3 and WS4 that were collected in 1988, 1994, and 2002 (Adams, DeWalle, Peterjohn, et al. 2006).

The higher NH_4^+ in soils of treatment WS3 is likely the direct result of the experimental additions of $(NH_4)_2SO_4$. Extractable NH_4^+ in WS3 was more than two times the levels measured in either WS4 or WS7 (Table 1). Surprisingly, although the levels of extractable NO_3^- were around three times higher in WS3 than in the reference watersheds, no detectable treatment effect on net NO_3^- production rates in these soils has been found since 1995 (Gilliam, Walter, et al., 2018). If net NO_3^- production rates are indeed the same across all watersheds, then the differences in the extractable pools, and higher stream NO_3^- concentrations, may reflect treatment-induced differences in vegetative or microbial demand. For example, Burnham, Cumming, Adams, and Peterjohn (2017) provided support for the idea that elevated Al^{3+} levels in the soils of the acidified watershed might lower the demand for NO_3^- by several of the dominant tree species. Regardless, it is clear that the acidification treatment has not only increased soil acidity in WS3 but has also greatly enhanced the leaching of mobile NO_3^- (Figure 3a), a result that is also important in understanding the response of soil cations (Qafoku, Summer, & Radcliffe, 2000). Furthermore, because most plant species can supply their N demand via uptake of either NH_4^+ or NO_3^- (Haynes & Goh, 1978), increased supply of NH_4^+ from the treatment further enhances the leaching potential of NO_3^- in WS3.

The previously documented lack of a detectable difference in net NO_3^- production rates in the well-drained soils at these sites (Gilliam, Walter, et al., 2018) is not likely to be attributable to substantially greater rates of gaseous N loss by either nitrification or denitrification in the fertilized watershed. Indeed, a limited number of measurements in these watersheds found that although losses of N gases in WS3 were greater, the magnitude of the combined loss of N as nitrous oxide (N_2O) and nitric oxide (NO) was small and likely to be <0.1 g N m^{-2} yr^{-1} (Peterjohn et al., 1998; Venterea et al., 2004). However, although rates of net NO_3^- production in the surface mineral soils of the fertilized watershed were not elevated, the significant reduction of soil pH in WS3 (Table 1) suggests the interesting possibility that the microbial community may have shifted toward a more prominent role for acid-stimulated NH_4^+ oxidation

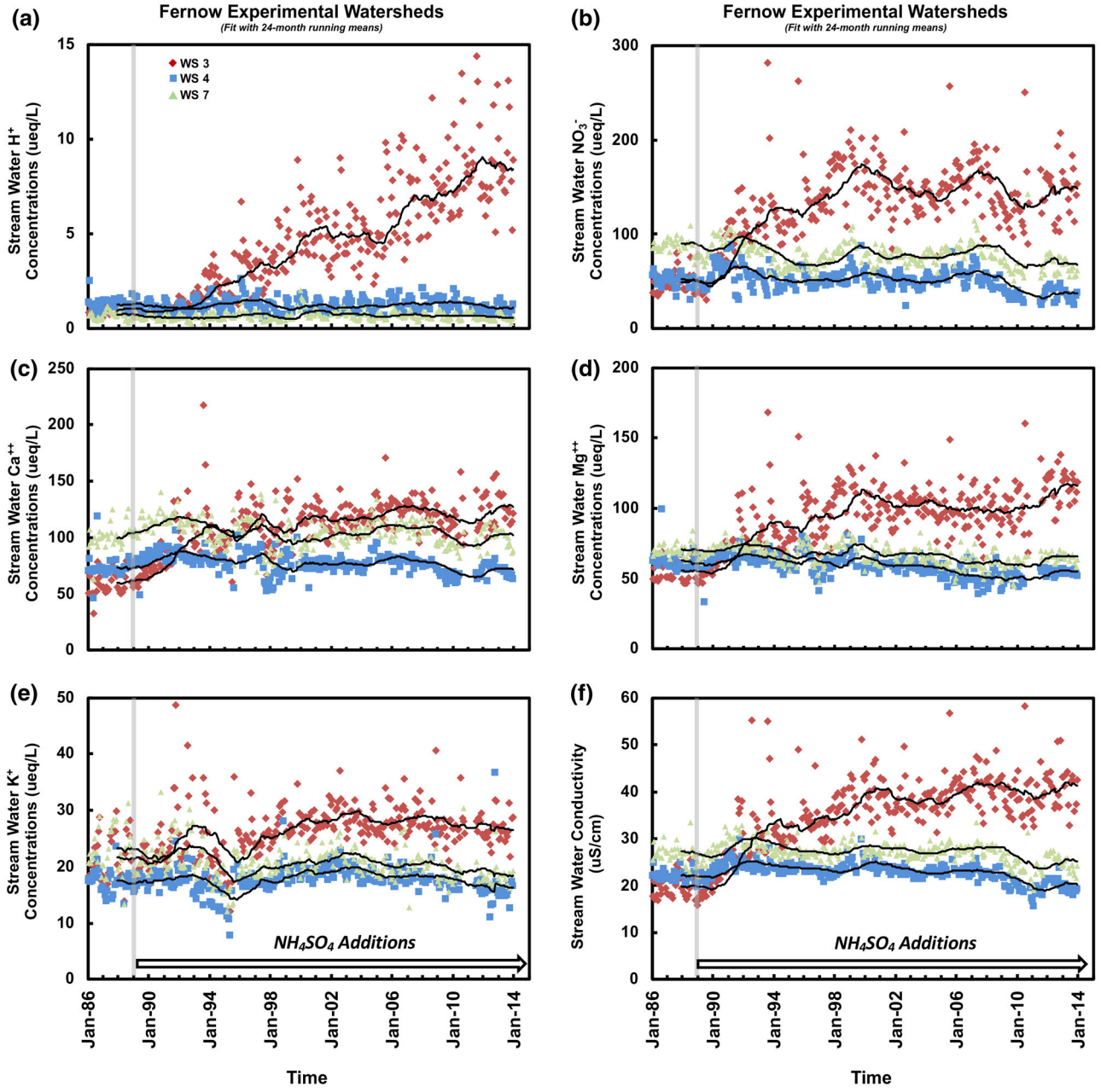

FIGURE 3 Volume-weighted mean monthly concentrations of major ions in stream water and electrical conductivity from 1989 to 2014 for three small watersheds at the Fernow Experimental Forest in West Virginia. Trend lines are 24-mo running means. Vertical bars indicate when fertilizer applications began

via archaea (Li, Chapman, Nicol, & Yao, 2018). Although low soil pH has traditionally been thought to inhibit nitrification (Barbour, Burk, Pitts, Gilliam, & Schwartz, 1999), recent work has shown that nitrification can not only occur at a pH as low as 3.0, but also that obligate acidophilic NH_4^+–oxidizing archaea (e.g., *Nitrosotalea* spp.) are stimulated at low soil pH (Norton & Stark, 2011).

For several years prior to the start of acidification treatments, stream concentrations of cations and electrical conductivity (EC) exhibited generally similar temporal patterns among the three watersheds (Figure 3). After the initiation of experimental additions of $(NH_4)_2SO_4$, reference WS4 and WS7 revealed minimal changes in stream chemistry over time, whereas WS3 showed notable increases in NO_3^-, hydrogen (H^+), Ca^{2+}, Mg^{2+}, K^+, and EC (Figure 3). Furthermore, all analytes with notable responses to treatment also displayed a time lag in such response—from 1 to 2.5 yr (Edwards et al., 2006). This time lag is also

consistent with the mean transit time of ~1.5 yr that has been estimated for baseflow in these watersheds using measurements of seasonal patterns in oxygen-18 (^{18}O) (DeWalle, Edwards, Swistock, Aravena, & Drimmie, 1997).

Despite differences in methods, our results, when coupled with those from previous measurements of exchangeable ions in the surface soils of these watersheds (Figure 2), suggest a pattern of change that is generally consistent with theoretical predictions for ion leaching after soil acidification and enhanced NO_3^- mobility (Galloway, Norton, & Church, 1983; Fernandez, Rustad, Norton, Kahl, & Cosby, 2003). In addition to the measurements reported here for 1991 and 2015, comparisons of extractable nutrients have also been made between WS3 and WS4 for samples collected in 1994 and 2002, and between WS3 and WS7 for soils collected in 1995 and 2000 (Tepp, 1995; Odenwald, 2002; Adams, DeWalle, Peterjohn, et al., 2006). Pretreatment values for a limited number of samples from the upper mineral soils (0- to 10-cm depth) have been reported for WS3 and WS4 (Adams, DeWalle, Peterjohn, et al., 2006), allowing some insight into the existence of any pretreatment differences between these two watersheds. For Ca, Mg, and K, the relative differences in average extractable concentrations between surface soils in the acidified (WS3) and mature reference (WS4) watershed have diminished over time (Figure 2).

Twenty-five years of the soil acidification treatment decreased extractable Ca in the surface mineral soil of WS3 relative to the two reference watersheds (Table 1). These results are consistent with previous observations indicating that enhanced leaching of NO_3^- is coupled to greater losses of Ca^{2+} in stream water leaving WS3 (Edwards et al., 2006) (Figure 3, Peterjohn et al., 1996). This is also in agreement with findings from the Hubbard Brook Experimental Forest based on a 30-yr dataset that show a tight coupling of NO_3^- and Ca^{2+} losses in stream water (Likens et al., 1998) that arises from the electrostatic anion and cation binding of NO_3^- and Ca^{2+} (Schlesinger, 1997).

The Ca/Mg ratios of ancient silicate sediments that gave rise to soils such as those of the study watersheds at FEF are close to 1 (Van Moort, 1973). Thus, because Mg^{2+} is biogeochemically similar to Ca^{2+}, it was not surprising that the response of Mg^{2+} to experimental N treatments closely resembled that of Ca^{2+} (Table 1). As found in earlier studies focusing on plant nutrient balances (Garten, 1976; Gilliam, 1988), Ca and Mg comprise the same foliar nutrient functional group (i.e., photosynthetic and structural; Garten, 1978). Previous results from the FEF found similar responses between Mg^{2+} and Ca^{2+} regarding N-mediated leaching and tree and herb foliar concentrations (Adams, DeWalle, Peterjohn, et al., 2006; Gilliam, Billmyer, et al., 2016; Peterjohn et al., 1996). Fernandez et al. (2003) also reported similarities between soil Ca^{2+} and Mg^{2+} in response to 9 yr of $(NH_4)_2SO_4$ additions at the Bear Brooks watersheds in Maine.

Although extractable K^+ displayed a response to the acidification treatment that was similar to other base cations (Table 1), we suggest that this may have been influenced more by enhanced plant uptake than from N-mediated leaching (as appeared to have occurred for Ca^{2+} and Mg^{2+}) for two reasons: (a) treatment-mediated increases in stream K^+ have been small, relative to Ca^{2+} and Mg^{2+} (Edwards et al., 2006, Figure 3), and (b) foliar K concentrations of dominant herb layer species were significantly greater in treated WS3 relative to the reference watersheds (Gilliam, Billmyer, et al., 2016), and overall herb layer biomass in WS3 is significantly higher than in WS4 (Gilliam, Welch, et al., 2016). Combining foliar K concentrations and biomass data from the two studies suggests that uptake of K^+ by herb-layer plants in WS3 may be ~2.5 times that in WS4 (similar current herb biomass data are unavailable for WS7).

Although soil P levels exhibited a similar response to acidification as the base cations (Table 1), the mechanisms for this are likely quite different. The biogeochemistry of soil P is complex (Marschner, 1995), as P can bind with other nutrients (e.g., Ca) and oxides of Al and Fe (Borggaard, Jørgensen, Møberg, & Raben-Lange, 1990). At the pH values of our soils (~4.0–4.4, Table 1), however, adsorption by oxides of Al and Fe is more likely (Borggaard et al., 1990) and is capable of influencing P availability (Tahovská, Čapek, Šantrůčková, & Kopáček, 2018). Furthermore, our results support earlier findings at FEF that excess N can initiate a greater biotic demand for P (Gress, Nichols, Northcraft, & Peterjohn, 2007) and are consistent with other studies showing that alleviation of N limitation can give rise to P limitation (Elser et al., 2007; Vitousek, Porder, Houlton, & Chadwick, 2010). At FEF, Gress et al. (2007) used several approaches to demonstrate the onset of P limitation by N additions to WS3. One facet of their study analyzed activity of phosphomonoesterase (PME), a plant enzyme produced under extreme P limitation in roots of *Viola rotundifolia* Michx., and found significantly higher root-associated PME in *V. rotundifolia* in WS3. Additionally, they used a root in-growth study in which they varied macronutrient additions (N, Ca, and P) to mesh bags containing vermiculite and measured the degree to which fine roots grew into the bags. They reported that the greatest fine root in-growth biomass occurred in bags treated with P, further demonstrating that additions of $(NH_4)_2SO_4$ may have led to P limitation (Gress et al., 2007).

The two extractable micronutrients included in this study were Fe and Mn. We hypothesized that extractable levels of both would increase in response to $(NH_4)_2SO_4$ applications to WS3. This was found, however, only for Fe and not for Mn (Table 1). Our expectation was based on

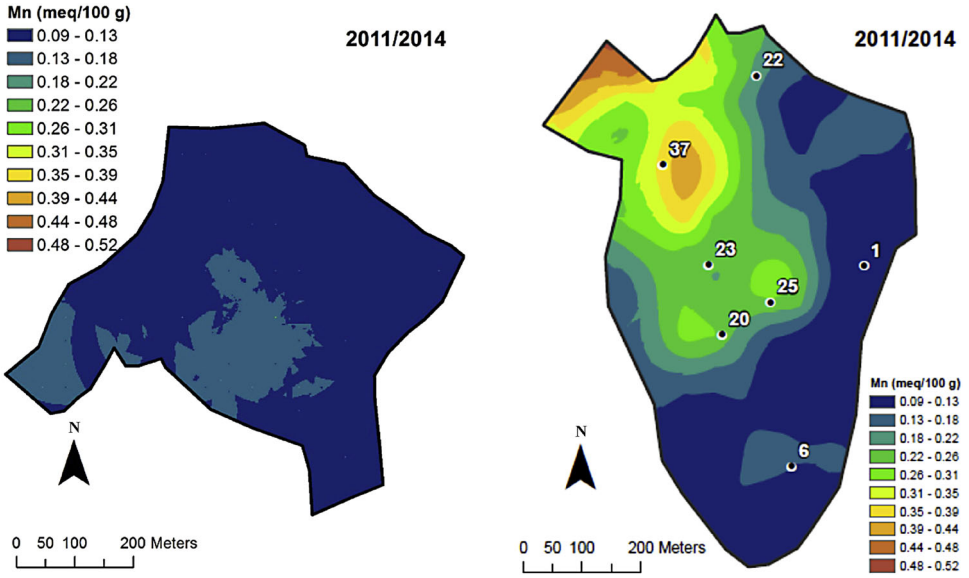

FIGURE 4 Kriged extractable soil Mn (from 2011 and 2014) for (a) reference watershed WS7 and (b) N-treated watershed WS3. Shown also for WS3 (data not available for WS7) are spatially explicit mean cover (%) values for *Rubus allegheniensis* in the seven permanent sample plots. Figures taken from Gilliam, Billmyer, et al. (2016). The unit meq 100 g^{-1} is equivalent to the unit $cmol_c$ 100 g^{-1} in our Table 1

(a) the known relationship between soil pH and Fe/Mn mobility (Barbour et al., 1999; Millaleo, Reyes-Diaz, Ivanov, Mora, & Alberdi, 2010), and (b) the acidifying nature of net nitrification in excess of plant uptake, which affects changes in several soil nutrients (Lukac & Godbold, 2011). The latter appears to have occurred in WS3, considering that soil pH was significantly lower (by nearly 0.5 pH units) there than in the reference watersheds (Table 1). Although this explains the significantly higher extractable Fe in WS3, it is less clear why we did not find similar results for Mn.

Our expectation for the response of Mn to acidification is based in large part on an intensive sampling of surface soils at 100 locations within each of WS7 and WS3, which revealed that extractable Mn was ~80% higher in WS3, along with a notable increase in the spatial heterogeneity in soil Mn levels that correlated closely with high cover of *Rubus allegheniensis*, a species that accumulates Mn at high levels in foliar tissue and litter (Gilliam, May, & Adams, 2018) (Figure 4; Kula, Hrdlicka, Hedbavny, & Svec, 2012). It is likely that differences in the response between the two studies is a result of differences in the extractants that were used, wherein the more intensive sampling used ammonium acetate (Gilliam, May, & Adams, 2018) and the current study used ammonium chloride.

In contrast with the micronutrients, Al is of no nutritional value to plants, but under conditions of increased mobility, it can be toxic to plant roots (Clarkson, 1966; Lukac & Godbold, 2011; Nagajyoti, Lee, Sreekanth, 2010). Increased N deposition has been shown to increase soil acidity and do so in ways that increases Al mobility in

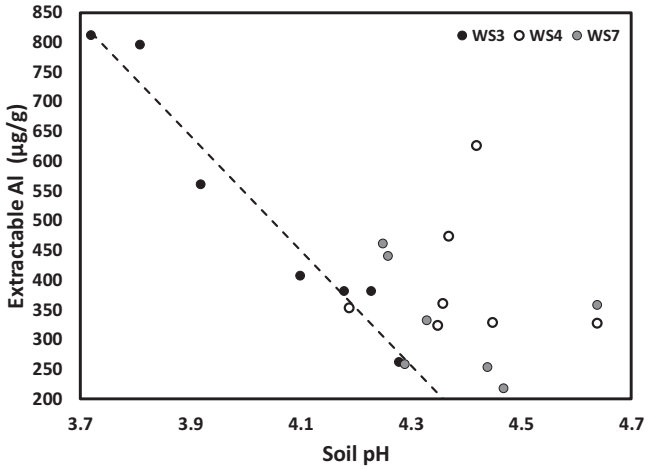

FIGURE 5 Extractable soil Al vs. soil pH for plots in the experimental watershed at Fernow Experimental Forest, West Virginia: WS3 (treatment watershed), black symbols, solid line; $Y = -964.9X + 4{,}406.0$, $r^2 = .95$; WS4 (reference watershed), gray symbols; WS7 (reference watershed), open symbols

forest soils (Lu, Mao, Gilliam, Luo, & Mo, 2014; Lynch & St. Clair, 2004). In our study, extractable Al was highest in soils of treatment WS3 (Table 1), which were also the most acidic, suggesting that acidification at FEF has increased mobility of Al. For WS3, extractable Al and soil pH were significantly correlated (Figure 5). These conclusions strongly support a study at FEF by Burnham et al. (2017) that examined soil solution Al in WS3 versus WS7. They not only reported that soil solution Al concentrations were 77% higher in WS3 but also found that elevated Al

in the soil solution altered the way in which tree species acquired available soil N—specifically, elevated Al caused a shift from NO_3^- uptake (which was inhibited by Al) to uptake of NH_4^+. In addition, the response of Al to acidification may have contributed to slowing the growth of some dominant hardwood trees in WS3, as reported by May, Burdette, Gilliam, and Adams (2005) and DeWalle et al. (2006).

Gilliam, Billmyer, et al. (2016) assessed the response of foliar Ca/Al ratios of prominent species of the herbaceous layer. Because there had been an N-mediated shift in herb community dominance, these data were for *Viola rotundifolia* at the beginning of the study (1993) and for *R. alleghaniensis* later in the study (2014). For *V. rotundifolia*, Ca/Al ratios were significantly lower in treated WS3 than on the reference WS7, but not in reference WS4. For *R. alleghaniensis*, Ca/Al ratios were significantly lower in WS3 than in both WS7 and WS4. Considering that foliar Ca/Al ratios may be useful indicators of soil nutrient conditions (Cronan & Grigal, 1995), these contrasts in foliar nutrients support soil nutrient data from this study showing treatment-mediated decreases in available Ca and increases in Al mobility.

4 | SYNTHESIS AND CONCLUSIONS

Several studies examining the effects of excess acidity and N deposition on the biogeochemistry of forest ecosystems throughout eastern North America have demonstrated deposition-mediated increases in loss of base cations (Currie, Aber, & Driscoll, 1999; Fernandez et al., 2003; Moore & Houle, 2009, 2013). The results for FEF suggest that, despite the apparent lack of an early response of exchangeable soil nutrients to acidification (Gilliam et al., 1994), detectable changes in some nutrient cations emerged after 25 yr of simulated acid deposition.

Current patterns in both surface soils and stream water chemistry suggest that chronic excess acidity, coupled with excess N deposition, has generally decreased base cation availability and increased Al mobility in this central Appalachian hardwood forest ecosystem. Not only does this represent a current concern for forest health, as there is evidence that suggests slowing growth rates for some prominent hardwood species at FEF (DeWalle et al., 2006; May et al., 2005), but it also represents an ongoing concern for the future management of such forests (Clark, Richkus, et al., 2019). This is especially relevant considering the high levels of acid and N deposition occurring in global temperate forests (Gilliam, 2016; Vet et al., 2014), the widespread signature of excess N in the Northern Hemisphere (Holtgrieve et al., 2011), and the likely long-term nature of recovery from N saturation of impacted forests (Gilliam et al., 2019; Schmitz et al., 2019; Stevens, 2016).

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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