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Temporal trends of sulfur levels in soils of northwest Ohio (USA) between 2002 and 2014

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ABSTRACT

Sulfur (S) is an essential nutrient for plant growth. Despite increasing reports of yield responses of crops to S fertilization, there is limited information about changes in the soil test concentrations of S. This study aimed to use a soil chemical analysis dataset from 2002 to 2014 to evaluate changes in soil S and other nutrient levels. The soil-test database comprised 8,428 topsoil samples (0 – 20 cm depth layer) collected from 143 farm fields located in the northwest Ohio counties of Defiance, Paulding, and Williams. Except for S, the database showed no significant changes in soil chemical properties from northwest

Ohio between 2002–2014. Soil sulfate (SO_4^{2-}) levels have linearly decreased by 63% from 2002 to 2014, reaching the range of concentration considered deficient for the main cereal crops. With no changes in soil organic matter (SOM) and pH, this result was attributed primarily to enactment of air quality regulations, since soil SO_4^{2-} decreases were directly correlated with the reductions of SO_2 emissions (-70%), SO_4^{2-} in rainwaters (-66%) and deposited (-52%) in NW Ohio between the years of 2002–2013. Further, combined increasing crop yields and insufficient compensation by fertilization had role on decreasing soil SO_4^{2-} levels. Current fertilization practices and wet deposition of S have not been sufficient to balance S removals from soil leading to the declines in the soil test S levels. It is imperative to paid more attention to practices that maintain soil S fertility levels to avoid yield penalties associated with soil S deficiencies.

Keywords: Atmospheric depositions – temporal trends – wet deposition – greenhouse gases – sulfur levels – soil sulfur fertility.

INTRODUCTION

Sulfur (S) is the ninth richest element on earth, being naturally found in the form of pure sulfide and sulfate minerals (Khan and Mazid, 2011). Although considered a secondary macronutrient, S is the fourth highest essential nutrient for plants (Franzen & Grant, 2008), performing several important roles in growth, development, and survival (Tripathi et al., 2014). Adequate soil levels of this nutrient are required in order to maintain satisfactory yields (Dick et al., 2008).

Plants uptake S mainly in the sulfate form (SO_4^{2-}), but soil retention of this anion, however, changes according to both soil chemical and physical properties (Raij, 2008). Soil surface layers have a lower capacity to retain SO_4^{2-} due to the predominance of negative charges generated by soil organic matter (SOM) and higher pH values (Scherer, 2009), and due to the presence of other competitive anions like phosphates and carbonates (Sokolova and Alekseeva, 2008; Eriksen, 2009).

The organic pool makes up almost 95% of the total S in non-calcareous soils and the mineralization of SOM pool often is capable of supplying much of the plant's requirement for S (Kovar and Grant, 2011). Therefore, any management practice that leads to decreases in both the amount of organic residue inputs and residual SOM will negatively affect S availability for crops (Blanco-Canqui et al., 2015; Kibet et al., 2016). Sulfur deficiencies are corrected by applying inorganic fertilizers that include elemental S, ammonium sulfate, simple superphosphate, FGD gypsum or phosphogypsum, and potassium and magnesium sulfates (Lucheta and Lambais, 2012; Camberato and Casteel, 2017).

Another critical source of soil S is atmospheric deposition (Aas et al., 2019). The S in the atmosphere is a result of energy production that comes from the burning of fossil fuels (Gautam et al., 2019). Gases containing S (e.g. sulfur dioxide - SO_2) that are generated by burning fossil fuels can return to the earth's surface dissolved in rainwaters or attached to solid particles (Eriksen, 2009). However, the adoption of strict regulations for emissions of greenhouse gases around the world has drastically reduced S atmospheric depositions (Haneklaus et al., 2008; Vieira-Filho et al., 2015; USEPA, 2020).

The U.S. approved its first federal regulation dealing with air quality control in 1955. This regulation, continuously improved until its current version and active since 1990, covers the control of acid rain and the emission levels for 189 gases (U.S. EPA, 2013). This decrease in S deposition has occurred at the same time as increased S uptake and extraction by plants that has greatly increased in the last 50 years. Not only is S removal due to higher plant yields that increased almost 200% for the most cultivated cereals (FAO, 2015), but also by the increases in the harvest indexes achieved by plant breeding (Pan and Deng, 2007; Koester et al., 2014).

Historically, over the most recent decades until now, S has generally had soil concentrations above the critical deficiency limits, mainly due to inputs of atmospheric depositions (Kost et al., 2008). As a result, S availability in soils has not been considered a limiting factor for plant growth and crop yields, resulting in S receiving less attention than other macronutrients such as N (Li et al., 2019). However, in the last decades, crops like soybean, wheat, and maize have shown positive yield and nutrition responses when supplying S under different pedoclimatic conditions in the USA (Sloam et al., 1999; Chen et al., 2005, 2008) and other countries around the world (Tisdale et al., 1986; Broch et al., 2011; Tiecher et al., 2012; Singh et al., 2013; Pias et al., 2019). These results provide evidence that both current fertilization practices and atmospheric depositions have not been sufficient to maintain adequate soil S levels, and consequently, leading to an inability of crops to realize their maximum yield potential (Mikkelsen and Norton, 2013).

Despite increasing reports of crop's positive response to S fertilization, there is limited information about temporal changes in soil S levels. This research hypothesizes that the current yield level of crops, the reduction of S atmospheric emissions and depositions, and the absence of compensation by the use of S fertilizers is leading to a gradual decrease in soil S levels over time. This study aimed to use a soil chemical analysis dataset from northwest Ohio (USA) farms to evaluate changes in soil S and other nutrient levels from 2002 to 2014.

MATERIAL AND METHODS

Characterization of the study area

The State of Ohio is located in what is called the eastern cornbelt of the United States. It is divided into 88 counties and totals approximately 116,096 km^2 of total area (Figure 1). The northwest (NW) region of Ohio is composed of 14 counties along with another 10 counties that are frequently reported as belonging to the NW region of the state (State of Ohio, 2010).

The climate in NW Ohio is classified as Dfa in the Köppen-Geiger scale (Köppen & Geiger, 1928) and is characterized by temperate temperatures that average between 3 ºC to 18 ºC in the three coldest months and above 10 ºC in the hottest month. There are well-defined winter and summer seasons and no dry periods. The data of annual accumulated rainfall and average temperatures to the northwest Ohio during the period of study (Figure 2) were obtained from National Oceanic and Atmospheric Administration (NOAA) weather stations.

Chemical elements deposition data were taken from the National Atmospheric

Deposition Program (NAPD) station located in Crawford and responsible for monitoring the NW Ohio area. Emissions data of S and N due primarily to coal burning were obtained from U.S. Energy Information Administration (U.S. EIA). Information about cereal crops area and historical yields in Ohio were taken from the National Agricultural Statistics Service (NASS).

Database description

The soil's database was originally made up of 9,080 soil chemical tests of soil samples (0-20 cm depth) of farms localized in the Ohio counties of Defiance, Paulding and Williams totaling an area of 5,900 ha (Figure 1 and Table 1).

The soil chemical data (Figure 3) included cation exchange capacity (CEC) by the sum of exchangeable cations, pH 1:1 in H_2O (McLean, 1982), H+Al by SMP (spell out SMP) solution (Shoemaker et al., 1961), soil organic matter (SOM) determined as the loss of mass by ignition at 360 ºC (Schulte & Hopkins, 1996), inorganic N extracted by 1 M KCl (Dahnke, 1990) and SO_4^{2-}, P, Ca^{2+}, Mg^{2+}, K^+ and Na^+ extracted by Mehlich III (Mehlich, 1984). The determination of SO_4^{2-}, was performed using the turbidimetric method according to Bartlett & Neller (1960). The soil chemical attributes which had values under or above one standard deviation (SD) when compared to the overall data average were considered outliers and removed from the statistical analysis.

The final database was composed by 8,428 soil chemical reports. The mean values and other descriptive statistics of chemical properties are shown in Figure 3.

Statistical Analysis

After the removal of the outliers, data from all soil chemical properties were separated by the respective years and submitted to the Shapiro-Wilk normality and Bartlett tests for variance homogeneity using the XLSTAT 2015 statistical package (ADDINSOFT, 2015). The P levels data did not show normal distribution and were transformed using the square root function. The data were then submitted to analysis of variance (ANOVA) and regression. Models were chosen based upon statistically significant ($p < 0.05$) values and the highest coefficients of determination (R^2). The correlation between independent variables was analyzed by the Pearson linear correlation ($p < 0.05$).

RESULTS AND DISCUSSION

Except for SO_4^{2-}, the database showed no significant differences in soil chemical properties from NW Ohio for the years of 2002 – 2014 ($p < 0.05$). Concentrations of SO_4^{2-}, however, significantly declined from 27.3 ± 6.1 to 10.0 ± 1.7 mg kg^{-1} (Figure 4). The concentrations were constant between 2002 and 2006 (average of 26.6 mg kg^{-1}), but then sharply decreased up to 2014, with an average concentration that was 52% lower than values observed in the first 4 years (2002 – 2006).

Soil SO_4^{2-} levels observed in 2014 (average of 10.1 ± 1.7 mg kg^{-1}) were in the range of concentrations (3.8 to 8.4 mg kg^{-1}) considered deficient for the main cereal crops (Blair et al., 1991; Chen et al., 2008; Horneck et al., 2011). If this trend is maintained, soil SO_4^{2-} concentrations will reach values considered restrictive for plant growth. Kost et al. (2008) evaluated 1,473 soil samples representing 443 of the 475 soil series in Ohio, and concluded that for a crop requiring 15 kg S ha^{-1}, most soils (62.5%) were classified as variably deficient, indicating the existence of potential for crop’s response to S supply. Camberato and Casteel (2017) summarized soil tests from northern and southern Indiana and concluded that the percentage of samples with soil SO_4^{2-} levels lower than 8 mg kg^{-1} has increased from less than 5% to about 70% in the period of 2005-2017.

Reduced availability of S has also the potential to compromise the uptake and assimilation of N by plants, given that S is a fundamental component of essential amino acids (Salvagiotti and Miralles, 2008; Hawkesford and Kok, 2011). On average, for each kg of crop´s S shortfall, 15 kg of N cannot be taken up by plants and, therefore, is subject to loss by leaching and/or volatilization (Haneklaus et al., 2008). Chen et al. (2008) verified interactions between N and S for the nutrition and yield of corn in Ohio soils and concluded that S addition increased yields even at the lower rates of N fertilizer, suggesting that N fertilizer use can be more efficiently utilized when combined with S sources. This can improve profitability in addition to reducing water contamination by sulfates and nitrates from fertilizers (Bindraban et al. 2015; Divito et al. 2015).

The occurrence of soil SO_4^{2-} fluctuations throughout the year is strongly dependent on variations in soil texture, the balance between atmospheric inputs, fertilizer addition, leaching, plant uptake, and microbial activity (Eriksen, 2009). Considering the organic pool, it is expected that soil levels of SO_4^{2-} will be lower over winter due to low mineralization rates associated with reduced soil temperature, moisture and microbial activity (Edwards, 1998). In NW Ohio, farmers usually grow a single crop each year (generally corn and soybean in rotation). Soil testing is generally performed in late autumn or early spring and represents a one-time picture of nutrient availability that is then used to make decisions regarding fertilization practices. As soils warm in the next spring and summer, more S is mineralized. This increases its availability for uptake and may mitigate some of the expected yield limitations associated with S nutrition.

Considering the agricultural soils evaluated, all under aerobic conditions, SOM and pH changes would be expected to have a key role in controlling soil SO_4^{2-} levels and its availability to crops (Lucheta and Lambais, 2012). The studied areas did not have significant changes in SOM levels between 2002-2014 (Figure 5), with an average value of 3.1%, and minimum and maximum values of 1.9 % and 4.3 % (Figure 3), respectively. The adoption of a long-term no-till system in all the evaluated farms (Table 1), with practices as growing cover crops, maintenance of crops straw on soil surface, and the absence of plowing kept SOM levels stable over the years (Blanco-Canqui et al., 2015; Kibet et al., 2016). Any practices that change SOM can affect SO_4^{2-} levels (Lu et al., 2016), since more than 95% of soil S is in the organic pool, and the mineralization process, which changes reduced S forms into SO_4^{2-} by oxidation, depends on the chemical (pH) and microbiological interaction with SOM (Dick et al., 2008; Eriksen, 2009).

The studied areas also did not have significant changes in pH values between 2002-2014 (Figure 5), with an average value of 6.56, and minimum and maximum values of 5.8 and 7.5 (Figure 3), respectively. Soil SO_4^{2-} adsorption has an inversely proportional relationship with pH (Fuentes-Lara et al., 2019), reaching its maximum at pH 3.0 and minimum at pH 6.5 (Scherer, 2009). Soils with slight acidity (i.e. pH values close to neutral), characteristic of surface layers (0-20 cm) in many agricultural soils including most of the soils in this study, have a predominance of negative charges (CEC), favoring the adsorption of cations instead of anions. However, soils with strongly acid conditions, more commonly found in subsurface profile layers, favor the retention of SO_4^{2-} by its adsorption on Fe and Al oxides as well on the edges of clay particles (Tabatai, 1987).

Given the pedoclimatic characteristics of the studied areas (Figures 2 and 3), neither reduced S-compounds nor S-minerals should have relevance in affecting soil SO_4^{2-} levels. Sulphur inputs by weathering of parent material is difficult to distinguish from other sources, such as mineralization, and don't provide more than 1 kg of S ha^{-1} $year^{-1}$, mainly because of its constant and slow release process (Haneklaus et al., 2000). Reduced sulfur compounds as sulfides (S^{2-}), elemental sulfur (S^0), and sulfites (SO_3^{2-}) are found, in small amounts, mostly in strongly acid and/or in reduced soils (Fuentes-Lara et al., 2019). Other sulfur minerals, as Ca and Mg sulfates, are significant for incipient soils and/or drier regions of the world, since in long-term agricultural soils or humid areas these minerals are leached by rainfall and rarely found (Dick and Chan, 2008).

The effects of anthropogenic SO_2 emissions results in increased S deposition that can cause acid rain and concurrent acidification of terrestrial and aquatic ecosystems worldwide (Lehmann, 2008). Despite these negative environmental effects, atmospheric S depositions also has been having an essential role in balancing soil S levels over the years. However, emissions of gases containing S, either from combustion of coal or other fossil fuels, systematically decreased in the United States since 1950. This change was especially evident after the 1990s decade when the U.S Environmental Protection Agency (U.S. EPA) started to adopt more rigid protocols to control the emission of greenhouse gases (U.S. EPA, 2013).

The SO_2 emissions by coal-burning from the Ohio electric power plants increased 46% between 1990 and 2001 whereas, in the period of 2002 – 2012, the emissions decreased by 70% (Figure 6, U.S. EIA, 2015). Similarly, to what was observed for soil SO_4^{2-} levels (Figure 4), the emissions of SO_2 were higher between 2002 – 2007, and then were significantly reduced after 2008, showing a linear decrease trend up to 2013 with averages 48% lower compared to the 2002 – 2007 period (Figure 6).

As a direct consequence of the reduction in SO_2 emissions, both wet depositions and S concentrations in rainwaters have been decreasing (Figures 7a and 7b). The major reductions in S wet depositions has been recorded in the States of Maryland, New York, West Virginia, Virginia, Pennsylvania and the region of Ohio River valley (U.S EPA, 1998). Data from NAPD (2014) indicate decreases of 66% in the concentration of SO_4^{2-} in rainwaters (Figure 7a) and 52% in the amount of SO_4^{2-} deposited in NW Ohio between the years of 2002 – 2013 (Figure 7b).

Soil SO_4^{2-} levels were positively correlated with both the concentrations of S SO_4^{2-} in rainwaters ($r = 0.89$, $p < 0.05$) and the amount of SO_4^{2-} deposited on soils ($r = 0.91$, $p < 0.05$). However, there was no correlation between these variables and the annual precipitation volume (Figure 2). Once SO_4^{2-} concentration in rainwater decreases, changes in the absolute amount of precipitation become more relevant in the final account of the SO_4^{2-} deposited on soil. Nevertheless, the variation in the average volume of precipitation in the evaluated period (Figure 2) did not correlate with the reduction of soil SO_4^{2-} levels. Besides the effects of precipitation volume on S depositions, the volume of rainwater that moves through the soil is important due to the potential of SO_4^{2-} leaching (Edwards, 1998; Scherer, 2009).

Further to the rainfall effects, the use of irrigation is another important aspect to considerate in the balance of soil SO_4^{2-}, especially in arid regions and/or for fruit and horticulture growing (USGS, 2018). Depending on the volume of water used to irrigate and the potential evapotranspiration (PE), irrigation can either increase or decrease soil SO_4^{2-} levels (Kivi and Bailey, 2017). If the applied irrigation volume is higher than PE, than there will be SO_4^{2-} leaching potential. Otherwise, if the irrigation volume is lower than PE, a positive balance of SO_4^{2-} will occur (Haneklaus et al., 2000). In the NW Ohio region, and especially in the evaluated farms, the use of irrigation to enhance production of grain crops is almost absent (Figure 2). In the three counties where the soil samples came from, the sum of the total irrigated area was about 356 and 570 ha in 2010 and 2015 years, respectively (USGS, 2018), and were mostly sprinkler and microirrigation system types which are not suitable for grain and forage crops.

Increases in nutrient export, mostly due to higher crop yields and harvest indices (HI), are also directly associated with decreases in soil S concentrations. In the past 50 years, major crops in Ohio such as soybean, corn, and wheat (USDA, 2014) had average yield increases of 104%, 258% and 166%, respectively (Figure 8). In the same period, the HI was increased 50% for soybeans (Koester et al., 2014) resulting in higher S export from soil since more of the total plant's biomass is being directed to harvested reproductive structures, in this case, grains.

Combining the northwest Ohio current average grain yields (Figure 8) with estimates of S removal by crops like soybean (3.25 kg of S Mg^{-1} of grains, Hitsuda et al., 2008), corn (1.30 kg of S Mg^{-1} of grains, Lamond, 1997), and wheat (1.50 kg of S Mg^{-1} of grains, Győri, 2005), it can be concluded that the average S export from soil has been higher than S depositions (Figure 7b). This contributes directly to the reduction of soil S levels over time.

Crop rotation also affects soil S concentration. Crops within the *Poaceae* family (wheat and corn) removed much more S from soil that crops within the *Fabaceae* family (soybean). Other crops, like species of *Brassica napus* and its cultivars, also have a high demand and capacity for soil S removal (up to 35 kg of S Mg^{-1} of grain, Mašauskiene and Mašauskas, 2012) mainly from soil subsurface layers (Franzen and Grant, 2008). Thus, both grain yield and growing crops with higher demand for S uptake and extraction, like oilseed rape crops (*Brassica napus* L.), can predispose the following crop to more severe S deficiencies (Mašauskiene and Mašauskas, 2012).

Sulfur reductions from wet depositions and increases in nutrient removal by crops create soil S deficits that can be compensated by the use of fertilizers. However, the use of S fertilizers in the USA has kept relatively constant since the beginning of the 1990s decade. The use of gypsum ($CaSO_4.2H_2O$) and elemental S in 2011 was similar to that the observed in 1990 (Figure 9). An exception to this trend is the application of fertilizers containing ammonium sulfate. However, utilization of this source is minor when compared to other options for N fertilization, and it is not considered a major fertilizer source of S (Figure 9).

As observed for S, the emissions of N compounds (i.e. NO, NO_2) from coal-burning plants in the State of Ohio decreased 38% between 1990 – 2001, and 77% between 2002 – 2012 (U.S. EIA, 2014). Consequently, a linear decrease of N concentrations in the rainwaters and wet depositions was also noticed (Table 2). However, in contrast to S, soil N concentrations in the NW Ohio were constant in the evaluated period, keeping the values close to the average of 39.0 g kg^{-1} (Table 2). The main difference between N compared to S is that between 1990 – 2011 the consumption of N fertilizers in North America increased by 47%. More specifically, the consumption of urea increased 67%, reaching 5.52 x 10^6 tons in 2011 (ERS USDA, 2013).

Differences in temporal trends for both soil S and N emissions in NW Ohio indicate that as soon as the SO_2 and NO emissions began to decrease, a cumulative deficit began for both elements. In this scenario, the use of fertilizers has become even more critical. Increases in the application of N fertilizers were an adequate and fast response to this condition, and efficiently balanced soil N concentrations, even considering the increases in the crop's yield and HI.

CONCLUSIONS

In this detailed study of soil SO_4^{2-} levels in northwest Ohio, the reduction of 70% in SO_2 emissions and 52% in SO_4^{2-} deposition, combined with increasing crop yields and insufficient compensation by fertilization, has led to a decreasing of 63% in soil SO_4^{2-} concentrations between 2002 – 2014. With this trend established, it is predicted that S soil concentrations will increasingly fall below critical levels needed to support optimum crops yields.

To overcome the S deficiencies in soil, several management options may be adopted including (i) adopting practices to increase soil organic matter levels and subsequent rates of S mineralization, and (ii) replace and replenish the S in soil lost by crop removal using S sources like organic and inorganic fertilizers or various types of industrial by-products.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author (leandromichalovicz@gmail.com) upon reasonable request.

DISCLAIMER

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Paulding%2BCounty%252CWilliams%2BCounty&wu_category_nms=--ALL%2BCategories--%252CIrrigation%252C%2BTotal%252CIrrigation%252C%2BCrop%252CIrrigation%252C%2BGolf%2BCourses

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Table 1 Description of the farms that provided samples which have composed the soil chemical analysis database

Farm	County	Number of samples	Area (ha)	Period (years)	Soil Series †	Additional Information
AD	Williams	900	809	2003-2013	Blount Loam, Glynwood Loam, Pewamo Silty Clay Loam, Mermill Loam, Fulton Loam, Haskins Loam	Long term no-till system, cover crops and wheat-soybean-wheat succession
BW	Williams	2,010	2,225	2000-2013	Blount Loam, Glywood Loam, Pewamo Silty Clay Loam, Haskins Loam	Milk production, corn (silage), soybean, alfalfa and wheat. Cattle manure applied to the soil every three years
KH	Defiance Paulding	1,393	1,012	2002-2013	Latty Silty Clay, Hoytville Silty Clay Loam, Fulton Loam, Nappanee Silty Clay Loam	Long term no-till system and cultivation of wheat-soybean succession.
MP	Williams	620	809	2002-2013	Blount Loam, Glywood Loam, Pewamo Silty Clay Loam	Long term no-till system and cultivation of wheat-soybean succession.
RC	Williams	236	303	2005-2013	Blount Loam, Glywood Loam, Pewamo Silty Clay Loam	Soil tillage before corn seeding.
RF	Defiance	2,746	1,618	2000-2014	Rensselaer Loam, Martinsville Loam, Whitaker Silt Loam, Blount Loam, Hoytville Silty Clay Loam	Long term no-till system and cultivation of wheat-soybean succession.
SM	Defiance Williams	1,015	809	2003-2013	Blount Loam, Glywood Loam, Pewamo Silty Clay Loam, Mermill Loam, Fulton Loam, Haskins Loam, Hoytville SCL, Nappanee SCL, Kibbie	No-till or reduced soil tilling. Cultivation of corn and soybean in succession.

	Loam, Colwood Loam

[†] Soil series classified according to Soil Survey Staff (1999).

Table 2 Soil N concentrations and wet depositions, N concentration in rainwaters, and emission of N compounds by electric power plants in the State of Ohio between 2002–2012

Year	N[†]	SD[‡]	[N] in rainwaters	N Depositions[§]	NO emissions[¶]
	----g kg^{-1}----		mg L^{-1}	kg ha^{-1}	x10^{6} Mg year^{-1}
2002	40.0	5.33	2.24	20.7	3.47
2003	40.3	5.37	2.17	16.1	3.31
2004	38.9	5.69	2.39	18.4	2.51
2005	39.4	5.29	2.10	21.2	2.38
2006	37.5	5.58	1.69	17.9	2.24
2007	38.9	5.69	1.77	18.2	2.27
2008	38.3	5.40	1.75	17.7	2.22
2009	38.6	6.03	1.43	15.8	1.10
2010	39.8	5.46	1.51	16.8	1.22
2011	38.7	5.19	1.38	10.9	1.21
2012	39.4	5.62	1.40	10.8	0.91
Regression	n.s	-	[N] =207**-0.10**year	N=1587*-0.80*year	NO =506-0.25**year
R^{2}	-	-	0.86	0.60	0.91

[†] Average concentration of inorganic N (NO_3^- + NH_4^+) in the soils of NW Ohio, calculated from the database; [‡] Standard deviation; [§] Depositions of inorganic N (NO_3^- + NH_4^+) obtained in the National Atmospheric Deposition Program obtained located in Crawford County (Lat. 40.55 Long. -82.99), northwest Ohio. [¶] Emission of N compounds by the coal burning in the electric power plants in the State of Ohio (EIA, 2014). *: $p < 0.05$, **: $p < 0.01$.

FIGURE CAPTIONS

Figure 1 Location of northwest Ohio counties in the state of Ohio, the United States of America**.**

Figure 2. Accumulated annual rainfall (circles) and average annual temperature (squares) in the northwest region of Ohio between the years of 2002 and 2014. The dotted lines represent the average values of annual precipitation and rainfall in the last 100 years. Source: NOAA (2015).

Figure 3 Descriptive statistics of the variables in the soil (0.0 – 0.20 m depth soil layer) data set. The central rectangle of the boxplots spans the first to the third input quartile. The thin line inside the rectangle is the median, the bold line is the mean, and the horizontal lines to the left and right of the rectangle extend to the minimum and maximum values, respectively. The solid circles represent the minimum and maximum outliers. † Cation exchange capacity; ‡ Soil organic matter; § Inorganic N levels ($NO_3^- + NH_4^+$).

Figure 4 Average sulfate (SO_4^{2-}) levels in topsoils (0 – 20 cm) from northwest Ohio for the years of 2002 – 2014. Bars indicate twice the standard deviation from the mean for each year. Statistical significance at $p < 0.01$ is denoted by two asterisks (**).

Figure 5 Average pH values and soil organic matter (SOM) levels in topsoils (0 – 20 cm) from northwest Ohio for the years of 2002 – 2014. Bars indicate the standard deviation from the mean at each year.

Figure 6 SO_2 emissions by coal burning for the production of electric power in northwest Ohio between 2002 and 2013. Statistical significance ($p < 0.01$) is denoted with two asterisks (**). Data from U.S. EIA (2015).

Figure 7 Sulfate (SO_4^{2-}) concentrations in rainwaters (a) and depositions (b) in northwest Ohio soils between the years of 2002 and 2013. Statistical significance ($p < 0.01$) is denoted with two asterisks (**). Bars indicate the standard deviation from the mean for each year. Source: Data from the National Atmospheric Deposition Program station (NADP, 2014), situated in the Crawford County (Lat. 40.55 Long. -82.99), northwest Ohio.

Figure 8 Average yields of corn, soybean and wheat in northwest Ohio between the years of 1950 and 2013. For the utilization of the equations, the x value should be accounted sequentially by considering 1950 =1 and 2013 = 64. Statistical significance ($p < 0.01$) is denoted with two asterisks (**). Source: USDA-NASS (2014).

Figure 9 Agricultural consumption of the main sources of S fertilizers in the USA between the years of 1990 and 2011. Statistical significance ($p < 0.01$) is denoted with two asterisks (**). Source: ERS USDA (2013).

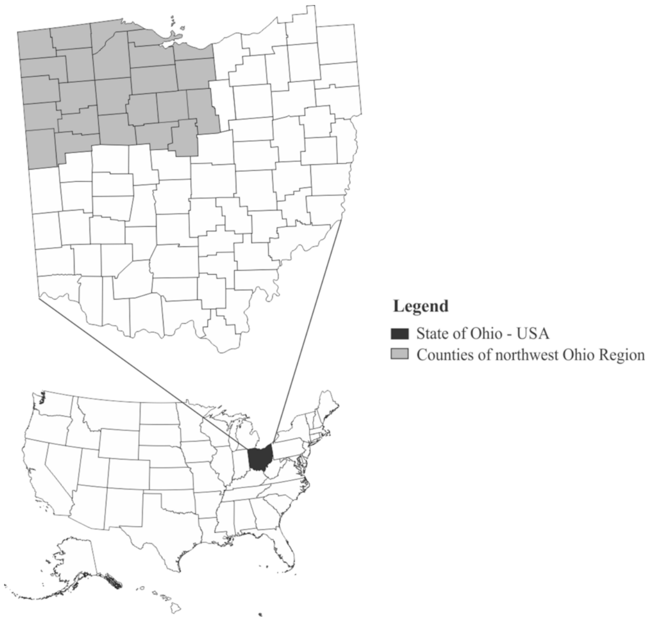

FIGURE 1.tif

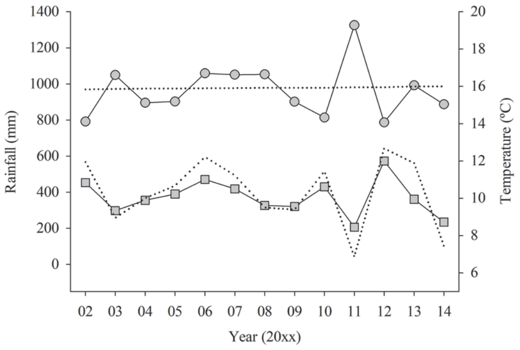
1400
1200
1000
800
600
400
200
0
Rainfall (mm)
20
18
16
14
12
10
8
6
Temperature (°C)
02
03
04
05
06
07
08
09
10
11
12
13
14
Year (20xx)

FIGURE 2.TIF

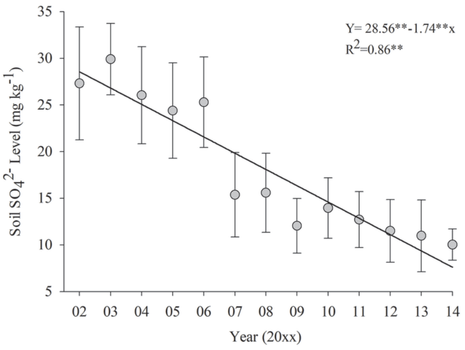
Y= 28.56**-1.74**x
R2=0.86**
Soil SO4 2- Level (mg kg-1)
35
30
25
20
15
10
5
02
03
04
05
06
07
08
09
10
11
12
13
14
Year (20xx)

FIGURE 4.TIF

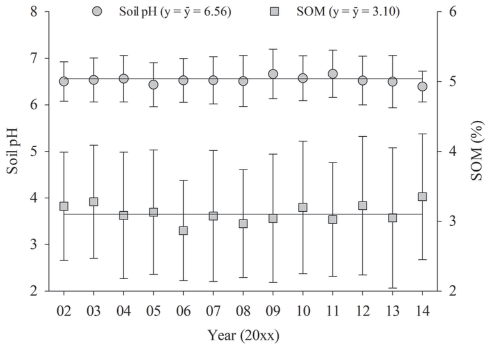
● Soil pH (y = ȳ = 6.56)
■ SOM (y = ȳ = 3.10)
Soil pH
8
7
6
5
4
3
2
SOM (%)
6
5
4
3
2
02
03
04
05
06
07
08
09
10
11
12
13
14
Year (20xx)

FIGURE 5.TIF

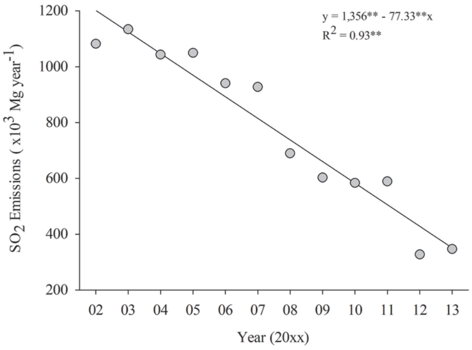
y = 1,356** - 77.33**x
R^2 = 0.93**
SO_2 Emissions (x10^3 Mg year^{-1})
1200
1000
800
600
400
200
02
03
04
05
06
07
08
09
10
11
12
13
Year (20xx)

FIGURE 6.TIF

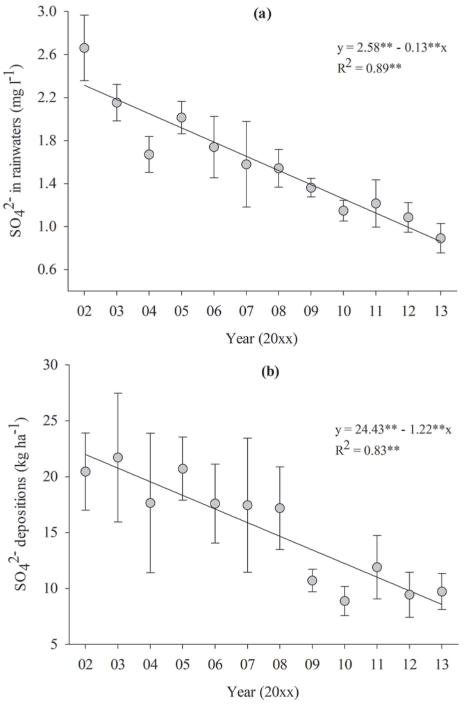
(a)
y = 2.58** - 0.13**x
R^2 = 0.89**
SO_4^{2-} in rainwaters (mg l^{-1})
3.0
2.6
2.2
1.8
1.4
1.0
0.6
02
03
04
05
06
07
08
09
10
11
12
13
Year (20xx)
(b)
y = 24.43** - 1.22**x
R^2 = 0.83**
SO_4^{2-} depositions (kg ha^{-1})
30
25
20
15
10
5
02
03
04
05
06
07
08
09
10
11
12
13
Year (20xx)

FIGURE 7.TIF

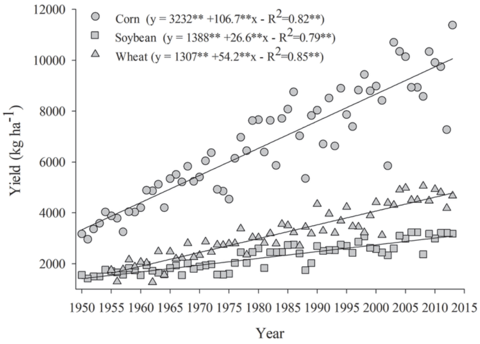
12000
10000
8000
6000
4000
2000
Yield (kg ha^{-1})
Corn (y = 3232** +106.7**x - R^2=0.82**)
Soybean (y = 1388** +26.6**x - R^2=0.79**)
Wheat (y = 1307** +54.2**x - R^2=0.85**)
1950
1955
1960
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
Year

FIGURE 8.TIF

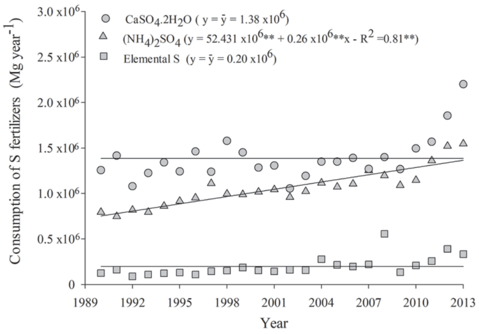
3.0 x10⁶
2.5 x10⁶
2.0 x10⁶
1.5 x10⁶
1.0 x10⁶
0.5 x10⁶
0
Consumption of S fertilizers (Mg year⁻¹)
● CaSO4.2H2O (y = ȳ = 1.38 x10⁶)
▲ (NH4)2SO4 (y = 52.431 x10⁶** + 0.26 x10⁶**x - R² =0.81**)
■ Elemental S (y = ȳ = 0.20 x10⁶)
1989
1992
1995
1998
2001
2004
2007
2010
2013
Year

FIGURE 9.TIF

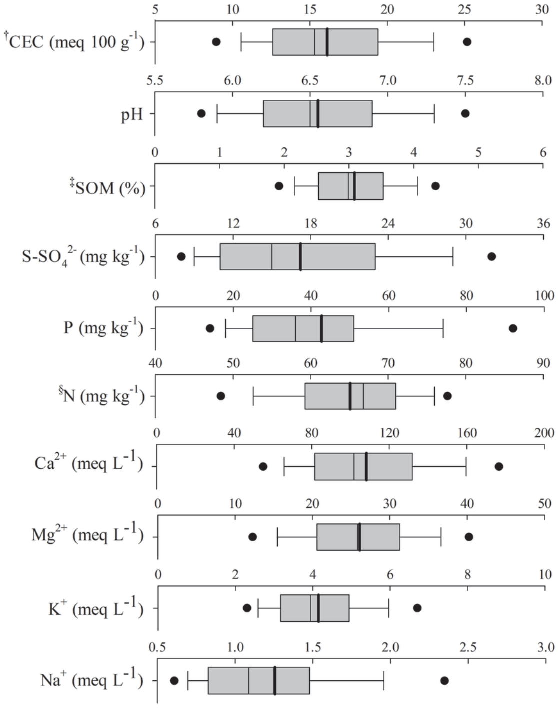
5 10 15 20 25 30
†CEC (meq 100 g-1)
5.5 6.0 6.5 7.0 7.5 8.0
pH
0 1 2 3 4 5 6
‡SOM (%)
6 12 18 24 30 36
S-SO42- (mg kg-1)
0 20 40 60 80 100
P (mg kg-1)
40 50 60 70 80 90
§N (mg kg-1)
0 40 80 120 160 200
Ca2+ (meq L-1)
0 10 20 30 40 50
Mg2+ (meq L-1)
0 2 4 6 8 10
K+ (meq L-1)
0.5 1.0 1.5 2.0 2.5 3.0
Na+ (meq L-1)

FIGURE_3.TIF

Temporal trends of sulfur levels in soils of northwest Ohio (USA) between 2002 and 2014

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Running Title: Temporal trends of sulfur levels in soils of northwest Ohio

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ABSTRACT

Sulfur (S) is an essential nutrient for plant growth. Despite increasing reports of yield responses of crops to S fertilization, there is limited information about changes in the soil test concentrations of S. This study aimed to use a soil chemical analysis dataset from 2002 to 2014 to evaluate changes in soil S and other nutrient levels. The soil-test database comprised 8,428 topsoil samples (0 – 20 cm depth layer) collected from 143 farm fields located in the northwest Ohio counties of Defiance, Paulding, and Williams. Except for S, the database showed no significant changes in soil chemical properties from northwest Ohio between 2002–2014. Soil sulfate (SO_4^{2-}) levels have linearly decreased by 63% from 2002 to 2014, reaching the range of concentration considered deficient for the main cereal crops. With no changes in soil organic matter (SOM) and pH, this result was attributed primarily to enactment of air quality regulations, since soil SO_4^{2-} decreases were directly correlated with the reductions of SO_2 emissions (-70%), SO_4^{2-} in rainwaters (-66%) and deposited (-52%) in NW Ohio between the years of 2002–2013. Further, combined increasing crop yields and insufficient compensation by fertilization had role on decreasing soil SO_4^{2-} levels. Current fertilization practices and wet deposition of S have not been sufficient to balance S removals from soil leading to the declines in the soil test S levels. It is imperative to paid more attention to practices that maintain soil S fertility levels to avoid yield penalties associated with soil S deficiencies.

Keywords: Atmospheric depositions – temporal trends – wet deposition – greenhouse gases – sulfur levels – soil sulfur fertility.

INTRODUCTION

Sulfur (S) is the ninth richest element on earth, being naturally found in the form of pure sulfide and sulfate minerals (Khan and Mazid, 2011). Although considered a secondary macronutrient, S is the fourth highest essential nutrient for plants (Franzen & Grant, 2008), performing several important roles in growth, development, and survival (Tripathi et al., 2014). Adequate soil levels of this nutrient are required in order to maintain satisfactory yields (Dick et al., 2008).

Plants uptake S mainly in the sulfate form (SO_4^{2-}), but soil retention of this anion, however, changes according to both soil chemical and physical properties (Raij, 2008). Soil surface layers have a lower capacity to retain SO_4^{2-} due to the predominance of negative charges generated by soil organic matter (SOM) and higher pH values (Scherer, 2009), and due to the presence of other competitive anions like phosphates and carbonates (Sokolova and Alekseeva, 2008; Eriksen, 2009).

The organic pool makes up almost 95% of the total S in non-calcareous soils and the mineralization of SOM pool often is capable of supplying much of the plant's requirement for S (Kovar and Grant, 2011). Therefore, any management practice that leads to decreases in both the amount of organic residue inputs and residual SOM will negatively affect S availability for crops (Blanco-Canqui et al., 2015; Kibet et al., 2016). Sulfur deficiencies are corrected by applying inorganic fertilizers that include elemental S, ammonium sulfate, simple superphosphate, FGD gypsum or phosphogypsum, and potassium and magnesium sulfates (Lucheta and Lambais, 2012; Camberato and Casteel, 2017).

Another critical source of soil S is atmospheric deposition (Aas et al., 2019). The S in the atmosphere is a result of energy production that comes from the burning of fossil fuels (Gautam et al., 2019). Gases containing S (e.g. sulfur dioxide - SO_2) that are generated by burning fossil fuels can return to the earth's surface dissolved in rainwaters or attached to solid particles (Eriksen, 2009). However, the adoption of strict regulations for emissions of greenhouse gases around the world has drastically reduced S atmospheric depositions (Haneklaus et al., 2008; Vieira-Filho et al., 2015; USEPA, 2020).

The U.S. approved its first federal regulation dealing with air quality control in 1955. This regulation, continuously improved until its current version and active since 1990, covers the control of acid rain and the emission levels for 189 gases (U.S. EPA, 2013). This decrease in S deposition has occurred at the same time as increased S uptake and extraction by plants that has greatly increased in the last 50 years. Not only is S removal due to higher plant yields that increased almost 200% for the most cultivated cereals (FAO, 2015), but also by the increases in the harvest indexes achieved by plant breeding (Pan and Deng, 2007; Koester et al., 2014).

Historically, over the most recent decades until now, S has generally had soil concentrations above the critical deficiency limits, mainly due to inputs of atmospheric depositions (Kost et al., 2008). As a result, S availability in soils has not been considered a limiting factor for plant growth and crop yields, resulting in S receiving less attention than other macronutrients such as N (Li et al., 2019). However, in the last decades, crops like soybean, wheat, and maize have shown positive yield and nutrition responses when supplying S under different pedoclimatic conditions in the USA (Sloam et al., 1999; Chen et al., 2005, 2008) and other countries around the world (Tisdale et al., 1986; Broch et al., 2011; Tiecher et al., 2012; Singh et al., 2013; Pias et al., 2019). These results provide evidence that both current fertilization practices and atmospheric depositions have not been sufficient to maintain adequate soil S levels, and consequently, leading to an inability of crops to realize their maximum yield potential (Mikkelsen and Norton, 2013).

Despite increasing reports of crop's positive response to S fertilization, there is limited information about temporal changes in soil S levels. This research hypothesizes that the current yield level of crops, the reduction of S atmospheric emissions and depositions, and the absence of compensation by the use of S fertilizers is leading to a gradual decrease in soil S levels over time. This study aimed to use a soil chemical analysis dataset from northwest Ohio (USA) farms to evaluate changes in soil S and other nutrient levels from 2002 to 2014.

MATERIAL AND METHODS

Characterization of the study area

The State of Ohio is located in what is called the eastern cornbelt of the United States. It is divided into 88 counties and totals approximately 116,096 km^2 of total area (Figure 1). The northwest (NW) region of Ohio is composed of 14 counties along with another 10 counties that are frequently reported as belonging to the NW region of the state (State of Ohio, 2010).

The climate in NW Ohio is classified as Dfa in the Köppen-Geiger scale (Köppen & Geiger, 1928) and is characterized by temperate temperatures that average between 3 ºC to 18 ºC in the three coldest months and above 10 ºC in the hottest month. There are well-defined winter and summer seasons and no dry periods. The data of annual accumulated rainfall and average temperatures to the northwest Ohio during the period of study (Figure 2) were obtained from National Oceanic and Atmospheric Administration (NOAA) weather stations.

Chemical elements deposition data were taken from the National Atmospheric Deposition Program (NAPD) station located in Crawford and responsible for monitoring the NW Ohio area. Emissions data of S and N due primarily to coal burning were obtained from U.S. Energy Information Administration (U.S. EIA). Information about cereal crops area and historical yields in Ohio were taken from the National Agricultural Statistics Service (NASS).

Database description

The soil's database was originally made up of 9,080 soil chemical tests of soil samples (0-20 cm depth) of farms localized in the Ohio counties of Defiance, Paulding and Williams totaling an area of 5,900 ha (Figure 1 and Table 1).

The soil chemical data (Figure 3) included cation exchange capacity (CEC) by the sum of exchangeable cations, pH 1:1 in H_2O (McLean, 1982), H+Al by SMP (spell out SMP) solution (Shoemaker et al., 1961), soil organic matter (SOM) determined as the loss of mass by ignition at 360 ºC (Schulte & Hopkins, 1996), inorganic N extracted by 1 M KCl (Dahnke, 1990) and SO_4^{2-}, P, Ca^{2+}, Mg^{2+}, K^+ and Na^+ extracted by Mehlich III (Mehlich, 1984). The determination of SO_4^{2-}, was performed using the turbidimetric method according to Bartlett & Neller (1960). The soil chemical attributes which had values under or above one standard deviation (SD) when compared to the overall data average were considered outliers and removed from the statistical analysis.

The final database was composed by 8,428 soil chemical reports. The mean values and other descriptive statistics of chemical properties are shown in Figure 3.

Statistical Analysis

After the removal of the outliers, data from all soil chemical properties were separated by the respective years and submitted to the Shapiro-Wilk normality and Bartlett tests for variance homogeneity using the XLSTAT 2015 statistical package (ADDINSOFT, 2015). The P levels data did not show normal distribution and were transformed using the square root function. The data were then submitted to analysis of variance (ANOVA) and regression. Models were chosen based upon statistically significant ($p < 0.05$) values and the highest coefficients of determination (R^2). The correlation between independent variables was analyzed by the Pearson linear correlation ($p < 0.05$).

RESULTS AND DISCUSSION

Except for SO_4^{2-}, the database showed no significant differences in soil chemical properties from NW Ohio for the years of 2002 – 2014 ($p < 0.05$). Concentrations of SO_4^{2-}, however, significantly declined from 27.3 ± 6.1 to 10.0 ± 1.7 mg kg^{-1} (Figure 4). The concentrations were constant between 2002 and 2006 (average of 26.6 mg kg^{-1}), but then sharply decreased up to 2014, with an average concentration that was 52% lower than values observed in the first 4 years (2002 – 2006).

Soil SO_4^{2-} levels observed in 2014 (average of 10.1 ± 1.7 mg kg^{-1}) were in the range of concentrations (3.8 to 8.4 mg kg^{-1}) considered deficient for the main cereal crops (Blair et al., 1991; Chen et al., 2008; Horneck et al., 2011). If this trend is maintained, soil SO_4^{2-} concentrations will reach values considered restrictive for plant growth. Kost et al. (2008) evaluated 1,473 soil samples representing 443 of the 475 soil series in Ohio, and concluded that for a crop requiring 15 kg S ha^{-1}, most soils (62.5%) were classified as variably deficient, indicating the existence of potential for crop's response to S supply. Camberato and Casteel (2017) summarized soil tests from northern and southern Indiana and concluded that the percentage of samples with soil SO_4^{2-} levels lower than 8 mg kg^{-1} has increased from less than 5% to about 70% in the period of 2005-2017.

Reduced availability of S has also the potential to compromise the uptake and assimilation of N by plants, given that S is a fundamental component of essential amino acids (Salvagiotti and Miralles, 2008; Hawkesford and Kok, 2011). On average, for each kg of crop´s S shortfall, 15 kg of N cannot be taken up by plants and, therefore, is subject to loss by leaching and/or volatilization (Haneklaus et al., 2008). Chen et al. (2008) verified interactions between N and S for the nutrition and yield of corn in Ohio soils and concluded that S addition increased yields even at the lower rates of N fertilizer, suggesting that N fertilizer use can be more efficiently utilized when combined with S sources. This can improve profitability in addition to reducing water contamination by sulfates and nitrates from fertilizers (Bindraban et al. 2015; Divito et al. 2015).

The occurrence of soil SO_4^{2-} fluctuations throughout the year is strongly dependent on variations in soil texture, the balance between atmospheric inputs, fertilizer addition, leaching, plant uptake, and microbial activity (Eriksen, 2009). Considering the organic pool, it is expected that soil levels of SO_4^{2-} will be lower over winter due to low mineralization rates associated with reduced soil temperature, moisture and microbial activity (Edwards, 1998). In NW Ohio, farmers usually grow a single crop each year (generally corn and soybean in rotation). Soil testing is generally performed in late autumn or early spring and represents a one-time picture of nutrient availability that is then used to make decisions regarding fertilization practices. As soils warm in the next spring and summer, more S is mineralized. This increases its availability for uptake and may mitigate some of the expected yield limitations associated with S nutrition.

Considering the agricultural soils evaluated, all under aerobic conditions, SOM and pH changes would be expected to have a key role in controlling soil SO_4^{2-} levels and its availability to crops (Lucheta and Lambais, 2012). The studied areas did not have significant changes in SOM levels between 2002-2014 (Figure 5), with an average value of 3.1%, and minimum and maximum values of 1.9 % and 4.3 % (Figure 3), respectively. The adoption of a long-term no-till system in all the evaluated farms (Table 1), with practices as growing cover crops, maintenance of crops straw on soil surface, and the absence of plowing kept SOM levels stable over the years (Blanco-Canqui et al., 2015; Kibet et al., 2016). Any practices that change SOM can affect SO_4^{2-} levels (Lu et al., 2016), since more than 95% of soil S is in the organic pool, and the mineralization process, which changes reduced S forms into SO_4^{2-} by oxidation, depends on the chemical (pH) and microbiological interaction with SOM (Dick et al., 2008; Eriksen, 2009).

The studied areas also did not have significant changes in pH values between 2002-2014 (Figure 5), with an average value of 6.56, and minimum and maximum values of 5.8 and 7.5 (Figure 3), respectively. Soil SO_4^{2-} adsorption has an inversely proportional relationship with pH (Fuentes-Lara et al., 2019), reaching its maximum at pH 3.0 and minimum at pH 6.5 (Scherer, 2009). Soils with slight acidity (i.e. pH values close to neutral), characteristic of surface layers (0-20 cm) in many agricultural soils including most of the soils in this study, have a predominance of negative charges (CEC), favoring the adsorption of cations instead of anions. However, soils with strongly acid conditions, more commonly found in subsurface profile layers, favor the retention of SO_4^{2-} by its adsorption on Fe and Al oxides as well on the edges of clay particles (Tabatai, 1987).

Given the pedoclimatic characteristics of the studied areas (Figures 2 and 3), neither reduced S-compounds nor S-minerals should have relevance in affecting soil SO_4^{2-} levels. Sulphur inputs by weathering of parent material is difficult to distinguish from other sources, such as mineralization, and don't provide more than 1 kg of S ha^{-1} year^{-1}, mainly because of its constant and slow release process (Haneklaus et al., 2000). Reduced sulfur compounds as sulfides (S^{2-}), elemental sulfur (S^0), and sulfites (SO_3^{2-}) are found, in small amounts, mostly in strongly acid and/or in reduced soils (Fuentes-Lara et al., 2019). Other sulfur minerals, as Ca and Mg sulfates, are significant for incipient soils and/or drier regions of the world, since in long-term agricultural soils or humid areas these minerals are leached by rainfall and rarely found (Dick and Chan, 2008).

The effects of anthropogenic SO_2 emissions results in increased S deposition that can cause acid rain and concurrent acidification of terrestrial and aquatic ecosystems worldwide (Lehmann, 2008). Despite these negative environmental effects, atmospheric S depositions also has been having an essential role in balancing soil S levels over the years. However, emissions of gases containing S, either from combustion of coal or other fossil fuels, systematically decreased in the United States since 1950. This change was especially evident after the 1990s decade when the U.S Environmental Protection Agency (U.S. EPA) started to adopt more rigid protocols to control the emission of greenhouse gases (U.S. EPA, 2013).

The SO_2 emissions by coal-burning from the Ohio electric power plants increased 46% between 1990 and 2001 whereas, in the period of 2002 – 2012, the emissions decreased by 70% (Figure 6, U.S. EIA, 2015). Similarly, to what was observed for soil SO_4^{2-} levels (Figure 4), the emissions of SO_2 were higher between 2002 – 2007, and then were significantly reduced after 2008, showing a linear decrease trend up to 2013 with averages 48% lower compared to the 2002 – 2007 period (Figure 6).

As a direct consequence of the reduction in SO_2 emissions, both wet depositions and S concentrations in rainwaters have been decreasing (Figures 7a and 7b). The major reductions in S wet depositions has been recorded in the States of Maryland, New York, West Virginia, Virginia, Pennsylvania and the region of Ohio River valley (U.S EPA, 1998). Data from NAPD (2014) indicate decreases of 66% in the concentration of SO_4^{2-} in rainwaters (Figure 7a) and 52% in the amount of SO_4^{2-} deposited in NW Ohio between the years of 2002 – 2013 (Figure 7b).

Soil SO_4^{2-} levels were positively correlated with both the concentrations of S SO_4^{2-} in rainwaters (r = 0.89, $p < 0.05$) and the amount of SO_4^{2-} deposited on soils (r = 0.91, $p < 0.05$). However, there was no correlation between these variables and the annual precipitation volume (Figure 2). Once SO_4^{2-} concentration in rainwater decreases, changes in the absolute amount of precipitation become more relevant in the final account of the SO_4^{2-} deposited on soil. Nevertheless, the variation in the average volume of precipitation in the evaluated period (Figure 2) did not correlate with the reduction of soil SO_4^{2-} levels. Besides the effects of precipitation volume on S depositions, the volume of rainwater that moves through the soil is important due to the potential of SO_4^{2-} leaching (Edwards, 1998; Scherer, 2009).

Further to the rainfall effects, the use of irrigation is another important aspect to considerate in the balance of soil SO_4^{2-}, especially in arid regions and/or for fruit and horticulture growing (USGS, 2018). Depending on the volume of water used to irrigate and the potential evapotranspiration (PE), irrigation can either increase or decrease soil SO_4^{2-} levels (Kivi and Bailey, 2017). If the applied irrigation volume is higher than PE, than there will be SO_4^{2-} leaching potential. Otherwise, if the irrigation volume is lower than PE, a positive balance of SO_4^{2-} will occur (Haneklaus et al., 2000). In the NW Ohio region, and especially in the evaluated farms, the use of irrigation to enhance production of grain crops is almost absent (Figure 2). In the three counties where the soil samples came from, the sum of the total irrigated area was about 356 and 570 ha in 2010 and 2015 years, respectively (USGS, 2018), and were mostly sprinkler and microirrigation system types which are not suitable for grain and forage crops.

Increases in nutrient export, mostly due to higher crop yields and harvest indices (HI), are also directly associated with decreases in soil S concentrations. In the past 50 years, major crops in Ohio such as soybean, corn, and wheat (USDA, 2014) had average yield increases of 104%, 258% and 166%, respectively (Figure 8). In the same period, the HI was increased 50% for soybeans (Koester et al., 2014) resulting in higher S export from soil since more of the total plant’s biomass is being directed to harvested reproductive structures, in this case, grains.

Combining the northwest Ohio current average grain yields (Figure 8) with estimates of S removal by crops like soybean (3.25 kg of S Mg^{-1} of grains, Hitsuda et al., 2008), corn (1.30 kg of S Mg^{-1} of grains, Lamond, 1997), and wheat (1.50 kg of S Mg^{-1} of grains, Győri, 2005), it can be concluded that the average S export from soil has been higher than S depositions (Figure 7b). This contributes directly to the reduction of soil S levels over time.

Crop rotation also affects soil S concentration. Crops within the *Poaceae* family (wheat and corn) removed much more S from soil that crops within the *Fabaceae* family (soybean). Other crops, like species of *Brassica napus* and its cultivars, also have a high demand and capacity for soil S removal (up to 35 kg of S Mg^{-1} of grain, Mašauskiene and Mašauskas, 2012) mainly from soil subsurface layers (Franzen and Grant, 2008). Thus, both grain yield and growing crops with higher demand for S uptake and extraction, like oilseed rape crops (*Brassica napus* L.), can predispose the following crop to more severe S deficiencies (Mašauskiene and Mašauskas, 2012).

Sulfur reductions from wet depositions and increases in nutrient removal by crops create soil S deficits that can be compensated by the use of fertilizers. However, the use of S fertilizers in the USA has kept relatively constant since the beginning of the 1990s decade. The use of gypsum ($CaSO_4.2H_2O$) and elemental S in 2011 was similar to that the observed in 1990 (Figure 9). An exception to this trend is the application of fertilizers containing ammonium sulfate. However, utilization of this source is minor when compared to other options for N fertilization, and it is not considered a major fertilizer source of S (Figure 9).

As observed for S, the emissions of N compounds (i.e. NO, NO_2) from coal-burning plants in the State of Ohio decreased 38% between 1990 – 2001, and 77% between 2002 – 2012 (U.S. EIA, 2014). Consequently, a linear decrease of N concentrations in the rainwaters and wet depositions was also noticed (Table 2). However, in contrast to S, soil N concentrations in the NW Ohio were constant in the evaluated period, keeping the values close to the average of 39.0 g kg^{-1} (Table 2). The main difference between N compared to S is that between 1990 – 2011 the consumption of N fertilizers in North America increased by 47%. More specifically, the consumption of urea increased 67%, reaching 5.52×10^6 tons in 2011 (ERS USDA, 2013).

Differences in temporal trends for both soil S and N emissions in NW Ohio indicate that as soon as the SO_2 and NO emissions began to decrease, a cumulative deficit began for both elements. In this scenario, the use of fertilizers has become even more critical. Increases in the application of N fertilizers were an adequate and fast response to this condition, and efficiently balanced soil N concentrations, even considering the increases in the crop's yield and HI.

CONCLUSIONS

In this detailed study of soil SO_4^{2-} levels in northwest Ohio, the reduction of 70% in SO_2 emissions and 52% in SO_4^{2-} deposition, combined with increasing crop yields and insufficient compensation by fertilization, has led to a decreasing of 63% in soil SO_4^{2-} concentrations between 2002 – 2014. With this trend established, it is predicted that S soil concentrations will increasingly fall below critical levels needed to support optimum crops yields.

To overcome the S deficiencies in soil, several management options may be adopted including (i) adopting practices to increase soil organic matter levels and subsequent rates of S mineralization, and (ii) replace and replenish the S in soil lost by crop removal using S sources like organic and inorganic fertilizers or various types of industrial by-products.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author (leandromichalovicz@gmail.com) upon reasonable request.

DISCLAIMER

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1 Description of the farms that provided samples which have composed the soil chemical analysis database

Farm	County	Number of samples	Area (ha)	Period (years)	Soil Series [†]	Additional Information
AD	Williams	900	809	2003-2013	Blount Loam, Glynwood Loam, Pewamo Silty Clay Loam, Mermill Loam, Fulton Loam, Haskins Loam	Long term no-till system, cover crops and wheat-soybean-wheat succession
BW	Williams	2,010	2,225	2000-2013	Blount Loam, Glywood Loam, Pewamo Silty Clay Loam, Haskins Loam	Milk production, corn (silage), soybean, alfalfa and wheat. Cattle manure applied to the soil every three years
KH	Defiance Paulding	1,393	1,012	2002-2013	Latty Silty Clay, Hoytville Silty Clay Loam, Fulton Loam, Nappanee Silty Clay Loam	Long term no-till system and cultivation of wheat-soybean succession.
MP	Williams	620	809	2002-2013	Blount Loam, Glywood Loam, Pewamo Silty Clay Loam	Long term no-till system and cultivation of wheat-soybean succession.
RC	Williams	236	303	2005-2013	Blount Loam, Glywood Loam, Pewamo Silty Clay Loam	Soil tillage before corn seeding.
RF	Defiance	2,746	1,618	2000-2014	Rensselaer Loam, Martinsville Loam, Whitaker Silt Loam, Blount Loam, Hoytville Silty Clay Loam	Long term no-till system and cultivation of wheat-soybean succession.
SM	Defiance Williams	1,015	809	2003-2013	Blount Loam, Glynwood Loam, Pewamo Silty Clay Loam, Mermill Loam, Fulton Loam, Haskins Loam, Hoytville SCL, Nappanee SCL, Kibbie Loam, Colwood Loam	No-till or reduced soil tilling. Cultivation of corn and soybean in succession.

[†] Soil series classified according to Soil Survey Staff (1999).

Table 2 Soil N concentrations and wet depositions, N concentration in rainwaters, and emission of N compounds by electric power plants in the State of Ohio between 2002–2012

Year	N[†]	SD[‡]	[N] in rainwaters	N Depositions[§]	NO emissions[¶]
	----g kg^{-1}----		mg L^{-1}	kg ha^{-1}	x10^{6} Mg year^{-1}
2002	40.0	5.33	2.24	20.7	3.47
2003	40.3	5.37	2.17	16.1	3.31
2004	38.9	5.69	2.39	18.4	2.51
2005	39.4	5.29	2.10	21.2	2.38
2006	37.5	5.58	1.69	17.9	2.24
2007	38.9	5.69	1.77	18.2	2.27
2008	38.3	5.40	1.75	17.7	2.22
2009	38.6	6.03	1.43	15.8	1.10
2010	39.8	5.46	1.51	16.8	1.22
2011	38.7	5.19	1.38	10.9	1.21
2012	39.4	5.62	1.40	10.8	0.91
Regression	n.s	-	[N] =207**-0.10**year	N=1587*-0.80*year	NO =506-0.25**year
R^{2}	-	-	0.86	0.60	0.91

[†] Average concentration of inorganic N (NO_3^- + NH_4^+) in the soils of NW Ohio, calculated from the database; [‡] Standard deviation; [§] Depositions of inorganic N (NO_3^- + NH_4^+) obtained in the National Atmospheric Deposition Program obtained located in Crawford County (Lat. 40.55 Long. -82.99), northwest Ohio. [¶] Emission of N compounds by the coal burning in the electric power plants in the State of Ohio (EIA, 2014). *: $p < 0.05$, **: $p < 0.01$.

FIGURE CAPTIONS

Figure 1 Location of northwest Ohio counties in the state of Ohio, the United States of America**.**

Figure 2. Accumulated annual rainfall (circles) and average annual temperature (squares) in the northwest region of Ohio between the years of 2002 and 2014. The dotted lines represent the average values of annual precipitation and rainfall in the last 100 years. Source: NOAA (2015).

Figure 3 Descriptive statistics of the variables in the soil (0.0 – 0.20 m depth soil layer) data set. The central rectangle of the boxplots spans the first to the third input quartile. The thin line inside the rectangle is the median, the bold line is the mean, and the horizontal lines to the left and right of the rectangle extend to the minimum and maximum values, respectively. The solid circles represent the minimum and maximum outliers. † Cation exchange capacity; ‡ Soil organic matter; § Inorganic N levels (NO_3^- + NH_4^+).

Figure 4 Average sulfate (SO_4^{2-}) levels in topsoils (0 – 20 cm) from northwest Ohio for the years of 2002 – 2014. Bars indicate twice the standard deviation from the mean for each year. Statistical significance at $p < 0.01$ is denoted by two asterisks (**).

Figure 5 Average pH values and soil organic matter (SOM) levels in topsoils (0 – 20 cm) from northwest Ohio for the years of 2002 – 2014. Bars indicate the standard deviation from the mean at each year.

Figure 6 SO_2 emissions by coal burning for the production of electric power in northwest Ohio between 2002 and 2013. Statistical significance ($p < 0.01$) is denoted with two asterisks (**). Data from U.S. EIA (2015).

Figure 7 Sulfate (SO_4^{2-}) concentrations in rainwaters (a) and depositions (b) in northwest Ohio soils between the years of 2002 and 2013. Statistical significance ($p < 0.01$) is denoted with two asterisks (**). Bars indicate the standard deviation from the mean for each year. Source: Data from the National Atmospheric Deposition Program station (NADP, 2014), situated in the Crawford County (Lat. 40.55 Long. -82.99), northwest

Ohio.

Figure 8 Average yields of corn, soybean and wheat in northwest Ohio between the years of 1950 and 2013. For the utilization of the equations, the x value should be accounted sequentially by considering 1950 =1 and 2013 = 64. Statistical significance ($p < 0.01$) is denoted with two asterisks (**). Source: USDA-NASS (2014).

Figure 9 Agricultural consumption of the main sources of S fertilizers in the USA between the years of 1990 and 2011. Statistical significance ($p < 0.01$) is denoted with two asterisks (**). Source: ERS USDA (2013).