Environmental Pollution 284 (2021) 117102

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Exploring the trend of stream sulfate concentrations as U.S. power plants shift from coal to shale gas☆

Xianzeng Niu [a, *], Tao Wen [b], Susan L. Brantley [a, c]

[a] Earth & Environmental Systems Institute, College of Earth and Mineral Sciences, Pennsylvania State University, 2217 EES Building, University Park, PA, 16802, USA
[b] Department of Earth and Environmental Sciences, Syracuse University, Syracuse, NY, 13244, USA
[c] Department of Geosciences, College of Earth and Mineral Sciences, Pennsylvania State University, 2217 EES Building, University Park, PA, 16802, USA

ARTICLE INFO

Article history:
Received 15 September 2020
Received in revised form
24 March 2021
Accepted 5 April 2021
Available online 9 April 2021

Keywords:
Coal
Natural gas
Power plant
Technology trend model
Stream SO_4^{2-} Concentration
SO_2 emissions

ABSTRACT

Since the early 2000s, an increasing number of power plants in the U.S. have switched from burning coal to burning gas and thus have released less SO_2 emissions into the atmosphere. We investigated whether stream chemistry (i.e., SO_4^{2-}) also benefits from this transition. Using publicly available data from Pennsylvania (PA), a U.S. state with heavy usage of coal as fuel, we found that the impact of SO_2 emissions on stream SO_4^{2-} can be observed as far as 63 km from power plants. We developed a novel model that incorporates an emission-control technology trend for coal-fired power plants to quantify potentially avoided SO_2 emissions and stream SO_4^{2-} as power plants switched from coal to gas. The results show that, if 30% of the electricity generated by coal in PA in 2017 had been replaced by that from natural gas, a total of 20.3 thousand tons of SO_2 emissions could have been avoided and stream SO_4^{2-} concentrations could have decreased as much as 10.4%. Extrapolating the model to other states in the U.S., we found that as much as 46.1 thousand tons of SO_2 emissions per state could have been avoided for a similar 30% coal-to-gas switch, with potential amelioration of water quality near power plants. The emission-control technology trend model provides a valuable tool for policy makers to assess the benefits of coal-to-gas shifts on water quality improvements as well as the effectiveness of emission control technologies.

1. Introduction

1.1. Impacts of fuel choices

During the last several decades, new technologies of natural gas (hereafter "gas") extraction from shale have led some to believe that shale gas can be a new "clean" energy source in the U.S. (de Gouw et al., 2014; Gilbert and Sovacool 2017; Massetti et al., 2017). However, such claims must rely on life cycle analysis to draw a whole picture of pros and cons of energy choices (Cooper 2017; Stamford and Azapagic 2014). The entire life cycle of gas includes exploration, drilling, production, transportation, and consumption. An important consideration that has drawn much interest is the relative release rates of two greenhouse gases, CO_2 and CH_4, during life cycle analysis of coal and shale gas, and their effects on climate (Barkley et al., 2019; Gilbert and Sovacool 2017). In addition to the release rates of CO_2 and CH_4, however, natural gas and coal differ in their emission rates of metals and trace gases during their life cycles as fuel. For example, gas releases much less SO_2 than coal when used as fuel (de Gouw et al., 2014) and the switch from coal to gas is found to be the second largest cause of reduction in SO_2 emission from 2004 to 2014 in the U.S., next to the adoption of sulfur-emission-control technology for coal-fired power plants (Lueken et al., 2016; Massetti et al., 2017). We hypothesized that the shift from coal to gas at power plants could also impact water quality of nearby streams, and if such impacts are measurable, they should be considered in future life cycle analyses. Although much of the deleterious effect of coal-burning emissions on surface water is related to the acidifying or metal-rich nature of these emissions (Chen et al., 2013; Sackett et al., 2010), we focused on sulfate (SO_4^{2-}) concentrations in streams as a proxy for the more difficult-to-follow effects of acid or metal emissions. We hypothesized that a study of SO_4^{2-} in surface waters could be a starting point for future assessments of the impacts of hydrocarbon-burning emissions as they deposit back onto the land surface.

☆ This paper has been recommended for acceptance by Sarah Harmon.
* Corresponding author.
E-mail address: xzniu@psu.edu (X. Niu).

https://doi.org/10.1016/j.envpol.2021.117102
0269-7491/

1.2. SO_2 emissions from coal-fired power plants

The electric power sector accounts for 64% of economy-wide SO_2 emissions in the U.S., and about 98% of the generated SO_2 is from coal-fired power plants (Massetti et al., 2017). For the last several decades, the U.S. has seen a dramatic decrease in SO_2 emissions from electric power plants, attributing to the implementation of environmental regulations (Taylor et al., 2005), adoption of new technologies (Baig and Yousaf, 2017; Taylor et al., 2005), a fuel switch from coal to gas (de Gouw et al., 2014; Lueken et al., 2016) and other clean energy sources, such as wind and solar energy (Millstein et al., 2017). For example, Massetti et al. (2017) reported that the U.S. SO_2 emissions in 2014 were 73% lower than those in 1970, and the rate of reduction increased rapidly after the ratification of the Clean Air Act (CAA) amendments in 1990. These amendments promoted the use of clean low-sulfur coal as well as innovative technologies to clean high-sulfur coal. Similar trends were also reported in other studies (de Gouw et al., 2014; Driscoll et al., 2016; Jiang et al., 2018). Many factors affect the SO_2 emissions from coal-fired power plants, including sulfur content in coal, total electricity generation, and the fraction of plants using flue gas desulfurization (FGD) (Massetti et al., 2017). Among them, numerous researchers have suggested that the adoption of new technologies, such as FGD, account for the majority of SO_2 reduction (Majumdar and Kar 2017; Massetti et al., 2017; Taylor et al., 2005). Therefore, when assessing the "true" environmental benefits of the shift from coal to gas in SO_2 emissions (and stream SO_4^{2-}), the contribution of technology adoption (hereafter "technology trend") must be taken into account to avoid overestimating the coal-to-gas effects.

1.3. SO_2 emissions vs. stream SO_4^{2-} concentrations

Decreases in SO_2 emissions to the atmosphere also result in decreases in SO_4^{2-} deposition back to the land surface. For example, studies show that SO_4^{2-} concentrations in surface waters in the northeastern U.S. have significantly declined since 1992 (Burns et al., 2020; Driscoll et al., 2016; Gavin et al., 2018; Patel et al., 2020; Shao et al., 2020), just as anthropogenic emissions of SO_2 in the U.S. have declined during the same time period. Similarly, as the anthropogenic SO_2 emissions decreased, Stoddard et al. (1999) found that SO_4^{2-} concentrations in lakes and streams in North America and Europe have also declined across regions, generally with more rapid declines during the 1990s.

Strong correlations between SO_4^{2-} in atmospheric deposition and surface water have been reported in numerous studies (Driscoll et al., 2016; Kline et al., 2016; Mitchell and Likens 2011; Shao et al., 2020; Smith and Alexander 1986; Watmough et al., 2016). However, the transit of sulfur from the atmosphere to stream water is often hard to determine because of retention in soils and vegetation (Burns et al., 2020; Patel et al., 2020; Rice et al., 2014; Siemion et al., 2018). The amount of precipitation and the types of soils and vegetation all affect the rate of sulfur transferal into the stream water (Mitchell and Likens 2011; Rice et al., 2014; Shao et al., 2020; Smith and Alexander 1986). In general, the higher the flux of SO_2 emitted into the atmosphere in a given region over a given time period, the more SO_4^{2-} is delivered to the nearby land surface, and the more likely it is to be taken up into soils and vegetation. When atmospheric sulfur deposition decreases, the sulfur is then slowly released from soil and vegetation to streams (Mitchell et al., 2011; Rice et al., 2014) and the rate of release varies with soil type and watershed runoff characteristics (Patel et al., 2020; Rice et al., 2014). The average lag time between monthly atmospheric deposition and stream chemistry in Appalachian forests (U.S.) from 1978 to 2012 was estimated by one research group to be as long as 48 months (DeWalle et al., 2016) but other researchers have identified much longer time lags (up to two decades) in other locations (Rice et al., 2014). These "buffer" or "legacy" effects of soils and vegetation on the transit of sulfur from atmosphere to stream water are location-dependent (Rice et al., 2014; Smith and Alexander 1986) because they depend upon thickness and adsorption capacity of soils as well as recharge ratios of watersheds (Burns et al., 2020; Patel et al., 2020; Rice et al., 2014). This buffering must be addressed in relating SO_2 emissions to stream SO_4^{2-} concentrations.

1.4. Research objectives

Although many researchers have demonstrated that coal-burning impacts waters and soils worldwide (Driscoll et al., 2016; Ma et al., 2014; Raymond and Oh 2009), no researchers have yet investigated whether the recent switch from burning coal to natural gas is currently affecting surface waters. We addressed this question by investigating streams in Pennsylvania, a state with a century-long history of hydrocarbon extraction and burning, and a publicly accessible record of water chemistry data that spans decades. Our first attempts to simply test for changes in SO_4^{2-} concentrations in streams near power plants showed that some streams showed effects. However, overall, the attempt was confounded by the small extent of change in SO_4^{2-} in stream waters and other factors, including variable effects of dilution by rainfall, the local nature of emissions on streams, the many changes in the histories of fuel usage and emission-control technologies at individual power plants, and the attenuating effects of soil and vegetation uptake of SO_4^{2-}. This is not surprising because many researchers have seen little to no change in sulfate concentrations in streams over the decades of decreasing atmospheric emissions in some parts of the USA (see summary in Rice et al., 2014). While Rice et al. (2014) developed a modeling approach to assess the effect of soil retention on stream SO_4^{2-} concentrations, they did not incorporate different (or changing) depositional histories in their model. We therefore developed a model to address some of these factors and that allowed assessment of the effects on local stream waters of the switch in fuel in PA. We then showed that this model also successfully describes the changes in emissions from power plants nationwide, and could, in a future study, be used to investigate nation wide impacts on U.S. stream waters.

In our stepwise approach to the problem, we set out to: 1) quantify the SO_2 emission intensity (hereafter, "*SO2EI*"); 2) develop an emission-control technology trend model to simulate the trend of *SO2EI* from coal-fired power plants (hereafter "$SO2EI_{trend}$"); 3) develop a stream SO_4^{2-} intensity trend model (hereafter "$SO4CI_{trend}$") to predict stream SO_4^{2-} concentration changes from atmospheric sulfur deposition; 4) extrapolate using the technology trend model from PA to assess the avoided SO_2 emissions (with implications for the potentially avoided stream water SO_4^{2-} contamination) as a result of the recent shift from coal to gas in power plants (hereafter coal-to-gas) across the U.S. By taking into account the emission-control technologies as well as other factors, our approach should provide a realistic and accurate assessment of the benefits of coal-to-gas shifts in terms of water quality at regional levels. Our findings are critical for future policy decisions.

2. Methods

In this section, we describe the methods used for the assessment of the impacts of power plant coal-to-gas switch on air (i.e. SO_2 emissions) and water quality (i.e. SO_4^{2-} concentrations). First, we applied a customized semivariogram analysis to determine the spatial range of the power plant impacts on stream water chemistry. We then developed emission-control technology trend

models to simulate the dynamics of SO_2 emissions from coal-fired power plants and SO_4^{2-} concentrations in nearby streams. Finally, we applied the trend models to assess the potential impacts of the coal-to-gas shift using a scenario analysis.

2.1. Research location, data, and data sources

We investigate Pennsylvania (PA, U.S.) because of the long history of hydrocarbon use (Raymond and Oh 2009), the general transition from coal to gas over the last decades, and the long record of water quality data (back to early 1990s) that is publicly available. A PA map and the locations of coal- and gas-fired power plants in 2017 and the PA Water Quality Network (WQN) sampling sites for water quality measurement are shown in Fig. 1.

All data used in this study were extracted from publicly available online data sources and quality-checked before use. The process of data cleaning includes unifying variable names and units, removing redundant data, and reformatting data structures to fit in a relational database (Niu et al., 2018a). Stream SO_4^{2-} concentration data were downloaded from PA WQN, which is a statewide, fixed-station water quality sampling system operated by the Bureau of Clean Water at PA Department of Environmental Protection (DEP) (http://www.dep.pa.gov/Business/Water/CleanWater/WaterQuality/Pages/Water-Quality-Network.aspx). WQN hosts data for 257 sites in PA (Fig. 1) from 1998 to 2016 (the year when data were downloaded). Although multiple water quality data sources are available (e.g., National Water Information System by U.S. Geological Survey and STORET by U.S. Environmental Protection Agency), our earlier investigations showed that the use of mixed datasets could lead to biased results because of the lack of equivalence in temporal coverage. In contrast, long term monitoring from WQN provided consistent stream water quality data for temporal trend analysis. A total of 23,816 non-censored (i.e., above the detection limits) SO_4^{2-} data from unfiltered surface waters in WQN were used for analyses, and a total of 756 censored data were excluded.

Annual data of net generation (netG) of electricity for coal and gas were extracted from the U.S. Energy Information Administration form EIA-923 (EIA, https://www.eia.gov/electricity/data.php#elecenv). This value, netG, is the total generation minus the energy consumption of the plant itself. This latter consumption, typically a few percent of total generation, depends on pollution control equipment. The state-level SO_2 emission data from 1990 to 2017 were extracted from the EIA website (https://www.eia.gov/electricity/data/emissions/). These data were estimated from calculations that applied an emissions factor to total fuel consumption (EIA electric power annual 2017, https://www.eia.gov/electricity/annual/). From 1990 to 2017, a total of 40,254 calculated SO_2 emissions (in metric tons) and 49,519 netG measurements (in kWh) at state level were discovered.

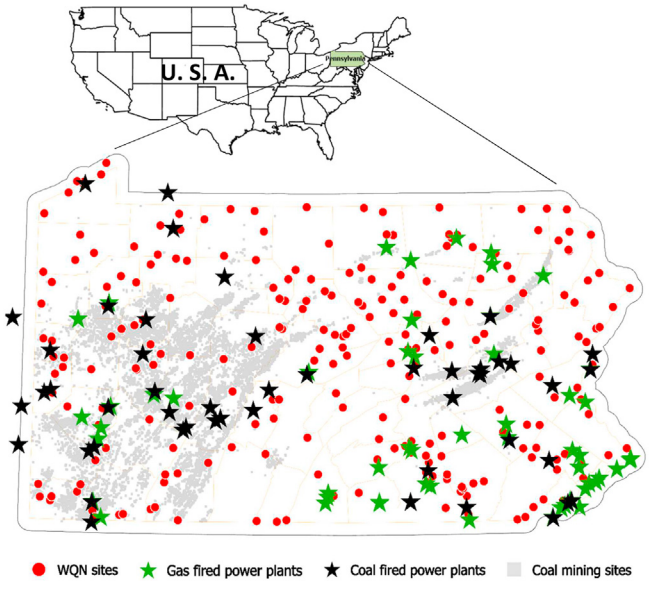

Fig. 1. Map of Pennsylvania (U.S.) with coal- and gas-fired power plants (as of 2017), water quality network (WQN) observation sites, and coal mining areas indicated as per the legend.

2.2. Spatial range of power plant impact on stream SO_4^{2-}

In this study, we applied a semivariogram analysis to determine the potential range of power plant impacts on stream SO_4^{2-} concentrations. Unlike the conventional semivariance which calculates the dispersion among all pairs of SO_4^{2-} observations, a modified semivariogram model (Eqn. A1, Appendix A) was developed in this study to consider only pairs of stream SO_4^{2-} concentrations (at each WQN-site) with their corresponding power plants. The model excludes site pairs between WQN water sampling sites. By doing so, the differences are evaluated between the semivariance and the distance of a WQN site to a power plant. We focused only on power plants that had used coal as a primary source (i.e. used coal more than any other fuel) for at least 10 years during 1990–2017 for the semivariance analysis. Not every power plant had a nearby WQN site to provide an on-site stream SO_4^{2-} value. Therefore, we first created a contoured stream SO_4^{2-} concentration surface by kriging the mean SO_4^{2-} values of each WQN sites using the ArcGIS Kriging function (Fig. B1; Appendix B). We then used the interpolated SO_4^{2-} values to represent the "stream" SO_4^{2-} concentrations at each coal-fired power plant site. Three semivariogram models were used (using the 'gstat' package in R): Exponential (*Exp*), Gaussian (*Gau*), and Spherical (*Sph*). Model performance was evaluated using the root mean square error (*RMSE*, Eqn. A2, Appendix A), which quantifies both the bias and the spread of the error distribution (Merino et al., 2001).

2.3. Technology trend models

2.3.1. Technology trend of SO_2 emission intensity

We employed a logistic function to simulate the trend of *SO2EI* of coal-fired power plants. The *SO2EI* is defined as the total SO_2 emissions per unit netG generated from coal (kg/MWh). We assumed that emission control technologies could be considered as yielding a cumulative effect and that the temporal trend in *SO2EI* after adoption of technologies would follow a typical inverse innovation diffusion cycle (Fig. 2). This cycle includes three stages: first, a stage characterized by a slow decrease in emission intensity that results from a few early adopters; second, a stage showing an accelerated decrease in emission intensity that happens as the majority of power plants adopts the technology; and third, a stage showing a slowdown in the rate of decrease in emissions as the slow-adopters eventually incorporate the technology.

The *SO2EI* for PA from 1990 to 2016 were calculated using the state SO_2 emissions and netG data reported by the EIA. To reduce non-technology related factors such as burner type, the *SO2EI* was normalized by a reference base value ($SO2EI_{norm}$, Eqn. (1)) for trend analysis. The base value was defined as *SO2EI* before adoption of a technology or when the first data were available. In this study, we used a median value of the first three years starting at 1990 as the base values to avoid any "extreme" values for the very first year of the data. $SO2EI_{norm}$ values were then used to fit an inverse logistic model to simulate the trend in SO_2 emissions for coal-fired power

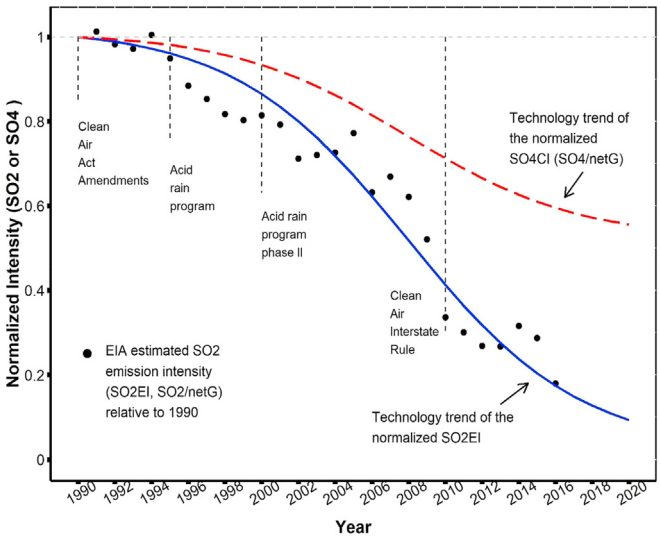

Fig. 2. EIA-estimated annual SO_2 emission intensities (*SO2EI*, black dots) for PA coal-fired power plants normalized to a base value in 1990. Solid line (blue) represents a fitted logistic model that describes the *SO2EI* emission-control technology trend. Dashed line (red) represents the trend of the SO_4^{2-} concentration intensity (*SO4CI*, also normalized to a base value in 1990) in PA streams, which is derived from the *SO2EI* trend model and adjusted by a soil/vegetation sulfur-legacy factor (see text for details). "Intensity" here refers to the annual SO_2 emissions (or mean stream SO_4^{2-} concentrations) for a given year for the entire state divided by the total net electrical power generation for the year under consideration. The timing of major U.S. environmental control regulations is indicated with black vertical dashed lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

plants ($SO2EI_{trend}$, see Eqn. (2)) as new technologies were adopted over time. The fitted model has an R^2 of 0.92 and a p-value <0.01. The *SO2EI* is a good indicator of coal burning efficiency with respect to SO_2 emissions. We refer to the trends of the *SO2EI* as technology trends for SO_2 emissions because *SO2EI* values were controlled largely by the adoption of emission-control technologies such as FGD (Massetti et al., 2017).

$$SO2EI_{norm}(i) = \frac{SO2EI\ (i)}{SO2EI_{base}} \tag{1}$$

$$SO2EI_{trend}(i) = \frac{1}{1 + e^{-(426.1792 - 0.21225\ *\ i)}} \tag{2}$$

where $SO2EI_{norm}$ represents the *SO2EI* normalized to a base value; *SO2EI(i)* is the *SO2EI* value at year *i*; $SO2EI_{base}$ is the *SO2EI* base value; and $SO2EI_{trend}$ (*i*) represents the simulated *SO2EI* trend value at year *i* normalized to the base value.

2.3.2. Technology trend of stream SO_4^{2-} concentration

As discussed above, SO_4^{2-} concentrations in atmospheric deposition strongly correlate to SO_2 emissions into the air because SO_2 dissolves into aerosols in the atmosphere to form dissolved sulfuric acid. Many authors have documented that deposition of this SO_4^{2-} containing rainwater increased the concentrations of protons and SO_4^{2-} in surface waters (DeWalle et al., 2016; Driscoll et al., 2016). While dissolved protons in the water tend to react with minerals and thus decrease in concentration, SO_4^{2-} tends to enter a watershed system and be held for various time periods before being released chemically unchanged. Thus, the long-term spatially generalized trends between stream SO_4^{2-} and SO_2 emissions have been shown to be similar (Stoddard et al., 1999) while the magnitudes of changes in stream water as a function of sulfur emissions over shorter time periods vary from place to place (e.g. Patel et al., 2020). These latter variations occur because SO_4^{2-} delivered to soils and vegetation is retained for different time periods in different locations (Driscoll et al., 1988; Rice et al., 2014). Currently, we are unable to predict these time lags from easily-observable watershed characteristics. We therefore proposed an empirical equation (Eqn. (3)) to predict the trend of SO_4^{2-} concentration intensity ($SO4CI_{trend}$) using the *SO2EI* trend and an empirical legacy sulfate adjusting factor.

Similar to the concept of *SO2EI*, the stream SO_4^{2-} concentration intensity (*SO4CI*) is defined as the stream SO_4^{2-} concentration resulting from sulfur emissions per unit of net electric generation (i.e. SO_4^{2-}/netG).

$$SO4CI_{trend}(i) = SO2EI_{trend}(i) + (1 - SO2EI_{trend}(i))*f_{ste} \tag{3}$$

where $SO4CI_{trend}$ and $SO2EI_{trend}$ represent the technology trend values of the normalized stream SO_4^{2-} concentration intensity and SO_2 emission intensity at a coal-fired power plant at year *i*, respectively. Both $SO4CI_{trend}$ and $SO2EI_{trend}$ are unitless values normalized to their respective base values. The value f_{ste} is a unitless sulfur transit efficiency factor (describing sulfur-transit from atmosphere to stream). The second part of Eqn. (3), referred to here as a legacy sulfate adjusting factor (LS), is calculated as a function of the f_{ste} and the difference between *SO2EI* values for the base year and a given year. When the *SO2EI* at a given year is greater than that of the base year (i.e. 1 as a normalized value), LS is negative, meaning that some sulfur deposited from the atmosphere has been stored transiently in soils and vegetation. When LS is positive, extra sulfur is released from the soils and vegetation and then delivered into groundwater/streams. The rate of sulfur uptake or release from soil and vegetation is controlled by f_{ste}, a parameter which varies by type of soil, vegetation, watershed hydrologic character, and climatic condition (Likens et al., 2002; Patel et al., 2020; Smith and Alexander 1986). Since the majority of the PA state is covered by sedimentary rock (shales, sandstones, limestones) and shares roughly the same climate (Niu et al., 2018b), we assumed a constant f_{ste} value across PA. Glaciation also has a big effect on the retention of SO_4^{2-} (Rice et al., 2014), such that glaciated soils are often young and less able to retain SO_4^{2-} while unglaciated soils are older and more able to retain SO_4^{2-}. Since only about 30% of PA land is covered by glaciated soils, the effect of glaciation was not incorporated in this study. Furthermore, we recognize that Rice et al. (2014), based on the theoretical framework of Cosby et al. (1986), have developed an approach to model SO_4^{2-} release from soils as a function of characteristics affected by glaciation, and we wanted instead to focus on investigating the effect of changing sources of fuel at power plants. In effect, we wanted to treat the legacy-related release of SO_4^{2-} from soils as an average value, recognizing that later models could explore more detailed approaches.

To calculate f_{ste}, we therefore estimated the value for previously determined "pristine" streams in the state that had been documented to maintain statistically constant SO_4^{2-}concentrations for at least 10 years (Fig. B2, Appendix B; See Niu et al., 2018b for more details). For these previously identified 19 "pristine" streams associated with WQN sites, we first regressed the mean SO_4^{2-} concentrations in the streams against the state-level SO_2 emissions from coal-fired power plants. Although these nominally pristine streams are not polluted by coal mines or other point sources, they are still somewhat affected by atmospheric deposition and thus can reveal an estimate of f_{ste}. Based on the work of Niu et al. (2018b), we also corrected the total sulfate concentrations in the streams by removing other sources of SO_4^{2-} (e.g. SO_4^{2-} from weathering of

sulfide minerals). This yielded an estimate of the stream SO_4^{2-} concentrations directly attributable to SO_2 emissions. We used 6.2 mg/L to represent an estimated minimum background SO_4^{2-} concentration in PA streams: this value was derived from the statewide mean SO_4^{2-} concentration (15.8 mg/L) for the pristine rivers minus one standard deviation (9.6 mg/L). The slope, 0.4901 (p-value = 0.003), of the fitted linear model between PA statewide SO_2 emissions and the mean SO_2-induced-stream-SO_4^{2-} was then used as the estimate for f_{ste} for the PA data (see Fig. B3; Appendix B).

2.4. Prediction of stream SO_4^{2-} concentrations

A WQN site may be impacted by several nearby coal-fired power plants. Assuming the sulfur content in coal is consistent over time, the total SO_2 emissions for a given WQN site is the product of *SO2EI* and the total netG generated from all the nearby relevant coal-fired power plants. In the following sections, methods for calculating the distance weighted total netG, SO_2 emissions, and SO_4^{2-} predictions are discussed.

2.4.1. Distance weighted total netG

The extent of impact of power plant emissions on stream SO_4^{2-} concentrations decreases with distance from the power plant. We explored buffer zones with distances of 20-, 40-, and 60-km (Fig. B4; Appendix B) to represent areas with intense, moderate, or low impacts, respectively (see section 3.1). Assuming that each zone received 30% of the total emitted sulfur as atmospheric deposition (with 10% of the sulfur transported outside the region by wind), the area-weighted densities of sulfur deposition were calculated and used as the weighting factor for each zone. The resulting weighting factors (W_{dist}, see Eqn. A3, Appendix A) are 0.652, 0.217, and 0.130 for the 20-, 40-, and 60-km zones, respectively. The total netG (T_{netG}) that affects a specific WQN site was then calculated as the sum of the distance-weighted netG from all power plants within 60-km of the WQN site (Eqn. (4)).

$$T_{netG}(i) = \sum_{j}^{n} (w_{dist} * netG_{ji}) \tag{4}$$

where T_{netG} is the total distance-weighted netG for a WQN site; W_{dist} is the distance weighting factor; $netG_{ji}$ is the netG for power plant j at year i; n is the total number of power plants that affect the specific WQN site.

2.4.2. Predictions of SO_2 emissions and stream SO_4^{2-}

The total SO_2 emissions from power plants affecting a WQN site is calculated from the product of *SO2EI* (i.e. a value from the $SO2EI_{trend}$ model) and the total netG (T_{netG}) from relevant coal-fired power plants. The predicted relative SO_2 emissions for year i ($RSO2_{pred}$) can be estimated from the $SO2EI_{trend}$ adjusted by a relative value of the T_{netG} at year i to the T_{netG} at the base year (Eqn. (5)).

$$RSO2_{pred}(i) = SO2EI_{trend}(i) * \frac{T_{netG}(i)}{T_{netG}(base)} \tag{5}$$

where $RSO2_{pred}(i)$ is the model predicted relative SO_2 emission from a coal-fired power plant at year i; $T_{netG}(i)$ and $T_{netG}(base)$ are the distance-weighted total netG from all relevant power plants (Eqn. (4)) at year i and at base year (1990), respectively; $SO2EI_{trend}(i)$ is the *SO2EI* trend value for year i.

Using the same concept as equation (3), the SO_4^{2-} concentration relative to the base value, $RSO4_{pred}$, can be estimated from the predicted SO_2 (i.e. $RSO2_{pred}$) and an empirical legacy sulfate adjusting factor as shown in equation (6):

$$RSO4_{pred}(i) = RSO2_{pred}(i) + \left(1 - RSO2_{pred}(i)\right) * f_{sce} \tag{6}$$

where $RSO4_{pred}(i)$ and $RSO2_{pred}(i)$ are the predicted relative stream SO_4^{2-} concentrations and SO_2 emissions from power plants for year i, respectively.

2.5. Observed stream SO_4^{2-} (WQN data)

SO_4^{2-} in streams derives from pollution from human activities (such as SO_2 emissions, coal mining, agriculture, etc.) and natural processes (i.e., geological phenomena). For example, based on Niu et al. (2018b), some streams in PA that are impacted heavily by coal mining have elevated SO_4^{2-} because of acid mine drainage. To keep our work from being biased by those sites, we only considered WQN sites where the minimum SO_4^{2-} concentration (i.e. min [SO_4^{2-}]) in the stream is less than a pre-defined threshold value. Specifically, we only chose the sites that meet the following criteria: min[SO_4^{2-}] < [mean-background-SO_4^{2-} + 2*StDev]. The mean-background-SO_4^{2-} and standard deviation (StDev) were adopted from Niu et al. (2018b) for "pristine" streams. The assumption here was that if min[SO_4^{2-}] was too high, the stream was likely contaminated by coal mining or other activities unrelated to power plant emissions. A total of 69 of the WQN sites that are categorized as pristine meet both this non-contamination criterion and the additional criterion of at least 10 years of data.

With data from these sites, we calculated the stream SO_4^{2-} concentrations ($SO4_{SO2}$) that are attributable to SO_2 emissions by subtracting background values ($SO4_{bg}$) from WQN observations ($SO4_{wqn}$; as shown in Eqn. A4, Appendix A). We then compared them to values predicted by the model. The background values vary with the type of bedrock and were calculated as mean SO_4^{2-} concentrations from "pristine" streams flowing over each bedrock type (see Fig. B2 in Appendix B; Adapted from Niu et al., 2018b). Stream SO_4^{2-} concentrations vary seasonally but the observations are not evenly distributed through the year. To avoid biases in annual mean calculations as a result of this seasonality, we created weighting factors for each month (W_j, i.e., annual mean divided by monthly mean; Eqn. A5, Appendix A), and then calculated the monthly-weighted annual mean (Eqn. (7)).

$$SO4_{obsv}(i) = \frac{\sum_j^n SO4_{SO2}(i,j) * W_j}{n} \tag{7}$$

where W_j is the weighting factor for month j; $SO4_{SO2}$ is the SO_2-induced SO_4^{2-} values calculated from Eqn. A5 at year i and month j; n is the total months of data available; $SO4_{obsv}(i)$ is the annual mean SO_2-induced SO_4^{2-} at year i.

2.6. Model validations and applications

In this section we extrapolate the *SO2EI* trend model from PA to predict SO_2 emissions for the 48 contiguous U.S. states and compare them with the EIA-estimated data. A comparison of root mean square error (*RMSE*, Eqn. A2, Appendix A) between predicted and EIA estimated *SO2EI* was used to evaluate the model's overall performance. Predicted stream SO_4^{2-} values were compared with the selected PA WQN observations as discussed in section 2.5. Since the WQN data starts at 1998, the mean $SO4_{obsv}$ value for the first three years (i.e. 1998-2000) was used as the base value for calculations of relative SO_4^{2-}. All statistical analyses were performed with R.

We then applied the *SO2EI* and *SO4CI* trend models to a scenario analysis for both the entire U.S. and for PA. The scenario we chose to

explore was based on the assumption that 30% of the electricity generated by using coal in 2017 was instead produced by burning gas (hereafter, 30% coal-to-gas scenario). Under this so-called "30% coal-to-gas scenario", we predicted the potentially avoided SO_2 emissions nationwide for every state in the U.S. We used this same calculation in turn to demonstrate the avoided SO_4^{2-} contaminations for streams nearby power plants in PA. We did not complete this assessment for the entire U.S. because we could not defensibly use our estimated f_{ste} for all geologies nationwide (such an extrapolation for stream chemistries nationwide must await better understanding of f_{ste} and use of models such as those proposed by Rice et al. (2014)). We also applied the model for assessment of effectiveness of emission control technologies to observations which led to identification of additional pollution sources at regional levels.

3. Results and discussions

3.1. Range of power plant impact on streams

Our semivariance analysis of the spatial correlation between SO_4^{2-} concentrations at WQN sites and at coal-fired power plant sites showed that the range varied from 20.4 to 62.7 km, depending on the model (Table B1; Appendix B). The variogram models (Fig. B5; Appendix B) also show that strong spatial autocorrelations exist within distances less than 20 km (corresponding to the range of the Gaussian model) and the autocorrelation clearly weakens after 60 km (corresponding to the range of the spherical and exponential models). Therefore, we used distances of 20-, 40-, and 60-km in this study to represent intense, moderate, and low impact zones of power plants. This three-impact-zone concept was adapted to calculate the overall distance-weighted impacts from multiple power plants as discussed in section 2.4.1.

These ranges are well aligned with previously published values. For example, a study of public health benefits in Massachusetts, U.S., showed that a maximum benefit was found within 25–40 km of a power plant when its emissions were reduced, while little to no benefit was observed out to 100 km from the source (Levy and Spengler 2002). Likewise, Högström (1973) used residence time analysis and found that sulfurous air pollutants from a local source could travel a distance of 50–100 km. Weber (1970) also found that almost 50% of the total atmospheric sulfur content could be lost from air samples in a period of 20 minutes to 1 hour. For the average wind speed of 26.7 km/hour in PA (www.climate.gov), this is equivalent to distances of 9–27 km (or an average of 18 km).

3.2. Technology trends of SO_2 emission intensity and stream SO_4^{2-} concentration intensity

The results of the *SO2EI* and *SO4CI* trends are shown in Fig. 2. The trend of *SO2EI* ($SO2EI_{trend}$) resembles an inverse typical technology diffusion pattern (e.g. Lotfi et al., 2014): slow decline in the beginning from innovators and early adopters (roughly 1990–2000), followed by a stage of accelerated decrease with the majority of adopters (2000–2012), and a mature, late slow down stage with slow-adapters (after 2013). Similar decline trends were reported in previous studies with various innovations (Baig and Yousaf, 2017; Jiang et al., 2018; Massetti et al., 2017; Taylor et al., 2005). Based on the model, the *SO2EI* of PA decreased by 84% between 1990 and 2016, reasonably consistent with the published estimates of a 71% decrease from 1997 to 2012 (de Gouw et al., 2014). The U.S. SO_2 emissions in 2014 were estimated to have reached about 73% below those in 1970 (Massetti et al., 2017).

The timing of major U.S. environmental control regulations after 1990 were also plotted in Fig. 2, including the Clean Air Act (CAA) Amendments in 1990, Acid Rain Programs in 1995 (Phase I) and 2000 (Phase II), and the Clean Air Interstate Rule in 2010. Following the CAA in the 1970s and especially after the CAA Amendments in 1990, numerous new technologies were developed and gradually adopted by the electric industry to reduce SO_2 emissions (Baig and Yousaf, 2017; Massetti et al., 2017). Among those initiatives, the U.S. Acid Rain Program is considered one of the most successful: it reduced more than 70% of power plant generated SO_2 emissions since the 1990s (Massetti et al., 2017). This decrease coincided with the observed rapid *SO2EI* decrease in our technology model. The installation of flue gas desulfurization (FGD) was found to be the biggest contributor of reductions in SO_2 emissions during this time period (Massetti et al., 2017).

The trend of stream SO_4^{2-} concentration intensity, $SO4CI_{trend}$ (red dashed line in Fig. 2), shows the same pattern as $SO2EI_{trend}$, except that the range of variations was reduced by a factor of 0.49 (i.e., by the atmosphere-to-stream sulfur transit efficiency factor, f_{ste}). This decreased variation range in stream SO_4^{2-}, when compared with that of *SO2EI*, can be at least partially explained by the modulation caused by sulfur sorption in soils and vegetation and the delayed release back to surface waters (DeWalle et al., 2016; Rice et al., 2014; Smith and Alexander 1986).

3.3. Validation of the technology trend models

3.3.1. Validation of the $SO2EI_{trend}$ model

To explore the validity of the technology trend model and its applicability to other states, we applied the $SO2EI_{trend}$ model (using Eqn. (5)) to predict the annual SO_2 emissions from 1990 to 2016 for 48 U.S. contiguous states. We then compared them with the EIA estimations. In general, the $SO2EI_{trend}$ model fairly predicted SO_2 emissions for 42 out of 48 of the states. The results show that our predictions significantly correlate with EIA-estimated values as shown in Fig. 3a ($R^2 > 0.4$ and p-value < 0.0001). One example of the comparison between EIA-estimates and model-predictions for the total emissions from the U.S. is shown in Fig. 3b ($R^2 = 0.91$). This result not only validates the $SO2EI_{trend}$ model, but also suggests that it can be applied to calculate SO_2 emissions in other states.

3.3.2. Validation of the $SO4CI_{trend}$ model

The $SO4CI_{trend}$ model was also validated against the observed stream SO_4^{2-} data from the PA water quality network (WQN). One comparison between model predicted and observed (WQN) stream SO_4^{2-} is shown in Fig. 4. In this case, the WQN site 21PA-WQX-WQN0154 (WQN0154) is located in the Valley Creek watershed in Chester County, PA, where five coal-fired power plants are located within 60 km (Fig. B6; Appendix B). From 1998 to 2016, some power plants switched from coal to gas and some were retired (as indicated by the number of "coal-fired" power plants in Fig. 4). The model predicted the trend of SO_4^{2-} concentrations with adequate accuracy ($R^2 = 0.58$ and p-value $= 0.00015$), reflecting the effect of the combination of changes in total netG from coal and the adoption of new emission control technologies. The model slightly under-predicted SO_4^{2-} concentrations after 2008, an effect that could be related to soil releases or land use changes as discussed in sections 3.7.2.

The overall decline in stream SO_4^{2-} concentrations for the 69 WQN sites is demonstrated in Fig. 5a and the accuracy is demonstrated by the histogram of root mean square error (RMSE) between predicted and observed values (Fig. 5b). The RMSE values are almost normally distributed around a mean value of 0.09. The slight positive skew in data show a mean RMSE of 9% that is most likely related to additional sources of SO_4^{2-} pollution as discussed below.

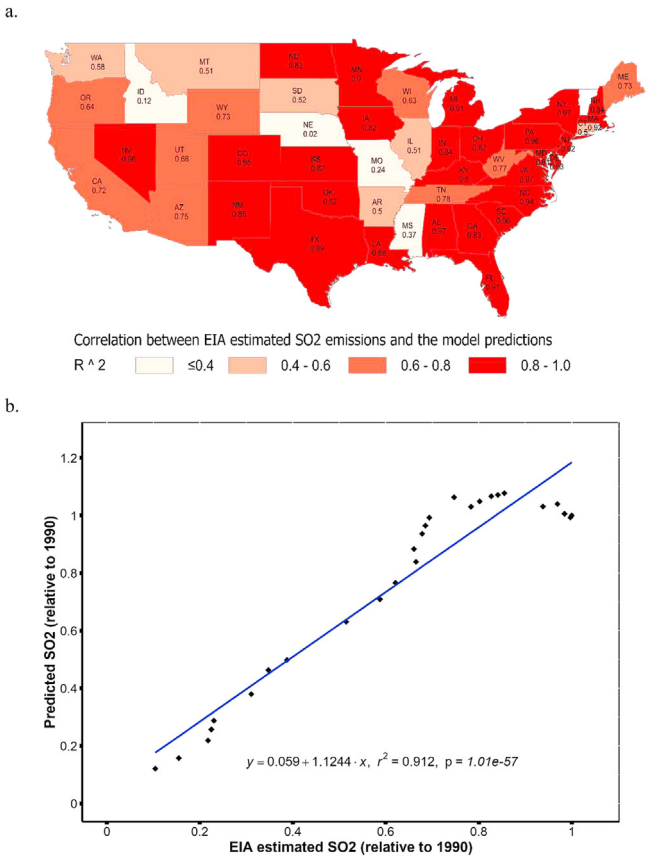

Fig. 3. Comparison between EIA-estimated annual SO_2 emissions and the technology trend model predictions. Panel (a) shows the correlations (R^2) between the two for each of the 48 U.S. contiguous states and panel (b) shows a scatter plot for the model predictions against the EIA-estimated U.S. total annual SO_2 emissions from 1990 to 2016. All values are normalized relative to values for 1990.

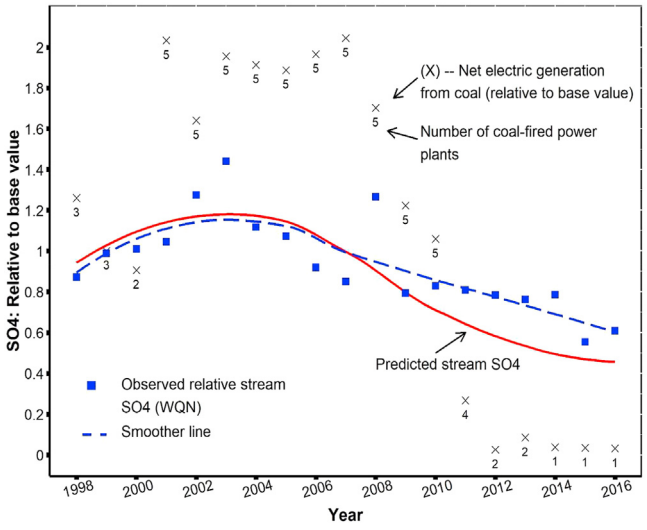

Fig. 4. Comparison between measured stream SO_4^{2-} concentration (blue squares) and predictions of the technology trend model (red solid line) at one stream site (WQN 0154 in Chester County, PA). All concentrations are relative to the base value (the median value of SO_4^{2-} for the first three years starting at 1998). A smoother line (dashed blue line, plotted using R-Loess smooth function) is also plotted to show the temporal pattern of the observed relative stream SO_4^{2-} concentrations. Black symbols (X) represent the net electricity generation (netG) from coal (relative to 1998). The accompanying labels are numbers of coal-fired power plants (EIA data) that potentially affect the WQN0154 site at respective years. The numbers change with time as coal-fired power plants come online or are retired or change fuels. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.4. Temporal trend of stream SO_4^{2-} concentrations as power plants abandon coal

Comparison between observed and model predicted stream SO_4^{2-} concentrations is consistent with the hypothesis that as power plants switch from coal to gas, less contaminating SO_4^{2-} reaches nearby streams. One example of trends of net electric generations and nearby stream SO_4^{2-} concentrations are shown in Fig. 6a and b, respectively.

In Fig. 6a, changes in the total amount of netG from both coal and gas from five power plants near water-sample site WQN0154 is shown. The total netG steadily increased to more than 3 times the 1998 level by 2016. However, in comparison to the 1998 level, coal consumption initially increased until 2008 and then began to dramatically decrease down to less than 5% by 2016. During the same time period, natural gas gradually replaced coal as the major source of fuel at the local power plants. As shown in Fig. 6b, the initially increasing coal consumption resulted in increasing stream SO_4^{2-} (the blue solid line), but stream SO_4^{2-} then began to decline once the power plants switched to dominantly gas. Fig. 6 is a good example showing why a model is needed to document the small improvements in stream chemistry that have ensued during the recent period of adoption of SO_2-emission-control technologies amid changing fuel choices.

In Fig. 6b, a plot of model predicted stream concentrations of SO_4^{2-} is also shown (black dashed line) from 1998 through 2016 for the same trend of total net power generation but assuming all electricity were generated by using coal. In that case, SO_4^{2-} increased over time until 2005 before starting to decline. This behavior is mainly determined by the competition between the increasing amount of netG from burning coal (i.e., increasing *SO4Cl*) and the adoption of emission control technologies (i.e., lowering *SO4Cl*). The difference between modeled and observed SO_4^{2-} (gray area between the dashed and solid lines in the figure) clearly define a gap, highlighting the avoided SO_4^{2-} stream contamination. Note that the gap (i.e. avoided SO_4^{2-} pollution) narrowed over time as the effects of emission control technologies became increasingly important with time. The results here clearly show the advantages of our technology model which avoids overestimating the benefit of the power plant switch from using coal to gas. The gap here demonstrates the environmental benefits to the stream that accrued from such coal-to-gas switch.

3.5. Avoided SO_2 emissions in the U.S

In 2017, a total of 1.21 billion MWh was generated for electricity in the U.S. from burning coal (eia.gov). Under the 30% coal-to-gas scenario, our model predicts that 402.6 thousand tons (k-tons) SO_2 emissions to the atmosphere could have been avoided. This result is compatible with the value derived from EIA estimations: based on EIA reporting Form EIA-923, 388.6 k-tons of SO_2 emissions would have been avoided if consumption of coal had been reduced by 30% in 2017. From state to state, the range of potentially avoided SO_2 emissions in 2017 varies from 0.1 to 46.1 k-tons, with the most reduction concentrated in the eastern parts of the U.S. as shown in Fig. 7. For PA, the reduction was predicted to be 20.3 k-tons under the 30% coal-to-gas scenario.

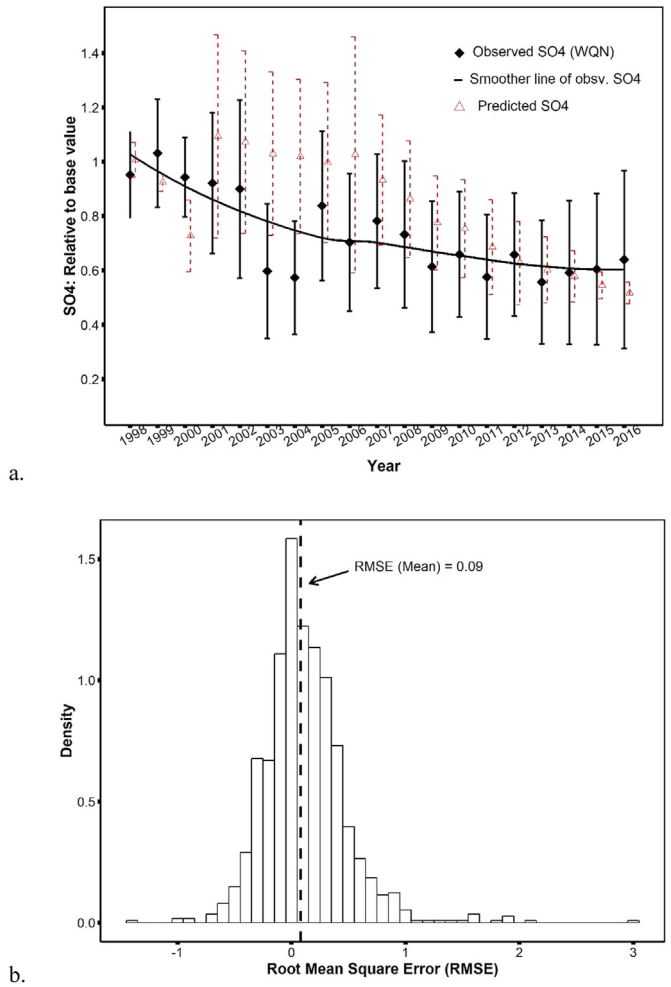

Fig. 5. Panel (a): Overall decreasing trend in stream SO_4^{2-} concentration (relative to 1998) for the mean of 69 sites in PA from the WQN database as described in the text. Data are shown with both measured (black diamonds with a smoother line using the Loess function in R) and model predictions (red triangle). Error bars represent ± one standard deviation. Panel (b): Histogram of values for root mean square error (RMSE) calculated between model predictions and the observations for the same 69 WQN sites. The mean of the RMSE for all sites is 0.09 (vertical dashed line in figure 5b). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

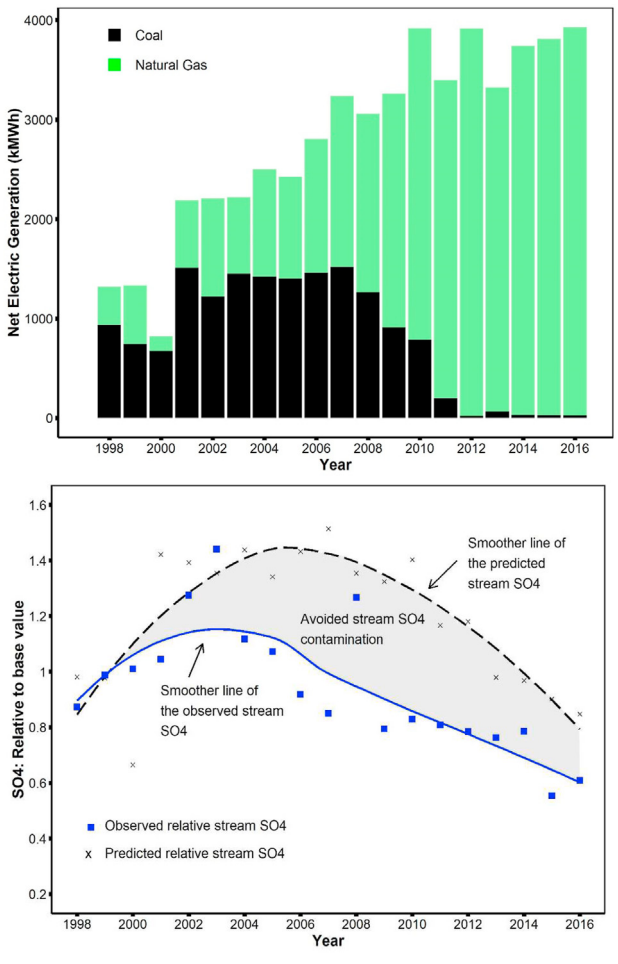

Fig. 6. Panel a): Annual total net electric generation (netG) from coal and natural gas for power plants within 60 km of a WQN site - WQN0154. Panel b): Comparison between predicted and measured stream SO_4^{2-} concentrations (relative to 1998) for the WQN0154 site. The solid-blue and dashed-black lines represent the smoother lines of the observed and model predicted SO_4^{2-} concentrations (plotted using the Loess function in R). The model predictions were executed under a scenario that the same total amount of annual netG were generated by burning coal, instead of using both coal and gas. The gaps between the smoother lines of the predicted and measured SO_4^{2-} (gray area) represent the potential avoided SO_4^{2-}contaminations after coal-to-gas switch of the surrounding power plants. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.6. *Avoided stream SO_4^{2-} contamination*

Under the same 30% coal-to-gas scenario as discussed in section 3.5, our model shows that stream SO_4^{2-} in PA could have been reduced by as much as 10.4%. This value is much smaller than the assumed amelioration in SO_2 emissions (30%) largely because of the attenuation factor that documents some SO_4^{2-} held in soils and vegetation.

To analyze these effects locally, we also conducted a hotspot analysis using the Getis-Ord Gi* statistic in ArcGIS to identify statistically significant spatial clusters of hot spots and cold spots where SO_4^{2-} reductions were significantly larger or lower than the surroundings, respectively. The results (Fig. 8) suggest that most of the predicted hot spots are in western PA where coal is still a major source for electricity generation. In effect, if 30% of the energy derived from coal in 2017 at each power plant was instead produced by burning gas, this would not have affected eastern PA significantly because power plants in that area were already mainly powered by gas. The implication is that stream water quality would have improved in western PA with such a switch from coal to gas. In addition, since glaciated soils release SO_4^{2-} to streams more quickly than unglaciated soils (Rice et al., 2014), the sites in the northwestern part of the state (especially glaciated soils) would most quickly show improvements in SO_4^{2-} concentrations in streams as compared to streams in the southern part of the state (unglaciated soils) after a 30% switch from coal to gas. However, that effect is not included in our current model.

Future research should take values such as we just calculated for emissions nationwide and use those to assess improvements in stream chemistry. However, as discussed previously, the effects on streams are attenuated by local soils and vegetation, and this is in turn a function of climate, land use, and geology. To make such a calculation nationwide will rely on better estimates of f_{ste} and could, for example, rely on models such as those suggested by Rice et al. (2014). For these reasons, we make the prediction here only for PA.

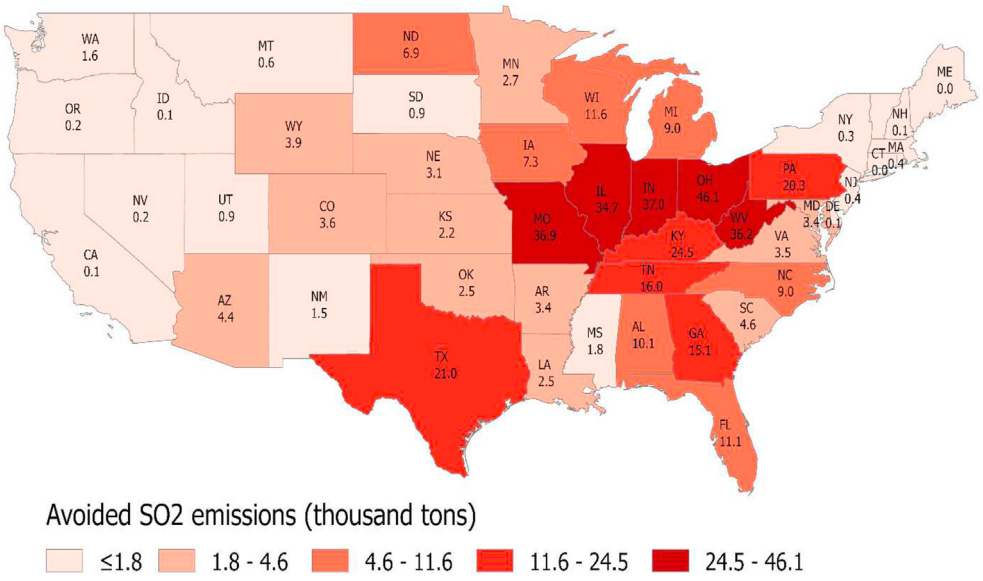

Fig. 7. Statewide potential for avoided SO_2 emissions (thousand of tons) from coal-fired power plants in the U.S. in 2017, assuming that 30% of the electricity generated by coal per state in 2017 had been replaced with energy from natural gas.

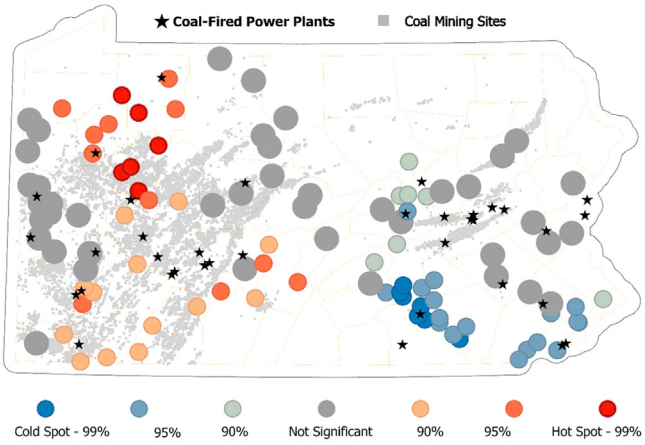

Fig. 8. Predicted hot spots for potentially avoided SO_4^{2-} contamination in PA streams. The calculations were based on an assumption that 30% of the electricity generated by coal in PA in 2017 was replaced by energy from natural gas. The red dots represent the hot-spots where reductions are predicted to be significantly larger than surroundings. The gray dots represents where the changes are not significant. The blue dots represent where the reductions are significantly lower than surroundings. Percentage values reflect significance levels for the hot/cold spots. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.7. Applications of the technology models

The technology trend of *SO2EI* discussed in section 3.2 represents the trend of SO_2 emission intensity predicted for a power plant that "fully" complied with regulations by adopting the most up-to-date emission control technologies. Any significant discrepancy from the trend indicates one of three scenarios: 1) lack of successful implementation of emission control technologies, 2) additional sources of pollution, or 3) additional approaches adopted to reduce SO_2 emission. We discuss implications below.

3.7.1. Evaluation of the efficiency of power plants in emission control

To represent the "ideal" situation where all power companies complied fully with pollution control regulations, we predicted the *SO2EI* for all 48 contiguous U.S. states using our $SO2EI_{trend}$ model and compared it with the *SO2EI* estimated from EIA reported SO_2 emissions (The difference between modeled ("ideal") and EIA estimated ("real") *SO2EI* in 2017 are shown in Figure B7; Appendix B). Results show that the majority of states in the east and west coast meet or exceed the standard in terms of emission control (here, we used the following criteria: [modeled-*SO2EI* − observed-*SO2EI*] > −0.05). However, some states (shown in blue in Fig. B7) in the midwest did not show the expected level of reduction. This indicates either i) full compliance was not achieved, ii) additional sources began emitting SO_2 in the study region during the study period, or iii) some of the states started with a low base *SO2EI* level and showed minimal changes. An example of the case-iii is Nebraska which was reported to release 3.71 kg-SO_2/MWh in 1990 as compared to the U.S. average of 8.96 kg/MWh. It is beyond the scope of this work to evaluate whether (i), (ii) or (iii) are the best explanations for the midwestern states, but the example shows how the trend model could be used to assess the efficiency of technology adoption at regional levels.

3.7.2. Identification of extra sources of pollution

The discrepancy between modeled and observed stream SO_4^{2-} values could be related to changes in the release rate of legacy SO_4^{2-} from soils or vegetation because of changing rainfall or other conditions, or could be an indicator of new sources of pollution in some areas. For example, in the case of the watershed where WQN0154 is located (Fig. 4), land use includes mixes of forest, agricultural land, and urban area. Increased urbanization and commerical use in recent years may have introduced extra emissions from automobile and industrial facilities (Jiang et al., 2018). This effect may partially explain why the observed actual SO_4^{2-} concentrations in streams were higher than the model indicated after year 2008.

Another example of additional sources of SO_4^{2-} to streams is coal mining (Raymond and Oh 2009). In the western part of PA where coal mining has been intensive, the observed stream SO_4^{2-} concentrations consistently exceeded the modeled values (e.g. WQN0404, WQN0422, WQN0820, WQN 0870, WQN0861, WQN0843, see Fig. B8; Appendix B). This discrepancy could be attributed to the presence of contamination from acid mine

drainage from mines.

3.8. Model implications and significances

Sulfur dioxide (SO_2) emissions are one of the major criteria pollutants from coal-fired power plants and the effect of such emissions on ecosystems is a matter of current research (Likens et al., 2002). For example, such emissions are acidic in nature and affect ecosystem pH balance deleteriously (Kline et al., 2016; Shao et al., 2020). In addition, coal burning also emits metals to the atmosphere which also are re-deposited in streams and soils. Few data are available for metal emissions nationwide, but numerous studies report SO_2 emissions from the electric power sector. Decreases in SO_2 emissions in the U.S. are largely attributed to the adoption of emission control technologies (Massetti et al., 2017; Mitchell and Likens 2011). However, the pattern of reduction in SO_2 emissions has not been quantitatively studied, impeding our ability to assess regional or country-wide reductions. While assessing changes in pH or in metal concentrations from decreased emissions might be a more direct method of analyzing the effect on stream biota, neutralization reactions and low metal concentrations obscure such temporal changes making them difficult to analyze. In this study, therefore, we applied a typical innovation diffusion (logistic) model to simulate the technology trend of SO_2 emissions from coal-fired power plants in the U.S. and to analyze its effects on stream sulfate concentrations as a way to assess how changing fuel choices (coal to gas) might be affecting stream chemistry. Our development of a technology trend model contrasts with previous studies where the SO_2 emission rate from coal-fired power plants was assumed from a reference value (e.g. de Gouw et al., 2014; Lueken et al., 2016). Using such a reference could lead to overestimations of the reduction in SO_2 emissions when assessing potential benefits of switching from coal to gas. Thus, the technology trend that we introduced here makes this study more robust in assessing the "true" benefit in avoided air (SO_2) as well as water (SO_4^{2-}) pollution when power plants switch from coal to gas.

Previous studies have detected correlations between SO_2 emissions from power plants and the SO_4^{2-} concentrations in atmospheric deposition and in surface water (Mitchell and Likens 2011; Smith and Alexander 1986). Some researchers have modeled the rate of release of SO_4^{2-} to streams from soils after atmospheric deposition (Rice et al., 2014) but our study is the first to quantify how changing fuel sources in local power plants may affect streams. To simplify our model of the effect of fuel choices, we simply treated the relationship between SO_2 emissions and stream SO_4^{2-} concentrations by introducing an empirically-derived legacy sulfur factor. The sulfur legacy factor is appropriate because it is known that sulfate accumulates in soils and vegetation and is not then released until after a time lag. This effect is variable with respect to climate, lithology, glaciation/lack of glaciation, and ecosystem conditions. For example, long-term analyses of budgets of sulfur reveal that the decline in SO_4^{2-} in precipitation resulting from decreases in SO_2 emissions have driven soils in the northeastern U.S. from acting as sinks of sulfur to acting as sources of sulfur (Mitchell and Likens 2011) but southeastern states have shown slower responses to lowered SO_2 emissions (Rice et al., 2014). By linking the power plant SO_2 emissions directly to the SO_4^{2-} in stream water, our model can be applied directly to assess the impacts in water quality caused by power plants as they switch from coal to gas.

Future work could address some assumptions made in this study. For example, we assumed that the sulfur content in coal is consistent when developing the technology model, and we also assumed no directional differences (i.e. wind directions) in power plant pollutant emission. These factors might be taken into account in future models. Perhaps most importantly, the sulfur-transit efficiency factor is highly location-dependent and, therefore, could be adjusted for different areas by using models such as those proposed by Rice et al. (2014). If this legacy factor were assessed more broadly, our approach could be used to predict changes in stream water quality across the U.S. or beyond.

4. Conclusions

As power plants switch from burning coal to gas because of economic factors, SO_2 emissions from the energy industry have decreased in the U.S. Our results showed that such a coal-to-gas switch in PA resulted in some reductions of SO_4^{2-} concentrations in streams nearby power plants. If 30% of the electricity generated by coal in 2017 in PA had been replaced by energy from natural gas, our model predicted that the reduction of stream SO_4^{2-} concentrations could have been as large as 10.4%. Extrapolating the model applications to the entire U.S., we found that a similar 30% coal-to-gas switch could result in a decrease of 0.1–46.1 thousand tons of total SO_2 emissions per state. We did not predict the nationwide effect on water quality because of lack of knowledge about differences in how soils and vegetation attenuate the release of SO_4^{2-} to streams in locations beyond PA. However decreases in SO_2 emissions, and in turn in stream SO_4^{2-} nationwide, are likely to benefit stream ecosystems in that less acidification and metal contamination would have occurred.

The relatively small improvements in stream water quality are difficult to detect amid all the temporal changes in power plant fuel and technology choices, as well as the effect of local soil/vegetation attenuation and variations in rainfall, etc. Our modeling approach to detect water quality change is robust because it takes into account emission-control technology trends. The technology trend models can be used to assess the ongoing and legacy impacts of coal-fired power plants on air and water quality. An added benefit of our models is that they can also be used to assess the effectiveness of the adoption of emission control technologies and region-specific benefits of coal-to-gas shifts. Such calculations are critical for policy evaluation and decision making.

Main findings

A technology trend model successfully predicts the rate of decrease in SO_2 emissions and the reduction of stream water SO_4^{2-} concentrations as power plants switch from coal to gas.

Credit author statement

Xianzeng Niu: Conceptualization, Methodology, Software, Data curation, Investigation, Writing – original draft preparation and revision; Tao Wen: Conceptualization, Data curation, Methodology, Investigation, Software. Susan Brantley: Supervision, Funding acquisition, Conceptualization, Review & editing,

Declaration of competing interest

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.

Acknowledgements

This work was partially funded by National Science Foundation Grant IIS-1639150 to Susan L. Brantley and Zhenhui Li, by the College of Earth and Mineral Sciences, and by the Earth and Environmental Systems Institute at the Pennsylvania State Univeristy. Tao

Wen was supported by the College of Earth and Mineral Sciences Dean's Fund for Postdoc-Facilitated Innovation at the Pennsylvania State University, USA.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117102.

References

Baig, K.S., Yousaf, M., 2017. Coal fired power plants: emission problems and controlling techniques. J. Earth Sci. Climatic Change, 08, 404.
Barkley, Z.R., Lauvaux, T., Davis, K.J., Deng, A., Fried, A., Weibring, P., Richter, D., Walega, J.G., DiGangi, J., Ehrman, S.H., Ren, X., Dickerson, R.R., 2019. Estimating methane emissions from underground coal and natural gas production in southwestern Pennsylvania. Geophys. Res. Lett. 46, 4531–4540.
Burns, D.A., McDonnell, T.C., Rice, K.C., Lawrence, G.B., Sullivan, T.J., 2020. Chronic and episodic acidification of streams along the Appalachian Trail corridor, eastern United States. Hydrol. Process. 34, 1498–1513.
Chen, J., Liu, G., Kang, Y., Wu, B., Sun, R., Zhou, C., Wu, D., 2013. Atmospheric emissions of F, As, Se, Hg, and Sb from coal-fired power and heat generation in China. Chemosphere 90, 1925–1932.
Cooper, J., 2017. Life cycle sustainability assessment of shale gas in the UK. In: The University of Manchester, p. 340.
Cosby, B.J., Hornberger, G.M., Wright, R.F., Galloway, J.N., 1986. Modeling the effects of acid deposition: control of long-term sulfate dynamics by soil sulfate adsorption. Water Resour. Res. 22, 1283–1291.
de Gouw, J., Parrish, D., Frost, G., Trainer, M., 2014. Reduced emissions of CO2, NOx and SO2 from U.S. Power plants due to the switch from coal to natural gas with combined cycle technology. Earth's Future *2*.
DeWalle, D.R., Boyer, E.W., Buda, A.R., 2016. Exploring lag times between monthly atmospheric deposition and stream chemistry in Appalachian forests using cross-correlation. Atmos. Environ. 146, 206–214.
Driscoll, C.T., Driscoll, K.M., Fakhraei, H., Civerolo, K., 2016. Long-term temporal trends and spatial patterns in the acid-base chemistry of lakes in the Adirondack region of New York in response to decreases in acidic deposition. Atmos. Environ. 146, 5–14.
Driscoll, C.T., Johnson, N.M., Likens, G.E., Feller, M.C., 1988. Effects of acidic deposition on the chemistry of headwater streams: a comparison between Hubbard Brook, New Hampshire, and Jamieson Creek, British Columbia. Water Resour. Res. 24, 195–200.
Gavin, A.L., Nelson, S.J., Klemmer, A.J., Fernandez, I.J., Strock, K.E., McDowell, W.H., 2018. Acidification and climate linkages to increased dissolved organic carbon in high-elevation lakes. Water Resour. Res. 54, 5376–5393.
Gilbert, A.Q., Sovacool, B.K., 2017. Benchmarking natural gas and coal-fired electricity generation in the United States. Energy 134, 622–628.
Högström, U., 1973. Residence time of sulfurous air pollutants from a local source during precipitation. Ambio 2, 37–41.
Jiang, Z., McDonald, B., Worden, H., Worden, J., Miyazaki, K., Qu, Z., Henze D, K., Jones, B.A., D Jr, A., Fischer, E., Zhu, L., Boersma, K., 2018. Unexpected Slowdown of US Pollutant Emission Reduction in the Past Decade.
Kline, K.M., Eshleman, K.N., Garlitz, J.E., U'Ren, S.H., 2016. Long-term response of surface water acid neutralizing capacity in a central Appalachian (USA) river basin to declining acid deposition. Atmos. Environ. 146, 195–205.
Levy, J.I., Spengler, J.D., 2002. Modeling the benefits of power plant emissions controls in Massachusetts. J. Air Waste Manag. Assoc. 52, 5–18.
Likens, G.E., Driscoll, C.T., Buso, D.C., Mitchell, M.J., Lovett, G.M., Bailey, S.W., Siccama, T.G., Reiners, W.A., Alewell, C., 2002. The biogeochemistry of sulfur at Hubbard Brook. Biogeochemistry 60, 235–316.
Lotfi, A., Lotfi, A., Halal, W., 2014. Forecasting Technology Diffusion: a New Generalisation of the Logistic Model.
Lueken, R., Klima, K., Griffin, W.M., Apt, J., 2016. The climate and health effects of a USA switch from coal to gas electricity generation. Energy 109, 1160–1166.
Ma, L., Konter, J., Herndon, E., Jin, L., Steinhoefel, G., Sanchez, D., Brantley, S., 2014. Quantifying an early signature of the industrial revolution from lead concentrations and isotopes in soils of Pennsylvania, USA. Anthropocene 7, 16–29.
Majumdar, D., Kar, S., 2017. Does technology diffusion help to reduce emission intensity? Evidence from organized manufacturing and agriculture in India. Resour. Energy Econ. 48, 30–41.
Massetti, E., Brown, M.A., Lapsa, M., Sharma, I., Bradbury, J., Cunliff, C., Li, Y., 2017. Environmental quality and the U.S. Power sector: air quality, water quality, land use and environmental justice. In: OAK RIDGE NATIONAL LABORATORY.
Merino, G.G., Jones, D., Stooksbury, D.E., Hubbard, K.G., 2001. Determination of semivariogram models to krige hourly and daily solar irradiance in western Nebraska. J. Appl. Meteorol. 40, 1085–1094.
Millstein, D., Wiser, R., Bolinger, M., Barbose, G., 2017. The climate and air-quality benefits of wind and solar power in the United States. Nature Energy 2, 17134.
Mitchell, M.J., Likens, G.E., 2011. Watershed sulfur biogeochemistry: shift from atmospheric deposition dominance to climatic regulation. Environ. Sci. Technol. 45, 5267–5271.
Mitchell, M.J., Lovett, G., Bailey, S., Beall, F., Burns, D., Buso, D., Clair, T.A., Courchesne, F., Duchesne, L., Eimers, C., Fernandez, I., Houle, D., Jeffries, D.S., Likens, G.E., Moran, M.D., Rogers, C., Schwede, D., Shanley, J., Weathers, K.C., Vet, R., 2011. Comparisons of watershed sulfur budgets in southeast Canada and northeast US: new approaches and implications. Biogeochemistry 103, 181–207.
Niu, X., Wen, T., Li, Z., Brantley, S.L., 2018a. One step toward developing knowledge from numbers in regional analysis of water quality. Environ. Sci. Technol.
Niu, X., Wendt, A., Li, Z., Agarwal, A., Xue, L., Gonzales, M., Brantley, S.L., 2018b. Detecting the effects of coal mining, acid rain, and natural gas extraction in Appalachian basin streams in Pennsylvania (USA) through analysis of barium and sulfate concentrations. Environ. Geochem. Health 40, 865–885.
Patel, K.F., Fernandez, I.J., Nelson, S.J., Malcomb, J., Norton, S.A., 2020. Contrasting stream nitrate and sulfate response to recovery from experimental watershed acidification. Biogeochemistry 151, 127–138.
Raymond, P.A., Oh, N.-H., 2009. Long term changes of chemical weathering products in rivers heavily impacted from acid mine drainage: insights on the impact of coal mining on regional and global carbon and sulfur budgets. Earth Planet Sci. Lett. 284, 50–56.
Rice, K.C., Scanlon, T.M., Lynch, J.A., Cosby, B.J., 2014. Decreased atmospheric sulfur deposition across the southeastern U.S.: when will watersheds release stored sulfate? Environ. Sci. Technol. 48, 10071–10078.
Sackett, D.K., Aday, D.D., Rice, J.A., Cope, W.G., Buchwalter, D., 2010. Does proximity to coal-fired power plants influence fish tissue mercury? Ecotoxicology 19, 1601–1611.
Shao, S., Driscoll, C.T., Sullivan, T.J., Burns, D.A., Baldigo, B., Lawrence, G.B., McDonnell, T.C., 2020. The response of stream ecosystems in the Adirondack region of New York to historical and future changes in atmospheric deposition of sulfur and nitrogen. Sci. Total Environ. 716, 137113.
Siemion, J., McHale, M.R., Lawrence, G.B., Burns, D.A., Antidormi, M., 2018. Long-term changes in soil and stream chemistry across an acid deposition gradient in the northeastern United States. J. Environ. Qual. 47, 410–418.
Smith, R.A., Alexander, R.B., 1986. Correlations between stream sulphate and regional SO2 emissions. Nature 322, 722.
Stamford, L., Azapagic, A., 2014. Life cycle environmental impacts of UK shale gas. Appl. Energy 134, 506–518.
Stoddard, J.L., Jeffries, D.S., Lükewille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D.T., Murdoch, P.S., Patrick, S., Rebsdorf, A., Skjelkvåle, B.L., Stainton, M.P., Traaen, T., van Dam, H., Webster, K.E., Wieting, J., Wilander, A., 1999. Regional trends in aquatic recovery from acidification in North America and Europe. Nature 401, 575–578.
Taylor, M., Rubin, S., Hounshell, D., 2005. Control of SO2 Emissions from Power Plants: A Case of Induced Technological Innovation in the. U.S.
Watmough, S.A., Eimers, C., Baker, S., 2016. Impediments to recovery from acid deposition. Atmos. Environ. 146, 15–27.
Weber, E., 1970. Contribution to the residence time of sulfur dioxide in a polluted atmosphere. J. Geophys. Res. 75, 2909–2914, 1896-1977.