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Use of Sulfur Isotope Ratios To Determine Anthropogenic Sulfur Signals in a Grassland Ecosystem

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Archived soil and herbage samples from the control plot of the Rothamsted Park Grass Experiment, established in 1856, were used to investigate the effects of dramatically changing SO₂ pollution inputs on the concentrations and stable isotope ratios of S in the samples. Both herbage S concentrations and $\delta^{34}\text{S}$ showed clear trends over the last 135 years. Herbage S concentrations correlated positively with annual total SO₂ emissions in the U.K. ($R^2 = 0.61$), whereas herbage $\delta^{34}\text{S}$ correlated negatively with SO₂ emissions ($R^2 = 0.83$). These results indicate that local variations of anthropogenic S inputs were not important at the site and verify the usefulness of this unique sample set for environmental monitoring. In contrast, the concentrations of total and extractable S in the topsoil were less sensitive to the changing pollution, although the $\delta^{34}\text{S}$ values of soil S also decreased significantly, particularly during the period 1900–1970. Based on these S isotope ratios, we estimated that anthropogenic S contributed up to 50% of the herbage S uptake at the peak of SO₂ emissions and still accounts for about 30% of the S presently stored in the topsoil.

Introduction

Human activities have dramatically altered the S cycle on Earth, increasing sulfur dioxide (SO₂) emissions by about 20-fold since 1850 (1). In 1990, global SO₂ emissions from anthropogenic sources were about three times those derived from natural processes (2). Anthropogenic emissions increased most rapidly from 1940 to 1970 in Europe and North America, but have been decreasing since 1970 (1, 3, 4). Despite this, current atmospheric S inputs still exceed the critical load for sensitive ecosystems in large areas of Europe (4). It is widely believed that increased inputs of acidifying compounds from the atmosphere, particularly those containing S, in some regions of industrialized countries have caused soil and water acidification, resulting in forest decline and loss of fisheries (5–7). In contrast, decreased S inputs in the recent decades have resulted in S deficiency in many agricultural crops in Europe and North America (8, 9).

The S concentrations of ice cores from Antarctica and Greenland and of lake sediments have been shown to reflect the dramatically increased S emissions, which were derived mainly from coal combustion, up to around the 1970s–1980s

(1, 10, 11). To study the health of ecosystems, it is essential to use soils and vegetation as records of the impacts of atmospheric pollution. However, this is more difficult, partly because of the dynamic nature of ecosystems and also because lengthy, reliable, in situ soil and vegetation records are very rare. Here we report evidence from a unique sample archive of dramatic changes in the isotopic composition and concentration of S in grassland herbage over the last 135 years, which show a close relationship with the changes in the anthropogenic SO₂ emissions. These isotopic results allow estimation of the impacts of anthropogenic S on the long-term cycling of S in the ecosystem and show how they are recovering in the post-heavy industrial era.

Materials and Methods

The Park Grass Experiment at Rothamsted started in 1856 on a semi-rural site in southern England (40 km north of London) that had been under permanent grass for several centuries (12, 13). The original objective was to test the effects of fertilizer on the yields of herbage. In this study, we used the herbage and soil samples from the unlimed control plot (plot 3d), which has never received any fertilizer treatments. The herbage from this plot contains a mixture of about 50:50 in dry weight of grass and dicotyledonous species, and there have been no significant trends in dry matter yield over the past century (13). Herbage is cut and removed twice yearly: in June and between September and November; only the first samples were used in this study. Subsamples of herbage are dried at 80 °C before being stored in sealed containers. Details of the experiment and of sample preparation have been described elsewhere (12–14). A total of 23 herbage samples were selected for analyses, including 14 samples from the single years of 1866, 1876, 1886, 1896, 1905, 1915, 1925, 1935, 1945, 1955, 1975, 1985, 1990, and 1991 and nine composite samples from the following periods: 1863–1865, 1901–1905, 1920–1923, 1940–1943, 1960–1963, 1971–1974, 1986–1989, 1990–1992, and 1993–1995.

Soil samples were taken from the top 23 cm depth in the following years: 1876, 1906, 1923, 1959, 1966, 1976, 1981, 1984, 1991, and 1996. In addition, subsoil was collected from 23 to 26 cm depth in 1876, 1981, and 1987. These were air-dried, ground to pass a 2 mm sieve, and stored in sealed glass jars. In 1876 and 1996, three and four topsoil samples, respectively, were taken from different areas of the control plot and analyzed separately. In other years, soils were bulked into one sample for the whole plot.

Soil and plant samples were digested with nitric and perchloric acids, and total S and phosphorus were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (15). Sulfur in the digest (>1 mg) was precipitated as barium sulfate and converted to SO₂ for the determination of the ³⁴S/³²S ratio using mass spectrometry (16). Soils were extracted with 0.016 M potassium phosphate in an 1:5 ratio. Aliquots of the extract were used for the determinations of SO₄²⁻ and total soluble S using ion chromatograph and ICP-AES, respectively (17). The extract was then digested with 30% hydrogen peroxide to convert all soluble S to SO₄²⁻, which was then precipitated as barium sulfate for mass spectrometric determination (16). Sulfur isotope results are reported as $\delta^{34}\text{S}$ (in ‰) on the VCDT scale. Assigning a $\delta^{34}\text{S}$ value of –0.3‰ to the reference material IAEA-S-1 silver sulfide, we obtained $\delta^{34}\text{S}$ values of 0.0‰ and 0.15‰ for Canyon Diablo Troilite and the reference material NBS 122, respectively. The overall analytical reproducibility was 0.1‰. All results are presented as means of duplicate analyses.

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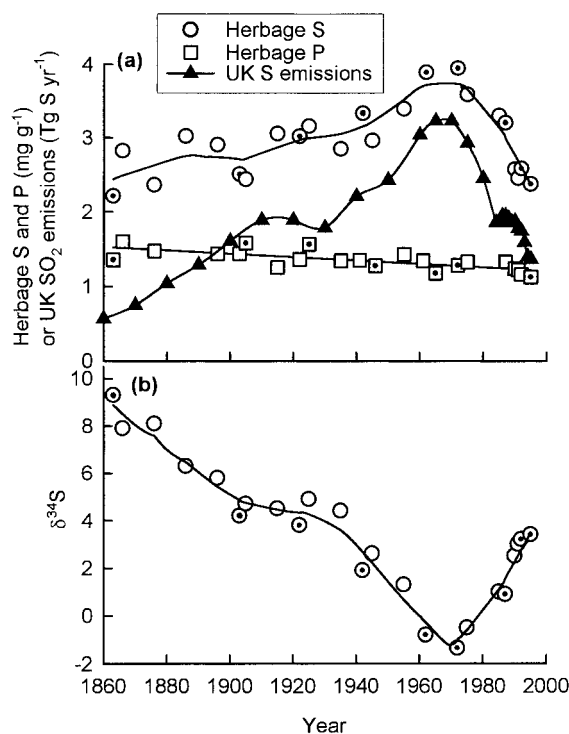


FIGURE 1. Changes in the total annual emissions of SO₂ in the U.K. and the concentrations of herbage S and phosphorus (a) and herbage δ³⁴S (b). Data for SO₂ emissions before 1970 were derived from ref 18, and after 1970 were from ref 19. Cubic smoothing splines are fitted to herbage S concentrations and δ³⁴S values and a linear regression line to herbage phosphorus concentrations. Symbols with a dot inside represent composite samples, and those without a dot represent single year samples. The data are available upon request.

Results and Discussion

Herbage Samples. The concentration of S in herbage sampled between 1863 and 1995 (Figure 1a) showed a trend remarkably similar to that of anthropogenic emissions of SO₂ in the U.K. (18, 19). There were two phases in the changes of herbage S concentration: a gradual increase between 1863 and the mid-1970s and a rapid decline since 1975. The S concentrations in the samples from the 1990s were similar to those in the earliest samples before widespread industrialization. Sulfur deficiency is unlikely to occur in this plot because the biomass production is mainly limited by nitrogen. However, large inputs of nitrogen fertilizers in agriculture and this rapid decrease in atmospheric S in the last 10 years have resulted in S deficiency and reduced crop yields in many areas in the U.K. and northern Europe (8).

The strong influence of atmospheric S from anthropogenic sources had a direct effect on the temporal pattern of herbage S (Figure 1a). This pattern is very different from that of the concentration of herbage phosphorus, a pedogenic element, which decreased slowly over the entire period studied due to a gradual depletion of the phosphorus supply in this unfertilized plot (Figure 1a). This is strong evidence that the changes in herbage S concentration cannot be attributed to changes in available S in soil.

The trend in the stable S isotope ratio δ³⁴S of the herbage S (Figure 1b) almost directly mirrored herbage S concentrations (Figure 1a) or U.K. SO₂ emissions (18, 19). The difference in δ³⁴S between the maximum in 1863 and the minimum in 1972 was 10.6‰. These results suggest that the isotopic composition of the pre-industrial native soil S differed markedly from that of anthropogenic S, the latter being much more depleted in ³⁴S, although there are no measurements of δ³⁴S in coal until recently (20).

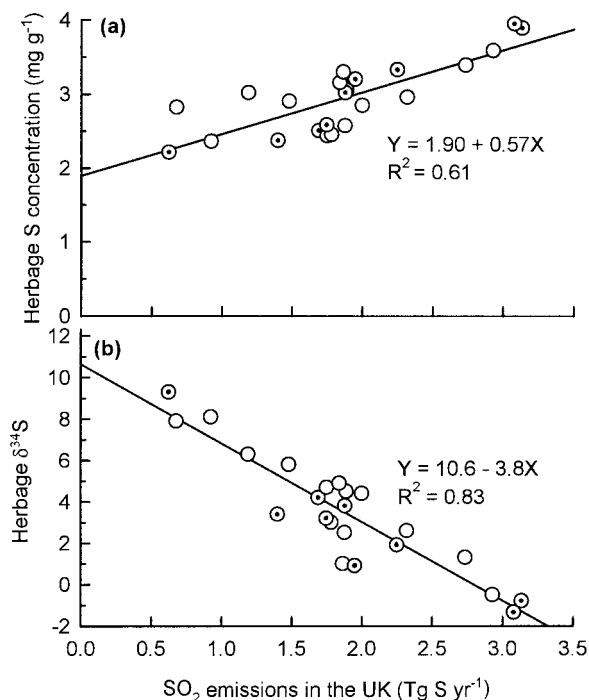


FIGURE 2. Correlations between total SO₂ emissions in the U.K. and herbage S concentration (a) and with herbage δ³⁴S (b). Symbols with a dot inside represent composite samples, and those without a dot inside represent single year samples.

The relationships between both herbage S concentration and δ³⁴S and the SO₂ emissions in the U.K. were linear (Figure 2), suggesting that increasing emissions increased plant uptake at the site proportionately and that the δ³⁴S of the anthropogenic S remained relatively constant. It is remarkable that the vegetation closely reflects a national trend, as this indicates that local sources or variations on a regional scale of S were not important in this case and verifies the usefulness of this sample set for environmental monitoring.

Soil Samples. Spatial variations within the plot in the soil S analyses were generally small in 1876 and negligible in 1996 (Figure 3a,b). Although S concentration in vegetation changed dramatically, the concentration of total S in the topsoil showed no clear trend over the period from 1876 to 1996, fluctuating around a mean of 355 mg kg⁻¹ with a coefficient of variation of 6.2% (Figure 3a). Phosphate-extractable S represents a mobile and available form of S in soils (17). This fraction included, on average, 73% SO₄²⁻ and 27% soluble organic S and accounted for 3–16% of the total S in all soil samples. The concentration of extractable S was about 30 mg kg⁻¹ between 1876 and 1984, except for a much higher value for the 1959 sample, and has decreased sharply since 1984 (Figure 3a). Therefore, the concentration of total S in the topsoil was not affected significantly by changing atmospheric inputs in the last century, and extractable S was not a sensitive indicator of anthropogenic inputs either. The latter is not surprising because the concentration of extractable S in soils can be influenced greatly by weather (particularly the amount of rainfall) prior to sampling.

The δ³⁴S of the total S in topsoil decreased from 8‰ in 1876 and 1906 to about 4‰ in the samples collected between 1966 and 1996 (Figure 3b). The δ³⁴S of extractable S was 1.5‰ less than that for the total S initially but decreased more rapidly than the δ³⁴S for total S during the first half of the century, and reached a value of about 1.5‰ over the last 30 years. The changes in the soil δ³⁴S reflect the influence of atmospheric deposition. The lack of a response of soil δ³⁴S to a marked decrease of SO₂ emissions since 1970 can be explained by two factors. First, the total amount of S in

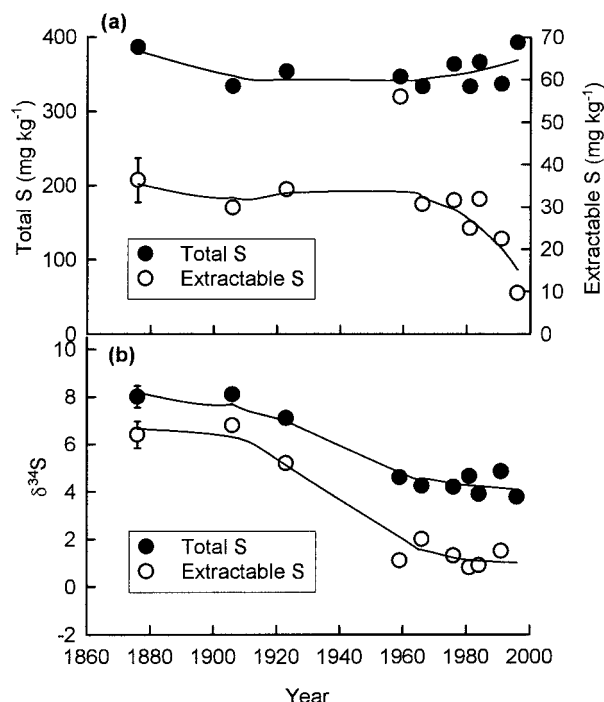


FIGURE 3. Changes in the concentrations of total and extractable S in the topsoils (a) and soil $\delta^{34}\text{S}$ (b). Curves are cubic smoothing splines. The data point for soil extractable S for the year 1959 was excluded from the curve fitting. Standard error bars are shown for the 1876 and 1996 soil samples. For the 1996 samples, the error bars were smaller than the symbols. The concentration of soil extractable S in the 1996 sample was too low to allow an accurate determination of $\delta^{34}\text{S}$.

TABLE 1. Total S Concentration and $\delta^{34}\text{S}$ of Topsoils and Subsoils

year	depth (cm)	total S (mg kg ⁻¹)	$\delta^{34}\text{S}$ (‰)
1876	0–23	386.2	8.0
	23–46	90.9	9.4
1981	0–23	333.3	4.7
	23–46	106.3	5.5
1991	0–23	336.7	4.9
	23–46	115.2	6.4

the topsoil (1000 kg ha⁻¹) is about 70 times the current annual deposition of S from the atmosphere. Second, mineralization–immobilization in the S cycle in soil causes a long lag before changes become apparent.

The concentrations of total S in the subsoils (23–46 cm) were about one-fourth to one-third of those found in the topsoils (Table 1). In three different years, $\delta^{34}\text{S}$ of soil total S was 0.8–1.5‰ more positive in the subsoils than in the topsoils (Table 1). There are two possible explanations for the differences in the $\delta^{34}\text{S}$ values between total S and extractable S and between topsoils and subsoils. The first is that the differences merely reflect the impact of atmospheric deposition, with topsoils and extractable S pool being affected more, hence having lower $\delta^{34}\text{S}$. The second is the effect of isotopic fractionation during mineralization of organic S, a process that is thought to produce SO_4^{2-} with depleted ^{34}S as compared to organic S (21, 22). There is still debate whether significant isotopic fractionation occurs during S mineralization (23). Dissimilatory sulfate reduction is known to result in significant isotopic fractionation (24), although this process is unlikely to be important in aerobic soils.

Estimation of Anthropogenic S Contributions. The large difference in $\delta^{34}\text{S}$ between native soil S and anthropogenic

S provides a basis for the isotopic ratio to be used to delineate contributions of S from different sources (25–28). We extrapolated the regression equation in Figure 2b to zero emissions to give a pre-industrial herbage $\delta^{34}\text{S}$ value of 10.6‰. This can be considered to be the isotopic signature of nonanthropogenic S. By plotting herbage $\delta^{34}\text{S}$ against the inverse of herbage S concentration (25), using data up to 1975 when emissions peaked, we obtain from linear regression an intercept of –12.2‰. This value represents anthropogenic S, probably derived from combustion of coal. The value of –12.2‰ for anthropogenic S obtained here is in the lower range of the $\delta^{34}\text{S}$ values reported for coal (between –30 and +30‰) (20). Using the calculated $\delta^{34}\text{S}$ values for the anthropogenic and nonanthropogenic S, we estimate that the contribution of anthropogenic S (both current deposition and that accumulated in the soil in previous years) to the herbage S pool increased from 6% in 1863 to a peak of 52% in 1972, and subsequently decreased to 30% in 1995. Furthermore, if we assume that the pre-industrial $\delta^{34}\text{S}$ for total S in the topsoil is similar to the pre-industrial herbage $\delta^{34}\text{S}$, on the basis that S uptake and assimilation by higher plants are usually associated with minimal isotope fractionation (25), we estimate that 30% of the total S stored in the top 23 cm soil in 1996 had been derived from atmospheric inputs of anthropogenic origin. These are rough estimates because there are no $\delta^{34}\text{S}$ records for anthropogenic S for the last 130 years.

In conclusion, vegetation samples are important for monitoring the long- and short-term changes in the health of the biosphere, while soil samples give information on the long-term turnover of S derived from pollution once it has entered the biospheric pool. The fact that a linear relationship between U.K. SO_2 emissions and herbage $\delta^{34}\text{S}$ was observed (Figure 2) indicates that these results may be representative of a wide geographical region. Therefore, this approach sheds light on the changes that have taken place in ecosystems across wide areas in the U.K. Similar studies in other zones may also confirm historical trends in $\delta^{34}\text{S}$ that can be used in a similar fashion.

Acknowledgments

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