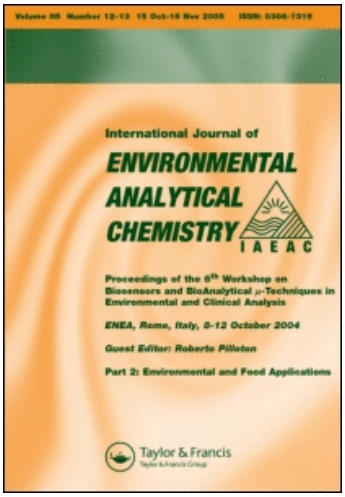

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Analysis of Organic and Inorganic Sulfur Constituents in Sediments, Soils and Water

D. H. Landers[ab]; M. B. David[a]; M. J. Mitchell[a]
[a] Department of Environmental and Forest Biology, State University of New York, College of Environmental Science and Forestry, Syracuse, New York, U.S.A. [b] State University Research Center at SUNY-Oswego, Oswego, New York

To cite this Article Landers, D. H. , David, M. B. and Mitchell, M. J.(1983) 'Analysis of Organic and Inorganic Sulfur Constituents in Sediments, Soils and Water', International Journal of Environmental Analytical Chemistry, 14: 4, 245 — 256
To link to this Article: DOI: 10.1080/03067318308071623
URL: http://dx.doi.org/10.1080/03067318308071623

Intern. J. Environ. Anal. Chem., 1983, Vol. 14, pp. 245–256
0306-7319/83/1404-0245 $18.50/0

Printed in Great Britain

Analysis of Organic and Inorganic Sulfur Constituents in Sediments, Soils and Water

D. H. LANDERS†, M. B. DAVID and M. J. MITCHELL

Department of Environmental and Forest Biology, State University of New York, College of Environmental Science and Forestry, Syracuse, New York 13210, U.S.A.

(*Received October 5, 1982*)

A suite of analytical methods for determining the amount of organic sulfur (carbon-bonded sulfur and ester sulfate) and inorganic sulfur (sulfate and sulfide) is described. Organic sulfur fractions, which have often been ignored, are major constituents of oxic substrates and have a major role in sulfur dynamics. Methods of sample preparation and a modification of the Johnson–Nishita digestion–distillation apparatus are given. HCl digestion, Zn–HCl reduction, hydriodic acid reduction, sulfate extraction, wet oxidation and dry oxidation are utilized for determining sulfur constituents. With only minor modifications these analyses were adapted for examining ^{35}S transformation rates. Results from these analyses on sewage sludge, lake sediment, soil, and water demonstrate the usefulness of these methods.

KEY WORDS: Organic sulfur, ester sulfate, radioisotope, carbon-bonded sulfur, inorganic sulfur.

INTRODUCTION

Sulfur is an important component of both natural and anthropogenic processes. Due to its importance both in the formation of acidic precipitation and as a macronutrient required by all organisms, sulfur's role in atmospheric, aquatic and terrestrial systems has been investigated.[1,2,3] Sulfur has a vast array of both inorganic and organic chemical species. The understanding of sulfur dynamics has been restricted due to lack of information on the role of specific sulfur constituents in

†Present Address: State University Research Center at SUNY–Oswego, Oswego, New York 13126.

affecting sulfur fluxes and transformations. For example, our work has shown the importance of organic sulfur in freshwater sediments of three lakes in New York (Oneida, South, Deer),[3] aerobically digested sewage sludge[4] and forest soils in the Adirondack Mountains.[5] Previous work on such substrates had generally ignored the organic sulfur constituents with most work focusing only on inorganic sulfate or sulfide.

We have combined and modified various analytical methods to determine the major sulfur constituents in lake waters, sediments, and soils. Independently these methods are useful. However, in combination with the same digestion–distillation apparatus, they provide a reliable and convenient group of analytical methods which have not been detailed elsewhere and can be used in investigations of sulfur dynamics. We have also expanded these techniques to use ^{35}S as a radioactive tracer in determining fluxes of sulfate into the major sulfur pools. This paper will describe the methodology and its application to the analysis of sulfur compounds in various materials.

Sample preparation

Unaltered wet sediment (60–95% wet mass) and moist soil samples (10–70% dry mass) are used for all analyses except total sulfur because major changes in sulfur constituents can occur upon drying of substrates,[5] while loss of sulfur by volatilization is negligible. Small sample sizes (ca. 2 mg) are often required due to the high sulfur content of certain substrates and the sensitivity of the analytical techniques. When handling small samples, the material is placed in glass weighing boats, formed by cutting in half lengthwise 1.5 cm lengths of 10 mm diameter glass tubing. Samples are added to the weighing boats with either a small spatula or a plastic syringe fitted with a 16 ga. 3.8 cm stainless steel hypodermic needle. Weigh boat and sample are added to digestion flasks. For sampling viscous substrates that clog needles (e.g., clayey lake sediments), a glass tubing extension is attached to a syringe with a plastic tubing connector.

With the exception of SO_4^{-2}-S sulfur fractionation has been routinely performed on lake water samples containing less than 0.031 μmoles total sulfur. To get samples within the detection range, flash evaporation is used to concentrate water samples. Samples are heated no higher than 25°C in a water bath to prevent alteration of labile forms of sulfur. After concentration the following methods can be performed on a maximum volume of 2 ml liquid.

Methods

For all our sulfur analyses the digestion–distillation apparatus of Johnson

and Nishita[6] is used except for SO_4^{-2}-S in water which may also be measured turbidimetrically.[7] We modified the apparatus by (1) adding a removable gas import tube, which allows thorough cleaning of all surfaces as well as interchange of parts if breakage occurs and (2) eliminating the two stopcocks on the gas washing column (Fig. 1). Eight digestion stations are connected to a common water supply for cooling the condensers. The nitrogen ($O_2 < 0.5$ ppm) purging gas is regulated individually via a group of stopcocks with needle valves. Electric mantles (50 ml, Glas-Col Co.) are connected to a variable transformer and samples are heated to boiling.

Reagents used in the following methods are described in Table I. An acetate trapping solution[6] is prepared daily and 80 ml added to each 100 ml volumetric flask before each analysis. The pyrogallol solution (10 ml) is added to the gas washing column. Samples are placed in the digestion flasks with specific reagents and the digestion–distillation procedure subsequently reduces various sulfur constituents to H_2S which is moved by a stream of N_2 into the trapping flasks where it forms ZnS, an insoluble precipitate. Colorimetric reagents, p-aminodimethyl-aniline sulfate and ferric ammonium sulfate, are added to the gas trapping flasks according to Johnson and Nishita[6] and samples are analyzed spectrophotometrically at 670 nm. Reagent blanks are run in each method and corrections made in results. Blanks are generally very low in all analyses (< 0.03 μmole S).

HCl digestion sulfur[8] (Acid digestible inorganic S). A wet sample (0.05–2.0 g) is placed into a digestion flask and 10 ml of 1:1HCl is added rapidly to the flask. All connections are closed quickly, the N_2 flow is started (about 2 bubbles per second) and the samples are refluxed for 1 hr. Na_2S is used as standard.

ZN–HCl reducible sulfur[9] (Non-sulfate inorganic S). A wet sample (0.05–0.20 g) is placed into a digestion flask containing ca. 2.0 g of granulated zinc metal. The system is flushed with N_2, 10 ml of 1:1 HCl is added, and the solution is boiled for 1 hr. The gas flow is continuous when adding the reagent to prevent liberated hydrogen gas from causing the sample to enter the gas import tubes. Extreme foaming has been a problem with some soil samples but the addition of 1.5 ml of an antifoam spray (A. H. Thomas Co.) has solved the problem and no interference has been found. $Na_2S_2O_3$ is used as a standard.

Hydriodic acid (HI) reducible sulfur[10] (Non-carbon bonded S). A wet sample (0.01–0.10 g) is added to the digestion flask and 4 ml of mixed reagent are added. Gas flow is started and the sample is refluxed for 1 hr. K_2SO_4 is used for a standard.

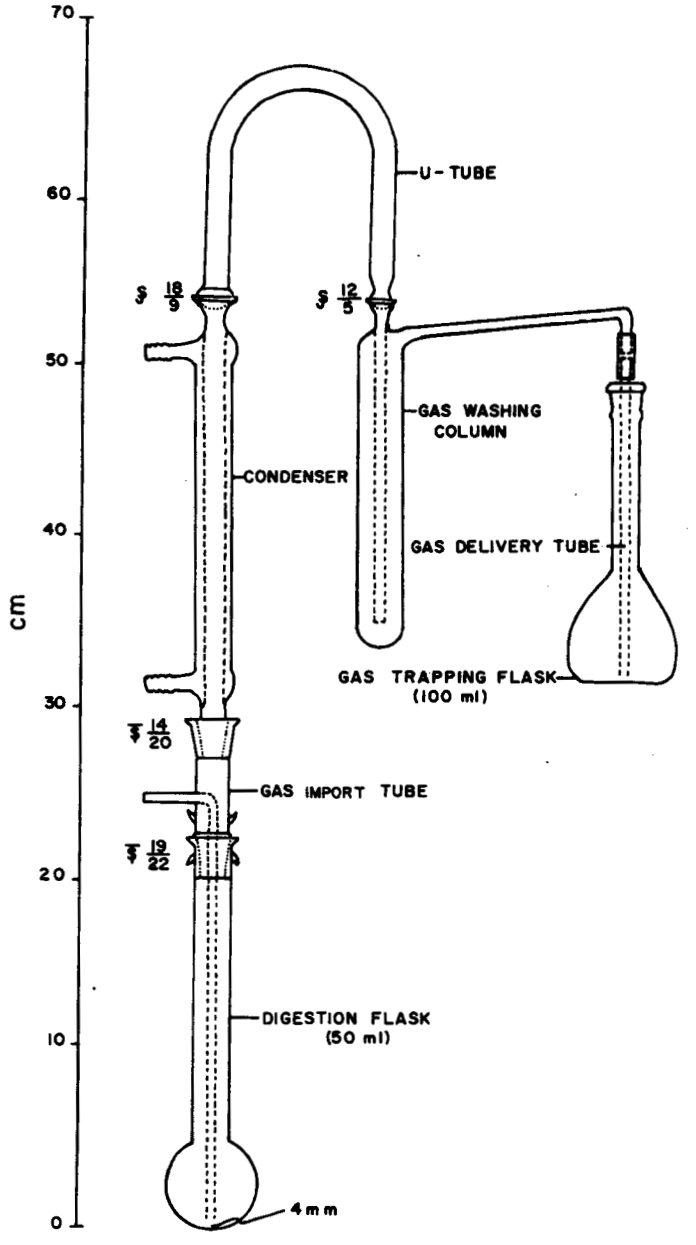

FIGURE 1 The digestion–distillation apparatus. Tapered glass joints are sealed with a few drops of water and the ball and socket connections are very lightly coated with silicon stopcock preparation. Condensers held by adjustable clamps are mounted to a permanent frame. Gas washing columns are rinsed with distilled water after use. All other parts are interchangeable and are assembled ahead of each takedown to minimize down time.

TABLE I

Analytical reagents used in sulfur analyses

Reagent	Preparation
1. DDW	Distilled deionized water.
2. 1:1 HCl	Concentrated HCl mixed in a 1:1 ratio with DDW.
3. Zinc metal	Granulated (20 mesh).
4. Hydriodic acid reducing mixture	Combine 300 ml of hydriodic acid, 75 ml hypophosphorus acid (50%) and 150 ml of 88% formic acid. Boil gently with a N_2 gas stream for 10 min after reaching 115°C. During the 10 min temperature is kept between 115° and 117°C. Upon completion the reagent may appear bright yellow or brown, apparently depending on the quality of the reagents used. We have found no performance difference related to color. The mixed reagent has a shelf life of about 2 wks.
5. Phosphate buffer	2.23 g of $Na_2H_2PO_4 \cdot H_2O$ dissolved in 1 liter of DDW (15 mmoles P).
6. Sodium hypobromite solution	3 ml of bromine is added slowly (0.5 ml $\cdot$ min^{-1}) with constant stirring to 100 ml of 2 M NaOH. Prepare immediately before use.
7. Mixed oxidant	25 g $NaHCO_3$ and 1 g Ag_2O thoroughly mixed in a mortar and pestle to a light grey color—kept in tightly sealed container.
8. Acetate trapping solution	Stock solution: dissolve 50 g of zinc acetate and 12.5 g of sodium acetate in DDW and dilute to 1 liter, filter. Before each analysis 100 ml of stock solution is mixed with 700 ml of DDW and 80 ml of this mixture added to each gas trapping flask.
9. Pyrogallol-sodium phosphate	Dissolve 10 g $NaH_2PO_4.H_2O$ and 10 g of pyrogallol in 100 ml DDW, bubble with nitrogen to dissolve. Prepare fresh daily and discard when brown color develops.
10. N, N-Dimethyl-p-phenylene-diamine sulfate (Eastman Kodak No. 1333)	Dissolve 2 g in 1500 ml of DDW, add 400 ml of concentrated sulfuric acid, allow to cool and dilute to 2 liters.
11. Ferric ammonium sulfate	Combine 25 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ and 5 ml of concentrated sulfuric acid, then add 195 ml of DDW, stir until dissolved.

Extractable sulfate. The amount of sulfate extracted from a given substrate depends on the extraction procedure as well as the adsorptivity and solubility of the sulfate constituents. A phosphate buffer solution will remove sulfate due to the higher affinity of phosphorus for anion exchange sites. Sediment samples up to 1 g are placed in 25 ml test tubes and extracted in 5 ml of phosphate buffer solution by shaking vigorously for 1 hr. The suspension is centrifuged to remove suspended particulates. The

supernatant is then placed into the barrel of a 10 ml disposable syringe fitted with a filter adapter and the sample filtered through a GF/C (Whatman, 98% retention of 1.2 μm) filter. Filtrate (up to 2 ml) is added to the digestion flasks and the HI reduction procedure followed. Significant amounts of ester sulfate in filtrates would cause an overestimate of the inorganic sulfate component. The same procedure is followed for soils, having generally lower sulfate concentrations than sediments, except that 5 g samples are shaken in a 250 ml flask with 100 ml buffer. To concentrate dilute aqueous sulfate samples, any volume of filtrate may be dried in the digestion flasks.

Total sulfur—wet oxidation. The sample (1.5–500 mg) is placed in a digestion flask and heated in a sand bath to dryness at 250° with 3 ml of sodium hypobromite solution.[11] The residue is resuspended with water, neutralized with formic acid, and then HI reduction of the sample is followed to quantitatively recover the inorganic sulfate formed by wet oxidation. This method is used for liquid and radioactive samples because it allows a larger sample size. K_2SO_4 is used as a standard.

Total sulfur—dry oxidation.[12] Dry, finely ground samples are used in this more rapid total sulfur method. The samples (1.5–100 mg) are combined with about 100 mg of mixed oxidant in small porcelain crucibles (18 mm dia, 12 mm h). The sodium bicarbonate in the oxidant should have a sulfur concentration less than 0.001% sulfur or high blanks may result. About 200 mg of the mixed oxidant is layered on top of the sample as a trap and the mixture heated in a cold muffle furnace to 550°C and maintained at that temperature for 3 hr. Larger samples can be used with proportional increases in the amount of mixed oxidant. After cooling, the mixture is transferred to the digestion flasks and an HI reduction used for determining total sulfur. When the hydriodic acid is added to the digestion flasks containing the solid sodium bicarbonate, considerable liberation of gas may occur. Consequently, to prevent entry of material into the gas import tubes, the N_2 gas glow should be started before adding the HI mixed reagent or, alternatively, up to 2 ml of DDW (distilled deionized water) can be added to decrease the rate of reaction. Beta-casein (0.8% sulfur) is used as a solid standard (personal communication J. R. Freney).

When analyses are complete, the fractionation scheme shown in Fig. 2 is used to determine organic and inorganic sulfur constituents. We perform Zn–HCl reduction on our samples but this fraction has not been adequately described in the literature for use with sediments.[13] Specifically, the recovery of iron–sulfur compounds by Zn–HCl reduction needs investigation. For example, in some reduced sediment samples the Zn–HCl

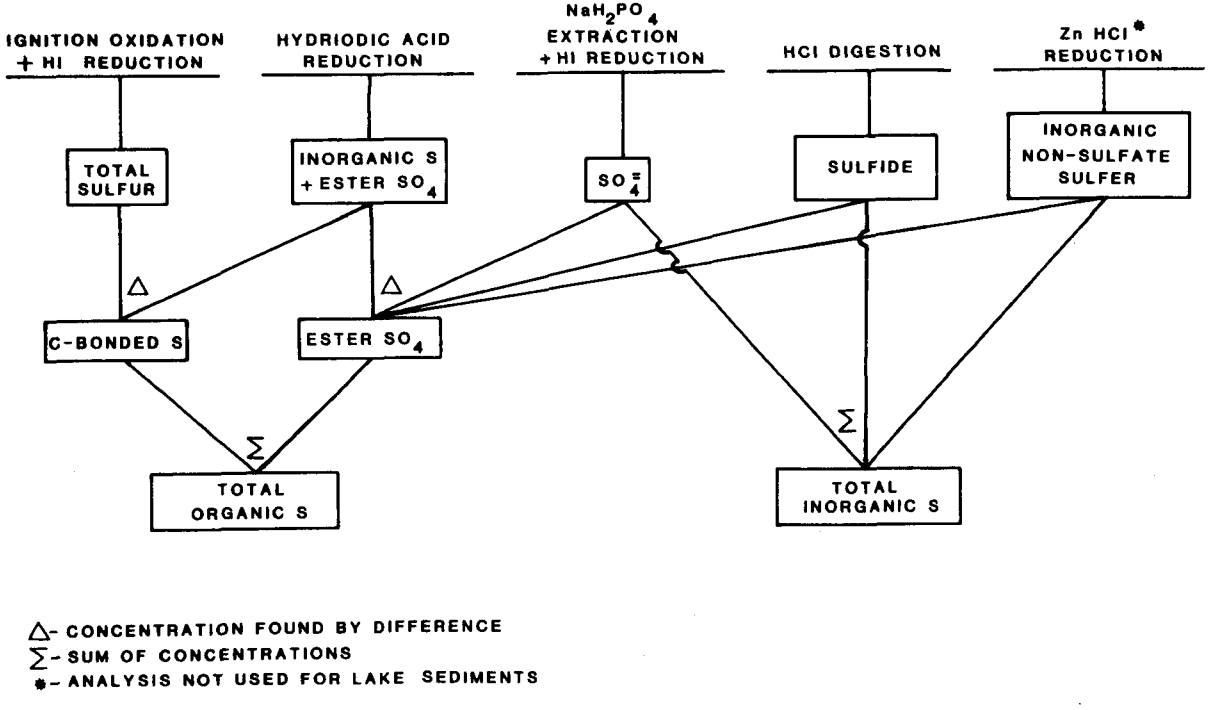

FIGURE 2 Determination of carbon-bonded sulfur, ester sulfate, and total organic sulfur from analyses of total sulfur, hydriodic acid reduction, extractable inorganic sulfate, HCl digestion and Zn–HCl reduction.

fraction was greater than the HI reducible fraction and additional work showed that HI reduction does not recover certain iron sulfide compounds (i.e., pyrite), while Zn–HCl reduction recovered a variable portion of these forms. In oxic soils,[5] however, the Zn–HCl fraction is subtracted to obtain an estimate of organic sulfur since these materials would not have significant quantities of iron sulfide compounds.

Analysis of marine and freshwater sediments for iron–sulfur compounds (e.g., pyrite, marcasite, greigite, mackinawite and pyrrhotite) has disregarded organic sulfur which, if present, would be included in many of these analyses.[14,15,16] Iron sulfur compound formation may occur in saturated soils and sediments when the oxygen concentration becomes low,[17] but would not be expected in oxic substrates. The lake sediments and soils we have studied are generally oxic and consequently the presence of iron sulfur compounds should be low. We have performed SEM–X-ray defraction analysis on bulk samples of sediments from three lakes[3] and found that particles containing iron–sulfur associations were not a major constituent of the total sulfur in the matrix. Mössbauer examination (Dr. Vaishnara, personal communication) of the same materials support these findings: pyrite was 37, 12 and 6% of total S in Oneida, South and Deer Lakes, respectively. As a result, we are confident that within the sediments we have examined iron sulfur compounds are usually a small component of the organic sulfur pool as defined by our analytical scheme (Fig. 2). The presence of iron–sulfur compounds would cause an over estimate of carbon-bonded sulfur but, if data are available, can be subtracted from the carbon-bonded sulfur pool.

After each digestion, flasks and gas import tubes are rinsed in tap water to remove reagents and samples and then submersed in aqua regia for at least 10 min. They are then rinsed thoroughly with tap water (3 X) and distilled water (3 X).

^{35}S techniques. Radioisotopes can be very useful in the precise measurement of the efficiency of laboratory operations as well as the investigation of movement of small amounts of labeled materials within soil or dediment systems.

Sediment, water, and soils labeled with ^{35}S are digested with the digestion–distillation apparatus. After methylene blue reagents are added to the Zn–Na acetate trapping solution and the color developed, we place a 500 μl sub-sample of this solution into 10 ml of ScintiVerse universal cocktail (Fisher Scientific Co.) Activity is determined with a liquid scintillation counter in the energy range 0–0.156 meV as CPM and converted to becquerels using efficiencies determined for each vial from the addition of an internal ^{35}S standard. Counting efficiencies generally have

ranged from 70–90% dpending upon the degree of color development in the acetate solutions with quenching increasing with color intensity. Sample size, isotope concentration, and the counting sample size may be adjusted so that both the colorimetric and radiometric analyses can be performed on the same samples after undergoing digestion and distillation.

There is a 200 fold dilution of sample when our methods are used. This should be considered when choosing the amount of isotope used in an experiment. ScintiVerse (Fisher Scientific Co.) can incorporate a large aqueous sample (i.e., greater than 0.5 ml per 10 ml) without becoming diphasic and the volume of the trapping flasks can be varied as an additional adjustment to the final activity in the scintillation vials.

Samples containing isotope were digested using the HI reduction procedure along with 20 μl sulfur as standard K_2SO_4 solution. We were able to account for 97% of the radioactive material; 87% was recovered from the volumetric trapping flask while 10% was recovered from the digestion flask and washings from the condenser.

Isotope contaminated apparatus is rinsed with tap water after soaking overnight in a potassium-dichromate cleaning solution and then put through out regular wash and rinse procedure described previously. Four replications of each sample are usually performed and using eight stations a competent technician can accomplish 5–6 runs (40–48 analyses) in a working day.

GENERAL RESULTS

We have found these procedures to be useful for analyzing sulfur in a variety of materials. We have used these methods to analyze thousands of samples for the major sulfur constituents in sediments, sludges and soils.[3,4,5,18,19,20] Furthermore, they have been easily adapted to other substrates ranging from liquid paint to wood containing different concentrations of sulfur constituents. Examples of some of these analyses are given in Table II and show that a wide range of sulfur concentrations can be measured with these procedures. In the sludge, soil and sediments, ester sulfate and carbon-bonded sulfur were the major sulfur constituents. However, the aerobically digested sludge and aerobic lake sediment substrates also had high concentrations of Zn–HCl–S, indicating that inorganic S constituents other than SO_4^{-2} may be important. In surface water from acidified, oligotrophic South Lake in the Adirondack Mountains, most of the S present was as SO_4^{-2}-S, though significant quantities of organic S were detected (>15% of total S). Organic S constituents have not been previously measured in lake water. Reduced

TABLE II

Sulfur constituents of various substrates.

Substrate	*n*	Total S	HCl–S	Zn–HCl–S	HI–S	SO_4^{-2}–S	[a]C–S	[a]C–O–SO_3
		(μmole·g^{-1} dry mass or μmole·l^{-1})						
Sewage sludge (aerobic) (Waugh and Mitchell)[4]	3	344±1.5	0.0	46.2±3.4	210±7.5	37±2.5	134±8.4(6)	126±2.5(100)
Forest soil Hardwood 01 Horizon (David *et al.*)[5]	4	50.0±9.3	U.D.	0.62±1.1	8.25±0.93	0.48±0.08	41.9	7.16
Forest soil Hardwood B22hir Horizon (David *et al.*)[5]	4	16.5±1.6	U.D.	0.69±0.03	5.00±0.62	0.72±0.13	11.5	3.59
South Lake sediment (unpublished)	12	229±18	1.56±0.36	75.9±9.4	82.5±12.5	35.3±2.5	146±17.7	45.3±12.4
South Lake water (unpublished)	6	0.064±0.002	U.D.	U.D.	0.060±0.002	0.053±0.002	0.004±0.002	0.007±0.0002

U.D.—undetectable.

[a]Not a direct measurement and pyritic S is not subtracted.

(*n*) if different from others.

non-sulfate inorganic S constituents were undetectable in all water samples.

We have also used these methods to ascertain the role of organisms in affecting the transformation and fluxes of sulfur on both aquatic and terrestrial systems.[3,4,18,20] The utilization of ^{35}S for studying the effect of a burrowing mayfly (*Hexagenia*) on sulfur fluxes is shown in Table III. In this study two nymphs were added to microcosms containing water and sediment from a mesotrophic lake. Microcosms were kept for 42 days in the dark at 20°C. The presence of *Hexagenia* increased the incorporation rate of sulfate into sediment and its transformation to organic forms.

TABLE III

Incorporation of radioactive sulfate ^{35}S into microcosms of lake sediment with and without the burrowing mayfly, *Hexagenia* (from Lawrence 1982).[19]

Microcosm type	Total sulfur	Organic sulfur
	k Bq · g^{-1} dry sediment ± S.E. ($n=6$)	
Hexagenia	575 ± 38	438 ± 71
Control	446 ± 22	295 ± 2

Much of this past work and our present research is focusing on the role of organic sulfur in both aquatic and terrestrial systems. This role has not been adequately investigated in previous work on sulfur dynamics and transformation in these ecosystems. To understand how both biogenic and anthropogenic sulfur affect sulfur dynamics, an assessment of the various sulfur constituents, especially the large proportion of organic sulfur, using appropriate analytical approaches is necessary.

Acknowledgements

The Office of Water Research Technology (Project No. B-096-NY) and McIntyre–Stennis provided partial financial support for this research.

References

1. J. O. Nriagu and J. D. Hem, p. 211–270. In: J. O. Nriagu (ed.) *Sulfur in the Environment* (Wiley–Interscience, NY, 1978) Part 2.
2. D. S. Shriner and G. S. Henderson, *J. Environ. Qual.* **7**, 392–397 (1978).
3. M. J. Mitchell, D. H. Landers and D. F. Brodowski, *Water, Air and Soil Pollution* **16**, 351–359 (1981).
4. J. H. Waugh and M. J. Mitchell, *Pedobiologia* **22**, 268–275 (1981).
5. M. B. David, M. J. Mitchell and J. P. Nakas, *Soil Sci. Soc. Am. J.* **46**, 847–852 (1982).
6. C. M. Johnson and H. Nishita, *Anal. Chem.* **24**, 736–742 (1952).

7. American Public Health Association, *Standard methods for the examination of water and wastewater*, (American Public Health Association, NY 1976) 14th ed.
8. J. Smittenberg, G. W. Harmsen, A. Quispel and D. Otzen, *Plant and Soil* **3**, 353–360 (1951).
9. R. B. Aspiras, D. R. Keeney and G. Chesters, *Analytical Letters* **5**, 425–432 (1972).
10. C. M. Johnson and A. Ulrich, *Calif. Agr. Exp. Sta. Bull.* No. 766 (1959).
11. M. A. Tabatabai and J. M. Bremner, *Soil Science Society of America Proc.* **34**, 62–65 (1970).
12. A. Steinbergs, O. Iismaa and J. R. Freney, *Anal. Chim. Acta* **27**, 158–164 (1962).
13. W. A. Dick, H. F. Chancy, Jr. and M. A. Tabatabai, *J. Environ. Qual.* **9**, 455–459 (1980).
14. R. W. Howarth and J. M. Teal, *Limnol. Oceanogr.* **24**, 999–1013 (1979).
15. R. W. Howarth, *Science* **203**, 49–51 (1978).
16. J. O. Nriagu, *Limnol. Oceanogr.* **13**, 430–439 (1968).
17. R. A. Berner, *Principles of Chemical Sedimentology* (McGraw–Hill Book Co., New York, 1971).
18. G. B. Lawrence, M. J. Mitchell and D. H. Landers, *Hydrobiologia* **87**, 273–283 (1982).
19. G. B. Lawrence, *M. S. Thesis*, CESF, SUNY, Syracuse, NY (1982).
20. M. J. Mitchell, M. B. David and C. R. Morgan, in press In: Ph. Lebrun, H. M. Andre, A. deMedts, G. Gregoire-Wibo and G. Wauthy (eds.) *New trends in soil biology VIII. Intl. Coll. Soil Zool.* (Dieu–Brichart, Belgium, 1983).