Sources of soil leachable sulphate in the Indian region using sulphur isotopic analysis

A Thesis

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by

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Certificate

This is to certify that this dissertation entitled ‘Sources of Sulphate in the Indian region using Sulphur isotopic ($\delta^{34}S$) analysis’ towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by Abdul Rauf Pat Indian Institute of Science Education and Research under the supervision of Dr. Shreyas Managave, Department of ECS, during the academic year 2022-2023.

Dr. Shreyas Managave

Committee:

Dr. Shreyas Managave

Dr. Anirban Das

This thesis is dedicated

to my parents and siblings

for their endless love and support

Declaration

I hereby declare that the matter embodied in the report entitled ‘Sources of Sulphate in the Indian region using Sulphur isotopic ($\delta^{34}S$) analysis’ are the results of the work carried out by me at the Department of Earth and Climate Science, Indian Institute of Science Education and Research, Pune, under the supervision of Dr. Shreyas Managave and the same has not been submitted elsewhere for any other degree

Abdul Rauf P

Date: 10/04/2023

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Abstract

Sulphur is an essential nutrient for the growth of plants and, in recent years, sulphur deficiency in the soils is becoming a serious problem. In order to manage the sulphur resources in the soil, it is necessary to understand various sources of sulphur and their relative contributions. The sulphur in the soil mainly comes from the substrate rock or via atmospheric deposition either as wet or dry deposition. As these sources have distinct sulphur isotopic compositions ($\delta^{34}S$), $\delta^{34}S$ study of leachable soil sulphate is a useful tool to study the origin of sulphur in the soil. $\delta^{34}S$ studies have been successful in understanding the biogeochemical cycle of sulphur by identifying the different sources of sulphur. Based on the limited number of $\delta^{34}S$ studies, it has been suggested that sulphur in the soils and rivers of peninsular India is mainly derived from atmospheric fallout or from rain, and the contribution from the bedrock is negligible. On the contrary, sulphur in the rivers from the western Himalayas is indicated to be derived from the rocks. However, such characterization is carried out at only a few locations and its spatial variability is not known. Further, because of contributions from deeper rocks or groundwater, $\delta^{34}S$ variation in the river or stream water may not reflect the $\delta^{34}S$ of the soils.
This study analysed the soils collected from various locations within India for their $\delta^{34}S$. Soil samples were collected employing a community-outsourced sampling scheme. Sulphate was leached out from the soil samples using an established protocol and was converted to barium sulphate whose $\delta^{34}S$ was determined at the IRMS facility of IISER Pune. $\delta^{34}S$ values of sulphate from the samples from the Indo Gangetic plain were depleted in ^{34}S compared to that in the rest of India. It is postulated that the soil sulphate in the Indo-Gangetic plain and Himalayan region is likely to be derived mainly from weathering of sulphide phases in the rocks while those from the soil in other parts of India are derived from atmospheric deposition. This contrast in the $\delta^{34}S$ values in soils between Himalaya-Gangetic plain and the rest of India mimics the spatial variability reported in the $\delta^{34}S$ of bird feathers from the Indian region. The $\delta^{34}S$ study of the riverine sulphate has implications for CO_2 budget estimation. This work will be helpful in assessing sulphate budget in the riverine system.

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Chapter 1 Introduction

1.1. Sulphur and its isotopes

Sulphur, which is the 16th element in the periodic table, is found in significant amounts and it's the 10th, 8th and 12th most abundant element in the solar system, bulk Earth and continental crust respectively. Sulphur has four stable isotopes, which are ^{32}S, ^{33}S, ^{34}S, and ^{36}S. These isotopes occur naturally and have varying abundances, with ^{32}S (94.99 % ± 0.26 %), ^{33}S (0.75 % ± 0.02 %), ^{34}S (4.25 % ± 0.24 %), and ^{36}S (0.01 % ± 0.01 %). The sulphur isotopic composition of a sample is expressed as

$$\delta^{34}S = [R_{\text{sample}} / R_{\text{standard}} - 1] \times 1000 \qquad (1)$$

Where, R is $[^{34}S/\,^{32}S]$, the ratio of abundances of ^{34}S and ^{32}S. Sulphur from meteorites Vienna Canyon Diablo Troilite (VCDT) is considered standard. The positive and negative values of $\delta^{34}S$ respectively indicate higher and lower $[^{34}S/\,^{32}S]$ in the sample relative to VCDT ($[^{34}S/\,^{32}S]$ = 0.044151) (Ding et al, 1999).

1.2. Sulphur isotopic fractionation

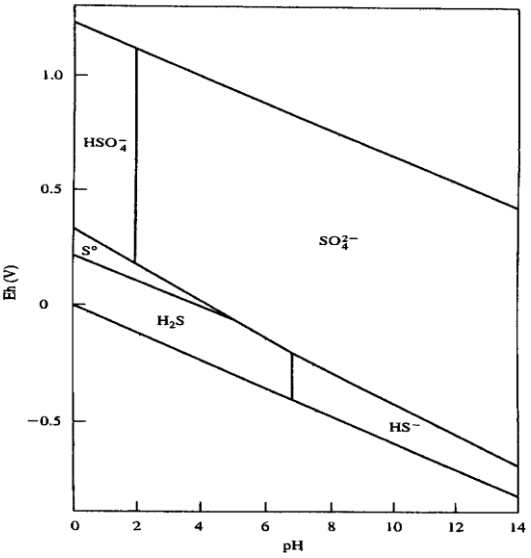

Figure 1.1: Eh-pH diagram for the system SO_2 - H_2O at 25°C (After Langmuir, 1997)

Eh - pH diagram of sulphur helps to understand the stability of sulphur containing species in different environments. In the Eh – pH diagram of sulphur (Figure 1.1), the higher Eh value indicates a stronger oxidative environment and smaller Eh value indicates a reducing environment. Highly acidic conditions lead to addition of H^+ to the species. Sulphate is the dominant form of sulphur in most environments. S^0, H_2S and HS^- exist only in highly reducing environments like deep sea vents and sediments. SO_4^{2-} and HSO_4^- are present in oxidising conditions like when it is in contact with water or exposed to oxygen.

Isotopic methods have been very successful in tracking sources of sulphur in the soil, and river water and thus understanding the geochemical cycle. Sulphur is an excellent element for studying the Earth's processes due to its presence in various forms in the lithosphere, atmosphere, and hydrosphere, and the significant mass difference between its most abundant isotopes (^{32}S and ^{34}S). However, interpreting its isotopic compositions is challenging due to its occurrence in different oxidation stages, which leads to complex fractionation patterns and its occurrence in various forms.

Isotopic fractionation is the natural process by which isotopes of an element are separated from each other in different chemical or physical processes. This process results in the enrichment or depletion of certain isotopes in a material or substance relative to the normal abundance of those isotopes in nature. Isotopic fractionation occurs to minimise the energy of the molecule and attains higher stability. Isotopic fractionations can be either equilibrium fractionation or Kinetic fractionation.

Sulphur isotopes can fractionate by mass-dependant and mass-independent ways. The mass-dependant fractionation can occur during equilibrium and kinetic processes. The former results from differential bond strengths of various sulphur isotopes while the latter is due to the energetics associated with the lighter isotopes.

Equilibrium fractionation occurs when the rates of all reactions and processes involving different isotopes are equal, resulting in a stable distribution of isotopes among the different species present in the system. In the reaction below, the isotopic exchange happening between $^{32}SO_4{}^{2-}$ and $H_2{}^{34}S$,

$$^{32}SO_4{}^{2-} + H_2{}^{34}S = {}^{34}SO_4{}^{2-} + H_2{}^{32}S$$

O’Neil (1986) explained temperature, chemical composition, crystal structure and pressure are some factors which lead to equilibrium isotopic fractionation. S-O bond is stronger compared to S-H bond. Strongly bonded molecules are enriched in heavier isotopes. Sulphur has oxidation states from -2 to +6. Heavier isotopes are enriched in Sulphur compounds in which sulphur is in higher oxidation states and the order of enrichment of ^{34}S in the compounds is $SO_4^{2-} > SO_3^{2-} > SO_x^0 > S^{2-}$ (Sakai, 1968; Bachinski, 1969). Therefore, seawater and evaporates in which Sulphur is mainly found as $SO_4{}^{2-}$ are enriched with ^{34}S and result in higher $\delta^{34}S$ values.

The equilibrium fractionation factor between two coexisting phases is temperature dependant. In the case of sulphur isotopes the temperature-dependence of the fractionation factor is shown in Table.1.

Compound or component (*i*)	**a**	**b**	**c**	***T* (°C) range***	**Data sources**
Sulfate minerals and aqueous sulfate	6.463		0.56	200 - 400	(2)
Sulfites	4.12	5.82	–5.0	> 25	(1)
SO_2	4.70		–0.5	350 - 1050	(1)
$S(=S_8)$	–0.16			200 - 400	(1)
H_2S aqueous-gaseous	0.71		–6.67	11 - 30	(3)
HS^-	–0.06		–0.6	50 - 350	(1)
S^{2-}	–0.21	–1.23	–1.23	> 25	(1)
FeS_2	0.40			200 - 700	(1)
FeS	0.10			200 - 600	(1)
$CuFeS_2$	–0.05			200 - 600	(1)
PbS	–0.63			50 - 700	(1)
ZnS	0.10			50 - 705	(1)
Ag_2S	–0.62			280 - 700	(4)
Cu_2S	–0.06			510 - 630	(4)
CuS	0.04			280 - 490	(4)
Bi_2S_3	–0.67			150 - 600	(5)

Table 1. Temperature effect on the equilibrium sulphur isotopic fractionation between different phases and H_2S (from Seal, 2006). Here, the coefficients **a**, **b** and **c** are as in $1000\ln\alpha_{i-H_2S} = \frac{\mathbf{a}\times10^6}{T^2} + \frac{\mathbf{b}\times10^3}{T} + \mathbf{c}$ (T in K).

Ohomoto and Lasaga (1982) the isotopic exchange of above reaction equilibrate faster at high temperature (T = 350 °C) and low pH (pH ≈ 2), also time to reach equilibrium increases considerably at lower temperatures unless the reaction occurs at an extremely acidic condition (Figure 1.2).

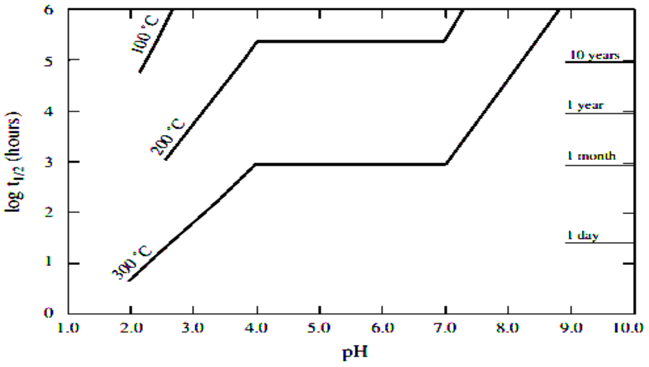

Figure 1.2: The kinetics of sulphur isotope exchange in terms of pH and log $t_{1/2}$. The bends in the isotherms are due to changes in the speciation of sulphur as a function of pH, Modified from Ohomoto and Lasaga (1982)

In kinetic isotopic fractionation of stable isotopes, the fractionation is unidirectional and the fractionation factors are more complicated. SO_4^{2-} gets reduced to H_2S by anaerobic sulphate reducing bacteria. ^{32}S-O bonds break easily compared to ^{34}S-O bonds which produce H_2S enriched with ^{34}S isotope and result in a lower δ^{34}S value. The reaction of reduction of sulphate to sulphide in an anoxic environment and the sediment–water interface is,

$$2\ CH_2O + SO_4^{2-} \rightarrow H_2S + 2\ HCO_3^{\ -}$$

The hydrogen sulphide formed gets fixed mainly as Iron sulphides or organic bound sulphur. Therefore, Pyrite (FeS_2) is enriched with ^{32}S, hence with negative δ^{34}S values. It has been shown that (Goldhaber and Kaplan 1975; Canfield and Teske 1996) the sulphur isotopic fractionation resulting from bacterial sulphate reduction ranges from 15 to 71‰ in marine settings.

The δ^{34}S of bacterogenic pyrite in a sedimentary basin follows the Rayleigh fractionation equation

$$\delta^{34}S_{SO_4^{2-}} = (\delta^{34}S^{o}_{SO_4^{2-}} + 1000)f^{\alpha-1} - 1000 \qquad (2)$$

Where, $\delta^{34}S^{o}_{SO_4^{-2}}$ is initial isotopic ratio of the sulphate reservoir and $\delta^{34}S_{SO_4^{-2}}$ the isotopic ratio at fraction of the reservoir remaining at a fraction, f; α is the fractionation factor associated with the formation of H_2S. The isotopic composition of H_2S and hence pyrite forming at any f is given as

$$\delta^{34}S_{pyrite} = (\delta^{34}S^{o}_{SO_4^{2-}} + 1000)\alpha f^{\alpha-1} - 1000 \qquad (3)$$

It can be followed from the above reaction that $\delta^{34}S_{pyrite}$ would be constant if $\delta^{34}S^{o}_{SO_4^{2-}}$ remains constant i.e. the sedimentary basin has infinite sources of sulphate, an open system. On the contrary, if the supply of sulphate is restricted i.e. a closed system, then $\delta^{34}S^{o}_{SO_4^{2-}}$ and $\delta^{34}S_{pyrite}$ would change with f; as f decreases both would become more positive.

It has been further observed that oxidation of reduced sulphur at the surface (oxidising) condition is associated with minimal isotopic fractionation (Balci et al., 2007). Therefore, oxidation of sedimentary pyrite in soil environment might not involve isotopic fractionation.

1.3. δ^{34}S variability in nature

Due to the Eh-pH conditions of the seawater, sulphur is found as sulphate and enriched in ^{34}S (δ^{34}S = 21.0 ± 0.2‰). Sedimentary sulphur speciation is controlled by the reduction of the sulphate by bacteria. At the bottom of the ocean, anaerobic sulphate reducing bacteria (*Desulphovibrio desulphuricans*) reduces the sulphate to ^{32}S enriched hydrogen sulphides. The sulphur in hydrogen sulphides with a -2 oxidation state will be converted to metal sulphides, especially FeS_2 (Pyrite). This process is a major flux of ^{32}S to the lithosphere from the hydrosphere as sulphides. The variable composition of marine sedimentary sulphide is partly due to Rayleigh isotopic fractionation and rate-dependent kinetic fractionation during sulphate reduction. This reduced sulphide when exposed to oxidising conditions may undergo oxidative weathering. Since oxidation of sulphide does not occur selective breakage of bonds of S, there is no or minimal fractionation observed (Diaz et al, 2020). So, the sulphate formed from oxidative weathering pyrite will be depleted in ^{34}S. Sulphur distribution in nature and their isotopic signature are shown in Figure 1.3.

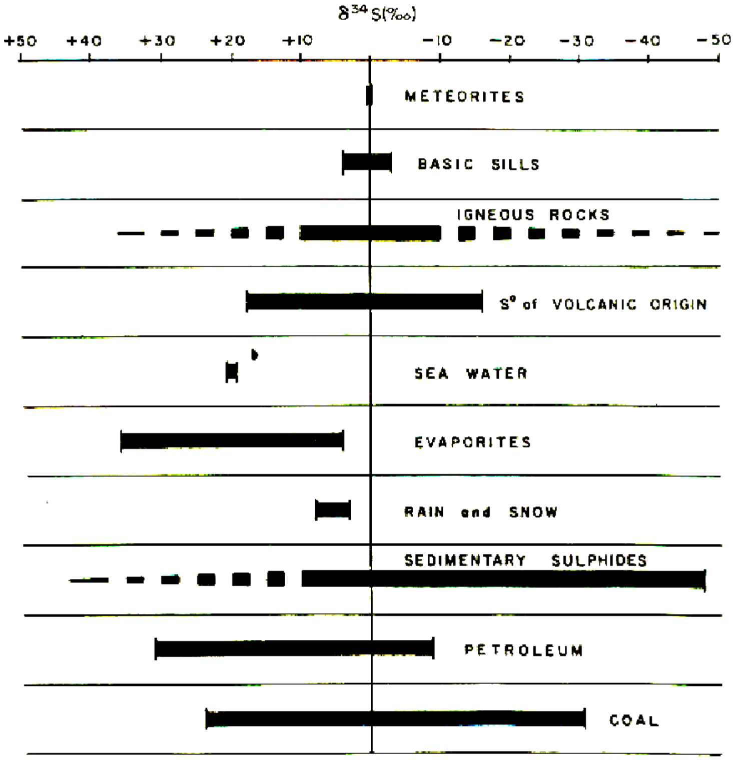

Figure 1.3: Sulphur isotope variation in nature (H., G.N., & Thode, 2005)

Igneous rocks and volcanic gases which originate from the deep crust and mantle have a range around $\delta^{34}S = 0$ ‰. In the atmosphere, sulphur is found as reduced gas. According to Maroulis and Bandy (1977) and Graedel (1979) dimethyl sulphide, which is produced by marine algae, might be a major source of sulphur in the atmosphere which is less enriched in ^{34}S. Also, H_2S formed in the deep sea reaches the atmosphere in special circumstances like heavy storms while in normal conditions H_2S gets oxidised by dissolved oxygen in the sea. Hansen et at. (1978)

measured H_2S from shallow littoral sediments of the North Sea which increased as the enrichment of organic matter in sediments got increased. Sulphur also reaches the atmosphere by anthropogenic sources such as the combustion of coal and petroleum. Sulphur sources in atmosphere and isotopic signature is shown in figure 1.4. Ocean spray having $\delta^{34}S$ similar to the marine sulphate also contribute significantly to the atmosphere. The contribution of marine sulphate to coastal aerosols has also been reported for location on the west coast (Kaushik et al., 2021).

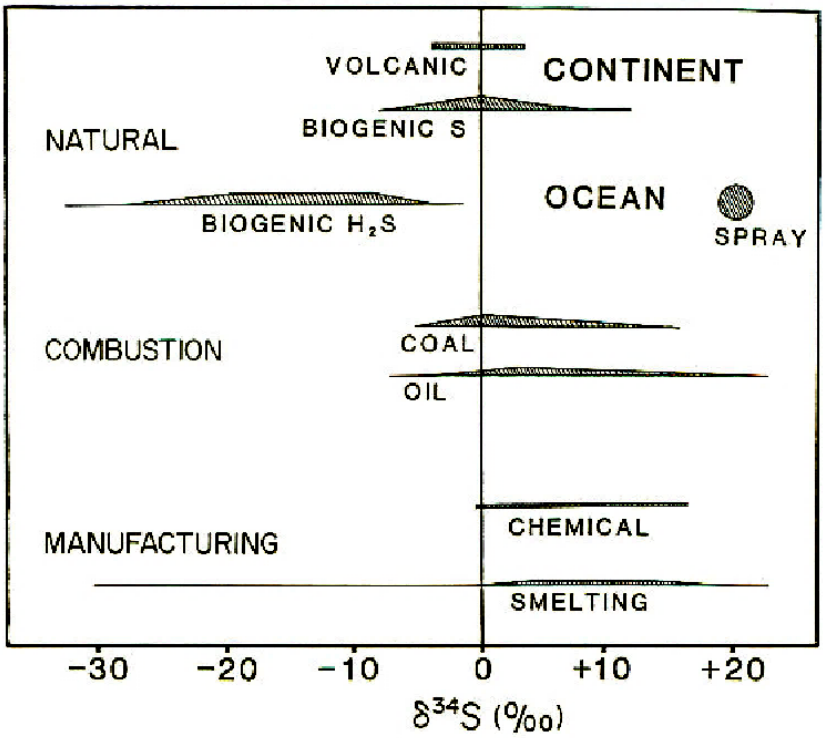

Figure 1.4: $\delta^{34}S$ distributions in major sources of atmospheric sulphur

(H., G.N., & Thode, 2005)

Ohmoto and Rye (1979) reviewed the available sulphur isotopic data for various types of hydrothermal mineral deposits, including sulphide deposits, epithermal deposits, and sedimentary exhalative deposits. The authors discussed the different mechanisms and processes that can lead to variations in sulphur isotopic compositions in these deposits. The authors noted that sulphide deposits associated with magmatic-hydrothermal systems often have distinctive sulphur isotopic compositions that reflect the contribution of sulphur from magmatic sources. In contrast, sedimentary deposits may have more complex and variable sulphur isotopic signatures that reflect the mixing of multiple sulphur sources and the influence of depositional environments.

1.4. δ^{34}S in rocks and rivers from Indian Region

Limited data exist about the isotopic composition of rocks from India. A compilation by Date et al., (2022) suggested δ^{34}S variability from 0.1 to 28.3‰. The sulphides associated with the Deccan basalts are expected to show δ^{34}S values <5‰ (Date et al., 2022). The sulphide minerals from different types of rocks from Dharwar Craton have shown δ^{34}S values of 0.1 ± 5.4 ‰ (range from -10.9 to 19.4 ‰) (Mishima et al., 2017). Charnokites and Peninsular Gneisses are the dominant rocks of southern India. They reveal δ^{34}S of 0.10 and 1.00 ‰, respectively.

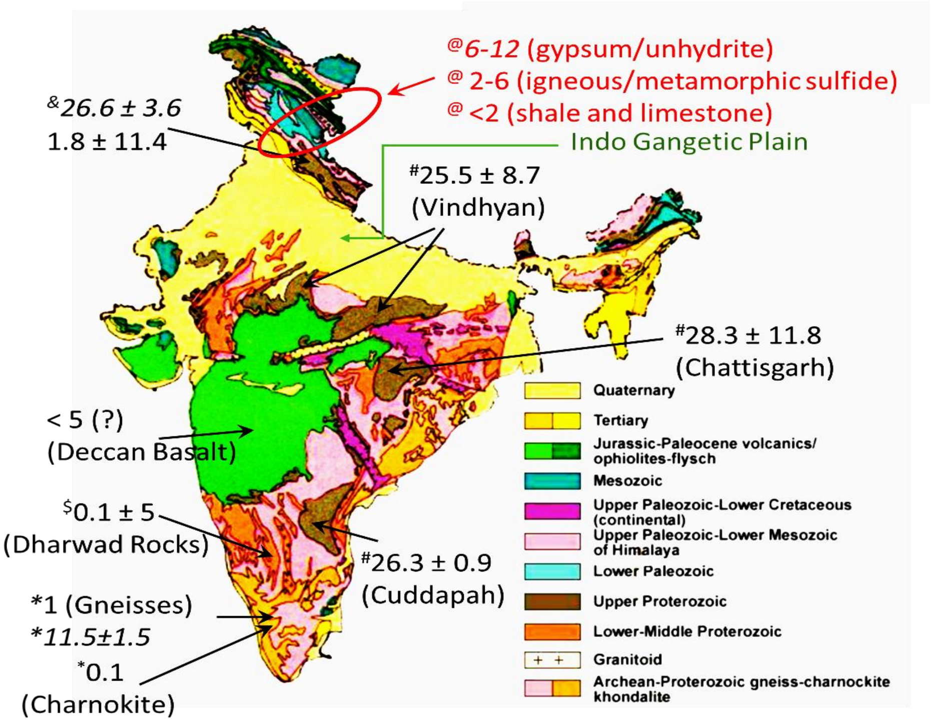

Figure 1.5: δ^{34}S values of underlying bedrocks in India. Values in italics are of sulphate. The δ^{34}S values for Deccan basalt, Charnokite and Gneiss are for the rock analyses whereas those for Vindhyan, Chattisgarh, Dharward and Cuddapah basins are for sulphides (map source Date et al., 2022).

Sulphides from the Proterozoic sedimentary basins of India show higher δ^{34}S values i.e. 25.5 to 28.3 ‰, mainly due to the closed nature of the sedimentary depositional environment where sulphate reduction followed by Rayleigh fractionation (Sarkar et al., 2010).

δ^{34}S studies of riverine sulphate from various rivers in India have shown lower δ^{34}S values of 3.4 ± 2.8 ‰ in the Alaknanda-Bhagirathi rivers (Chakrapani and Veizer, 2006). The sulphate from the Peninsular river Krishna showed δ^{34}S of 14.5 ± 2.8 ‰ (Das et al. 2011).

1.5. Sulphur in soils

The sulphate in the soil majorly comes from (1) Atmospheric deposition (2) Chemical weathering of sulphides in sedimentary rocks (3) Anthropogenic sources (Mizota & Sasaki, 1996).

From the atmosphere, the heavy isotopes get deposited in soil easily by dry and wet deposition and it has got higher $\delta^{34}S$ compared to sulphide weathering. The major source of sulphate in rainwater over the ocean is sea spray and it has small $\delta^{34}S$ compared to seawater $\delta^{34}S$. The rainwater over land has low $\delta^{34}S$ compared to rainwater over the ocean. The small $\delta^{34}S$ values of sulphate in and rainwater over the ocean compared to oceanic water can be accounted for by the merging of biogenic sulphur (H., G.N., & Thode, 2005). Also, higher contribution from biogenic sulphur in land compared to the sea leads to low $\delta^{34}S$ in land rainwater compared to those found in the ocean.

The sulphate in the atmospheric deposition is Secondary atmospheric sulphate (SAS) and sea salt sulphate (SS). Sulphate derived from the secondary atmospheric sulphate is produced by the oxidation of reduced sulphur gases and compounds by interacting with H_2O_2, carbonyl sulphide (COS), and ozone (Diaz et al, 2020). Sea salt sulphate is of sea origin. Seaspray which has a sulphate composition of seawater and is carried by winds to the terrestrial part is another source of sulphur in the soil.

The sulphide in sedimentary rock is mostly found as pyrite (FeS_2). Oxidative weathering of pyrite leads to sulphate in soil which will be less enriched in $\delta^{34}S$ compared to atmospheric deposition. $\delta^{34}S$ values of underlying bedrock in India are depicted in Figure 1.5 according to literature values,

Another sulphur source in soils is from fertilizers. Fertilizers like NPK, Zinc Sulphate, and Ammonium Sulphate have sulphate concentration which affects soil sulphate and its isotopic signature. In this study all soil samples are collected from non-agricultural areas and thus have minimal effect on the study of $\delta^{34}S$ values of Indian soil sulphur.

Mixing compounds with different isotopic composition causes isotopic variation following the mass balance equation

$$\delta_{mixture} = X_A \delta_A + X_B \delta_B \qquad (4)$$

Where $\delta_{mixture}$ is the resulting isotopic composition of the mixture, δ_A and δ_B are the isotopic compositions of components A and B, and X_A and X_B are the mole fractions of components A and B. The above equation can be used to ascertain contributions from various sources to the soil using the isotopic characterization of different end-members.

Anion concentrations in soil leachate can also help in constraining sources of sulphur in the soil. SO_4 to Cl ratio is expected to increase as the distance from the coast increases (Diaz et al, 2020). The average SO_4/Cl ratio in seawater is 0.14 (Morris & Riley, 1966). The input of Chloride from the weathering process is minimal compared to atmospheric deposition. The dry and wet atmospheric near coastal deposition will contribute to higher chloride concentration.

1.6. About this study

The sulphur isotopic studies in river water samples is how the rivers act as a source of CO_2 in the carbon budget while studies have been considering rivers as a sink of CO_2. Oxidative weathering of pyrite (OWP) produces sulphuric acid, which will lead to the chemical weathering of carbonate minerals and further leads to a net release of CO_2, in contrast to the sink of CO_2 associated with silicate weathering (Calmels et al., 2007). Sulphur isotopes in rivers can provide insight into how much riverine sulphate is sourced from the dissolution of sedimentary sulphate minerals versus oxidative weathering of pyrite (OWP). The major sources of sulphate considered in this study are groundwater influx, oxidative weathering of pyrite, dissolution of evaporate, pollution and soil leaching (Das et al., 2011). The sources of sulphate in these studies are determined by $\delta^{34}S$ values. So the sulphur isotopic composition in soils done in this study of nearby areas of the rivers will be helpful to give a confirmation on whether the sulphate came from the soil or not.

Sulphur Isotopic studies in museum bird feathers have been used to track the migration patterns of birds recently (Date et al, 2022) all over India. According to Date et al (2022), irrespective of the trophic level of the species, the $\delta^{34}S$ values in bird feathers in Himalayan and Gangetic regions are low compared to the rest of the part of India. Thus it was felt necessary to explore whether the soil sulphur which eventually gets reflected in the food chain also shows a spatially distinct pattern. This study on soil sulphur will shed light on confirming the source of sulphur in the feathers and food source of birds as the soil samples have covered almost all of the areas where the feather samples have been collected. This study mainly focuses on the source of sulphur in soil through its isotopic signature. It can reveal whether the sulphate in the soils of these locations originated from underlying bedrock or other sources.

Chapter 2 Materials and Methods

2.1 Sample collection

Soil samples were collected from 80 locations (Figure 2.1). all over India through a community-outsourced sampling scheme. All the samples collected in this study are from the non-agricultural area. Each sample is collected from 3 pits of 0.3 m depth which are 5 – 10 m apart from each other. Soil samples were well mixed and separated 1 kg of soil from it through coning and quartering. The latitude and longitude of the sample locations were marked. The samples, if wet, were dried (at 40 ^{0}C) and kept in Ziploc bags under non-contaminating conditions until analysis. The sampling locations are marked in

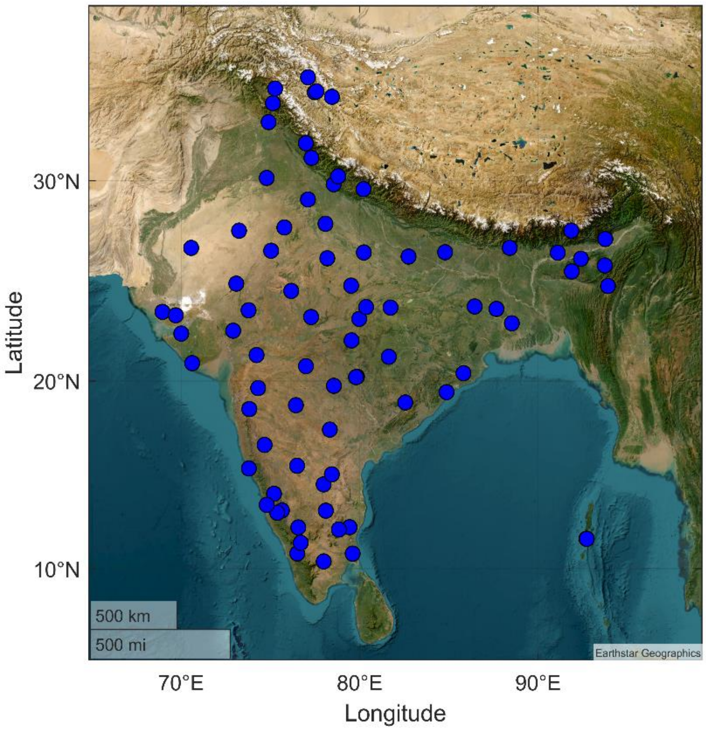

Figure 2.1: Soil sampling locations from India

2.2 Sample processing

Roots and leaf remains were carefully removed from the samples using forceps. 120 g of representative soil sample was taken after coning-quartering and sieving through a 2mm sieve. The sampling processing was done following Diaz et al, 2020. Aggregated soil parts were well crushed and collected after sieving. Samples were soaked with Milli-Q water in a 1:5 ratio. The leached samples were shaken for 1 hour in an orbital shaker after keeping them undisturbed for 24 hours. The samples were ultrasonicated for 10 minutes to get the maximum sulphate to leach out by dislodging them. Centrifugation was done after that to the leached sample to make the filtration faster. Leachate was filtered through 0.2 micron nylon membrane (47 mm diameter) filter paper. Milli-Q water was added to the sludge in the same ratio for the second cycle and kept for 1 hour and the leachate was filtered again. The anion concentrations were measured using the Ion chromatography instrument (Figure 2.2).

Figure 2.2: Ion Chromatography for anion analysis

2.3 Anion concentration analysis using Ion Chromatography

Ion chromatography (IC) was used to determine concentrations of major anions (Cl^{1-}, SO_4^{2-}, NO_3^-) in the liquid phase. It is a separation technique that is based on the differential partitioning of ions between a stationary phase and a mobile phase. The stationary phase is typically a resin or polymer that contains ion-exchange functional groups. The mobile phase is a liquid that carries the sample through the column and elutes the separated ions. The resin used for anion analysis as the stationary phase in the Metrohm Ion Chromatography instrument is a quaternary amine ($R\text{-}NR_3+$). The mobile phase or eluent used is a solution of Na_2CO_3 and $NaHCO_3$. When the sample is injected into the ion chromatography column, the ions in the sample interact with the stationary phase based on their charge and size. The ions with the highest affinity for the stationary phase will be retained longer and will elute later from the column, while the ions with lower affinity will elute earlier. Fluorides will get eluded earlier, then Chlorides, Nitrates, Phosphates and Sulphates respectively. The separated ions are then detected by a conductivity detector, which generates a signal that is proportional to the amount of each ion eluting from the column. The detector used in Metrohm ion chromatography is a conductivity detector, which measures the conductivity of the eluent as ions pass through it.

To prepare a sample for ion chromatography measurement, 1 ml portion of leachate was pipetted from each sample and diluted by 10 times before being loaded. 5 – 6 ml of the diluted sample is loaded after washing the vial 6 times with Milli – Q water and drying.

Eluent and Acid preparation

The eluent for anion analysis is a mixture of 3.3 mM of Na_2CO_3 and 1 mM of $NaHCO_3$. Eluent was filtered through 0.45 μm nylon filter paper to avoid small particles. Then ultrasonication was done to make it free of air bubbles. The eluent was freshly prepared before each analysis as it may change in its character and properties if kept for a long time.

H_2SO_4 of concentration 0.2 M is used for the regeneration of the column In IC. For the dilution of acids Ultra High Pure (UHP) water was used.

Standards preparation

0.1 μM, 0.25 μM, 0.5 μM, 1 μM, 2 μM, and 4 μM solutions of combined Fluoride, Chloride, Nitrate, Phosphate, and Sulphate were prepared as standards from a stock solution of 50 μM using the equation below,

$$N_1V_1 = N_2V_2$$

The soil leachate samples generally have concentrations in this range.

Where N and V are the Normality and Volume of solutions respectively. Each standard will have an area as the output in the plot of conductivity and retention time. The concentration of samples was calculated from the standard curve equation of standards (area vs concentration). The concentration of anions calculated from the standard curve is in μM/L. Sulphate concentration in 1 ml leachate was calculated by multiplying the concentration by 10. The total sulphate concentration in 120g of soil (μM) was calculated by multiplying the concentration of sulphate in 1 ml with leachate volume. Sulphate concentration per gram of soil (μM/g) was calculated by dividing the total sulphate concentration by soil weight (120g). The precision and accuracy of the measurements were better than 6 % (1-sigma).

2.4 $BaSO_4$ Precipitation

1 M HCl was added to the leachate to get rid of the carbonates and bicarbonates. 35 ml of 20 percentage ACS grade $BaCl_2$ was added to the leachate in a 1L beaker to precipitate sulphate in the leachate as $BaSO_4$. The leachate was kept undisturbed for 24 hours to precipitate $BaSO_4$. Since the concentration of the sulphate in the leachate was too less, the precipitated $BaSO_4$ had to be scratched from the walls of the beaker. The precipitate is filtered using 0.2 μm nylon filter

paper (30 mm diameter). The precipitate was rinsed several times with Milli–Q water. The filtered $BaSO_4$ is carefully transferred to a 2 ml centrifuge tube by spraying Milli-Q water and ultrasonicated for 2 minutes to get the maximum precipitate out of filter paper to centrifuge tube. Centrifugation at 10000 RPM for 20 minutes was done to completely separate the precipitate. The supernatant water was carefully removed with pipette and the precipitate was allowed to dry at 80^0 C overnight. The filter papers of 20 samples with the least $BaSO_4$ concentration which were not able to transfer to the centrifuge tube were kept in a small ziplock bag.

0.2 mg of $BaSO_4$ of each sample was used to measure the sulphur isotopic composition. $BaSO_4$ was packed in a tin capsule using a small spatula. The packing was done carefully without any material coming out of it. The filter papers of samples with small concentrations were packed in a bigger tin foil. The spatula and the working space were cleaned thoroughly with Kim wipes between every sample packing.

2.5 Sulphur Isotopic ($\delta^{34}S$) measurements

$\delta^{34}S$ measurements of sulphate were measured using Isoprime precisION with Elemental analyzer vario PYRO cube. The isotopic measurements were done in the combustion mode. The packed $BaSO_4$ was loaded in carousel. The combustion was done in oxygen rich environment at 1150 ^{0}C. He was used as carrier gas. Tungsten Oxide (WO_3) granules and Al_2O_3 wool are used in combustion tube, they are high-purity, thermally stable, and chemically inert material that allows for efficient and complete combustion because of its large surface area and porous nature. WO_3 also act as catalyst and help to reduce the temperature required for complete combustion. CO_2, SO_2, SO_3, H_2O, N_2 and NO_X produced from combustion were further carried through reduction tube which is kept at 850 $^{\circ}$C. Copper was used as the reducing material in the reduction tube which leaves the species for analyses as CO_2, SO_2 and N_2. Silver wool is used in the reduction tube to remove halogens. A tube filled with phosphorus pentoxide acted as a moisture trap.

The sulphur dioxide gas is passed through the SO_2 column, where it is trapped. The column is then heated to release the sulphur dioxide gas, which can be introduced into the mass spectrometer for isotopic analysis without any interference from other gases. In the mass spectrometer, the SO_2 gas gets ionised by the electron impact. These ionised species are then accelerated by an electric field and separated according to their mass to charge ratio using a magnetic field. The resulting ion beam is detected by Faraday cup, which produces an electrical signal that is proportional to the abundance of ions with a given mass to charge ratio. The ratio of the abundances of ^{34}S to ^{32}S is then calculated, and this ratio is compared to a standard or reference material to determine the isotopic fraction. Linearity and stability runs were done between each batch.

The sulphur isotopic composition of the samples is then reported as a delta value ($\delta^{34}S$), expressed in parts per thousand (‰), as

$$\delta^{34}S = [(R_{sample} / R_{standard}) - 1] \times 1000$$

where R_{sample} is the ratio of ^{34}S to ^{32}S in the sample and $R_{standard}$ is the ratio of ^{34}S to ^{32}S in the standard VCDT. A positive delta value indicates that the sample has a higher $^{34}S/^{32}S$ ratio than the reference material, while a negative delta value indicates the opposite. Repeat measurements of internal laboratory standards and reference material yielded reproducibility of 0.2 to 0.3 ‰ (1-sigma).

Chapter 3 Results and Discussion

3.1 Salt concentration variation

Chloride and Sulphate concentrations in the soil showed a large range (Figure 3.1). The maximum SO_4 concentration in the analysed soil samples was 280.2 µM/g in the sample from Matanomadh. 8 samples had sulphate values that were less than the detection limit of the instrument. Chloride concentration varied from 0.033 µM/g (kapoli River) and 68.85 µM/g (Matanomadh). The maximum accuracy of all these anion concentration analyses was 6 %. Flouride and Nitrate concentrations were below the detection level for many of the samples.

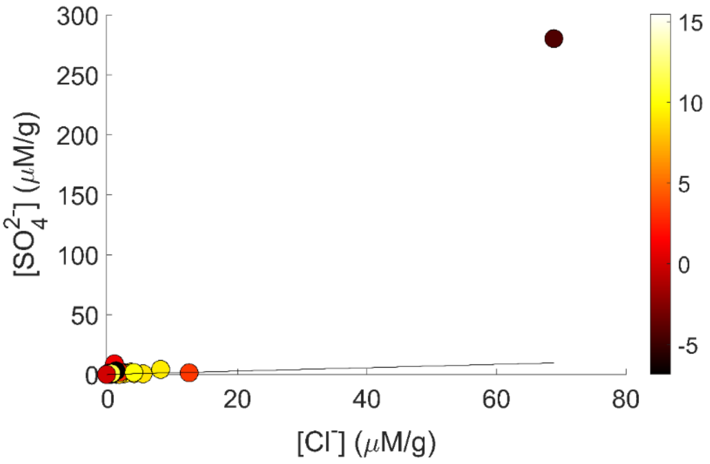

Figure 3.1(a): SO_4 and Cl concentration variation of samples from the Sea level standard. Black solid line represents the sulphate to Chloride ratio in seawater which is 0.14. $\delta^{34}S$ values are indicated in color bar.

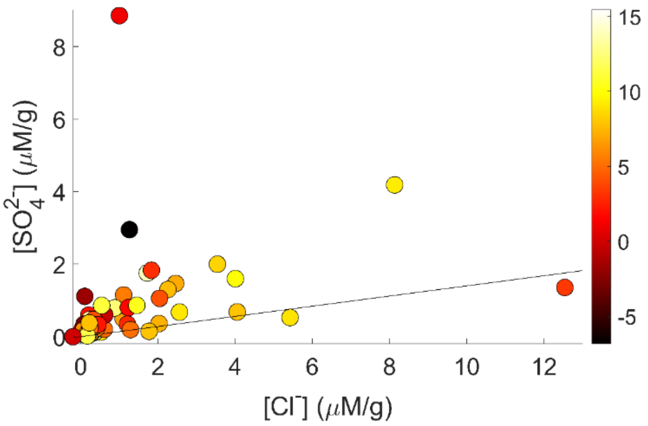

Figure 3.1(b): An enlarged view of Figure 3.1 (a). Matanomadh and Shimla samples are not included in this figure.

The sulphate to chloride concentration in seawater is 0.14. Sulphate and chloride concentrations in all 81 samples are plotted with respect to sea salt concentrations in Figure 3.1(a) and Figure 3.1(b). The sample from Matanomadh had very high concentrations of sulphate and chloride. Also, in most of the samples, the sulphate by chloride ratio is more than that in the ocean. It is interesting to note that the samples with high ratios of sulphate to chloride are mostly from the orogenic belt. The ratios (given in the bracket) are Bogdang, Ladakh (8.8), Darjeeling (10.4), Ahotguri near Kapoli river (6.03), Matanomadh, Gujarat (4.0) and near Neil beach, Andaman (4.0).

Atmospheric transport of ocean spray and sea salt can deposit sulphate and chloride inland. On a larger scale, we did not observe any systematic variation in the variation of sulphate and chloride concentrations and their ratios to change systematically from the coastline (Figures 3.2 and 3.3). The distance from the coastline was calculated by the average wind trajectories in the monsoon period in India. However, chloride concentrations seemed to show a decreasing trend till to a distance of about 1000 km (Figure 3.3). The Southern part of India does not show a decreasing relation of salts with increasing coastline distance. This indicates the possibility of other potential sources of sulphate and chloride in the soil samples. Figures 3.4(a) and 3.4(b) shows sulphate to chloride ratio does not have any systematic variation in Indo Indo-Gangetic plain.

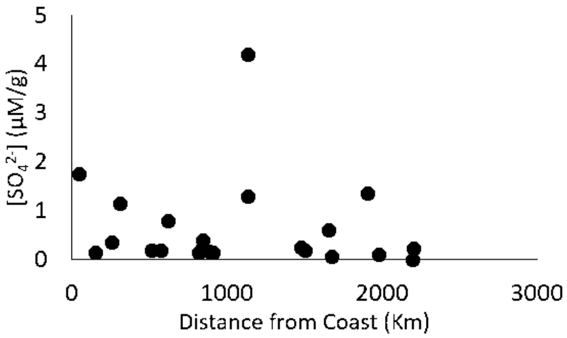

Figure 3.2: Sulphate concentration in soil leachate of samples in Indo-Gangetic plain region

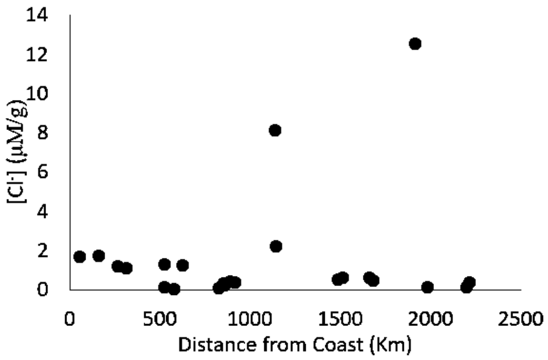

Figure 3.3: Chloride concentration in soil leachate of samples in Indo-Gangetic plain region

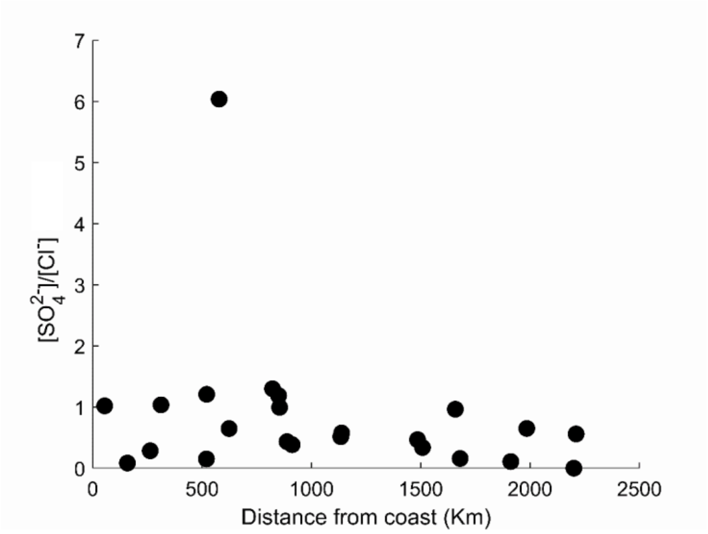

Figure 3.4 (a): Sulphate to chloride concentration variation of samples in Indo-Gangetic plain.

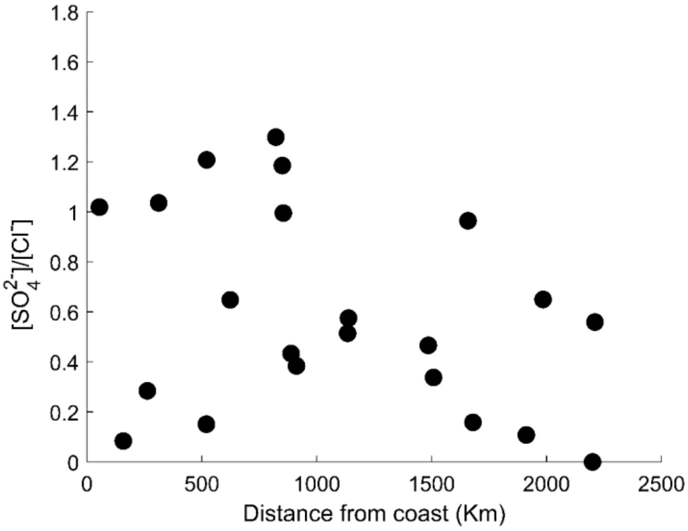

Figure 3.4 (b): enlarged view of Figure 3.4 (a). Kapoli river sample is not included in this figure.

3.2 Sulphur isotopic signature ($\delta^{34}S$) variability in soil samples all over India

$\delta^{34}S$ of soils analysed in the present study vary from -6.8 to 15.4 ‰. Figure 3.5 shows the histogram of distribution of $\delta^{34}S$ of soils analysed in the present study. Although the samples are not strictly collected with uniform spatial resolution throughout India, the histogram gives an idea about the abundance of samples as per their $\delta^{34}S$ values. The mode of the $\delta^{34}S$ distribution suggested that the highest number of samples belonged to 7 to 8 ‰. The median of the distribution is 7.5 ‰. The negative skewness of the distribution, however, reflects relatively lower proportion of the Himalaya with respect to the rest of India.

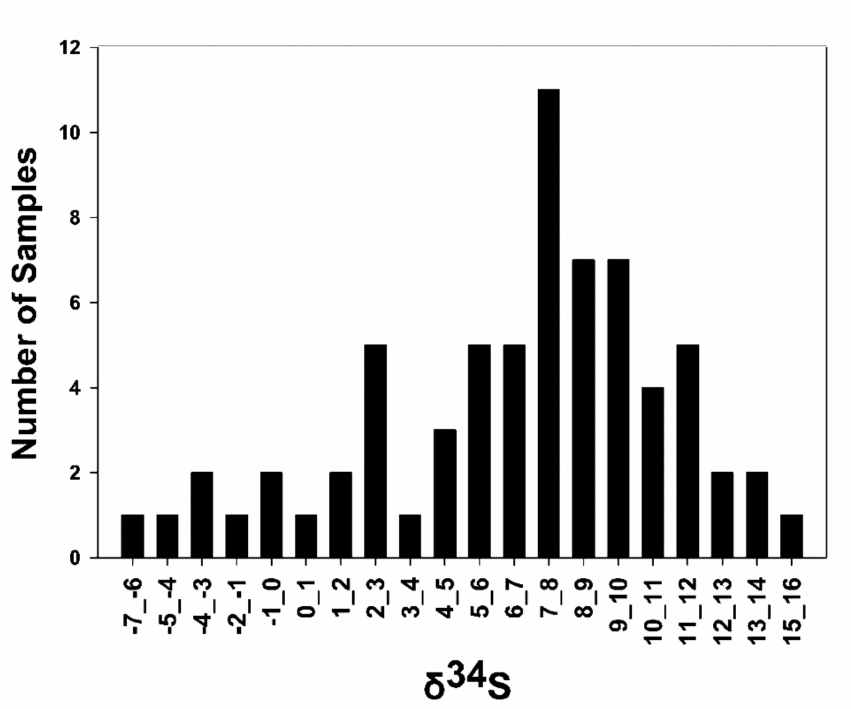

Figure 3.5: Histogram showing number of soil samples belonging to δ^{34}S bins of 1 ‰ size. The first and the last bins are from -7‰ to -6‰ and 15‰ to 16‰, respectively.

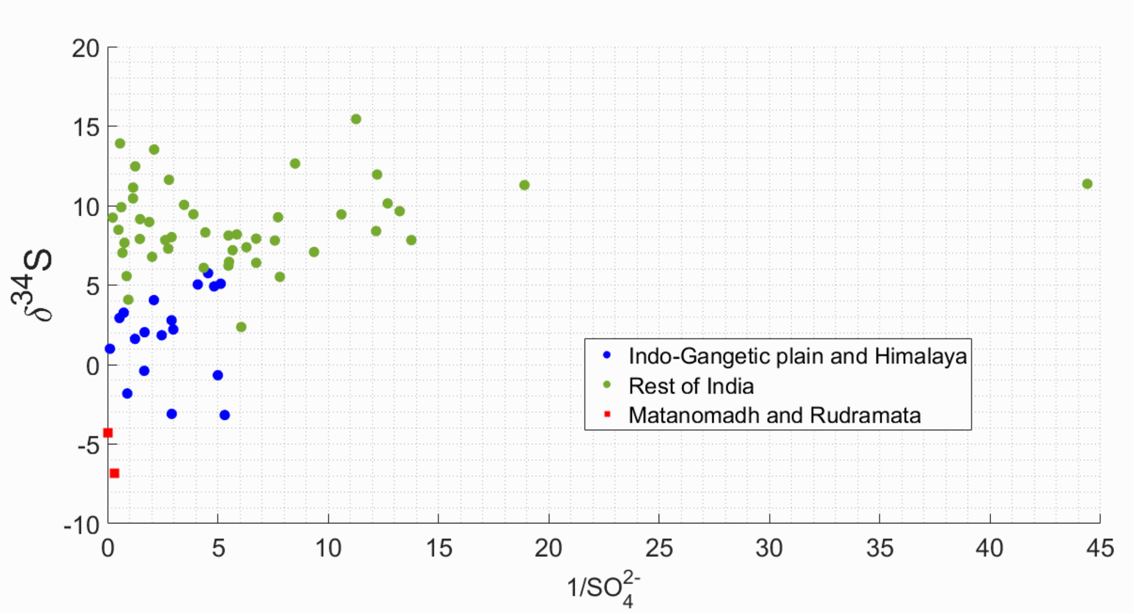

Figure 3.6: δ^{34}S values (‰) of all the soils samples versus the reciprocal of SO_4^{2-} concentrations (µM^{-1}).

As with the δ^{34}S variations, a large spread was also observed with respect to SO_4^{2-} concentrations. Figure 3.6 shows δ^{34}S values plotted against the reciprocal of SO_4^{2-} concentrations. Depending upon the sample locations and their δ^{34}S and SO_4^{2-} concentrations three main categories could be seen in Figure 3.6: (i) the samples with lower $\delta^{34}S$ values and relatively higher SO_4^{2-} concentrations were from the Himalaya and Indo-Gangetic plains; (ii) the samples with variable SO_4^{2-} concentrations and relatively higher $\delta^{34}S$ values were from the rest of India, and (iii) two samples with the lowest $\delta^{34}S$ values and very high SO_4^{2-} concentrations were from locations where reduced sediments were reported.

Figure 3.7 shows spatial variability in the isotopic composition of leachable soil sulphur from the Indian region. Many samples had sulphate concentrations too low for the mass spectrometric measurements (shown by hollow circles in Figure 3.7). Such samples had sulphate concentrations typically less than 0.02 μmol/g. The $\delta^{34}S$ values varied from -6.8 to 15.4 ‰ with a mean of 6.7 ± 4.5 ‰ (1-σ).

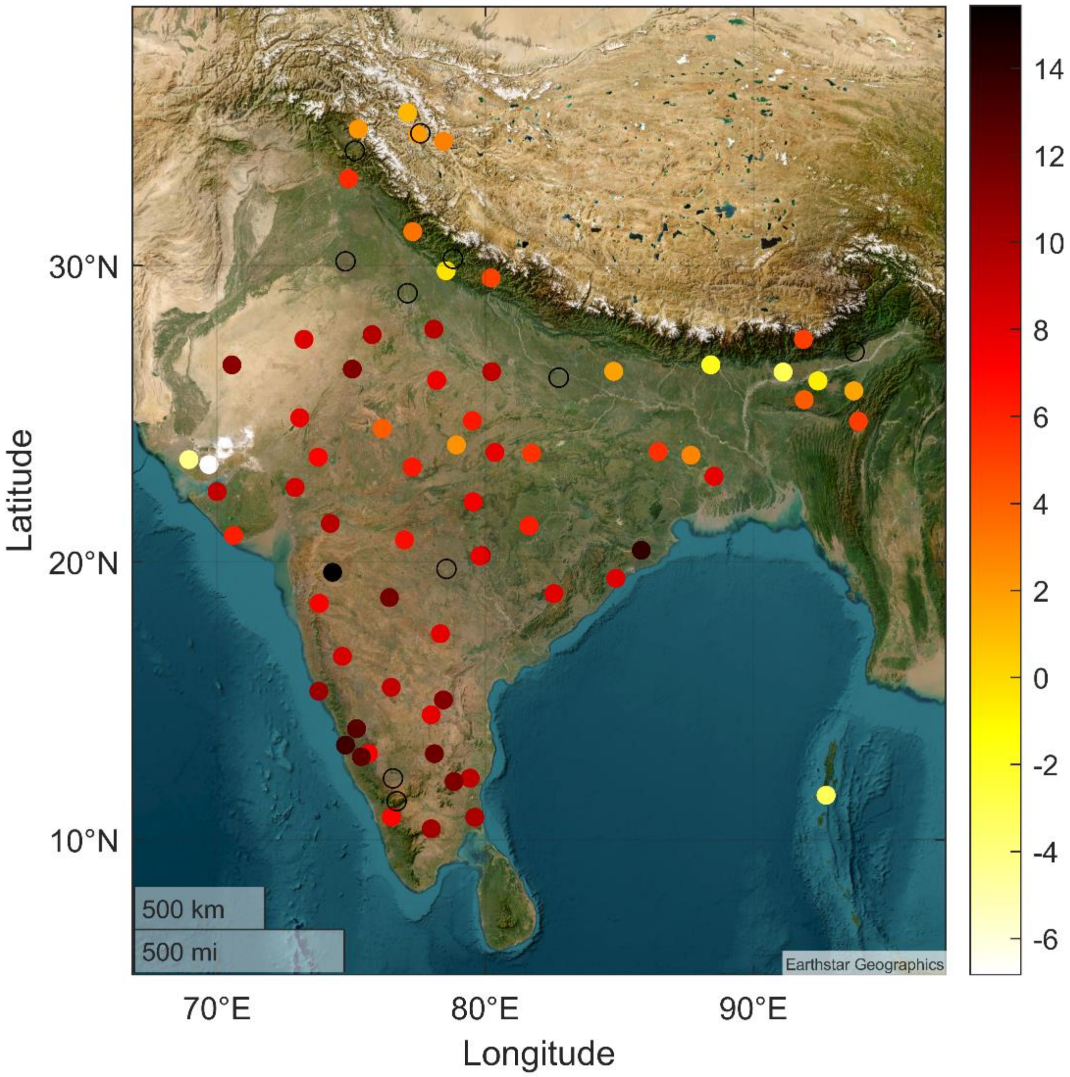

Figure 3.7: $\delta^{34}S$ of soil samples all over India. Colour bar represents $\delta^{34}S$. Hollow black circles represent samples with low sulphate concentration (typically less than 0.02 μmol/g)

The $\delta^{34}S$ values in the Indo Gangetic plain and Himalayan region analysed clearly showed lower values compared to the rest of India (Figure 3.7). $\delta^{34}S$ values were <6 ‰ in the Indo-Gangetic plain whereas for the samples from the rest of India, it varied from ~6 to 16 ‰. Peninsular India soil revealed higher $\delta^{34}S$ values compared to the rest of the locations. Samples near to coast yielded the highest $\delta^{34}S$ among all other samples. In the west coastal side, soil samples from Neelavara, Dharmasthala, and Shimoga showed $\delta^{34}S$ of 13.5 ‰, 12.5 ‰, 12.6 ‰ respectively. In the east coastal side, Bhuvaneshwar shows the highest $\delta^{34}S$ value of 13.9 ‰. The lowest $\delta^{34}S$ values are shown by Rudramata and Matanomadh -6.8 ‰ and -4.3 ‰ respectively from Gujarat. These locations are separated by less than 100 Km and had very high sulphate concentrations in the leachate. The sample from Andaman from Neil beach showed $\delta^{34}S$ of -3.1 ‰.

Figure 3.8 shows the variation in sulphate by chloride ratio of the samples with their $\delta^{34}S$. It can be seen that the lower $\delta^{34}S$ values of the samples had higher sulphide by chloride ratios. This suggested that such samples could have a significant contribution from non-marine sources.

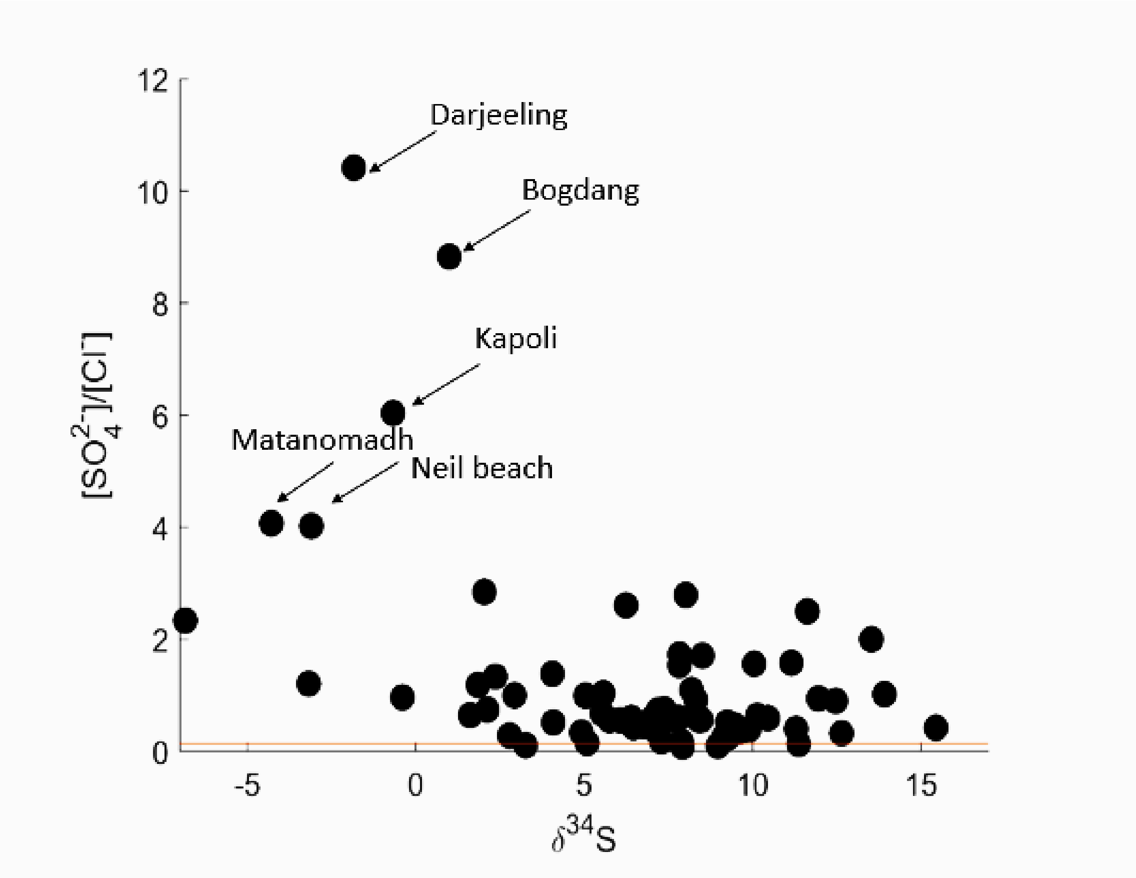

Figure 3.8: SO_4 to Cl concentration of samples variation with $\delta^{34}S$. Red solid line represents sulphate by Chloride ratio in seawater which is 0.14

3.3 Constraining end-member $\delta^{34}S$ values

The sulphate in the soil is likely derived from multiple sources each having different $\delta^{34}S$ values. However, $\delta^{34}S$ values of the possible sources have not been fixed and have variability associated with it. The likely end-member sources are (i) marine sources, (ii) lithology, and (iii) anthropogenic sources. One of the important sources of sulphur is seawater. The reported $\delta^{34}S$ value of modern seawater sulphate i.e. sea salt sulphate, is 21.0 ± 0.2 ‰ (Rees et al. 1978). Sea spray over land near the ocean is an important source of sulphate in soil which has $\delta^{34}S$ of seawater. Phytoplankton and bacteria produce dimethylsulfonopropionate (DMSP) in the ocean. The transportation of DMSP from the ocean to the atmosphere during turbulence and diffusion and later breakdown produces dimethyl sulphide (DMS) (Norman et al., 1999). It has been further shown that the fractionation associated with the formation of DMS from DMSP is minimal (< +1 ‰) and a small fractionation (−0.5 ± 0.2‰) occurs during the emission of DMS to the atmosphere (Amrani et al., 2013). The oxidation of the DMS produces biogenic sulphate aerosols in the atmosphere. As a result, the reported $\delta^{34}S$ value of the ocean atmosphere which is far from offshore was in the range of 12 ‰ to 18 ‰ (Chukhrov et al 1980). On the western coast of India, $\delta^{34}S$ values of aerosols collected in summer showed a value of 9.0 ± 2.8 ‰ (Agnihotri et al., 2015) which originated from dimethyl sulphide. While analysing the soils from the Shackleton Glacier region of Antarctica, Bao and Marchant (2006) considered the end-member $\delta^{34}S$ values of secondary atmospheric sulphate (SAS), sea salt sulphate (SS) and terrestrial sulphate formed by weathering of sulphides as 12.0, 22.0 and 5 ‰, respectively. However, based on studies in six different ocean provinces Amrani et al., (2013) showed that the sea-salt sulphate ($\delta^{34}S = +21.1‰$) had a similar $\delta^{34}S$ value to DMS or DMSP (+18.9 to +20.3‰). $\delta^{34}S$ of rain water in India is reported 11.4 ± 2.3 ‰ (Jacks et al., 1994).

Chakrapani and Veizer (2006) based on the $\delta^{34}S$ of sulphate in Alkhandra – Bhaghirati rivers in western Himalaya concluded that $\delta^{34}S$ values of 6-11 ‰ are originated from sulphates, samples with $\delta^{34}S$ of 2-6 ‰ indicated the source as the oxidation of sulphides from igneous and metamorphic rocks while $\delta^{34}S$ values of < 2 ‰ indicated the sulphide oxidation of sedimentary rocks. Another study of $\delta^{34}S$ values of sulphate in the water of the Indus River basin (Karim & Veizer, 2000) indicated the presence of three distinct sources of sulphur. The first source was the result of the oxidation of sulphide minerals from igneous and metamorphic rocks, which had a $\delta^{34}S$ value of less than 12 ‰. The second source was the result of the oxidation of sulphide minerals from sedimentary rocks, which had a $\delta^{34}S$ value of approximately -5 ‰. Finally, the third source was anthropogenic in nature and had a $\delta^{34}S$ value of 5 ± 1 ‰.

Rock from Peninsular India shows varying $\delta^{34}S$ values. The $\delta^{34}S$ values of rocks have been discussed in the Introduction (see Section 1.4) with a geological map of India.

The $\delta^{34}S$ studies of common fertilizers such as NPK, $ZnSO_4$ and NH_4SO_4 have been done: $\delta^{34}S$ value of NPK-based fertilizers was 1 – 10.3 ‰ (Moncaster et al., 2000) and of $ZnSO_4$ was 3.7 ‰ (Das et al., 2011). Jacks et al (1994) have reported the $\delta^{34}S$ value of NH_4SO_4 as 7.3 ‰.

3.4 $\delta^{34}S$ variations in Indo-Gangetic plains and Himalaya

$\delta^{34}S$ values of the samples from the Indo-Gangetic plain and Himalaya (Figure 3.7) varied from -3.2 to 5.8 with a mean of 2.1 ± 2.5 (1-σ, N = 17). The lowest $\delta^{34}S$ value was from Barpett, Assam ($\delta^{34}S$ = -3.2‰). We did not observe any systematic variation in $\delta^{34}S$ with altitude or latitude or longitude. It may not be possible to do so given the sampling resolution employed in this study. Nevertheless, their lower values as compared to samples from rest of the India was apparent (Figure 3.7).

The rivers from High Mountain Asia have been analysed for $\delta^{34}S$ in dissolved sulphate. Chakrapani and veizer (2006) reported $\delta^{34}S$ of 3.4 ± 2.8 ‰ in Alaknanda – Bhaghirati rivers in western Himalaya. Sulphate from Indus river yielded $\delta^{34}S$ of 5 ± 1‰ in Punjab rivers (Karim & Veizer, 2000). These values are similar to the $\delta^{34}S$ of soil samples from the Himalayan region observed in this study. From this, it appears that the sulphate in the soil from this region is mainly from the oxidative weathering of sulphides from the sedimentary/igneous or metamorphic rocks. The lower $\delta^{34}S$ values in the soils from the Indo-Gangetic plain are likely due to the sediments derived from the Himalayas. Contribution or mixing of sulphate from marine sources (either DMS or sea salt) appears to be minimal in this region. It is interesting to note that a sample from Neil beach, Andaman, despite being from an ocean island, showed $\delta^{34}S$ value of -3.1‰ suggesting non-marine sulphide source.

3.5 $\delta^{34}S$ variations in central and peninsular India

In contrast to the $\delta^{34}S$ variability in the Himalaya or Indo-Gangetic plains, $\delta^{34}S$ values in rest of India were higher. It varied from 2.4 to 15.4 with a mean of 8.8 ± 2.6 (1-σ, N = 48). This did not include samples from Matanomadh (δ^{34}S = -4.3‰), Rudramata (δ^{34}S = -6.8‰) and Neil beach, Andaman (δ^{34}S = -3.1‰).

Apart from the general trend in the variation of values in δ^{34}S, few samples showed some exceptions. The notable lower δ^{34}S values were from Singrauli (5.5‰), Jhalawar (4.1‰), and Banda (2.4‰). The reduced sulphides from coal deposits around Singrauli might have yielded lower δ^{34}S values. These values are low and show variation from the general trend as we expected higher values from these locations. These locations might have sulphate sources apart from atmospheric sulphate which might be from rock weathering or anthropogenic sources. Very low δ^{34}S values of the samples from Matanomadh and Rudramata might have originated from shale. These samples showed sulphate concentrations in the leachate which are too high compared to other sample leachates which also indicates its origin from shale or intense sulphide weathering.

The δ^{34}S values (8.8 ± 2.2‰, N = 48) of the soils from the rest of India were higher than that in the Himalaya or Himalaya-derived sediments. If three samples with lower δ^{34}S values are ignored, the mean δ^{34}S value is 9.2 ± 2.2‰ (N = 45). This clearly shows that the rest of India showed higher δ^{34}S values than the Himalaya and Indo-Gangetic plain (at $p<0.0005$).

Unlike the rivers from Himalaya, the peninsular rivers yielded higher δ^{34}S values. The δ^{34}S range of Bhima river and its tributaries were around 14 ± 2 ‰ and Krishna river and its tributaries showed a wide range of 8 ‰ to 20 ‰ (Das et al., 2011). The study (Das et al., 2011) has also concluded that the sulphate input in these rivers from oxidative weathering of sulphides is minimal and the major input of sulphate is from the leaching of saline salts.

The higher δ^{34}S values (δ^{34}S > 11‰) showed samples were from the area near the coast indicating the major sulphate source is from atmospheric deposition from a marine source. It has been reported that during the rainy season, the west coast of India consistently experiences winds blowing from the southwest direction (Pant et al, 1997) and it will lead to sea spray deposition. The reported δ^{34}S of the modern seawater sulphate is 21 ± 0.2 ‰ (Rees et al. 1978). However, as the δ^{34}S of samples near to the coast is greater than the rainwater deposition less than sea salt, sulphate in it might be entirely from sea salt origin. The rainwater in these areas might have consisted of sulphur which is biogenic in origin like dimethyl sulphide produced by marine algae which has lower δ^{34}S compared to sea spray deposition.

The variation in soil δ^{34}S values in the soil (8.8 ± 2.6 ‰) is too less than that reported for rocks (varying from 0.1 to 28 ‰). Further, the δ^{34}S values of samples from rest of the India did not mimic δ^{34}S values of underlying rocks (Figure 1.5 and 3.7). Since the δ^{34}S signature is preserved during oxidative chemical weathering (Balci et al., 2007), this shows that sulphate in it is mainly derived from sources other than the lithology.

Further, $\delta^{34}S$ values were less than that reported for rainwater in India (11.4 ± 2.3 ‰, Jacks et al., 1994). This rainwater end-member value is from only one study i.e. Jacks et al., (1994) carried out in southern India. Whether similar values of rainwater exist in various locations throughout India is not known. If one assumes that it does, then the observed values (8.8 ± 2.6 ‰) cannot be explained by rainwater contribution alone. All the samples collected in this study are from non-agricultural areas so the fertilizers could not contribute to the sulphate budget of the soil. It thus appears that the sulphate in the soil is mainly coming from atmospheric deposition with a minor contribution from lithology.

The $\delta^{34}S$ values of atmospheric sulphate aerosol are known to get affected by local and regional coal burning (Han et al., 2016; Lv et al., 2018). For example, $\delta^{34}S$ values of the Beijing aerosols varied from 2.8‰ to 9.9‰ (Average 6.0 ± 1.8 ‰). In the absence of robust estimation of this component, it was not possible to assess the role of anthropogenic pollution in controlling $\delta^{34}S$ of soil sulphate.

3.6 Implications of the present study

One of the aims of this study was to check whether the spatial pattern in $\delta^{34}S$ of bird feathers in India (Date et al., 2022) is also reflected in $\delta^{34}S$ of soils. Such association will strengthen the use of $\delta^{34}S$ studies in feathers to reveal migration. Date et al., (2022) observed that in Himalayan region and Gangetic plains the feather samples showed lower $\delta^{34}S < 6.4$ ‰ values. It was concluded that the $\delta^{34}S$ of feathers in peninsular India is derived from the atmospheric deposition since the moisture advection over India during the summer monsoon period from Arabian Sea and Bay of Bengal. Also apart from deposition as rain and sea spray, marine food sources of birds also might have led to higher $\delta^{34}S$ values. The $\delta^{34}S$ of feathers indicated in Himalayan and Gangetic plains is derived from underlying rocks and the anthropogenic sulphate sources in those areas are minimal according to previously reported values from the studies.

The conclusions of sulphate sources in this study which indicate the difference in Indo-Gangetic plain and Himalayan region with the rest of India is mimicking the study done by Date et al, 2022 in bird feathers. In the Indo Gangetic plain - Himalayan region feather samples showed 6‰ which has a similar range of $\delta^{34}S$ in soils done in this study. It's safe to assume that the $\delta^{34}S$ of these bird's feathers is derived from the soil through the food they consumed in that region.

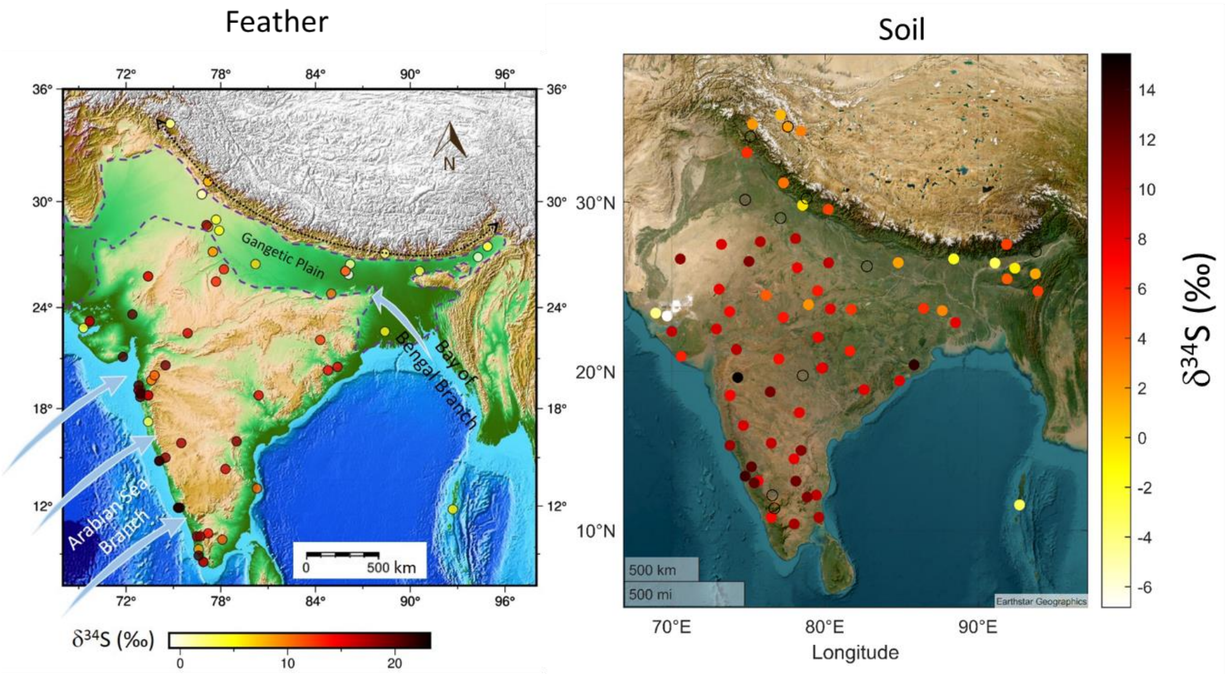

Figure 3.9: Comparison of soil $\delta^{34}S$ (left) with feather $\delta^{34}S$ (right)

Quantifying the sources and sinks of sulphur is crucial in understanding riverine fluxes of sulphur and thereby $\delta^{34}S$ values of the oceanic sulphate reservoir. $\delta^{34}S$ values of modern rivers have been used to estimate chemical weathering fluxes, especially how much of the riverine sulphate is derived from oxidative weathering of reduced (e.g. pyrite) and oxidised (e.g. gypsum) sources. However, Das et al., (2011) have shown that the saline soils also contribute significant sulphate to the rivers suggesting an additional end-member to pyrite and gypsum. The $\delta^{34}S$ values reported in the soils all over India suggested relatively similar $\delta^{34}S$ values of the samples from the rest of India. These values of similar to that reported by Das et al., (2011). If the inference of Das et al., (2011) applies to other regions, then this work suggests that atmosphere-derived soil sulphate as a major source of sulphate in the river waters from the rest of India. As suggested previously (Chakrapani et al., 2006; Turchyn et al., 2013; Karim & Veizer, 2000) pyrite is the major source of sulphur to the sulphates of rivers in the Himalayas.

Conclusions

The terrestrial sulphur cycle is influenced by various biogeochemical processes. The $\delta^{34}S$ of various sources of sulphur has been used to constrain the budget of riverine $\delta^{34}S$. Pyrite and oxidized sulphur (gypsum) are considered as the two major natural sources of sulphur. The importance of other sources of sulphur on a regional scale is unknown. Further, sulphur in the soil is also invoked as a plausible source of sulphur. This work attempts to identify sources of sulphur in the soils from the Indian region. The following are the important findings from this study.

- Strong segregation in $\delta^{34}S$ values of leachable soil sulphate between the Himalayas and Gangetic Plain, and the Rest of India.
- $\delta^{34}S$ values in the soils from the Himalayas and Indo-Gangetic plain varied from -2.5 to 5.9‰. $\delta^{34}S$ values in the soil from central and peninsular India showed 9.2 ± 2.2‰ (N = 45). It thus appears that the soil from the Himalayas and Indo-Gangetic Plain derive sulphur mainly from the rock whereas the soils from the rest of India are from atmospheric deposition. Sea spray and biogenic sulphate appear to be a major sources of sulphur for atmospheric deposition.
- Soil sulphate is showing a similar spatial pattern of $\delta^{34}S$ values in rivers reported in India and leaching of soils can be a potential source of sulphate in rivers.
- The spatial pattern in $\delta^{34}S$ values in the soil mimics the $\delta^{34}S$ values in feathers done by Date et al., (2022) and this will help to understand bird migration using $\delta^{34}S$ values.
- The anthropogenic inputs to the atmosphere (and soil) and their influence on $\delta^{34}S$ values could not be assessed.
- It would be interesting to see whether the $\delta^{18}O$ value of the soil sulphate also shows the strong spatial segregation between the Himalaya-derived sediments and the Rest of India. Such a study would determine the source of the water that was involved in forming the sulphate and further constraint the end-members and their relative contributions in the various parts of India.

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