Release of Sulphur Nutrient to Overlying Waters from Selectively Fertilised Soils Reference with Limnology

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Abstract: ***One of the most important aspects of understanding nutrient dynamics in aquatic environments, notably in limnology, is the release of sulphur nutrient to overlying waters from soils that have been selectively fertilised. This study evaluates the complex relationship between how soil fertilisation methods are carried out and the subsequent leaching of sulphur nutrient into aquatic habitats. The study sheds light on the pathways and mechanisms responsible for mobilising sulphur nutrient from soils and their subsequent transportation to overlying waters. This is accomplished through the utilisation of selective fertilisation techniques. The research sheds light on soil management practices' influence on sulphur nutrient release dynamics by employing sophisticated analytical methods such as chemical analysis and isotopic tracing. The findings highlight the significance of considering soil management strategies to reduce sulphur nutrient fluxes to aquatic systems. This, in turn, helps to define sustainable approaches to nutrient management and ecosystem conservation. This research contributes significantly to the overall comprehension of nutrient cycling in aquatic ecosystems. It offers insightful information that may be utilised by policymakers, land managers, and conservationists, among other groups.***

Keywords: Sulphur nutrient, soil fertilisation, limnology, nutrient dynamics, aquatic ecosystems, soil management

1. Introduction

The existence of sulphate in the water is the outcome of the sulphur cycle, which is always present in the medium. Sulphur is utilised in inorganic or organic form by all living organisms and exists predominantly as sulphate in the water body. Plants and animals reduce the sulphate to sulfhydryl (-SH) groups in protein synthesis. Thus, it is of nutritional value for the aquatic biota. The requirement is small, but the normal distribution of sulphate, sulphide, and organic sulphur-containing compounds always meets the same. The decomposition of proteinaceous sulphur within the organic compounds and anaerobic reduction of sulphate from ferrous sulphate all together provide nutritional sulphate and affect the cyclin of other nutrients. This ultimately determines the productivity of the ecosystem and the consequent distribution of biota.

Sulphur comes to natural waters through the solubilisation of rocks, agricultural fertilisers, atmospheric precipitation and air-dried deposition. In the latter's case, the last source of sulphate has recently been observed as dominant in the total sulphur input because of industrial expansion, which releases sulphur-containing gases into the atmosphere. Calcium sulphate is the most common constituent of sedimentary rocks and is soluble in water. Thus, the drainage from calcareous regions, such as around Udaipur, should usually contain a higher sulphate concentration. A similar situation has been observed elsewhere by Nriagu and Hem (1978) and Kilham (1984). The bacteria also contribute to the oxidation of sulphide and elemental sulphur. The anoxic decomposition of organic matter releases sulphur as hydrogen sulphide, which oxidises rapidly when it comes in contact with toxic water conditions. Protein-decomposing bacteria belonging to the genus Proteus are primarily active in the soil. On the other hand, sulphate-reducing bacteria such as *Desulfovibrio* and *Desulfotomaculum* are anaerobic. These are laws in the oxygen-devoid layer of the soil.

The lowest sulphate concentration in oxic water is slightly<1 mg/l (Talling & Talling, 1965); however, the highest has been recorded in saline lakes P50 gm /). The normal range is about $-30 mg per litre. The lack of sulphate has been reported to limit algal productivity (Fish, 1956), but Lehman and Branstrator (1994) have also observed negative results recently.

2. Materials and Methods

Experiments were carried out on two different soil types using two different fertilisers. The soils utilised in this study are the two commonly found types in the Mewar region of Rajasthan. The soils are dark and crimson. Black cotton soil is frequently regarded as black, although soil scientists identify it as red. The routine examination of these soils for agriculture, plant development, and perhaps the prevalence and abundance of phytoplankton in the aquatic environment is as outlined:

Nutrients	**Red Soil**	**Black Soil**
Sulphur	0.0280 mg/g	0.0320 mg/g

Sulphate ions were estimated using the Turbidimetric method (NEERI, 1987). They usually occur in natural water. Many sulphate compounds are readily soluble in water. Most originated from the oxidation of sulphite or gypsum ($CaSO_4$) and anhydrite, shales rich in organic compounds. Sulphate ions react with barium chloride and precipitate as $BaSO_4$ in acidic media. The absorbance of this precipitated suspension was measured on a spectrophotometer at 420 nm. A calibration curve was prepared by running standard sulphate solutions ranging from 0.0 to 40 mg/l with 5 mg/l increment. The final concentration was obtained from the standard calibration curve.

3. Experimental Results

Temperature:
In the elevated temperature of 32°C, the red soil gave the average per hour sulphate release at 1.258 ppm, while the black indicated a little lesser release at 0.528 ppm (Table 6.1). In the gradient of release, the oscillative behaviour of sulphate, through observable, was negatively lowly significant in red soil and positive but non-significant in black soil (Fig. 6.1 and 6.2). The behaviour patterns in red and black soils were similar but, on closer observation, were found to differ at the beginning of the experimentation itself, as indicated by the first three readings of both soils. The statistically treated data also supports the above inference that the behavioural pattern of sulphate in these two soils is only apparently similar (Fig 6.1 and 6.2). The control also showed some sulphate in the water medium, as did other nutrients. The highest sulphate release in red soil was 16.0 ppm, obtained right in the first reading, taken at 48 hours. Higher readings were observed from 76 to 104 hours, 10.0 to 11.0 pm. The release was low throughout the experimentation in black soil and oscillated between zero at 28 hours to 7.0 ppm at $4 and 56 hours. The 54 to 80-hour period showed higher readings similar to that described earlier for the red soil. The percentage drop in the average per-hour sulphate release was 58,03% in black concerning the red soil.

At the lower temperatures of 4 and 5°C, the average per hour release was 0.966 and 0157 ppm in the red and black soil, respectively. The oscillative behaviour, however, was more distinct at the lower temperature and was relatively regular, as seen from the plots of empirical data (Fig. 6.3). In general, the red soil exhibited a regular and elevated release of sulphate throughout the experimentation in comparison to that of black soil, which at times showed zero readings of sulphate (Table 6.2). In the case of black soil, the highest reading of sulphate release was observed to be 5.0, while the same in the red soil was 11.0, showing more than twice the difference. The statistical plots (Fig 6.4) showed non-significant "P" values in both soils. The regression was negative for the red soil. In general, sulphate release was higher in red than in black soil. The percentage drop in the average per-hour sulphate release was 83.75% in black about red soil.

pH (Hydrogen ion concentration):
In the acidic pH of 4.5, the red soil had an average release of 1.067 ppm per hour compared to the black soil, which had a sulphate release of only 0.134 ppm, the difference approximately eightfold. The highest level of sulphate release was 17 ppm in red soil compared to only 3.0 ppm in black soil. The time of release was different in the two cases; thus, there was no definitive pattern concerning the types of soils studied. In the case of black soil, there were intermittent zero readings in the sulphate release experiment (Table 6.3). However, the oscillative pattern of behaviour in sulphate release was evident at an elevated level in the red soil and a lesser level in the black soil (Fig.6.6).

In the alkaline pH of 9.0, there was a degree of release of an elevated level in red soil where the average per hour release was 0.595 ppm, with the highest release being 7.0 pm. On the other hand, the black soil revealed consistently depressed per hour release of sulphate, though the highest was 8.0 ppm. There was little similarity in the release status in the two soils throughout the experimental period (Table 6.4). The graphical presentation of the empirical data showed marginal similarity in both soils through different elevation levels (fig 6.7). Statistically, the regression coefficients were negative and lowly significant in both soils (Fig.6.8). The average per hour sulphate release was 0.280 ppm in black soil and 52,95% less in red soil.

Photic intensity:
The degree of sulphate release at different photic intensities was studied similarly to that of earlier major micronutrients. The photic intensity obtained by a 1-watt bulb showed lux values of 904 in control, 565 in red and 590 in black soil. The results obtained were as follows:

The sulphate release was consistently higher in red soil than in black soil. The average per hour release in the former was 0.719 ppm, while the same was only 0.370 ppm in black soil. The highest hourly release of sulphate observed in red soil was 10.0 ppm, and the lowest was zero ppm. On the other hand, the black soil indicated the highest release within the first 24 hours with a reading of 8 ppm, the minimum being Zero ppm. This zero reading was obtained at the end of the experiment in both soils. There was no similarity in the release pattern at different periodicity levels in the two soils. Still, the plotted empirical data shows a declining release trend in both soils (Table 6.5, Fig 6.9). The percentage drop in the average per-hour sulphate release was 48.54% in black with red soil. The control, as expected, showed continued zero readings, barring stray instances. The oscillatory behaviour in these lux intensities was observed but had little rhythmicity in red and black soils (Fig 6.9). A statistically significant negative correlation was observed only with red soil. Black soil showed a non-significant and negative correlation (Fig 6.10)

With a 60-watt bulb giving the lux values of 4500 in control, 3800 in red soil and 3900 in black soil, the observed results were regular and relatively higher with red soil than with black soil. In the latter case, readings were obtained in the first 28 hours after settlement and nil readings until the end of the experimentation. In the case of red soil, the highest release was 15 ppm, and the lowest was 2 ppm. The average per hour release for the red soil was 0.988 ppm, while for black soil, it was only 0.134 ppm (Table 6.6), the drop being 86.44%. The oscillative behaviour in sulphate release was seen only with red soil (Fig.6.I1), and statistically, this was negative but marginally significant (Fig_6.12).

The 100-watt bulb with light intensities of 7200 lux in control and 6000 lux in red and black soils gave the same release pattern as in the earlier cases. The average per hour sulphate release was higher in red soil (0.910 ppm) than in black (0.550 ppm). The percentage sink was 39.57 % in the black soil. The highest reading in the red soil was 10.0 pm, with the least at 2 ppm. On the other hand, in the case of black soil, the highest was 8 ppm and the lowest 2 ppm. As in the case of the previous study, there was little similarity and rhythmicity for the hourly release pattern of sulphate in both soils (Table 6.7). However, there was a marginal increase in sulphate release, especially in red soil after 76 hours. In Fig 6.13 and 6.14, the marginal oscillative behaviour of sulphate release is depicted with a scant similarity in the general pattern of fluctuations. The correlation coefficient obtained with sulphate concentration plotted against periodicity in red soil was found to be positively significant, and in the black, it was negative and non-significant.

With a 200-watt bulb giving a light intensity of 7500 lux in control and 6500 lux in red and black soils, the situation was more or less the same as in earlier photic experiments. The average per-hour release was 0.404 ppm in red soil and 0.337 ppm in black (Table 6.8). The percentage of the sink was 16.59% in black soil compared to the red soil. The control consistently showed nil reading and hence was not tabulated. The oscillative behaviour of sulphate release was better seen in this last photic experiment (Fig 6.15). Statistically, the relations were negative and non-significant (Fig 6.16)

Turbation

In the turbation experiment, the hourly release of sulphate was distinctly elevated in red soil than in black, the average being 0539 ppm in red soil and 0.235 ppm in black. The percentage drop was 56.41 % in black soil with red. The release quantum was highest at 10.0 ppm in red soil and 7.0 ppm in black soil. The lowest readings were zero ppm in red and black soils (Table 6.9). The oscillative behaviour of sulphate release was distinct and declined towards the end of the experiment, as seen in Fig 6.17. The statistical treatment of the data gave adverse marginal correlation soils (Fig. 6.18).

4. Discussion

Sulphur is an integrated protein component and is considered a part of some amino acids. Sulphur performs the role of an activator of enzymes and co-enzymes. It thus is not a part of the enzyme but is essential in closer coordination with enzymes. Sulphur is also a flavouring compound in certain horticultural crops (Franzen Dave, Tech file obtained from the internet). As an oxygen source, anaerobic bacteria also use sulphate, which converts it into hydrogen sulphide.

In natural waters, the sulphate concentration is reported to vary from 2 to 80 mg./l. However, in industrial areas and arid regions, it may exceed 1000 mg/l. High sulphate content may be expected in Rajasthan owing to the relatively higher occurrence of gypsum, especially in the northwestern region. In Karnataka, the sulphate content is 22.66 mg/l in two reservoirs (paper- obtained from the internet). The latter author found a decreasing trend in the sulphate from winter to spring season, which he related to the water's suitability for irrigation. The highest sulphate concentrations are in saline lakes, as stated earlier.

The sulphur transport in the aquatic system has both chemical and biotic influences. It has been reported that the lowest concentration of sulphate (< 1ppm) is a common feature of several African lakes with basins situated in crystalline rock formations (Talling & Talling, 1965). These lakes were of oxic waters with probably orthograde oxygen profile. This indicates that the availability of sulphate in natural waters is phytoplankton-dependent. The higher the phytoplankton, the higher the dissolved oxygen will be, consequently lowering the sulphate. This hypothesis is likely to be operating in the African lakes and probably in all lakes situated in tropical regions; however, this has been contradicted by Lehman and Branstrator (1994), as stated earlier.

From the above-stated experimental results, it could be said that the per-hour sulphate release has been consistently higher in red soil, at times to the extent of a several-fold increase. The heating experiment showed a higher sulphate release amongst all the experiments again in the red soil. The experimental conditions are anaerobic due to glass distilled water covered with a paraffin layer. In nature, under such circumstances. The sulphate release is related to the existence of a heterotrophic bacterial metabolism occurring in t the decomposing of organic material (Butin, 1953). In this case, the bacterium *Proteus species* and a few others are reportedly active in soil systems. This sulphate release is reduced by HS-to H_2S (Jorgensen, 1983). All the sulphate-reducing bacteria are anaerobic. It is necessary to mention here that in the present experimental setup, there is little possibility of a bacterial population in the soil bed of the jar. The soil was in dry condition before use. Except for spores of bacteria, there may not be any possibility of live active anaerobic bacteria in the soil. As such, sulphate in the jar's water column results from the dissolution of sulphurous elements because of anoxic conditions. This, however, needs further detailed study, especially of the water interface.

In the natural lacusterine and closed water systems, such an anaerobic condition would occur only at the organic matter-laden bottom at the interface between anoxic and oxic layers. The former is the consequence of anaerobiosis produced by anaerobic bacteria. The sulphate is higher in Udaipur waters, primarily bottom waters (Durve & Sharma, 2007). This is probably the result of anaerobic bacterial metabolism in the anoxic bottom layer, as Butlin (1953) and Jorgensen (1983) observed. This sulphate has come to the upper water column by diffusion. The existence of sulphate in the water column of Udaipur lakes in appreciable quantities is thus the outcome of anoxic conditions overlaid by relatively lower oxic hypolimnetic waters. Therefore, The presently reported experiments attempt to explain the probable functioning of lake metabolism in sulphate in Udaipur Lake systems. The sulphate in the ground waters of Udaipur has been investigated by Agrawal and Jagetia (1997), who recorded values ranging from 15 to 570 ppm.

Sulphur is utilised by all living organısms in both inorganic and organic forms. Sulphate is released during the geochemical weathering of rocks and soils containing either sulphides or free sulfur, which are oxidised in the presence of water to form sulphuric acid (Zobell, 1973). This acidity may adsorb to soil particles. Sulphur is also found in the soil's organic matter (Houle & Carignan, 1995).

Table 6.1: Sulphur levels under different simulated temperatures and conditions.
Variable- Heating (32ºC)

Red soil		Black soil	
Periodicity of reading (hours)	Sulphur in ppm	Periodicity of reading (hours)	Sulphur in ppm
48	16.0	24	2.0
50	15.0	26	3.0
52	8.0	28	0.0
76	10.0	52	5.0
78	11.0	54	7.0
80	11.0	56	7.0
104	10.0	80	6.0
106	5.0	82	2.0
108	5.0	84	1.0
132	8.0	108	4.0
134	7.0	110	5.0
136	6.0	112	2.0
Average per hour	1.258	Average per hour	0.528

The percentage drop in the average per-hour release of sulphur in black soil was 58.03% compared to red soil.

Table 6.2: Sulphur levels under different simulated temperature conditions. Variable- Heating (32ºC)

Red soil 4⁰C		**Black soil 5⁰C**	
Periodicity of reading (hours)	Sulphur in ppm	Periodicity of reading (hours)	Sulphur in ppm
48	6.0	24	0.0
50	8.0	26	0.0
52	11.0	28	3.0
76	10.0	52	1.0
78	9.0	54	1.0
80	5.0	56	0.0
104	10.0	80	2.0
106	6.0	82	0.0
108	5.0	84	5.0
132	9.0	108	2.0
134	3.0	110	0.0
136	4.0	112	0.0
Average per hour	0.966	Average per hour	0.157

The percentage drop in the average per-hour release of sulphur in black soil was 83.75% compared to red soil.

Table 6.3: Sulphur levels under different simulated pH conditions Variable – Acidic pH 4.5

Red soil		**Black soil**	
Periodicity of reading (hours)	Sulphur in ppm	Periodicity of reading (hours)	Sulphur in ppm
48	2.0	24	0.0
50	9.0	26	3.0
52	3.0	28	3.0
76	2.0	52	0.0
78	15.0	54	0.0
80	4.0	56	1.0
104	11.0	80	0.0
106	17.0	82	1.0
108	4.0	84	0.0
132	11.0	108	1.0
134	10.0	110	3.0
136	7.0	112	0.0
Average per hour	1.067	Average per hour	0.134

The percentage drop in the average per-hour release of sulphur in black soil was 87.45% compared to red soil.

Table 6.4: Sulphur levels under different simulated pH conditions Variable – Alkaline pH 9.0

Red soil		Black soil	
Periodicity of reading (hours)	Sulphur in ppm	Periodicity of reading (hours)	Sulphur in ppm
48	6.0	24	3.0
50	6.0	26	3.0
52	7.0	28	2.0
76	3.0	52	1.0
78	7.0	54	8.0
80	6.0	56	6.0
104	6.0	80	1.0
106	2.0	82	0.0
108	4.0	84	1.0
132	2.0	108	0.0
134	2.0	110	0.0
136	2.0	112	0.0
Average per hour	0.595	Average per hour	0.280

The percentage drop in average per hour release of

Table 6.5: Sulphur levels under different simulated photic conditions Variable- Photic intensity (15-watt bulb)

Red soil		Black soil	
Periodicity of reading (hours)	Sulphur in ppm	Periodicity of reading (hours)	Sulphur in ppm
48	10.0	24	8.0
50	10.0	26	3.0
52	9.0	28	3.0
76	6.0	52	3.0
78	8.0	54	4.0
80	2.0	56	2.0
104	5.0	80	2.0
106	4.0	82	1.0
108	2.0	84	1.0
132	4.0	108	4.0
134	4.0	110	2.0
136	0.0	112	0.0
Average per hour	0.719	Average per hour	0.370

The percentage drop in average per hour release of sulphur was 48.54% in black soil in relation to red soil.

Table 6.6: Sulphur levels under different simulated photic conditions Variable- Photic intensity (60-watt bulb)

Red soil		Black soil	
Periodicity of reading (hours)	Sulphur in ppm	Periodicity of reading (hours)	Sulphur in ppm
48	13.0	24	5.0
50	15.0	26	5.0
52	12.0	28	2.0
76	7.0	52	0.0
78	2.0	54	0.0
80	7.0	56	0.0
104	7.0	80	0.0
106	4.0	82	0.0
108	7.0	84	0.0
132	6.0	108	0.0
134	3.0	110	0.0
136	5.0	112	0.0
Average per hour	0.988	Average per hour	0.134

The percentage drop in average per hour release of sulphur was 86.44% in black soil in relation to red soil.

Table 6.7: Sulphur levels under different simulated photic conditions Variable- Photic intensity (100-watt bulb)

Red soil		Black soil	
Periodicity of reading (hours)	Sulphur in ppm	Periodicity of reading (hours)	Sulphur in ppm
48	7.0	24	8.0
50	4.0	26	3.0
52	6.0	28	5.0
76	2.0	52	2.0
78	5.0	54	2.0
80	6.0	56	4.0
104	8.0	80	5.0
106	9.0	82	4.0
108	8.0	84	4.0
132	7.0	108	3.0
134	9.0	110	4.0
136	10.0	112	5.0
Average per hour	0.910	Average per hour	0.550

The percentage drop in average per hour release of sulphur was 39.57% in black soil in relation to red soil.

Table 6.8: Sulphur levels under different simulated photic conditions Variable- Photic Intensity (200-watt bulb)

Red soil		Black soil	
Periodicity of reading (hours)	Sulphur in ppm	Periodicity of reading (hours)	Sulphur in ppm
48	8.0	24	8.0
50	1.0	26	1.0
52	1.0	28	1.0
76	7.0	52	6.0
78	4.0	54	3.0
80	0.0	56	0.0
104	2.0	80	0.0
106	3.0	82	2.0
108	4.0	84	3.0
132	0.0	108	0.0
134	0.0	110	0.0
136	6.0	112	6.0
Average per hour	0.404	Average per hour	0.337

The percentage drop in average per hour release of sulphur was 16.59& in red soil in relation to black soil.

Table 6.9: Sulphur levels under simulated turbation condition Variable- Turbulence

Red soil		Black soil	
Periodicity of reading (hours)	Sulphur in ppm	Periodicity of reading (hours)	Sulphur in ppm
48	10.0	24	7.0
50	5.0	26	2.0
52	4.0	28	2.0
76	7.0	52	4.0
78	3.0	54	0.0
80	3.0	56	1.0
104	4.0	80	2.0
106	3.0	82	0.0
108	5.0	84	3.0
132	2.0	108	0.0
134	2.0	110	0.0
136	0.0	112	0.0
Average per hour	0.539	Average per hour	0.235

The percentage drop in average per hour release of sulphur was 56.41% in red soil in relation to black soil.

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