Article

Sulphur Contents in Arable Soils from Four Agro-Ecological Zones of Ghana

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Abstract: There is limited data on Sulphur (S) contents in arable soils for appropriate fertilizer recommendations in Ghana. Five study areas in a reconnaissance survey (RS), followed by an in-depth study of two areas comprising farms of different durations of cultivation, were investigated for the current total S and sulphate contents. Basic soil properties were measured using standard laboratory procedures. Total S and sulphate contents were determined using LECO instrument dry combustion and HPLC, respectively. The results showed wide variations in total S contents from 31 to 603 mg kg^{-1} in the Guinea Savannah (GS) zone. The mean trend was Forest > Forest-Transition (F-S) > north Guinea Savannah (nGS) > Deciduous Forest (DF) > south Guinea Savannah (sGS) in the RS sites, with a similar trend in the main study sites. Sulphate contents ranged from 5 to 25 mg kg^{-1}, constituting 0.8 to 37% of the total S. The mean percent trend was sGS = DF > Forest > nGS > F-S. Soil organic carbon (SOC) was the major predictor of total S along with pedogenic minerals. Total S and crystalline pedogenic minerals predicted the sulphate contents. The results highlight the need for ecologically-based S fertilizer programmes to boost crop yields.

Keywords: crop yields; duration of cultivation; HPLC; native vegetation; pedogenic minerals; sulphate; total S

1. Introduction

Low soil fertility, leading to yield reduction and increasing yield gaps [1,2], is recognized as a driver of farmland expansion in Sub-Saharan Africa [3,4]. Integrated soil fertility, using a combination of inorganic and organic soil amendments, is considered to be the most appropriate approach in a smallholder farming context [5]. However, major nutrient combinations in the form of nitrogen (N), phosphorus (P) and potassium (K) dominate the Sub-Saharan African fertilizer market in NPK compound fertilizers without added sulphur (S), calcium (Ca) or magnesium (Mg). The continuous use of these fertilizers creates a nutritional imbalance, as observed in the widespread soil S deficiency [6,7]. The imbalances have implications for soil microbial community structure and activity [8,9], crop yields [10], ecosystem health [10,11], and agricultural sustainability [11]. The S deficit has been widely attributed to reduced atmospheric S deposition, increased use of low S mineral fertilizers, low utilization of animal manure, continuous cultivation with low nutrient inputs and high crop residue removal, intense use of high-yielding crop cultivars, etc. [6,12]. Sulphur and N define crop productivity [13] because of the close N-S functions in cellular processes and secondary metabolism [14]. This makes S the fourth important plant nutrient [6,15,16]. A review of the effects of secondary nutrients and micronutrients in sub-Saharan Africa [17] revealed that the application of S achieved agronomic efficiencies in many countries. They, therefore, concluded that soil S deficit is a setback to crop productivity due to the current low yields compared to those obtained through S application. Thus, the inclusion of S fertilizers (inorganic and organic) could boost crop yields and food security [15] for the following reasons: (1) Crops have similar requirements for S and P [16]; (2) S deficiency

affects N uptake [12,18] since S and N play synergistic roles in the biosynthesis of protein and Vitamin B1 [19,20]; (3) Sulphur is essential because it is a component of some amino acids (i.e., cysteine, cystine and methionine), vitamins, coenzymes, glucoside oils and is indispensable for their synthesis [14,21]; (4) Sulphur is also a component of several compounds that are responsible for aroma, taste and flavour of foods and beverages [22]. This implies that low soil S contents may affect not only yield but also the quality of crops and food nutrition.

Sulphur deficiency could be one of the drivers of the existing large yield gaps in West Africa [23] because the application of S and micronutrients increased maize yield by 25% [17] and 29% [24] compared to regular NPK compound fertilizers. Specifically, the inclusion of S fertilizer increased rice grain in the Guinea Savannah zone by 65% [23]. A study conducted in lowland soils of the Equatorial forest, Guinea savanna, Sudan savanna, and Sahel savanna zones of West Africa found limited but highly variable quantities of sulphate [25]. According to the 2017 annual report of the Ghana Ministry of Food and Agriculture (MoFA) (i.e., "Facts and Figures"), the actual yields of major cereals, legumes and root crops in Ghana range between 32.6 and 55% of potential yields [26]. This implies that yield gaps of 45 to 67.4% in Ghana remain to be closed. The current flagship programme (Planting For Food and Jobs), which aim to boost agriculture in Ghana, promote the increased use of fertilizers through subsidies. Over the years, there has been an enormous focus on fertilizers such as urea, NPK compound fertilizers of varying ratios, and ammonium sulphate (the only S-supplying, but acidifying, fertilizer) [26]; personal communication with farmers at the study sites). Moreso, the MoFA annual Facts and Figures report does not report S data as part of the information on soil properties relevant for crop production.

Sulphur research in Ghana dates back over four decades [25,27–29]. Safo and Sekou [29] focused only on available S (sulphate) in soils of cocoa plantations and cassava farms in the Deciduous Forest zone and found varied amounts of 3.3 to 23.4 mg kg^{-1}. Acquaye and Beringer [27] studied S forms and distributions in soil profiles, whereas Acquaye and Kang [28] studied S status in surface soils of the Forest, Deciduous Forest and Guinea Savannah zones of Ghana. They found total S in the range of 9 to 347 mg kg^{-1} in both cases with sulphate contents of 3 to 39 mg kg^{-1}, where the Forest zone had consistently higher S contents than the Guinea Savannah zone. The study by Buri et al. [25] covered lowland areas of the West African sub-region. They also found variations across the flood plains, where the sulphate contents were 3.4 and 4.9 mg kg^{-1} for river flood plains and inland valley swamps, respectively. Currently, it is uncertain what the S contents in Ghanaian soils are. The only other recent S data are from Tsujimoto et al. [23], who investigated the effects of S on rice yields on cultivated and non-cultivated White Volta floodplain soils of the Guinea Savannah zone. Given the existing yield gaps, the adoption of appropriate S fertilizers could contribute to closing the yield gaps. If S fertilization (applied as elemental S, gypsum, ZnS, $(NH_4)_2SO_4$ at 5 to 68 kg ha^{-1}) increased maize yields by >20% and rice yields by >60%, a conscious S countrywide fertilizer programme (an integration of both inorganic and organic sources) could contribute to closing the current yield gaps of maize and rice under recommended growing conditions. To achieve this, adequate data on current soil S contents in Ghanaian soils will be required. It also calls for a drastic shift from the continuous use of only NPK fertilizers to the inclusion of suitable S fertilizers to enhance yields from the already degraded soils.

Consequently, this study was conducted to investigate S contents in selected arable soils from four agro-ecological zones of Ghana involving over one hundred farms of different durations of continuous cultivation. It was hypothesized that S levels in the arable soils will vary due to continuous crop production with limited fertilizer use, farming systems, and types of fertilizers used. The research questions considered are: What are the current total S and sulphate levels in soils of farms of different duration of cultivation and wealth categories? What factors drive these S contents? How could these contents influence crop yields and yield gaps? Which S fertilizers could address the gaps?

2. Materials and Methods

2.1. Study Sites

The study was conducted in two stages, as part of the Sentinel Project (Social and Environmental Trade-offs in African Agriculture—https://www.sentinel-gcrf.org/, accessed on 20 October 2022). The first stage was conducted in five out of six areas located in different agro-ecological zones of Ghana selected for a reconnaissance survey of the Sentinel Project (Figure 1). The ecological zones are listed from the wet to relatively dry zones below (except for Apataim, which had similarities with the Dompem area):

- *Dompem*, *Forest zone*: native vegetation, a mature cocoa (*Theobroma cacao* L.) plantation, a young cocoa plantation and a mixed farm comprising plantain (*Musa paradisiaca* L.), banana (*Musa* sp. L.), cassava (*Manihot esculenta* Crantz), and pineapple (*Ananas comosus* (L.) Merr.) with one-year old cocoa seedlings. The geology of the Dompem site is dominantly Birrimian formation comprising argillaceous sediments, volcanic and calcareous materials that metamorphosed into folded granite, and Tarkwaian formation comprising sandstones, phyllites and conglomerates.

- *Sefwi-Ahokwa*, *Deciduous Forest zone*: native vegetation under the Taungya agroforestry system, mature cocoa and oil palm plantations. The geology is Birrimian with argillaceous sediments, volcanic and calcareous materials that metamorphosed into folded granite or intruded by granite.

- *Adansam*, *Forest -Savannah Transition zone*: native vegetation, a mango plantation and two yam (*Dioscorea* sp.) farms located on two different soil types. The geology is located on the Voltaian system comprising mudstone, sandstone, conglomerates, tillites and limestone.

- *Lito*, *Guinea Savannah zone*: native vegetation and two yam farms. The geology is located on the Voltaian system comprising mudstone, sandstone, conglomerates, tillites and limestone.

- *Wallembelle*, *Guinea Savannah zone*: native vegetation, maize (*Zea mays* L.) and soybean (*Glycine max* (L.) Merr.) farms. The geology is dominantly granite.

Random sampling was employed at the reconnaissance survey sites to observe the variability across the fields. Five independent samples were taken to 20 cm depth at different spots at about 5–10 m apart, depending on the size and nature of the site.

The second stage of the study focused on two locations: the Dompem-Pepesa area located in the Tarkwa-Nsuaem Municipality in the Forest zone and the Adansam-Kokuma area within the Kintampo South District in the Forest-Savannah Transition zone of Ghana (Figure 1). Whereas the reconnaissance survey farms and native vegetation were selected based on site and farmer availability, the farms for the final study were selected based on wealth categories and duration of cultivation (farm types) [30]. The basis for selecting the sites, description of the two sites and sampling have already been described by Neina and Agyarko-Mintah [30].

2.2. Laboratory Procedures

The basic properties of the soil such as pH, exchangeable bases, effective cation exchange capacity (ECEC), pedogenic minerals (Al and Fe), total carbon (C) (i.e., SOC since no carbonates were present in the soil) and total S have already been described in Neina and Agyarko-Mintah [30]. The available S (sulphate) contents in the soils were determined by Ion Chromatography (Shimadzu HPLC IC 20A System), after extracting air-dried soil (<2 mm) using 500 ppm P of Monocalcium Phosphate ($Ca(H_2PO_4)_2$) at 2.5:1 extractant to soil ratio [31].
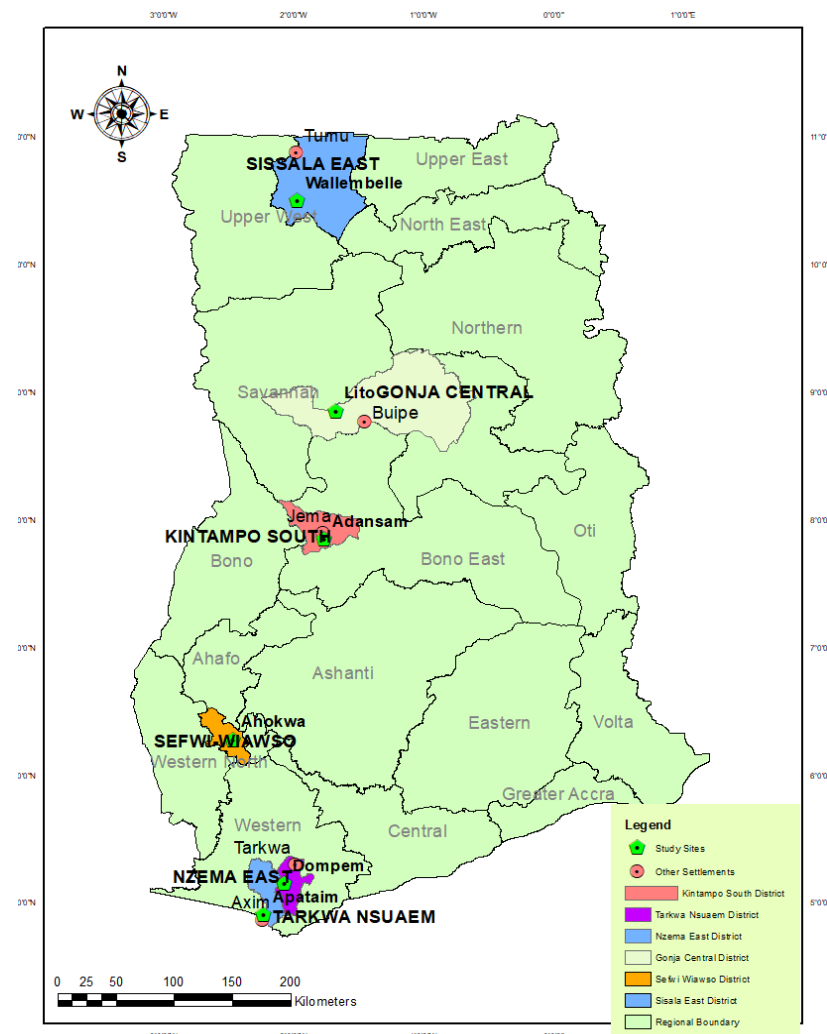
Figure 1. Location of the reconnaissance survey and the two main study areas.

2.3. Statistical Analyses

Some samples were below detection for total S both in the reconnaissance survey and the main study samples. Therefore, only farms containing total S were used to identify the farms for statistical analyses. This defeated the aim of including wealth rank as a factor along with farm types in the main study. Consequently, nine farm replicates were obtained for Dompem, whereas five were obtained for Adansam. All the data were checked for conformity to Analysis of Variance (ANOVA), bivariate correlation and multiple linear regression using SPSS Version 20 (IBM, New York, NY, USA). Where necessary, non-normal data were log- or square root transformed. The data were assessed to examine whether the duration of cultivation had significant impacts on the soil properties using One-Way ANOVA and the means were compared using Tukey HSD tests at a 5% level of significance. In the case of non-normal data, non-parametric statistics such as Kruskal-Wallis/Mann-Whitney U Tests were applied. Multiple regression was run to identify the predictors of the total S and sulphate contents, using the stepwise forward method in SPSS version 20. All regression models were tested for normality, constancy of variance, absence of correlation between the residuals (Durban–Watson statistics) and absence of multi-collinearity, calculating the variance inflation factor (VIF). Pearson's and Spearman's correlations were conducted for normal and non-normal data to test relationships among the soil properties. The graphs were created using Sigma Plot 12.

3. Results

3.1. Basic Properties of the Soils

The texture of the reconnaissance survey sites were dominantly clayey textures for the Forest, sandy clay for the Deciduous Forest, sands for the Forest-Savannah Transition and sandy loams for soils of the Guinea Savannah zones (Table 1). Further, the Forest, Deciduous Forest and Forest-Savannah Transition zones had lower bulk densities (<1.3 g cm^{-3}) than the Guinea Savannah zone (≤ 1.5 g cm^{-3}). The soil organic carbon (SOC) contents in the reconnaissance survey soil decreased by about 70% as one traverses from the Forest zone and Deciduous Forest zones towards the Forest-Savannah Transition zone, but increased by 20 to 30% towards the Guinea Savannah zone (Table 2). For the main study, the basic properties of the soils have already been described in Neina and Agyarko-Mintah [30]—although the data overlaps because of differences in the S contents.

Table 1. Bulk density, particle size and textural classes of soils from native vegetation and croplands of each of the reconnaissance survey sites ($n = 5 \pm$ One standard error of means).

Site	Bulk Density (g cm^{-3})	Sand (%)	Silt (%)	Clay (%)	Textural Class
Dompem (Forest zone)					
Native vegetation	1.0 ± 0.1	60.0	16.0	24.0	Sandy clay loam
Old cocoa	1.1 ± 0.2	38.4	36.6	25.0	Loam
Young cocoa	1.2 ± 0.1	44.6	26.7	28.8	Clay loam
Vegetable farm	0.9 ± 0.2	43.0	25.8	31.3	Clay loam
Sefwi—Ahokwa (Semi-Deciduous Forest zone)					
Native vegetation	0.9 ± 0.1	71.8	7.7	20.5	Sandy clay loam
Oil palm	1.2 ± 0.3	82.4	4.1	13.5	Loamy sand
Cocoa	1.3 ± 0.2	64.9	11.6	23.5	Sandy clay loam
Adansam (Forest-Savannah Transition zone)					
Native vegetation	1.2 ± 0.1	90.0	4.0	6.0	Sand
Mango	1.3 ± 0.1	88.0	6.0	6.0	Sand
Yam (Ferric Luvisol)	1.1 ± 0.1	90.0	4.0	6.0	Sand
Yam (Fluvisol)	1.2 ± 0.1	95.0	2.0	3.0	Sand
Lito (Guinea Savannah zone)					
Native vegetation	1.7 ± 0.0	69.2	11.8	19.0	Sandy loam
Yam	1.3 ± 0.2	70.0	17.5	12.5	Sandy loam
Grassland	1.7 ± 0.1	70.8	7.7	21.5	Sandy clay loam
Mixed yam	1.5 ± 0.1	79.5	7.0	13.5	Sandy loam
Wallembelle (Guinea Savannah zone)					
Native vegetation	1.4 ± 0.1	79.0	6.5	14.5	Sandy loam
Maize	1.5 ± 0.2	76.8	7.2	16.0	Sandy loam
Soybean	1.5 ± 0.1	86.2	4.8	9.0	Loamy sand

3.2. Total S Contents and Trends

The results of the reconnaissance survey showed a wide variation in the total S contents among the croplands and native vegetation in the ecological zones. The mean total S content ranged from 31 mg kg^{-1} in the native vegetation of Lito to 603 mg kg^{-1} in the maize farm of Wallembelle, both in the Guinea Savannah zone (Table 2). A wavy trend in the total S content is observed from the Forest zone in the south toward the Guinea Savannah zone in northern Ghana. For instance, the total S contents decreased by about 75% as one traverses from the Forest zone to the Deciduous Forest zones, increased by 52% in the Forest-Savannah Transition zone, decreased again by 60% in the Forest-Savannah Transition zone followed by another increase by 62% in the Guinea Savannah zone (Table 2). The total S content was detected in all independent replicates and sites of the Rain Forest and Deciduous Forest agro-ecological zones of Ghana, i.e., Dompem and Sefwi- Ahokwa (Table 2). The mean total S trend was Dompem > Adansam > Wallembelle > Sefwi- Ahokwa > Lito. In the Guinea Savannah zone, total S was detected in all independent replicates

and sites of Lito. For Wallembelle, in the same agro-ecological zone, S was detected in all three sites but not in all samples (i.e., one replicate for forest, three for maize and two for soybean farms). In the soils of the Forest-Savannah Transition the total S was generally below detection. For instance, the total S contents of most of the croplands from Adansam were below detection. Sulphur was detected in only two of the four sites sampled, i.e., only one replicate of the yam farm and three replicates of the mango farm (Table 2). As a result, ANOVA was only performed on the total S contents of the Dompem and Sefwi-Ahokwa soils because of missing data points. However, no significant differences were observed in the total S contents of the two sites (Table 2). A Spearman correlation revealed a weak positive correlation ($r = 0.37$, $p < 0.01$) between the total S and SOC of all the sites (Figure 2).

Table 2. Soil pH, total C, N, S and sulphate contents of soils from native vegetation and croplands the reconnaissance survey sites ($n = 5 \pm$ One standard error of means).

Site	Soil pH	Total C (g kg^{-1})	Total S (mg kg^{-1})	Sulphate (mg kg^{-1})
Dompem (Forest zone)				
Native vegetation	4.5 ± 0.2	20.9 ± 9.4	597.2 ± 109.0	4.8 ± 0.2 a
Old cocoa	5.2 ± 0.2	18.4 ± 8.3	456.0 ± 100.8	23.4 ± 2.7 b
Young cocoa	4.9 ± 0.2	16.6 ± 7.4	398.0 ± 56.2	25.8 ± 2.7 b
Vegetable farm	5.2 ± 0.1	19.4 ± 8.7	516.2 ± 48.3	6.9 ± 1.2 c
p-value	-	>0.05	>0.05	0.024
Sefwi—Ahokwa (Semi-Deciduous Forest zone)				
Native vegetation	6.2 ± 0.4	22.0 ± 9.8	138.8 ± 27.6	14.8 ± 0.6 a
Oil palm	6.4 ± 0.3	14.9 ± 6.7	106.8 ± 25.5	8.7 ± 0.2 b
Cocoa	6.2 ± 0.2	14.2 ± 6.4	121.4 ± 36.2	15.4 ± 0.2 a
p-value	-	>0.05	>0.05	0.05
Adansam (Forest-Savannah Transition zone)				
Native vegetation	5.9 ± 0.1	5.2 ± 2.3 a	BD	7.5 ± 0.6
Mango	6.1 ± 0.1	6.5 ± 2.9 a	498.7 ± 105.0	7.2 ± 0.2
Yam (Ferric Luvisol)	6.4 ± 0.1	7.4 ± 3.3 b	259.0 ± 0.0 *	7.1 ± 0.1
Yam (Fluvisol)	6.5 ± 0.2	4.4 ± 2.0 c	BD	6.9 ± 0.6
p-value	-	0.001	-	>0.05
Lito (Guinea Savannah zone)				
Native vegetation	5.4 ± 0.1	6.8 ± 3.0	31.4 ± 18.4	11.7 ± 0.6 a
Yam	5.8 ± 0.1	8.1 ± 3.6	69.6 ± 40.8	11.6 ± 0.3 a
Grassland	5.4 ± 0.3	11.8 ± 5.3	95.8 ± 25.2	6.9 ± 0.4 b
Mixed yam	5.8 ± 0.3	8.8 ± 4.0	147.1 ± 72.6	7.2 ± 0.8 b
p-value	-	>0.05	-	<0.001
Wallembelle (Guinea Savannah zone)				
Native vegetation	6.6 ± 0.1	7.8 ± 3.5	230.0 ± 0.0 *	7.9 ± 0.2
Maize	6.5 ± 0.1	17.6 ± 7.9	603.3 ± 27.5	9.2 ± 0.3
Soybean	5.8 ± 0.1	7.0 ± 3.1	339.5 ± 91.4	8.1 ± 0.6
p-value	-	>0.05	-	>0.05

BD: Below detection; * Total S was detected in only one sample. No total S was detected in two of the Adansam sites; Data in columns followed by different letters depict significant differences at *p –value < 0.05*.

For the main research at the final two sites, total S was below detection in 21% of the 51 farms sampled from Adansam. The mean S contents of the Dompem soils ranges from 98.5 to 236.2 mg kg^{-1} and differed ($p = 0.043$) among the farm types. The total S contents of the Dompem soils decreased with the duration of cultivation by 28, 91 and 19 mg kg^{-1} in years three, five and ten, respectively. It was almost three-fold (Table 3) those of Adansam, which also differed among farm types with the highest and lowest total S contents in the ten and five years farms, respectively. A Pearson correlation revealed strong positive correlations ($r = 0.62$, $p < 0.001$) between the Dompem total S and total C (Figure 3a) and ECEC ($r = 0.57$, $p < 0.001$) (Figure 4a). A non-parametric Spearman correlation also showed a moderate correlation between the Dompem total S and Al$_d$ ($r = -0.38$, $p < 0.05$) (Figure 4b). The regression model showed that SOC alone accounted for 38.1% of total S in

the Dompem soils, while Fe_{ox} contributed 7.1%, giving a coefficient of determination (R^2) of 45.2% ($p < 0.001$). A Pearson correlation revealed a moderate positive correlation between the Adansam total C and total S ($r = 0.48$, $p < 0.033$) (Figure 3b). Again, the regression model revealed that the clay content accounted for 35.2% ($p < 0.01$) of the total S in the Adansam soils.
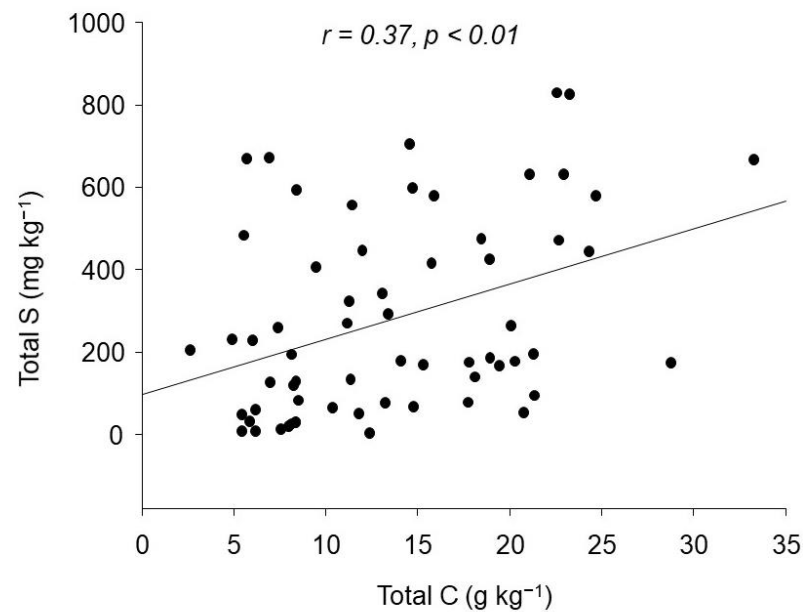

Figure 2. Spearman between reconnaissance survey total S and SOC.

Table 3. Soil and δpH, total C, N, S and sulphate contents of soils from different farms in Dompem ($n = 9 \pm$ One standard error of means) and Adansam ($n = 5 \pm$ One standard error of means).

Farm Type	[1] Soil pH		[2] δpH	[3] Total C	Total S	Sulphate
	Water			g kg^{-1}	mg kg^{-1}	mg kg^{-1}
Dompem						
Year one	4.1 ± 0.2		−0.5 ± 0.1	33.2 ± 6.9	236.2 ± 40.2 a	11.3 ± 1.3 a
Three years	4.4 ± 0.2		−0.4 ± 0.0	25.5 ± 4.7	208.4 ± 57.5 b	12.4 ± 2.0 a
Five years	4.5 ± 0.1		−0.5 ± 0.1	18.2 ± 1.3	117.1 ± 17.0 c	12.0 ± 1.8 a
Ten years	4.5 ± 0.1		−0.6 ± 0.0	19.9 ± 3.4	98.5 ± 13.1 d	5.8 ± 1.1 b
p-value	-		*>0.05*	*>0.05*	*0.043*	*0.004*
Adansam						
Year one	6.6 ± 0.3		−0.2 ± 0.2	8.6 ± 1.7	54.6 ± 1.7 a	5.7 ± 0.7 a
Three years	6.3 ± 0.0		−0.1 ± 0.2	10.4 ± 0.8	61.3 ± 9.1 a	6.7 ± 0.7 a
Five years	6.4 ± 0.1		0.0 ± 0.2	8.3 ± 1.3	39.7 ± 6.8 ab	16.3 ± 1.9 b
Ten years	6.0 ± 0.1		0.0 ± 0.1	10.7 ± 0.8	73.3 ± 7.5 ac	12.4 ± 1.8 b
p-value	-		-	*>0.05*	*0.023*	*<0.001*

[1,2,3] Overlapping data with part published in Neina and Agyarko-Mintah [30]; Data in columns followed by different letters depict significant differences at *p-value < 0.05*.
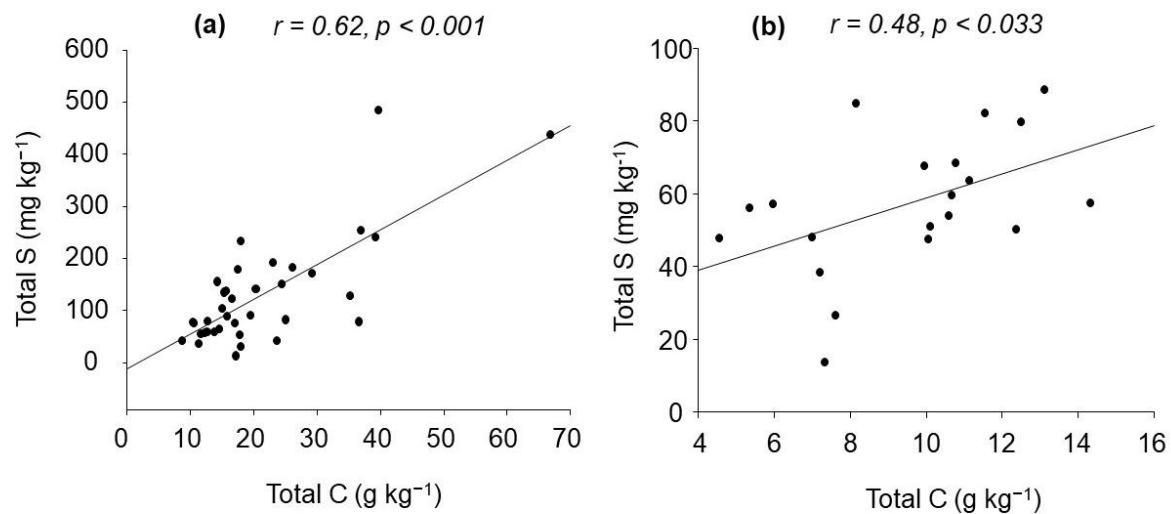
Figure 3. Pearson correlation between (**a**) Dompem total S and SOC and (**b**) Adansam total S and SOC.
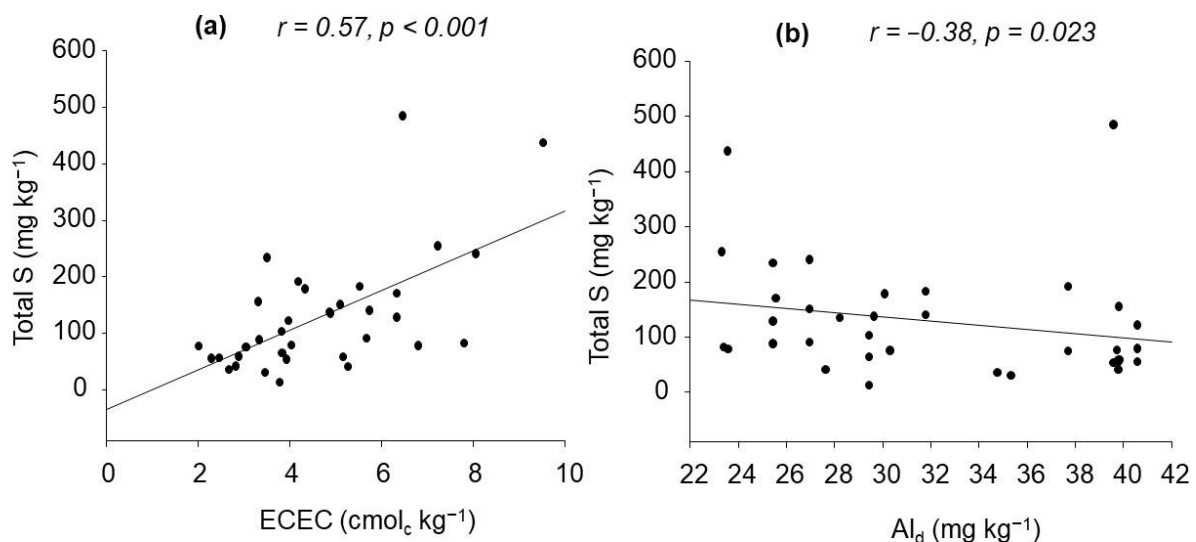

Figure 4. Spearman correlations, showing a positive correlation between Dompem total S and (**a**) ECEC and a negative correlation with (**b**) Al_d.

3.3. Sulphate Contents and Trends

Unlike the total S, sulphate was detected in all five replicates of all the reconnaissance sites from all the agro-ecological zones, ranging from 5 to 25 mg kg^{-1} for the Dompem sites. The sulphate contents constituted 0.8 to 7.5% of the total S for Dompem, 8.2 to 12.7% for Sefwi, 1.5 to 2.7% in Adansam, 4.5 to 37% in Lito and 1.5 to 3.4% in Wallembelle soils. The mean percent trend was Lito = Sefwi- Ahokwa > Dompem > Wallembelle > Adansam. For the main study in Dompem and Adansam, the mean sulphate contents of both study sites were similar (i.e., 10.4 and 10.3 mg kg^{-1}), but differed among the farms ($p < 0.05$) (Table 3). There was no clear trend in the sulphate contents in both study areas with regards to the duration of cultivation. However, they appeared to mirror each other, where the sulphate content in the Dompem soils decreased by almost half in year ten, whereas those of Adansam more than doubled in years five and ten (Table 3). The Dompem sulphate contents ranged from 4.8 to 10.2% of total S, whereas those of Adansam ranged from 10.4 to 41% of total S. A Pearson correlation between the Dompem total S and sulphate showed a weak positive correlation ($r = 0.39, p < 0.05$). For the Adansam soils, Spear-

man correlations showed strong negative relations between sulphate and Al_d ($r = -0.73$, $p < 0.001$) and sulphate and Fe_d ($r = -0.70$, $p < 0.01$). The regression model showed that Fe_d alone accounted for 72% of the sulphate content, whereas Al_d contributed 14.5%, yielding a coefficient of determination (R^2) of 86.5% ($p < 0.001$) for the Adansam soils.

4. Discussion

The basic properties of the study areas are a reflection of the interactions between the geology and agro-ecological zone. Consequently, the textural classes, along with the SOC contents, produced increasing trends in bulk densities as one moves from the wet ecological zones of southern Ghana to the relatively drier and low biomass ecological zones of northern Ghana. Generally, cultivation increases bulk density [32] depending on the tillage method and crops grown [33], as observed in most of the cultivated soils (Table 1). In the reconnaissance survey soils, specific differences can be observed at the different locations due to effects of particle size distributions and SOC contents. For instance, the bulk densities of the Dompem cocoa plantations were higher than that of the native vegetation, except for the vegetable farm. The observation is attributed to small scale differences in the particle size distributions and SOC contents. The vegetable farm had 17, 9.0 and 7.3% less sand, silt and clay in addition to 1.5 g kg^{-1} less SOC compared to the native vegetation (Table 1). The Sefwi-Ahokwa soils showed increased bulk densities in the croplands. There was no particular trend in bulk densities of the Adansam croplands. However, the bulk densities of the yam farms were almost similar to those of the native vegetation because mounding reduces soil bulk density to enhance yam tube expansion [34]. The difference between the two yam farms is caused by soil type, particle size distribution and SOC contents (Tables 1 and 2). The SOC content of the Adansam native vegetation is due to the nature of the site, which affected the C turnover. The vegetation was thick and had a turf of root network, which limits rainwater flow through the canopy and subsequent infiltration into the deeper soil layers. Such conditions affect microbial activities and organic matter decomposition. Generally, most of the soils have been exposed to prolonged leaching, resulting in a loss of the original nutrients in the parent materials [35]. This has fashioned out soil types with the soil pH, δpH ECEC, SEB and pedogenic Al and Fe of the soils [30]. The properties presented have both direct and indirect effects on soil S and its dynamics in each agro-ecological zone.

The study confirmed a wide variability in total S contents in both reconnaissance survey sites and the main study farm types (Tables 2 and 3). These may be attributed to the different crops grown either in sole or mixed patterns. Interviews conducted with the farmers revealed that 71% of the farms sampled in Dompem were mixed crop systems, dominated by heavy-feeding crops such as cassava, maize and rice. For the Adansam soils, only 16% of the farms were a mixed crop system, but the sole crops were mostly heavy-feeding yam. The differences in the cropping patterns tend to produce differences in SOC contents and turnover as well as crop nutrient uptake [36,37], leading to different residual effects. The positive correlations between total S and SOC (Figures 2 and 3) confirm that over 90% of total S is bound in organic matter [6,16,38]. The correlations also corroborate previous findings [25,27,39,40]. There seem to be variations in the fraction of total S that is bound in the organic fraction. For instance, Acquaye and Beringer [27] and Acquaye and Kang [28] discovered that organic S constituted 56 to over 95% of the total S in soil profiles of the same agro-ecological zones of Ghana, although the land uses of the profiles locations were not indicated. This observation is attributed to the various factors that influence S status in soils. Apart from SOC, the other drivers of total S in this study are pedogenic minerals for the Dompem soils and clay content for the Adansam soils. Based on their results, Acquaye and Beringer [27] and Acquaye and Kang [28] concluded that the total S contents of the Ghanaian soils depend on the agro-ecological zone, the topographic position, parent material, SOC content, vegetation cover and soil pH (with a limited effect). The findings of this study depict the same trends, starting from the reconnaissance survey sites. Similar to our study, Acquaye and Beringer [27] and Acquaye and Kang [28] observed that

soils formed over Birrimian rocks and phyllite and basic rocks in the Forest and Deciduous Forests zones had higher total S than soils formed over acidic rocks, alluvium, and shales or sandstones and tertiary sands [28]. It was expected that the native vegetation will contain more total S than the arable soils, as seen in those of the Forest and Deciduous Forest zones (Table 2). However, the native vegetation of the Forest-Transition and Guinea Savannah zones showed a different trend with relatively low total S contents compared to the croplands. This may be attributed partially to the nature of the vegetation and partly to the geology, as suggested earlier. Unlike the native vegetation, the total S contents of the croplands were substantial for the Forest-Transition and Guinea Savannah zones. This may be due to the use of ammonium sulphate, the only prevalent S-containing N fertilizer used in Ghana, and cattle manure in the case of the Lito Pasture. Generally, the total S contents are influenced by fertilizer type (e.g., manure, mineral fertilizer) used [20,41], climatic conditions, soil type, atmospheric S depositions, and crop type [41], and agronomic practices such as conservation agriculture and cover cropping [13,39]. More applications of ammonium sulphate fertilizer, animal manure, S-rich crop residues [42], crucifer-legume cover crop mixtures [43], cover cropping crop fertilization [13], conservation agriculture with high residue retention [39] tend to increase S contents.

Although SOC is the main source of S, the type and quality are of great importance. In SOC, the organic S exists in two essential forms including (i) Ester organic S bonded to O or N [7,38] and (ii) Carbon-bonded S comprising of direct C-S bond) [38]. Organic ester sulphate-S constitute a reserve form of S for microbes, notably fungi [7,44]. Because the total soil S fraction is mostly organically-bound, it is not readily available to plants and must mineralize into inorganic or available S form (sulphate, SO_4^{2-}), which affects crop yields [45]. Sulphate is the most satisfactory index of S availability for plants [46], although thiosulfate ($S_2O_3^{2-}$) uptake is possible [14]. The range of sulphate values (5 to 25 mg kg^{-1}) found in this study is slightly similar to those (3 to 22 mg kg^{-1}) obtained by Acquaye and Kang [28] in Ghanaian soils and those (7.9 to 21.6 mg kg^{-1}) of Kumar et al. [39] in soils of Bangladesh, much higher than those (2.7 to 8.1 mg kg^{-1}) found in the White Volta floodplain soils of Ghana [23] and those (<5 mg kg^{-1}) of Safo and Sekou [29] in selected forest soils of the Deciduous Forest zone of Ghana, but lower than values found by Acquaye and Beringer [27] in the Forest zone of Ghana. Despite these variations, the mean sulphate contents for each agro-ecological zone were in the order Dompem > Sefwi- Ahokwa > Lito > Wallembelle > Adansam for reconnaissance survey and Dompem = Adansam.

Studies show that a small fraction of sulphate (<5% of total S) is present in soils during the growing season [19,20]. However, in this study, the fraction of total S that constituted the available S varied widely from <1 to >30% for the reconnaissance survey samples and 4.8 to 41% for the two study areas. The trend did not follow that of total S for the latter, but Adansam had a higher fraction of sulphate in total S. Acquaye and Kang [28] found a mean value of 6% in the different agro-ecological zones. The variations in the sulphate fraction of total S are attributed to total S for the Dompem and the crystalline pedogenic minerals (Al_d and Fe_d) for the Adansam soils, according to the correlations and regression models. These findings corroborate those of Zhang et al. [47], Amberger [48] and Tanikawa et al. [49]. The pedogenic minerals contribute to the net positive surface charges which retain sulphate in soil, particularly in warm and wet climates [47]. Further, S availability is also controlled by soil pH [19,50] and soil texture, and is particularly low in light-textured soils [41,51]. Owing to these factors, Zhang et al. [47] have proposed a conceptual model of S dynamics in soil of different climates.

How could these sulphate levels influence crop yields and yield gaps? Saito et al. [52] already called for the need to close yield gaps in various agro-ecological zones. Research shows that the threshold soil sulphate content for a definite effect on crop yields is 10 mg kg^{-1}, according to Grobler et al. [45] and Cate and Nelson [53]. This implies that 67% of the reconnaissance survey sites, ten years farms of Dompem and years one and three of Adansam all contain sulphate contents below the 10 mg kg^{-1} threshold, based on the mean values presented in Tables 2 and 3. For the individual farms in the main study, only

36% of farms Dompem and 40% Adansam meet the proposed threshold (same or above). However, the sulphate contents, which fall below the 10 mg kg^{-1}, do exceed the range of 4–5 mg kg^{-1} which are characteristic of S-responsive sites observed by Zhao et al. [22] after S fertilizer application in malting barley. The proposed threshold sulphate content seems to be crop-specific, as Meyer et al. [54] found a higher threshold of 20 mg kg^{-1} for sugarcane.

To overcome these crop-specific S requirements, previous researchers categorised crops into those with high S (e.g., oil rapeseed, mustard, cruciferous vegetables, alfalfa, etc.), medium S (e.g., cotton, grasses, sugarcane, coffee, etc.) and low S (cereals, groundnut, sugar beet, etc.) requirements [6]. Sadly, no specific rate of S fertilizer application has been recommended for these categories of S requiring crops, although 10 to 75 kg ha^{-1} [22,41,48,55,56] have been proposed for different crops and conditions. Despite the recommendations, crop yield responses also depend on the initial sulphate and SOC contents in the soil [57], crop response, type of inorganic and organic S fertilizer [41,48,58] and whether S-containing agrochemicals are used or not [55,56,59]. Therefore, it is essential to adopt inorganic fertilizer such as elemental or bentonite S, gypsum, Kieserite, Epsom salt, sulphate of potash, single super Phosphate [48]; and organic S sources such as legume cover [43,60,61], cattle manure, poultry manure, pig manure [62], composted agro-processing wastes [58,63], tithonia (*Tithonia diversifolia* (Hemsl.) A. Gray) biomass [61], in addition to agroforestry, conservation agriculture, and other integrated aspects of integrated soil fertility management. It is important to note that the application of elemental S fertilizer and ammonium sulphate could reduce soil pH, depending on the type used [41], and are not recommended for acidic soil conditions.

5. Conclusions

The study confirmed variations in total S and sulphate contents in all the soils, which showed a wavy trend across the ecological spectrum. This was pronounced in the reconnaissance survey sites, starting from the Forest zone in the south towards the Guinea Savannah zone in the north. The SOC content was the main factor controlling the total S contents in the soils, in addition to the pedogenic minerals. Unlike the total S contents, which were below detection in some samples after dry combustion, sulphate was present in all the soils. The contents ranged from 5 to 25 mg kg^{-1} and constituted 0.8 to 37% of total S, where the Lito soils of southern Guinea Savannah had the highest fraction. Total S and crystalline pedogenic minerals were the main predictors of the sulphate contents. The results suggest that climatic conditions, geology, crop type grown and cropping pattern and the types of fertilizers used possibly influenced the S levels in the soils. Finally, the results highlight the need for ecologically-based S fertilizer programmes and an intense promotion of integrated soil fertility management to augment the current crop yields. Soil pH and texture, particularly in the Forest-Savannah, should be a guide to the choice of S fertilizers applied.

6. Patents

There are no patents related to this manuscript.

Author Contributions: Conceptualization, Introduction, Methodology, and Sample analysis, Soil sampling, Data analysis, Original Draft Preparation, D.N.; Project Administration, Review & Editing, Validation, D.N. and B.A. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: Data available on request due to privacy restrictions. The data presented in this study are available on request from the corresponding author. The data are not publicly available due to continuity of the study.

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