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Sulfur and molybdenum fractionation in marine and riverine alluvium paddy soils

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ABSTRACT

Intermittently submergence and drainage status of paddy fields can cause alterations in morphological and chemical characteristics of soils. We conducted a sequential fractionation study to provide an insight into solubility of Sulfur (S) and Molybdenum (Mo) in flooded alluvial paddy soils. The samples (0–15 and 15–30 cm) were taken from marine and riverine alluvial soils in Kedah and Kelantan areas, respectively, and were sequentially extracted with NaHCO₃, NaOH, HCl, and HClO₄–HNO₃. Total S in upper and lower layers of Kedah and Kelantan ranged between 273 and 1121 mg kg⁻¹, and 177 to 1509 mg kg⁻¹, respectively. In upper layers and subsoil of Kedah, average total Mo were 0.34 and 0.27 mg kg⁻¹, respectively. Average total Mo in Kelantan were 0.25 mg kg⁻¹ (surface layer) and 0.28 mg kg⁻¹ (subsoil). Cation exchange capacity (CEC) was positively correlated with plant available amounts of Mo in upper layers of Kedah area. Also, total and medium-term plant-available S was correlated with total carbon (C) at lower layers of Kelantan soil series. But in surface layers of Kelantan soil series, CEC was strongly correlated with total and medium-term plant-available S. Our results indicates that the influence of flooding conditions on soil S and Mo contents in paddy fields may cause long-term changes in S and Mo chemical reactivities.

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Paddy; molybdenum; sulfur; alluvial soil

Introduction

Flooding soils with water causes drastic changes in normal physical, chemical and biological processes, and reactions. The heterogeneity of these soils, in terms of fluctuations in redox potential and their chemical specificities, are result of changes in distribution of microorganisms, mineral phases, and mixing different redox reaction substrates and products.[1]

Rice, as a traditional staple food in Asia, is grown as wet land rice and is arguably the most important crop in the world. In peninsular Malaysia, rice-growing areas are categorized into three groups as follows: (1) coastal alluvial plains that are mainly found on the west coast; (2) river terraces of the large rivers which are mainly seen on the east coast; (3) floodplains and valleys of the small rivers.[2] Sulfur, as an important element in paddy fields, undergoes redox transformations. In oxidizing conditions, sulfate ions (SO₄²⁻) can move easily with soil solution and in this form they are taken up by plants. In acidic soils, if microbial activities are reduced, plant available form of sulfur will be decreased due to low S oxidation.[3] It is generally stated that pH values, type of cation present, presence of competing anions, extractable amounts of Al³⁺ and Fe³⁺, organic C, clay content, and

soil horizon type govern to a vast extent sulfate sorption in various soils.[4] Aluminium- and Fe-humus complexes and inhibition of crystallization of Al and Fe oxides by organic matter are accounted for increased reactive surfaces toward sulfate adsorption.[5] The initial increase in water-soluble sulfate at the beginning of submergence and then a slight decrease for several months is seen in acid soils.[6]

It was reported that some coastal sediments in west coast of peninsular Malaysia contain up to 2–3% pyrite as a result of thousands years of pyritisation process.[7] Pyrite (cubic FeS₂) is the most thermodynamically stable iron sulfide mineral in soils [8] which is produced by transformations of unstable monosulfides.[9] When sulfate is reduced, hydrogen sulfides (H₂S), which are second mechanism for pyrite formation, are formed. Prevalence of this gas is only seen in sandy soils low in reducible iron or the soils contain large amounts of organic matter under flooding conditions.[1] In the presence of H₂S, thiooxymolybdates such as MoO₆S²⁻, MoO₃S²⁻, and MoO₂S₂²⁻ are formed and MoO₂S₂²⁻ becomes dominant when concentration of sulfide enhances.[10] According to Wang et al. [11], The presence of relatively stable residual Mo (VI) under high concentrations of H₂S supports

the assumption that thiomolybdates are of diagenetically importance in sulfidic sediments.

However, mineralization of organic sulfur compounds or immobilization of them into organic compounds are seen in oxidized and reduced zones of waterlogged soils but production of sulfide prevails mainly in reduced soil layers.[12] Molybdenum occurs in different potential soil fractions including positively charged surfaces, crystalline material, soil solution, organic material, and discrete compounds.[13] Molybdenite (MoS_2) is the most abundant form of Mo in igneous rocks. In general, rates of 0.5–5 mg kg^{-1} are considered normal, and soils contain 0.5 or less could be considered low.[14] Prevalence of Mo in soil in different oxidation states (2–6) have made the chemistry of Mo more complex. Lindsay, [15] displayed that molybdenum species in soil solution declined in the order $\text{MoO}_4^{2-} > \text{HMoO}_4^- > \text{H}_2\text{MoO}_4^0 > \text{MoO}_2(\text{OH})^+ > \text{MoO}_2^{2+}$, and solubility of them decreased in the order $\text{CuMoO}_4 > \text{ZnMoO}_4^{2-} > \text{MoO}_3 > \text{H}_2\text{MoO}_4^0 > \text{Ca H}_2\text{MoO}_4 > \text{Pb H}_2\text{MoO}_4$. Molybdenum could be traced in some fractions such as soil solution, organic matter, and solid phases and are mainly bound with oxides. Inner and outer – sphere surface complexes for Mo adsorption were found on Fe and Al oxides, respectively, but MoO_4^{2-} forms inner-sphere surface complexes on both Al and Fe oxides at low pH and outer-sphere surface complexes at high pH. Adsorption of Mo on a weight basis on all soil Fe and Al oxides is higher than adsorption on clay minerals, and its adsorption on montmorillonite is higher than illite and kaolinite.[16] McGrath et al. [17] also stated that molybdate sorption on amorphous iron oxides largely affects Mo toxicity under different pH regimes. It was also reported that retention of molybdate on $\gamma\text{Al}_2\text{O}_3$ was higher than sulfate, and molybdate considerably inhibited adsorption of sulfate on aluminum oxides but sulfate did not have any effect on molybdate adsorption.[18] During oxic conditions, molybdenum exists in oxidation state of 6 in oxyanionic form but in anoxic conditions, sulfide mineral molybdenite is predominant.[19] Under water-logged conditions, two layers are produced. The surface layer contains high levels of dissolved oxygen, whereas oxidized oxygen is not present in underlying layers. Hence, redox potential is low at surface layers and increases with depth. Fox and Doner, [20] reported that maximum accumulation of Mo was found near water-sediment interface which might resulted from formation of MoS_2 and MoS_4^{2-} . Case studies with a focus on total molybdenum status in soils have been rarely done in Malaysia and this is the first study, to our knowledge, to test molybdenum concentrations in different fractions of alluvial paddy soils of two major rice production areas in this country. This study was conducted to determine S and Mo concentrations in different rice soils developed on marine

and riverine alluvial materials from Kedah and Kelantan states, Malaysia.

Materials and methods

Site description

Kedah (Latitude: 5°52'59.57" N, Longitude: 100°31'46.58" E) and Kelantan (Latitude: 6°7'20.15" N, Longitude: 102°14'16.56" E) states are situated in Peninsular (east) Malaysia (Figure 1). The soils from Kedah are of marine alluvium parent material while soils from Kelantan are of riverine alluvium parent material.

The average annual rainfall in Kedah and Kelantan is 2201.9 and 2854.4 mm, respectively.[21] In Kedah and Kelantan, the lands under rice cultivation were about 50.8 and 10.5% of their whole land areas, respectively. [22] Also, the mean temperatures were not so different between Kedah (27.6 °C) and Kelantan (27.4 °C) states.[21] Rice harvested area in Kedah (187,413 ha) was approximately 5 times larger Kelantan (38,641 ha). [22] We collected different samples of soils from two above-mentioned areas on paddy fields (Table 1).[23]

Determination of soil properties

The integrated soil samples were collected from depths of 0–15 and 15–30 cm. For analysis, soil samples were oven-dried and visible macro fauna and root pieces were removed. Samples were crushed and sieved to <2 mm. Silt and clay concentrations were determined by pipette method, and fine and coarse sand particles were separated by sieving (50–250 and 250–2000 μm diameter). Soil pH was measured by a glass electrode in distilled water and 0.01 M CaCl_2 at a soil-to-solution ratio of 1:2.5 (w/v).

Soil samples (0.5 g) were accurately weighed and placed in ceramic crucibles along with combustion accelerators. The crucibles were placed in a high temperature furnace which was then flooded with oxygen (Trumac Determinator, Leco USA). The furnace was heated to 1350 °C and caused the combustion of the carbon and sulfur in soil samples. Cation exchange capacity (CEC) was calculated by sum of cations using 1 M NH_4OAc (pH 7.0). Amorphous iron (Fe ox) and aluminum (Al ox) were determined by extraction in solution using oxalic acid and ammonium oxalate (pH 3) for 4 h in the dark,[24] following by detection using inductively-coupled plasma optical-emission spectrometry (ICP-OES) (Optima 8300, PerkinElmer, USA). The samples high in clay contents were centrifuged at high speeds. Total molybdenum (Mo) was determined independently of fractionation procedure by solubilizing Mo with HCl at 120 °C and use of heptan-2-one as a solvent with detection by ICP-OES. [25]

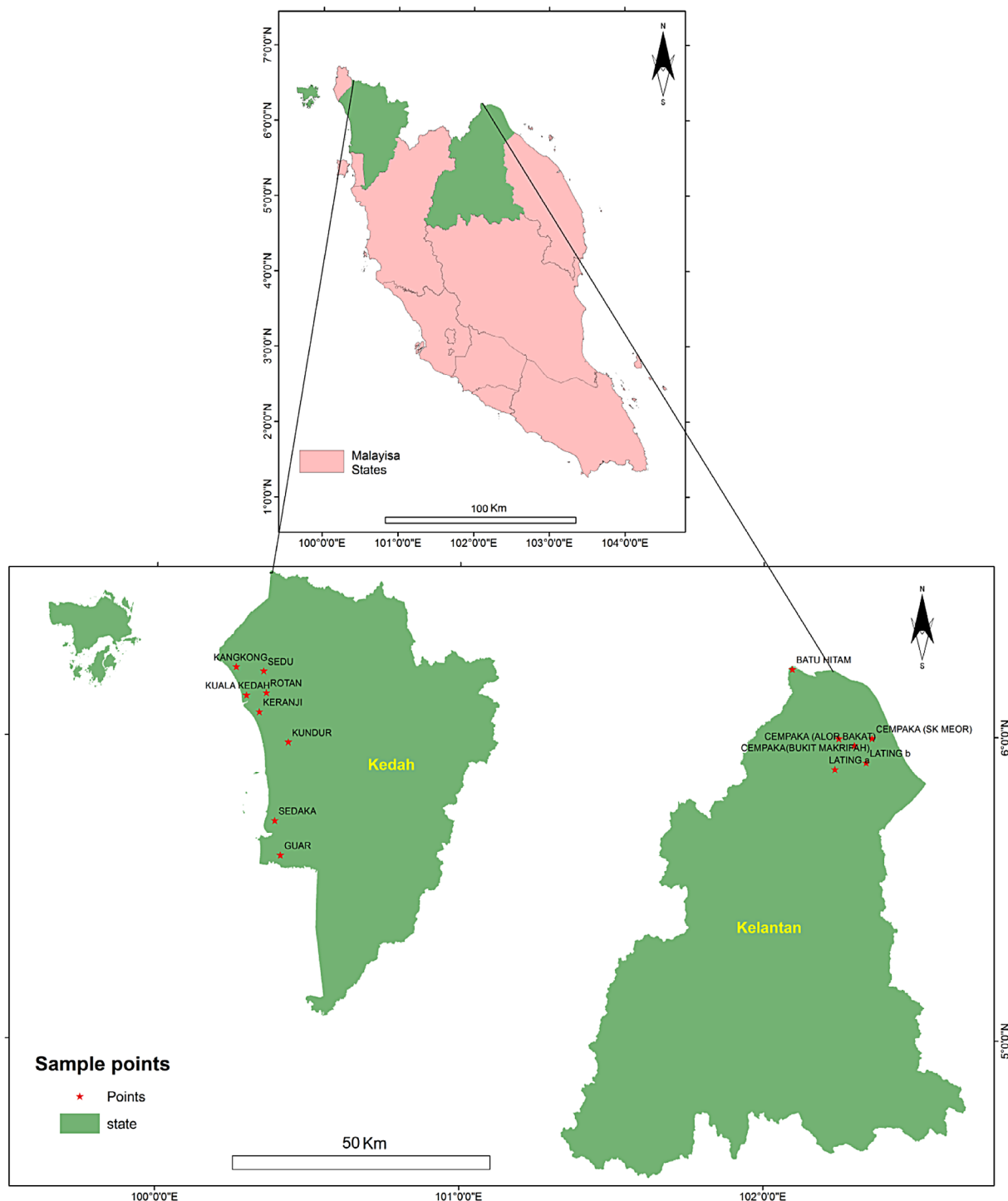


Figure 1. Map of the Kedah and Kelantan illustrating the location of sampling sites.

Table 1. Morphological classification and location of sampled profiles on Kedah and Kelantan, Malaysia.

Location	Soil series	Geology	Soil morphological type	US taxonomy
Kedah	Guar	Marine alluvium	Brown very fine	Typic Sulfaquept
	Sedaka	Marine alluvium	Pale very fine	Typic Pelludert
	Keranji	Marine alluvium	Pale very fine	Typic Sulfaquent
	Kuala Kedah	Marine alluvium	Pale very fine	Typic Fluvaquent
	Kangkong	Marine alluvium	Pale very fine	Sulfic Tropaquepts
	Sedu	Marine alluvium	Brown very fine	Typic Sulfaquept
	Rotan	Marine alluvium	Pale very fine	Typic Pelludert
Kelantan	Kundur	Marine alluvium	Pale very fine	Sulfic Tropaquepts
	Cempaka	Riverine alluvium	Red-yellow fine	Orthoxic Tropudults
	Lanting	Riverine alluvium	Yellow fine	Aquoxic Tropudult
	Batu Hitam	Riverine alluvium	Pale fine	Typic Paleaquult

Table 2. Properties of eight soils series of lowland rice paddy field on Kedah Province.

Soil location	Depth	Textural class	Clay		Soil pH		CEC meq 100 g ⁻¹	Total C g kg ⁻¹	Al ox g kg ⁻¹	Fe ox g kg ⁻¹	Total Mo mg kg ⁻¹	Total S
			%	H ₂ O	CaCl ₂	H ₂ O						
Guar	0–15	Silty clay	49.89	4.59	4.12	20.85	37.95	0.43	2.84	0.37	850	
	15–30	Silty clay	52.04	4.44	3.96	9.36	41.29	0.44	2.60	0.37	1076	
Sedaka	0–15	Silty clay loam	39.53	4.64	4.07	16	20.74	0.34	0.95	0.37	501	
	15–30	Silty clay	44.40	4.56	4.08	19.38	15.75	0.35	0.87	0.10	447	
KerANJI	0–15	Silty clay	43.46	5.13	4.48	23	33.17	0.34	1.01	0.31	444	
	15–30	Silty clay	52.79	5.19	4.56	10.38	26.65	0.45	1.20	0.15	377	
Kuala Kedah	0–15	Silty clay	53.54	5.85	5.16	13.26	23.76	0.44	1.07	0.35	273	
	15–30	Silty clay	55.90	6.13	5.66	27.31	17.47	0.40	0.83	0.32	220	
Kangkong	0–15	Silty clay	40.55	4.85	4.51	15.76	24.03	0.17	1.00	0.32	740	
	15–30	Silty clay	43.24	5.59	5.41	18.78	16.46	0.14	0.79	0.27	560	
Sedu	0–15	Clay	61.29	4.83	4.50	15.55	42.45	0.44	0.59	0.35	1033	
	15–30	Silty clay	58.04	4.69	4.46	16.48	36.71	0.56	0.53	0.52	1509	
Rotan	0–15	Silty clay	42.09	5.22	4.68	18.92	21.73	0.26	0.84	0.35	372	
	15–30	Silty clay	45.67	5.27	4.72	21.36	19.03	0.32	0.96	0.37	387	
Kundur	0–15	Silty clay	40.69	4.92	4.20	16.75	25.15	0.31	0.93	0.31	1121	
	15–30	Silty clay	52.41	4.92	4	22.67	16.54	0.47	1.05	0.10	194	

Notes: Al ox: oxalate-extractable aluminum, Fe ox: oxalate extractable iron.

Sulfur and molybdenum fractionation

Triplicate 1 g soil samples were placed into 50 mL centrifuge plastic tubes and sequentially extracted according to a modified version of sequential fractionation procedure by Hedley et al. [26], represented by Lilienfein et al. [27]. This sequential extraction method was used to assess S and Mo concentrations because these elements are of certain general similarity in chemical characteristics. Labile or weakly adsorbed S and Mo were extracted using 0.5 M sodium bicarbonate (NaHCO₃). After 16 h of shaking (end-over-end), supernatants were centrifuged and filtered. Bounded S and Mo to Al and Fe hydrous oxides (medium term plant available S and Mo) were determined by extracting the soil with 0.1 M NaOH. Samples were shaken for 16 h, followed by centrifuging and filtering. Acid soluble S and Mo (associated S and Mo with calcium and iron oxides) were extracted using 1 M HCl, and after 16 h supernatants were centrifuged and filtered. Residual fraction (highly resistant and occluded S and Mo) were digested by application of 5 M HNO₃ and concentrated HClO₄ at 200 °C. After filtering, all aliquots were analyzed by ICP-OES.

Data analysis

Sulfur and Mo are demonstrated as the mean of the three replicate extracts. Correlations between soil properties and S and Mo fractions were determined using SAS 9.4, Sigma plot version 12.0 and Excel softwares. Significant differences between soil depths were calculated using Student's *t*-test at *p* < 0.05. All results were stated on the basis of oven dried soils at 105 °C for 24 h.

Results

Soil properties

Chemical and physical properties of soils are illustrated in Tables 2 and 3. In upper layers of Kedah and Kelantan, contents of clay varied from 39.5 to 61.2% and 5.8 to

46.6%, respectively. In lower layers Kedah and Kelantan, the clay contents varied from 43.2 to 58% and 13.8 to 55.6%, respectively. The pH of all soil series ranged between 4.3 (Cempaka Sk Meor) and 6.7 (Cempaka Bukit Makrifah). Also, the average pH of surface layers of Kedah soil series was higher than others. In surface soils of Kedah and Kelantan areas, total carbon varied from 20.74 to 42.45 g C kg⁻¹ and 9.28 to 28.65 g C kg⁻¹, respectively. Total C decreased with depth in both areas except in Guar soils. Total Mo ranged from 0.1 to 0.525 mg Mo kg⁻¹ at both soil depths. In Kedah, the average total Mo contents of all soil series declined with depth, but were found greater in subsoils of Kelantan. In Kedah and Kelantan, total sulfur ranged from 194 to 1509 mg S kg⁻¹ and 177 to 1036 mg S kg⁻¹, respectively. According to results, total sulfur concentration declined with depth in both areas except in Guar, Rotan and Batu Hitam series.

Amorphous iron varied from 0.53 to 2.84 g Fe kg⁻¹ (Kedah), and 0.04 to 1.05 g Fe kg⁻¹ (Kelantan), and total amorphous aluminum between 0.14 to 0.56 g Al kg⁻¹ (Kedah) and 0.08 to 0.55 g Al kg⁻¹ (Kelantan). In Kedah soil series, CEC values varied from 13.26 to 20.85 meq 100 g⁻¹ (0–15 cm) and (9.36) to 27.31 meq 100 g⁻¹ (15–30 cm) and increased with depth except in Guar and KerANJI series. CEC of Kelantan soil series ranged from 2.9 to 13.49 meq 100 g⁻¹ (0–15 cm) and 2.67 to 9.13 meq 100 g⁻¹ (15–30 cm) and declined with depth except in Lating b series. Average clays percentage of the soils in Kedah found to be higher than Kelantan soil series at both depths. Sedu series had highest clay content (61%) while the lowest was seen in Lating a series in the both layers. There was no significant difference in values of soil pH, CEC, amorphous iron and amorphous aluminum between soil depths except in total C contents of Kelantan soil series (**p* < 0.05).

Concentrations of sulfur fractions

In this experiment, total sulfur and portions of sulfur are illustrated in Tables 4 and 5 and Figures 2 and 3.

Table 3. Properties of six soils series of lowland rice paddy field on Kelantan Province.

Soil location	Depth	Textural class	Clay	Soil pH		CEC	Total C	Al ox	Fe ox	Total Mo	Total S
				H ₂ O	CaCl ₂						
Cempaka (Sk Meor)	0–15	Loam	26.08	5.27	4.60	7.68	19.00	0.37	0.47	0.32	363
	15–30	Clay loam	31.03	4.36	3.93	6.03	10.61	0.36	0.59	0.15	211
Cempaka (Alor Bakat)	0–15	Silty clay	46.66	5.04	4.28	9.50	27.10	0.55	1.05	0.26	451
	15–30	Clay	55.6	4.97	4.40	8.14	11.07	0.48	1.04	0.35	247
Cempaka (Bukit Makrifah)	0–15	Clay loam	24.6	6.78	6.52	7.75	22.63	0.21	0.63	0.22	429
	15–30	Clay loam	30.69	5.26	4.59	5.63	9.65	0.25	0.81	0.3	225
Lating a	0–15	Loamy sand	5.87	6.08	5.72	2.90	9.28	0.08	0.15	0.32	297
	15–30	Sandy loam	13.85	5.04	4.44	2.67	2.99	0.11	0.04	0.42	177
Batu Hitam	0–15	Clay loam	36.67	5	4.38	13.49	28.65	0.42	0.67	0.20	892
	15–30	Clay loam	38.56	4.77	4.17	9.13	16.76	0.43	0.25	0.21	1036
Lating b	0–15	Sandy clay loam	27.23	4.97	4.21	5.25	11.69	0.24	0.66	0.22	300
	15–30	Sandy clay	37.03	5.22	4.27	6.22	6.76	0.31	0.49	0.30	195

Notes: Al ox: oxalate-extractable aluminum, Fe ox: oxalate extractable iron.

Table 4. Average of sulfur concentrations in the fractions of the sequential extraction in Kedah area.

Soil location	Depth (cm)	NaHCO ₃ -S		NaOH-S		HCl-S (mg kg ⁻¹)		HNO ₃ -HClO ₄ -S	
		(mg kg ⁻¹)	RSD (%)	(mg kg ⁻¹)	RSD (%)	(mg kg ⁻¹)	RSD (%)	(mg kg ⁻¹)	RSD (%)
Guar	0–15	218	10.16	391	4.76	51	14.53	17.66	18.38
	15–30	337.30	10.34	308.60	7.66	13	20.88	3.94	8.40
Sedaka	0–15	199.85	11.08	200.40	9.30	25	19.64	6.69	7.62
	15–30	242.63	14.38	130.20	18.14	7.62	13.02	5.6	5.91
KerANJI	0–15	89.90	14.64	219.25	8.50	27.80	17.08	9.79	12.06
	15–30	131.45	16.54	95.82	14.66	4.40	9.59	13.34	14.84
Kuala Kedah	0–15	63.40	14.95	127	14.67	51.90	14.50	16.22	19.42
	15–30	81.80	12.65	83	18.41	9.33	13.10	12.91	10.07
Kangkong	0–15	302.50	7.32	298	6.25	24.85	3.30	99	21.12
	15–30	317.70	10.98	191.50	12.33	10	4.03	36	9.20
Sedu	0–15	363.80	6.09	382.65	4.87	19.70	18.22	2.57	19.84
	15–30	730.50	4.77	401	5.88	13.21	20.53	3.40	9.72
Rotan	0–15	117.80	18.81	158.45	11.77	57.84	13.01	10.51	16.72
	15–30	187	18.65	112	21.11	9	14.77	7.15	16.36
Kundur	0–15	72.70	3.04	119	15.66	66.80	11.27	8.50	5.99
	15–30	72.30	4.82	85	17.83	nd	–	11	10.49

Notes: nd: not detected, RSD: relative standard deviation.

Table 5. Average and sulfur concentrations in the fractions of the sequential extraction in Kelantan area.

Soil location	Depth (cm)	NaHCO ₃ -Mo		NaOH-Mo		HCl-Mo		HNO ₃ -HClO ₄ -Mo	
		(mg kg ⁻¹)	RSD (%)	(mg kg ⁻¹)	RSD (%)	(mg kg ⁻¹)	RSD (%)	(mg kg ⁻¹)	RSD (%)
Cempaka (Sk Meor)	0–15	72.14	13.75	129	14.75	37	2.27	121.81	11.60
	15–30	59.75	12.62	68.55	18.79	1.16	8.54	79.15	10.59
Cempaka (Alor Bakat)	0–15	120.73	14.20	140.54	13.53	44	18.95	142.5	9.91
	15–30	61.45	12	71.26	17.70	nd	–	110	19.20
Cempaka (Bukit Makrifah)	0–15	250	6.85	130	14.62	9.91	8.46	30.71	15.95
	15–30	50.12	16.98	62.75	11.45	nd	–	111	18.85
Lating a	0–15	58.43	19.32	83.88	12.69	45.51	18.41	102	13.81
	15–30	41.93	12.26	44.83	14.01	5.55	17.71	83	18.57
Batu Hitam	0–15	211	8.10	352	5.40	65.72	12.75	250	5.64
	15–30	169.21	7.99	260	7.57	30	12.60	568	5.65
Lating b	0–15	43	19.81	60.80	3.12	8.60	17.44	181.65	7.77
	15–30	32	12.25	37	5.25	5	19.66	116.47	7.60

Note: nd: not detected.

In surface layers of marine alluvium soil series (Kedah area), NaOH and HCl fractions extracted the largest and smallest average S contents, respectively (Figure 2). Sulfur in NaOH and HCl extracts accounted for between 10.6 to 49.2% and 1.9 to 18.9% of the total S in higher layers of marine alluvium soil series,

respectively (Figure 2). In subsoils of Kedah soil series, NaHCO₃ and HCl extracted the largest and smallest S fractions, respectively (Figure 3). NaHCO₃-extractable S accounted for between 31.3 and 56.7% of the total S in lower layers of Kedah soil series, respectively (Figure 3).

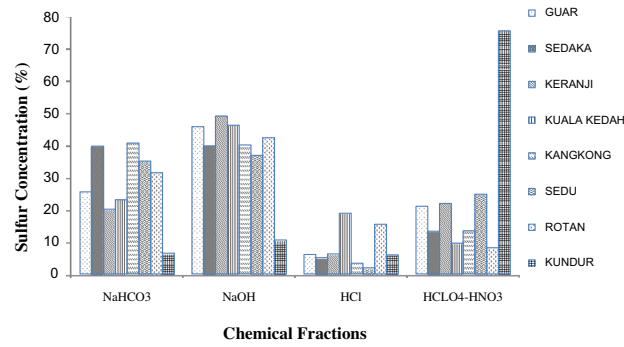


Figure 2. Average portions of sulfur of the total concentrations in Kedah soil series (0–15 cm).

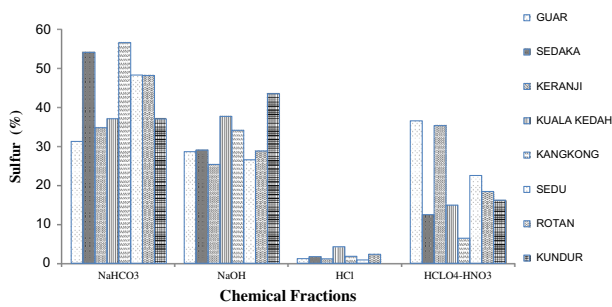


Figure 3. Average portions of sulfur of the total concentrations in Kedah soil series (15–30 cm).

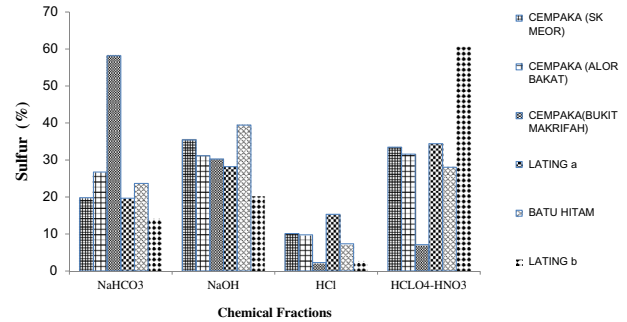


Figure 4. Average portions of sulfur of the total concentrations in Kelantan soil series (0–15 cm).

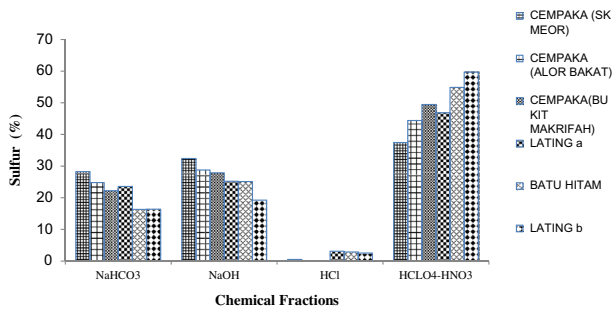


Figure 5. Average portions of sulfur of the total concentrations in Kelantan soil series (15–30 cm).

Also, greatest amounts of extracted S were observed in NaHCO_3 ($730.5 \text{ mg S kg}^{-1}$) and NaOH ($401.6 \text{ mg S kg}^{-1}$) fractions in subsoils of Sedu series (Table 4).

The maximum level of S ($850.45 \text{ mg S kg}^{-1}$) was extracted by $\text{HClO}_4\text{-HNO}_3$ in surface layers of Kunder series, while the lowest amount of S ($19.7 \text{ mg S kg}^{-1}$) was extracted by HCl in Sedu series of Kedah Area (Table 4). In subsoils of Kedah soil series, amounts of extracted S in a descending order were as follows: $\text{NaHCO}_3 > \text{NaOH} > \text{HClO}_4\text{-HNO}_3 > \text{HCl}$ (Figure 3).

According to the results, the proportions of S decreased along the line $\text{HClO}_4\text{-HNO}_3 > \text{NaOH} > \text{NaHCO}_3 > \text{HCl}$ in surface layers of riverine alluvium soil series (Kelantan area) (Figure 4). Sulfur extracted by NaOH and HCl from upper layers accounted for between 20.2 to 39.4% and 2.3 to 15.3% of the total soil S in surface layers of riverine soil series, respectively (Figure 4). In subsoils of Kelantan

area, proportions of S declined along the line $\text{HClO}_4\text{-HNO}_3 > \text{NaOH} > \text{NaHCO}_3 > \text{HCl}$ (Figure 5).

Cempaka (Bukit Makrifah) soil series contained the highest NaHCO_3 -extractable S ($250.05 \text{ mg S kg}^{-1}$) in surface layers but the largest amounts of S, which were extracted by NaOH, HCl, and $\text{HClO}_4\text{-HNO}_3$, were seen in Batu Hitam soil series (Table 5). Also, the lowest amounts of extracted S in HCl (8.6 mg S kg^{-1}), NaHCO_3 ($43.05 \text{ mg S kg}^{-1}$), and NaOH ($60.8 \text{ mg S kg}^{-1}$) extracts were seen in upper layers of Lating B series (Table 5).

In lower depths, Batu Hitam series contained highest extracted S in all chemical fractions as follows: $\text{HClO}_4\text{-HNO}_3$ ($568.15 \text{ mg S kg}^{-1}$), NaOH ($260.6 \text{ mg S kg}^{-1}$), NaHCO_3 ($169.2 \text{ mg S kg}^{-1}$), and HCl ($30.15 \text{ mg S kg}^{-1}$) (Table 5). Total carbon was significantly correlated with NaOH-extractable S ($r^2 = 0.86$; $p < 0.05$) and total S ($r^2 = 0.97$; $p < 0.05$) at lower depths of Kelantan soil series. Also, total CEC was strongly and positively correlated with total S ($r^2 = 0.81$; $p < 0.05$) and NaOH-extractable S ($r^2 = 0.80$; $p < 0.05$) of surface layers of Kelantan soil series.

Concentrations of molybdenum fractions

Molybdenum concentrations in sequential extractions are shown in Figures 6–9. In Kedah area, most of Mo levels were extracted with NaHCO_3 and NaOH fractions at both depths. Molybdenum in NaHCO_3 extracts accounted for 16.5–83.7% of total Mo at upper layers of marine alluvium soil series (Kedah area) (Figure 6). Mean concentrations of Mo extracted by NaHCO_3 and NaOH

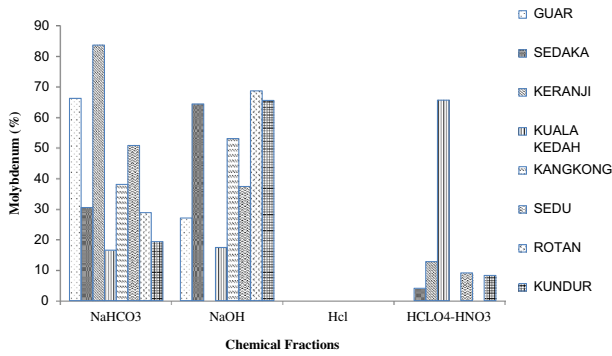


Figure 6. Average portions of molybdenum of the total concentrations in Kedah soil series (0–15 cm).

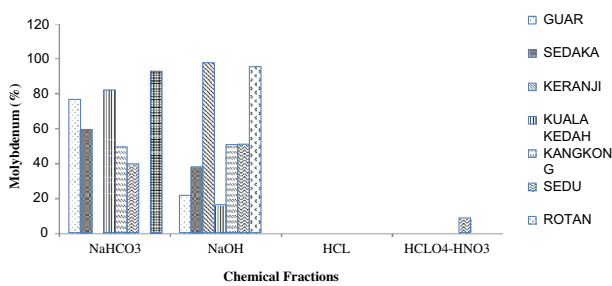


Figure 7. Average portions of molybdenum of the total concentrations in Kedah soil series (15–30 cm).

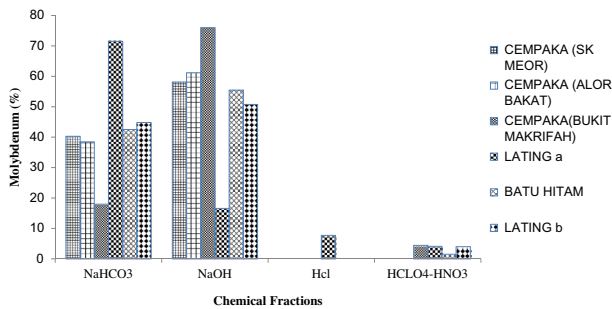


Figure 8. Average portions of molybdenum of the total concentrations in Kelantan soil series (0–15).

were greater at surface soils than subsoils in Kedah (Table 6) but they were not significantly different. Although Mo was not detected in NaOH extract of Kundur series (subsoil), but NaOH-extractable Mo accounted for between 16.1 and 98% of total Mo at lower layers of Kedah soil series (Figure 7).

According to results, Mo concentrations in NaHCO₃ extracts were not detected in lower depths of Keranji and Rotan soils series (Table 6) whereas, 98 and 95% of total Mo were obtained in NaOH extract in subsoils of Keranji and Rotan series, respectively (Figure 7). The highest amount of Mo in NaHCO₃ extracts was achieved in subsoil of Guar series (0.28 mg Mo kg⁻¹) (Table 6).

Rotan soils contained the highest NaOH-extractable Mo (0.35 mg Mo kg⁻¹) in lower depths (Table 6). We did not detect any Mo in HCl extracts at both depths of Kedah soils (Table 6). In Kedah, residual Mo of upper layers was found in different soils but in Guar, Kangkong and Rotan series (Table 6). In lower layers, residual Mo was not detected in any soils except in Sedu series (0.04 mg Mo kg⁻¹) (Table 6). In riverine alluvium soil series (Kelantan area), mean concentrations of NaHCO₃-extractable Mo in subsoils (0.25 mg Mo kg⁻¹) were nearly two times higher than surface layers (0.11 mg Mo kg⁻¹) (Table 7).

In subsoils of Kelantan area, proportions of Mo decreased along the line NaHCO₃ > HCl > NaOH > HClO₄-HNO₃. The results show that maximum Mo concentration (0.37 mg Mo kg⁻¹) was achieved in NaHCO₃ extracts of lower depths of Lating a soil series (Table 7). Also, NaHCO₃ extracted 99, 98, 96, and 93% of Mo from subsoils of Cempaka AB, Lating b, Cempaka BM, and Cempaka SK series, respectively (Figure 9). In upper layers, NaOH extracted Mo of all soils, but we did not detect any Mo in NaOH fractions of subsoils except in Batu Hitam series (0.07 mg Mo kg⁻¹) (Table 7). At both layers, Mo was not obtained in HCl fraction except in Lating a (both layers) and Batu Hitam series (subsoil). The proportions of Mo declined along the line NaOH > NaHCO₃ > HClO₄-HNO₃ > HCl in surface layers of Kelantan soil series (Figure 8). In lower layers, residual Mo was only seen in Cempaka BM, but in surface layers was found in Cempaka BM, Lating a, Batu Hitam, and Lating b series. Results showed that there was no correlation between total Mo and soil properties. Also, CEC was linearly correlated with NaHCO₃-extractable Mo ($r^2 = 0.61; p < 0.05$) at upper layers of Kedah soil series.

Principal component analysis of sulfur

Principal component analysis (PCA) was conducted on the data of soil properties and extracted S and Mo

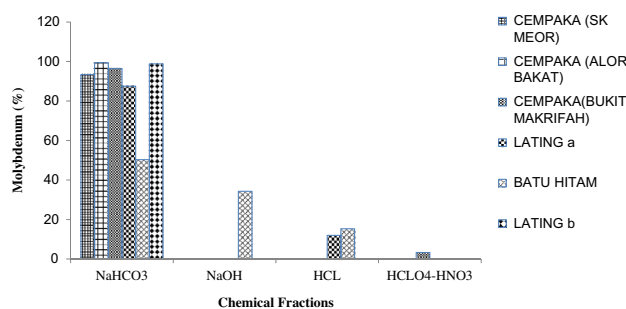


Figure 9. Average portions of molybdenum of the total concentrations in Kelantan soil series (15–30 cm).

Table 6. Average of Mo concentrations in the fractions of the sequential extraction in Kedah area.

Soil location	Depth (cm)	NaHCO ₃ -Mo (mg kg ⁻¹)	RSD (%)	NaOH-Mo (mg kg ⁻¹)	RSD (%)	HCl-Mo (mg kg ⁻¹)	RSD (%)	HNO ₃ -HClO ₄ -Mo (mg kg ⁻¹)	RSD (%)
Guar	0-15	0.25	2.8	0.10	16.66	nd	-	nd	-
	15-30	0.28	3.90	0.08	18.47	nd	-	nd	-
Sedaka	0-15	0.11	6.11	0.24	7.03	nd	-	0.01	15.74
	15-30	0.06	18.43	0.03	3.79	nd	-	nd	-
KerANJI	0-15	0.26	2.69	nd	-	nd	-	0.03	16.77
	15-30	nd	-	0.14	10.20	nd	-	nd	0
Kuala Kedah	0-15	0.05	12.08	0.06	27.86	nd	-	0.23	10.34
	15-30	0.27	4.22	0.05	28.29	nd	-	nd	-
Kangkong	0-15	0.12	5.74	0.17	9.99	nd	-	nd	-
	15-30	0.13	8.37	0.13	10.72	nd	-	nd	-
Sedu	0-15	0.17	3.91	0.13	12.89	nd	-	0.03	17.50
	15-30	0.21	5.42	0.27	5.55	nd	-	0.04	21.07
Rotan	0-15	0.10	6.91	0.24	7.46	nd	-	nd	-
	15-30	nd	0	0.35	4.17	nd	-	nd	-
Kundur	0-15	0.06	11.66	0.20	8.53	nd	-	0.02	19.58
	15-30	0.09	12.13	nd	-	nd	-	nd	-

Note: nd: not detected.

Table 7. Average of Mo concentrations in the fractions of the sequential extraction in Kelantan area.

Soil location	Depth	NaHCO ₃ -Mo (mg kg ⁻¹)	RSD (%)	NaOH-Mo (mg kg ⁻¹)	RSD (%)	HCl-Mo (mg kg ⁻¹)	RSD (%)	HNO ₃ -HClO ₄ -Mo (mg kg ⁻¹)	RSD (%)
Cempaka (Sk Meor)	0-15	0.13	4.91	0.18	2.55	nd	-	nd	-
	15-30	0.14	7.85	nd	-	nd	-	nd	-
Cempaka (Alor Bakat)	0-15	0.10	6.4	0.15	3.01	nd	-	nd	-
	15-30	0.34	3.16	nd	-	nd	-	nd	-
Cempaka (Bukit Makrifah)	0-15	0.04	15.82	0.17	2.80	nd	-	0.01	17
	15-30	0.28	3.80	nd	-	nd	-	0.01	12
Lating a	0-15	0.23	17.70	0.05	8.95	0.02	4.03	0.01	12.78
	15-30	0.37	19.56	nd	-	0.05	4.35	nd	-
Batu Hitam	0-15	0.08	7.51	0.11	4.32	nd	-	0.003	5.66
	15-30	0.10	10.40	0.07	4.06	0.03	6.89	nd	-
Lating b	0-15	0.10	6.34	0.11	4.20	nd	-	0.009	18.88
	15-30	0.29	3.71	nd	-	nd	-	nd	-

Note: nd: not detected.

in order to better understand their interrelationships. In surface layers of Kelantan soil series, the results showed that three factors all had eigenvalues higher than one so that 94% of total variance with the first three principal components can be explained (Table 8). The first principal component explains about 58.6% of the total variance, the second factor explains about 19.2%, and the third factor explains about 16.7%. The first eigenvector has high positive loadings on variable CEC, total S and NaOH-S and high negative loadings on variable pH. According to this, CEC, total S and medium term plant available S were fairly close together, representing a close relationship among them. Furthermore, the pH appears to be a non-effective factor, influencing plant available S in surface layers of riverine alluvium soil series. The second eigenvector has high positive loadings on the variables NaHCO₃-S and pH and high negative loadings on variables HClO₄-HNO₃-S. The third eigenvalue

has high positive loading on the variables HCl-S and NaOH-S and high negative loadings on Fe ox and clay.

In lower layers of Kelantan soil series, PCA results illustrated that three factors all had eigenvalues higher than one (Table 9). The three principal components explain 97% of total data-set variance. The first principal component explains about 61.5% of the total variance, the second factor explains about 27.03%, and the third principal component explains about 8.9%. The first eigenvector has high positive loadings on variable total S, carbon and NaOH-S and high negative loadings on variable pH. According to this result, carbon, NaOH-S and total S were close together and pH seems to be a non-effective factor, affecting availability of S in lower layers of riverine alluvium soil series. The second eigenvector has high positive loadings on the variables Fe ox and clay and high negative loadings on variables HCl-S-S. The third eigenvalue has high positive loading on the variables pH and high negative loadings on Al ox.

Table 8. Varimax rotated matrix for soil properties and extracted sulfur in upper layers of riverine alluvium soil series (Kelantan area) (0–15 cm).

	Factor 1	Factor 2	Factor 3
NaHCO ₃ -S	0.20	0.57	-0.06
NaOH-S	0.33	0.18	0.33
HCl-S	0.22	-0.07	0.47
HClO ₄ -HNO ₃ -S	0.25	-0.37	0.32
Clay	0.23	-0.13	-0.35
pH	-0.21	0.57	-0.05
CEC	0.38	0.12	0.01
Total C	0.30	0.21	-0.16
Total S	0.34	0.18	0.28
Al ox	0.23	-0.193	-0.25
Fe ox	0.27	-0.097	-0.50
Eigenvalue	6.4	2.1	1.8
% Variance explained	58.6	19.2	16.7
% Cumulative variance	58.6	77.9	94.6

Table 9. Varimax rotated matrix for soil properties and extracted sulfur in lower layers of riverine alluvium soil series (Kelantan area) (15–30 cm).

	Factor 1	Factor 2	Factor 3
NaHCO ₃ -S	0.26	-0.13	-0.02
NaOH-S	0.36	-0.15	0.02
HCl-S	0.32	-0.29	0.12
HClO ₄ -HNO ₃ -S	0.25	-0.18	0.16
Clay	0.18	0.48	0.16
pH	-0.13	-0.00	0.93
CEC	0.32	0.28	0.08
Total C	0.35	0.15	-0.09
Total S	0.36	-0.17	0.10
Al ox	0.27	0.39	-0.12
Fe ox	-0.019	0.55	0.07
Eigenvalue	6.7	2.9	0.9
% Variance explained	61.5	27.03	8.9
% Cumulative variance	61.5	88.6	97.5

Table 10. Varimax rotated matrix for soil properties and extracted molybdenum in surface layers of marine alluvium soil series (Kedah area) (Mo).

	Factor 1	Factor 2	Factor 3
NaHCO ₃ -Mo	0.47	-0.21	-0.15
NaOH-Mo	-0.36	-0.24	0.46
HClO ₄ -HNO ₃ -Mo	-0.03	0.54	-0.22
Clay	0.30	0.36	0.40
pH	-0.13	0.46	-0.43
CEC	0.39	-0.33	-0.45
Total C	0.38	0.01	0.28
Al ox	0.33	0.33	0.24
Fe ox	0.30	-0.142	-0.10
Eigenvalue	3.49	3	1.21
% Variance explained	38.8	33.3	13.5
% Cumulative variance	38.8	72.2	85.7

PCA of molybdenum

Table 10 illustrates the factors, eigenvalues, and associated variance explained in the physico-chemical data and communities. According to results, three factors all had eigenvalues higher than one (the most significant one). Also, three extracted factors explain 85.7% of data-set variance. The first principal component explains about 38.8% of the total variance, the second factor explains about 33.3%, and the third factor explains about 13.5%. The first eigenvector has high positive loadings on variable NaHCO₃-Mo, CEC and total carbon, and high negative loadings on variable NaOH-Mo. The second eigenvector has high positive loadings on the variables

HClO₄-HNO₃-Mo and pH and high negative loadings on variables NaOH-Mo and CEC. The third eigenvalue has a high positive loading on the variables NaOH-Mo and clay and high negative loadings on CEC and pH. According to the results, the first component seems to reflect the strong association between CEC and available amount of Mo in surface layers of marine alluvium soils series hence, this finding could confirm the correlation result. Although PCA results showed second and third components were correlated with HClO₄-HNO₃-Mo, pH, NaOH-Mo, clay, and CEC but correlation analysis indicated that there was not significant relationship between other values except CEC and NaHCO₃-Mo.

Discussion

In this study, the paddy soils of peninsular Malaysia were found to contain low levels of Mo (0.41–0.87 mg kg⁻¹) compared with high Mo contents (6–8 mg kg⁻¹) derived from swampy lowland paddy fields of east Malaysia. [28] Concentration of Mo in alluvial soils, spodosols, and inceptisols are quite low, and are generally ranged between 0.2 and 5 mg kg⁻¹ in soils. [29] The current results illustrated that CEC was positively correlated with NaHCO₃-extractable Mo in surface layers of Kedah soil series. Molybdate (MoO₄²⁻) is the oxyanion which is commonly found in solutions under oxidizing conditions. In a laboratory study, Mo was immobilized under reducing conditions and remobilized under oxic conditions, and iron minerals became major sinks for Mo adsorption in reducing conditions. [30] Also, CEC enhancement coincided progressively with decline in E_h in the AP horizon of a waterlogged rice field. [31] Redox potential is high in surface layers of flooded soils and decreases with depth to low negative values. [32] According to our results, Keranji series had the highest CEC and the highest amount of Mo in NaHCO₃ fraction in surface layers of Kedah soil series. It has mentioned that molybdenum deficiency is not a problem in paddy fields on acid sulfate soils. [33]

It can therefore be concluded that when CEC is high in surface layers of waterlogged soils, MoO₄²⁻ availability might be enhanced to the plants. In reducing conditions of flooded soils, molybdate is transformed to MoS₄²⁻ and binds to Al, Fe, and organic matter phases through sulfur bridges [34] and consequently its availability is decreased.

Because of very poor drainage status of Keranji series comparing with other series in Kedah area, increased solubility of Mo from parent material might also be accounted for higher Mo availability in such soils. It was also cited that various pastures of New Zealand, which produced forage high in Mo (>5 ppm), were found on acidic soils (pH 5.3–6.4). This could be due to the poor drainage status of soils that are intermittently wet with low redox potential during the year. [35,36] However, further studies are needed to elucidate the chemistry of Mo in poorly drained soils of paddy, and the factors influencing mobility of Mo in such soils.

The increase of CEC and surface negative charges following submergence could enhance exclusion of anions from pores, and cause reduction of impedance factor. [37] At low pH, hydroxides of iron are precipitated on kaolinite surfaces and occurrence of positive charges on these surfaces bring about a decline in negative charges of complex. [38] In flooded conditions, sulfate reducers are active at pH values above 5, resulting in a reduction of plant available form of sulfur but at a pH less than 4.5, sulfate concentration increases in soil solution. [39] Megonigal et al., [40] illustrated that production of methane was hindered once reduction of sulfate dominated

anaerobic decomposition in brackish marshes, resulting in regulation of carbon reservoir of soil. This means that large contents of sulfur in the form of sulfate in reducing layers can be directly related to carbon contents in lower reduced layer of flooded soils.

Our findings showed that average portion of NaHCO₃-extractable S was higher in surface layers than lower depths of Kelantan soils. It has demonstrated that high concentrations of sulfate in oxic conditions at higher E_h zones of paddy fields can be attributed to activities of sulfur-solubilizing bacteria, while formation of sulfide at lower E_h in paddy subsoils might be due to sulfate-reducing bacteria function. [41] The current results show that as CEC reached the highest value and maximum carbon content was achieved in surface layers of Kelantan (Batu Hiam series), the largest amount of S (352 mg kg⁻¹) was also recorded. It demonstrates that medium-term plant available S contents, which are adsorbed more strongly on iron and aluminum hydrous oxides, were increased as capacity of cation exchange and organic content of flooded soils in surface layers were enhanced. In subsoils of Kelantan, concentrations of NaOH-extractable S were high as carbon content increased. Although amorphous iron contents were not correlated with S concentrations in NaOH fractions in lower layers of Kelantan soil series, but their greater levels might have affected the sorption of S concentrations in NaOH fractions of Cempaka series. Recalcitrant S concentrations in HClO₄-HNO₃ fraction of subsoils were higher than concentrations of recalcitrant S of upper layers of Kelantan soil series. These soils are slightly light textured and vertical or lateral soil solution movements may account for sulfur losses in such soils. Furthermore, reduction of ferric forms of iron to ferrous forms and formation of amorphous iron from ferrous iron in lower depths of flooded soils lead in increases of anion sorption capacity and immobilization of S. If the contents of other competing anions for the sorbing surfaces, such as phosphate, are large in reduction layers of soils, the concentration of sulfate in solution will be increased. [42]

It was shown that organic Al and crystalline Fe contents accounted for the sorption of sulfate in some spodosols, [43] but in ultisols, retention of sulfate was associated to only amorphous iron not amorphous Al. [44] In contrast to ultisols, retention of sulfate was positively correlated with inorganic amorphous Al in podzolic soils. [45] According to current results, the average total amounts of S declined with depth of soil following same pattern as average total carbon in all soil series. Our results are in agreement with those of Möller et al. [46] who presented that status of S in tropical soils depended closely on the turnover rate and content of organic matter. Also, a positive relationship between organic carbon of soils and water soluble sulfate in forested soils was observed by Neary et al. [47].

In contrast to Kedah, Kelantan soils series contained higher available S in NaHCO₃ fraction in surface layers

than lower ones. In Kedah area, Guar and Sedu had the highest amounts of total S at both layers. Our results are also in agreement with Paramanathan and Daud, [48] who indicated that Guar and Sedu were grouped as soils with sulfuric horizons having large levels of elemental S.

Conclusion

The results demonstrate minute concentrations of Mo fractions detected in both studied areas, but S contents were high. Only CEC and total C were significantly correlated with S and Mo contents in comparison with other soil properties. None of soil properties contributed to Mo (extractable in chemical fractions)-except CEC. Total amount of Mo had a moderate correlation with CEC in surface layers of Kedah soil series. There was no correlation between Mo and soil properties of Kelantan soil series. In contrast to Mo, we found strong and positive correlations between some soil properties (CEC and total C) and S in Kelantan soil series. No correlation was achieved between S and soil properties in Kedah area. Although there is not enough data on speciation of Mo in flooded paddy soils, it can be stated that increase of CEC in oxic soil surface layers may enhance solubility of Mo in marine alluvial soil solution. Also, the results reveal that sorption of S could be enhanced by increase in CEC and carbon contents in riverine alluvial soils.

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