

Original Article

Sources and Generation Mechanisms of High SO_4^{2-} Concentrations in Soil water, Groundwater and Streamwater in a Small Watershed, Lambir Hills National Park, Malaysia

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Introduction

Floodplains, lowlands, swamps, and wetlands are increasingly being developed for agriculture, aquaculture, resorts, and urban use across the world. Significant environmental damage due to drainage and changes in land use has been identified in these areas (LJUNG *et al.*, 2009; BUSCHMANN *et al.*, 2008), which are often underlain by sediments containing sulfide minerals. When the reduced and non-oxidized sulfide materials are exposed to the air by excavation, uplift, or drainage, oxidation occurs and sulfuric acid is ultimately produced when the acid neutralizing capacity of the soil by the adsorbed bases and easily weatherable minerals (e.g., CaCO_3) is exceeded (LJUNG *et al.*, 2009; WHITE *et al.*, 1997). Such soils, commonly described as acid sulfate soils, have been reported mainly from coastal mangrove forests (SIMPSON and PEDINI, 1985) and coastal wetlands (DENT and PONS, 1995; LIN *et al.*, 1995; SAMMUT *et al.*, 1995; 1996; WILLETT *et al.*, 1982) underlain by Holocene marine sediments.

In recent years, however, similar acidification of soils and rocks has been identified further inland, along former coastlines and in marine sedimentary rock of Tertiary age (VUAI *et al.*, 2003). It has become apparent that extensive distribution of metal sulfide and sulfate materials in the geological units in a region has the potential to affect the environmental performance and structural integrity of other types of earthworks and construction (FITZPATRICK *et al.*, 1996; SAMMUT, 2004).

In Malaysia and Indonesia, oil palm plantations were not only developed in the flatlands, but also in the sloped areas along former coastlines and in marine sedimentary rocks. Although the acidification of soils due to such disturbances has not yet been reported, such agricultural land development requires the cutting and excavation of soil and rock. The subsequent oxidation of sulfidic materials, the acidification of soils and waters, and the leaching of toxic metals such as Al and Fe may occur, which can affect oil palm growth and damage surrounding aquatic ecosystems.

To predict the magnitude of the impact of such anthropogenic land development, it is vital to

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study natural systems in undisturbed areas. Even in undisturbed tropical lowland rain forests, one of the highest SO_4^{2-} concentrations in streamwater in the tropics has been reported from Lambir Hills National Park (LHNP), Sarawak, Malaysian Borneo ($287.4\mu\text{mol}_c\text{L}^{-1}$; GOMYO *et al.*, 2009). In contrast, some ecological studies have indicated that the toxic effects of Al and Fe leaching may be one of the possible explanations for reduced seedling growth in LHNP (PALMIOTTO *et al.*, 2004). To understand the relationship between high SO_4^{2-} concentration and the leaching of Al and Fe into soil water, groundwater, and streamwater in undisturbed natural lowland rain forests, it is necessary to investigate (1) the temporal and spatial variation of SO_4^{2-} concentration in the watershed, (2) the relationships among SO_4^{2-} , Fe, and Al concentrations and pH, and (3) the origin of SO_4^{2-} , Fe, and Al in soil water, groundwater, and streamwater. Thus, in this paper we describe a case study that used nested experimental watersheds covered by undisturbed tropical lowland rain forests in LHNP to better understand the above-mentioned topics.

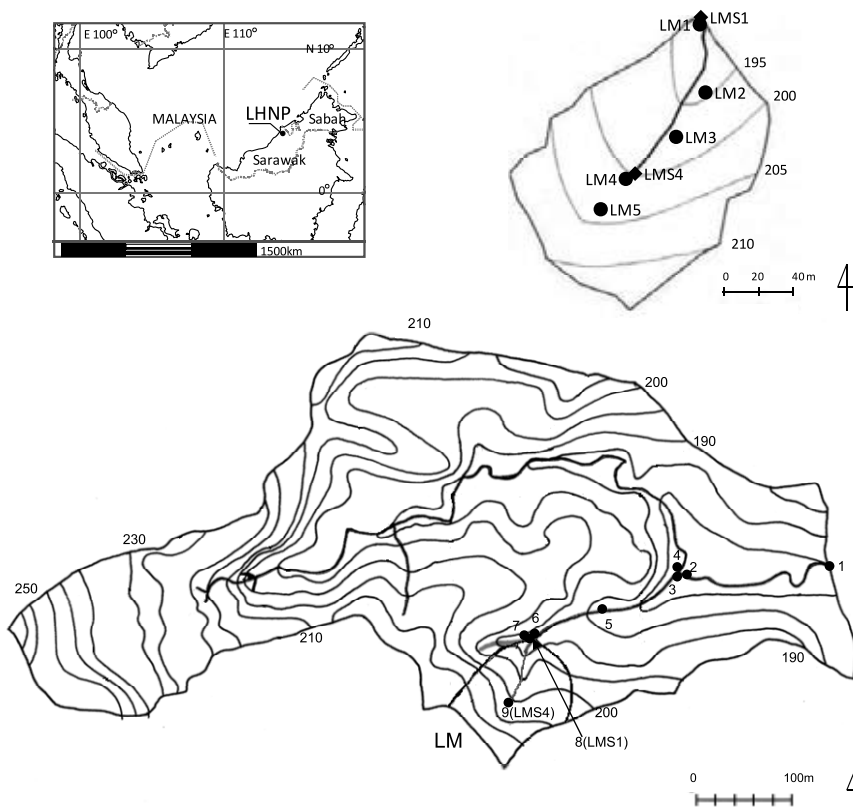


Fig. 1. Maps showing the location and topography of the LC and LM watersheds in Lambir Hills National Park (LHNP), Sarawak, Malaysian Borneo. The locations of the streamwater, soil water, and groundwater sampling sites are shown. The LM watershed was one of the sub watersheds of LC; sampling points No. 8 and No.9 appear on the LC map at the same places as LMS1 and LMS4 on the LM map, respectively.

Materials and methods

Study watershed

Two experimental nested watersheds were set up in LHNP, 25 km southwest of the city of Miri in the state of Sarawak, Malaysian Borneo (Fig. 1): Lambir Crane (LC; elevation 180–212 m above sea level (asl); watershed area 22.0 ha) and Lambir Micro, a sub-watershed of Lambir Crane (LM; elevation 190–212 m asl; watershed area 0.59 ha). Between 2000 and 2007, the annual mean temperature and rainfall in the area were 25.9°C and 2649 mm, respectively. This area has a humid tropical maritime climate and no distinct seasonal change in air temperature. The monthly rainfall during our study period (November 2005–January 2008) is shown in Fig. 2, and was never <90 mm. A higher amount of rainfall was observed in December than in any of the other months.

Geologically, the study area is situated within the approximately 2100 m thick Lambir Formation, a muddy sandstone unit between 13 and 6 million years old (Middle and Late Miocene) (ASHTON, 1998). The sea probably reached its greatest depth near Lambir about 12.8 million years ago, as shown by the concentration of fossils in massive blue clay stones, which are thought to represent a peak in the abundance and biodiversity of the animals living in, on, and above the sea bed (HAZEBROEK and ABANG KASHIM, 2001). The rocks of the Lambir Hills were uplifted and gently folded from the seabed at the beginning of the Pleistocene (WILFORD, 1961). From previous studies of soil chemical properties in LHNP, the soils of the study area can be roughly divided into two groups: the Sandy Humult Ultisols (hereafter referred to as SHU), and the Clay Udult Ultisols (hereafter referred to as CUU) (ASHTON, 1998; PALMIOTTO *et al.*, 2004).

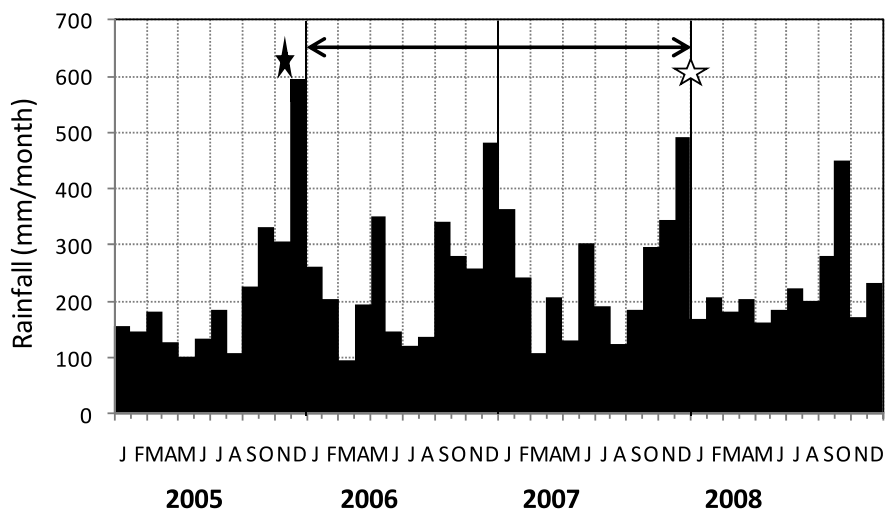


Fig. 2. Monthly rainfall in Lambir Hills National Park (LHNP) during the study period. The two-headed arrow, the black star, and the white star indicate the long-term sampling period, the spatial sampling of sub-watersheds in LC on 22 November 2005, and the intensive soil water and streamwater sampling at LM, respectively.

The SHU are present on sandstone ridges and dip slopes, and are characteristically deep, yellow, nutrient poor, leached, and drought-prone, with a thick (5–15 cm) surface horizon of densely rooted raw humus. In contrast, the CUU are present in gullies and lower areas overlying shale, and are characteristically deep and yellowed, with higher nutrient concentrations and a greater water-holding capacity than the SHU, and a thin (<1 cm) surface organic layer of leaves lacking a root mat. The study area is located in a tropical lowland mixed Dipterocarp forest (YAMAKURA *et al.*, 1995; ASHTON, 1998; POTTS *et al.*, 2002), within which the spatial distribution of tree species is related to soil variation. *Dryobalanops aromatica* and *Shorea lava* naturally aggregate on the SHU, and *Dryobalanops lanceolata* and *Hopea dryobalanoides* on the CUU (PALMIOTTO *et al.*, 2004).

Sampling design and chemical analyses

Water

We sampled streamwater at the LC watershed outlet weekly for two years (2006–2007), and collected a total of 123 samples. On 22 November 2005, we also sampled streamwater at the nine different sub-watersheds within LC, including the outlet of LC (No. 1), the outlet of LM (No. 8, also LMS1), and the stream source in LM (No. 9, also LMS4). These sampling points were numbered and are shown in Fig. 1.

In LM we sampled soil water at five different sites along the main stream (Fig. 1). LM1 represents the lowest point near the watershed outlet (LMS1), and LM4 represents the point just above the spring (LMS4). At all sites, we sampled the soil water using a suction soil water sampler (DIK-8392; Daiki Rika Kogyo Co., Ltd., Japan), which consisted of a ceramic porous cup (18 × 95 mm), a lead pipe, and a syringe buried in the soil to extract the soil water from three different depths (10–20, 50–60, and 90–100 cm), except at LM2 (10–20 and 50–60 cm only). A groundwater well made of a PVC pipe (10 cm diameter) was installed at LM4 for groundwater sampling. The average groundwater depth for two years (January 2007–December 2008) was 170 cm (WAKAHARA, unpublished data). Streamwater was sampled at LMS1 and LMS4. Soil water, groundwater and streamwater were sampled in LM was performed on 6 days: 30 and 31 December 2007 and 3, 4, 11, and 13 January 2008. During this period, the mean volumetric ratio of soil water contents at depths of 10, 30, and 60 cm at LM4, observed continuously by thermo-time domain reflectometry sensors (CS616; Campbell Scientific, Inc., USA), was 0.35, 0.32, and 0.34, respectively, slightly higher than the two-year averages from January 2007 to December 2008 (0.33, 0.31, and 0.33, respectively) (WAKAHARA, unpublished data). pH was measured on site using the glass electrode of a pH meter (D-54; Horiba Co., Kyoto, Japan). The calibration of the pH meter was confirmed with standard solutions of pH 4 and 7.

Bottles containing the samples were brought to the field laboratory within 30 min of sampling and were immediately stored at 2°C. All samples were filtered through a 0.2 µm hydrophilic regenerated cellulose filter (Minisart RC15; Sartorius Stedim Japan Co., Ltd., Japan), kept in a cold box with refrigerant, and transported to Japan for chemical analysis. The cation (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) and anion (Cl^- , NO_3^- , and SO_4^{2-}) concentrations were analyzed using an ion

chromatograph analyzer (HIC-6A; Shimadzu Co., Kyoto, Japan). The total dissolved Fe and Al concentrations were analyzed with inductively coupled plasma emission spectrometry (SPS 1500VR; Seiko Instruments, Inc., Japan) for soil water, groundwater, and streamwater from the LM watershed. In this report, we define the total anion concentration (TA) as $([\text{Cl}^-] + [\text{NO}_3^-] + 2[\text{SO}_4^{2-}] + [\text{OH}^-])$ and the total cation concentration (TC) as $([\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{H}^+])$, where $[\text{X}]$ represents the concentration of X measured in $\mu\text{mol}_c\text{L}^{-1}$.

Soil

Soils were sampled on 18 June 2009 at LM1, LM4, and LM5 (Fig. 1). The depths of sampling were 10–20 and 30–40 cm at LM1; 10–20, 30–40, 50–60, and 90–100 cm at LM4; and 10–20, 30–40, and 50–60 cm at LM5. All soil samples were filtered without drying through a 2-mm mesh sieve, immediately followed by pH (H_2O) measurements in the field laboratory. The pH was measured with a glass electrode pH meter (D-54; Horiba Co.) using a fresh soil-to-solution (H_2O) ratio of 1:5.

Discharge

Discharge data were collected from an adjacent watershed (23.3 ha). Water height was measured every 10 minutes by an automatic water level data recorder (KADEC21-MIZU, Northone Co. Ltd. Japan) in a natural pool on exposed bedrock where a rapid flow was generated at the outlet. SHIRAKI and WAKAHARA (2005) describe how to convert from water level to the discharge. Hourly discharge data for 2 years (2006–2007) were used in this study to determine the relationship between discharge and SO_4^{2-} concentration.

Results

Long-term spatial variation in streamwater chemistry in LC and its sub-watersheds

Fig. 3(a) shows the relationship between SO_4^{2-} concentration and hourly discharge and Fig. 3(b) shows the relationship between SO_4^{2-} concentration and watershed area. The mean concentration of SO_4^{2-} was $135.2 \pm 55.3 \mu\text{mol}_c\text{L}^{-1}$ (\pm standard deviation). The relationship between the concentrations of SO_4^{2-} and the areas of the sub-watersheds in LC observed on a single day are shown in Fig. 3(b). The range of SO_4^{2-} concentrations among the sub-watersheds in LC was within the range from 65 to $341 \mu\text{mol}_c\text{L}^{-1}$ (Fig. 3(a)), which is comparable to the range of long-term variation in SO_4^{2-} concentrations in LC (from 30 to $272 \mu\text{mol}_c\text{L}^{-1}$; Fig. 3(b)).

Fig. 4 shows the SO_4^{2-} concentrations in soil water, groundwater, and streamwater at the five sites and at various depths in LM. The SO_4^{2-} concentration in soil water was lowest at LM2 ($0.5 \mu\text{mol}_c\text{L}^{-1}$), followed by LM1. The concentration increased from LM3 to the upstream sites. The highest value of $420.5 \mu\text{mol}_c\text{L}^{-1}$ was observed at LM5. At LM4, the concentration of SO_4^{2-} did not differ significantly between groundwater and soil water (Fig. 4). The concentration of SO_4^{2-} in streamwater at LMS1 was significantly higher than those in soil water at LM1, LM2, and LM3, but was significantly lower than that in soil water at LM5 (Fig. 4). The concentration of SO_4^{2-} in streamwater at LMS4 was significantly higher than that in soil water from a depth of

10–20 cm at LM4, but was significantly lower than that in soil water from depths of 50–60 and 90–100 cm at LM5 (Fig. 4).

Fig. 5 shows the relationship between SO_4^{2-} and Mg^{2+} concentrations, and Fig. 6 shows the relationship between SO_4^{2-} and Ca^{2+} concentrations. The SO_4^{2-} concentration in soil water increased with Mg^{2+} concentration. A similar relationship was observed in groundwater and streamwater. However, if the SO_4^{2-} concentration in soil water is the same as that in groundwater and streamwater, the Mg^{2+} concentration in soil water is always 40–60 $\mu\text{mol}_e\text{L}^{-1}$ higher than that in groundwater and streamwater. The Ca^{2+} concentration was higher in the lower part of the LM watershed (LM1 through LM3) than in the upper part (LM4 through LM5) (Fig. 6).

Fig. 7 shows the relationship between SO_4^{2-} and the anion charge deficit (TC–TA), and Fig. 8 shows the relationship between SO_4^{2-} and the pH. The anion charge deficit was positive in the lower part of the LM watershed, but zero or negative in the upper part of the LM watershed except at a depth of 10–20 cm at LM4. The pH was higher in the upper part of LM than that in the lower part of the LM watershed. The streamwater in LC and its sub-watersheds including LM

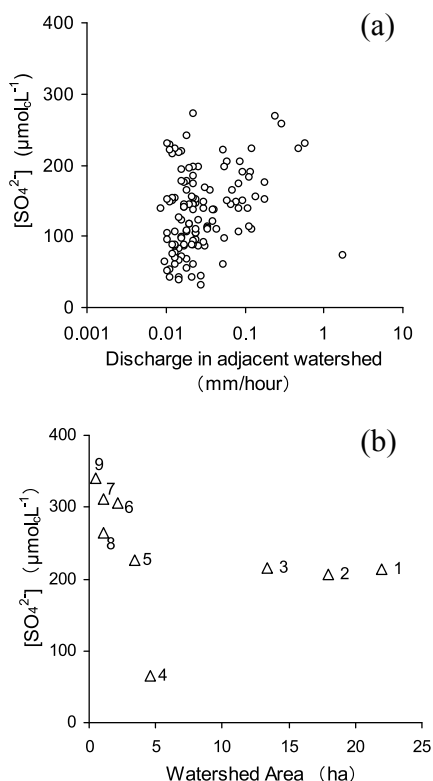


Fig. 3. The relationship between SO_4^{2-} concentrations and (a) discharge in the adjacent watershed used for long-term sampling at the outlet of LC and (b) the watershed areas used for spatial sampling of the sub-watersheds in LC observed on 22 November 2005. The numbers on (b) indicate spatial sampling points on the LC map (Fig. 1). The [X] indicates the concentration of X ($\mu\text{mol}_e\text{L}^{-1}$).

(LMS1 and LMS4) was of the same quality for Ca^{2+} , TC-TA and pH as the soil water in the upper part of LM, except at the sampling point No. 4, located at the outlet of a northern sub-watershed of the LC watershed (Fig. 1). The streamwater from the LM watershed does not reach the sampling point No.4.

Figs. 9 and 10 show the relationship between the concentration of SO_4^{2-} and the concentrations of total dissolved Fe and Al, respectively. Although the concentration of total dissolved Fe was less than $15 \mu\text{mol}_c\text{L}^{-1}$ in most cases, exceptionally high concentrations (34.5 and $53.8 \mu\text{mol}_c\text{L}^{-1}$) were measured at LM5 at depths of 50–60 and 90–100 cm, respectively. The higher the SO_4^{2-} concentration, the higher the total dissolved Al concentration. A similarly high total dissolved Al concentration ($15\text{--}25 \mu\text{mol}_c\text{L}^{-1}$) was also observed in the streamwater at LMS1 and LMS4.

Table 1 lists the pH of soil water in LM and the soil pH (H_2O) at LM1, LM4, and LM5. The soil pH (H_2O) values (4.34–5.64) were similar to the soil water pH values at the equivalent sites and depths, as well as with the soil pH (H_2O) reported by HIRAI *et al.* (1997) from a 52 ha permanent vegetation plot in LHNP (4.18–5.49).

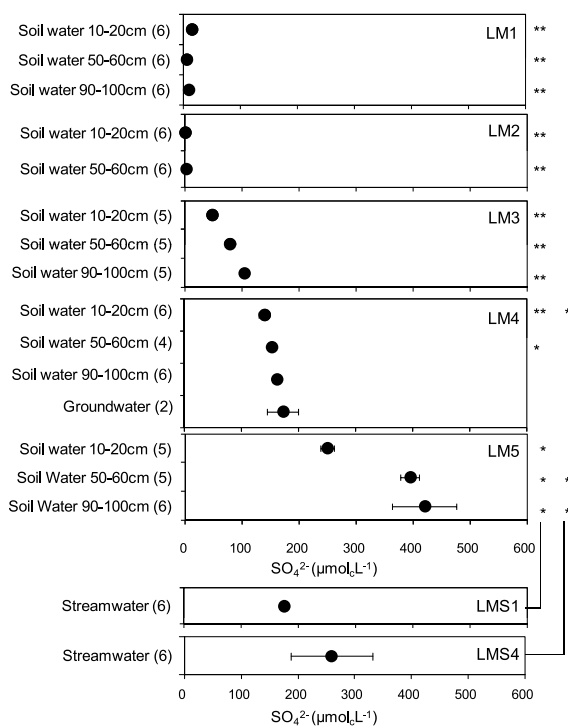


Fig. 4. Mean SO_4^{2-} concentrations in soil water, groundwater, and streamwater in the LM watershed. The numbers in parentheses indicate the number of samples, and the bars are the standard deviations. * and ** (on the right side of the figure) indicate significant differences between LMS1 streamwater and LMS4 streamwater; between all soil water and groundwater; and between LMS4 streamwater and LM4 and LM5 soil water and groundwater (*t*-test; **, $p < 0.001$; *, $p < 0.01$).

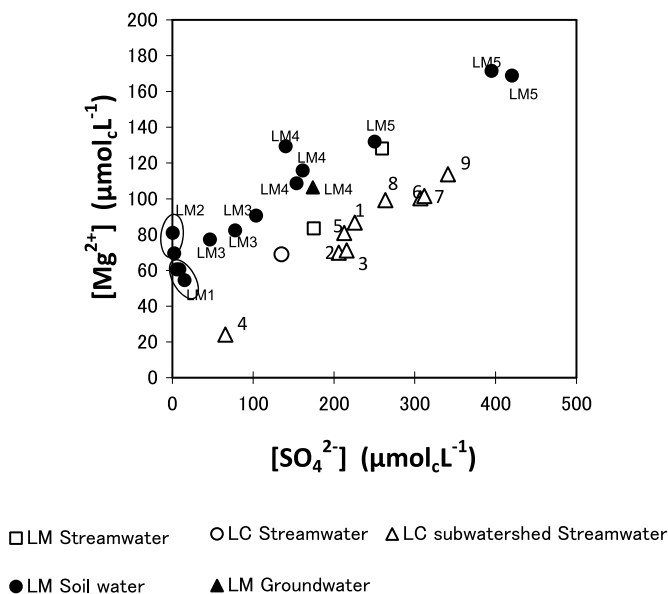


Fig. 5. The relationship between $[\text{SO}_4^{2-}]$ and $[\text{Mg}^{2+}]$ for long-term LC streamwater observations (means), LC sub-watershed streamwater observation, and LM soil water, groundwater, and streamwater. The numbers on \triangle indicate spatial sampling points on the LC map (Fig. 1) observed on 22 November 2005. The $[X]$ indicates the concentration of X ($\mu\text{mol}_c\text{L}^{-1}$).

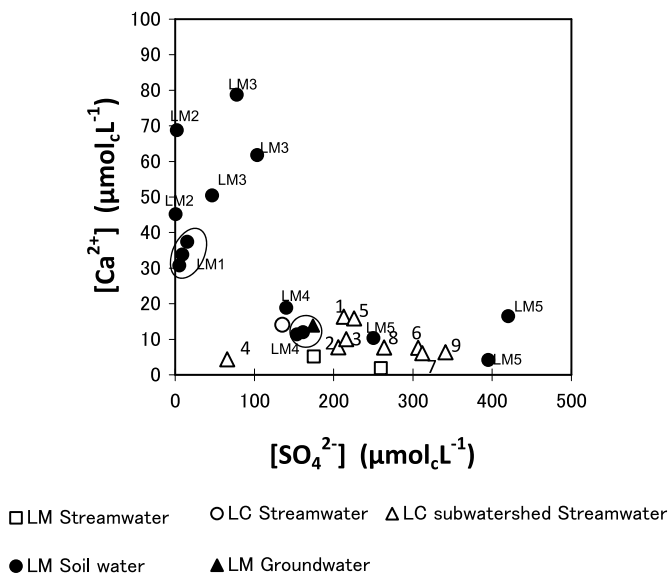


Fig. 6. The relationship between $[\text{SO}_4^{2-}]$ and $[\text{Ca}^{2+}]$ for long-term LC streamwater observations (means), LC sub-watershed streamwater observations, and LM soil water, groundwater, and streamwater. The numbers on \triangle indicate spatial sampling points on the LC map (Fig. 1) observed on 22 November 2005. The $[X]$ indicates the concentration of X ($\mu\text{mol}_c\text{L}^{-1}$).

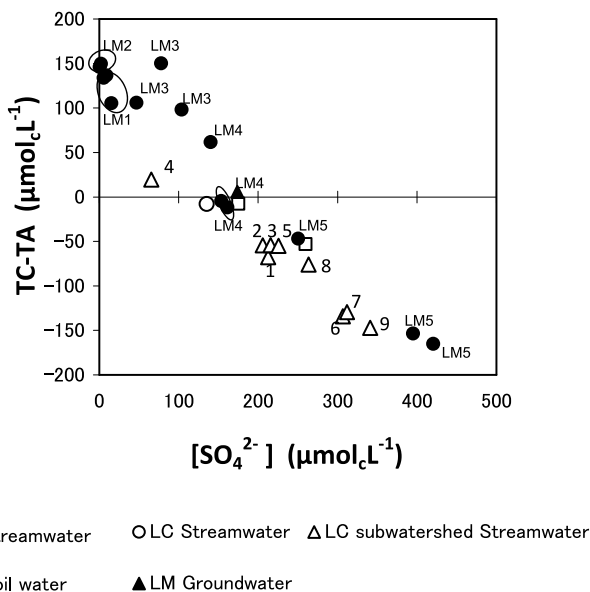


Fig. 7. The relationship between $[\text{SO}_4^{2-}]$ and $[\text{TC} - \text{TA}]$ for long-term LC streamwater observations (means), LC sub-watershed streamwater observations, and LM soil water, groundwater, and streamwater. The numbers on \triangle indicate spatial sampling points on the LC map (Fig. 1) observed on 22 November 2005. The $[\text{X}]$ indicates the concentration of X ($\mu\text{mol}_c\text{L}^{-1}$).

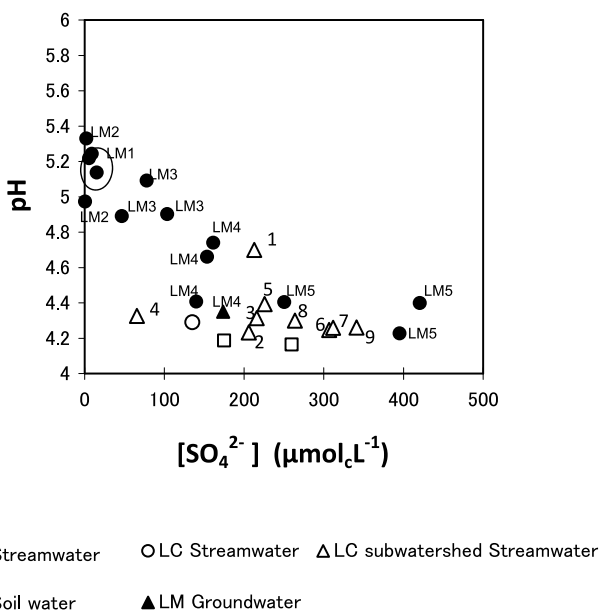
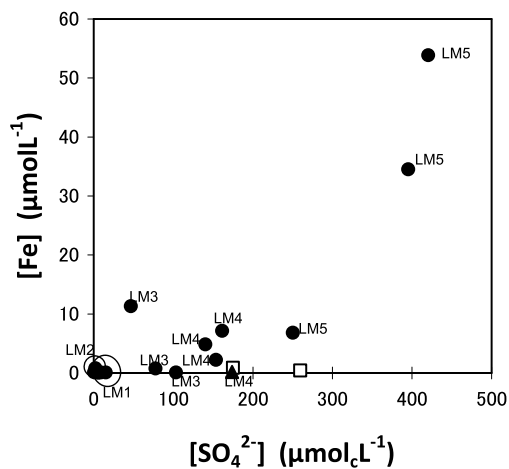
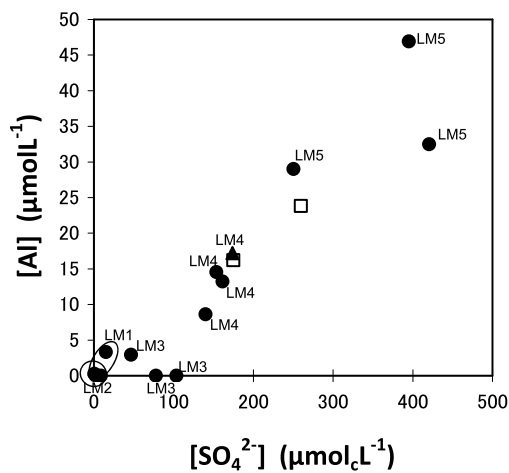


Fig. 8. The relationship between $[\text{SO}_4^{2-}]$ and pH for long-term LC streamwater observations (means), LC sub-watershed streamwater observations, and LM soil water, groundwater, and streamwater. The numbers on \triangle indicate spatial sampling points on the LC map (Fig. 1) observed on 22 November 2005. The $[\text{X}]$ indicates the concentration of X ($\mu\text{mol}_c\text{L}^{-1}$).



□ LM Streamwater ● LM Soil water ▲ LM Groundwater

Fig. 9. The relationship between [SO₄²⁻] and [Fe] is only shown for LM soil water, groundwater, and streamwater. The [X] indicates the concentration of X (μmol_cL⁻¹).



□ LM Streamwater ● LM Soil water ▲ LM Groundwater

Fig. 10. The relationship between [SO₄²⁻] and [Al] is only shown for LM soil water, groundwater, and streamwater. The [X] indicates the concentration of X (μmol_cL⁻¹).

Table 1. The pH of soil water and soil samples.

	Soil water pH	Soil pH (H_2O)
LM1 10-20cm	5.19	5.64
LM1 30-40cm		5.52
LM1 50-60cm	5.27	
LM1 90-100cm	5.27	
LM4 10-20cm	4.50	4.61
LM4 30-40cm		4.81
LM4 50-60cm	4.68	4.62
LM4 90-100cm	4.75	4.57
LM5 10-20cm	4.41	4.42
LM5 30-40cm		4.41
LM5 50-60cm	4.24	4.34
LM5 90-100cm	4.44	

Discussion

SO_4^{2-} concentration in streamwater

The SO_4^{2-} concentration in streamwater (arithmetic mean) in LC, LMS1, and LMS4 ranged from 135.2 to 259.7 $\mu\text{mol}_c\text{L}^{-1}$. This level is 9.4–18.0 times higher than that of rain water, which contains concentrations of SO_4^{2-} (volume weighted mean 14.4 $\mu\text{mol}_c\text{L}^{-1}$; GOMYO, 2010). Thus, the high SO_4^{2-} concentration in streamwater cannot be explained by condensation via evapotranspiration alone; rather, the SO_4^{2-} in streamwater probably originates from a terrestrial source within a watershed. The oxidation of sulfide may be one of the principal reactions producing SO_4^{2-} (e.g., STRAUSS, 1997; KOHFAHL *et al.*, 2008; FITZHUGH *et al.*, 2001).

In the Mendolong 1 experimental watershed (18.2 ha, hereafter referred to as M1) in Sabah, Malaysia, GRIP *et al.* (1994) reported a high concentration of SO_4^{2-} in streamwater (volume weighted mean 142.8 $\mu\text{mol}_c\text{L}^{-1}$), which was comparable to that in LC. The SO_4^{2-} concentration in rain water at M1 (1.17 $\mu\text{mol}_c\text{L}^{-1}$) was 122 times lower than that in streamwater (GRIP *et al.*, 1994) which is too low to explain the high concentration in streamwater. In contrast, the SO_4^{2-} concentration in an adjacent experimental watershed (volume weighted mean 11.8 $\mu\text{mol}_c\text{L}^{-1}$) named Mendolong 2 (4.5 ha, hereafter referred to as M2) was 12 times lower than that at M1. GRIP *et al.* (1994) showed that the SO_4^{2-} concentration difference between M1 and M2 may have been the result of a high S concentration in the soil and bedrock at M1; weathering would thus produce a higher SO_4^{2-} concentration at M1 than at M2.

Soil and streamwater chemistry comparisons

Table 2 shows selected streamwater chemistry values for M1 and M2 from GRIP *et al.* (1994) and for LC, LMS1, and LMS4 from this study. The SO_4^{2-} concentrations in LC, LMS1, and LMS4 were comparable with that in M1 (142.8 $\mu\text{mol}_c\text{L}^{-1}$), but higher than that in M2 (11.8 $\mu\text{mol}_c\text{L}^{-1}$). The pH in LC, LMS1, and LMS4 ranged from 4.2 to 4.3, which was comparable with that in M2 (4.9), but lower than that in M1 (6.3). These results show that the streamwater

Table 2. The pH, SO_4^{2-} , Total cation minus total anion, Ca^{2+} concentration, $\text{Ca}^{2+} : \text{SO}_4^{2-}$ ratios, total Fe and Al concentrations of streamwater at LC, LMS1, LMS4, M1 and M2.

	pH			SO_4^{2-} ($\mu\text{mol}_c\text{L}^{-1}$)			TC-TA ($\mu\text{mol}_c\text{L}^{-1}$)			Ca^{2+} ($\mu\text{mol}_c\text{L}^{-1}$)			$\text{Ca}^{2+}/\text{SO}_4^{2-}$		
	n	SD		n	SD		n	SD		n	SD		n	SD	
LC	4.3	123	0.8	135.2	123	55.5	-7.9	123	62.4	14.1	123	10.2	0.10	123	0.2
LMS1	4.2	6	0.6	175.0	6	9.0	-7.7	6	37.6	5.1	6	2.8	0.03	6	0.0
LMS4	4.2	5	0.4	259.7	6	71.4	-53.1	6	67.0	1.9	6	2.2	0.01	6	0.0
M1	6.3	NA	NA	142.8	NA	NA	202.7	NA	NA	84.8	NA	NA	0.59	NA	NA
M2	4.9	NA	NA	11.8	NA	NA	58.1	NA	NA	11.0	NA	NA	0.93	NA	NA

	Fe ($\mu\text{mol}_c\text{L}^{-1}$)			Al ($\mu\text{mol}_c\text{L}^{-1}$)		
	n	SD		n	SD	
LC	NA	NA	NA	NA	NA	NA
LMS1	0.9	2	0.0	16.2	2	4.2
LMS4	0.4	2	0.0	23.8	2	6.5
M1	2.0	NA	NA	1.5	NA	NA
M2	7.2	NA	NA	10.4	NA	NA

Note: TC = Total cation ($[\text{H}^+] + [\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}]$), TA = Total anion ($[\text{Cl}^-] + [\text{NO}_3^-] + 2[\text{SO}_4^{2-}] + [\text{OH}^-]$), where [X] shows the concentration of X ($\mu\text{mol}_c\text{L}^{-1}$), M1 and M2 stands for Mendolong W3 and W6, respectively (GRIP *et al.* 1994). n = The number of samples, NA = Not available, SD = standard deviation.

chemistry in LC, LMS1, and LMS4 is similar to that in M1 but different from that in M2 in terms of SO_4^{2-} concentration, whereas in terms of pH it is similar to M2 but different from M1. To explain the similarities and differences between Lambir and Mendolong, we compared the anion charge deficits (TC-TA), Ca^{2+} , and the total dissolved Al and Fe concentrations in the two watersheds.

Table 2 shows that the anion charge deficit of streamwater in LC, LMS1, and LMS4 was negative, but was positive in M1 and M2. This anion charge deficit difference was mainly due to the lower Ca^{2+} concentration in Lambir than in Mendolong. The $\text{Ca}^{2+} / \text{SO}_4^{2-}$ was higher in M1 and M2 (0.594 and 0.929, respectively) than that in LC, LMS1, and LMS4 where it ranged from 0.007 to 0.104. GRIP *et al.* (1994) showed that the large anion charge deficit (about 40% of the total cation charge in M1 and 70% in M2) may partly be due to organic acids, and partly to hydrogen carbonate not accounted for in HCO_3^- (as calculated from the temperature and pH of streamwater in equilibrium with atmospheric CO_2). In LMS1, and LMS4, however, the cation charge deficit may partly be due to other metal cations such as Al and Fe, which may leach under low pH conditions. The low Ca^{2+} concentrations in streamwater in LC, LMS1, and LMS4 may be the result of all the calcium in the soil and bedrock having been leached by sulfuric acid.

The total dissolved Al concentration was lower in the higher pH watershed (M1) than in the lower pH watersheds (M2, LMS1, and LMS4). However the leaching mechanisms in M2 and Lambir may be very different. In M2, the total dissolved Al was leached while neutralizing the HCO_3^- and organic acid, whereas in LMS1 and LMS4, the total dissolved Al was leached while neutralizing SO_4^{2-} that exceeded the total cation charge from the concentrations of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ . The total dissolved Fe concentration pattern was different from that for Al; it was higher in M2 ($7.2 \mu\text{mol}_c\text{L}^{-1}$) but lower in LMS1 and LMS4 ($0.4\text{--}0.9 \mu\text{mol}_c\text{L}^{-1}$). This difference

suggests that the leaching mechanism of Al and Fe in LMS1 and LMS4 differs from that in M2. We assume that in LMS4 and LMS1, the Fe in the soil water is precipitated rapidly by bacterially-induced (SMITH and TUOVINEN, 1985), redox-controlled reactions when Fe appears to the stream. In M2, however, no such reactions were occurred, and there were no SO_4^{2-} sources in the soil.

The origins of SO_4^{2-} in soil water and streamwater

One of the main novel findings of this study was the large variation in inorganic chemical properties of soil water even within a small watershed (Figs. 4 and 5). The large difference between the SO_4^{2-} concentrations in the upper and lower parts of the watershed (Fig. 4) suggests different sources and generation mechanisms as follows.

The upper part of the LM watershed, including LM4 and LM5, was dominated by *Dryobalanops aromatica* and the soil can be categorized as SHU, whereas the soil of the lower part of the LM watershed including LM1 can be categorized as CUU. The soil water SO_4^{2-} concentration in LM5 was two orders of magnitude higher than that in LM1 (Fig. 4). This result was also supported by HIRAI *et al.* (1997), who examined the relationship between the distribution of tree species and the soils in LHNP and found that *D. aromatica* develops on SHU soil with dominantly drier soil moisture conditions, a low nutrient status (lower exchangeable Ca and Mg), and high acidity. If the origin of high SO_4^{2-} levels was primarily the acidification of organic sulfur, the SO_4^{2-} concentration should be higher in the CUU soil in the lower part of the watershed because of the higher nutrient condition, rather than in the SHU soil in the upper part of the watershed.

PALMIOTTO *et al.* (2004) reported that a 5–15 cm surface horizon of densely rooted raw humus was common in SHU. The SO_4^{2-} concentrations of soil water at LM3, LM4 and LM5 were higher deeper soil depth than shallower in the lower soil depth. The highest concentrations of SO_4^{2-} were detected at 90–100 cm depths in LM5 soil, which is far deeper than the densely rooted raw humus layer common in SHU. These results suggest that the major origin of SO_4^{2-} in LM soil water is not be the organic sulfur in the raw humus, but is that from the acidification of inorganic sulfur, such as FeS_2 .

There was a linearly increasing correlation between SO_4^{2-} and Mg^{2+} concentrations in soil water (Fig. 5) in both the lower and the upper watersheds. The relationship between SO_4^{2-} and Ca^{2+} concentrations in soil water (Fig. 6), however, exhibited a different pattern. In the lower part of the watershed, the Ca^{2+} concentration in soil water exceeded $30 \mu\text{mol}_c\text{L}^{-1}$ and increased with increasing SO_4^{2-} concentration, whereas in the upper part of the watershed, the Ca^{2+} concentration in soil water was less than $20 \mu\text{mol}_c\text{L}^{-1}$ and remained relatively stable regardless of changes in the SO_4^{2-} concentration.

The soil water in the lower part of the watershed was characterized by a higher Ca^{2+} concentration (Fig. 6), lower SO_4^{2-} concentration, with total cations exceeding total anions (Fig. 7), a higher pH (Fig. 8), and lower total dissolved Fe and Al concentrations (Figs. 9 and 10). The soil water in the upper part of the watershed was characterized by a lower Ca^{2+} concentration

(Fig. 6), higher SO_4^{2-} concentration, with total anions exceeding total cations (Fig. 7), a lower pH (Fig. 8), and higher total dissolved Fe and Al concentrations (Figs. 9 and 10). A possible explanation for this clear difference between the lower and the upper watershed may be the role of SO_4^{2-} in chemical weathering. At CUU sites, the pH was >4.8 , the SO_4^{2-} production rate was lower than at SHU sites, and the acid buffering capacity of Ca^{2+} exceeded the SO_4^{2-} concentration. At SHU sites, the pH was <4.4 , and a higher production of SO_4^{2-} than at CUU sites exceeded the Ca^{2+} resources, resulting in complete leaching of Ca^{2+} , triggering the leaching of Al and Fe.

If the total dissolved Al exists in the form of Al^{3+} and contributes to the ion balance, the cation charge deficit (TA–TC) of all soil water will be positive, except at 50–60 and 90–100 cm depths of LM5 soil water. The cation charge deficit including Al^{3+} at 50–60 and 90–100 cm depths of LM5 soil water was -12.8 and $-67.6 \mu\text{mol}_c\text{L}^{-1}$, respectively. This means that there are other uncounted cations that can compensate for the negative cation charge deficit at 50–60 and 90–100 cm depths of LM5 soil water. One possibility is the contribution of dissolved Fe to the ion balance. If the total dissolved Fe exists in the form of Fe^{3+} , the Fe^{3+} concentrations at 50–60 cm and 90–100 cm depths of LM5 soil water were 103.5 and 161.5 $\mu\text{mol}_c\text{L}^{-1}$ respectively. These concentrations partly explain the cation charge deficits including Al^{3+} at 50–60 and 90–100 cm depths of LM5 soil water, respectively. This supports the hypothesis that the acidification of FeS_2 may be one of the origins of the high SO_4^{2-} concentrations and the total dissolved Fe concentrations of LM5 soil water at the 50–60 and 90–100 cm depths.

Conclusions

This study found that (1) the spatial variation of streamwater SO_4^{2-} concentrations was greater than the temporal variation, (2) the soil water SO_4^{2-} concentration in the SHU soils distributed on ridges and in headwater areas in the LM watershed was two orders of magnitude greater than that in the CUU soils distributed on the lower slopes of the LM watershed. Al leaching was initiated when the soil water pH dropped below 4.8 and the Ca^{2+} concentration fell below about 20 $\mu\text{mol}_c\text{L}^{-1}$. Fe leaching began when the SO_4^{2-} concentration reached about 400 $\mu\text{mol}_c\text{L}^{-1}$.

These findings suggest that the source of SO_4^{2-} may be FeS_2 that is unevenly distributed in the watershed and that different mechanisms may control the leaching of dissolved Al and Fe into the soil water.

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Summary

To understand the origin of the high SO_4^{2-} concentrations in soil water, groundwater, and streamwater in undisturbed natural lowland rain forests and the link between such high SO_4^{2-} concentrations and Al and Fe leaching, we undertook a case study in nested experimental watersheds covered by undisturbed tropical lowland rain forests in Lambir Hills National Park, Sarawak, Malaysia. Streamwater at the outlet of a 22 ha watershed was sampled weekly for 2 years and an intensive study of soil water, groundwater, and streamwater was conducted within a 0.59 ha sub-catchment. It was found that that (1) the spatial variation of SO_4^{2-} concentration in streamwater was larger than the temporal variation, (2) the soil water SO_4^{2-} concentrations in the Sandy Humult Ultisols distributed on the ridges and in the headwater areas in the sub-watershed were two orders of magnitude greater than in the Clay Udult Ultisols distributed on the lower slopes of the sub-watershed. Al leaching began when soil water pH dropped below 4.8 and Ca^{2+} concentration levels fell below approximately $20 \mu\text{mol}_c\text{L}^{-1}$. Fe leaching started when the SO_4^{2-} concentration reached about $400 \mu\text{mol}_c\text{L}^{-1}$. These findings suggest that the SO_4^{2-} may be derived from FeS_2 , which is unevenly distributed in the watershed, and that different mechanisms may control the leaching of dissolved Al and Fe into the soil water.

Keywords: Lambir Hills National Park, SO_4^{2-} concentration, Fe and Al, Soil water, Streamwater

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マレーシア・ランビル国立公園小流域における土壤水、地下水、渓流水の高濃度硫酸の起源と生成機構

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要 旨

低地熱帯雨林における土壤水、地下水、渓流水の SO_4^{2-} 濃度の起源とメカニズム、および、高 SO_4^{2-} 濃度と Al, Fe 溶出との関係を明らかにするために、マレーシアランビルヒルズ国立公園内の低地熱帯雨林に覆われた小流域を対象に、ケーススタディを実施した。22ha の流域末端部で週 1 回、渓流水の採水を 2 年間継続し、0.59ha の支流で土壤水、地下水、渓流水の集中観測を実施した。(1) 渓流水 SO_4^{2-} 濃度の空間分布の範囲は、時系列分布の範囲よりも大きいこと、(2) 支流の尾根および上流域に分布する砂質土壌の土壤水 SO_4^{2-} 濃度は、下流域の斜面下部に分布する粘土質土壌の土壤水 SO_4^{2-} 濃度より 2 オーダー大きいことが明らかになった。土壤水の pH が 4.8 以下、 Ca^{2+} 濃度が約 $20\mu\text{mol}_c\text{L}^{-1}$ 以下になると Al の溶出が始まり、さらに、 SO_4^{2-} 濃度が約 $400\mu\text{mol}_c\text{L}^{-1}$ に達すると Fe の溶出が始まった。これらの結果は、 SO_4^{2-} 濃度の起源は、流域内に不均一に分布する FeS_2 である可能性を、また、Al の土壤水への溶出は、Fe の溶出とは異なるメカニズムで起きていると推察された。

キーワード：ランビル国立公園・硫酸イオン濃度・鉄とアルミニウム・土壤水・渓流水