Nutrient and trace element concentrations influence greenhouse gas emissions from Malaysian tropical peatlands

Received: 20 July 2020 | Revised: 6 October 2020 | Accepted: 10 October 2020

DOI: 10.1111/sum.12669

RESEARCH PAPER

Soil Use and Management BRITISH SOCIETY OF SOIL SCIENCE WILEY

Nutrient and trace element concentrations influence greenhouse gas emissions from Malaysian tropical peatlands

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Funding information
This work was supported by Crops For the Future (CFF), Malaysia [Biop1-011] and The School of Biosciences, University of Nottingham, UK. We are thankful to people of Kampung Raja Musa, Selangor State Forestry Department and Global Environment Centre for access to field sites. We are thankful to Dr Saul Vazquez Reina and Prof. Scott Young, University of Nottingham for help with laboratory analyses.

Abstract

Tropical peatlands are unique and globally important ecosystems for carbon storage that are generally considered nutrient poor. However, different nutrient and trace element concentrations in these complex ecosystems and their interactions with carbon emissions are largely unknown. The objective of this research was to explore the concentrations of macro- and micronutrients and othertrace elements in surface peats, and their relationship with greenhouse gas emissions in North Selangor peatlands subjected to different land use. All nutrient and trace element concentrations except chromium exhibited significant differences between sites. Most macronutrients and some micronutrients showed significant differences between seasons, typically with a reduction over time from wet to dry seasons, possibly due to leaching. CO_2 emissions were positively related to organic matter content and manganese concentrations and negatively correlated with selenium. CH_4 emissions were positively correlated with organic matter content, manganese, copper, barium, cobalt and aluminium, and negatively correlated with molybdenum, selenium, lithium and vanadium. This research has detected loss of essential nutrients over time, aiding to increase nutrient limitation in tropical peatlands due to drainage. The observed significant correlation between trace elements and greenhouse gas emissions strengthens the importance of including trace element analyses in understanding the biogeochemical functions of these understudied peatlands.

KEYWORDS

carbon dioxide, trace elements, methane, oil palm, soil nutrients, tropical peatlands

1 | INTRODUCTION

Tropical peatlands are unique ecosystems that provide numerous ecosystem services such as carbon and water storage, flood prevention, biodiversity conservation and other socio-cultural services (Dohong et al., 2017; Yule, 2010). These carbon-rich ecosystems are formed due to delicate yet complex interactions between several environmental factors such as topography, climatic conditions, hydrology, biogeochemistry and microbial ecology (Andersen et al., 2013; Page et al., 1999). However, the most important factor of all these is a consistently high water table that creates anoxic conditions, which prevents microbial decomposition even under tropical temperatures which are conducive to microbial activity

(Andersen et al., 2013; Wösten et al., 2008). Due to this, tropical peatlands in their natural state have acted as carbon sinks for millennia and played important role in the climatic balance of the Earth (Page et al., 2011). Nevertheless, anthropogenic disturbance in recent decades that lower the water table of these peatlands, turn them from carbon sinks to sources by exposing peat for aerobic decomposition (Dhandapani et al., 2019a; Dohong et al., 2017).

Oil palm plantation development is one of the major causes for this high rate of deforestation and peatland degradation (Dislich et al., 2017; Miettinen et al., 2016). Oil palm is the fastest expanding equatorial crop and the world's most consumed vegetable oil in the past decade (Lam et al., 2019; Tan et al., 2009). About 40% of the world's palm oil production comes from smallholder plantations (Azhar et al., 2017; Saadun et al., 2018), while small holder plantations also often follow more diverse cropping systems and management practices than industrial monocropping (Azhar et al., 2011; Dhandapani et al., 2019a, 2019b; Matysek et al., 2017). Despite this, smallholder plantations and different cropping systems are understudied in comparison with monocropping (Dhandapani et al., 2020). Tropical peatlands are considered naturally nutrient poor, and however, concentrations of nutrients and different elements are not well explored in these landscapes (Dhandapani, Ritz, Evers, Yule, et al., 2019; Sjögersten et al., 2011). The effects of land conversion on these nutrient and heavy metal concentrations in these ecosystems are virtually unknown. This is important because some of the macro- and micronutrients are known to exhibit functional relationships with greenhouse gas emissions in natural peat swamp forests (Dhandapani, Ritz, Evers, Yule, et al., 2019). Therefore, the role of these nutrients and heavy metals and their functional interactions within the diverse cropping systems needs to be further explored for a better understanding of these complex ecosystems.

Soil nutrients can be divided into macronutrients that are needed in large quantities (Maathuis, 2009), and micronutrients that are essential but needed in smaller quantities for physiological functions of living organisms (Harmsen & Vlek, 1985). Both macro- and micronutrients play important roles for life and species distribution in an ecosystem (John et al., 2007). The rest of the trace and heavy metal elements other than the macro- and micronutrients, can be further divided in to five groups, namely alkali metals, alkaline earth metals, transition metals, rare earth metals, and other metals and metalloids that do not belong to any other groups (Arevalo, 2016; Krämer et al., 2007). Some of these micronutrients and heavy metals are toxic in higher concentrations and have plant and animal health impacts (Wuana & Okieimen, 2011). The nutrient poor condition is particularly problematic in agricultural peatlands, where some of these elements are essential for crop growth (Yonebayashi et al., 1994). This is further strained by very low pH that makes some essential nutrients unavailable for plants (Fageria et al., 1990; Melo et al., 2013).

The concentrations of these nutrients and heavy metals in peat can influence greenhouse gas emissions via a few different pathways: (a) directly through chemical and mechanistic control over processes (Warren et al., 2017); (b) indirectly through changes in microbial community properties such as community structure, diversity, activity and biomass (Dowrick et al., 2006; Wang et al., 2019); (c) in natural habitats, nutrients and trace elements can also influence plant species distribution (John et al., 2007) that affects microbial communities through rhizosphere or plant litter inputs, which can further impact GHG emissions (Bezemer et al., 2006; Burns et al., 2015; Fan et al., 2019). However, the lack of research on nutrient and trace element concentrations in different peatlands, particularly tropical peatlands leave these processes and interrelations unexplored. The understanding of the different roles played by various elements in these ecosystems would provide new insights into management of agricultural peatlands to protect peat functions and reduce environmental impacts.

These nutrients and trace elements can directly influence peat functions mainly through carbon storage, either chemically interacting with carbon compounds and influence their lability or indirectly through interacting with other life forms such as plants and microbes that are involved in the carbon storage process. However, currently knowledge is lacking regarding these interactions and their potential importance for controlling greenhouse gas emissions in tropical peatlands. Accordingly, this research aimed to identify the concentrations of these nutrients and trace elements in North Selangor peatlands and their interactions with greenhouse gas emissions. We address the following specific research questions:

1. Do nutrient and trace element concentrations in the North Selangor peatlands differ across a range of land uses?
2. How are these differences impacted by seasons?
3. What are the relationships between peat nutrient/trace element concentrations and greenhouse gas emissions across different land uses?

2 | MATERIALS AND METHODS

2.1 | Study sites

The study sites were located in a single peat dome in the North Selangor peatlands (3°34′32N 101°15′44E), the second largest area of peatlands in Peninsular Malaysia, a detailed site description is in Dhandapani et al. (2019a). The soil classification comes under Histosols and the climatic conditions are tropical. Study sites were selected to represent forest and different cropping systems practiced by small holders: (a)

Historically drained secondary peat forest, hereafter denoted as 'Forest'; (b) first-generation oil palm monocropping, denoted '1st gen OP'; (c) cleared of first-generation oil palm monocropping, denoted 'Cleared'; (d) second-generation oil palm and pineapple intercropping, denoted 'Pineapple Intercropping'; (e) second-generation oil palm and yam intercropping, denoted 'Yam Intercropping' (f) second-generation oil palm monocropping, denoted '2nd gen OP'. The forest site is located in the northern edge of the peatlands within Sungai Karang Forest Reserve, and agricultural sites are located in Kampung Raja Musa village in the southern edge of the peatlands (Figure 1). The species composition of the forest site can be found in Dhandapani et al. (2019a) and Dhandapani, Ritz, Evers, Yule, et al. (2019). All the agricultural sites used in this study are smallholder plantations and are 2 hectares in size, consistent with small holdings in the region. The peat depth ranged from 0.5 to 3.5 m and average rainfall in the region is 1,359 to 2,480 mm per annum (Global Environmental Centre, 2014). The water table was below the surface for all sites during both the wet and dry season measurements, except for few wet season measurements in oil palm and pineapple intercropping site.

2.2 | Sampling strategy

Random sampling was used with 25 independent measurement within a site for each visit (Dhandapani et al., 2019a). Each site was visited 3 times each in wet and dry seasons, resulting in 150 individual measurements for each site. The gas measurements and physico-chemical properties for all sampling points are reported in Dhandapani et al. (2019a). However, in this correspondence research, only 10 random samples from one visit in each season were taken for nutrient and heavy metal analyses. The surface peat samples (0–5 cm) were collected from the exact same spot where the greenhouse gas measurement was made, and thus, peat properties, nutrient and heavy metal concentrations were directly related to each individual greenhouse gas emission measurements.

2.3 | Nutrient and trace element analyses

The exact same method used in Dhandapani, Ritz, Evers, Yule, et al. (2019) was used for nutrient analyses in this study. The peat nutrient and heavy metal concentrations were

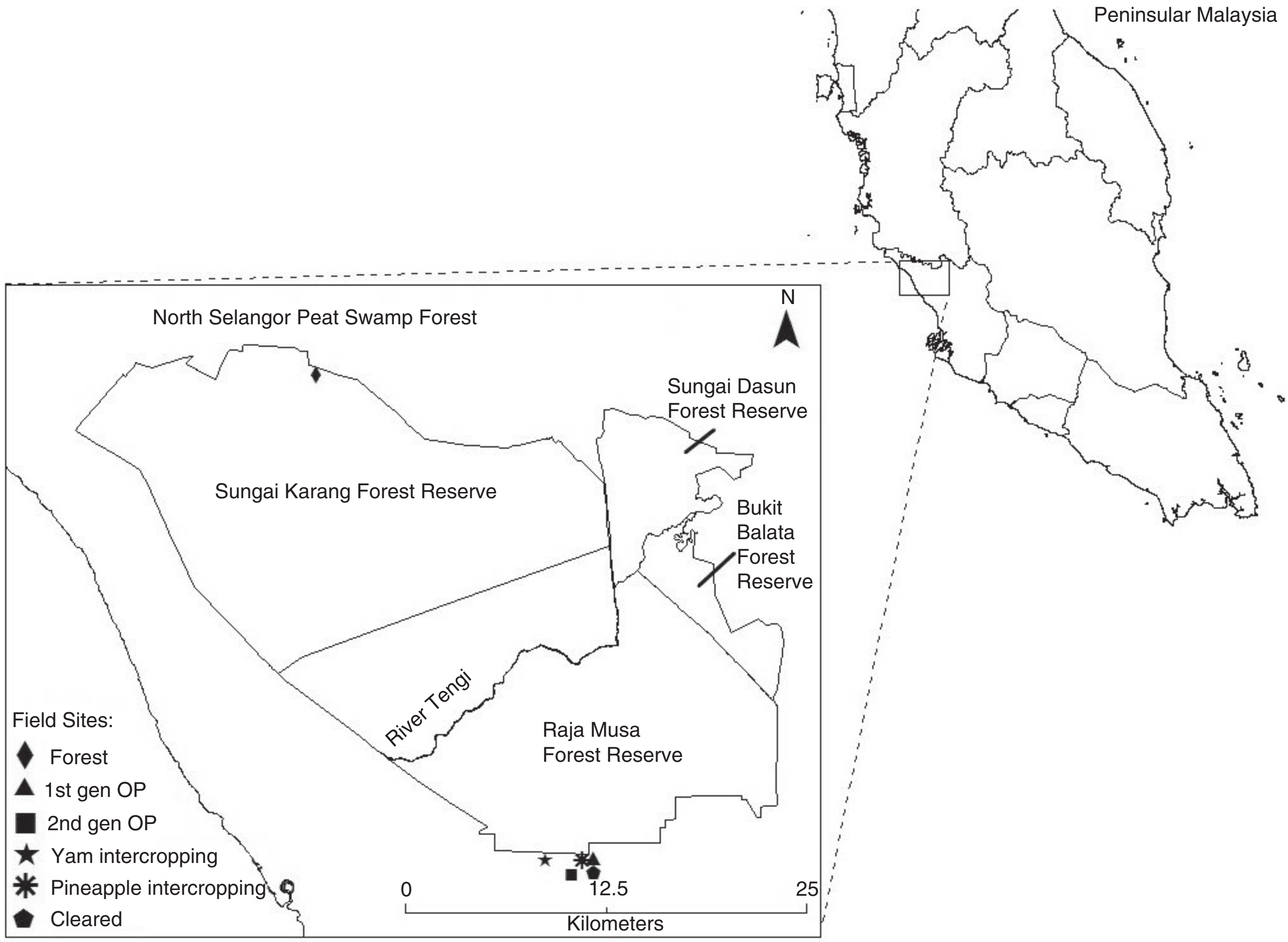

FIGURE 1 Site locations

analysed using inductively coupled plasma mass spectroscopy (ICP-MS). For this, approximately 0.1 g of oven dried (105°C for 48 hr) and ball-milled peat were weighed in Digitubes (Fisher Scientific). The Digitubes were then placed in the heating blocks and 8 ml of nitric acid was added to each sample. The samples were left overnight, and then, 2 ml of hydrogen peroxide was added, and the tubes were closed with watch glasses. Samples were then heated at 95°C for 2 hr. After the heat block digestion, the samples were diluted by filling milliQ water up to 50 ml, 1 ml of each sample was transferred in to 10 ml tube and further diluted with 9 ml of milliQ water. The samples were then analysed using 'Thermo Scientific ICAP Q' ICP-MS fitted with "CETAC™ A5X- 520" auto sampler' (Dhandapani, Ritz, Evers, Yule, et al. (2019).

2.4 | Peat properties and greenhouse gas emissions

The CO_2 and CH_4 emissions were measured using the Los Gatos Ultraportable Greenhouse Gas Analyser. Description of methods for the field sampling, laboratory analyses and gas emission calculations can be found in Dhandapani et al. (2019a). The peat properties reported in Dhandapani et al. (2019a) were peat surface temperature, volumetric moisture, pH and organic matter content.

2.5 | Statistical analyses

All the statistical analyses were carried out using Genstat® 17th edition (VSN International, Hemel Hampstead). The significance of differences between sites for nutrient and heavy metal concentrations were evaluated using linear mixed models with restricted maximum likelihood (REML) incorporating seasons and sites as fixed affects. For the data sets that were not normally distributed, the data were log-transformed. Principal component (PC) analysis using correlation matrix was performed on nutrient and heavy metal concentrations to identify the difference in overall nutrient profile among sites.

Backward stepwise multiple regression was performed with CO_2 and CH_4 as response variables, and the four measured peat properties and 29 elemental concentrations as fitted terms. Measurements made in the forest site, and in 1st gen OP that are near mature oil palm crop that had significant autotrophic contributions (Dhandapani et al., 2019b) were removed from the regression model for CO_2 emissions to account for only heterotrophic emissions that relate directly to peat decomposition. Similarly, wet season measurements from Pineapple Intercropping site that had very high CH_4 emissions due to above surface water level is removed from the regression model, as waterlogged conditions override all the other relationships (Dhandapani et al., 2019a).

3 | RESULTS AND DISCUSSION

Macronutrients are essential group of elements that are supplied by soil to plants in large quantities (Maathuis, 2009). All the studied macronutrient concentrations were significantly different among the sites, with phosphorus concentrations showing no significant difference between the seasons (Figure 2; Table 1). However, phosphorus

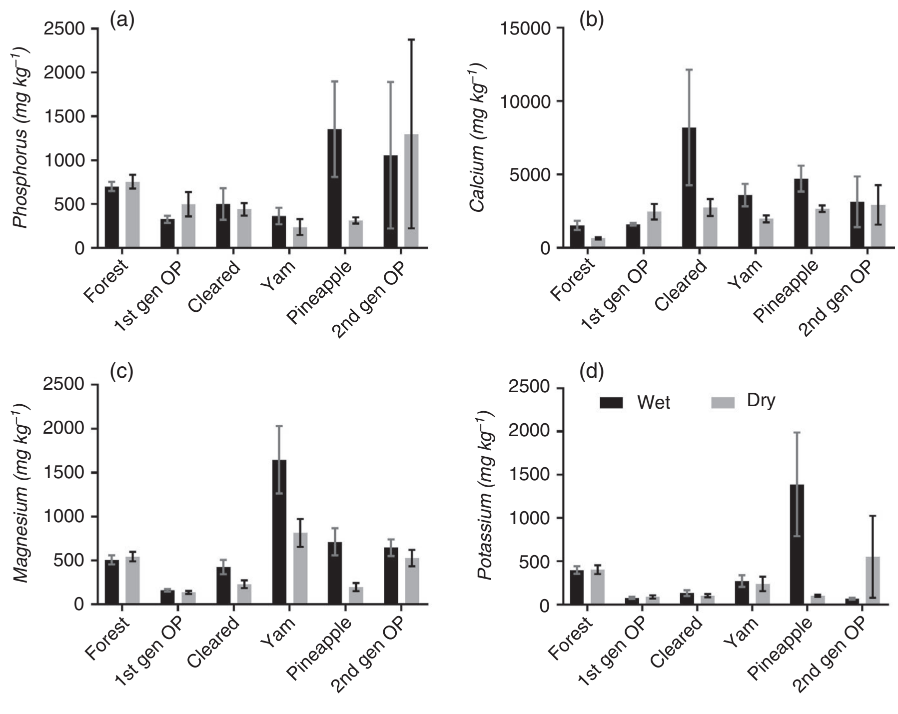

FIGURE 2 Effect of site and season upon macronutrients: (a) phosphorus, (b) calcium, (c) magnesium and (d) potassium between different study sites during wet (black) and dry (grey) season. Bars denote mean values ($n = 10$), and whiskers denote standard errors. Note 1st gen OP denotes 1st generation oil palm monocropping, yam denotes 2nd generation oil palm and yam intercropping, pineapple denotes 2nd generation oil palm and pineapple intercropping, 2nd gen OP denotes 2nd generation oil palm monocropping

concentrations were highly variable within 2nd gen OP showing high standard error. This high intra-site variation is possibly due to the legacy effect of previous generation plantations, where dead oil palm wood relatively rich in phosphorus (Dhandapani & Evers, 2020) were left to degrade in certain regions within the site, spiking phosphorus concentrations in those regions. Calcium concentrations were significantly reduced in dry season compared to the wet season measurements for most of the sites, and there were no significant interactions between site and season. Magnesium concentrations stayed at the same level for both seasons for Forest, 1st gen OP and 2nd gen OP, while it was reduced for the rest of the sites resulting in significant interaction between site and season. Potassium concentrations were significantly reduced in Pineapple Intercropping and increased in 2nd gen OP from wet season to dry season, while there was no change between seasons for the rest of the site resulting in significant seasonal interactions.

All macronutrients either stayed at the same levels from the wet season to dry season measurements or reduced over time with decrease in dry season (Figure 2). This suggests that despite many of the sites being used for agriculture, there may have been no additional input over time, and there is possible leaching of these important nutrients in these ecosystems (Dhandapani & Evers, 2020). Leaching is highly plausible in these acidic environment where there are ample H+ ions to replace cations, such as ionic forms of magnesium, calcium and potassium (Guicharnaud & Paton, 2006; Haynes & Swift, 1986). All the agricultural sites in this study were also actively drained, further adding to the leaching pressure (Kløve et al., 2010; Laiho & Laine, 1995; Sallantaus, 1992). All macronutrients except calcium stayed at the same level for the forest over the seasons, showing minimal loss. Calcium decreased over time in the forest site, possibly of loss through leaching as previously observed in North Selangor peatlands (Dhandapani & Evers, 2020). Calcium is one of the most mobile nutrients in soils (Mengel et al., 2001a; Neilsen & Stevenson, 1983) and is highly prone to leaching especially in acidic soils (Leys et al., 2016) such as the forested peatlands studied here (Dhandapani et al., 2019a). The changes between different agricultural sites were highly variable, possibly attributed to the difference in their management regimes such as types of fertilizer (Sundram, 2019) and pesticide (Taiwo & Oso, 1997) used in the sites, which is unknown. Some notably high concentrations of macronutrients are high phosphorus, calcium, magnesium and potassium concentrations in the wet season measurements of Pineapple Intercropping, Cleared, Yam Intercropping, respectively. However, all of these concentrations were greatly reduced in dry season that were comparable to those nutrient concentrations in other studied sites (Figure 2). Relatively higher level of phosphorus and potassium concentrations in the Forest can be attributed to leaf litter addition in this site, which is lacking in all the other agricultural sites, as these two nutrients were found to readily leach from leaf litter to the soil (Ong et al., 2017; Staaf, 1980). None of the macronutrients exhibited any significant correlation with greenhouse gas emissions in a multiple regression including all 29 studied elements and four other peat physico-chemical properties reported in Dhandapani et al. (2019a; Table 2).

Similar to the macronutrients, all micronutrients were also significantly different among the sites, while significant seasonal changes characterized by reduction in concentrations from wet to dry season were observed only for manganese, zinc and copper (Table 1; Figure 3). The interactions between site and season were significant for copper, molybdenum, nickel and selenium, as all these four micronutrients were reduced from wet season to dry season for Forest and Yam Intercropping sites, while they stayed at the same level for all the other sites, except for a significant increase in selenium concentration from wet season to dry season in Pineapple Intercropping (Figure 3). It is notable that these four micronutrients exhibited similar trend in all these site even though they take different ionic forms in soil (Kirkby, 2005; Mengel et al., 2001b; Oorts, 2013; Yamada et al., 1998). This indicates that other characteristics of these nutrients other than their ionic forms had greater influence on their dynamics in these studied sites.

Some of the micronutrients were significantly correlated with greenhouse gas emissions in the multiple regressions including peat physico-chemical properties and 29 different elements (Table 2). Manganese was positively related to both CO_2 and CH_4 emissions. Manganese concentrations were significantly higher in the second-generation plantations compared to the forest and 1st gen OP. Manganese is an essential element that plays a role in photosynthesis, nitrogen metabolism and synthesis of 35 different enzymes in plants (Mousavi et al., 2011). However, higher concentration of manganese also has potential for toxicity especially in acidic soils (Sparrow & Uren, 2014). The reported levels of manganese for all studied sites were below the limit of 250 mg kg^{-1} for any toxic effects on plants (Min et al., 2019). Manganese is known to significantly alter soil microbial communities with increased biomass and diversity (Marschner et al., 2003; Min et al., 2019), which could have indirectly effected the increase in greenhouse gas emissions (Stendahl et al., 2017). Due to its role in enzymatic decomposition, manganese is found to play crucial part in litter degradation and carbon loss from humus layers in northern ecosystems (Berg et al., 2010, 2015; Keiluweit et al., 2015; Perez & Jeffries, 1992; Stendahl et al., 2017). Our results suggest that they play a similar role of enhancing carbon loss through gaseous emissions in tropical peatlands.

Copper is known to have antimicrobial properties against microbes involved in aerobic decomposition (Berg

TABLE 1 Linear mixed model (REML) for different nutrient and trace element concentrations, showing statistical significance of the effects of site, season and the interactions between site and season

	Site	Season	Site*Season
Macronutrients			
logP	**$F_{5,108} = 5.18$, $p < .001$**	$F_{1,108} = 1.94$, $p = .167$	$F_{5,108} = 1.64$, $p = .155$
logCa	**$F_{5,108} = 11.3$, $p < .001$**	**$F_{1,108} = 8.33$, $p = .005$**	$F_{5,108} = 1.95$, $p = .091$
logMg	**$F_{5,108} = 23.31$, $p < .001$**	**$F_{1,108} = 21.45$, $p < .001$**	**$F_{5,108} = 3.57$, $p = .005$**
bocoxK	**$F_{5,108} = 16.87$, $p < .001$**	**$F_{1,108} = 7.09$, $p = .009$**	**$F_{5,108} = 3.03$, $p = .013$**
Micronutrients			
logFe	**$F_{5,108} = 32.64$, $p < .001$**	$F_{5,108} = 3.59$, $p = .061$	$F_{5,108} = 1.93$, $p = .095$
logMn	**$F_{5,108} = 22.89$, $p < .001$**	**$F_{1,108} = 12.03$, $p < .001$**	$F_{5,108} = 1.98$, $p = .087$
logZn	**$F_{5,108} = 7.71$, $p < .001$**	**$F_{1,108} = 13.63$, $p < .001$**	$F_{5,108} = 1.39$, $p = .234$
logCu	**$F_{5,108} = 7.18$, $p < .001$**	$F_{1,108} = 2.65$, $p = .106$	**$F_{5,108} = 2.69$, $p = .025$**
Mo	**$F_{5,108} = 33.44$, $p < .001$**	**$F_{1,108} = 11.63$, $p < .001$**	**$F_{5,108} = 4.88$, $p < .001$**
logNi	**$F_{5,108} = 8.78$, $p < .001$**	$F_{1,108} = 3.87$, $p = .052$	**$F_{5,108} = 4.54$, $p < .001$**
logSe	**$F_{5,108} = 30.53$, $p < .001$**	$F_{1,108} = 1.04$, $p = .310$	**$F_{5,108} = 3.7$, $p = .004$**
logNa	**$F_{5,99} = 6.73$, $p < .001$**	$F_{1,99} = 3.59$, $p = .061$	$F_{5,99} = 2.13$, $p = .068$
Alkali and Alkaline Earth metals			
logLi	**$F_{5,101} = 3.77$, $p = .004$**	$F_{1,101} = 2.04$, $p = .156$	$F_{5,101} = 0.46$, $p = .808$
logRb	**$F_{5,108} = 26.11$, $p < .001$**	**$F_{1,108} = 12.08$, $p < .001$**	$F_{5,108} = 0.53$, $p = .752$
logCs	**$F_{5,108} = 13.1$, $p < .001$**	**$F_{1,108} = 9.29$, $p = .003$**	$F_{5,108} = 1.23$, $p = .301$
Be	**$F_{5,108} = 7.21$, $p < .001$**	$F_{1,108} = 2.70$, $p = .103$	$F_{5,108} = 0.37$, $p = .866$
logSr	**$F_{5,108} = 7.64$, $p < .001$**	$F_{1,108} = 0.64$, $p = .424$	$F_{5,108} = 0.7$, $p = .621$
logBa	**$F_{5,108} = 8.36$, $p < .001$**	**$F_{1,108} = 5.85$, $p = .017$**	**$F_{5,108} = 2.84$, $p = .019$**
Transition metals			
logTi	**$F_{5,108} = 15.96$, $p < .001$**	$F_{1,108} = 0.26$, $p = .613$	$F_{5,108} = 1.84$, $p = .112$
logV	**$F_{5,108} = 3.88$, $p = .003$**	$F_{1,108} = 2.63$, $p = .108$	$F_{5,108} = 0.36$, $p = .878$
logCr	$F_{5,108} = 1.42$, $p = .224$	$F_{1,108} = 0.62$, $p = .434$	$F_{5,108} = 0.48$, $p = .791$
logCo	**$F_{5,108} = 19.68$, $p < .001$**	$F_{1,108} = 0.92$, $p = .168$	$F_{5,108} = 1.83$, $p = .113$
Ag	**$F_{5,107} = 7.93$, $p < .001$**	$F_{1,107} = 0.72$, $p = .397$	**$F_{5,107} = 6.56$, $p < .001$**
logCd	**$F_{5,108} = 13.69$, $p < .001$**	$F_{1,108} = 2.80$, $p = .097$	$F_{5,108} = 1.09$, $p = .372$
Other metals and metalloids			
logAl	**$F_{5,108} = 4.06$, $p = .002$**	$F_{1,108} = 1.86$, $p = .176$	$F_{5,108} = 0.43$, $p = .825$
logTl	**$F_{5,108} = 20.74$, $p < .001$**	**$F_{1,108} = 23.17$, $p < .001$**	**$F_{5,108} = 2.40$, $p = .042$**
logPb	**$F_{5,108} = 6.66$, $p < .001$**	**$F_{1,108} = 10.89$, $p = .001$**	**$F_{5,108} = 9.28$, $p < .001$**
logAs	**$F_{5,108} = 11.25$, $p < .001$**	$F_{1,108} = 1.12$, $p = .292$	$F_{5,108} = 1.58$, $p = .171$
logU	**$F_{5,108} = 3.80$, $p = .003$**	$F_{1,108} = 1.83$, $p = .179$	$F_{5,108} = 0.61$, $p = .689$

Note: Statistically significant figures are presented in bold.

TABLE 2 Backward stepwise elimination regression for the relationship between peat properties, nutrient and trace element concentrations, and CO_2 and CH_4 emissions

	logCH_4	logCO_2
Constant	1.8374	2.449
Peat properties		
Organic matter content (%)	+0.001875 ($p < .001$)	+0.00338 ($p = .020$)
Micronutrients		
Mn	+0.001827 ($p < .001$)	+0.001743 ($p = .001$)
Cu	+0.00654 ($p = .011$)	
Mo	−0.0830 ($p < .001$)	
Se	−0.0911 ($p < .001$)	−0.08 ($p = .042$)
Alkali and Earth Alkaline metals		
Li	−0.24 ($p < .001$)	
Ba	+0.001562 ($p = .007$)	
Transition metals		
V	−0.04443 ($p < .001$)	
Co	+0.0933 ($p < .001$)	
Other metals and metalloids		
Al	+0.0000807 ($p < .001$)	
Degrees of freedom	10, 95	3, 91
F statistic	13.53	4.66
p value	<.001	.005
% variance	56.9%	10.80%

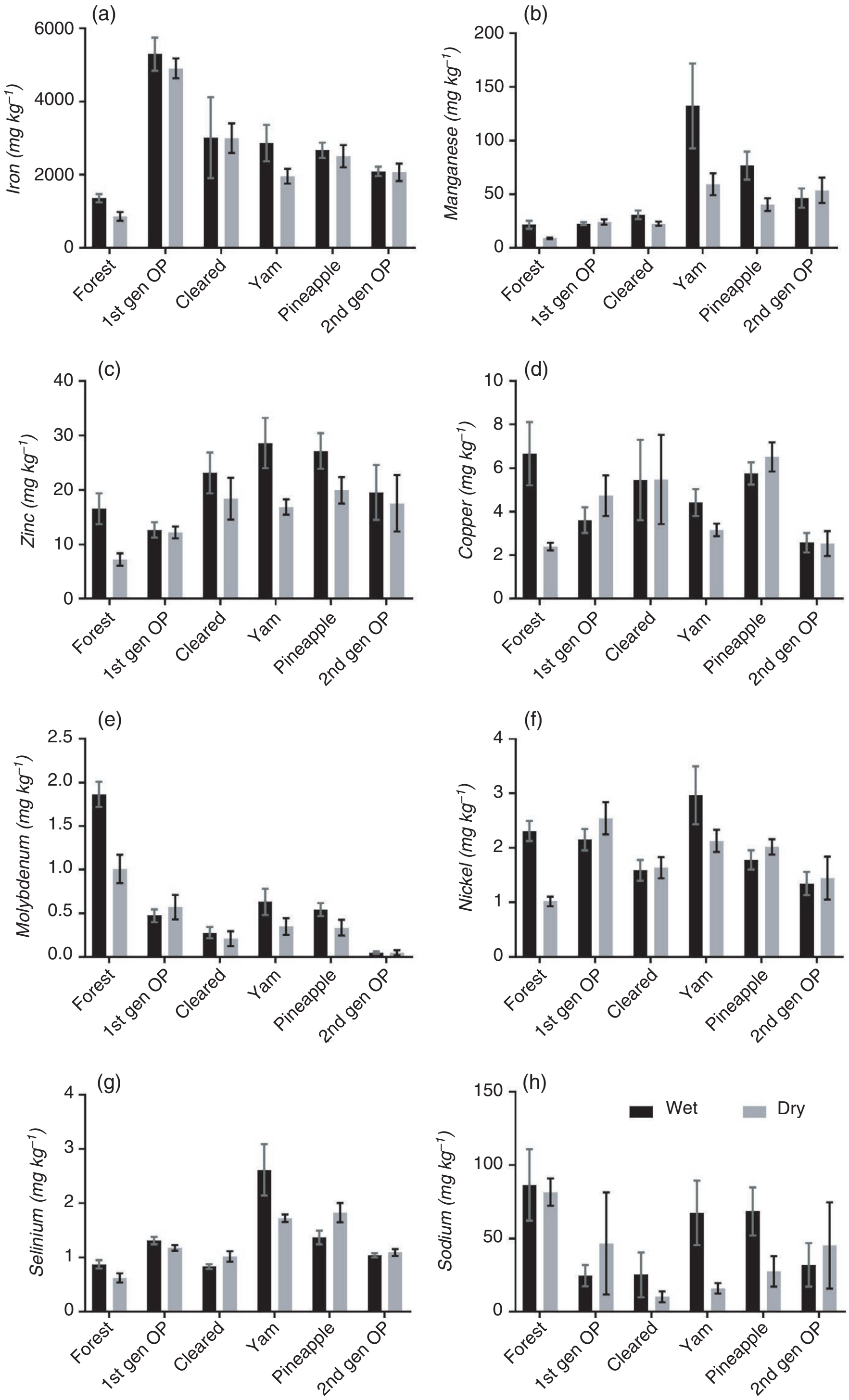

FIGURE 3 Effect of site and season upon micronutrients: (a) iron, (b) manganese, (c) zinc, (d) copper, (e) molybdenum (f) nickel (g) selinium and (h) sodium between different study sites during wet (black) and dry (grey) season. Bars denote mean values ($n = 10$), and whiskers denote standard errors. Note 1st gen OP denotes 1st generation oil palm monocropping, yam denotes 2nd generation oil palm and yam intercropping, pineapple denotes 2nd generation oil palm and pineapple intercropping, and 2nd gen OP denotes 2nd generation oil palm monocropping

et al., 2005; Gajjar et al., 2009; Wheeldon et al., 2008). Adding to this, Dhandapani, Ritz, Evers, Yule, et al. (2019) found negative correlations between copper concentrations and CO_2 emissions. However, reports of such negative impact on anaerobic microbes are scarce, in fact a few studies show copper to enhance CH_4 emissions especially in an environment with high organic content as in our sites (Dhandapani et al., 2019a; Jiao et al., 2005).

Molybdenum is an important element in soil for nitrogen and sulphur cycling (Kaiser et al., 2005; Warren et al., 2017), and it was negatively correlated with CH_4 emissions in the multiple regression. This negative correlation between molybdenum concentrations and CH_4 emissions was also previously observed in tropical peat swamp forests (Dhandapani, Ritz, Evers, Yule, et al. (2019). Molybdenum is an important element for N_2 fixation (Kaiser et al., 2005), and the majority of nitrogen-fixing bacteria in peatlands are methanotrophs that consume CH_4 (Larmola et al., 2014; Vile et al., 2014), thus indirectly influencing lower CH_4 fluxes from these ecosystems. On the other hand, molybdenum also facilitates sulphate-reducing bacteria that compete with methanogens (Dowrick et al., 2006; Kaiser et al., 2005), further reducing CH_4 emissions. Selenium is also closely associated with sulphate transporters and thus linked to sulphur cycle (Schiavon et al., 2017), which unsurprisingly exhibited a similar trend to that of molybdenum in relation to CH_4 emissions (Table 2).

Alkali and alkaline earth metals constitute important groups of elements in soils, which characteristically form alkaline solution when reacted with water, and are generally highly reactive with other elements. All alkali and alkaline earth metals (excluding macro- and micronutrients) were significantly different among sites (Figure 4; Table 1), and only rubidium and caesium were significantly reduced from wet to dry season, while there was no significant difference between seasons for other alkali and alkaline earth metals. Alkali and alkaline earth metals constitute a diverse group of elements from macronutrients such as potassium and calcium, and micronutrients such as sodium and magnesium to other toxic elements. These alkali and alkaline earth metals that are not macro- or micronutrient, are mostly associated with environmental deterioration and contamination in their higher concentrations (Asylbaev & Khabirov, 2016). In soils, these elemental distributions are based on parent material, topography, the characters of pedogenesis and above-ground vegetation (Asylbaev & Khabirov, 2016). In peat, the dependence may be greater on the vegetation and characters of underlying material beneath peat layers. In multiple regression, lithium was negatively correlated with CH_4 emissions and barium was positively related to CH_4 emissions (Table 2). Both lithium and barium are non-essential elements for living beings and mostly associated with soil contaminations and toxicity (Anderson et al., 1988; Shahzad et al., 2016). Lithium concentrations in all studied sites were below the toxic level for plants (Shahzad et al., 2016). Though the concentrations of these elements were very low, their observed functional relationship with greenhouse gas emissions shows the importance of further research in understanding their dynamics in tropical peatlands.

Transition metal elements such as iron, copper, zinc and molybdenum are essential micronutrients for plant functioning (González-Guerrero et al., 2016), and their dynamics in soil were known to be influenced by soil organic matter

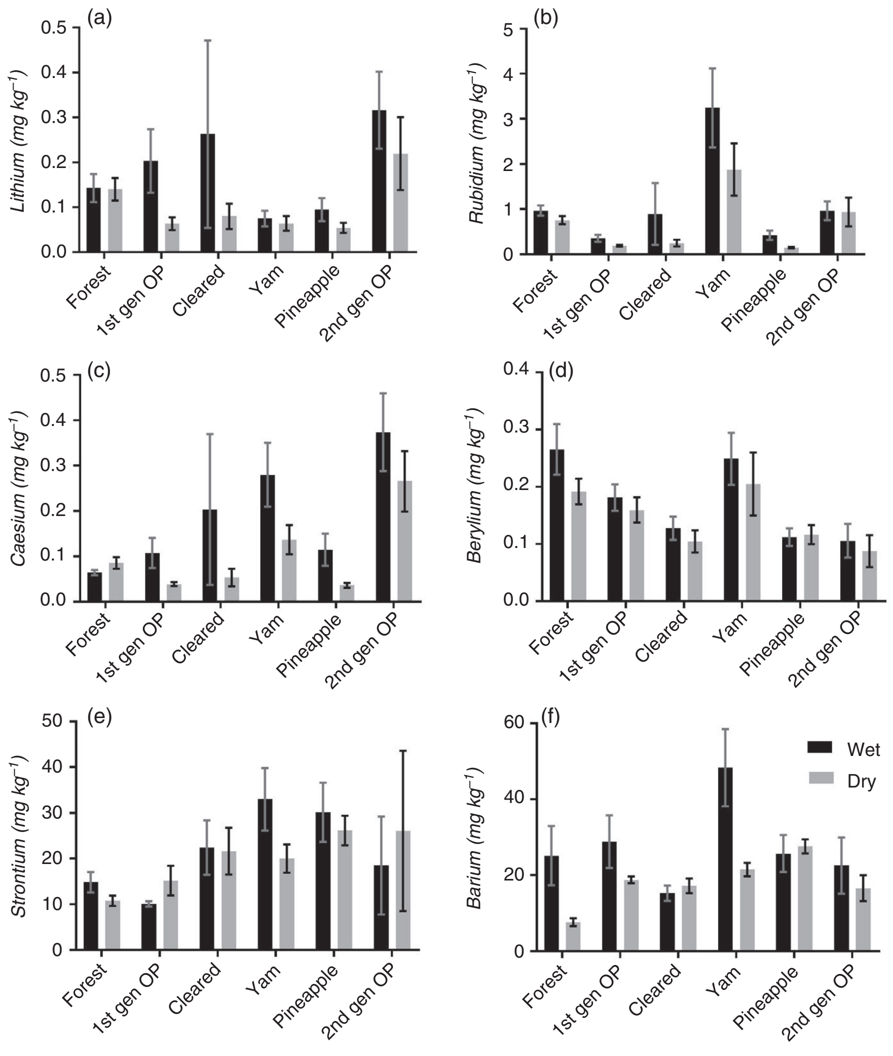

FIGURE 4 Effect of site and season upon alkali and alkaline earth metals: (a) lithium, (b) rubidium, (c) caesium, (d) beryllium, (e) strontium and (f) nickel between different study sites during wet (black) and dry (grey) season. Bars denote mean values ($n = 10$) and whiskers denote standard errors. Note 1st gen OP denotes 1st generation oil palm monocropping, yam denotes 2nd generation oil palm and yam intercropping, pineapple denotes 2nd generation oil palm and pineapple intercropping and 2nd gen OP denotes 2nd generation oil palm monocropping

(Linehan, 1985). Most transition metals including the micronutrients in higher concentrations are associated with soil contamination and toxicity (Wuana & Okieimen, 2011). All transition metal concentrations (excluding essential micronutrients) except chromium were significantly different between sites and none of the transition metal concentrations exhibited any significant seasonal change (Figure 5). Silver exhibited significant interaction between site and season, as the concentration decreased from wet to dry season for Forest, while it increased from wet to dry seasons for Cleared and 2nd gen OP sites (Figure 5; Table 1). Vanadium was negatively related, and cobalt was positively related to CH_4 emissions (Table 2). Vanadium is an element that is toxic in higher concentrations but also plays a role in enzyme activities (Anke, 2005). Vanadium concentration in the sites is much lower than global average for peat (Anke, 2005). Vanadium is an essential element for several nitrogen-fixing microbes, which in peatlands are associated with methanotrophy (Anke, 2005; Larmola et al., 2014; Vile et al., 2014), explaining the negative correlation of vanadium concentrations with CH_4 emissions. Cobalt is an essential element for optimal growth of some methanogens (Demirel & Scherer, 2011). Considering that cobalt concentrations were very low in the studied sites, increase in such concentrations positively increased CH_4 production by promoting methanogens. Similar positive correlation was also observed in paddy fields, where cobalt promoted the abundance and activity of methanogens (Wang et al., 2019). The same study also found that optimum cobalt concentrations for CH_4 production in paddy soil are 50 mg kg^{-1}, which is multi-fold higher than the concentrations in studied tropical peatlands, showing a strong potential for further increase in CH_4 emissions with changes in cobalt concentrations.

All the rest of the heavy metals and metalloids also showed significant changes between study sites, while only thallium and lead showed significant difference between seasons and also significant interaction between sites and seasons (Figure 6; Table 1). These elements (aluminium, thallium, lead, arsenic and uranium) that do not belong to other reported classifications of metals are generally non-essential

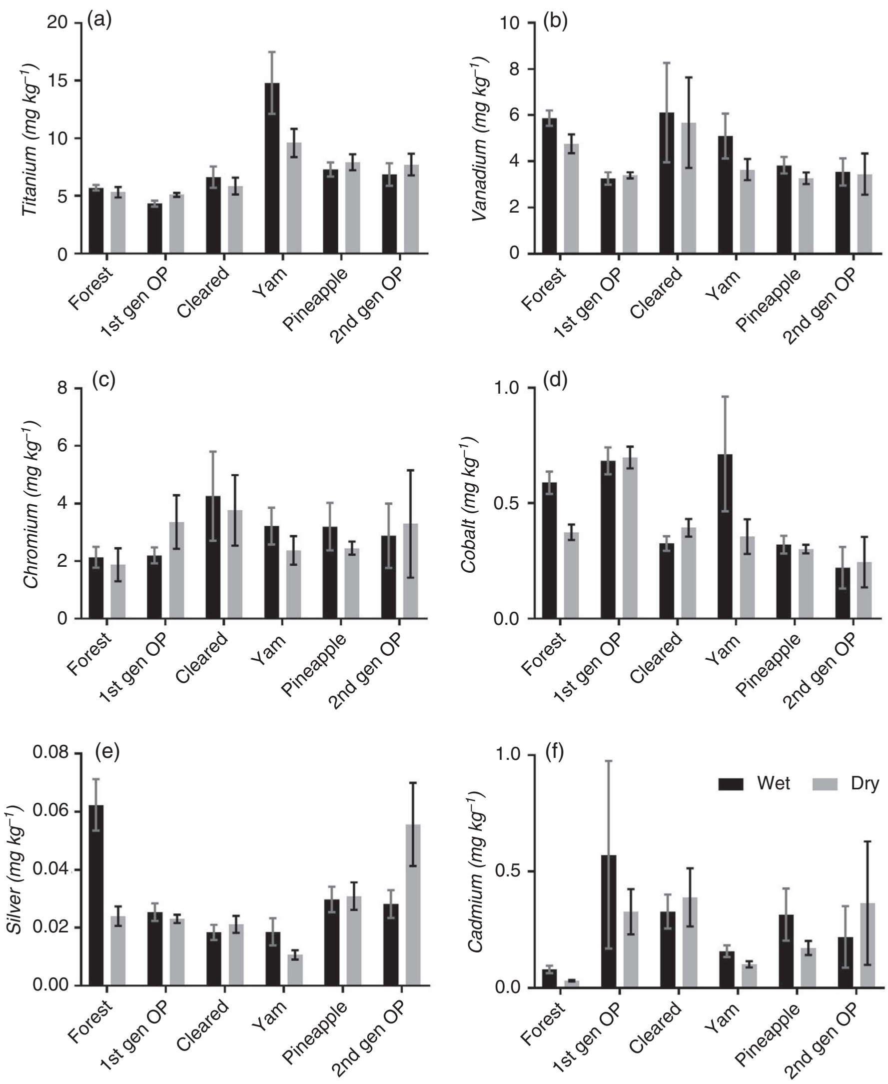

FIGURE 5 Effect of site and season upon transition metals: (a) titanium, (b) vanadium, (c) chromium, (d) cobalt, (e) silver and (f) cadmium between different study sites during wet (black) and dry (grey) season. Bars denote mean values ($n = 10$), and whiskers denote standard errors. Note 1st gen OP denotes 1st generation oil palm monocropping, yam denotes 2nd generation oil palm and yam intercropping, pineapple denotes 2nd generation oil palm and pineapple intercropping, 2nd gen OP denotes 2nd generation oil palm monocropping

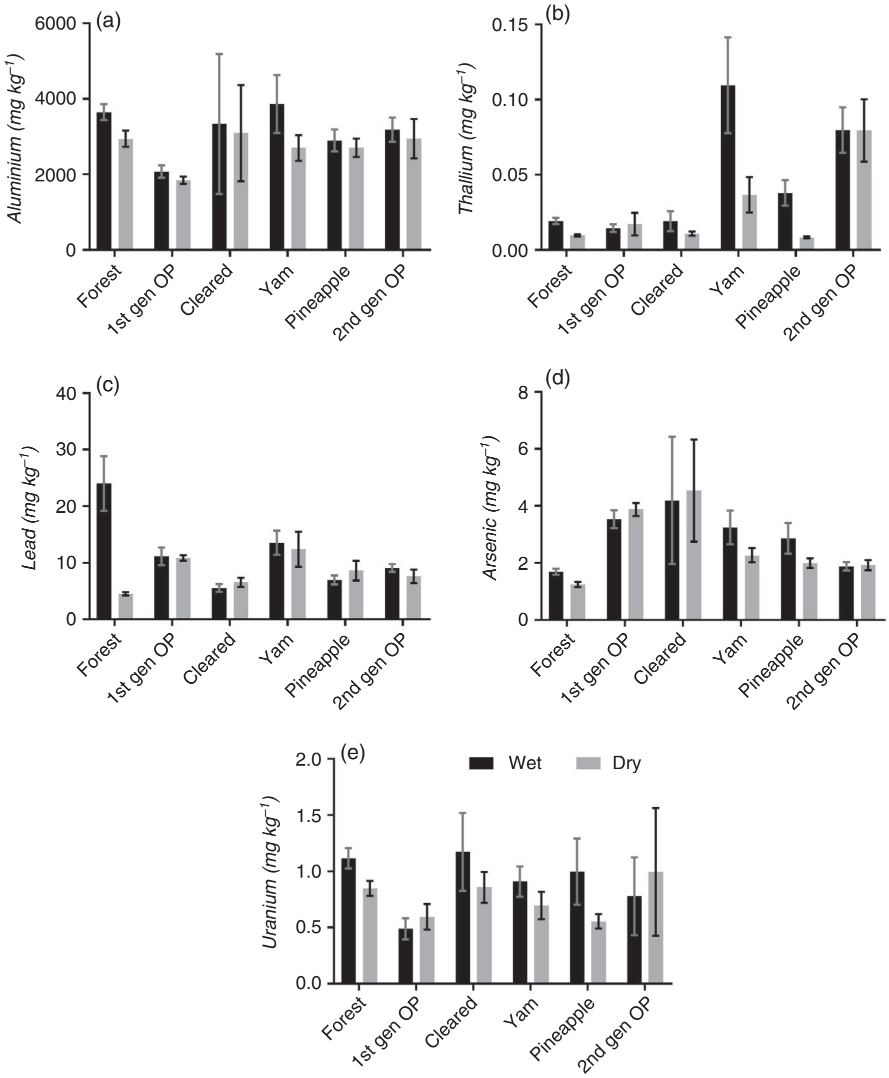

FIGURE 6 Effect of site and season upon other metals and metalloids: (a) aluminium, (b) thallium, (c) lead, (d) arsenic and (e) uranium between different study sites during wet (black) and dry (grey) season. Bars denote mean values ($n = 10$), and whiskers denote standard errors. Note 1st gen OP denotes 1st generation oil palm monocropping, yam denotes 2nd generation oil palm and yam intercropping, pineapple denotes 2nd generation oil palm and pineapple intercropping, and 2nd gen OP denotes 2nd generation oil palm monocropping

and toxic in most environments (Tchounwou et al., 2012). Aluminium concentrations also exhibited negative correlations with CH_4 emissions (Table 2). As most of the past studies were focused on toxicity of aluminium and its effect on plants and animals (Pina & Cervantes, 1996), their role in carbon cycling are not well known. Because of their pH levels—well below 4—North Selangor peatlands are at high risk for aluminium toxicity (Kochian et al., 2004). Considering that it is the most abundant metal in earth's crust (Bojórquez-Quintal et al., 2017), its higher concentrations in low pH tropical peatlands (Figure 6) and its potential to interrupt biogeochemical processes (Bojórquez-Quintal et al., 2017; Kochian et al., 2004; Pina & Cervantes, 1996), there is a need to research aluminium and its biogeochemical interactions in tropical peatlands.

Taken together, the multiple regressions with all the measured parameters in Dhandapani et al. (2019a) and the 29 elements have shown that the micronutrients and other trace elements exhibited significant correlations overshadowing the macronutrients and some physico-chemical properties such as peat temperature and pH, showing the functional importance of these trace elements (Table 2). Organic matter content is one exception that was significantly correlated with both CH_4 and CO_2 emissions. However, it should also be noted that unusually high CH_4 emissions at the Pineapple Intercropping site during wet season was associated with high water table level, which is the ultimate control for CH_4 emissions and was left out of the regression model (Dhandapani et al., 2019a).

4 | CONCLUSIONS

All the nutrients and trace element concentrations except chromium were significantly different among the sites, showing the significant spatial variations and potential impacts of different smallholding practices. As all of the studied sites were drained, the reduction in most of the macronutrients and some of the micronutrient concentrations from wet season to dry season show the potential loss through leaching over time, further increasing nutrient limitations in these peatlands. The fact that many micronutrients exhibited significant correlations with GHG emissions, over the commonly studied peat physico-chemical properties such as peat moisture, temperature, pH and organic matter content shows the need to further explore these trace elements and their functional interactions in tropical peatlands. This study showed that nutrient and trace element concentrations significantly varied among different land uses within a single peat dome, and nevertheless, there is a need for large scale study exploring different land uses in the wider region, especially considering that small holder oil palm plantations vary widely in their management practices regionally. These fields observed correlations provide valuable insights, and however, there is a need for controlled experiments to fully understand the mechanistic role of these different elements in GHG emissions from peat. Such understanding would help in making informed management decisions to control carbon loss through GHG emissions from tropical peatlands.

DATA AVAILABILITY STATEMENT

Data is available on request to the corresponding author.

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How to cite this article: Dhandapani S, Evers S, Ritz K, Sjögersten S. Nutrient and trace element concentrations influence greenhouse gas emissions from Malaysian tropical peatlands. *Soil Use Manage*. 2021;37:138–150. https://doi.org/10.1111/sum.12669