

Distribution of Exchangeable Al, Fe and Mn in Forest Soils from Two Contrasting Watersheds in the Oil Sands Region in Northern Alberta, Canada

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A better understanding of the behavior of metals such as Al and Fe in soils receiving atmospheric acidic deposition will help us understand why certain forest ecosystems are sensitive to acidification and ecological stress [Jansen *et al.*, 2005; Xue *et al.*, 2006]. In general, pH and organic matter content are two important parameters affecting the mobilization of metals in the soil [Ok *et al.*, 2002; Ok *et al.*, 2003]. However, the factors governing the mobilization of metals in forest ecosystems are not fully understood. The objectives of this study were to (i) quantify the distribution of metals (Al, Fe and Mn) in the soil profiles of two contrasting watersheds; and (ii) evaluate the relationship between exchangeable metals and other soil chemical variables in order to understand possible mechanisms for metal retention and/or mobilization in the forest soils in the oil sands region of northern Alberta, Canada.

Two contrasting watersheds, Lake 185 (57.15°N, 110.86°W) located north of Fort McMurray and Lake 287 (56.21°N, 111.20°W) located near Stony Mountains were studied in the oil sands region in northern Alberta. Five representative upland sites were selected for soil sampling in each watershed, and three of the five selected plots in each watershed were jack pine (*Pinus banksiana* Lamb.) dominated stands and the other two were aspen (*Populus*

tremuloides Michx.) dominated stands. In July 2005, five soil pits in each watershed were dug to describe and classify the soils, and then soil samples were collected by horizon. Thick (>5 cm) forest floors were developed from each upland site where low temperatures retarded decomposition. Luvisolic (Boralf) soils, developed under mixed deciduous and coniferous vegetation, were common mineral soils in this area. Soil samples were air dried and passed through a 2 mm sieve prior to analysis. Soil pH was measured in 1 mol/L KCl using 10 g of mineral soil or 2 g of organic sample in 20 ml solution. Indirect measurement of acid-buffering capacity was performed by reacting 2 g of soil with 25 ml 0.40 mol/l acetic acid for 16 h [Ashworth and Kirk, 1999]. Exchangeable base cations, Al, Fe and Mn were determined after extraction with 1 mol/l NH₄Cl at a ratio of 5 g of sample to 100 ml extraction solution [Sullivan *et al.* 2006]. The filtrates were analyzed for Ca, Mg, K, Na, Al, Fe and Mn using ICP-MS. Each sub-sample was further ground and used for total C and N analysis using an element analyzer.

Soil pH was extremely acidic especially for the organic horizon (the forest floor) in the two watersheds (Table 1).

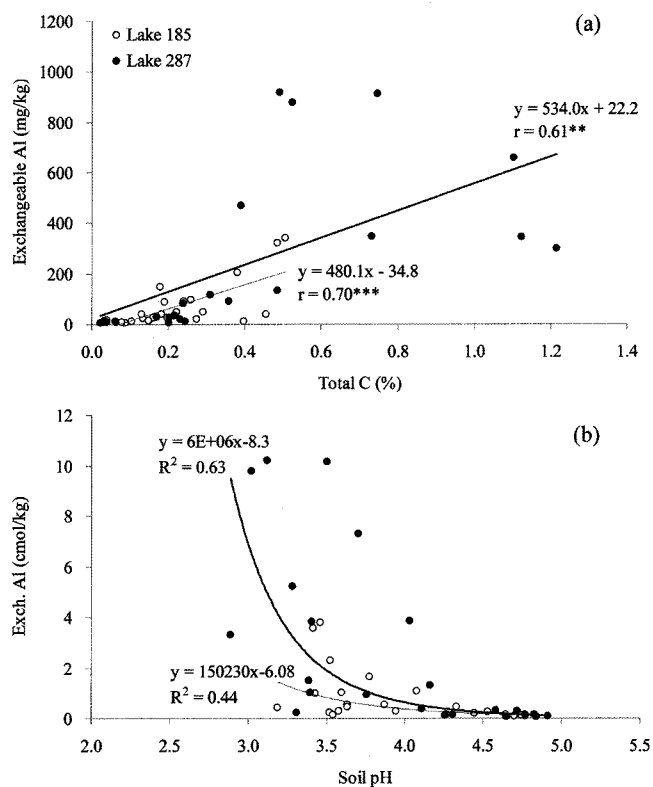


Fig. 1. The relationship between total C and exchangeable Al concentration (a), and soil pH and exchangeable Al concentration (b) in mineral horizons of forest soils from two watersheds in the oil sands region of northern Alberta. **Significant at $p < 0.01$; ***Significant at $p < 0.001$.

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Table 1. Chemical properties (means with standard deviations in parentheses) of forest soils from two watersheds in the oil sands region in northern Alberta

Site	Horizon	pH	pH	Total C	Total N	CEC _e	BS	Ca-s ¹⁾	Al-s ²⁾
		(KCl)	(acetic acid)	(%)		(cmol _e /kg)		(%)	
L185	Organic	3.66 ^a (0.72)	2.91 ^a (0.17)	31.57 ^a (6.68)	1.21 ^a (0.57)	35.32 ^a (23.25)	91.53 ^a (7.36)	68.22 ^a (10.81)	4.87 ^a (6.56)
	Mineral ³⁾	3.94 ^a (0.50)	2.50 ^b (0.11)	0.23 ^b (0.14)	0.03 ^b (0.01)	2.83 ^b (2.44)	70.13 ^a (20.01)	45.30 ^a (14.16)	26.86 ^b (19.46)
L287	Organic	3.23 ^a (0.43)	2.87 ^a (0.10)	33.81 ^a (2.90)	1.40 ^a (0.51)	30.62 ^a (10.32)	89.90 ^a (6.40)	64.38 ^a (5.54)	5.12 ^a (5.05)
	Mineral	3.95 ^a (0.66)	2.66 ^a (0.06)	0.40 ^a (0.36)	0.04 ^a (0.02)	6.32 ^a (7.17)	54.68 ^b (26.04)	35.33 ^a (19.20)	41.23 ^a (25.29)

¹⁾Ca-s: Ca saturation (%); ²⁾Al-s: Al saturation (%); and ³⁾The values for the mineral horizon were means of all mineral soil horizons in the soil profile. Values in the same column followed by different superscript letters are significantly different at $\alpha = 0.05$ when compared at the same soil horizon for two lakes.

Table 2. Pearson correlation coefficients for chemical variables of forest soils from two watersheds in the oil sands region in northern Alberta

Parameter	Coefficient	
	Organic horizon (n = 10)	Mineral horizon (n = 10)
Exch. Al \times pH _{KCl}	-0.83**	-0.54***
Exch. Fe \times pH _{KCl}	-0.84**	-0.47***
Exch. Mn \times pH _{KCl}	0.47 ^{ns}	-0.03 ^{ns}
Exch. Al \times Total C	-0.40 ^{ns}	0.65***
Exch. Fe \times Total C	-0.49 ^{ns}	0.84***
Exch. Mn \times Total C	0.77**	0.10 ^{ns}
Exch. Al \times Exch. Fe	0.96***	0.63***
Exch. Al \times Exch. Mn	-0.46 ^{ns}	-0.05 ^{ns}
Exch. Fe \times Exch. Mn	-0.65*	-0.04 ^{ns}

^{ns}Not significant; *Significant at $p < 0.05$; **Significant at $p < 0.01$; ***Significant at $p < 0.001$.

Acid-buffering capacity was higher in the forest floor than in the mineral soil horizons as a result of higher organic matter content. For the mineral horizon, base saturation was significantly lower in Lake 287 (L287) than in Lake 185 (L185). In contrast, Al saturation was significantly higher in L287 than in L185, even though other chemical parameters related to acid buffering capacity (e.g., CEC_e and total C) were significantly higher in L287 than in L185 (Table 1).

For mineral horizons, concentrations of exchangeable Al and Fe, but not Mn, were significantly correlated to organic matter content (Fig. 1 and Table 2). The slope of regression equation (i.e., exchangeable Al/total C) for mineral horizons was greater in L287 than in L185. The effect of pH on exchangeable Al content in the soil was also more evident in L287 than in L185 (Fig. 1). Both

exchangeable Al and Fe contents in the soils were linearly correlated with soil pH in the two watersheds (Table 2). Pearson correlation analysis showed that exchangeable Al was highly correlated with exchangeable Fe for both the forest floor ($r = 0.96$, $p < 0.001$) and mineral horizons ($r = 0.63$, $p < 0.001$).

In this study, forest soils were more acidified in L287 than in L185 based on pH, and Ca, Al and base saturations (Table 1). When soil pH was < 4.0 , exchangeable Al concentration in mineral horizons increased sharply especially in L287 (Fig. 1). Exchangeable Al and Fe were related to soil organic matter content in mineral horizons (Fig. 1 and Table 2). It might be postulated that the release of Fe was accompanied by the increase of exchangeable Al in mineral horizons due to their similar behavior in acidic conditions and tendency to complex with organic matter [Tyler, 1981; Xue *et al.*, 2006].

Unlike Al and Fe, most of the exchangeable Mn (up to 95% of the total present) was retained in the forest floor (data not shown). Organic matter mineralization and leaching out of the forest floor may have increased concentrations of Al and Fe in soil solution infiltrating the mineral horizon [Broquen *et al.*, 2005].

The complexation of Al with organic matter is known as a major mechanism for its mobility in forest soils [Jansen *et al.*, 2005]. Thus, it is possible for the metals to be transported to the deeper mineral horizon with the dissolved organic matter (DOM) originating from the forest floor [Tyler, 1981; Merrington *et al.*, 2002]. The mobilization of Al, Fe and Mn was more evident in L287 than in L185. Further research will be conducted to elucidate the mechanisms of metal (especially for Mn) retention by organic matter under different environmental conditions in this region.

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