Long-term effects of paper mill biosolids and liming materials on soil properties, trace metals availability and distribution in a loamy soil

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Introduction

Residues from pulp and paper Kraft mills contain crop nutrients and trace metals (**TM**) that can harm the environment when applied in large amounts to agricultural lands (Gagnon *et al.* 2010). Lime addition to prevent soil acidification would be one of the aspect to reduce TM availability (Alloway 1995).

Speciation of TM can help assess how strongly they are retained in soil and how easily they may be released into soil solution (Tessier 1979; Gleyzes *et al.* 2002).

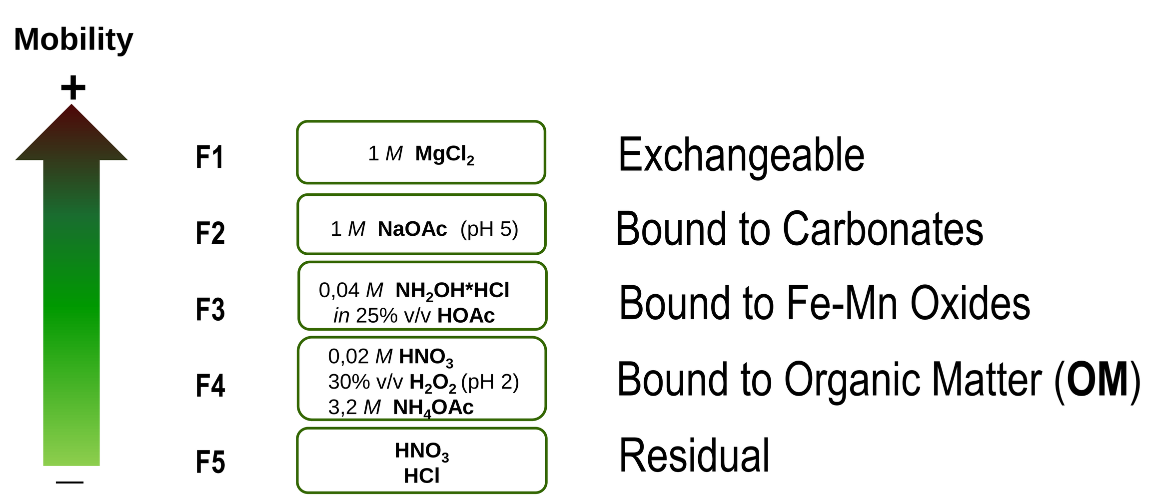
Objective

This study investigated the effects of annual repeated applications after nine years of paper mill biosolids (**PB**) and liming materials on the chemical forms of four TM, namely cadmium (**Cd**), copper (**Cu**), nickel (**Ni**), and zinc (**Zn**).

Materials & Methods

- This study was conducted (2000-2008) near Trois-Rivières, QC, Canada (46°17' N; 72°50' W) on a loamy soil.
- Treatments applied in post-seeding (mid-June) of each year are:
  - Mineral N fertilizer (120 kg N ha^{-1});
  - PB rates: 0, 30, 60, 90 t ha^{-1} (wet basis);
  - Liming materials: lime mud (**LM**), wood ash (**WA**) and calcitic lime (**CL**), applied at 3 t ha^{-1} to the 30 t PB ha^{-1} (wet basis).

  On average, 45 kg ha^{-1} mineral N were added to 30PB to meet the needs of the crop.
- Soil samples (0-30 cm) were collected on 2008 after the corn harvest.
- Soils were analyzed for:
  - pH;
  - Extractable Cd, Cu, Ni and Zn with Mehlich-3 (**M-3**) (Mehlich 1984) and DTPA-TEA (Liang and Karamanos 1993);
  - Sequential extraction (Tessier 1979) to fractionate TM into five operationally defined groups:



- The mobility factor (**MF**) were calculated as follows:

$$MF = \frac{Exchange + Carbonate}{Exchange + Carbonate + Oxides + O.M + Residual} \times 100$$

(Salbu et al. 1998)

Results & Discussion

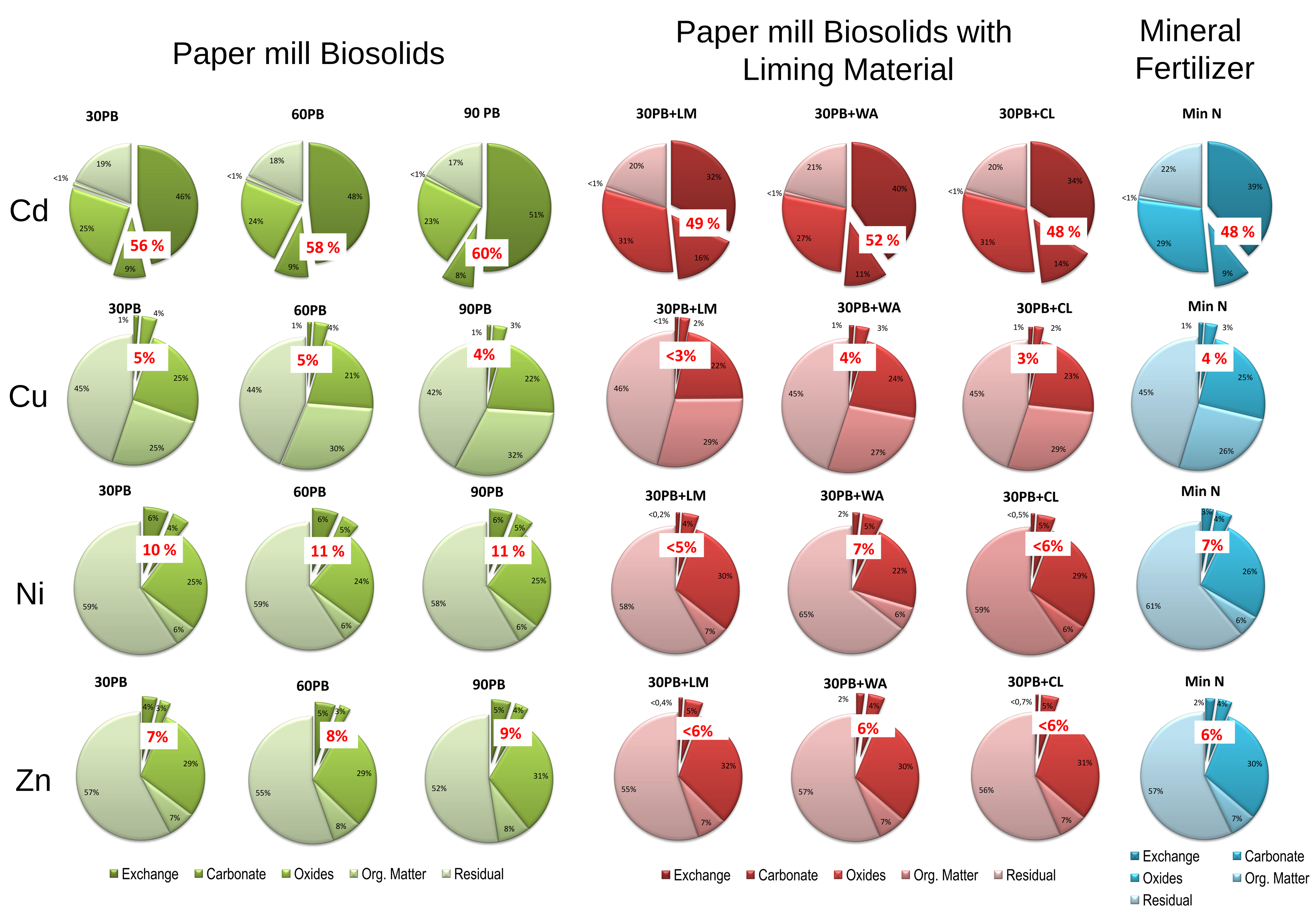


Fig. 1. Distribution of Cd, Cu, Ni and Zn in each step of the Tessier sequential extraction procedure.
The more mobile forms of TM are shown as over-exposed in each graph. The red percentage represents the mobility factor (MF).

Table 1. Availability of some soil TM in the 0-30 cm depth.

Treatments	Cd F1+F2*	Cd M-3	Cd DTPA	Cu F1+F2*	Cu M-3	Cu DTPA	Ni F1+F2*	Ni M-3	Ni DTPA	Zn F1+F2*	Zn M-3	Zn DTPA
	mg kg^{-1}			mg kg^{-1}			mg kg^{-1}			mg kg^{-1}		
Control (0PB)	0.073^{c}	0.061^{f}	0.061^{cd}	1.07^{a}	5.68^{a}	10.10^{a}	6.08^{a}	1.71^{ab}	1.73^{a}	4.9^{c}	6.4^{bc}	5.2^{b}
30PB	0.095^{b}	0.076^{cde}	0.077^{b}	0.87^{ab}	5.58^{a}	9.20^{ab}	5.87^{a}	1.77^{a}	1.70^{ab}	5.0^{bc}	6.2^{c}	5.4^{b}
60PB	0.105^{ab}	0.091^{ab}	0.099^{b}	0.80^{ab}	5.85^{a}	8.33^{abc}	6.19^{a}	1.79^{a}	1.77^{a}	6.8^{ab}	8.4^{ab}	7.3^{a}
90PB	0.113^{a}	0.097^{a}	0.102^{b}	0.76^{ab}	6.31^{a}	9.03^{ab}	5.99^{a}	1.53^{ab}	1.69^{abc}	7.1^{a}	9.2^{a}	7.7^{a}
30PB+LM	0.080^{bc}	0.086^{abc}	0.071^{b}	0.65^{b}	5.71^{a}	6.79^{c}	2.55^{b}	1.72^{ab}	1.42^{bc}	4.0^{c}	7.2^{abc}	4.1^{b}
30PB+WA	0.087^{bc}	0.081^{bcd}	0.072^{b}	0.81^{ab}	6.00^{a}	8.91^{ab}	3.91^{b}	1.48^{b}	1.65^{abc}	5.1^{bc}	7.3^{abc}	5.2^{b}
30PB+CL	0.069^{c}	0.073^{def}	0.060^{b}	0.56^{b}	5.21^{a}	7.54^{bc}	2.88^{b}	1.69^{ab}	1.40^{c}	3.9^{c}	6.3^{c}	4.3^{b}
Mineral N	0.072^{c}	0.068ef	0.057^{d}	0.74^{b}	5.92^{a}	9.43^{a}	3.83^{b}	1.59^{ab}	1.48^{abc}	4.8^{c}	6.3^{c}	4.7^{b}

Different letters represent significant differences at $P = 0.05$ according to a LSD test.
*F1+F2 = Exchangeable fraction + Bound to Carbonate fraction.

Soil pH

- Soil pH increased with liming materials application (data not shown).
  - Specifically, in the order LM ≥ CL ≥ WA after nine years of repeated applications (Robichaud *et al.* 2010).

Soil Trace Metals

- The residual fraction was by far the most abundant pool for Cu, Ni and Zn with 42-65% (fig. 1).
- By contrast, the pools considered as readily and potentially available (exchangeable and carbonate) represented between 3-12% for Cu, Ni and Zn.
- Cd showed a different pattern being mostly present in exchangeable fraction (32-51%) and up to 48-60% if we add that bound to carbonate fraction.
- Rates of PB increased the availability of TM specifically in the exchangeable fraction, whereas the addition of lime allowed to reduce it, especially for Cd and Ni (Fig. 1 and Table 1).

The first two forms (exchange and bound to carbonate) can be considered readily available to plants, while the other become available in the long term (Xian 1989)

- The higher amount of M3- and DTPA-Cu compared with (F1+F2) can be explained by the effect of chelating agents which extract part of Cu bound to OM. Indeed, $MgCl_2$ and NaOAc do not affect OM (Vidal-Vàzquez *et al.* 2005).
- Conversely, chelating agents were not effective in extracting the bioavailable Ni (Mehlich 1984; Filgueiras *et al.* 2002).

Conclusion

The application of PB in combination with liming materials contributed to decrease TM in the most mobile fractions compared with the control plots. Cd and Zn most affected TM by PB and liming materials.

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