Leaching of heavy metals (Cu, Mn, Zn, Ni, Pb and As) after six months application of raw and composted recycled paper mill sludge

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Abstract
Sludge from paper mill with recycled paper feedstock (RPMS) is a waste from secondary process of paper making, generated at final stage of paper production after biological treatment. Land application of RPMS could provide substantial benefit to plant growth and contributes to increase in organic matter that may result in chemical and physical changes in soil. Nevertheless, the potential for groundwater contamination from land application of RPMS is an important concern. Therefore, the objective of this study is to evaluate the cumulative amount of heavy metals (Cu, Mn, Zn, Ni, Pb and As) leached at 15, 30, 60 and 120 cm depths after six months application of raw and composted RPMS.The cumulative amount of Cu, Mn, Zn, Ni, Pb and As leached after six months application of raw and composted RPMS ranged from 7.9 to 72 µg, 8.6 to 212 µg, 17.9 to 462 µg, 1.2 to 18.4 µg , 0.4 to 3.5 µg and 0.05 to 2.4 µg, respectively. After 6 months of application of raw and composted RPMS, the trend of heavy metals leached seemed to increase with increasing depth (15, 30, 60 and 120 cm) for every treatment. The general trend was that only very small fractions (below 1%) of Cu, Mn, Zn, Ni, Pb and As leached relative to the total amount added with the raw and composted RPMS after six months of experiment. The percentage and cumulative amounts of heavy metals leached were very low; possibly maybe the sludge was not fully mineralized within the duration of this experiment.

Key Words
Leaching, heavy metals, recycled paper mill sludge, cumulative.

Introduction
Utilization of organic by-products as soil amendments in agricultural production exemplifies a strategy for converting wastes to resources. At present, Malaysia generates about 1,000,000 metric tons annually of recycled paper mill sludge and the quantity that needs to be disposed of is accumulating every year. Some of the wastes from the paper manufacturing mill are categorized under hazardous toxic waste by the Department of Environment, Malaysia, due to which, paper mill sludge is not well utilized in Malaysia. Paper manufacturing mills opted for land fill disposal, which might not be viable in the long run as land cost is becoming expensive. Recycled paper mill sludge is an active organic material and has potential benefits to supply nutrients for crop growth. The trial showed encouraging plant growth and demonstrated the effect of sludge in improving soil fertility and nutrient properties, as well as soil physical properties (Bellamy *et al.* 1995; Phillips *et al.* 1997; Ritter *et al.* 1992). However, if excessive pollutants are introduced by application of low quality sludge, the practice may have an adverse effect on soil and groundwater quality, and lead to contamination of the food chain. Direct utilization of raw RPMS for plant growth needs close monitoring. In this study, RPMS were turned into compost for converting these chemically complex materials into useful soil amendments. The objective of this study was to evaluate the cumulative amount of heavy metals (Cu, Mn, Zn, Ni, Pb and As) leached at 15, 30, 60 and 120 cm depths after six months application of raw and composted RPMS.

Methods
Experimental design
The field study was located at University Agriculture Park, Puchong, Selangor, Malaysia. Twelve plots (10m × 6 m) were established and each plot consists of 9 plants of *Khaya senagelensis* seedlings planted at 4m × 3m distance with 3 treatments and 4 replications arranged in a completely randomized block design (CRBD). *Khaya senegalensis* is a forest tree identified under the 9th Malaysian Plan as one of the potential timber species for large scale forest plantation. Composted and raw RPMS were air dried and passed through a 4.7 mm sieve and applied around the tree within 50 cm radius. Treatments established were control, 0.7 t/ha raw RPMS and 1.3 t/ha composted RPMS.

Soil, raw and composted recycled paper mill sludge
Raw RPMS from the biological treatment pond was collected from the United Paper Mill in Selangor, Malaysia. Raw RPMS mixed with EFB fibres at 1:1 ratio (v/v) was used in this study as composted RPMS was found suitable for land application (Rosazlin *et al.* 2009). pH and mean concentrations of heavy metals in the soil, composted and raw RPMS used in this experiments are shown in Table 1.

Table 1. pH and mean concentrations of heavy metals in the soil, composted and raw recycled paper mill sludge used in the experiments (on a dry weight basis).

	pH	Cu (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	As (mg/kg)
Soil	5.06	7.3	23	30	5.7	7.9	35
Composted RPMS	7.84	72	342	183	22	89	150
Raw RPMS	7.18	88	325	251	26	177	186

Sampling
Leachate solutions were sampled at 15, 30, 60 and 120 cm depth, with 1905 slim tube water sampler (Soil Moisture Equipment Corp., SA). Slim tube water samplers were located at 50 cm radius from the plant. Water samples were collected every week to avoid overflow of water in the tube. On dry season, water samples were combined for following weeks to get enough water samples for analysis. Finally, a total of 11 water samples were collected between July 2009 and January 2010 with total rainfall of 1609mm. Leachate were sampled by application of a vacuum to the sampler at a level of 70 kPa, and then transported to the laboratory and stored in a refrigerator at ≤4 ºC.

Laboratory Analysis
Water samples were filtered and concentrations of Cu, Mn and Zn in the leachate samples were determined by atomic absorption spectrophotometer (5100 PerkinElmer, USA). Given the low concentration of Ni, Pb and As in the leachate, these elements were measured out using atomic absorption spectrophotometer with graphite chamber (4100 Graphite Perkin Elmer Zeeman).
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Results
The cumulative amount of Cu, Mn, Zn, Ni, Pb and As leached after six months application of raw and composted RPMS ranged from 7.9 to 72 µg, 8.6 to 212 µg, 17.9 to 462 µg, 1.2 to 18.4 µg, 0.4 to 3.5 µg and 0.05 to 2.4 µg, respectively (Figure 1). The amounts were very low, maybe the applied sludge was not fully mineralized within duration of this experiment. Generally, quantities of metal leached followed the order of Zn > Mn > Cu > Ni > Pb > As.

After 6 months of experiments, the composted RPMS gave the highest cumulative leached amount at 120 cm depth compared raw RPMS. Treatment with raw RPMS shows significantly higher leaching compared to composted RPMS and control in cumulative leached amount of Mn and As except 60 and 30 cm depth, respectively. Application of raw RPMS was significantly different at 60 and 120 cm depth but not significant different at 15 and 30cm in leached Zn. Meanwhile, the cumulative amount of leached Zn is highest compared to other metals. These observations support assertions that there is a soluble or mobile fraction of heavy metals in soil (Sloan *et al.* 1997). The cumulative amount of Ni and Pb after six months application of raw and composted RPMS was significantly higher than control for every depth except at 60 cm depth, despite their differing chemical properties (Table 1). This suggests that soil physical processes may be more important than chemical processes in determining the distribution and mobility of these metals.

After 6 months of application the raw and composted RPMS, trend of heavy metals leaching seemed to increase with increasing depths for every treatments. This observation is supported by Chaney and Ryan (1993) who reported that the specific metal adsorption capacity added to soil by sludge plays a significant role in controlling phytoavailability of metals. Overall, treatment with raw RPMS showed significantly higher heavy metal in the leachate than composted RPMS indicative of more rapid leaching compared composted RPMS and control even the amount of application is half than composted RPMS.

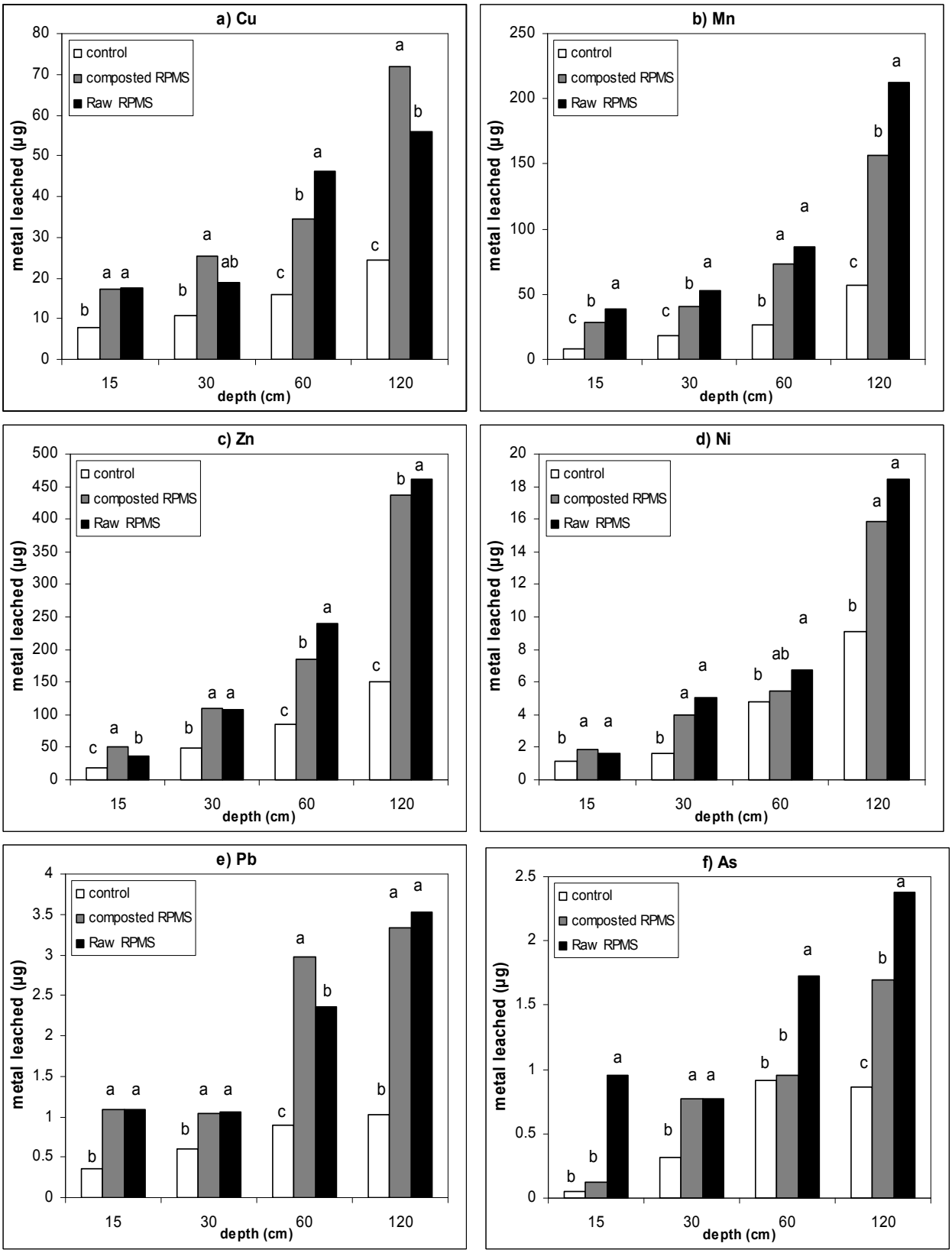

Figure 1. Cumulative amount of a) Cu, b) Mn, c) Zn, d) Ni, e) Pb and f) As leached at different depths after 6 months application of raw and composted recycled paper mill sludge. Similar letter above bar within treatment in each depth indicate the bar are not significantly different at $p<0.05$, according to the Tukey.

Table 2 shows the percentage of total amounts of leached Cu, Mn, Zn, Ni, Pb and As relative to the corresponding total amount added with the raw and composted recycled paper mill sludge after six months of experiment. There was no significant difference for Cu, Ni, Pb and As in the percentage leached between raw and composted RPMS treatments. Generally, only very small fractions (below 1%) of the total amounts of Cu, Mn, Zn, Ni, Pb and As were leached after six months for the raw and composted RPMS treatments. Six months duration of experiment is not enough to show the trend of percentage loss as water through soil profile. According to Egiarte *et al.* 2008, after 2.5 years study, application of 17 Mg/ha sludge only gave 1.5% and 0.7% of Zn and Pb leached at 50 cm depth.

Table 2. Percentage of total amounts of Cu, Mn, Zn, Ni, Pb and As leached relative to the corresponding total amount added with the raw and composted recycled paper mill sludge after six months of experiment.

	Cu	Mn	Zn	Ni	Pb	As
Composted RPMS	0.08% a	0.04% b	0.20% b	0.05% a	0.02 %a	0.001% a
Raw RPMS	0.16% a	0.12% a	0.32% a	0.10% a	0.02% a	0.003% a

Letter with the same alphabet list in the column are not significant different at $p<0.05$, according to the T-Test

Conclusion

Application of raw and composted RPMS for six months showed an increase in cumulative amount of leached Cu, Mn, Zn, Ni, Pb and As with increasing depth (15, 30, 60 and 120 cm) for every treatments. Generally, the amount of metal leached followed the order of Zn > Mn > Cu > Ni > Pb > As. Only very small fractions (below 1%) of the total amounts of Cu, Mn, Zn, Ni, Pb and As were leached after six months for the raw and composted RPMS treatments.

References

Bellamy KL, Chong C, Cline RA (1995) Paper sludge utilization in agriculture and container nursery culture. *Journal of Environmental Quality* **24,** 1074-1082.

Chaney RL, Ryan JA (1993) Heavy metals and toxic organic pollutants in MSW-compost. In 'Science and engineering of composting: Design, environmental, microbiological and utilization aspects. Renaissance Publication (Ed Keeneer HM). pp. 451-506 (Renaissance Publication: Ohio).

Egiarte G, Pinto M, Ruíz-Romera E, Camps Arbestain M (2008) Monitoring heavy metal concentrations in leachates from forest soil subjected to repeated applications of sewage sludge. *Environmental Pollution* **156,** 840-848.

Phillips R, Kirkpatrick K, Scotford IM, White RP, Burton RGO (1997) The use of paper mill sludges on agricultural land. *Bioresource Technology* **60**, 73-80.

Ritter WF, McDermott JG, Chirnside AEM (1992). Use of paper mill residuals as soil amendments. *Communication Soil Science ad Plant Analysis* **23**, 469-488.

Rosazlin A, Fauziah CI, Wan Rasidah K, Rosenani AB (2009) Characteristics of compost from recycled paper mill sludge mixed with oil palm empty fruit bunches. In 'Proceedings of the Agriculture Congress' (Ed Dzolkifli O), pp. 286-288 (UPM Publication; Malaysia).

Sloan JJ, Dowdy RH, Dolan MS, Linden DR (1997) Long-term effects of biosolids applications on heavy metal bioavailability in agricultural soils. *Journal of Environmental Quality* **26,** 966-974.