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Degradation and Ecotoxicity of C14 Linear Alpha Olefin Drill Cuttings in the Laboratory and the Field

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Abstract

Laboratory and field studies were conducted on C14 linear alpha olefin (LAO) mud drill cuttings. In the laboratory, LAO drill cuttings applied to a loam soil at a total extractable hydrocarbon (TEH) concentration of 4.8% (wt:wt) degraded by 92% to a TEH residual of 0.38% after 3 months. This residual was nontoxic to plants, earthworms, springtails and Microtox™ bacteria based on both acute and chronic toxicity bioassays. Earthworm growth and reproduction after 2 months exposure to soil with remediated LAO cuttings were greater than in the untreated soil. In the field, LAO cuttings were spread over a silty loam soil in southern Alberta at an inital concentration of 3.1% (wt:wt) during the fall. The following spring the field was tilled, fertilized and planted with barley. The LAO in the soil degraded by 68% to a 1% LAO level by harvest (11 months treatment), and was further reduced to 0.25% after 23 months of landfarming treatment. At 1% LAO, barley growth was not significantly reduced in the laboratory or the field. In contrast, 1% LAO significantly inhibited earthworm growth and reproduction, and killed the springtails. The Microtox™ bioassay revealed no toxicity in water extracts of the soil. Co-composting studies in northern British Columbia involved mixing LAO cuttings with wood fibre at a ratio of 1:3 and applying fertilizer. After 22 months treatment, the TEH at two separate sites had decreased by 95%, from initial concentrations of 8.1 and 15.2% to final concentrations of 0.4 and 0.6%, respectively. Results to date indicate that C14 LAO drill cuttings degrade readily under both laboratory and field conditions, and that both landfarming and co-composting are effective means for eliminating and detoxifying C14 LAOs.

Introduction

Linear alpha olefins (LAOs) are clear, colorless, synthetic, hydrocarbon liquids made by the polymerization of ethylene. They are being used extensively as base fluids for offshore drilling, primarily because of their low toxicity and high biodegradability (Anonymous 2002). Recently, research was initiated to evaluate the potential of LAOs as base fluids for terrestrial drilling, and to compare the environmental properties of olefins to diesel oil, a base fluid commonly used in drilling muds in western Canada. Laboratory studies to assess the biodegradation and ecotoxicity of 2% C14 LAO (wt:wt) in soil revealed that this olefin degraded readily with no toxic residues remaining in the soil after 3 months incubation (Visser et al. 2002). In contrast, diesel oil degraded more slowly and was still extremely toxic after incubation. These results strongly suggested that drilling wastes generated from drilling muds containing C14 LAOs would be more amenable to bioremediation, and pose less of an environmental risk in the field, than similarly generated diesel cuttings.

Although the biodegradation and ecotoxicity potential of C14 LAO fluid in soil has been studied, the degradation and toxicity of C14 LAO, when it forms a component of drill cuttings, has not been determined, either in the laboratory or the field. Therefore, research was conducted to evaluate the degradability and toxicity of C14 LAO drill cuttings in silty loam in the laboratory. Since laboratory observations may not accurately reflect response in the field, field studies were initiated also to evaluate landfarming and co-composting technologies for treating LAO drill cuttings.

Objectives. Specific objectives of the research were: (1) to determine the potential degradability and ecotoxicity of C14 LAO drill cuttings when mixed into silty loam soil and bioremediated for 3 months in the laboratory; (2) to monitor the degradation and ecotoxicity of C14 LAO cuttings during landfarming treatment in a barley field in southern Alberta, and to compare the degradation/toxicity dynamics in the field with that observed in the laboratory (objective 1), and (3) to evaluate co-composting as a field technology for treating C14 LAO drilling wastes.

Properties of C14 LAO Fluid and Drill Cuttings.

C14 LAO (BP trade name: Amodrill® 1410) was the base fluid used in all of the drilling muds used to generate the drill

cuttings tested in the following experiments. Some of the physical/chemical/biological properties of this fluid are:

- aromatic content: 0%
- polynuclear aromatic hydrocarbons (PAH): <0.001%
- viscosity 40ºC, cSt: 2.09
- pour point: -18ºC
- flash point: 116ºC
- biodegradation potential: 96%

(Anonymous 2002).

The C14 LAO-based invert mud contained 11.4% C14 hydrocarbon with potassium formate as the internal phase (90:10 olefin: internal phase). The LAO drill cuttings used in the laboratory and landfarming studies had hydrocarbon contents ranging from 6.1 to 13.7%, an alkaline pH (9.6 to 12.2) and ECs ranging from 2.6 to 9.7.

1. Laboratory Study to Determine Degradation and Ecotoxicity of C14 LAO Drill Cuttings.

The objective of this research was to monitor the degradation and ecotoxicity of C14 LAO drill cuttings in the lab under conditions simulating those in a landfarming operation. It was also of interest to determine the C14 LAO residual remaining in the soil following bioremediation to a stable hydrocarbon endpoint, and to assess the ecotoxicity associated with this residual.

Methods. After conducting an initial assessment of the drilling waste, receiving soil and the area available for landfarming, an application rate of approximately 3.3 cm of drill cuttings to 15 cm of soil was recommended. For the laboratory study, it was necessary to convert this application rate to a mass basis, and this was found to be 60 g of cuttings in 100 g dwt receiving soil. The receiving soil originated from the landfarm site, and was a silty loam that had been amended with cow manure to improve nutrient conditions for hydrocarbon bioremediation. The soil was sieved (4 mm) and homogenized prior initiation of the experiment, and had a $pH_{1:2}$ of 7.0, an $EC_{1:2}$ of 0.24 dS/m and a background TEH content of 710 µg/g dwt.

Biodegradability. Aliquots of field moist receiving soil, each equivalent to 100 g dwt, were treated with 60 g LAO drill cuttings. Three replicates with no cuttings (controls) and 3 replicates with LAO cuttings were tested. Each LAO cuttings replicate was amended with 400 µg N/g dwt and 80 µg P/g dwt so that LAO degradation would not be constrained by low nutrient conditions. Previous studies demonstrated that it is essential that available nitrogen be sufficient to allow rapid and complete degradation of the highly bioavailable carbon in the C14 LAO. Soil moisture was adjusted to approximately 35% (dwt), and each sample was placed in a glass tube and incubated at 22ºC. Respiration, measured as CO_2 efflux using an Infrared Gas Analyzer (IRGA), was determined at regular intervals for 90 days to determine the potential for degradability and to identify the biological treatment endpoint. The treatment endpoint is defined as the point at which respiration stabilizes, and there is very little difference in CO_2-C release between successive sample times. This endpoint signals the exhaustion of easily available hydrocarbons and the initiation of a slow decay phase. In the case of the LAO cuttings, a treatment endpoint had been achieved after 90 days incubation.

In addition, TEH in both control and LAO cuttings treatments were analyzed at the initiation of the biodegradability study, and after 90 days when a biological treatment endpoint had been achieved, as indicated by stable respiration measurements. Extractable hydrocarbons (C11-C40+) were quantified using the capillary column gas chromatography/flame ionization detection (GC/FID) method described in Method No. G108.0 (Alberta Environment 1992). This method involves extraction of soil with methanol and methylene chloride, centrifugation, and the analysis of the methylene chloride layer by injection into a gas chromatograph. Individual carbon groups are separated according to boiling point and quantified. Carbon scans and chromatograms were used to quantify changes in the C14 LAO hydrocarbon, which was readily identifiable as a distinct C14, C15 peak. All hydrocarbon data in the LAO cuttings treatment were corrected for background carbon associated with the soil organic matter.

Ecotoxicity. Four ecotoxicity tests, representing various tropic levels, were conducted immediately following cuttings application, and after 90 days bioremediation when LAO degradation had stabilized. The assays included a phytotoxicity test with barley; assessments of earthworm survival, growth and reproduction; springtail survival; and the Microtox™ bioassay. Because of the amount of soil required to conduct the assays, bulk samples of soil with and without LAO cuttings were incubated in conjunction with, but separate from, the respiration samples. Moisture, nutrient and temperature conditions of the bulk samples were identical to those of the respiration samples.

Phytotoxicity bioassay. Twenty barley seeds were planted in undiluted soil from each of the control and LAO cuttings treatments. There were 3 replicates per treatment and the plastic dishes containing the soil were incubated under controlled moisture, temperature (23-28ºC) and light conditions in a growth chamber with a photoperiod of 16 h light and 8 h dark. After 5 days, emergence was evaluated by counting the number of seedlings that had emerged at least 3 mm above the soil surface. Also, shoot and root lengths and weights of 10 randomly selected seedlings per replicate were measured. This bioassay is a measure of acute toxicity.

Earthworm bioassay. Three replicates of 500 cc soil for each of the control and LAO cuttings treatments were placed in 900 ml glass jars. Ten large, healthy earthworms (*Eisenia andrei*) were placed on the surface of the soil in each jar, and the jars were closed with a vented lid. The test units were incubated at room temperature (22±2ºC) under continual illumination. After 14 days exposure, percent survival of the earthworms was determined for each replicate, and earthworms and soil returned to the jar. After 90 days incubation, earthworm survival was measured again. Also, the mass of adult earthworms was determined by oven drying the adult earthworms at 80ºC, and earthworm reproduction per 10 adult earthworms was assessed by counting juvenile earthworms in each jar. The 14-day survival assay is indicative of any acute toxicity associated with the LAO cuttings, while earthworm mass and reproduction are

measures of any chronic toxicity that may be caused by a soil contaminant.

Springtail bioassay. Three replicate aliquots of 30 g moist soil from each of the two treatments were placed in 125 ml glass jars and 10 healthy, adult springtails (*Folsomia candida*) were introduced into each replicate. After 7 days exposure, surviving springtails were floated out of the soil with a fine jet of deionized water, and counted. Results of this assay are a measure of acute toxicity.

Microtox™ bioassay. Duplicate 25 g dwt equivalent soil samples from each of the control and LAO cuttings treatments were slurried in deionized water at a ratio of 1:4 (wt:wt) for 24 hours. The slurries were centrifuged and the supernatent tested for reductions in light production by *Vibrio fischeri* using the protocol outlined in Report EPS 1/RM/24 (Environment Canada 1992). This bioassay measures acute toxicity.

Results and Discussion

Biodegradability.

Respiration. The microbial biomass responded extremely rapidly to the presence of the LAO cuttings. Respiration peaked at 74 µg CO_2-C/g dwt/hr within 3 days of adding the LAO cuttings to the soil, demonstrating that the LAO was highly bioavailable (Fig. 1). Following the peak, respiration subsided quickly indicating rapid exhaustion of the LAO carbon source. After 90 days incubation, respiration had stabilized at 10 µg CO_2-C/g dwt/hr. Higher respiration in the LAO cuttings treatment than in the control soil throughout the monitoring period shows that the LAO contributed significantly to the amount of carbon available for growth and reproduction by the microbial biomass. This is especially evident when the cumulative CO_2-C loss from soil with and without LAO drill cuttings is considered. Fig. 2 clearly shows that cumulative respiratory carbon loss from the LAO cuttings was considerably greater than that from the untreated soil. Indeed, the amount of LAO carbon lost through respiration over the course of the study was approximately 23000 µg/g dwt soil-cuttings mixture which constitutes about 48% of the LAO carbon that was added to the soil. During the degradataion process, C14 LAO would also be incorporated into microbial biomass.

Hydrocarbon Analyses. Since the main form of carbon in the LAO cuttings was C14 hydrocarbon, it was possible to identify it on a chromatogram, and to quantify it from the accompanying carbon scans. In this study, carbon scans of the untreated receiving soil made it possible to correct the C14 LAO carbon for background carbon in the soil organic matter.

Rapid disappearance of the LAO observed in the respiration profiles was confirmed by the TEH measurements. After 90 days incubation the amount of LAO carbon decreased from 48000 µg/g dwt soil (4.8%) initially to 2500 µg/g dwt soil (0.25%), which represents a loss of 95% of the LAO (Fig. 3). The linear molecular structure of the C14 LAO, with a double bond at the end of the chain, make this olefin highly biodegradable, as is evident from these data.

Ecotoxicity.

Phytotoxicity. Barley emergence was not sensitive to fresh 4.8% LAO in the cuttings, since there was no significant difference in emergence between control and LAO cuttings treatments prior to bioremediation (Table 1). Also, root length was not significantly reduced by fresh LAO cuttings, while shoot length, and shoot and root mass were (Table 1; Fig. 4). Therefore, barley growth, but not emergence, was inhibited by 4.8% C14 LAO. After 90 days incubation of the cuttings, no acute phytotoxicity was evident as barley shoot length and barley mass production were almost identical in the control and LAO cuttings treatments (Table 1, Fig. 4).

Earthworm bioassays. Although earthworm survival was not significantly reduced by the presence of 4.8% LAO in cuttings either before or after bioremediation, earthworms in soil containing fresh cuttings were visibly smaller than those in the control soil (Table 1). However, any earthworm toxicity that may have been associated with the fresh LAO cuttings was eliminated after 90 days incubation and 95% loss of the LAO carbon. Earthworm survival in the presence of bioremediated LAO cuttings was 100%, adult earthworm biomass was not significantly different from that in the control soil, while juvenile production/10 adult earthworms was significantly higher in the LAO cuttings treatment than in the untreated soil (Table 1, Fig. 5). More earthworm reproduction in the LAO cuttings treatment than in the control treatment can be explained by more food availability in the LAO cuttings soil caused by an increase in microbial biomass in this treatment.

Springtail Survival. Springtails (*F. candida)* were extremely sensitive to fresh C14 LAO cuttings since there was complete mortality of this species after 7 days exposure (Table 1). However, after 90 days bioremediation, springtail survival was 100% demonstrating that there was no acute toxicity associated with the LAO residual remaining in the soil after incubation.

Microtox™ Bioassay. A water extract from soil containing 4.8% fresh LAO in cuttings tested moderately toxic, but this toxicity was completely eliminated after 90 days bioremediation of the cuttings (Table 1).

Summary. When applied to loam soil at 4.8%, C14 LAO in drill cuttings has the potential to degrade almost completely, leaving a small residue (0.25%) that has no acute toxicity to barley, earthworms, springtails and Microtox™ bacteria, and no chronic toxicity to earthworm growth and reproduction. Similar results were obtained for LAO base fluid in a previous study (Visser et al. 2002).

2. Landfarming Study to Determine Degradation and Ecotoxicity of C14 LAO Cuttings in the Field.

Field studies to confirm that C14 LAO drill cuttings degrade as rapidly in the field as they do in the laboratory are lacking. Thus, a biomonitoring study was performed to evaluate landfarming as a technology for biodegrading C14 LAO drill cuttings, and for reducing any ecotoxicity associated with the cuttings.

Methods. Landfarming of the C14 LAO drill cuttings was conducted in a barley field in southern Alberta. The receiving soil was a silty loam amended with cow manure to improve soil fertility as described previously for the laboratory study. The 0-15 cm deep soil had a pH (saturated paste) of 6.4 and an EC (saturated paste) of 0.4 dS/m.

In September 2001, C14 LAO drill cuttings were spread on the soil surface over an area of 0.75 ha with a grader, to achieve an approximate thickness of 3 cm cuttings. The site was disced lightly following cuttings application. An untreated control plot was established adjacent to the landfarm plot. In May 2002, the LAO cuttings were incorporated into the topsoil to a target depth of 10 cm. Both landfarm and control plots were fertilized with 365 kg/ha 46-0-0 and 55 kg/ha 12-51-0, and seeded with barley at a rate of 2 bushels/ha.

Biomonitoring was initiated approximately 2.5 months after applying the LAO cuttings. On each monitoring date, 15 soil samples were removed from across each of the landfarm and control plots and combined for a total of two bulk samples, one from each plot. Soil sampling was repeated 7, 8, 10.5, 20 and 22 months following application of the cuttings. At each sample time, the bulk soil samples were sieved (4 mm), homogenized and assessed for hydrocarbon content. Soil respiration and ecotoxicity were evaluated at 2.5, 7, 8 and 10.5 months following the application of the LAO cuttings.

Hydrocarbon Analyses. Extractable hydrocarbons (C11-C40+) at each sample time were quantified as described previously for the laboratory study. Since the C14 LAO was readily identifiable on the chromatogram and in the carbon scan, data are reported as C14 LAO.

Respiration. Because carbon metabolism by the microbial biomass is dependent on adequate nutrients, especially nitrogen (N) and phosphorus (P), respiration with and without added N and P can reveal if hydrocarbon degradation is being constrained by a lack of nutrients. Thus, at each sample time, 50 g dwt equivalent soil samples from the control and LAO cuttings plots were moistened to 35% (dwt) with deionized water and were left unfertilized or were fertilized with N and P. Duplicate samples of each fertilized and unfertilized treatment in each plot type were attached to an IRGA, and respiration was monitored for 31 days as described above.

Ecotoxicity.

Barley response in the laboratory. A long-term barley bioassay was used to monitor phytotoxicity in the landfarm soil over the first 10 months of treatment. At each sample time, 500 cc of sieved soil was moistened with deionized water, fertilized, placed in a plastic cup and planted with 5 healthy, unblemished barley seeds. Three replicates were established for each of the control and LAO cuttings treatment at each sample time. Plants were grown in a growth chamber as described for the laboratory study. Soil moisture was adjusted daily.

After 14 days growth, emergence, shoot and root elongation, and shoot and root mass of all seedlings were determined as described previously. This longer-term bioassay is recommended for monitoring chronic toxicity.

Barley response in the field. Barley production in the control and LAO cuttings treated plots was determined between 8 and 10.5 months following application of the LAO cuttings application (spring/summer 2002). At 10.5 months, barley shoots in each of 10, 50x50 cm quadrats per treatment were clipped 1-2 cm above the soil surface. Seed heads were separated from the shoots and dried at 80ºC to obtain a dry weight estimate/m^2.

Earthworm bioassays. At each sample time, earthworm survival after 14 days exposure, was determined using the methodology described previously. No earthworm mortality was observed on any of the sample times; therefore, a longer term (70 day) earthworm bioassay was conducted 10.5 months after LAO cuttings application, to test for chronic toxicity. After measuring 14 day survival, the earthworms and soil were returned to the jars and incubated for a total of 70 days. Earthworms were fed cooked oatmeal weekly to standardize food availability in the control and LAO cuttings treatments. Adult earthworm survival and dry mass, and juvenile production/10 earthworms were assessed after 70 days exposure using the techniques already described.

Springtail bioassay. Springtail survival after 7 days exposure (acute toxicity) was determined at each sample time in the landfarm and control soils using methodologies outlined above.

Microtox™ bioassay. This bioassay was conducted at each sample time until any toxicity associated with the LAO cuttings treated soil had dissipated relative to the control soil. Methodologies for conducting this bioassay have been given previously.

Results and Discussion

Hydrocarbons. TEH was not measured immediately following application of the C14 LAO drill cuttings. However, based on the hydrocarbon content of the cuttings and the application rate (3 cm layer), it was estimated that the amount of hydrocarbon applied with the cuttings at the initiation of the study was approximately 27000 µg/g dwt. The TEH level in the landfarm soil 2.5 months after LAO cuttings application was 31000µg/g dwt. Because the estimated initial TEH content and the actual amount measured 2.5 months after cuttings application were similar, it was assumed that there was very little degradation of the LAO between the time the cuttings were applied (Sept 2001) and the first sample time (Dec 2001), 2.5 months after application.

Approximately 20% of the C14 LAO dissipated between December and April, demonstrating that LAO degradation can proceed over the winter period (Fig. 6). A significant reduction in C14 LAO between 7 and 8 months after cuttings application is attributed to enhanced degradation of the LAO due to tillage of the cuttings into the soil 2 weeks prior to sampling. Prior to spring tillage, the cuttings were located primarily at the soil surface, and tillage may have improved moisture, temperature and nutrient conditions for degradation. Between 8 and 10.5 months, the amount of C14 LAO did not decline, but appeared to stall at a residual level of approximately 1%. This lack of LAO degradation during the summer months may have been caused by a deficiency in available soil N that is required by the microbial biomass to metabolize LAO carbon.

Monitoring of C14 LAO continued in spring and summer 2003, 20 and 23 months after LAO cuttings application. Between 10.5 and 20 months, LAO levels declined significantly to 3900 ug/g dwt, and were further reduced to 2500 ug/g after 23 months. Thus, two years of landfarming treatment resulted in almost complete degradation of the C14 LAO (92%) introduced with the cuttings. This

demonstrates that landfarming is an effective means for treating C14 LAO drill cuttings. Rapid degradation of alpha olefins has been observed also by Melchor et al. (2001) in a field study conducted with drill cuttings applied to a tropical wetland in Venezuela.

Although the concentration of C14 LAO tested in the laboratory study (48000 µg/g dwt) was greater than the amount treated at the landfarm site (31428 ug/g dwt), residual LAO remaining in the soil after 3 months incubation in the laboratory was identical to the residual LAO in the soil after 23 months landfarming treatment, i.e. 2500 µg/g dwt. This confirms that C14 LAO is highly biodegradable both in the laboratory and the field, but that less than optimal environmental conditions in the field (moisture, temperature, nutrient extremes) can significantly reduce degradation rates and lengthen the treatment time.

Respiration. Respiration was monitored over the first 10.5 months of the study. At each sample time, CO_2 efflux was greater in the LAO cuttings soil than in the control soil, which shows that there was significantly more bioavailable carbon in the LAO soil, and that this LAO was being actively metabolized (Fig. 7). Respiration was relatively stable or increased slightly between 7 and 10.5 months landfarming treatment. Relatively high soil respiration in the landfarmed soil, compared with the control, at the termination of the monitoring period shows that the LAO carbon had not degraded to a stable endpoint after landfarming the cuttings for 10.5 months.

The respiration pattern observed for LAO cuttings incubated under laboratory conditions (Fig. 1) differed from that observed for the LAO cuttings landfarmed in the field. A rapid increase in CO_2 evolution immediately following incorporation of the LAO cuttings into the soil was evident in the laboratory, but not in the field. Degradation of C14 LAO in the field may have been constrained by a lack of N, thereby changing, and possibly stalling, the degradation process. When C14 LAO soil, sampled after 2.5, 7, 8 and 10.5 landfarming treatment, were fertilized with N and P, respiration increased significantly (Fig. 8). Cumulative carbon loss from landfarmed soil supplemented with nutrients was significantly greater than that from unamended landfarmed soil after 31 days incubation. This suggests that degradation of C14 LAO in the field was inhibited by a lack of nutrients, particularly between the 7 and 10.5 month sample times. That LAO degradation was repressed was evident also in the rapid response of the microbial biomass in the landfarmed soil to nutrient amendation. Regardless of sample time, respiration in the landfarmed LAO cuttings soil peaked at relatively high rates (e.g. 50 µg CO_2-C/g dwt/h in the 10.5 month samples) within 24 hours of nutrient addition. It is possible that with additional fertilizer and tillage at the landfarm site, C14 LAO would have degraded more rapidly than was observed in this study, thereby shortening the treatment time.

Ecotoxicity.

Barley response in the laboratory. Barley shoot lengths, shoot weights and total plant weights were significantly reduced by C14 LAO cuttings following 2.5 and 7 months landfarming treatment, when LAO contents ranged from 2.5 to 3.1% (Table 2; Fig. 9). Following tillage of the LAO cuttings into the soil at 8 months, and a reduction in C14 LAO to 8000 µg/g dwt, significant effects on barley growth could no longer be detected. Also, barley growth was not significantly affected by the 10000 µg LAO/g dwt measured in soil that had been landfarmed for 10.5 months. Thus, barley productivity is not compromised by 1% LAO in the soil, but levels of 2.5% will reduce growth significantly.

Barley response in the field. In the field, neither barley shoot nor seed production were significantly reduced in the landfarm plots between 8 and 10.5 months, when LAO levels in the soil ranged from 8000 to 10000 µg/g dwt. Barley shoot and seed production (mean±SD) in the control plot was 282±66 g dwt and 164±48 g dwt/m^2, respectively, compared with 208±98 and 138±84 g dwt/m^2 in the landfarmed LAO cuttings plot. Barley crop response in the field supported the observations made in the laboratory in that 1% LAO did not inhibit barley crop production.

Earthworm response. Based on the 14 day earthworm survival bioassay, there was no acute toxicity associated with the LAO cuttings-treated soil at any of the sampling times, since there was 100% survival in both control and landfarm soil on each occasion (Table 2). However, long-term exposure (70 days) of the earthworms to 10.5 month old landfarmed soil revealed that 10000 µg LAO/g dwt significantly reduced adult earthworm growth, and completely inhibited reproduction as no juveniles were produced in the LAO soil (Fig. 10). Earthworm bioassay data from the landfarm study corroborate those obtained in the laboratory, and clearly show that earthworm growth and reproduction endpoints are more sensitive indicators of LAO toxicity than earthworm survival. Of all the ecotoxicity endpoints measured in this study, earthworm survival was the least sensitive.

Springtail response. As was observed in the laboratory study, *Folsomia candida* was extremely sensitive to the presence of LAO in the soil because there was virtually complete mortality of this species in landfarmed soil on all sampling dates (Table 2). Since this springtail species is extremely sensitive to C14 LAO, it may be an excellent candidate for monitoring LAO detoxification.

Microtox™ response. The Microtox™ was conducted to determine if there was any toxicity associated with leachates potentially generated by the landfarmed soil over the term of the study. Although there was slight Microtox™ toxicity in the landfarmed soil, 2.5 and 7 months after C14 LAO cuttings application, no LAO toxicity was detected after tillage at 8 months when the LAO concentration was reduced to less than 1% (Table 2).

Summary. By landfarming C14 LAO drill cuttings, LAO contents in the soil were reduced from 31400 to 10000 µg/g dwt (68% mass loss) after 10.5 months treatment. Additional treatment resulted in further degradation of the LAO to 2500 µg/g dwt (92% mass loss) after 23 months. Respiration monitoring of the landfarmed soil over the first 10.5 months of treatment, revealed that the CO_2 efflux pattern characteristic of C14 LAO treated soil in the laboratory (i.e. high initial CO_2 peak, followed by a rapid decline and low stable respiration when the LAO has been degraded) was not observed in the field. Fertilization of landfarm soil with N and P significantly increased respiration and this suggests that

LAO degradation in the field was constrained by a lack of nutrients.

From the various bioassays used to monitor ecotoxicity, it can be concluded that approximately 1 year following application of the LAO cuttings, there was very little phytotoxicity and Microtox™ toxicity remaining in the landfarmed soil. However, the earthworm reproduction and the springtail survival test revealed extreme toxicity associated with the C14 LAO cuttings after 1 year landfarming treatment. These results show that 10000 ug LAO/g dwt soil may be acceptable for barley crop production, but it is not protective of the soil fauna. With additional degradation of the LAO to levels of 2000 – 3000 ug/g dwt, it is highly likely that toxicity to the soil fauna would be eliminated also, as was demonstrated in the laboratory study.

Based on sensitivity to LAO, the following endpoints were ranked from most to least sensitive: springtail survival = earthworm juvenile production > earthworm mass production > barley shoot length = barley shoot weight > total barley plant weight > Microtox™ > barley root weight > barley root length = earthworm survival. Because of the variable sensitivities of the test species and measurement endpoints, it is imperative that more than one test species, and both short- and long-term bioassays be considered in a biomonitoring protocol. The discrepancy in sensitivity between species is illustrated by data from the springtail and earthworm survival bioassays; in contrast to the springtails, which exhibited virtually 100% mortality in LAO cuttings-treated soil on all sampling dates, earthworms exhibited 100% survival throughout the study. However, the earthworm reproductive assay proved to be as sensitive to the C14 LAO as the springtail bioasssay.

3. Co-Composting Study to Determine Degradation of C14 LAO Drill Cuttings in the Field.

Petroleum hydrocarbons (PHCs) such as gasoline, diesel fuel, jet fuel and grease can all degrade extensively when co-composted with organic material such as wood residues or leaf litter (EPA530-R-98-008). In Alberta, PHC-contaminated drilling wastes have been co-composted with wood fibre generated by the forestry industry, usually at a ratio of 3:1 or 2:1 wood fibre:drilling waste. Advantages of using wood residue as the organic matrix for co-composting are:

- PHC cuttings can be mixed with wood residue as the cuttings are generated at the drilling site, thereby reducing the risk of soil and groundwater contamination.
- PHC bioremediation time is extended as a result of heat generation during the composting process. The heat generated is sufficient to allow biodegradation to continue over the winter months.
- the wood residue is sorptive and may stabilize PHCs sooner by binding and incorporating recalcitrant residues.
- wood decay fungi, such as white rots, may contribute significantly to the degradation of resistant PHCs bound to the wood matrix.
- bioremediation of PHC drilling wastes can be conducted on sites with limited area available for biotreatment (e.g. remote drilling sites).
- production of a stable, nontoxic, organic compost high in available nutrients may be a useful amendment for the reclamation of a drilling site.

Because co-composting offers many advantages for biotreatment of drilling wastes, this technology is currently being evaluated for its effectiveness in treating C14 LAO drill cuttings at various sites in northern British Columbia. Results from two separate drilling sites, referred to as Noel and Cutbank, are summarized below.

Construction and Monitoring of Noel and Cutbank Co-Compost Windrows. C14 LAO drill cuttings, that had been stored in onsite tanks during the drilling operation, were mixed with wood fibre at a ratio of approximately 3:1 wood:cuttings and placed in windrows on a wood fibre bed in October 2001. The wood fibre used to construct the windrows was a mixture of spruce, pine and aspen poplar. Conditions for microbial activity were optimized by the addition of nutrients, especially N, and by turning and aerating the co-compost piles with an ALLU bucket at 0 and 13 months. Progress of the composting process was monitored 0, 6, 13, 18 and 22 months after construction of the windrows and included measurements of compost temperature, TEH, bulk density, moisture, C:N ratio, available N and P, pH and EC. The TEH (C10-C40+) was determined as described previously with the exception that silica gel cleanup was applied to the compost extract to remove background hydrocarbons originating from the wood residue. Throughout the monitoring period, moisture in the co-composts exceeded 23% (wwt), available N was greater than 100 µg/g, the pH (saturated paste) ranged from 7 to 8, and the EC (saturated paste, 25ºC) ranged from 6 to 7. After 22 months the maturity of each compost was assessed by measuring its temperature, evaluating the C:N ratio, determining the oxygen uptake (BNQ 1996) and conducting cress and radish plant bioassays for emergence, shoot height and wet biomass (CCME Guidelines for Compost Quality 1996). Seedling emergence and plant growth were tested in a 2:1 mixture of receiving soil:compost over a period of 14 days (OECD 1984). In addition, a 4:1 compost:water extract was tested for toxicity using the bacterial luminescence bioassay (Microtox™).

Results and Discussion. Temperatures in the co-compost piles peaked at 52-59ºC, 18 months after initiating treatment. At this time, approximately 90% of the TEH (C10-C32) had disappeared. After 22 months, TEH (C10-C32) in the co-composts at the Noel and Cutbank sites had been reduced by 95%. These data demonstrate conclusively that C14 LAO degrades readily, and that co-composting is an effective method for treating LAO drill cuttings (Fig. 11). Monitoring of the two co-compost piles is continuing, and it is expected that when the windrows are dismantled in spring 2004, almost all of the LAO will have degraded, and that the drilling waste will meet the British Columbia Generic Numerical Soil Standards for PHCs (C10-C19 = 1000 µg/g; C19-32 = 1000 ug/g) (British Columbia Ministry of Water, Land and Air Protection 1996).

According to the CCME Guidelines for Compost Quality (1996) a compost is considered mature when:

- it no longer generates heat

- the C:N ratio is less than or equal to 25
- oxygen uptake is less than 125 mg O_2/kg organic matter/hour
- cress and radish seed emergence is 90% of the control and radish wet mass production in compost –soil mix is not less than 50% of the control.

At 22 months, both composts no longer generated heat, and both had C:N ratios less than 25 (22 at Noel; 13 at Cutbank). In the Noel co-compost, oxygen uptake (62 mg/kg) was less than 125 mg O_2/kg solids/hour, while oxygen uptake by the Cutbank co-compost (169 mg/kg) slightly exceeded the CCME guideline, indicating that this compost was approaching maturity. Cress and radish seed emergence, shoot height and wet seedling biomass all met the CCME guideline. All plant measurements were greater than 100% of the control, with the exception of cress wet biomass in the Noel co-compost which was 95% of the control (Figs. 12 to 14). Based on these guidelines, both co-composts were at, or near, maturity after 22 months treatment.

The bacterial luminescence bioassays conducted on the 22 month-old co-composts revealed that there was no toxicity associated with water extracts from either compost (EC50s >91). Thus, it can be concluded that C14 LAO, contained in drill cuttings at concentrations up to 15.2%, degrades almost completely when co-composted with wood residues for 2 years, leaving a mature compost that can be used for reclamation of the drilling site. In addition, there is no toxicity associated with water extracts from the mature compost. The average lifespan of a drill cuttings/wood residue co-compost in Alberta is 2.3 years (Samuelson 2003). The present study suggests that, in the case of C14 LAO drill cuttings/wood residue co-compost, this lifespan can be shortened to 2 years, thereby making the composting technology a cost-effective method for treating these types of cuttings, particularly in remote areas.

General Conclusions

1. In the laboratory, C14 LAO present in drill cuttings at a concentration of 4.8%, was almost completely degraded after 3 months incubation in loam soil. Optimum moisture, temperature and nutrient (N, P) conditions promoted the rapid degradation of this highly bioavailable olefin, leaving a residue that was not toxic to plants and soil fauna.
2. Landfarming C14 LAO drill cuttings in the field also resulted in almost complete removal of the LAO; however, the rate of degradation was much slower than that observed in the laboratory. Variability in moisture, temperature and nutrient availability, particularly N, extended the treatment time in the field. In the present study, 3.1% LAO in drill cuttings had been reduced by 68% after almost 1 year of treatment, and by 92% after almost 2 years. After landfarming 3.1% LAO drill cuttings for almost 2 years, the LAO residual remaining in the soil was identical to that observed after incubating 4.8% LAO drill cuttings for 3 months in the laboratory, i.e.2500 µg/g dwt. Soil respiration of landfarmed soil, with and without added nutrients, indicated that LAO degradation in the field was limited by a lack of N.
3. After almost 1 year landfarming treatment and a reduction in C14 LAO from 3.1% to 1% in soil, no toxicity to barley productivity was detected in the laboratory or in the field. However, 1% LAO in the soil caused 100% mortality of the springtails, and completely inhibited earthworm reproduction. Based on the laboratory study, a reduction to 0.25% LAO in soil is necessary to eliminate toxicity to springtails, and earthworm growth and reproduction.
4. Co-composting C14 LAO drill cuttings with wood residues in the field was also successful at eliminating relatively high levels of LAO in drill cuttings (8.2%, 15.2%). After 22 months, the amount of C14 LAO that had been removed by co-composting was very similar to that observed in the landfarm over the same period of time, i.e. 95% of the total. Based on CCME guidelines, the LAO cuttings composts were at, or near, maturity after 22 months treatment.

Acknowledgements

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Table 1. LABORATORY. Barley response, earthworm and springtail survival and Microtox™ measurements in loam soil with and without C14 LAO drill cuttings before and after 90 days bioremediation.

Parameter	Before bioremediation		After 90 days bioremediation	
	Control	4.8% C14 LAO cuttings	Control	4.8% C14 LAO cuttings
BARLEY				
Emergence (%)	100	90	98	100
Shoot length cm/plant	13.1	3.9	11.9	10.0
Root length cm/plant	10.1	10.5	8.4	12.7
EARTHWORMS				
% Survival after 14 days exposure	100	93	100	100
SPRINGTAILS				
% Survival after 7 days	100	0	100	100
MICROTOX™				
EC50 %*	>100	55	>100	>100

EC50 = effective concentration of 1:4 soil:water extract (%) that caused a 50% reduction in bacterial luminescence after 15 minutes exposure. >100 = non toxic; 55 = moderately toxic.

Table 2. FIELD. Barley response, earthworm and springtail survival and Microtox™ measurements in landfarm soil, 2.5, 7, 8 and 10.5 months after application of C14 LAO drill cuttings.

Parameter	Treatment	Time after application of LAO drill cuttings			
		2.5 months	7 months	8 months	10.5 months
BARLEY					
Shoot length (cm/plant)	Control	29.9±1.2*	31.6±1.7	32.2±1.9	35.6±2.8
	LAO	**16.4±1.9**	**13.4±5.1**	33.5±1.3	35.7±2.8
Root length (cm/plant	Control	20.6±0.6	19.7±1.5	20.3±2.2	19±1.7
	LAO	17.2±2.7	23.2±4.7	23.4±2.5	19.9±0.7
EARTHWORMS					
% Survival after 14 days	Control	100	100	100	100
	LAO	100	100	100	100
SPRINGTAILS					
% Survival after 7 days	Control	100	100	100	97
	LAO	3.3	3.3	0	0
MICROTOX™					
EC50 %**	Control	>100	>100	>100	>100
	LAO	78	93	>100	>100

* Data are mean (n=3) ± SD. Bold face indicates significantly different from control ($p < 0.05$).
** EC50 = effective concentration of 1:4 soil:water extract (%) that caused a 50% reduction in bacterial luminescence after 15 minutes exposure. >100 = non toxic; 55 = moderately toxic.

Fig. 1. Respiration of soil with and without LAO drill cuttings in the laboratory.

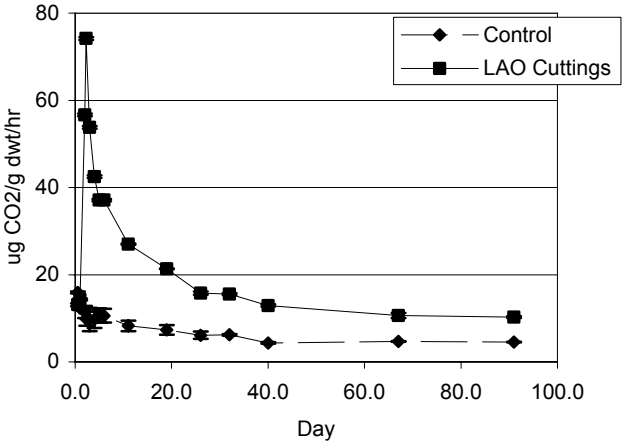

Fig. 2. Cumulative CO2-C Loss from soil with and without LAO drill cuttings in the laboratory.

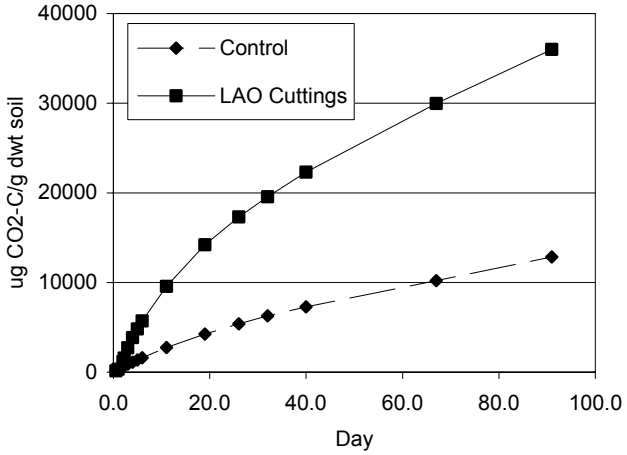

Fig. 3. C14 LAO in soil before and after 90 days bioremediation.

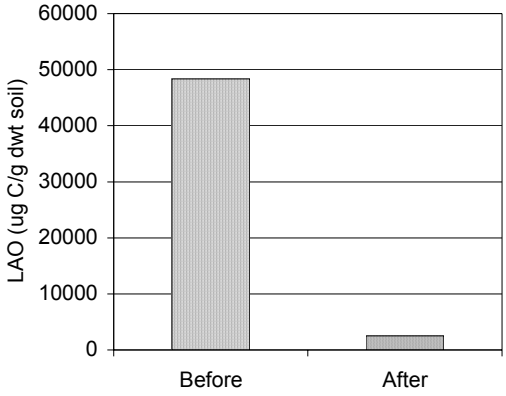

Fig. 4. Barley shoot and root mass before and after 90 days remediation of LAO cuttings in soil.

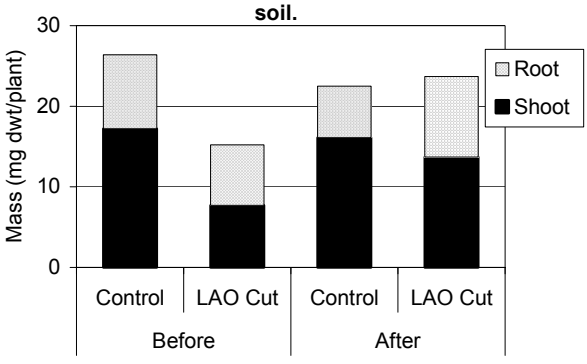

Fig. 5. Earthworm mass and juvenile production in soil with and without LAO cuttings after 90 days treatment.

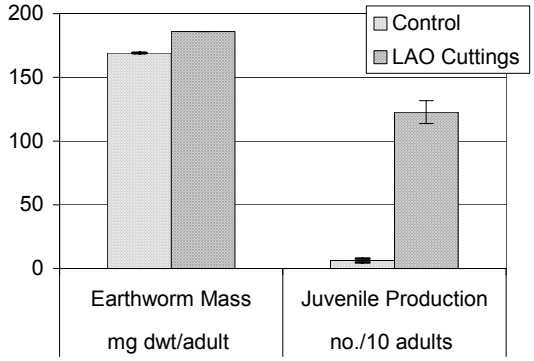

Fig. 6. C14 LAO in landfarm soil over 23 months

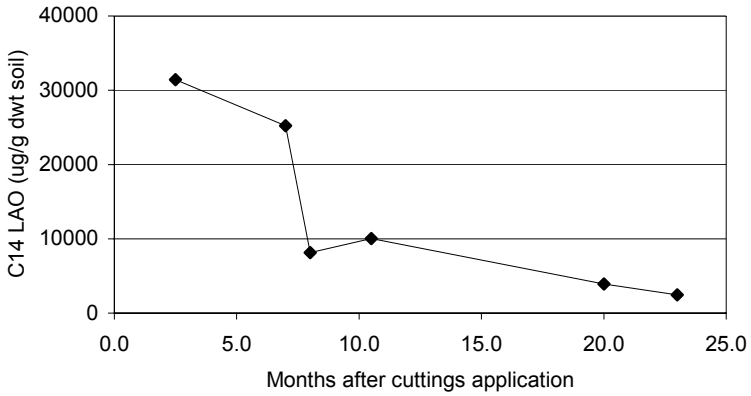

Fig. 7. Respiration in control and LAO landfarm soil over 10.5 months.

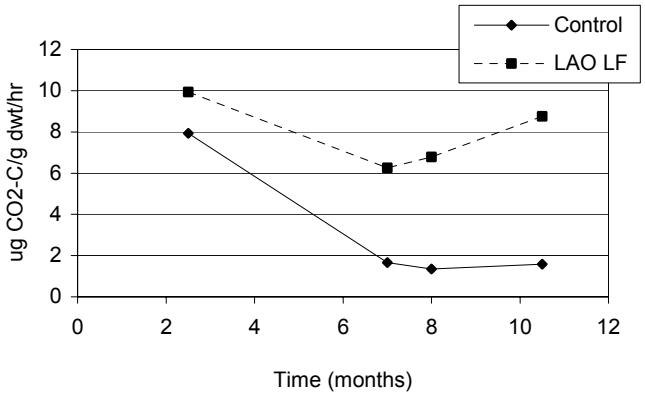

Fig. 8. Respiration of 10.5 month landfarm soil with and without fertilizer

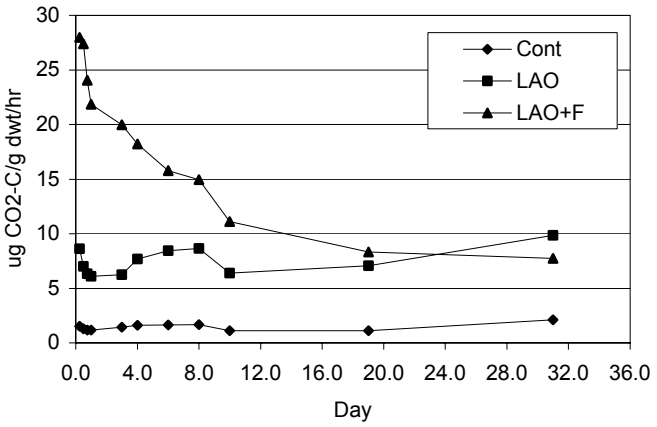

Fig. 9. Barley shoot mass over 10.5 months of landfarming treatment. Data are means and SDs.

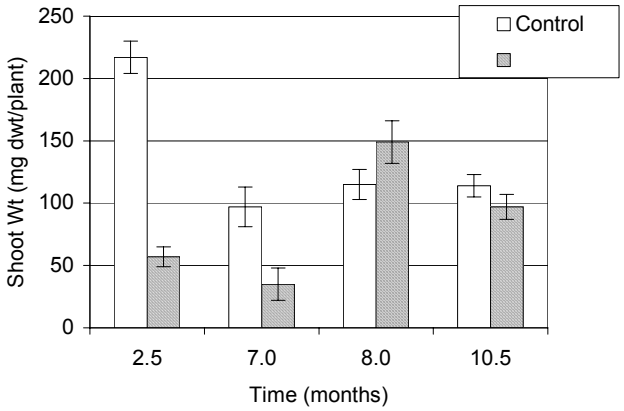

Fig. 10. Earthworm mass and juvenile production in 10.5 month landfarm soil with and without LAO drill cuttings.

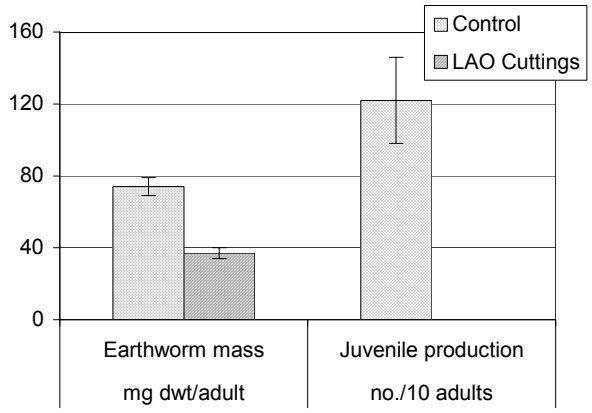

Fig. 11. TEH (C10-C32) in co-compost over time.

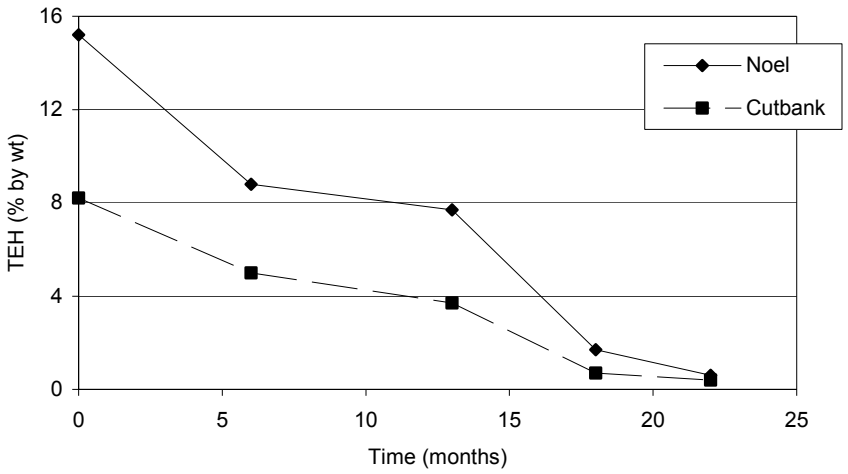

Fig. 12. Emergence in 22 month co-compost.

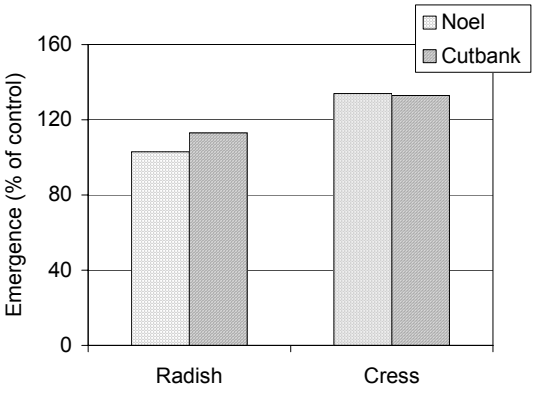

Fig. 13. Shoot height in 22 month co-compost.

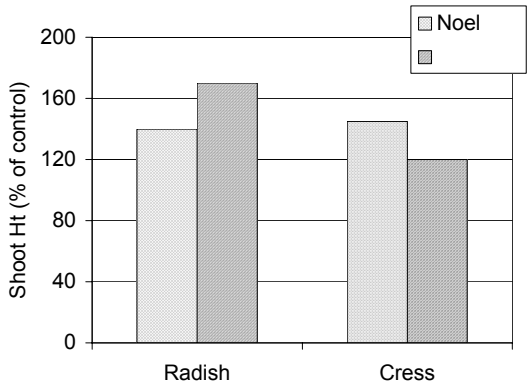

Fig. 14. Wet seedling biomass in 22 month co-compost.