

# Feasibility Study of Potential Use of Pulp and Paper Mill Fly Ash as a Co-Composting Material



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Submission: October 01, 2017; Published: October 16, 2017

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## Abstract

The fly ash waste from local pulp and paper industry was mixed with municipal sewage sludge (bio solids) as a co-composting material to investigate the feasibility of applying carbon-enriched fly ash in improving the quality of bio solids generated from water treatment facility. Parallel experiments were conducted under the same composting conditions, only in one of which the fly ash was added. The other without adding fly ash was used as a control. The composting parameters, including pH, moisture content and carbon to nitrogen ratio, electrical conductivity and germination index, of the parallel experiments were monitored for 30 days. Meanwhile, the microbial activity, an important indicator of compost maturity, was examined through plate counting. Free PAHs in the compost system was also measured to investigate the degree of biodegradation in the composting system. The results of parallel experiments were compared to evaluate the feasibility of using ash as a stabilizer.

**Keywords:** Pulp and paper fly ash; Bio solids; Co-composting; Waste management

**Abbreviations:** CBPP: Corner Brook Pulp and Paper; FA: Fly Ash; GI: Germination Index; RHWTF: Riverhead Wastewater Treatment Facility; NAP: Naphthalene; AC: Activated Carbon

## Introduction

Corner Brook Pulp and Paper (CBPP) Ltd. play an important role in promoting the economic growth of the western Newfoundland in Canada. The plant utilizes a thermo-mechanical pulping process to produce standard newsprint and other specialty newsprint grades for almost 700 metric tons per days. Each year, approximately 10,000 metric tons of fly ash (FA) are generated from mill operation and disposed to landfills [1]. However, the leach ate of landfill has become a rising concern since it contains non-biodegradable organic matters and heavy metals which can cause surface and ground water pollution [2-4]. Meanwhile, the landfill space starts getting deficient and the cost of waste disposal is increasing. Hence, there is an urgent need for CBPP Ltd. to seek sustainable waste management strategies to treat their fly ash waste.

Because of its physical properties and chemical content, FA has been used as an additive in cement and concrete [5,6], soil stabilizer [7], colour ingredient in ornamental concrete [8,9] and an adsorbent to remove organic and inorganic contaminants from water and wastewater [10-12]. CBPPFA has high carbon content (more than 80%) [13]. it is possible to be utilised as a soil amendment or a co-composting material with municipal sewage sludge [14,15]. The municipal sewage sludge waste,

also known as biosolids can be converted into composts for treatment because the nutrients such as nitrogen, phosphorus, iron, calcium and magnesium contained are essential for plant growth.

The sludge based composts can improve the soil properties, such as enhancing the water retention capacity of soil, keeping soil particles together and improving soil porosity. Due to the presence of heavy metals, PAHs, and organic contaminants (OCs), which are harmful to human health and the ecosystem, the application of such composts are commonly inspected by communities [16]. When biosolids are co-composted with activated carbon (AC) and biochar, the immobilization of metals and the reduction of organic contaminants and PAHs [17] can significantly improve the compost quality; because of the high cost of activated carbon, however, the composting of biosolids is not economically feasible.

On the contrary, composting with the addition of fly ash can help stabilize the organic matter and PAHs in the biosolids as well [18], and the heat generated during the thermophilic phase also kills pathogens. In this way, the quality of sludge based composts will be improved and the cost will be decreased. Meanwhile, good compost should have a carbon to nitrogen ratio (C/N) of 25:1,

while the locally-available biosolids from Riverhead Wastewater Treatment Facility (RHWTF) has a C/N ratio of only 8:1. Since the CBPP FA is rich in carbon content, it is expected that the co-composting of CBPP FA with biosolids will significantly increase the C/N ratio to an acceptable level. Therefore, the main objective of this study is to assess the feasibility of applying CBPP FA as a co-composting material to improve the quality of biosolids generated by the local wastewater treatment facility. The benefits are relevant for the province, where soil has little organic matter and, due to its geological characteristics, a thin top layer. The high-quality compost thus produced can be commercialized and used to improve soil fertility and develop greenbelts, landscaping, and golf courses.

## Methods

### Characterization of FA and Biosolids

The fly ash and municipal sludge samples were collected from CBPP and RHWTF, respectively. Both samples were characterized by pH, moisture content, and carbon to nitrogen ratio. The pH and the moisture content were measured according to ASTM method C311. The C/N ratio was measured by a PE 2400 CHN analyzer. The PAHs in both samples was also determined through solvent extraction and followed by GC-MS analysis [19]. The trace metals in the FA and biosolids samples were analyzed using modified EPA method 3050 and followed by inductively coupled plasma mass spectrometry (ICP-MS). Specifically, a 100 ± 10 mg sample was weighed, placed in a 15 ml Teflon vial (Savillex) with a screw cap, and the vial weight recorded. Then 3 ml of 8N nitric acid (HNO<sub>3</sub>) was added to the vial and heated on a hot plate at 70°C for two days.

The vial cap was tightly closed to reflux the acid and generate pressure to speed up digestion. The samples were then dried and cooled; 1 ml of HNO<sub>3</sub> and 1 ml of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were added to the system and heated at 70°C for two days to remove organic matters. The samples were then dried and cooled. An additional 2 ml 8N HNO<sub>3</sub> and 1 ml hydrofluoric acid (HF) were added to the samples and heated at 70°C for two days. After drying and cooling, 3 ml of aqua regia was added to the sample and heated at 70°C for one day. The sample was dried, cooled, and dissolved in 2% HNO<sub>3</sub>. All the solution was transferred to a 50 ml conical centrifuge tube and deionized water was added to 45 g. The solution was then filtered by a 0.45 µm syringe filter. Finally, 0.5 g of the solution was transferred to an 11 ml tube and deionized water was added to 10 g. The solution was analyzed by an Elan DRC II ICP-MS analyzer. Besides, the surface area and porosity of the FA sample was measured by N<sub>2</sub> adsorption

at 77K using an automated adsorption apparatus Tristar II Plus micrometric analyzer.

### Composting Process

Composting reactors with dimensions of 50 L (cm) × 20 W (cm) × 25 H (cm) was previously designed by [20] and used in this study. Two parallel experiments were conducted under the same conditions with CBPP FA added to one of the reactors. Seven kilograms of digested wastewater sludge and 2 kilograms of fish waste processed in a food processor were added to both reactors. Fish waste was added as the nitrogen source to balance the initial C/N ratio to 25:1. An additional 500 grams of the CBPP FA was added to one reactor. Originally, no PAH was detected in the sludge, FA, or fish waste samples.

Crude oil was spiked as the PAH source at a 20 g/kg oil to solid weight ratio. The composting samples were turned twice a day to maintain homogeneity and air flow, and the composting process was continued for 30 days. In each reactor, approximately 30 grams of samples were taken randomly in the first 9 days and every 3 days after that for the analysis of pH, electrical conductivity (EC Meter, Orion Star A222 and A322, Thermo Scientific), moisture content, C/N ratio and germination index (GI) (TMECC, 2001). The results of the parallel experiments were then compared to evaluate the feasibility of applying this type of fly ash as a stabilizer.

## Results and Discussion

### Characterization of FA and biosolids

The pH, C/N ratio, moisture content, and conductivity of the sludge and FA were measured and reported in (Table 1). The pH of the biosolids and the FA are 8.7 and 12 respectively; both are alkaline. The biosolids from RHWTF show a high moisture content, while the FA is very low, which can reach the ideal mixture moisture content of 55-60%. The specific surface area of 249.4 m<sup>2</sup>/g of the FA sample indicates a relatively high surface area. Commercial ACs normally has specific surface area of 800-1200 m<sup>2</sup>/g, while coal and oil fly ash have that of 2m<sup>2</sup>/g. The high surface area of FA enables it to act as an adsorbent, absorbent, and moisture controller. However, the absorption of moisture can cause decomposition of the FA, and the addition of bulk agents, such as saw dust and chips are required to keep the system aerated. The high C/N ratio of FA indicates that it is a good source of carbon. The ICP-MS result shows that both samples are dominated by Al, Ca, Fe, Mg, and P. The concentrations of hazardous metals are relatively low in the CBPP FA than that in the biosolids.

**Table 1:** Characteristics of CBPP FA and Biosolids.

CBPP FA		Biosolids	
pH	12	pH	8.7
Density	0.45 g/cm <sup>3</sup>	Density	-
PAHs	Not detected	PAHs	Not detected
Moisture content	0.89 %	Moisture content	73%

Surface area	249.4 m <sup>2</sup> /g	Surface area	NA
C/N ratio	572.95	C/N ratio	7.18
<b>Metal content in solid (Unit: mg/Kg)</b>			
Mg	512	Mg	6234
Al	947	Al	19509
Fe	784	Fe	17019
P	114	P	7011
S	<LD	S	<LD
Cl	11634	Cl	28608
Zn	12	Zn	879
Cu	7	Cu	633
Pb	2.3	Pb	85
As	<LD	As	2.7
V	15	V	37
Cr	5	Cr	42
Ni	16	Ni	22
Ca	2656	Ca	7178

LD: Lower than detection

### SEM and elemental analysis of crushed CBPP FA

The SEM analysis of the FA indicated a wood fiber structure with pores evenly distributed on the particle surface (Figure 1). The porous structure also matches the high micro-pore volume from the BET result. Free metal oxides found in untreated

FA mainly contain CaO, MgO, and Al<sub>2</sub>O<sub>3</sub>. Micro- to meso-pore structures can be found on the 100 nm scale SEM photo. The point elemental analysis in (Figure 2) indicates that FA is the carbon-dominated material and Ca and Al the major metal components. This also matches the ICP-MS result.

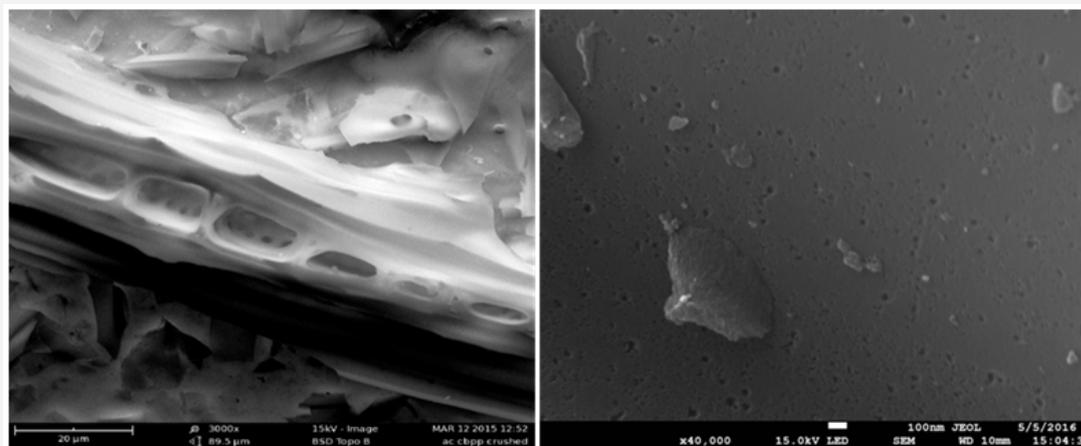


Figure 1: SEM analysis of CBPP FA.

Table 2: Results of composting parameters.

Time (days)	Moisture content (%) - W	Moisture content (%) - W/O	GI (%) - W	GI (%) - W/O	pH - W	pH - W/O	EC - W	EC - W/O	C/N ratio - W/O	C/N ratio - W
1	68.45	71.30	21.35	21.37	7.52	7.24	10.16	10.03	10.70	14.02
3	69.95	71.10	23.45	28.01	7.66	7.54	10.09	9.48	10.63	14.78
6	68.98	70.48	21.14	26.00	8.20	7.95	9.8	8.98	10.55	14.56
9	68.79	69.39	24.30	23.20	8.16	8.02	9.505	8.47	10.48	14.27
12	69.80	71.58	28.89	25.07	8.29	8.13	8.5	8.25	10.26	14.18
15	70.57	72.15	26.59	27.26	8.50	8.22	8.16	8.41	10.17	14.12

18	70.20	70.85	29.22	30.79	8.47	7.96	8.29	8.57	10.20	13.95
21	70.19	69.92	31.42	32.92	8.79	7.84	9.905	8.62	10.07	13.74
24	72.37	72.75	28.08	32.94	8.82	8.01	9.18	8.71	9.67	13.85
27	71.65	71.56	33.20	35.33	8.45	7.84	9.28	8.14	9.57	13.64
30	70.54	70.59	29.26	38.22	8.68	8.12	8.84	7.86	9.76	13.72

W: With FA; W/O: Without FA; GI: Germination Index; EC: Electrical Conductivity.

### Composting Process

The stability and maturity of a compost are generally determined by the C/N ratio C/N and the GI. In addition to these two parameters, the pH and moisture or water content of a final compost product are also tested. The results are shown in (Table 2).

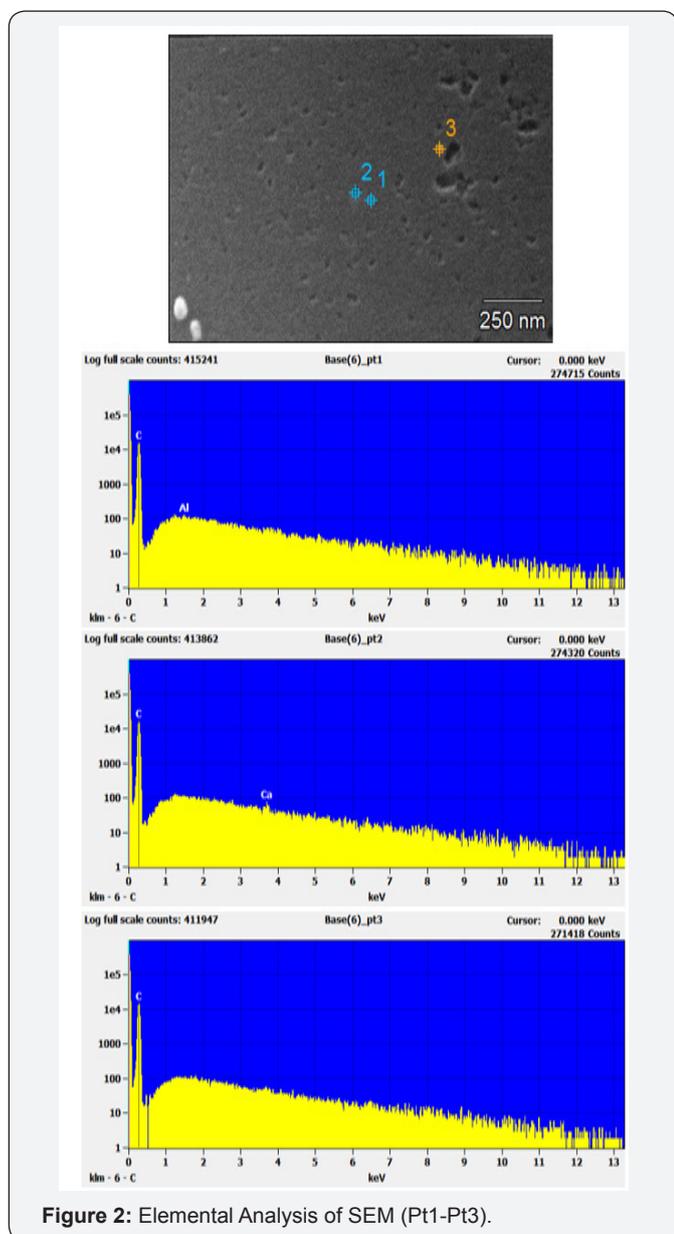


Figure 2: Elemental Analysis of SEM (Pt1-Pt3).

### C/N ratio

Carbon and nitrogen are important nutrients; microbes use carbon for energy and growth, and nitrogen for protein and reproduction. Biosolids mixed with fly ash in a ratio of 14:1 have been composted for 30 days, and the biosolids only is treated under the same conditions for comparison (Figure 3) shows the C/N ratio change with two types of compost, biosolids and biosolids with fly ash; over a 30-day composting process and that the addition of fly ash can significantly increase the C/N ratio. However, the C/N ratio change for the two types of compost for this time period has similar trends and slope, which indicates that fly ash, may not accelerate composting. The C/N ratio of biosolids with fly ash decreased from 14.0 to 13.7, while that of biosolids only dropped from 10.7 to 9.8. Both types of compost have a slight C/N ratio change, indicating that composting is quite slow in both.

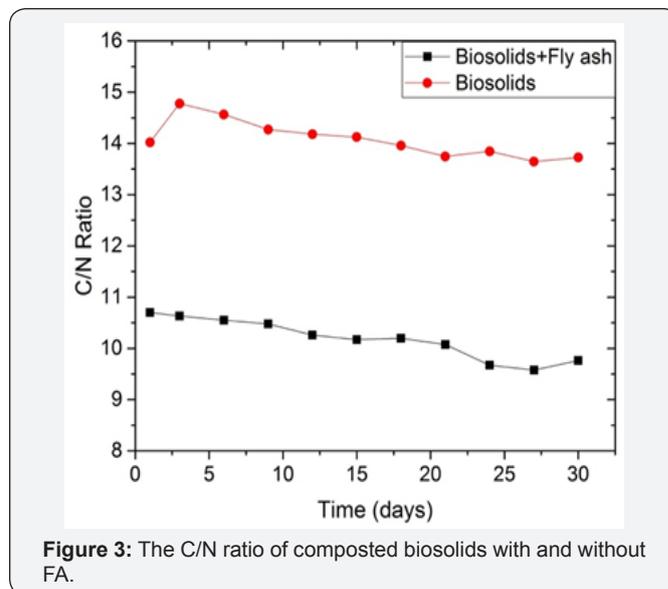


Figure 3: The C/N ratio of composted biosolids with and without FA.

### Germination index (GI)

GI is usually used for evaluating compost maturity, especially when compost products are applied to soil supplements or used as fertilizers, (Figure 4) displays seeds sprouting in biosolids with fly ash and in sole biosolids. Within a 30-day period, the highest GI in biosolids with fly ash is 33.2%; in sole biosolids it is 38.2%. Compost with a GI value of more than 80% indicates phytotoxic-free and mature compost [20]. The result reveals that both types of compost are not mature enough. An extended

composting time is necessary. Compared with biosolids without FA, the addition of FA hinders seed germination. Therefore, a further study is necessary to investigate phyto toxic compounds in FA.

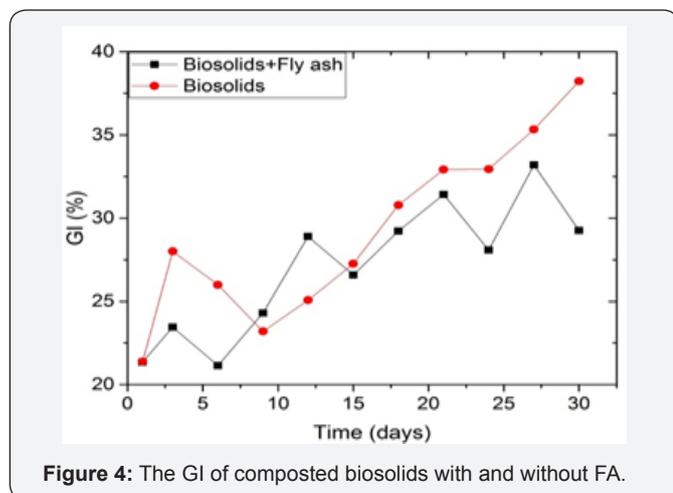


Figure 4: The GI of composted biosolids with and without FA.

**Moisture content**

Moisture is essential for microbe growth, and the ideal level is 40%-60%, Figure 5 shows the change of moisture in two types of compost during the composting process. A fluctuation of moisture is observed in both materials. The moisture content of biosolids with and without FA fluctuates between 68.5% and 72.4%, and 69.4% and 72.7%, respectively. This illustrates that both have moisture content slightly higher than 60%, which could be why the degradation process is slowed down.

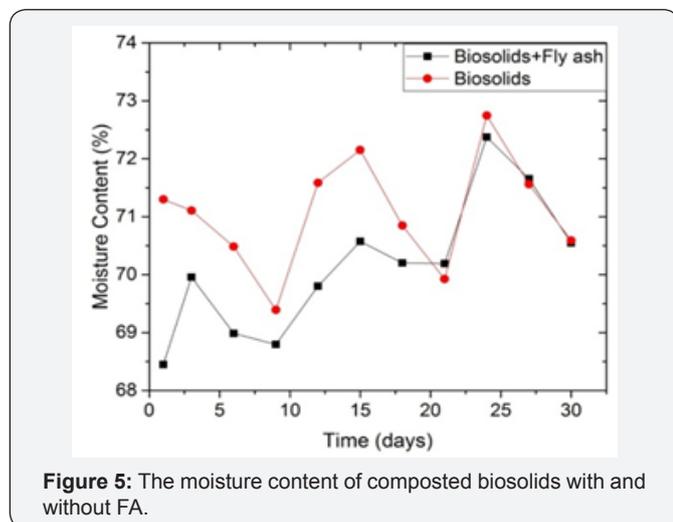


Figure 5: The moisture content of composted biosolids with and without FA.

**pH**

The pH value indicates the alkalinity or acidity of the compost. During the microbial decomposition of organic compounds, ammonium (NH<sup>4+</sup>) is usually generated, and leads to a pH increase to above 8. As biodegradation continues, NH<sup>4+</sup> is emitted from the medium as NH<sub>3</sub>; meanwhile, some produced organic acid neutralizes the compost, which further decreases the pH. The pH of the compost will stabilize [21], (Figure 6) demonstrates the change of pH in two types of compost over 30

days. The pH of both biosolids with fly ash and sole biosolids gradually increases to above 8 at the end of the 30-day period. This implies that both materials are possibly in the process of ammonium generation, and not mature yet. This is in good agreement with the results of other parameters.

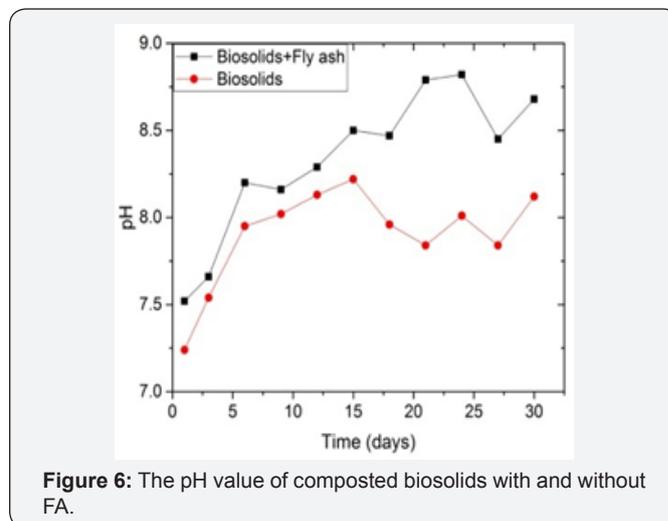


Figure 6: The pH value of composted biosolids with and without FA.

**Electrical Conductivity**

EC is determined at different sampling points to estimate the salinity and soluble nutrients in the compost. This value indicates whether the compost can be applied as a growth medium or an organic fertilizer. High levels of salt in compost can reduce crop yields as it hinders the root from extracting water from the soil-compost solution. In general, the majority of crops can grow in compost with an EC below 10 mmhos/cm. Once the EC is above 10, the compost is better utilized as an organic fertilizer. As shown in (Figure 7), the EC values of the two types of compost fluctuate between 7.9 and 10.2 mm hos/cm, which denotes that both can potentially be applied as a growth medium.

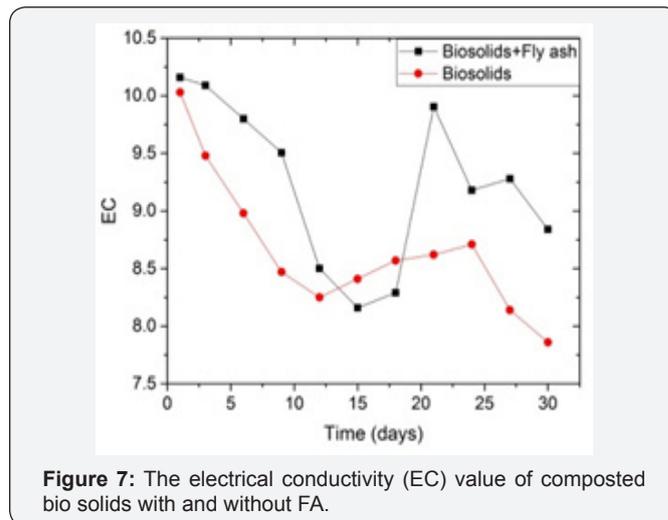


Figure 7: The electrical conductivity (EC) value of composted bio solids with and without FA.

**Microorganism Counting**

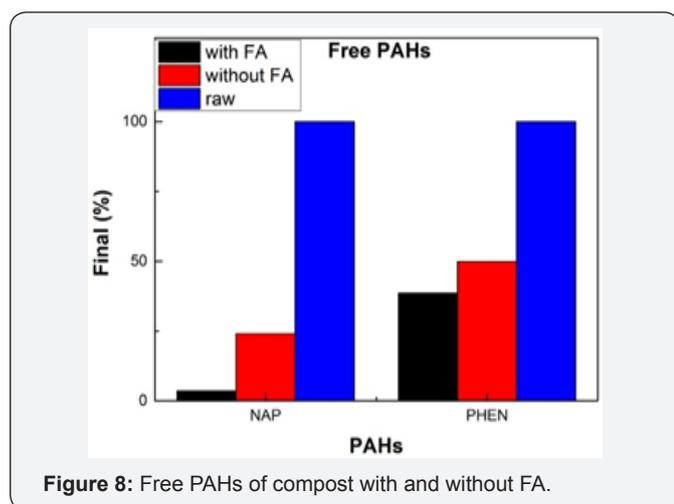
Microbial activity, another important indicator of compost maturity, is represented by plate counting. Microorganism colonies were counted by the spread plate counting method. The

culture medium for total thermophilic and mesophilic bacteria was 10% strength tryptic soy broth agar. A 10 grams sample was weighed in a 250 ml Erlenmeyer flask with the addition of 90 ml of a 0.85% (w/w) sterile NaCl solution. The flask was sealed and mixed on a mechanical shaker at 200 rpm for 30 minutes at room temperature. The supernatant was diluted into ten serial concentrations ranging from  $10^{-2}$  to  $10^{-10}$ . Four dilution factors were selected that could best characterize the microorganisms of the samples. Then 100  $\mu$ L diluted solution was spread in a petri dish with the medium, and placed in a 30°C incubator for three days [22-24].

The results are shown in (Table 3). The microorganism of the sample with FA begins with higher starter and then slightly decreased in the first three days. It reaches a peak at the sixth day, and begins to decrease, at last reaches another peak at 21st day. This could be due to the unstable conditions of composting in first week, and with the increase of temperature and aeration, thermophile bacteria began growing and then decrease after the peak. The sample without FA shows a more stable trend than the one with FA; this could be because, without FA, there is not enough carbon for bacteria growth, thus causing the slower maturity of the composting process.

**Table 3:** Results of microbial counting.

Days	Sample with FA	Sample without FA
1	1	$51 \times 10^5$
3	3	$52 \times 10^7$
6	6	$18 \times 10^8$
9	9	$46 \times 10^6$
12	12	$17 \times 10^7$
15	15	$70 \times 10^6$
18	18	$28 \times 10^7$
21	21	$5 \times 10^8$



**Figure 8:** Free PAHs of compost with and without FA.

### PAH Degradation

Free PAHs in the compost system is one indicator of biodegradation. As shown in (Figure 8), the concentration of extractable naphthalene (NAP) from both compost samples

decreases during composting. The one with FA shows a better performance of NAP than the one without FA; this could be because the addition of high surface area FA can eventually improve PAH adsorption. Illustrated that AC can effectively adsorb PAHs with 5-6 rings; however, for 2-4 rings PAHs are barely effective. In this study, the better performance of compost with FA could have been due to better microbial activity [25,26].

### Conclusion

The CBPP FA showed good potential as a carbon source in the composting of biosolids in this research. The process of co-composting FA with municipal sludge seemed extremely slow that the compost was not matured after 30 days composting process. However, the concentration of PAHs was reduced through this co-composting process because of the microbial activity and physical adsorption. It is certain that the municipal sludge alone cannot be a suitable raw material for composting due to the low carbon to nitrogen ratio.

### Acknowledgement

The support provided by the Harris Centre at Memorial University in the form of the Harris Centre - MMSB Waste Management Applied Research Fund is highly appreciated. Appreciation is also extended to the Corner Brook Pulp and Paper Limited and Riverhead Wastewater Treatment Facility for providing material for this project.

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DOI: [10.19080/IJESNR.2017.05.555675](https://doi.org/10.19080/IJESNR.2017.05.555675)

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