

New Generation of Iron-Enhanced Compost for Stormwater Treatment

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- **Problem and Research Objectives**

Stormwater is the major conduit of pollutants into the Puget Sound. Many streams and wetlands have been degraded by urban development and associated stormwater impacts and require habitat and water quality improvement, while others still support endangered salmon and require protection. Improving stormwater management to reduce levels of pollutants entering the Sound is one of six key state policy objectives of the Puget Sound Partnership to protect water quality, habitat, and aquatic resources, thus reversing the Sound's decline and restoring it to health by 2020. In the Puget Sound, more than 13,000 lb of toxic metals are released into the Sound daily (Ecology and King County 2011). Lead (Pb) is one of the major toxic heavy metals that pose threats to human health and environmental quality statewide. The major sources of Pb in stormwater in the Puget Sound area include human activities such as shooting and fishing, leaching from roofing material, and fuel combustion. In the Spokane area, Pb contamination sources include Pb-based paint and residual deposits from past use of leaded gasoline, pesticides containing Pb, and mine waste from the Coeur d'Alene Basin. Elevated nutrients in stormwater is another major concern that impairs environmental habitats through. In the state of Washington, more than 260 bodies of water are known to be polluted with nutrients such as P and N.

Compost is one of most popular amendments used in bioretention systems for stormwater treatment because it retains a variety of stormwater constituents. Traditional compost made with various organic wastes improves retention of toxic heavy metals and organic pollutants but, over time, it can contribute to P export as the compost decomposes. Iron-enhanced compost, in which Fe is added to complex with organic functional groups in the compost, has been developed specifically for sequestering both heavy metals and oxyanion contaminants (Brown et al. 2012; Shi et al. 2012). Using Fe-enhanced compost for stormwater treatment has several advantages, such as superior ability to remove both toxic metals and P, low cost by using natural and waste materials (both plant materials and Fe compounds), improved soil properties such as increased water retention and fertility, and urban agriculture promotion while minimizing the impact on stormwater quality. However, critical questions remain concerning the capacity and stability of Fe-enhanced compost for contaminant removal both in existing bioretention systems and in development of urban gardens. There are no predictive tools for the efficiency of Fe-compost and its long-term effects on environmental quality.

The goals of the proposal are to evaluate the stormwater treatment capabilities of our newly developed Fe-compost for the retention/removal of stormwater pollutants. Our specific objectives include:

- (1) Characterize reactive sites in Fe-compost with a suite of chemical and spectroscopic techniques and determine the capacity of Fe-compost retention of Pb;
- (2) Evaluate the efficiency, stability, and longevity of Fe-compost for stormwater treatment in stirred-flow experiments and develop mechanistic-based kinetics models for predicting stormwater quality and fate of sequestered contaminants.

- **Methodology**

- 1. Preparation of the Fe-compost.**

Initial Compost Development. The compost used for this study was pulled from Washington State University Composting Facility, Pullman, Washington. The compost feedstock was derived from university food and chemical laboratory waste, as well as local woody biomass and

animal bedding. The compost product in our study was the result of a 30-day thermophilic composting method utilizing 12 ft wide x 5 ft tall windrows with an initial C:N ratio of 35/40:1 and a moisture content of approximately 65% impregnated with treatment bags. 21 fine-mesh bags were inserted in three separate but relatively close (1 m apart) locations within a composting pile. The mesh bags contained two iron treatments at three concentrations each (50, 150, 300 g/kg for iron (II) gluconate (FG); 31, 93, and 190 g/kg for iron (II) sulfate (FS) incorporated into 1 kg of compost, plus three control bags containing no amendments. At the end of the 30-day composting process, the bags were removed and the contents air dried and stored at -20 °C to halt microbial activity in sealed ziplock bags.

Second Compost Development: Minimizing Dissolved Organic Carbon (DOC). Compost utilized in bioretention systems requires a stable, well-developed, and uniform media. The maturity of compost can have a direct impact on its sorption capacity for metals in the environment and ultimately their transport. One such transport mechanism correlated to compost maturity is the lower molecular-weight mobile component of compost, dissolved organic carbon (DOC) which, in turn, is connected to microbial decomposition of organic matter during the various composting stages (Zmora-Nahum, 2005). To assess DOC as a function of compost maturation time, 63 fine-mesh bags were separated by month (1 month, 2 month, and 3 month) and inserted in three separate but relatively close (1 m apart) locations within a composting pile. A single set of mesh bags (21) contained three varying amounts of each treatment (50, 150, 300 grams for iron (II) gluconate; 31, 93, and 190 grams for iron (II) sulfate) incorporated into 1 kg of compost, plus three controls bags containing no amendments, and all 3 sets were identical. The bags were removed in one month increments. Upon removal, the bags were weighed, and air/oven dried weights were determined. Roughly 400 grams was air dried, ground, and stored in a 1-liter ziplock bag; the rest was refrigerated at -20 °C to halt microbial activity.

Third Compost Development: Minimizing DOC by Managing the Carbon Source. Beginning in the fall of 2014, 4×4×4 foot composting bins were purchased from O2 Compost® Company (Snohomish, WA) and assembled. Seven bins were constructed as outlined in diagram 1: 3 Fe-sulfate treatments (31, 93, and 131 g Fe/kg compost), 3 Fe-gluconate treatments (50, 150, 300 g Fe/kg compost), and one control. Similar to the previous approaches, each bin will house one treatment and will be composted until the final curing stage is reached.

2. Compost Characterization

Solid State Nuclear Magnetic Resonance (NMR). Removal of paramagnetic material is required prior to analysis due to the magnetic interference of iron in NMR spectroscopy. Compost sample preparation for solid-state NMR analysis followed a modified version of Skjemstad et al (1994). Compost samples were sieved (2 mm) and approximately 3 grams were placed in 30 mL of 2% HF solution in a 50 mL polypropylene centrifuge tubes. The tubes were then placed on a reciprocal shaker on low for 24 hours. They were then spun at 20,000 rpm for 20 minutes, and the supernatant was removed and disposed. A successive 5 rinses with deionized water followed, coupled with spinning and removal of the supernatant. The compost was removed and air dried for 2 days.

Compost samples were initially milled with a mortar-and-pestle, and processed sequentially under the same NMR acquisition parameters. A 5 mm zirconia rotors (Revolution NMR, LLC, AMP4089-001 5 mm, 160 ul, Rotor Assembly, Teflon Caps, Zirconia, CS) was filled with approximately 100 mg of milled compost. Solid state ¹³C cross polarization/magic angle spin (CP/MAS) analyses was conducted using the Bruker Avance 400 spectrometer (400 MHz), with

a frequency of 100.63 MHz (Bruker AXS, Inc., Madison, WI, U.S.A.) at Washington State University's NMR Center (Pullman, WA). The spectrometer employed a 7.5 mm double resonance HX MAS probe (Chemagnetics, Varian, Inc., Palo Alto, CA, U.S.A.). ^{13}C CP/MAS NMR spectra acquisition used a spinning speed of 6 kHz, with a cross polarization contact time of 1 ms followed by an acquisition time of 5.1 ms, a pulse width of 14 μs , and a relaxation delay of 4s. The spectra produced were the result of 17,261 scans, with chemical shifts set at units of parts per million (δ).

Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR). ATR-FTIR analysis utilized dried and ground compost samples. Sixty scans per sample were acquired using a Shimadzu IR-Prestige 21 (Columbia, Md., USA) analyzer modified with an Attenuated Total Reflectance (ATR) unit (PIKE Technologies, Madison, Wis., USA). Focusing on the spectral range of 4000 to 500 cm^{-1} , absorbance intensities were used to compare changes across the sample set, disclosing differences in both carbon and functional groups.

3. Batch Adsorption Experiments

Adsorption Edge Experiment. Pb adsorption on selected iron-compost samples was studied at a fixed total Pb concentration (~0.8-1.0 mM) for each compost while reaction pHs varied from low to high (pH 3 – 8) using a batch method. The reaction pHs were adjusted by adding NaOH or HCl. The solid:solution ratio was fixed at 5 g/L.

Adsorption Isotherm Experiment. The Pb adsorption on selected iron-compost samples was studied at pH 6.0 and 7.0 while total Pb concentrations varied from low to high (up to about 0.8 mM). The reaction pHs were adjusted by adding NaOH or HCl. The solid:solution ratio was fixed at 5 g/L (for pH 6.0) and 10 g/L (for pH 7.0).

4. Stirred-flow Kinetics Experiments

Pb adsorption was conducted by continuously pumping Pb stock solution through the stir flow chamber at varying flow rates and Pb concentrations. About 0.02 g of compost was put in stir flow chamber with background electrolyte and a stir bar, which was covered with a filter (Figure 1). Filtrate was collected by a fraction collector. Filtrate samples were analyzed using a Microwave Plasma-Atomic Emission Spectrometer (MP-AES).

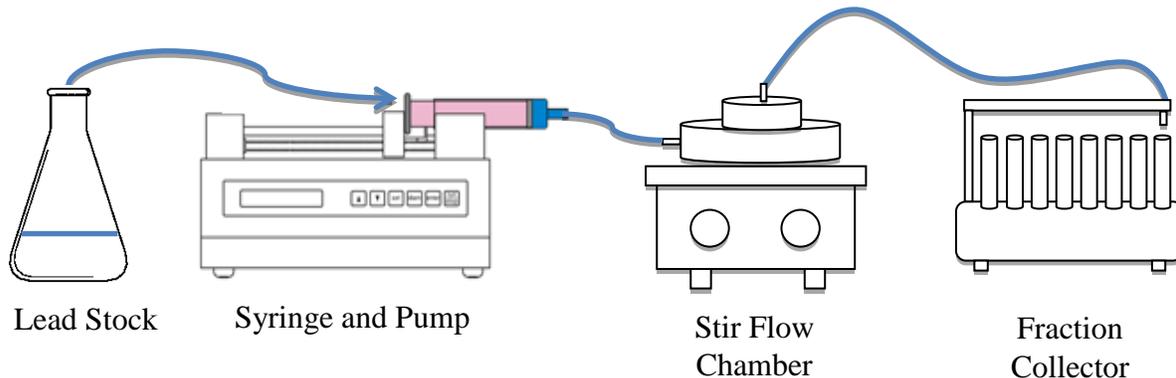


Figure 1: Illustration of Pb adsorption experiment.

- **Principle Findings and Significance**

1. Preparation of the Fe-compost.

During our initial experiments, Fe was successfully amended into the Fe-compost samples, while higher Fe loadings were achieved using FG compared with FS salts. The final Fe concentrations in Fe-compost samples were summarized in Table 1.

Samples	Estimated [Fe] mol/kg	[Fe] mol/kg	Std	pH
Control	---	0.0569	0.030 8	8.6
FG50	0.2	0.206	0.021 8	5.9
FG150	0.6	0.493	0.066 8	4.9
FG300	1.2	1.47	0.180	4.6
FS31	0.2	0.214	0.036 2	5.9
FS93	0.6	0.293	0.048 4	5.1
FS190	1.2	0.308	0.054 7	3.3

Table 1. Iron gluconate (FeG) and Iron sulfate (FeS) final concentrations in compost after 1 month

In our second trial, we observed varying DOC concentrations in different Fe-compost samples. Table 2 shows the final DOC (g/kg) of various treatments after three months of composting process. The large windows at the WSU Compost Facility housing the treatment bags were found to be a source of excess DOC in the final compost product. It was understood that to ultimately minimize DOC in the final compost product, limiting the total carbon source used for our compost was required so that the final maturation stage and lowest release of DOC can be achieved. Instead of using large, compost windrows, smaller composting bins were employed.

Treatment	DOC (g/kg)
FG300B1	50.6
FG300A3	14.5
FS93B1	4.37
FS93A3	4.51
Control	15.5

A1	
Control	
B3	18.4

Table 2. Dissolved organic carbon in compost samples with various treatments. FG300 represents the Fe-gluconate 300g/kg treatment; FS93 represents the Fe-sulfate 93g/kg treatment

The results from the first two trials help to produce Fe-compost with low DOC concentrations, which is in process for our third trial.

2. Characterization of Fe-compost using both NMR and FTIR

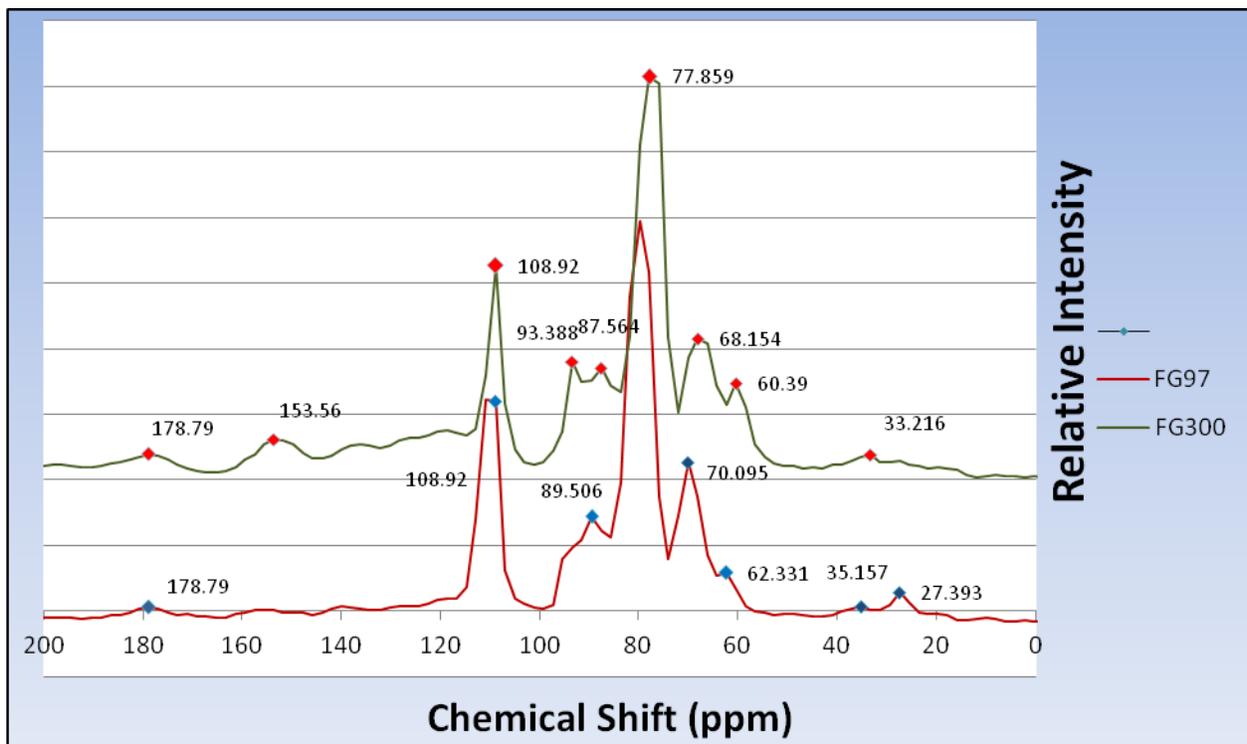


Figure 2. ^{13}C -NMR spectra of FG300 and FG97 samples.

The ^{13}C -NMR spectra pictured above were sourced from two different iron-gluconate concentrations, 300g Fe/kg (FG300) and 97g Fe/kg (FG97). Besides the iron concentrations, the other difference in the sample treatments was the FG97 compost, a compost product composted to completion (i.e. reached the final, low temperature curing phase of the composting process). FG300 was 30 day compost, by comparison, a relatively young compost. Both spectra show very similar peaks with prominent differences in various carbon groups. The peak assignments are based on findings from the literature (Spaccini and Piccolo, 2008; Gao et al., 2015). For both spectra pictured, the major peaks of interest occurred in the regions of 0-110 ppm (aliphatic) and 160-190 (carboxylic).

For the higher iron treatment, FG300, the most intense peaks occurred at 68.1, 77.9, 87.6, and 108.9 ppm, which are specific to carbons of cellulose (Spaccini and Piccolo, 2008; Gao et al., 2015). The peak at 60.4 ppm denotes lignon methoxy carbons groups (Gao et al., 2015). FG300 Phenolics are associated with the peaks at 153.6 and carboxylic carbons are noted at 178.8 ppm (Gao et al., 2015). Comparatively, FG300 shows a much higher concentration of carbon phenolics and available ligno-cellulose, with lower recalcitrant aliphatic region (33.2 ppm), especially when compared to FG97. There is a similar composition, overall, in both in carbon types, showing a relatively similar composition of the two compost samples.

ATR-FTIR Solid Compost Samples

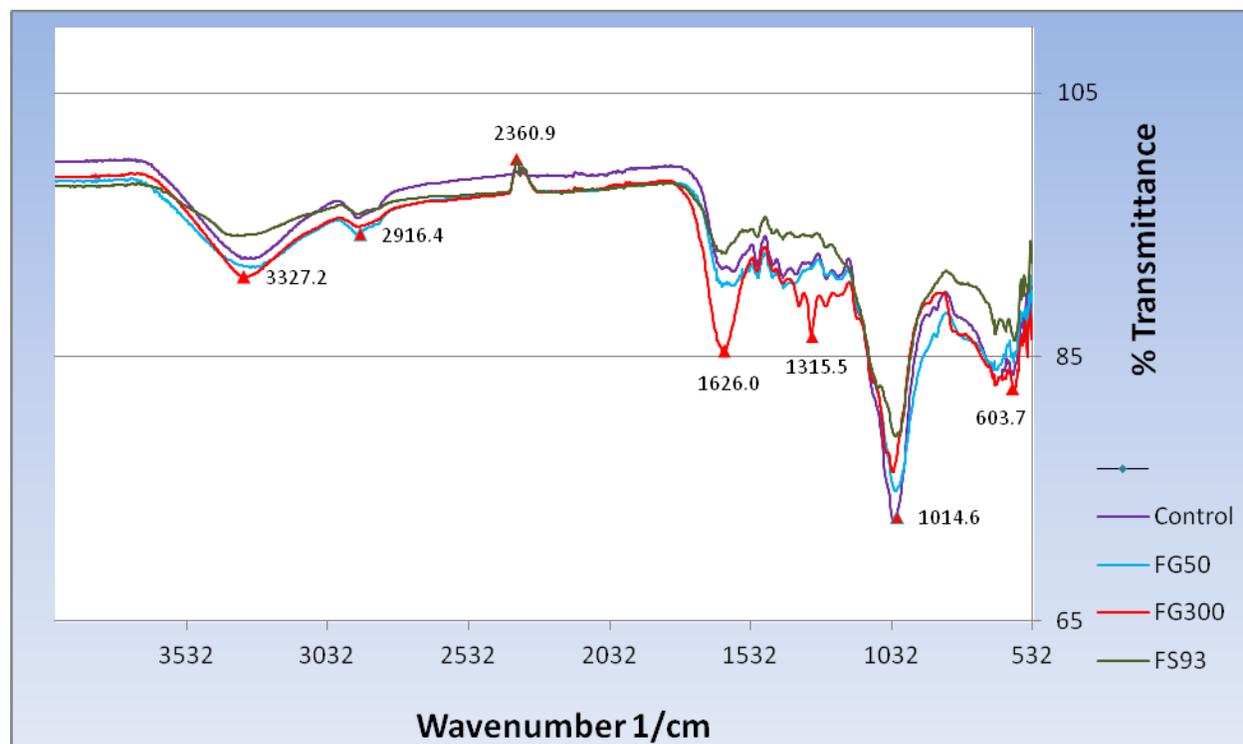


Figure 3. ATR-FTIR of four compost products: control (no iron), FG50 (50g/kg Fe), FG300 (300g/kg Fe), and FS93 (93g/kg Fe from Fe-sulfate)

Selected samples were analyzed using ATR-FTIR. Disclosing the stretch and vibrational nature of various covalent bonds within a sample, ATR-FTIR supports not only the compost NMR data but may also show iron complexation with organic functional groups within our selected samples (Sharma, Ofner, & Kappler, 2010). Assignments were gathered from published literature (Smidt & Meissl, 2007; Huang et al, 2006; and Carballo et al. 2008). Analysis of the solid compost shows nearly identical peaks. When overlain, it was difficult to compare and extrapolate from the various peak intensities, but the highest iron treatment, FG300, showed the most unique peaks overall.

The greatest peak intensities in all samples were at the 1014-1024 peak (between Abs = 0.14 to 0.10). This peak range is indicative of either C-O-C or C-O-P bonds in polysaccharides. Both the C-O-C and C-O-P bonds correlate with the high fraction of structural cellulose as indicated in the solid state carbon NMR. The slightly higher intensity of the polysaccharide region in both

the FT-IR and the solid state ^{13}C -NMR are expected with the younger FG300 compost, as this region is highly accessible and subject to microbial degradation during the composting process; an older compost of the same feedstock will show an overall decrease in the region (Spaccini & Piccolo, 2008).

The next highest peak intensities were seen in the very broad region between 594-665 range for all compost samples (Abs: control = 0.081, FG50 = 0.076, FG300 = 0.079, FG 93 = 0.064 for both). This broad peak is associated with the S-O bending of sulfate, but the upper broader shoulder on the FG300 peak might be more associated with the C-O bending of carbonate. The FS (iron-sulfate) treatment did not show any prominent peaks with these regions. Given the high solubility of FeSO_4 and the higher anion competition with DOC during the composting process, less inorganic sulfate would likely remain in the pile after completely composting.

The next highest peak intensities were seen at the peak range marked at 1626. This large peak is associated with C=C bonding in aromatic ring structures. FG300, by far, had the largest and most distinctive peak in this region among all the spectra. According to Sharma et al (2010), this specific peak may be indicative of iron complexation with carboxylic groups within organic matter, shifting the peaks slightly to the right in the spectra. This occurs at roughly 1600 and at <1350 range in the IR spectra for both COO- and phenolic groups, respectively (Sharma, Ofner, & Kappler, 2010).

Closely behind are the peaks marked at 1315 (Abs = 0.03 - 0.06). This specific peak is associated with the COO- stretch of carboxylic acid groups or the C-O stretch of carbonate. Compared to the organic carbon source, inorganic carbonate would likely have a less prevalent influence in peak intensities. A small fraction of the peak at 1014 may be attributed to the Si-O stretch of clays as the peak at 3327 is indicative of the SiO-H stretch sourced from clay minerals within the compost.

3. Batch Adsorption Experiments

Lead adsorption on various compost samples is presented in Figures 4-6. Pb adsorption was linear at low Pb concentrations, and Pb adsorption linearly increased with solution Pb concentrations. Pb adsorption approached saturation at high Pb concentrations and is well-described by the Langmuir equation. Pb adsorption to the Fe-gluconate compost was comparable to that of the FeSO_4 - compost even though the concentration of Fe was lower.

At pH 7 in the linear adsorption range, compost samples with Fe-gluconate showed higher adsorption than that of compost samples with FeSO_4 , suggesting Fe-gluconate may be more effective than FeSO_4 for Pb adsorption at the low Pb concentrations expected in soils and water.

The adsorption edge occurs at a significantly lower pH on the FeSO_4 -based compost than that made using Fe-gluconate. This indicates that the nature of Pb-sorbing sites on FeSO_4 -based compost are different than those on the Fe-gluconate-based compost. One possibility is that there are more Pb-OM sorption sites in the FeSO_4 -based compost whereas the Fe-gluconate sample has more Fe-OH sites.

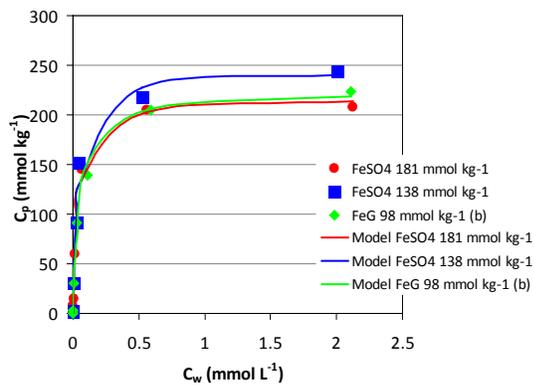


Figure 4: Pb adsorption isotherms with selected composts at pH 6 and modeling results obtained using Langmuir equation. Model parameters are presented in Table 1.

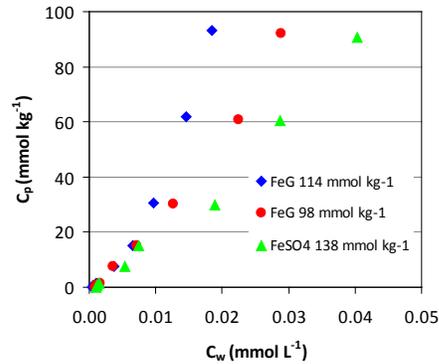


Figure 5: Pb adsorption isotherms with three selected composts at pH 7.

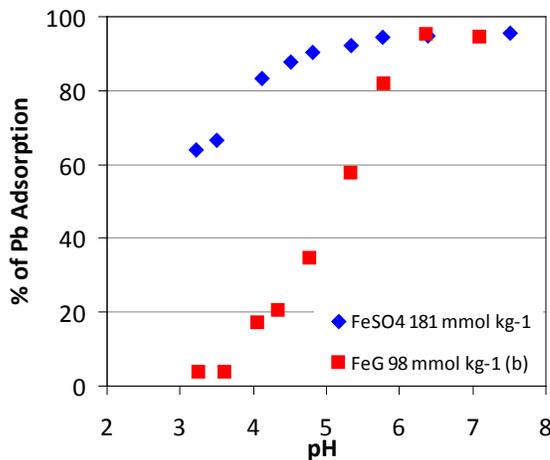


Figure 6: Pb adsorption edge curves made by representative compost samples of FeSO₄ and FeG.

Overall, all iron-compost samples showed high Pb adsorption ability based on our adsorption experiments. The effect of Fe content in compost on Pb adsorption is not conclusive, and a better understanding of both Fe-OH and OM sites in the mixed system will be required. Pb adsorption is more effective in a higher pH solution because there is less H⁺ to compete with Pb for both organic and Fe-OH adsorption sites, and the capacity and affinity of selected compost samples for Pb adsorption can be estimated by the Langmuir adsorption model. At pH 6, the capacity of the Fe-gluconate-based compost is comparable to those of the FeSO₄-based composts with much higher Fe contents. Interestingly, the higher affinity of Pb for the FeSO₄-based composts is the opposite of what is observed at pH 7, implying the nature of sorption sites depends on Fe source.

4. Stirred-flow Kinetics Experiments

During the stirred-flow kinetics experiments, the effluent Pb concentrations increased with longer leaching time, due to more binding sites occupied by the adsorbed Pb, and then approached a plateau close to the influent Pb concentration. The adsorption rates of Pb on FG 97 and FG 134 are dependent on the flow rates (Figures 7-8), with lower flow rates favor Pb adsorption since slower flow rates allowed for more time and contact for chemical reactions to occur.

At the similar experimental conditions, Pb adsorption ability FG 134>FG97>FS 138 (Figure 9), suggesting that FG compost generally has higher adsorption ability than FS compost. Consistent with the batch adsorption experiments, all Fe-composts demonstrate a high Pb adsorption capability.

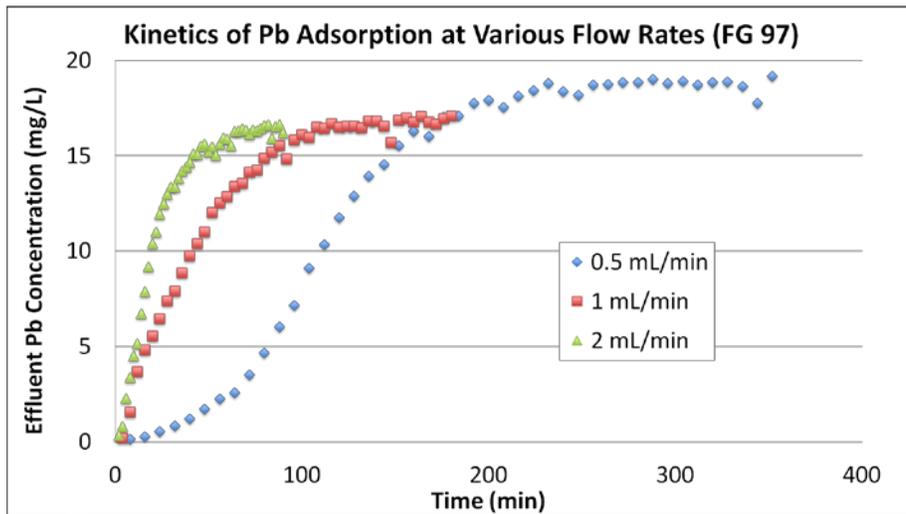


Figure 7. Kinetics of Pb adsorption on FG97 compost at various flow rates.

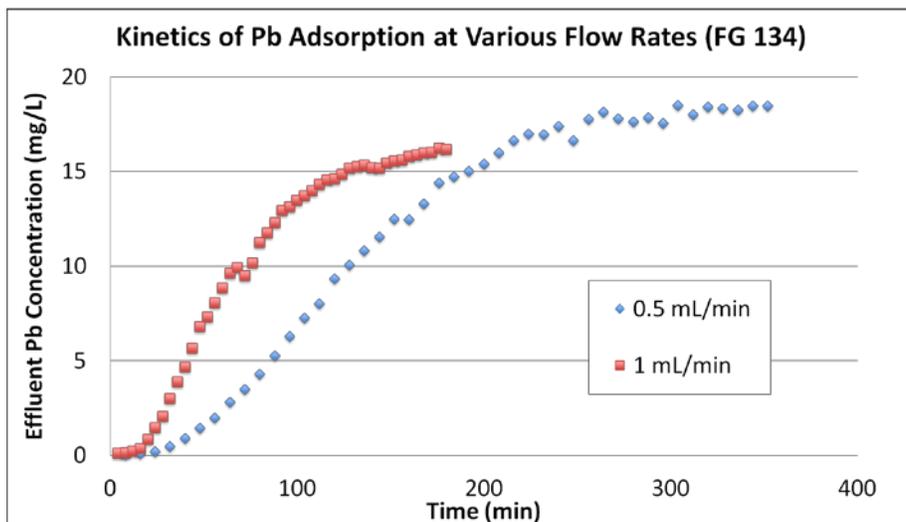


Figure 8. Kinetics of Pb adsorption on FG134 compost at various flow rates.

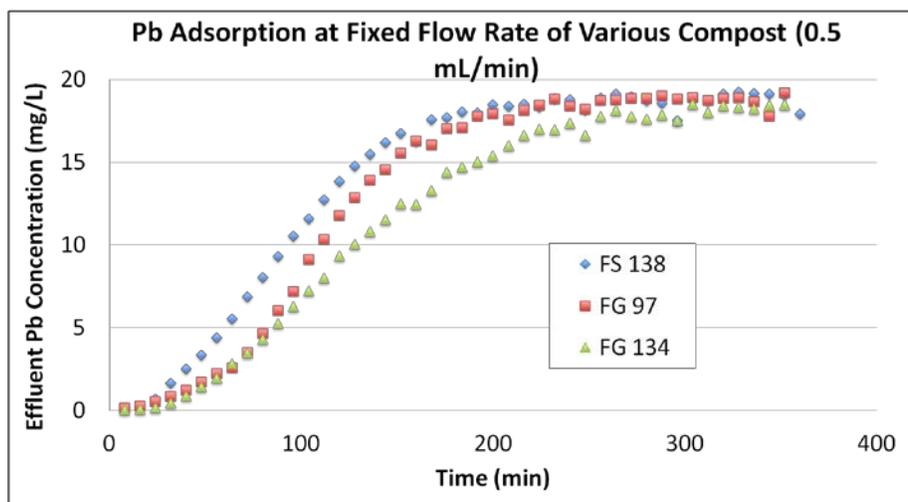


Figure 9. Kinetics of Pb adsorption on various compost samples at the fixed flow rate.

5. Discussion and Summary

Given we are able to achieve a final maturation/curing stage during the final compost process with the bins from O₂ Compost®, the DOC should be low enough to minimize transport of heavy metals within our study. This is also important for field applications in general as bio-filtration systems may facilitate heavy metal transport if improper composting methods are used. Zmora-Nahun et al (2005) focused on dissolved organic carbon as a function of feedstock material and composting time and found that, regardless of the source material, an average DOC concentration of 4 g/kg was achieved with all compost, the ultimate variable being composting time. The measure of this level of decomposition can be tied to the water-extraction or soluble carbon phase of the decomposition process, which makes DOC analysis useful for metal sorption and transport studies (Bernal, Sánchez-Monedero, Paredes, & Roig, 1998).

The NMR coupled with ATR-FTIR data is a useful method for characterization of compost. Overall, the compost samples sourced from 30 day composting show a relatively young media, rich in labile carbon groups. With the successive subsampling during the composting process, we would be able to see a gradual decrease in cellulose carbon and an increase in stable, aromatic carbon groups (Spaccini & Piccolo, 2008). The FG97 compost, a fully composted media, shows lower labile carbon and more recalcitrant or stable (lignin) components. With DOC analysis during these same subsampling points, we would be able to relate DOC behavior with compost maturity. Comparing compost maturity with solid-state NMR has been demonstrated to be a useful and even quantitative method for compost analysis (Spaccini & Piccolo, 2008). As our compost is amended with iron and requires a pretreatment removal step prior to NMR analysis, ATR-FTIR would likely be a useful and feasible approach for iron analysis within organics (Sharma, Ofner, & Kappler, 2010), especially coupled with other adoption analyses (arsenate or phosphate adsorption).

Both batch and stirred-flow experiments demonstrated that Fe-compost is a promising product for removing Pb from the stormwater, with high Pb adsorption capacity and fast adsorption rates. To further understand the mechanisms of Pb reactions with Fe-compost, the

characterization of Fe associated functional groups is essential. Currently we are conducting experiments at the Pacific Northwest National Laboratory to investigate Fe species in Fe-compost using Mossbauer Spectroscopy at EMSL. A mechanistic model is also under development to predict Pb reactions with Fe-compost. Furthermore, we will investigate the ability of P removal with our latest Fe-compost products from the 3rd trial.

As a whole, we have learned that compost used in biofiltration systems, specific for urban settings, is something that should be approached with a complete understanding of the biological, chemical, and physical controls that go into proper compost production. Improper development would likely result in the compost serving as a contamination source rather than a sink, a result directly counter to its primary purpose, which is mitigating the impacts of environmental contaminants sourced from urban development. Iron compost as a novel product will significantly improve the current practice to design effective bioretention systems for stormwater treatment.

- **List of Students Supported**

1. Patrick M. Freeze, Ph.D. Graduate Research Assistant, Department of Crop and Soil Sciences, Washington State University, Pullman
2. Jonathan Abarca, Undergraduate Intern, Department of Crop and Soil Sciences, Washington State University, Pullman

- **Publications**

1. Zhenqing Shi, Patrick Freeze, Jonathan Abarca, Markus Flury, and James B. Harsh. A new generation of Fe-enhanced compost for urban stormwater treatment. In preparation for *Water Research*
2. Jonathan Abarca, Zhenqing Shi, Jeff Boyle, James Harsh. Iron-Enhanced compost for soil remediation. Poster for 2014 WSU SURCA.
3. Jonathan Abarca, Zhenqing Shi, Jeff Boyle, James Harsh. A new iron-enhanced compost for stormwater treatment. Poster for 2014 WSU SURCA.

- **Awards and Achievements**

1. The U.S. Fulbright award (2015-2016) for Patrick Freeze.
2. The Association of International Agriculture and Rural Development Future Leader Forum (AIARD-FLF) award for Patrick Freeze.

Reference:

- Bernal, M. P., Sánchez-Monedero, M. A., Paredes, C., & Roig, A. (1998). Carbon mineralization from organic wastes at different composting stages during their incubation with soil. *Agriculture, Ecosystems & Environment*, 69(3), 175-189.
- Brown, S. L., I. Clausen, M. A. Chappell, K. G. Scheckel, M. Newville and G. M. Hettiarachchi (2012). High-Iron Biosolids Compost-Induced Changes in Lead and Arsenic Speciation and Bioaccessibility in Co-contaminated Soils. *Journal of Environmental Quality* 41(5): 1612-1622.
- Carballo, T., Gil, M., Gomez, X., Gonzalez-Andres, F., & Moran, A. (2008). Characterization of different compost extracts using Fourier- transform infrared spectroscopy (FTIR) and thermal analysis. *Biodegradation*, 19(6), 815-830.
- Ecology and King County (2011). Control of toxic chemicals in Puget Sound: assessment of selected toxic chemicals in the Puget Sound basin, 2007-2011. Washington State Department of Ecology, Olympia, WA and King County Department of Natural Resources, Seattle, WA.
- Gao, X., Laskar, D. D., Zeng, J., Helms, G. L. and Chen, S. (2015). A ¹³CCP/MAS-based nondegradative method for lignin content analysis. *ACS Sustainable Chem. Eng.* 3, 153-162.
- Huang, G., Wu, Q., Wong, J., & Nagar, B. (2006). Transformation of organic matter during co-composting of pig manure with sawdust. *Bioresour. Technol.*, 97(15), 1834-1842.
- Sharma, P., Ofner, J., & Kappler, A. (2010). Formation of Binary and Ternary Colloids and Dissolved Complexes of Organic Matter, Fe and As. *Environ. Sci. Technol.*, 44(12), 4479-4485.
- Shi, Z., Y. W. Chan and J. B. Harsh (2012). Lead adsorption on iron-amended composts. The 22nd V.M. Goldschmidt Conference. Montreal, Canada.
- Smidt, E., & Meissl, K. (2007). The applicability of Fourier transform infrared (FT- IR) spectroscopy in waste management. *Waste Manage.*, 27(2), 268-276.
- Spaccini, R., & Piccolo, A. (2008). Spectroscopic Characterization of Compost at Different Maturity Stages. *CLEAN – Soil, Air, Water*, 36(2), 152-157.
- Zmora-Nahum, S. M. O. T. J. C. Y. (2005). Dissolved organic carbon (DOC) as a parameter of compost maturity. *Soil Biology & Biochemistry*, 37(11).