



Great Lakes Maritime Research Institute

*A University of Wisconsin - Superior and
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Title: Combining Fine Dredged Material and Biosolids for Beneficial Reuse: Wet vs. Dry Water Quality Implications

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Progress Report

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Background/Objectives

The beneficial use of environmental materials has the potential of providing sustainable solutions for solids management in many different arenas. Both dredged material from the Duluth-Superior Harbor and biosolids from the Western Lake Superior Sanitary District in Duluth, MN have been used with some success for the purpose of creating topsoil and establishing vegetation in the challenging setting of mineland reclamation. While experimental-scale and pilot-scale field applications have taken place in upland situations, there is frequently a need to create wetland habitat during mineland reclamation and other restoration projects. The use of dredged material and biosolids carry with them potential water quality concerns, which are heightened in the setting of wetlands due to typically direct connectivity with ground and surface water as well as the wetland habitat itself. Many of the chemical and biological processes controlling the release of metals and nutrients differ in settings where soil is continuously saturated (wetland) versus occasionally wetted (upland). The purpose of the work described herein was to investigate how metals and nutrients are released from different mixture ratios of fine dredged material and biosolids under saturated and occasionally-wetted conditions.

Methods/Analytical

Five different blend ratios outlined in Table 1 were tested in the lab using ~2.5 inch diameter polycarbonate columns with a nylon mesh screen installed in the bottom to support solid materials. Four columns for each blend ratio were incubated at constant temperature and controlled humidity conditions under either dry (Figure 2a) or wet (Figure 2b) conditions for a period of 8 weeks. Once per week, water was added to the top of the columns and allowed to equilibrate with the solids for a period of 2 hours after which the leachate from columns was collected and analyzed for a suite of water quality parameters including alkalinity, conductivity, nitrate, ammonia, pH, and metals. Though water addition occurred consistently on a weekly basis, samples were preserved and analyzed at 0, 1, 2, 3, 5, and 8 weeks. Alkalinity was measured by titration, ammonia was measured spectrophotometrically, pH and conductivity were quantified with electrodes, nitrate and phosphate were quantified by ion chromatography, and metals were measured by Inductively Coupled Plasma-Mass Spectrometry.

Results

Alkalinity & Conductivity

Alkalinity differed markedly amongst the wet and dry lab experiments. Regardless of blend ratio, alkalinity remained below 2 millimoles per liter (mM) for dry experiments while alkalinity was above 4mM after the initial flushing for all wet experiments. If alkalinity is taken as a surrogate for mineral dissolution (total conductivity showed similar trends), it is clear from these results that the 2 hour equilibration time was not sufficient to allow pore waters to fully interact with minerals present in the solids. Although a consistent trend was not observed with respect to mixture ratios, the 0 and 10% biosolids columns appeared to have lower alkalinity leachate under saturated conditions and higher alkalinity under dry conditions compared to other blend ratios.

Nutrients: Nitrate, Ammonia, and Phosphate

Total nitrogen concentrations in leachate from the dredged-biosolids mixtures generally increased with increasing biosolids content under both saturated and unsaturated conditions (Figure 2). Total N

concentrations ranged from 10 to 70 mg/L as N in dry conditions and from less than 1 to greater than 140mg/L in wet conditions. The composition of the nitrogen in leachate changed dramatically as the biosolids content increased. The labile carbon provided by biosolids likely facilitated microbial processes which converted nitrate to ammonia. Under dry conditions, mixtures with biosolids contents of 50% and less had 80% to 90% of total N in leachate comprised of nitrate. For mixtures stored under wet conditions, nitrate comprised a majority of total N in leachate only for the 0 and 10% biosolids mixtures (Figure 2). These observations provide strong evidence that continuously saturated conditions not only affected mineral dissolution but also resulted in a characteristically different redox environment.

In both dry and wet conditions, phosphorus concentrations in leachate from dredged-biosolids mixtures of 0%, 10%, 20%, and 50% biosolids were all relatively low (<4mg/L, Figure 3). However phosphorus concentrations in leachate from the 100% biosolids material were higher under dry conditions (7-9mg/L) and extremely elevated in saturated conditions (75-275mg/L). After nitrate, the next most energetic electron acceptor in most natural systems is ferric iron oxide which often represents a strong binding phase for phosphate. Ferric iron minerals are reduced by bacterial communities which thrive in anoxic environments that are also depleted of nitrate. The absence of exposure to oxygen and nearly complete consumption of nitrate in the saturated conditions with significant biosolids fraction likely facilitated the release of phosphate from the solid phase in the saturated experiments. Extremely elevated phosphate concentrations were only observed in leachate from the saturated 100% biosolids mixture (Figure 3) although nitrate observations suggest that both the saturated 50% and saturated 20% biosolids mixtures were also depleted of nitrate (Figure 2). The reason for why iron reduction did not result in the mobilization of iron (and consequently phosphate) in the saturated 50% and 20% biosolids mixtures is not known.

Metals

The metals measured in leachate which exceeded potentially applicable water quality standards (Table 2) were arsenic, cobalt, and copper (Figure 4). Leachate from dry columns contained higher arsenic and cobalt concentrations than those stored saturated. Leachate from saturated columns contained higher concentrations of copper. Aside from initial conditions, a distinct trend of increasing leachate metal concentration with increasing biosolids content (up to 50%) was observed for arsenic as well as cobalt and zinc to some extent. Although at the surface, this would suggest that these metals are originating from the biosolids material, evidence suggests that geochemical conditions facilitated by the presence biosolids may lead to the mobilization of metals originating from either material. Elucidating the specific mechanisms responsible for the leaching of metals from the dredged-biosolids mixtures will require further study. For example, sulfide plays an important role in controlling the mobility of many metals, but its effects were not quantified directly in this study.

Hydraulics

Perhaps the largest difference between wet and dry incubation conditions was the observed change in hydraulic characteristics in blend ratios containing predominantly dredged material. After approximately 5 weeks, the 0%, 10%, and 20% biosolids content stored under saturated conditions essentially stopped draining. Typically less than 10mL of volume was recovered from these columns despite an attempt to drain for >12 hours. This evidence suggests that dredged material (predominantly clay) took several weeks to completely saturate. Alternatively, previous research has shown that biological organisms,

which exist predominantly under saturated conditions, can bind together inorganic and organic portions of soils, forming a crust and reducing hydraulic conductivity. The practical implication of slow hydrologic drainage under saturated conditions for the beneficial use of dredged material for land application or wetland habitat creation is that very little drainage through the dredged material will occur if it remains saturated. This is important to consider when interpreting some of the water quality measurements which showed higher concentrations in leachate under saturated conditions. Although concentrations in leachate were observed to be higher under continuously saturated conditions for ammonia, phosphate, and copper; a greatly reduced volume of drainage through saturated clay material would limit the total mass of these chemicals transported to ground water from a wetland created with dredged material.

Conclusions

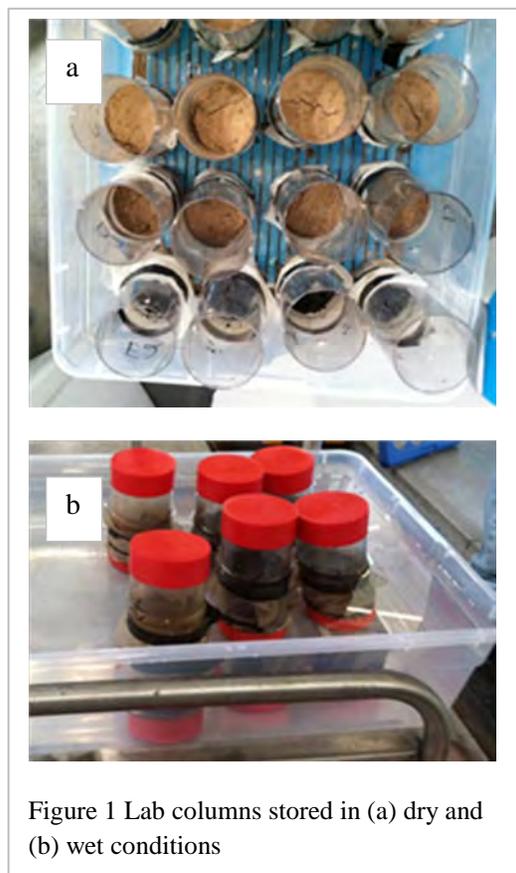
The results of this study demonstrated that important differences can be expected between the water quality impacts of upland and wetland applications of dredged material, biosolids, or some combination thereof. The composition of total nitrogen (nitrate vs. ammonia) in leachate shifted dramatically depending on both the biosolids content and the saturation conditions. Phosphate was generally higher in saturated conditions likely owing to the more reducing environment induced by a lack of access to atmospheric oxygen. In some instances metals concentrations in leachate were related to biosolids content; however, the origin of the metals (dredged material or biosolids) as well as the mechanism leading to their mobilization are related to a complex set of interrelated biogeochemical processes likely influenced by the high carbon content of biosolids. In addition to geochemical controls on nutrient and metal mobility, results suggest that hydrogeologic controls may drastically reduce transport of water and dissolved chemicals from continuously saturated fine dredged material. This consideration should lessen the effects from wetland reuse applications on local groundwater, but does not alleviate concerns about effects on the local wetland ecosystem or potential connectivity via surface water.

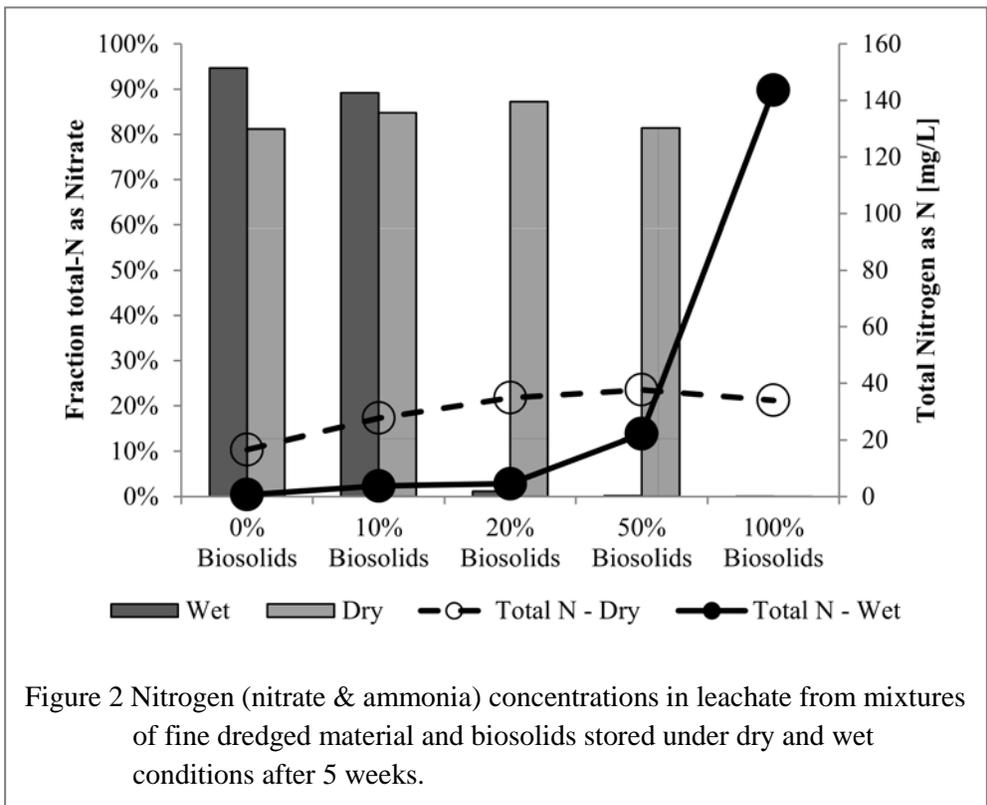
Acknowledgements

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Table 1 Blend ratios for lab experiments

Blend Ratios	Fraction Biosolids (by mass)	Fraction Fine Dredged (by mass)
A	0	1
B	0.1	0.9
C	0.2	0.8
D	0.5	0.5
E	1	0





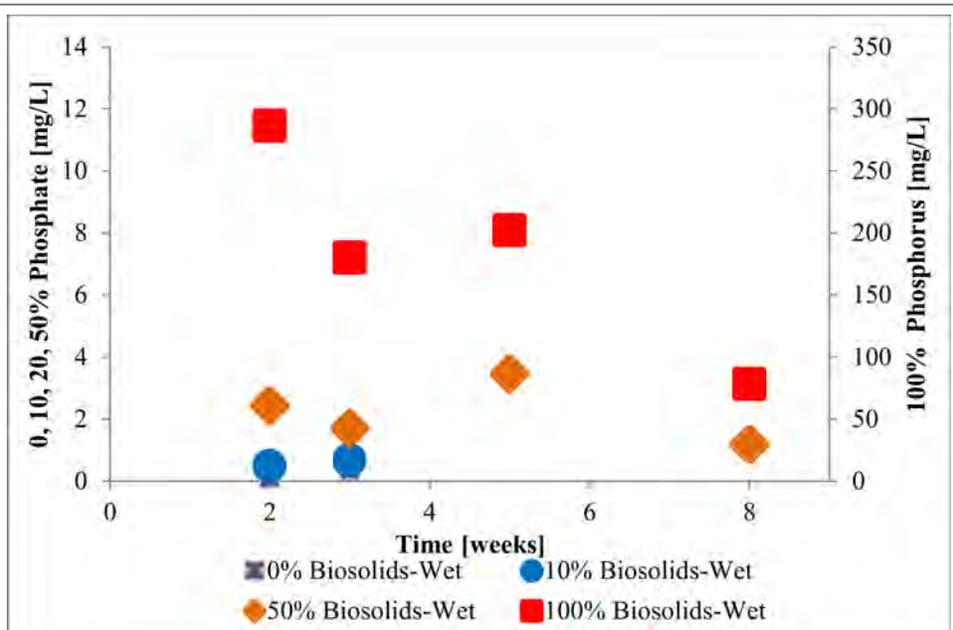


Figure 3 Phosphate concentrations measured 2, 3, 5, and 8 weeks after the initiation of lab experiments in leachate from mixtures of fine dredged material and biosolids stored under wet conditions.

Table 2 Potentially applicable water quality standards for the protection of human health and ecosystem health (toxicity/wildlife) in Minnesota and the Lake Superior Watershed in particular.

Chemical	EPA-MCL ¹ [mg/L]	State of MN – Class 2B/C/D toxicity-based ² [ug/L]	State of MN – Human health-based ² [ug/L]	State of MN – Class 2B/C/D toxicity based Lake Superior ² [ug/L]	State of MN – Human health- based Lake Superior ² [ug/L]
Nitrate	10,000				
Ammonia		40			
Arsenic	10		53		2.0
Cobalt		5.0			
Copper	1,300	9.8		9.3	

¹Maximum Contaminant Levels for drinking water: <http://water.epa.gov/drink/contaminants/index.cfm>

²Guidance Manual for Assessing the Quality of Minnesota Surface Waters for Determination of Impairment: 305(b) Report and 303(d) List. Minnesota Pollution Control Agency: wq-iw1-04.

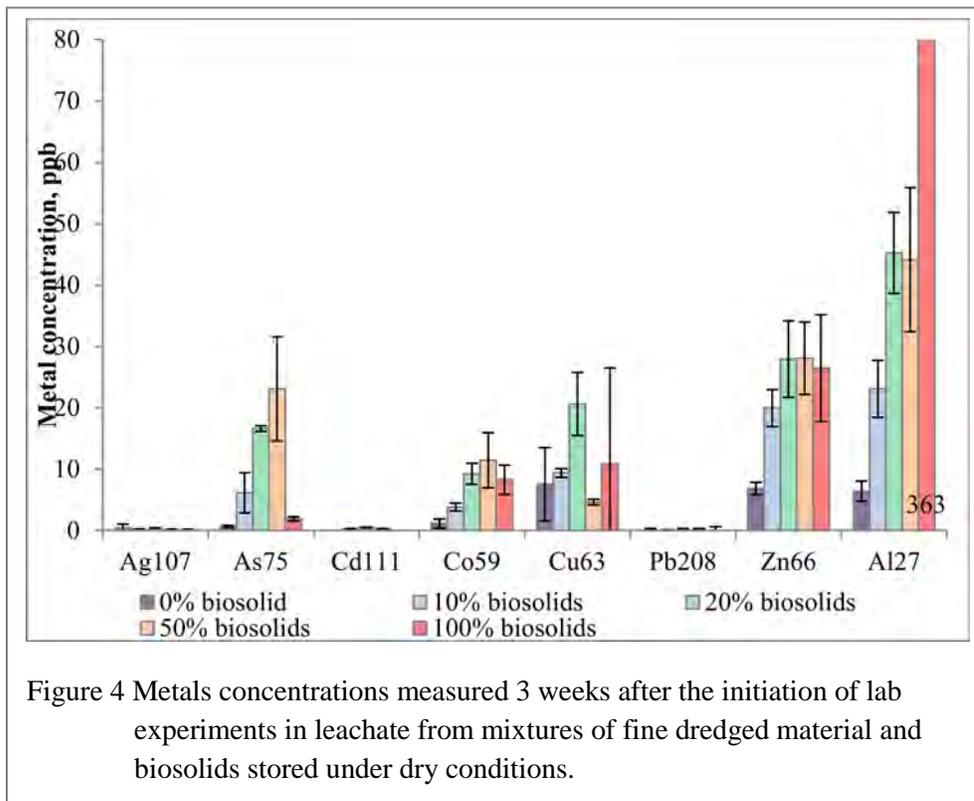


Figure 4 Metals concentrations measured 3 weeks after the initiation of lab experiments in leachate from mixtures of fine dredged material and biosolids stored under dry conditions.

Bio

Dr. Johnson is an assistant professor in the University of Minnesota - Duluth Department of Civil Engineering. He received his PhD from the University of Texas and has been teaching classes and performing research related to engineered solutions to water quality problems since arriving at UMD in 2009. He is currently involved in projects related to the environmental impacts of mining in NE Minnesota and the risk posed by contaminated sediments in the St. Louis River Estuary.

