

Nickel Removal from the Water Column

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Introduction

European regulatory requirements have created a need to define whether or not metals are removed from freshwaters and into the substrates in a timely manner, reducing their potential for adverse ecological effects. Discussions amongst industry sponsors and academic scientists of the Environmental Toxicity Advisory Panel (ETAP) suggested research in this area as a priority. Metals Research Organizations (MERA) decided to fund a research effort to begin addressing the issue, of which this project is one component. The overall goals of this research project were to 1) Initiate research to better demonstrate substrate-associated Ni is “irreversibly” and rapidly removed from the water column using a range of freshwater substrate types and 2) Initiate research to better demonstrate once Ni removed from the water column it is not released from substrates during remobilization in an ecologically significant manner. Specific project aims were to: 1) Select from a variety of substrates the optimal types for conducting metal removal studies. These would include a low binding potential (LBP) substrate and one that is optimal for metal removal; 2) Conduct the OECD 29 Transformation/Dissolution Protocol (T/DP extension, part 1) testing of the water removal and binding of Ni using LBP (CANMET and Raisin) and optimal removal (Buffalo) substrates; 3) Evaluate remobilization of metals (part 2); and 4) Begin studies on the role of pH, Eh and Kd in the T/DP Extended Assay and mesocosm systems to determine whether there is reversibility (with and without remobilization).

Following discussions with scientists MERA, a series of experiments were designed to evaluate their influence of Ni removal from the water column. These initial tests have included evaluations of 4 substrates, introduced in a dry, wet or rewetted condition, incubated or non-incubated, and studied how pH responded to the introduction of CO₂ by a capillary tube or airstone (T/D P extension part 1 – removal) and metals response of remobilization (part 2). The basic T/DP protocol was followed with slight modifications. Results are presented below in Figures 1 – 12.

Methods

Tests were conducted using 10x diluted OECD 203 solution in 1 liter Erlenmeyer flasks on a shaker table (4 treatments x 2 replicates = 8 flasks per exposure). One gram of substrate was added to solution and briefly allowed to settle. Then, nickel chloride (1 mg/L) was added to flasks and shaken ~5 minutes at 150 rpm on an orbital shaker table, followed by time 0 water sampling. Water samples were taken at various times during exposure. In the first three tests, airstones were used to diffuse 0.5% CO₂ either directly into solution or in the overlying head space, and included Buffalo, River Raisin, and Plum Creek substrates. The ideal target pH throughout the exposure was 6 (+/- 0.2). At least one blank treatment was included in each test without substrate or nickel. Nickel chloride (1 mg/L) solution was in 10x diluted OECD 203 solution (time sample -1). Time 0 samples were taken approximately 5 minutes after substrate was added to flasks. Chronic tests (28 d exposure) were sampled frequently on day 1, followed by weekly samples. A 28 d test was also conducted with 10x diluted OECD solution spiked with 1 mg/L of copper

chloride a 1 mg/L of nickel chloride together, utilizing CANMET LBP, Raisin Non-Incubated, Raisin Incubated, and Buffalo substrates (10 g treatments). Seventy percent removal was calculated based on an initial -1h time sample for results in Tables 1 - 3.

Raisin Non-Incubated substrates were represented by dried Raisin substrate, while Raisin Incubated substrate was prepared as followed: 1) weigh desired amount of dried Raisin substrate in Pyrex bottle, 2) dampen substrate with DI water, 3) purge headspace of bottle with nitrogen, 4) seal bottle and let rest for at least 7 days.

A remobilization experiment was conducted at the end of a 96 h exposure by placing test flasks on an orbital shaker table at 150 rpm for 1 h. Water samples were taken for dissolved Fe and Ni at various times post shaking (e.g. R0, R1, R2, etc.).

In addition, osmotic effect tests were conducted to investigate the mechanistic process of Ni removal. Osmotic strength was adjusted by KCl addition to OECD 203 solution to achieve 0.01 M, 0.1 M, and 1.0 M solutions. Given the rapid rate of outer sphere complexation, samples were taken at time 0, 1, 3, 5, 10, and 20 minutes.

Results

The ability of different substrates to influence Ni removal from the water column was evaluated, with substrates pre-treated in various ways. The substrates and their pre-treatments consisted of tests with Plum Creek substrate, Buffalo and Raisin substrates. Table 1 summarizes substrate chemistry and characteristics. Buffalo substrate is a NIST certified substrate and several factors (total organic carbon, copper substrate values, and texture) were not reported. Total iron is reported in percentage for CANMET and Buffalo while Raisin and Plum are reported in $\mu\text{g/g}$. Raisin and Plum are most similar among 4 substrates, particularly in total Fe and Ni, Cu, Zn, and Pb substrate concentrations. Texturally, Raisin and CANMET are classified as sand while Plum is sandy loam.

The substrate treatments were Dry (dried at 60° C for > 48 h); Rewetted (dry + wetted with Milli-Q water); and Wet (non-manipulated substrate direct from field sample bottle). The Dry Plum substrate removed Ni more rapidly than Plum Wet and Plum Rewetted treatments (Figure 1). Another test exposed test solutions to different methods of diffusing CO₂ (capillary tubing or airstones in head space) (Figure 2). The pH was difficult to control due to flow variability and differences in substrate characteristics; however, pH was similar among treatments. In Figure 1, the maximum pH increase was 0.4 units to 6.78, with the other three treatments remaining within 0.1 unit. In Figure 3, pH increased between 0.7 and 1 unit. While in Figure 4, pH was relatively stable with increases between 0.2 and 0.7 units (maximum of 6.7). The greatest increase in pH occurred with the Buffalo Dry treatment. A comparison of all 3 substrates wet vs. dry showed dry Buffalo to have the optimal removal of ~69% in 4 days. Another test exposed Buffalo and Raisin dry substrates (1 g vs 10 g treatments) for 28 days (Figure 5, Table 2). Buffalo and Raisin dry 10 g treatments removed nickel at similar rates, though Buffalo removed a higher amount in the first 4 hours. Buffalo 1 g treatment removed Ni more rapidly compared to Raisin 1 g treatment. Throughout the 28 days, pH varied greatly; ranging from 6.09 – 6.35 at time period - 1, increasing approximately 0.5 pH units at 120 hours, and increasing approximately 1.0 pH units at the end of 28 days.

Results from a 28 d test with Buffalo, CANMET, Raisin Incubated, and Raisin Non-Incubated exposed to Ni and Cu are presented in Figure 6, Figure 7, Table 3, and Table 4. All test substrates achieved 70% removal of both metals in 28 d.

The acid volatile sulfide/simultaneously extracted metal ratio (AVS/SEM) of Raisin substrates (pre/post exposure, incubated vs non-incubated substrates) are displayed in Table 5. SEM elements analyzed include Ni, Cu, Cd, Zn, and Cr. Cd values were reported as non-detects by ICP-OES. All treatments were

predicted to be toxic based on SEM-AVS values greater than 0. Pre-exposure Non-Incubated sulfide was 0, while post exposure Non-Incubated exhibited a slight increase in sulfide (0.021 $\mu\text{mol/g}$). On the other hand, a post exposure Incubated treatment showed a slight decrease in sulfide compared to pre-exposure Incubated.

Figures 8 – 10 show the osmotic ionic strength testing. Seventy percent removal of Ni was achieved with Raisin Incubated and Raisin Non-Incubated substrates in 0.01 M Raisin Incubated, in 0.1 M Buffalo and Raisin Incubated, and Raisin Non-Incubated in the 1.0 M exposures. CANMET LBP substrate did not achieve 70% Ni removal in 4 days.

Results from 96 h exposure and 1 h remobilization are shown in Figure 11, Figure 12, Table 6, and Table 7. Canmet treatment reached 70% removal between sample periods R24 and R96 (between 120 – 192 h from experiment initiation), Raisin Non-Incubated at 96 h, Raisin Incubated between 24 and 96 h, and Buffalo between R6 and R24 (102 – 120 h). No Ni or Fe flux was noted post remobilization. pH varied greatly with minimum of 5.98 and maximum of 8.7. Highest pH was exhibited by Raisin Incubated treatment, while Canmet was most stable post 24 h, where pH dropped from 6.43 to 6.18 at R96. pH increased slightly in all treatments after remobilization (R0) except Canmet.

Table 8 provides a summary of all experiments while Table 9 provides approximate removal times for selected experiments. Seventy percent removal could not be calculated in all experiments due to failure to obtain time zero values (background).

Discussion

The experiments demonstrated that Ni is rapidly removed from the water column, under a wide variety of conditions using T/DP extended methods. The removal rates vary depending on the conditions and the substrates, but most resulted in rapid removal (over 70%) within 96 hrs.

Substrate mass and pH had an important role when comparing 1 g and 10 g loading regardless of substrate type. The 10 g treatments are more efficient at removing Ni, compared to 1 g; however, both removed 70% in 4 days. Buffalo substrate appears to be more efficient at removing nickel compared to Plum Creek. Buffalo 10 g, Buffalo 1 g, and Raisin 10 g. All substrates removed 70% of nickel within 120 h, while Raisin 1 g failed at the end of 28 d with only 54% removed (Fig. 5).

Based on early results from the 28 d test with combined Ni and Cu, it appeared these metals may compete for binding sites. Only the Raisin treatments achieved 70% removal of Ni in 96 h, while all four treatments achieved 70% removal of copper within 96 h (10 g loading). However, all treatments achieved 70% removal of nickel within 28 d (Fig. 6).

Shaking at 150 rpm for 1 h did not cause Ni or Fe remobilization into overlying water. At time of remobilization, Raisin Non-Incubated and Raisin Incubated had achieved 70% removal, with Buffalo and Canmet close at 63% and 60%, respectively. However, Buffalo and Canmet achieved 70% removal within time constraints of the test (~8 d) which further supports removal of Ni within 28 d.

Sulfide concentrations in Raisin substrates, both pre/post exposure and incubated/non-incubated values, were low with slightly elevated SEM values, resulting in potential for toxicity based on SEM-AVS. This is expected in oxic systems. Pre-exposure Non-Incubated substrate had no sulfide, however, post-experiment, non-incubated substrates had slightly elevated levels of sulfide. Non-Incubated treatments were only dried Raisin substrate and the AVS test is typically conducted on wet substrates. The drying resulted in low AVS, thus creates an artifact when considering the SEM-AVS based bioavailability model. Sulfide likely only had time to reduce in substrate micropores given similar results between Incubated and Non-Incubated treatments.

Next Steps

Current and near-future research is focused on identifying the properties of a Reasonable Worst Case sediment for broad-scale application of the T/DP Extended Assay. A large number of substrates are being analyzed for low binding potential. These, are those substrates tested in this study, and by CANMET and Kent State University are being characterized these traits related to metal removal. Once the substrate traits are identified for a RWC sediment it will allow for the collection and identification of RWC substrates world-wide.

Results of the T/DP Extended Assay (part 1 and part 2) studies from CANMET, KSU and University of Michigan experiments will be integrated (along with prior documentation) to strengthen the weight-of-evidence decision-making for identifying research gaps and metal rapid removal hazard classification.

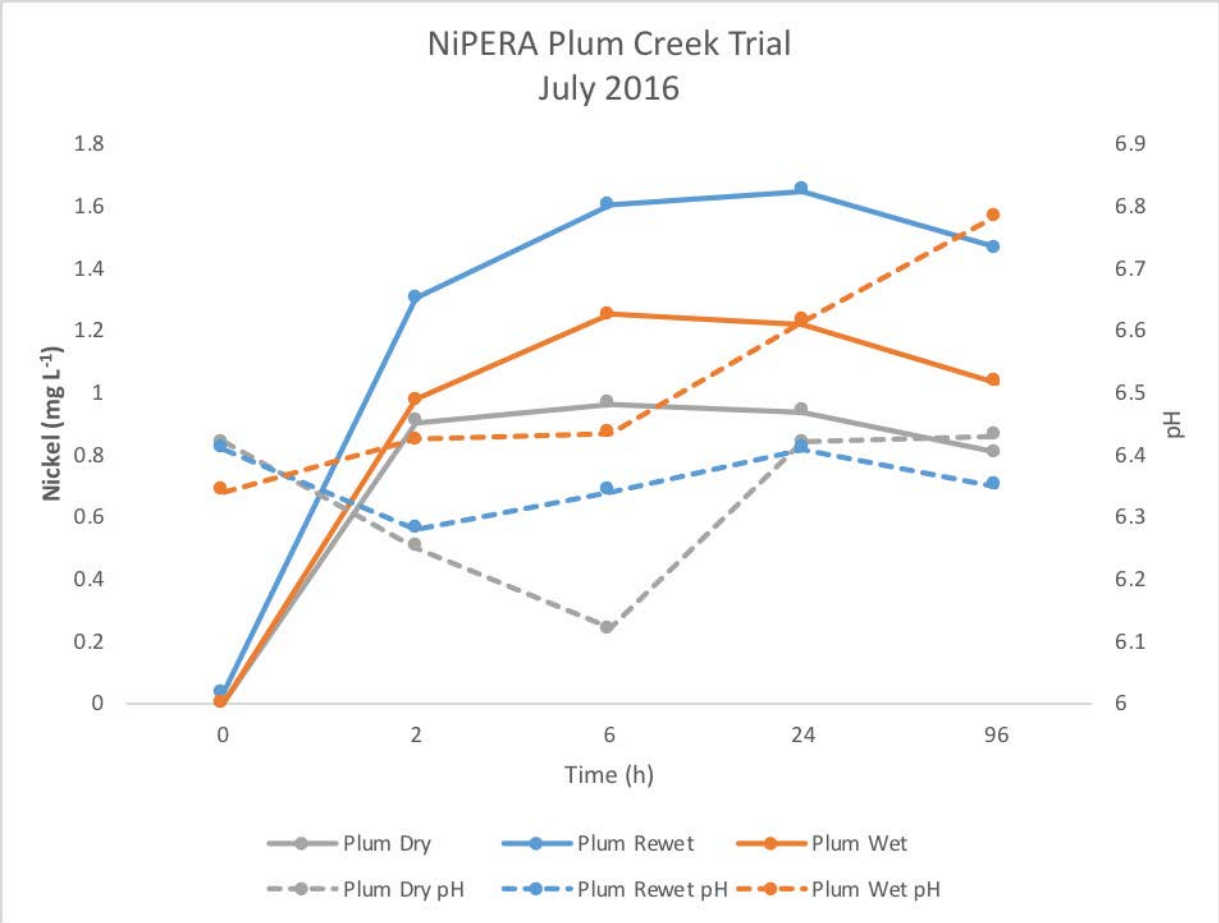


Figure 1. Plum Dry vs Rewet vs Wet exposure with 1 mg/L nickel chloride.

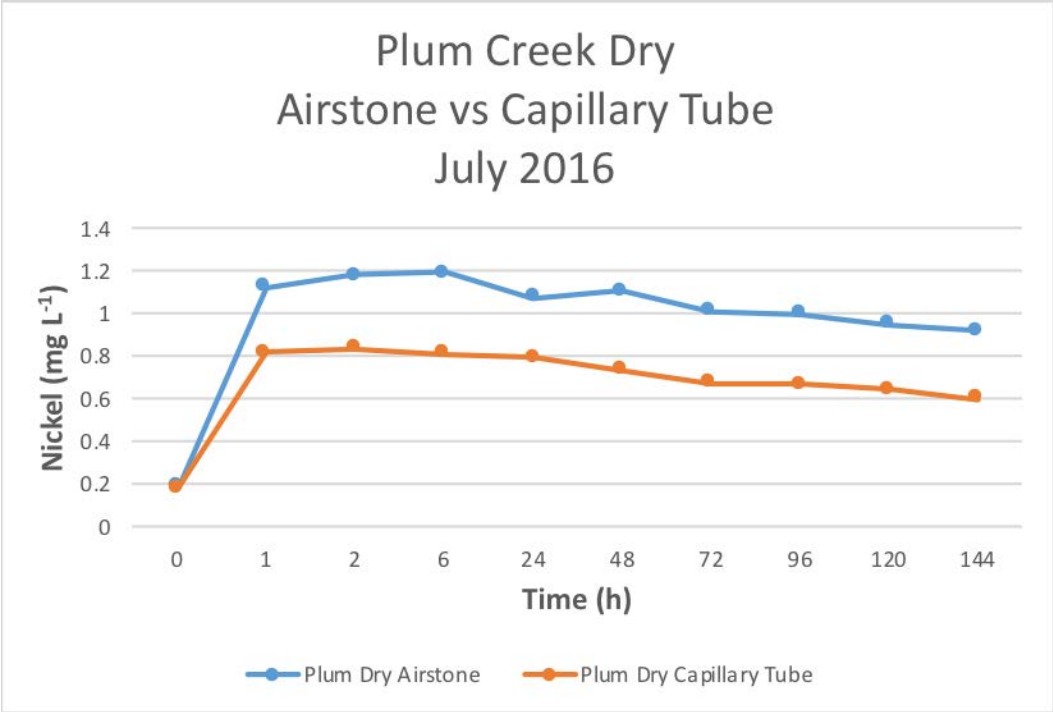


Figure 2. Airstone vs Capillary tube exposure

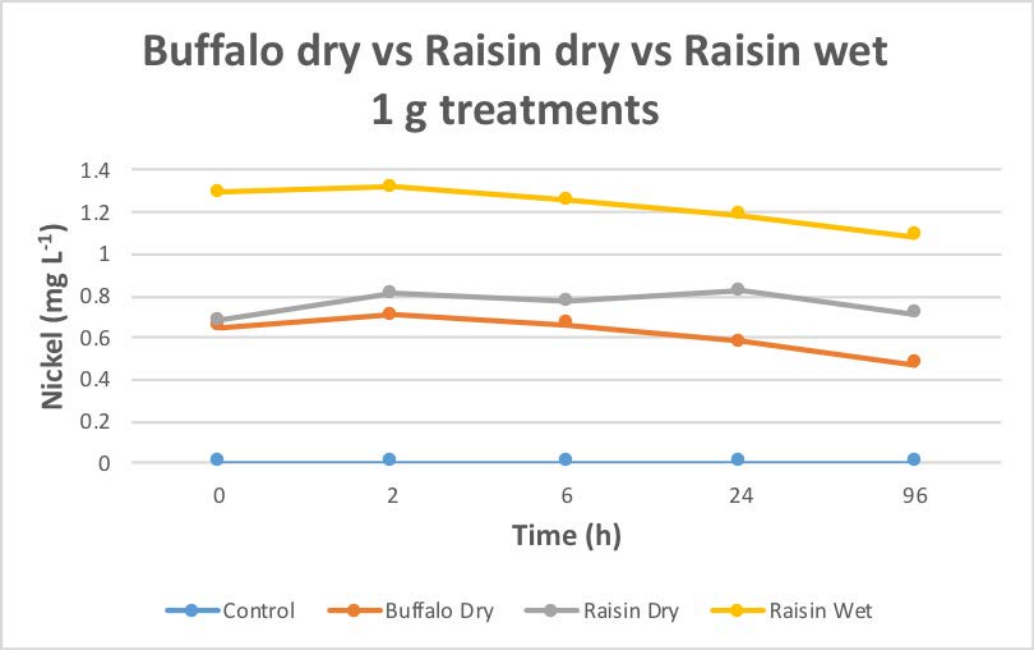


Figure 3: Dry vs. Wet testing Round 1 (time 0 sample was collected after Ni added)

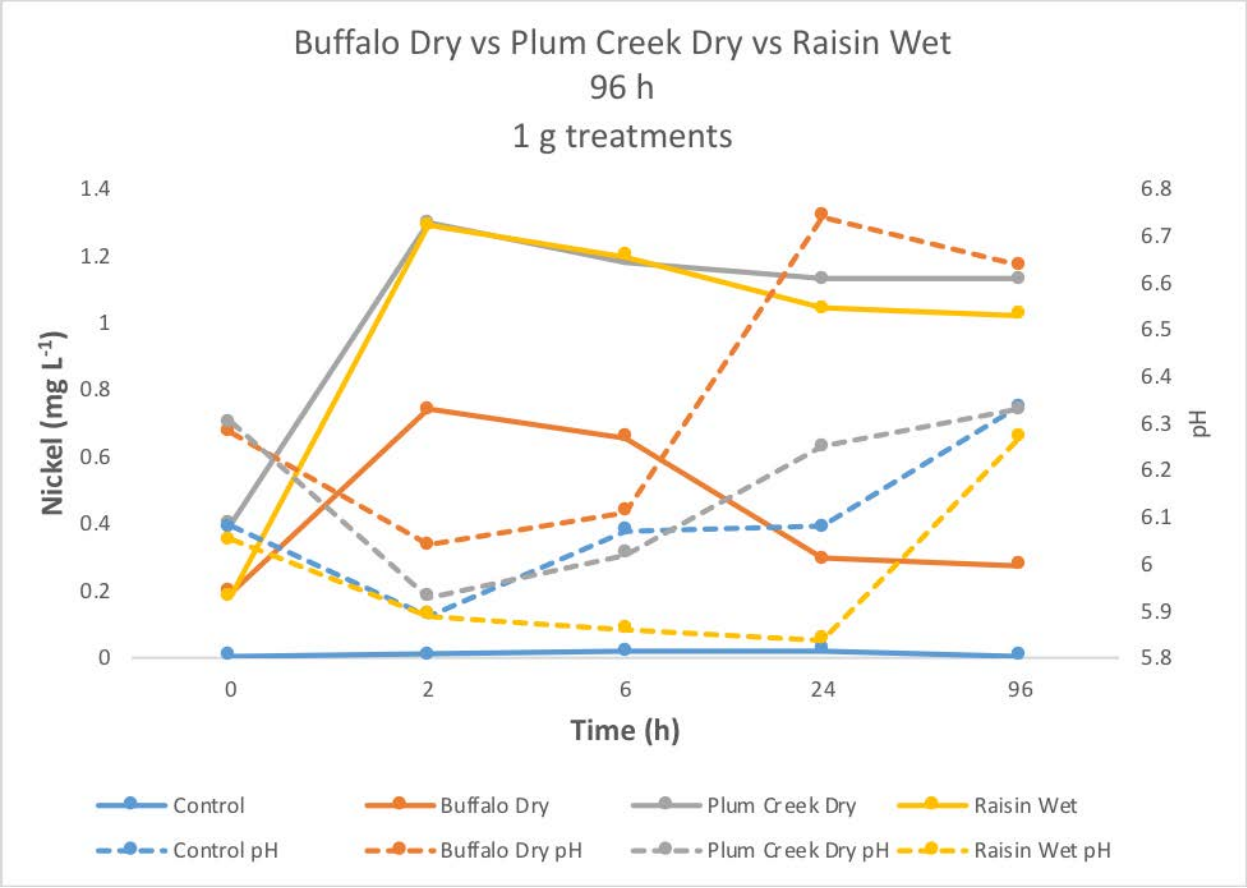


Figure 4: 96 h exposure with Raisin Wet, Plum Creek Dry, and Buffalo Dry to determine optimal wet vs dry state.

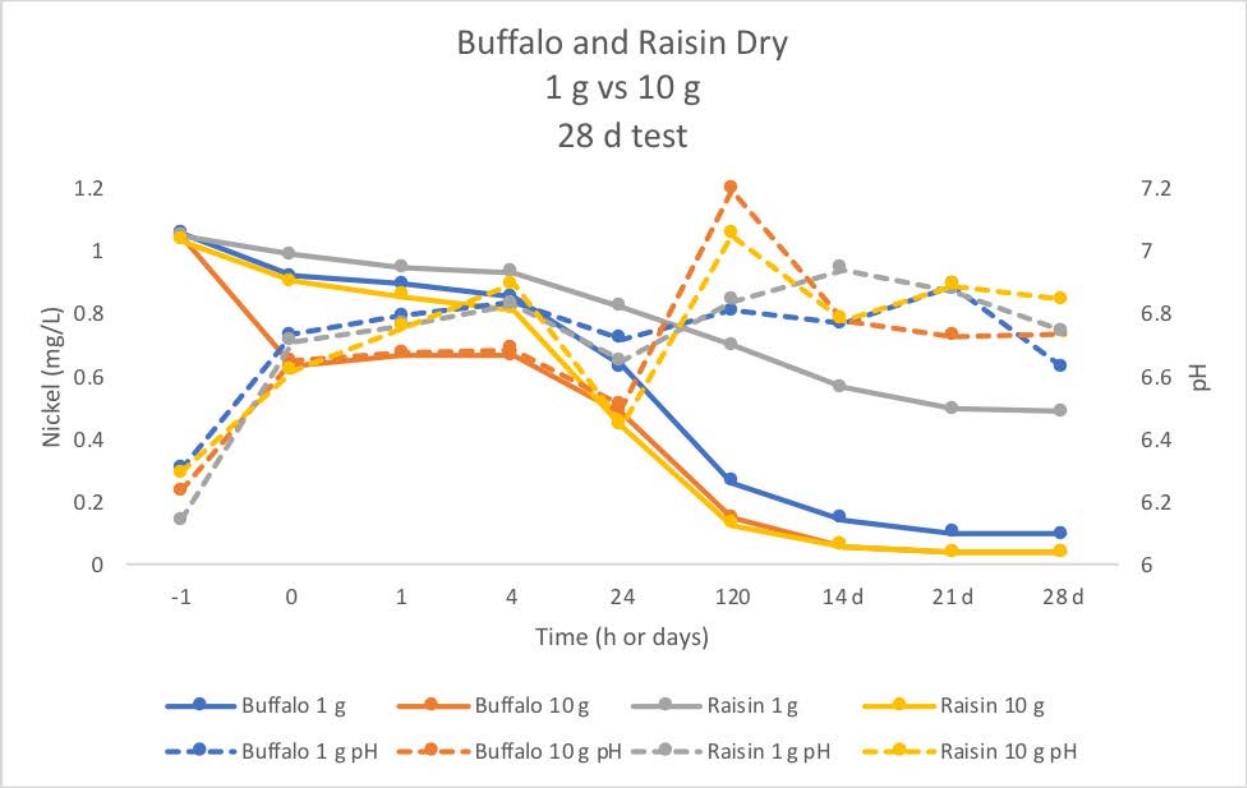


Figure 5: 28 d Buffalo and Raisin Dry 1 g vs 10 g (time -1 sample was nickel chloride in 10x diluted 203 OECD, time 0 sample was post substrate addition)

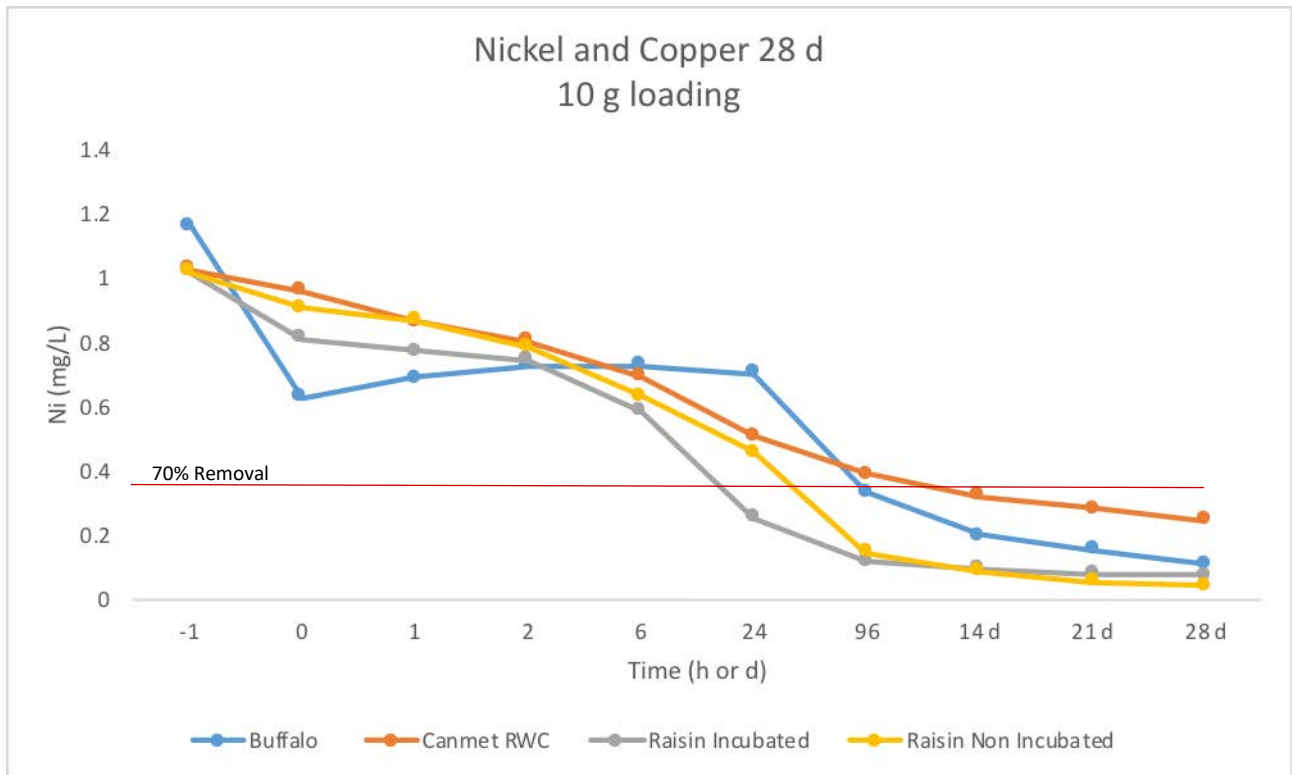


Figure 6: *Nickel and Copper 28 d exposure, nickel only shown here. Buffalo time 0 h and 2 h are reported lower than subsequent sampling. Substrate was stuck to the side of flasks, and with 10 x OECD 203 addition (after each sampling time to replenish volume) substrate was rinsed into flask which may account for this difference. Raisin non-incubated and Raisin Incubated treatments achieved 70% removal of nickel within 96 h.*

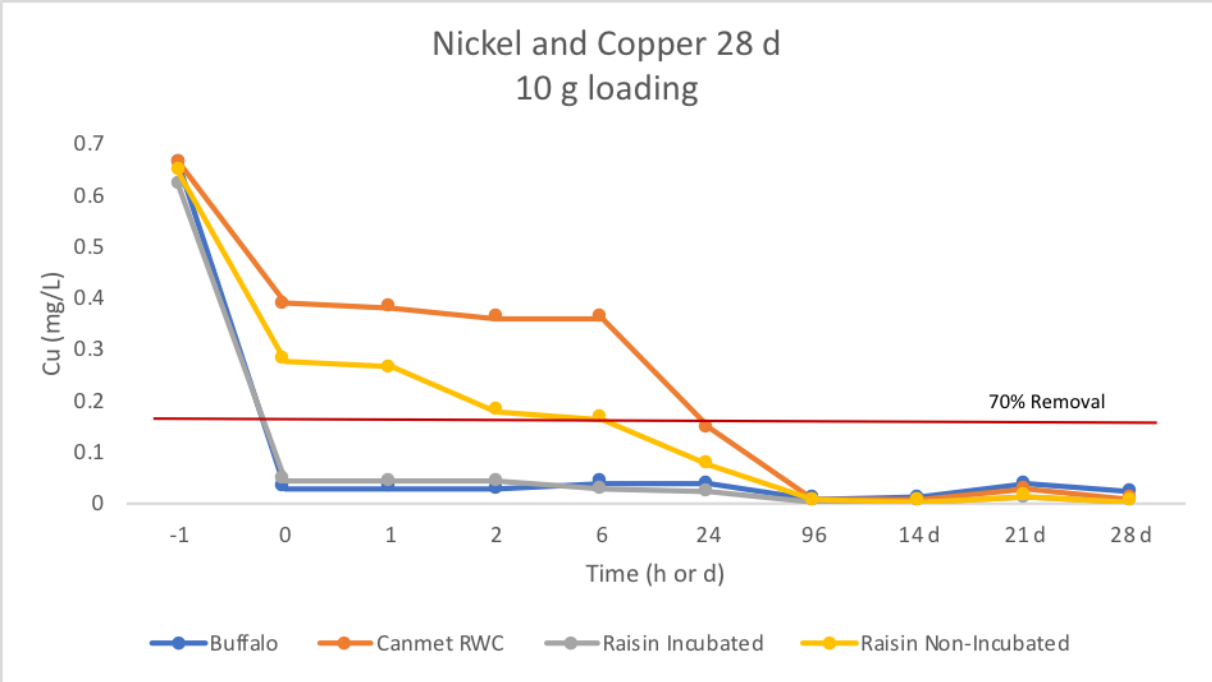


Figure 7: Nickel and Copper 28 d exposure, copper only shown here. All treatments achieved 70% removal within 96 h.

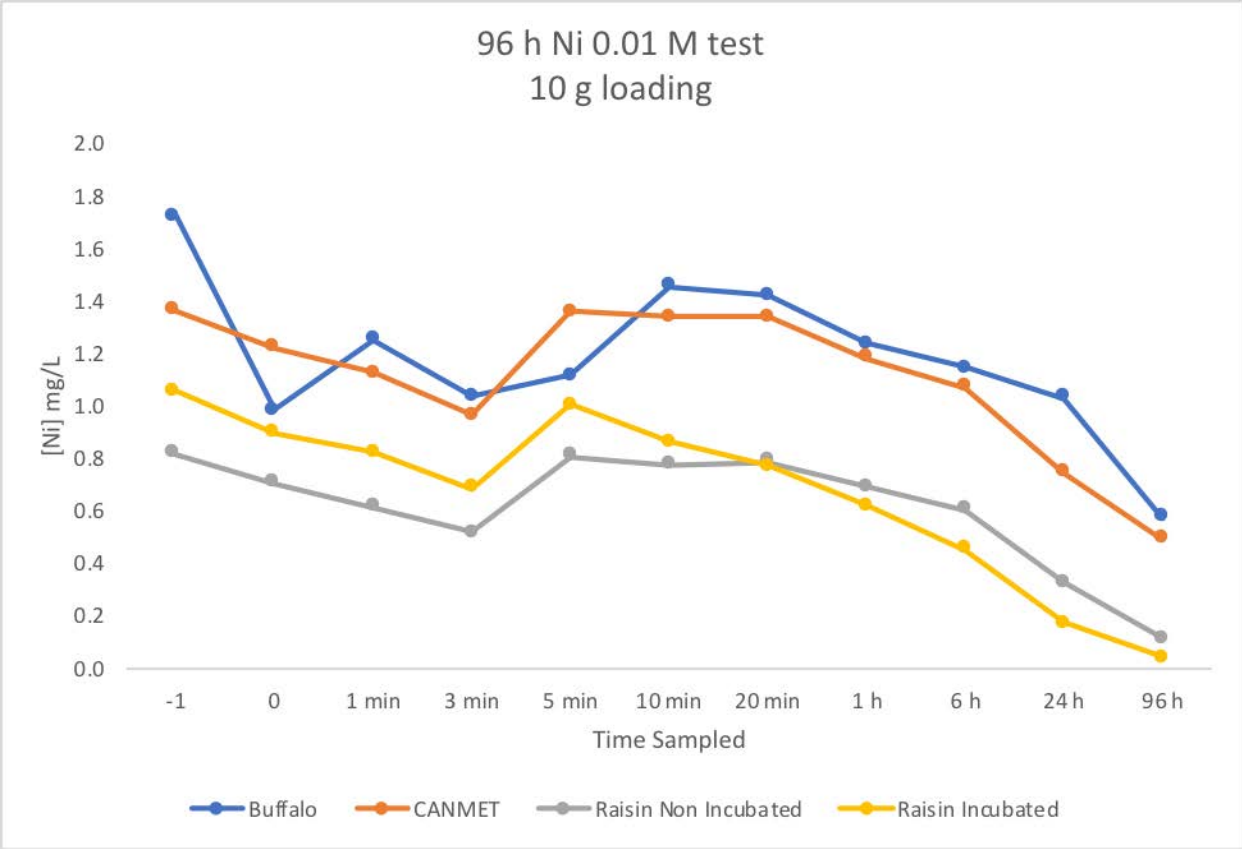


Figure 8: 0.01 M Ionic Strength results. Note variable initial values of nickel solution.

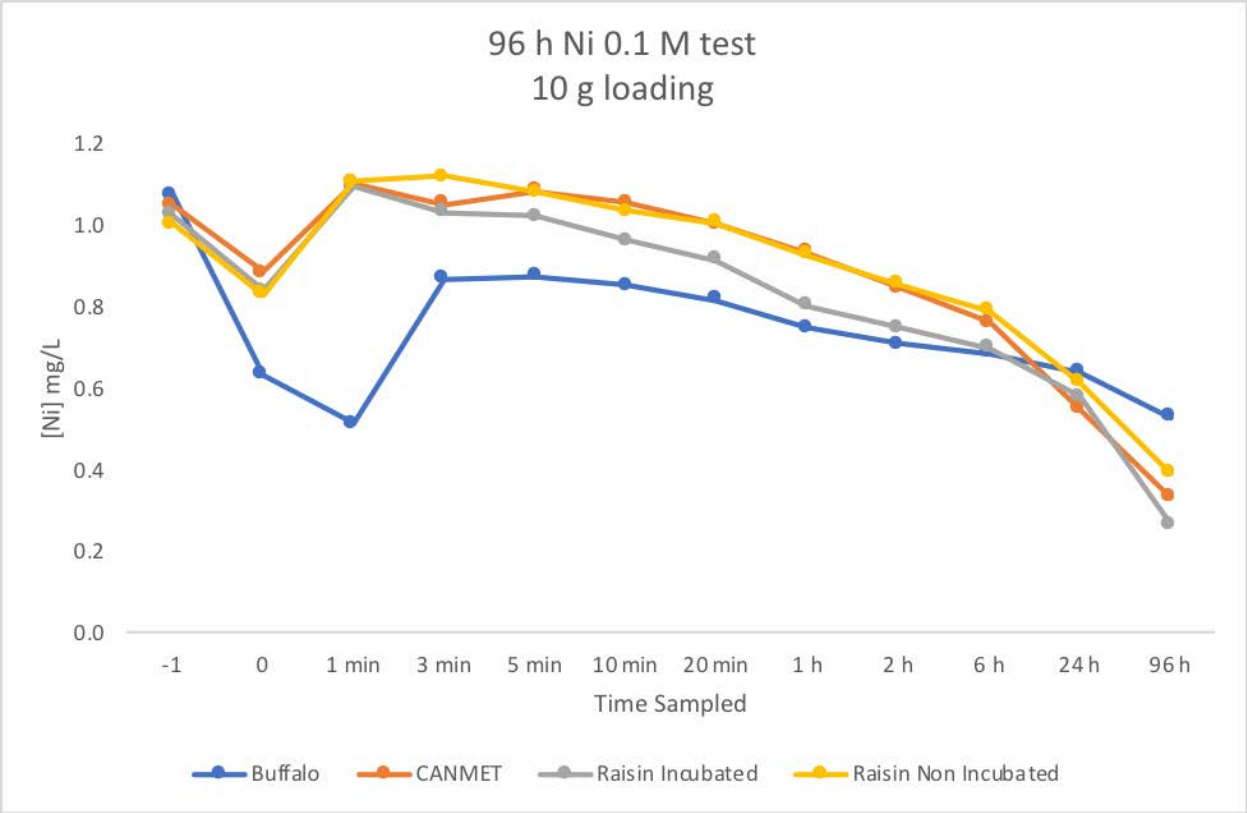


Figure 9: 0.1 M Ionic Strength Results

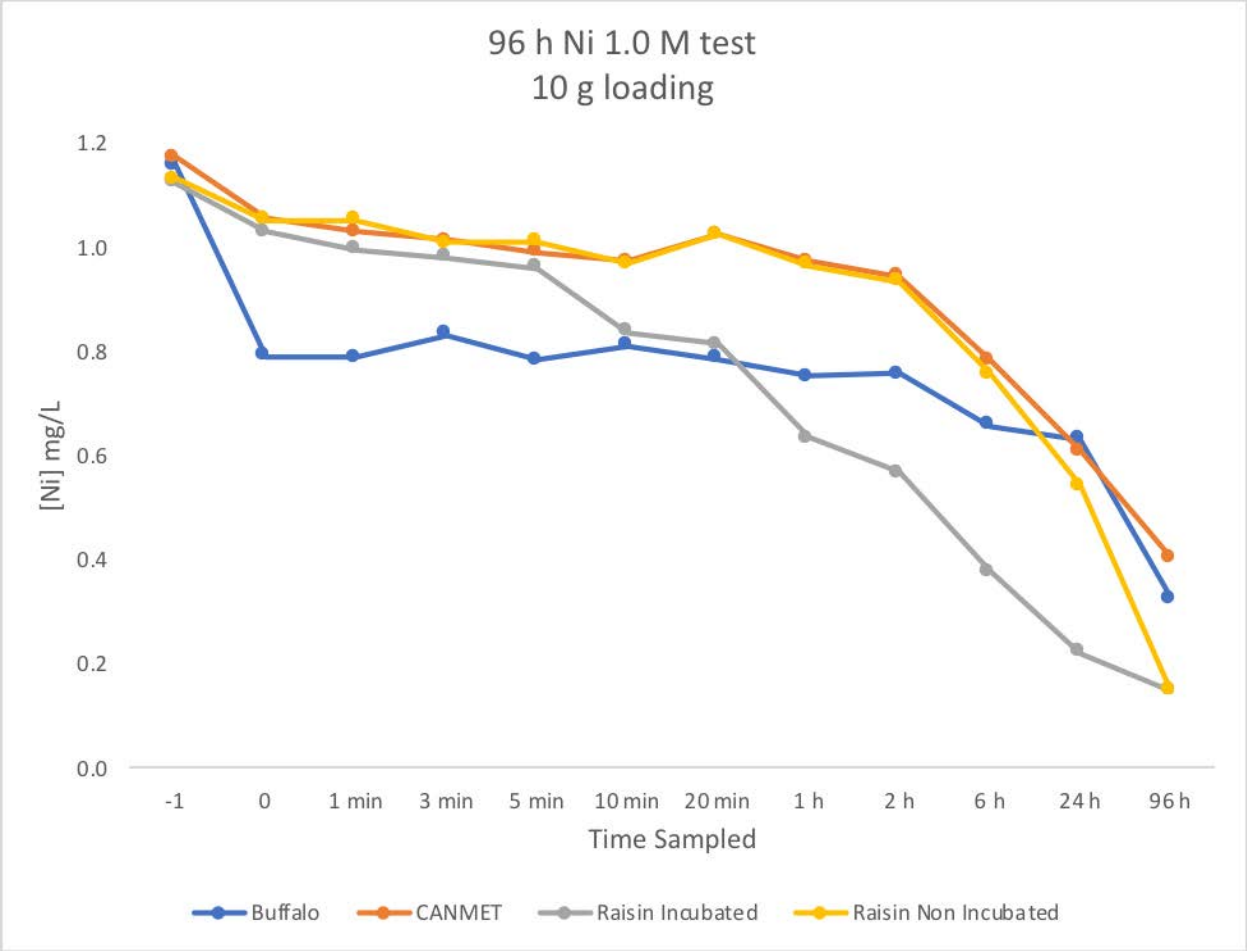


Figure 10: 1.0 M Ionic Strength results

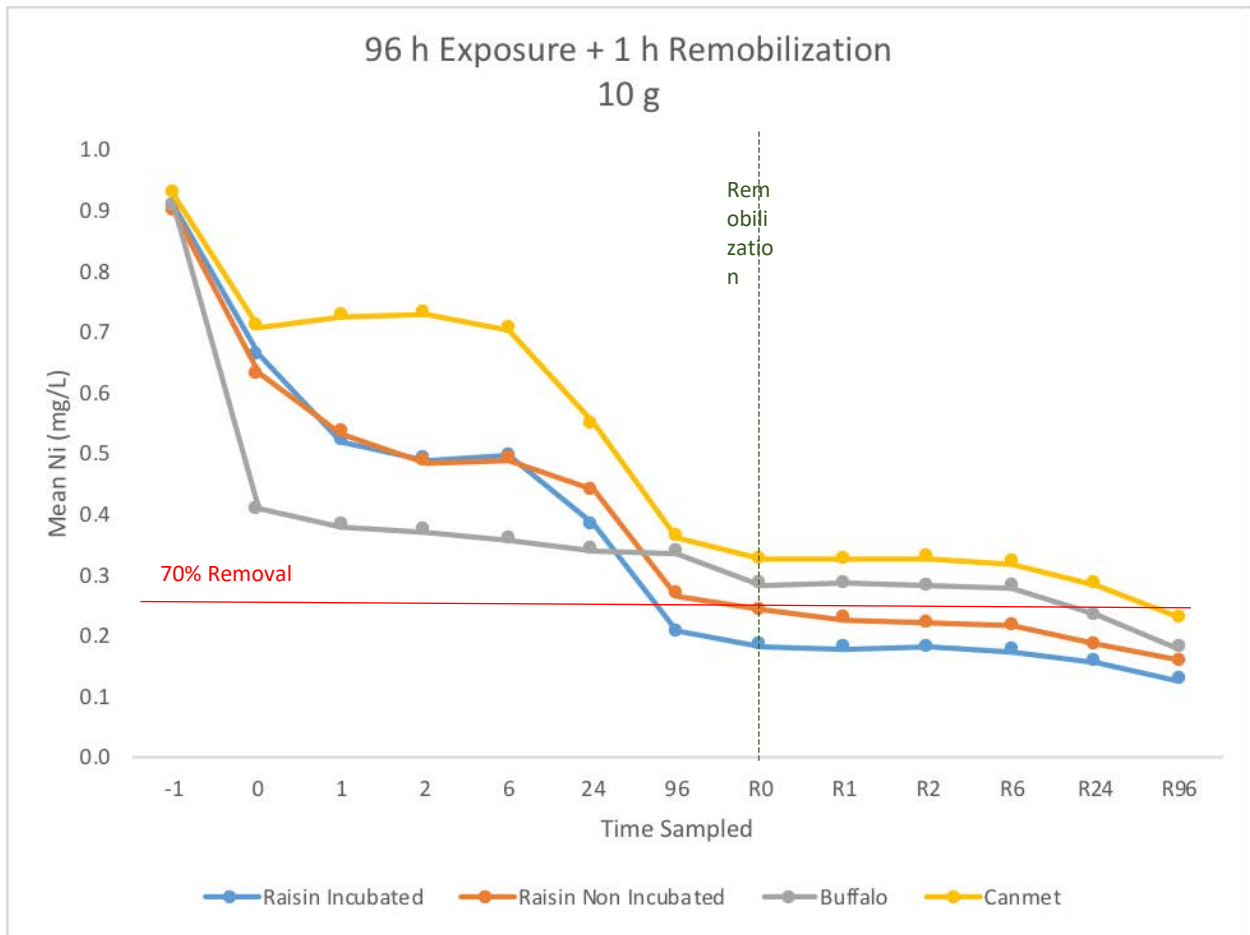


Figure 11: 96 h exposure with 1 h remobilization at 150 rpm on orbital shaker table. No flux of Ni was detected post remobilization. All treatments achieved 70% removal within time constraints of experiment.

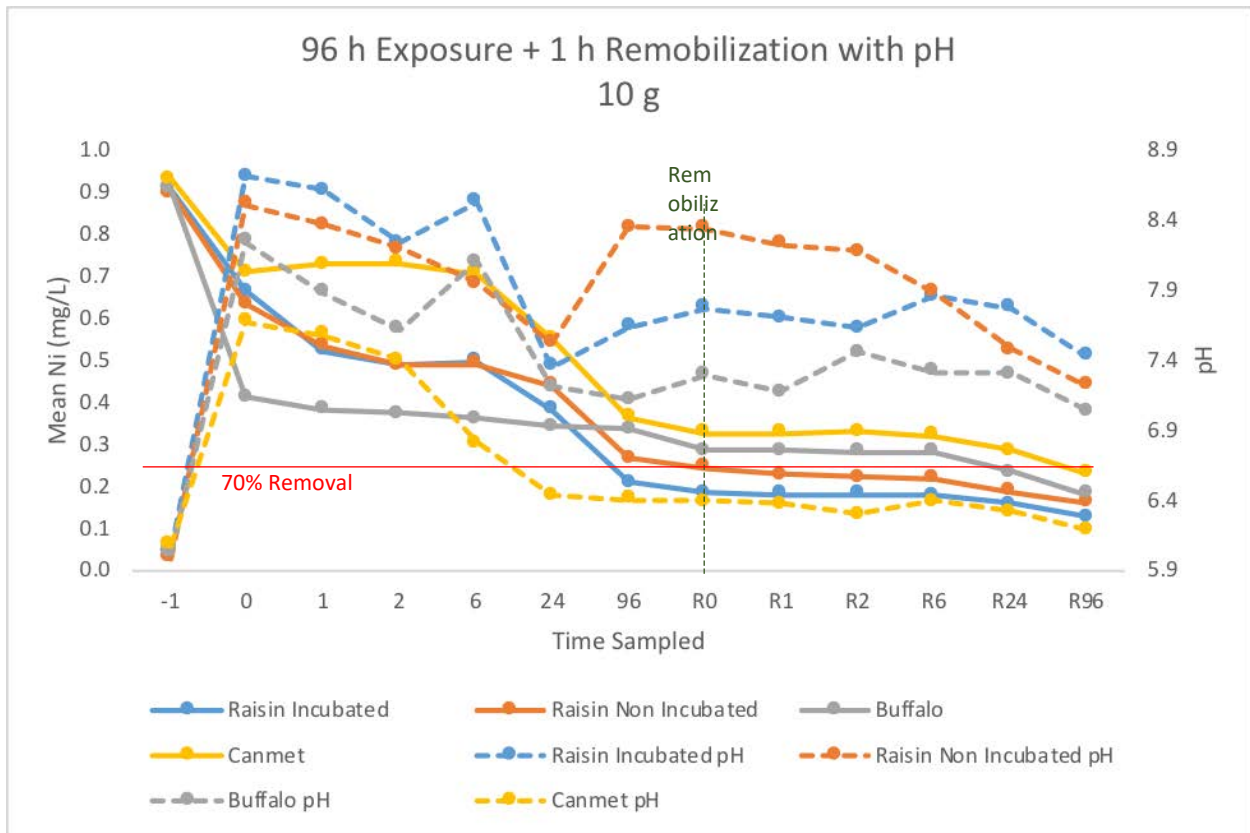


Figure 12: 96 h exposure with 1 h remobilization at 150 rpm on orbital shaker table with pH overlay. pH ranged from 5.98 – 8.7 but remained stable in control flask (pH 5.98 – 6.11, not shown on graph).

Table 1: Summary of substrate chemistry. TOC, Cu, or texture data not provided by NIST.

	TOC (% dry)	Total Fe	Mn (µg/g)	Ni (µg/g)	Cu (µg/g)	Zn (µg/g)	Pb (µg/g)	Texture
Raisin	18.72	9,077 ug/g	454	11.7	6.67	30.7	3.58	Sand
CANMET	1.1	1.56 %	506	34	18	54.7	13.5	Sand
Buffalo	--	3.97 %	544	42.9	--	408	150	--
Plum Creek	1.9	9,300 ug/g	2,900	9.1	4.09	24.3	1.88	Sandy loam

Table 2: Buffalo vs Raisin Dry, 1 g vs 10 g 28 d test results

Treatment	Time (h)	Mean Ni (mg/L)	70% Removal
Buffalo 1 g	-1	1.058	

Buffalo 1 g	0	0.9215	
Buffalo 1 g	1	0.896	
Buffalo 1 g	4	0.8535	
Buffalo 1 g	24	0.6335	
Buffalo 1 g	120	0.266	0.3174
Buffalo 1 g	14 d	0.147	
Buffalo 1 g	21 d	0.1045	
Buffalo 1 g	28 d	0.101	
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Buffalo 10 g	-1	1.047	
Buffalo 10 g	0	0.633	
Buffalo 10 g	1	0.671	
Buffalo 10 g	4	0.665	
Buffalo 10 g	24	0.483	
Buffalo 10 g	120	0.1495	0.3141
Buffalo 10 g	14 d	0.063	
Buffalo 10 g	21 d	0.0415	
Buffalo 10 g	28 d	0.0405	
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Raisin 1 g	-1	1.0495	0.3148 (not achieved)
Raisin 1 g	0	0.99	
Raisin 1 g	1	0.946	
Raisin 1 g	4	0.933	
Raisin 1 g	24	0.8235	
Raisin 1 g	120	0.6985	
Raisin 1 g	14 d	0.566	
Raisin 1 g	21 d	0.498	
Raisin 1 g	28 d	0.488	
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Raisin 10 g	-1	1.033	
Raisin 10 g	0	0.9025	
Raisin 10 g	1	0.8555	
Raisin 10 g	4	0.8155	
Raisin 10 g	24	0.442	
Raisin 10 g	120	0.129	0.3099
Raisin 10 g	14 d	0.06	
Raisin 10 g	21 d	0.0415	
Raisin 10 g	28 d	0.0415	

Table 3: 28 d Ni and Cu test values (Ni only below) with 70% removal calculated

Treatment	Time (h)	Mean Ni (mg/L)	70% removal
Buffalo	-1	1.166	
Buffalo	0	0.63	
Buffalo	1	0.69	
Buffalo	2	0.73	

Buffalo	6	0.73	
Buffalo	24	0.704	
Buffalo	96	0.334	
Buffalo	14 d	0.199	0.3498
Buffalo	21 d	0.1555	
Buffalo	28 d	0.106	
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Canmet	-1	1.029	
Canmet	0	0.961	
Canmet	1	0.8655	
Canmet	2	0.8055	
Canmet	6	0.6945	
Canmet	24	0.5085	
Canmet	96	0.39	
Canmet	14 d	0.3185	0.3087
Canmet	21 d	0.283	
Canmet	28 d	0.2445	
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Raisin Incubated	-1	1.019	
Raisin Incubated	0	0.8125	
Raisin Incubated	1	0.7745	
Raisin Incubated	2	0.7465	
Raisin Incubated	6	0.5875	
Raisin Incubated	24	0.252	0.3057
Raisin Incubated	96	0.115	
Raisin Incubated	14 d	0.094	
Raisin Incubated	21 d	0.08	
Raisin Incubated	28 d	0.073	
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Raisin Non-Incubated	-1	1.0205	
Raisin Non-Incubated	0	0.909	
Raisin Non-Incubated	1	0.8715	
Raisin Non-Incubated	2	0.789	
Raisin Non-Incubated	6	0.634	
Raisin Non-Incubated	24	0.4585	
Raisin Non-Incubated	96	0.1465	0.3061
Raisin Non-Incubated	14 d	0.086	
Raisin Non-Incubated	21 d	0.0525	
Raisin Non-Incubated	28 d	0.0435	

Table 4: Ni and Cu 28 d test values (Cu only below) with 70% removal calculated

Treatment	Time (h)	Cu mg/L	70% removal
Buffalo	-1	0.661	
Buffalo	0	0.0295	0.1983

Buffalo	1	0.0295	
Buffalo	2	0.0275	
Buffalo	6	0.0385	
Buffalo	24	0.0375	
Buffalo	96	0.008	
Buffalo	14 d	0.0105	0.3498
Buffalo	21 d	0.0365	
Buffalo	28 d	0.021	
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Canmet	-1	0.664	
Canmet	0	0.389	
Canmet	1	0.38	
Canmet	2	0.36	
Canmet	6	0.36	
Canmet	24	0.1465	0.1992
Canmet	96	0.0065	
Canmet	14 d	0.006	
Canmet	21 d	0.026	
Canmet	28 d	0.0085	
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Raisin Incubated	-1	0.619	
Raisin Incubated	0	0.045	0.1857
Raisin Incubated	1	0.0415	
Raisin Incubated	2	0.0425	
Raisin Incubated	6	0.027	
Raisin Incubated	24	0.022	
Raisin Incubated	96	0.003	
Raisin Incubated	14 d	0.003	
Raisin Incubated	21 d	0.01	
Raisin Incubated	28 d	0.0045	
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Raisin Non-Incubated	-1	0.646	
Raisin Non-Incubated	0	0.278	
Raisin Non-Incubated	1	0.265	
Raisin Non-Incubated	2	0.178	0.1938
Raisin Non-Incubated	6	0.163	
Raisin Non-Incubated	24	0.0755	
Raisin Non-Incubated	96	0.0055	
Raisin Non-Incubated	14 d	0.0035	
Raisin Non-Incubated	21 d	0.0125	
Raisin Non-Incubated	28 d	0.0035	

Table 5: AVS/SEM values for Raisin pre- and post- exposure, Incubated vs Non-Incubated substrates.

Treatment	[S²⁻] (μmol/g)	SEM (μmol/g)	SEM-AVS
Pre-exposure Non-Incubated	0.00	1.20	1.20
Post-exposure Non-Incubated	0.02	0.39	0.38
Pre-exposure Incubated	0.04	0.07	0.04
Post-exposure Incubated	0.02	1.06	1.04

Table 6: 96 h Exposure + 1 h remobilization Ni results. No Ni flux noted post 1 h remobilization.

Treat	Sample time	Mean Ni (mg/L)	70% Removal
Raisin Incubated	-1	0.907	
Raisin Incubated	0	0.663	
Raisin Incubated	1	0.521	
Raisin Incubated	2	0.489	
Raisin Incubated	6	0.497	
Raisin Incubated	24	0.382	
Raisin Incubated	96	0.207	0.272
Raisin Incubated	R0	0.183	
Raisin Incubated	R1	0.180	
Raisin Incubated	R2	0.181	
Raisin Incubated	R6	0.175	
Raisin Incubated	R24	0.157	
Raisin Incubated	R96	0.126	
Raisin Non Incubated	-1	0.898	
Raisin Non Incubated	0	0.631	
Raisin Non Incubated	1	0.534	
Raisin Non Incubated	2	0.486	
Raisin Non Incubated	6	0.491	
Raisin Non Incubated	24	0.440	
Raisin Non Incubated	96	0.266	0.269
Raisin Non Incubated	R0	0.243	
Raisin Non Incubated	R1	0.228	
Raisin Non Incubated	R2	0.220	
Raisin Non Incubated	R6	0.216	
Raisin Non Incubated	R24	0.186	
Raisin Non Incubated	R96	0.159	
Buffalo	-1	0.908	
Buffalo	0	0.409	
Buffalo	1	0.381	
Buffalo	2	0.372	
Buffalo	6	0.359	

Buffalo	24	0.34	
Buffalo	96	0.336	
Buffalo	R0	0.284	
Buffalo	R1	0.285	
Buffalo	R2	0.282	
Buffalo	R6	0.281	
Buffalo	R24	0.234	0.272
Buffalo	R96	0.179	
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Canmet	-1	0.928	
CANMET	0	0.710	
CANMET	1	0.726	
CANMET	2	0.731	
CANMET	6	0.705	
CANMET	24	0.549	
CANMET	96	0.363	
CANMET	R0	0.325	
CANMET	R1	0.326	
CANMET	R2	0.327	
CANMET	R6	0.319	
CANMET	R24	0.284	
CANMET	R96	0.230	0.278

Table 7: 96 h Exposure + 1 h remobilization Fe results. No Fe flux noted post remobilization.

Treatment	Time Sampled	Mean Fe (mg/L)
Raisin Incubated	-1	0.085
Raisin Incubated	0	0.083
Raisin Incubated	1	0.081
Raisin Incubated	2	0.082
Raisin Incubated	6	0.083
Raisin Incubated	24	0.089
Raisin Incubated	96	0.030
Raisin Incubated	R0	0.007
Raisin Incubated	R1	0.000
Raisin Incubated	R2	0.000
Raisin Incubated	R6	0.000
Raisin Incubated	R24	0.000
Raisin Incubated	R96	0.000
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Raisin Non Incubated	-1	0.079
Raisin Non Incubated	0	0.099
Raisin Non Incubated	1	0.099
Raisin Non Incubated	2	0.101

Raisin Non Incubated	6	0.100
Raisin Non Incubated	24	0.104
Raisin Non Incubated	96	0.027
Raisin Non Incubated	R0	0.031
Raisin Non Incubated	R1	0.013
Raisin Non Incubated	R2	0.008
Raisin Non Incubated	R6	0.009
Raisin Non Incubated	R24	0.000
Raisin Non Incubated	R96	0.000
Buffalo	-1	0.075
Buffalo	0	0.088
Buffalo	1	0.083
Buffalo	2	0.081
Buffalo	6	0.081
Buffalo	24	0.083
Buffalo	96	0.004
Buffalo	R0	0.017
Buffalo	R1	0.009
Buffalo	R2	0.007
Buffalo	R6	0.008
Buffalo	R24	0.007
Buffalo	R96	0.007
Canmet	-1	0.075
Canmet	0	0.083
Canmet	1	0.084
Canmet	2	0.089
Canmet	6	0.093
Canmet	24	0.099
CANMET	96	0.014
CANMET	R0	0.018
CANMET	R1	0.009
CANMET	R2	0.007
CANMET	R6	0.008
CANMET	R24	0.006
CANMET	R96	0.000

Table 8: Summary of experiments

Figure #	Treatments	Exposure length	Loading	Notes
1	Field collected (Plum Creek) dry, rewet, wet treatments	96 h	1 g	Dry substrate most efficient at removing Ni from water column

2	Plum dry	96 h	1 g	No significant differences between airstone and capillary tube for gas introduction to control pH
3	RR dry, RR wet, Buff dry	96 h	1 g	Dry substrate most efficient at removing Ni from water column
4	Buffalo, Plum Dry, Raisin Wet	96 h	1 g	Buffalo most efficient at removing Ni from water column, Plum Dry and Raisin wet similar
5	Buffalo and Raisin Dry	28 d	1 g, 10 g	Buffalo and Raisin dry 10 g treatments removed Ni at similar rates, though Buffalo removed higher amount in first 4 h. Raisin 1 g never achieved 70% removal in 28 d. pH varied greatly throughout 28 d
6, 7	River Raisin (RR) (incubated & non-incubated), CANMET LBP, Buffalo	28 d	10 g	70% removal of Cu achieved in all treatments and Ni removal in Raisin Incubated treatment within 96 h, Cu seemed to out compete Ni for binding sites on substrate
8	River Raisin (incubated & non-incubated), CANMET LBP, Buffalo	96 h	10 g	Refer to modeling data provided by Mutch Associates
9	River Raisin (incubated & non-incubated), CANMET LBP, Buffalo	96 h	10 g	Refer to modeling data provided by Mutch Associates
10	River Raisin (incubated & non-incubated), CANMET LBP, Buffalo	96 h	10 g	Refer to modeling data provided by Mutch Associates
11, 12	River Raisin (incubated & non-incubated), CANMET LBP, Buffalo	96 h + 1 h remobilization	10 g	No Ni flux post remobilization

Table 9: Approximate 70% removal times for selected experiments

Figure #	Treatment and Loading (all 10 g unless otherwise listed)	Approximate 70% Removal Time
5	Buffalo 1 g	120 h
5	Buffalo 10 g	120 h
5	Raisin 1 g	not achieved
5	Raisin 10 g	120 h
6	Buffalo	96 h - 14 d
6	Canmet	14 d
6	Rais Inc	24 h

6	Rais Non-Inc	96 h
7	Buffalo (Cu)	< 1 h
7	Canmet (Cu)	24 h
7	Rais Inc (Cu)	< 1 h
7	Rais Non-Inc (Cu)	6 h
8 - 0.01 M test	Buffalo	not achieved
8 - 0.01 M test	Canmet	not achieved
8 - 0.01 M test	Rais Inc	24 h
8 - 0.01 M test	Rais Non-Inc	96 h
9 - 0.1 M test	Buffalo	not achieved
9 - 0.1 M test	Canmet	not achieved
9 - 0.1 M test	Rais Inc	96 h
9 - 0.1 M test	Rais Non-Inc	not achieved
10 - 1.0 M test	Buffalo	96 h
10 - 1.0 M test	Canmet	not achieved
10 - 1.0 M test	Rais Inc	24 h
10 - 1.0 M test	Rais Non-Inc	96 h
11 - remobilization	Buffalo	R6 – R24 (6 - 24 h post remobilization, 102-120 h from initiation)
11 – remobilization	Canmet	R24 - R 96 sample times (~120 - 192 h)
11 – remobilization	Rais Inc	24 – 96 h
11 - remobilization	Rais Non-Inc	96 h