PROPOSAL FOR WOODASH APPLICATION TO MUD LAKE

WITHIN THE " WASTE MANAGEMENT AREA "
AT THE ABANDONED SOUTH BAY MINE SITE

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1.0 BACKGROUND

Wood ash has long been recognized as a valuable and safe additive to agricultural soils. Composed primarily of calcium- and potassium-oxides, it also contains major and minor elements common in the environment and yet essential to plant growth. Field and greenhouse research have shown that it has a liming effect of up to 90% of the total neutralizing power of lime. Almost by definition, since ash is derived from the combustion of clean and virgin woods, it is not offensive to the environment.

In summer 2000, 4 t of wood ash, generated in Ear Falls by Weyerhaeuser sawmill, was applied on an experimental basis to the slopes of the recently enlarged Backfill-Raise Ditch at the Abandoned South Bay Mine Site, which provides a pathway for seepages from the underground workings. Lacking a ground cover, the contaminated slopes were vulnerable to erosion. Experiments in the previous year, with one truck load of wood-ash indicated that the wood ash would both raise the pH of the waste rock, and provide nutrients to stimulate the growth of a terrestrial moss. In fact, this was accomplished. The resulting carpets of moss in the cracks between the rocks stabilized the ground and reduced the infiltration of the contaminated run-off into the waste rock of the mill site. During the summer of 2001, with the approval of the MOE, approximately 100 tonnes of wood ash were spread over Mill Pond, Mine site and on the Backfill Raise ditch slopes. The results will be documented by fall 2002 but so far are very promising.

Concurrent with those terrestrial experiments, in May 2000, wood ash was added to samples of acidic water taken from Mud Lake and Boomerang Lake, both of which lie within the waste management area. The pH of Mud Lake is presently at 2.5; Boomerang Lake is 3.0. The object of the experiment in two 1 m^3 containers was to determine the amount of wood ash required to raise the pH to 4.5, at which level phytoplankton and microbial activity accelerate, to counteract acidification and promote biological polishing, mainly for the removal of zinc.

Wood ash has two reaction components; it contains potassium oxide (1.6 % wt/wt), which reacts immediately, and calcium oxide (11.4 % wt/wt), which settles with the remaining inert materials in the ash, which is about 80% by weight, to the sediment of the lake to be treated. From there it gradually releases its neutralizing capacity.

Table 1a provides the composition of the active and inactive elements in wood ash, determined based on ICP analysis of the air-dried wood ash. The table also contains the elemental concentrations obtained from a 1:5 (weight: volume) distilled water slurry, to show which elements are released to distilled water.

Table 1a: Neutralizing and inert components in wood ash and wood ash slurry

Neutralizing oxides	%	Dissolved 20 g : 100mL (mg/L)	Inert	Dissolved 20 g : 100mL (mg/L)	Total Elements in Dry Wood Ash (ug/g)
Ca	8.1	5.4	Ag	< 0.001	1.9
K	1.34	1700	Al	8.1	6800
Mg	0.71	<0.01	B	2.8	80
Fe	0.63	0.17	Be	<0.001	< 0.05
P	0.25	0.25	Cd	0.005	2.3
Mn	0.37	0.37	Cr	0.058	13
Na	0.17	0.17	Co	<0.001	4.8
Ba	0.08	0.084	Cu	0.021	33
Zr	0.0024	0.0024	Mo	0.4	1.6
Sr	0.026	0.026	Ni	<0.001	8.9
			Pb	<0.002	4
			Si	-	25
			Ti	<0.001	480
			V	0.03	12
			Zn	0.065	590

Table 1b: Slurry nutrients and chemistry

NH_3-N	0.34	Em (mv)	-65
(NO_2 + NO_3)-N	3.6	Conductivity (uS/cm)	4996
TKN	1.6	Alkalinity (mg/L	975.3
pH	11.535		

As can be seen from Table 1a, generally low concentrations of metals were released with distilled water, and at a very high pH. The main constituents, who are liberated, are potassium, as can be anticipated, calcium and due to the extreme high pH Al, which would precipitate immediately at lower pH values. Some phosphate can also be expected to be released, which would have along with the nitrogen compounds a beneficial effect, if indeed some slow release of the nutrients can be anticipated. Solubility in distilled water is not representative of the conditions in Mud Lake

Further tests were carried out with water samples from Mud Lake and Boomerang Lake water to assess the true conditions of the solubility of the wood ash in AMD water, which again is likely to exaggerate the liberation, as 95 % by volume of the wood ash sinks to the bottom within 24 h, and in the sediments different conditions would prevail for mobilization of metals Table 2. For Boomerang Lake decreases in concentration of Al, Cu, Fe and S are noted, to which a decrease in S and Zn is added for Mud lake water. The elements A, Be, Cd, Co, Cr, Mg, Mn, Mo, Ni, P Pb, S Si Ti V, Zn and Zr remain the same for Boomerang Lake, where S, Zn, Ni and Mn differ to Mud Lake. Increases in concentrations are noted for B, Ba, Ca, K, Mo, Na, Sr in Boomerang Lake, whereas slight increase in Ni and Mn are present in Mud Lake. The difference in solubilites to distilled water is clearly demonstrated. The 1-m3 tank with Boomerang lake water received 4 L of wood ash, and the Mud lake tank received 12 L of wood ash. Both samples were obtained after 2 days where the pH had increased in Boomerang from 3.0 to 4.7 and in Mud Lake from 2.8 to 6.3. From this work it is not possible to derive negative effects on the water quality, rather for both lakes, the treatment would be beneficial precipitating Al, Cu, Fe, Zn and S. Higher levels of Zn precipitated from the Mud Lake water in the containers due to co-precipitation with Fe. In turn this can only assist downstream water quality in Armanda Lake.

Table 2: Comparison of Water Chemistry Before and After Wood ash Treatment on Site

Parameter Mg/L	Boomerang Lake		Mud Lake	
	Before Wood Ash	After Wood Ash	Before Wood Ash	After Wood Ash
Temp ^{c}o	17.8	10.7	19.2	12.7
PH	3.17	4.76	2.846	6.33
Condo us/cm	910	810	1260	110
L*Eh mV	714	633	774	609
L*Acid	162.5	90.2	297.9	44.7
Lower Concentration following Wood Ash Treatment				
Al	5.7	3	0.11	0.005
Cu	0.45	0.36	0.045	0.007
Fe	9.8	1.1	97	8.7
S			200	190
Zn			10	7.6
Same Concentration following Wood Ash Treatment				
Ag	0.001	0.001	0.001	0.001
Be	0.001	0.001	0.001	0.001
Cod	0.046	0.044	0.007	0.006
Co	0.11	0.12	0.056	0.047
Cr	0.001	0.001	0.002	0.002
Mg	19	20	19	22
Man	7.2	7.5		
Mo			0.001	0.002
Ni	0.031	0.042		
P	0.01	0.02	0.01	0.01
Pub	0.005	0.004	0.005	0.003
S	150	150		
Si	12	11	5.5	5.8
Ti	0.001	0.001	0.001	0.002
V	0.001	0.001	0.001	0.001
Zn	31	32		
Zr	0.001	0.001	0.002	0.002
Higher Concentration following Wood Ash Treatment				
B	0.002	0.041	0.003	0.11
Ba	0.027	0.18	0.02	0.25
Ca	94	110	98	180
K	2.2	17	3.7	32
Mn			6.3	8.1
Mo	0.001	0.014		
Na	2.9	4.9	4.6	8.1
Ni			0.001	0.004
Sr	0.24	0.33	0.16	0.39

As the tables illustrate, wood ash is an ideal agent for the treatment of severely acidic water bodies and their sediments. The two fold reaction of the calcium and potassium in wood ash makes it especially attractive as an amendment to acidified water bodies in mining waste management areas in general. Here at South bay a unique opportunity exists to test recycling of a waste product from the lumber industry for the remediation of mining related environmental issues. No project could be more in keeping with the spirit of sustainable development advocated by the report of the Brundtland Commission.

2. The specific conditions of Mud Lake

The volume of the contaminated ground water, which is discharged into Mud Lake, is estimated to be 1 l/s. This relatively small amount is contributing to a total outflow volume per year of about 14 l/s. No other sources of contaminants enter Mud Lake, which is a shallow lake with a mean depth of 1- to 1.5 m, with gyttia (organic rich) sediment extending to a depth of more than 8 m. Mud Lake turns over about 3 times per year, mainly in the spring and fall.

In May 1994, it became evident that the discharge from Mud Lake to Amanda Lake had become contaminated, from which point on Amanda Lake was monitored. The pH level in Amanda Lake did not change from pH 6.5 until March 2000 when a reduction was noted to pH 5.5, after 5 years of discharge. This slow decrease suggested, that Armanda Lake had a relatively strong natural buffering capacity and thus the discharge of Mud Lake water did not give cause for major concern, given efforts then underway to control the source of contamination into Mud lake (from the tailings).

In 1997, research was initiated to develop a microbial in-situ treatment process of the small ground water discharge into Mud Lake. Pilot tests were approved in late 2001, too late for start up of the test facility, but they are presently in progress. Carbon and urea are to be injected with the AMD, which will stimulate microbial activity, which in turn will raise the pH causing contaminants to precipitate. The final preparations for the start up of the pilot treatment were completed in July 2002. Data relating to the velocity of the injected ground water and the volume of AMD that can be delivered passively to the gyttia sediments, from a depth of about 12 m have been generated in July 2002. These hydro-geological data to confirm the flow conditions in the pilot test system have been submitted to the hydro geologist for final assessment prior to start up, which is planned for early August 2002.

The activity of beavers raised the water level in Mud Lake by 0.6 meters by early 2000, which lead to more contaminant generation in the tailings drainage basin, a highly undesirable state. In June, a pulse of 30 t of acidity was released to Armanda Lake prior to the installation of flow control at the outflow of Mud Lake. By December, this had significantly depleted the natural buffering capacity of the Armanda Lake resulting in pH 3.9.

Samples of Amanda Lake water that were tested for the treatment with wood ash showed promising results. Here caution was taken not to add to much wood ash, which given the conditions in Mud Lake is not possible. Using thermodynamic modelling of the entire drainage basin, containing Lena Lake, a dosage of wood ash of the addition of one tonne of wood ash per day, during periods of peak flow to the outflow of Mud Lake would have stabilize the pH possibly over one year. Although the calculations and the experiments in the laboratory agreed with each other in the tonnage required, continues additions could not be implemented practically. We opted to propose a one-time dose of 70 t taking advantage of the large volume of spring melt water for mixing.

Accordingly, seventy tonnes of wood ash were shipped to the Waste Management Area, and stored under a tarp pending approval by the regulatory agencies to disperse it in Amanda Lake during the winter of 2001/2002. However, regulatory approval was never given for this undertaking. For Armanda lake the application of wood ash may have raised the pH higher than desired, and thus the emphasis in the proposed application was on taking care not to overdose with wood ash.

We are now proposing to use the same wood ash to improve the highly contaminated sediments in Mud Lake in the area of the outflow and the main ground water discharge (Map 1). We are also initiating pilot testing for the in-situ treatment of ground water entering Mud Lake, which will result in reduction of the contaminant load to Mud Lake. These measures are expected to reduce the acidity and contaminants leaving Mud Lake and prevent the further deterioration of Amanda Lake.

2.0 Mud Lake Wood-ash treatment

Concurrent with the onset of the in-situ treatment research, the final configuration for the passive treatment approach for Mud Lake was developed, which required measures for the sediments in Mud Lake, which are becoming increasingly enriched with iron and zinc. As a first measure, in 1997 we treated Mud Lake with 40 t of natural phosphate, which decreased the iron concentrations immediately and controlled the pH for nearly 3 years. The phosphate application followed a failed attempt to reduce the impact of the incoming ground water discharge through installation of an ARUM cover in the discharge region of the ground water in 1996. Potato waste was added to the sediments, but the cover became too heavy to stay afloat, due to iron encrustment. The final close out scenario envisaged for Mud Lake is a functioning in-situ treatment and biological polishing in the lake, similar to Boomerang Lake.

Laboratory work with Mud Lake sediments have been underway for 5 years, defining organic carbon additions and sediment pore water chemistry, to ensure that a functioning sediment can be provided when the brush is introduced to assist with biological polishing in Mud Lake. A survey of the sediments carried out in 2000 indicated that on average the acidity of the sediments in Mud Lake (combined metal measure) is about 2 times higher than that of the water. The acidity is mainly due to iron (220 mg/l to 990 mg/l) and zinc (184 - 100 mg/L). These metals concentrations lead to physical gradient of electrical conductivity of approximately 1000 uS/cm (water 200 to 3320 uS/cm sediment) between water and the sediment. The Mud Lake sediments are 80 % to 90 % water with a wet density of about 1.

Due to the physical conductivity gradient, the water does not mix readily. A mass balance of the contaminant distribution for Mud Lake, including ground water input, freshwater output and summarizing the contaminant load since the year discharge started indicated, that 80 % of the contaminant load remains in the uppermost layer of the sediments, establishing this physical gradient. The mass balance was completed in March 2000. We have since tested the ability of wood ash to precipitate the metal load contained in the sediments in Mud Lake. These experiments focused on elucidating a rate of application, which would remove all of the acidity in the sediment and at the same time demonstrating that the prescribed application of wood ash will have no adverse effect on the outflow of Mud lake and hence on Armanda lake.

Three open-bottomed, 1-m3 tanks were set up in Mud Lake to test wood ash addition to the sediment in June 2001. A first round of three application rates of additions of 2.4 kg 9 kg and 19 kg of wood-ash was added to the sediment, respectively. The additions were based on the results obtained with the wood-ash experiments carried out for Amanda

Lake. Then water samples were collected from within the sediments (sediment pore water) and from the free water above the sediments in the tanks. The sediments pore-water has generally a pH of around 4.2 to 5.5 and the results from the container test were too varied to give confidence in an effective application rate. The pH of samples collected of pore water in untreated sediment in the vicinity of the containers (Control) ranged around 5.6 with and acidity between 520 to 677 $CaCO_3$ mg/L. The high application rate (19 kg wet weight) reduced the acidity in the sediment to 129 to 250 $CaCO_3$ mg/L, a reduction of about 50 %. One promising readings in the test tanks indicated a sediment acidity of 16 $CaCO_3$ mg/L and a pH of 6.5. We did not consider these results sufficiently firm to derive a sediment application rate and we set up the experiment again in October 2001 by moving the tanks to new locations. Only two tanks could be moved, one had to be abandoned, since it was mired too deeply into the sediment.

However the first round of experiments provided a firm basis upon which to calculate the application rate for the second experiment. We considered the fast reaction based on potassium content in the wood ash alone in order to predict the expected reduction in acidity. As these neutralizing reactions are stoichometric reactions it has to be possible to derive application rates for which the effects on the sediments are predictable, i.e. x amount of alkalinity added reduces x amount of acidity. Variables might be introduced if the water infiltrated through the sediment into the tanks, or if waves introduced fresh water over the top; the bottom seals were carefully checked but overtopping could not be prevented during windy periods.

In Table 3a the calculations on which the application rates are based are presented. In a 1-m3 tank of Mud Lake water there are 379 g of acidity. Wood ash itself when titrated generated potassium alkalinity of 1760 mg/L or per gram of wood-ash, or 9 mg of calcium carbonate equivalent alkalinity. In order to consume all of the acidity in the water with the potassium alkalinity in the wood-ash alone, we calculated that we needed to add 43 kg to one 1-m3 tank or 1 m^2 of sediment. As we do not have a measure for the slow release capacity of the calcium oxide alkalinity this time, the low application rate of the first experiment was used, resulting in 4.7 kg of wood-ash. From this application, if we had correctly assessed the fast reaction rate, we expected an 11 % reduction of the acidity in the top water. The differences between 43 kg and 4.7 result from the moisture content of the wood ash of the pile in the field as compared to that calculated based on oven dried wood ash. One of the tanks received 4.7 kg, whereas two tanks received 32.8 kg (adjusted based on the actual wet/dry weight ratio of the material applied in the field), which was less than should have been added to remove all the acidity or 100 %. Two tanks were used with the same application rate to account for variability in sediment and wood ash.

Table 3a Chemistry of surface water and water on top of sediment for Wood Ash Expt ($1m^3$ tank #1)

Estimated Amount of Wood Ash Needed for 1 m^3 of Mud Lake Water		
Total Water Volume Used for Each Tank	m^3	1
pH of Test Water	Unit	2.99
Acidity of Test Water	mg/L	380
Total Acidity of Test Water	mg	379,800
Potassium Alkalinity generated in wood ash	mg/L	1760
$CaCo_3$ Alkalinity generated per gram wood ash	mg	9
Estimated Amount of Wood Ash Needed to Consume All the Acidity from the Test Water	ton/m^3	0.0432
	kg/m^3	43
Actual Amount of Wood Ash Used to Treat the Test Water	L/m^3	10
	kg/m^3	4.7
The Acidity Reduction Due to 4.7 kg of Wood Ash Added to the Test Water, Comparing to Control	%	11

Table 3b and 3c present the results, where tank # 1 produced nearly perfect results for the water neutralisation, that is the addition of 4.7 kg of wood ash produced the expected 10 % reduction within 2 days. Tank # 2 resulted in a lower reduction of 6 %, but must have received new water overtop of the rim of the tank from outside Mud Lake. The wood ash particles settle in less than a day to the bottom, therefore no turbidity is generated in water.

Confident that our calculations were correct and that the application of wood ash would not result in an unreasonably high pH we tested the second application rate, to confirm our calculations. Here with 32.8 kg we expect a 100 % decrease in acidity in the water and in the sediments. We added to the same tanks more wood ash resulting in an application rate of 32.8 kg a reduced application rate which resulted due to the differences in wet and dry weight.

Table 3b: Chemistry of surface water and water on top of sediment for Wood Ash Tank #1

Top water chemistry after **4.7 kg** of wood ash addition on Sept. 15, 2001					
Days After Wood Ash	pH	Eh (mv)	Cond (uS/cm)	Acidity (mg/L)	Acidity Reduction %
0	2.85	806	1475	434	0
0.01	2.96	821	1620	418	-4
0.08	3.04	828	1620	374	-14
0.25	3.05	832	1618	358	-18
1	3.07	833	1600	397	-9
2	3.07	839	1609	392	-10
Top water chemistry after **32.8 kg** of wood ash addition on Oct. 8, 2001					
0	2.87	786	1750	337	0
0.01	7.26	440	1815	234	-30
0.02	8.77	359	1842	8.5	-97
0.21	8.59	380	1864	0	-100
1.1	8.58	374	1860	0	-100
261	2.86	643	1045	528.7	57
275	2.90	739	934	418.4	24
Chemistry of sediment pore water after **32.8 kg** of wood ash addition on Oct. 8, 2001					
0	2.99	782	1747	234.4	0
0.01	9.99	334	1898	0	-100
0.02	8.66	379	1813	0	-100
0.21	8.56	367	1857	0	-100
1.1	8.55	376	1897	0	-100
261	5.51	348	1019	104	-69
275	6.00	181	937	391	16

For this assessment, we again sampled top water and sediment pore water. Sediment pore water was sampled by immersing a bottle on a stick to immerse the bottle completely in the sediment. The result in both tanks, the total removal of acidity with the first day, confirmed expectations. Even with this high application rate, the top water pH ranges between 6.5 to 8.5, which is acceptable and does not result in any adverse drastic pH increases, which could be released to Armanda Lake.

After 275 days, nearly a full year, the acidity in the sediment pore water in both tanks had been reduced, by 69 per cent in Tank 1 and 97 per cent in Tank 2 with a slight increase in the second sampling in 2002. Based on these findings, which include the long-term effects on the sediments, we propose a conservative application rate of 20 kg/m^2 to Mud Lake sediments, or 70 tonnes total. This should achieve a 50 % reduction in the sediment acidity in the areas treated.

The results from the additions of wood ash to the tanks (i.e. " Top water" data presented above) demonstrate that it is not possible to over neutralize the outflow of Mud Lake at these application rates. We can therefore confirm that no extreme pH increases are to take place while the wood-ash is applied at these rates.

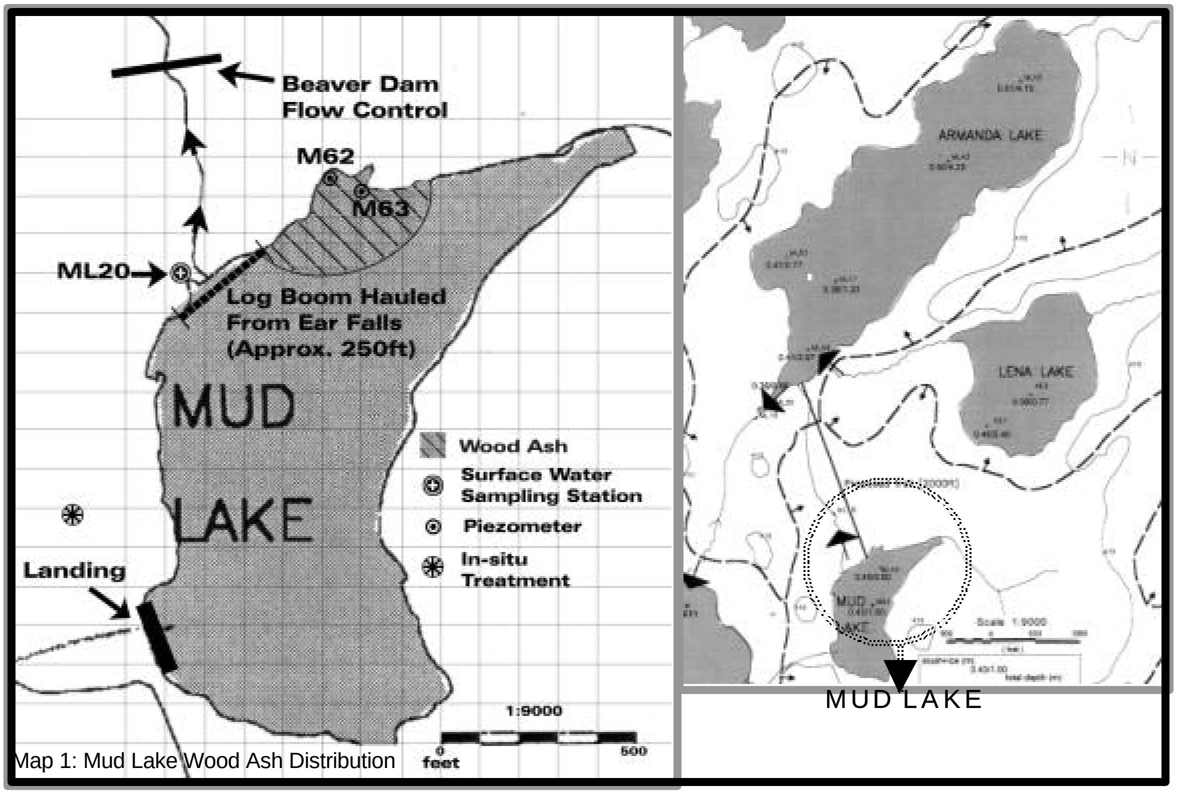
Table 3c: Chemistry of surface water and water on top of sediment for Wood Ash Tank #2

Days After Wood Ash	PH	Eh (me)	Condo (cm/cm)	Acidity (mg/L)	Acidity Reduction %
Top water chemistry after **4.7 kg** of wood ash addition on Sept. 15, 2001					
0	3.00	838	1119	380	0
0.01	3.24	661	1342	405	6.6
0.08	3.46	627	1289	355	-6.6
0.25	3.52	622	1276	370	-2.7
1	3.38	656	1294	399	5.0
2	3.32	672	1303	386	1.7
Top water chemistry after 32.8 kg of wood ash addition on Oct. 8, 2001					
0	2.87	800	1559	339	0
0.01	5.99	545	1678	26	-92
0.02	6.16	483	1707	18	-95
0.21	6.57	460	1730	19	-94
1.1	6.52	445	1748	17	-95
261	2.61	646	1042	873	158
275	2.87	749	954	433	28
Chemistry of sediment pore water after **32.8 kg** of wood ash addition on Oct. 8, 2001					
0	2.89	664	2810	456.1	0
0.01	7.12	494	1744	12.0	-96
0.02	6.59	463	1726	18.6	-94
0.21	6.58	448	1755	18.2	-95
1.1	6.96	432	1829	11.7	-97
261	6.44	259	870	39.6	-88
275	6.46	236	1016	11.3	-97

3.0 Application method

We have made two attempts to devise systems by which the wood ash would be gradually released from containers in the tank by the action of waves. However, neither worked and the idea has been abandoned. We now propose to suspend the wood-ash in the same fashion as we distributed the phosphate rock. Two barges will be used. One will carry the solid wood-ash. The second, which is equipped with 2 1m^3 tanks will disperse it as a slurry - wood ash mixed with water from the lake - through a fire hose.

The location where the wood ash application should take place is the northern section of Mud Lake, where both the groundwater discharge is taking place, and major inflow of the fresh water occurs. (Map 1). The rational for using this location as a first trial area is that if the sediments are improved here, they will not contaminate the inflow of fresh water, and therefore bring about the fastest improvement of overall water quality. The monitoring point for the wood-ash application is the mouth of Mud Lake outflow.



Map 1: Mud Lake Wood Ash Distribution

Water will be sampled after each 10 t application of wood ash. If pH exceeds 8.0, the wood ash application will be terminated. After 70 tons of wood-ash is distributed a survey of the sediment acidity will be carried out in the northern end of the lake to define the reduction of sediment acidity achieved. A baseline sediment survey was carried out in 2001.

Log booms will be constructed at the outflow of Mud Lake to prevent the escape of any wood ash that has not yet sunk. As our application method will slurry the wood -ash, it is highly unlikely that larger particles will survive the strong slurring action. However as a safety measure, the log boom will be in place. Once the entire lake sediment is improved, and confirmed by measurements in 2003 spring, brush cuttings will be added to the lake, to provide an anchor for the algae blooms that are expected as a result of the nutrients in the ash; this, in turn will further promote the precipitation of zinc and iron.

With a reduction in acidity in the sediment surface layer, we expect an improvement in the fall run-off water quality leaving Mud Lake. If the first application is successful, we may propose a further treatment of the remainder of Mud Lake with an application rate dictated from the application of the first 70 t to the sediments.