ARSENIC AND NICKEL REMOVAL FROM WASTE ROCK SEEPAGES USING MUSKEG SEDIMENT

FINAL REPORT

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EXECUTIVE SUMMARY

Passive treatment systems for mine waste water have, over the past 10 years, received increasing attention from the research community. These types of treatment options are particularly attractive for decommissioning in situations where effluent loadings are low and flows seasonal. The effluent-cleansing processes are natural in passive systems, and are biologically-mediated. Wetland sediments are the most important aspect of these natural treatment systems.

The use of sediments for passive treatment in ponds within a muskeg area surrounding a waste rock pile is being investigated. Acidic seepage from that waste rock pile requires treatment, specifically for the removal of As and Ni. Microbial activity is stimulated in the sediment with additions of degradable carbon. Field enclosures set up in the muskeg ponds have removed As and Ni from seepage water and the pH has been increased. Detailed laboratory studies confirmed the removal at similar rates in batch conditions.

A literature review on As and Ni in sediments indicates that adsorption/desorption are the main processes which control both metals' chemistry in the sediment; these processes are affected by Eh and pH. Arsenic can be precipitated as ferrous-arsenate and Ni as nickel sulphide. Both precipitates can be microbially mediated in the lower parts of the sediment.

Sediments were spiked with these precipitates and recovered using sequential extractions. The sequential extractions identify the exchangeable forms of the precipitates, those which are organically bound, the carbonate forms of the precipitates, and finally with a nitric acid extraction, the mineralized forms of the precipitates. Arsenic was extracted mainly in the organically-bound fraction, ranging from ***86*** % to 98 % of the spike. Nickel was partitioned between the exchangeable fraction and the organic fraction. In the presence of sulphide, a significant shift was noted in that more Ni was extracted as exchangeable (86 %) and less remained in the pore water (1.3 %). This suggests indirectly that the sediment adsorption properties change in the presence of sulphide reduction, which increases the stability of the sediment as a Ni sink.

The laboratory reactor sediments, which facilitated the removal of As and Ni from the seepage, were sampled destructively to determine pore water chemistry and the chemical forms of As and Ni which had accumulated in the top 1 cm of the sediment.

The pore water chemistry indicated that in reactors where microbial sulphate reduction took place, the lowest Ni concentrations (0.43 mg/L) were detected in the pore water. In the control reactor, the concentrations were 7.8 mg/L. The highest **As** concentrations were reported in the control reactors, at 11 mg/L, which was reduced to 3 mg/L when carbon amendments were added to the sediment. The original seepage water concentrations were 39 mg/L and **61** mg/L of **As** and Ni respectively.

The **As** in the top layer of the sediment is present either as organically bound or extractable with the carbonate fraction. Through carbon additions, a shift takes place to the carbonate form. None of the **As** is present in the mineral fraction of the sediments. The distribution of the precipitated Ni is different from **As** in that about 43 % to 84 % is present in the exchangeable form, 42 % to **69** % as organically bound, and the remainder as either carbonate (3 % to 8 %) or in the mineral form (6.8 % to **16** %).

A final mass balance on the reactors suggests that, overall, only a small fraction of the **As** and Ni is available in the pore water. In the reactors where organic matter was added to the sediment, generally higher fractions are retained in the sediment.

Experiments were carried out in 2 **L** column reactors to repeat the previously noted removal capacity of muskeg sediments to treat seepage high in **As** (85 mg/L) and Ni (74 mg/L). The results were repeated and effective removal (> 90 %) was achieved for both elements within 56 days. Organic amendments (potato waste) stimulated microbial activity and generated reducing conditions.

Further work will be required to compare the laboratory results to the field results. To date however, the stimulation of microbial activity in muskeg sediments appears to be a promising option for decommissioning.

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1.0 INTRODUCTION

Wetlands have been employed for the mitigation of acid mine drainage. Most of these wetlands are for the treatment of coal drainage and function by precipitation of iron as iron(III) hydroxides in aerobic conditions (Brodie 1990). Treatment of base-metal-rich mine drainage has been less extensively investigated. Emphasis has been placed on anaerobic microbial treatment where, in sediments, alkalinity generation takes place through iron and sulphate reducing bacteria. The pH is elevated as a result of the microbial activity which, in turn, facilitates the precipitation of metals as either sulphides and/or hydroxides (Bell et al 1989, Kalin 1993, Wildeman 1992). These processes take place in wetland and lake sediments and might be utilized as a decommissioning option for seepage treatment.

A waste rock pile of a uranium operation in northern Saskatchewan generates acidic seepages with elevated concentrations of arsenic, nickel, phosphate, sulphate and nitrate. The quantity of seepage from the waste rock pile is not extremely large and only emerges seasonally. The waste rock pile is surrounded by muskeg, which has several open shallow ponds; the ponds have been assessed as to their usage as seepage treatment areas. The muskeg/wetland is a perched water body, supplied only by atmospheric precipitation with diffuse inflow and oufflow.

The feasibility of using the open water ponds in the muskeg has been addressed through a series of field and laboratory experiments. It has been proposed that if microbial activity can be stimulated in the muskeg sediments through additions of carbon to generate alkalinity, then the production of reducing conditions would lead to the precipitation of contaminants. **As** the concentrations of nutrients in the seepage are relatively high, the biomass expected to be produced in the ponds could utilize both phosphate and nitrate present in the seepage. This biomass, in turn, could provide a continuous source of carbon for the microbial activity in the sediments. Since 1992, seepage water has been introduced to field enclosures and laboratory reactors in which the rates of removal of both **As** and Ni have been determined.

Results are summarized in Smith et al (1993), and Fyson et al (1994). The field enclosures and the laboratory reactor experiments established that, under reducing conditions and in the presence of potato waste or alfalfa pellets, the sediment from the wetland was able to remove As and Ni from seepage water in batch conditions.

Prior to large-scale treatment in the field, it is essential to assess the treatment capacity **of** the muskeg sediment and the stability of the removed contaminants in the sedirnents, with particular reference to the possibility that the pond water chemistry could change over the season (e.g. an influx of spring runoff water could result in dilution of the pond seepage water).

The objective of the work carried out jointly with CANMET and CAMECO seeks to characterize the chemical forms of **As** and Ni removed from the seepage water to the sedirnents. Laboratory reactor experiments will be initiated to determine the capacity of sediments to remove As and Ni under flow conditions. The sediments from the laboratory reactors, from which the initial data were collected on the removal of As and Ni, will be used to determine the stability of the precipitates formed in the sediments. Sequential extractions are used to determine the chemical form of the precipitates, either as an organocomplex or in an adsorbed form.

A literature review on both arsenic and nickel biogeochemistry is used to identify the main chemical factors controlling the water-sediment interface, as this is the driving force of the proposed seepage treatment system.

2.0 ARSENIC AND NICKEL IN THE AQUATIC ENVIRONMENT - A LITERATURE REVIEW

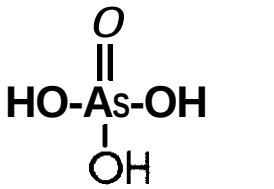
2.1 Species of Arsenic

The average concentrations of arsenic in shales, igneous rocks and sandstones is **13,** 1.8 and **1.0** mg/kg respectively (Onishi and Sandell 1955, Lemmo et al 1983). Arsenic is an element of multiple oxidation states. The common species of arsenic found in water, sediment and soil systems are arsenate(+5), arsenite(+3), monomethylarsonate (MMAA +3) and dimethylarsonite **(DMAA** +1) (Andreae 1979, 1983). Their respective chemical structures are presented in Figure 1. **Most** of the natural arsenic pool in water exists in the inorganic forms of arsenite **(As+3)** and arsenate **(As+5)**. The organic forms MMAA and DMAA are very small components of the total **As** pool, representing up **to 5%** in water or sediments (Faust et al 1987a).

The inorganic **As** species are primarily controlled by Eh and pH. Figure **2** is a pH - Eh diagram of **As** which shows the interchange between **As(+5)** and **As(+3)**. The thermodynamic data are from Kotz and Purcell (1987) and Stumm and Morgan (1981).

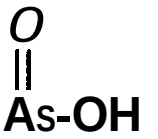
Generally, **As(+5)** dominates in surface waters, sediment surfaces and aerobic environments. In some sandy sediments, even under anaerobic conditions, As(+5) is the dominant species. This is probably due **to** the absence of electron donors (i.e. organic matter in the sandy sediments) (Faust et al 1987a), or due to the presence of oxidizing material in the sediments (Oscarson et al 1980). **As(+3)** exists in the deep sediments and pore water under anaerobic conditions.

Figure 1. The **Major Arsenic Species in Nature**



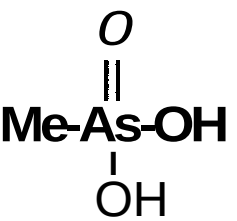
H_3AsO_4 (+5)

Arsenic acid



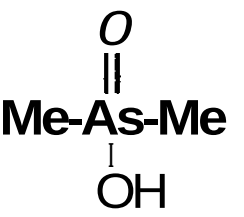
$HAsO_2$ (+3)

Arsenious acid



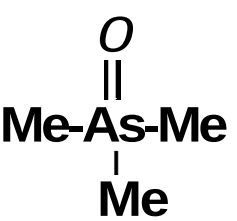
MMAA (+3)

Monomethylarsonic acid



DMAA (+1)

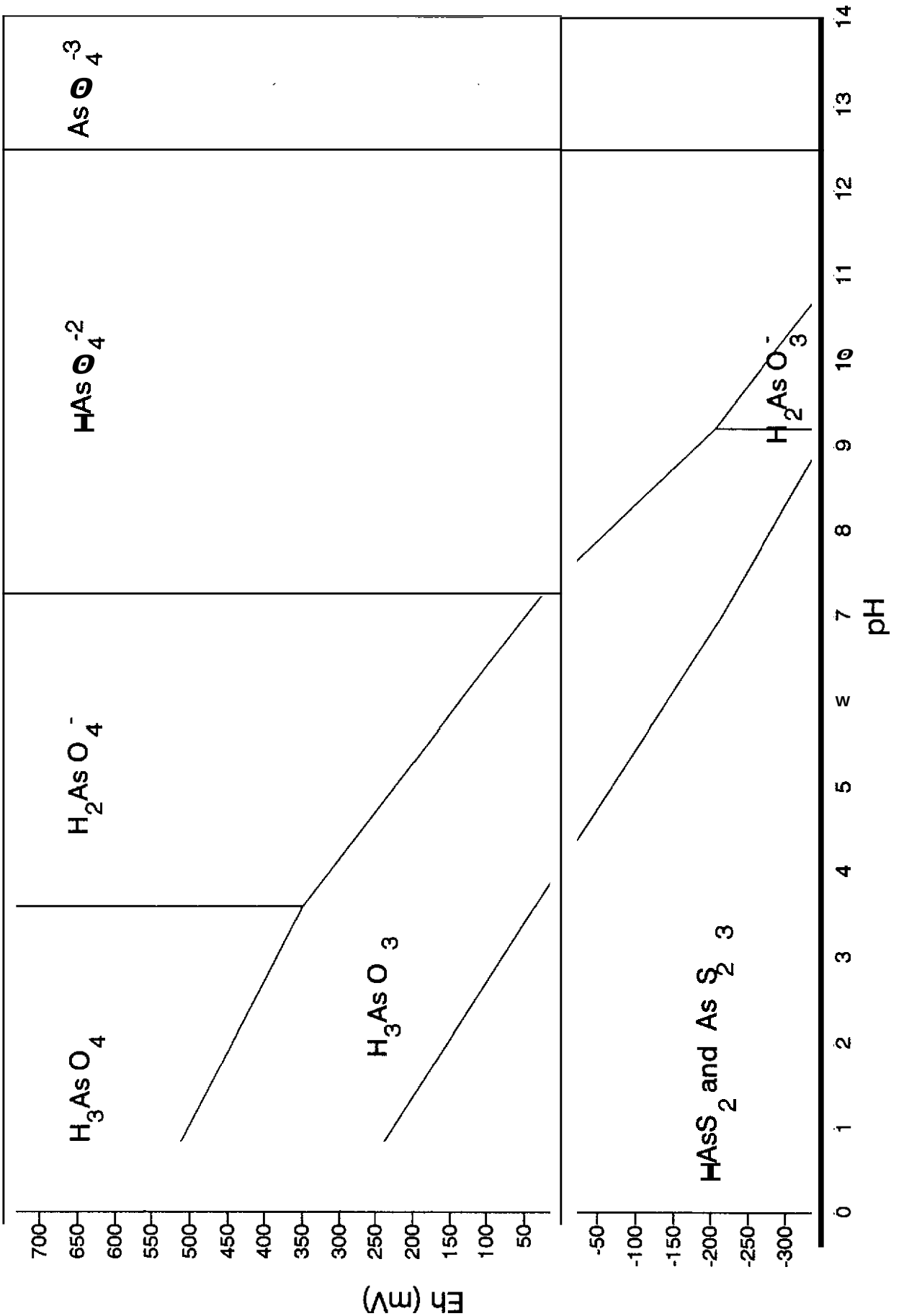
Dimethylarsinic acid



TMAO (-1)

Trimethylarsine oxide

Figure 2. Eh-pH Diagram of Arsenic



2.1.1 Biological Cycling of Arsenic

Arsenic can enter a biological system similar to the phosphorus cycle in the environment; the As cycle and balance in nature are important. Arsenic is toxic due to its ability to form covalent bonds with sulphur, and As(+3) has a high affinity for thiol groups of proteins. This reaction inactivates many enzymes, making this radical more toxic than As(+5) (Tamaki and Frankenberger 1992).

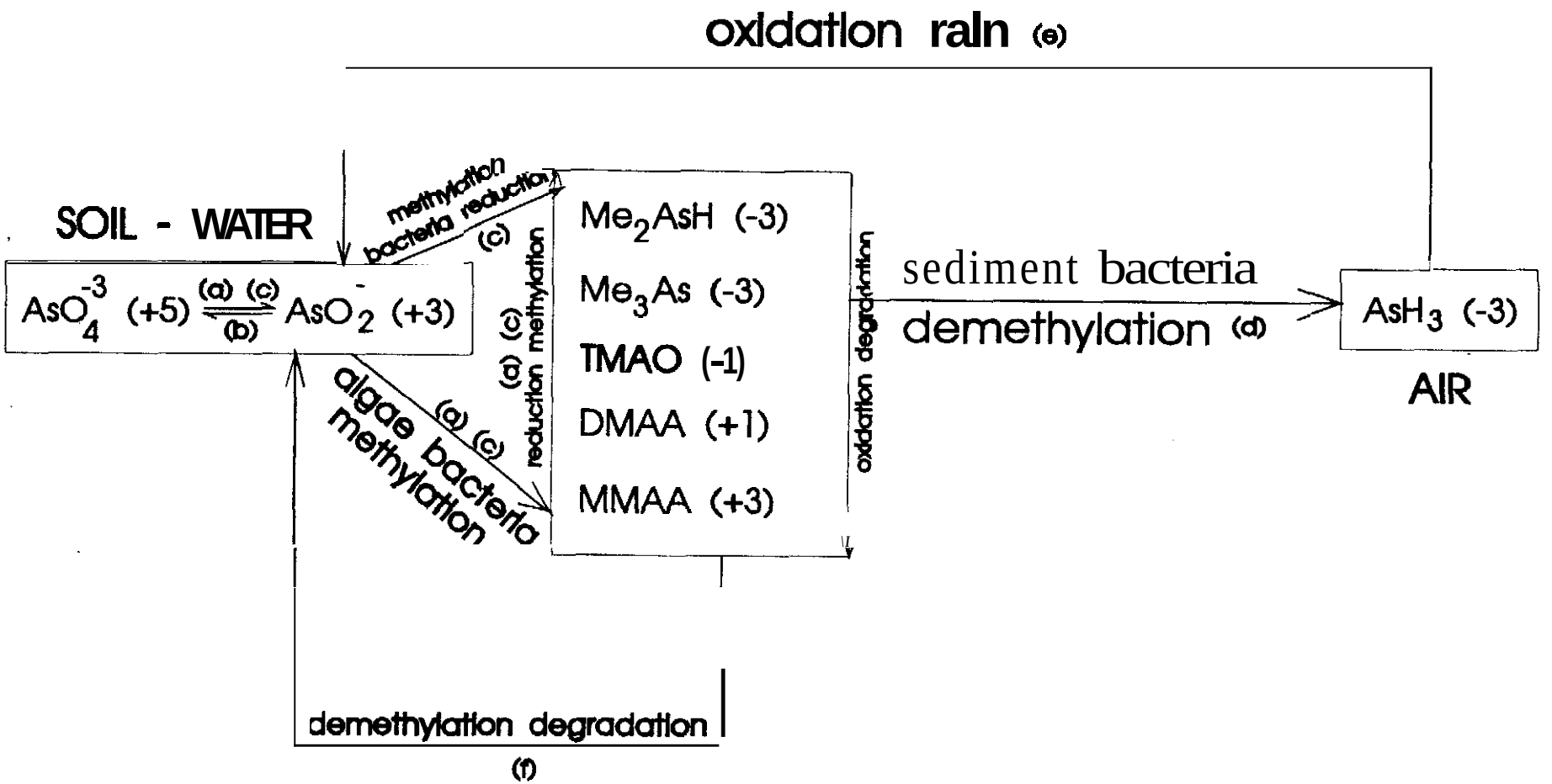
In highly productive ecosystems in the water, up to 80% of the total As pool may undergo reduction and methylation by algae (Sanders 1983). Arsenic uptake is not influenced by external phosphate (Budd and Craig 1981), however the presence of As may depress the uptake of phosphorus by algae (Brunskill et al 1980).

In aerobic conditions algae can reduce As(+5) to As(+3), and methylate As(+3) to the non-volatile compounds (Baker et al 1983) monomethylarsonic acid (MMAA +3), dimethylarsinic acid (DMAA +1) or trimethylarsine oxide (TMAO -1) (Johnson and Burke 1978, Andreae 1983). Methylation is equivalent to a biological detoxification process for As. In Figure 3 all biological reactions for As are summarized and lettered, starting with "(a)" for the algal reduction and methylation.

Bacteria are approximately 10-fold more resistant to As(+5) than to As(+3) (Osborne and Ehrlich 1976). Under aerobic conditions, bacteria catalyse 78-96% of the As(+3) oxidation into As(+5) (Wakao et al 1988) (see Figure 3(b)).

Under anaerobic conditions, bacteria reduce As(+5) to As(+3) and methylate As(+3) into MMAA (+3), DMAA (+1) and further into dimethylarsine (see Figure 3(c)). Some fungi generate trimethylarsine (Tamaki and Frankenberger 1992).

Figure 3. Arsenic Cycle in Nature



Soil and sediment bacteria can demethylate dimethylarsine and trimethylarsine into arsine; this is the primary mechanism for As loss to the atmosphere (see Figure 3(d)). Arsine in the air can be oxidized into As(+3) and As(+5) forms, and fall down to the ground with rain (Figure 3(e)).

Since As can enter the food chain, microbial metabolism is another facet of its biological cycling. The end product of As in the higher trophic levels (e.g. shrimps) is arsenobetaine (Norin and Christakopoulos 1982). Such organic forms of *As* can be broken down by bacteria to As(+5) and carbon dioxide. The general degradation process follows the direction below (Kaise et al 1987, Hanaoka 1987):

arsenobetaine → trimethylarsine oxide → DMAA →
→ MMAA → AsO_2^-(+3) → AsO_4^{-3}(+5) (see Figure 3(f))

2.1.2 Stability of Arsenic Species

The residence times of arsenic in various environmental components are listed below (Mackenzie et al 1979, Woolson 1983):

Environment	Residence Time (years)
Sediments	99,800,000
Ocean (dissolved)	9,400
Land	2,400
Terrestrial Biota	17
Oceanic Biota	0.07
Air (total)	0.03

Overall, organic fractions comprise only about 5% of the total As. These organic forms are chemically less stable than inorganic arsenate and arsenite - the more desirable forms of arsenic - which can remain in the sediments as stable precipitates.

2.1.3 Arsenic Adsorotion Processes

Arsenic chemistry in soils and sediments is believed to be mainly controlled by adsorption-desorption mechanisms; both As(+3) and As(+5) can be adsorbed. The adsorption process is controlled by Eh and pH (Goldberg and Glaubig 1988) which are the same factors controlling the chemical species of the inorganic As forms.

Elkhatib et al (1984) used a modified Freundlich equation to describe the kinetics of the As(+3) adsorption process in soil. They found that Fe(+3) oxides and Eh are the main soil properties controlling the As adsorption rate.

Pierce and Moore (1982) studied the adsorption of As(+5) and As(+3) on amorphous iron hydroxide. Their conclusion was that As(+5) adsorbs more readily than As(+3); the optimum pH condition for As(+5) adsorption is pH 4, and for As(+3) pH 7.

The adsorption of As to oxides (Fe, Al, and Mn), clays and sediments has been studied. Strong linear correlations exist between total As concentrations and both Fe and Mn concentrations (all elements are determined by neutron activation analysis) in the surface sediments of Lake Washington. A poor linear correlation of total As concentration with organic carbon concentration (oven-dried sediment treated with HCl and then with a LECO carbon analyzer) was observed in the same sediments (Crecelius 1975).

Although adsorption of As occurs on the surfaces of both Fe(+3) and Mn(+4) oxides, the situation is different. The surface of Mn(+4) oxide is mostly negatively charged. When Mn(+4) oxide is reduced to Mn(+2) in the deeper sediment, it dissolves and diffuses into the porewater. Mn(+2) may then be adsorbed by the surface of Mn(+4) oxide. This changes the sediment-bound Mn(+4) oxide's surface charge from negative to positive, which then adsorbs the negatively charged As(+5) anions (Takamatsu et al 1985). These oxidation/reduction processes can be affected by microbial activity in the sediment.

Mn(+4) oxide can oxidize As(+3) into As(+5) (Takamatsu et al 1985). For example, As(+3) is observed to be oxidized by Mn(+4) in fresh sediments from a southern Saskatchewan lake into As(+5) through an abiotic process. The reaction activation energy *is* only 3.3-8.5 kcal/mole. This low activation energy required for the reaction indicates that the oxidation process is very fast and mainly diffusion-controlled (Huang et al 1982). It has been shown that under **N,** gas flow, As(+3) is oxidized by Mn(+4) and Fe(+3) in the sediments. These oxidations can take place according to the following reactions:

$$HAsO_2 + MnO_2 + 2H^{+} = H_3AsO_4 + Mn^{+2}$$
$$HAsO_2 + 2Fe^{+3} + 2H_2O = H_3AsO_4 + 2Fe^{+2} + 2H^{+}$$

Sorption of As is occurring simultaneously with the oxidation of As(+3) to As(+5) (Oscarson et al 1980).

The Fe(+3) oxide surface is mostly positively charged, hence it readily adsorbs the negatively charged As(+5) anions. However, the adsorption is only favoured by a low pH. At a higher pH (> 5.5 - **6),** the Fe(+3) hydroxide surface becomes negatively charged and this makes the adsorbed **As** unstable (Dzombak et al 1990, Brewster preprint).

There is disagreement in the findings about the relationship between As and Al(+3) oxide components in the sediments. Some reports showed a positive correlation effect between them (Huang 1975, Livesey and Huang 1981), whereas a poor correlation was indicated by others (Crecelius 1975).

Phosphate (P+5) and sulphate (S+6) sometimes compete with As in the adsorption process. Addition of phosphate or sulphate after As(+5) or As(+3) had been adsorbed had very little affect on the adsorption of As. A significant effect on the adsorption of As at low concentrations was evident after phosphate or sulphate had already been adsorbed (Pierce and Moore 1982). Barrow (1974) found that high concentrations of

As(+5) solution (As(+5) = 37.5 g/L) can displace phosphate (200 μg phosphate per g of soil) from soil. Livesey and Huang (1981) examined the influence of anions (nitrate (N+5), chloride (Cl-1), sulphate, and phosphate) on the adsorption of As by active soil components. The molar ratio of anions to As(+5) ranged from 100 to 10000 (As(+5) = 0.10 mg/L to 2.15 mg/L). Nevertheless, other anions, which were tested in relation to affecting the adsorption of **As** by the soils, did not vary significantly with increased concentrations of chloride, nitrate and sulphate. Only phosphate substantially suppressed the adsorption of As.

As mentioned above, adsorption-desorption equilibria with sediments are considered to dominate the As concentrations in the aqueous phase. Part of the adsorbed **As** is related with Fe(+3) oxide and may be extracted by oxalate solution, while the remainder is complexed with organic molecules and, hence, is not oxalate-extractable.

Faust et al (1987a, b, and c) did a series of experiments to test the stability of **As** in sediments of the Maurice River, Blackwater Branch, and Union Lake. They found that both sandy and organic sediments have 43% to 81% As non-extractable by distilled water or 1 N HCl solutions (Faust et al, 1987a). Among the extractable As, less than 1% is released from organic sediments while 28-48% is released from sandy sediments. This indicates that organic sediments have a stronger affinity and a greater capacity for sorption of **As** than sandy sediments (Faust et al, 1987b).

As(+3) is more mobile than As(+5). Under reducing conditions therefore, where this form will predominate, As concentration increases greatly (Masscheleyn et al 1991). The **As** release is strongly dependent on the oxidation states and the surface charge of Fe(+3) hydroxide in sediments. Under anaerobic conditions, 10 times as much As is released from sediment than in aerobic conditions (Clement and Faust, 1981). Arsenic is not released within the aerobic range of 10% to 100% oxygen saturation in the sediment.

2.1.4 Arsenic Precipitation Processes

Besides adsorption to the sediments, arsenic may also precipitate or coprecipitate in the sediments. Various metal ions can form precipitates with arsenate (As+5). Hess and Blanchar (1976) used ion products of Al, Ca, Fe, Mn, and Pb arsenate compounds to study the equilibrium states of As in some soil samples. They found that Pb arsenate and Mn arsenate are more stable than Fe, Al, Pb and Ca arsenate precipitates in their soil samples, and both Mn and Pb concentrations control the level of As in solution. Under reducing conditions, As can react with sulphur to form the stable sulphides As_4S_4 (realgar) and As_2S_3 (orpiment).

Overall, adsorption of As in sediments with Fe(+3) and Mn(+4), Al(+3), and precipitation of As with sulphide (S-2) and other metal ions are the major mechanisms for arsenic removal from aqueous environments.

2.2 Species of Nickel

Most nickel is produced from sulphide ores, such as pentlandite ($(Fe,Ni)_9S_8$), the arsenide ores, such as niccolite (NiAs), chloanthite ($NiAs_2$) and nickel glance (NiAsS) (Nicholls 1973). Nickel can form compounds in a series of valence states from -1 to +4; the most common state is Ni(+2). Additionally, nickel can form organometallic compounds (Nicholls 1973), while free nickel ions can form a large number of complexes with organic phosphorus and nitrogen compounds. Nickel also has quite a high adsorption ability (Weider, 1990).

In a study of the Yukon and Amazon rivers, 2.2% to 2.7% of the total nickel was found in solution as free ions and complexes. The rest was found adsorbed on suspended materials in metallic coatings, **or** incorporated in solid biological materials, **or** in crystalline structures (Gibbs 1973).

The mobility of nickel in soil and sediment pore water is low. In Sudbury, nickel and copper concentrations in surface samples of soil and sediment were found to be elevated (Hutchinson et al 1975). However, the elevated concentrations were confined to the top 15 cm. This indicates that the nickel does not move vertically downward through the sediment or soil profile.

2.2.1 Bioloaical Cycling of Nickel

Nickel is one of the essential trace elements for living organisms (Mertz 1974, Nielsen 1971). It is an essential component of bacterial enzymes such as hydrogenases (Hausinger 1987), but it is also very toxic to most bacteria (>5.87 mg/L).

Bacteria with high nickel resistance have been isolated from heavy-metal-rich sites. Four hundred nickel tolerant "isolates" have been collected (Schmidt et al 1991) and some were able to grow in the presence of 2.35 mg/L $NiCl_2$.

Nickel resistance is determined by the presence of genes on a DNA plasmid which can be transferred between bacteria and can, therefore, potentially spread within heavy-metal-polluted ecosystems. The plasmids carrying nickel resistance may show resistance to other heavy metallic ions such as cobalt, chromate, and mercury (Mergeay et al 1985, Schmidt et al 1991).

Algae (*Scenedesmus acutiformis* var *alternans*) isolated from heavy-metal-polluted lakes near Sudbury, Ontario are tolerant to nickel (Stokes et al 1973). This study found that growth rates were sub-maximal in solutions containing 1.5 mg/L nickel; some algal growth occurred at 3 mg/L nickel. In the laboratory, 0.25 mg/L nickel solutions had no effect on the growth of the cultured isolate (Stokes et al 1973).

Stokes et al (1973) established a positive correlation between nickel concentrations in water and algae, and between sediment and roots of the water lily Nymphaea. The highest concentrations of nickel were found in the algal periphyton which had 20,000

times more nickel than in the water. In the vegetation, nickel concentrations uniformly exceeded both copper and zinc levels at the contaminated sites.

A few flowering plants, termed nickel-hyperaccumulators, can survive in heavily contaminated soils and may accumulate 1% dry weight as nickel (Schlegel et al 1991). The oral toxicity of nickel to man is very low. Nickel does not accumulate in human tissues and is eliminated via the faeces and urine.

2.2.2 Stability of Nickel Soecies

In aquatic ecosystems, the biogeochemical processes that may contribute to the removal of nickel from polluted waters include: (1) uptake by vegetation; (2) binding to organic matter as organic complexes; (3) adsorption to sediment by cation exchange or coprecipitation; (4) the formation of insoluble metal oxides/oxyhydroxides; (5) insoluble metal sulphides; and (6), other insoluble metal precipitates. The ability to form organic complexes assists nickel removal and retention by organic sedirnents.

An experiment to measure the maximum binding capacities for ten cations to sphagnum peat and sawdust showed that Ni^{+2} was one of the more strongly bound ions (Weider 1990) . The ions are listed below in decreasing order of binding capacity:

$$Al^{+3} = Zn^{+2} > Fe^{+3} > Ni^{+2} = Cd^{+2} > Na^{+} = Mn^{+2} > K^{+} > Ca^{+2} > Mg^{+2}$$

Eger and Lapakko (1989) and Lapakko and Eger (1988) showed that, at a neutral pH, peat could remove up to **20** mg Ni per g peat (dry weight). Removal rates were reduced at lower pH.

2.2.3 Nickel Adsorption Processes

The removal of nickel from the aquatic environment is mainly a result of adsorption on other metal oxide surfaces (Theis and Richter 1980). Sediments rich in iron hydroxide (goethite) and manganese oxide are effective scavengers of heavy metals in the aquatic environment (Singh and Subramanian 1984). The adsorption of Ni on goethite has been studied under different conditions - pH **4** to 8, concentration of Ni from $5.87*10^{-2}$ mg/L to 5.87 mg/L, and temperature from 5°C to 35°C (Bruemmer et al 1988). Ni adsorption on MnO_2 solid has also been studied (Laitinen and Zhou 1988). The adsorption was in agreement with the Langrnuir equation and it was found that the adsorption increased with pH, reaction time and temperature.

2.2.4 Nickel Precipitation Processes

Precipitation as sulphides under reducing conditions is a further common mechanism by which nickel is precipitated in the sediment. Reactor studies (Hammack and Edenborn 1992, Dvorak et al 1992) have shown that nickel is effectively removed from solutions in batch-reactor conditions into sulphide precipitates. The resulting sulphide precipitates are stable over a wide range of pH's and can be expected to trap the nickel as long as reducing conditions prevail.

The nickel sulphide formation may be closely linked to the presence of nickel organic complexes since, in nature, metal sulphides commonly exhibit a close association with high-molecular-weight organics in fine-grained sediments (Kirchner 1985), and several studies suggest that organo-metallic complexes which form *in situ* play an important role in the transfer of metallic ions to sulphide phases (Nissenbaum and Swaine 1976, Lett and Fletcher 1980).

Nickel may form organic complexes at the bacterial cell surface, then further react with microbially produced S^{-2}. Ferris et al (1987) found microcrystalline millerite (NiS)

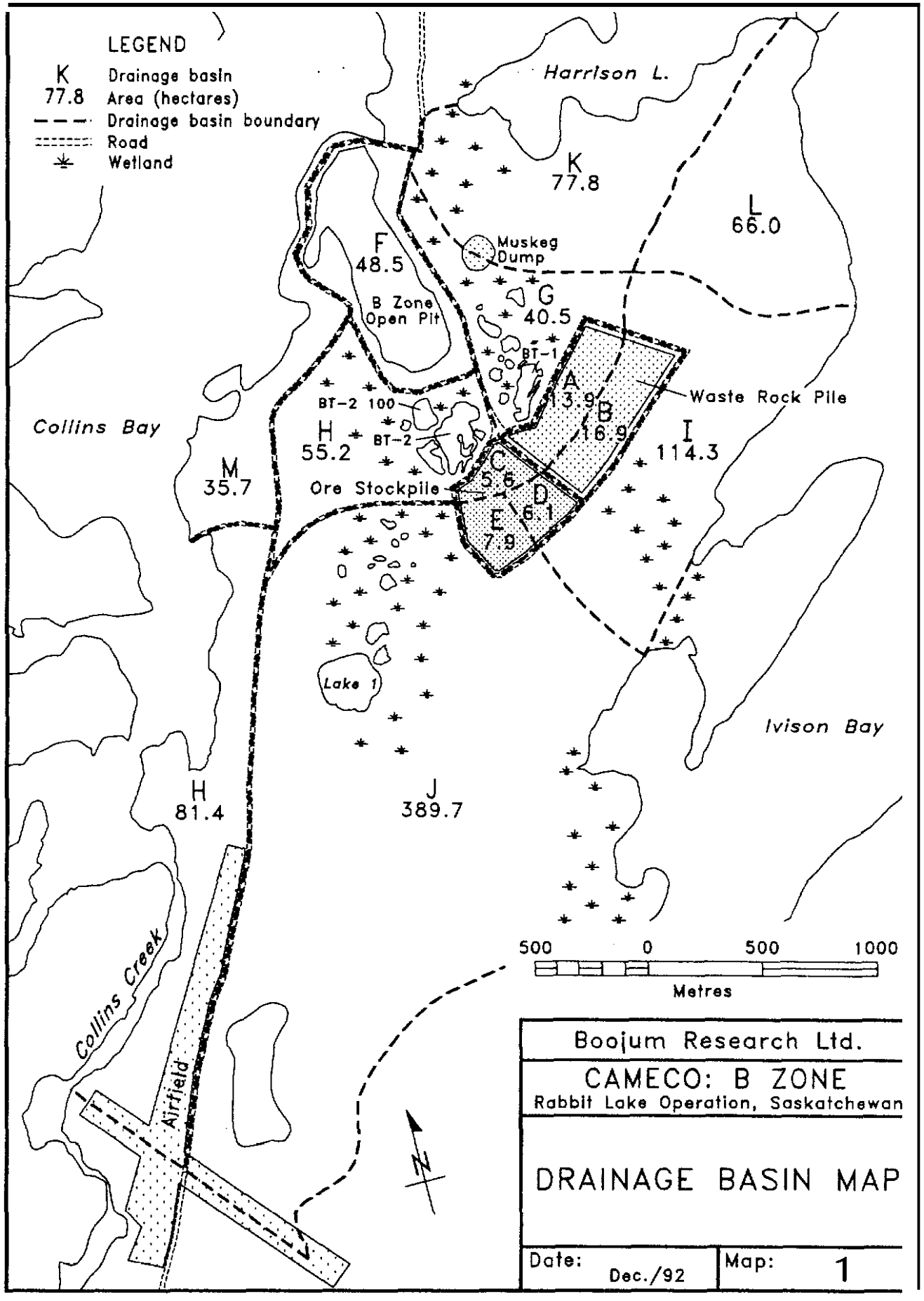
associated with bacterial surfaces in a lake sediment contaminated from mine drainage near Sudbury, Ontario. Ferris et al **(1989)** also showed that bacterial biofilms formed on slides suspended in lakes accumulated more Ni in neutral conditions than in acidic conditions, indicating that an increase in pH may be important in determining Ni removal rates.

3.0 MATERIALS AND METHODS

3.1 Site description

The study was conducted at CAMECO's Rabbit Lake uranium operation in northeastern Saskatchewan (Collins Bay, Wollaston Lake). Located northwest of the waste rock pile in the B-Zone area is the BT-1 wetland which covers 40.5 hectares, and drains primarily towards the flooded B-Zone open pit (Map 1). The BT-2 wetland is immediately adjacent to the northwest side of the ore stockpile, and covers 55.2 hectares; water from this wetland also drains towards the flooded pit. A series of ponds, with an average depth of 0.5 m and underlain by 1 m of sediment primarily composed of peat particles, is located in the northeast section of the BT-2 wetland. An overview of the BT-2 wetland is depicted in Plate 1.

Plate 1: Overview of the BT-2 Wetland


LEGEND
K
77.8
Drainage basin
Area (hectares)
Drainage basin boundary
Road
Wetland
Harrison L.
K
77.8
L
66.0
F
48.5
Muskeg
Dump
G
40.5
B Zone
Open Pit
BT-1
A
13.9
B
16.9
Waste Rock Pile
BT-2 100
BT-2
H
55.2
I
114.3
Collins Bay
M
35.7
C
5.6
D
6.1
E
7.9
Ore Stockpile
Lake 1
Ivison Bay
H
81.4
J
389.7
Collins Creek
Airfield
N
500
0
500
1000
Metres
Boojum Research Ltd.
CAMECO: B ZONE
Rabbit Lake Operation, Saskatchewan
DRAINAGE BASIN MAP
Date:
Dec./92
Map:
1

3.2 Preparation and Operation of Reactors

3.2.1 1993 Laboratory Reactors

Six acrylic cylinders (9.5 cm internal diameter and 42 cm high) were used as "reactors" for the water column experiment, as well as two 2 L glass jars. They were cleaned and rinsed with distilled water. The reactors are shown in Plate 2.

The experiment was set up on May 3, 1993 and terminated on January 10th 1994. To each reactor, 500 mL of original BT-2 station 250 muskeg sediment was added and left to settle for 24 hours. Then 760 mL of 6.11 water from the Waste Rock Seepage was carefully added to the top of the sediment in each reactor. Reactor R1 was the control without organic amendments, reactors R2 and R3 were used for the potato waste anaerobic treatment, and reactors R4 and R5 were used for the alfalfa anaerobic treatment.

Plate 2: 1993 Laboratory reactors used to study biological arsenic removal

Six days after adding the 6.11 water (May 10, 1993), 5 g of potato waste was added to R2 and R3, and alfalfa pellets (55 mL or 31.5 g) were added to R4 and R5. At the same time, glass jars 1 and 2 were set up as controls with 760 mL 6.11 water and no sediment. Jar 1 was amended with 5 g potato waste and Jar 2 was amended with 55 mL alfalfa pellets. All the reactor cylinders and jars were tightly sealed.

3.2.2 1994 Laboratory Reactors

The sediment contained in the 1993 reactors was used in sequential extractions to determine the form of the As and Ni which had accumulated in the sediment. The same reactors were washed and reused to set up the 1994 experiment; the set-up of the reactors was identical to the experiments carried out in 1993.

900 mL of sediment collected at the BT-2 250 m section of the transect, and 900 mL of 6.11 seepage water was added carefully by siphoning to minimize sediment disturbance. Glass jars were set up with 6.11 water (900 mL) to which no sediment was added. The slightly milky appearance of the seepage water in the reactor is depicted in Plate 3; the reactor shown is following set-up with 5 g of potato waste (McCain Foods) after a 24 h settling period. Potato waste was added to the top of the water and reached the sediment surface within 1 hour.

The sediment in the reactors received the following treatments:

A. Reactors 1,2,3,7,8 & 9	- no further treatment
B. Reactors 4,5,& 6	- replace 500 mL of the water column weekly, simulating continuous flow of the seepage in the "field"
C. Jar 1 & 3	- no further treatment
D. Jar 2	- replace 500 mL of the water column weekly

Plate 3: 1994 Laboratory reactor at set-up

3.3 Monitoring and Analytical Methods

Water was drawn from the sediment with a syringe while seepage water was carefully replaced from above to minimize or avoid sediment disturbance. The following parameters were monitored:

pH	acidity	Ni
Em	alkalinity	As
conductivity	NO_3	Fe

The pH was measured with a Canlab probe and Jenco meter, Em with Fisher probes and Corning Model 103 meter, and conductivity with an Orion 140 meter and probe. Em values were converted to Eh values by means of the formula:

$$Eh\ (mV) = Em\ (mV) + (241 - 0.66(T-25))$$

where T is the measured temperature (°C). Acidity was determined by titration against NaOH with a Metrohm 702 SM Titrino autotitrator. Nickel was determined with a colorimetric test (Rollet's dimethylglyoxime complexation) and reading absorbance at 445 nm. Arsenic was measured with the Merck Merckoquant strip test which measures the reaction between hydrogen arsenide gas and mercury(+2) bromide. Iron was determined by a phenanthroline test (absorbance at 510 nm) and NO_3-N with a Hach cadmium reduction (absorbance at 545 nm). For the colorimetric tests, a Bausch and Lomb Spectronic 70 spectrophotometer was employed.

The colorimetrically-determined concentrations were compared to those determined by ICP (Inductively Coupled Plasma Spectrophotometry). These analyses are carried out by a certified laboratory in Toronto; the laboratory's QA/QC procedures are given in Appendix 7. For the seepage water which was treated, the agreement between the colorirnetric concentrations and those determined by ICP were reasonable, but nickel concentrations in the solutions derived from the sequential sediment extraction were unacceptable due to interference. Therefore, all Ni concentrations in solutions from the sequential sediment extractions were determined by ICP.

3.4 Sediment Sampling in the 1993 Reactors

After 35 weeks (January 10, 1994) of operation the sediments were sampled. The water overlying the sediments in the reactors was syphoned carefully not to disturb the sediment. The seepage water overlying the sediments in the reactors was referred to as the **Top** water sample. Water filtered from the top and middle layers of the sediments was referred to as the Middle water sample. Water filtered from the bottom sediments was referred to as the **Bottom** water sample.

Sediments in the reactors were divided into three layers - the top 1 cm was referred to as the top sediment sample of the reactors while the 5 cm section of sediment immediately below it was referred to as the middle sediment sample. The remaining sediment below this was referred to as the bottom sediment sample.

Each layer of sediment was collected with a spoon and filtered immediately. The pore water derived in this manner was used to quickly measure Em, pH and electrical conductivity.

All of the pore water samples were purged with N_2 gas, sealed in plastic bottles and refrigerated (4°C). ICP analysis was carried out within 48 h of removal from the sediment. Concentrations of sulphide and sulphate were determined in the pore water.

Each of the sediment layers were well mixed and then separated into two portions. One portion was sealed under nitrogen gas and kept in the refrigerator (4°C) for sequential extraction analysis. One portion was used for measurement of wet volume, dry weight and loss on ignition (LOI), a measure of the organic content of the material.

The sequential analysis of sediment is designed to determine: (1) the form of metal deposit in the sediment, and (2) the stability of the various As and Ni precipitates.

The sequential extractants are referred to in previous metal extraction studies (Salomons and Forstner 1984, Bupp and Ghosh 1991, Henrot and Wieder 1990). The extraction steps are:

(1) 1M KNO, solution for exchangeable metals, solidlsolution ratio 1:50, 2 hours shaking.

(2) 0.1M $Na_4P_2O_7$ + 0.01N EDTA solution for organically-bound metals, solidlsolution ratio 1:50, 24 hours shaking.

(3) 1M ammonium acetate solution (pH=5) for metal carbonate, solidlsolution ratio 1:50, **5** hours shaking.

(4) concentrated HNO, solution for other metal precipitates (arsenates, hydroxides and sulphides), solidlsolution ratio 1:50, 2 hours heating at 120°C.

3.5 Sequential Extraction **of 'Spiked' Sediments**

To test the applicability of the sequential extraction method to the sedirnents and determine the reliability ***of*** the colorimetric tests as monitoring tools for the experiment, extractions were carried out with sediments spiked with precipitates. The proposed As and Ni precipitates were synthesized as described below and mixed with the sediment; this allowed for an assessment of the effectiveness of the extraction method with respect to the relevant elements which were removed from the seepage water in the reactors.

BT-2 250 sediment (collected in 1993) was used to adsorb all the precipitates in the spike experiment. The sediment moisture was measured by drying the sediments at 104°C in an oven for 24 hours (Clesceri et al 1989).

In the reactors, to which seepage water was added, the concentrations **of As** and Ni were reported as 50 mg/L and 82 mg/L respectively. The total volume of seepage water added to the reactors was 700 mL which resulted in a total quantity of **As** and Ni (precipitated or adsorbed onto the sediments) of about 35 mg and 57.4 mg respectively.

To precipitate the total loading of As and Ni added to the reactors, it required 26 mg of Fe and 121.3 mg $Na_2CO_3 \cdot H_2O$ or 234.7 mg $Na_2S \cdot 9H_2O$.

In order to run the spike experiment within a similar concentration range, precipitate was produced in solutions which considered concentrations of reagents in stoichiometric proportions to achieve the desired concentration range of total As and Ni.

Sediment was prepared once to produce a combination of iron arsenate precipitate and nickel carbonate, referred to as sample #2, while a second combination produced a sediment spiked with iron arsenate and nickel sulphide, referred to as sample #3 . For each preparation 20 g of the wet sedirnents were used. Sample #1 sediment was used as a control with no precipitates added.

To make precipitates of $FeAsO_4$ and $NiCO_3$, a solution consisting of 98.6 mg Na_3AsO_4 (22.2 mg As) and 260 mg $NiSO_4 \cdot 6H_2O$ **(58** mg Ni) was prepared and added to the sediments in 20 mL distilled water. A second solution containing 167 mg $FeCl_3 \cdot 6H_2O$ and 119 mg Na_2CO_3 solutions was prepared in 10 mL distilled water and slowly dropped into the slurry of the sediment. Thus in the sediment, the respective precipitates were expected to form (sample #2). Finally, the pH was adjusted to 6.35 by dilute NaOH or H_2SO_4 solutions, and the slurry was allowed to settle for **1** hour.

To form the combination of $FeAsO_4$ and NiS precipitates (sample #3), solutions of 93 mg Na_3AsO_4 (20.5 mg As) and 266 mg $NiSO_4 \cdot 6H_2O$ (59.4 mg Ni) were dissolved in 20 mL distilled water and added to the sediments. This was followed by adding a solution of 158 mg $FeCl_3$ and 205 mg Na_2S dissolved in 10 ml **of** distilled water **to** the sediment. The sediment changed colour to a dark black and the pH was adjusted with 1N NaOH to 6.30.

Afler the sediments and their respective precipitates settled for one hour, the sediments were filtered with a 0.45 μm filter paper. Before each extraction, the sediments were rinsed twice with 50 mL distilled water to wash away the remaining extractants. The washing water was combined with the extraction solutions to give a total volume of 150 mL. The sequential extractions, as described above, were carried out on the washed sediments.

Solutions derived from each extraction were assayed using the colorimetric methods to determine the concentrations of iron, arsenic and nickel which were released from the sediment during the extractions.

4.0 RESULTS

4.1 1993 Experiment - Arsenic and Nickel Forms in Sediments

In the **1993** reactors, where arsenic and nickel was removed from the seepage water to the sediment, a known amount of both contaminants can be expected when the sediments are extracted. Through (a) destructive sampling of these reactors, (b) analysis of the pore water collected from different depths, and (c) analysis of the sediment in the reactors, estimates can be derived as to the fraction of the contaminants removed by the sediments. The pore water concentrations are those which are potentially available to diffuse throughout the sediment layers and to the water column. The results from the pore water analysis are presented in Section **4.1.1**.

The chemical form in which the contaminants are present in the sediment can be determined through their extractability using sequential extractions; exchangeable metals are recovered in the first extraction with potassium nitrate, followed by the extraction of organically-bound metals with a sodium diphosphate and EDTA solution in the second step. The third extraction is carried out with ammonium acetate, which recovers carbonate precipitates formed in the sediment, and finally a hot nitric acid extraction is employed to recover all remaining metals not bound in a silicate matrix.

Although the sequential extraction steps will provide good estimates as to the form of metals bound to the sediment, it can not be expected that a complete recovery of all precipitates formed in the sediments is possible with such an extraction process. Each extraction step will have its own methodological error as well as an analytical error. Thus, in order to assess the ability of the procedure to allow for accurate quantification of the extracted fractions, a spiked sediment extraction was carried out.

The results of the spiked sediment extraction are presented in Section **4.1.2.**, and the sequential extractions carried out on the top **1** cm layer of the sediments in the reactors are presented in Section **4.1.3.**

4.1.1 Seeoaae Water and Sediment Pore Water Analysis

Laboratory measurements of pH, Eh and conductivity of the reactor seepage water overlying the sediments, and pore water derived from filtrations of the sediments are summarized in Table 1. The **Top** layer refers to the treated seepage water overlying the sediments, the **Middle** layer to the pore water derived from a combination of the top and middle layers of the sediment, and the **Bottom** layer to the pore water derived from the lower part of the sediment. Also included in Table 1 are the concentrations of As, Ni, Fe, P, sulphate and hydrogen determined by the assay laboratory.

Table 1: 1993 Reactor Experiment - Chemistry of Water Overlying Sediment & Sediment Pore Water after 35 Weeks of Operation, Jan. **10,1994**

REACTOR	Layers	pH	Eh (mV)	Cond. (umhos/cm	As (mg/L)	Fe (mg/L)	Ni (mg/L)	P (mg/L)	HS (mg/L)	SO4 (mg/L)
R-1	Top	4.31	518	474	11	0.034	7.85	0.25	<0.01	235
Control	Middle	5.17	402	477	7	0.038	5.17	0.15	<0.01	242
	Bottom	5.32	201	393	3.5	0.056	1.82	0.1	<0.01	199
R-2	Top	6.44	221	470	3	0.266	0.66	1.56	<0.01	84.4
Potato	Middle	6.53	173	393	6	0.177	1.41	1.19	<0.01	44.9
Waste	Bottom	6.43	152	268	3	0.581	0.18	0.68	<0.01	12.5
R-3	Top	6.35	223	376	0.7	0.094	0.28	0.78	<0.01	47.8
Potato	Middle	6.42	123	328	6	0.161	1.36	0.76	0.01	21.9
Waste	Bottom	6.16	111	318	3	1.45	0.37	1	<0.01	12.4
R-4	Top	7.48	2	3650	3	0.488	0.46	6.97	0.17	4.93
Alfalfa	Middle	7.48	131	3860	4.5	0.778	0.43	7.47	0.05	4.62
Pellets	Bottom	7.02	106	4030	5.5	1.21	0.53	7.66	<0.01	5.81
R-5	Top	7.33	167	3890	3	0.176	0.33	6.01	<0.01	
Alfalfa	Middle	7.47	96	3910	3	0.132	0.6	7.31	<0.01	23.9
Pellets	Bottom	7.16	101	4100	3.5	0.368	0.63	2.49	<0.01	4.08
6.11 Water*		4.41	208	1541	39.6	0.48	61.0	20	n.d.	22

assayed by SRC **on Aug.** 14, 1993

n.d. = **not determined**

Note: all **parameters measured at room temperature** (20-21 **C)**

To determine the fractionation of the contaminants between pore water (mobile fractions) and sediments, the calculations have **to** be based on the pore water concentrations. This is the potentially mobile fraction which can move out of the sediment and become available for release into the water column. The results obtained from the analysis of the seepage water overlying the sediment and the pore water are briefly discussed for each reactor below.

R I (no organic amendment to sediment): It is evident that pH values for R I (6.11 seepage water and E-6 sediment) were lower than those of the other reactors. However, they were much higher than the seepage water added at the start of the experiment (pH 4.41). In this reactor, redox potential (Eh) was much higher in the top samples (+518 mV) than in the middle **(+402** mV) or bottom samples (+201 mV) where more reducing conditions prevailed. The pH was higher at the bottom of the reactor (pH 5.32) than in the middle (pH **5.17)** or top (pH 4.31) indicating that alkalinity generating processes, such as denitrification, iron reduction and sulphate reduction have taken place. The lower conductivity in the bottom sample (393 μmhos/cm compared **to 477** μmhos/cm in the middle and **474** μmhos/cm at the top) suggests that precipitation or other ion removal processes have occurred or that ions have been removed from the seepage water before **it** reaches this zone. The chemistry data (Table **1)** indicates that concentrations of **As** and Ni were substantially lower at the bottom (3.5 mg/L and **1.82** mg/L) than at the surface (11 mg/L and 7.85 mg/L). In contrast, iron concentrations were highest in the bottom sample (0.056 mg/L compared **to** 0.034 mg/L for the surface sample).

R2 and R3 (with potato waste): The water from these reactors had a higher pH (6.44 and 6.35 for surface samples) and lower Eh (221 mV and 223 mV for surface samples) than the control reactor (pH 4.31 and Eh 518 mv). The fermentation of the potato waste can result in development of more reducing conditions than with the sediment alone. This in turn results in promotion of alkalinity generating anaerobic processes. There was no clear difference in pH between top and bottom samples but as observed for R I, the Eh and conductivity were lower at the bottom of the reactors. There were

no substantial differences in top and bottom samples for As and Ni. Iron concentrations were higher in the bottom samples (0.58 mg/L and 1.45 mg/L for R2 and R3 respectively) than the top samples (0.27 mg/L and 0.09 mg/L for R2 and R3 respectively) indicating that iron (III) reduction and dissolution may have taken place here in reducing conditions. Overall, conductivity was lower than in the control reactor (R1) indicating the enhancement of metal removal processes by the potato waste.

R4 and R5 (with alfalfa pellets): The pH of reactors with alfalfa pellets was higher and the Eh lower in the top, middle and bottom layers of R4 and R5 than both that of the control (R1) and the potato waste reactors (R2 and R3). The conductivity was an order of magnitude higher than in the other reactors (approximately 4000 μmhos/cm compared to approximately 400 μmhos/cm). In R4, arsenic concentrations were higher at the bottom (5.5 mg/L) than at the top (3 mg/L) whereas in R5 they were consistent throughout (3 mg/L to 3.5 mg/L). Iron concentrations increased with depth from 0.49 mg/L (R4) and 0.18 mg/L (R5) at the surface to 1.21 mg/L (R4) and 0.37 mg/L (R5) at the bottom. Sulphide was detected in R4 sediments but not in any of the other reactors. This sulphide was associated with the lowest Eh values and may indicate the occurrence of sulphate reduction and subsequent precipitation of metal sulphides. Very high phosphate concentrations (2.5 to 7.3 mg/L) were found in the alfalfa pellet reactors.

Comparison of the pore water Concentrations of all the reported elements clearly indicates that changes have taken place. For example, the highest concentration of As in the pore water was reported as 11 mg/L in the control reactor (R1), but the seepage water contained 39.6 mg/L of As. In all other reactors, where organic amendments were added to stimulate microbial activity, the concentrations of As in the pore water were lower ranging between 3 mg/L to 5 mg/L. Similar trends are seen for Ni in that the control reactors had the highest pore water concentrations with 7.8 mg/L in the surface water, but considerably lower concentrations were noted (0.3 mg/L to 1.4 mg/L) in sediments of reactors with organic amendments.

For the nutrient phosphate, the conditions were reversed as expected, since no additions of phosphate-rich organic amendments were made to the control reactors. Here the control had the lowest concentration of **P** at **0.25** mg/L (top sample), **followed** by the potato waste reactors (R2 and **R3)** with concentrations of 0.8 mglL to 1.6 mglL in the surface layer. The alfalfa-pellet amended reactors **(R4** and **R5)** had the highest P concentrations with 6.0 mglL to 7.0 mg/L in the surface layer.

The fact that sulphide reduction can take place in the presence of alfalfa pellets is indicated by the presence of sulphide in **R4** and also the reduced concentrations of sulphate in sediments at the bottom of reactors. The highest sulphate concentrations are present in the control reactor sediments with **235** mglL in the surface sample. In the potato waste amended reactors ***(R2*** and ***R3)*** a reduction to **47.8** mg/L and **84.4** mglL at the surface and lower in the lower layers of the reactors was observed. In **R4** (alfalfa-pellet amended) the lowest sulphate concentrations are reported with **4.9** mglL at the surface where concurrently HS concentrations are noted. In order to detect hydrogen sulphide in the pore water, the availability of metals to react with the sulphide must be low. This is suggested by the relatively low Ni concentrations in **R4,** where the highest hydrogen sulphide concentrations are reported. The pore water data strongly indicate, that the sediments are instrumental in changing the chemical composition of the seepage water.

4.1.2 Seauential Extraction Effectiveness and Specificity

Sediments were spiked with precipitates of $FeAsO_4$ and $NiCO_3$ to produce one combination, called sample #2, and a second combination was made by spiking sediment with $FeAsO_4$ and NiS, called sample #3. Sample #1 was the original sediment without a spike.

The results from the spike sequential extractions are summarized in Table 2a for As, Table 2b for Ni, and Table 2c for Fe. **All** data determined in the experiment, including data required for the calculations to arrive at summary Table 2 are given in Appendix Table A1.

Metal concentrations in the original solution and in each extraction were measured. The total extracted metal values in each solution were calculated by multiplying the assays by the solution volume. The percentages of extracted metals in each extraction were determined by comparison with the total extracted metal value. In Table 2, the final column "total measured %" is the sum of all the measured amounts divided by the original added amount.

The **As** present in the original sediment is bound mainly as organic complexes, as this was the only extraction in which **As** was detected (Table 2a). For Ni, fractions are present in the sediment as exchangeable Ni, organically-bound Ni, and Ni in a mineral form, while no Ni is present as a carbonate (Table 2b). For Fe, the original sediment does not contain exchangeable iron. **A** large fraction of Fe is organically-bound, followed by mineral forms (Table 2c); no other forms of Fe exist in the sediment.

Sample #2 was spiked with iron arsenate and nickel carbonate to concentrations of known amounts. With these extractions it is possible to examine the behaviour of these precipitates in the selective extractions. Sample #2 for **As** indicates that the largest fraction is organically-bound, followed by some recovery as a carbonate but none in the exchangeable form or the mineral phase. For Ni, the results are different as a large

Table **2:** Spike Extraction Data

a.

		original solution		1M KNO3 solution		1M Na4P2O7 + EDTA sol'n		1M HN4 acetate sol'n		conc. HNO3 solution		total measured
sample No	added As(mg)	tot.As mg	%	tot.As mg	%	tot.As mg	%	tot.As mg	%	tot.As mg	%	As %
#1	0	0	0	0	0	0.04	100	0	0	0	0	
#2	22.2	0.23	1.30	0	0	15.0	85.8	2.3	12.9	0	0	78.6
#3	20.9	0.05	0.31	0	0	15.0	98.3	0.2	1.4	0	0	72.9

b.

		original solution		1M KNO3 solution		1M Na4P2O7 + EDTA sol'n		1M HN4 acetate sol'n		conc. HNO3 solution		total measured
sample No	added Ni(mg)	tot.Ni mg	%	tot.Ni mg	%	tot.Ni mg	%	tot.Ni mg	%	tot.Ni mg	%	Ni %
#1	0	0	0	0.1	4.7	0.2	6.6	0	0	2.1	88.7	
#2	58	16.1	40.8	5.6	14.2	17.5	44.4	0.3	0.6	0	0	68.1
#3	59.4	0.1	1.3	9.8	86.2	1.4	12.5	0	0	0	0	19.1

c.

		original solution		1M KNO3 solution		1M Na4P2O7 + EDTA sol'n		1M HN4 acetate sol'n		conc. HNO3 solution		total measured
sample No	added Fe(mg)	tot.Fe mg	%	tot.Fe mg	%	tot.Fe mg	%	tot.Fe mg	%	tot.Fe mg	%	Fe %
#1	0	0	0	0	0	4	64.7	0.2	0	2.0	32.0	
#2	34.6	0.04	0.1	0	0	23	79.5	1.3	4.5	4.6	15.9	83.5
#3	32.7	4.7	14.7	0	0	26.9	84.3	1.2	3.7	-0.9	0	100.3

Note: tot.M(mg) = [M](mg/L) * vol.(mL)/1000

% M extracted = tot.M/tot.M(extract orig. + extract1 + extract2 + extract3 + extract4)

where: M = As. Ni. Fe

fraction remained in the pore water, not bound in any form to the sediment. The second largest fraction was the organically- bound, while some fraction was present in the exchangeable phase; none of the Ni was extracted in the mineral form. The Fe results were very comparable to the original sediment in that most was organic, none exchangeable, and some present as carbonates and in the mineral form.

Sample #3 contained iron arsenate together with nickel sulphide. For arsenic, one would expect very similar results to sediment sample #2 unless the formation of nickel sulphide changes surface charges in the sediment thereby facilitating different adsorptions for the arsenic forms. This indeed seems to be the case, as lower recoveries were reported in the pore water solutions than in sample #2; this was also the case for the carbonate extractions which reported lower "% recoveries" than in sample #1. In the presence of nickel sulphide, the largest fraction of As is organically-bound in the sediment while none is present in the mineral extraction.

For Ni, the distribution of the forms changes drastically, in that very low fractions remain in the original pore water. The largest fraction is present as extractable Ni followed by organically-bound Ni in the sediment. The two last extractions - carbonate and mineral forms - yielded no nickel.

Nickel concentrations in sample #'s 2 and 3 display a different distribution in five solutions. Sample #2 contains synthesized $NiCO_3$ precipitates. Sample #3 contains synthesized NiS precipitates. The sequential extraction analysis shows that, for $NiCO_3$, almost 40 % of Ni remained in solution, while for sample #3 only 1.3 % was measured in the original solution. Most of the nickel was adsorbed as organic complexes onto the sediment in both samples. For NiS, 3.6 % and 1.2 % of the measured Ni was present in the 3rd and 4th extractions respectively; these are the weak-acid-soluble or mineral-stable precipitates (most likely NiS).

In the presence of nickel sulphide, Fe concentrations in the original pore water were the highest of all three samples, which might suggest that some FeS had also been formed in the sediment. None of the iron was in the exchangeable form, which was consistent with all the previous extractions. The largest fraction was, again, organically-bound Fe followed by extracted fractions as carbonate an in the mineral phase (although very little).

In summary, the spiked sediment extractions suggest that, for **As,** the presence of sulphide reduction produces a larger fraction of organically-bound **As,** while for Ni the presence of sulphide suggests a shift towards exchangeable Ni forms. Iron is mainly present in the organically-bound form, which is essential to the microbially-driven sediment contaminant removal process.

In Table 3, the concentrations of **As** , Ni and Fe determined colorimetrically in the laboratory are compared to concentrations determined by ICP in the same solutions recovered from the sequential extractions. In-house colorimetric determinations were required due to time limitationss (given the large set of analyses required to complete the examination of the reactors) and economic constraints.

Table 3: Comparison of Boojum and EPL Data

		original solution		1M KNO3 solution		1M Na4P2O7 +EDTA solution		1M NH4 acetate solution		conc. HNO3 solution		total measured
	added (mg)	mg/L	total mg	mg/L	total mg	mg/L	total mg	mg/L	total mg	mg/L	total mg	%
Lab As	20.9	0.4	0.0	0.0	0.0	100.0	15.0	1.4	0.2	0.0	0.0	72.9
EPL	20.9	0.2	0.0	0.5	0.1	124.0	18.6	6.9	1.0	0.3	0.1	94.6
Sample #2												
Lab Ni	58.0	121.0	16.1	38.2	5.6	117.9	17.5	1.7	0.3	0.0	0.0	68.1
EPL	58.0	123.0	16.4	50.1	7.4	322.0	48.1	61.8	9.3	31.4	5.7	149.7
Sample #3												
Lab Ni	59.4	1.3	0.1	65.8	9.8	10.5	1.4	0.0	0.0	0.0	0.0	19.1
EPL	59.4	100.0	11.8	68.7	10.2	183.0	27.3	12.1	1.8	3.6	0.6	86.0
Lab Fe	32.7	39.9	4.7	0.0	0.0	206.4	27.0	9.3	1.2	6.5	-0.9	100.3
EPL	32.7	39.5	4.7	0.05	0.01	158.0	19.7	14.0	1.9	14.7	0.5	80.3

Comparing the reported elements for both analyses with respect to concentrations and total measured %, it is evident that the results for iron and arsenic are in good agreement and acceptable. However, the nickel determinations show large deviations in concentrations between the two laboratories.

In summary, the laboratory measurements **of** arsenic and iron are similar to those determined by ICP. For higher concentrations, the differences between the analyses are somewhat larger, as the colorimetric determinations have to go through several dilution factors.

With respect to the effectiveness **of** the sequential extractions, it can be concluded, based on the summary of the total measured concentrations from the spiked sediment extractions, that **As** can be accounted for in the range **of** 73 % to 95 %. Nickel determined by ICP is accounted for between ***86%*** and >100 % (some **of** the Ni was extracted from the original sediment in addition to the spiked concentrations added). The methods yield reliable results on which conclusions can be based with respect to the sediment's capacity to act as an environmental sink for both Ni and As.

4.1.3 1993 Reactor Sediment Extraction Test

The first series **of** sequential extractions on the reactors were carried out on the top samples of the sediments. The top layer of the sediments (about 1 cm thick) can be expected to have the largest component **of** accumulated As and Ni from the treated seepage water. The summary results **for** As, Ni, and Fe are given in Table **4. All** analytical results are presented in Appendix Tables A3a and A3b with a detailed explanation of the calculations for the approach taken. Table 5 presents a summary **of** the mass balance in the reactors.

Arsenic

The sum **of** all measured As amounts (last column in Table **5)** are low; they are only 22 % to 38 % **of** the total As content in the R2 to R5 columns. However in R1, the control column, the measured As amount is 117% of total estimated original As. The difference is probably caused by the distribution **of** As in the reactor sediments.

Table 4: Extraction of As, Ni, and Fe in top 1 cm of Sediment in Reactors

	1M KNO3 solution			1M Na4P2O7+EDTA sol'n			1M NH4 acetate sol'n			conc. HNO3 solution		
sample	% As	% Ni	% Fe	% As	% Ni	% Fe	% As	% Ni	% Fe	% As	% Ni	% Fe
R1	0	45.9	0	84.3	42.0	87.8	2.3	0	3.9	0	0	8.3
R2	0	28.6	0.8	57.1	58.0	69.8	23.1	6.4	16.2	0	6.8	12.9
R3	0	32.6	0	73.5	47.9	24.1	8.8	3.2	5.9	0	15.8	69.4
R4	0	3.8	0	43.2	68.9	48.7	15	8.1	13.5	0	18	36.9
R5	0	2.2	0	51.8	79.1	57.5	26.9	8.1	16.2	0	9.9	26.1

Table 5: Mass Balance of As, Ni, and Fe in Reactors

	measured			measured to
sample	total (mg)	sediment %	pore water %	total %
R1 As	31.9	86.6	13.4	117.3
Ni	24.2	88	12	52.5
Fe	79.1	100	0	
R2 As	10.5	80.1	19.9	38.7
Ni	136.0	99.7	0.3	306.1
Fe	88.8	99.8	0.2	
R3 As	8.1	82.3	17.7	30.2
Ni	60.4	99.5	0.5	132.8
Fe	50.0	99.4	0.6	
R4 As	6.4	58.2	41.8	22.1
Ni	23.6	98.8	1.2	47.1
Fe	62.5	99.2	0.8	
R5 As	9.2	78.7	21.3	33.4
Ni	49.6	99.3	0.7	98.9
Fe	109.5	99.9	0.1	

The pore water data show that **As** is mostly concentrated in the top water in R1, therefore the surface sediment should contain more as. In the pore water of the **R2** to **R5** reactors, the **As** concentrations increased with depth. This indicates that **As** may be more concentrated in lower layers of sediments.

Since only the top layers of sediments were used in the extraction experiment, and the calculated total **As** amounts in the sediments were based on the top sediment values, the measured **As** amounts are lower than the real values. In most reactors **As** was concentrated in the sediments **(78.7 %** to **86.6** %). Reactor **R4** sediment only contained **58.2 %** of the total **As,** the reason probably being that most **As** in the lower layers was not detected.

In all reactors, none of assayed **As** in the sediments was in the ion-exchangeable form (1st extraction) or in the least soluble form (4th extraction), as shown in Figure 4. **All** the **As** found was in the form of organic complexes and weak-acid-soluble **forms.**

In R I sediment, **84.3 %** of **As** (Table **4)** was adsorbed as organic complexes, while the rest was extracted as weak-acid-soluble precipitates. In reactors **R2** to **R5,** the **As** organic complexes ranged from **73.5 %** to **43.2 %** in the sediments. The weak-acid-soluble form increased from **8.8 %** to **26.9** %. This indicates that the as has moved into relatively stable precipitate forms.

Nickel

The final Ni "accounted for" amounted to about **50 %** to 100 **%** of the feed Ni in reactors R I, R4, and **R5.** In reactors **R2** and **R3** (potato waste as substrate) the "accounted for" Ni was higher than the original content. The Ni was concentrated in the sediments, especially in the **R2** to **R5** reactors (Figure **5).**

Fig 4: Reactor sediments
As in sequential extractions

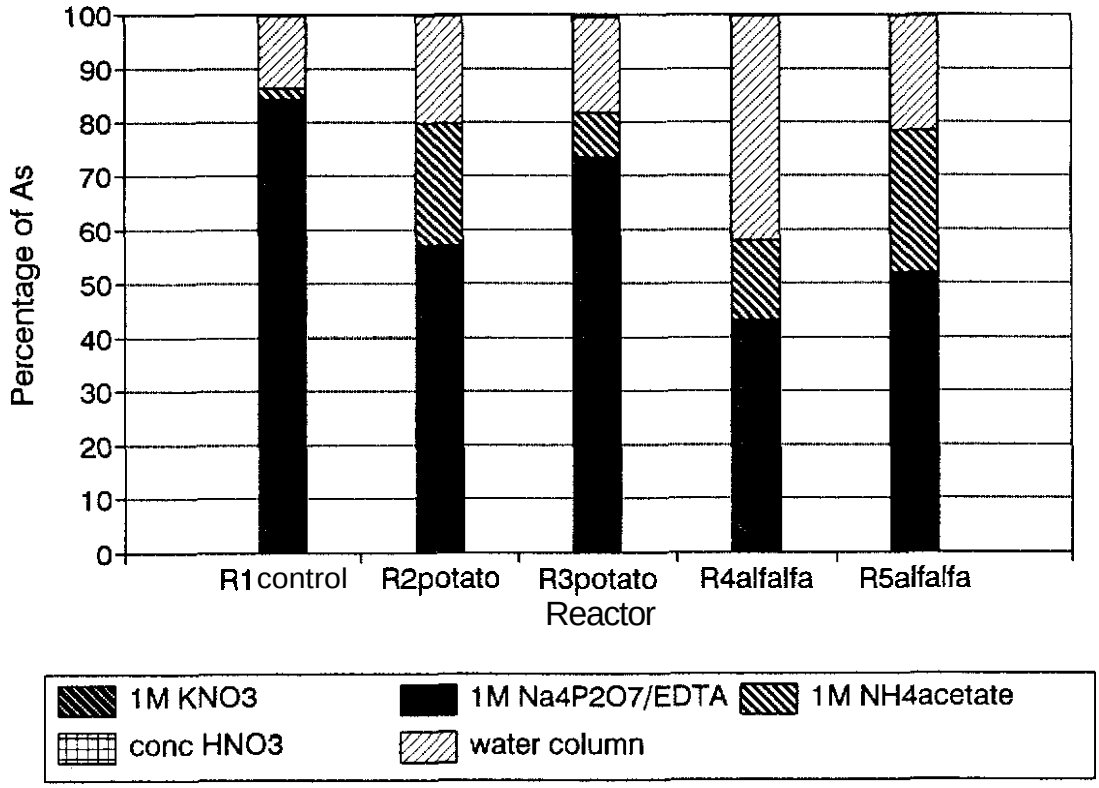
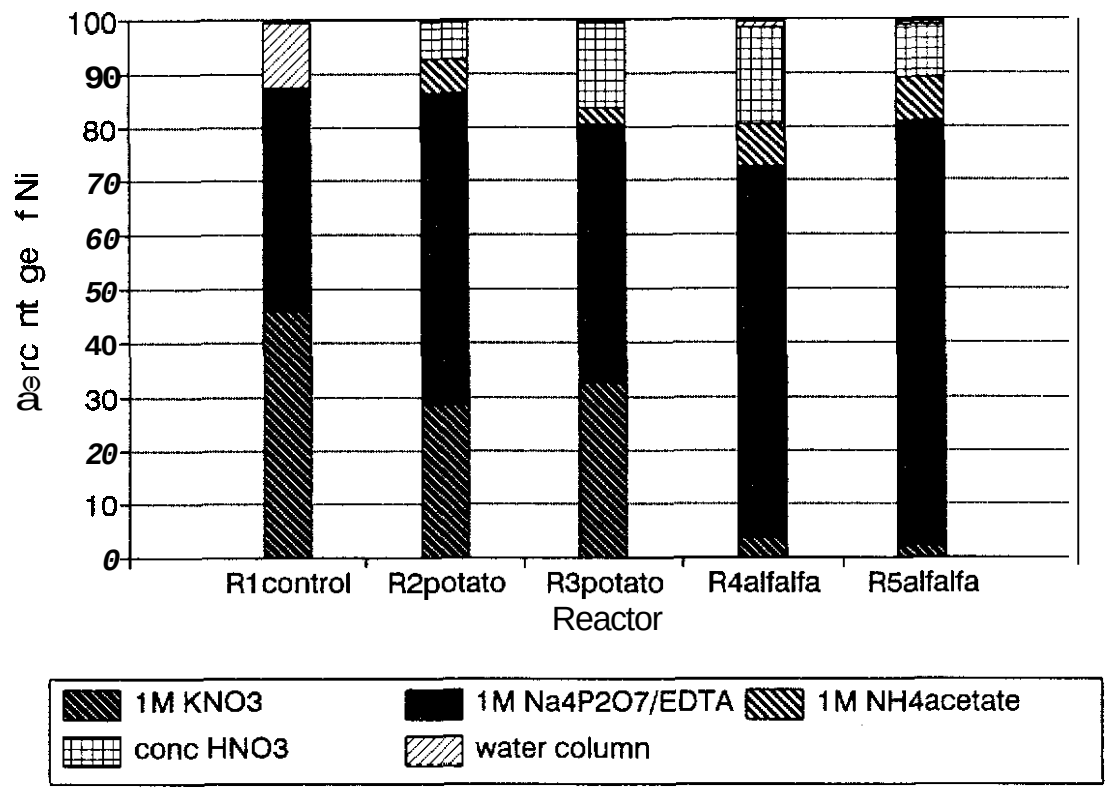


Fig 5: Reactor sediments
Ni in sequential extractions



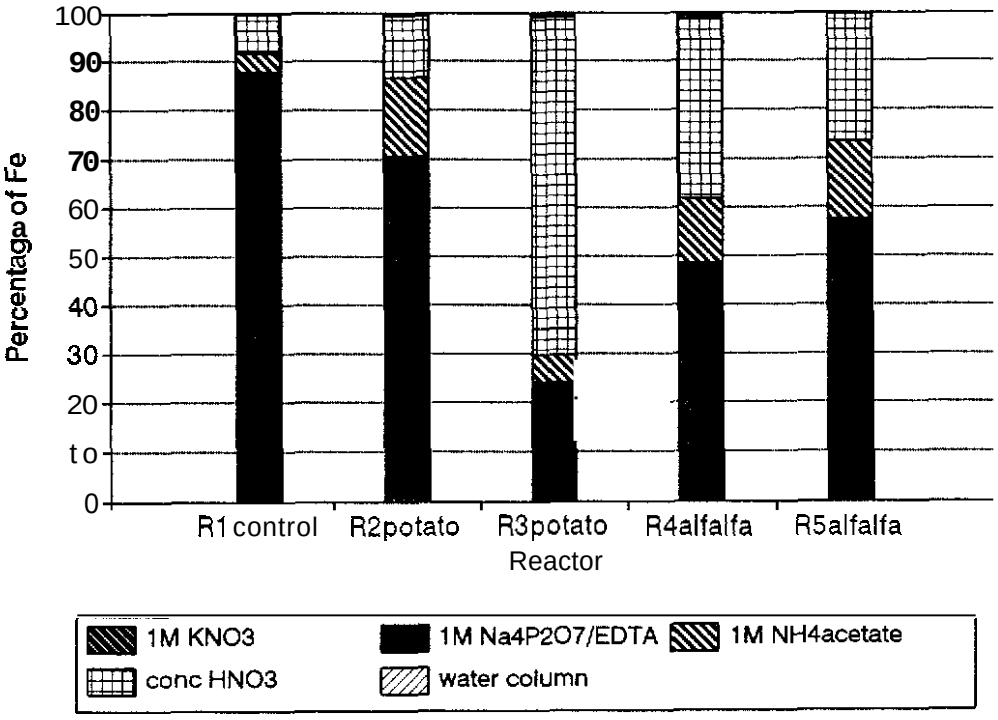
Nickel was detected in all four extraction fractions. The adsorbed Ni indicated by the first extraction fraction was less in **R4** and **R5** reactors (alfalfa as substrate). The percentage of Ni in organic complexes was similar in all reactors (Figure **5).** Nickel formed weak-acid-soluble and strong-stable precipitates only in reactors **R2 to R5.**

Iron

As the initial Fe concentration in 6.1**1** water was very low, most of the extracted Fe was from the original sediments therefore no original amount of Fe was estimated. In Table A3b, the "accounted for" Fe contents are listed. The values from reactors **R I , R2** and **R5** are very close and indicate that the calculations are rational. The **R3** and **R4** bottom pore water samples had relatively high Fe concentrations, therefore it was expected that the bottom sediment samples would have the highest Fe concentrations. This, however, was not the case.

The extraction data showed that over 99 % of the Fe was in the sediment, and almost none was ion-exchangeable. In **R I ,** 87.8 % of the Fe was organically-complexed and about **12.2** % was in the form of weak-or-strong-acid-soluble precipitates (Figure 6). This **is** consistent with the spike experiment.

Fig 6: Reactor sediments
Fe in sequential extractions



In the R2 to **R5** reactors, the amount of organically-complexed Fe decreased to 24 % to 70 %, while the acid-extractable precipitates increased to 29 % to 75 %. Most of the Fe precipitates were in the stable form and only concentrated nitric acid could dissolve it (Figure 6).

4.2 1994 Experiment - As and Ni Removal Capacity *of* Sediments

This experiment was designed to test the capacity **of** muskeg sediment to treat a seasonal seepage from the waste rock pile.

Measurements made on the water columns **of** the reactors after set-up but prior to addition of potato waste are shown in Table 6. The initial readings for the columns indicate that the water chemistry is similar to that of the seepage water. Mixing with sediment pore water results in an elevated pH (4.3 to 5.0 compared to 3.85 for 6.11 water) and reduced conductivity (1155 μmhos/cm to 1262 μmhos/cm compared to 1386 μmhos/cm for the seepage water) and Eh (367 mV to 445 mV for column water and 522 mV for the seepage water).

After 4 to 5 days **of** incubation with potato waste, samples from all reactors and jars were analyzed together with the added seepage water and sediment pore water. The data is shown in Table 7. By this time, dramatic changes in the Eh had occurred in some of the columns due to the hydrolysis and fermentation of potato waste. In 5 of the 9 reactors, reducing conditions had established negative Eh values. The fermentation of potato waste was reflected in the increased acidity in the reactors with low Eh values. Under these conditions, denitritication had commenced as indicated by lower NO_3-N concentrations compared to the seepage water. **Also,** the reducing conditions were responsible for the appearance of dissolved iron in solution. There was no detectable dissolved iron in 6.11 water. In general, the lower the Eh value for the reactor column, the higher the iron concentration. Arsenic concentrations were consistently lower in the reactor columns than in the seepage water. Nickel concentrations were somewhat lower in the reactors than in the seepage water. The lower values in the reactors with the lowest Eh values indicates that some precipitation may already be occurring in reducing conditions.

The chemistry of water samples from the controls (seepage water and potato waste) was very similar to that of 6.11 water. There was no clear indication that hydrolysis

Table 6: Sediment Treatment Capacity Reactors, Chemistry after 24 h.

Reactor	pH	Eh (mV)	Cond. (umhos/cm)	Temp. (C)
1	4.97	432	1155	21.3
2	4.68	435	1197	21.5
3	4.55	389	1207	20.2
4	4.49	445	1195	21.5
5	4.39		1221	21.7
6	4.44		1237	20.1
7	4.36		1237	21.7
8	4.5	368	1163	20.3
9	4.36	409	1262	20

Table 7: Sediment Treatment Capacity Reactors, Chemistry after 96 h.

Reactor	pH	Eh (mV)	Cond. umhos/cm)	Temp. (C)	As (mg/L)	Fe (mg/L)	Ni	NO3-N (mg/L)	Acidity (mg/L)*
1	4.81	278	1255	20.9	56	2.6	51.a	26.3	171.4
2	4.87	257	1301	20.8	50	2.8	61.3	23.9	150.3
3	4.69	-272	1313	20.6	50	4.99	48.4	11.7	234.5
4	4.76	299	1269	20.8	56	2.8	56.1	20	172.2
5	4.59	319	1306	20.8	62	2.6	77	31.1	154.5
6	4.62	-272	1291	20.8	50	5.44	37.2	10.4	241.1
7	4.54	146	1334	20.7	50	2.3	59.6	24.7	154.4
a	4.49	-72		20.7	45	4.28	35	23.9	178.8
9	4.41	-243	1384	20.9	50	3.83	58.7	16.8	214.7
jar 1	4.04	469	1570	20.1	a5	0.37	48.4	26.3	165.1
jar 2	4.03	471	1568	20.3	85	0.38	62.2	33.4	152.8
jar 3	3.98	469	1587	20.5	a5	0.24	69.9	27.1	168.7
6.11	3.85	522	1386	21.6	a5	0.08	72.5	27.1	106.7

Sediment 5.68 173 196 20.9
BT 2 Stn 250

*(mg/L) equivalent of CaCO3

and fermentation of potato waste had commenced. The presence of sediment factors is clearly important for the rapid commencement of potato decomposition, the establishment of reducing conditions, and the removal of nitrate, arsenic and nickel ions from solution.

The reactors were sampled weekly after the first sampling. The data are summarized in Figures **7** to **18.** The data for individual jars is shown in Appendix Table **A4.**

Eh

By the second sampling (10 days after set-up), negative Eh values were established in all reactors. For **7** of the **9** reactors and all the jars, Eh was **-190** mV or less as shown in Figure **7.** At the next reading **(17** days after set-up), there had been an increase in Eh with only one of the reactors maintaining a negative value. The Eh of the jars was generally lower than for the reactors at this sampling and all remained negative. The upward trend was maintained for the following sample **(26** days) but then the values declined again in both the reactors and jars.

At **40** days, negative values were found for all **6** of the unchanged reactors (range of -102 mV to **-74** mV). Values for the 'recharged' reactors were a little higher (+3 mV to **+5** mV). The removal of organic acids in these reactors has reduced the capacity to generate reducing conditions. The jars exhibited low, positive Eh values **(+48** mV to **+86** mV). There was no clear difference in Eh values between the reactors and the jar with weekly water changes (reactors **4-6,** jar **2)** and the other reactors.

Acidity

The seepage water had an acidity of **107** mg/L (equiv. $CaCO_3$). Acidity increase **for** the first two measurements is largely attributable to hydrolysis and fermentation of potato waste to volatile fatty acids as similar values were found in reactors and jars **(187** mg/L to **508** mg/L by day **12).** After this time, acidity declined in the 're-charged' reactors and jars due to dilution of potato waste decomposition products (Figure 8). In the 'unchanged' reactors, acidity also declined from the first measurement to **59-97** mg/L

Fig. 7: Reactor water column
Redox potential (Eh)

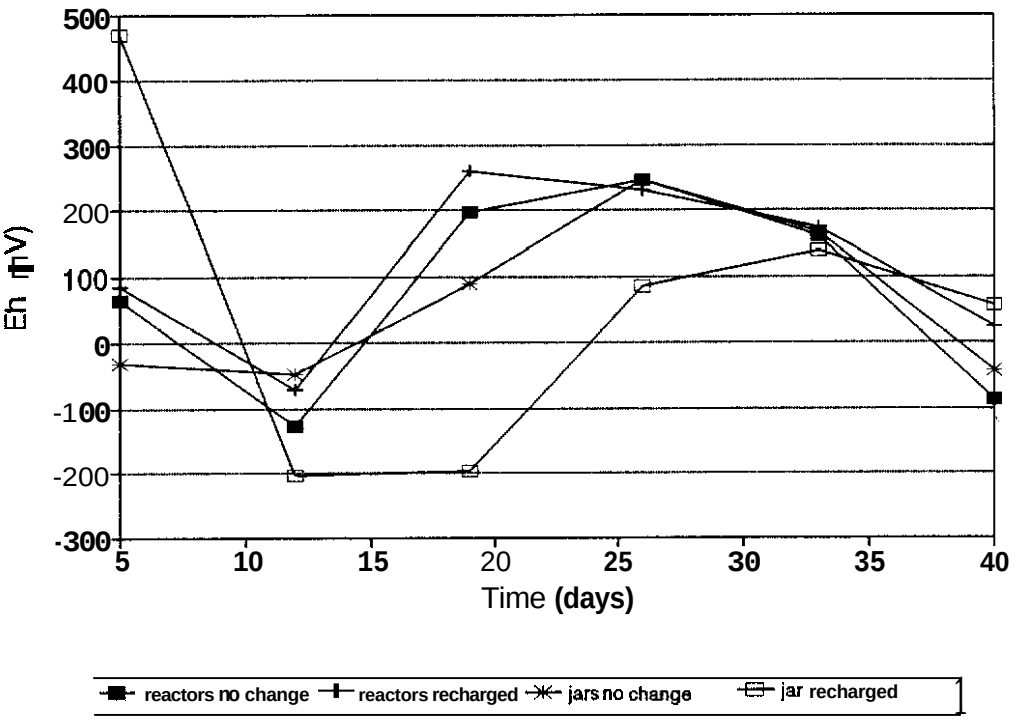
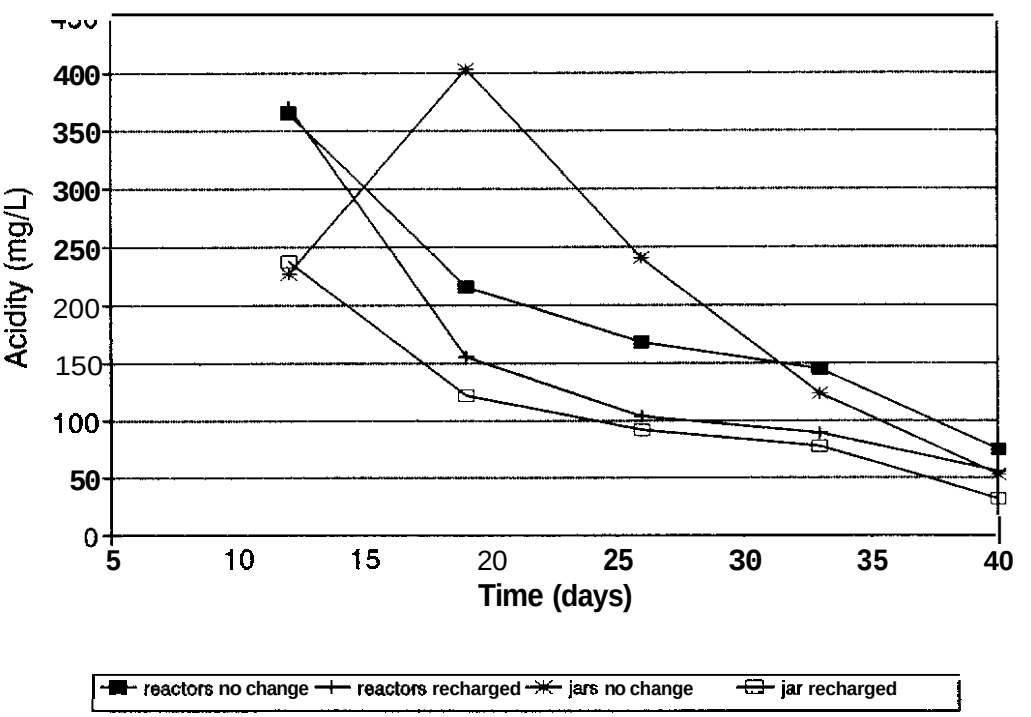


Fig 8: Reactor water column
Acidity



at day 40. By this time, 250-300 mg/L of acidity had been consumed in both unchanged reactors and unchanged jars.

pH

The seepage water had a pH of 3.95. The first readings at 10 days showed little change (pH 4.31 to 4.87 in reactors and pH 4.75 **to** 5.55 in jars). There was a steady rise in pH from the second sample onwards for all reactors to around pH 6-6.5 by day 40 (Figure 9). In other words, the 'recharge' reactors exhibited the same pH rise as the 'unchanged' reactors. There was **a** similar pH rise in the jars.

Conductivity

For reactors not receiving 'fresh seepage water, there was a fairly steady decline in conductivity through the course of the experiment from around 1300 μmhos/cm to around 960 μmhos/cm (Figure 10). This decrease was not apparent in the control jars. Initially, the conductivity was considerably higher in these jars compared to the reactors (around 1600 μmhos/cm). Thereafter, values were steady at around 1300 μmhos/cm. The reactors receiving 'fresh' seepage water weekly exhibited an initial decline in conductivity between the first two readings, comparable to that observed for the other reactors. Thereafter, values were steady at around 1150 μmhos/cm.

Nickel

The nickel concentration in the reactors was generally lower (25-61 mg/L) than the control jars (60-70 mg/L) at the first sampling (4 to 5 days), attributable to dilution by sediment water in the reactors (Figure 11). In contrast, in the reactors with no further additions of seepage water, there was a decline to approximately 20 mg/L at day 26 after which the concentration remained steady. Nickel concentration in the control jars remained more or less constant throughout the course of the experiment.

Fig. 9: Reactor water column

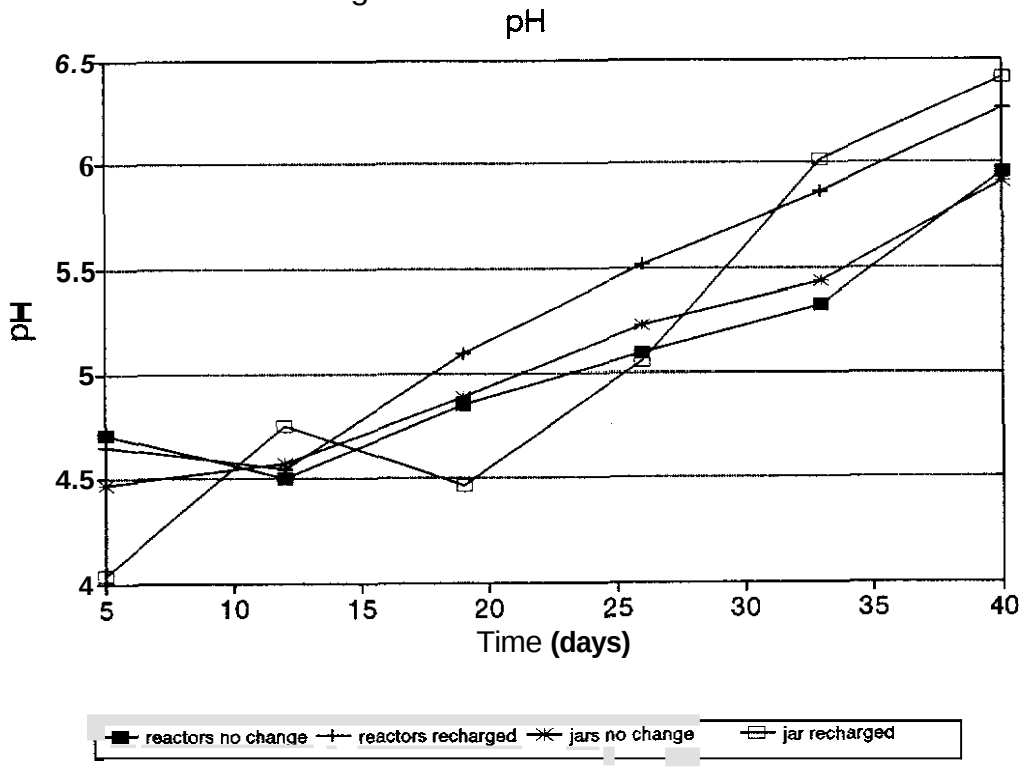


Fig 10: Reactor water column

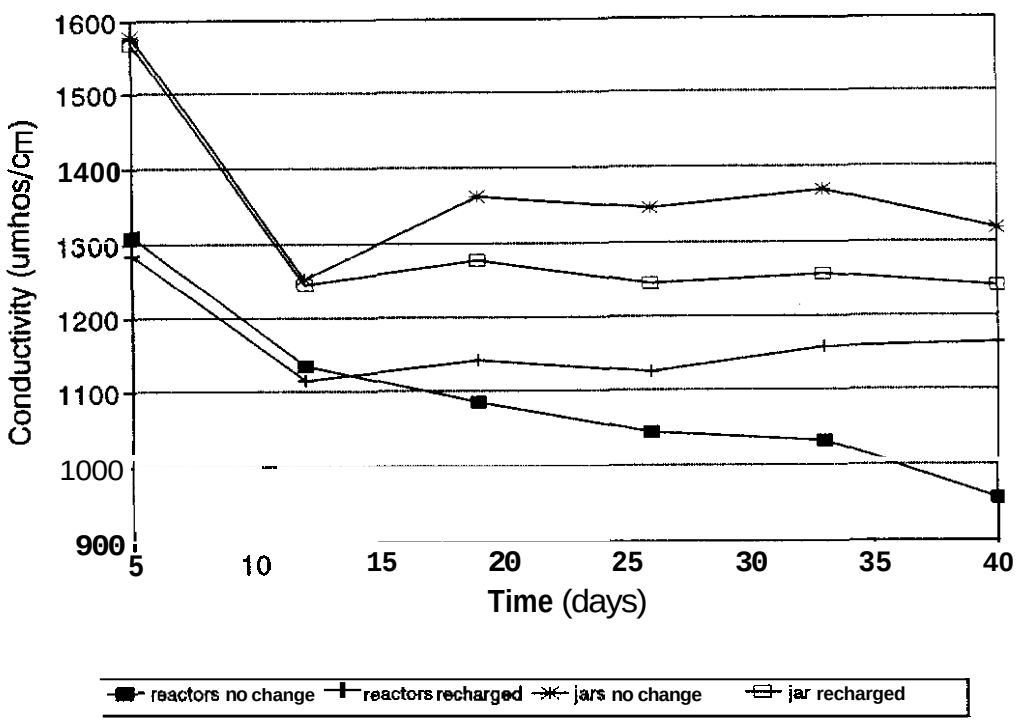


Fig. 11: Reactor water column
Nickel

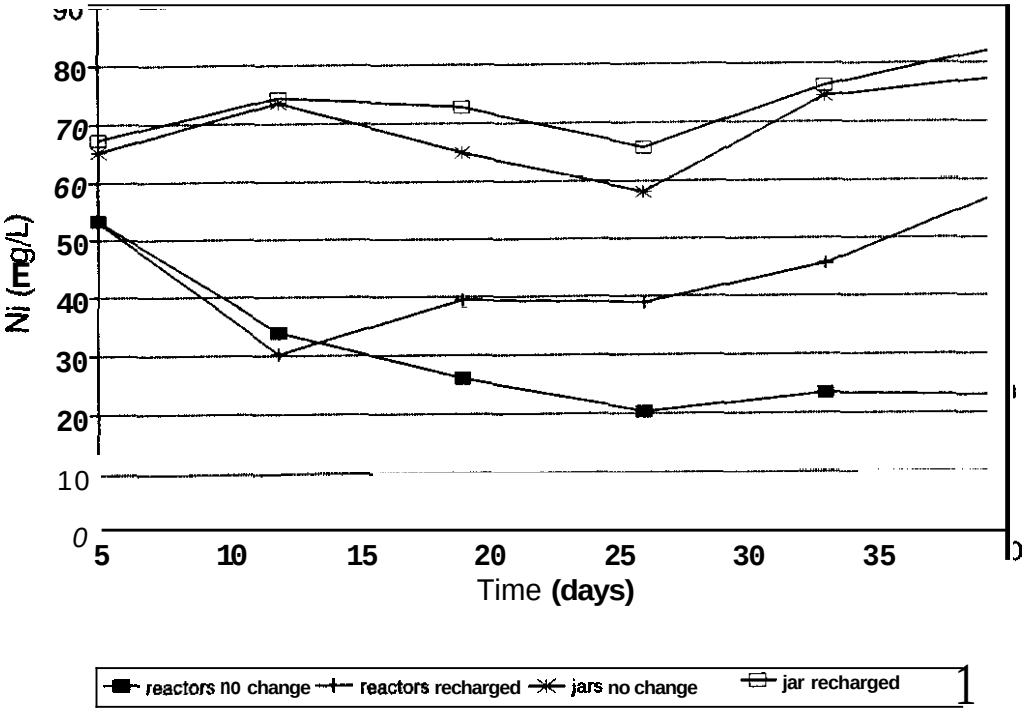
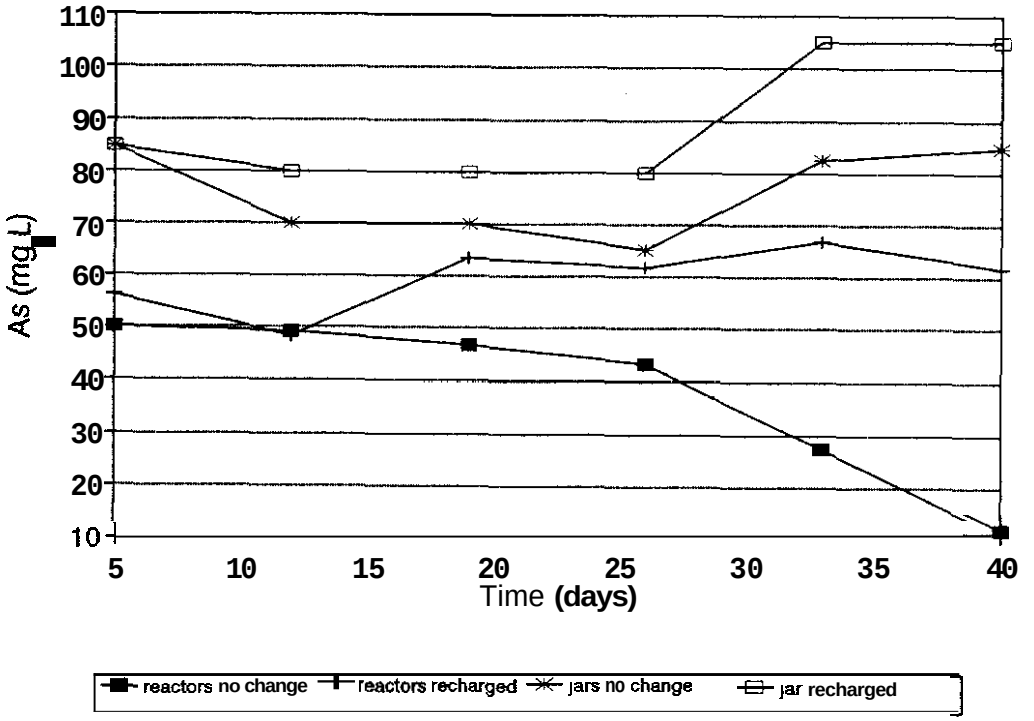


Fig 12: Reactor water column
Arsenic



Arsenic

The seepage water contained **90** mg/L dissolved arsenic (Figure 12). By the **first** reading (10 days), the As concentration had dropped to 50 mg/L. Much of this change is attributable to dilution by water in the sediment, although removal by other means cannot be discounted.

In the jars, there was no decline in As concentration over the course of the measurements. After this time, the As concentration in the reactors without water change declined to a mean value of 10 mg/L by 40 days from 50 mg/L at **4** to 5 days.

Iron

There was an increase in iron in both jars and reactors (Figure 13). The Fe in the jars is released from the potato waste as it decomposes. The maximum concentration observed was around **4** mg/L. The concentration was lower in the 'recharged' jar due to removal at the time of water change. In the 'no change' reactors, Fe concentration rose to a mean of 16.5 mg/L. The dramatic dip at 33 days may be due to settling of weakly-suspended solids. Iron in the reactors came both from the potato waste and the sediments.

Nitrate-N

There was a dramatic decline in nitrate-N concentrations in all reactors and jars from day 5 to day 12 (Figure 14). Thereafter, the decline continued in reactors until day **40** when concentrations were 0.13 mg/L or less for the 'unchanged' reactors and **0.49** mg/L or less for the 'recharged' reactors. For the 'unchanged' jars, there was a substantial increase in nitrate-N from day 12 to day 19 followed by a decline to < 0.5 mg/L by day **40.**

Ammonium-N

There was a steady decline in ammonium-N in all reactors and jars to day 26, after which values recovered to near initial values (Figure 15). There was no clear effect of 'recharging' with 6.11 water on the ammonium-N concentration.

Fig. 13: Reactor water column
Iron

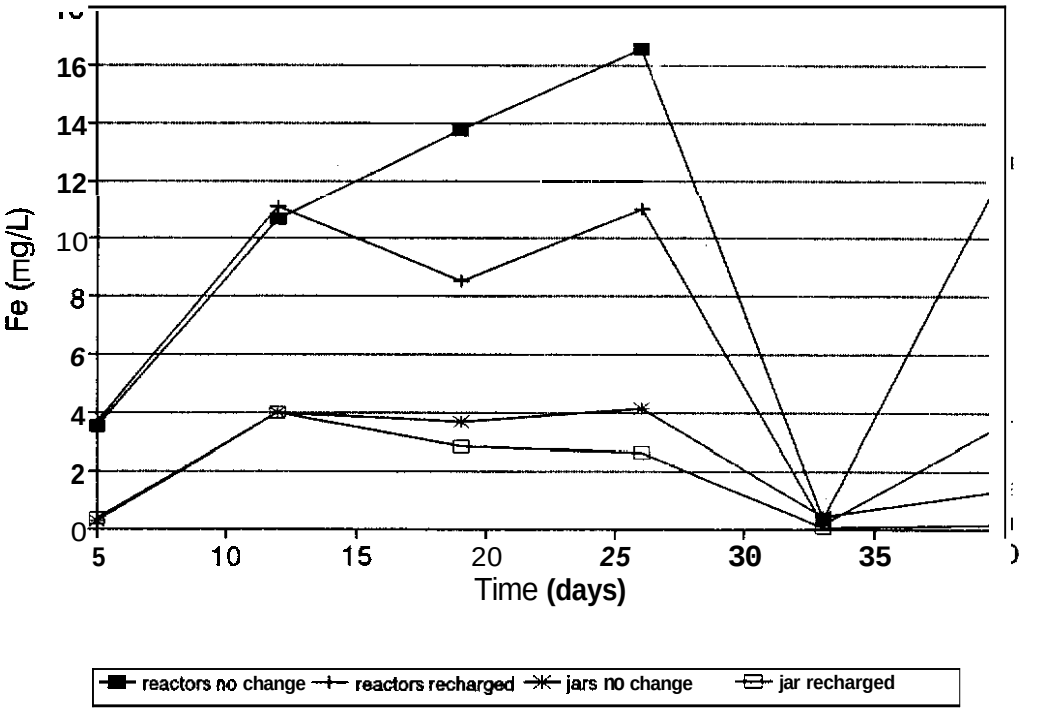


Fig. 14: Reactor water column
Nitrate-N

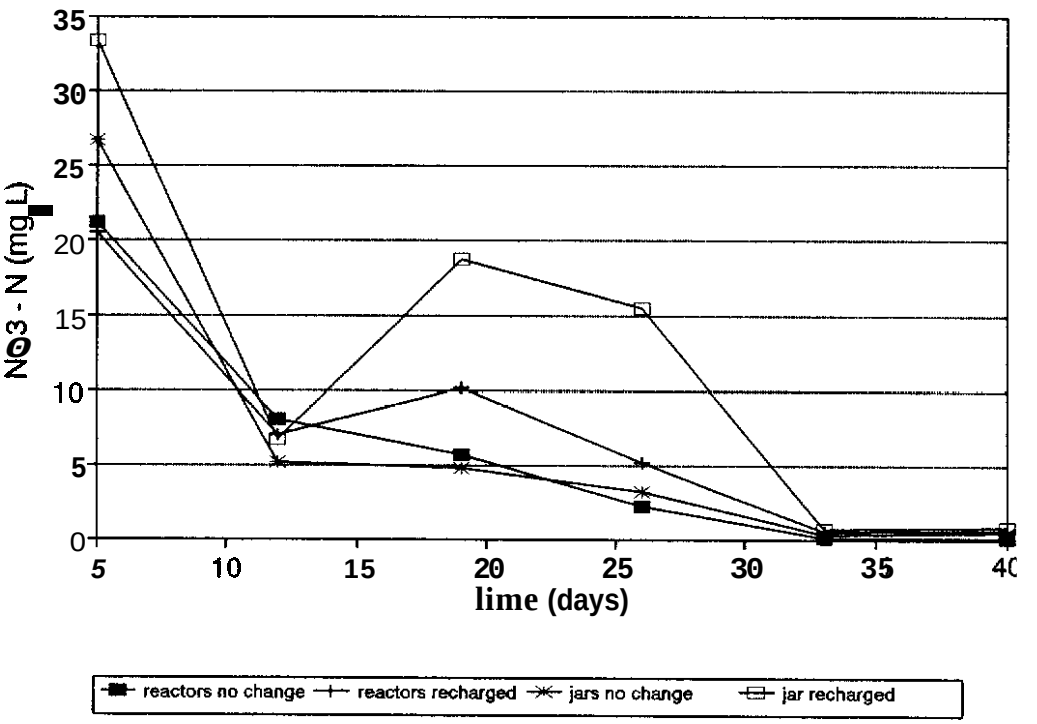


Fig. 15: Reactor water column
Ammonium-N

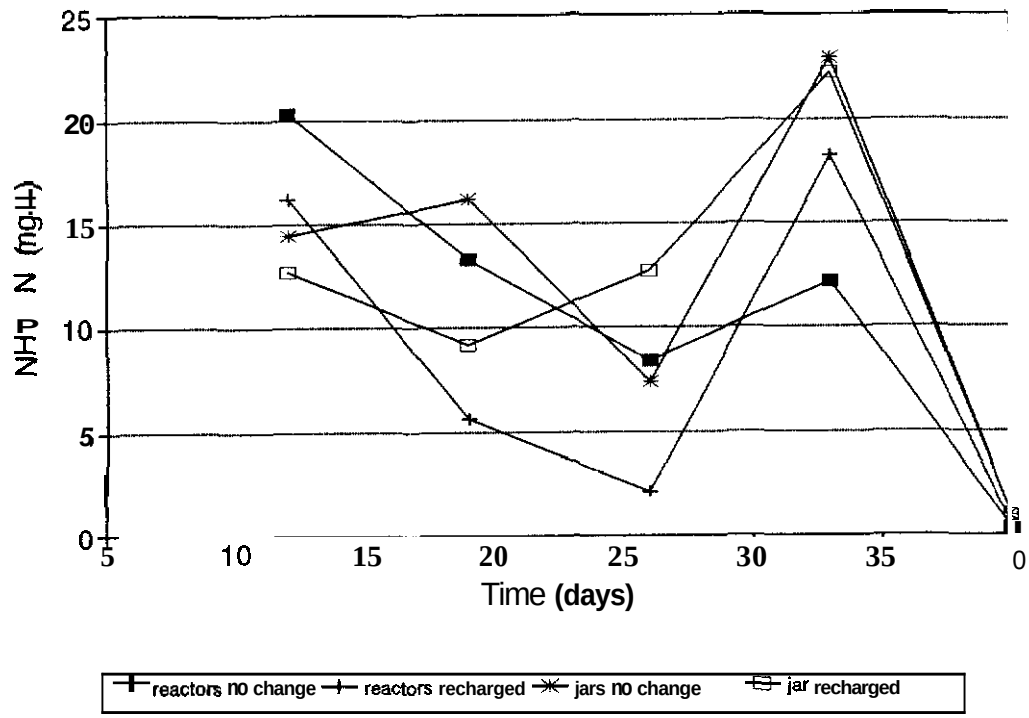
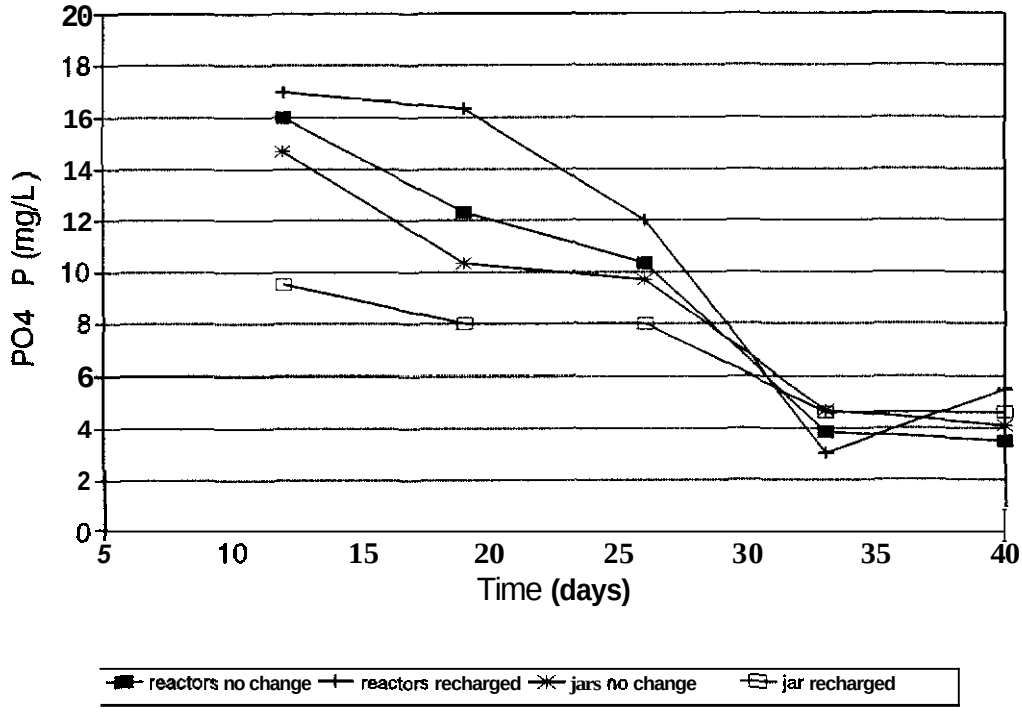


Fig. 16: Reactor water column
Phosphate-P



Phosphate

Phosphate-P concentrations were higher in reactors than in jars up **to** 26 days, presumably due to release from the sediments (Figure 16). Overall there was a steady decline in phosphate-P concentrations in all reactors to **4-6** mg/L and control jars until day 33. From this time **to** day **40,** concentrations were steady in both reactors and control jars.

Overall

The data for the unchanged control jars shows the effects of potato waste on seepage water. The early decline in Eh and establishment of reducing conditions is associated with the decomposition of potato waste and probable release of volatile fatty acids which contributes to the increase in acidity. The reducing conditions thus established support the reduction of nitrate (denitrification) and iron. The removal of phosphate and ammonium may be due in part to uptake by microorganisms. The lack of arsenic and nickel removal are attributable to a lack of ferric and sulphide ions respectively for precipitation andlor surface sites for adsorption processes. The steady conductivity in the jars suggests little overall removal of ions from solution.

In contrast to the jars, there was a steady reduction in conductivity in the reactors indicating a net removal of ions from solution. The drop in Eh and rise in acidity exhibited a similar. pattern to that of the jars. The removal of nitrate, ammonium and phosphate was also similar. Iron concentrations were much higher in the reactors, undoubtedly due to reduction and dissolution of iron from the sediments. Iron reduction inhibits sulphate reduction if ferrous iron is present (Lovley and Phillips 1987). Therefore sulphate reduction may not have occurred. In some reactors, Eh values were lower at the initial reading **(4-5** days) than the theoretical maximum value (-220 mV) at the initial reading at which sulphate reduction occurs (Zehnder and Stumm 1988). The removal of approximately 70 % of the Ni from solution before a steady state was achieved is interesting. If nickel is removed as a sulphide precipitate, sulphate reduction must occur for generation of sulphide. This may have occurred early on. Some removal by adsorption processes is possible. However, the available sites would likely be tilled within hours of set-up as indicated by the data of Eger and

Lapakko (1989). The steady decline in Ni is more suggestive of a precipitation process. The steady decline in **As** is also indicative of precipitation. The low **Eh** and release of ferrous iron from the sediments suggests that precipitation of ferrous arsenate may be occurring.

Weekly changing of 500 mL of water with 'fresh' seepage water resulted in concentrations of Ni and **As** similar to the original values after 2 weeks for **As.** This suggests that for **As,** the net removal ceases. For Ni, on the other hand, some removal continued. It is possible to estimate the total Ni removed from the water column in these reactors during the period of observations. The estimated total removal (mean of 3 reactors) together with the total Ni in the reactors is summarized in Figure 17.

It is assumed that the volume of water in the reactors being treated is 0.9 **L.** The data indicate that by day **40,** a total of 93 mg of Ni had been removed from a total of 145 mg added to the reactors. This is nearly double that removed from the 'unchanged' reactors. However by the end of the observations the amount of Ni removed with each addition of seepage water was small. Clearly the system is approaching saturation.

Calculations of **As** removal form the 'recharged' reactors **4,** 5 and 6 have also been made (Figure 18). With additions of seepage water, the **As** concentration in the water column remains fairly constant (Figure 11) but is considerably lower than in the seepage water (85 mg/L), therefore the **As** is being removed from the reactor water throughout the period ***of*** observations. Figure 18 shows that by day **40,** a total of 83 mg had been removed. The rate of removal remained constant over the observation period. In other words there is no indication that the removal process(es) is nearing full capacity.

Since the **As** concentration in the 'unchanged' reactors was still declining at the end of the observation period, the water column in reactors 7, 8 and 9 was not changed. It is planned to run these reactors until there is no longer any net removal of **As** and Ni at which point, 500 mL of the water column will be replaced with 'fresh' seepage water.

Fig. **17:** Recharged reactors
Nickel removal

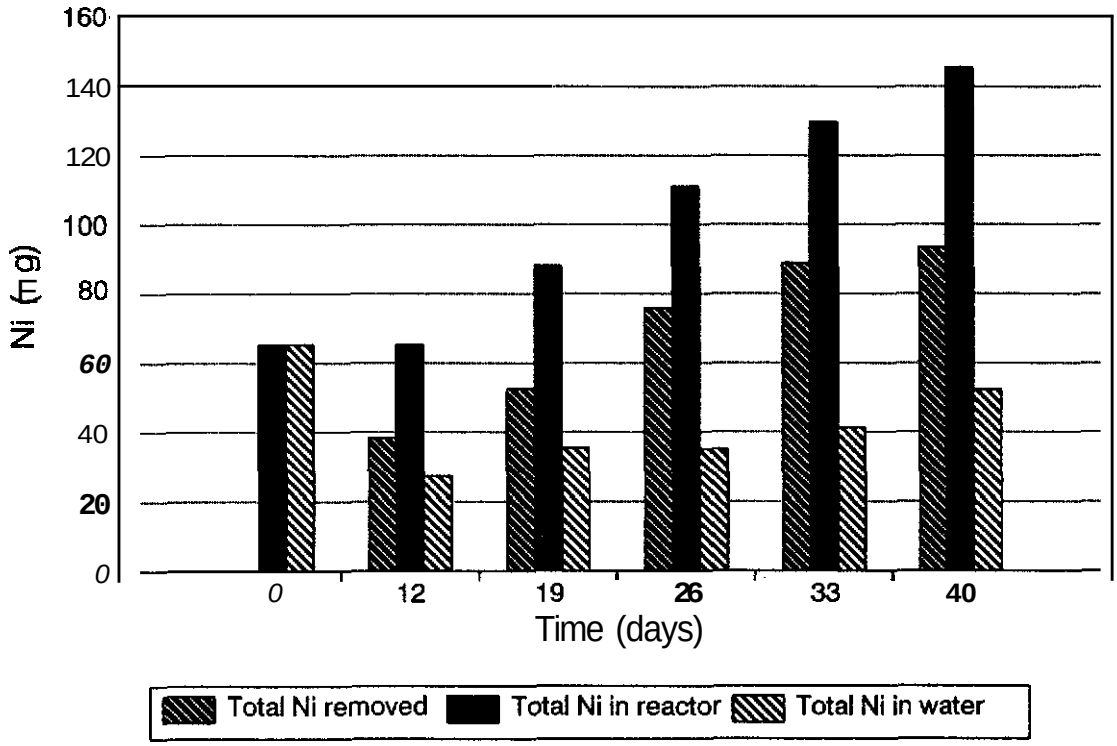
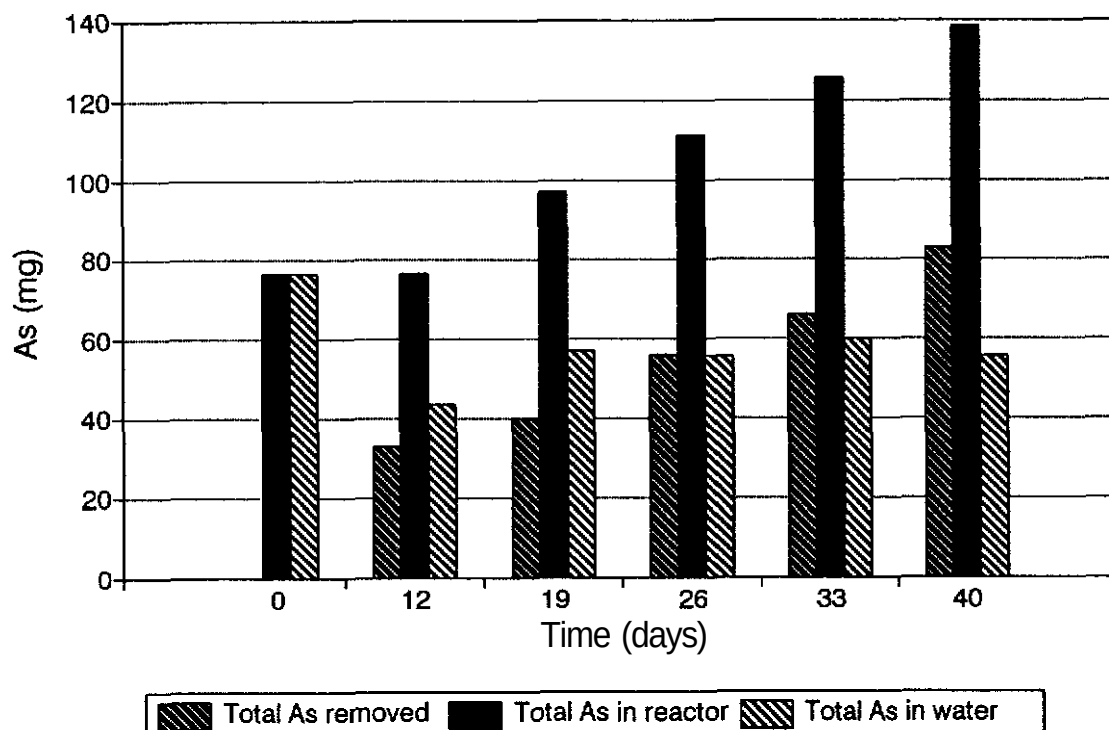


Fig. 18: Recharged reactors
Arsenic removal



5.0 DISCUSSION AND CONCLUSIONS

To date, analyses have demonstrated that the muskeg sediment was effective in removal of Ni and As from added acid mine drainage, especially when organic supplements (potato waste, alfalfa pellets) were added.

Analysis of the 1993 reactors provided a test for sequential extraction techniques for determination of amounts and forms of As and Ni held in sediments. The method was found to be reproducible for As and Fe but yielded highly variable results for Ni.

The sequential analysis suggests that much As is held by the sediment in organic complexes. In the presence of organic amendments in the reactors, a substantial amount of precipitate was present. This indicates that reducing conditions, established through addition of potato waste or alfalfa pellets, can lead to removal of arsenic as precipitates. The Eh/pH diagram suggests that the conditions found soon after addition of the organic amendments were favourable for formation of arsenite. This form of As has recently been detected in anaerobic soils contaminated by waste waters from a gold mine (Bowell et al, 1994). Although reducing conditions were no longer present in the water column at the time of sampling for the sediment analysis, pre-formed precipitates would be expected to be stable in the conditions observed. In the absence of organic amendments, less As was removed. The As removed was entirely as organic complexes. These are likely to be less stable than inorganic precipitates when conditions change.

The Ni data from the sequential analysis is too variable for quantitative estimation of forms removed. However it is clear that precipitates are formed only when organic amendments (potato waste or alfalfa) have been added to the reactors. As for arsenic, reducing conditions produced through decomposition of organic matter can lead to precipitation of nickel salts which will be more stable in sediments than complexed forms.

The 'sediment treatment capacity' experiment yielded valuable data on the dynamics of *As* and Ni removal and began to examine the treatment capacity of the 6-Zone muskeg sediments. Over the **40** day period of observations, As concentrations in the water column declined from **85** mg/L to 10 mg/L. In previous experiments with similar conditions, dissolved As concentration eventually declined to stable values of 0.5 mg/L to 1 mg/L. In the present experiment, Ni declined from 70 mg/L **to** 20 mg/L. Further decline was likely inhibited by the high Fe in solution (reduced Fe released under reducing conditions). This will inhibit sulphate reduction (Lovley and Phillips 1991) **so** sulphide ions would not be present for precipitation of nickel sulphides.

Exchange of 6.11 water in the water column of reactors determined that the sediment can remove considerably more Ni and As than present in a 'single dose.' Arsenic removal continued at a linear rate through 5 changes of water. Nickel removal rates declined towards the end **of** the observations. The third treatment, where 6.11 is exchanged when a steady state concentration of As and Ni prevails in the water column, has not yet commenced.

To summarize, both As and Ni can be removed from 6.11 water as potentially stable precipitates if exposed to reducing conditions induced through decomposition of organic amendment and the sediment environment.

6.0 REFERENCES

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List of Appendices

		original solution				1M KNO3 solution				1M Na4P2O7+EDTA solution				1M HN4 acetate solution				conc.HNO3 solution				total
sample No	added As(mg	vol. mL	[As] mg/L	tot.As mg	%	vol. mL	[As] mg/L	tot.As mg	%	vol. mL	[As] mg/L	tot.As mg	%	voi. mL	[As] mg/L	tot.As mg	%	vol. mL	[As] mg/L	tot.As mg	%	measured As%
#1	0	0	0	0	0	150	0	0	0	150	0.3	0.04	100	150	0	0	0	150	0	0	0	
X2	22.2	133	1.7	0.23	1.30	150	0	0	0	150	100	15.0	85.8	150	15	2.3	12.9	180	0	0	0	78.6
#3	20.9	118	0.4	0.05	0.31	150	0	0	0	150	100	15.0	98.3	150	1.4	0.2	1.4	170	0	0	0	72.9

		original solution				1M KNO3 solution				1m Na4P2O7+EDTA solution				1M NH4 acetate solution				conc. HNO3 solution				total
sample No	added Ni(mg)	vol. mL	[Ni] mg/L	tot.Ni mg	%	vol. mL	[Ni] mg/L	tot.Ni mg	%	voi. mL	[Ni] mg/L	tot.Ni mg	%	vol. mL	[Ni] mg/L	tot.Ni mg	%	vol. mL	[Ni] mg/L	tot.Ni mg	%	measured Ni%
#1	0	0	0	0	0	150	0.8	0.1	4.7	150	1.1	0.2	6.6	150	0	0	0	150	14	2.1	88.7	
#2	58	133	121	16.1	40.8	150	38.2	5.6	14.2	150	117.9	17.5	44.4	150	1.7	0.3	0.6	180	0	0	0	68.1
#3	59.4	118	1.3	0.1	1.3	150	65.8	9.8	86.2	150	10.5	1.4	12.5	150	0	0	0	170	0	0	0	19.1

		original solution				1M KNO3 solution				1M Na4P2O7+EDTA solution				1M NH4 acetate solution				conc. HNO3 solution				total
sample No	added Fe(mg	vol. mL	[Fe] mg/L	tot.Fe mg	%	vol. mL	[Fe] mg/L	tot.Fe mg	%	vol. mL	[Fe] mg/L	tot.Fe mg	%	vol. mL	[Fe] mg/L	tot.Fe mg	%	vol. mL	[Fe] mg/L	tot.Fe mg	%	measured Fe %
#1	0	0	0	0	0	150	0	0	0	150	26.6	4	64.7	150	1.4	0.2	0	150	13	2.0	32.0	
#2	34.6	133	0.3	0.04	0.1	150	0	0	0	150	179.7	23	79.5	150	10.0	1.3	4.5	180	37	4.6	15.9	83.5
#3	32.7	118	39.9	4.7	14.7	150	0	0	0	150	206	26.9	84.3	150	9.3	1.2	3.7	170	6.5	-0.9	0	100.3

Table A2. Comparison of Boojum and EPL Data

		original solution				1M KNO3 solution				1M Na4P2O7+EDTA solution				1M NH4 acetate solution				conc. HNO3 solution				total
	added (mg)	vol. mL	mg/L	total mg	%	vol. mL	mg/L	total mg	%	vol. mL	mg/L	total mg	%	vol. mL	mg/L	total mg	%	vol. mL	mg/L	total mg	%	measured %
Lab As	20.9	118	0.4	0.05	0.3	150	0	0	0	150	100	15.0	98.3	150	1.4	0.2	1.4	170	0	0	0	72.9
EPL	20.9	118	0.2	0.02	0.1	150	0.5	0.1	0.4	150	124	18.6	94.0	150	6.9	1.0	5.2	170	0.3	0.06	0.3	94.6
Lab Ni	58	133	121	16.1	40.8	150	38.2	5.6	14.2	150	117.9	17.5	44.4	150	1.7	0.3	0.6	180	0	0	0	68.1
EPL	58	133	123	16.4	18.8	150	50.1	7.4	8.5	150	322	48.1	55.4	150	61.8	9.3	10.7	180	31	5.7	6.5	149.7
Lab Ni	59.4	118	1.3	0.1	1.3	150	65.8	9.8	86.2	150	10.5	1.4	12.5	150	0	0	0	170	0	0	0	19.1
EPL	59.4	118	100	11.8	23.1	150	68.7	10.2	19.9	150	183	27.3	53.4	150	12.1	1.8	3.6	170	3.6	0.6	1.2	86.0
Lab Fe	32.7	118	39.9	4.7	14.4	150	0	0	0	150	206.4	27.0	82.5	150	9.3	1.2	3.6	170	6.5	-0.9	0	100.3
EPL	32.7	118	39.5	4.7	14.2	150	0.05	0.01	0.02	150	158	19.7	60.3	150	14	1.9	5.8	170	15	0.5	0	80.3

Appendix 3. Explanation of Sequential Extraction Calculations

In Table A3a the second column gives the metal loadings which have been added with the seepage to the reactors, and represents the mg/L multiplied by the volume of seepage added. In the third column, the accumulated As and Ni losses due to the weekly sampling where water is withdrawn from the reactors is presented.

The fourth column represents the amount of As and Ni which remained in the reactors for removal by sediments. The sediment ratios represented in the fifth column are the ratios of the dry weight of the total sediment in the reactors to the dry weight of the sediment used in the extractions.

For each of type of sequential extraction, the extracted metal concentrations and the volumes of the extraction solutions were measured, from which the total quantity of metal extracted (representing the respective form of the metal present in the sediment) was calculated. The percentage of each fraction is referenced back to the original amount present in the reactor sediments.

The concentrations of each metal in the reactors' water columns are shown in Table A3b. The waters are divided into three layers; the "top" solution is the water above the sediment (the treated seepage in the reactors), the "middle" solution is the pore water from sediment layers **1** and **2,** and the "bottom" solution is the pore water from sediment layer 3. The metal content and percentages were calculated. The "pore water %" is the sum of the dissolved metals in the three solutions, and the "sediment %" is the total extracted.

The percentage comparison of the amounts of metal in the sediment and those in the water body, assessed by analysis, is listed in the three columns under the "measured" section of Table A3b. The last column in Table A3b shows the comparison of the "head" less the "sampling loss" (the 3rd column in Table A3a) with the total metal analyzed in the pore water and the sediment.

Table A3a. Extraction and Mass Balance of As, Ni, and Fe in Reactors

					1M KNO3 solution				1M Na4P2O7+EDTA solution				1M NH4 acetate solution				conc.HNO3 solution			
sample	As(mg) added	As(mg) sampled	As(mg) left	sediment ratio	vol. mL	[As] mg/L	tot. As mg	%	vol. mL	[As] mg/L	tot. As mg	%	vol. mL	[As] mg/L	tot. As mg	%	vol. mL	[As] mg/L	tot. As mg	%
R1	38	10.8	27.2	19.0	130	0	0	0	50	28.3	26.9	84.3	130	0.3	0.7	2.3	112	0	0	0
R2	38	10.8	27.2	26.7	130	0	0	0	50	4.5	6.0	57.1	130	0.7	2.4	23.1	134	0	0	0
R3	38	11.3	26.8	18.3	130	0	0	0	50	6.5	5.9	73.5	130	0.3	0.7	8.8	116	0	0	0
R4	38	9.2	28.8	24.5	130	0	0	0	50	2.3	2.8	43.2	130	0.3	1	15	145	0	0	0
R5	38	10.6	27.4	63.3	130	0	0	0	50	1.5	4.7	51.8	130	0.3	2.5	26.9	141	0	0	0
					1M KNO3 solution				1M Na4P2O7+EDTA solution				1M NH4 acetate solution				conc. HNO3 solution			
sample	Ni(mg) added	Ni(mg) sampled	Ni(mg) left	sediment ratio	vol. mL	[Ni] mg/L	tot. Ni mg	%	vol. mL	[Ni] mg/L	tot. Ni mg	%	vol. mL	[Ni] mg/L	tot. Ni mg	%	vol. mL	[Ni] mg/L	tot. Ni mg	%
R1	56.4	10.4	46.0	19.0	130	4.5	11.1	45.9	50	10.7	10.1	42.0	130	0	0	0	112	0	0	0
R2	56.4	12.0	44.4	26.7	130	11.2	38.8	28.6	50	59.1	78.8	58.0	130	2.5	8.7	6.4	134	2.6	9.3	6.8
R3	56.4	10.9	45.5	18.3	130	8.3	19.7	32.6	50	31.7	28.9	47.9	130	0.8	1.9	3.2	116	4.5	9.5	15.8
R4	56.4	6.3	50.1	24.5	130	0.3	0.9	3.8	50	13.3	16.3	68.9	130	0.6	1.9	8.1	145	1.2	4.3	18
R5	56.4	6.3	50.1	63.3	130	0.1	1.1	2.2	50	12.4	39.2	79.1	130	0.5	4	8.1	141	0.6	4.9	9.9

		1M KNO3 solution				1M Na4P2O7+EDTA solution				1M NH4 acetate solution				conc. HNO3 solution			
sample	sediment ratio	vol. mL	[Fe] mg/L	tot. Fe mg	%	vol. mL	[Fe] mg/L	tot. Fe mg	%	vol. mL	[Fe] mg/L	tot. Fe mg	%	vol. mL	[Fe] mg/L	tot. Fe mg	%
R1	19.0	130	0	0	0	50	73.2	69.4	87.8	130	1.2	3.1	3.9	112	3.1	6.6	8.3
R2	26.7	130	0.2	0.7	0.8	50	46.5	62.0	69.8	130	4.2	14.4	16.2	134	3.2	11.4	12.9
R3	18.3	130	0	0	0	50	13.2	12.1	24.1	130	1.2	2.9	5.9	116	16.4	34.7	69.4
R4	24.5	130	0	0	0	50	24.9	30.5	48.7	130	2.7	8.5	13.5	145	6.5	23.1	36.9
R5	63.3	130	0	0	0	50	19.9	63.0	57.5	130	2.2	17.8	16.2	141	3.2	28.6	26.1

Table A3b. Extraction and Mass Balance of As, Ni, and Fe in Reactors

	top column solution				middle column solution				bottom column solution				measured			measured
sample	vol. mL	[As] mg/L	tot. As mg	%	vol. mL	[As] mg/L	tot. As mg	%	vol. mL	[As] mg/L	tot. As mg	%	total As(mg)	sediment %	pore water %	total %
R1	270	11	3	9.3	70	7	0.5	1.5	235	3.5	0.8	2.6	31.9	86.6	13.4	117.3
R2	270	3	0.8	7.7	102	6	0.6	5.8	222	3	0.7	6.3	10.5	80.1	19.9	38.7
R3	270	0.7	0.2	2.3	116	6	0.7	8.6	180	3	0.5	6.7	8.1	82.3	17.7	30.2
R4	191	3	0.6	9	135	5	0.6	9.5	270	5.5	1.5	23.3	6.4	58.2	41.8	22.1
R5	125	3	0.4	4.1	210	3	0.6	6.9	270	3.5	0.9	10.3	9.2	78.7	21.3	33.4
	top column solution				middle column solution				bottom column solution				measured			measured
sample	vol. mL	[Ni] mg/L	tot. Ni mg	%	vol. mL	[Ni] mg/L	tot. Ni mg	%	vol. mL	[Ni] mg/L	tot. Ni mg	%	total Ni(mg)	sediment %	pore water %	total %
R1	270	7.9	2.1	8.8	70	5.2	0.4	1.5	235	1.8	0.4	1.8	24.2	88	12	52.5
R2	270	0.7	0.2	0.1	102	1.4	0.1	0.1	222	0.2	0	0	136.0	99.7	0.3	306.1
R3	270	0.3	0.1	0.1	116	1.4	0.2	0.3	180	0.4	0.1	0.1	60.4	99.5	0.5	132.8
R4	191	0.5	0.1	0.4	135	0.4	0.1	0.2	270	0.5	0.1	0.6	23.6	98.8	1.2	47.1
R5	125	0.3	0	0.1	210	0.6	0.1	0.3	270	0.6	0.2	0.3	49.6	99.3	0.7	98.9
	top column solution				middle column solution				bottom column solution				measured			
Sample	vol. mL	[Fe] mg/L	tot. Fe mg	%	vol. mL	[Fe] mg/L	tot. Fe mg	%	vol. mL	[Fe] mg/L	tot. Fe mg	%	total Fe(mg)	sediment %	pore water %	
R1	270	0	0	0	70	0	0	0	235	0.1	0	0	79.1	100	0	
R2	270	0.3	0.1	0.1	102	0.2	0	0	222	0.6	0.1	0.1	88.8	99.8	0.2	
R3	270	0.1	0	0.1	116	0.2	0	0	180	1.5	0.3	0.5	50.0	99.4	0.6	
R4	191	0.5	0.1	0.1	135	0.8	0.1	0.2	270	1.2	0.3	0.5	62.5	99.2	0.8	
R5	125	0.2	0	0	210	0.1	0	0	270	0.4	0.1	0.1	109.5	99.9	0.1	

able

Reactor	pH	Eh (mV)	Cond. umhos/cm)	T-C (C)	Ni (mg/L)	As (mg/L)	Fe (mg/L)	N03-N (mg/L)	NH4-N (mg/L)	PO4-P (mg/L)	Acidity (mg/L)*
February											
1											
2	4.37	-215	1150	20.5			9.5	10.0	19.7	19	436.8
3	4.87	75	1110	20.7			11.3	7.6	16.2	13	230
4	4.44	-231	1111	20.6			11.8	9.2	12.7	15	374.4
5	4.49	-232	1165	20.7			6.8	9.2	26.8	22	320.6
6	4.73	209	1068	20.6	32.9		14.5	2.8	9.2	14	415
7		-188	1160	20.6	39.8		11.2	6.8	5.6	17	508.1
8	4.78	196	1135	20.7	31.2	45	13.0	6.0	19.7	14	284.2
9	4.68	-191	1144	20.5	45.0		13.8	10.8	16.2	13	357.7
jar-1	4.75	-204	1264	20.4	72.6		4.2	4.4	12.7	9.5	269.5
jar-2	5.17	-193	1245	20.4	74.3	80	4.0	6.6	12.7	8.7	237.4
jar-3	5.55	-275	1241	20.5	74.3	65	3.8	6.0	16.2	10	183
February											
1	4.76	222	1055	20.2	22.6	45	12.3	6.0	12.7	13	195
2	4.77	210	1091	20.3	24.3	45	14.2	9.2	16.2	15	258
3	5.m	155	1065	20.3	29.5	45	12.8	5.2	16.2	9	154.8
4	5.33	234	1140	20.4	39.8	65	7.8	9.2	2.1	8	117.7
5	4.89	280	1176	20.3	39.8	65	11.2	8.4	12.7	19	217.6
6	5.21	226	1108	20.4	38.1	60	6.5	13.2	2.1	22	130.7
7	4.72	-114	1098	20.4	27.8	50	14.2	6.0	5.6	12	296.9
8	5.08	113	1062	20.3	26.0	45	14.3	5.2	12.7	10	158.6
9	4.93	226	1135	20.4	34.7	50	14.7	2.8	18.2	9	233.6
jar-1	4.46	-197	1365	20.2	65.7	75	3.7	4.4	12.7	8	387.1
jar-2	5.05	-177	1278	20.1	72.6	80	2.8	16.7	9.2	18	121.5
jar-3	4.43	-203	1381	20.1	64.0	65	3.7	5.2	19.7	10	418.5
Fe	4										
1	5.03	248	1063	20.4	19.1	40	15.7	2.8	5.6	10	171.2
2	5.06	257	1032	20.5	19.1	40	16.7	3.6	2.1	12	186.6
3	5.22	233	1038	20.6	22.6	45	16.3	1.2	5.6	9	137.3
4	5.54	220	1108	20.6	38.1	60	10.7	3.6	2.1	9	94.5
5	5.41	229	1126	20.6	41.6	55	11.0	2.8	2.1	13	136.9
6	5.67	202	1142	20.6	38.4	70	11.3	9.2	2.1	14	78.4
7	5.17	236	1035	20.7	17.4	45	14.7	1.2	2.1	11	171 5
8	5.29	230	1011	20.6	18.1	45	16.3	2.8	5.6	10	142.6
9	5.25	232	1076	20.6	24.3	45	19.7	2.0	5.6	6	194.8
jar-1	5.06	86	1356	20.4	58.8	60	4.0	2.8	9.2	6	168.2
jar-2	5.18	-48	1245	20.3	65.7	80	2.7	15.5	12.7	15	92.2
jar-3	4 5 6	-13	1336	20.4	57.1	70	4.3	3.6	5.8	13	310.7
February											
1	5.26	151	1017	21.5	17.4	25	0.2	0.1	10.3	3.5	137.3
2	5.31	180	1031	21.4	20.9	30	0.1	0.1	13.1	3.8	129.1
3	5.43	152	1011	21.6	19.1	25	0.7	0.1	12.4	4.2	111.2
4	5.81	161	1156	21.5	45.0	60	0.1	0.5	17.3	2.5	92.6
5	5.83	171	1175	21.6	46.4	70	0.1	0.6	19.4	2.1	86.9
6	5.94	144	1144	21.5	43.3	70	0 3	0.6	18.0	4.5	86.4
7	5.43	175	1059	21.6	19.1	20	0.2	0.1	12.4	4.8	162.2
8	5.51	108	987	21.5	24.3	20	0 3	0.1	10.3	4.9	159.9
9	5.38	171	1078	21.6	39.8	45	0.7	0.1	14.5	4.3	169.6
jar-1	6.01	138	1388	21.4	76.0	65	0.3	0.3	25.1	4.6	108.2
jar-2	5.52	206	1257	21.3	76.0	105	0.1	0.7	22.3	4.8	77.4
jar-3	5.31	186	1353	21.2	72.6	80	0.6	0.3	20.8	4.7	138.3
March 2/9											
1	5.91	-88	985	21.5	24.0	10	10.5	0.1	0.6	3	77.7
2	5.89	-84	928	21.4	23.1	10	9.2	0.1	0.3	3.5	62.7
3	6.08	-93	940	21.3	21.4	10	11.2	0.1	0.2	4	71.3
4	6.19	10	1155	21.5	58.5	60	3.5	0.5	0.5	6	56.2
5	6.27	8	1165	21.6	63.6	65	4.5	0.6	0.7	5.5	56.9
6	6.34	9	1150	21.6	51.6	60	3.0	0.7	0.3	5	53.1
7	5.92	-69	1010	21.6	16.1	5	16.3	0.1	0.1	4.1	79.3
6	6.08	-89	820	21.5	16.3	10	9.7	0.1	0.1	4.3	59
9	5.77	-15	1050	21.4	3 . 3	20	18.7	0.1	0.7	3.8	98.5
jar-1	6.41	56	1310	21.1	75.7	80	1.5	0 3	1.0	4.6	45.4
jar-2	6.39	92	1240	21.2	62.6	105	0.16	0.9	1.0	5.2	30.8
jar-3	6.45	79	1325	21.1	79.2	90	1.2	0.6	1.0	4.7	59.9
6.	3.95	528	1398	21.5	87.6	90	0.16	21.5	20.8	56	89.5

Appendix 7. Environment Protection Laboratories QA/QC Procedures

Appendix 8. Saskatchewan Research Council QA/QC Procedures

EPL

February 2, 1993

Mr. Paul Douris
Boojum Research Ltd.
468 Queen Street East
Suite 400, Toronto, Ontario
M5A 1T7

Dear Paul:

Further to your request for information on EPL's round robin participation and QA/QC documentation, I am enclosing three separate packages.

1.0 QUALITY ASSURANCE, QUALITY CONTROL, DETECTION LIMITS

This is a precis of our QA Manual, which is at least three inches thick. This precis describes EPL's QA/QC goals and objectives as well as the laboratory applications and (p. 5) a listing of specific, routine QA/QC steps that we perform on every project. EPL is probably unique among labs in going to these lengths, and in actually providing the customer with a full QA/QC report on each project.

2.0 EPL LABORATORY CERTIFICATION

This describes our certification in Canada and the U.S., as well as a listing of the round robins we've participated in. Our performance in these round robins is always among the top 1-5 participants.

3.0 MISA ATG # CHART

A listing of EPL's methods, keyed to MISA test group, U.S. EPA method code, and EPL's method detection limits - all of which meet the MISA requirements, as well as the other existing regulatory requirements.

If you require further information please give me a call.

Yours very truly,

J.N. Bishop
Vice President

JNB/no
Enclosures

Saskatchewan
Research Council

ANALYTICAL SERVICES LABORATORY

15 Innovation Blvd Saskatoon, Saskatchewan Canada S7N 2X8 Phone: (306) 933 6932 Fax: (306) 933 7922

QUALITY ASSURANCE IN THE SRC ANALYTICAL LABORATORY

The SRC analytical laboratory has been providing commercial analytical services for over 35 years. It is currently one of the most modern, well equipped laboratories in Canada. The laboratory has instrumentation in excess of $3 million and is well equipped to provide a wide range of analytical services.

The laboratory maintains an extensive in house quality control and quality assurance program. It is designed to continuously evaluate and improve the procedures in place in order to ensure the reliability of analytical data.

A computerized Laboratory Information Management System is used to uniquely identify each sample, set up the analytes for each, monitor the work flow and store the generated analytical results. This system incorporates the QC data and is used to prepare the analytical reports and invoices. All generated analytical data is the property of the client and will not be released to a third party except at the request of the client.

A variety of Quality Control techniques are used to ensure the validity of the analytical results. Some of these techniques may have constraints that will limit their use for certain analyses; the SRC laboratory endeavours to use as many techniques as possible for each procedure. Some of these techniques are described below:

- **Laboratory Prepared Control Standards.**
  Control standards are prepared by spiking water with the parameters being analyzed. These are analyzed with each batch of samples; results must agree within a certain specified range.

- **Duplicates.**
  Duplicates are analyzed on a regular basis; in most cases every tenth sample is duplicated. Results are checked for agreement.

- **Standard Reference Materials.**
  For some sample matrices a variety of certified standards are available for a wide range of analytes. When available, these are analyzed with each batch of samples.

- **Recovery of Known Additions.**
  Sample matrix effects are checked by spiking samples with a known amount of standard and subsequently measuring the recovery of the analyte in the sample.

- **Calibration.**
  Instruments are calibrated prior to running samples and checked periodically to ensure the stability of the instrument response.

- **Comparison of Results.**
  When it is known that analyte levels for a particular sample site remain consistent over time, the laboratory compares each result to previous results. Any inconsistencies are rechecked for lab error. If the change is confirmed, the client is immediately notified.

The Quality control results in the database are used to identify problems within a sample run. If a problem occurs the samples involved are repeated until satisfactory results are obtained. Specific quality control information regarding a group of samples can be provided for an additional charge.

The laboratory has a full time QA/QC manager who regularly reviews the QC data for all laboratory procedures and assesses their performance. In addition, the QA/QC manger coordinates the laboratory's participation in a number of interlaboratory performance assessment programs.

- **Canadian Association of Environmental Analytical Laboratories (CAEAL)**
  The association provides certification for various parameters when acceptable results are demonstrated in their interlaboratory performance evaluation program. CAEAL also provides an accreditation program that includes on-site evaluation of the laboratory procedures and facilities. The SRC laboratory is currently certified and accreditted for a wide range of parameters with CAEAL. The CAEAL accreditation conforms to the ISO-9000 series and ISO Guide 25 laboratory standards.

- **Environment Canada, LRTAP Program**
  This program examines selected major ions, nutrients and physical parameters.

- **Ecosystems Interlaboratory (Federal-Provincial) Quality Assurance Program.**
  The SRC laboratory participates in the trace metals portion of this program.

- **U.S. Environmental Protection Agency programs.**
  The laboratory participates in several of these programs dealing with the radiochemical measurement of a wide range of radionuclides.

- **Alberta Water Analysts Committee (AWAC)**
  The laboratory participates in the interlaboratory studies sponsored by AWAC each year. These studies examine major ions, nutrients, trace metals and demand parameters.

- **Health and Welfare Canada.**
  The laboratory participates in an interlab program on the determination of Uranium in urine.

For further information contact the laboratory's QA/QC program manager, Jeff Zimmer, at (306) 933-5204.

SRC
Saskatchewan Research Council

QUALITY ASSURANCE, QUALITY CONTROL, DETECTION LIMITS, LIMS

QUALITY ASSURANCE PROGRAM

EPL's Quality Assurance Program (QAP) develops information which can be used to provide on indication of the need for corrections to the analytical system (QA). The QA Program measures whether or not the lab is in overall control. Quality Control (QC) becomes a subset of the QAP and evaluates the accuracy and precision of analytical data to establish the quality of data.

The following section provides an overview of EPL's Quality Assurance Program.

EPL's QA Manual is available for review upon request. An outline is attached (Appendix 1). The complete document which is several inches thick is available for viewing anytime at the EPL office.

OBJECTIVES AND GOALS

Quality Objectives

The Quality Assurance Program (QAP) assures the accuracy, precision, and reliability of the analytical data produced by EPL. Management, administrative, statistical, investigative, preventive, and corrective techniques are employed to achieve this objective through the following goals.

Quality Goals

- To develop and implement approved methods capable of meeting EPL client needs for precision, accuracy, sensitivity, and specificity.
- To ensure that all EPL staff receive training in quality technology enabling them to carry out their QAP responsibilities.
- To establish and keep under review a baseline of quality performance against which the effectiveness of quality improvement efforts are measured.
- To monitor the routine operational performance of the laboratory through participation in appropriate interlaboratory testing programs and to provide for corrective actions as necessary.
- To improve and validate laboratory methodologies by participation in method validation studies.

Quality Tactics

This section lists the tactics EPL follows to achieve the QAP goals.

- Quality activities emphasize the prevention of quality problems rather than detection and correction of problems after they occur.
- Quality cost figures are computed quarterly and reported to the President.
- All employees undergo training programs commensurate with their positions, duties, and responsibilities.
- EPL uses only published and approved methods.
- EPL retains copies of all test and analytical reports in a manner and for a period specified by regulatory or accrediting bodies.
- EPL has a comprehensive calibration program involving all instrumentation used for making analytical determinations.
- EPL uses appropriate, reagents and chemicals, Certified when necessary, and appropriate calibrated glassware, certified when necessary.
- EPL establishes and maintains a total interlaboratory quality management system to assure continued precision and accuracy of laboratory results.
- EPL participates in interlaboratory testing programs on its own initiative and as prescribed by accrediting organizations.

Laboratory Facilities

EPL's state-of-the-art laboratory is located at 6850 Goreway Drive, Mississauga, Ontario L4V 1P1. Specific features include:

- A high security building with restricted access to laboratory area.
- Emergency electrical back up to essential services including, fumehoods, storage refrigerators, lab lighting etc.
- Controlled laboratory suitable for trace analysis.
- Centralized services, library with on-line data searching, centralized glassware washing, maintenance, chemical and labware stores.

- Projects are defined by assigning the specified test codes to the lab sample within a given project.
- On-line LIMS reports display the real time status of lab workstations.
- EPL follows the U.S. EPA's recommended frequency for processing QC samples. These requirements are predefined and enforced by the LIMS system.
- Each analytical run contains as a minimum 1 process blank and 1 process recovery spike per 15 samples, as well as 1 replicate and 1 matrix spike per client within the run.
- Hardcopy worksheets containing all of the pertinent information are generated for each run.
- Signed and dated records of each laboratory activity are maintained.
- Lab staff have ready access to LIMS status reports including:
  - work in progress
  - work due dates
  - overdue work
  - project status etc.
- The LIMS audit trail documents all key events:
  - sampling date
  - date received
  - process data
  - analysis data
  - report data

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

- All analytical services are based upon accepted (MOE, U.S. EPA) procedures and are fully validated prior to use.
- Analytical standards are prepared from neat solids or from certified solutions.
- Calibration standards are validated against external reference standards wherever possible.
- Extensive use is made of Standard Reference Material (SRM) For routine procedure evaluation.
- Surrogate standards are used.
- Routine submission of blind samples is standard practice.
- Analytical sequences are predefined and ensure all results are traceable to calibration and QC data.
- Hardcopy reports displaying all of the required data are generated for each instrument analysis.
- Analytical results are determined only from instrument responses that fall within the demonstrated calibration range.
- Acceptable QC sample performance must be demonstrated prior to the authorization of data, (data are subjected to 3 levels of QC review: technician, supervisor, and manager).
- On-going method and instrument performance records are maintained for all analysis.
- A QC certificate is issued with each project. The QA/QC data reported is specific to your project, and it consists of:
  - full spike/recovery determination
  - blank
  - standard reference material
  - replicate analysis
- Records containing all pertinent data are securely archived for seven years.
- The LIMS database is backed up daily.

Interlnboratory Comparison

- **EPL is** accredited by **CAEAL** as of June 1991.
- EPL is accredited by New York State, as of January 1992
- EPL welcomes audits and inspections by current and potential clients.
- Whenever possible EPL participates in interlaboratory round robin studies. A list of round robins EPL has participated in is attached (Appendix 2).

ANALYTICAL METHODS & INSTRUMENTATION

EPL analytical methods are listed in Appendix 3. We have **also** included information on standard holding times and preservation methods. Methodologies specific to this contract **are** referenced on 'Attachment **A'.**

EPL METHOD DETECTION LIMITS

EPL follows EPA and Ontario Ministry of the Environment (MOE) analytical methods. Method Detection Limits (MDL's) are established following MOE Analytical Protocols.

Method Detection Limit (MDL) - in a given matrix and with a specific method is ***defined as the minimum concentration of an analyte that can be identified, qualitatively or quantitatively measured, and reported to be greater than zero at the 99% confidence level.***

An MDL is a statistically defined decision point. Measured results falling at or above this point are interpreted to indicate the presence of **an** analyte in the sample with a **specified** probability, **and** assumes that there are no known sources **of error in** identification or biases in measurement.
It should be noted that when **MDL** estimates ***are*** developed using clean samples (i.e. reagent blanks) they represent an optimum achievable value. MDL's obtained in this fashion are useful for establishing performance criteria and allowing comparison of interlaboratory method capabilities, but are not applicable in defining the quantitation capability for other samples which introduce matrix effects. EPL MDL's have been established for the matrix being analyzed. As such, real sample MDL's ***can*** be higher than instrument detection limits. MDL's specific to this proposal are available upon request.

LIMS

Environment Protection Laboratories have a proprietary PC **based** LIMS system. **MOE and** OGS systems supplied by BMB Compuscience served as the genesis LIMS. **The** software

has been customized for EPL's specific needs. The system is capable of both sample/data handling and reporting as well as a data management to log workload, throughput and costing.

All major components of the LIMS have a backup which can be easily installed should the original fail. Data are stored on the host/server PC (33 Compaq 386) hard drives, and it is backed up to tape nightly.

("'There are two levels of security on the LIMS system, one at the network operations level requiring that the user know both a user number and a password. As well, the LIMS software has security, restricting access to certain modules and various levels within those modules (i.e. browsing, updating, approvals).

The system has a sophisticated costing and invoicing module. Invoices and Certificates of Analysis are generated by the LIMS on completion and approval of sample analysis. Reports of Analysis are available electronically through EPL's bulletin board, in ASCII delimited files if requested.

EPL's instrument data capture module has a QC checking routine which flags QC data that fall out of tolerance. The routine also compares the present QC data to long term trends. The analyst receives a QC error report with each run of samples which lists all QC exceptions. In addition, the percent spike recovery is calculated and listed. All control charts are updated and generated each night by the LIMS. All QC data are stored in databases for long term precision and accuracy tracking.

The data undergoes *three* levels of approval before release to the client. Each approval is time stamped along with the LIMS usercode of the individual who approved it.

All written methods are available on the LIMS for referral by the analyst.

INTERLABORATORY *COMPARISON* STUDIES

EPL routinely participates in government and industry sponsored interlaboratory comparative studies. Appendix 2 lists all the studies EPL has participated in since start up. Two round robins are of special interest - the Canadian Association of Environmental Analytical Laboratories accreditation for metals and anions and the O'Connor Associates BTEX evaluation; both demonstrate that EPL's data falls in the upper decile. More recent robins such as the air filter study from the Association of the Chemical Profession of Ontario (ACPO), January 1992, and the Atmospheric Environment Studies 1991 air filter study have established EPL as a leading air analysis laboratory. EPL has also recently been certified by New York State, and their certification involved analyses of interlaboratory check samples.

EPL
ENVIRONMENT PROTECTION LABORATORIES INC.

EPL LABORATORY CERTIFICATION

Neither the Government of Canada nor the Provincial Government of Ontario has a formal approval process for laboratories. However, EPL is recognized as a top quality laboratory by senior officials in the Canadian Federal Government and the Ontario Ministry of the Environment, and we have been approved by these agencies to perform analytical work for them.

EPL has performed extensive testing for the Province of Ontario, and has taken part in numerous interlaboratory studies for water and other materials. Our laboratory has always performed very well, and on the basis of our data quality we have been contacted by the Ontario Ministry of the Environment to perform environmental analyses.

EPL has also performed testing for several departments of the Federal Government of Canada, including Agriculture Canada and Environment Canada. Before selecting EPL, the Canadian Government examined EPL's data quality and put the lab through an extensive cross-comparison with several U.S. laboratories. The fact that both the Provincial Government of Ontario and the Canadian Federal Government have approved EPL for their work constitutes de facto acceptance of EPL's capabilities. The Ontario Ministry of the Environment has even used EPL to act as a referee laboratory to settle questions about data from different provincial government laboratories.

EPL is a member of the International Association of Environmental Testing Laboratories (IAETL), an organization made up of laboratories working on issues such as accreditation.

We are also members of the Ontario Bottled Water Association (OBWA) and the Canadian Bottled Water Association. EPL was selected by the OBWA as their laboratory of choice for 1991 and 1992.

EPL has been certified by the Canadian Association of Environmental Analytical Laboratories (CAEAL). CAEAL is the only organization in Canada that formally certifies analytical laboratories.

In the U.S., EPL has been granted Certification by New York State, through the Department of Health. EPL's certification covers bottled water, effluent, air samples and the range of other environmental analyses. Certification by New York State is regarded as primary certification by a large number of other states.

6850 Goreway Drive, Toronto, Ontario, Canada L4V 1P1 Telephone (416) 673-3255 • FAX (416) 673-7399

EPL
ENVIRONMENT PROTECTION LABORATORIES INC

Environment Protection Laboratories **Inc.**
Round Robin Studies

DATE	SPONSOR	TYPE OF ANALYSIS
Jan 1990	MOE # 90-1	Cyanide / Water
Jan 1990	MOE ENV890543	Metals / Sediment
Aug 1990	MOE # 90-5	BTX and Acrylonitrile
Aug 1990	MOE St. Bruno	Metals / Sediment
Sept 1990	MOE	PAH / Sediment
Oct 1990	MOE # 90-6	Mercury
Nov 1990	MOE # 90040	Lithium / Water
Nov 1990	MOE Sludge	Metals / Sludge
Jan 1991	CCIW # G-1	Chlorinated Hydrocarbons / Sediment
Feb 1991	O'Connor Associates	BTX / Water
Mar 1991	AES	Metals / High Vol Filters
April 1991	CAEAL	Metals / Anions
May 1991	MOE	PCDD/DF / PUFs
May 1991	Proctor & Redfern	PAH / PCDD/DF / Metals
Oct 1991	CAEAL	Metals / Anions
Oct 1991	MOE # 91-3	Phenols by 4AAP
Nov 1991	MOE # 91-4	Oil & Grease
Nov 1991	MOE # 91-5	TOC / DOC in Water
Nov 1991	ACPO	Metals / Anions on Filters
Dec 1991	WTC	Cyanide / Water
Dec 1991	ESSO	BTX / VCM
Dec 1991	CCIW CEPA CP-3	PCDD/DF / Ampules
Jan 1992	ACPO	Metals / Anions on Filters
Feb 1992	WTC	Cyanide / Effluents
Feb 1992	State of New York	Metals / Anions / Pesticides / Volatiles
Feb 1992	Labatts	Metals / BTX
March 1992	CAEAL	Metals
April 1992	ACPO	Metals / Anions
April 1992	State of New York	Metals / Anions / Pesticides / Volatiles
April 1992	O'Connor Associates	BTEX
April 1992	Golder/Shell	BTX / EHC / Lead
July 1992	State of New York	Metals / Anions / Pesticides / Volatiles
Oct 1992	CCIW CEPA CP-4	PCDD/DF / Ampules
Nov 1992	State of New York	Metals / Anions / Pesticides / Volatiles
Nov 1992	CAEAL	Metals

eplrrs2/cn

6850 Goreway Drive Toronto Ontario Canada L4V 1P1 Telephone (416) 673-3255 • FAX (416) 673-7399

NEW YORK STATE **DEPARTMENT OF HEALTH**

D A W **AXELROD, M. D.** *COMMISSIONER*

Expires 12:01 AM April 1, 1993
ISSUED April 1, 1992
REVISED June 30, 1992

INTERIM CERTIFICATE OF APPROVAL FOR LABORATORY SERVICE

Issued in accordance with and pursuant to section 502 Public Health Law of New York State

Lab ID No.: 11284

Director: MR. TIM MUNSHAW
Lab Name: ENVIRONMENT PROTECTION LABORATORIES WC
Address : 6850 GORENAY DRIVE
MISSISSAUGA ONTARIO CAN

is hereby APPROVED as an Environmental Laboratory for the category

ENVIRONMENTAL ANALYSES NON POTABLE WATER

All approved subcategories and/or analytes are listed below:

Hydrocarbon Pesticides :
4'-DDD
4'-DDE
4'-DDT
pha-BHC
drin
eta-BHC
aptan
lordane Total
lta-BHC
eldrin
odrin aldehyde
adrin
dosulfan I
dosulfan II
Endosulfan sulfate
Heptachlor
ptachlor epoxide
odrin
indane
Mirex
thoxychlor
CB
raphene

Wastewater Miscellaneous :
Bromide
Boron, Total
Cyanide, Total
Color
Phenols
Oil & Grease Total Recoverable
Hydrogen Ion (pH)
Specific Conductance
Silica, Dissolved
Sulfide (as S)
Surfactant (MBAS)
Temperature
Organic Carbon, Total
Purgeable Aromatics (ALL)

Mineral :
Acidity
Alkalinity
Chloride
Sulfate (as SO4)
Hardness, Total
Acrolein and Acrylonitrile (ALL)
Wastewater Bacteriology (ALL)
Chlorinated Hydrocarbons (ALL)
Demand (ALL)
Wastewater Metals I (ALL)
Nitroaromatics and Isophorone (ALL)
Polynuclear Aromatics (ALL)
Phthalate Esters (ALL)
Purgeable Halocarbons (ALL)

Wastewater Metals III :
Cobalt, Total
Molybdenum, Total
Tin, Total
Thallium, Total
Nitrosoamines :
N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine
Dioxins (ALL)
Haloethers (ALL)
Wastewater Metals II (ALL)
Nutrient (ALL)
Polychlorinated Biphenyls (ALL)
Priority Pollutant Phenols (ALL)
Residue (ALL)

Serial No.: 12864

Lawrence S. Stamman

Lawrence S. Stamman, M.D., Ph.D., Acting Director
[illegible], Ph.D., Director
Wadsworth Center for Laboratories and Research

XIV

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NEW YORK STATE DEPARTMENT OF WEALTH

DAVID AXELROD, M. D. COMMISSIONER

Expires 12:01 AM April 1
ISSUED April 1, 1992
REVISED June 30, 1992

INTERIM CERTIFICATE OF APPROVAL FOR LABORATORY SERVICE

Issued in accordance with and pursuant to section 502 Public Health Law of New York State

Lab ID No.: 11284

Director: MR. TIM MUNSHAW
Lab Name: ENVIRONMENT PROTECTION LABORATORIES INC
Address : 6850 GOREWAY DRIVE
MISSISSAUGA ONTARIO CAN

is hereby APPROVED as an Environmental Laboratory for the category

ENVIRONMENTAL ANALYSES/ POTABLE WATER

All approved subcategories and/or analytes are listed below:

Drinking Water Non-Metals :
- Alkalinity
- Chloride
- Color
- Fluoride, Total
- Nitrate (as N)
- Hydrogen Ion (pH)
- Solids, Total Dissolved
- Sulfate (as SO4)

D.W. Organohalide Pesticides :
- Endrin
- Lindane
- Methoxychlor
- Toxaphene

D.W. Chlorinated Acids :
- 2,4-D
- 2,4,5-TP (Silvex)

Drinking Water Metals I (ALL)
Volatile Halocarbons (ALL)

Drinking Water Bacteriology :
- Standard Plate Count

Drinking Water Trihalomethane (ALL)
Volatile Aromatics (ALL)

Lawrence S. Sturman

Serial No.: 12865

Lawrence S. Sturman, M.S., Ph.D., Acting Director
[illegible], D. Director
Wadsworth Center for Laboratories and Research

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DOH-3317 (11/90)

NEW YORK STATE DEPARTMENT OF HEALTH

DAVID AXELROD. M. D. *COMMISSIONER*

Expires 12:01 AM April 1, 1993
ISSUED April 1, 1992
REVISED June 30, 1992

INTERIM CERTIFICATE OF APPROVAL FOR LABORATORY SERVICE

Issued in accordance with and pursuant to section 502 Public Health Law of New York State

Lab ID No.: 11284

Director: MR. TIM MUNSHAW
Lab Name: ENVIRONMENT PROTECTION LABORATORIES INC
Address : 6850 GOREWAY DRIVE
MISSISSAUGA ONTARIO CAN

is hereby APPROVED as an *Environmental Laboratory for* the *category*

ENVIRONMENTAL ANALYSES/AIR AND EMISSIONS

All approved subcategories and/or analytes are listed below;

[redacted] (ALL)

Lawrence S. Stanman

Lawrence S. Stanman, M.D., Ph.D., Acting Director
[redacted], Director
Wadsworth Center for Laboratories and Research

Serial No.: 12866

xvi

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DOH-3317 (11/90)

NEW YORK STATE DEPARTMENT OF HEALTH

DAVID AXELROD, M.D. COMMISSIONER

Expires 12:01 AM April 1, 1993
ISSUED April 1, 1992
REVISED June 30, 1992

INTERIM CERTIFICATE OF APPROVAL FOR LABORATORY SERVICE

Issued in accordance with and pursuant to section 502 Public Health Law of New York State

Lab ID No.: 11284

Director: MR. TIM MUNSHAW
Lab Name: ENVIRONMENT PROTECTION LABORATORIES INC
Address : 6850 GOREWAY DRIVE
MISSISSAUGA ONTARIO CAN

is hereby APPROVED as an Environmental Laboratory for the category

ENVIRONMENTAL ANALYSES/SOLID AND HAZARDOUS WASTE

All approved subcategories and/or analytes are listed below:

Miscellaneous :
Cyanide, Total
Hydrogen Ion (pH)
Sulfide (as S)
Priority Pollutant Phenols (ALL)

Characteristic Testing :
Toricity - Metals Only
Metals I (ALL)
Polynuclear Arom. Hydrocarbon (ALL)
Purgeable Aromatics (ALL)

Acrolein and Acrylonitrile (ALL)
Chlorinated Hydrocarbons (ALL)
Metals II (ALL)
Polychlorinated Biphenyls (ALL)
Purgeable Halocarbons (ALL)

Chlor. Hydrocarbon Pesticides (ALL)
Haloethers (ALL)
Nitroaromatics Isophorone (ALL)
Phthalate Esters (ALL)

Lawrence S. Stuman

Lawrence S. Stuman, M.D., Ph.D., Acting Director
[illegible] Director
Wadsworth Center for Laboratories and Research

Serial No.: 12867

xvii

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DOH-3317 (11/90)

E: JUNE 1, 1991

CAEAL LABORATORY CERTIFICATION PROGRAM

REGISTRATION STATUS

LABORATORY: ENVIRONMEN PROTECTION LABS
REGISTRATION NO: 1380
ISTRATION DATE: JUNE 7, 1991

PARAMETER	METHOD	AUDIT DATE	PE SCORE	STATUS
TRIX: FRESH WATER				
CHLORIDE	ION CHROMATOGRAPHY	91.03.01	100	Y
CALCIUM - DISSOLVED	ICP	91.03.01	100	Y
CADMIUM - DISSOLVED	ICP	91.03.01	100	Y
COBALT - DISSOLVED	ICP	91.03.01	100	Y
CHROMIUM - DISSOLVED	ICP	91.03.01	100	
COPPER - DISSOLVED	ICP	91.03.01	100	
IRON - DISSOLVED	ICP	91.03.01	100	
MAGNESIUM - DISSOLVED	ICP	91.03.01	95	
MANGANESE - DISSOLVED	ICP	91.03.01	100	
NICKEL - DISSOLVED	ICP	91.03.01	100	
LEAD - DISSOLVED	ICP	91.03.01	100	
VANADIUM - DISSOLVED	ICP	91.03.01	100	
ZINC - DISSOLVED	ICP	91.03.01	100	
POTASSIUM	FLAME PHOTOMETRIC	91.03.01	80	
SODIUM	FLAME PHOTOMETRIC	91.03.01	100	
NITRATE	ION CHROMATOGRAPHY	91.03.01	90	
NITRATE + NITRITE	ION CHROMATOGRAPHY	91.03.01	100	
SULPHATE	ION CHROMATOGRAPHY	91.03.01	100	

PROVISIONAL REPORT

ACLAE

CAEAL

This is to certify that

Environment Protection Laboratories

6850 Goreway Drive
Toronto, Ontario

is a member of
The Canadian Association for
Environmental Analytical Laboratories

CAEAL 1992 ACLAE

Dr. John Lawrence, President

Member until: June 18, 1991

MISA ATG #	Parameter	Method Code	Method Identifier	MISA MDL mg/L	EPL MDL mg/L	EPL SRI mg/L	HIGH CAL mg/L
1	Chemical Oxygen Demand (COD)	EP011A	Potassium Dichromate/Sulphuric Acid Reflux Colourimetric Determination (HACH DR/3000)	10	5	1	100/500
2	Total Cyanide	EP022A	Acid Distillation into Alkaline Absorber Pyridine - Barbituric acid Colourimetric Determination (Hach DR/3000)	.005	.002	0.001	.1
3	pH (Hydrogen Ion)	EP031D	Combination Electrode (Hach) pH meter	.01 units	.01 units	.01	10
4a	Ammonia + Ammonium	EP042A	Alkaline Distillation into Boric Acid (Buechi 321) Nesslerization Colourimetric Determination (Hach DR/3000)	.25 (as N)	.05 (as N)	.01	2.5
4a	Total Kjeldahl Nitrogen (TKN)	EP044A	Acid Digestion - H2SO4/HgSO4/K2SO4 (Buechi 430) followed by alkaline distillation into Boric acid (Buechi 321) Nesslerization Colourimetric Determination (Hach DR/3000)	.5 (as N)	.10 (as N)	.1	2.5
4b	Nitrate plus Nitrite	EP042A	Copper-Cadmium Reduction. NED Colourimetric Determination (Hach Dr/3000)	.25 (as N)	.10 (as N)	.05	1.25
5a	Dissolved Organic Carbon (DOC)	EP051A	Filtration - 0.45u Membrane Filter, UV/ persulphate oxidation followed by Colourimetric Determination (Skalar SA 20/40)	.5 (as C)	.5 (as C)	.1	2.5
5b	Total Organic Carbon (TOC)	EP053A	UV/persulphate oxidation followed by Colourimetric Determination (Skalar SA 20/40)	5 (as C)	1.0 (as C)	.1	2.5
6	Total Phosphorous (TP)	EP062A	Acid Digestion - HNO3/H2SO4 - Ascorbic acid Colourimetric Determination (Hach DR/3000)	.1	.02	.01	1.0
7	Specific Conductance	EP071D	Conductivity Cell with Resistance Thermometer (MetrOhm) Conductometer (MetrOhm 660)	5 uS/cm	.1 uS/cm	.1 uS/cm	.1
8	Total Suspended Solids (TSS)	EP081C	Filtration - 2 um glass fibre, drying @ 103 C (Precision STM 135), Gravimetric Determination (Sartorius R200D)	2	1	1	.1
8	Volatile Suspended Solids (VSS)	EP082C	Filtration - 2 um glass fibre, ignition @ 550 C (Neytech 85P), Gravimetric Determination (Sartorius R200D)	4	1	1	.1
9	Copper * Cobalt * Nickel Silver Zinc * (Cadmium) (Lead)	EP092B	Nitric evaporation Air-acetylene AAS (TJA Smith-Hieftje 22) * A 5 fold preconcentration is carried out for Co, Cu, and Zn	.01 .02 .02 .03 .01	.005 .01 .005 .03 .005	.001 .01 .001 .01 .001	5 5 5 5 5 5 5

Department of Commerce
Juanita M. Kreps
Secretary

National Bureau of Standards
Ernest Ambler, Acting Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 1571

Orchard Leaves

This Standard Reference Material is intended for use for the calibration of apparatus and the validation and/or verification of methods used in the analysis of agricultural and other botanical materials for major, minor, and trace elements.

Certified Values of Constituent Elements: The certified values for the constituent elements are shown in Table 1. The analytical techniques used and the names and affiliations of the analysts are shown in Tabk 3. Certified values arc based on results obtained by reference methods of known accuracy and performed by two or more analysts; or alternatively, from results obtained by two or more independent, reliable analytical methods. Non-certified values are given for information only in Tabk 2. All values arc based on a minimum sample *s i n of* 250 mg of *the* dried material.

Notice and Warnings to Users:

Expiration of Certification: This certification is invalid after 5 years from the date of shipping. Should it k shown invalid prior to that time, purchasers will k notified by NBS.

Stability: The material should be kept in its original bottle and stored at temperatures between 10-30 °C. It should not be exposed to intense sources of radiation, including ultraviolet lamps or sunlight. Ideally, the bottle should be kept in a desiccator in the *dark* at the temperature indicated.

Use: A minimum wmpk of 250 mg of the *dried* material (see Instructions for Drying) should k wed for m y analytical determination to be related to the certified values of this certificate.

The overall direction and coordination of the technical measurements leading to this certificate were performed under the chairmanship of P. D. LaFleur. The overall coordination of the cooperative work performed by the Commission of European Communities, Joint Research Center, Ispra Establishment, Italy. was by G. Rossi of thc Chemistry Division.

The technical and support aspects involved in the preparation, certification, and issuance *of* this S——— Reference Material were coordinated through the oftie of Standard Reference Materials by T. W. Mears.

Washington, D.C. 20234
(January 28, 1971)
(Revised August 15, 1976)
(Revised August 31, 1977)

J. Paul Cali, Chief
Office of Standard Reference Materials

Table 1. Certified Values of Constituent Elements[a]

Major Constituents

Element	Content Wt. Percent
Nitrogen	276 ± 0.05
Calcium	2.09 ± 0.03
Potassium	1.47 ± 0.03

Minor Constituents

Element	Content Wt. Percent
Magnesium	0.62 ± 0.02
Phosphorus	0.21 ± 0.01

The uncertainties shown above include both the imprecision, expressed as the standard deviation of a single measurement, and an allowance for unknown sources of systematic error.

Trace Constituents[a]

Element	Content µg/g
Iron	300 ± 20
Manganese	912 4
Sodium	822 6
Lead	45k 3
Strontium	37 ± I
Boron	332 3
Zinc	25 ± 3
Copper	12 ± I
Rubidium	12k I
Arsenic	10 ± 2

Element	Content µg/g
Antimony	29 ± 0.3
Chromium	26 20.3
Nickel	1.3 i0.2
Molybdenum	0.3 ± 0.1
Mercury	0.155 ± 0.015
Cadmium	0.11 ± 0.01
Selenium	0.08 ± 0.01
Thorium	0.064 ± 0.006
Uranium	0.029 ± 0.005
Beryllium	0.027 ± 0.010

The uncertainties shown above are the imprecisions expressed as either two standard deviations of a single determination (commonly. but perhaps incorrectly, called the "95 percent confidence limit"), or the entire range of observed results -whichever of the two is larger. No additional allowance for the uncertainty from unknown sources of systematic error has been included, since these are considered to be small relative to the imprecision as expressed.

[a]Analytical values are based on the "dry-weight" of material (See Instructions for Drying).

Table 2. Non-certified Values for Trace Constituent Elements[a]

NOTE: The following values arc not certified because they are not based on the results of either a reference method or of two or more independent methods. These valuer are included for information only.

Element	Content µg/g
Sulfur	(1900)
chlorine	(690)
Barium	(44)
Bromine	(10)
Fluorine	(4.)
Lithium	(0.6)

Element	Concent µg/g
Cobalt	(0.2)
Iodine	(0.17)
Bismuth	(0.1)
Gallium	(0.08)
Cesium	(0.04)
Tellurium	(0.01)

[a]Analytical values are based on the "dry-weight" of material (See Instructions for Drying).

Additional Information on Analyses: Digestion procedures should be designed to avoid loss of volatile elements such as arsenic, mercury, etc. It was found that digestion of the orchard leaves in nitric and perchloric acids was incomplete, a small residue of siliceous material remaining. This residue must be considered an integral part of this Standard Reference Material. Therefore, dissolution procedures must be capable of complete dissolution of the leaves, but must not result in losses of volatile elements.

Iron and lead in the nitric-perchloric acid soluble portion were determined to be 270 $\mu g/g$ and 44 $\mu g/g$, respectively. These two values, not to be confused with the *total* material values given in Table 1, are not certified, but given for information only.

Source and Preparation of Material: The orchard leaves for this Standard Reference Material were collected and prepared under the direction of A. L. Kenworthy of Michigan State University. These leaves were hand picked from an orchard near Lansing, Michigan, and air dried. The dried leaves were ground in a comminuting machine to pass a 40-mesh sieve (about one-third passing a 60-mesh sieve). After grinding the material, it was dried at 85° C and thoroughly mixed in a feed blender. The prepared leaves were packaged in polyethylene-lined fiber drums and sterilized *in situ* with 4.9 megarad of cobalt-60 radiation. The sterilization procedure was carried out at the U. S. Army Natick Laboratories under the direction of A.Brynjolfsson.

Homogeneity Assessment: The homogeneity of this material was established on the premise that the minimum sample size be 250 milligrams. Assessment of homogeneity was made using analyses for nitrogen, potassium, and magnesium. A statistical analysis of the data shows that there is evidence for a small degree of variability between samples with respect to potassium. The data for the other elements do not reveal such an effect. Statistical design and analysis of data were performed by J. Mandel of the NBS Institute for Materials Research.

Instructions for Drying: Before weighing, samples of this Standard Reference Material *must* be dried by either:

1. Drying in air in an oven at 85 °C for at least 4 hours.
2. Lyophilization using a cold trap at or below −50 °C at a pressure *not greater* than 30 Pa (0.2 mm Hg) for at least 24 hours.

NOTE: Drying at 135 °C results in large losses and discoloration and should *not* be used.

Analysts and Analytical Methods Used

Analytical Methods

A. Atomic absorption spectroscopy
B. Flame emission spectrometry
C. Gravimetry
D. Intersociety Committee Method 12204-01-68T for fluorine
E. Isotope dilution mass spectrometry
F. Isotope dilution spark source mass spectrometry
G. Kjeldahl method for nitrogen
H. Neutron activation
I. Nuclear track technique
J. Optical emission spectroscopy
K. Photon activation
L. Polarography
M. Spectrofluorimetry
N. Spectrophotometry

Analysts

Analytical Chemistry Division. National Bureau of Standards

1. T. C. Rains
2. M. S. Epstein
3. T. A. Rush
4. W. P. Schmidt
5. B. S. Carpenter
6. E. R. Deardorff
7. R. A. Paulson
8. L. P. Dunstan
9. L. J. Moore
10. E. L. Garner
11. T. J. Murphy
12. L. A. Machlan
13. J. W. Gramlich
14. R. Alvarez
15. K. M. Sappenfield
16. C. Mueller
17. P. 1. Paulsen
18. D. A. Becker
19. I. E. Gills
20. W. D. Kinard
21. P. D. LaFleur
22. L. T. McClendon
23. H. I. Rook
24. G. J. Lutz
25. E. J. Maienthal
26. S. I. Diamondstone
27. S. A. Wicks

Cooperating Analysts

28. Nuclear Chemistry Section. Josef Stefen Institute, Ljubljana, Yugoslavia.
    V. Ravnick, A. R. Byrne, L. Kosta, M. Dermelj
29. Chemistry Division. Standards and Reference Substances Secretariat, Commission of European Communities, Joint Research Center, Ispra Establishment. Italy.
    F. Giradi, R. Pietra, G. Guzzi, E. Sabhioni
30. L. A. Rancitelli, Pacific Northwest Laboratories. Battelle Memorial Institute. Richland, Washington.
31. J. S. Jones, Jr., University of Georgia, Athens, Georgia.
32. A. L. Kcnwonhy. Michigan State University, East Lansing, Michigan.
33. L. Rengan, Eastern Michigan University. Ypsilanti, Michigan.

Table 3 Methods and Analysis*

METHOD / ELEMENT	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Sb								19				25		
As	1,2							18,19,20, 22,31,34				25		n
a					9,11									
a	B												28	
Bi												25		
B					10,15				J	32,33				
Br								19						
Cd	1,3							30				25		
Ca	1,3	1,3												
Cs								P						
Cl								19,30						
Cr					8,10			18						
Co								19						
Cu						14.1417		19,20,29, 30		32				
F				7										
Ga								30						
I								23						
Fe	1,2					14,16,17		19,30,31				25		
Pb						14.1417					24	25		
Li														
Mg	1,3,29							30		32				
Mn	1,3							18,20,30						
Hg	1,3					14,16,17		19,23,29, 30						
Mo					9.12			21,30						
Ni						14,16,17		30				25		
N							4,7							
P			4,7					30		32,33				
K	1,3	1,3						30						
Rb		1329			9.11.12			30,31						
Se						14,16,17		23,30						
Na		1,3						20,30,31						
Sr					9.12									
S			5.6											
Te								23						
Th					10,12									
U					12,13			18	J					
Zn	1,3					14,16,17		18,29,30, 31		32,33				

*Numbers in body of table refer to analysts named above.

MISA ATG #	Parameter	Method Code	Method Identifier	MISA MDL mg/L	EPL MDL mg/L	EPL SRI mg/L	HIGH CAL mg/L
9 con't.	Aluminum	EP093B	Nitric evaporation	.03	.001	.001	25
	Chromium		Nitrous oxide - acetylene AAS	.02	.0005	.0001	25
	Molybdenum *		(TJA Smith-Hieftje 22)	.02	.02	.01	25
	Vanadium *		* A 10 fold preconcentration is carried out for	.03	.03	.01	25
	(Beryllium)		Mo and V.				10
	Beryllium	EP094B	HNO3 Digestion, Graphite Furnace AAS	.01	.0002	.0001	.05
	Cadmium		(TJA Smith-Hieftje 22/CTF 188)	.002	.0002	.0001	.05
	Lead			.03	.001	.001	.05
	Thallium			.03	.002	.001	.05
10	Arsenic	EP101B	HNO3/H2SO4/HClO4 Acid Digestion	.005	.001	.001	^^
	Selenium		Hydride Generation AAS	.005	.0001	.001	.02
	Antimony		(TJA Smith-Hieftje 22/Varian V6A 76)	.005	.0001	.001	.02
11	Hexavalent Chromium	EP112A	Diphenylcarbazide Colourimetric Determination (Hach DR/3000)	.01	.01	.01	.5
12	Mercury	EP121B	Oxidative acid digestion Cold Vapour AAS (TJA Smith-Hieftje 22/Varian V6A 76)	.0002	.0002	.0001	.005
13	Tetra Alkyl Lead		Liquid/Liquid Extraction, Colourimetric	.002	.002	.001	10
	Tri Alkyl Lead	EP131A	Determination (Hach DR/3000 or Graphite Furnace)				
		EP132B	AAS (TJA Smith-Hieftje 22/CTF 188)				
14	Phenolics (4AAP)	EP142A	Acidic Distillation Solvent Partition/Colourimetric Determination (Hach DR/3000)	.002	.002	.001	.2
15	Sulphide	EP152A	Flocculation/Filtration, Methylene Blue Colourimetric Determination (Hach Dr/3000)	.02	.02	.01	.5

MISA ATG #	Parameter	Method Code	Method Identifier	MISA MDL ug/L	EPL MDL ug/L	EPL SRI ug/L	HIGH CAC ug/L
16	1,1,2,2-Tetrachloroethane	EP161A	Purge and Trap. GCIELCDIPID	4.3	0.3	.1	40
	1,1,2-Trichloroethane			0.6	0.3	.1	40
	1,1-Dichloroethane			0.8	0.6	.1	40
	1,1-Dichloroethylene			2.8	0.6	.1	40
	1,2-Dichlorobenzene			14	0.7	.1	40
	1,2-Dichloroethane			0.8	0.7	.1	40
	1,2-Dichloropropane			0.9	0.7	.1	40
	1,3-Dichlorobenzene			1.1	0.7	.1	40
	1,4-Dichlorobenzene			1.7	0.7	.1	40
	Bromoform			3.7	0.8	.1	40
	Bromomethane			3.7	3.3	.1	40
	Carbon tetrachloride			1.3	0.2	.1	40
	Chlorobenzene			0.7	0.7	.1	40
	Chloroform			0.7	0.4	.1	40
	Chloromethane			3.7	3.5	.1	40
	Cis-1,3-Dichloropropylene			1.4	0.5	.1	40
	Dibromochloromethane			1.1	0.7	.1	40
	Ethylene Dibromide			1.0	1.0	.1	40
	Methylene Chloride			1.3	0.6	.1	40
	Tetrachloroethylene			1.1	0.8	.1	40
	Trans-1,2-Dichloroethylene			1.4	0.8	.1	40
	Trans-1,3-Dichloropropylene			1.4	0.3	.1	40
	Trichloroethylene			1.9	1.0	.1	40
	Trichlorofluoromethane			1.0	5.0	.1	40
	Vinyl Chloride			4.0	4.6	.1	40
17	Benzene	EP171A	Purge and Trap. GCIELCDIPID	0.5	0.4	.1	40
	Toluene			0.5	0.5	.1	40
	o-Xylene/Styrene			0.5	0.5	.1	40
	m/p-Xylene			1.1	0.05	.1	40
18	Acrolein	EP181A	Purge and Trip, GCIMS using capillary column	4.0	4.0	.1	40
	Acrylonitrile			4.2	4.0	.1	40
19	Acenaphthene	EP191A	Liquid/liquid extraction capillary column GC/MS	1.3	1.0	.1	40
	5-nitro-acenaphthene			4.3	2.0	.1	40
	Acenaphthylene			1.4	1.0	.1	40
	Anthracene			1.2	1.0	.1	40
	Benz(a)anthracene			0.5	1.0	.1	40
	Benzo(a)pyrene			0.6	0.5	.1	40

I A		Method Code	Method Identifier	MISA MDL ug/L	EPL MDL ug/L	EPL SRL	HIGH CAL ug/L
19	Benzo(b)fluoranthene	EP191A		0.7	0.7	.1	20
con't.	Benzo(g,h,i)perylene			0.7	0.7	.I	20
	Benzo(k)fluoranthene			0.7	0.7	.1	20
	Camphene			3.5	2.5	.1	20
	1-Chloronaphthalene			2.5	1.0	.I	20
	2-Chloronaphthalene			1.8	1.0	.I	20
	Chrysene			0.3	0.2	.I	20
	Dibenz(a,h)anthracene			I.3	1.0	.1	20
	Fluoranthene			0.4	0.3	.1	20
	Fluorene			1.7	1.0	.I	20
	Indeno(1,2,3-c,d)pyrene			1.3	I.0	.I	20
	Indole			1.9	2.0	.I	20
	1-Methylnaphthalene			3.2	1.0	.1	20
	2-Methylnaphthalene			2.2	I.0	.1	20
	Naphthalene			1.6	I.0	.I	20
	Perylene			I.5	I.0	.I	20
	Phenanthrene			0.4	0.3	.1	20
	Pyrene			0.4	0.4	.I	20
	Benzylbutylphthalate			0.6	0.6	.I	20
	Bis(2-ethylhexyl)phthalate			2.2	2.0	.1	20
	Di-n-butylphthalate			3.8	I.0	.1	20
	4-Ernophenyl phenylether			0.3	0.3	.I	20
	4-Chlorophenyl phenylether			0.9	0.8	.1	20
	Bis(2-chloroisopropyl)ether			2.2	I.0	.I	20
	Bis(2-chloroethyl)ether			4.4	1.0	.1	20
	2,4-dinitrotoluene			0.8	0.7	.1	20
	2,6-dinitrotoluene			0.7	0.7	.1	20
	Bis(2-chloroethyoxy)methane			3.5	2.0	.1	20
	Diphenylamine			14	4.0	.1	20
	N-Nitrosodiphenylamine			14	4.0	.1	20
	N-Nitrosodi-n-propylamine			3.I	2.8	.1	20
	Biphenyl			2.0	I.6	.I	20
20	2,3,4,5-Tetrachlorophenol	EP201A	Liquid/liquid extraction capillary column GC/MS	0.4	0.4	.I	40
	2,3,4,6-Tetrachlorophenol			2.8	1.5	.1	40
	2,3,5,6-Tetrachlorophenol			I.6	1.3	.1	40
	2,3,4-Trichlorophenol			0.6	0.6	.1	40
	2,3,5-Trichlorophenol			1.3	1.3	.I	40
	2,4,5-Trichlorophenol			1.3	I.0	.1	40

MISA ATG #	Parameter	Method Code	Method Identifier	MISA MDL ug/L	EPL MDL ug/L	EPL SRI ug/L	HIGH CAL ug/L
20 con't.	2,4,6-Trichlorophenol	EP201A		1.3	1.2	.1	40
	2,4-Dimethylphenol			7.3	1.0	.1	40
	2,4-Dinitrophenol			42	2.0	.1	40
	2.4-Dichlorophenol			1.7	1.7	.1	40
	2,6-Dichlorophenol			2.0	1.9	.1	40
	4,6-Dinitro-o-cresol			24	4.0	.1	40
	2-Chlorophenol			3.7	2.0	.1	40
	4-Chloro-3-methylphenol			1.5	1.5	.1	40
	4-Nitrophenol			1.4	1.3	.1	40
	m-Cresol			3.4	1.0	.1	40
	o-Cresol			3.7	1.0	.1	40
	p-Cresol			3.5	1.0	.1	40
	Pentachlorophenol			1.3	1.0	.1	40
	Phenol			2.4	1.0	.1	40
23	1,2,3,4-Tetrachlorobenzene	EP231A	Liquid/liquid extraction, florisil clean up, dual capillary column ECD/GC	0.01	0.01	0.01	20
	1,2,3,5-Tetrachlorobenzene			0.01	0.01	0.01	20
	1,2,4,5-Tetrachlorobenzene			0.01	0.01	0.01	20
	1,2,3-Trichlorobenzene			0.01	0.01	0.01	20
	1,2,4-Trichlorobenzene			0.01	0.01	0.01	20
	2,4,5-Trichlorotoluene			0.01	0.01	0.01	20
	Hexachlorobenzene			0.01	0.01	0.01	20
	Hexachlorobutadiene			0.01	0.007	0.01	20
	Hexachlorocyclopentadiene			0.01	0.005	0.01	20
	Hexachloroethane			0.01	0.01	0.01	20
	Octachlorostyrene			0.01	0.005	0.01	20
	Pentachlorobenzene			0.01	0.01	0.01	20
24	2,3,7,8-Tetrachlorodibenzo-p-dioxin	EP241A	Liquid/liquid extraction, multi col chemically modified adsorbent colu clean up SIM GC/MS analysis	0.000020	0.000015	.000005	.0005
	Octachlorodibenzo-p-dioxin			0.000030	0.000025	.000005	.0005
	Octachlorodibenzofuran			0.000030	0.000025	.000005	.0005
	Total heptachlorinated dibenzo-p-dioxins			0.000030	0.000025	.000005	.0005
	Total heptachlorinated dibenzofurans			0.000030	0.000025	.000005	.0005
	Total hexachlorinated dibenzo-p-dioxins			0.000030	0.000025	.000005	.0005
	Total hexachlorinated dibenzofurans			0.000020	0.000015	.000005	.0005
	Total pentachlorinated dibenzo-p-dioxins			0.000020	0.000015	.000005	.0005
	Total pentachlorinated dibenzofurans			0.000015	0.000010	.000005	.0005
	Total tetrachlorinated dibenzo-p-dioxins			0.000020	0.000020	.000005	.0005
	Total tetrachlorinated dibenzofurans			0.000015	0.000010	.000005	.0005

MISA ATG #	Parameter	Method Code	Method Identifier	MISA MDL ug/L	EPL MDL ug/L	EPL SRI ug/L	HIGH CAL ug/L
25	Oil and Grease	EP252C	Liquid/liquid extraction (Freon) Gravimetric Determination (Sartorius R200D)	1	.5	.5	50
27	Polychlorinated Biphenyls (PCB)	EP271A	Identification of Arochlors present, and total concentration, by liquid/liquid extraction, florisil clean up, capillary ECD/GC analysis	0.1	0.07	.01	5
28a	Open Characterization - Volatiles	EP281A	Purge and Trap GC/MS using capillary column	1	1	0.1	20
28b	Open Characterization - Extractables	EP282A	Liquid/liquid extraction, capillary column GC/MS	1	1	[redacted]	40
29	Al, Ba, Be, Bi, B, Cd, Ca, Ce, Cr, Co, Cu, Dy, Er, Eu*, Gd, Ga, Ge, Au, Hf*, Ho*, In, Ir, Fe, La*, Pb, Lu*, Mg, Mn, Mo, Nd, Ni, Nb, Os, Pd, P*, Pb, K*, Pr, pH*, Re*, &, Ru, Sm, &, &*, Ag, Na, Sr, S*, Ta, Tb, Th, Tm, Sn, Ti, W, U*, V, Yb, Y, Zn, Zr	EP291B	Nitric digestion/aqua regia digestion Inductively Coupled Plasma (TJA ICAP 61E) Argon Emission Spectrometry	0.05	0.05	0 01	10
	Cs*, Li, Rb	EP292B	Flame Atomic Absorption (TJA Smith-Hieftje 22)	0.05	0.05	0.01	10
	As, Se, Sb	EP293B	Hydride Generation Atomic Absorption (TJA Smith-Hieftjs 22/Varian VGA 76)	0.005	0.001	0.001	0.02
	Hg	EP294B	Cold Vapor Atomic Absorption (TJA Smith-Hisftje 22/Varian VGA 76)	0.0002	0.0002	0.0001	0.005
	Tl	EP295B	Graphite Furnace Atomic Absorption (TJA Smith-Hieftje 22/CTF 188)	0.03	0.002	0.001	0.05
	XXX		* A 5 fold preconcentration is carried out for Cs, Eu, Hf, Ho, La. Lu. P, K, Pt, Re, Si, S, U				
M1	Chloride	EP312A	Mercuric thiocyanate reaction Ferric Nitrate Colourimetric Determination (Hach Dr/3000)		0.5	.1	10
M2	Cyanates	EP321A	Acidic Reflux/Neutralization Nesslerization Colourimetric Determination (Hach Dr/3000)		0.05	.01	8.0
M3	Total Dissolved Solids	EP331C	Filtration - 2 ug glass fibre, evaporation @ 103 C (Precision STM 135) Gravimetric Determination (Sartorius R200D)		1	1	500
M4	Sulphate	EP342A	Ion Chromatograph Dionex Series 4500I AS4A Anion exchange column		0.5	0.1	15.0
M5	Iron	EP351A	Nitric digestion Inductively Coupled Plasma (TJA ICAP 61E) Argon Emission Spectrometry		0.005	0.001	10
M6	Thiocyanate	EP361A	Absorption (Ion Exchange Resin)/Filtration Ferric Nitrate Colorimetric Determination (Hach Dr/3000)		0.05	.01	2.0
M8	Cyanide-free	EP381A	Acidic Distillation into buffering absorber Isonicotinic Acid/Barbituric Acid Colourimetric Determination (Skalar SA 20/40)		0.02	.01	[redacted]