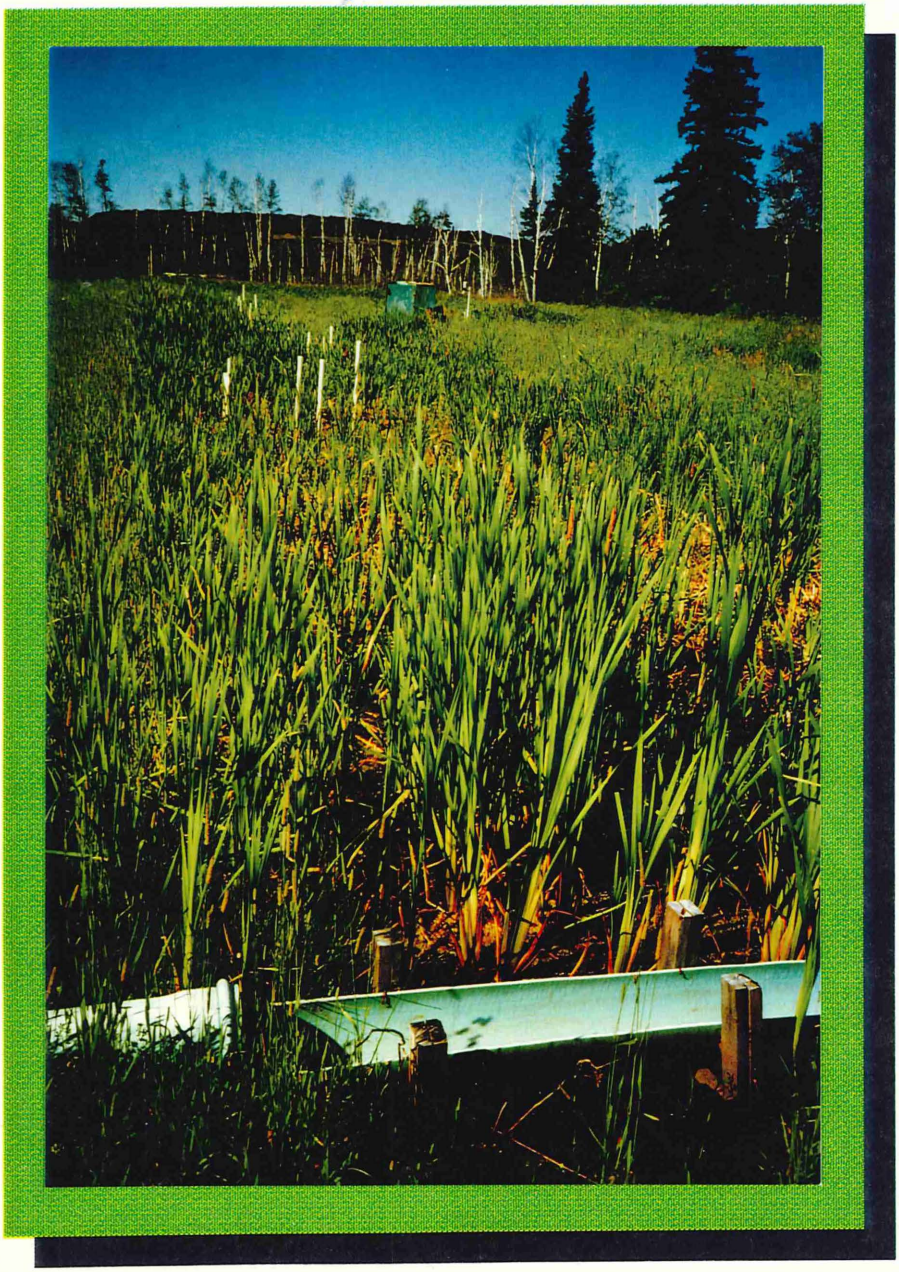
THE USE OF OVERLAND FLOW WETLANDS TO REMOVE METALS FROM NEUTRAL MINE DRAINAGE AT LTV STEEL MINING CO.'S DUNKA MINE



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Minnesota Department of Natural Resources
Division of Minerals
St. Paul, Minneota

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Executive Summary

Four wetland treatment cells were used to remove nickel from a neutral drainage which flowed from a stockpile containing Duluth Complex rock. The pH of the drainage was around 7 and nickel concentrations generally varied from 1-2 mg/L. The cells were designed so that a variety of water levels, vegetation, and flow distribution methods could be examined. The initial design of the cells included the following:

Cell 1 Unmodified natural wetland with 5 cm of water; flow dispersed across the width of the cell.

Cell 2 Modified wetland with 5 cm of water and shallow trenches dug perpendicular to the flow path; flow dispersed across the width of the cell.

Cell 3 Serpentine flow established with hay bales; 15 cm of water; 5 cm of hay placed on the surface of the entire cell; planted with cattails.

Cell 4 Peat berms used to established serpentine flow; 15 cm of water; planted with cattails. In 1991, a 15 cm mixture of peat and peat screenings (a waste product generated during the processing of horticultural peat) was added to the cell.

Although all cells removed nickel from the drainage, the following generalizations can be made:

1) The reduction in nickel concentrations was greatest in the cells with a water depth of 5 cm, a result of better contact between the drainage and the peat substrate.

2) Removal generally increased as the residence time of the drainage within the cell increased. For the cells with a 5 cm water depth, summer residence times greater than or equal to 36 hours were required to reduce nickel concentrations to meet water quality standards (0.213 mg/L). Removal efficiency decreased in the fall and outflow nickel concentrations failed to meet water quality standards despite residence times of 66 hours.

3) Over 99% of the nickel removed was associated with the peat substrate, with less than 1% of the removed nickel associated with the vegetation.

4) Metal removal was confined to the top 20 cm of the peat, and 60% of the total nickel removed was bound to organics in the peat via adsorption, complexation, ion-exchange and chelation reactions. These reactions are dependent on the number of available reaction sites in the peat, and therefore the peat has a finite capacity to remove nickel from solution.

5) Although a wetland can be designed that will, in theory, function in perpetuity, very large wetland areas and very low flow rates would be needed to create a balance between the input metal load and the rate of generation of new removal sites (produced by the decomposition of biomass).

Wetland treatment of neutral mine drainage offers an effective alternative to conventional treatment technology. However, the following limitations need to be incorporated in any decision to use this technology:

1) Removal efficiency decreased in the fall. Steps must be taken to increase treatment effectiveness during this time.

2) A given wetland has a finite and limited capacity to remove metals. For long-term water quality problems, such as mine drainage, treatment plans must contain provisions to replace the peat or supply new binding sites.

3) The enhanced wetland concept, used in cell 4, in which a fresh peat mixture was added to the surface of the existing wetland, provides a method to periodically replace the peat mixture and consequently restore the metal removal capacity of the peat.

4) Removal efficiency decreased when flow rates exceeded the design flow (i.e. residence time decreased). Systems must be designed with storage for water generated during periods of high flow, or must be sized to treat these flows.

Section 1. Introduction.

LTV Steel Mining Company operates an open pit taconite mine (the Dunka Mine) in northeastern Minnesota. In order to mine the iron formation, waste material from the Duluth Complex (which contains copper, nickel and iron sulfides) was removed and then stockpiled adjacent to the mine. When the mine began in 1962, the potential water quality problems which could be caused by the oxidation of the sulfides in this material was not recognized. Over 60 million tons of this material covering 320 acres has now been stockpiled. Drainage from these stockpiles contains elevated concentrations of nickel, copper, cobalt, and zinc; this drainage had increased metal concentrations in nearby receiving waters to levels which are as much as 500 times the natural background concentrations. These concentrations exceeded water quality guidelines established by the Minnesota Pollution Control Agency (MPCA), and in 1985 the company signed a stipulation agreement with the MPCA which established a time line for achieving the water quality goals.

As part of this agreement, the company conducted a feasibility study which analyzed various treatment options and their associated costs (Barr Engineering, 1986). A large number of options were examined, ranging from a full-scale treatment plant (lime precipitation with reverse osmosis) to various passive treatment alternatives (e.g. stockpile revegetation).

The feasibility analysis concluded that a treatment plant capable of treating all the drainage (6×10^8 L/yr) could generally achieve the guidelines, but would have a capital cost of 8.5 million dollars and an annual operating cost of 1.2 million dollars (1985 dollars). However, similar reductions in metal loading to the watershed might also be achieved through a series of passive (low cost, low maintenance) methods. This approach would combine infiltration reduction, alkaline treatment and wetland treatment to produce reductions in both flow and metal concentrations. The capital cost for this approach would be about 4 million dollars, with annual operating costs of around $40,000. Wetland treatment is a crucial aspect of this passive approach, and although previous work (Eger and Lapakko, 1988; Lapakko and Eger, 1988; Lapakko, et al., 1986) had demonstrated the effectiveness of peat to remove trace metals from mine drainage, no field data from an actual treatment system existed.

In 1986, LTV Steel Mining Company and the Minnesota Department of Natural Resources (MDNR) began a cooperative program to develop data on optimal wetland treatment design and system life. The goal of the program was to provide data for the design of full-scale treatment systems for all of the stockpile drainages at the Dunka Mine.

Construction of test cells commenced in 1988. The four test cells began receiving input water on August 1, 1989, and they continued to receive stockpile drainage input for the rest of the 1989 field season, and then for the entire 1990 and 1991 field seasons. Data collected and design criteria established during this study were then used to guide establishment of full-scale peat/wetland treatment systems at LTV's Dunka Mine, which were built during the winter of 1992 to treat drainage from the northern portion of the mine site. In addition, in 1992 LTV began operation of a lime treatment plant to treat water from the southern portion of the mine.

This treatment plant and the wetland systems now treat all the stockpile drainage, and the mine is currently in compliance with its NPDES permit. LTV's goal is to eventually replace the treatment plant with a series of constructed wetlands.

Section 2. Site description and wetland characterization.

Site description The Dunka Mine is a large open pit taconite operation. The pit is approximately 4 km long, 0.4 km wide, and has a maximum depth of 110 meters. The Duluth Complex (an igneous metalliferous intrusion) overlies the taconite ore at this location, and must be removed and stockpiled. The Duluth Complex material was separated based on copper and nickel content and stockpiled along the east side of the open pit (Figure 1).

Stockpiles at the mine are presently built with 13 m lifts, with side slopes at the angle of repose (approximately 45^0). The stockpiles contain a total of about 63 million metric tons of material, and cover about 140 hectares. Drainage from the stockpiles that contain Duluth Complex rock flows to Unnamed Creek or Flamingo Creek, and eventually to Bob Bay of Birch Lake (Figure 1). Discrete seepages have been identified along the bases of the stockpiles and are identified in Figure 1 as EM8, Seep 3, Seep 1, W-1D, W-2D, W-3D, and Aquifer X. Smaller diffuse seepage has also been observed along the toe of some of the stockpiles, but this seepage is not a major contributor to the overall metal load to the watershed. In general, seeps begin to flow during spring thaw, typically around the beginning of April, and flow continuously until freeze up (usually near the end of November). Average flows vary from 0.5 L/sec to 14 L/sec (8 to 220 gpm), but maximum flows exceeding 100 L/sec (1600 gpm) have been observed after periods of heavy precipitation.

The stockpile drainage could generally be characterized as a high-hardness, neutral drainage whose primary contaminant is nickel, with annual median nickel concentrations on the order of 3-30 mg/L. Copper, cobalt, and zinc are also present, but these metals are generally present at concentrations less than 5% of the nickel values. Median pH ranges from 5.0 to 7.5, but most of the stockpile drainages have pH greater than 6.5. Prior to 1992, stockpile drainage had increased the average concentrations of trace metals in the receiving streams to levels that are 200 to 500 times above natural background levels, and which exceeded water quality guidelines by factors of 3 (Table 1). Metal release to the watershed decreased by over 90% after the wetland and lime treatment systems were installed.

Wetlands are located near all the stockpiles and appear to offer potential treatment area for each of the seepages (Figure 1). These wetlands are typical of the many small lowland areas in northern Minnesota, and would generally be associated with any mining operation in this region.

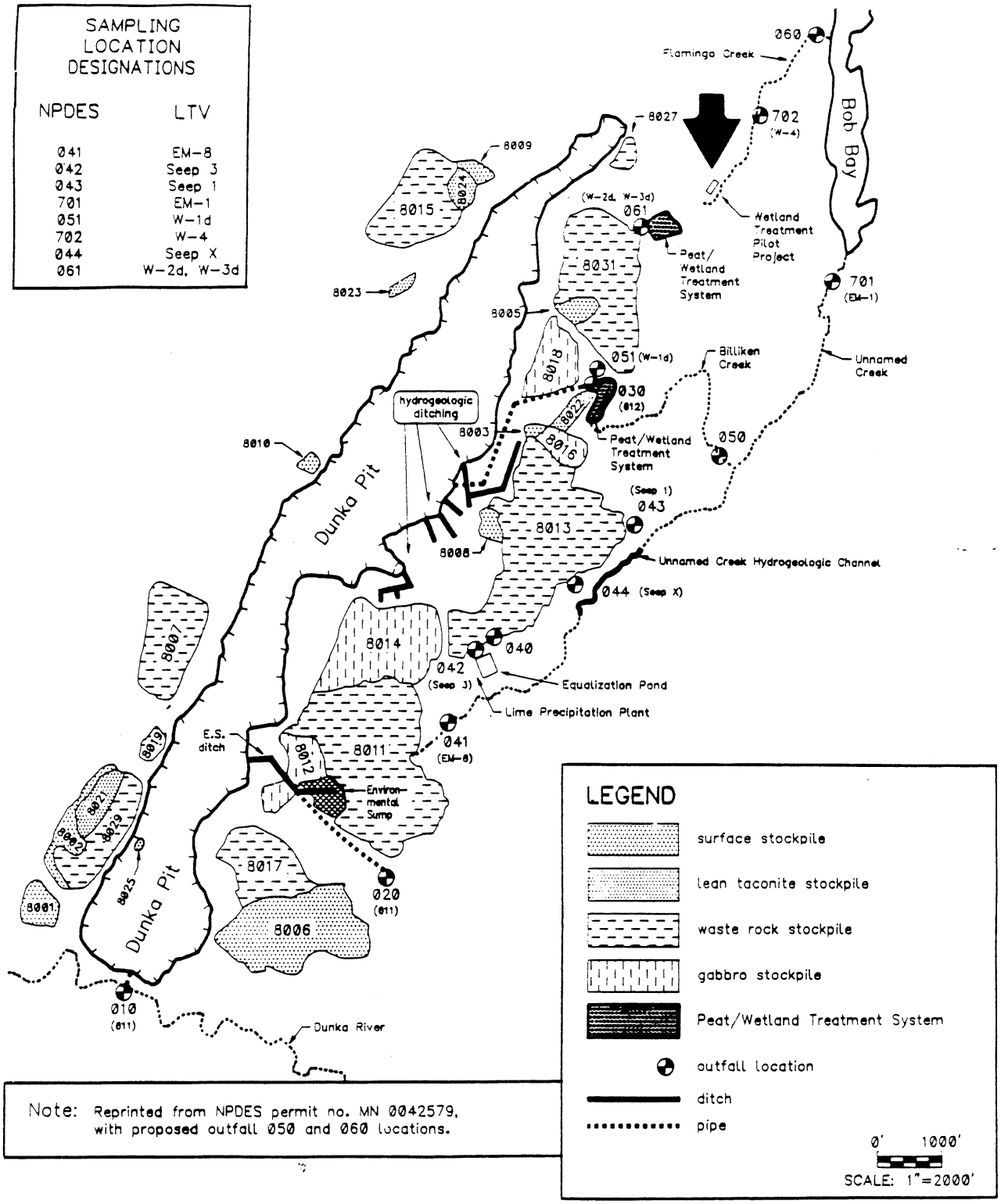


Figure 1. Dunka Mine site map.

Table 1. 1989 Dunka Mine water quality (the first year of system operation).

	Average Concentrations				
	pH (s.u.)	Cu (mg/L)	Ni (mg/L)	Co (mg/L)	Zn (mg/L)
Stockpiles[1]	5.2 - 7.1	0.07 - 1.1	3.1 - 37	0.09 - 2.0	0.06 - 3.4
Receiving[2] streams	7.0 - 7.2	0.007 - 0.013	0.18 - 0.49	0.005	0.01 - 0.05
Water[3] quality standards	6.5 - 8.5	.013	.213	.005	.149
Natural[4] background	6.9	.001	.001	.0004	.002

[1] Stockpile drainage (EM8, Seep 3, W1D, Seep 1).
[2] Stream stations (EM1, W4).
[3] MPCA guidance document for closure plan development.
[4] Regional Copper Nickel Study, median values Minnesota Environmental Quality Board, 1979.

Wetland characterization An initial survey was conducted to determine the capability of each wetland to treat stockpile drainage (Lapakko and Eger, 1987). At each prospective wetland, survey lines were established, peat depths were measured every 50-100 m, and the peat was characterized every 100-200 meters. The number and spacing of samples depended on the size and shape of the wetland.

Characterization included a botanical description of the entire peat profile, a measurement of the degree of decomposition (using the Von Post scale), and chemical and physical analyses (pH, % ash, metal and nutrient concentration, and cation exchange capacity). Samples for chemical and physical analyses were collected at intervals of 0-20, 20-50, 50-100, and 100-200 cm, and then at 100 cm intervals for the rest of the peat profile. All samples were collected with a 5 cm Macaulay sampler.

Peat pH was measured in 0.01 M $CaCl_2$ solution, and peat samples were dried at 105°C for 24 hours and processed in a blender to produce a homogenous material. The peat was digested with a concentrated HCl/HNO_3 mixture, and metal concentrations were determined by atomic absorption (using a Perkin Elmer Atomic Absorption Spectrophotometer, Model #603).

The wetlands ranged in size from 1 to 20 ha, with average depths ranging from 0.2 to 1.2 m (Table 2). The peat was generally well decomposed, with decomposition increasing with depth, and was primarily a sedge peat with wood fragments. Metal concentrations in the peat

Table 2. Characteristics of wetlands at LTV's Dunka Mine, Babbitt, Minnesota.

Wetland	Total Area (ha)	Mean Depth (m)	pH	CEC (meq/ 100 g)	Cu (mg/kg)	Ni (mg/kg)	% Ash	Drainage associated with the wetland	
								Mean [Ni] (mg/L)	Mean Daily Flow (L/s)
EM-8	20	1.2	5.8	180	92	38	16	1.7	14
W-1D	4.2	0.25	5.65	90	239	57	60	5.9	2.5
Seep 1	1.2	0.2	5.50	130	180	740	33	15.4	0.4
W-2D	11	0.5	5.45	120	620	90	38	0.9	1.5*

Note: Peat chemical characteristics are average values for the wetland. * = estimate

varied depending on the sites' proximity to existing stockpile drainage. Copper concentrations in the peat ranged from 40 to 724 mg copper per kg of dry peat, while nickel ranged from 19 to 740 mg/kg. The pH (measured in $CaCl_2$) ranged from 5.25 to 7.45, which was in the expected range for shallow sedge-type peat deposits. Ash content ranged from 10 to 60%, with the highest ash content found in areas where the peat depth was less than 30 cm.

In order to determine if wetland treatment was a viable treatment alternative, the metal retention capacity for each wetland was estimated. Laboratory and field data from previous MDNR studies were used to develop a nickel retention capacity. The maximum nickel concentration observed in field samples was 6400 mg/kg, while concentrations as high as 20,000 mg/kg were measured in laboratory experiments (Eger and Lapakko, 1988, Lapakko and Eger, 1988). Based on these data, a nickel removal value of 10,000 mg/kg nickel dry peat was used to determine the total removal potential of each wetland area. Since most of the flow in peatlands occurs across the surface and within the top 30 cm (1 foot) of the peat (Romanov, 1968), an active removal depth of 20 cm was selected. Data collected from a nearby white cedar peatland which had received mine drainage had demonstrated that the metal concentrations in the peat decreased with depth, and that the majority (>90%) of the metal removal had occurred in the upper 20 cm of the peat (Eger and Lapakko, 1988).

A total removal capability was calculated and divided by the annual average nickel loading to determine the treatment system life for each seep (Table 3). Lifetimes ranged from about 20 years to several hundred years. These calculations do not include the effect of other reclamation activities which should also reduce the annual nickel loading and therefore increase the lifetime of the wetland treatment system. For example, covering a stockpile with soil and establishing vegetation typically reduces annual flow and mass load by about 40% (Eger and Lapakko, 1981) and would therefore extend the minimum treatment system life from 20 to 33 years.

Table 3. Lifetimes of wetland treatment systems at the Dunka Mine, as projected prior to the MDNR wetland treatment study.

Wetland	Peat Mass in Top 20 cm (metric tons) *	Annual Nickel Loading (metric tons)	Treatment System Life (yr) **
EM-8	4000	0.47	90
W-1D	840	0.43	20
Seep 1	240	0.12	20
W-2D	2200	0.03	780

* Assumes there is 0.1 grams dry peat per cubic centimeter.
** Assumes that 100 g of dry peat can sequester 1 g of nickel.

Section 3. Selection of test area.

Based on the estimated lifetimes of the treatment systems, wetland treatment appeared to be a useful, long-term mitigation method. A site for test plot construction was selected based on the following criteria:

(1) A peat depth of at least 50 cm - Although the majority of metal removal occurs within the top 20 cm, peat from the white cedar peatland had elevated metal concentrations in the 20 to 50 cm interval.

(2) Peat metal concentrations less than several hundred mg/kg - Wetland areas that had already received stockpile drainage had metal concentrations greater than 1000 mg/kg, so a significant amount of removal potential had already been used.

(3) A low degree of decomposition, H3 or H4 on the Von Post scale - The lower the degree of decomposition, the more fibrous the peat, and therefore less resistance to flow through the peat. As the resistance to flow decreases (i.e. hydraulic conductivity increases), more stockpile drainage can contact the peat and metal removal should increase.

(4) The drainage had to have adequate flow to supply input to several test plots, and a chemistry typical of the majority of the stockpile drainages at the Dunka mine - Specifically, the drainage should have nickel concentration on the order of 1 to 5 mg/L with a flow rate of 0.6 to 0.9 L/sec (10-15 gpm).

(5) An open area for easy test cell construction - Although a wooded area could be used, large areas of open wetland exist at this mine, and construction costs are minimized if an open area can be utilized.

(6) Good access - Easy access reduces the overall cost of the project.

Based upon these selection criteria, a location for test cell work was chosen in the W3D wetland (Figure 1). The objectives of the test cell work were the following:

(1) To determine the optimum treatment efficiency through the use of different flow distribution methods and different vegetation types.

(2) To measure the system life.

(3) To develop data applicable to full-scale operation.

Additional information on the site selection process is provided in detailed reports on the wetland survey work (Lapakko and Eger, 1987, Eger, 1987) and in Appendix 1.

Section 4. Test cell design, construction, modifications, and operation.

Four cells were designed so that a variety of water levels, vegetation, and flow regimes could be tested (Figure 2). Each cell was 6 meters wide x 30.5 meters long (20 ft. wide by 100 ft. long) and was surrounded by a compacted peat berm. (Additional design and construction details are given in Appendices 2 and 3.)

Drainage from the 8031 stockpile, site W3D, provided most of the input water to the cells during the course of the experiment. This water was a high hardness, neutral pH drainage, and had about 1-2 mg/L nickel in solution, and was fairly typical of the drainages at Dunka (Table 1). In the fall of 1990, short-term tests were conducted in cell 1 that used drainage from Seep 1 and Aquifer X as input water; see Section 7.7 and Appendix 22 for details. The other three cells received nothing but W3D drainage throughout the duration of the experiment.

A retaining dam was constructed near the toe of the stockpile to provide storage and to provide a hydraulic head with which to supply the cells through a 10-cm (4-inch) flexible plastic pipeline. The pipeline transported stockpile drainage, which was to have nickel concentrations in the 1 - 3 mg/L range, to the cells. Before the pipeline was constructed, natural wetland treatment had reduced the nickel concentrations in the vicinity of the cells to less than 0.1 mg/L (Appendix 1).

Water was dispersed across the cell with a perforated PVC pipe and collected with an open half pipe at the outflow. The original cell designs were as follows:

Cell 1: Unmodified natural wetland; water dispersed across natural wetland; vegetation primarily sedges (*Carex sp.*) and grasses (*Calamagrostis sp.*); water depth of 5 cm (2 inches; 5 cm).

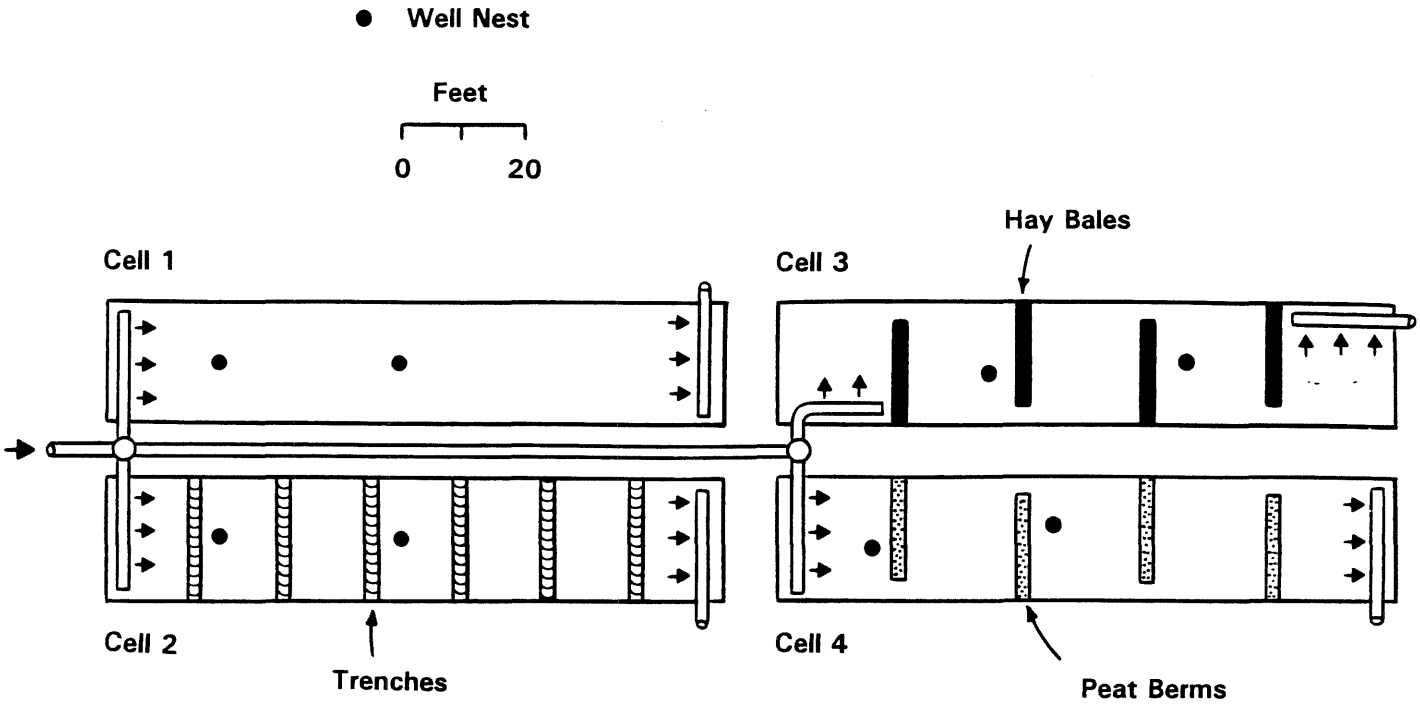


Figure 2. Design schematic of MDNR wetland treatment cells.

Cell 2: Modified wetland; shallow trenches were constructed with a backhoe; these trenches were spaced about 4.5 meters apart and were about 60 cm deep (15 feet by 2 feet) and were dug perpendicular to the flow path; the spoil material from the trench was cast down stream; sedges and grasses from the surrounding area were transplanted into the cell; water depth, 5 cm (2 inches).

Cell 3: Modified wetland; hay bales placed to create serpentine flow, 5 cm (2 inches) of straw placed on the bottom of the entire cell to encourage sulfate reduction; cell planted with cattails (*Typha sp.*; 1 per square meter); water depth, 15 cm (6 inches).

Cell 4: Modified wetland; peat berms constructed across the cell, perpendicular to flow; cattails planted (1 per square meter); water depth, 15 cm (6 inches).

Based on the results of previous laboratory studies (Lapakko et al., 1986), a design residence time in the range of 40-48 hours was selected for the cells. Input flow rates were set at 3.8 liters per minute (1 gallon per minute) for cells 1 and 2, and 11.4 liters per minute (3 gallons per minute) for cells 3 and 4 (Table 4).

Construction of the cell berms occurred in March of 1988, and installation of the plumbing and final contouring of the berms was completed during June 1988. Cattails were planted in cells 3 and 4, and additional grasses and sedges were planted in cells 1 and 2 in July, 1988. (Additional details on plot construction are provided in appendices 4 and 22).

Initial water level measurements indicated that up to 8 liters per minute (2 gpm) leakage was occurring through the berms, and a dye study indicated that the cells were interconnected (Appendix 5). A bentonite cut off wall was designed and installed in April 1989 (Appendix 6). Bentonite was mixed with sand and placed into a trench which was cut in the center of the berms with a Ditch Witch power trencher. The ditch was cut into the mineral soil underlying the cells so that any lateral flow into or out of the cells would be minimized. Subsequent dye and water level measurements indicated that seepage in all cells had been reduced to less than 10% of the input flow (Appendix 7).

With the exception of cell 4, all cells functioned according to design. The peat berms in cell 4 did not transmit water at a rate equal to the inflow rate of 11.4 L/min (3 gpm), and the water level began to rise in the cell. To keep the water level in the cell below the top of the cut off wall, slots were cut into the peat berms to provide serpentine flow. (Figure 2 depicts the final configuration of cell 4.)

A mixture of peat and peat screenings was added to cell 4 in June 1991, at a depth of approximately 15 cm (6 inches), in an attempt to improve the generally poor performance of the cell. The mixture was 1 part well-decomposed reed sedge peat from an unimpacted wetland to 2 parts peat screenings from a sphagnum peat processing facility. The peat/peat screenings

Table 4. Initial water levels, flow rates and residence times for the MDNR wetland treatment cells.

Cell	Design Water Level (in.)	Initial[a] Water Level Calculation (in.)	Final[b] Water Level Estimate (in.)	Design Flow Rate (gpm)	Range of [c] Residence Time (hrs.)
1	2	2.6	1.9	1	40-55
2	2	2.6	1.9	1	40-55
3	6	6.2	6.2	3	42-43
4	6	6.2	6.2	3	42-43

a Based on survey information; see Table A2-3.
b Calculation based on final outlet elevation - average peat surface elevation (see Table A2-3).
c Range based on design flow rate and the initial and final estimates of water level, and on a plot size of 20 ft. wide x 100 ft. long; Residence time = 21 hr / inch of standing water / gpm input

mixture was a relatively more permeable substrate which was expected to improve subsurface flow, and it provided a source of newly available binding sites in the cell for the removal of the metal ions from solution. (A description of this material is presented in Appendix 2.) The outlet elevation was set to allow 5 cm (2 inches) of water depth, assuming that the peat would settle about 50%. Complete settling of the peat did not occur during 1991, and the water depth in the cell varied from 0 cm to about 5 cm for the rest of the 1991 field season.

The input water used in cells 2, 3 and 4 was exclusively water from stockpile 8031 (W3D drainage); cell 1 received the same input except from 9/17/90 to 10/28/90, when short term tests were conducted that used drainage from Seep 1 and Aquifer X (Figure 1, Section 7.7, Appendix 21). The change in the operation of cell 1 was made because the input nickel concentrations began declining in the summer of 1990. By the beginning of September 1990, input nickel concentrations to the cells had dropped below 0.2 mg/L, due to decreased nickel concentrations at the seep itself, and to nickel removal occurring behind the dam at the toe of the stockpile (Appendix 2).

In an attempt to gather additional information on the effect of higher concentrations and shorter residence times on metal removal, the tests with Seep 1 and Aquifer X were initiated in cell 1 on 9/17/90. Tanker trucks were used to transport both Seep 1 and Aquifer X water to the site. Seep 1 water was mixed with W3D water on a 1:1 volume basis, and used as cell 1 input water from 9/17/90 to 10/8/90. Aquifer X water was fed directly to cell 1 from 10/11/90 to 10/28/90. The target residence time for the Seep 1 study was 48 hours, while the residence time in the Aquifer X test was varied between 48 and 24 hours (Section 6.3, Appendix 12).

Prior to system start-up during the 1991 field season, another smaller dam was constructed directly at the W3D seep. Significant amounts of nickel removal was observed to be occurring in the ponding area behind the original dam near the toe of stockpile 8031, and so the new dam at the toe was constructed to allow collection of water that had considerably higher nickel concentrations than the water obtained from the dam at the toe of the stockpile. A 4" (10 cm) flexible polyethylene pipe was then installed to route this drainage directly to a settling barrel (Appendix 2) that fed the treatment cells; all input water to the four treatment cells during 1991 came via this pipe from the new dam at the W3D seep. As a result, 1991 input metal concentrations were considerably higher than corresponding 1990 values (see Appendices 15-17).

Section 5. Methods.

5.1 Flow.

Flow data collection commenced in August 1989, and continued during the course of each field season. The cells were shut down for the winter and early spring (roughly November through May), and received no input flow during these periods.

Input flow came from the base of the 8031 stockpile, where a retaining dam had been built to supply water to the cells (Appendix 2). Water was routed from the dam in a 10-cm diameter polyethylene pipe. The input water was distributed across one end of each cell with a 5-cm perforated PVC pipe, while the outflow was collected at the other end of the cell in a collection trough which was set to maintain the desired water level within the cell. In 1990, a settling barrel was installed prior to the cells to remove particulate matter from the input and to minimize plugging of the flow meter (Appendix 10).

Input and output flow from each cell was measured continuously with a Data Industrial electronic flow meter and recorded with a Campbell Scientific micrologger, which also recorded precipitation, temperature, and relative humidity (Appendix 29). These flow data were then used (in conjunction with the results of the dye studies) to determine the residence time within each cell, and to calculate the mass loadings into and out of the cells. The flow meters were calibrated in the laboratory prior to initiation of the study, and were periodically checked during the field seasons.

5.2 Water quality samples.

Water quality grab samples of the inflow and outflow were typically collected about twice per week during each field season. The input samples were collected from the common feed that supplied all four cells, and the output samples were collected from the outlet pipe of each cell. Samples were analyzed for pH, specific conductance, alkalinity, acidity, calcium, magnesium, sodium, potassium, sulfate, copper, nickel, cobalt, zinc, iron and manganese. Metals were analyzed with a Perkin Elmer atomic absorption unit (Model No. 603) in either flame or

flameless mode. Sulfate was analyzed by the barium chloride turbidimetric method (Standard Methods 426C, HF scientific model DRT-100 turbidimeter), and alkalinity and acidity were determined by titration.

Groundwater samples were collected several times during 1989 and 1990. Samples were taken from each cell to observe variations in water quality with peat depth and with distance from the input. Two well nests were installed in each cell and included a shallow-peat well, and a deep-peat well. Samples of the surface water were also collected at these sites. The wells were constructed from 5-cm PVC and were designed to collect a sample from a distinct layer of peat (Figure 3). (Details on the design of these wells are presented in Appendix 13.)

5.3 Vegetation samples.

Vegetation varied between the cells, with cells 1 and 2 containing primarily the original vegetation of grasses and sedges, while cells 3 and 4 were planted with cattails. The surface of cell 1 was not disturbed during construction, and this cell maintained its original vegetation, with the sole exception being the addition of approximately 150 clumps of sedge and grass that were dug up from the surrounding area and placed into the cell in an attempt to fill in some bare spots within the cell. Since cell 2 had been disturbed by scarification and ditching (see cell description in Section 4), clumps of grasses and sedges were transplanted into the cell from the surrounding area. Cattails were planted into cells 3 and 4 at a spacing of one plant per square meter. The cattails that were used to plant cell 4 were excavated with a backhoe from a site near LTV's main office building at Hoyt Lakes. These were loaded on trucks and brought to the site. These plants were in thick clumps and had to be chopped apart prior to planting. Cell 3 was planted with cattails that were dug from the surrounding area by hand. As a result of the wet conditions, these cattails could be pulled by hand from the wetland, and then transplanted directly into the cell.

Baseline vegetation samples (cattails, grasses/sedges and duckweed) were collected from the cells in July 1989, prior to system start-up. Sedge and grass leaves were collected randomly at five sites within cells 1 and 2, duckweed samples were collected from approximately 12 open-water sites within cells 1-4, and two sets of entire cattail plants were collected; one set came from Hoyt Lakes, and the other from the surrounding (W3D) area.

The cattails from Hoyt Lakes were kept separate from the W3D plants, and analyzed separately for metals content. Four composite samples of about three plants each were made for each of the two groups of cattails. The plants were placed in plastic bags for transport to the laboratory. At the laboratory the cattail samples were gently rinsed with tap water, and then separated into leaves, roots, and rhizomes. The samples were then rinsed with distilled water and then allowed to air dry, after which any visible soil was removed from the roots and rhizomes. The samples were oven dried at 80°C for 24 hours, at which time the samples were ground in a Wiley mill with a minus 20 mesh screen. (The grinding chamber was thoroughly cleaned between each sample with a brush and compressed air.) The samples were then ashed, digested with

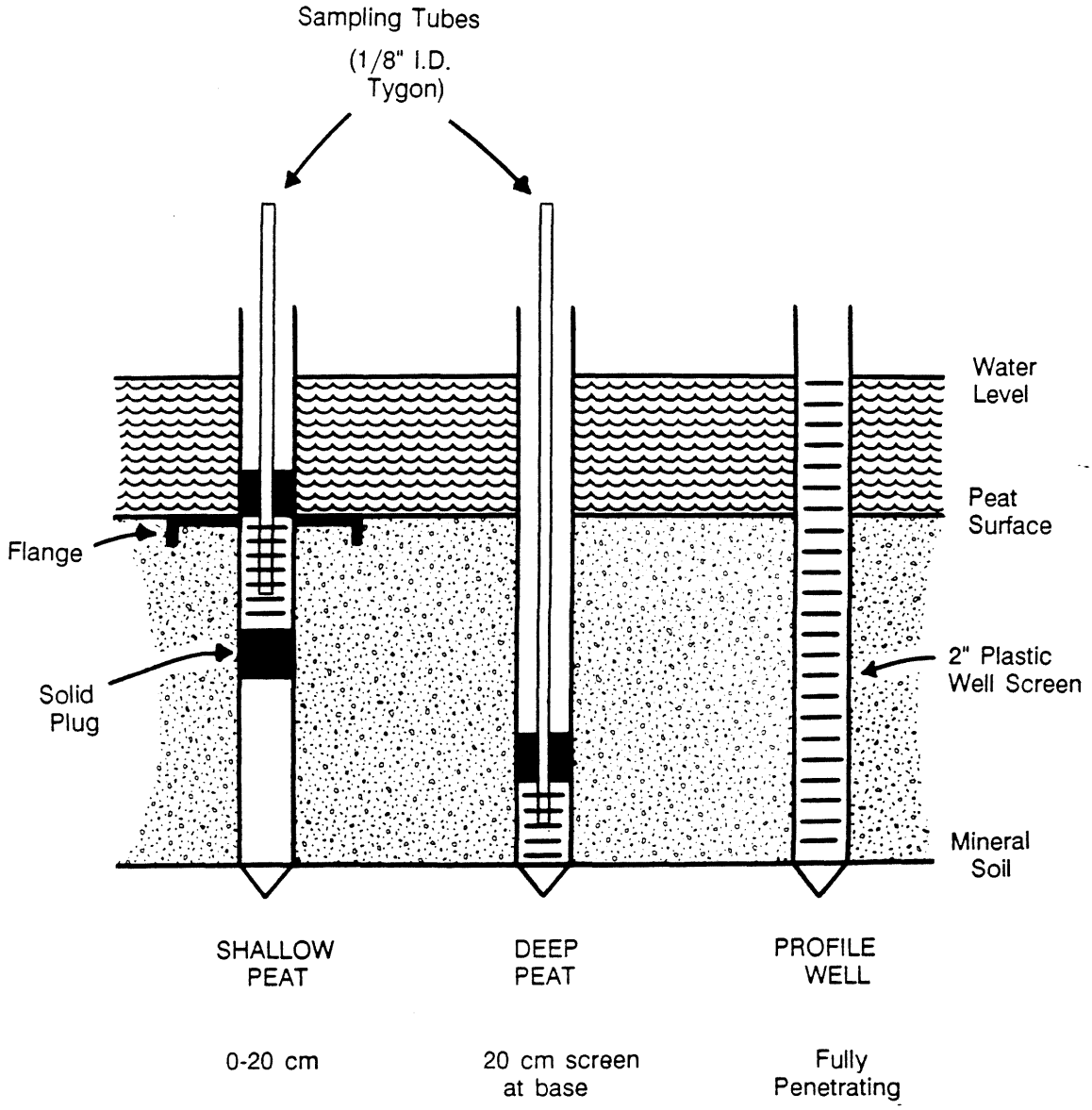


Figure 3. Design schematics of monitoring wells.

concentrated nitric acid, and then analyzed for metal content by atomic absorption using a Perkin Elmer Atomic Absorption Spectrophotometer, Model #603.

Additional vegetation samples were collected in the summer of 1991, after approximately two seasons of exposure to the input drainage. Cattails, grasses and sedges were collected at 12 sites within cells 1, 2 and 3. The sites were spaced at 1.5 meter intervals across the width of the cell and were located 6, 12, 18 and 24 m from the inlet end of the cell. Samples were composited across the width of each cell. Duckweed samples were collected randomly from open water sites within the cell and composited. Care was taken so that the roots and rhizomes of the cattails were maintained intact, and then the whole plant was gently rinsed in water from the site to remove the majority of soil from the plant. The plants were then placed in plastic bags for transport to the laboratory, where they were carefully rinsed, and allowed to air dry. After transport to the MDNR Hibbing lab, the samples were then oven dried at 80°C for 24 hours, at which time the samples were then processed and analyzed in a manner similar to that used for the baseline samples.

In August 1991, percent cover was estimated by inspecting random 0.5-m^2 subplots at ten foot intervals down the length of the cell. Above ground biomass was collected from within a 0.1 - m^2 frame placed within the larger 0.5-m^2 frame. The above ground biomass was then separated into cattails, grasses and sedges, and duckweed, oven dried at 80°C for 24 h, and then weighed. Total above ground biomass was calculated by multiplying the total area of the cell (163 - 191 m^2; Appendix 3) by the average of the biomass values determined for each vegetation type.

Below ground biomass was not directly measured. Literature values (Zhang et al. 1991, Hill 1987) indicate that the ratio for Typha roots-rhizomes-leaves biomass is approximately 1:18:14. Mass calculations for metal uptake by the underground portion of cattails were based on this ratio, though it is recognized that the actual values of the vegetation in the MDNR cells may vary considerably from this ratio due to local climatic and growing conditions.

5.4 Peat samples.

Baseline peat samples were collected in September 1988. Six core samples were collected using a Macauley sampler. Triplicate samples were collected in the center of the cell at the well nest at distances of 4.5 and 14 m from the inlet (Figure 2). Samples were collected at depths of 0 to 20 cm, 20 to 50 cm, and then at 50 cm intervals until mineral soil was encountered.

The peat samples were oven dried at 105° C for 24 hours, processed with a blender to break up clumps, and sieved to minus 80 mesh. Greater than 70% of all the processed samples were less than 80 mesh. All samples were digested using a total digestion procedure, in which 0.5 g of sample was digested with a concentrated acid solution containing 1 mL HCl, 2 mL HNO_3, and 0.5 mL HF at 90°C for 2 h.

In late May 1991, after 2 yr of operation, additional peat samples were collected from the 0 to 20 cm segment and from the 20 to 50 cm segment, at the sites shown in Figure 2. Triplicate samples were collected at several of the sites (for both surface and deep segments) to determine the variability between samples. The deep samples were collected with a Macauley sampler, while the shallow samples were collected with a power soil auger that had been modified to accept a 10-cm-ID stainless steel tube with serrated cutting teeth. Shallow samples that were at first collected with a Macauley sampler were small in volume and difficult to collect due to the loose consistency of the surface peat; in contrast, the power auger samples were larger in volume, and therefore less apt to be influenced by local concentration variations within the peat, and more likely to accurately represent the actual conditions within the cell. These samples were processed and analyzed with the same methods used for the baseline samples (with the exception that a microwave digestion procedure was performed on the 1991 samples).

5.5 Sequential extractions of peat samples.

After 3 yr of operation, another set of peat samples was collected to allow determination of the depth and form of metal removal. These samples were collected with the power soil auger in March 1992 when the wetland was frozen. Three cores were collected at each site, and each core was 20 to 40 cm long. The cores were extracted from the core tube, wrapped in freezer paper, and stored in the freezer. Each core was cut into 2 to 4-cm segments while the core was still frozen. These sections were stored in the freezer until the sequential extraction procedure was performed.

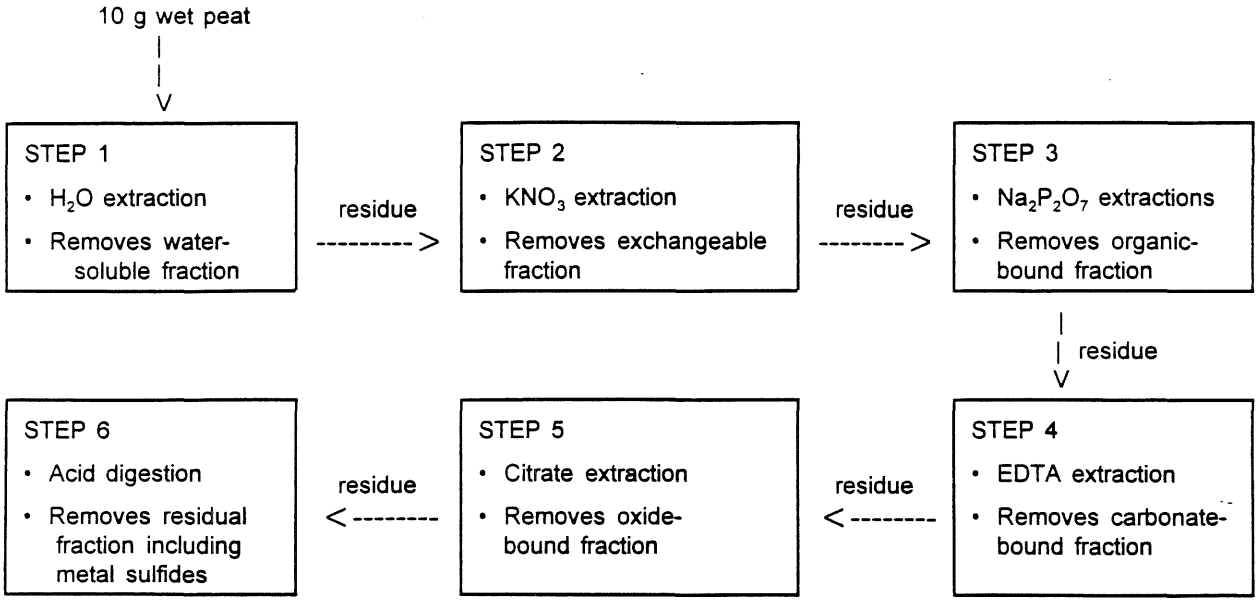
A series of laboratory extraction steps was then used to differentiate the form of the metal in the core (Figure 4). In general, the procedure was the same as the one developed by Wieder (1991, Miller et al., 1983), except that the peat was not rinsed and centrifuged between each step. A comparison of samples run with and without rinsing showed little difference between the results. The only major difference in our extraction procedure was the inclusion of additional pyrophosphate extraction tests. Initial results indicated that a large fraction of metal removal occurred in the carbonate form (EDTA extraction). Since EDTA can also extract metals that are bound to organics, a total of six pyrophosphate extractions were performed to determine if additional metal would be extracted. Based on these results, it was determined that four extraction steps were needed to extract the majority (>90% extraction) of the metals associated with the organics. A 10 g subsample of the substrate was analyzed using a total digestion with HNO_3, HF, and HCl. (Additional information is presented in Appendix 24.)

Section 6. Flow.

6.1. Flow rates.

Initial flow rates were about 3.8 L/min for cells 1 and 2 and 11.4 L/min for cells 3 and 4. These were selected to achieve a residence time in the range of 40 - 48 hours, and were

Figure 4. Sequential extraction procedures used to differentiate the metal forms present in 1992 peat samples.



calculated based on the depth of standing water and the area of the cell. Operational problems in 1989 (which included plugging of flow meters and valves) caused inflow values to vary considerably. Actual flows ranged from about 1.9 L/min (0.5 gpm) to about 18.9 L/min (5gpm) across the four cells (Appendix 11).

In July of 1990, a settling barrel was installed to allow any debris to settle prior to flowing into the cells (Appendix 3). After the barrel was installed, clogging problems were virtually eliminated and the inflows were fairly stable. Inflow rates for cells 1 and 2 generally ranged from 3.8 to 5.3 L/min (1.0-1.4 gpm).

Flow rates were adjusted periodically to study the effect of residence time on metal removal and in an attempt to increase treatment efficiency. Water levels were lowered in both cells 3 and 4 in an attempt to provide better contact between the drainage and the peat substrate. Flow rates and changes in water level are summarized in Table 6.1.1 and a more detailed description of the variation in flow is given in Appendix 11. Figures 5 - 7 depict 1989-91 flow rates vs. time for all four cells.

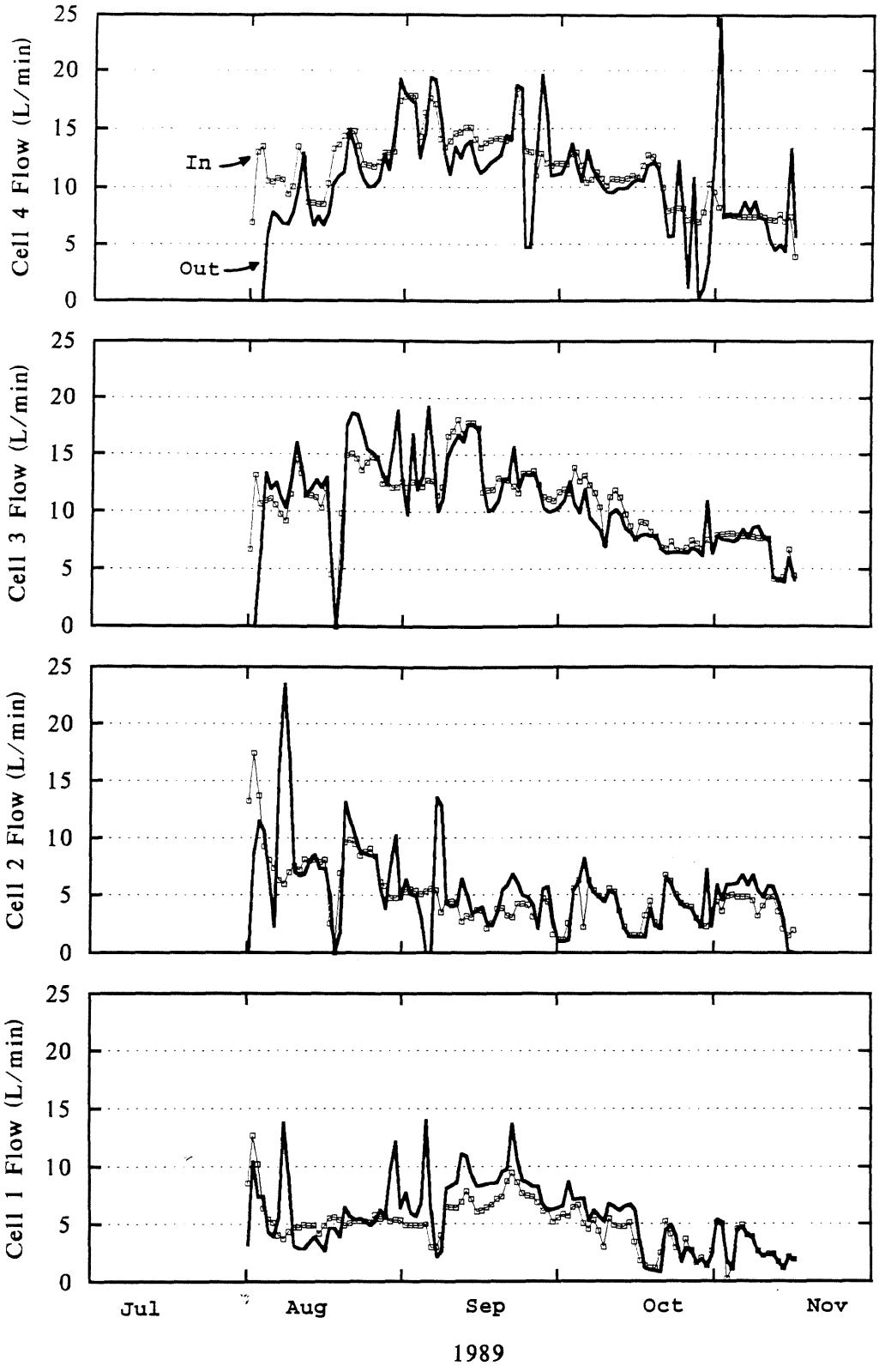


Figure 5. 1989 flow rates vs. time, cells 1-4.

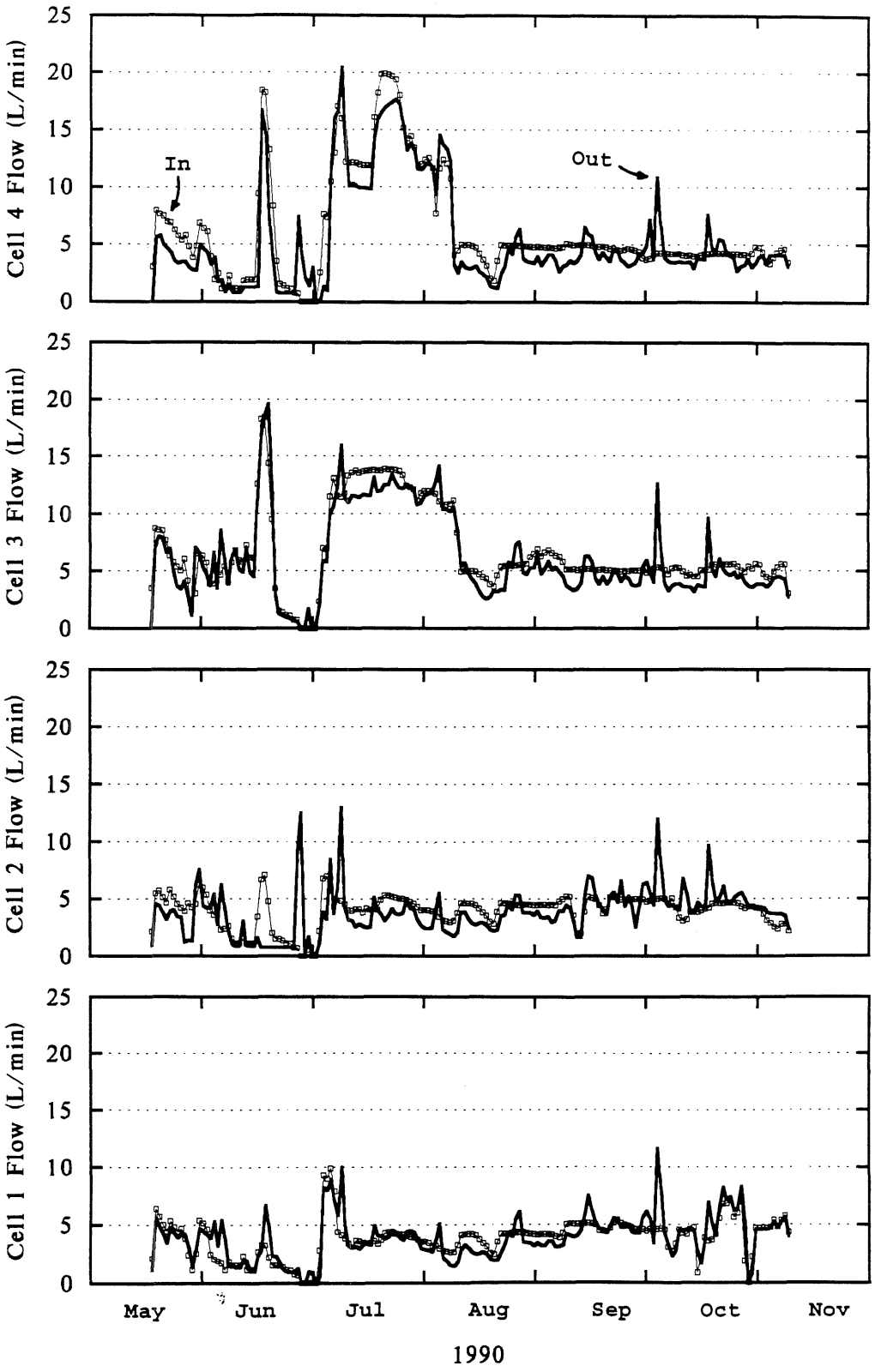


Figure 6. 1990 flow rates vs. time, cells 1-4.

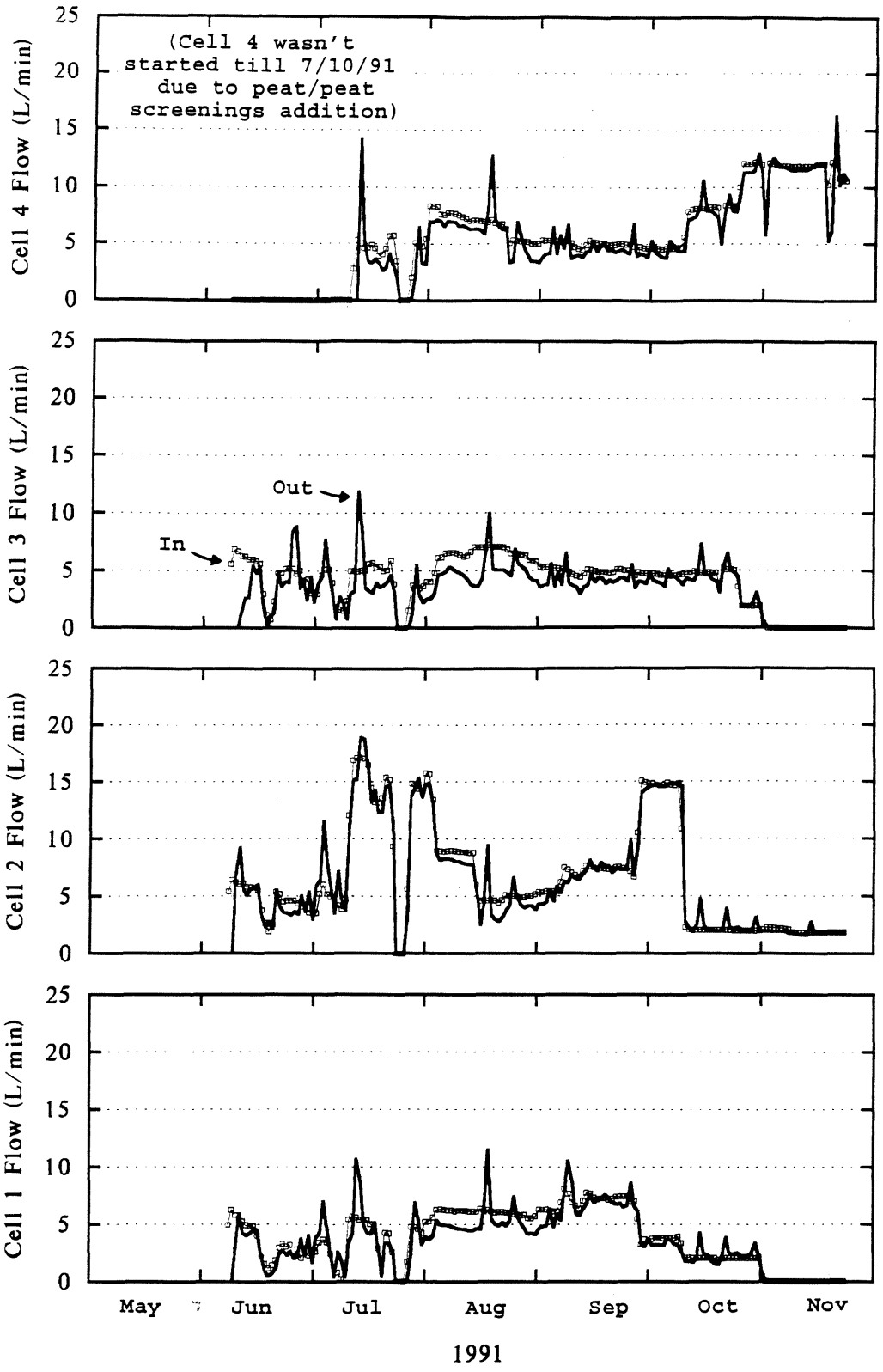


Figure 7. 1991 flow rates vs. time, cells 1-4.

6.2 Residence time

Residence time is a measure of the stockpile drainage's contact time within the wetland treatment system and is defined as the volume of exchangeable water in the cell divided by the flow rate of water through the cell. Residence time increases as the size of the wetland's water volume increases and as the flow into the cell decreases.

Residence time is an important design parameter since it provides a means to calculate an appropriate size for a wetland treatment system. Input metal concentrations are reduced by a smaller percentage in a wetland treatment system with a short residence time as compared to an equivalent system with a longer residence time (Section 7.6). One of the goals of this study was to design a system which would provide the maximum metal removal with a minimum residence time.

Residence times were regulated by adjusting input flow rates into the cells, but were calculated from daily outflow in order to account for changes in flow due to evapotranspiration (ET) and precipitation.

Although residence time is a measure of the time needed to replace the volume of free-standing water in a cell and is a function of inflow rate, it is virtually impossible in the field to get uniform replacement of water across the entire cell. The lack of uniform flow is due to the uneven wetland surface and variations of flow velocity with water depth. The result of the non-uniform flow is that less water is displaced than called for in the design specifications, which means flow velocity in the system is increased, resulting in a shorter residence time and therefore less treatment. Some additional exchange of water probably occurs in the upper portions of the wetland substrate which would increase residence time slightly.

In 1990, dye studies were conducted to determine the effective residence time in each of the cells (Appendix 12). Effective residence times were estimated by measuring the time the dye was added to the time when the peak dye concentration was detected in the outflow of each cell. These values were multiplied by the average flow rates of each cell to determine the exchangeable water volume. The exchangeable water volumes for each cell were calculated from these dye studies so that daily residence times and flow rates needed to achieve desired residence times could be calculated for each cell. The residence times in cells 1 and 2 were 43 and 49 hours, respectively, and were within the design range that was expected to provide adequate removal. The residence times in cells 3 and 4, however, were only 18-22 hours, or about a factor of 2 below the design residence time. Additional tracer studies were conducted in the fall of 1990 and in 1991 to verify residence time estimates (Appendix 12).

Although residence times (flow rates) were relatively constant during the dye studies, there were several situations which caused residence times to vary substantially over the course of the project. These problems included the following:

1. plugging of the feed line to the cells
2. plugging of the input or output flow meters, or both
3. input from precipitation
4. influence of ET

As a result, the residence time of all the cells varied from less than 1 day to around 12 days. A detailed description of these problems and their effects on flow rates and residence time is given in Appendix 12.

6.3 Water balance

Annual water balances were calculated for each cell to determine if the cells were closed systems, and to evaluate the role of evapotranspiration in system performance.

The water balance equation used was as follows:

- Total inflow + precipitation (100% falling on water surface and 50% falling on side slopes of cells) - Total outflow = Total loss (or gain)

Total loss is an estimate of evapotranspiration (ET) and seepage into or out of the cells. It was assumed that the bentonite cutoff walls prevented significant lateral flow into or out of the cells, and that the 1 meter of decomposed peat on top of the silty clay and/or bedrock prevented significant vertical inflow or outflow. Therefore, all of the loss was assumed to be a measure of ET.

Calculated ET values on a seasonal basis are presented in Table 5. In 1990, ET ranged from 0.3 cm/day in cell 1 to 0.9 cm/day in cell 4. In 1991, ET was higher than 1990 in all cells except cell 4. The values ranged from 0.6 cm/day in cell 2 to 1.1 cm/day in cell 3. Cell 4 was unchanged from 1990, which may be due to the later start-up date or the addition of the peat/peat screenings mixture, which decreased the live biomass.

Data from a pan evaporation study conducted in 1990 near the rim of the north pit at the Dunka mine (about 520 meters (1700 ft) W-NW of the plots) was compared to the results from this water balance. The pan evaporation data showed that the average daily evaporation for 1990 (May through October) was 0.37 cm/day (Appendix 26). For this part of northern Minnesota a pan correction factor of 0.78 is generally applied to pan measurements to estimate evaporation from lakes. No correction factor is available for estimating shallow ponds or marshes.

ET in wetlands is quite complex. Although emergent vegetation contributes to the transpiration loss, it shades the water and diminishes evaporation from the water surface, and it is unclear how the presence of emergent vegetation affects the loss of water from a body of water (Mitsch and Gosselink, 1993). Some studies have shown that ET from heavily vegetated water bodies

Table 5. 1989-91 water balances for cells 1-4.

	Cell 1	Cell 2	Cell 3	Cell 4
· 1989 total inflow (m^3)	755	775	1667	1786
· Precipitation* (10.39")	76	74	77	73
· 1989 total outflow (m^3)	878	855	1645	1624
· Loss or gain (-) from ET or Seepage (m^3)	-47	-6	99	235
· Loss per day, n=108, (cm/day)	-0.3	0.0	0.5	1.2
· 1990 total inflow (m^3	964	1002	1709	1579
· Precipitation (16.05")	117	114	119	112
· 1990 total outflow (m^3)	981	964	1575	1395
· Loss or gain (-) from ET or seepage (m^3)	100	152	251	296
· Loss per day, n=176, (cm/day)	0.3	0.5	0.7	0.9
· 1991 total inflow (m^3)	930	1570	1007	1359
· Precipitation (17.30")	125	122	127	81**
· 1991 total outflow (m^3)	862	1532	832	1261
· Loss or gain (-) from ET or seepage (m^3)	193	160	302	179
· Loss per day, n=154,** (cm/day)	0.8	0.6	1.1	0.9

* Precipitation input includes 50% surface runoff from cell watershed. See Appendix 3 for as-built cell dimensions.

** Cell 4 did not start receiving input in 1991 until July 11 because of the addition of 6" of a peat/peat screenings mixture. Cell 4 received 11.59" of rain over 114 days. (The other cells started receiving input on 6/7/91.)

Note 1 The average (1960-1977) Class A pan evaporation at Hoyt Lakes (about 32 km southwest) for the months June - October is 52.12 cm/153 days = 0.34 cm/day. The average for May - October = 64.67 cm/184 days = 0.35 cm/day (Baker et al., 1979).

Note 2 The average Class A pan evaporation at a site 520 meters west for May - October, 1990 was 0.37 cm/day (John Adams, Minnesota Dept. Natural Resources, Division of Waters, unpublished).

may be up to three times the evaporation rate of an open water surface while other studies have shown that vegetation has no or even a negative effect on ET (Idso, 1981, Kadlec, 1993). The overall effect of vegetation on ET is a function of biomass and the transpiration rate of the specific vegetation. Estimated ET in our cells is generally higher than pan evaporation measurements.

The difference between the input and output flow lines in Figures 6.1.1 through 6.1.3 represents water losses believed to be due to ET. The greatest difference occurs in August, with substantial differences also occurring in July and early September. This is consistent with

general climatic conditions for this region. Potential sources of error in the estimate of ET are presented in Appendix 26.

Section 7. Surface water quality.

7.1. Introduction.

The results presented in this section are generally for filtered metal values. In 1989 only filtered samples were analyzed, while in 1990 and 1991, analyses of unfiltered and total digested samples were also conducted. In general, the difference between filtered, unfiltered and total digested values were less than 10% (Appendix 18). For those cases where there was a significant difference between total and filtered values, both are presented.

Concentrations in the outflow of the cells are compared to water quality standards that existed at the time of system construction (1988). It should be noted that these standards have since been modified, and may be modified further in the future. LTV performed bioassay tests which demonstrated that the cobalt standards was too restrictive, and in 1991 the MPCA increased the cobalt standard from 0.005 to 0.050 mg/L. In 1994, the nickel standard was changed from 0.213 to 0.509 mg/L. However, the standards referred to in this paper pertain to the standards that were in place at the time of system construction.

7.2. Input Water

W3D stockpile drainage can be characterized as a high-hardness neutral drainage whose primary contaminant is nickel. Average hardness in the input was around 2300 mg/L as $CaCO_3$, with a pH range of 6.5 - 7.9, and a mean nickel concentration of 1.27 mg/L (1989-1991 data). Copper and zinc concentrations generally met the water quality criteria established by the MPCA, while nickel and cobalt routinely exceeded the criteria, sometimes by almost an order of magnitude (Table 6).

In September/October 1990, two short-term studies were conducted in cell 1. Water from Aquifer X and Seep 1 was trucked to the wetland treatment area and used as input to cell 1 (the other three cells continued to receive W3D input during this time period). These short-term tests are discussed in Section 7.7.

The average input/output water quality data for 1989, 1990 and 1991 are summarized in Tables 7, 8 and 9. The water quality data used to generate these summaries are presented in Appendix 15, box plots are in Appendix 16, concentration vs. time figures are in Appendix 17, quality assurance data is presented in Appendix 19, and summary statistics are presented in Appendix 20. Since nickel is the contaminant of primary concern, it will be discussed in detail after a discussion of the other major parameters (i.e. pH, SO_4, Cu, Co, Zn and the major cations Ca, Mg, Na and K).

Table 6. Input water (W3D) quality summary and comparison to (1988) MPCA water quality standards. (The data presented refer to the input water quality as it enters the treatment cells, which is not necessarily the same as the water quality at the W3D seep itself.)

Parameter	Concentrations (mg/L)		
	W3D Drainage		MPCA Standards
	Average	Range	
pH (s.u.)	7.24	6.5 - 7.9	6.5-8.5
Copper	0.017	0.002 - 0.25	0.013
Cobalt	0.025	0.003 - 0.047*	0.005
Nickel	1.27	0.11 - 3.84	0.213
Zinc	0.033	0.01 - 0.12	0.149
Specific conductance (μmhos/cm)	3805	2600 - >5000	1000
Hardness+	2360	1890 - 2590	250

* This is the second highest value observed; the maximum value was 0.170 which appears to be an anomaly.
\+ Calculated from calcium and magnesium (hardness = 2.5*Ca + 4.2*Mg)

This table includes data from 8/1/89 - 11/15/89, 5/22/90 - 11/7/90, and 6/13/91 - 11/22/91.

7.3. Water quality results.

Water quality results for all the cells are summarized by year in Tables 7, 8 and 9. Individual parameters are discussed in the following separate subsections.

7.3.1. pH.

The pH of the input water (W3D) was relatively constant over the course of the study, ranging from 6.5 to 7.9, with a mean value of 7.24. The pH of the output water from each treatment cell was generally about 0.1 to 0.3 units less than the corresponding input pH values (Appendix 17). The only exception to this was in cell 4 during 1991, at which time the output pH values were up to 1.5 units less than the corresponding input pH values, a result of the peat/peat screenings amendment to the cell prior to the 1991 season (Figure 8). At the beginning of

Table 7. 1989 surface water quality summary (average concentrations of input and cell outflows).

Site	pH	S.C.	Alk	Acy	Net Alk	Cu	Ni	Co	Zn	Ca	Mg	Na	K	Mn	Fe	SO_4	% Ni removal
Input	7.21	3390	104	23	82	0.009	0.62	0.007	0.03	392	308	118	10	0.27	0.09	2510	--
Cell 1	6.86	3290	107	38	69	*	0.11	0.007	0.02	370	298	115	8	0.23	0.19	2460	82
Cell 2	6.95	3310	111	34	77	0.009	0.08	0.005	0.02	367	293	116	9	0.32	0.19	2430	87
Cell 3	6.89	3350	130	41	89	0.008	0.23	0.005	0.02	380	302	115	12	0.28	0.32	2430	63
Cell 4	7.07	3330	103	29	75	0.008	0.50	0.005	0.02	378	300	113	9	0.20	0.08	2430	19

* Copper concentrations in outflow were significantly greater than inflow values; see Appendix 16.

Note: Metals values are in mg/L, pH values are in standard units, and specific conductance (SC) values are in μmhos/cm.

Table 8. 1990 surface water quality summary (average concentrations of input and cell outflows).

Site	Time Period	pH	s.c	Alk	Acy	Net Alk	Cu	Ni	Co	Zn	Ca	Mg	Na	K	Mn	Fe	SO_4	% Ni removal
Input	May 22 to Sept. 17	7.33	3850	90	24	66	0.010	0.71	0.020	0.03	374	337	120	11	0.30	0.06	2350	--
Cell 1		6.97	3750	112	38	74	0.008	0.06	0.017	0.01	354	319	118	8	0.24	0.20	2290	92
Cell 2		7.09	3860	100	29	74	0.008	0.08	0.019	0.02	363	327	120	9	0.25	0.18	2300	89
Cell 3		7.10	3830	112	29	84	0.008	0.16	0.018	0.02	363	325	118	11	0.27	0.16	2280	77
Cell 4		7.08	3780	91	25	67	0.010	0.38	0.017	0.02	357	316	115	9	0.16	0.08	2230	46
Input	May 22 to Nov. 7	7.33	3760	85	21	64	0.010	0.76	0.025	0.03	371	327	119	11	0.27	0.06	2320	
Cell 2		7.08	3780	94	26	69	0.009	0.10	0.017	0.02	362	321	118	9	0.22	0.18	2280	87
Cell 3		7.11	3730	101	24	77	0.009	0.23	0.017	0.02	359	316	116	10.	0.24	0.13	2220	70
Cell 4		7.08	3710	86	22	64	0.010	0.41	0.016	0.02	356	310	114	9	0.15	0.09	2200	46

Note: Water quality data for two time periods are presented because of the short-term tests (the Seep 1 and Aquifer X tests) conducted in cell 1 from 9/17/90 to 10/26/90. Until September 17, all four cells received W2D input water.

Metals values are in mg/L, pH values are in standard units, and specific conductance (SC) values are in μmhos/cm.

Table 9. 1991 surface water quality summary (average concentrations of input and cell outflows).

Site	pH	S.C.	Alk	Acy	Net Alk	Cu	Ni	Co	Zn	Ca	Mg	Na	K	Mn	Fe	SO_4	% Ni removal
Input	7.12	4480	71	23	48	0.035	1.99	0.015	0.062	425	377	117	9.2	0.12	0.04	2430	--
Cell 1	6.84	4390	98	31	67	0.007	0.92	0.008	0.025	407	366	113	7.4	0.37	0.27	2390	54
Cell 2	6.94	4500	91	25	66	0.006	0.92	0.008	0.024	408	358	110	7.8	0.17	0.27	2330	54
Cell 3	6.92	4460	92	25	67	0.007	0.58	0.007	0.014	414	362	112	8.0	0.21	0.36	2420	71
Input	7.11	4510	67	23	44	0.039	1.92	0.010	0.046	426	380	115	9.1	0.05	0.04	2450	--
4	6.31	4000	60	43	17	0.008	0.49	0.009	0.019	368	312	99	8.2	1.29	2.61	2280	74

Note: Metals values are in mg/L, pH values are in standard units, and specific conductance (SC) values are in μmhos/cm. Cell 4 was started later than the other 3 cells in 1991 due to the addition of peat/peat screenings to the cell in June. The input values that appear above the cell 4 results reflect only the data after the time of cell 4 start-up, while the input values shown at the top of the table include the entire data set for 1991.

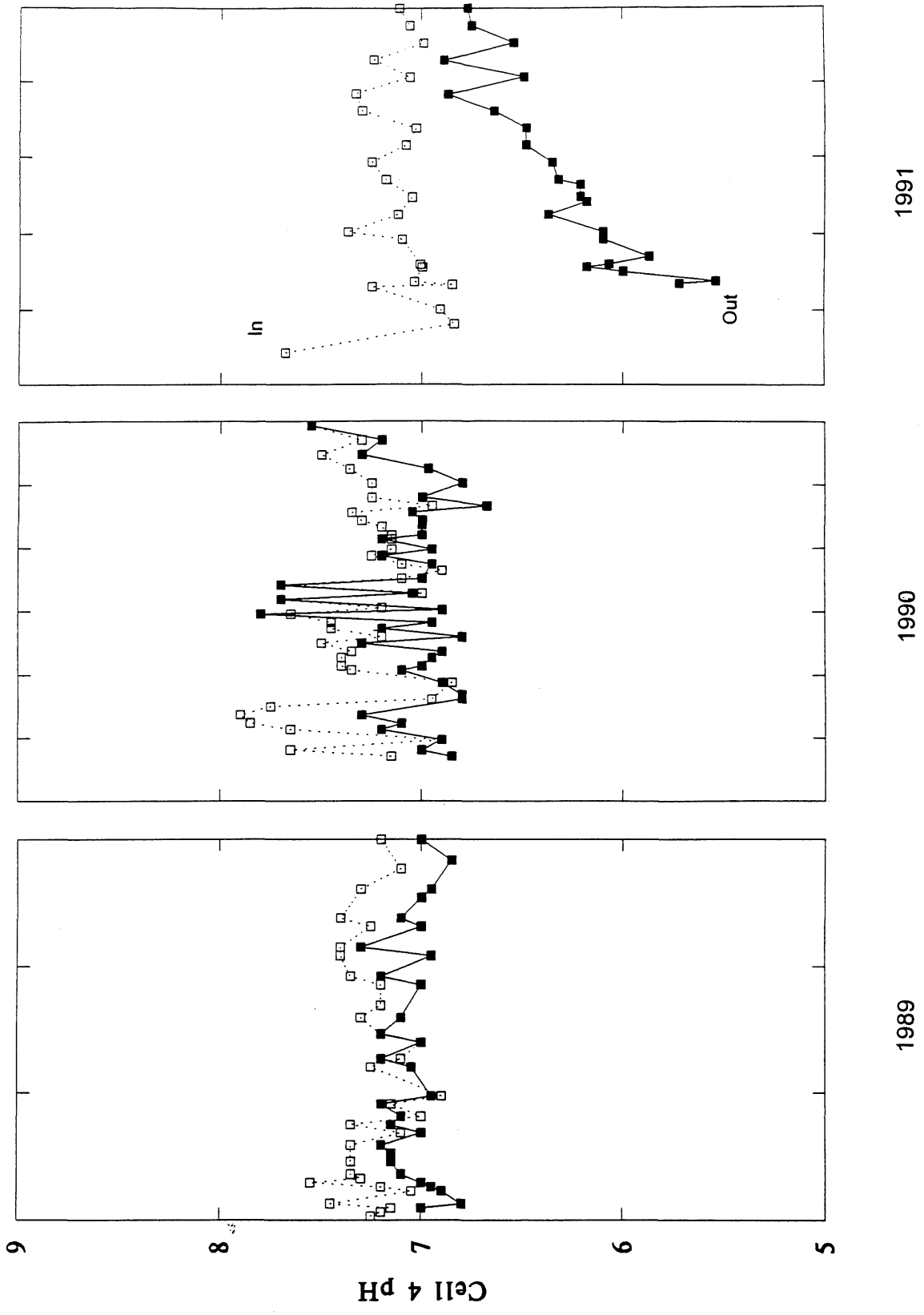


Figure 8. Cell 4 pH vs. time (1989-91).

the 1991 season, output pH values from cell 4 were about 5.5 while input values were about 7.0. During the course of the season this difference became smaller, and by the end of the year the output values were about 0.1 to 0.3 units less than the input values.

7.3.2. Sulfate.

Output sulfate concentrations were generally less than or equal to input concentrations (Appendix 17). Box plots comparing the input to the output from each cell failed to demonstrate a significant decrease in the sulfate concentrations from any of the cells (Appendix 16).

7.3.3 Major cations (Ca, Mg, Na, K).

In cells 1, 2 and 3, there was no statistically significant difference between 1989-91 input and output concentrations of the major cations; calcium, magnesium, sodium and potassium. (See Appendices 15-20 for details.) Output concentrations of these four parameters closely reflected the corresponding input concentrations, indicating that little removal (or addition) of these parameters occurred as the result of drainage flowing through the wetland cells.

In each of these three cells, however, there was a short period in the beginning of the field season in which the output concentrations of these parameters were noticeably lower than the corresponding input values. This phenomenon was likely the result of dilution; water that had accumulated in the cell prior to system startup probably combined with the input water early in the field season. Concentrations of the major cations in this 'storage' water would be very low, since it was the result of snow and rain, and the storage water diluted the initial pulse of input water as it moved through the cells. Output concentrations generally approached input concentrations within one to two weeks.

Cell 4 also generally showed no difference in input/output concentrations of these parameters (except for the above-mentioned early season effect), but in 1991 there was a large difference in the first part of the season, during which time the output concentrations were substantially lower than the input concentrations. Prior to start-up in 1991, a 15 cm (6 inch) mixture of peat and peat screenings had been added to the cell in an attempt to improve performance (see Section 4). About 9 cm (3.5 inches) of rain had fallen the week before the new peat mixture was added, and an additional 5 cm (2 inches) fell immediately after the peat addition. As a result there was a substantial amount of dilution water contained within the cell and within the pores of the new substrate. Some removal of calcium and magnesium could also have occurred through ion exchange with the new substrate.

7.3.4. Copper.

During 1989 and 1990, copper concentrations in the input water averaged 0.010 mg/L, and there was little to no difference between input and output copper concentrations in any of the four treatment cells. The only measurable copper removal occurred in cell 1 during the September/October 1991 short term tests which used drainage from Aquifer X and Seep 1 as input water (see Section 7.7).

In 1991, the average copper concentration in the input increased to 0.035 mg/L and all four cells removed measurable amounts of copper (percent removal was about 80% for all cells). Output copper concentrations were generally less than the PCA standard of 0.013 mg/L until fall when several values exceeded the standard. The maximum output value was 0.026 mg/L, which was observed in the outflow of cell 3 on November 13. Average copper concentrations in all the cells were below the PCA standard (Table 6.1.4).

7.3.5. Cobalt.

Cobalt removal efficiencies closely paralleled those observed for copper; there was little to no removal during 1989-90, but in 1991 all four cells removed cobalt from the input drainage. Percent removal ranged from 10% in cell 4, to 50% in cells 1 ,2 and 3. None of the output concentrations routinely met the proposed standard of 0.005 mg/L, and the average values for each of the cells exceeded the standard by about 50%.

7.3.6. Zinc.

In general, all four cells removed zinc from the input drainage. Except for cells 1 and 4 in 1989, there were statistically significant differences between the input and output zinc concentrations in all four cells during all three years; 1989, 1990 and 1991. (Cell 1 showed very little difference between the input and output concentrations during 1989, while cell 4 showed some difference, but not enough to be statistically significant.) Percent removal was about 33% for all four cells. In 1991, zinc input concentrations doubled from about 0.03 to 0.06 mg/L and the percent removal also increased. Percent removal ranged from 60% in cells 1,2 and 4, to around 75% in cell 3. Zinc removal appeared to be independent of water level and flow rate/residence time effects.

7.3.7. Nickel.

W3D drainage was used for input water to cells 2, 3 and 4 during the entire duration of the study. Cell 1 received primarily W3D drainage as well, but two short term tests were conducted in the cell in the fall of 1990 which used water from Seep 1 and Aquifer X as input to the cell (Section 7.7). Metal concentrations in the W3D drainage had fallen below 0.2 mg/L by

September 1990, and the short-term tests in cell 1 were initiated to observe the effects of higher metal concentrations and decreased residence time on effluent water quality. Prior to the 1991 field season, input concentrations were increased by changing the location of the input pipe at the stockpile (Appendix 2).

In 1991 a series of residence time tests were run on cell 2, and new material was added to cell 4. The effects of these changes are discussed in Section 7.6.

All four cells were successful in removing nickel from the input water, but cells 1 and 2 were considerably more effective than cells 3 and 4 during 1989 and 1990. The overall change in nickel concentration in 1989 and 1990 ranged from 82-92% in cells 1 and 2, to 63-77% in cell 3 and 19-46% in cell 4.

Figures 9, 10, 11 and 12 depict input/output nickel concentrations and residence time vs. time for each of the four cells. The following is a summary of input/output nickel concentrations vs. time for each cell:

Cell 1

1989 Cell 1 performed very well in the first year of operation (1989), with all but one output nickel concentration value (n=35) less than the proposed MPCA standard of 0.213 mg/L, even though input concentrations had steadily increased from about 0.2 mg/L on August 28 to about 1.2 mg/L by November 15. Overall nickel concentrations were reduced by 82%. The percent removal was fairly constant throughout the year and no seasonal effects on metal removal performance was observed.

1990 The cell again removed about 92% of the input nickel until October 1, at which time the short-term tests with Seep 1 and Aquifer X water were initiated. Nickel concentrations in the W3D input had steadily dropped throughout the summer until they were less than 0.2 mg/L, which resulted in an insufficient metal load to the cells. The tests with Aquifer X and Seep 1 were conducted to examine the ability of the wetland treatment system to treat drainage with higher metal concentrations. The results of these tests are discussed in Section 7.7.

1991 When the source of the input water was changed (Section 4) nickel concentrations into the cell increased by about a factor of 3. Input nickel concentrations averaged about 2.0 mg/L during 1991, with a high of almost 4.0 mg/L early in the season. Nickel concentrations in the output were generally on the order of ~ 0.1 - 0.3 mg/L until about September 1, at which time output concentrations increased to around 1.2 mg/L. Overall nickel concentrations were reduced by about 54%, although removal averaged around 90% prior to September.

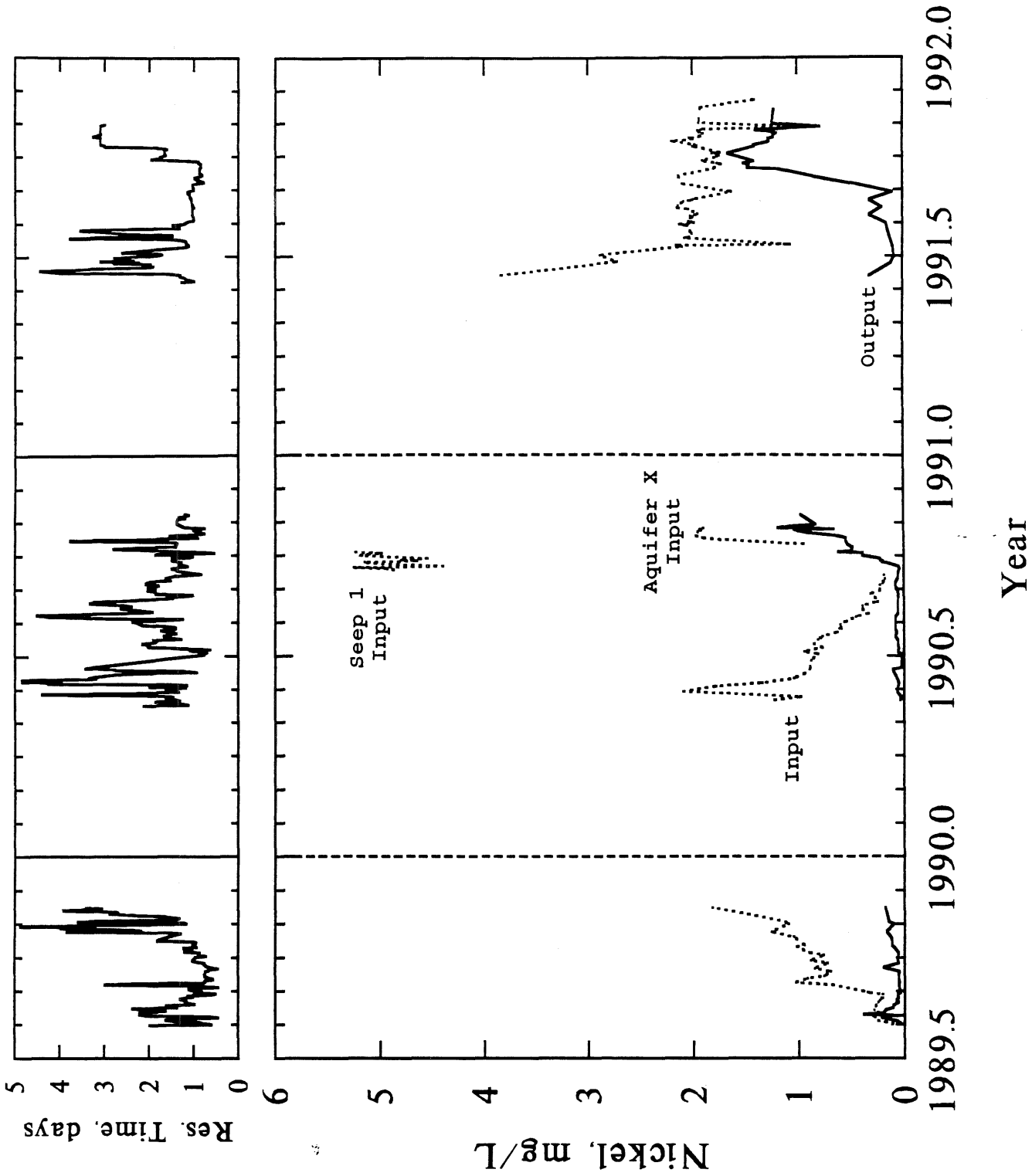


Figure 9. Cell 1 input/output nickel concentrations and residence times.

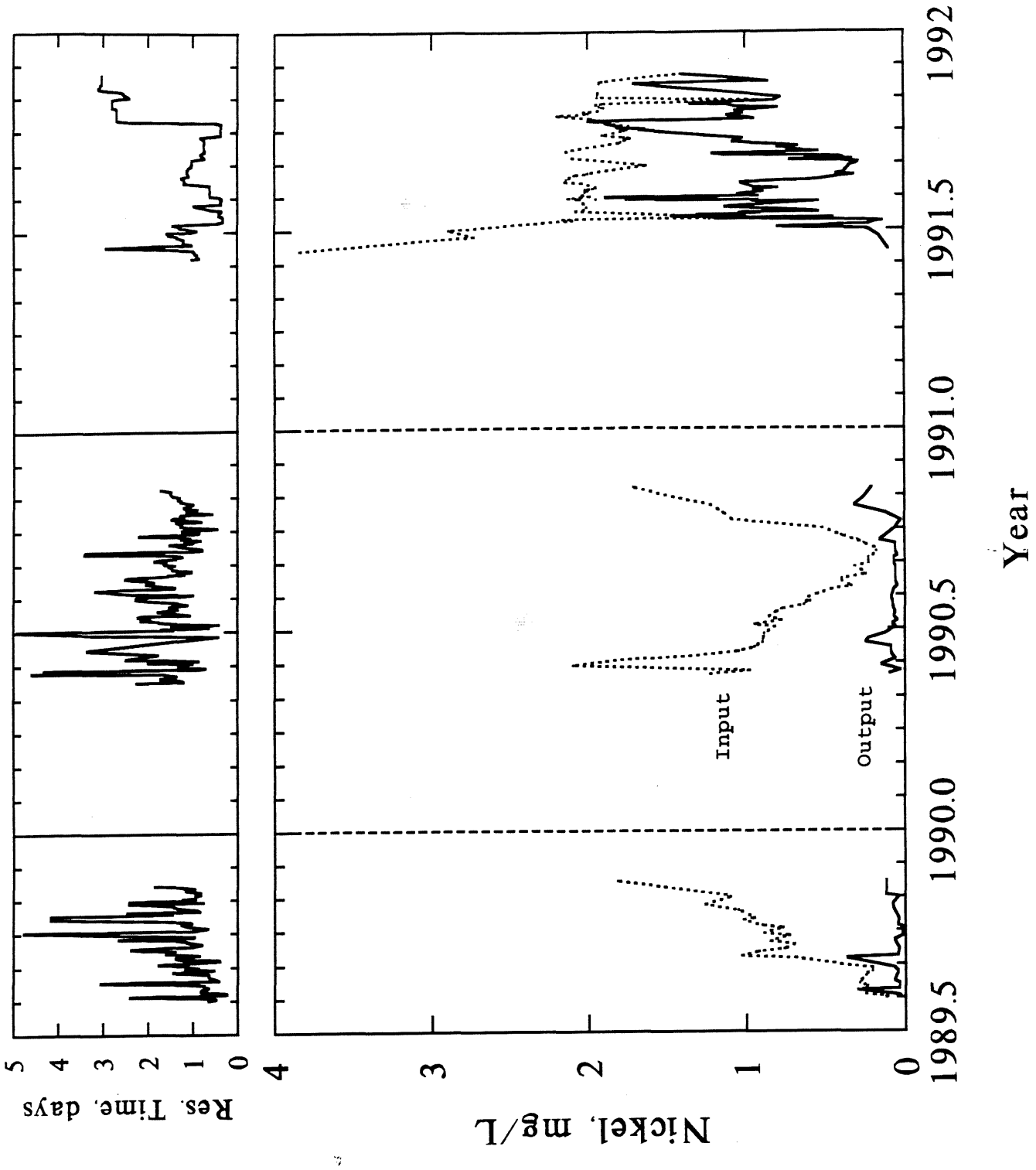


Figure 10. Cell 2 input/output nickel concentrations and residence times.

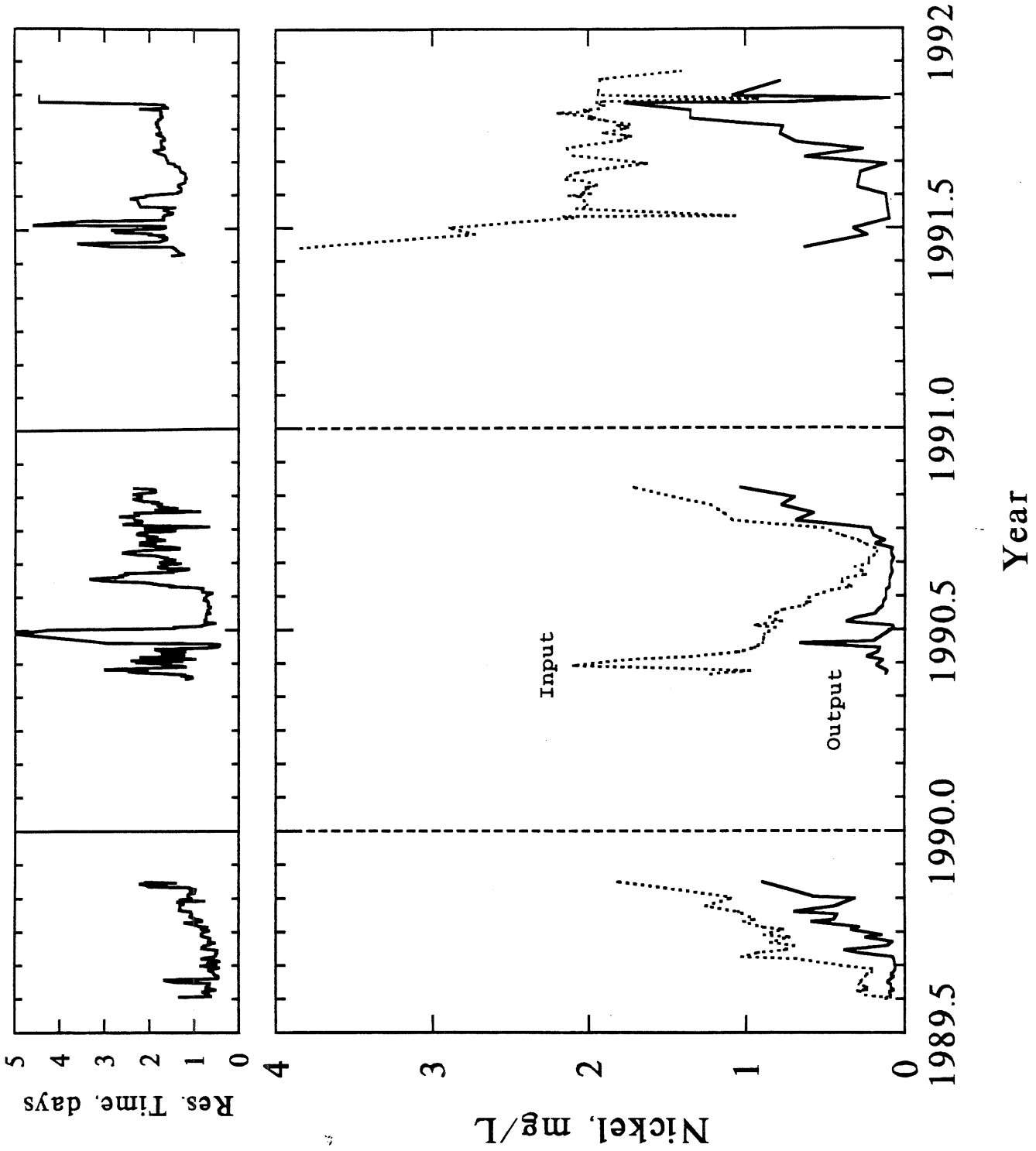


Figure 11. Cell 3 input/output nickel concentrations and residence times.

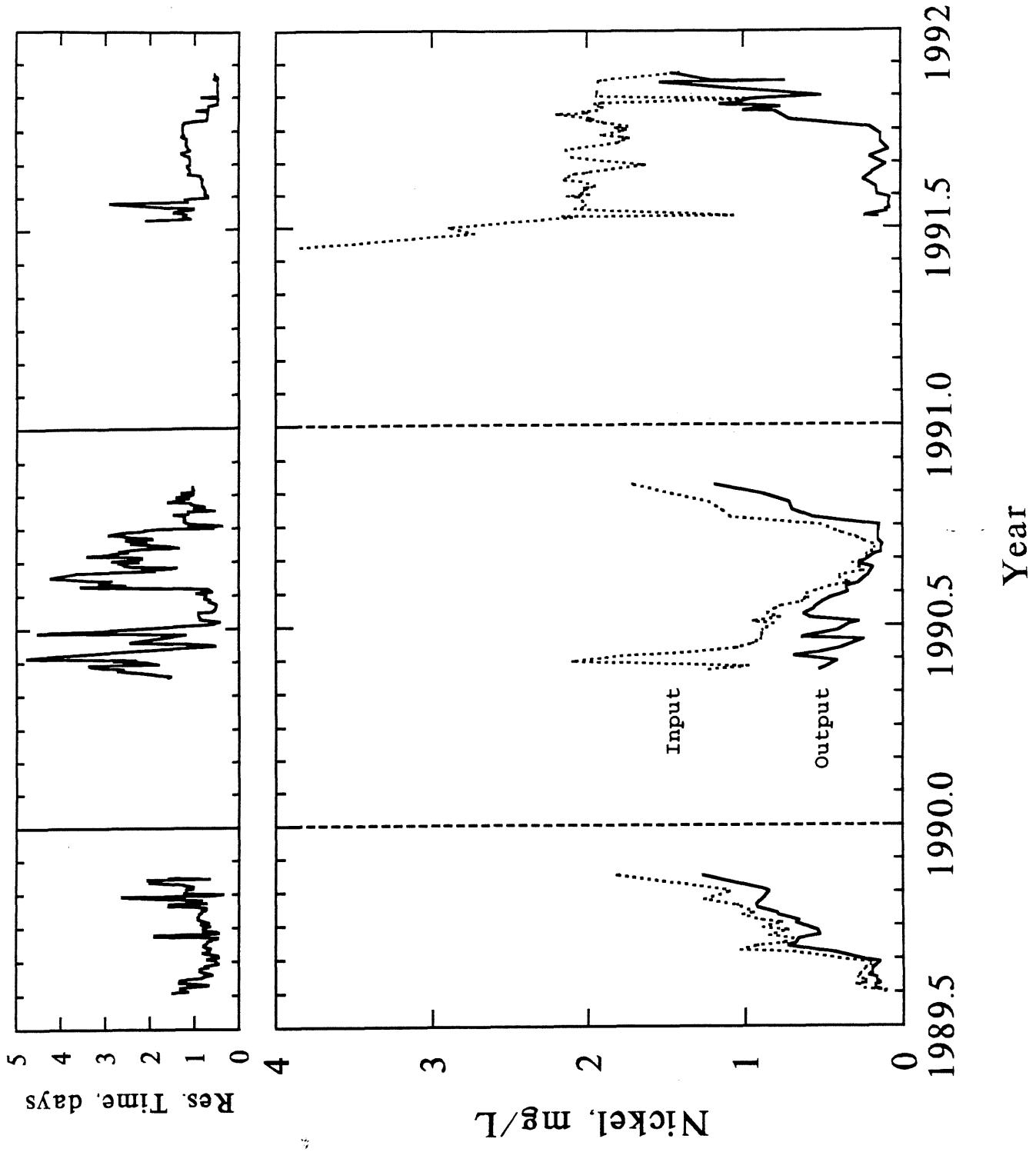


Figure 12. Cell 4 input/output nickel concentrations and residence times.

Cell 2

1989 Like the other shallow water cell (cell 1), cell 2 generally performed very well in 1989, with only 3 of 29 samples over the 0.213 mg/L proposed standard, even though input concentrations had risen from ~0.2 mg/L on August 28 to ~1.2 by the end of the season. Nickel concentrations were decreased by 87% by the cell. No seasonal effects on system performance were observed.

1990 The cell again performed very well, with nickel concentrations dropping by 89%. Output concentrations increased slightly in the fall, from less than 0.1 mg/L to around 0.2 mg/L.

1991 In 1991, residence time was altered in cell 2, with residence times ranging from 12 to 96 hours. The purpose of these tests was to collect data on the effect of residence time on metal removal. As a result of these tests, the reduction of nickel concentration in cell 2 decreased. The results are discussed more fully in section 7.6. Almost all output concentrations exceeded the 0.213 proposed standard (Appendix 17).

Cell 3

1989 Nickel concentration decreased by 63%, a smaller removal than measured in either cells 1 or 2. Input concentrations increased from about 0.2 mg/L on August 28 to about 1.2 by November 15, and output concentrations displayed a similar trend, increasing from 0.08 on September 12 to 0.9 mg/L by November 15. Output concentrations increased over the course of the year with concentrations increasing in the fall.

1990 The cell performed quite well in the first part of the year, averaging about 0.1 mg/L while input concentrations decreased from about 1.0 mg/L to about 0.2 mg/L by September 13. After September 13, both input/output concentrations rose considerably. Overall nickel concentrations were decreased by 77%.

1991 Even though input concentrations were higher (due to new collection point at W3D), output concentrations were lower, and overall concentrations were decreased by 71%. From September 1 and on, however, output concentrations rose dramatically, even though input concentrations remained relatively constant.

Cell 4

1989 In 1989, output concentrations were quite similar to corresponding input concentrations, indicating that little removal was occurring in the cell. The overall reduction in nickel was only 19%.

1990 Nickel concentrations decreased by 46% in 1990, but this removal was significantly less than the removal that occurred in the other three cells over this same time period. By the time

input concentrations had decreased to about 0.2 mg/L in mid-September, removal was essentially negligible, and during the remainder of the season, when input concentrations increased from about 0.2 mg/L to about 1.8 mg/L, output concentrations followed a very similar trend, with little metal removal occurring. In August 1990, the input flow rate was decreased from around 11 L/min to 4 L/min (3 gpm to 1 gpm), but since input concentrations were so low, no improvement in removal was observed. In September the water level in the cell was lowered by about 5 cm (2 inches). This was to provide better contact with the peat, but again there was no improvement in removal efficiency.

1991 A layer of peat/peat screenings was added to cell 4 (at a depth of about 15 cm) prior to the start of the 1991 season (July 11 for this cell) and resulted in a dramatic increase in the metal removal performance of this cell. Even though input concentrations were consistently about 2.0 mg/L during most of the 1991 season, output concentrations consistently stayed below 0.2 mg/L, and nickel removal averaged over 90%. In October, input flow was increased from 4.5 L/min to 8.3 L/min (1.2 to 2.2 gpm), and then to 12 L/min (3.2 gpm), and removal decreased to around 50%. (Only 1 of 18 samples collected during from the time of system start-up to October 5 exceeded the proposed MPCA standard of 0.213 mg/L, while all 13 samples collected after October 5 were above the standard.)

7.4. Nickel concentrations in surface water within the cells.

Several types of surface water samples were taken within the cell to examine the variation of concentration within the cell. In 1990 and 1991, surface water samples were taken at each of the 2 well sites that were located 4.5 m (15') from the inlet side (and 1/2 the width of the cell), and at 14 m (45') from the inlet side. In September 1991 a more detailed survey examined the variation of concentrations across the width of the cell as well as across the length (Figures 13, 14 and 15). This data indicated that 1) concentrations varied across the width of the cell by factors of from 2 to 10, and 2) that concentrations increased in the cell during the month (i.e. the zones of high concentration within the cells spread). These changes are most noticeable in the 1991 data set, when input concentrations were at their highest, around 2 mg/L. In 1990 input concentrations generally decreased throughout the field season, and when the samples were collected the input concentrations were less than 0.5 mg/L (Appendix 15).

7.5. Seasonal effects on metal removal performance.

Although the data is not totally consistent with respect to the performance of the wetland cells as a function of season, there does seem to be some evidence that metal removal efficiency can decrease when temperatures decrease in the fall. This loss of performance seems to be particularly noticeable when input concentrations are elevated, on the order of several mg/L. Evidence for this seasonal effect on system performance include:

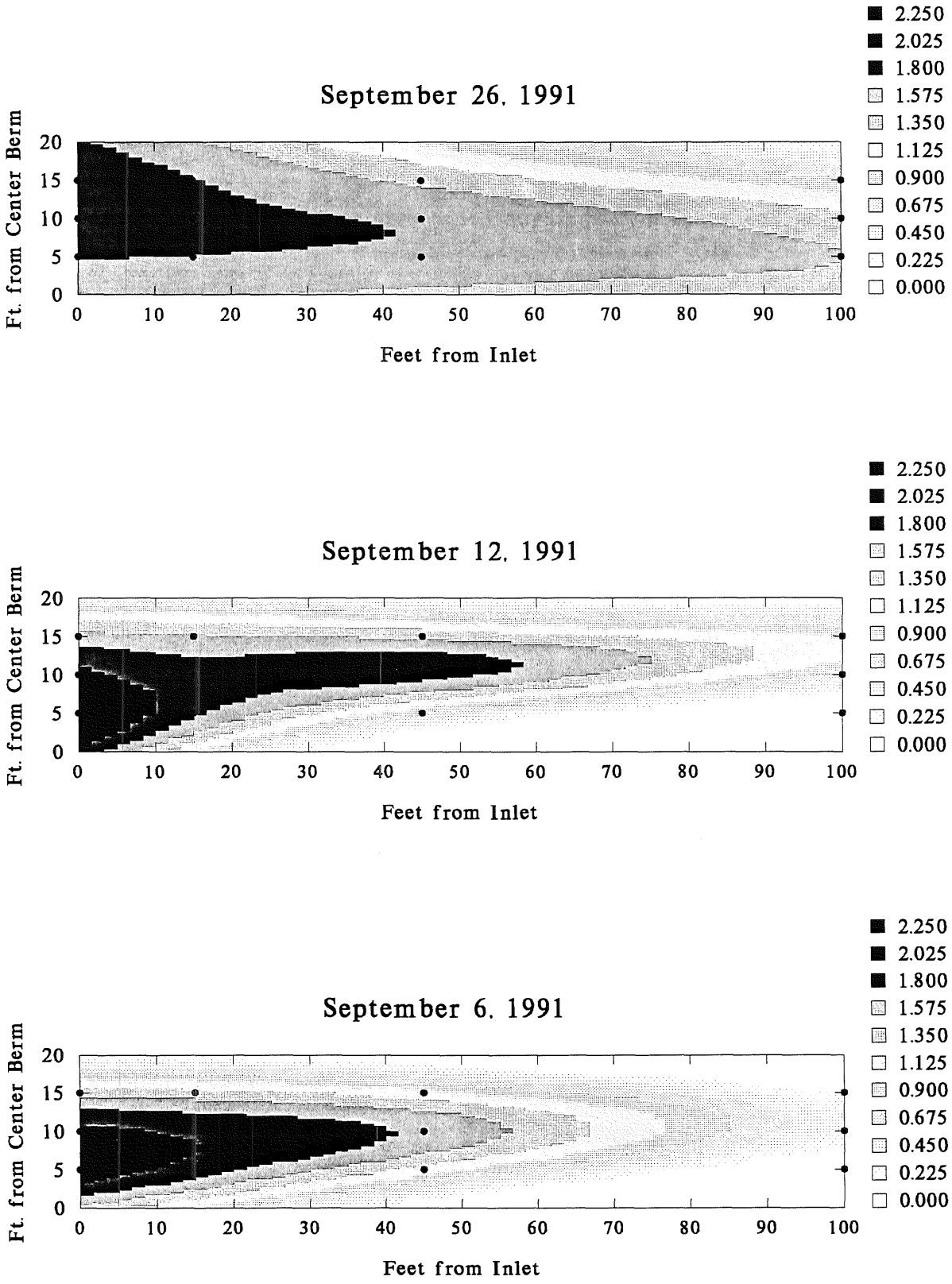


Figure 13. Cell 1 surface nickel concentrations (September, 1991).

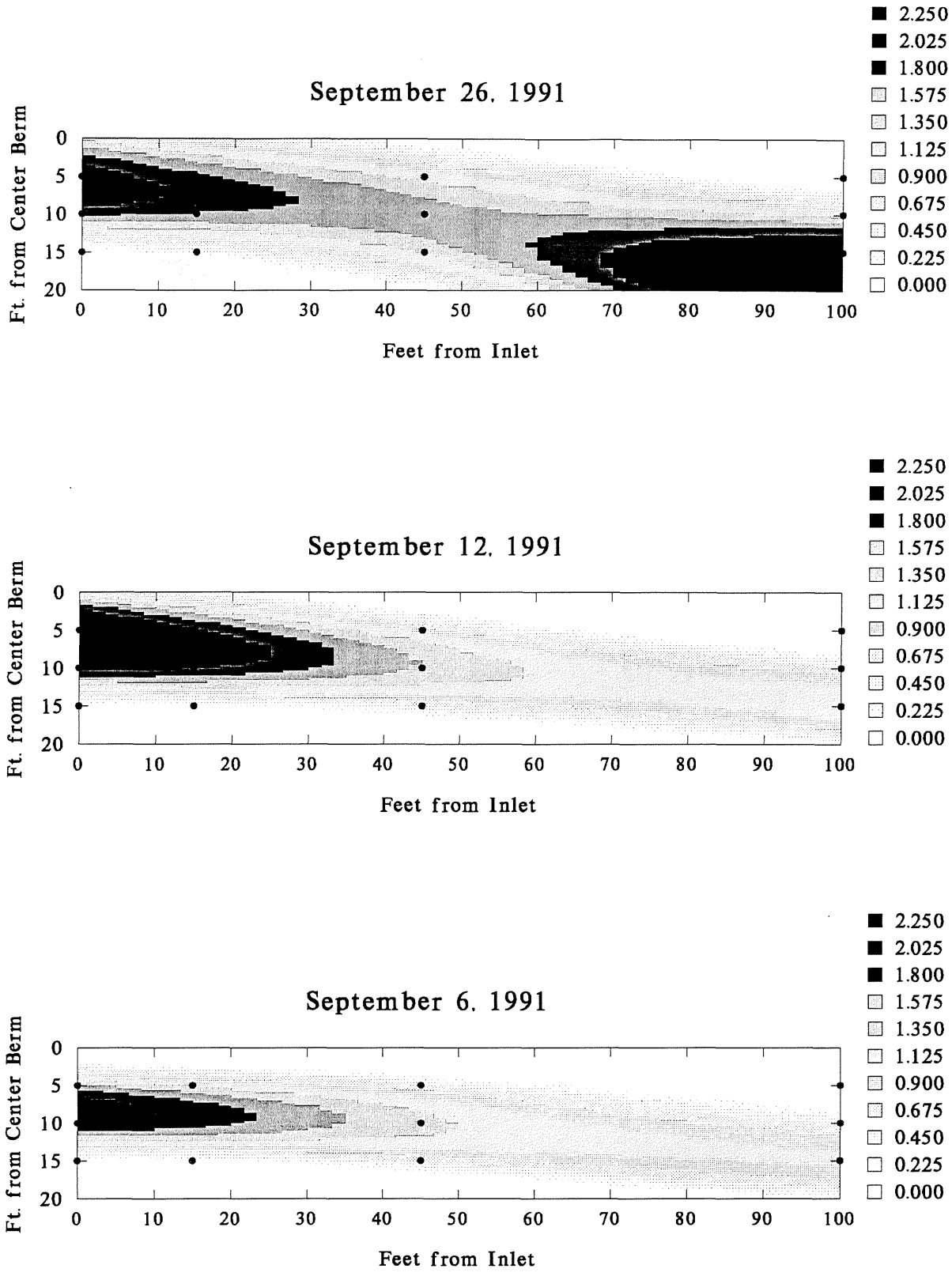


Figure 14. Cell 2 surface nickel concentrations (September, 1991).

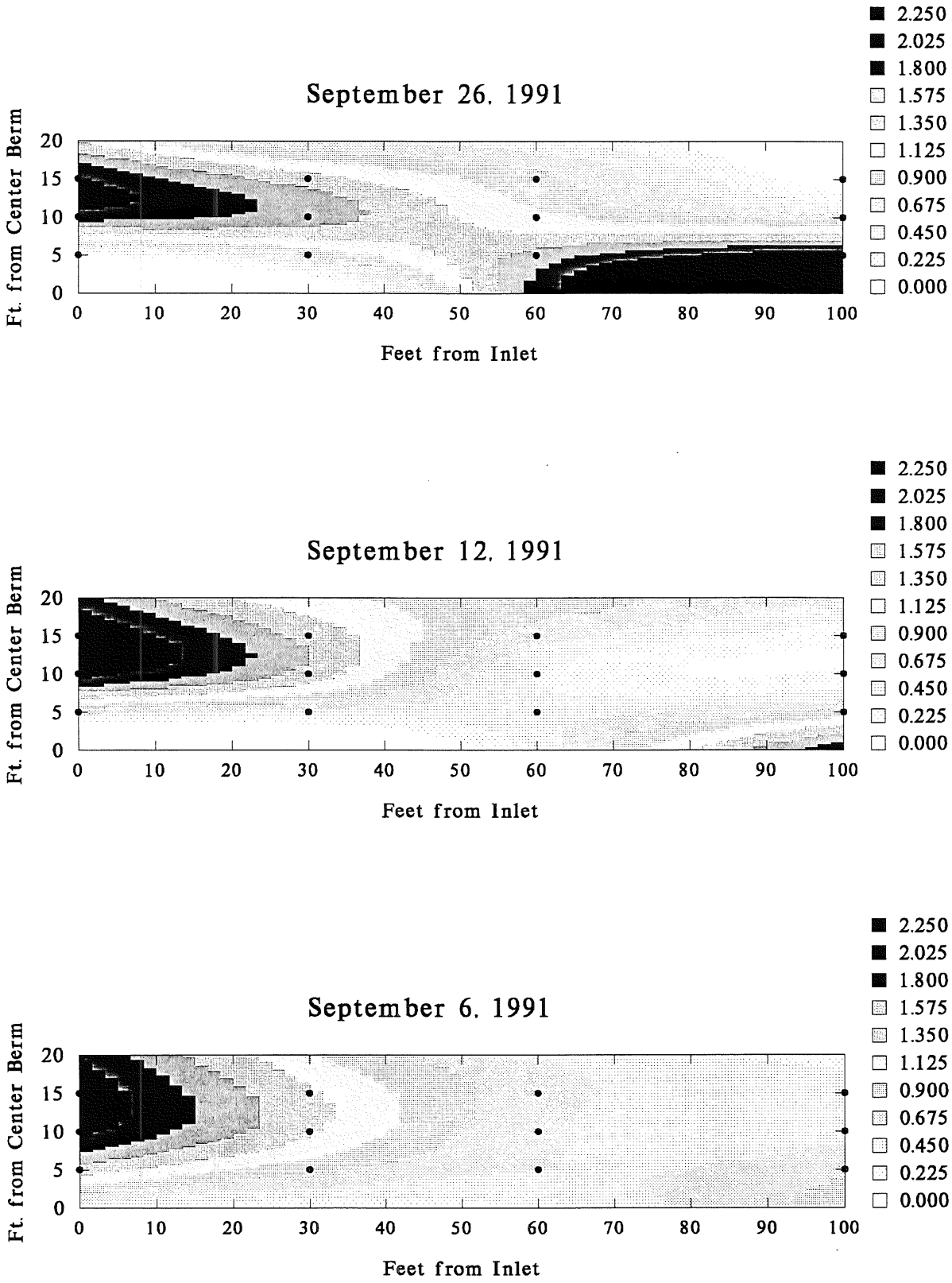


Figure 15. Cell 3 surface nickel concentrations (September, 1991).

- Removal performance decreased dramatically in cell 1 in the fall of 1991, even when residence time and input concentrations remained constant. Output increased from the 0.2 - 0.3 mg/L range to about 1.5 mg/L, even though the input concentration remained at about 2 mg/L, and even though average residence time increased from about 1 day to about 2-3 days.

- System performance was often much more efficient after system start-up in spring/summer than in the fall, even when input concentrations and residence times were similar to the fall values. For example, in the spring of 1990, input concentrations and residence times in cell 3 were similar to the last 1989 values, yet metal removal performance was considerably better in spring 1990 (Figure 7.3.7.3).

7.6. Residence time effects on metal removal performance.

Although the residence time varied in all cells, specific controlled tests were conducted during 1991 in cell 2 to examine the effect of residence time on metal removal. Flows to the cell were adjusted to provide residence times ranging from 12 to 96 hours, with most of the data being collected in the range of 12 to 48 hours. Figures 16 and 17 summarize the output concentration as a function of residence time in the cell.

Outflow nickel concentrations generally increased as residence time decreased. Concentrations in cell 2 increased from around 0.2 mg/L at a residence time of around 36 hours to over 1 mg/L when the residence time was decreased to 12 hours. Based on 1990 data, residence time had a larger effect on the outflow concentration when the input concentration exceeded 1 mg/L. At input concentrations below 1 mg/L the cell 2 outflow concentration appeared to be independent of the residence time (Figure 18).

In the fall of 1991, outflow concentrations in cell 2 increased despite increased residence times. Nickel concentrations increased to over 1 mg/L despite residence times of 66 hours. At a residence time of 12 hours the outflow concentration was 1.7 mg/L in the fall, but at similar residence times in the summer the concentration was around 1 mg/L. Although no specific tests were conducted on cell 1, the same general trends as those found in cell 2 were observed (Figure 19). Again, the higher outflow concentrations in the fall appear to be more related to loss of treatment efficiency in the fall (i.e. the seasonal effect) than to residence time effects.

In cell 4 in 1991, residence time was not changed until October. Although there does seem to be a seasonal effect (i.e. concentrations are higher at comparable residence times), there also seemed to be a decrease in efficiency as the residence time decreased (Figure 20). Nickel concentrations in cell 4 met the water quality standard at much shorter residence times than the other cells. Nickel concentrations in cell 4 were below 0.2 mg/L at residence times as low as 16 hours, while in cell 2 the nickel exceeded 0.2 mg/L when residence time fell below 36 hours.

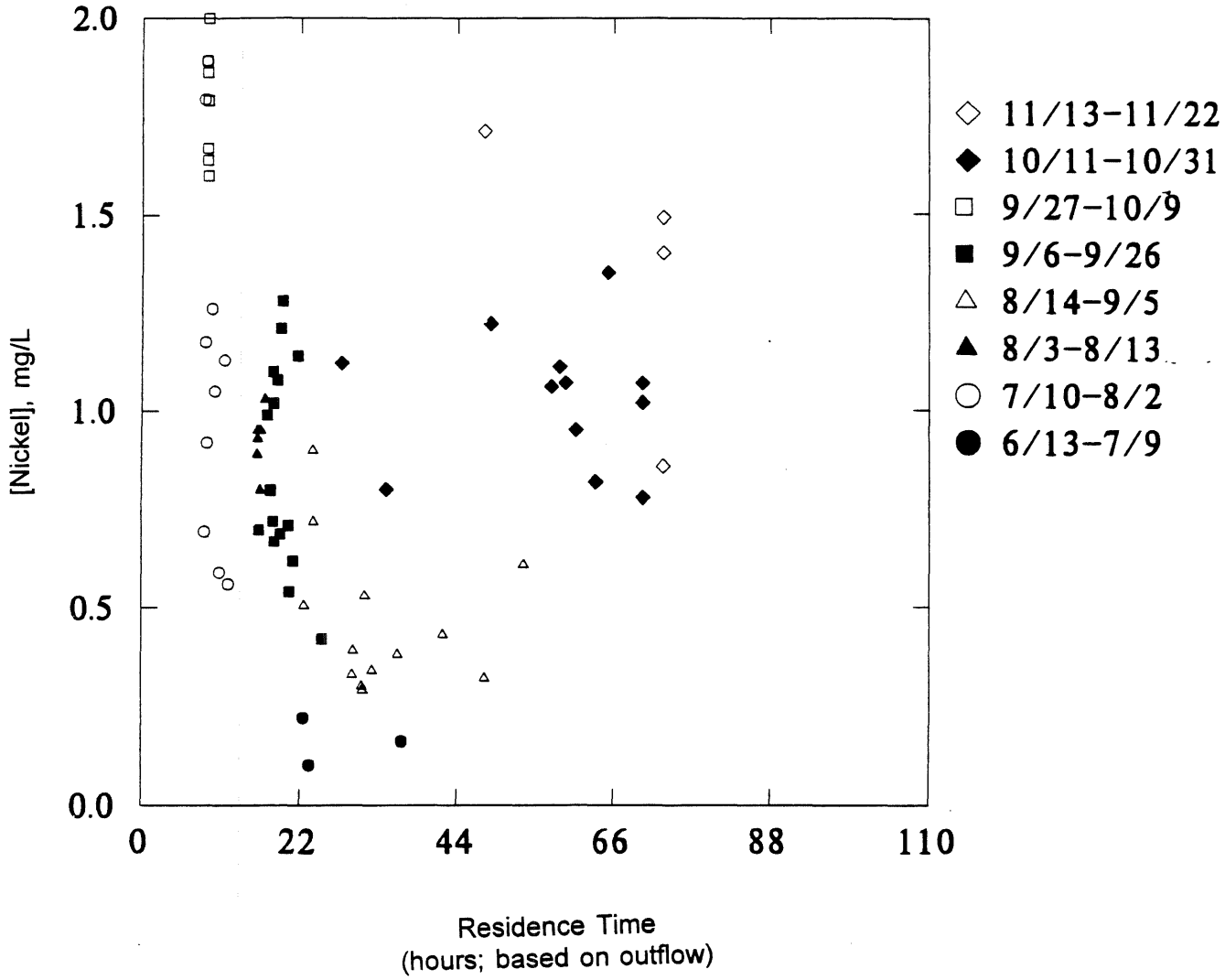


Figure 16. Cell 2 output nickel concentrations vs. residence time, 1991.

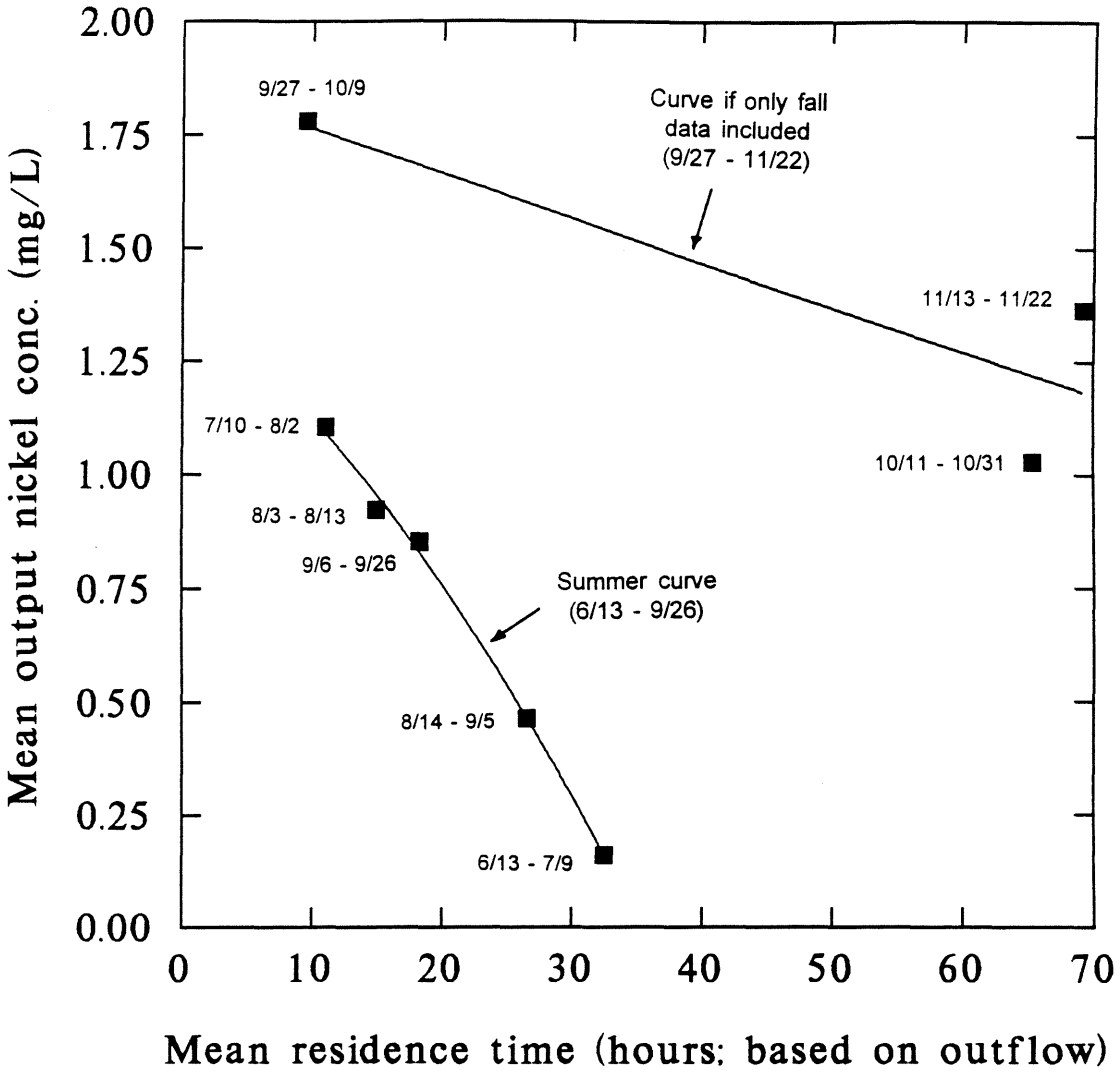
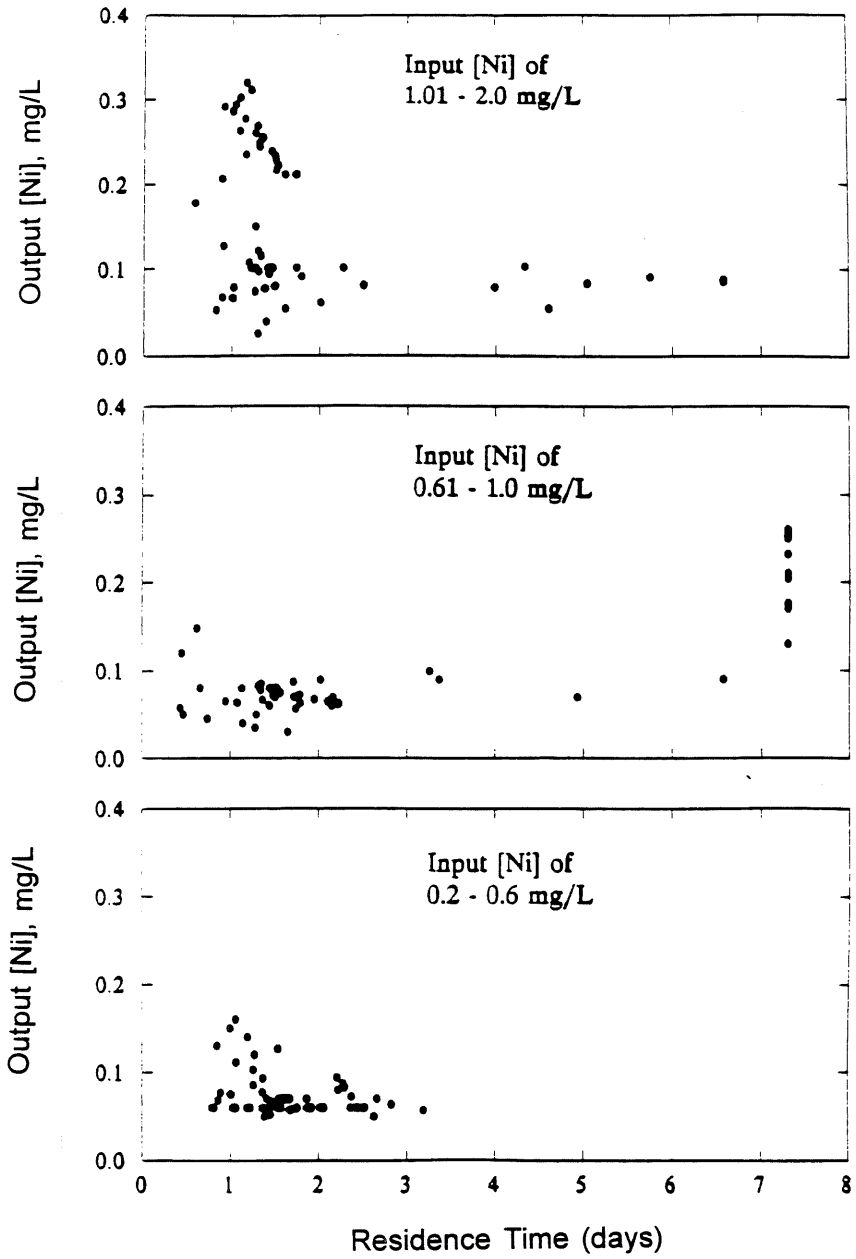


Figure 17. Relationship between average cell 2 output nickel concentrations and residence time, 1991.



Notes: 1. Residence times were calculated from daily flow rates.

2. Daily output concentrations were estimated by linearly interpolating between measured values.

Figure 18. 1990 output nickel concentrations in cell 2 as a function of input concentration and residence time.

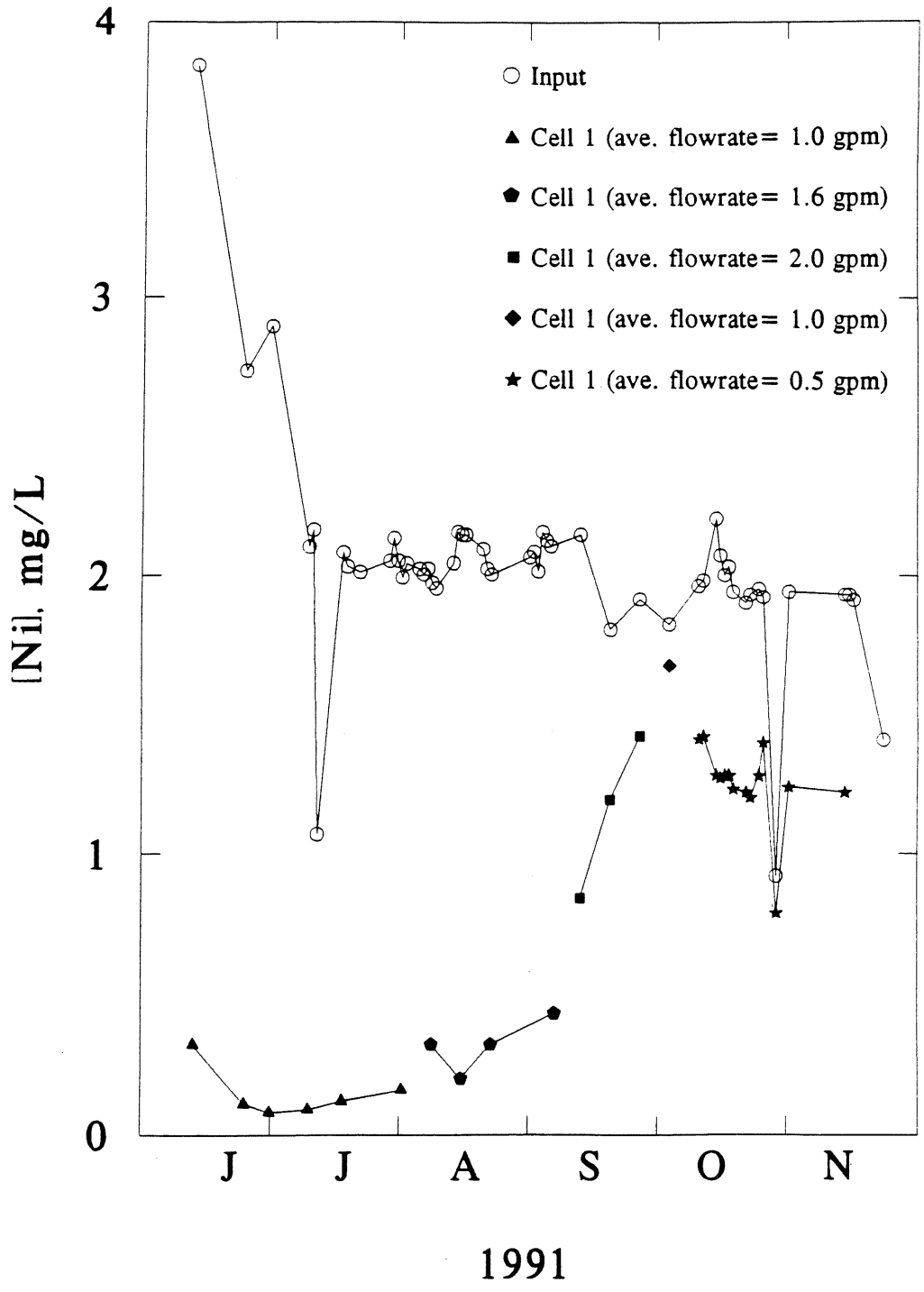


Figure 19. Cell 1 input/output nickel concentrations for periods of constant residence time, 1991.

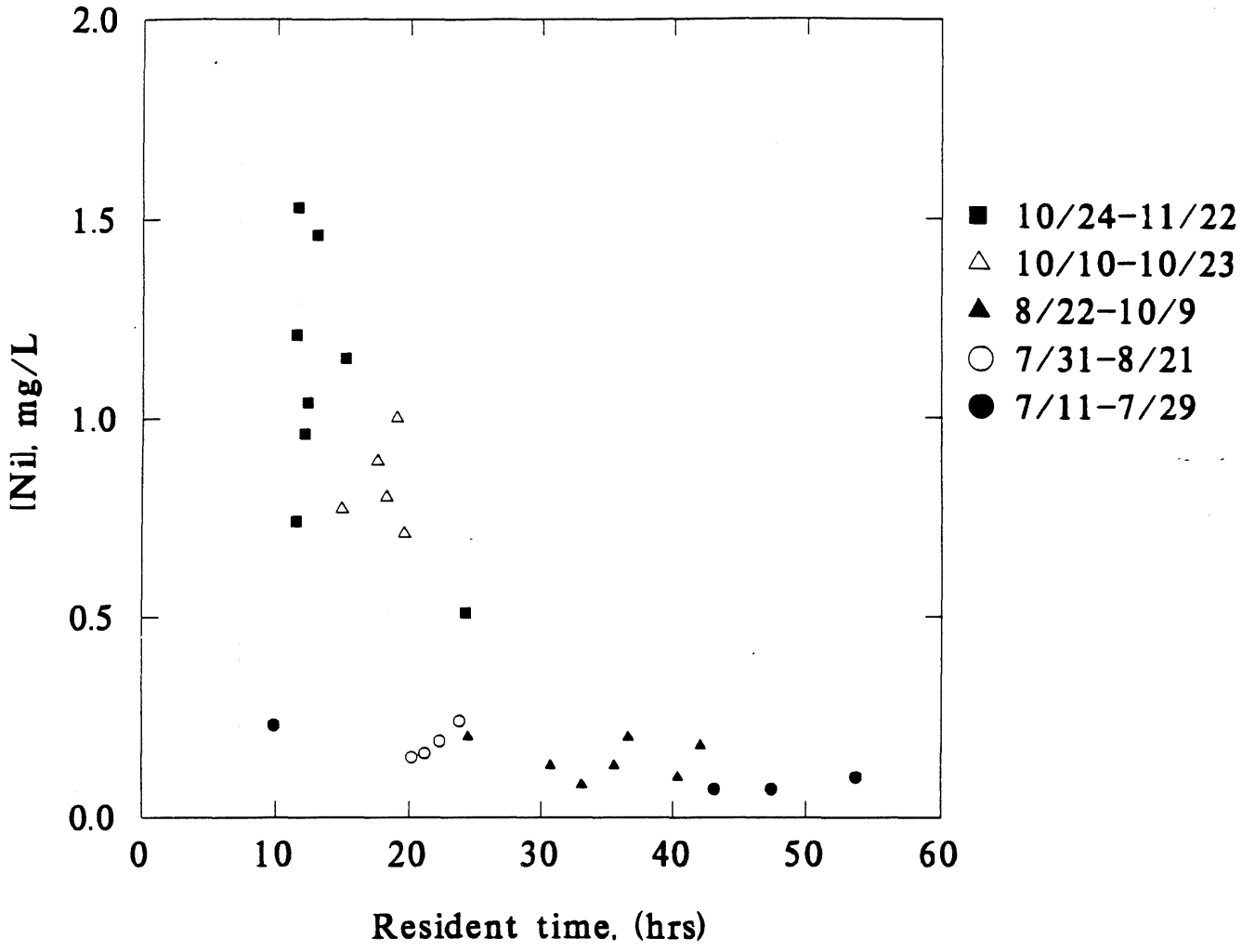


Figure 20. Cell 4 output nickel concentrations vs. residence time, 1991.

7.7. Aquifer X and Seep 1 tests; cell 1, 1990.

In September and October of 1990, two special tests were conducted in cell 1 which used mine drainage from stockpiles at the Dunka Mine other than 8013 (W3D); Seep 1 and Aquifer X (Figure 1). By September 1990 the metal concentrations in the W3D input water had decreased substantially, with mean nickel concentrations less than 1 mg/L, and the Seep 1 and Aquifer X tests were conducted to examine the ability of the cell to treat drainage with higher concentrations of nickel and elevated concentrations of the other trace metals, copper, cobalt and zinc. The Seep 1 test was conducted first, running from 9/17/90 through 10/5/90, with the Aquifer X test was run from 10/11/90 through 10/26/90. Table 10 summarizes the water quality data of the Seep 1 and Aquifer X tests, with the results of the Aquifer X test broken down into two parts based on residence time.

Seep 1 Test

Stockpile drainage from Seep 1 was mixed with the W3D input to the treatment cells on a 1:1 volume basis (Appendix 21). The input pH ranged from 6.6-7.4 and contained elevated levels of copper, 0.11-0.18 mg/L; cobalt, 0.27-0.5 mg/L; nickel, 4.27-6.12 mg/L; and zinc, 0.65-0.94 mg/L, all of which exceeded the water quality standards that are presented in Table 1.

Table 10. Summary of water quality data from the Aquifer X and Seep 1 tests in cell 1.

Input Source		Input Concentration Range (mg/L)	Output Concentration Range (mg/L)	Water Quality Standards	Overall mass Removal (%)	Median Residence Times (hours)
Seep 1 + W3D 9/17/90 - 10/5/90	pH	6.6- 7.4	6.6-7.45	6.5-8.5	NA_p	34
	Cu	0.11-0.18	0.006-0.023	0.013	90	
	Ni	4.27-6.12	0.04-0.63	0.213	94	
	Co	0.27-0.5	0.006-0.050	0.005	90	
	Zn	0.65-0.94	0.019-0.037	0.149	96	
Aquifer X 10/11/90 - 10/19/90	pH	6.65-7.15	6.45-7.00	6.5-8.5	NA_p	34
	Cu	0.08-0.24	0.005-0.007	0.013	95	
	Ni	1.75-1.98	0.56-0.64	0.213	59	
	Co	0.18-0.26	0.003-0.008	0.005	97	
	Zn	1.42-1.76	0.024-0.058	0.149	96	
Aquifer X 10/20/90 - 10/26/90	pH	6.73-7.30	6.73-7.35	6.5-8.5	NA_p	22
	Cu	0.21-0.35	0.004-0.022	0.013	73	
	Ni	1.91-1.96	0.95-1.20	0.213	41	
	Co	.21- .24	0.029-0.040	0.005	81	
	Zn	1.87-1.96	0.055-0.320	0.149	90	

NA_p = not applicable, pH values are in standard units, all other values are mg/L.

In general, for the majority of the wetland treatment data, the difference between filtered and total metals was less than 10% (Appendix 19). This was also generally true for both the Seep 1 and the subsequent Aquifer X test, except that there was a significant difference between total and filtered copper in the input water, ranging from 35-80%. However, there was little difference between total and filtered copper in the outflow during these tests (Appendix 19), and therefore only the total copper results are presented in this discussion.

Outflow pH was generally 0.1-0.2 pH units less than the input and had a minimum value of 6.47, which was essentially at the minimum water quality standard of 6.5 (Appendix 21). All trace metal concentrations in the outflow were significantly lower than the input concentrations.

Copper concentrations decreased by over 90%, and although only 58% of the outflow samples were below the proposed standard of 0.013 mg/L, the maximum copper concentration was only 0.023 mg/L (Figure 21). Although cobalt was generally reduced by more than 90% to concentrations in the range of 0.006-0.050 mg/L (Figure 22), the last sample of the Seep 1 test had a cobalt concentration of 0.180 mg/L, which appears to be an anomaly. All subsequent concentrations were about an order of magnitude less than this value (See Aquifer X results). Zinc concentrations decreased by over 95% to 0.019-0.037 mg/L, and consistently met the proposed water quality standard (Figure 22).

Nickel concentrations decreased by 90-99% to values ranging from 0.04-0.63 mg/L. Outflow nickel concentrations were initially less than the proposed standard but began to increase, exceeding 0.21 mg/L after about the tenth day of the test. Concentrations continued to increase to around 0.5 mg/L at the end of the test. However, the nickel removal at the end of the test was still around 90% (Figure 21).

During the Seep 1 test, surface water samples were collected at the two well sites within cell 1. Site 1-AS is 4.5 m (15 feet) from the inlet, while Site 1-BS is 8.3 m (45 feet) from the inlet. For copper, almost all removal occurred in the first 4.5 m. For the other trace metals, although greater than 40% of the metal removal occurred in the first 4.5 m, significant removal occurred from the second well to the outlet (Figures 21 and 22).

Aquifer X Test

Beginning on 10/11/90, water from stockpile drainage Aquifer X was the only water input to cell 1 for the rest of the season. This water had a pH of 6.65-7.30 with elevated trace metal concentrations; copper 0.034-0.390 mg/L; cobalt, 0.14-0.25, mg/L; nickel 0.96-1.98 mg/L; and zinc 0.70-1.96 mg/L. The minimum value for all the metals was measured in the first sample and appears to be anomalous since subsequent samples from the same tanker were about a factor of two higher (Appendix 19). All input metal values exceed the proposed water quality standards (Table 10). Total copper values of the input water averaged 52% higher than filtered values, yet there was little difference in the output (Appendix 19), so only total values are discussed.

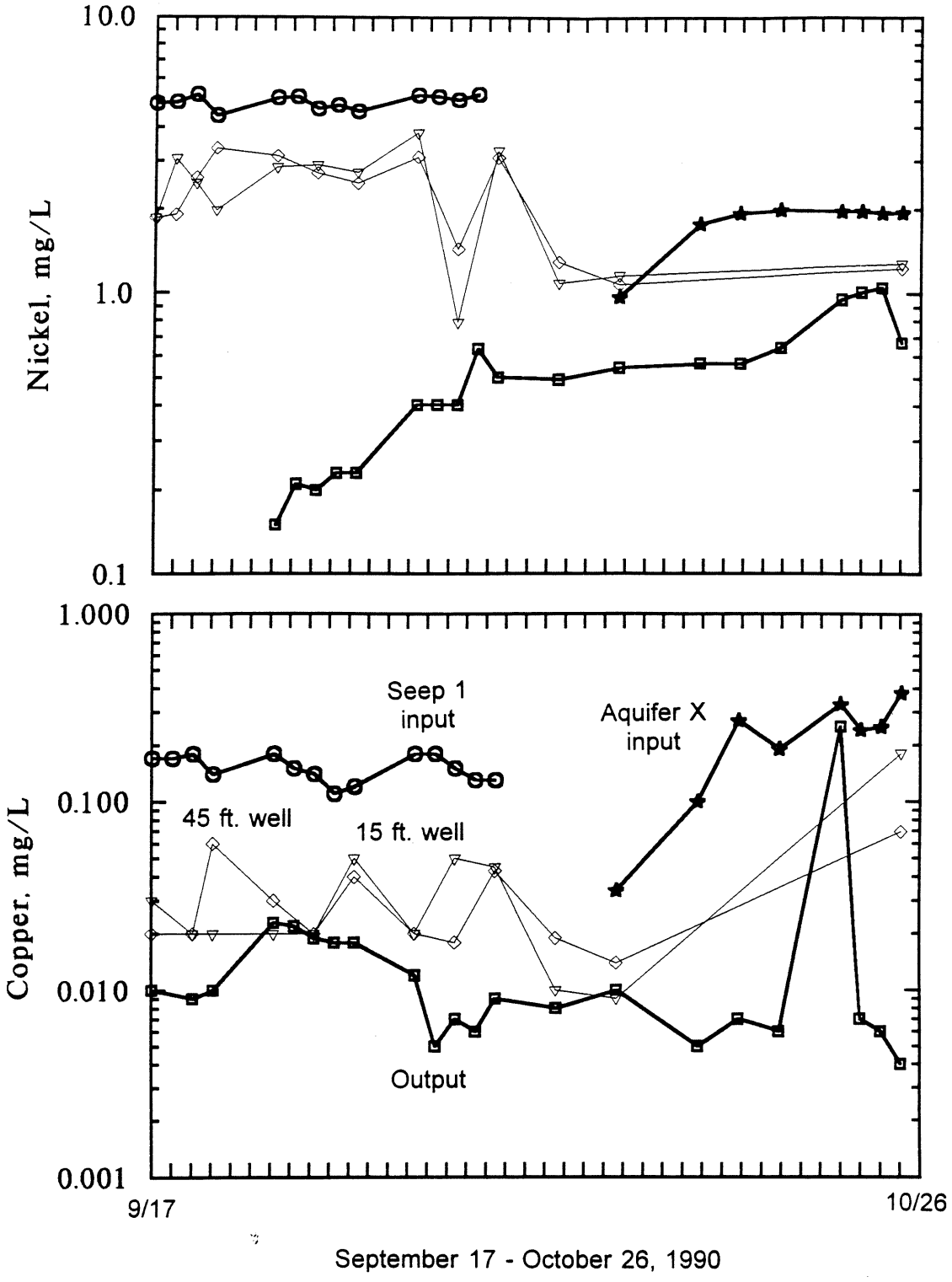


Figure 21. Seep 1 and Aquifer X tests; copper and nickel concentrations in outflow and within cell.

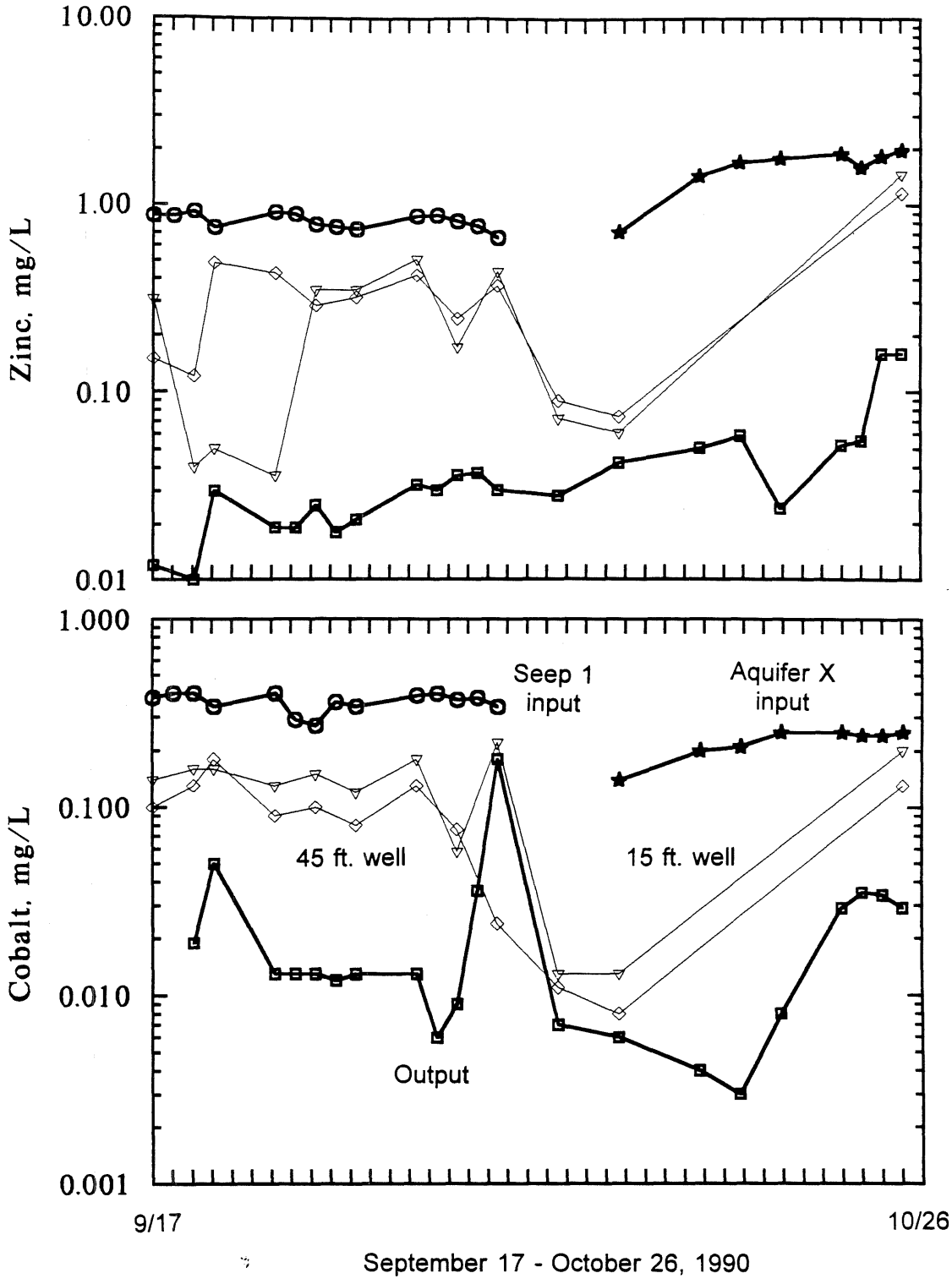


Figure 22. Seep 1 and Aquifer X tests; cobalt and zinc concentrations in outflow and within cell.

One of the objectives of the Aquifer X test was to determine the effect of residence time on metal removal. The residence time during the first week of the test was to be 48 hours and would then decrease to 24 hours during the second week. Actual residence time during the first week ranged from 22 to 91 hours, with a median of 34 hours. The large fluctuation in residence time was the result of plugging in the feed line from the tanker and 1.69 inches of precipitation on October 3. The range of residence times during the second week was much smaller, 19-24 hours, with a median of 22 hours (Appendix 21, Figure 23).

Removal of copper, cobalt, and zinc ranged from 82-95% throughout the test (Figures 21 adn 22). Copper concentrations in the outflow were below the proposed standard of 0.013 mg/L until the last sample of the test, which was 0.022 mg/L. Copper removal appears to be independent of the residence times used in this test. Cobalt concentrations were below or near the proposed standard during the initial part of the test but increased by a factor of 5 and exceeded 0.005 mg/L after the residence time in the cell was decreased. Zinc concentrations were below the proposed standard until near the end of the test when they increased to 0.16-0.32 mg/L.

Nickel removal (based on the percentage difference between inflow and outflow concentrations) was much lower than for the other metals, and none of the outflow concentrations met the proposed standard. Nickel removal was initially on the order of 70% and decreased to around 43% at the end of the test. Nickel concentrations in the outflow increased by nearly a factor of 2, from around 0.6 mg/L to about 1.1 mg/L, as residence time decreased from 34 to 22 hours.

Section 8. Groundwater quality.

A limited set of groundwater samples were collected from each cell (Appendix 14). Samples were collected from the surface of the wetland and at depths of 0-20 cm and at about 1 meter in depth. The initial set of samples was collected in 1989 prior to the addition of drainage to the cells. Initial specific conductance values ranged from 240-2000 µmhos/cm in the deep samples, and from 2000-3200 µmhos/cm in the shallow samples. The lowest values were observed in the deep wells of cell 4. The variation in the specific conductance was probably an indication of preferential flow paths in the wetland prior to construction of the cells. Nickel in all the initial samples averaged 0.020 mg/L and ranged from 0.020-0.050 mg/L.

Samples collected after the drainage was introduced into the cells showed that concentrations of all parameters generally decreased with depth in the wetland. This was particularly true for nickel. Surface nickel concentrations reflected the input concentration, while concentrations in the shallow wells ranged from 0.150 to 0.040 mg/L (median 0.070 mg/L), and from 0.010 to 0.0140 mg/L in the deep wells (median 0.040 mg/L). Specific conductance in the shallow wells generally reflected the input values, although several unusually high values (4000-5000 µmhos/cm) were recorded. Deep wells showed a general slow increase in specific conductance during the time period of the study.

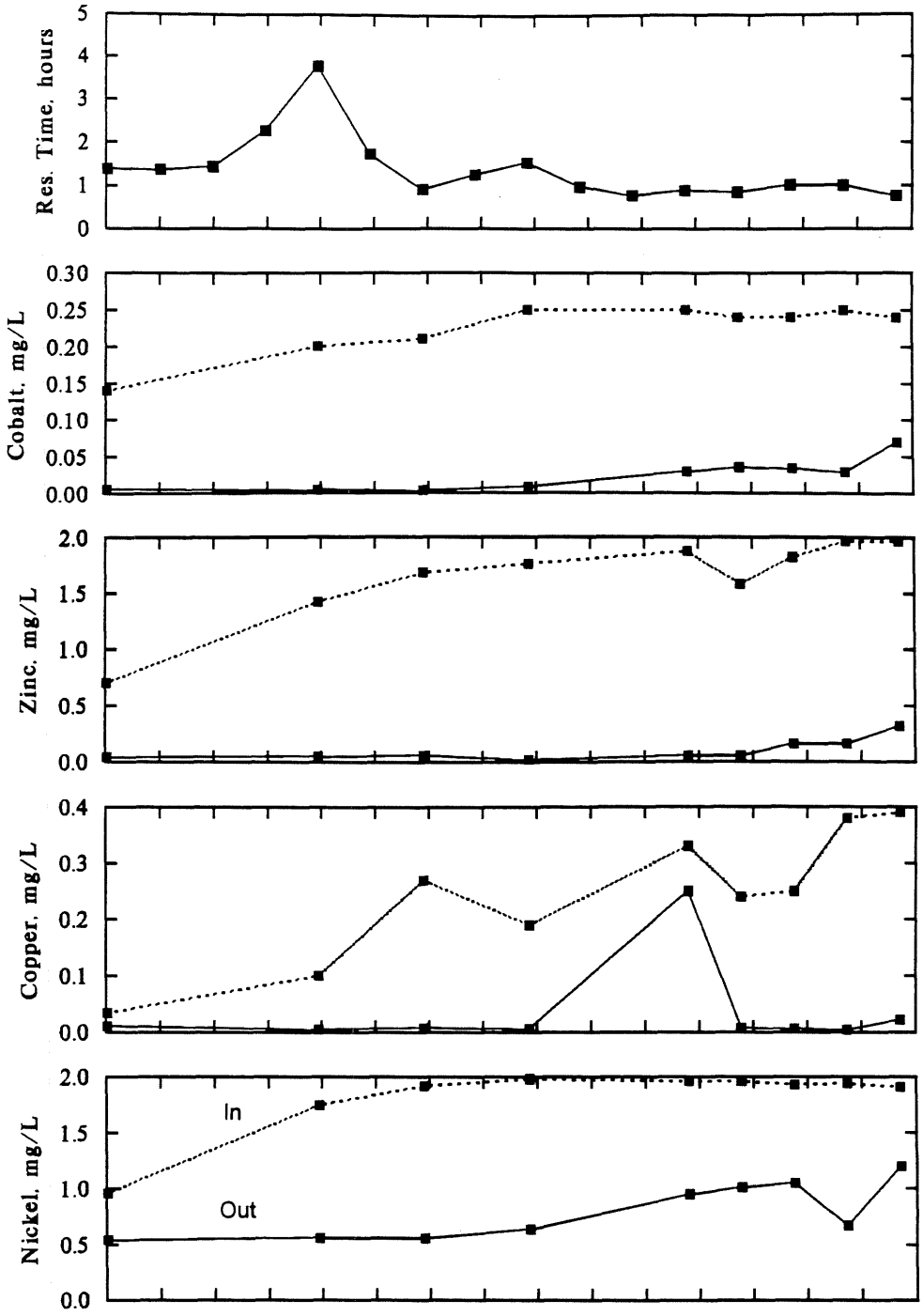


Figure 23. Aquifer X test; water quality results and residence times.

Section 9. Peat and vegetation data.

9.1. Introduction.

Many processes, including filtration, sedimentation, adsorption, precipitation, plant uptake, and microbiologically-mediated reactions (i.e. sulfate reduction) may play a role in the overall metal removal that occurs in a wetland treatment system (Watson et al., 1989). Regardless of the specific processes involved, a generalization can be made that metals can accumulate in two main compartments; in the vegetation or in the (peat) substrate. Metal accumulation within the DNR wetland cells was calculated by comparing the baseline data (collected prior to the addition of stockpile drainage to the treatment cells) with data collected near the end of the study.

Though other metals such as copper, cobalt and zinc are present in the wetland treatment input water, the concentrations of these metals are low in comparison with the nickel concentrations; thus nickel will be the focus of this discussion. Data on the other metals can be found in Appendix 22, which also includes a discussion of the specific assumptions and calculations that were used to generate the mass values. In general, there was little to no significant accumulation of copper, cobalt or zinc by the vegetation or by the peat.

9.2. Vegetation data.

9.2.1 Introduction.

Though other species may have been present in small quantities, the major vegetation present in the wetland treatment cells were cattails (*Typha sp.*), grasses (*Calamagrastis sp.*), sedges (*Carex sp.*), and minor amounts of duckweed (*Lemna sp.*) on the open water portions of the cells. These four plant groups were assumed to be responsible for all metal removal by the vegetation in the cells, and the following 3 sections address the metal mass removal due to each plant group.

Cattails: Cattails have been used extensively in constructed wetlands; they quickly produce a dense stand and large biomass, and they may be innately resistant to heavy metals (McNaughton et al., 1974). Cattails were planted in the two high water cells (3 and 4), they also became established and abundant in cell 2, and they were also present in the natural wetland cell (cell 1), though to a lesser degree (a large portion of cell 1 was already populated with grasses/sedges).

The above ground biomass was measured in July 1991 and the below ground biomass was estimated using values obtained from the literature. Zhang et al. (1991) reported that for cattails the ratio of root/rhizome/leaves biomass is 1:18:14, respectively. Using these values (19 parts below-ground biomass per 14 parts above-ground biomass), below-ground values ranging from 25.4 kg in cell 1 to 142.8 kg in cell 2 were calculated (Appendix 22). (Below-ground cattail biomass is assumed to have remained the same from year to year, with no dieoff between

seasons, even though it probably increases somewhat from year to year as the root network develops and matures.)

Total cattail biomass ranged from 44 kg in cell 1 to 248 kg in cell 2 (Appendix 22). Cattail biomass in Cell 4 in 1991 was only 155.8 kg, despite a very dense and healthy population in 1990. The lower standing biomass resulted from the addition of the peat/peat screenings mixture in June 1991; when this material was added to the cell, most of the cattails were bent over, broken or covered.

Grasses (*Calamograstis sp.*) and Sedges (*Carex sp.*):

Grasses and sedges were the original dominant vegetation types in the wetland, and were maintained in cell 1. For the purpose of this study these species were lumped together into a "grass like" group. These species often grew together and it would have been too time consuming to carefully separate each species. Since the vegetation in cell 2 was destroyed during the scarification of the surface and the construction of the trenches, clumps of grasses and sedges were removed from the surrounding area and transplanted into the cell in an attempt to reestablish the original vegetation.

Above ground biomass was measured in 1991. Although the root structures of grasses/sedges are quite small in relation to the above-ground portion of the plant, no definitive above-ground/below-ground biomass ratio could be found for these species. Bernard et al. (1988) report that "standing crops in *Carex* wetlands are in the range of about 500-1050 g/m^2 above ground, and about 150-900 g/m^2 below-ground", and for our calculations a ratio of 2:1 above/below was used. In 1991, the biomass for this group ranged from 9 kg in cell 3 to 72 kg in cell 1.

Duckweed (Lemna sp.): Duckweed was found on open water sections of the wetland in cells 1 through 3, but contributed less than 2% of the overall biomass in the cells. Duckweed has essentially no root structure; the entire plant was collected when they were skimmed from the water surface.

9.2.2. Baseline (1989) vegetation metal concentrations.

The initial set of vegetation samples were collected on July 20, 1989; these samples represent the pre-operational conditions within the cell. Nickel concentrations in these samples ranged from 3.4 mg/kg in the cattail leaves from Hoyt Lakes, to 175 mg/kg in the duckweed sample from cell 1.

The duckweed samples generally contained the highest concentrations of nickel, followed by the cattails, and then by the grasses and sedges (Table 11). The highest cattail metal concentrations were found in the roots, followed by the rhizomes and then by the leaves. This

pattern is consistent with that reported by Taylor and Crowder (1983) for cattails collected near the International Nickel Company facility at Sudbury, Ontario.

Nickel concentrations in the cattails that existed at the site prior to system start-up (the W2D plants) contained higher concentrations of nickel than the cattails brought in from the Hoyt Lakes area. (Appendix 22) These higher levels were most likely due to previous exposure to drainage from the 8031 stockpile (Figure 1).

9.2.3. July 1991 tissue metal concentrations.

Vegetation samples were collected in July 1991 and analyzed for metal content; these data are summarized in Table 11. For the cattails, these same data, grouped by distance from the inlet side, are presented in Appendix 22. Again the roots had the highest nickel concentrations (with a mean concentration of 247 ppm), followed by the rhizomes (47 ppm) and then by the leaves (15 ppm).

There appeared to be no definitive relationship between metal content and the distance from the inlet. In general, however, nickel concentrations in the cattail roots tended to reach a maximum value near the middle (length) of the cell, which roughly coincides with the maximum concentrations observed in the 1991 peat samples (Section 9.3.3). The concentrations in the rhizomes and leaves showed no distinct pattern.

Table 11. Mean metal concentrations in vegetation from the wetland treatment cells (baseline and 1991 samples).

	Copper		Nickel		Cobalt		Zinc	
	Baseline	1991	Baseline	1991	Baseline	1991	Baseline	1991
Cattails								
· roots	19.0	45.9	18.0	246.6	9.8	11.3	97.7	31.8
· rhizomes	9.0	17.4	8.5	47.3	4.8	3.4	27.0	14.8
· leaves	8.0	8.0	4.9	14.8	3.2	1.6	42.8	15.6
Grasses/ sedges	4.5	6.5	7.2	26.2	1.8	2.3	36.2	17.7
Duckweed	44.4	18.0	40.9	418.0	10.2	19.0	51.2	30.5

Note: metal concentrations are ppm

9.3. Peat data.

9.3.1. Introduction.

Four sets of peat samples were collected to determine the mass and forms of metals removed in the wetland cells; in 1987, 1988, 1991 and 1992.

Five peat samples were collected from the W2D wetland in April 1987 as part of the survey to find a suitable site for test cell construction (Lapakko and Eger, 1987). In September 1988, after the test cells had been constructed (but prior to start-up of the system), additional samples were collected from each of the four cells at each well location (4.5 m and 8.3 m from the input side of the cells).

Additional peat samples were taken from cells 1 and 2 during late May and early June of 1991. In cell 1, these samples were taken from sites located 3.0, 7.6, 10.6, 16.8 and 22.9 m (10, 25, 35, 55 and 75 ft) from the inlet ends of the cells, and 1.5, 3.0 and 4.5 m (5, 10 and 15 feet) from the center berm located between cells 1 and 2 (Figure 24). In cell 2, samples were collected at the 5 peat berms, which were 4.9, 9.6, 13.1, 18.9 and 23.5 m (16, 31.5, 43, 62 and 77 ft) from the inlet side of the cell. At each of the 5 berms, samples were collected 1.5, 3.0 and 4.5 m (5, 10 and 15 ft) from the center berm that separates cells 1 and 2. Both surface (0-20 cm) and deep (20-50 cm) peat samples were taken at each site, and triplicate samples were collected at some of the sites.

During the winter of 1992, three sets of frozen peat cores were collected from cells 1, 2 and 3 (3 cores from each cell) to analyze the form and depth of metal removal. These results are presented in Section 9.3.4.

All samples were analyzed for copper, cobalt, nickel and zinc, but over the course of the study, only nickel was removed in sufficient quantities to produce a measurable difference in the peat. The results for all the metals are presented in Appendix 23. The results for nickel are discussed in the following sections.

9.3.2. Baseline peat metal concentrations.

Nickel concentrations ranged from 100 to 310 mg/kg in the upper (0-20 cm) segment of the peat, and from 100 to 150 mg/kg in the deeper 20-50 cm segment; these data are summarized in Table 12. The difference between replicate samples varied from 5% - 79%, with an average difference of 26% (Appendix 23). Average concentrations in the 0-20 cm segment were generally equal to or higher than the 20-50 cm samples, with the largest difference occurring in cell 2. Surface concentrations were most likely elevated due to the proximity of the wetland to the 8031 stockpile.

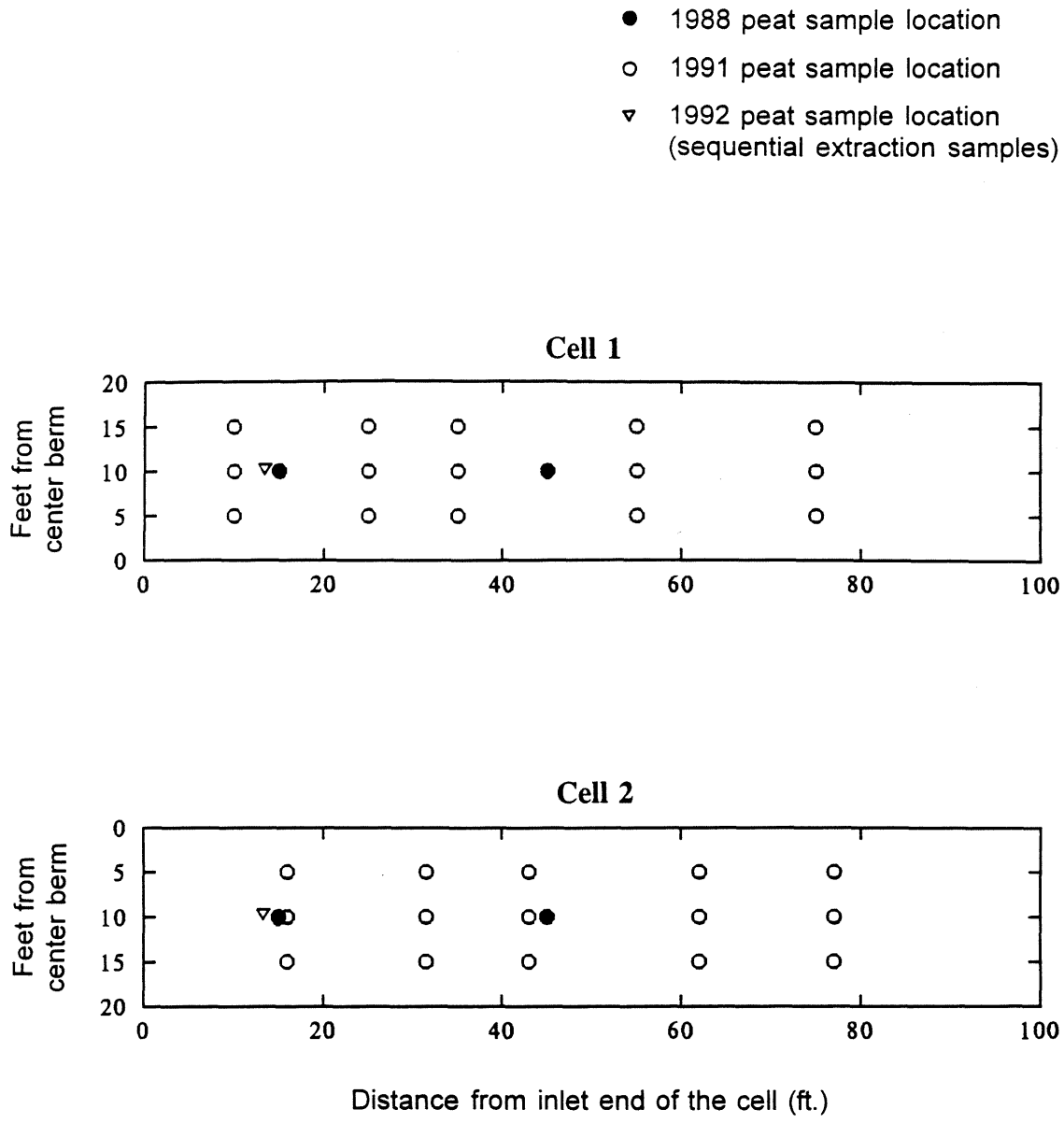


Figure 24. Peat sampling locations (1988, 1991 and 1992).

Table 12. Mean 1988 (baseline) and 1991 peat nickel concentrations.

	Surface peat (0-20 cm)				Deep Peat (20-50 cm)			
	Baseline (1988)		1991		Baseline (1988)		1991	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cell 1	174.0	139 - 225	1051	291 - 3200	134.5	121 - 145	202	128 - 361
Cell 2	223.3	130 - 310	692	131 - 1460	128.3	110 - 150	288	116 - 1343
Cell 3	153.7	140 - 170	na	na	128.3	100 - 150	na	na
Cell 4	125.0	100 - 180	na	na	120.0	100 - 140	na	na
Mean	169.0	nap	872	nap	127.8	nap	245	nap

na: not analyzed (peat samples weren't collected from cell 3 or cell 4 in 1991).

nap: not applicable

9.3.3. Peat metal concentrations as of May 25, 1991.

Cell 1 showed the highest increase in peat nickel concentrations, particularly in the surface segment (0-20 cm), where the mean concentration increased from 174.0 to 1051 mg/kg, and where the maximum observed concentration increased from 225.0 to 3200 mg/kg (Table 12). Nickel concentrations in the deep peat also increased, but the increase was smaller than in the surface peat. (The low vertical gradient and the low hydraulic conductivity of the peat limited transport of the drainage to the deeper peat.) The mean nickel concentration in the deep peat of cell 1 increased from 134.5 to 202.0 mg/kg, with the maximum concentration increasing from 145.0 to 368.0 mg/kg.

Cell 2 also showed elevated peat nickel concentrations in 1991 as compared to 1988, but to a lesser degree than in cell 1. The mean nickel concentration in the surface peat increased from 223.3 to 691.8 mg/kg, and the maximum concentration increased from 310.0 to 1430.0 mg/kg. In the deep peat, the mean concentration increased from 128.3 to 287.7 mg/kg, and the maximum concentration increased from 150.0 to 544.0 mg/kg. The box plots presented in Figure 25 summarizes the 1988 and 1991 peat nickel data for all four cells (though only cells 1 and 2 were sampled in 1991). A key for interpreting the box plots is presented in Figure 26.

As depicted in Figures 27, 28, 29 and 30, the 1991 peat nickel concentrations varied considerably within the two cells. In cell 1, the maximum surface and deep peat nickel concentrations were observed at a distance of about 7.6 m (25 ft) from the inlet end of the cell, and toward the side near the center berm (which separates cells 1 and 2), possibly indicating the

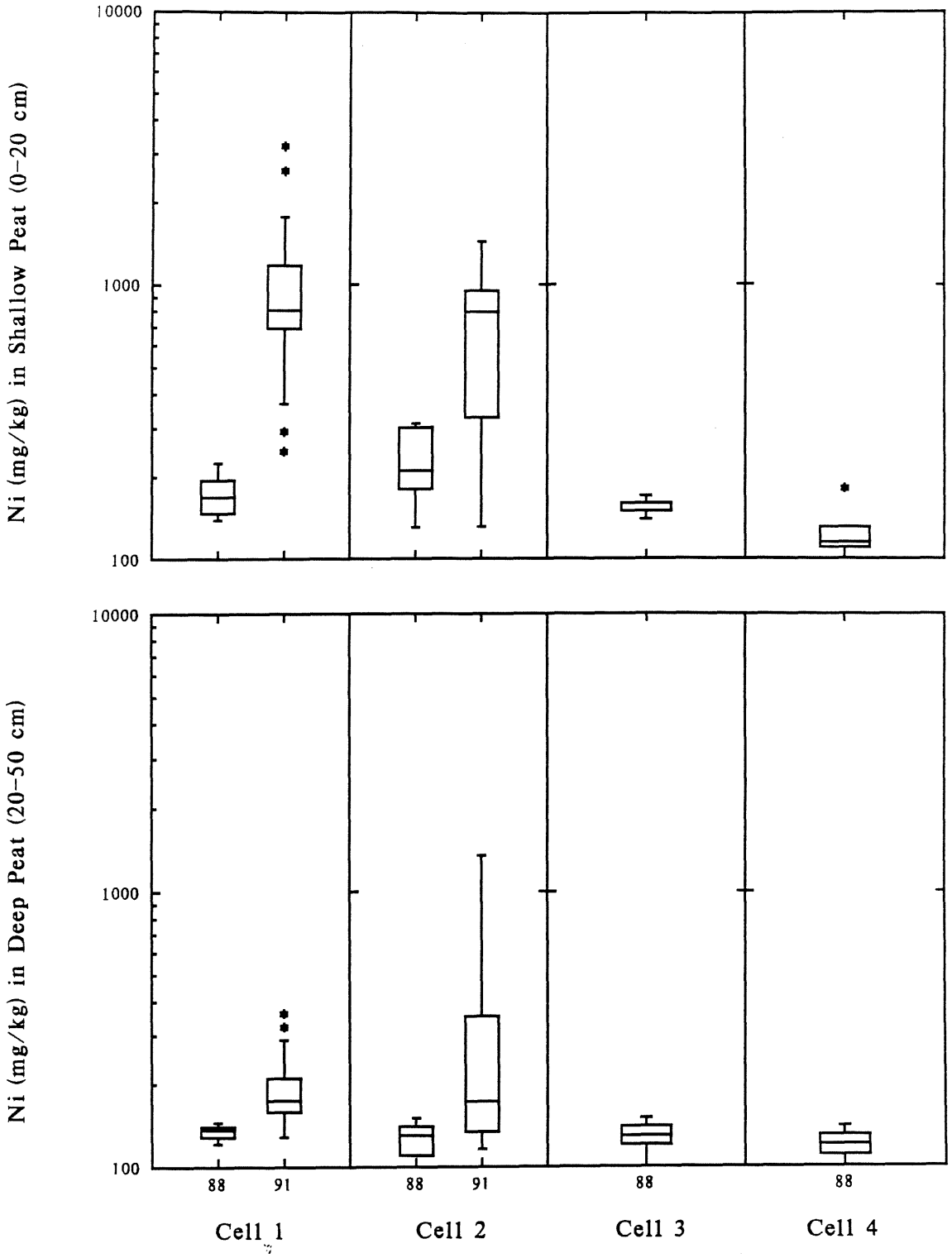


Figure 25. 1988 and 1991 peat nickel concentrations in the shallow and deep peat.

The box plot is comprised of the *central box*, the *whiskers*, and the *outliers*.

- Within the *central box*, the *median* of the data set is depicted by the center horizontal line, and the *lower and upper hinges* are depicted by the other two horizontal lines of the central box. The median splits the ordered data set in half, and the hinges split those two resulting halves in half again (i.e. the three horizontal lines in the central box represent the 25th, 50th, and 75th percentiles of the entire data set). The distance between the two hinges is called the *H-spread (H)*.

- The *whiskers* (the two vertical lines) represent the range of values that fall within 1.5 H-spreads of the two hinges.

- The *outliers* represent values that fall outside of the *Inner and Outer Fences*. Asterisks represent those values which lie outside of the inner fences but within the outer fences. Open circles represent those values which lie outside of the outer fences. The inner and outer fences are defined as:

$$\begin{aligned} \text{Inner fences} &= \text{lower hinge} - 1.5H \\ &= \text{upper hinge} + 1.5H \end{aligned}$$

$$\begin{aligned} \text{Outer fences} &= \text{lower hinge} - 3H \\ &= \text{upper hinge} + 3H \end{aligned}$$

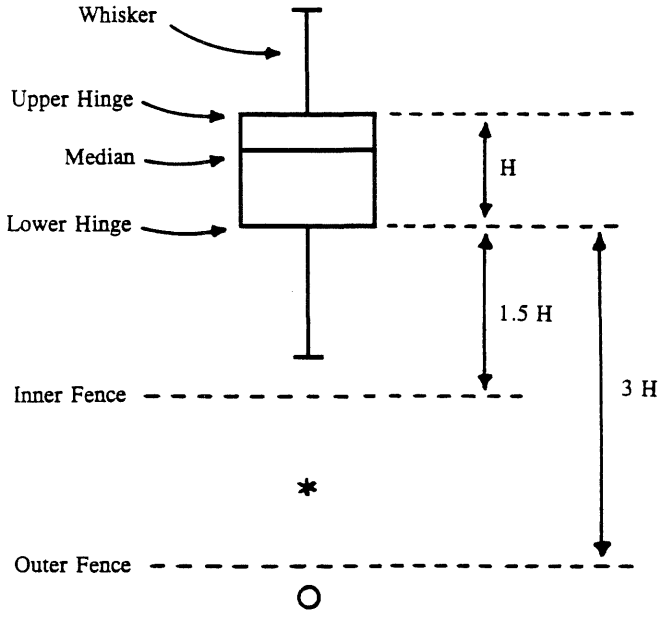


Figure 26. Key for box plot interpretation.

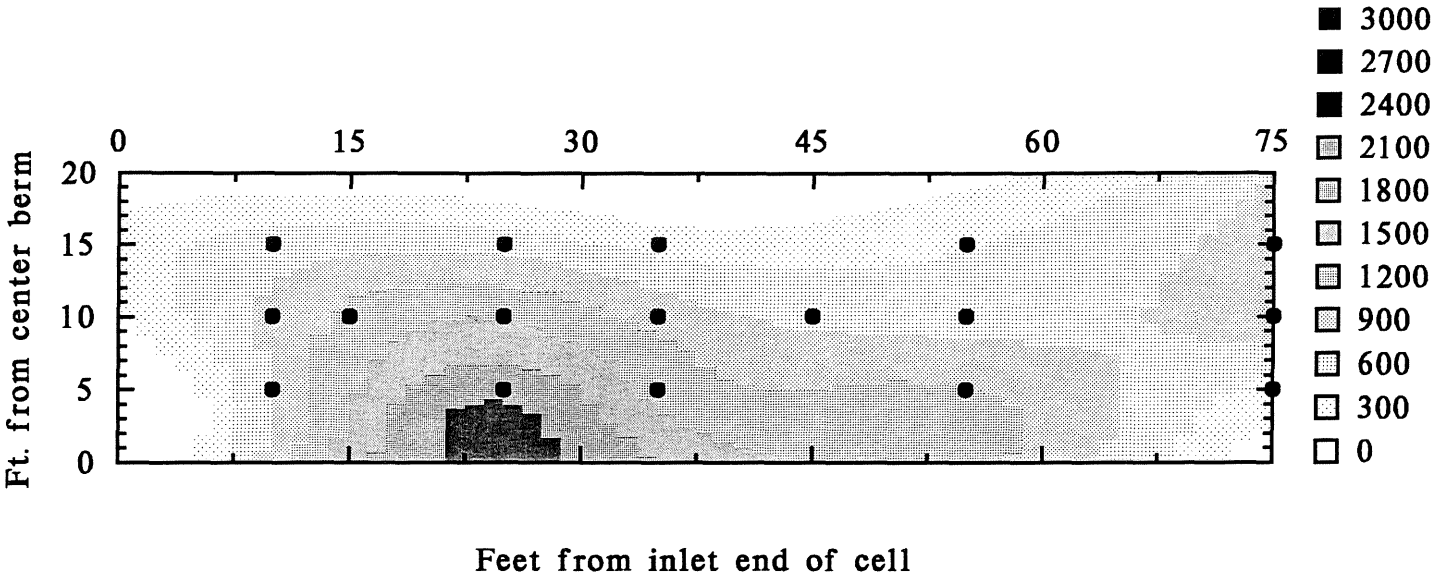


Figure 27. Nickel concentrations in the surface peat (0-20 cm) of cell 1.

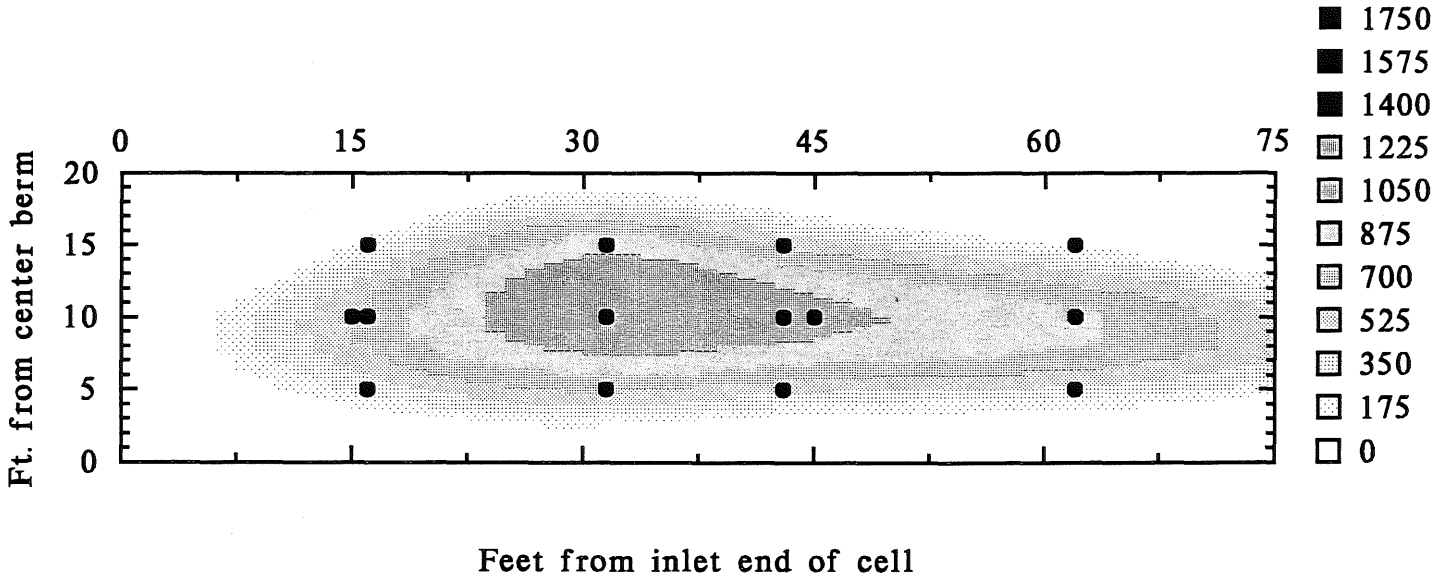


Figure 28. Nickel concentrations in the surface peat (0-20 cm) of cell 2.

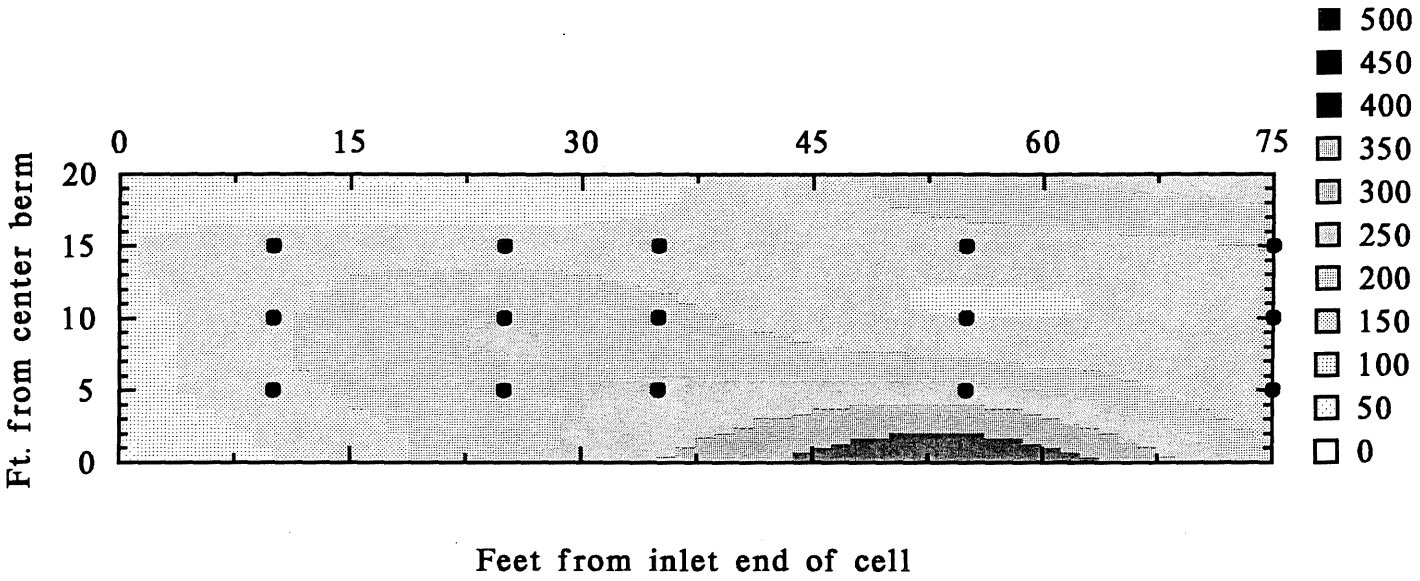


Figure 29. Nickel concentrations in the deep peat (20-50 cm) of cell 1.

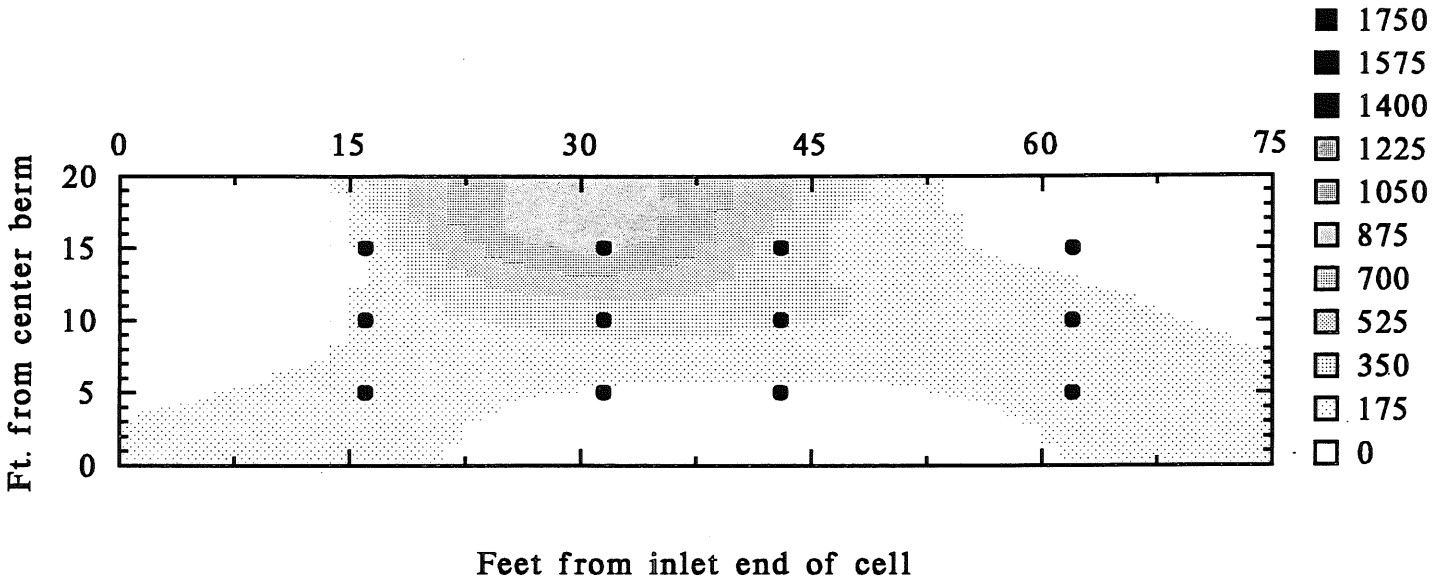


Figure 30. Nickel concentrations in the deep peat (20-50 cm) of cell 2.

presence of preferential flow paths within the cell. In cell 2, the maximum concentrations were observed at a distance of about 9-12 m (30-40 ft) from the inlet side of the cell, and near the center width of the cell.

9.3.4. Sequential extraction results; depth and form of metal removal.

Nickel

Results from the sequential extraction procedures indicate that peat nickel concentrations generally decreased with depth, eventually reaching background concentrations, and that the majority of the removed nickel was bound with organic material in the peat substrate. The nickel values from each sequential step were added together and compared to the value obtained from a total digestion. In general, the difference between the sum and the total digestion value was within 30% (Appendix 26). Significant differences in the magnitude and shape of the concentration vs. depth profiles were observed between each cell. As a result, the nickel results for each cell will be discussed separately.

Cell 1 Nickel concentrations were generally highest in the shallowest peat, with concentrations decreasing with depth until background levels were approached or reached at a depth of approximately 20 cm. Figure 31 presents nickel results for cell 1; the data used to generate this figure are the averages of all 3 cores. The average nickel value in the 0-2 cm segment was somewhat lower than the value for the subsequent 2-4 cm segment. The surface of one of the cores was mounded above the water table, and as a result the surface concentrations in this core approached background levels (Appendix 26).

In the shallower peat, where the highest nickel concentrations were on the order of 3500 to 4000 mg/kg, the sodium pyrophosphate extraction step removed the bulk of the nickel ($\sim$60%) from the peat, indicating that the nickel in this area was primarily bound to organic material in the peat substrate. As peat depth decreased, and as the total nickel concentration also decreased, the proportion of nickel removed in the pyrophosphate step decreased as well, while the proportion removed during the HNO_3 extraction step increased, reaching a value of about 60% when the nickel concentrations in the peat reached background levels ($\sim$150-200 mg/kg at $\sim$20 cm deep). This indicates that the nickel in the deeper peat was associated with residual forms, and it is assumed that the majority of this nickel is associated with sulfides. This distribution in the deeper segments of the peat represents conditions prior to the beginning of the wetland treatment experiment.

Of the other four extraction steps, the water extraction step and the subsequent KNO_3 extraction step removed little nickel ($\sim$2-5%), indicating that little of the nickel taken up by the peat was in a water soluble form or in an exchangeable form.

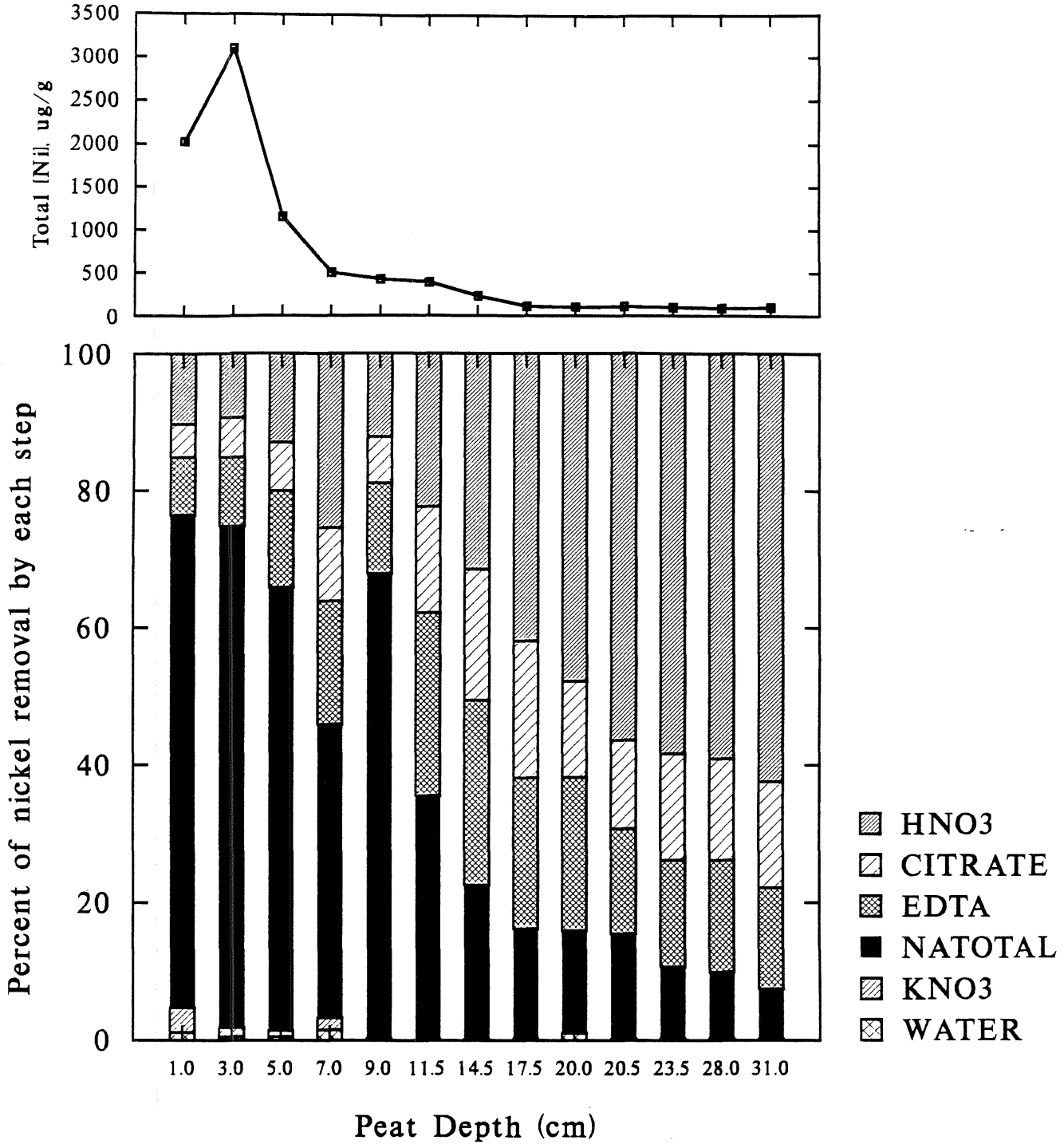


Figure 31. Sequential extraction results; cell 1 nickel.

The remaining two extraction steps (with EDTA, which removes carbonate bound forms, and with citrate, which removes oxide-bound metals) each extracted about 10-20% of the total nickel (Figure 31). The percent nickel removal tended to increase somewhat with depth, roughly concurrent with the decreasing proportion removed by depth in the sodium pyrophosphate extraction step.

Cell 2 Total nickel concentrations in this cell also generally decreased with peat depth, but the decrease was less abrupt than was the case in cell 1, and concentrations remained above background concentrations to a slightly greater depth (~25 cm) than was the case in cell 1 (Figure 32). The greater depth of nickel removal in cell 2 may have been a result of the series of trenches and berms that were constructed in the cell. These trenches were constructed to better distribute flow, both horizontally and vertically, and may have produced better contact between the drainage and the peat.

The sodium pyrophosphate step again extracted most of the nickel (~60%) in the zone where removal took place in this cell (the ~0-20 cm segment), again indicating that the nickel in this segment was primarily bound to organic material in the peat. However, as can be seen in Figure 32, the transition from the organically-bound nickel to the residual nickel was much slower and less abrupt in this cell than in either cell 1 or 3. The sodium pyrophosphate step removed about 60% of the total nickel at depths as deep as 15-20 cm.

In the deeper peat (i.e. greater than 20 cm), where little to no nickel removal occurred, the HNO_3 step removed the bulk of the nickel (~60%), indicating that nickel in this segment was primarily in the residual form.

Cell 3 Nickel concentrations in the upper sections of cores collected from this cell were the highest observed for any cell, and ranged from about to 4000-7700 mg/kg. Nickel concentrations again decreased with peat depth, with the overall pattern being similar to that observed for cell 1. As can be seen in Figure 33, peat nickel concentrations dropped steadily from the maximum of ~7700 mg/kg in the top (0-2 cm) segment, reaching background levels at a depth of ~14 cm. The transition from organically-bound nickel to residual nickel was very abrupt in the cores taken from this cell, and coincided with the depth at which background levels were reached (~14 cm). Although the majority of the nickel was bound to the organic material in the peat, the residual form in the upper portions of the core comprised up to about 25% of the nickel. This was almost twice the percent nickel extracted in cell 1, and exceeded the 10-20 % extracted in cell 2.

Copper

The concentration vs. depth profile for copper was dramatically different than the one observed for nickel (Figures 34, 35 and 36). Copper concentrations in all three cells tended to be at a minimum near the surface, and to increase with depth. In general, surface concentrations ranged from ~100-150 mg/kg in the top peat segment, to maximum concentrations in the peat segment

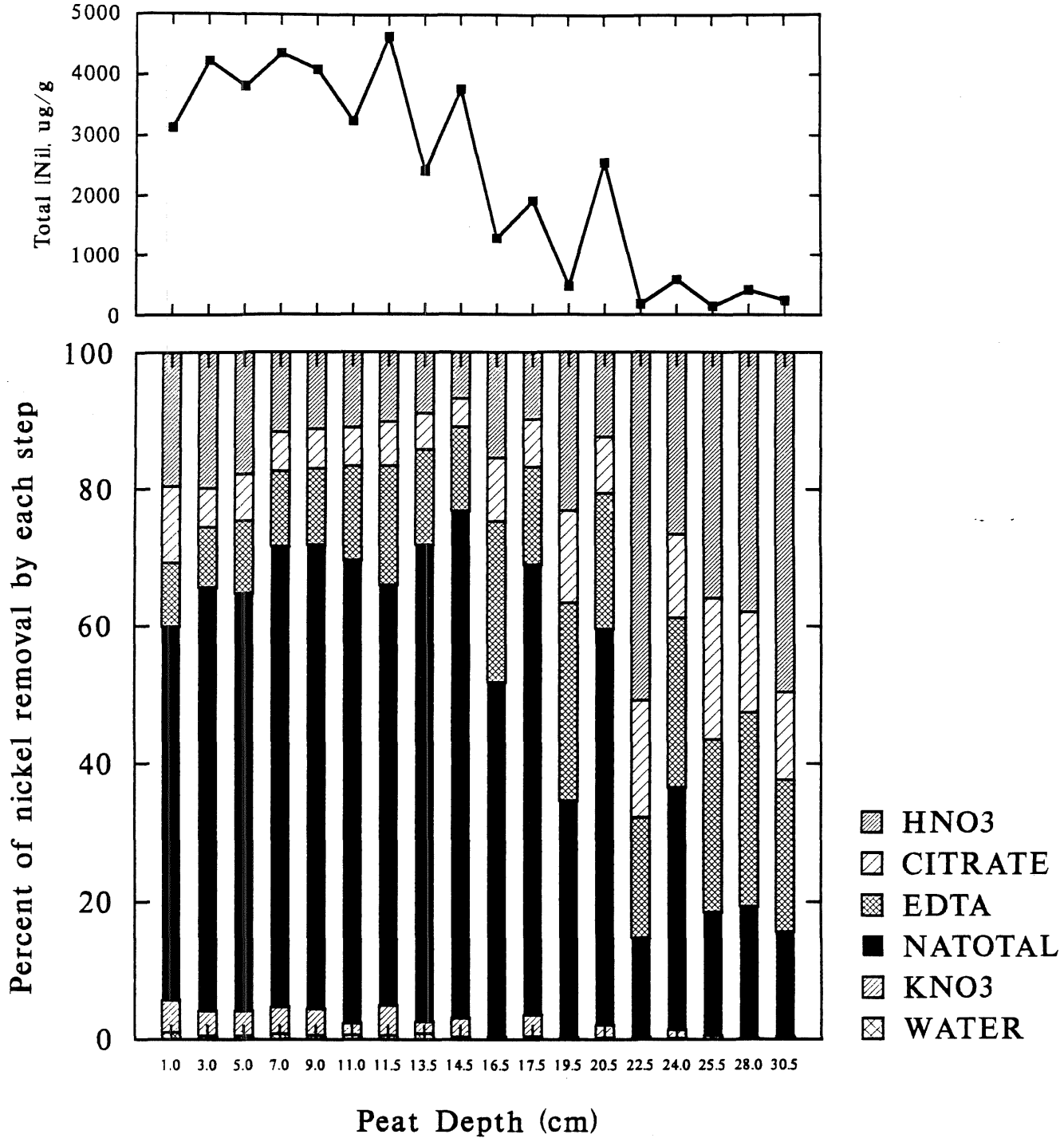


Figure 32. Sequential extraction results; cell 2 nickel.

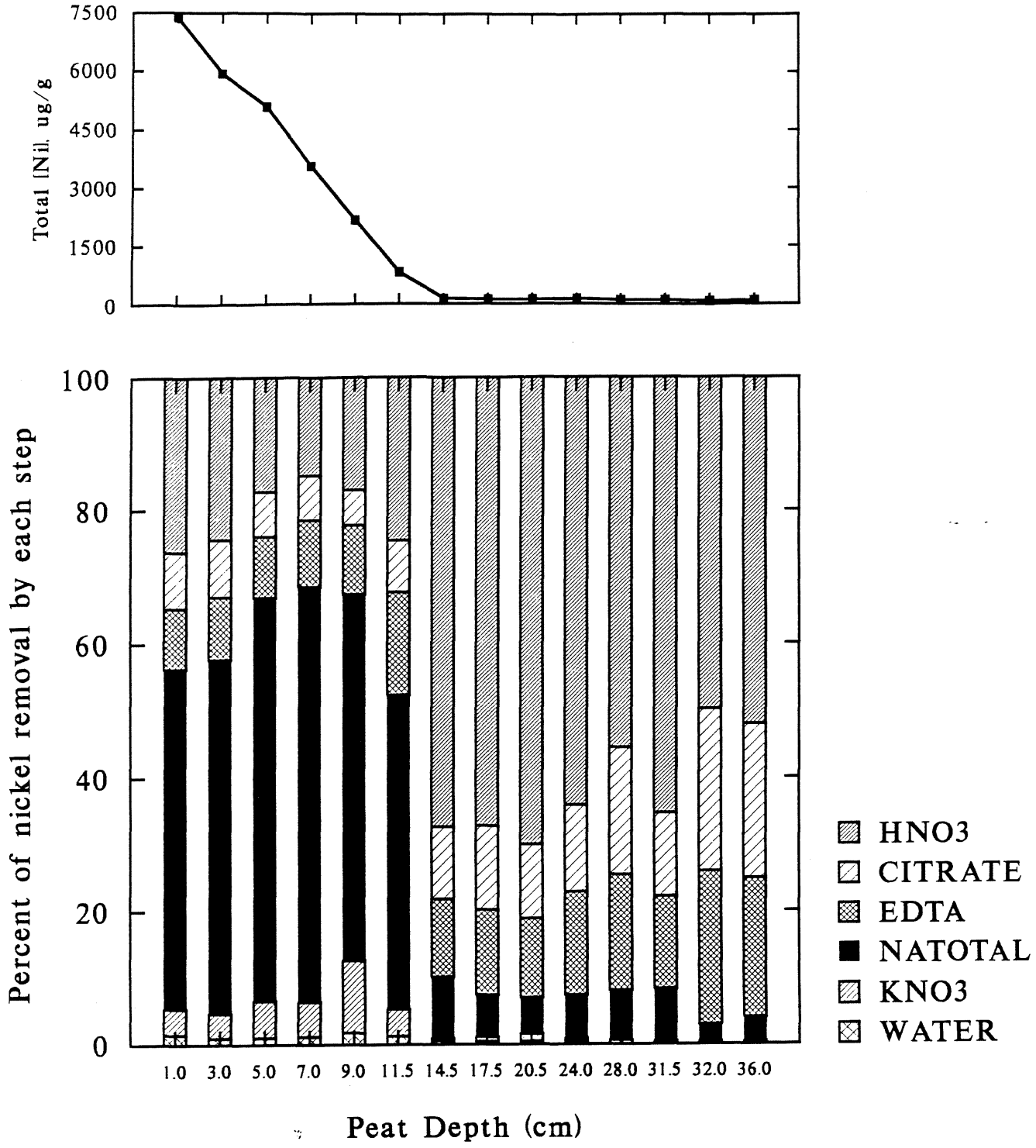


Figure 33. Sequential extraction results; cell 3 nickel.

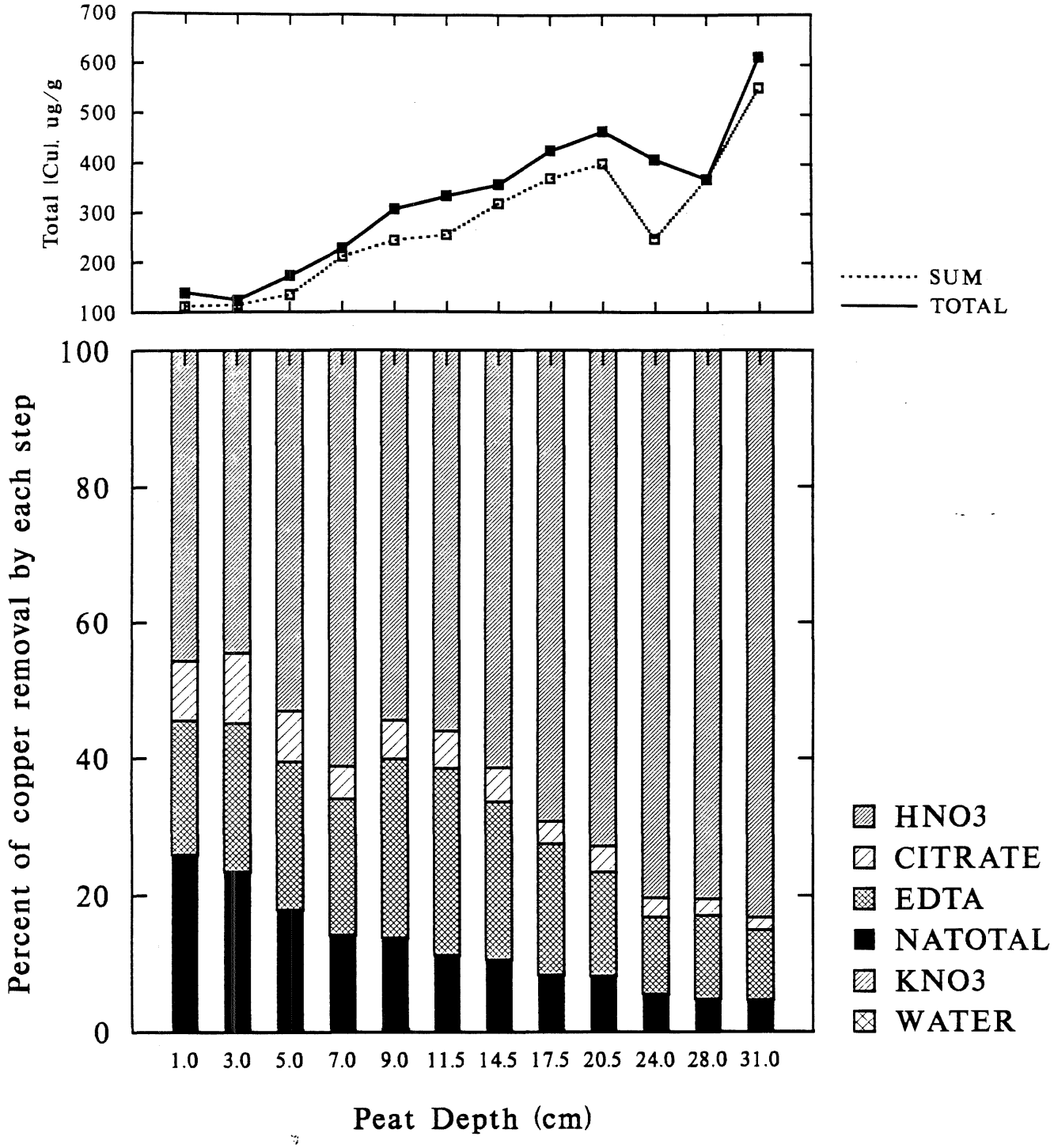


Figure 34. Sequential extraction results; cell 1 copper.

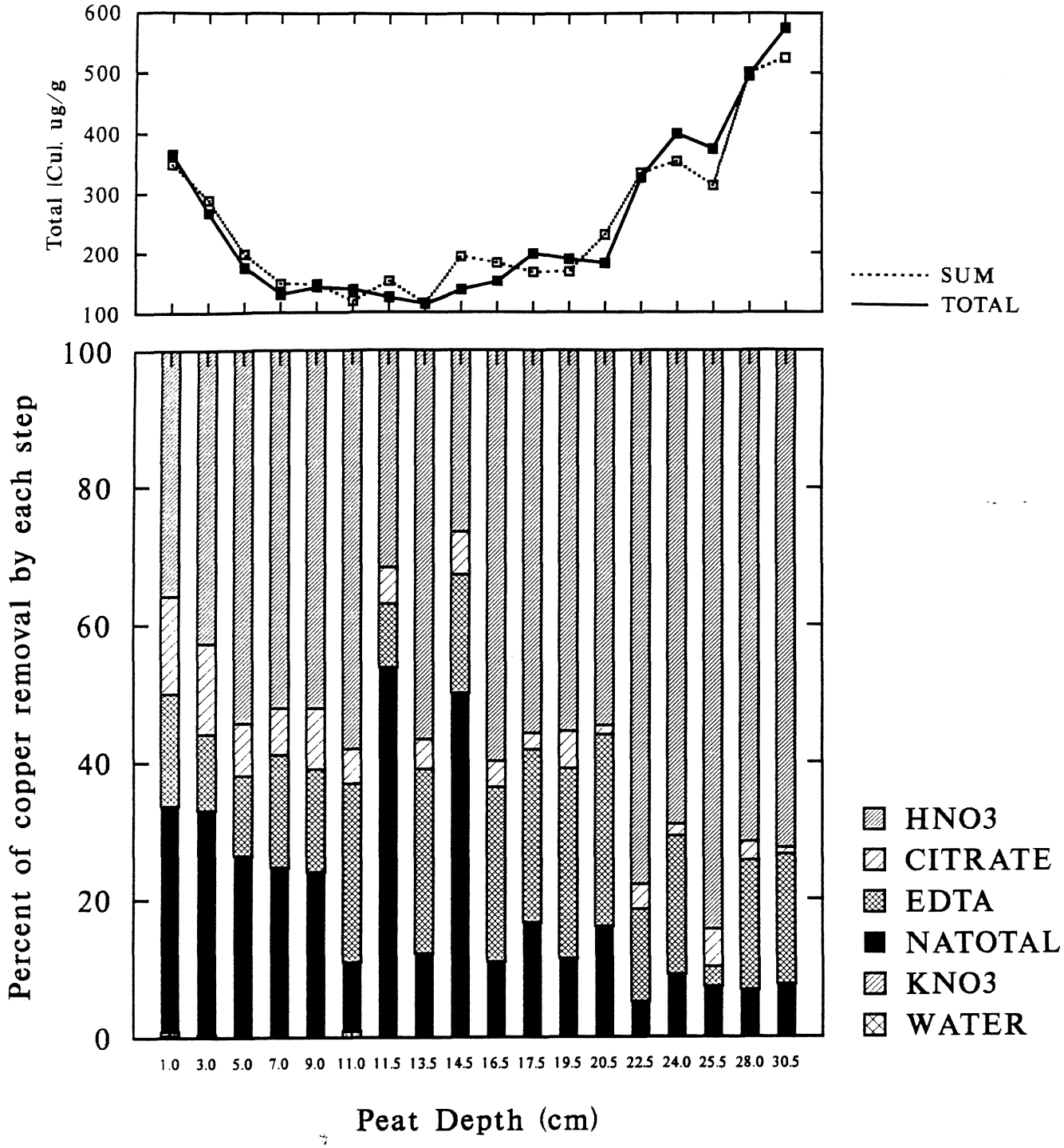


Figure 35. Sequential extraction results; cell 2 copper.

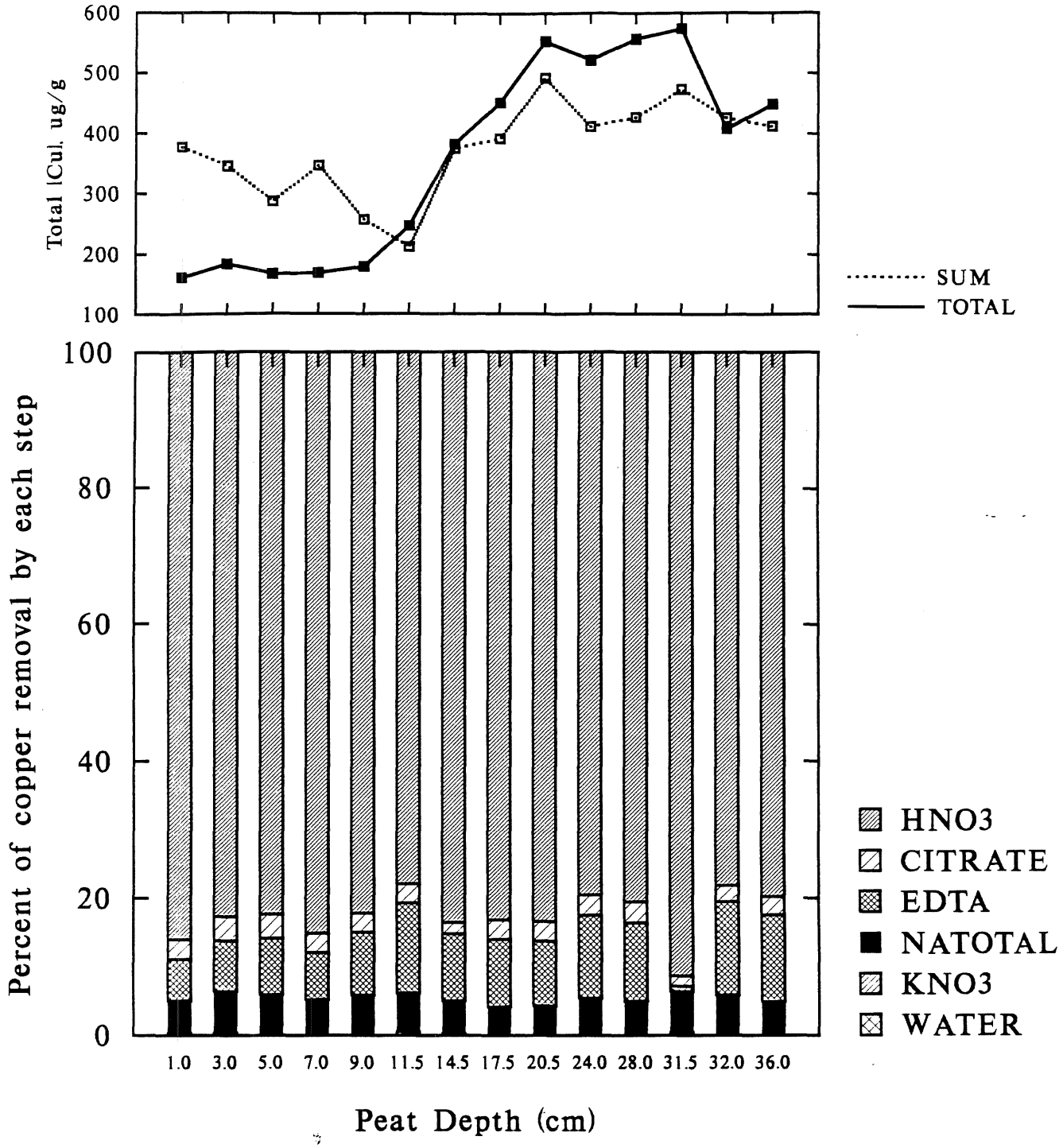


Figure 36. Sequential extraction results; cell 3 copper.

of ~600 mg/kg. In cell 2, copper concentrations were somewhat elevated in the top 6-8 cm of the peat, possibly indicating measurable copper removal in this cell.

The higher concentrations in the deeper peat of the wetland indicate a watershed source for copper. This area has relatively thin soils (<4.5 m to bedrock) and bedrock outcrop occurs immediately west of the cells. Copper was removed from water draining from this area and was concentrated in the peat. Lake sediment samples collected in Bob's Bay of Birch Lake (Figure 1) also have elevated copper concentrations at depth, providing additional evidence to support the theory of a watershed copper source (Lapakko and Eger, 1981).

In general, the copper loadings from the input to the cells were quite low, and the small amount of removal may not have increased concentrations in the upper portion of the peat to a level sufficient to be detected. The vast majority (>80%) of the copper present in the deep peat was in the residual form (i.e. removed by the HNO_3 extraction step), and even in the surface peat over 60% of the copper was present in the residual form. In cell 2, which had elevated copper concentrations, the organically bound fraction accounts for about 35% of the concentration in the upper portions of the peat. In general, the sodium pyrophosphate step removed less than 20% of the total copper in the upper portions of the core, and decreased to around 5-10% in the deeper sections of the core.

Cobalt

Cobalt generally followed the same trend as nickel, with concentrations being highest in the top (0-2 cm) segment and decreasing with depth. The major difference is that the concentrations were much lower than were the nickel values, a result of the relatively low cobalt load into the cells from the input water. The highest cobalt values were on the order of 130 mg/kg, as compared to values as high as 7700 mg/kg for nickel. Most of the cobalt, even at depth, was bound to the organic material in the peat, with a maximum of 75-80% in the zone of highest concentration.

Even though the general trends were the same for all three cells, cell 2 generally had higher cobalt levels than cells 1 and 3 (Appendix 26). This may be the result of a somewhat higher cobalt load into cell 2 which resulted from increased flow rates.

Zinc

Zinc also generally decreased with peat depth, going from a high of about 200 mg/kg in the top layer (in cells 2 and 3) to a low of 30 to 50 mg/kg in the deepest peat layers (Appendix 26). The proportion of zinc removed by each extraction step remained generally the same throughout the entire peat cores, with little variation with depth.

Section 10. Mass removal.

10.1. Introduction.

Wetland treatment is widely recognized as a potentially effective treatment option for acidic coal mine drainage, and for municipal wastewater treatment facilities. Much less is known, however, about the suitability of such systems for use at metal mining operations, and the little data that does exist deals primarily with input/output concentrations. (Often the projects which generate such data are motivated by regulatory requirements, which tend to define system success in terms of effluent concentrations.)

As a result, there are often insufficient data to complete an overall mass balance for the system, or to determine the fate of the removed metals. These type of data are important not only because they allow better estimations of system performance, but also better predictions of system lifetime and future availability of the removed metals. Mass removal was calculated by 2 methods:

1. the input/output concentrations were combined with the flow data, and
2. the increase of nickel mass in the peat and vegetation was calculated.

10.2. Metal mass removal estimates made from flow and concentration data.

The mass of metal entering and exiting the treatment cells was estimated by multiplying the total daily flows by the measured or calculated input/output concentrations. Input and output flow values were continuously measured throughout this study (Section 5.1, Appendix 11). Metals samples were typically collected about once a week, and concentrations between the measured values were estimated by using the average of the preceding and subsequent measured values. The daily concentrations were then multiplied by the daily input/output flows to arrive at daily mass loads. These daily mass values (presented in Appendix 25) were then summed over the course of the study to arrive at the total mass into and out of the cell. The total mass removed was the difference between the input and output values. The overall mass removal is summarized in Table 13.

Nickel: Approximately 3 kg of nickel was removed in each of the four cells over the course of the study (Table 13). Even though the reduction in concentration was lower in cells 3 and 4 the higher flow rates through the cell resulted in an overall mass removal comparable to cells 1 and 2. Nickel mass removal increased significantly in cell 4 after the peat/peat screenings mixture was added to the cell in 1991. The fresh binding sites provided by the new organic material resulted in much better removal efficiency in the cell. The mass removed in 1991 was 80% greater than the sum of the mass removed in 1989 and 1990. All four cells had the highest mass removal in 1991, a direct result of the consistently increased input metal concentrations that resulted from the construction of a dam right at the W3D seep (Section 4).

Table 13. Summary of nickel mass removal, as calculated from input/output water quality and flow data.

	Time Period	Annual Flow ($L \times 10^4$)		Nickel mass (g)		Total mass removed	Percent removal
		Input	Output	Input	Output	(g)	
Cell 1	1989	75	88	525	85	440	84
	1990	96	98	1450	260	1190	82
	1991	91	84	1780	490	1290	73
	Total			3760	840	2920	Ave = 80
Cell 2	1989	78	85	500	80	420	84
	1990	100	96	810	100	710	88
	1991	157	153	3050	1440	1610	53
	Total			4360	1620	2740	Ave = 75
Cell 3	1989	167	165	1210	400	810	67
	1990	171	158	1370	410	960	70
	1991	100	82	2010	410	1600	80
	Total			4590	1220	3370	Ave = 72
Cell 4	1989	179	162	1300	920	380	29
	1990	158	139	1240	620	620	50
	1991	132	122	2490	700	1790	72
	Total			5030	2240	2790	Ave = 50

Copper, Cobalt, Zinc: With the exception of the Seep 1 and Aquifer X study, mass removal of the other metals was considerably lower, reflecting the lower concentrations of these metals in the input water. Daily mass values for these parameters (copper, cobalt, zinc) are presented in Appendix 25; a summary of these data for cell 1 are presented in Table 14.

In general, zinc was removed in all cells during the entire study, while copper and cobalt removal was measurable only in 1991, a result of the higher input concentrations. (Mass calculations indicated that small amounts of copper and cobalt were removed during 1989 and 1990. Since input concentrations were low and there was no statistically significant difference between the input and output concentrations, the mass values were not considered significant.)

10.3. Mass removal by peat.

Three methods were used to estimate the total nickel mass removed by the peat in cells 1 and 2. In general, each method multiplies the nickel concentration by the mass of peat that is assumed to contain that specific nickel concentration. The results of these calculations are summarized in Table 15; values calculated from input/output flow and concentration data

Table 14. Summary of copper, cobalt and zinc mass removal as calculated from input/output water quality and flow data.

	Copper (g)			Cobalt (g)			Zinc (g)		
	In	Out	Rem.	In	Out	Rem.	In	Out	Rem.
Cell 1									
1989	9.8	65.0[A]	~0[A]	19.6	19.8	~0	20.1	19.7	~0
1990	55.0	15.2	39.8	89.3	21.4	67.9	309.8[B]	39.6	270.2
1991	80.6	6.6	74.0	13.1	6.2	6.9	53.6	21.1	32.5
Total	145.4	86.8[A]	113.8	122.0	47.4	74.8	383.5	80.4	302.7
Cell 2									
1989	10.5	8.9	1.6	22.6	20.6	2.0	21.8	15.6	6.2
1990	11.6	11.1	0.5	29.5	17.2	12.3	29.0	16.6	12.4
1991	89.8	11.8	78.0	23.0	11.2	11.8	89.4	41.8	47.6
Total	111.9	31.8	80.1	75.1	49.0	26.1	140.2	74.0	66.2
Cell 3									
1989	22.0	18.0	4.0	43.0	36.2	6.8	43.1	25.9	17.2
1990	18.9	13.8	5.1	42.8	30.0	12.8	48.3	26.2	22.1
1991	72.7	6.5	66.2	15.6	5.5	10.1	99.1	13.9	85.2
Total	113.6	38.3	75.3	101.4	71.7	29.7	190.5	66.0	124.5
Cell 4									
1989	23.4	20.0	3.4	46.0	36.6	9.4	47.5	36.6	10.9
1990	17.1	14.6	2.5	38.3	21.9	16.4	44.4	27.9	16.5
1991	68.9	6.5	62.4	12.9	10.0	2.9	58.6	22.4	36.2
Total	109.4	41.1	68.3	97.2	68.5	28.7	150.5	86.9	63.6

A: The 1989 cell 1 outflow copper concentrations were abnormally elevated, yet the samples were destroyed before reanalyses could be conducted. The other three cells yielded reasonable values, implying that the cell 1 values were somehow compromised. If cell 1 removal in 1989 was zero, as seems probable, the total output mass would be 21.8 instead of 86.8 g, and removal would have been 113.8 g.

B: The 1990 cell 1 cobalt and zinc values were elevated due to the Aquifer X and Seep 1 tests, which used input sources that contained elevated cobalt and zinc concentrations. (The 1990 cell 1 output copper values were not noticeably higher than other years because the copper concentrations in the Aquifer X and Seep 1 inputs were not very high.)

are also presented in this table for comparison purposes; these values include only data through the 1990 field season, because the 1991 peat samples were collected in June, prior to the commencement of flow in the cells. Details of the calculation methods are presented in Appendix 25.

The mass removal estimates arrived at by the various methods were generally comparable. Since there are a greater number of assumptions and estimates in the methods which compute the mass accumulated in the peat and vegetation, the values computed from the input/output calculations are believed to be the most accurate.

Table 15. Comparison of nickel mass removal estimations for cells 1 and 2.

	Nickel mass (kg) as calculated from 1989-1990 flow and concentration data	Method 1	Method 2	Method 3	Average
Cell 1:					
Shallow	1.63	3.15	2.85	2.14	2.4
Deep	na	0.36	0.33	--	
Cell 2:					1.2 (excluding method 3 value)
Shallow	1.13	1.49	0.90	0.25 [A]	
Deep	na	0.58	0.54	--	

na: Not analyzed. (Nickel removal calculations that are based on input/output mass loadings assume that all removal occurs in the shallow peat.) All mass values are kg.

A: The calculated mass (0.25 kg) was abnormally low. This was a result of the specific distribution of nickel concentration values in this cell. Based on this distribution the program assigned nickel values of zero to a large area of the cell (Appendix 25).

Method 1: The mean nickel concentrations in the shallow and deep peat layers of cells 1 and 2 were multiplied by the total peat mass of the two peat layers, and then the mass of nickel calculated to have been in the baseline peat was subtracted from this value. This method (which was used to calculate the initial nickel mass present in the peat) may not adequately account for the variation of nickel within the cell.

Method 2: In 1991, cell 1 and 2 peat samples were collected from 15 sites within each cell. For this method, each cell was divided into 15 portions, with each sample point at the center of a section; see Appendix 23. The mass of peat calculated to be in each of these sections was then multiplied by the corresponding nickel concentration value, and then the nickel retained was calculated by subtracting the original nickel mass from this calculated value.

Method 3: A software graphics program was used to create concentration contour lines. The volume of peat calculated (by a planimeter) to be within each contour segment was multiplied by the nickel concentration of that segment. The nickel mass calculated to be in the baseline peat was then subtracted from the sum of these contour segments to determine the mass retained.

10.4. Mass removal by vegetation.

The biomass estimates were combined with the tissue metals analyses to calculate the metal mass load taken up by the vegetation over two seasons of operation (Table 16). These data were then added to the metal loads taken up by the peat, to yield a total mass removal value for the peat and vegetation. This was then compared to corresponding mass estimations that were calculated from input/output flow and water quality data (Section 10.3.1).

Table 16. Vegetative nickel mass removal estimates.

	Mean 1989 [Ni] (mg/kg)	Mean 1991 [Ni] (mg/kg)	Biomass[1] (g/m^2)	Total[2] Biomass (kg)	Nickel Removed (g)
Cell 1					
Cattails					
· Leaves[3]	4.9	12.0	101	37.6	0.26
· Roots	17.9	72.0	-	1.3	0.07
· Rhizomes	8.5	16.8	-	24.2	0.20
Grasses/Sedges	6.0	7.5	260	145	0.22
Duckweed[4]	17.5	455.0	12	4.4	1.92
					Total 2.7 g
Cell 2					
Cattails					
· Leaves[3]	6.4	8.2	567	211	0.38
· Roots	27.0	91.1	-	7.5	0.48
· Rhizomes	13.9	42.8	-	135	3.90
Grasses/Sedges	8.5	34.5	64	36	0.94
Duckweed[5]	39.5	100.0	11	4.1	0.25
					Total 6.0 g

1: These biomass estimations (i.e. 101 for cattails) are from a 1991 biomass survey conducted by Anne Jagunich (MDNR, Hibbing) which did not consider belowground biomass. The belowground cattail biomass estimates are based on above/below ground biomass ratios as determined by Zhang et al. (1 root: 18 rhizome: 14 leaves).
2: Total biomass values assume that two growing seasons have been completed (so total aboveground biomass generated during the two year period was twice that of the 1991 biomass), and that the underground biomass (i.e. roots, rhizomes) remained constant in the two years prior to the 1991 biomass survey.
3: "Leaves" includes all plant material above the soil.
4: Only one duckweed sample was collected from cell 1 (735 mg/kg) during the original survey; the values presented in this table are based on that single sample, and may be significantly in error.
5: No duckweed sample was collected from cell 2

10.5. Peat mass removal as compared to vegetative mass removal.

Previous work has indicated that the mass of nickel removed by plant uptake is a small percentage of total removal (Eger et al., 1988, Wildeman, 1991, Gersberg, 1984, Dunbabin and Bowmer, 1992). In this study, less than 1% of the overall mass removal was removed by the vegetation, while more than 99% of the removal was associated with reactions that occurred at the peat substrate (i.e. adsorption, chelation, complexation, ion-exchange, sulfate reduction, precipitation, etc.)

Nickel concentrations in the vegetation within the cells appeared to peak near the middle of the cell, similar to the pattern for nickel concentrations in the peat. These areas could be where water tends to pool or where there is better contact with the peat.

10.6. Areal removal rates.

Areal removal rates were calculated by dividing the total mass removed by the area of the cell and by the total time the system was in operation. This provides a rate of metal removal per unit area and per unit time. For the three year period of the experiment, the areal nickel removal rates were similar for all the cells and ranged from 34 to 42 $mg/m^2/day$ (Table 17, Appendix 25).

Removal rates for the other metals (copper, cobalt, zinc) were more than an order of magnitude lower than nickel, the result of the lower input concentrations (Table 17). During the Seep 1 and Aquifer X study, when input concentrations were higher, removal rates increased by factors ranging from 2.5 for copper to 65 for zinc. The removal rate for zinc during those studies was comparable to the overall rate for nickel (Appendix 25).

Section 11. Discussion.

11.1. Metal removal.

A variety of metal removal processes occur in wetland systems. Physical processes such as sedimentation and filtration remove particulate metals from solution. In this study, over 90% of all the metals were present in the dissolved form and required either biological or chemical reactions for their removal. Biological processes (which include vegetative uptake and microbial mediated processes such as sulfate reduction) also occurred, but the major mode of metal removal was through the chemical processes, particularly those that occurred at the substrate surface. Peat contains a complex mixture of organic compounds with a series of functional groups. These groups provide a variety of sites for metals to bind.

Based on the mass balance calculations and the sequential extraction results (Section 9.3.4), it was determined that most of the metal removed in the wetland cells was associated with the

Table 17. Areal mass removal rates.

	Total days of operation (1989-91)	Cell area (m^2)	Areal removal rate ($mg/m^2/day$)			
			Nickel	Copper	Cobalt	Zinc
Cell 1	431	163	41.6	1.1	1.1	4.3
Cell 2	444	168	36.7	1.0	0.4	0.9
Cell 3	431	191	40.9	0.8	0.4	1.5
Cell 4	453	179	34.4	0.8	0.4	0.8

Note: Cell 1 removal rates were higher than the other three cells due to the 1990 Aquifer X and Seep 1 tests.

organic fraction of the peat substrate. A series of reactions, including adsorption, ion exchange, complexation and chelation are responsible for this removal. In some of these reactions metal ions in solution replace hydrogen ions located at binding sites on the peat. The net result of this process is a release of hydrogen ions to solution, which has the effect of depressing solution pH. The total change in pH will be a function of the character of the peat, the amount of ion exchange that occurs, and the alkalinity of the solution. In the wetland treatment cells, output pH values were approximately 0.1 to 0.3 units lower than the corresponding input values (see Appendices 15-18).

Since the ability of peat to remove metals from solution decreases as the pH of the solution decreases, and because effluent pH must remain above 6.5 for successful wetland treatment (due to regulatory requirements), the input pH must be greater than 6.5. Stockpile drainage at the Dunka Mine generally has a pH greater than 6.5, alkalinity greater than 80 mg/L (as $CaCO_3$), and from 1-10 mg/L nickel. The outflow from any wetland treatment systems at Dunka should thus remain above the standard (6.5) if the influent pH is 6.7 or greater. If the stockpile drainage is less than 6.7, the input pH could be increased by passing the drainage through a limestone bed before it is directed to the wetland treatment system (Lapakko and Antonson, 1990). The limestone bed could be used to adjust the effluent pH from the wetland, but there may be a greater possibility of plugging the limestone bed with organic material from the wetland.

A larger decrease in pH was observed in cell 4 in 1991, at which time the output values were up to 1.5 units less than the corresponding input values. This was caused by the addition of the peat/peat screenings material prior to the 1991 field season. The screening material was a waste product from the production of horticultural peat, and has a pH generally less than 5 and a low

metal content (Appendix 23). As a result there was a large amount of hydrogen ions being released to solution in the early part of the year. As the easily exchangeable hydrogen ions were replaced, the difference between input and output pH decreased (Figure 8).

The specific mechanisms of metal removal are important because they affect the overall lifetime of the wetland. Long term treatment of mine drainage is an important regulatory issue, and the ability of wetlands to provide continued treatment has not been demonstrated. As a result, the Office of Surface Mining has required back-up chemical treatment for wetlands built to control coal mine drainage (O.S.M., 1988). If the removal is primarily due to removal by organics, then the system lifetime is limited by the total amount of removal sites that are available in the top portion of the wetland. The length of time a wetland can successfully treat a specific mine drainage will be a function of the effective number of removal sites and the total metal load into the system. These factors are discussed more fully in Section 11.5.

Sulfate reduction is a bacteriologically-mediated process in which sulfate is reduced to sulfide. In the absence of oxygen, the bacteria can oxidize organic matter and use sulfate as the electron acceptor, which results in sulfate being reduced to sulfide. The sulfides can then react either with metal ions to produce highly insoluble metal sulfides, or with hydrogen ions to produce hydrogen sulfide (H_2S) gas (Hedin et al., 1989). The gas can then volatilize, resulting in the distinctive H_2S odor. This reduction process also has the effect of producing alkalinity (HCO_3^-), which has the effect of consuming acid and raising solution pH (Dollhopf et al., 1990).
This reaction is dependent only on an anaerobic environment, and adequate supplies of small chain organic compounds and sulfate (Postgate, 1984). Since sulfate is always present in elevated concentrations in problematic mine drainage and all wetlands have anaerobic zones, the amount of sulfate reduction will be a function of the supply of small chain organics, and the transport of metals from the aerobic upper zone of the wetland to the deeper anaerobic layers. Sulfate reduction processes offers the possibility of longer-term treatment, since this process can continue to remove metals as long as there is a source of small chain organics and sulfate.

There was no significant difference between input and output sulfate concentrations in the four treatment cells and mass balance calculations did not show any substantial sulfate removal in any of the cells (Appendix 25). Given the high concentrations of sulfate in the drainage (several thousand mg/L), small changes in sulfate mass would be difficult to detect. All four cells gave off a definite H_2S odor, which would indicate that at least some sulfate reduction had occurred within the cells. In cell 3, where hay had originally been placed in an attempt to encourage sulfate reduction (by providing a readily consumable organic carbon source), this odor was strongest in 1989, and coincided with elevated net alkalinity values in the initial month of the study (Appendix 17). Ten to twenty percent of the nickel in the upper sections of the peat cores from cell 1 and 2 was associated with the residual form which would include the metal sulfides, while in cell 3, the percentage was somewhat higher, ranging from 15 to 25% Although sulfate reduction occurred, its contribution to the overall removal was much less than the complexation reactions that occurred with the organic matter in the peat.

11.2. Water level effects on system performance.

Although all the cells were successful in removing nickel from mine drainage, the reduction in nickel concentration was always highest in the cells with 5 cm (2 inches) of water. Since over 99% of the metal removal is associated with the peat, a shallow water depth provides for better contact of the drainage with the substrate.

This difference in contact was demonstrated by the first dye study conducted in 1990 (Appendix 12). Rhodamine WT was used in this study to determine the residence time in each of the cells. Since this dye is adsorbed onto organics, dye removal can be used to indicate the degree of water and substrate contact. The dye removal in the deep water (15 cm; 6 inches) cells was significantly less than the removal in the shallow water cells (Figure 37). The higher removal was the result of better contact between the dye in solution and the substrate.

Preferential flow paths also developed more readily in the deep water cells. The design residence time for each of the cells was on the order of 40 to 48 hours. The initial flow rate was calculated by determining the volume of water above the peat and determining the flow rate that would produce a residence time in that range. Dye studies indicated that while the actual residence times for the shallow water cells were close to the design values, the residence times in the deep water cells were too low by about a factor of two. The lower residence times indicated that preferential flow paths and incomplete exchange of water existed in the deeper water cells.

11.3. The effects of residence time and seasonal factors on system performance.

Previous laboratory kinetic data indicated than nickel removal for a drainage with water quality similar tho the W3D input was 68% complete after 24 hours and 80% complete after 48 hours (Lapakko et al, 1986). Initially all cells were designed to have a residence time on the order of 40-48 hours, but residence time varied somewhat throughout the study due to fluctuations in flow. One of the objectives of this study was to provide design data for full scale wetland treatment systems at the Dunka Mine, and in 1991 a series of tests were conducted in an attempt to specifically identify the relationship between residence time and removal (Eger and Melchert, 1992).

The residence time is a critical design parameter since the size of the wetland is directly proportional to its value.

$$\text{Residence time} = \frac{\text{Area of wetland X water depth}}{\text{flow rate}}$$

Based on the variation of outflow concentrations with residence time in the various cells, several conclusions can be drawn:

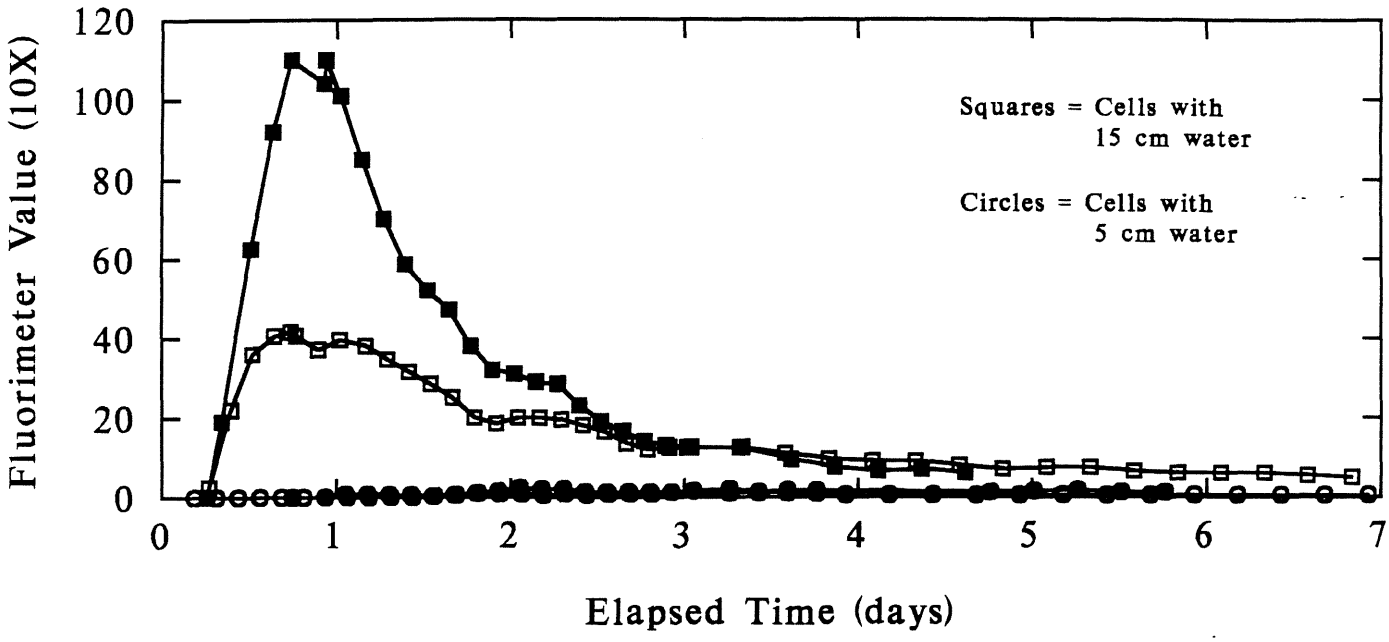


Figure 37. Comparison of dye recovery in wetland cells with differing water levels.

1. Outflow concentrations generally increase as residence time decreases.

2. As input concentration increases the importance of residence time increases.

3. There appears to be a seasonal factor, such that the removal at a given residence time is less in the fall than during the summer.

For the W3D drainage, when the input concentration exceeded 1 mg/L, and during summer conditions, a residence time greater than 36 hours was required to produce an effluent that met the proposed standard of 0.213 mg/L (Figure 15). At input concentrations below 1 mg/l the outflow concentration appeared to be independent of the residence time (Figure 7.6.3).

Based on the current data the residence time required for adequate treatment in the fall could not be determined. In general, there was a loss of treatment efficiency when temperatures decreased in the fall. Outflow concentrations increased even when residence times were increased; outflow nickel concentrations in cell 2 exceeded water quality standards even with residence times of 66 hours. Both chemical and biological reactions are affected by temperature, and it is likely that the loss of efficiency is related to slower reaction and diffusion rates. Although metal removal still occurred, water quality standards were not met. Newer systems will have to be designed to either store flow in this time period or size for lower efficiency in the fall.

Cell 4, during its first year of operation with the added peat/peat screenings mixture, was able to produce nickel concentrations below the standard at residence times as low as 20 hours (Figure 7.6.5). This better performance was most likely the result of the large number of new adsorption sites that were added with the new material.

11.5. System lifetime estimates.

Initial estimates of lifetime were made using laboratory and field data collected during previous studies (Eger and Lapakko, 1989). The two assumptions were that:

1. The nickel capacity in one kg of dry peat was 10,000 mg/kg.
2. The effective depth of metal removal in overland flow wetlands was 20 cm.

Based on these assumptions and using an input flow of 7.6 L/min, a nickel concentration of 2 mg/L, and 225 days of flow each year, the lifetime of each cell would be on the order of 15 years:

$$\text{Lifetime (years)} = \frac{\text{total removal capacity in cell (mg)}}{\text{annual nickel load (mg/year)}}$$

$$= \frac{\text{(Area of cell (cm}^2\text{) x Effective removal depth (cm) x Density of peat (g/cm}^3\text{) x 10,000 } \mu\text{g Ni/g)}}{\text{Conc. (mg/L) x Flow (L/min) x 1440 min/day x 225 days/yr)}}$$

Although additional adsorption sites will be generated annually as plants die and decompose, the formation of new sites is minimal. To provide a balance between the input of metals and the formation of new removal sites in our test cell, input flow would need to be reduced by about an order of magnitude (Table 18).

Another method to increase the treatment life of the wetland is to construct the system so that the surface peat can be replaced. This approach has been used by LTV Steel Mining Company at their Dunka Mine in northeastern Minnesota, where a peat mixture was placed on top of an existing wetland (Frostman et al., 1993). New material can be added when the removal capacity of the mixture is exhausted.

Table 18. Comparison of annual production of metal removal sites with current annual metal input.

Annual input of removal sites:	
• Peat accumulation rate	1 mm/yr[1]
• Bulk density	0.1 g/cm^3
• Removal capacity	10 g Ni/kg dry peat[2]
• Area of cell	186 m^2
• Annual removal capacity	0.2 kg Ni/yr
Present loading rate to cell	
• Flow	3.8 L/min
• Concentration	2.0 mg/L
• Average days of flow	225
• Annual metal input	2.5 kg Ni/yr
Flow reduction needed to balance input with annual generation of sites	92%

[1] Craft and Richardson, 1993
[2] Eger and Lapakko, 1988

Another factor that limits the removal in natural wetlands is the transport of metals to reaction sites. Although peat depth in our wetland was about 1 m, only the upper 20 cm was effective in removing metals. In natural wetlands, flow occurs primarily across the surface, generally within the upper 30 cm (Romanov, 1968). Flow is minimal in the deeper layers as a result of a low vertical hydraulic gradient and a decrease in hydraulic conductivity with depth. However, wetlands can be constructed to encourage vertical flow and provide more contact with the substrate. This type of wetland requires additional engineering design, but the increase in treatment per unit area can be significant (Eger and Melchert, 1992).

Section 12. Conclusions.

- All four cells were successful at removing metals from mine drainage, but the cells with 5 cm of water depth (cells 1 and 2) were more efficient than the cells with 15 cm of water depth (cells 3 and 4). The shallower water depth allowed more intimate contact of the water with the organic substrate (peat) in the cell, and produced greater removal of metals.

- Outflow nickel concentrations generally increased as residence time decreased. A residence time of 24-48 hours was usually necessary for adequate treatment.

- Metal removal efficiency in all four cells tended to decrease in the fall. Although the specific reasons are for this loss in efficiency are unclear, it is likely related to decreased chemical/biological activity due to colder air/water/ground temperatures. This loss of efficiency will need to be incorporated into the design of future systems to provide adequate treatment in the fall.

- More than 99% of the nickel removal in the cells was associated with the peat.

- The vegetation in the cells (cattails, grasses/sedges and duckweed) accounted for less than 1% of the mass removal. However, vegetation plays other indirect roles in metal removal which are important, such as preventing erosion of the substrate, distributing flow and minimizing the development of preferential flow paths, filtering particulates, increasing the permeability of the peat substrate, and affecting sediment chemistry and microbial activity (Dunbabin and Bowmer, 1990).

- The majority (about 60%) of the metal removal in the peat substrate occurred through association with the organic material in the peat. The processes involved include adsorption, ion exchange, and complexation and chelation of metal ions onto binding sites in the peat. Most of the removal occurred in the top 20 cm of the peat, though some removal was detected in the 20-50 cm layer as well. This was particularly true in cell 2, where trenches had been constructed to increase the contact of the drainage with the deeper peat layers.

- The metals bound in the peat via adsorption should remain in the peat. The large molecular weight humic materials produced by anaerobic decomposition of plants have a strong affinity

for metals, which are therefore largely insoluble (Simpson, et al., 1983). Desorption tests indicated that greater than 80% of the metals were strongly bound by the peat (Lapakko and Eger, 1986).

- Metal removal by reactions which bind metals to the organic material in the peat, accounted for about 60% of the total removal. These reactions depend on the availability of removal sites and therefore have a finite capacity. Other removal mechanisms with finite capacities, such as ion exchange, accounted for about another 15% of metal removal. As the binding sites in the peat become filled with metal ions, the ability to remove metals from solution becomes exhausted.

- The addition of new adsorption binding sites via decaying plant matter is not sufficient to counter the exhaustion process. To maintain the effectiveness of such a system without physically altering the cell, it would be necessary to either 1) decrease input concentrations, or 2) decrease input flow rates.

  Neither alternative may be possible or practical, and to maintain system effectiveness it would be necessary to replace and/or amend the spent peat with fresh peat (or other organic substrate materials).

- The cell may be considered to be exhausted even if some metal-removal capacity remains. System success is usually defined by the ability to meet water quality standards. Once output concentrations exceed standards, then the cell is by definition no longer successful, even if some removal capacity remains within the peat.

- Though input/output sulfate concentrations seemed to indicate that little sulfate reduction was occurring in the cells, all of the cells had an H_2S odor. This odor was strongest in cell 3, which had straw added to it in an attempt to encourage sulfate reduction by supplying a readily available food source for the sulfate-reducing bacteria. The superior treatment observed for cell 3 in relation with the other deep-water cell (cell 4) may be the result of sulfate reduction.

- Aerobic processes occurring in wetlands can remove metals from neutral mine drainage. These processes are limited by the amount of available exchange sites in the substrate, and by the transport of contaminants to these sites. Aerobic processes cause pH to decrease (as hydrogen ions at the binding sites are exchanged for metal ions), and are less effective at removing metals as solution pH decreases.

  Anaerobic processes are effective in not only removing metals, but also in elevating pH; this is the best treatment for acid mine drainage. Systems designed for anaerobic treatment can handle a higher volume of flow than similar-sized aerobic systems, but flow rates through the substrate may decrease over time as the substrate decomposes.

A mining research site being constructed by MDNR in Hibbing, MN, will combine aerobic and aerobic wetlands to treat neutral metal mine drainage. It is hoped that the anaerobic wetland(s) will remove the bulk of the metals, and the subsequent aerobic wetland (and possibly a soil filter) will remove remaining metals and other contaminants such as nitrogen and total phosphorous, which are often associated with anaerobic systems.

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