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METAL MOBILIZATION FROM A NEAR-SHORE LAKE SEDIMENT UNDER SIMULATED ACIDIC GROUNDWATER INPUTS

by

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Approved by:

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Abstract

Simulation of acidic groundwater passing through lake sediments was conducted under controlled conditions in a laboratory. Three sediment cores collected intact from the near-shore region of an acidic lake were subjected to simulated groundwater inputs of initially identical chemistry for a seven day period. Following this period water being used in the simulation for two of the sediment cores was acidified by hydrochloric acid (HCl) addition to examine the ability of these sediments to neutralize acidic groundwater with varying H^+ concentration.

Simulated acidic water passing through the sediment cores mobilized significant amounts of metals. The sediment acted as a sink or a source of metals dependent on H^+ concentration of water leaving the sediments. Following influent acidification, the sediments acted as a source of aluminum (Al) until the end of the experimental period. In all cores, influent H^+ was neutralized predominately by the mobilization of Al. Fluoride release from the sediments was episodic following acidification. The majority of the fluoride released was complexed with Al forming AlF^{2+} which was the predominant (>99%) Al-F species. Unlike Al, both manganese (Mn) and lead (Pb) mobilization was episodic with the influent acidification. For one core in the period before acidification, the sediment acted as a sink for Pb, however, this Pb was remobilized following influent acidification. The sediment was a "strong" sink for iron (Fe) prior to and following the influent acidification period. Acidification showed no effect on the mobilization of Fe, and over 99% of the influent Fe was lost to the sediments. Comparison of sediment metal fractions showed substantial variation in total metal content among the cores, however, the percentage distribution of the sediment metal fractions among the cores was similar. The inter-core variation in sediment chemistry and it's effects on groundwater chemistry as observed during the initial seven day period, suggest that the chemistry of groundwater inputs to lakes should exhibit high spatial variability.

ACKNOWLEDGMENTS

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1.0 INTRODUCTION

1.1 SOURCES AND TRANSPORT OF ACIDIC DEPOSITION

Extensive release of acid precursors to the atmosphere occurs from many industrialized regions of the world (USEPA, 1984). These acid precursors result from the combustion of fossil fuels for the production of energy which has increased substantially in the last few decades (USEPA, 1984). Emissions of nitrogen and sulphur oxides to the atmosphere occur during fossil fuel combustion and subsequently H_2SO_4 and HNO_3 are formed by oxidation and hydrolysis. The eventual fate of these acids that are formed is deposition to the earth's surface. Research in the 1960's manifested low pH values in precipitation in northern Europe and eastern North America (Likens et al., 1979; Likens and Butler, 1981). Recently acidic deposition has been reported in western North America (Likens et al.,1980).

Acidic deposition has been observed in many studies in regions remote to urban industrialized areas (Johannes and Altwicker, 1980). These regions are "downwind" of industrialized regions and have been observed at distances exceeding 1000 km from acid precursor source areas (Likens and

Butler, 1981).

On an annual basis, atmospheric inputs of sulphuric acid exceed those of nitric acid inputs in North America and Europe (Johannes et al. 1984). However during winter periods, atmospheric inputs of nitric acid have been observed to be approximately equal to sulphuric acid inputs (Galloway and Likens 1981). This occurrence may partly explain the increased importance of nitric acid inputs to surface water acidification during snow melt events (Driscoll and Schafran 1984). Atmospheric inputs of both nitric and sulfuric acid can occur by wet (rain, snow, fog) and dry (aerosol) deposition processes. Dry deposition of acids to watersheds is strongly influenced by the receptor surfaces (e.g. vegetative types, water) present in the watershed and consequently is spatially variable (Hicks 1984).

1.2 EFFECTS OF ACIDIC DEPOSITION ON SURFACE WATER CHEMISTRY AND AQUATIC LIFE

1.2.1 SURFACE WATER ACIDIFICATION

Apparent acidification of surface water by acidic atmospheric inputs has been well documented by extensive research (NAS, 1981, US/Canada, 1981, NRCC, 1981). In eastern

North America many acid-sensitive (low alkalinity) lakes appear to have lost up to 40% of pre-acidification alkalinity. These lakes are very sensitive (little buffering capacity) to acidic deposition, such that small increases in acidic inputs could cause substantial decreases in pH values. Acidic waters have been observed to mobilize and dissolve various metals (e.g. Al, Fe, Mn, Pb) from soils and surface water sediments (Schindler et al., 1980) and result in increased concentration of metals in groundwater and surface waters (Wright and Henrickson, 1978; Seip, 1980). Aluminum has been observed to be the most readily mobilized metal within watersheds containing acidic waters (Johnson et al., 1981; Driscoll et al., 1984).

Within surface water systems, certain watershed characteristics have been identified as having significant control over surface water chemistry. Watersheds having high lake surface area to watershed area ratios (LS:WS) will have greater amounts of atmospheric deposition deposited directly to the lake. As a result terrestrial processes will have a lower influence over surface water chemistry. As an example, very acidic surface waters have been observed in regions where acidic atmospheric inputs occur and little terrestrial input of water to a lake occurs (Driscoll and Newton, 1985). Watersheds with low LS:WS ratios will have the majority of atmospheric deposition intercepted by the terrestrial system before reaching the lake and consequently terrestrial processes will exert a greater influence over surface water chemistry.

Surface waters acidified by atmospheric acid inputs are characteristically elevated in sulfate and the sum of the concentration of strong acid anions (SO_4, Cl, NO_3 in eq/l) exceeds the sum of the concentration of base cations (Ca, Mg, Na, K in eq/l) (Cronan and Schofield 1979; Johnson et al. 1981). Since aqueous solutions must be electrically neutral, these waters are elevated in H^+ or H^+ and metals other than the base cations such that the cationic and anionic charges are equivalent.

1.2.2 SOURCES OF TRACE METALS IN ACIDIC AQUATIC ENVIRONMENTS

Three important sources can contribute to trace metal concentrations in surface waters. First, atmospheric deposition, which includes dry particulate deposition or wet deposition (both dissolved and particulate matter scavenged from the atmosphere). Mineral weathering reactions and bacterially-mediated decomposition processes are second important sources where soils can yield both soluble and particulate trace metals to the surface waters. Surface water sediments, both lentic and lotic sediments, can also serve as reservoirs of trace metals. The relative abundance of trace metals in the atmosphere varies and depends on it's atmospheric transport. Lentzy and Mackenzies (1979) compared atmospheric and fluvial contributions in surface waters and reported that the Pb contribution from atmospheric sources was up to 12% of fluvial path way, whereas for Al, Fe, and Mn it was up to 25% of fluvial path way. Jeffries and Snyder (1981) have summarized the available data for potential atmospheric inputs of trace metals to rural North America (Table 1.1).

In a watershed system, the terrestrial environment can serve as an important source for trace metals. The pools for trace metals in terrestrial systems include soils, parent bedrock, soil solutions and vegetation. The interactions between these pools form a complex network which serves as a source and sink for these metals. Among these pools, trace metals in soil solutions are readily available for transport to surface waters, whereas transport of mineral bound metals and metals retained by inorganic and organic soil components are controlled by mobilization processes. The decay of plant material results in accumulation of these metals on soil surfaces and higher concentrations of these metals in the upper few centimeters of soil profiles (Bohn et al., 1979).

In the southwestern Adirondack Mountain region of New York, a region identified as acid sensitive (Driscoll and Newton, 1985), the predominant minerals that are susceptible to mineral weathering with H^+ transfer are plagioclase, amphiboles, pyroxenes, and biotites (Troutman and Peters,

Table 1.1

Range and Median Concentration (μM) and Deposition (μM $m^{-2}yr^{-1}$) for Pb, Zn, Al[a], Mn, Fe in Bulk Precipitation of Rural North America

	Concentration (μM)		Deposition (μM $m^{-2}yr^{-1}$)	
	Range	**Median**	**Range**	**Median**
Pb	0.001 - 0.193	0.08	0.008 - 0.0153	0.081
Zn	0.34 - 11.6	0.47	0.14 - 1.49	0.72
Al	5.93 - 17.4	8.15	5.93 - 13.7	8.67
Mn	0.042 - 0.69	0.31	0.044 - 0.19	0.055
Fe	0.61 - 15.9	0.81	0.27 - 11.8	3.92

From Jeffries and Snyder (1981). Collection dates span 1965 to 1977.

a. Only European values available.

1982). Elevated concentrations of trace metals in the surface waters of this area were attributed to the increased mobilization of these metals by mineral weathering reactions (Troutman and Peters, 1982). From their detailed examination of three lakes in the southwestern Adirondack Mountains, they suggested that variation in pH values among lake waters resulted predominantly from differences in the quantity of neutral groundwaters flowing in to these lakes. Since the solubility of these metals increases at low pH values (Stumm and Morgan, 1981), the extent of neutralization of acid inputs can strongly affect metal mobility. These authors observed that the transport of Mn and Zn correlated well with the extent of neutralization of acid precipitation; lead transport was mainly a function of hydrology and groundwater regimes; and iron transport was largely the result of mobilization and complexation with organic matter. In this geographic area during snow melt periods, increased transport of Al, Fe, and Mn have been attributed to increased solubility of these metals, accelerated weathering of glacial till, and the decomposition of biotite and amphibole in the bed rock (Davis and Galloway, 1982). In a study of watershed, Swanson and Johnson (1980) reported that net accumulation of Pb, Cu, and Ni, and net loss of Mn and Fe occurred in highly acidic soils and water, and was strongly influenced by mobile organic matter (fulvic, humic acids, dissolved and colloidal organic matter). Within the watershed Pb and Fe mobilization was interpreted to be a result of complexation with mobile organic matter.

Elevated metal concentrations, particularly Al, are associated with elevated H^+ concentrations in acidic waters (Johnson et al., 1981; Driscoll, 1980; Wright and Henrikson, 1978; Henrikson and Wright, 1978). These elevated metal concentrations are attributed to the higher rate of dissolution and increased solubility of metals at lower pH values of water (Troutman and Peters, 1982). Studies in the United States (Driscoll, 1980; Cronan and Schofield, 1979; Johnson et al., 1971), southern Norway (Seip, 1980), and Sweden (Hulteberg and Johansson, 1981) have shown that low pH waters can readily mobilize Al from soils. Driscoll (1984) observed that inorganic Al concentration increased exponentially with decreases in soil pH. Due to electroneutrality constraints the transport of conservative anions (e.g. Cl^-, SO_4^{2-}) through an ecosystem will result in an equivalent flux of cations. When these conservative anions pass through soils in an acid sensitive region (i.e. soils with low CEC and base saturation), base cation mobilization may be insufficient to neutralize H^+. Hence, the result is the transport of acidic cations (H^+, Al^+, trace metals) from soils to surface waters with the conservative anions.

Aluminum can occur as dissolved or particulate aqueous forms (Driscoll, 1985) and its mobilization and immobilization can control the transport of other metals (White, 1984).

Dissolved aluminum mobilized with H^+ ion can occur in groundwater and surface waters as aqua Al (Al^{3+}) as well as OH^-, F^-, SO_4^{2-} and organic complexes (Lind and Hem, 1975; Roberson and Hem, 1969). Aqua Al as well as important inorganic complexes of Al (OH^-, F^-, SO_4^{2-}) constitute a fraction of Al that has been referred to as labile Al (Driscoll, 1984; Johnson and Driscoll, 1981). Concentrations of this fraction of Al are predominately controlled by the concentration of H^+ and inorganic complexing ligands in solution. It has been observed that below a pH value of 5.5 fluoride is a strong complexer of Al and can be the dominant Al-inorganic ligand complex in acidified waters (Johnson et al. 1981). Dissolved Al can also occur as an organic complex and can comprise a significant portion of the total dissolved Al in solution (Driscoll 1981; Driscoll et al. 1984). The concentration of dissolved aluminum present in solution as an organic complex appears to be directly related to the dissolved organic carbon concentration in solution (Driscoll et al. 1984). Organically bound Al has been referred to as nonlabile Al due to the apparent lack of influence of H^+ and inorganic complexing ligand concentrations on this fraction.

1.2.3 EFFECTS OF ACIDIC DEPOSITION ON AQUATIC LIFE

Biological stress due to acidic deposition has been well documented in a number of ecosystems (Dannevig, 1959;

Beamish and Harvey, 1972; Almer et al., 1974; Cowling, 1980; Schindler et al., 1980a; Baker, 1981; Charles et al., 1987). In a lake acidification study (Schindler et al., 1985) a decrease in lake water pH value from 6.8 to 5.0 over a period of eight years resulted in dramatic changes in the biology of the lake. Mysis relecta and Pimephales promelas which were key organisms in the food web were completely removed from the lake at pH 5.8. Results of the acidification induced stress on the aquatic system were observed to be irreversible over the period of study. Changes in phytoplankton species, cessation of fish reproduction, disappearance of benthic crustaceans and appearance of filementous algae were attributed to changes in the lake's food web as a consequence of increased lake water H^+ concentration.

Fish population losses have been observed in many acidic surface waters and have been attributed to acidic deposition (Beamish and Harvey, 1972; Cowling, 1980). Decreased pH in a surface water can cause direct effects on growth rate, failure of recruitment of young fish, and reproduction of fish populations (NRCS, Canada, 1981). Beamish et al., (1975) reported that a decline of pH from 5.3 to 4.8 over a period of one year resulted in a substantial decrease in the growth rate for white suckers and was apparently associated with acidification. Additionally, increased concentrations of aluminum associated with acidification are toxic to fish (Baker and Schofield, 1982) and other aquatic organisms (Hall et al., 1985). The most toxic forms of Al have been reported as aqua Al, Al^{3+} and hydroxide complexes of Al (Baker and Schofield 1982). Fluoride and organic complexation of aluminum was reported to mitigate aluminum toxicity to fish fry (Baker and Schofield, 1982). Potential factors contributing to fish mortality include ion regulatory failure (Wood and McDonald, 1982) and gill accumulation of aluminum (Driscoll et al., 1980; Baker, 1981; Grahn, 1980; Baker and Schofield, 1982; Harvey, 1982). Elevated Mn in bone tissues of fish has also been linked to structural deformation in fish vertebrae (Harvey and Fraser, 1982).

1.3 NEUTRALIZATION PROCESSES IN TERRESTRIAL AND AQUATIC SYSTEMS

1.3.1 BIOGEOCHEMICAL PROCESSES IN ACID NEUTRALIZATION

A number of biogeochemical processes can contribute to the production of alkalinity and neutralization of acidic precipitation as acidic waters are transported through terrestrial and aquatic systems. Alkalinity is defined as the ability of an aqueous solution to neutralize H^+ added to the solution. This determination is measured relative to a fixed reference point which is traditionally the carbonic acid equivalence point ($HCO_3^- = H^+$; Stumm and Morgan, 1981). For most natural waters alkalinity can be defined as the sum of the equivalent concentrations of the carbonate species plus OH^- minus the H^+ concentration (Equation 1.1; Table 1.2; Stumm and Morgan, 1981).

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad [1.1]$$

Where: [] is the molar concentration

Alkalinity can also be defined in terms of electroneutrality as the sum of the equivalence of strong base cations minus the sum of the equivalence of strong acid anions (Equation 1.2).

$$\text{Alkalinity} = [Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + [NH_4^+] + n[Me^{n+}] - [Cl^-] - 2[SO_4^{2-}] - [NO_3^-] - [SA^-] \qquad [1.2]$$

Where: Me are metals other than the base cations
SA^- is the strong organic acid concentration

Within natural waters containing low concentrations of carbonate and OH^- (alkalinity < 100 μeq l^{-1}), additional aqueous components may contribute significantly to alkalinity. Weak organic acids (WA) and hydrolyzed forms of dissolved Al have also been identified as significant contributors to alkalinity in low alkalinity, acid-sensitive waters and may exceed carbonate and OH^- alkalinity (Equation 1.3); Henriksen and Seip, 1980; Driscoll and Bisogni, 1984)

Table 1.2

Mechanisms for Neutralization of Acids in Lake Sediments[1].

Congruent dissolution (1.4)

$Al(OH)_3 + 3H^+ \longleftrightarrow Al^{3+} + 3H_2O$

(gibbsite)

Incongruent dissolution (1.5)

$2NaAlSi_3O_8 + 2H^+ + 9H_2O \longleftrightarrow 2Na^+ + Al_2Si_2O_5(OH)_4 + 4Si(OH)_4$

(albite)

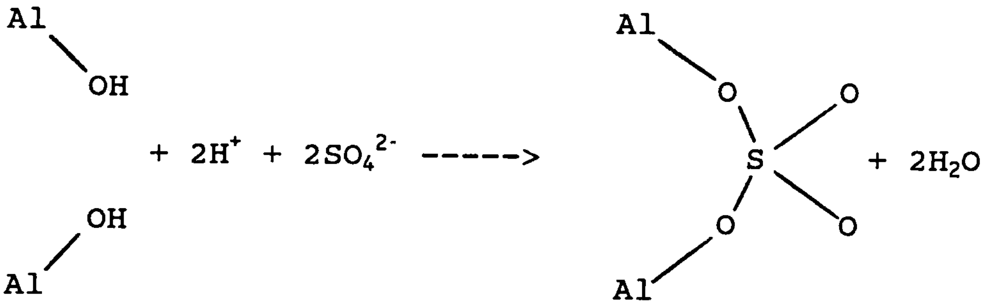
Cation exchange (1.6)

$M^{n+} - X + nH^+ \longleftrightarrow M^{n+} + nH^+ - X$

Precipitation of humic acids (1.7)

$R\text{-}COO^- + H^+ \longleftrightarrow RCOOH_{(s)}$

Sulphate adsorption (1.8)



Sulphate reduction

Production of H_2S (1.9a)

$2H^+ + SO_4^{2-} + 2CH_2O \longrightarrow H_2S_{(s)} + 2CO_2 + 2H_2O$

Precipitation of H_2S (1.9b)

$2H^+ + SO_4^{2-} + Fe(OH)_3 + 9/4CH_2O \longrightarrow FeS_{(s)} + 19/4H_2O + 9/4CO_2$

1(Stumm and Morgan, 1981)

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [WA^-] + x[Al(OH)_x^{3-x}] - [H^+] \qquad [1.3]$$

Water transported from a terrestrial system is generally enriched with alkalinity when compared to water entering the terrestrial system (Schnoor and Stumm, 1986). Many biogeochemical processes have been identified as contributing to terrestrial generation of solution alkalinity, with the relative contribution of each process varying among watersheds (Table 1.2; Schnoor and Stumm 1986).

Congruent dissolution of oxy-hydroxy Al minerals, such as gibbisite, increases alkalinity and releases Al to solution (Equation 1.4). Incongruent dissolution (Equation 1.5) similarly consumes H^+ as evidenced by the example reaction of albite conversion to kaolinite. Cation exchange associated with soil organic matter and clays can contribute to solution alkalinity by exchanging basic cations for H^+ (Equation 1.6). Precipitation of organic humus from soil solutions will also consume H^+ (Equation 1.7) and may significantly contribute to the cation exchange capacity of soils. Sulphate adsorption (Equation 1.8) can also consume H^+ by substitution of SO_4^{2-} into the inner sphere of metal hydroxides (Rajan, 1978). Sulphate adsorption in soils has been directly correlated with Fe and Al content of soils and negatively correlated with organic content of soils (Johnson et al., 1980). Sulphate reduction is one of the dominant neutralizing processes in anoxic environments (Nriagu and Hem, 1978). In an experimental lake acidification study (Cook and Schindler, 1983) half of the H_2SO_4 added was neutralized by sulphate reduction. In other studies a 65% loss of SO_4^{2-} was observed in eutrophic Weber Lake, Michigan (Kilham, 1982), 30% loss of SO_4^{2-} in soft water Langtern Lake, Norway (Wright and Johannessen, 1980), and 44% loss of SO_4^{2-} in Bog-Lake watershed, Nova Scotia (Ogden, 1982) were attributed to sulphate reduction. Microbial utilization of SO_4^{2-} as an electron acceptor results in the formation of sulfide and the consumption of two moles of H^+ for every mole of SO_4^{2-} reduced. The fate of sulfide formed by this process will determine whether alkalinity production can be considered permanent. No net alkalinity production occurs if the sulphide is reoxidized to SO_4^{2-}. For net alkalinity production to occur, the sulfide produced should leave the system as H_2S (Equation 1.9a) or dimethyl sulphide or precipitate as FeS (Equation 1.9b).

Atmospheric NO_3^- from precipitation is retained in terrestrial and bog systems by assimilation or denitrification (Kerekes et al., 1982; Hemond, 1980; Wright Johannesen, 1980). Consumption of one equivalent of H^+ takes place per mole of NO_3^- consumed (Equation 1.10 and 1.11). Retention of NH_4^+ in terrestrial systems results in the consumption of solution alkalinity. However, NH_4^+ deposition in most cases is less than NO_3^- deposition and the retention of inorganic nitrogen in these systems contributes to solution alkalinity. Among these reactions, cation exchange and mineral dissolution are usually the dominant alkalinity producing reactions (Henriksen, 1980; Thomson, 1982).

1.3.2 BIOGEOCHEMICAL PROCESSES IN TERRESTRIAL SYSTEMS: PROCESSES INFLUENCING ACID/BASE CHEMISTRY

Changes in acid/base chemistry that occur after precipitation has reached a surface water body have been suggested to be of secondary importance relative to changes that occur in the terrestrial system (Driscoll and Newton, 1985). Consequently, watersheds having high lake surface to watershed area ratios would have greater amounts of atmospheric input deposited directly to the lake and the lake waters would be characteristically have a high H^+ concentration. In these types of lakes, in-lake neutralization processes would predominantly control the acid/base chemistry.

The assimilation of acidic atmospheric inputs by terrestrial systems (geology) is affected by:

1) the chemical nature of soils, in particular cation exchange capacity (CEC) and base saturation (BS),
2) the permeability of soils,
3) the surface area of soil particles,
4) the soil depth in the watershed (USEPA, 1984a).

The terrestrial system can act as a source or sink of cation exchange capacity which has direct control on acid neutralization (McFee et al., 1976; Henriksen, 1980; Thompson, 1982). The cation exchange capacity of the soil is mainly dependent on the components of soils (Table 1.3; McFee et al., 1976).

It has been hypothesized that the role of geology in controlling the chemistry (acidity/alkalinity) of surface water bodies in the Adirondack Mountain region of New York can be up to 70% (Newton et al., 1987). These authors observed that where thick soils were present, significant amounts of acidic precipitation infiltrated to the groundwater system. Precipitation that infiltrates to groundwater has a longer contact with geological materials (than water flowing through shallow soils) and appears to undergo complete neutralization by geochemical weathering reactions taking place within the soil. Thus, acid-sensitive regions (as defined by soil CEC and percent base saturation) having deep permeable overburden can neutralize considerable amounts of H^+. Hence, acid sensitive soils are generally those with a low base exchange capacity and short retention time within geologic materials (Goldstein et al., 1984; Chen et al., 1984). Neutralization occurs quickly when the soils develop from carbonate bed rock due to the readily available base cations available. Consequently, regions with predominately siliceous soils with low base exchange capacity are primarily at risk for surface water

Table 1.3

Average Cation Exchange Capacity of Some Soil Components

Soil component	CEC(meq $100g^{-1}$)
Organic matter	200
Silicate clays	
Vermiculite	150
Montmorillonite	100
Kaolinite	10
Illite	30
Hydrous oxide clays	4
Silt and sands	negligible

acidification.

Chemical weathering of geologic materials is the ultimate source of base cations for groundwater. Water plays an important role in the transport of various metal fractions and base cations from soils and transporting them to surface waters. The relative solubilities and mobilities depend on the concentration and type of cations and anions in water passing through these materials and the physicochemical properties of the subjected soils (Schnoor et al., 1986).

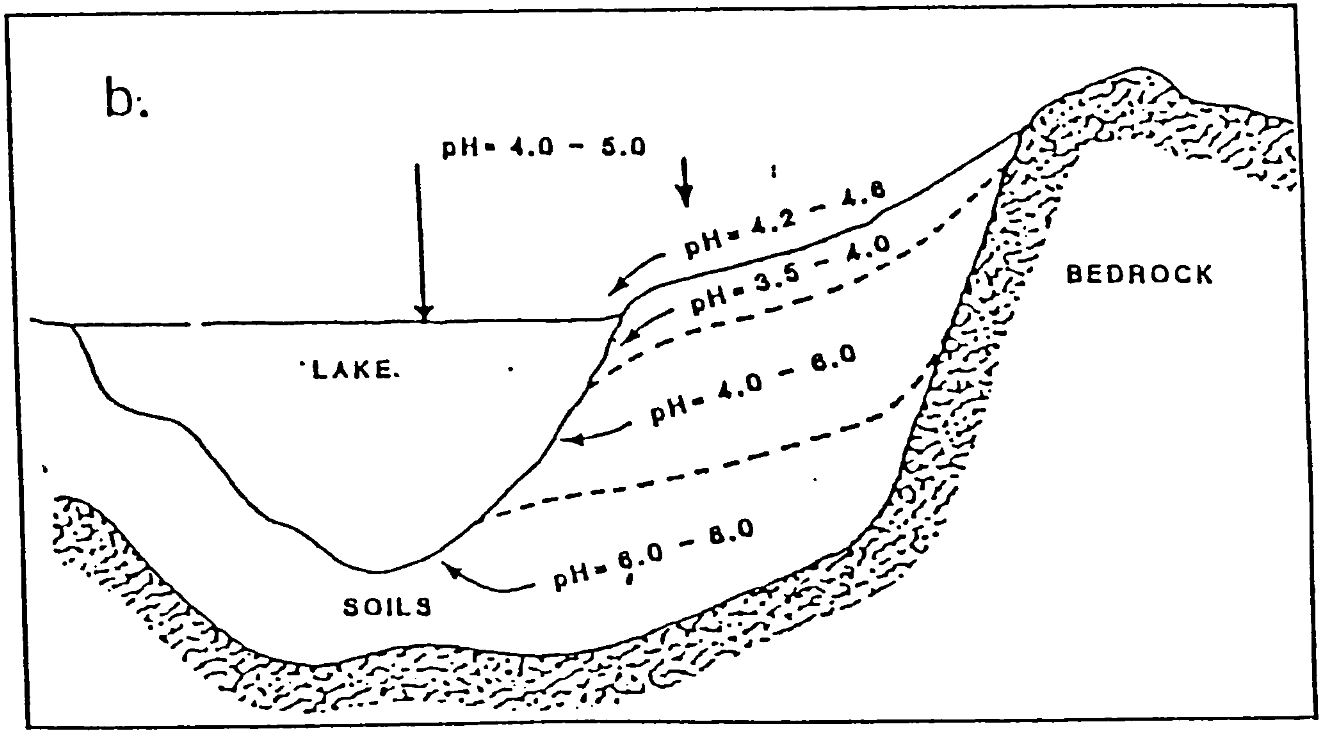
The extent of neutralization of acidic precipitation passing through silicious soils largely depends on the rate at which chemical weathering can supply base cations to cation exchange sites. Chemical weathering produces free base cations and acid neutralizing capacity to groundwater and ultimately surface water. Hence the magnitude of the pool of readily available base cations controls the extent of neutralization (Goldstein et al., 1984) and lakes are susceptible to acidification when the base cation production for exchange sites is less than the hydrogen ion inputs (Schnoor and Stumm, 1986).

1.4 HYDROGEOLOGY AND SURFACE WATER CHEMISTRY

1.4.1 GROUNDWATER FLOW PATHS

Groundwater flow paths through terrestrial systems are largely determined by the geologic setting. Geologic controls include topography of the drainage basin, infiltration capacity of soils and the thickness of soils in the drainage basin. Steep slopes are characteristic of surface run off dominated drainage basins whereas a low relief generally results in a greater portion of precipitation infiltrating the soils. Permeability characteristics of soils and the type of plant cover also significantly influence infiltration (Searcy, 1959). For two different drainage basins of similar relief and receiving similar precipitation inputs, the contribution of precipitation to groundwater will be largely controlled by differences in soil permeability between the two basins. The percentage of infiltration in general is greater in silicious soils than carbonate soils due to higher permeabilities of silicious soils.

The thickness of permeable soil material has been reported to control the pH of groundwater (Chen et al., 1984a; Fig. 1.1). This relationship is a result of the neutralization that occurs when acidic groundwater has a "long" period of contact with the soil/overburden. For example, if bedrock is


b.
pH= 4.0 - 5.0
pH= 4.2 - 4.6
pH= 3.5 - 4.0
pH= 4.0 - 6.0
pH= 6.0 - 8.0
LAKE.
SOILS
BEDROCK

mantled with thick tills, groundwater flow paths can penetrate deep within the soil and the contact time is long. In contrast, groundwater flow lines are short and water quickly exits the soil/overburden when the bedrock is covered with thin layers of till.

1.4.2 GROUNDWATER FLOW PATHS NEAR THE LAKE SHORE

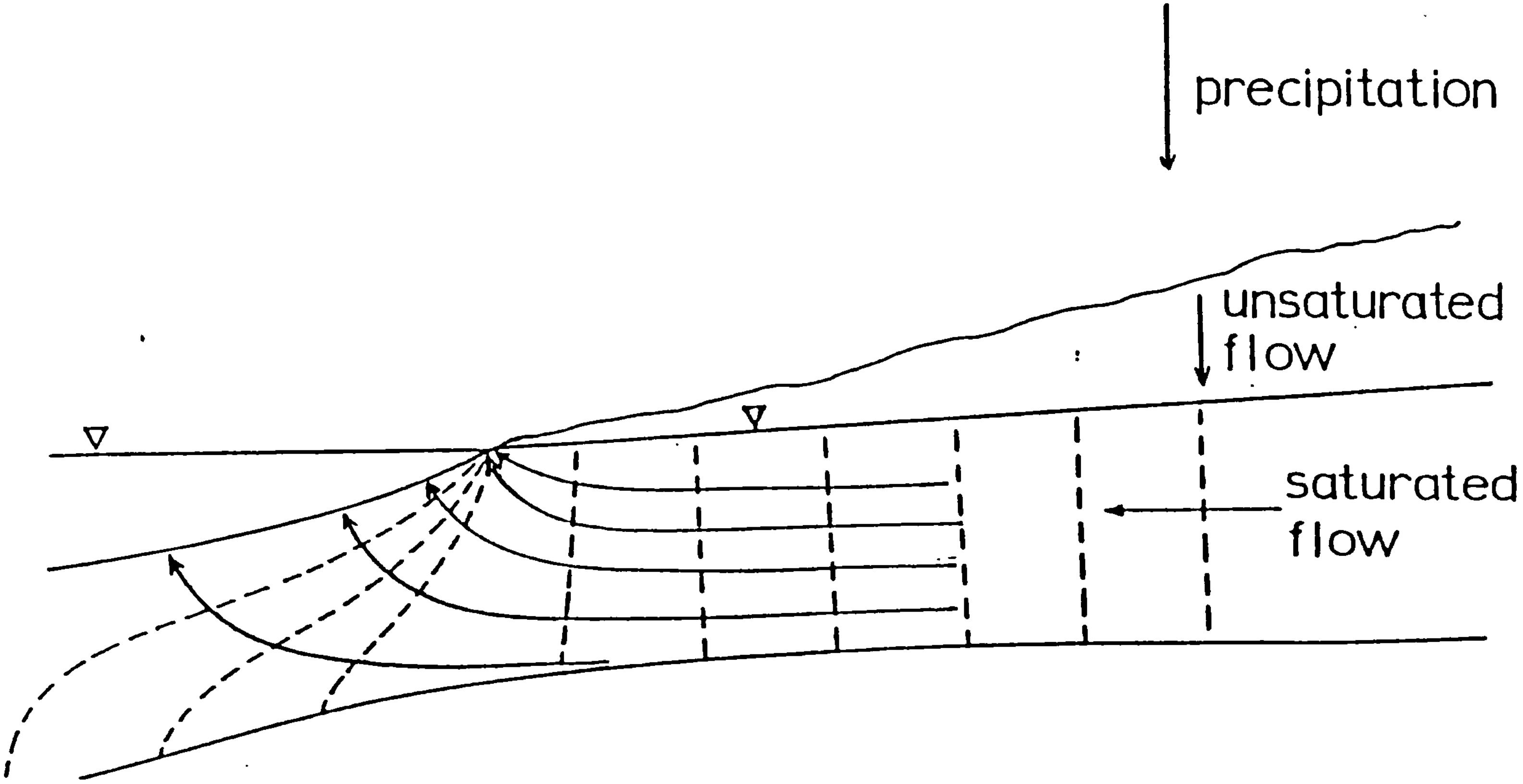
Previous studies of groundwater flow into lakes (Lee et al., 1980; McBride and Pfannkuch, 1975; Pfannkuch and Winter, 1984/1985; Winter and Pfannkuch, 1984/1985) indicate the highest rates of groundwater seepage to lakes generally occur within a few meters of the shore and decrease exponentially with distance away from the shore ($f = f^0e^{-cx}$, where f is the total flux, f^o is the flux at the shore line, c is a constant, and x is the distance from the shore; Lee et al., 1980). Hence, near-shore regions of lakes can be sites of high groundwater inputs. The sediments along the lake edge are the last that the groundwater comes in contact with before entering the lake, thus the chemistry as well as the mineralogy of these sediments may be important in controlling lake water chemistry.

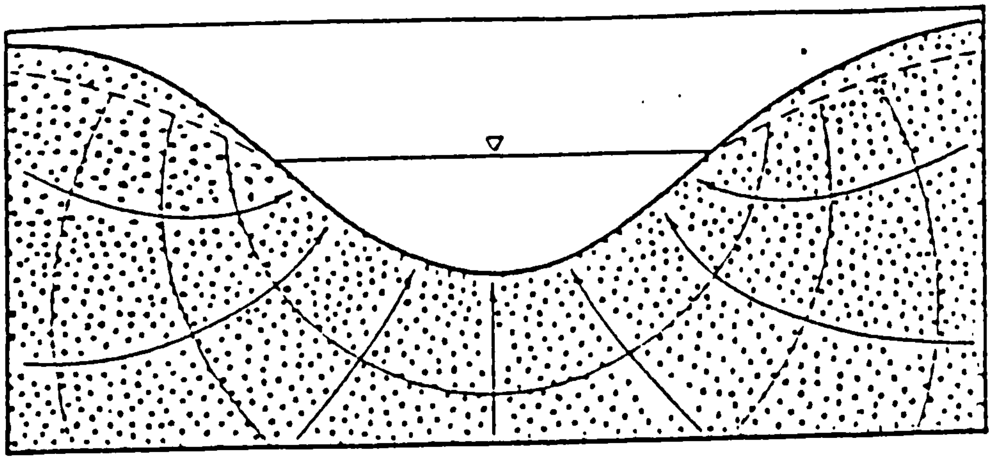
The magnitude of the contribution of groundwater inputs to lake hydrologic budgets has recently been manifested by various workers studying the water movement between lakes and surrounding aquifers (Winter, 1978a; Anderson and Munter, 1981; Hurley et al., 1985). In lakes (hydraulically connected to the surrounding groundwater system), modelling of various settings and groundwater flow paths has been carried out by various workers (McBride and Pfannkuch, 1975; Winter, 1978b; Winter and Pfannkuch, 1984/1985). Both field investigations (Lee et al., 1980) and modelling studies (McBride and Pfannkuch, 1975; Winter and Pfannkuch, 1984/1985) have revealed that in lakes receiving groundwater, flowlines converge and reflect upwards through the sediments in the vicinity of the lake shore (Figures. 1.2 and 1.3). In general, groundwater inputs are highly variable among lakes with the percentage contribution controlled by the physical characteristics of surficial geology and groundwater flow paths.

1.4.3 INFLUENCE OF HYDROLOGIC FLOWPATHS ON SURFACE WATER CHEMISTRY

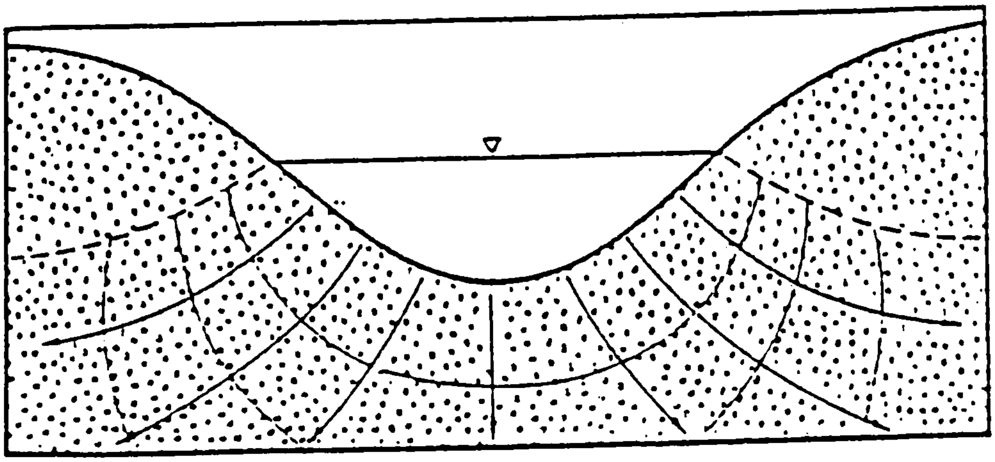
Recent evidence suggests that surface water chemistry in acid sensitive regions is substantially influenced by groundwater flow paths through the terrestrial systems (Chen et al., 1984a; Goldstein et al., 1984). Driscoll and Newton (1985) depicted the importance of the hydrologic flow path to surface water chemistry by conceptualizing the relationship

GROUNDWATER FLOW TO LAKES

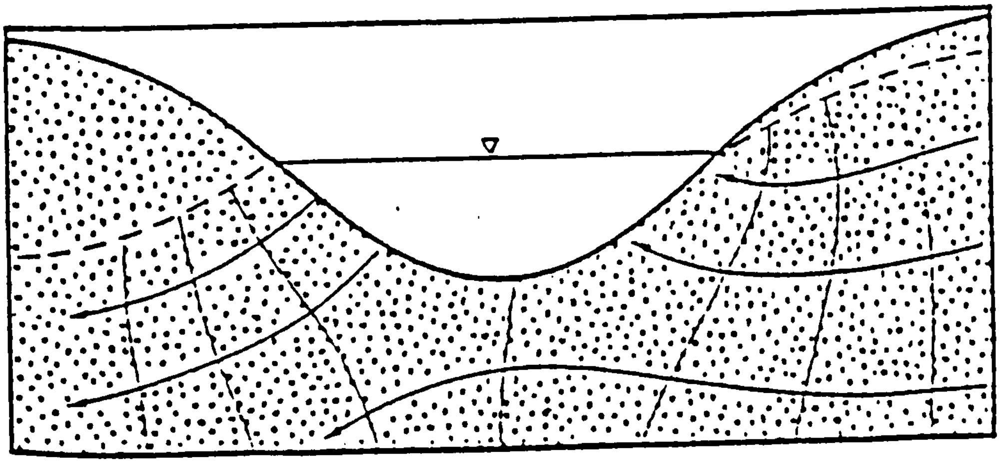




a) Discharge lake



b) Recharge lake



c) Flow-through lake

between soil flowpath and chemistry. When precipitation with high H^+ concentration infiltrates through deep soils (lower mineral horizon) containing pools of readily exchangeable basic cations, water entering the lake along this flowpath is enriched with basic cations and lower in H^+ concentration. Since this horizon contains a pool of readily exchangeable basic cations, basic cations are mobilized during H^+ removal. Whereas in the water passing through upper mineral horizons, Al is readily mobilized by H^+ removal due to the low concentration of readily exchangeable basic cations.

In a study of the relationships between groundwater flowpaths and chemistry, Schafran (1988) observed that geochemical reactions occurring in the near-shore sediments of an acidic lake could effect the chemistry of the groundwater inputs. Particularly noted in this study was the mobilization and immobilization of Al that readily occurred in response to changing pH values of groundwater. Mobilization of Ca^{2+} and F^- were also noted during periods when groundwater pH values declined. Groundwater concentrations of Pb also appeared to be influenced by changes in pH values; however, no conclusive relationship between groundwater pH values and the mobilization/immobilization of Pb in these sediments was developed.

1.5.0 PROPOSED RESEARCH

The following research was conducted to investigate the ability of a near-shore sediment in an acidic lake to chemically modify acidic groundwater transported through the sediment. Specifically, the ability of the sediments to neutralize H^+ through metal mobilization from the sediments will be evaluated. In this study, sediment cores taken from a field site underwent simulated groundwater input in a controlled laboratory setting. The cores received "groundwater" adjusted to different pH values to assess the sediments ability to neutralize H^+ and to determine the processes/reactions responsible for the neutralization.

1.5.1 RESEARCH HYPOTHESES

The following null-hypotheses are to be examined in this research:

1. Significant changes in water chemistry as well as sediment chemistry are not expected after acidification

2. Aluminum in water leaving the sediments will not be significantly affected by fluoride concentration

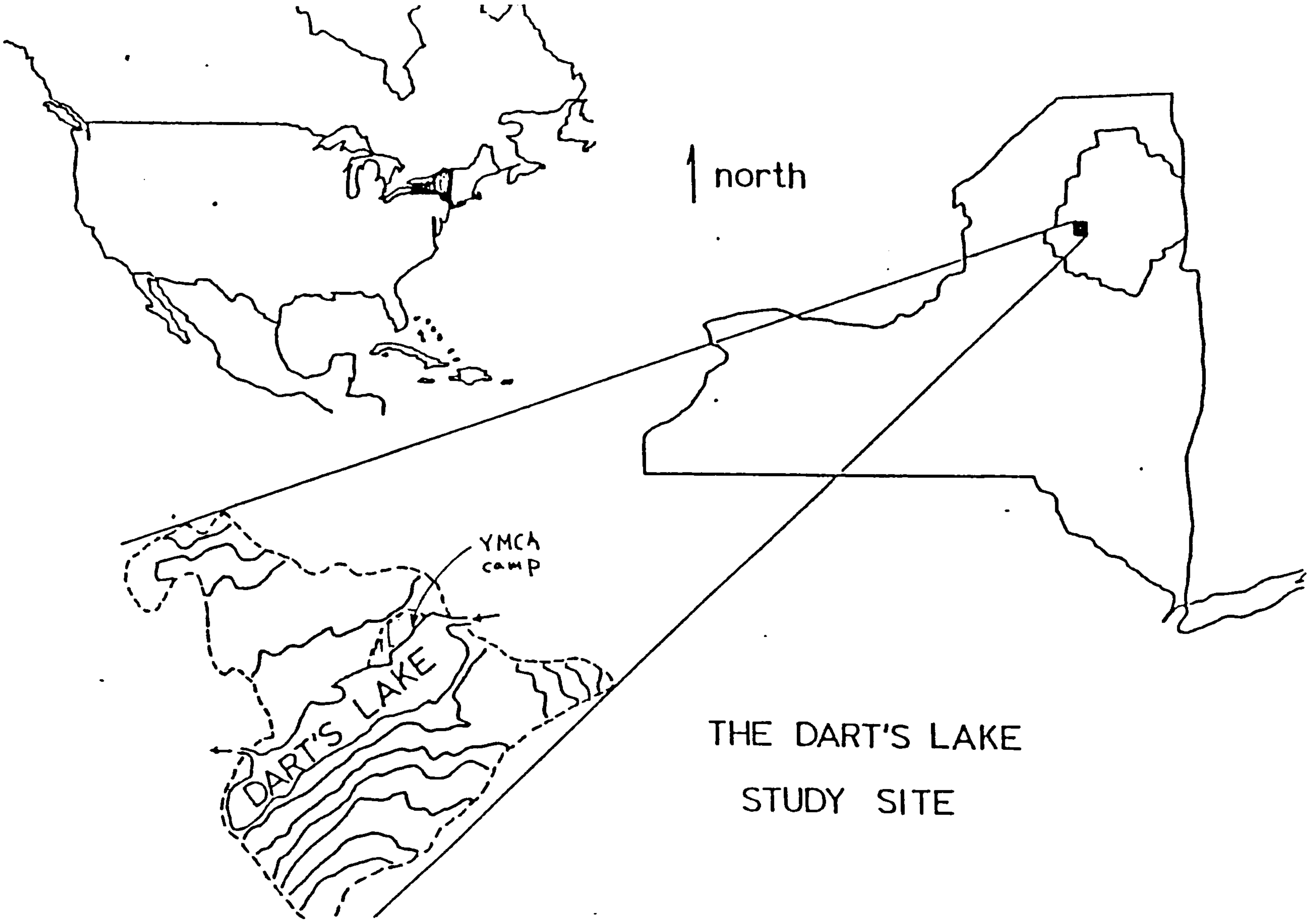
3. Mutual releases of metals and basic cations will be gradual and time dependent when the seepage rate is constant

4. No correlation between effluent pH and effluent metal and base cation concentrations will be observed.

In order to understand the effects of acidic deposition on hydrogeochemical processes, detailed laboratory investigations were carried out under controlled conditions. The main objective of the following experimental set-up was to simulate field conditions in the laboratory. Simulation involved the matching of groundwater flow rates and temperature with typical field conditions.

1.6 STUDY SITE

Dart's Lake (43° 47' N, 74° 51' W) which is located in the Adirondack Mountain region of New York was selected as the field study site where sediment cores were collected (Figure 1.4). The Dart's Lake site was selected due to previous work at a number of near-shore sediment sites where both groundwater and sediment chemistry had been determined (Schafran, 1988). Results of that study suggested that the near-shore lake sediments could influence the chemistry of groundwater inputs through metal mobilization/immobilization reactions. Substantial variations in surface water acid/base



THE DART'S LAKE
STUDY SITE

chemistry are present in this region (Schofield, 1977; Pfeiffer and Festa, 1980), even though most of the region is covered with "acid-sensitive" soils. These variations have been attributed to variations in geological and hydrological characteristics among watershed areas (Newton and April, 1982). The wide range in chemical characteristics of surface waters include acid neutralizing capacity, NO_3^-, Ca^{2+}, Al and dissolved organic carbon concentrations. Soils within the region are predominately Spodosols, which have minimal SO_4^{2-} absorption capacity (Fuller et al., 1985). Atmospheric inputs of the strong acid anions SO_4^{2-}, and Cl^- are not substantially retained by the soils in this region and are instead transported to surface waters (Schafran and Driscoll, 1987). This region receives substantial amounts of acidic deposition (0.5-0.75 keq/ha-yr SO_4^{2-}; 0.25-0.4 keq/ha-yr NO_3^-) (Stensland, 1984) and contains many acidic surface waters.

This site has been extensively studied by various workers. General geology and mineralogy (Newton et al.,1987), chemical characteristics (Driscoll and Newton, 1985), and water column chemistry (Driscoll et al., 1987; Driscoll and Schafran, 1984; White and Driscoll, 1985; Schafran and Driscoll, 1987) have been investigated within Dart's Lake and its watershed. The average bulk chemistry of surficial material in the Dart's Lake watershed was analyzed by Newton et al. (1987) (Table 1.4).

Table 1.4

Average Bulk Chemistry of Surfacial Materials in the Dart's Lake Watershed

(Newton et al. 1987)

SiO_2	74.09%
Al_2O_3	11.34%
Fe_2O_3	6.23%
MgO	0.40%
CaO	1.13%
Na_2O	1.53%
K_2O	3.88%
TiO_2	1.21%
P_2O_5	0.13%
MnO	0.06%

The bedrock surrounding this lake consists of metasedimentary rocks, granitic, charnockitic, syenitic, and gneisses (Newton et al., 1987). Watersheds with this kind of bedrock are acid sensitive when covered with a thin layer of soil due to the non-availability of readily exchangeable basic cations (C_B: Ca^{2+}, Mg^{2+}, Na^+, K^+) to neutralize hydrogen ion inputs. These watersheds are unable to retain the atmospheric inputs of acidic anions(SO_4^{2-}, NO_3^-, Cl^-) hence they are transported through the watershed. The transport of these acidic anions through the watershed without equivalent concentrations of basic cations results in incomplete neutralization (Vestal et al., 1976).

Studies of Mn and Pb in Dart's lake have shown that Al cycling can substantially affect Mn and Pb concentrations in the water column (White and Driscoll, 1985, 1987). Results from a recent study indicating the near-shore sediments of an acidic lake showed that many significant biogeochemical reactions occurred which were unique to this sediment region of the lake (Schafran, 1988). Such processes such as NO_3^- and SO_4^{2-} reduction have also been observed to produce alkalinity, increase pH values, and result in the precipitation of Al from hypolimnetic waters of Dart's Lake (Schafran and Driscoll, 1987). Rudd et al. (1986 a, b) observed similar findings for epilimnetic sediments in the lake and reported that the areal rate of alkalinity production in these sediments was similar to other lakes in the Adirondack region and Canada. Physical and chemical characteristics for Dart's Lake (Table 1.5; Schafran and Driscoll, 1987), indicate the setting for the field study site.

Table 1.5

Physical and Chemical* Characteristics of Dart's Lake

surface area	58 ha
maximum depth	15 m
mean depth	7 m
elevation	517 m
hydraulic retention	0.06 yr
catchment area	10700 ha
pH	5.18
NO_3^-	24.4 ueq/l
SO_4^{2-}	137.6 ueq/l

* mean concentrations for the whole lake (25 October 1981 to 21 November 1982; Schafran and Driscoll 1987)

2.0 RESEARCH METHODOLOGY

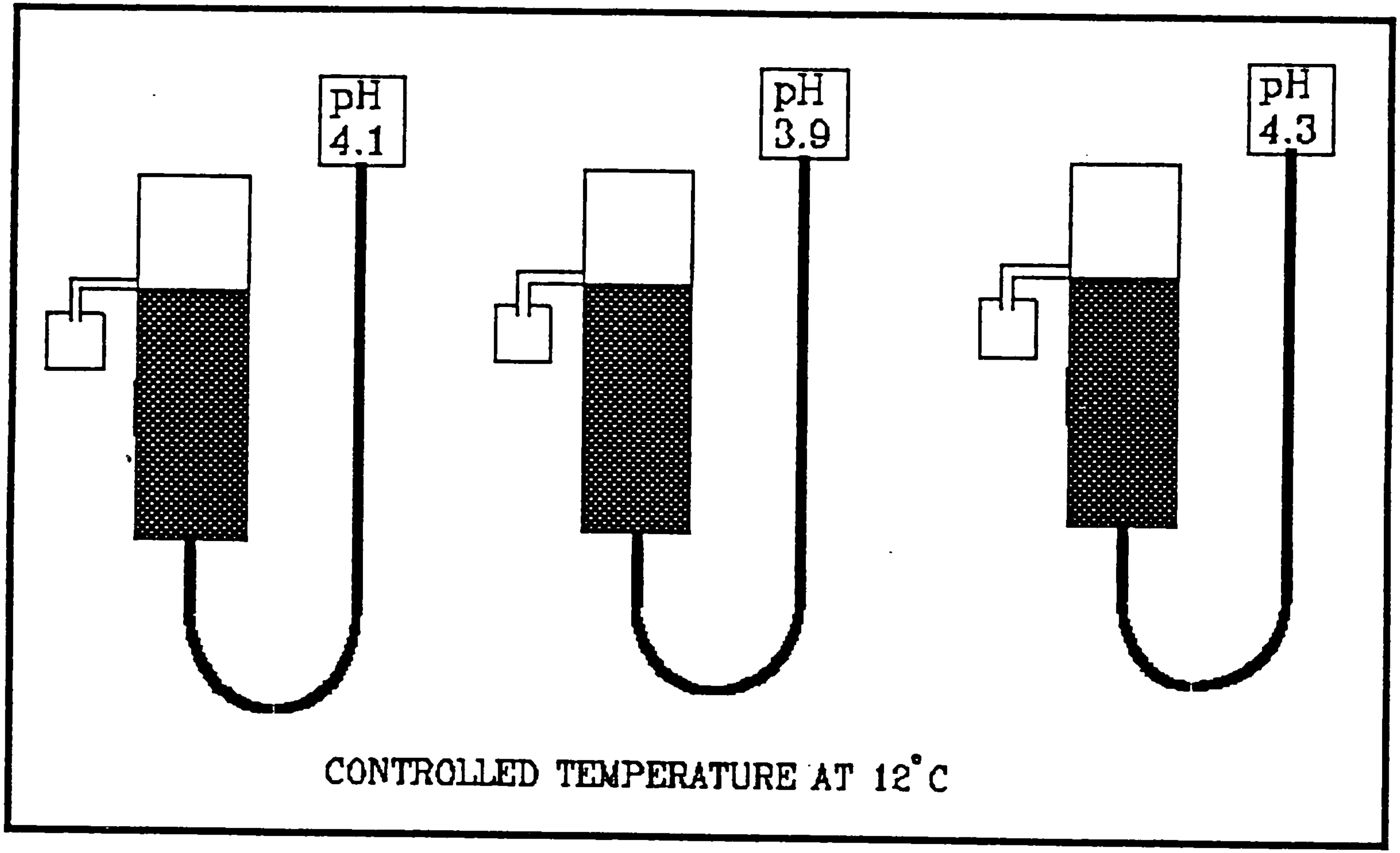
2.1 FIELD SAMPLING

Field sampling was conducted to collect the sediments and water to be used in the laboratory simulation experiment. Four sediment cores were collected from Dart's Lake on 17 and 18 June, 1988. The site where the cores were collected was adjacent to a site where groundwater and sediment chemistry were previously studied (Schafran 1988). Seepage rates at the study site have been observed to decrease exponentially as a function of distance away from the shore (Schafran and Driscoll, 1988) which is consistent with the theoretical modelling of lake-groundwater interactions (McBride and Pfannkuch, 1975; Pfannkuch and Winter, 1984). The sediment cores were taken by hand with a 4.7 cm diameter plastic core liner. One core was collected near the shoreline (water depth = 5 cm) on 17 June and served as a control for sediment metal extraction profiles. After removal from the sediment this core was immediately sectioned (1 cm sections for the top 8 cm, and 2 cm from 9 to 22 cm and placed in individual whirlpak bags. Three cores that were utilized in the laboratory simulation were collected on 18 June at the same location and water depth but 50 cm distance from the control core. All three core liners were inserted into the sediment before any were removed to minimize sediment disturbance. A 5 cm distance separated each core. The three core liners were then removed from the sediment and contained sediment ranging from 15 to 18 cm depth. Upon removal from the sediment, the cores were immediately sealed on the bottom with a cap to avoid the loss of sediment and pore water. The bottom cap was sealed immediately using silicone caulking. Small diameter (I.D = 0.5 mm) polyethylene tubing for the seepage experiments was inserted in to the bottom caps. The end of the tubing not connected to a cap was placed above the top of the core during transport to prevent water from draining from the core. The sediment cores were placed vertically into a well-insulated carrier. This carrier was designed specifically to transport the three cores and to minimize disturbance during transport. This carrier was subsequently filled with ice and the cores were returned to the laboratory approximately twelve hours after collection. A polyethylene bag was placed between the cores and ice to prevent possible contamination of the cores by melting ice.

Water used in the groundwater simulation experiment was collected from a small, unnamed stream that drains into Dart's Lake. Water was collected by siphoning stream water into three 20 litre polyethylene carboys. In order to insure a similarity of chemical composition among the three carboys, the three carboys were filled by alternately siphoning water from the stream into each carboy for three minute periods, until all were filled.

2.2 GROUNDWATER SIMULATION EXPERIMENTS

As soon as the cores were brought to the laboratory, they were connected to the groundwater seepage simulation set-up inside a refrigerator. The simulation set-up consisted of a linear polyethylene (LPE) tube (I.D. = 0.5 mm) connected to the top of a two litre LPE bottle (Figure 2.1). The 2 litre bottle served to hold water that would pass through the sediment cores. The 2 litre bottles were initially placed at a predetermined height (determined from a "trial" run) inside the refrigerator to achieve the desired seepage rates (140 ml/24 hrs.). For the first four days of the simulation the elevations of the two litre bottles were varied until similar flow rates existed in all three cores. Following this period, flow of water through the sediment cores was controlled by establishing a constant elevation (hydraulic gradient) between water surfaces in the two litre bottles and the water elevation above the cores. A hole was drilled approximately 0.5 cm above the sediment in each core liner and a 0.5 cm diameter Nalgene tube (effluent tube) was connected. Water passing through each core exited the core through the effluent



EXPERIMENTAL SETUP

tube and was collected in a 250 ml LPE bottle. Effluent samples were transferred to 60 ml LPE bottles every 24 hours and stored at 4°C. The volume collected was quantified gravimetrically using the relationship between the volume and mass of water (1 g H_2O = 1 ml H_2O). During the period of simulation, the volume of water drained from each two liter bottle was replaced every 24 hours by the water in the respective carboy. All three carboys were stored at 4°C.

The groundwater temperature at the field site was measured by lowering a thermometer inside an existing piezometer located at the field site. A temperature of 12° C was measured for water present in the piezometer at the field site. To establish similar temperature conditions for the laboratory simulation a temperature of 12° C was maintained throughout the experimental period.

During the simulation experiment, each core received water from a single carboy. During the first seven days of the simulation the cores received water of nearly identical chemistry. On the eighth day of the experiment, two carboys were acidified by the addition of HCl until the pH values in the carboys were lowered to 4.1 and 3.9. The two litre bottle connected to core 1 and core 2 were emptied on this day and refilled with the acidified waters. The time period during this change (10 minutes) was minimized to avoid changes that might occur due to non-seepage conditions. The pH of the third carboy (Control carboy) was not altered and remained at 4.3

throughout the experiment. Following the acidification, cores 1, 2, and 3 received water with pH values of 4.1, 3.9, and 4.3, respectively. The simulation experiment was conducted for 46 days.

2.3 CHEMICAL ANALYSIS OF SEDIMENTS AND EFFLUENT

The effluent pH was measured immediately after collection. Portions of the effluent samples were transferred to 60 ml LPE bottles from 250 ml bottles. Approximately 30 ml of the overflow was transferred to another 60 ml LPE bottle followed by acidification to pH 1.5 with redistilled HNO_3 and stored at 4° C.

Overflow samples were analyzed for pH with an Orion Research (model 811) pH meter and a Ross combination pH electrode. Calcium, Mg, Na, K concentrations were measured by flame atomic absorption spectroscopy (AAS) with a Perkin-Elmer atomic absorption spectrometer (Model 603). Analytical standards for Ca, Mg, Na, and K were prepared using Fisher Scientific AAS stock solutions with 5% Sr and 0.02% HNO_3 addition to standards to avoid ionization effects. Samples received identical amounts of Sr and HNO_3 to match the matrix of the standard. Aluminum, Mn, Fe, and Pb were measured with graphite furnace AAS. Deuterium arc background correction was utilized during the analysis of these metals.

Fluoride concentrations of selected effluent samples (30% of total number of effluent samples at regular intervals before as well as after acidification) were measured with an Orion Fluoride Electrode (model 94-09-00). Standards were prepared with Fisher Scientific Fluoride Stock Solution. Measurements were made following addition of TISAB (total ionic strength adjustment buffer, Orion TISAB III) resulting in decomplexation of bound fluoride and allowing determination of the total F in solution.

The dissolved organic carbon concentrations of selected overflow samples collected were measured with a TOC analyzer (Model PR-1 Module). The reagent solution consisted of 5% potassium persulphate and 5% v/v of 85% phosphoric acid in the matrix of low carbon content Milli-Q water. Carbon standard solutions were prepared with potassium hydrogen phthalate salt.

The concentrations of free and organically complexed fractions of Pb on selected effluent samples (22% of total number of samples) collected before and after acidification were measured using stripping voltammetry (OSWV) with high purity 0.1 M KCl solution as the electrolyte medium. Standards were prepared with Fisher Scientific Pb Stock Solution and 0.1 M KCl in Milli-Q water. Organically bound Pb in the overflow solutions was calculated by subtracting free Pb from total Pb.

Sulphate and Cl^- were analysed in selected samples using ion chromatography (Dionex model 2020i). Mixed standards were made from high purity chemicals.

2.3.1 SEDIMENT EXTRACTIONS AND ANALYSIS

2.3.2 SEQUENTIAL EXTRACTION OF SEDIMENT SAMPLES FOR METALS

At the termination of the laboratory simulation the three cores were sectioned at 1 cm intervals and stored in polyethylene bags. The sediment samples were subsequently sieved through a nylon (1 mm) mesh with deionized H_2O to remove coarse sand grains (≈20% of total sample) and then homogenized. Homogenized sediments were stored at 4° C. prior to the commencement of extraction procedures.

2.3.3 SEDIMENT EXTRACTIONS

Four to five grams of wet sediments were placed in 50 ml Nalgene LPE centrifuge tubes with caps. The sediments were extracted in a sequential manner with solutions of 1) potassium chloride, 2) sodium pyrophosphate, and 3) acid ammonium oxalate. These sediment extractions were employed to quantify different metal fractions in the sediments. The metals extracted by these solutions represent operationally defined metal fractions that have been associated with certain metal-solid phases in sediment (Figure 2.2). These metals would likely represent the most labile metal fractions that would mobilize due to acidification.

Extractant	**Metal fraction**
KCl	Easily exchangeable metals
Sodium Pyrophosphate	Organically bound metal
Acid Ammonium oxalate	Metals present as amorphous oxides

In the sequential extraction procedure, sediments were first mixed with 1 N KCl to extract an "exchangeable metal" fraction (USDA, 1972). This metal fraction is generally perceived as the most labile metal fraction and most easily solubilized. Twenty ml of 1 N KCl was added to each centrifuge tube and placed on a shaking table for 30 minutes. The sediments were then centrifuged at 2000 rpm for 30 minutes to separate the particulate matter. The supernatant was then pipetted into 30 ml Nalgene LPE bottles and stored at 4° C.

A 0.1 M sodium pyrophosphate solution was used to extract what is believed to be metals bound to organic matter (USDA, 1972). A 25 ml aliquot of the sodium pyrophosphate solution was added to each tube containing sediment and then placed on a shaking table for 16 hours. Following shaking, the tubes were centrifuged at 2000 rpm for 45 minutes and the supernatant was pipetted into 30 ml Nalgene LPE bottles.

A 0.02 M ammonium oxalate solution was used to extract metals believed to represent the hydrous oxide metal fraction (USDA, 1972). The pH of the ammonium oxalate solution was adjusted to 3.0 by adding 17.56 g/l of oxalic acid. Twenty-five ml of ammonium oxalate solution was added to each centrifuge tube and placed on a shaking table for 4 hours in the dark. The extracts were then centrifuged at 2000 rpm for 2 hours and the supernatant pipetted into 30 ml Nalgene LPE bottles. Extraction samples were stored at 4° C prior to analysis.

2.3.4 METAL ANALYSIS OF EXTRACTIONS

Samples obtained from sediment extractions were analysed for Al, Mn, Fe, and Pb by flameless atomic absorption spectroscopy. Al, and Fe concentrations were measured following 75 fold and 55 fold dilutions, respectively, using deionized water that was also used for standards preparation. Concentrations in the sediment extracts were reported as $\mu g/g$ of dry sediment. Standards were made using KCl, sodium pyrophosphate, and ammonium oxalate solutions in proportions similar to the extraction solutions in order to match the matrix of the extractions. Standard AAS procedures (Perkin-Elmer, 1977) were followed.

2.4 MOISTURE AND ORGANIC MATTER CONTENT

To determine the moisture content of the sediments, approximately 3 to 4 g of wet sediment was placed into pre-weighed aluminum pans, weighed, dried at 104°C overnight, placed in a dessicator and then reweighed. Dry weight of the sediment was calculated from the difference in weights before and after drying. The sediment was then placed in a 550°C oven for 12 hours to combust organic matter. The organic matter content was determined as the difference in weights prior to and after combustion at 550°C.

2.5 POROSITY MEASUREMENTS

The porosity of Dart's lake near-shore sediments were measured on a volume basis. Porosity was determined by saturating a known volume (75 cc) of sediment with water and measuring the volume of water required to saturate the unit volume of dry sediment.

2.6 DATA ANALYSIS AND CHEMICAL EQUILIBRIUM CALCULATIONS

Statistical correlations (linear and regressions) between all metal concentrations in the overflow and duration of leaching, TOC, Fluoride, NO_3, SO_4, base cations were carried-out. The comparison of leached metal fractions between treated and untreated cores and graphical representation of temporal relationships were done. Metal budgeting calculations were carried-out and were compared with organic budgeting values. Standard deviations of all the analytical data were also conducted. A chemical equilibrium model (MINTEC) was used to assess the speciation of metals measured in the overflow (USEPA, 1984). This model utilizes the equilibrium constant approach, subject to mass balance constraints.

2.7 REPLICATES AND QUALITY CONTROL

Three replicate measurements were taken for all metals in the sediment extracts (Al, Fe, Mn, Pb) and for selected components in the effluent samples (metals, base cations, TOC, free Pb and Al concentrations) to calculate the analytical coefficient of variation. Additionally, a triplicate extraction of at least one sediment section per core was conducted to evaluate the variability of the extraction procedure. Standards were checked against EPA standards to assure quality control. Standards were also checked with the standards available in the geochemical laboratory of the Geological Sciences Department at Old Dominion University. This interdepartmental standard checking was done with matrix matching.

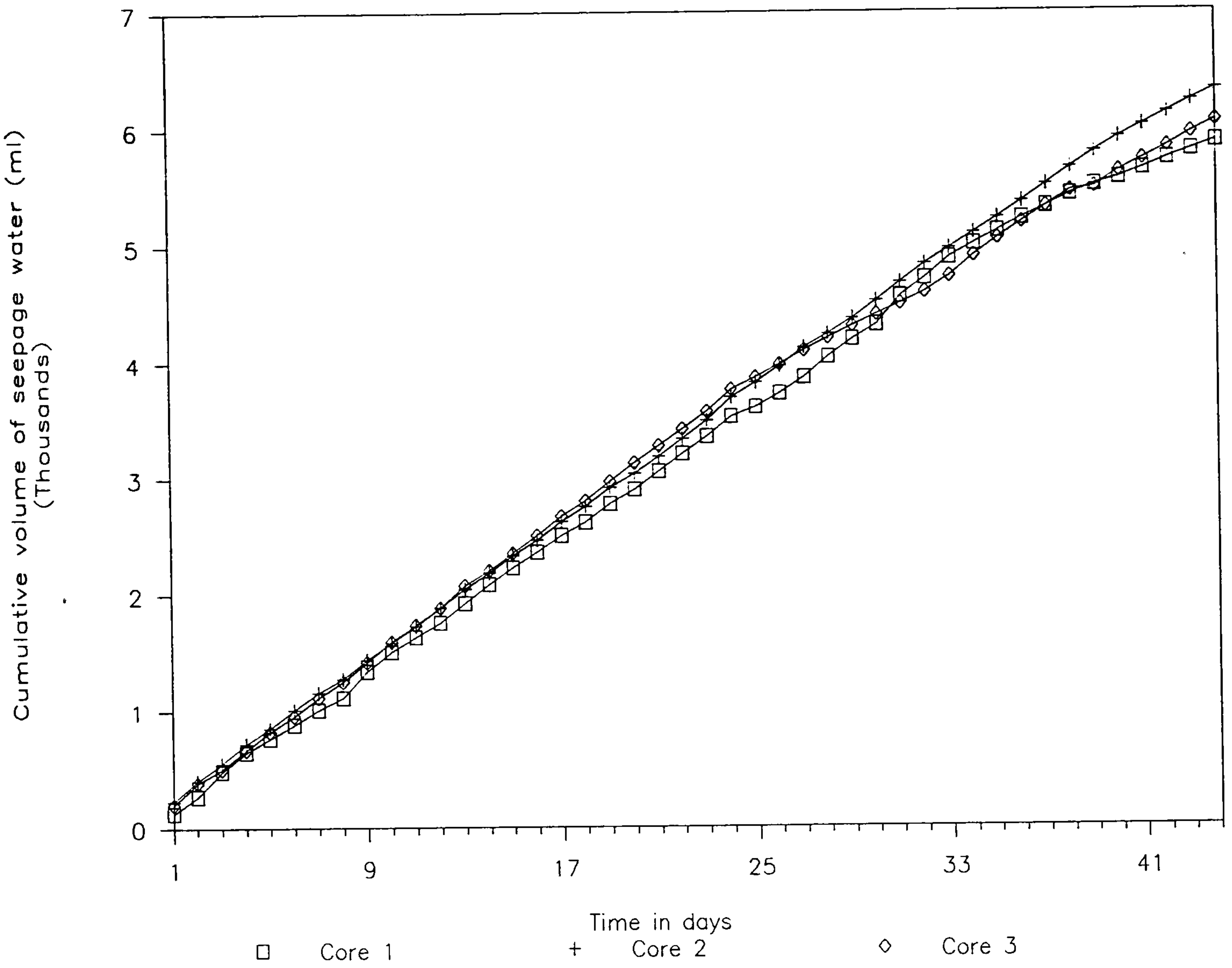
3.0 RESULTS

3.1 GROUNDWATER SEEPAGE

The seepage rates through the three cores were adjusted approximately to 140 ml/day which was determined to be similar to rates observed previously at the field site (Schafran, 1988). Variation in temporal seepage rates were observed even though the hydraulic gradients were constant. However, the cumulative volume of water through all three cores was approximately similar (5876, 6326, and 6057 ml/44 days in cores 1, 2, and 3, respectively; Figure 3.1) by the end of the experiment with average seepage rates of 134 (S.D. = 25), 144 (S.D. = 19), and 137 (S.D. = 21) ml/day in cores 1, 2, and 3, respectively. Retention times of influent water were calculated as (Equation 3.1):

$$t = V_p/Q, \qquad [3.1]$$

where V_p = pore volume of sediment
Q = flowrate
and t = retention time.



Cumulative volume of seepage water (ml)
(Thousands)
0
1
2
3
4
5
6
7
1
9
17
25
33
41
Time in days
□ Core 1
+ Core 2
◇ Core 3

The following retention times were calculated from this expression:

t for core 1 = 0.73 day

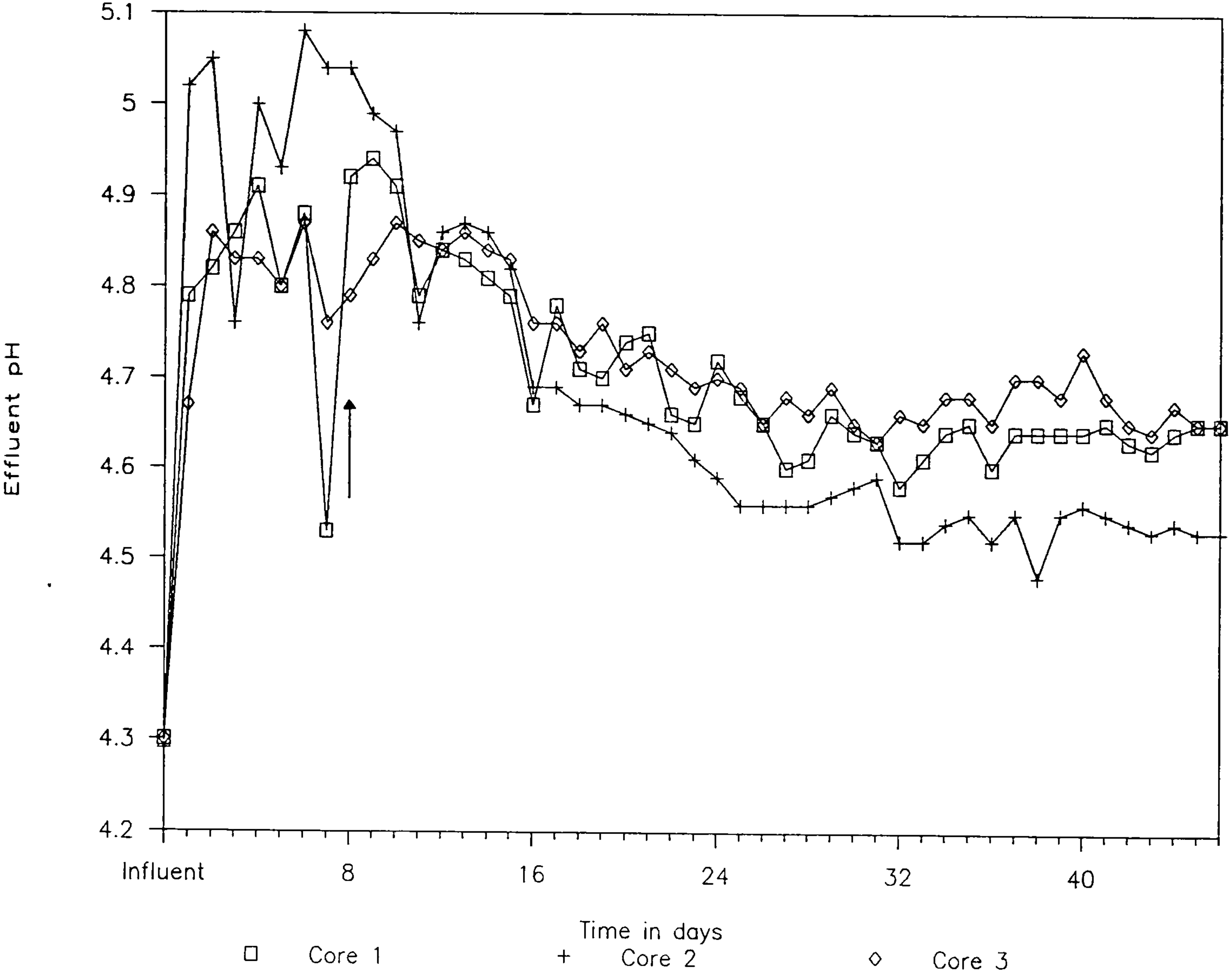
t for core 2 = 0.77 day

t for core 3 = 0.74 day.

3.2 pH

The pH value of water collected in the field and used as simulated groundwater was 4.3, and a constant weekly monitoring of pH in the unacidified carboy showed a slight drop to 4.28 over the experimental period. All three sediment cores showed significant neutralization of influent H^+ ion concentration with the largest neutralization occurring in the beginning period (days) of the experiment. As evidenced by the change in pH values of the overflow solutions over time (Figure 3.2), the sediment capacity to neutralize H^+ inputs decreased with time in all three cores.

The influent H^+ concentration passing through core 1 was substantially neutralized (mean of seven days = 71%; S.D. = 5%) prior to acidification from a pH value of 4.30 to 4.94 over a period of seven days. Following acidification (influent pH = 4.1), overflow pH values decreased when compared to leachate before acidification but represented approximately a 70% reduction in H^+ concentration for ten days. Overflow pH


Effluent pH
5.1
5
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

values slowly decreased for twenty-seven days and then stabilized at 4.64 (reduction of influent H^+ = 54%).

Prior to influent acidification, the greatest neutralization observed in any of the cores occurred in core 2 where H^+ concentration decreased (mean = 78%; S.D. = 4%) and pH values >5.0 were present in overflow solutions over the first seven days of the experiment. Following acidification, the pH decreased rapidly and attained equilibrium (steady effluent H^+ concentration) approximately 27 days after acidification. Similar to core 1 and core 2, the pH of effluent samples from core 3 was highest during the early period of the experiment and decreased with time until equilibrium was attained approximately 25 days after the seepage experiment began. The pH trend of core 3 was not substantially different from cores 1 and 2 even though the water supplied to core 3 received no acid addition.

3.3 ALUMINUM

3.3.1 TOTAL ALUMINUM

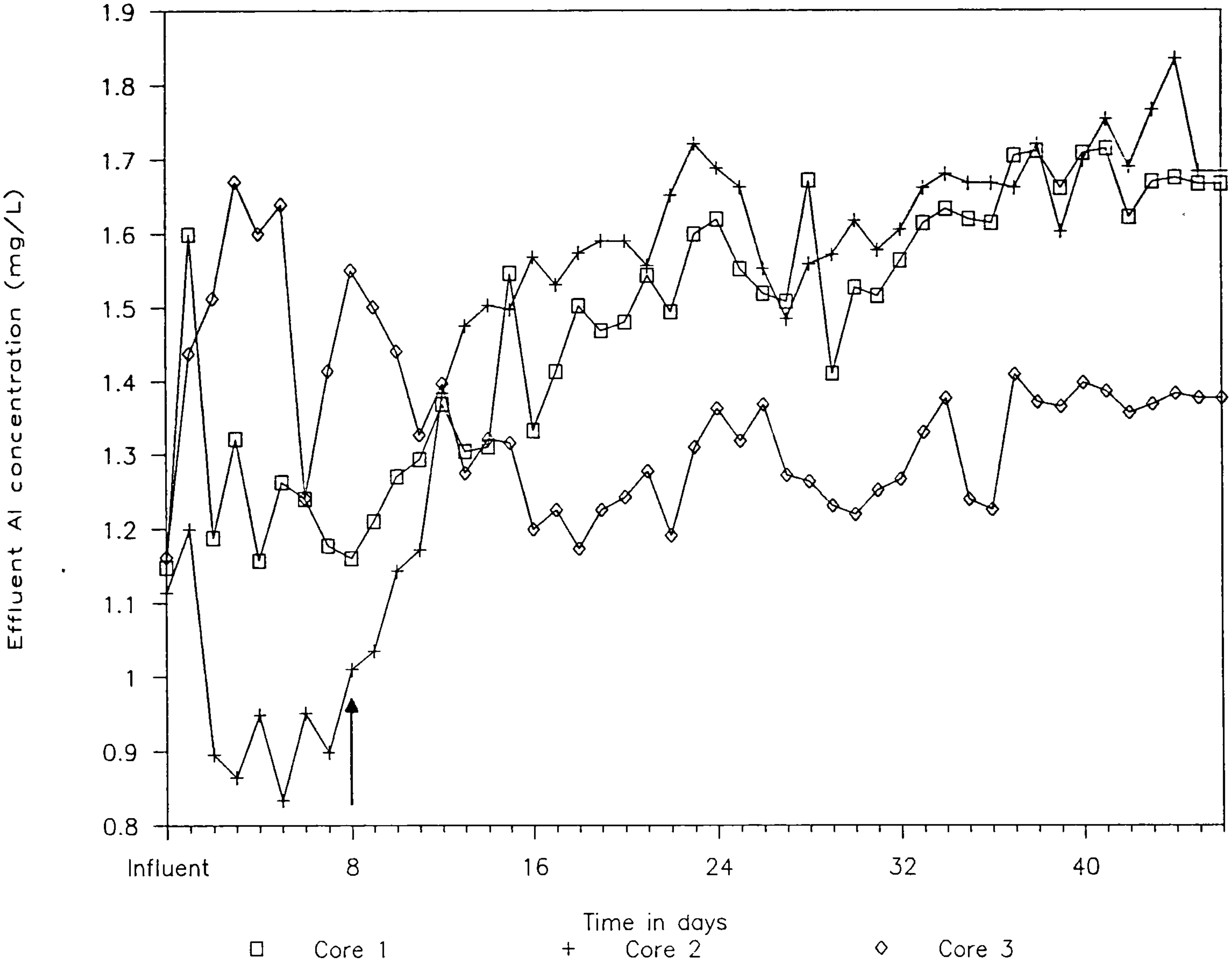
Total Al concentrations in the influent "groundwater" were 1.15, 1.11, and 1.16 for core 1, core 2, and core 3, respectively. Al concentrations in the overflow of core 1 increased to 1.6 mg/l within 24 hours of seepage, and then dropped to approximately the influent concentration until the seventh day of the experiment whereupon it began a gradual rise to slightly above 1.7 mg/l (Figure 3.3). Following acidification (day 7), substantial amounts of Al were mobilized from the sediment of core 1 representing a 49% increase over the influent concentration.

Until the influent was acidified on the seventh day, Al was removed (22%) from the seepage solution by the sediment. Following acidification a dramatic increase in Al concentrations in the effluent solutions occurred for ten days (Al = 92 ug Al l^{-1} d^{-1}), and then increased at a much lower rate (Al concentration = 10 ug Al l^{-1} d^{-1}) until the end of the experiment. At the experiment's termination, the Al concentration was 64% higher than in the influent and a 100% higher than the overflow immediately before acidification.

Overflow Al concentrations from core 3 manifested that Al was mobilized from the sediment throughout the experiment. In the initial 9 day period of the experiment, overflow concentrations were greater than cores 1 and 2.

3.3.2 ORGANICALLY BOUND ALUMINUM

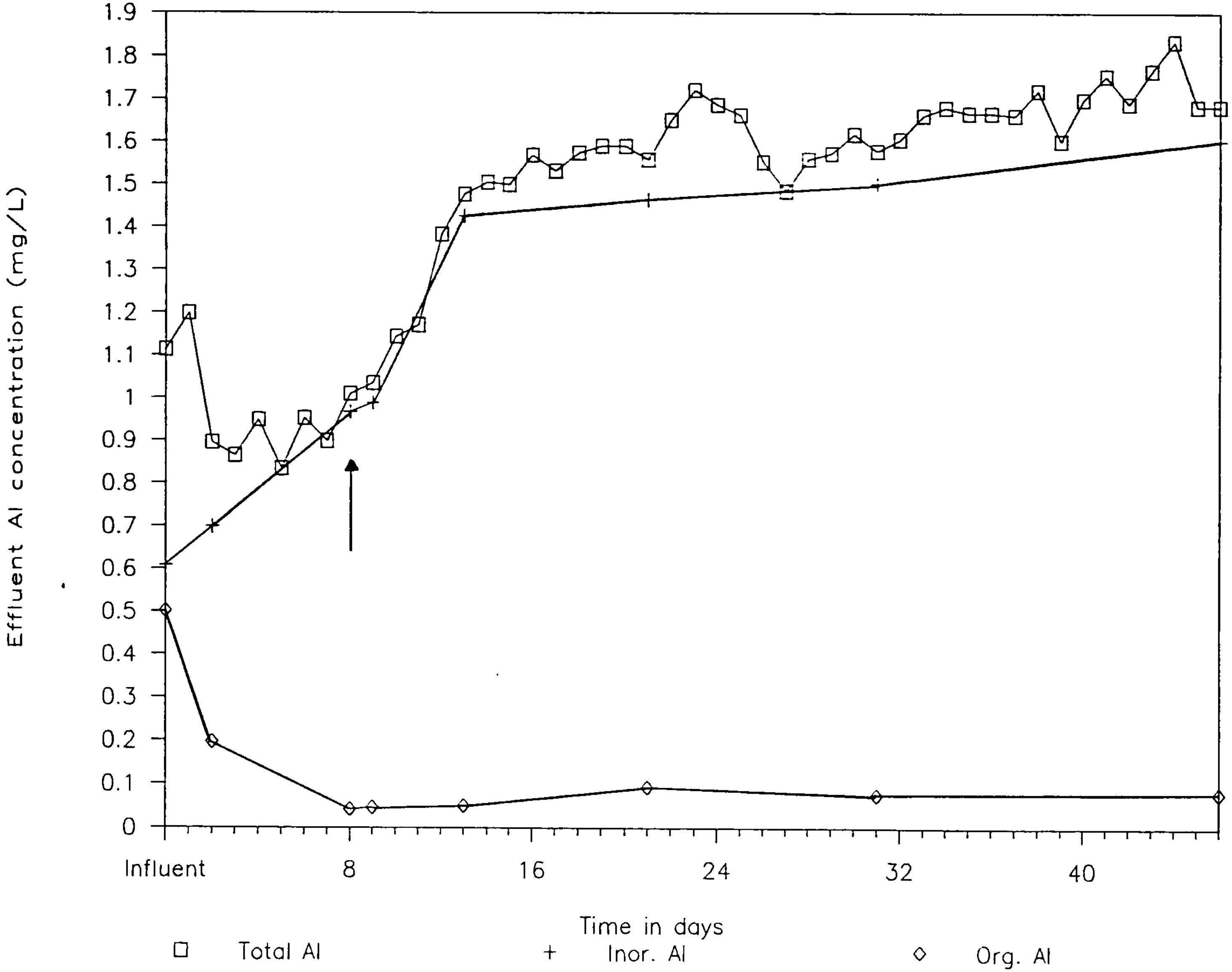
In all three cores substantial amounts (<75%) of organically bound Al was lost from influent solutions to the sediment during the simulation. Removal of organically bound Al from seepage solution reached apparent equilibrium from day 8 to 31 in all the cores. Removal of organically bound Al from

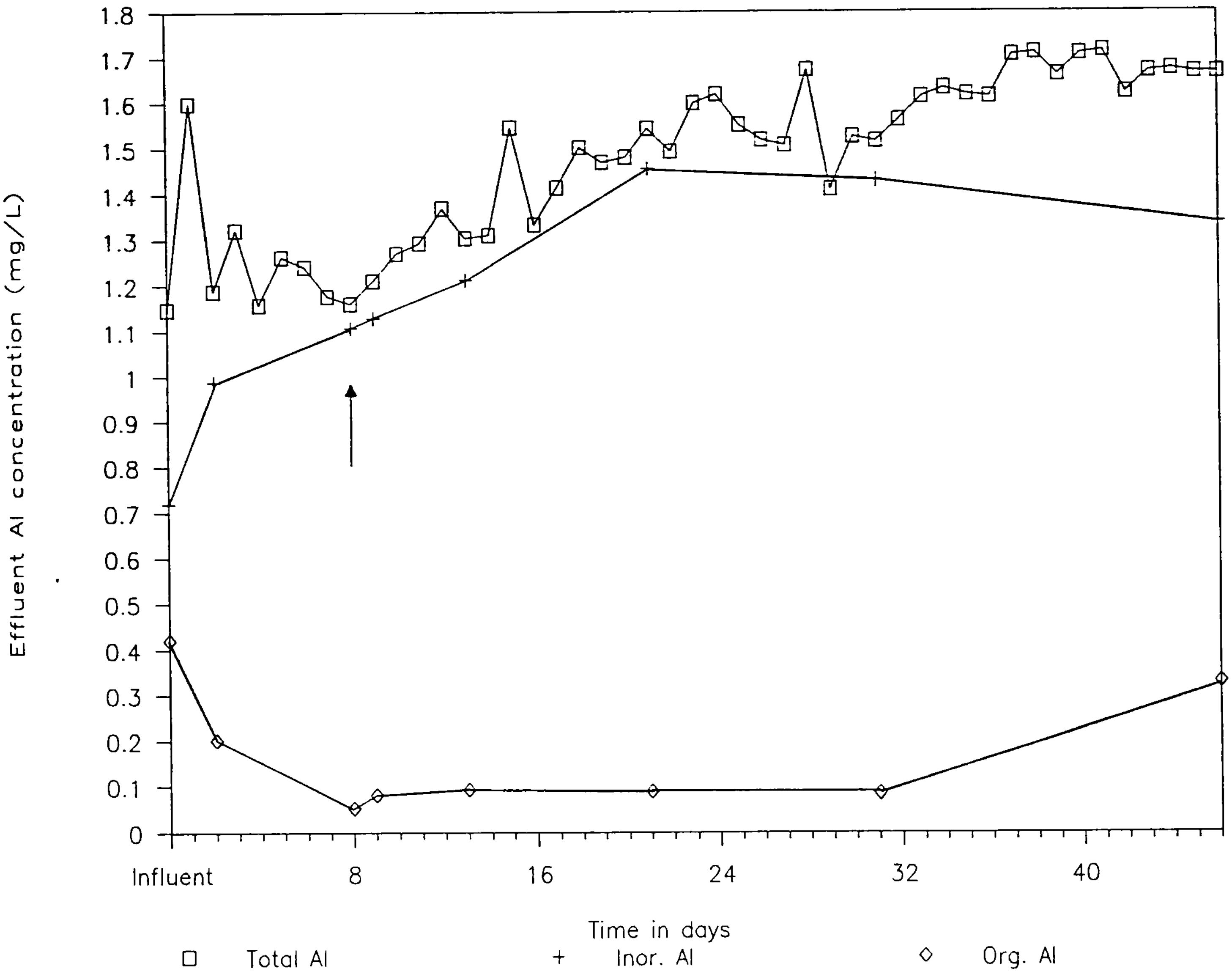

Effluent Al concentration (mg/L)
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

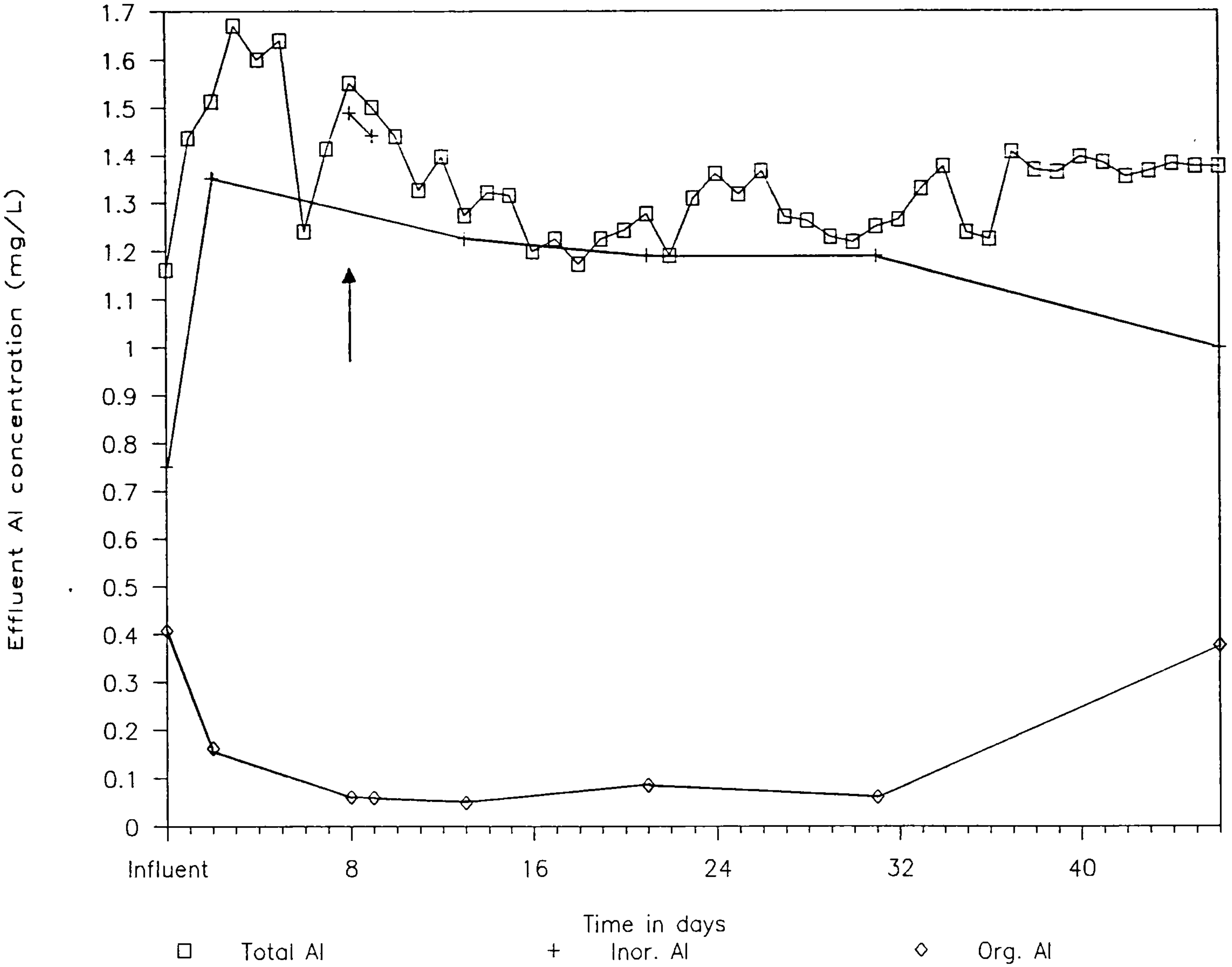
the seepage solution in core 2 (Figure 3.4) appears to have remained constant through the end of the experiment whereas in core 1 (Figure 3.5) and 3 (Figure 3.6), organically bound Al was observed at approximately influent concentrations on the last day of simulation. Organically bound-Al was approximately 37% of the total Al in the influent solutions.

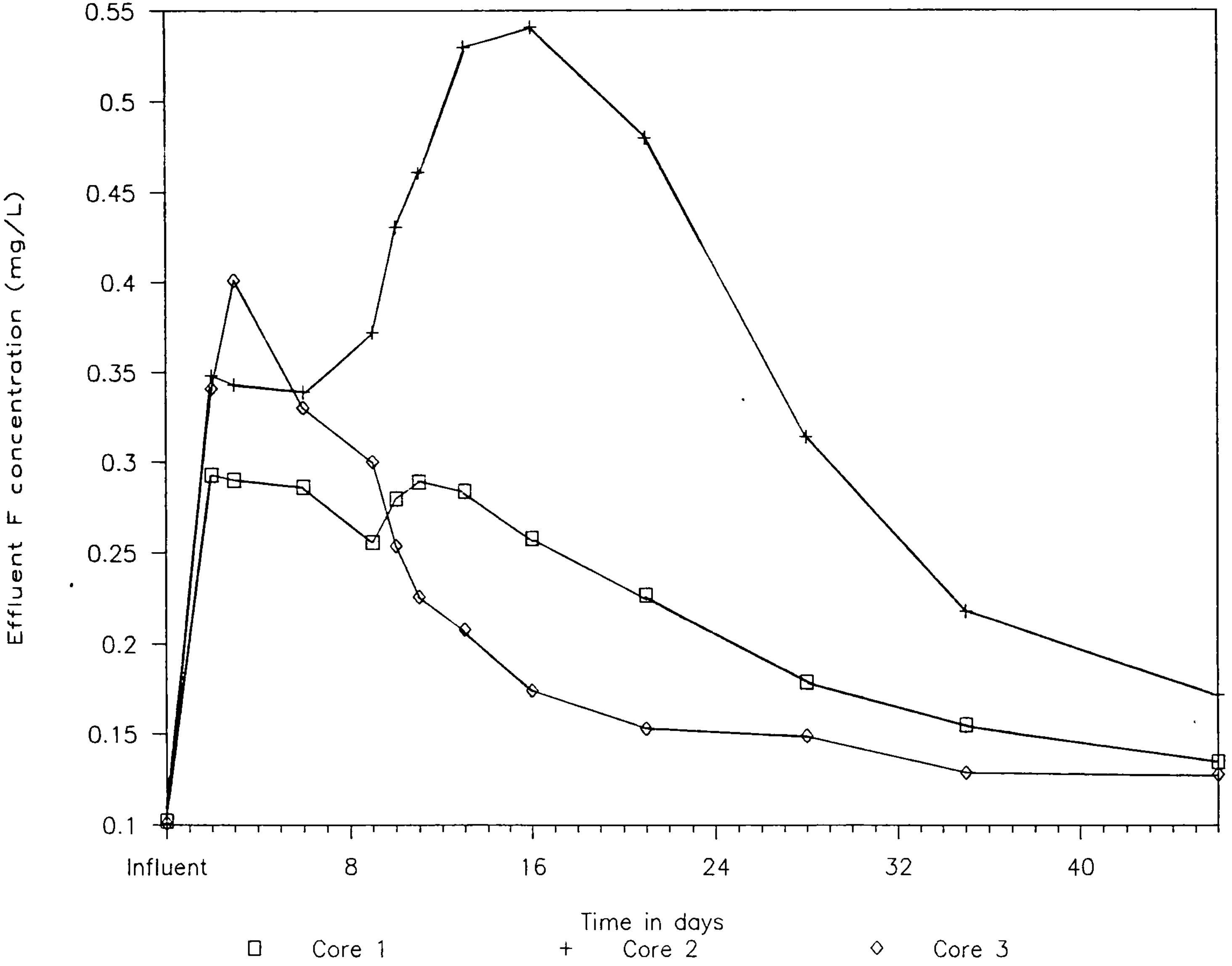
3.4 FLUORIDE

Fluoride was released from the sediments of all three cores as evidenced by increased effluent F concentrations relative to influent concentrations (Figure 3.7). A F concentration of 0.10 mg/l was present in the influent solutions passing through all three cores. Increased F concentrations in the overflows were observed both before and after acidification. In core 1, F concentration in effluent increased up to 187% above influent concentration before acidification. Following acidification a slight increase in F concentration was observed (13% higher than before acidification) followed by a gradual but substantial decrease until the end of the experiment. At this time, F concentration in the overflow was approximately 40% higher than influent concentration indicating that the sediment continued to leach F.


Effluent Al concentration (mg/L)
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Influent
8
16
24
32
40
Time in days
□ Total Al
+ Inor. Al
◇ Org. Al


Effluent Al concentration (mg/L)
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Influent
8
16
24
32
40
Time in days
□ Total Al
+ Inor. Al
◇ Org. Al


Effluent Al concentration (mg/L)
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Influent
8
16
24
32
40
Time in days
□ Total Al
+ Inor. Al
◇ Org. Al


Effluent F concentration (mg/L)
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

Fluoride releases from core 2 after acidification were more substantial than either core 1 or 3. For a five day period following acidification F increased in the effluent waters at a rate of 0.0287 mg F/l/day. For the 20 days following acidification F concentrations in effluent were > 0.1 mg/l higher than in either core 1 or core 3. Fluoride concentrations peaked on the fifteenth day (0.541 mg/l) representing a 450% increase over influent concentrations and then decreased rapidly to concentrations of 0.172 mg/l by the end of the experiment. At the termination of the experiment effluent F concentrations were 70% higher than influent concentrations.

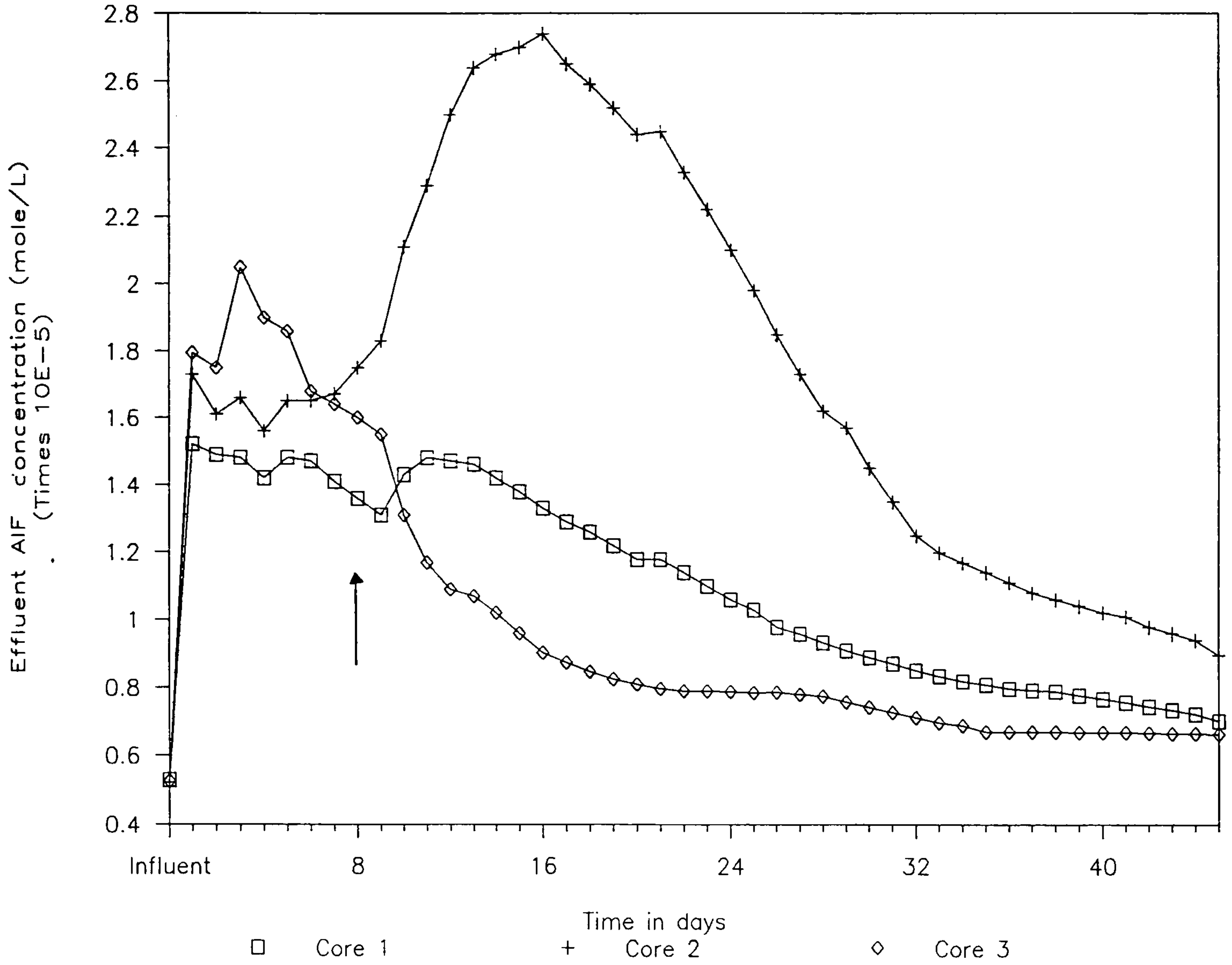
The overflow from core 3 exhibited the highest concentration of F prior to acidification. The F concentration in the overflow peaked on the second day and decreased through the remainder of the experiment. After the acidification of core 1 and 2, fluoride concentrations in the core 3 effluents were consistently lower than effluent solutions from core 1 and 2. At the termination of the experiment, F release was still occurring from the sediment as evidenced by effluent F concentrations that were 26% greater than influent concentrations.

3.5.0 INORGANIC ALUMINUM SPECIES

3.5.1 ALUMINUM FLUORIDE COMPLEXES

Speciation calculations for Al showed that fluoride complexes of Al were the dominant Al species both prior to and following passage of water through the cores. Aluminum fluoride was the dominant Al-F species comprising > 99% of such species. In core 1 immediately after seepage, AlF^{2+} concentrations increased up to 699 ug/l (186% increase), and then gradually decreased until the date of acidification (Figure 3.8). Following acidification, AlF^{2+} concentrations increased slightly (9% with reference to the concentration before acidification) for three days and then gradually decreased until the end of the experiment.

Aluminum fluoride concentrations in the overflow water from core 2 were similar to the concentrations from core 1 prior to acidification. Following acidification, a substantial increase (425% increase over influent concentration and 57% increase over the concentration before acidification) of AlF^{+2} at a rate of 17.5 ug l^{-1} d^{-1} occurred for nine days and then decreased rapidly until the end of the experiment.

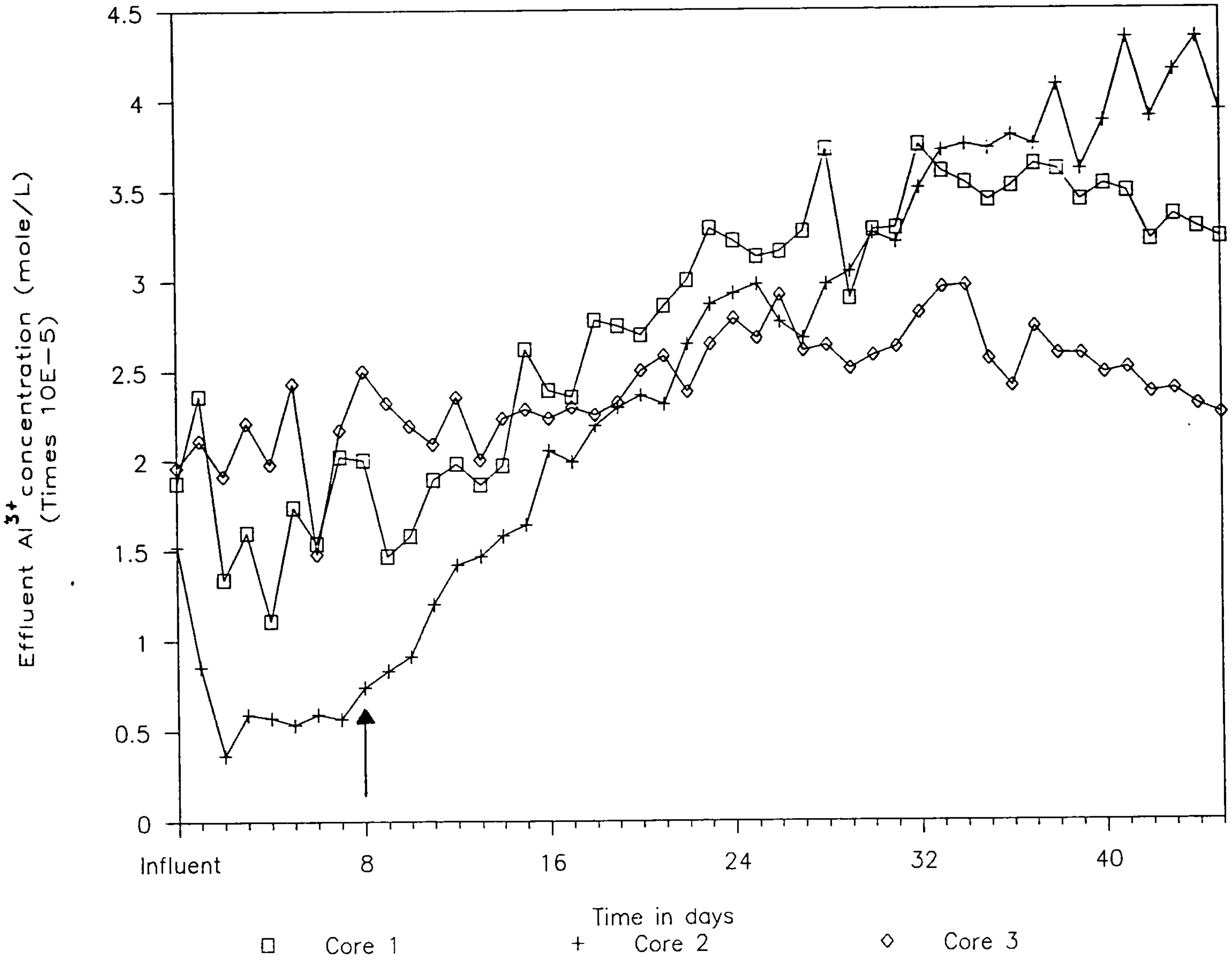

2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
Effluent AlF concentration (mole/L)
(Times 10E−5)
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

Aluminum fluoride concentrations in core 3 behaved similar to core 1 and 2 with substantial increases (290%) calculated for the overflow in the early period of the experiment. Concentrations of AlF^{2+} decreased from day 3 onward and experienced no subsequent increase as observed in cores 1 and 3.

3.5.2 Al^{3+}

Influent Al^{3+} concentrations ranged between 1.5 X 10^{-5} and 1.95 X 10^{-5} M/l and represented 36 to 44% of the total Al concentrations. Temporal trends of Al^{+3} concentrations in the overflows from the three cores were similar to the trends of total Al (Figure 3.9). In the period before acidification loss of Al from the water passing through sediment core 2 included a substantial amount of Al^{3+}. Following acidification there was a consistent increase of Al^{3+} in this core (189% increase with reference to influent concentration and 485% increase with reference to the concentration before acidification) at a rate of 27 ug l^{-1} d^{-1} until the end of the experiment.

Overflow concentrations of Al^{3+} were generally lower than influent concentrations for core 1 prior to acidification. Following acidification Al^{3+} concentrations increased similar to core 2 (34. ug l^{-1} d^{-1}) for 23 days. Overflow Al^{3+} concentrations decreased over the last 13 days of the experiment but were 80% higher than influent

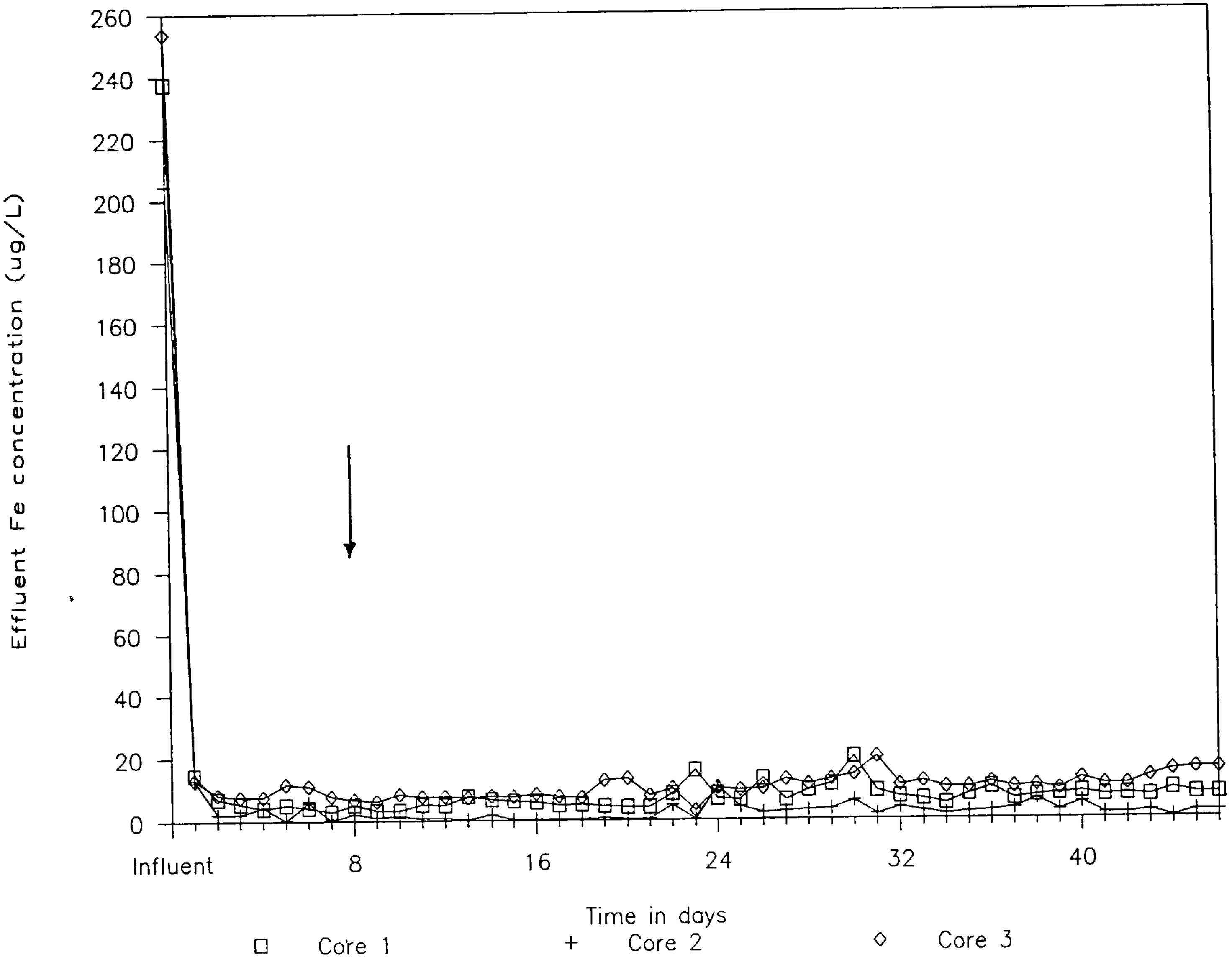

Effluent Al^{3+} concentration (mole/L)
(Times 10E−5)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

concentration at the termination of the experiment.

Overflow Al^{3+} concentrations in core 3 were only slightly elevated relative to the influent concentration. From day 18 to 36, Al^{3+} concentrations increased slightly but decreased over the final 10 days to concentrations observed prior to this period.

3.6 IRON

Iron concentrations in the influent solutions were elevated (204-253 ug/l) relative to effluent concentrations (<30 ug/l). Iron was most likely present as an organic complex in the influent solutions because of the elevated organic matter concentration of the influent solutions and low solubility of Fe in oxic waters at these pH values (pH = 4.3; Stumm and Morgan, 1981). For all three cores, the sediments served as a sink for Fe present in the influent water. Acidification of the influent solutions had little effect on Fe concentrations in the overflow solutions (Figure 3.10).


Effluent Fe concentration (ug/L)
260
240
220
200
180
160
140
120
100
80
60
40
20
0
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

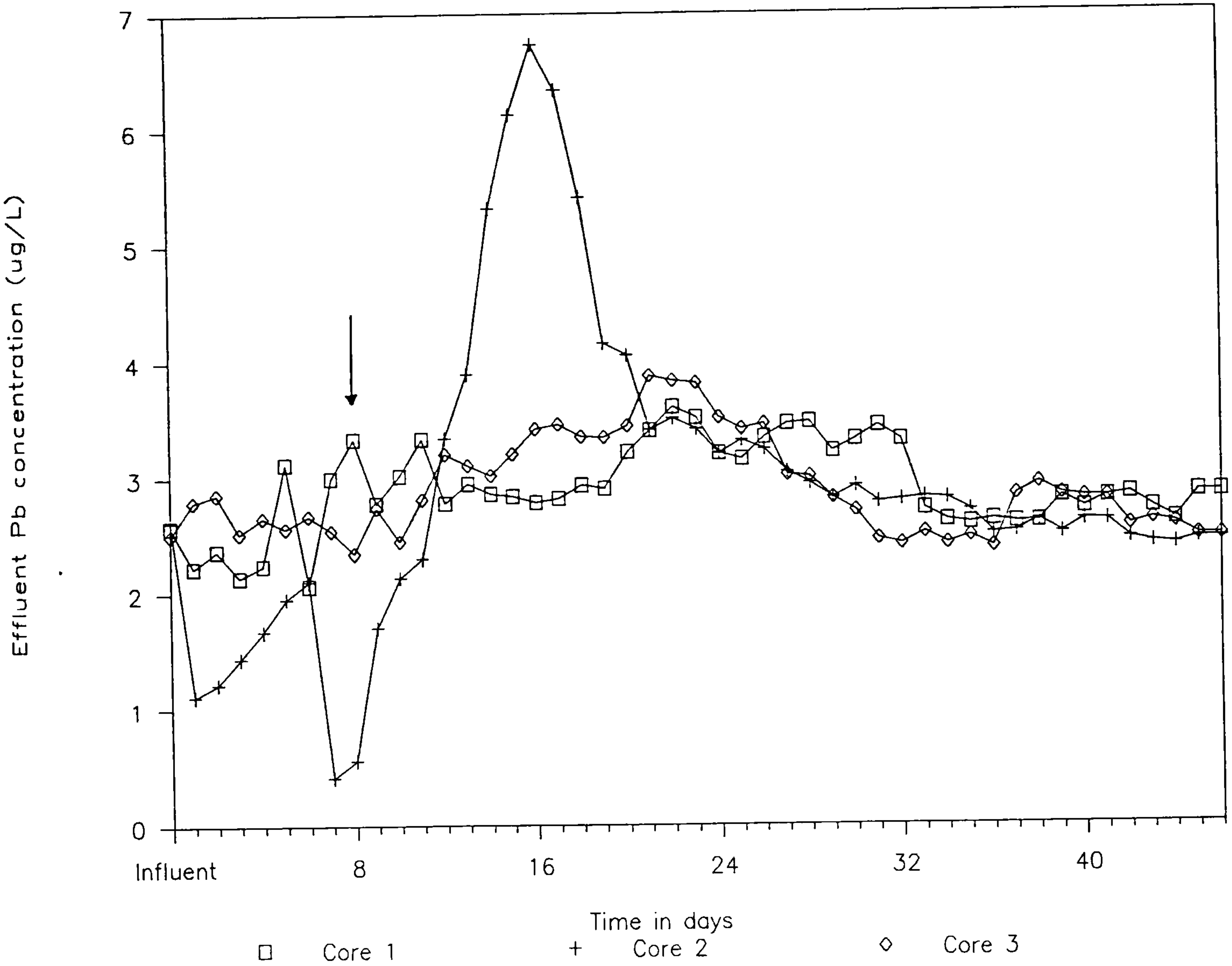
3.7.0 LEAD

3.7.1 TOTAL LEAD

Concentrations of Pb in effluent samples from core 3 were not substantially different from the influent concentration (2.5 ug/l) during the first 11 days of the experiment (Figure 3.11). Slight increases occurred in effluent concentrations from this core from day 12 to 30, but returned to the influent concentration thereafter.

Lead concentrations in effluent solutions from core 1 followed a similar trend to the control core (core 3). Slight increases in Pb concentrations were observed for the period directly following acidification but were similar to the influent concentration by the end of the experiment. From these results, it appears that only small amounts of Pb were mobilized from the sediment from these two cores.

Effluent Pb concentrations from core 2 behaved substantially different from cores 1 and 3 before as well as after acidification. During the first 24 hrs. of seepage, effluent Pb concentrations decreased (> 40%) indicating removal into the sediment. During the next six days Pb concentrations remained below the influent concentration but


Effluent Pb concentration (ug/L)
0
1
2
3
4
5
6
7
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

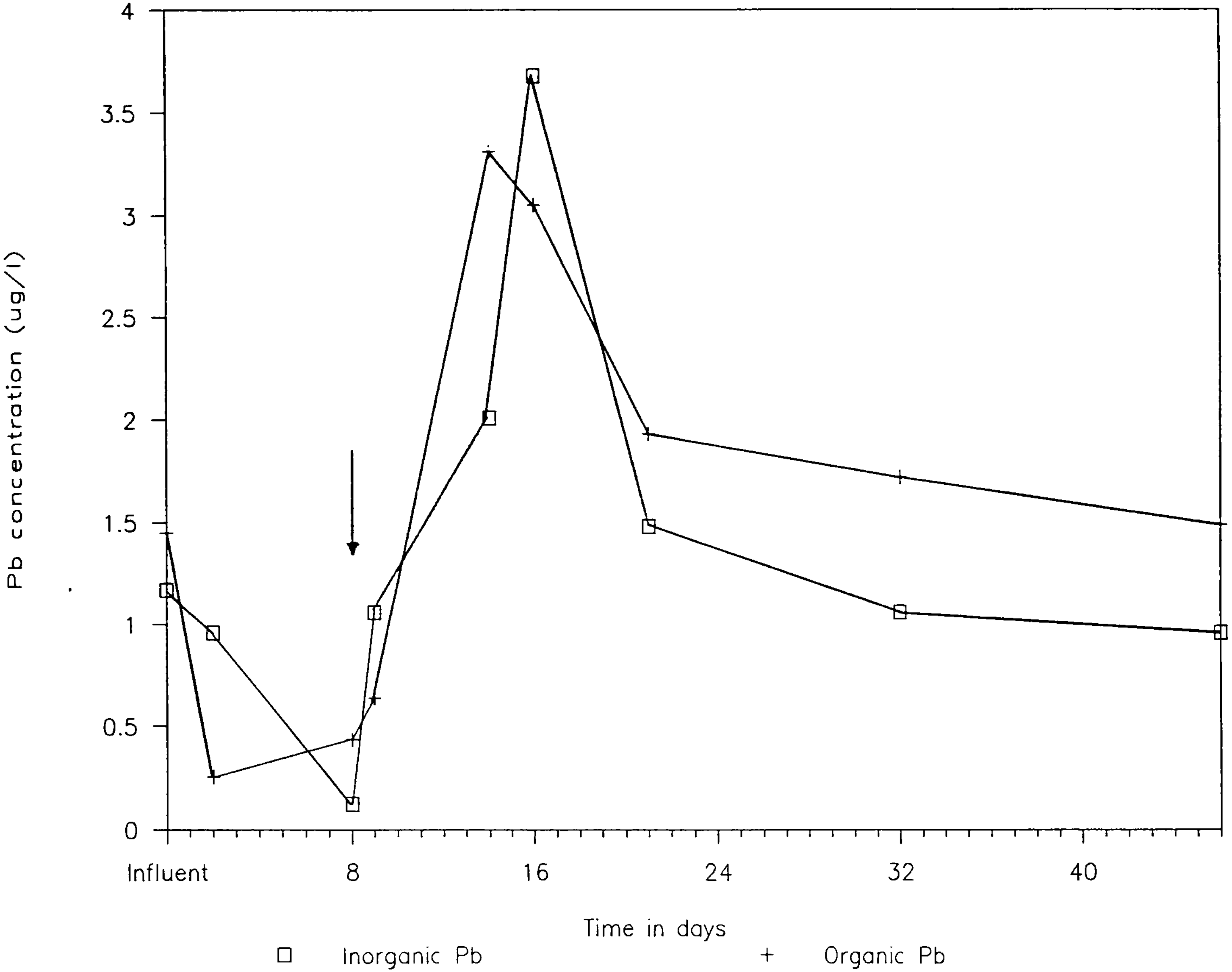
gradually increased. Following acidification a substantial increase of total Pb (156% of influent at the peak) occurred over nine days and then dropped to that of the influent concentration within seven days. Lead concentrations over the remainder of the experiment were relatively constant and equivalent to influent concentration. For all three cores, Pb behaved conservatively beyond the 35th day of the experiment.

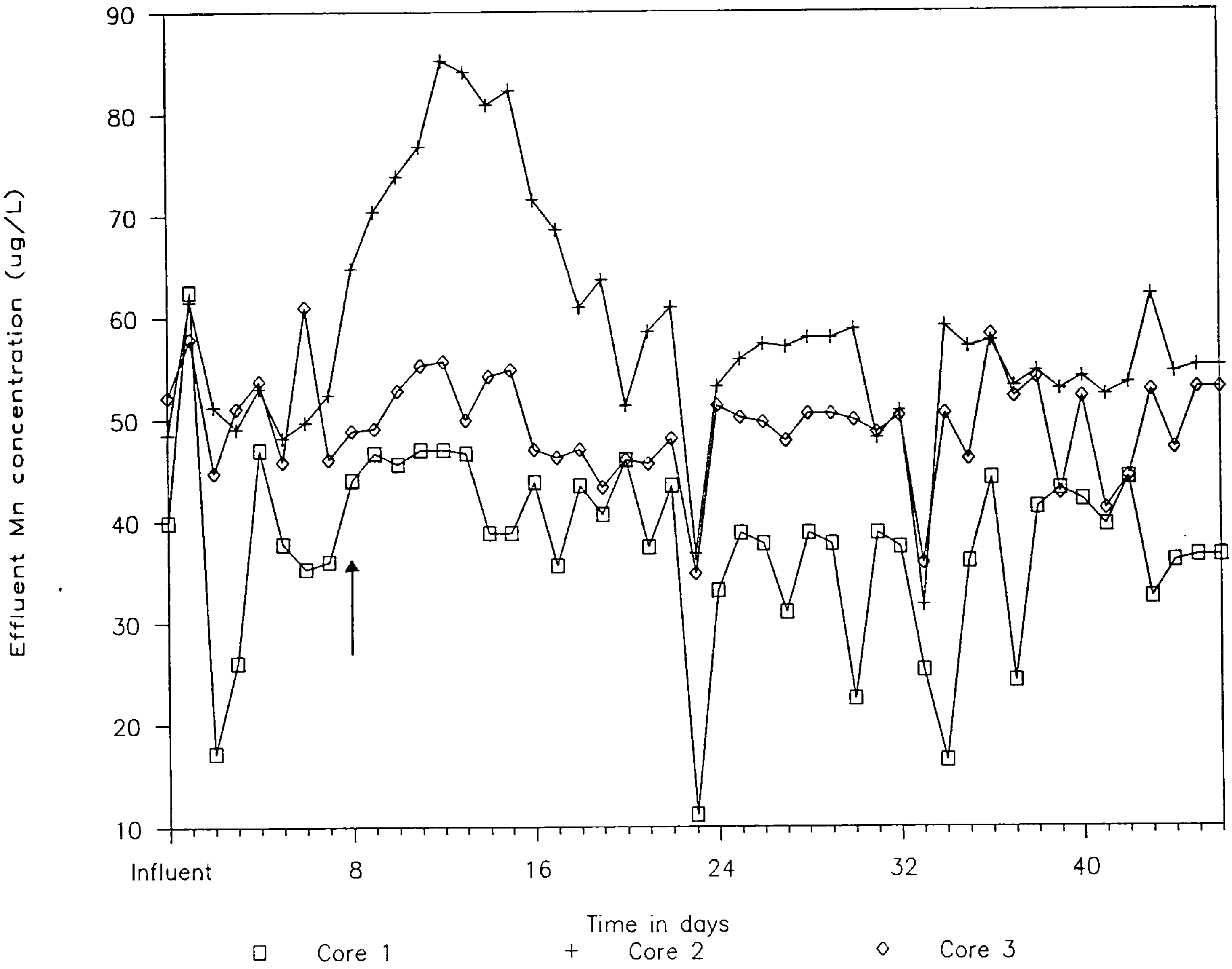
3.7.2 INORGANIC AND ORGANIC LEAD

Fractions of the inorganic and the organically bound Pb in the influent water to core 2 were approximately equal (Figure 3.12). Effluent solutions were also evenly distributed between the inorganic and organic fractions both before and after acidification. Because a considerable increase in total Pb concentration was observed following acidification, either the Pb mobilized from the sediment was equally distributed between these two fractions or it achieved this equilibrium distribution following mobilization.

3.8 MANGANESE

Manganese was higher than the influent (40-52 ug/l) in the effluents from all three cores during the initial 24 hours of leaching (Figure 3.13). Manganese concentrations increased by 57% in core 1 during the first 24 hours of


Pb concentration (ug/l)
4
3.5
3
2.5
2
1.5
1
0.5
0
Influent
8
16
24
32
40
Time in days
□ Inorganic Pb
+ Organic Pb


Effluent Mn concentration (ug/L)
90
80
70
60
50
40
30
20
10
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

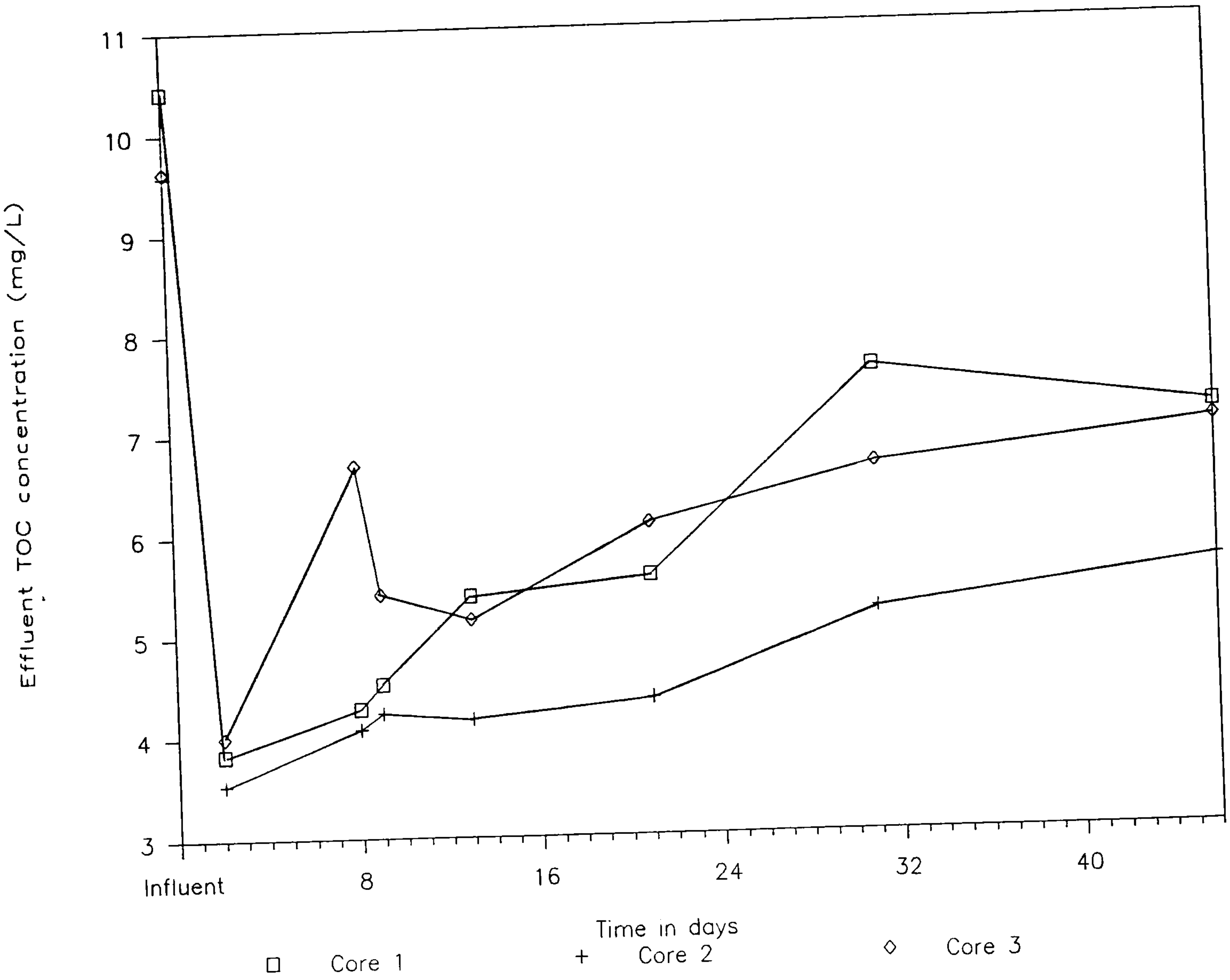
leaching and then decreased sharply (72%) in the following 24 hour period. Manganese concentrations fluctuated from approximately 17 to 63 ug/l before acidification. Following acidification, they increased gradually to 45 ug/l and then decreased to between 18 and 40 ug/l with large daily variations.

Except for the elevated concentrations observed during the initial 24 hours of leaching, Mn concentrations of effluent waters before acidification were similar to the influent concentration (approximately 48 ug/l). Following acidification, Mn concentrations increased substantially (76% of influent) by day 12. From day 25 until the end of the experiment, Mn concentrations were relatively constant in the overflow solutions (19% higher than the influent concentration)

Minor variations in overflow Mn concentrations were observed throughout the experimental period in core 3 but no significant variation (mean = 51 ug/l; S.D = 4 ug/l) compared to the influent concentration (52 ug/l) was observed.

3.9 TOTAL ORGANIC CARBON

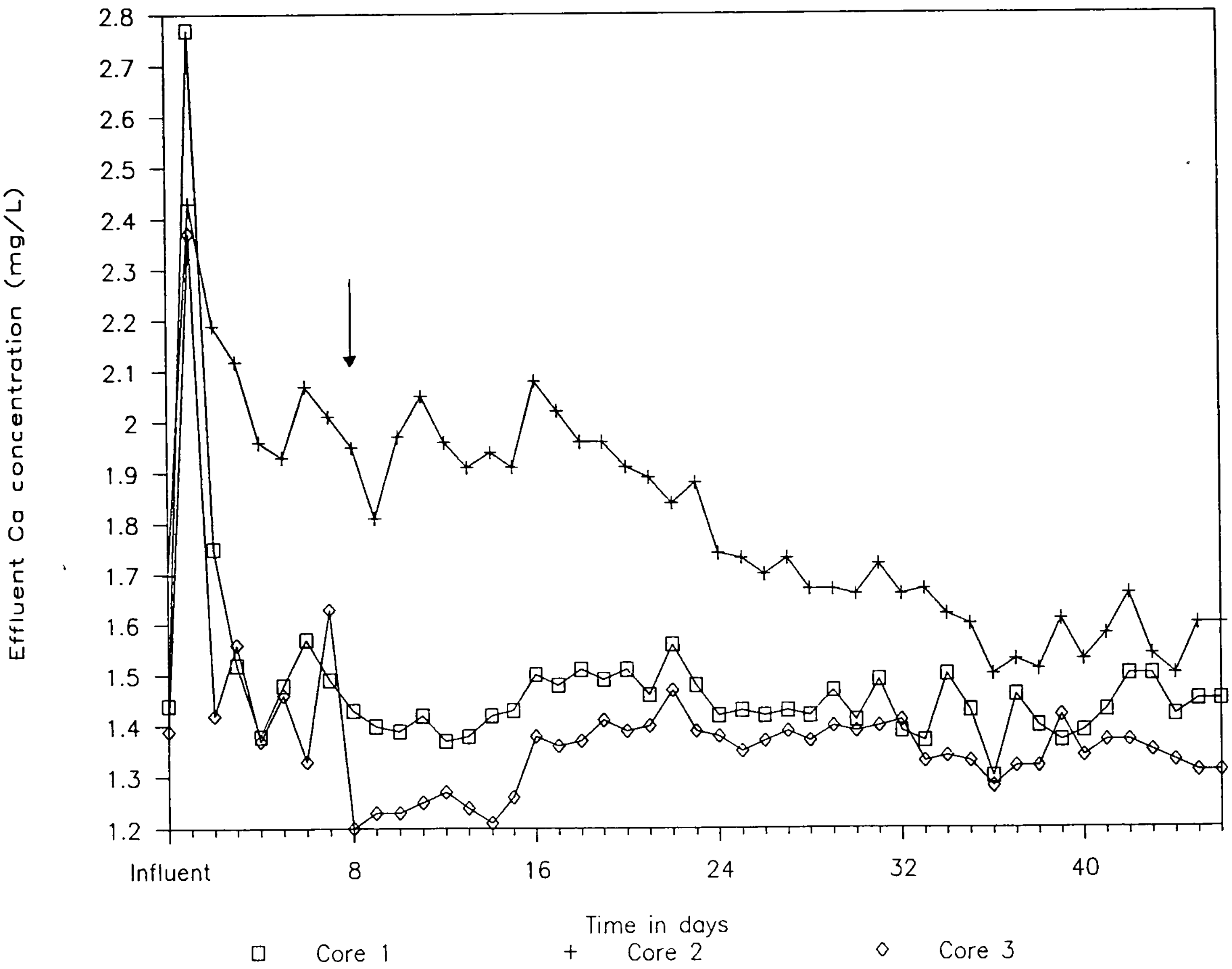
Effluent TOC concentration was reduced substantially in all the cores relative to influent TOC concentration (9.6 to 10.4 mg/l) (Figure 3.14). Trends in TOC retention by the


Effluent TOC concentration (mg/L)
11
10
9
8
7
6
5
4
3
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

sediments were similar for all cores and showed no substantial response following acidification. The greatest retention in the sediment occurred during the first three days in all three cores (63, 63 and 58% in core 1, core 2, and core 3, respectively). The amount of TOC retained in the sediment decreased gradually over the remainder of the experiment (31, 41 and 27% in core 1, 2 and 3, respectively at the end of the experiment).

3.10 BASE CATIONS

Calcium was the dominant base cation (C_B) and contributed 79 to 81% of the total C_B charge. Substantial amounts of Ca were released from all three cores during the first 24 hours of seepage (Figure 3.15). Following this period, temporal trends of overflow Ca concentrations were significantly different among the three cores. Substantial changes were not observed in the effluents of core 1 with reference to influent concentration, except the initial peak during first twenty-four hours of seepage. The Ca concentration in the effluent of core 2 was 2.77 mg/l during the first twenty-four hours of seepage and dropped to approximately 1.95 mg/l. Effluent Ca concentrations remained relatively constant until eleven days after acidification. Eleven days after acidification, the concentrations of Ca

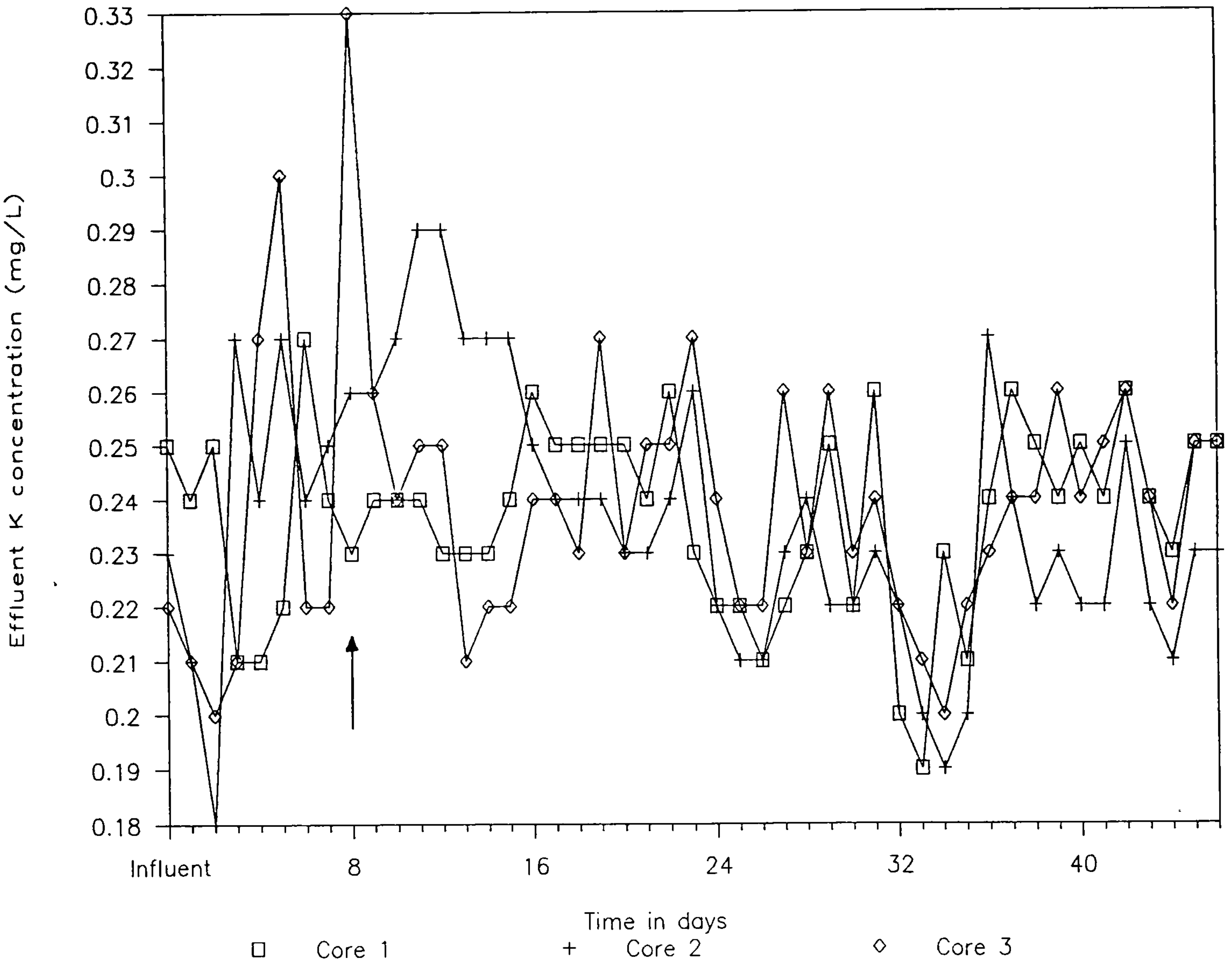

Effluent Ca concentration (mg/L)
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

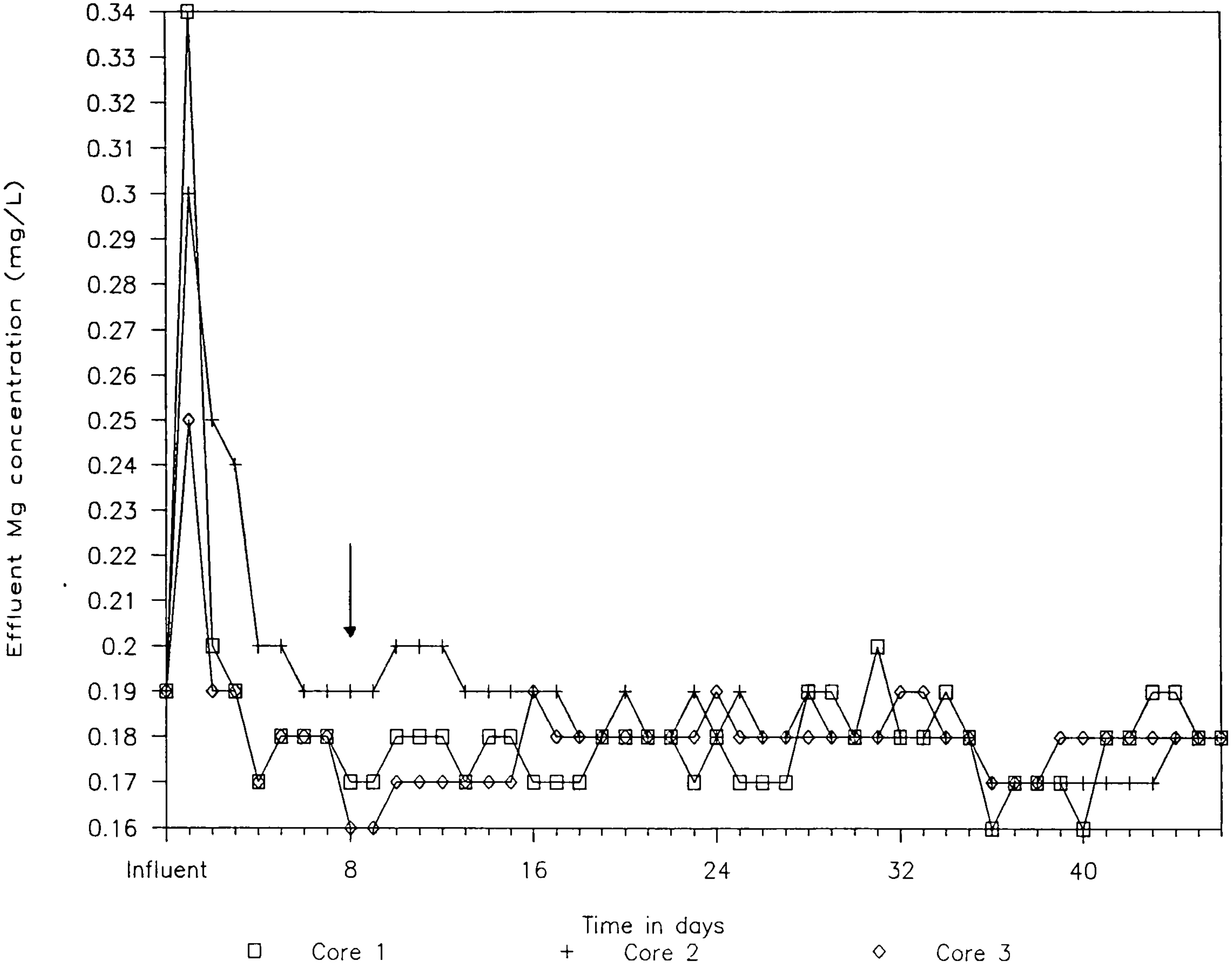
decreased gradually until ten days before the end of the experiment, and then remained constant at approximately the influent concentration until the end of the experiment.

In core 3, except for an initial peak after twenty-four hours of seepage, effluent concentrations were maintained approximately at the same level of influent concentration during the first seven days of the experiment. Calcium concentrations were 10% lower for days 8-15 and from the sixteenth day until the end of the experiment were maintained approximately at influent concentrations. The temporal trend of Ca in core 1 effluent was similar to that of core 3 but with slightly higher concentrations. Concentrations of Ca in effluent solutions appear related to H^+ as a positive relationship between overflow Ca concentration and influent H^+ concentration was exhibited among the cores.

Little variation in K and Mg were observed in the effluent samples of the three cores (Figures 3.16 and 3.17). Influent K concentrations were between 0.22-0.25 mg/l. Effluent concentrations of K in all cores showed no consistent temporal relationships and were not substantially different than influent concentrations. A sudden peak in effluent concentrations of Mg occurred immediately after seepage but dropped approximately to the influent concentrations (0.18 mg/l) in all three cores.

Effluent Na concentrations in core 2 and core 3 were approximately equal to influent concentrations throughout the


Effluent K concentration (mg/L)
0.33
0.32
0.31
0.3
0.29
0.28
0.27
0.26
0.25
0.24
0.23
0.22
0.21
0.2
0.19
0.18
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3


Effluent Mg concentration (mg/L)
0.34
0.33
0.32
0.31
0.3
0.29
0.28
0.27
0.26
0.25
0.24
0.23
0.22
0.21
0.2
0.19
0.18
0.17
0.16
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

experiment, except an initial peak during the initial periods of seepage 3.18). Sodium concentrations in effluent samples of core 1 varied considerably with several peaks over time. These peaks do not appear to be correlated with any other parameter.

3.11 SULPHATE

From the limited number of sulphate measurements made for samples at selected intervals during the study it appears that sulphate was relatively conservative passing through the sediment cores (Figure 3.19). Individual points that were either higher or lower than the influent sulphate concentrations do not show any relationship with any parameters.

3.12.0 SEDIMENT METAL CONCENTRATIONS

The following sediment-metal extraction results are for the three cores which underwent seepage and the fourth core which did not undergo seepage. In order to understand the changes in various fractions of sediment-metals due to a change in seepage chemistry, the three cores were sectioned at 1 cm intervals, extracted, and analysed for exchangeable, organically bound, and hydrous oxide metal fractions upon

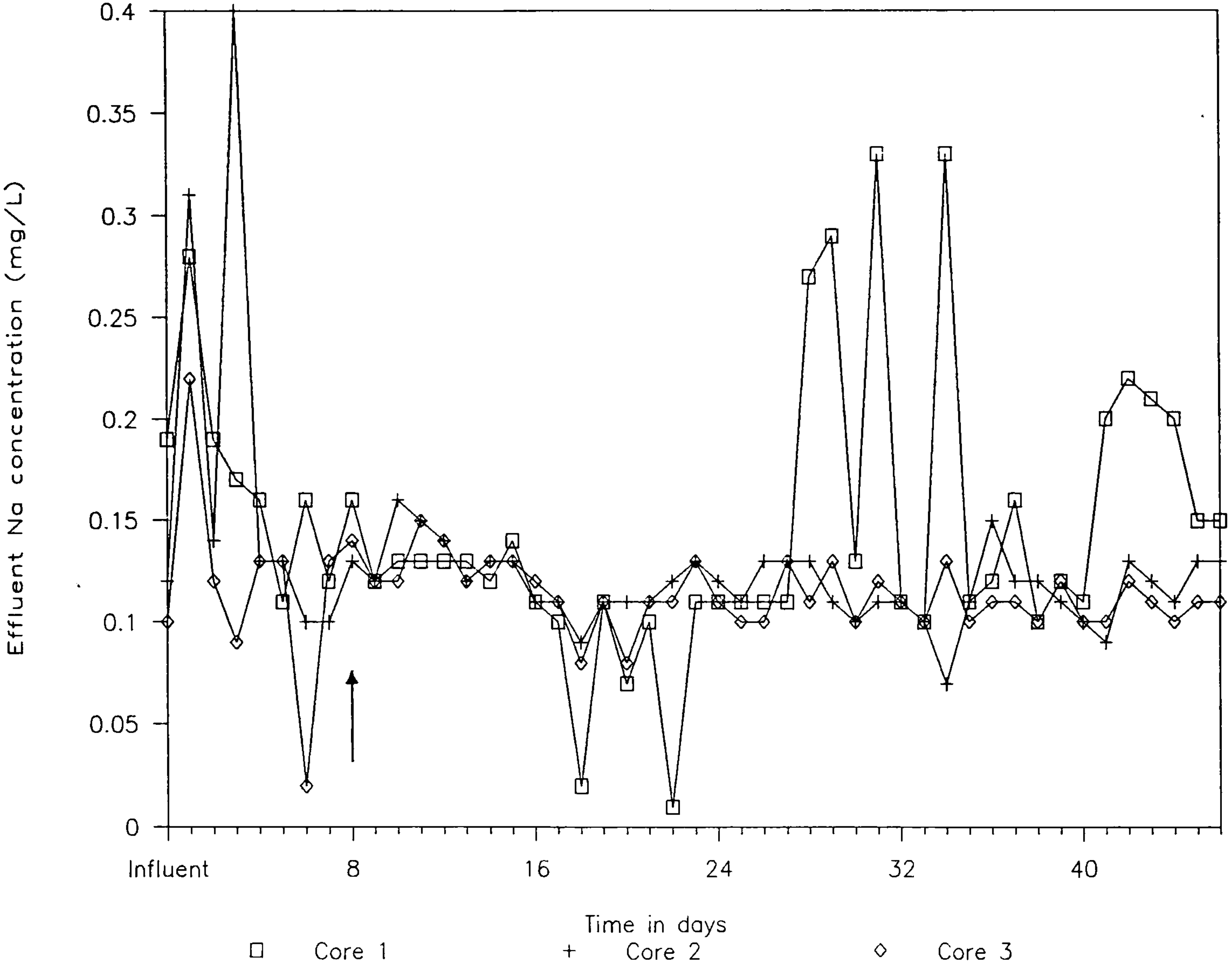
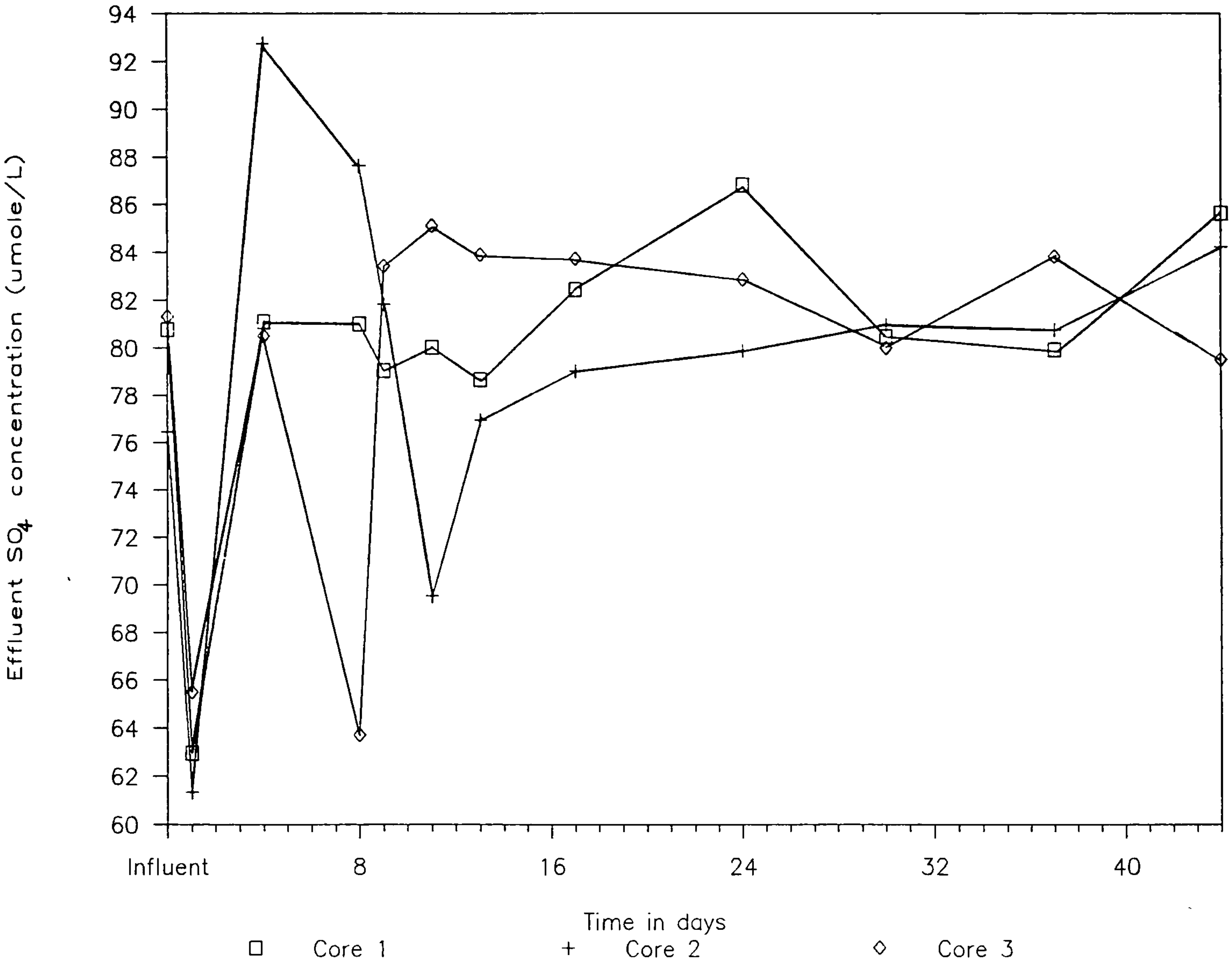

0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Effluent Na concentration (mg/L)
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

Figure 3.19 Effluent sulphate concentration as a function of time.


Effluent SO_4 concentration (umole/L)
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
Influent
8
16
24
32
40
Time in days
□ Core 1
+ Core 2
◇ Core 3

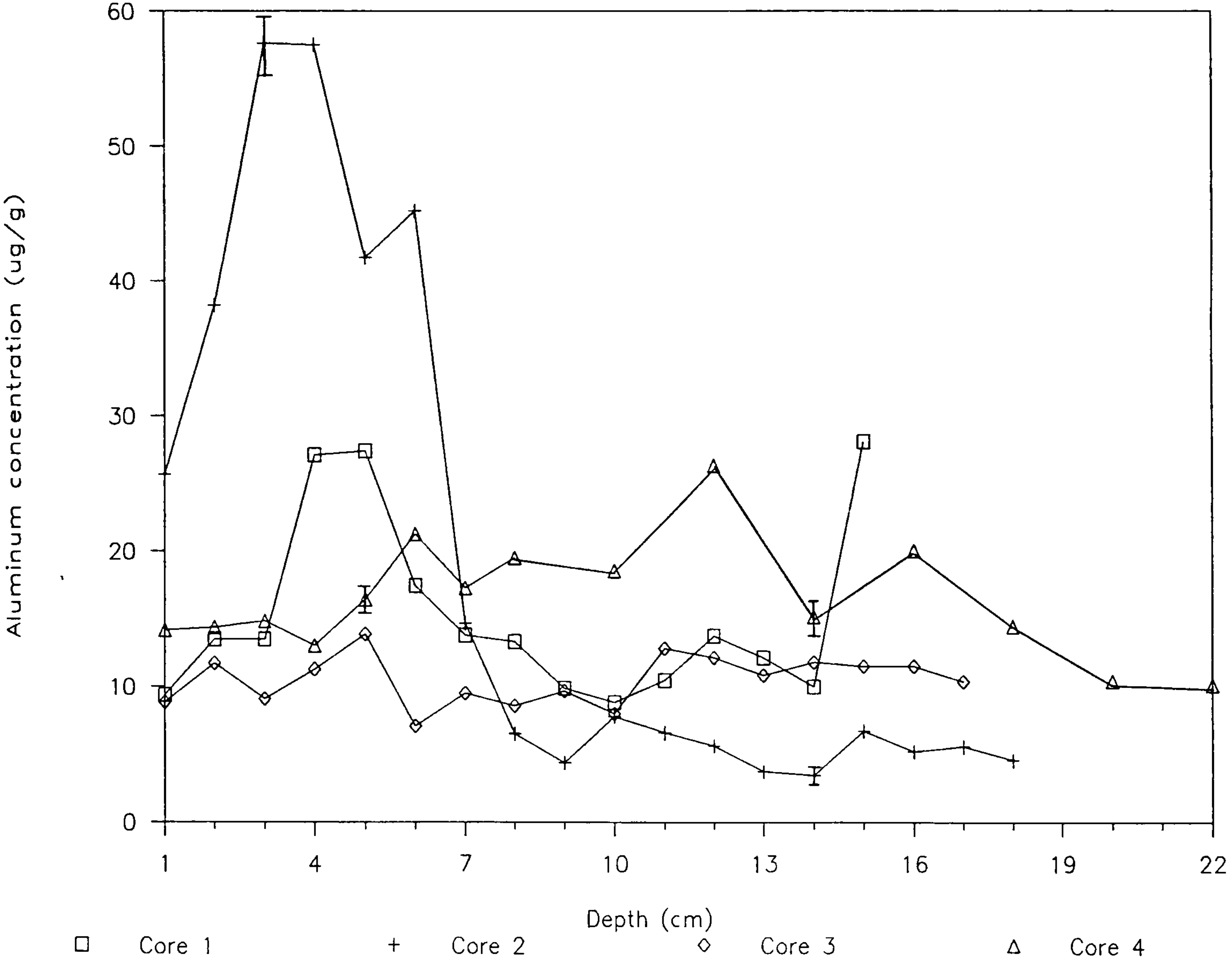
termination of the experiment. A fourth core which was sectioned immediately in the field and followed the same extraction procedures, served as the reference core for comparision studies. Metal concentrations were represented as mass of metal/mass dry weight of sediment.

3.12.1.0 SEDIMENT ALUMINUM FRACTIONS

3.12.1.1 POTASSIUM CHLORIDE EXTRACTABLE ALUMINUM

The exchangeable Al fraction in cores 3 and 4 along the depth profile were similar and had no substantial variation in concentrations with depth (Figure 3.20).

The concentration profile of exchangeable Al at depth in the sediments of core 2 (treated at pH of 3.9) was substantially different than the sediments collected in cores 3 and 4. Core 2 had the highest surface concentration (25.7 ug/g) of any core increasing to 57 ug/g at 4 cm and decreasing dramatically to 4 ug/g at 9 cm depth. Below this depth (11 cm) it was relatively constant (±3 ug/g) through to the bottom of the core (22 cm) and had the lowest concentrations observed in any of the cores observed at these depths. The concentration profile in core 1 was similar to core 2, in that there was a well defined peak in concentration in the top 8 cm of the sediment. The concentration profile peaked (27.4 ug/g) at 5 cm and dropped to 9 ug/g at the 10 cm depth. A



Aluminum concentration (ug/g)
60
50
40
30
20
10
0
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4

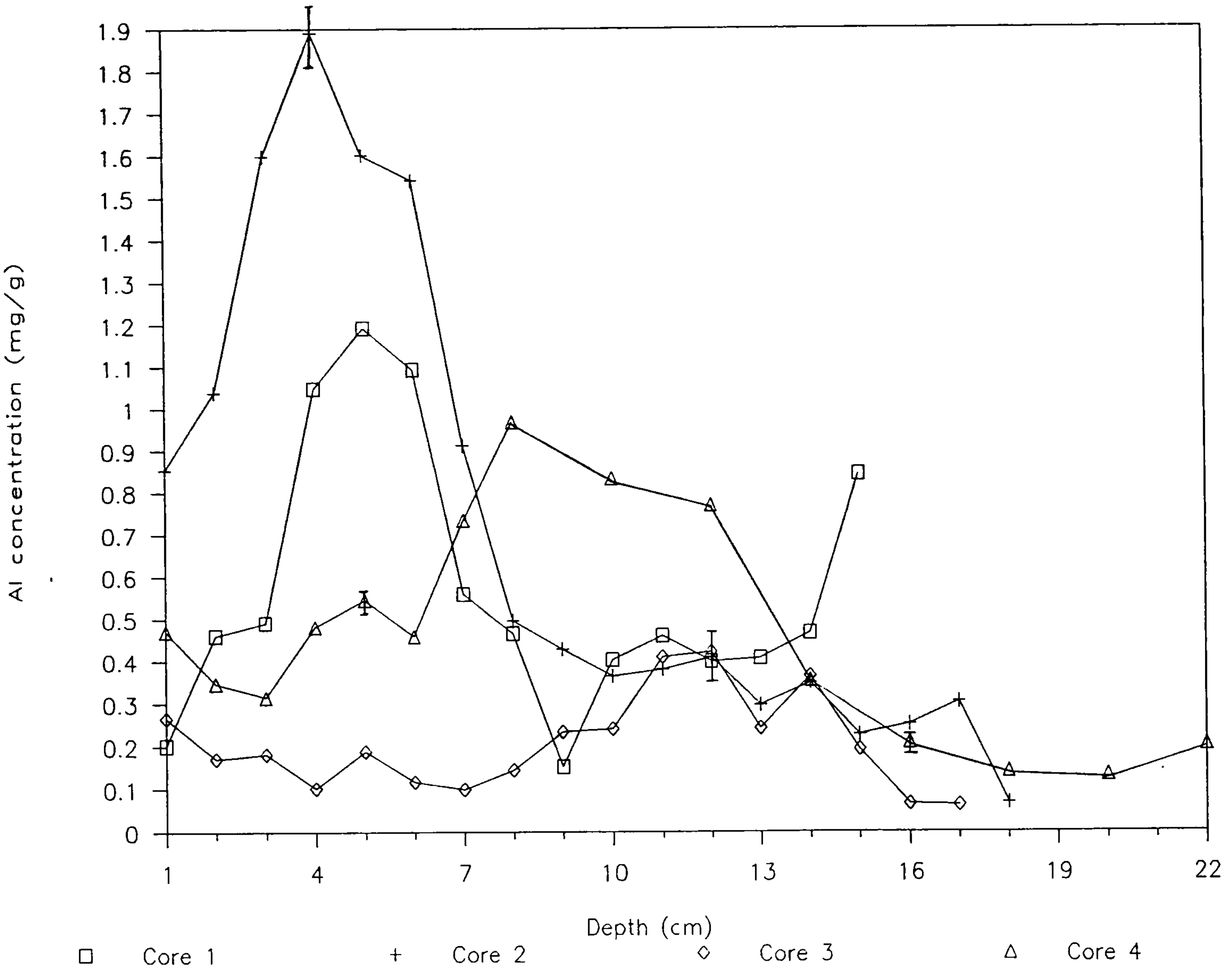
sharp peak of 28 ug/g was present at the 15 cm depth. No other core exhibited this trend.

3.12.1.2 SODIUM PYROPHOSPHATE EXTRACTABLE ALUMINUM

Sediment profiles of sodium pyrophosphate extractable Al (NaP-Al) were markedly different for cores 1 and 2 compared to cores 3 and 4 (Figure 3.21). On a "whole core" basis, the sediments of core 3 had the lowest NaP-Al concentration of any core. Concentrations varied from a low of <0.1 mg/g (16 and 17 cm depth) to 0.423 mg/g at 12 cm depth. Concentrations were elevated at the 9-15 cm depth and formed a distinguishable enriched region relative to the remainder of the core.

Concentrations of NaP-Al in the sediments of core 4 were generally 100% higher than core 3 but reflected a similar trend. NaP-Al concentrations peaked (0.969 mg/g) at 8 cm and decreased to <0.200 mg/g at 18 cm. An enriched region of NaP-Al was found at mid-core depth (6-14 cm) similar to core 3.

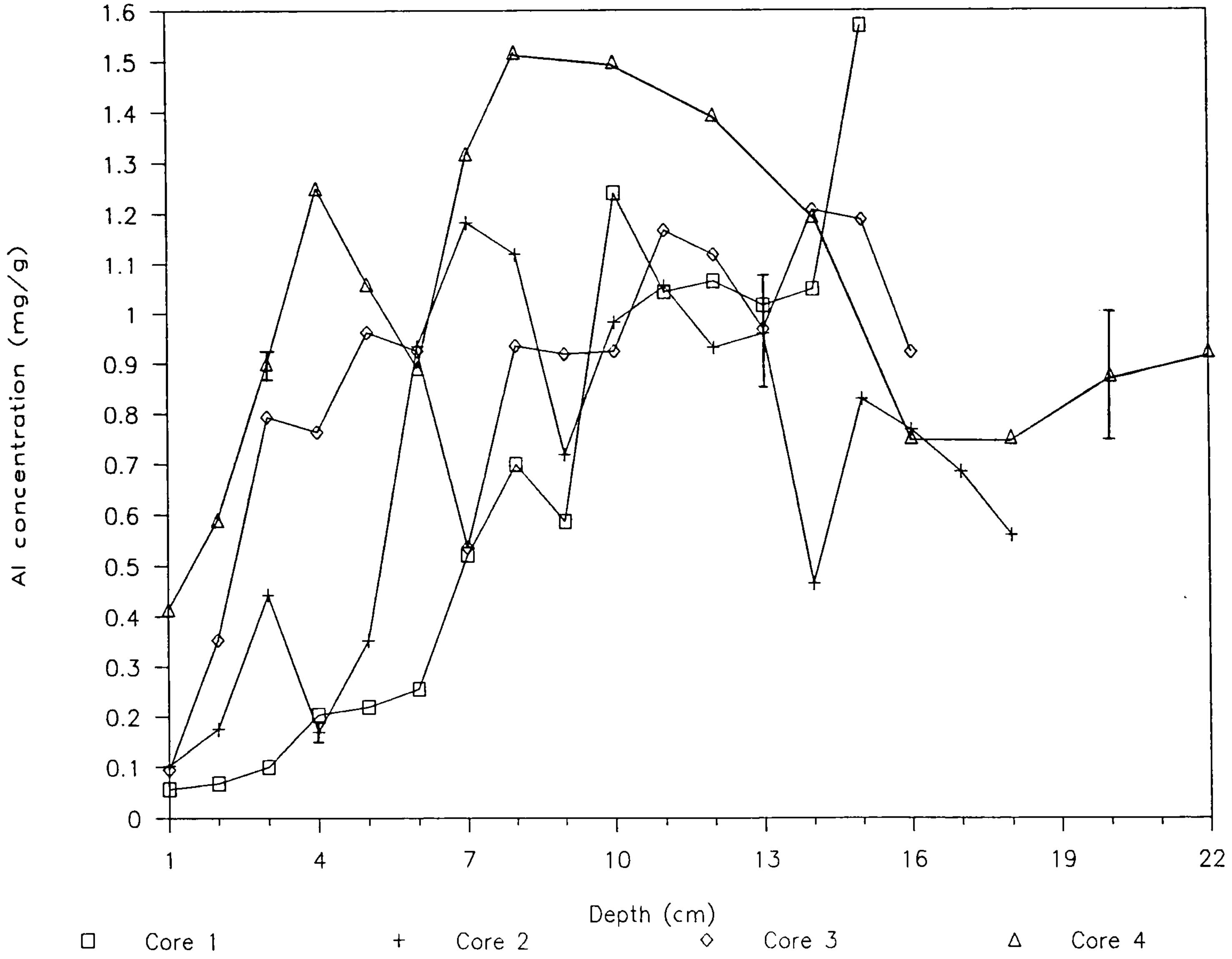
The concentration profiles in the acidified cores (core 1 and core 2) were different from the unacidified and field sectioned cores (core 3 and core 4). In core 2, the lowest concentration (0.068 mg/g) was present at the bottom of the core (18 cm depth). Sediment NaP-Al concentrations increased to 1.89 mg/g at 4 cm depth and then decreased to 0.85 mg/g at the surface. The region between the surface and 8 cm was the most highly enriched of any of the cores. The


Al concentration (mg/g)
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4

concentration profile of NaP-Al in core 1 was similar to core 2 with a region of elevated concentration between 0 and 8 cm. The trend in concentration below the enriched region was dissimilar to core 2 in that NaP-Al concentrations increased at the bottom of the core.

3.12.1.3 AMMONIUM OXALATE EXTRACTABLE ALUMINUM

Trends in ammonium oxalate-extractable Al (Amo-Al) were less distinguishable and more variable than observed with the KCl and NaP extractions (Figure 3.22). The lowest Amo-Al concentration for each core occurred at the surface of the core. Concentrations generally increased with depth in all cores to 11 cm below the surface. Below this depth Amo-Al concentrations decreased in core 2 and core 4 while core 3 increased to it's highest concentration at the bottom of the core. The trend in Amo-Al in core 1 at 15 cm is consistent with observations of KCl-Al and NaP-Al in core 1 with sharply higher concentrations present at the bottom of the core. For core 3, minimal Amo-Al variation with depth was observed between 11 cm and the bottom of the core.


1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Al concentration (mg/g)
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4

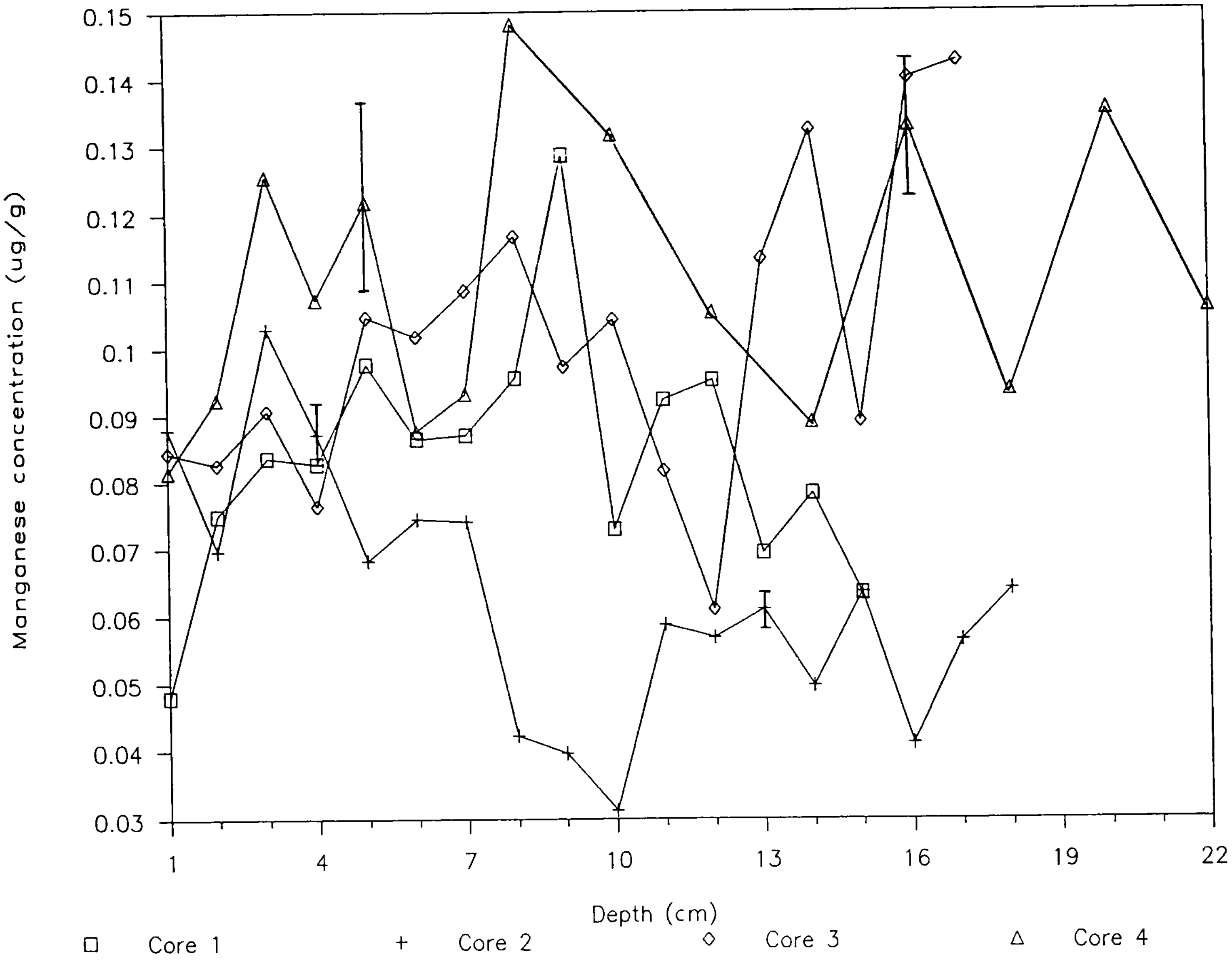
3.12.2.0 SEDIMENT MANGANESE FRACTIONS

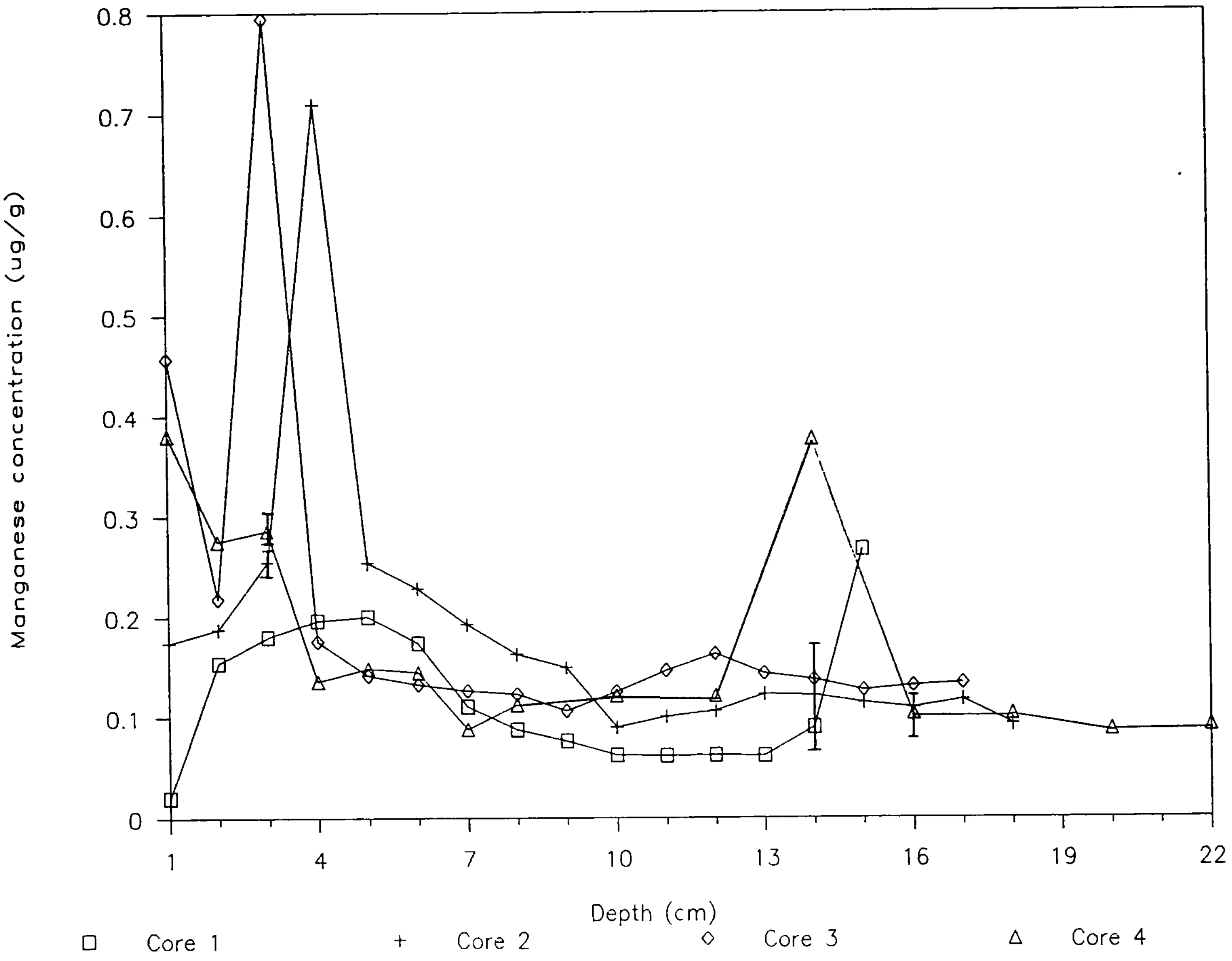
3.12.2.1 POTASIUM CHLORIDE EXTRACTABLE MANGANESE

The KCl-exchangeable Mn concentrations (KCl-Mn) in each core exhibited considerable variability with depth. The lowest KCl-Mn concentrations were observed in core 2 which, below 4 cm, had the lowest concentration of any core (Figure 3.23). The lowest concentration at the sediment surface was observed in core 1 (0.05 ug/g). Within this core KCl-Mn concentrations increased below the surface to a peak concentration at 9 cm (0.129 ug/g) and the decreased below this depth. Cores 3 and 4 exhibited considerable variability with depth but no discernible trends were apparent.

3.12.2.2 SODIUM PYROPHOSPHATE EXTRACTABLE MANGANESE

Concentrations of sodium pyrophosphate-extractable Mn (NaP-Mn) were generally elevated at shallow sediment depths in all cores (Figure 3.24). Narrow, highly enriched zones of NaP-Mn were observed in both cores 2 and 3 at depths of 4 and 3 cm, respectively. Core 1 and core 4 exhibited no similar enriched zones. Below 9 cm, all cores had similar concentrations of NaP-Mn. Core 4 had the highest concentration of NaP-Mn at the surface (0.46 ug/g) but dropped to <0.2 ug/g by 4 cm depth. Concentrations remained relatively constant below 4 cm except for a sharp peak at 14 cm depth.


Manganese concentration (ug/g)
0.15
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4


Manganese concentration (ug/g)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4

The NaP-Mn concentration profile in core 1 was substantially different from the rest of the cores. It had the lowest surface concentration (0.02 ug/g) among the cores and had its maximum concentration at the bottom of the core (0.27 ug/g). Except the surface concentration, the concentrations were >0.1 ug/g until 7 cm and <0.1 ug/g below the 8 cm depth except for the bottom section.

3.12.2.3 AMMONIUM OXALATE EXTRACTABLE MANGANESE

The ammonium oxalate extractable-Mn concentrations in the extracts from all four cores were less than the detection limit (0.02 ug/l) of furnace atomic absorption spectroscopy.

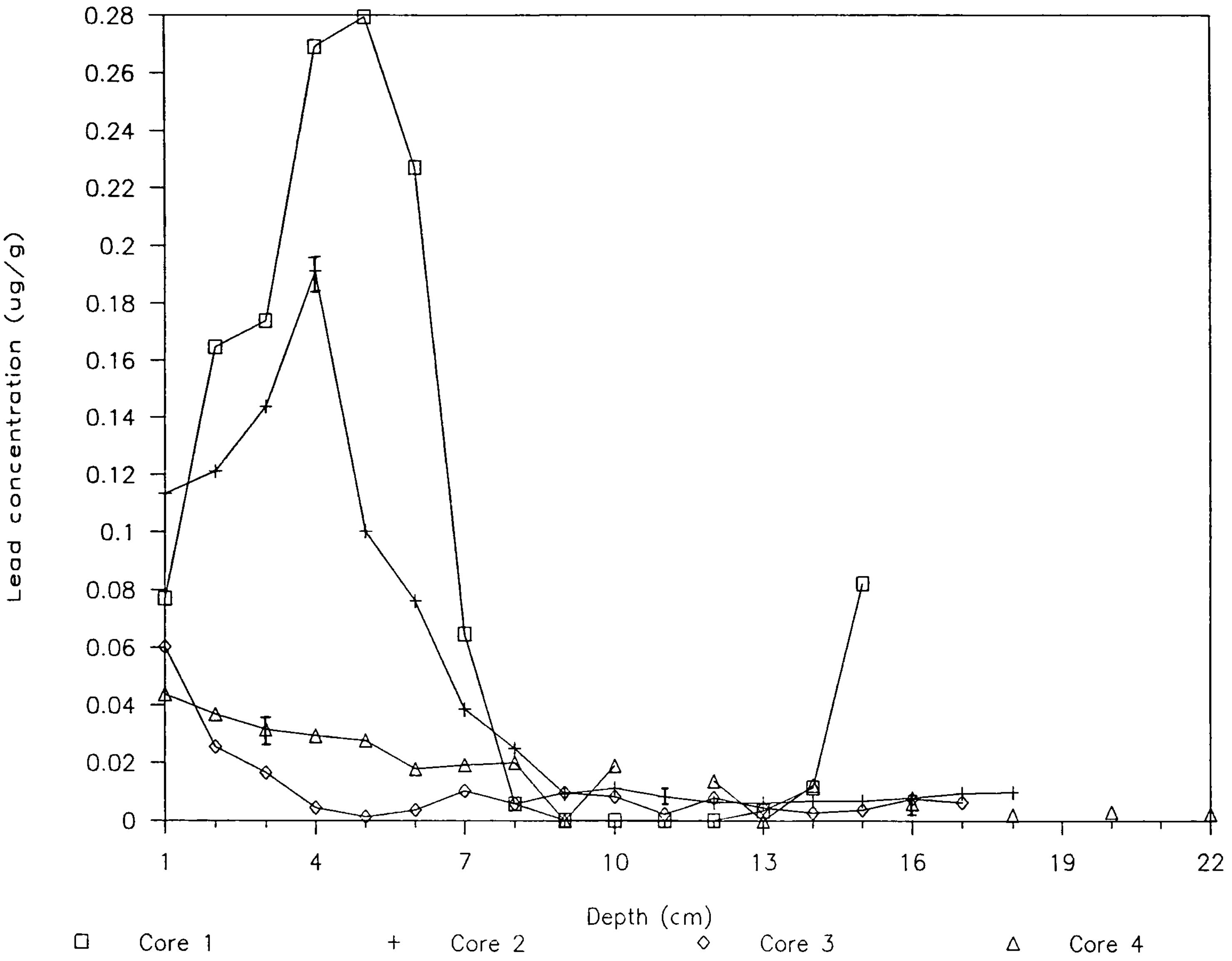
3.12.3.0 SEDIMENT LEAD FRACTIONS

3.12.3.1 POTASSIUM CHLORIDE EXTRACTABLE LEAD

The KCl-exchangeable Pb concentration in all the cores were less than the detection limit (0.2 ug/l) of furnace atomic absorption spectroscopy for the KCl extractions.

3.12.3.2 SODIUM PYROPHOSPHATE EXTRACTABLE LEAD

Significant variations were observed among the cores in the concentration of sodium pyrophosphate extractable Pb (NaP-Pb) in the top 8 cm (Figure 3.25). Below 8 cm the

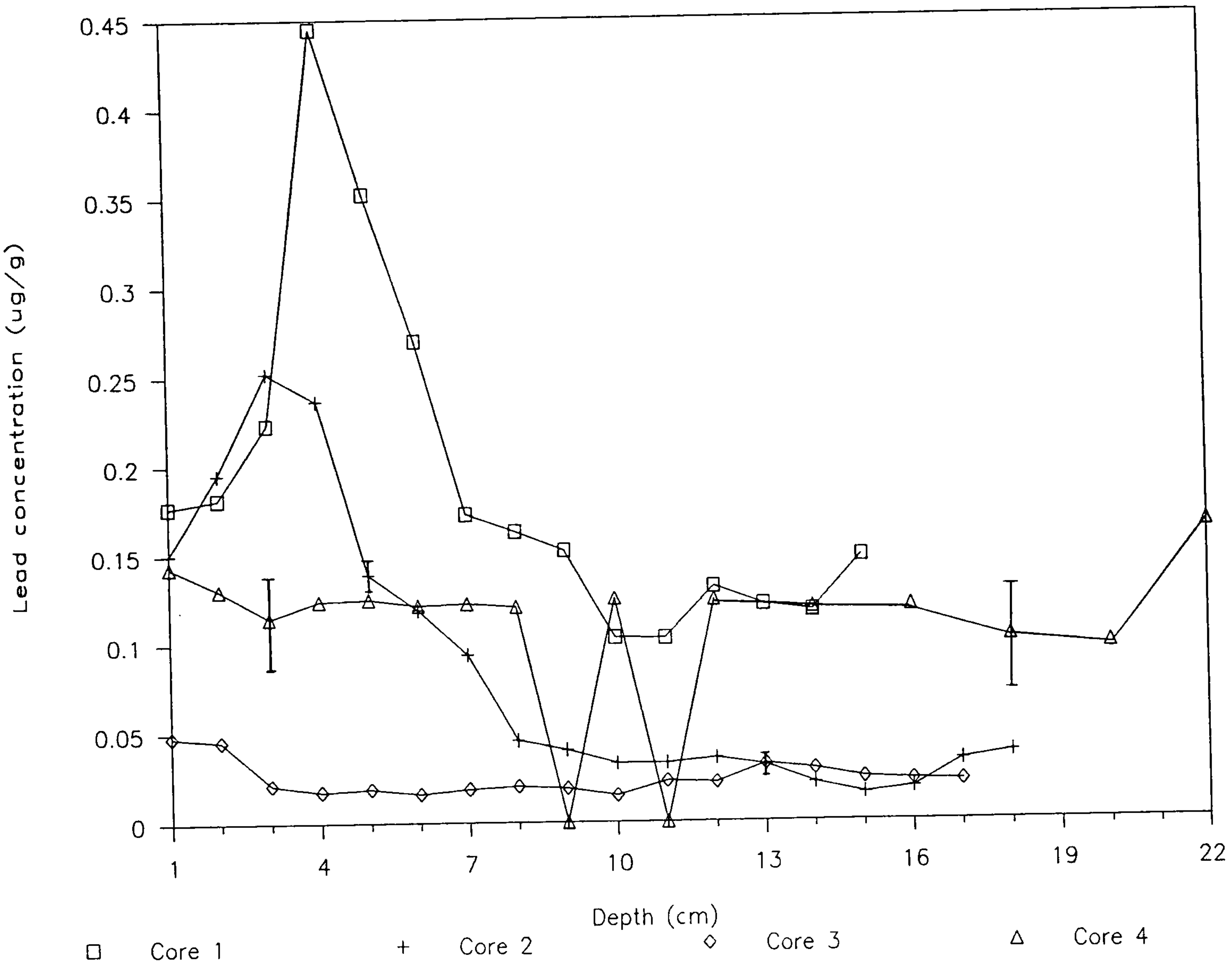

0.28
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Lead concentration (ug/g)
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4

concentrations were less than 0.03 ug/g in all the cores except at the lowest depth in core 1. The surface concentrations of NaP-Pb concentrations in core 3 and 4 were 0.060 and 0.044 ug/g and decreased downward through the core.

In core 1 and 2 concentration profiles of NaP-Pb from 0 to 9 cm depth were substantially different from trends in core 3 and 4. In core 1, a steep increase of NaP-Pb concentration observed from 0.077 ug/g at the surface to 0.279 ug/g at 5 cm depth followed by a steep decrease to 0.010 ug/g at 8 cm depth. The distribution of NaP-Pb concentrations in core 2 was similar to core 1. Concentrations of NaP-Pb increased from 0.113 ug/g at the surface to 0.190 ug/g at 4 cm depth and then dropped steeply to 0.010 ug/g at the 9 cm depth. Concentrations of NaP-Pb were <0.020 ug/g for both cores below 8 cm.

3.12.3.3 AMMONIUM OXALATE EXTRACTABLE LEAD

The concentrations of ammonium oxalate extractable Pb (Amo-Pb) in core 3 were relatively constant and low (approximately 0.03 ug/g ± 0.01) throughout the depth profile (Figure 3.26). Similarly in core 4, Amo-Pb concentrations were relatively constant with depth but were present at much higher concentration than core 3 (0.13 ± 0.03 ug/g). Variations in the profiles of Amo-Pb concentrations were more depth variable in cores 1 and 2 than in cores 3 and 4. The Amo-Pb


Lead concentration (ug/g)
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4

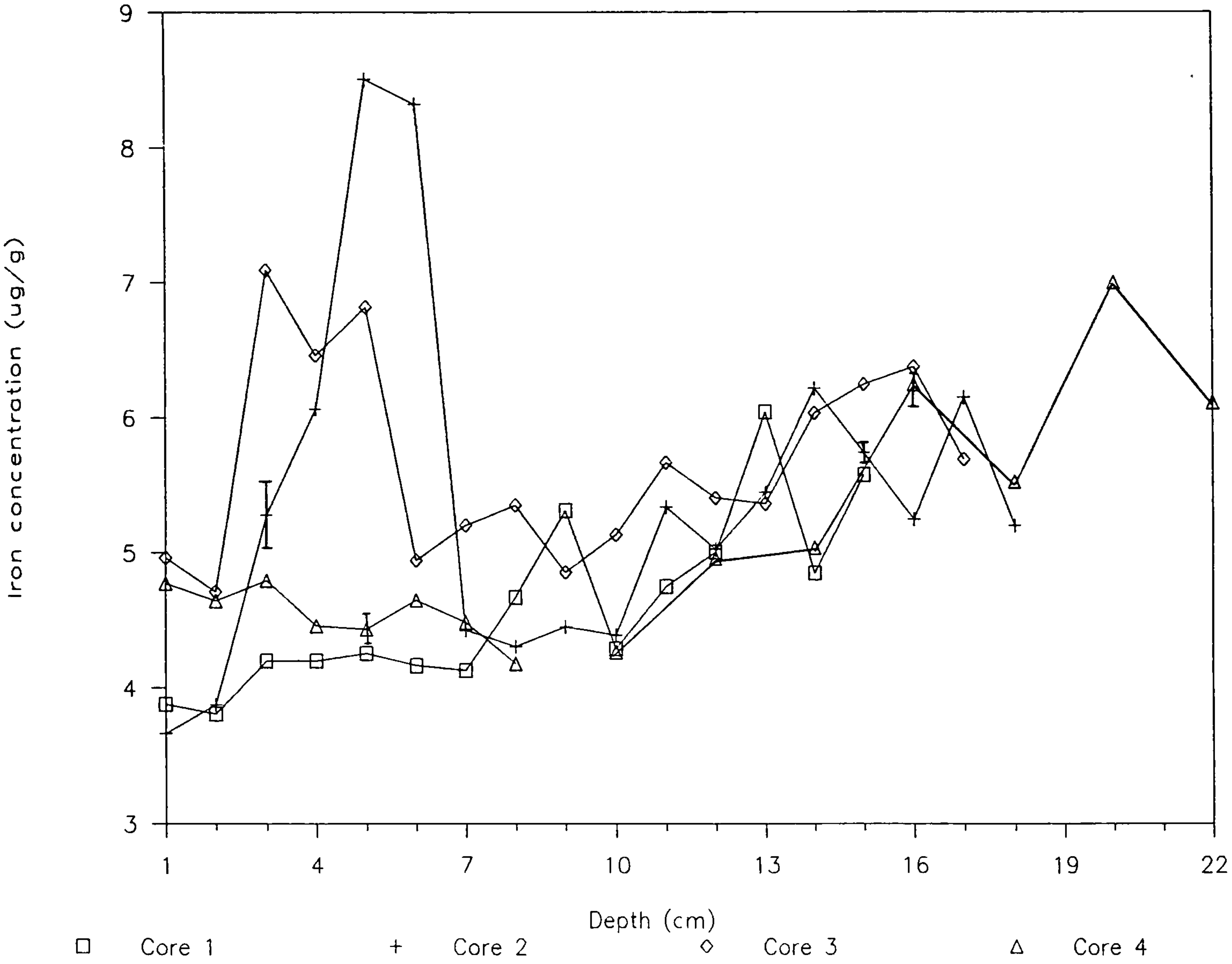
concentrations in core 1 and 2 increased sharply from 0.177 and 0.151 ug/g at the surface to 0.445 and 0.252 ug/g at 4 and 3 cm, respectively and then dropped steeply by the 9 cm depth.

3.12.4.0 SEDIMENT IRON FRACTIONS

3.12.4.1 POTASIUM CHLORIDE EXTRACTABLE IRON

The trend and concentration of the KCl-exchangeable fraction of Fe (KCl-Fe) were similar for core 1 and core 4 with gradually increasing concentrations with depth (Figure 3.27). The KCl-Fe concentrations in core 1 increased from approximately 4 ug/g at the surface to 5 ug/g near the bottom of the core. For core 4, KCl-Fe concentrations were 4.8 ug/g at the surface, decreased to 4.2 ug/g at 8 cm depth and then increased to 6 ug/g at the bottom of the core.

The concentration profiles of the KCl-Fe fraction were similar for core 2 and core 3. Each core exhibited elevated KCl-Fe concentrations, relative to the rest of the core, between the 2 and 6 cm depths. In core 2, KCl-Fe concentrations increased from 4 ug/g at the surface to 8.5 ug/g at the 5 cm depth and dropped sharply to 4.5 ug/g at 7 cm depth. In core 3 KCl-Fe concentrations increased from 5 ug/g at the surface to approximately 7 ug/g at the 3-5 cm depths then decreased sharply to 5 ug/g at 6 cm depth. Below 7 cm KCl-Fe in all cores was similar and not substantially different when the variability associated with the extraction


Iron concentration (ug/g)
9
8
7
6
5
4
3
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4

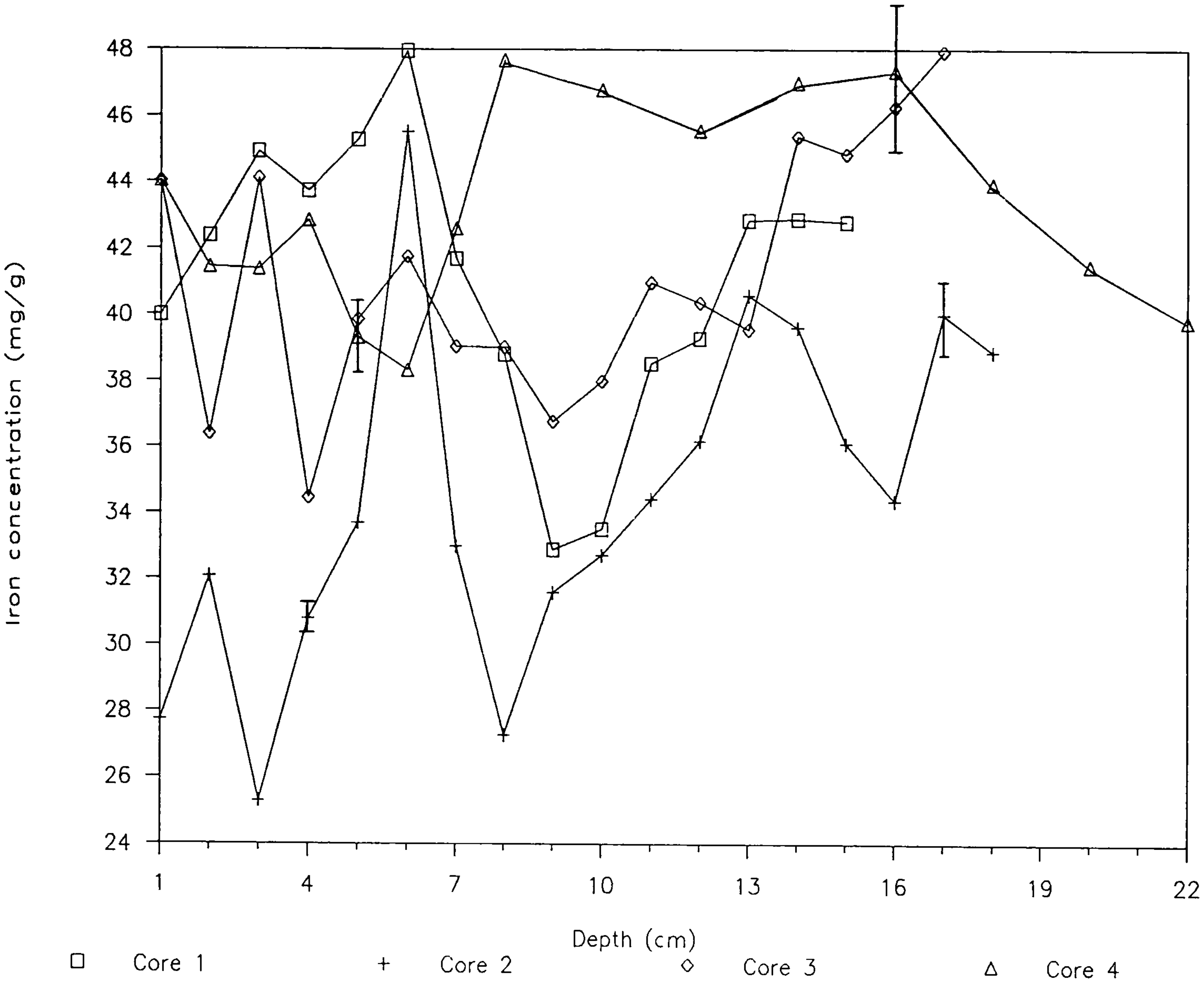
and analysis is considered.

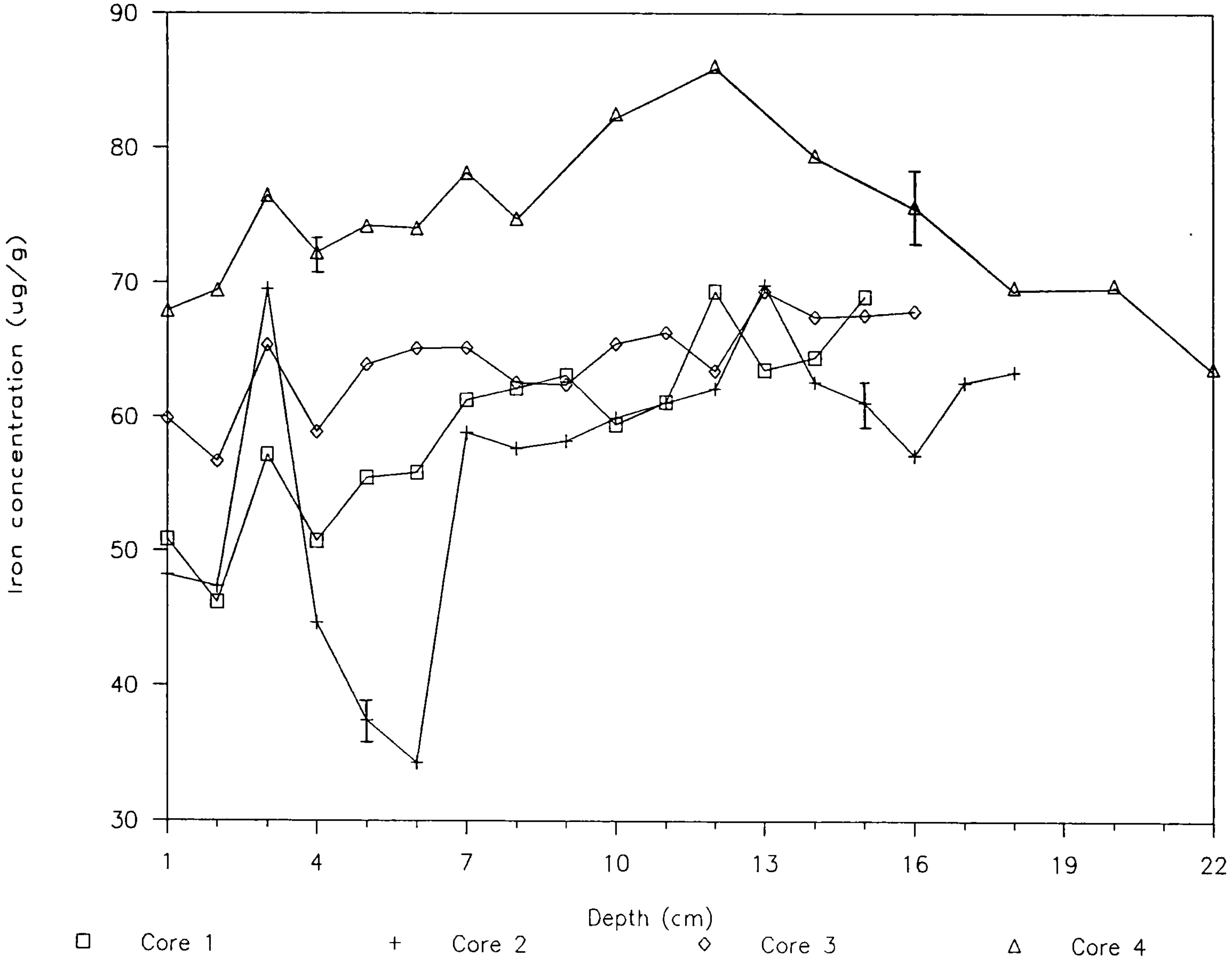
3.12.4.2 SODIUM PYROPHOSPHATE EXTRACTABLE IRON

Minimal depth variation in sodium pyrophosphate-extractable Fe (NaP-Fe) was observed in core 3 and 4 (Figure 3.28). In core 1, the NaP-Fe profile was highlighted by a region of lower concentrations between 6 and 13 cm. The NaP-Fe concentration was 40 ug/g at the surface and maintained higher concentrations between 2-6 cm than the other cores. A dramatic decrease in NaP-Fe concentration occurred from 48 ug/g at 6 cm to 33 ug/g at 9 cm depth and was followed by an increase to the 13 cm depth. The NaP-Fe concentrations profile in core 2 was similar to the profile observed in core 1 except that NaP-Fe concentrations were lower in core 2. Near-surface (0-3 cm) concentrations of NaP-Fe were substantially lower (<10 ug/g) than the other cores while concentrations below 9 cm were only slightly (<5 ug/g) lower than the other cores.

3.12.4.3 AMMONIUM OXALATE EXTRACTABLE IRON

The trends of ammonium oxalate-extractable Fe (Amo-Fe) concentrations) in core 1, core 3, and core 4 were parallel from 0-6 cm depth, with surface concentrations of 51, 60 and 68 ug/g, respectively (Figure 3.29). The concentration profile in core 4 remained higher than core 1 and 3 below 6


Iron concentration (mg/g)
48
46
44
42
40
38
36
34
32
30
28
26
24
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4


90
80
70
60
50
40
30
Iron concentration (ug/g)
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4

cm whereas cores 1 and 3 exhibited similar concentrations below this depth.

For core 2 the trend and concentration of ammonium oxalate extractable-Fe was essentially the same as core 1 and 3 below the 7 cm depth. However, between the surface and 6 cm the trend in Amo-Fe was substantially different than the other cores. A peak concentration was observed at 3 cm depth (70 ug/g) followed by a sharp drop to 6 cm (34 ug/g). A sharp increase occurred between 6 and 7 cm depth (59 ug/g) and then remained approximately at that concentration level (±10 ug/g) until the bottom of the core.

3.13 SEDIMENT CORE METAL BUDGETS

Total extractable metal concentrations in each core were calculated to evaluate the potential sediment sources for the metals monitored in this study (Table 3.1).

$$\text{Metal}_T = \text{Sum }[\text{KCl extractable + Sodium pyrophosphate extractable + Ammonium oxalate extractable metal}]$$

Percentages of each fraction of metals were also calculated in each core to understand the relative contribution of each fraction to the total metal (Table 3.2). Significant

Table 3.1

Total extractable metal and organic matter concentrations in sediment cores

Core #	Al(mg)	Fe(mg)	Mn(ug)	Pb(ug)	TOC (g)
1	855	72.51	141	194	12.49
2	1186	79.74	203	112	20.62
3	643	86.78	235	27	5.55
4	725	75.5	241	32	6.26

Table 3.2

Relative percentages of metal fractions

Metal	Core #	KCl-extr. %	NaP-extr. %	Amo-extr. %
Al	1	2	46	52
	2	1	51	48
	3	1	19	80
Fe	1	5	39	56
	2	5	36	59
	3	5	37	58
Mn	1	41	59	-
	2	26	74	-
	3	34	66	-
Pb	1	-	32	68
	2	-	37	63
	3	-	31	69

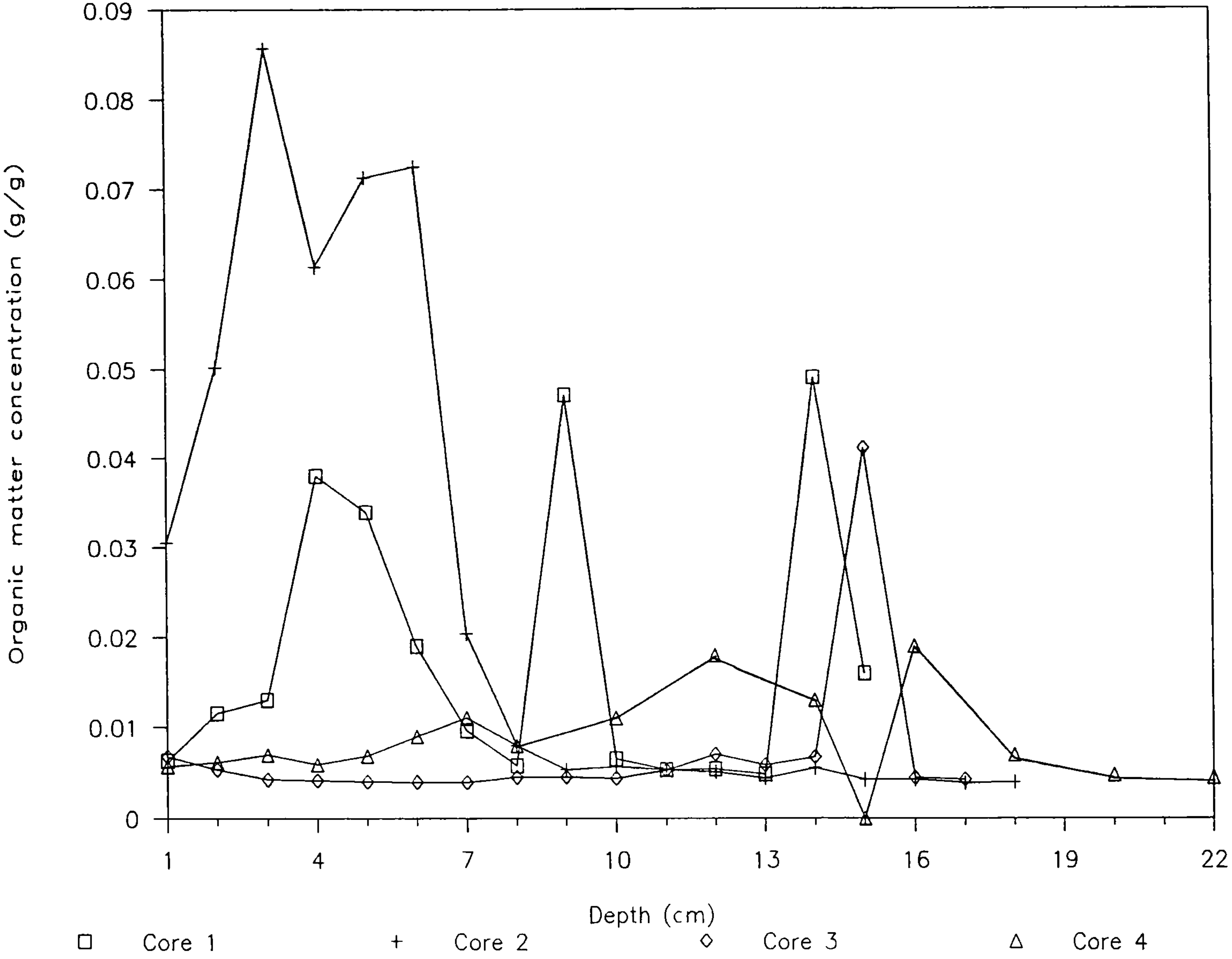
KCl-extr. includes exchangeable metal fraction

NaP-extr. includes organically bound metal fraction

Amo-extr. includes hydrous oxide metal fraction

"-" indicates metal concentrations below detection limit differences in the total organic matter content was observed among the cores. Total organic matter present was 12.49, 20.62, and 5.55g in core 1, core 2, and core 3, respectively. Organic matter profiles exhibited elevated concentrations just below the surface in core 1 and core 2 with generally lower values below this region (Figure 3.30). Organic matter concentrations in core 3 and 4 were generally below 0.01 g/g and were essentially depth invariable.

Figure 3.30 Organic matter concentration in sediment as a function of depth.


Organic matter concentration (g/g)
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1
4
7
10
13
16
19
22
Depth (cm)
□ Core 1
+ Core 2
◇ Core 3
△ Core 4

4.0 DISCUSSION

4.1.0 EFFECTS OF SEDIMENT HETEROGENEITY ON GROUNDWATER CHEMISTRY

The syngenetic chemical and mineralogical composition of sediments is largely controlled by post-depositional groundwater seepage and depositional processes as well as sediment sources during the depositional processes. In this study, considerable sediment heterogeneity was observed for four sediment cores taken in very close proximity. The cause of this heterogeneity is undiscernible from this work but may be related to groundwater chemistry and flux. The sediment cores taken for this experiment were collected in a line parallel to the shore line in an effort to reduce inter-sediment core variations that might be related to groundwater flowing along flowpaths from different depths in the terrestrial watershed. From field monitoring analysis (Schafran, 1988) and theoretical modelling studies (McBride and Pfannkuch, 1975) groundwater flux and chemistry should have been essentially the same through this sediment region. However, detailed analysis of groundwater flowpaths and the associated chemistry in near-shore sediments has not been extensively conducted and variations of groundwater chemistry may occur over relatively short distances. Thus without further analysis of this situation at the field site, sediment chemical heterogeneity is assumed to be related to syn- as well as post-depositional processes.

Even though all four cores were collected within a one meter distance parallel to the lake shore, they showed significant variation in extractable (KCl, sodium pyrophosphate, and ammonium oxalate) metal (Fe, Mn, Al, Pb) fractions. Prior to the influent acidification, the effluent chemistry was observed to be substantially different among the cores due to the variation in sediment chemistry. The difference in the rates of mobilization of metals from each core was likely dependent on the extent of disequilibrium with cation exchange, dissolution and sorption reactions and the amount of metal present.

In the pre-acidification period, core 2 exhibited the greatest capacity for removing H^+ from influent water through mobilization of Ca^{2+} from the sediment. The increase in the pH values of water passing through this core also resulted in Al removal. Thus, the mobilization of Ca^{2+} caused core 2 to behave as a sink for Al while core 1 and 3, which exhibited lower Ca^{2+} mobilization, were sources of Al during the entire study. The release of Ca^{2+} after acidification continued to be greater in core 2 but was insufficient to prevent the mobilization of Al from the core due to the lower pH values (core 2 influent was lowest pH, 3.9).

Decreases in Al concentration in the effluent was most likely due to immobilization through exchange reactions or precipitation of an Al hydroxide at higher pH conditions. Following acidification, the pH values of effluent solutions decreased gradually. This was probably a result of the lack of equivalent exchangeable cations to compensate increased H^+ concentrations. An exponential increase in Al concentrations occurred with decreasing pH values which is consistent with previous observations in natural waters (Dickson, 1978; Driscoll et al., 1984; Hutchinson et al., 1978).

During pre-acidification, the overflow Pb concentrations of core 2 were significantly different from the other cores. In cores 1 and 3 no substantial removal or release of Pb occurred, but in the overflows of core 2, significant decreases in Pb concentration (> 50% reduction with reference to influent concentration) occurred. Dissolved organic matter can act as a strong chelator of Pb and may be responsible for its retention in this core (Schnitzer and Khan, 1975). Because sediment in core 2 was enriched with organic matter (relative to the other cores) lead may have become complexed with the sediment organic matter. The variation in the organic matter content among the cores also explains the heterogeneity of organically bound Pb fraction among the cores. This explanation is supported by the increased fraction of organically bound Pb in the effluents during the post acidification period. Following acidification, organically bound Pb in the overflows increased to approximately 50% of the influent concentration.

4.2.0 EFFECTS OF ACIDIFICATION ON EFFLUENT METAL CONCENTRATIONS

Acidification of the influent water substantially increased Al, Mn and Pb concentrations in the effluent and showed no apparent effect on Fe concentrations. Substantial removal of Fe (96-98%) occurred in all cores both prior to and after acidification. Core 2, which removed the highest amount of TOC from the influent water, also removed the greatest amount of Fe from the water. Because the waters were well oxygenated and inorganically complexed or free Fe at these pH values is very low (Stumm and Morgan, 1981), it is likely that the majority of Fe present in these waters was present as an organo-iron complex. However, no significant correlation was observed between effluent TOC and Fe concentrations. The mechanism causing the accumulation of organic carbon and Fe is unknown but may have been the result of adsorption of the Fe-organo complex to sediment metal oxides or a mechanical straining/filtering process.

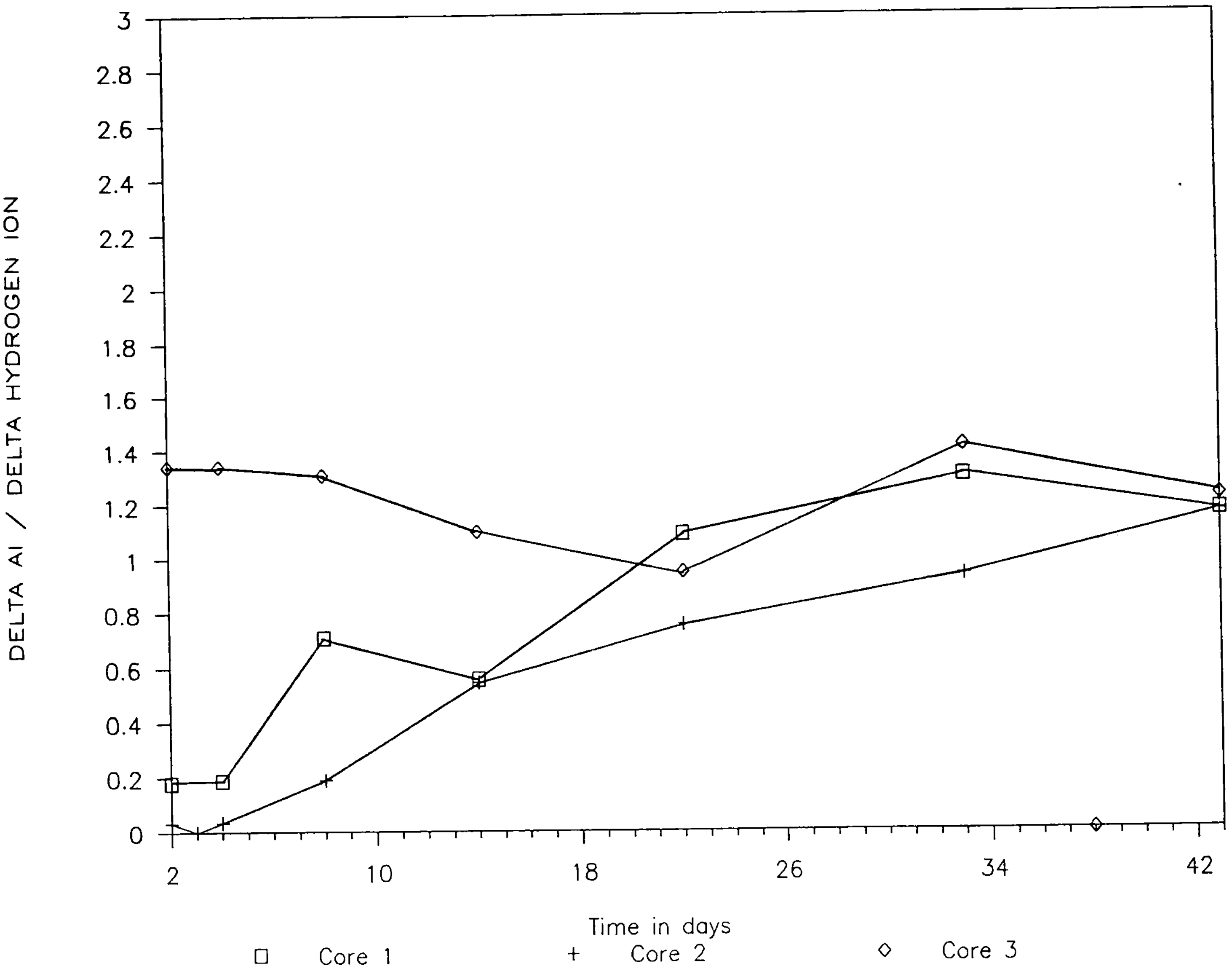
Acidification showed a prominent direct impact on Al mobility from the sediments. In core 2, which received water with the lowest pH value (3.9) following acidification, the sediments served as a sink (19% removal) for Al until the day of acidification. After acidification Al concentrations increased drastically with an approximately 100% increase by the end of the experiment; a 49% increase was observed in core 1 over the same period. The rate of increase of Al concentrations was inversely proportional to pH. Sediment releases of Al were largely responsible for the neutralization of H^+. To compare the relative importance of H^+ neutralization by Al mobilization the ratio of Al change to H^+ ($\Delta Al_{equivalence}/\Delta H^+_{equivalence}$) in the influent and overflow waters was calculated as follows:

$$Al_{equivalence} = \text{Effluent } \Sigma\{3[Al^{+3}] + 2[AlF^{2+}] + 2[AlOH^{+2}] + [Al(OH)_2^+]\} - \text{Influent } \Sigma\{3[Al^{+3}] + 2[AlF^{2+}] + 2[Al(OH)^{2+}] + [Al(OH)_2^+]\}$$

$$H^+ = [\text{Influent } H^+] - [\text{Effluent } H^+]$$

where: [] indicates M/l

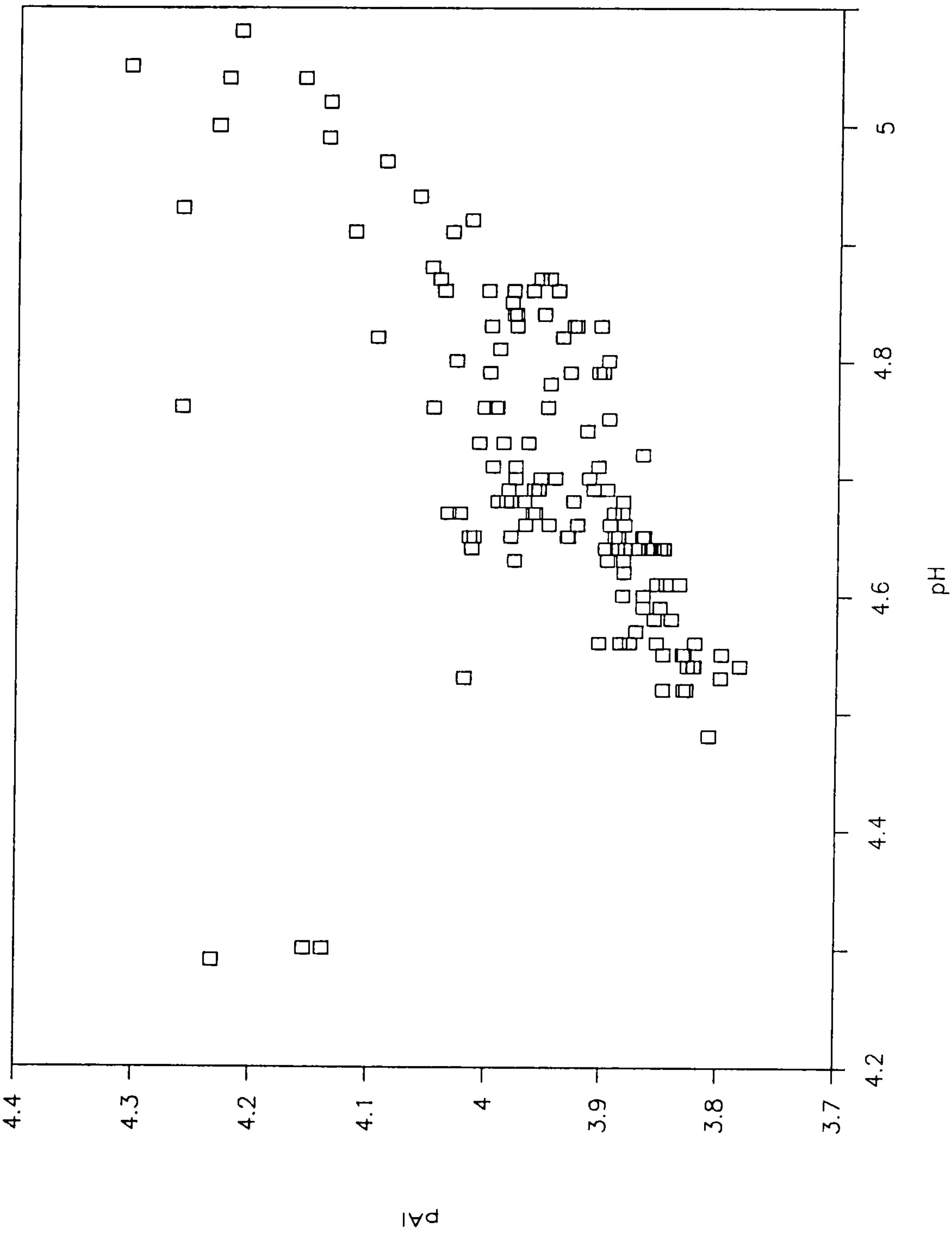
The temporal relationship of $\Delta Al/\Delta H^+$ (Figure 4.1) appeared to be considerably different in each core. During initial periods, in cores 1 and 2, the $\Delta Al/\Delta H^+$ ratio was very low (<0.2). By the end of the experiment the ratio

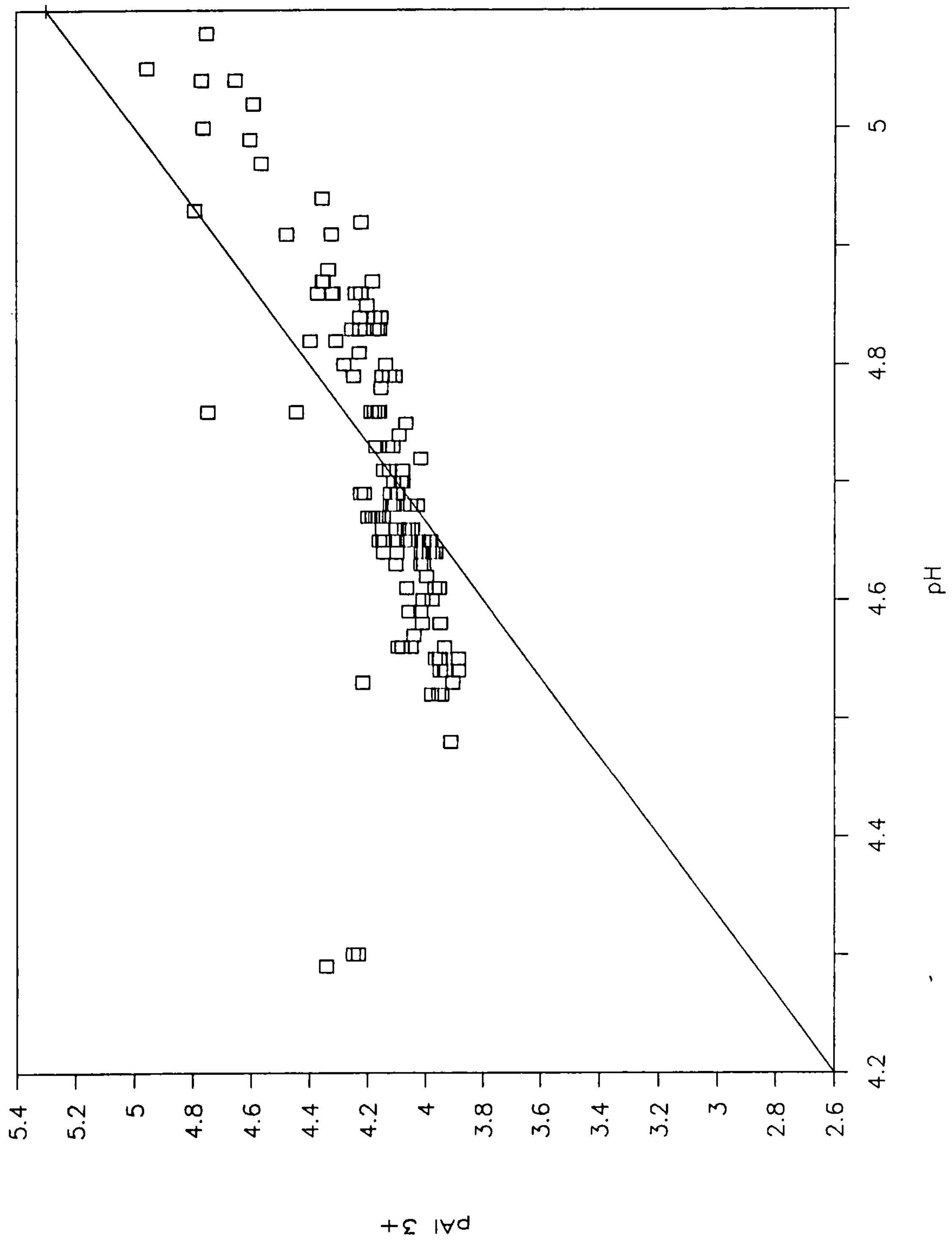

DELTA Al / DELTA HYDROGEN ION
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
2
10
18
26
34
42
Time in days
□ Core 1
+ Core 2
◇ Core 3

gradually approached 1 indicating Al mobilization was totally responsible for H^+ neutralization. In cores 1 and 2, $\Delta Al/\Delta H^+$ values less than 1 were likely due to H^+ utilization by reactions not involving Al mobilization such as congruent dissolution (Table 1.2, equation 1.4), cation exchange (Table 1.2, equation 1.6), and precipitation of humic acids (Table 1.2, equation 1.7). Since significant amounts of total organic carbon were lost from the influent water, it is possible that a certain amount of H^+ was consumed by the precipitation of organic humus from the seepage water. In core 1 and core 2 the relative contribution of these reactions to H^+ neutralization during the early period of the experiment was significantly higher, hence the $\Delta Al/\Delta H^+$ ratio was lower, whereas the ratio of nearly 1 near the end of the study indicates that by this period most of the H^+ was neutralized via the mobilization of Al. In core 3, this ratio decreased gradually for 21 days before increasing through the end of the experiment. Another supporting observation that significant amounts of H^+ were neutralized with the precipitation of organic humus was the differences among the temporal ratios in the cores could be well correlated with the differences in the organic budgeting values of the cores. The temporal ratio between ΔAl and ΔH^+ was lowest in core 2, which had the highest amount of organic matter, and the temporal ratio was highest in core 3, which had the least amount of organic matter.

A strong correlation between the pH and labile aluminum was observed, consistent with the findings of many other workers in dilute acidic systems (Driscoll, 1980; Johnson et al., 1981). The distribution of -log of total Al (pAl_T) as a function of pH is shown in the Figure 4.2. Higher total Al concentrations were associated with lower pH values which is consistent with the pH dependent solubility of Al (Stumm and Morgan, 1981). Many researchers have reported that the concentrations of inorganically complexed and free Al in acidic surface waters exhibit apparent equilibrium with a form of gibbsite (May et al., 1979; Johnson et al., 1981; Driscoll and Schafran, 1984). Effluent samples with pH values between 4.7 and 5.1 appeared (Figure 4.3) to be slightly oversaturated with respect to the gibbsite mineral phase, while overflows with pH values less than 4.7 appeared to be undersaturated with respect to the gibbsite mineral phase. Effluent samples with low pH values and undersaturated with respect to gibbsite could possibly be due to the slow dissolution kinetics at these pH values. This explanation has been proposed to explain the same relationship observed in natural systems (Hooper and Schoonmaker, 1986). This kind of trend has also been reported for Dart's lake (Driscoll and Schafran, 1984).

Fluoride is a strong complexing ligand with Al (Johnson et. al., 1981) and following acidification fluoride released from the sediments in this study was predominantly


pAl
4.4
4.3
4.2
4.1
4
3.9
3.8
3.7
pH
4.2
4.4
4.6
4.8
5


pAl 3+
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4
3.2
3
2.8
2.6
pH
4.2
4.4
4.6
4.8
5

bound to Al as an AlF^{2+} complex. Concentrations of fluoride in the overflows peaked within eight days of acidification and then decreased to relatively constant concentrations in the overflow from each core. Because Al concentrations remained elevated until the end of the study a substantial decrease in the proportion and absolute concentration of Al complexed by F occurred. The complexation of Al^{+3} by F has been shown to mitigate the toxicity of Al to aquatic biota (Baker and Schofield, 1982). Therefore, the release of fluoride can be viewed as a mitigating factor to Al toxicity. However for these sediments, the "mitigation potential" of F following acidification was temporally variant and was greatest for the short period following acidification.

Elevated Al concentrations observed at low pH values are consistent with the pH dependent solubility of Al and has similarly been viewed in many natural systems (Nordstrum and Ball, 1986; Driscoll et. al., 1984). According to a laboratory study (Sprauge, 1964) the toxic level of Al to various fish population was 40 ug/l. Effluent concentrations of Al in my study exceeded 1830 ug/l which is 45 x higher than the toxic levels. Hence, acidic waters that pass through these sediments would be expected to negatively impact fish and other aquatic organisms in the lake.

Lead and manganese concentrations in seepage water were also influenced by seepage through the sediment cores.

Previous research (Henrickson and Wright, 1978; Dickson, 1980; Fjerdingstad and Nilssen, 1983) has shown that elevated Pb concentrations occur in lakes that have low pH values. A similar relationship between total Pb and pH values was observed in my study suggesting that low pH values in groundwater could mobilize Pb from these sediments. In addition, unlike the other metals observed in this study, Pb showed an episodic release from core 2 with the introduction of lower pH value waters. In core 2 until the day of acidification, significant amounts of Pb were removed from the seepage water. Retention of Pb was likely a result of exchange reactions with sediment organics in the core or due to coprecipitation with Al. White (1985) observed that the removal of Pb from the water column in Dart's lake was related to the precipitation of Al. Aluminum precipitation from solution in the sediment porewaters may similarly remove Pb from groundwater. At low pH values the release of Pb could be from sediment organics through organic ligand protonation reactions (Schnitzer and Khan, 1972) and/or from oxide mineral surfaces through dissolution or surface-site protonation reactions (James and Healy, 1972; Schindler et al., 1980b; Schindler, 1981; Stumm and Morgan, 1981).

Sprague (1964) reported that a concentration of 2.07 ug Pb/l in solution caused complete reproductive failure in American Flag fish and death of fish fry occurred within 6 days of exposure. It has also been reported that adults show reduction in egg hatchability at these low concentrations of Pb (Hutchinson and Sprague, 1982). Effluent Pb concentrations were three times greater than the toxic levels for fish reported in these studies. Aqua (uncomplexed) forms of trace metals have been reported as more toxic to aquatic organisms than complexed forms (Leivestad et al., 1976; Schofield, 1976b; Stumm and Morgan, 1981). In the presence of complexing ligands, such as humic acids, the toxicity of Pb can decrease because the aqua concentration of the metal is lowered due to complexation with available ligands. Lead concentrations in the effluents of core 2 showed that both organically bound and inorganic Pb were approximately 50% each before as well as after influent acidification periods. This same core acted as a sink for both organically bound and inorganic Pb before acidification and a source after acidification. Following acidification both fractions of Pb were released from the sediment. Organically bound Pb mobilization is believed to be due to organic ligand exchange reactions (Schnitzer and Khan, 1972). However other studies (Fjerdingstad and Nilssen, 1983) have emphasized that as the pH of the water decreases, humic acid concentration decreases resulting in an increase in the free form (not complexed with organics) of trace metals at toxic levels. Although TOC concentrations were substantially reduced in the effluents, removal of Pb was not associated with TOC retention.

Mn is a potentially toxic trace metal whose mobility can be influenced by solution pH values and also by the redox state of the water. Results from a computer generated chemical equilibrium model (Hoffmann and Eisenreich, 1981) have shown that pH is the primary variable controlling Mn chemistry in oxic environments. However when oxygen is depleted, Mn solubilization as Mn^{2+} readily occurs through Mn reduction (Hem, 1978; Stumm and Morgan, 1981). Many researchers (Hem, 1978; Hem, 1979; Swanson and Johnson, 1980; Stumm and Morgan, 1981; Ehrlich, 1981) emphasized that Mn is one of the group of elements involved in redox reactions in trace metal cycling and whose redox processes may indirectly affect the fate of Al, Pb, Zn, Cd, Cu, Co and Ni. In this study the probability of Mn release to effluents due to Mn reduction reactions was minimized due to the conditions of simulation.

Similar to Pb, substantial mobilization of Mn occurred following acidification. The Mn release was similar to Pb in that a substantial increase after acidification was followed by a rapid decrease. Organic matter, due to its polyelectrolytic week acid character, can form strong complexes with metal ions (Schnitzer and Khan, 1972; Gamble et al., 1980). Since there was an abundance of organic matter in the influent solutions, much of the Mn may have been complexed with organic matter. Exponential release of Mn into the effluent following acidification, was similar to experimental observations of Schnitzer and Khan (1972) which they suggested was due to organic ligand protonation reactions.

In core 2, where substantial amounts of Mn were released, the organically bound sediment Mn fraction was estimated to be 74% of total sediment Mn concentrations, whereas the hydrous oxide Mn fraction was below the detection limit. Since most of the Mn was apparently bound to sediment organics, it can be hypothesized that following acidification, Mn release took place by the following model reaction:

$$R\text{-}Mn + nH^{+} \text{-----}> R\text{-}H_{n} + Mn^{n+}$$

where: R-Mn is the Mn-organic complex in the sediment

Mn^{n+} is free form in solution,

$R\text{-}H_n$ is the H^+ organic complex in the sediment

With the input of hydrogen ions, the Mn bound to organic ligands as a co-ordinate complex, was released as the organic complex became protonated. This reaction is possible based on the chemical kinetic constraints that covalent compounds are more stable than the co-ordinate complexes. This reaction reached equilibrium after an initial peak in Mn concentration and no further release of Mn occurred after this period because of the lack of available Mn. The rate and magnitude of transformation from co-ordination complex to the stable covalent compound depends on the strength of the acid when the metal is bound to sediment organics. This mechanism is consistent with the lower release of Mn at 4.1 influent pH (in core 1), and higher release at 3.9 pH (in core 2).

Hydrogen ion concentration acts as a master variable in controlling metal solubility (Stumm and Morgan, 1981). In Adirondack lakes Schofield (1976a) has suggested that manganite ($MnOOH_{(s)}$) is the mineral that controls Mn chemistry. Saturation index (SI) values for manganese concentrations with manganite as a reference mineral were calculated with the following equilibrium relationship:

$$MnOOH + 3H^+ + e^- \text{--->} Mn^{2+} + 2H_2O$$

where K_{so} is equilibrium constant

$\log K_{so} = 25.27$ (Lindsay, 1979)

since $SI = \log (Q_p/K_p)$

where: $Q_p = \{Mn^{2+}\}/\{H^+\}^3 \{e\}$

then $SI = \log Mn^{2+} + 3\ pH + pE - 25.27$

where: SI = 0, solution is in equilibrium

= -, solution is undersaturated

= +, solution is oversaturated

Saturation indices were calculated for influent and selected effluents using data derived from the MINTEC chemical equilibrium model and the above equation and determined to be highly negative (not shown). The release or retention of Mn^{2+} if controlled by manganite should be reflected in the SI values. Net loss from solution to sediment should occur when the SI values are positive and net release of Mn^{2+} should occur when SI values are negative. Since SI values for both influent and effluents were highly negative these values indicate the aqueous system was undersaturated with respect to manganite. These undersaturated conditions were consistent with White's (1984) SI values for Dart's Lake during snow melt period, when pH values declined markedly.

5.0 CONCLUSIONS

Assimilation of H^+ by lake sediments decreased over time when subjected to seepage with acidic waters. The hydrogen ion acted as the master variable in controlling metal mobilities and changes in effluent acid/base chemistry. Under constant seepage, the extent of neutralization of H^+ depended mainly on the extent of availability of exchangeable basic cations and the mobilization of metals. Presence of organic matter in the sediment also appeared to contribute to neutralization of H^+ as observed. As evidenced by these results, silicious sediments of Dart's Lake are vulnerable to acidic deposition because mineral weathering reactions are much slower than the rate of groundwater transport through these sediments.

Acidification represented a prominant role in Al mobilization which was the predominant H^+ neutralization reaction. Acidification of influent solutions increased Al concentrations in the overflow solutions 45x higher than the toxic levels reported for fish. Over 75% of the organically bound Al was lost in to the sediment during seepage and over 90% of the total Al mobilized was inorganic Al which is a more toxic form than organically complexed Al.

Acidification caused fluoride concentrations to increase and peak dramatically in the effluent solutions. Most of the F released was complexed with Al, forming AlF^{2+} which represented >99% of the total Al-F species. Following acidification, Al^{3+} in effluent solutions was >4x higher than the influent concentrations and several times higher than the toxic levels reported for fish. Unlike other metals, Al release increased through the end of the study, which showed that Al mobilization was increasing as a source of H^+ neutralization as the base cation concentration decreased.

Unlike other metals, Fe was substantially removed from the influent solutions with over 99% of the influent Fe lost to the sediment. Acidification showed no apparent impact on Fe mobilization or removal.

Acidification of influent solutions directly controlled Pb release from the sediment. Prior to acidification the sediment acted as a sink for both organically bound and inorganic Pb. Following acidification Pb concentrations increased dramatically (over 6x) which was 3x more than the toxic level that has been reported for fish. Acidification mobilized both organically bound and inorganic Pb maintaining approximately equal ratios.

Sediments acted as a potential sink for organic matter with removal occuring most likely by adsorption or by mechanical straining. Sediment microbial activity could also have consumed influent organic matter. However, the organic matter in solution was likely humic in origin and resistant to microbial consumption. Therefore, given the short contact time and origin of organic material, removal of the majority of the organic matter was likely non-microbial in nature. Organic matter may have an important role in metal mobilization and removal as evidenced by changes in organically bound Al and Pb and removal of Fe because organic matter participated in the H^+ neutralization. Calcium contributed >79% of the total C_B charge and increased in effluent solutions following acidification. However, Ca^{2+} mobilization was a minor contributor to H^+ neutralization by the end of the study. Following acidification, no sediment release of Na, K, or Mg occurred.

Sediment metal concentrations in three closely spaced cores revealed that considerable spatial variation can occur over short distances in near-shore sediments. Sediment-metal concentrations varied drastically among the cores, however, the proportion of each metal fraction among cores was similar. The exchangeable fraction of Al and Pb was negligible, whereas exchangeable Mn was 25% of the total Mn metal concentrations. Direct correlation between organically bound metal fractions and organic matter was observed. Except for Mn, the hydrous oxide metal (Al, Fe, Pb) fraction in each core was the predominant fraction of the total extractable metal thus reactions involving hydrous oxide metals are likely to substantially influence the chemistry of groundwater passing through these sediments.

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