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Preliminary Analysis of In Situ Bioremediation in Hamilton Harbour

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Preliminary Analysis of In Situ Bioremediation in Hamilton Harbour

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Abstract

Approximately 14 tonnes of calcium nitrate was injected into sediments of Hamilton Harbour. Three areas in total of about 1.8 ha were treated. Initial results indicate rapid oxidation of about 80% of the hydrogen sulphide (293 µg/L to 53 µg/L at deep basin). Oxidation resulted in precipitation of about 98% of the porewater iron in the surface 15 cm of sediment but the concentration of most trace metals like zinc and lead were unchanged. The nitrate treatment did not significantly affect the concentration of acid volatile sulphides. In the Dofasco boatslip biodegradation of organic contaminants varied from 79% for low molecular weight compounds (BTXs), to 25% for petroleum hydrocarbons, and 15% for polynuclear aromatic hydrocarbons. These rates of biodegradation are consistent with many studies; more time is required for bacteria to metabolize the organic wastes.

Management Perspective

Pilot-scale in place sediment treatment was evaluated in Hamilton Harbour. The oxidation of the sediments by nitrate is primarily a microbial process; the sediment toxicity does not appear to inhibit the bacteria. The oxidation of the sediments was detected by a 80% removal of the most reactive reduced sulphur compound hydrogen sulphide. The microbes are then able to biodegrade most of the smaller toxic organic compounds. The larger organic compounds were only partially decomposed (15%). The treatment is not finished. More time is required for the microbes to biodegrade the larger organic contaminants. The sediment treatment equipment performed very well, and the worst case scenario is that more oxidant is required and the treatment would have to be repeated. The cost of in place sediment treatment is 50-200 times less than dredging and subsequent treatment; thus, either the sediments could be retreated or the treatment could be redesigned to accelerate the biodegradation process. Ideally, we would retreat one of the three sites and monitor the biodegradation of the other two untreated sites.

The intent of this project is to evaluate in situ bioremediation of organic contaminants. In oxic environments, coal tar is biodegradable. Low molecular weight compounds like naphthalene biodegrade quickly, i.e., half lives as short as two weeks (Lee and Ward 1985, Heitkamp et al. 1987, Heitkamp and Cerniglia 1987, Keck et al. 1989, Howard 1991), but without the addition of an oxidant, the coal tar would persist. A number of laboratory studies have shown that nitrate addition can stimulate the biodegradation of polynuclear aromatic hydrocarbons (PAHs) (Al-Bashir et al. 1990, Mihelcic and Luthy 1991, McFarland and Sims 1991, Murphy et al. 1992). Lee et al. (1988) and Nowicki (1991) review the use of nitrate in treating PAH contaminated groundwater. Successful in situ treatment would reduce the toxicity of the Hamilton Harbour hotspots to that of the main harbour. Presently the hotspots can act as point source discharges of PAHs when ships or storms resuspend the sediments.

Sediments in the hotspots are acutely toxic to Hexagenia limbata, Daphnia magna, Escherichia coli, Photobacterium phosphoreum, Hyalella azteca, Chironomus riparius, and Tubifex tubifex (Hamilton Harbour Stage 1 Remedial Action Plan, 1992). Some sublethal effects on wildlife appear obvious. Seventy-two percent of the barbels of brown bullheads in Hamilton Harbour were reduced to short stubby projections (Hamilton Harbour Stage 1 Remedial Action Plan, 1992). Chemical burns to technicians by these sediments confirms that Hamilton Harbour sediments can react with flesh.

The most common concern with PAHs is their potential to induce cancer in wildlife at concentrations below the acute toxicity concentration. A main RAP/Stakeholder goal for Hamilton Harbour is a healthy fishery (Rodgers et al. 1988). This goal can not be achieved without treatment of these carcinogenic substances. The concentration of PAHs in the Hamilton

Harbour hotspots (>800 µg/g, Murphy et al. 1990) is higher than those reported by Fabacher et al. (1988) for several sites on the Great Lakes and is higher than the PAH concentration reported by Shiaris and Jambard-Sweet (1986) for contaminated estuaries of the world. Sediments from other sites with lower PAH concentrations than the Hamilton Harbour hotspots have been linked to the induction of the fish lesions and tumours; Elizabeth River Norvolk, Virginia (Hargis et al. 1984), Eagle Harbor, Washington (Myers et al. 1987, Swartz et al. 1989), Black River, Ohio (Fabacher et al. 1988), and Vancouver Harbour, British Columbia (Goyette et al. 1988, Brand and Goyette 1989, Burrard Inlet Environmental Improvements 1990). The concentration of papillomas on white suckers from Hamilton Harbour is high (35%, Hamilton Harbour Stage 1 RAP, 1992). Within 14 months after exposure of the yolk sacs to sediment extracts from outside of a Hamilton Harbour hotspot, 12% of the white sucker fry developed tumours (Metcalfe et al. 1988). Neoplasms in fish of Hamilton Harbour are likely caused by PAHs.

2. METHODS

2.1 Site

Hamilton Harbour (43°14'N, 79°51'W) is located at the western end of Lake Ontario. It is roughly triangular in shape with an east-west length of 8 km and a north-south width of 5 km (Fig. 1). It has a mean depth of 13 m, a maximum depth of 24 m, and an area of approximately 2150 ha. The Dofasco Boatslip is about 1 km long and 100 m wide. Dredging and ship traffic have removed most of the contaminated sediments from the slip. However, the south-west corner of the slip is still badly contaminated with coal tar. Most of the contamination is historical and the steel mill has implemented advanced waste treatment.

2.2 The Sediment Treatment

The Department of Fisheries and Oceans' vessel, the Gander, was used to support and transport the sediment injection equipment. This vessel was powered by twin Volvo four cylinder diesel motors with two propellers. The boat was 8.2 m long, 3.0 m wide, had a draft of 0.4 m and it could be loaded with about 6 tonnes of calcium nitrate and gear. The calcium nitrate was dissolved in lake water to form a 60% solution. It was retained in a large tank on the Gander for pumping into an 8 m wide injection boom. The details are being submitted for a patent.

About 5000 m^2 of sediments at the south west corner of the Dofasco Boatslip were treated in 1992. On July 28, and Sept. 15-17, 3.6 tonnes and 3.89 tonnes respectively, of farm grade calcium nitrate [$5Ca(NO_3)_2.NH_4NO_3.10H_2O$] were injected into the sediments. Also 4.5 tonnes of calcium nitrate were injected near Randle Reef (Stelco Boatslip) in about 10,000 m^2 of sediment July 15-17. A small area in the deep basin of Hamilton Harbour (21 m deep, 3,200 m^2), was treated with 0.38 tonnes and 2.16 tonnes of calcium nitrate on May 20 and July 30, respectively.

2.3 Sampling

Surface sediments (0-15 cm) were collected with either a Shipek grab sampler, or a modified KB corer (Mawhinney 1987, Mudroch and MacKnight 1991). Samples were returned to NWRI, subdivided, and either placed in a fridge or freezer within 24 h. Control reference sediments consisted of samples collected from the treatment zone before treatment and samples

collected from untreated areas next to treatment sites collected simultaneous with those from the treated zone.

2.3.1 Peepers

Diffusion chambers (Mudroch and MacKnight 1991) were placed into the treated sediments of the deep basin treatment 20 weeks after the first treatment and 11 weeks after the second treatment and left to equilibrate for three weeks. The porewater was sampled within minutes of retrieval and acidified. The metal content of samples was analysed by ICP-AES.

2.4 Chemical Analyses

The pH and redox of samples were measured with meters. Total sulphur was analyzed by a furnace method by the Waste Water Centre (WTC).

2.4.1 Air Monitoring

Battery powered air sampling pumps were supplied by Dofasco to monitor gases emitted to the air from disturbance of the sediment bottom. Air was pumped through tygon tubing mounted near the worker's face into a charcoal collection tube. The tube was then analyzed in a gas chromatograph (GC) for benzene, toluene, and xylene (BTXs). The concentrations of BTXs were divided by the exposure time to determine exposure levels of the staff.

Hydrogen sulphide concentrations were monitored with a Drager datalogger unit. The datalogger digitally recorded ambient hydrogen sulphide levels and time weighted exposure levels. If a concentration of 10 ppm had been reached, an alarm would have been activated.

2.4.2 Purge and Trap Analysis for Volatile Organic Compounds

Volatile organic compounds were measured by GC/MS in the Waste Water Treatment Centre (WTC) laboratory. A sample of 0.5 - 1.0 gram wet sediment was weighed and diluted with 5.0 mL of distilled water. The internal standards and surrogates were added. This volume was heated to 40^{0}C and purged for approximately 10 minutes with helium gas. The sample was trapped on a Tenax-charcoal trap, run through a DB624 30 m column and analyzed on a GC/MS.

2.4.3 Total Petroleum Hydrocarbons

A 20 g sample of wet sediment was extracted with 80 mL dichloromethane for 5 hours on a shaker table. The extract was first dried by filtration through sodium sulphate and then concentrated by evaporation through a Snyder column. A GC was used to analyze the concentrate.

2.4.4 PAHs

Liquid-liquid extraction was used to prepare sediment samples containing a high percentage of moisture (Dofasco boatslip). A 20 mL sediment sample was diluted with 500 mL of distilled water and extracted with dichloromethane. A Soxhlet extraction was used for sediment samples with relatively lower moisture contents (Stelco boatslip). The sample was spiked with surrogate PAHs (6 deuterium isotopes) and extracted in a Soxhlet apparatus with an acetone-hexane mixture. The organic extract was base-partitioned. The aqueous medium was back-extracted with hexane and the organic fractions were combined. The combined extract was dried through sodium sulphate and concentrated. A GC/MS was used to analyze the concentrates.

Recovery of the six deuterium labelled PAHs varied from 66% to 100% (mean 77%). No efficiency corrections were made to the GC/MS analyses.

2.4.5 Acid Volatile Sulphide Analysis

Sediment samples for acid volatile sulphide (AVS) analyses were either processed the day of sample collection or were frozen and processed within two weeks. Wet sediment (1.0 mL) was added to 5 mL of N_2-purged distilled water in a 15x125 mm test tube fitted with a two-hole rubber stopper containing a 6 mm o.d. gas delivery tube going to the bottom of the test tube, an outlet tube connected to the trap solution, and a syringe needle. The hydrogen sulphide trap solution was prepared by adding 3.5 mL of sulphide anti-oxidant buffer (SAOB) stock solution (2 M NaOH, 0.1 M ascorbic acid and 0.1 M EDTA) (Arowolo and Cresser 1991) to 10.0 mL of de-aerated distilled water. The apparatus was purged for about 5 min. with oxygen-free nitrogen gas after which 2.5 mL of 6 M HCl was slowly added through a syringe needle inserted through the rubber stopper. Purging was continued for an additional hour at a flow rate of about 20 mL/min. To determine the sulphide concentration in the trap solution, the emf was measured using a sulphide ion selective electrode (ISE) (Orion 94-16), a double junction reference electrode (Orion 90-02), and a Corning Model 240 pH meter. Standard sulphide ion solutions, prepared in SAOB solution over the range of 10^{-1} to 10^{-5} M from 0.5 M Na_2S stock solution (actual concentration was determined iodometrically), were used to prepare the calibration curve.

2.4.6 Free Hydrogen Sulphide

The free or dissolved hydrogen sulphide in the sediment was determined similarly to the AVS. Wet sediment (30 mL) was added to 70 mL de-aerated distilled water in a 125 mL polyethylene bottle. Two holes were made in the cap and a gas delivery tube and an outlet tube were sealed through the holes using hot melt glue. The sediment was kept in suspension using a magnetic stirrer for the duration of the purging process (1 hour). Hydrogen sulphide in the nitrogen stream was trapped in SAOB solution (3.5 mL stock SAOB and 10.0 mL de-aerated water) and the resulting sulphide ion concentration was measured with the ISE.

2.4.7 Ion Chromatograph Analysis of Nitrate and Sulphate

Sediment samples were weighed into 50 mL polypropylene test tubes and deionized distilled water was added on an equal wet weight to volume basis. The tubes were capped, shook vigorously and placed on an end over end shaker for two hours. At this time, the tubes were centrifuged at 4000 rpm for 25 minutes. The supernatant was collected and filtered through a GF/F filter. Samples were spiked with sodium carbonate and sodium bicarbonate so that the final concentration of these salts was 0.03%. They were stored at 4°C for up to 48 h until analysed on the Dionex model 2010i ion chromatograph.

3. RESULTS

The sediments of the Dofasco boatslip were black with a strong hydrocarbon odour. The extremely high concentration of acid volatile sulphide (AVS, Fig. 2) confirmed redox measurements that these sediments were highly reduced (redox <-200). Some samples contained

as much as 2.0% AVS (dry weight) and the mean concentration in the boatslip was 0.8%. These AVS concentrations are unusually high relative to other sites with anoxic sediments (Fig. 2). The concentration of total sulphur in the Dofasco boatslip is also higher than the two other areas of the harbour studied (Table 1). It seems that historic discharges of sulphur were less diluted in the Dofasco boatslip. The nitrate treatment had no effect upon the concentration of AVS (data not shown); much of the AVS is relatively stable to nitrate treatment. However, the concentration of free H_2S was significantly reduced by the nitrate treatment (Table 2). The concentration of H_2S in the pretreatment sediments (mean 293 µg/L) would be very toxic to many organisms; the mean concentration of hydrogen sulphide in the posttreatment samples (53 µg/L) would not be toxic to Hexagenia (Oseid and Smith 1975). Further discussion of toxicity is premature. Other toxins are present; the focus of the oxidation of hydrogen sulphide is the signal that microbes now have an oxic environment to biodegrade organic contaminants.

Table 1 Total Sulphur Content (mg/g dry weight)

	Dofasco Boatslip	Deep Basin	Stelco Boatslip
mean	18.07	5.20	3.97
standard deviation	6.87	.80	1.09
number of samples	9	12	12

Table 2 Free H_2S in Deep Basin Sediment (Nov. 25/92)#

Site	H_2S			
	Pretreatment		Posttreatment	
	(µg/g)	(µg/L)	(µg/g)	(µg/L)
S-1	0.44	100	0.21	50
S-2	2.25	490	0.09	20
S-3	1.39	290	0.35	90
Mean	1.36	293	0.22	53

#These results of surface sediments (0-10 cm) are expressed either per unit dry weight (µg/g) or per volume of wet sediments (µg/L). By comparison, species sensitive to H_2S, like Hexagenia limbata have acute (96 h) LC_{50} of 165 µg/L (Oseid and Smith 1975).

3.1 Nitrate Injection

The nitrate injection was most efficient at the Stelco site (Fig. 3) and deep basin site. At these sites, virtually all of the nitrate was injected as a tight peak. However, the injection of nitrate was not as efficient in the Dofasco boatslip. The first two treatments on July 28 were only 20% as efficient and the second set of treatments on Sept. 15-17 were about 50% as efficient as treatments at other sites. The irregular bottom left by earlier dredging caused the sediment injection equipment to bounce. The treatment appeared to flatten the bottom and the

following treatment efficiency increased. Trash like old cables and rope on the sediment surface were not a problem. Occasionally the boat would shutter as we hit something but no damage occurred to the equipment. Similar obstructions can shut down a hydraulic dredge and cause most bucket dredges to lose their contents in the water column.

The nitrate injection resulted in a rapid (within two weeks) increase of redox of about 100 units. The denitrification of the nitrate resulted in the oxidation of reduced sulphur to sulphate. In Figure 4 the peak of sulphate is broader than the nitrate peak presumably because of diffusion, but the dense solution could also be falling through the sediments.

3.2 Metals/Phosphorus

The depth of treatment can be seen best in the porewater data from the deep basin (Fig. 5). The oxidation of the sediments decreased the iron concentration of the porewater from 50 mg/L to 1 mg/L in the top 15 cm of sediments. The precipitation of iron resulted in precipitation of phosphorus from about 1.5 mg/L to 0.5 mg/L (Fig. 6). Manganese also precipitated but the concentration of other metals was unchanged (data not shown).

3.3 Air Quality

The air quality was not changed by the sediment treatment. The four charcoal canisters worn by staff (two on treatment boat and two on boat following treatment boat) detected no measurable concentrations of benzene, xylene, or naphthalene (<0.01 ppm). Two samples did detect about 0.1 ppm of toluene but this was not a significant health concern. Ambient hydrogen

sulphide concentrations rose to 2 ppm but the time weighted average was below 1 ppm; again this was not a concern.

3.4 BTX Biodegradation

The in place treatments in 1992 resulted in excellent biodegradation of several organic compounds (mean of three samples, reductions as follows; toluene 80%, ethylbenzene 86%, m/p-xylene 76%, 3/4-ethyltoluene 89%, and dichloromethane 65%) (Fig. 7). These relatively rapid biodegradation rates are similar to those reported in laboratory studies where nitrate was added to enhance biodegradation (Hutchins 1991).

3.5 TPH Biodegradation

Analysis of three samples indicates that 25% of the petroleum hydrocarbons were biodegraded in the Dofasco boatslip treatment (Fig. 8).

3.6 PAH Biodegradation

The biodegradation of the PAHs (polynuclear aromatic hydrocarbons) is more complex. About 15% (450 µg/g to 383 µg/g, mean of 3 samples) of 15 PAHs were biodegraded and in the process the naphthalene content increased 196% (280 µg/g to 549 µg/g, mean of 3 samples, Fig. 9). The imbalance in the concentration of naphthalene suggests that other higher molecular weight compounds not measured in the standard priority pollutant PAH analysis are decomposing to produce naphthalene. Approximately 50% of the PAHs in coal tar pitch contain more than

seven rings (Enzminger and Ahlert 1987); we are capable of measuring less than 50% of the PAHs.

The sediment samples from near Stelco are not all analyzed but one aspect from an earlier study supports the hypothesis that during biodegradation of PAHs, naphthalene is formed (Fox et al. 1992). The Stelco sediments are more oxic than Dofasco sediments (about 100 redox units higher) with only 20% of the AVS of the Dofasco Boatslip. Since the coal tar cannot be biodegraded in anoxic sediments (Heitkamp and Cerniglia 1987, Mihelcic and Luthy 1988), there should be more PAH biodegradation in the Stelco sediments. Before treatment, the concentration of naphthalene in the Stelco sediments was more than 100 times higher than sediments near Dofasco with a similar concentration of the other 15 priority pollutant PAHs. Since large PAHs produce naphthalene, other small PAHs could also be formed during biodegradation. Rates of biodegradation could be determined more accurately with labelled compounds. With adequate oxidant and time, the PAH biodegradation could be resolved with GC/MS analysis.

3.7 Comparison to Other Biodegradation Treatments

The biodegradation of TPH was greater in a reactor experiment with sediments from the St. Marys River (Fig. 8). About 90% of the petroleum hydrocarbons biodegraded. Sediments from both the Dofasco boatslip and the St. Marys River had similar concentrations of TPH (2%). The incubation with St. Marys River sediments has continued about 6 times longer than the Dofasco treatment and more time is required to evaluate the Dofasco treatment.

The biodegradation of PAHs was much faster in a reactor with sediments from Red Rock (Fig. 8). About 70% of the PAHs biodegraded in 42 days. These sediments are rich in wood

fibre. The greater microbial metabolism may have been responsible for the fast PAH biodegradation. In the wood fibre, the microbes produce cellulases that might also be effective in biodegrading PAHs. However, extrapolation from a site with a low concentration of PAHs (Fox et al. 1993) to Hamilton Harbour is uncertain. It should be possible to enhance the biodegradation in Hamilton Harbour sediments and studies are proceeding to evaluate organic enrichments.

The Dutch have observed rates of PAH biodegradation in landfarming that are consistent with our Hamilton Harbour studies (Fig. 8, Van Dillen 1991, Van Veen and Annokkee 1990). Note that in Figure 8, the biodegradation of petroleum hydrocarbons in our studies is also similar to the Dutch experience. The Dearborn landfarming process for biodegrading PAHs apparently takes nine months to biodegrade more than 90% of the PAHs (Seech and Marvan 1992). The Dearborn process utilizes a large organic amendment and the decay produces heat (+10°C). The in situ treatment will be slower because of temperature limitations (Maliszewska-Kordyback 1991). Larger PAHs take more than several months to biodegrade (Heitkamp and Cerniglia 1987). Our treatment has only had several weeks to react and not much biodegradation is expected to occur in the winter. Although in situ treatment is slower, it merits further evaluation. The expense of landfarming is 50-200 times the cost of in situ treatment, a large land area is required for treatment, dredging is required, and disposal of the treated sediment is necessary.

Soil reclamation using biodegradation has occurred without excavation. The success of these treatments has varied greatly (Lee et al. 1988). Some contaminants cannot be readily biodegraded. In place treatments cannot provide optimal environmental conditions for the microbes to completely biodegrade the organic wastes. However, all sites can contain some

PAHs locked in microsites which are therefore not biodegradable (Van Dillen 1991). Presumably these refractory PAHs would not be toxic. In similar studies it was found that coal dust contains PAHs but relative to coal tar and creosote, it is biologically inert (Alden and Butt 1987). Coal tar appears to be more difficult to bioremediate than petroleum hydrocarbons and future analysis should include carcinogen bioassays to assay the efficiency of treatment.

4. CONCLUSIONS

The in situ treatment was deeper than anticipated. Since nitrate can diffuse into the deeper sediments, some toxins (H_2S, CH_4 etc.) deep in the sediments can diffuse to the surface. The diffusion of nitrate deeper into sediments requires that the treatment dose be increased.

The oxidation of free hydrogen sulphide is rapid, but most of the sulphides appear to be relatively resistant to oxidation by nitrate treatment. It does not appear necessary to oxidize all sulphides to provide an oxic environment for microbes to bioremediate coal tar. Initial results could not detect the solubilization of metals from nitrate oxidation. It seems that precipitation of iron dominated the trace metal solubility.

Many of the smaller molecular weight aromatics biodegrade quickly, whereas, PAHs biodegrade slowly. During the first stage of biodegradation, naphthalene appears to be produced. Confirmation is required with either radioisotopes or more GC/MS analysis next year. In the future, we hope to monitor the long-term effectiveness of the 1992 treatments. If the biodegradation proceeds for a few years, for some sites the existing approach would be successful. However, there are many ways, such as organic enrichment to enhance bacterial metabolic rates and we hope to enhance the biodegradation rates. Also we have rebuilt the

injection boom so that it will bounce less in irregular bottoms and inject nitrate deeper. The efficiency of treatment in the Dofasco boatslip can be improved.

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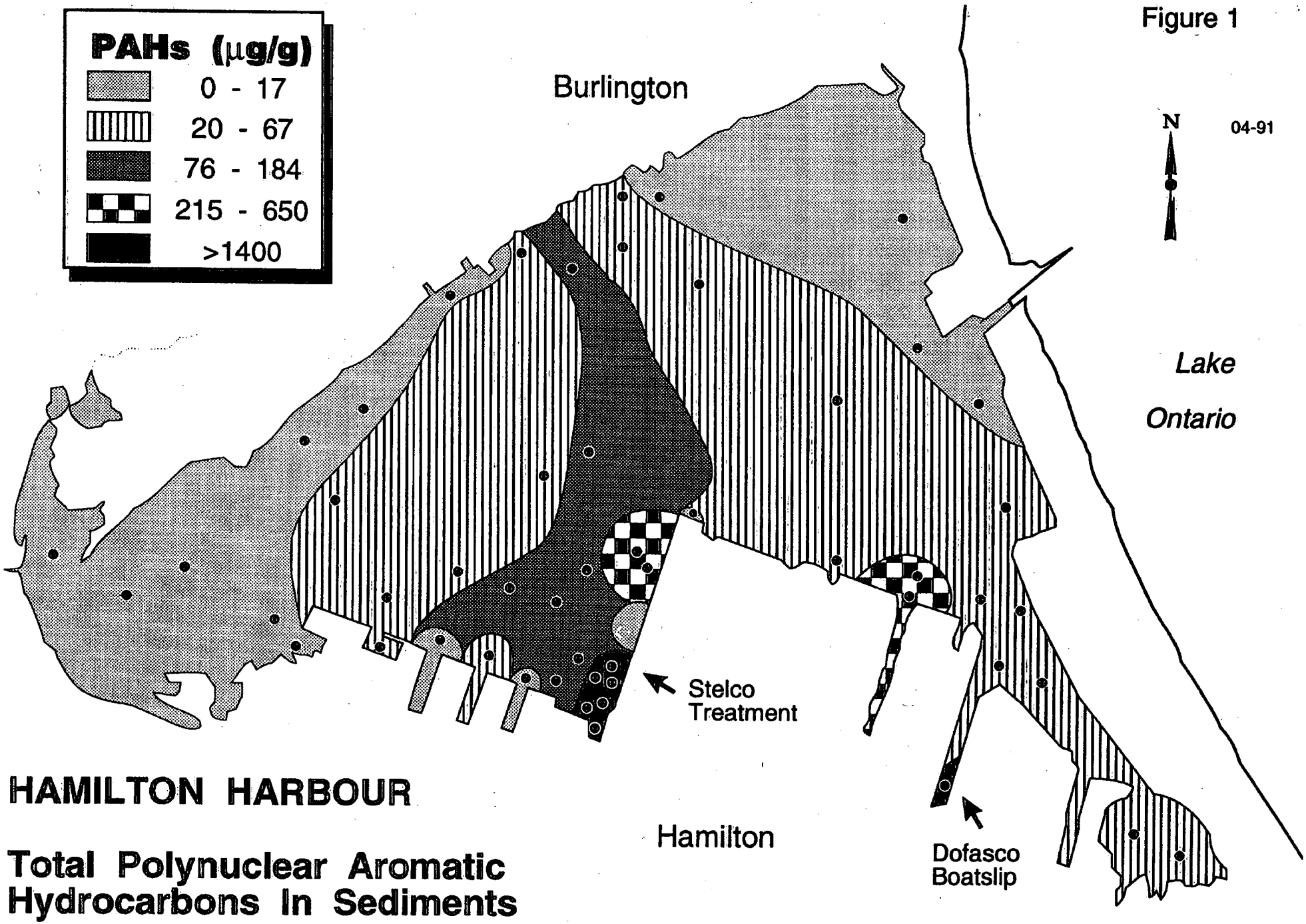
List of Figures

Figure 1



HAMILTON HARBOUR

Total Polynuclear Aromatic Hydrocarbons In Sediments

Acid Volatile Sulphide

Average Amounts in Sediments

Figure 2

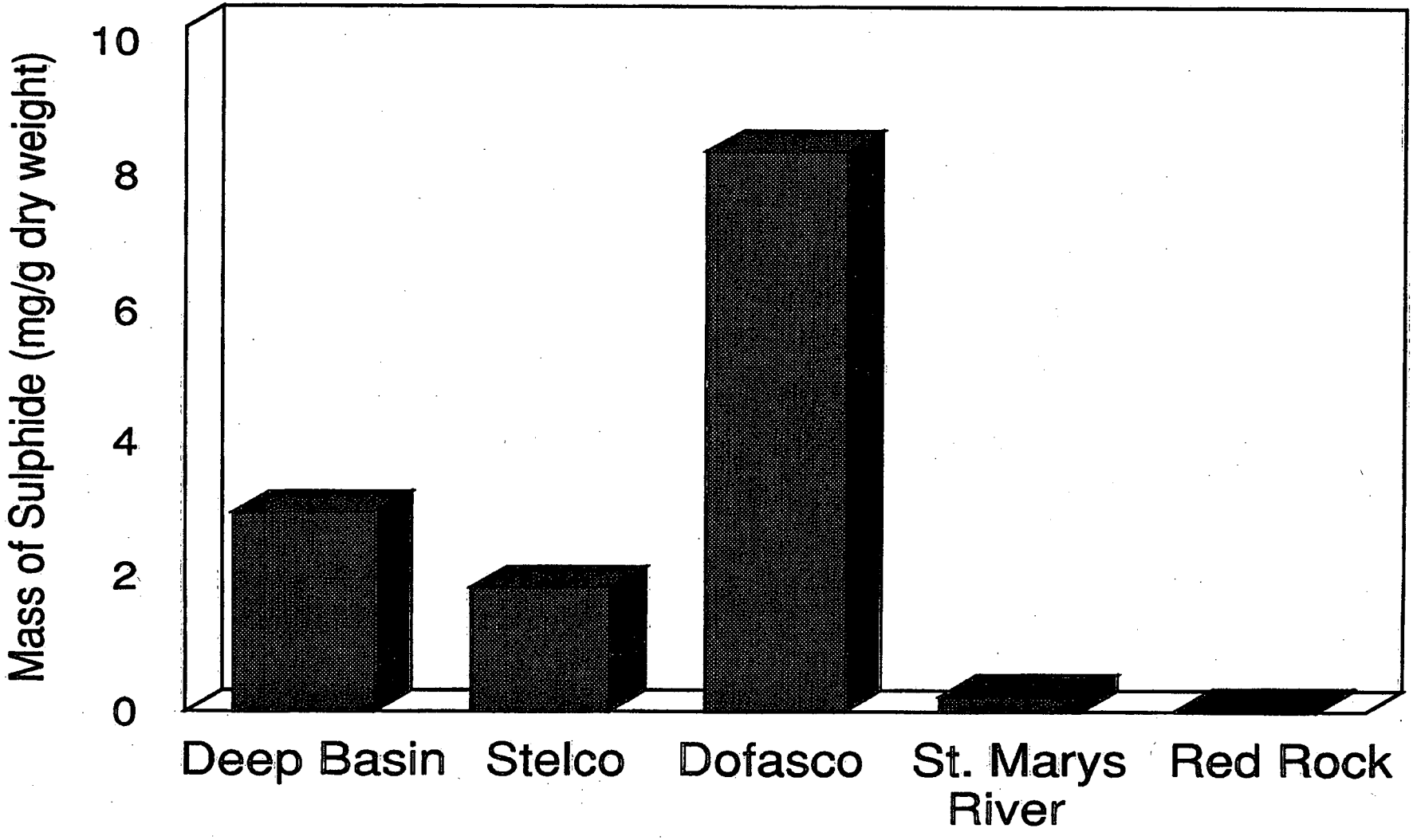


Figure 3

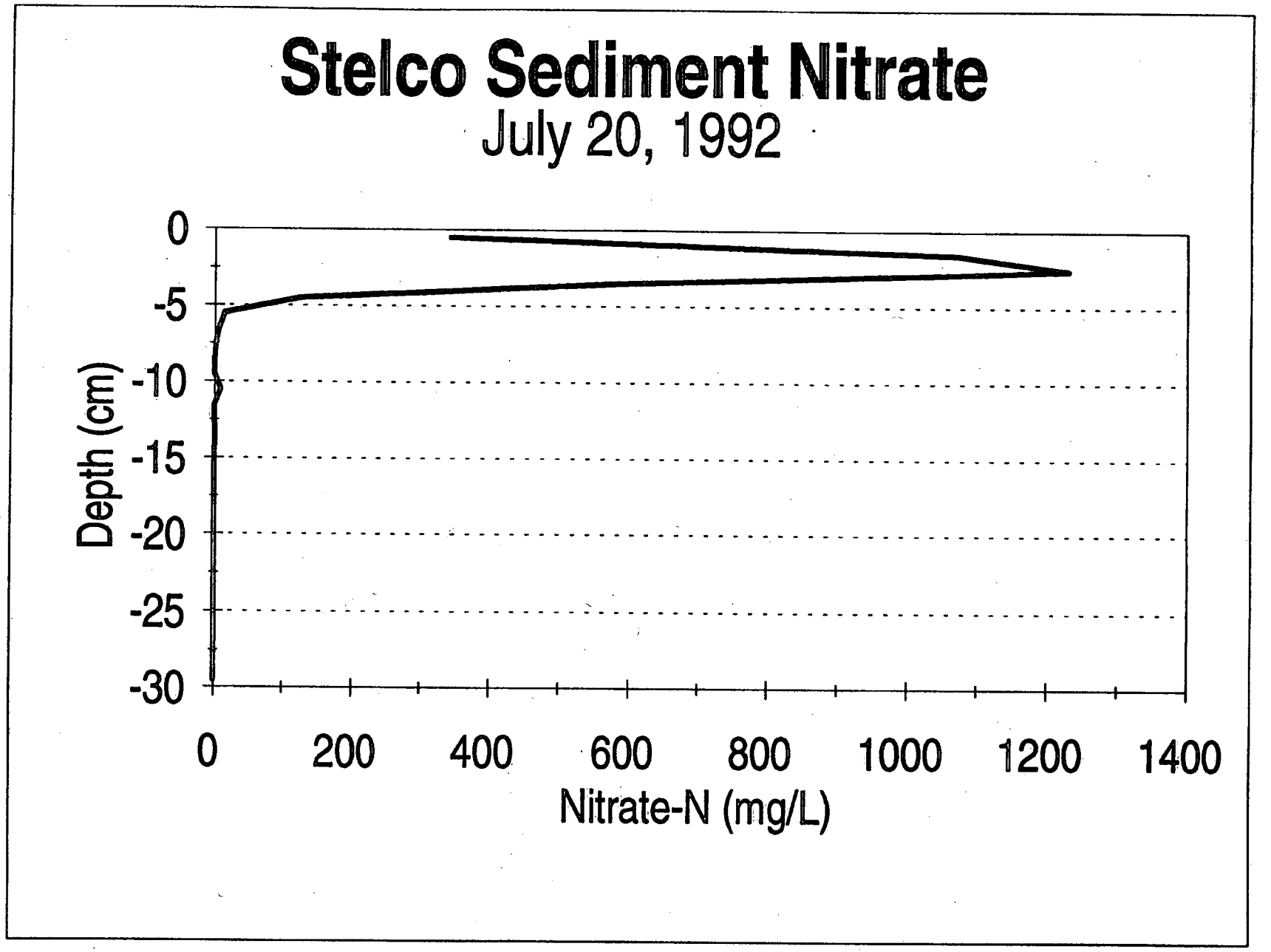

Stelco Sediment Nitrate
July 20, 1992
Depth (cm)
0
-5
-10
-15
-20
-25
-30
0
200
400
600
800
1000
1200
1400
Nitrate-N (mg/L)

Figure 4

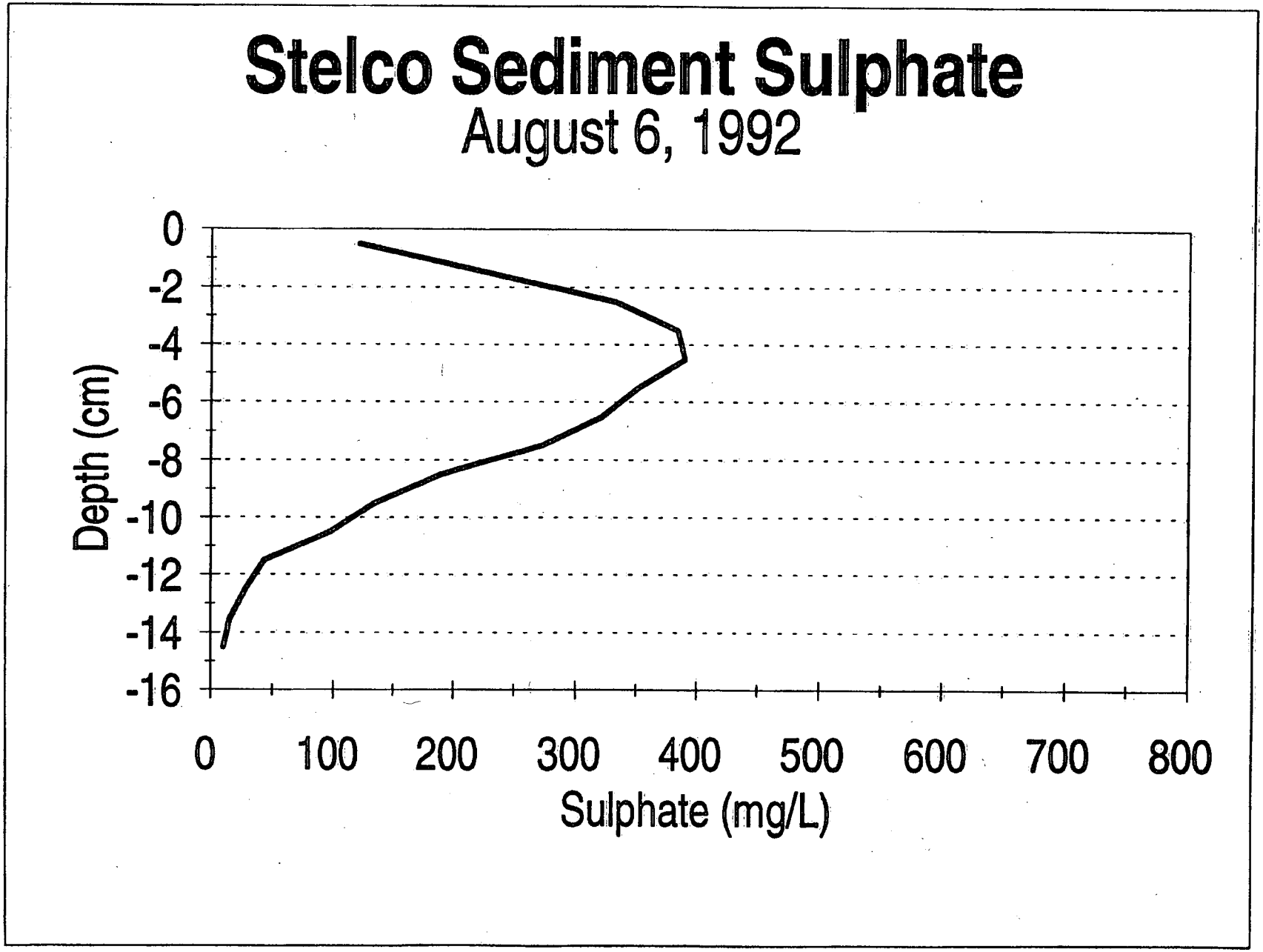

Stelco Sediment Sulphate
August 6, 1992
Depth (cm)
0
-2
-4
-6
-8
-10
-12
-14
-16
0
100
200
300
400
500
600
700
800
Sulphate (mg/L)

Figure 5

Pore Water Iron Concentrations

Deep Basin, Hamilton Harbour 1992

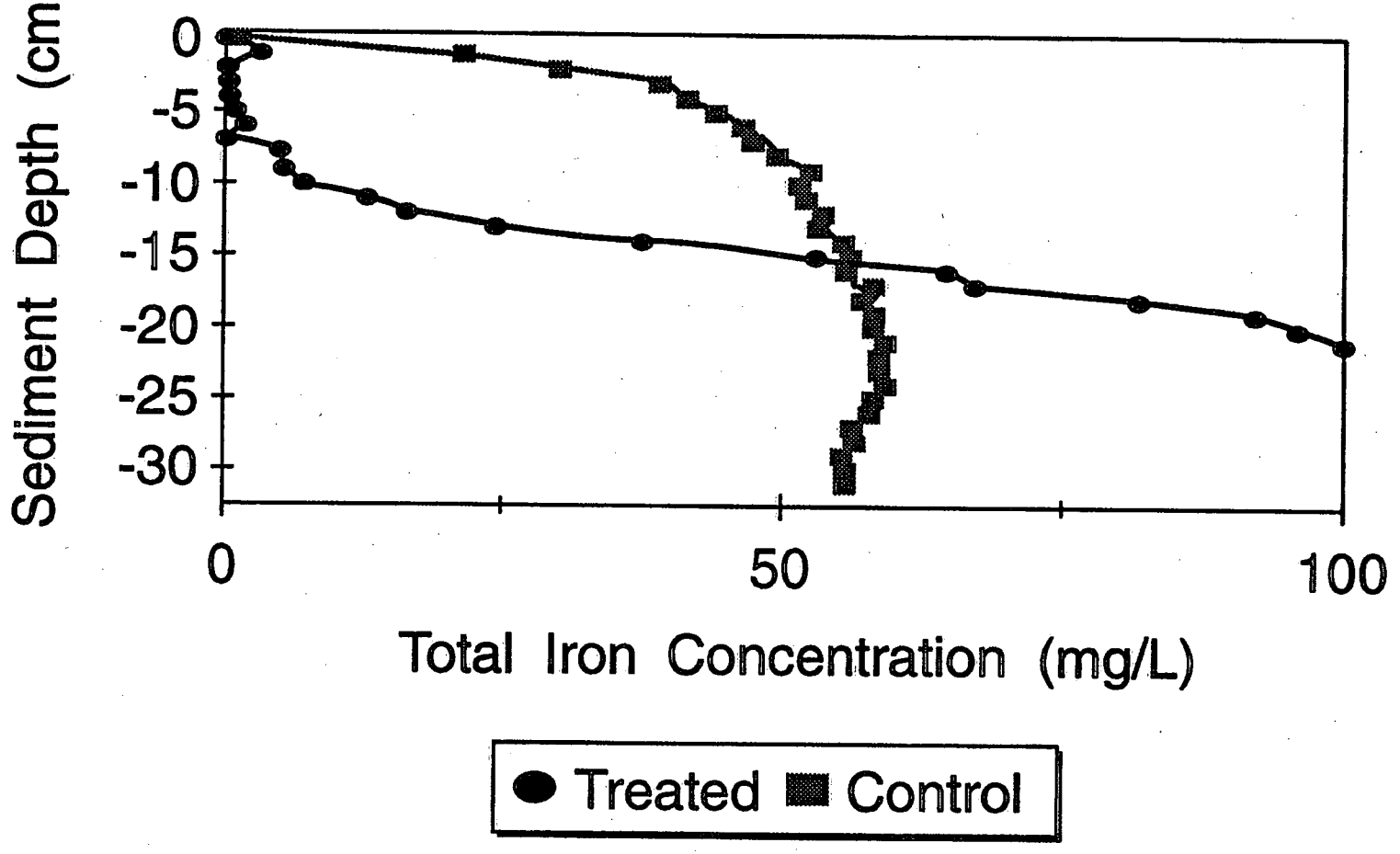


Figure 6

Soluble Reactive Phosphorus

Pore Water, Deep Basin, HH

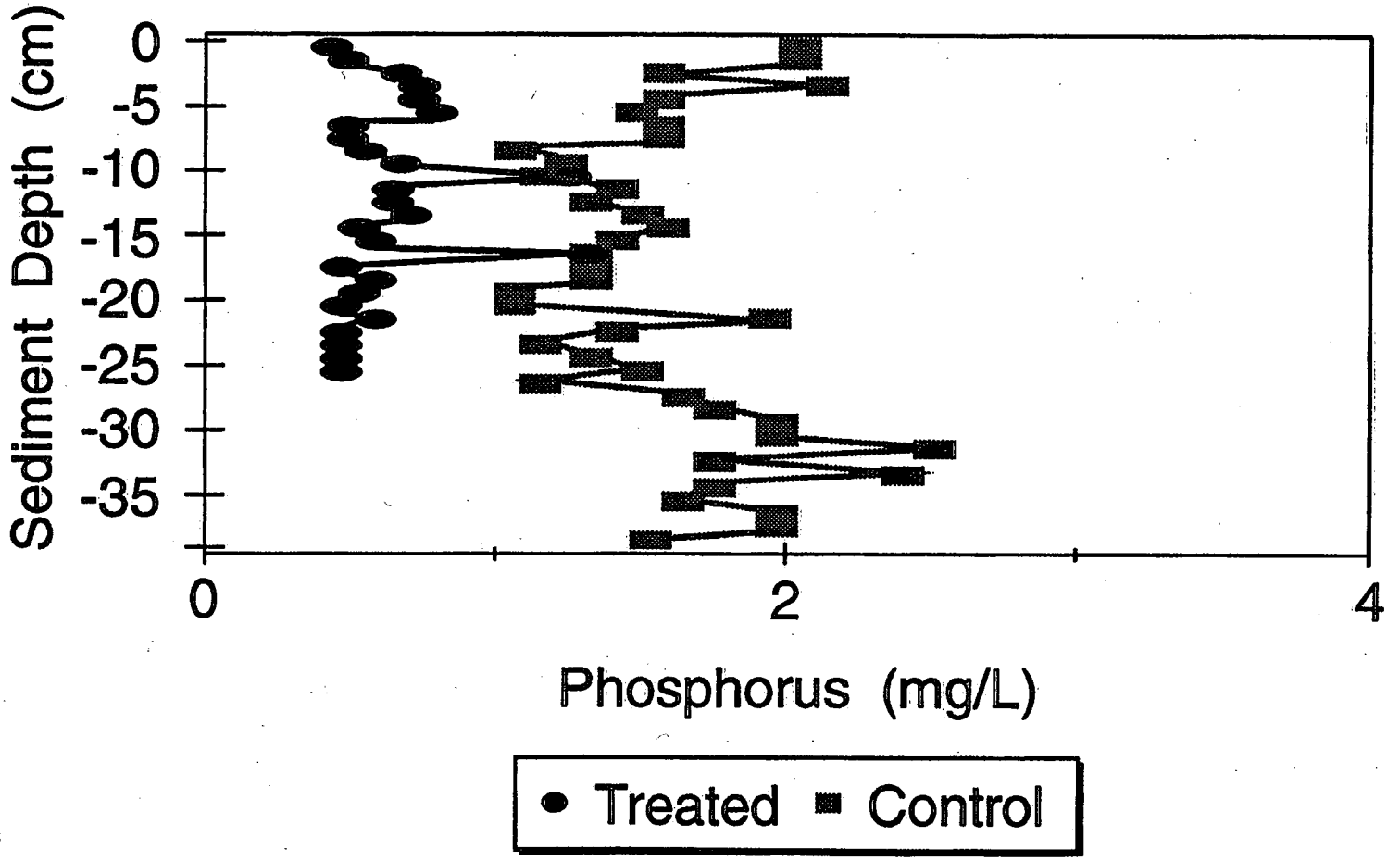


Figure 7

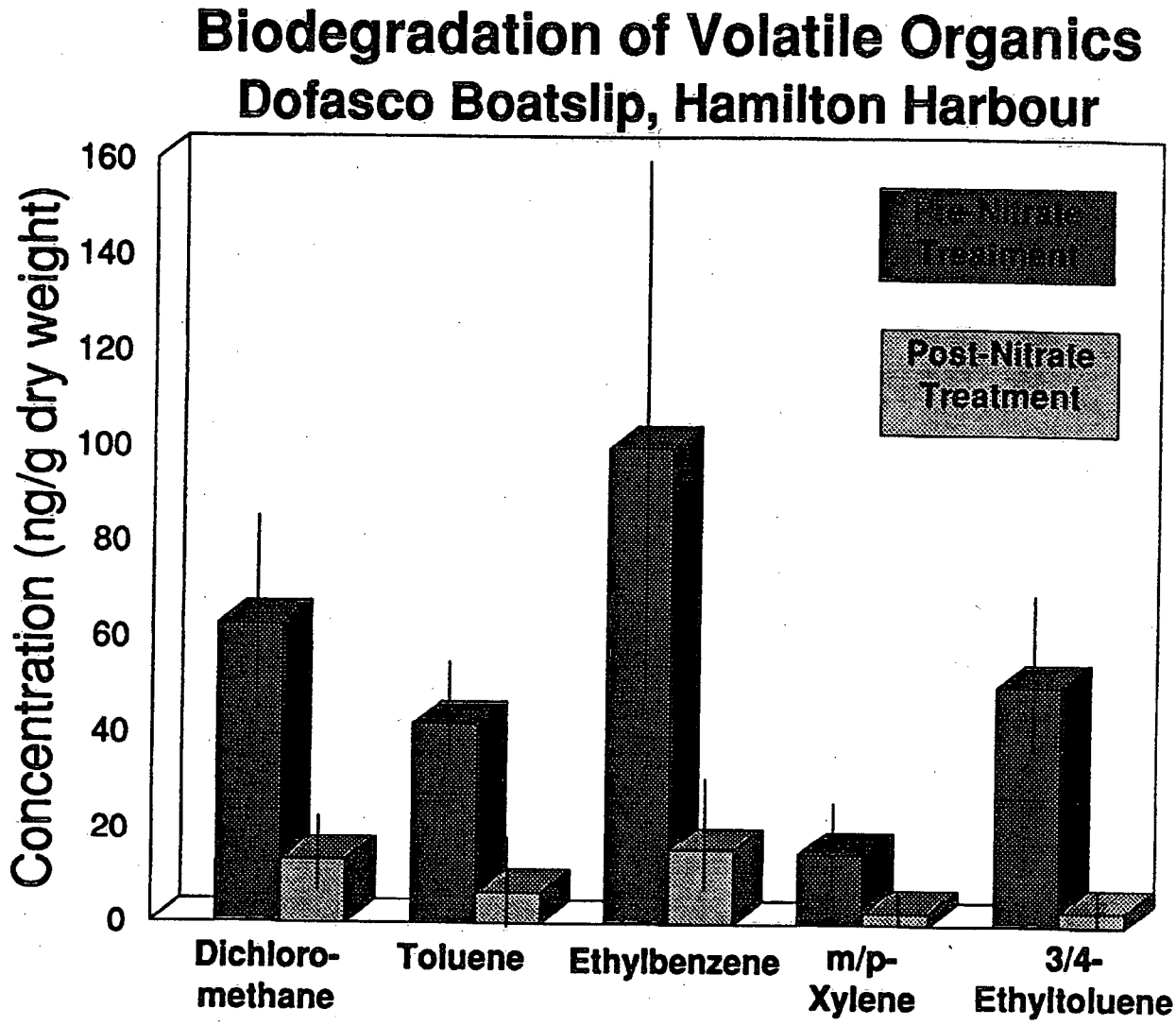
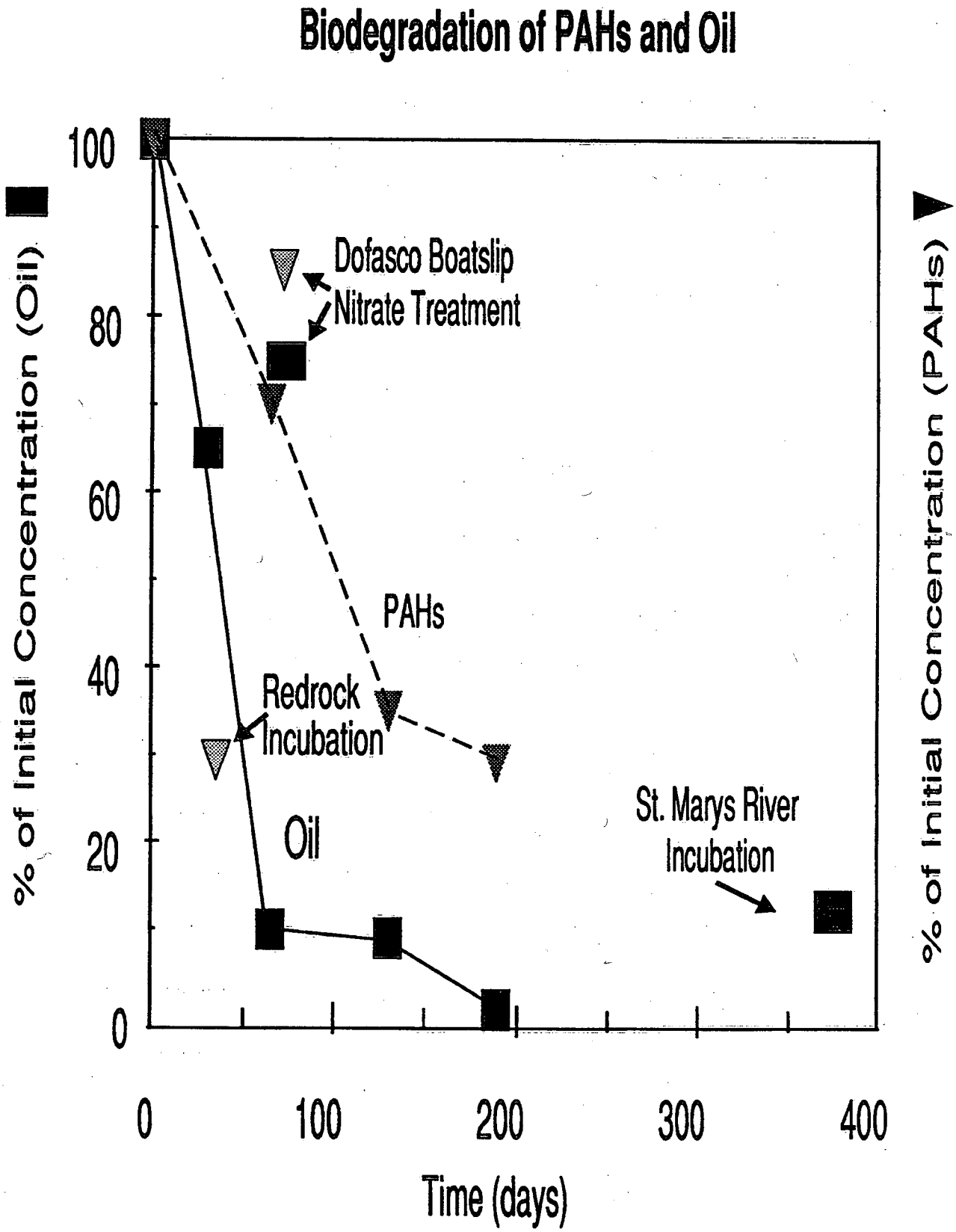
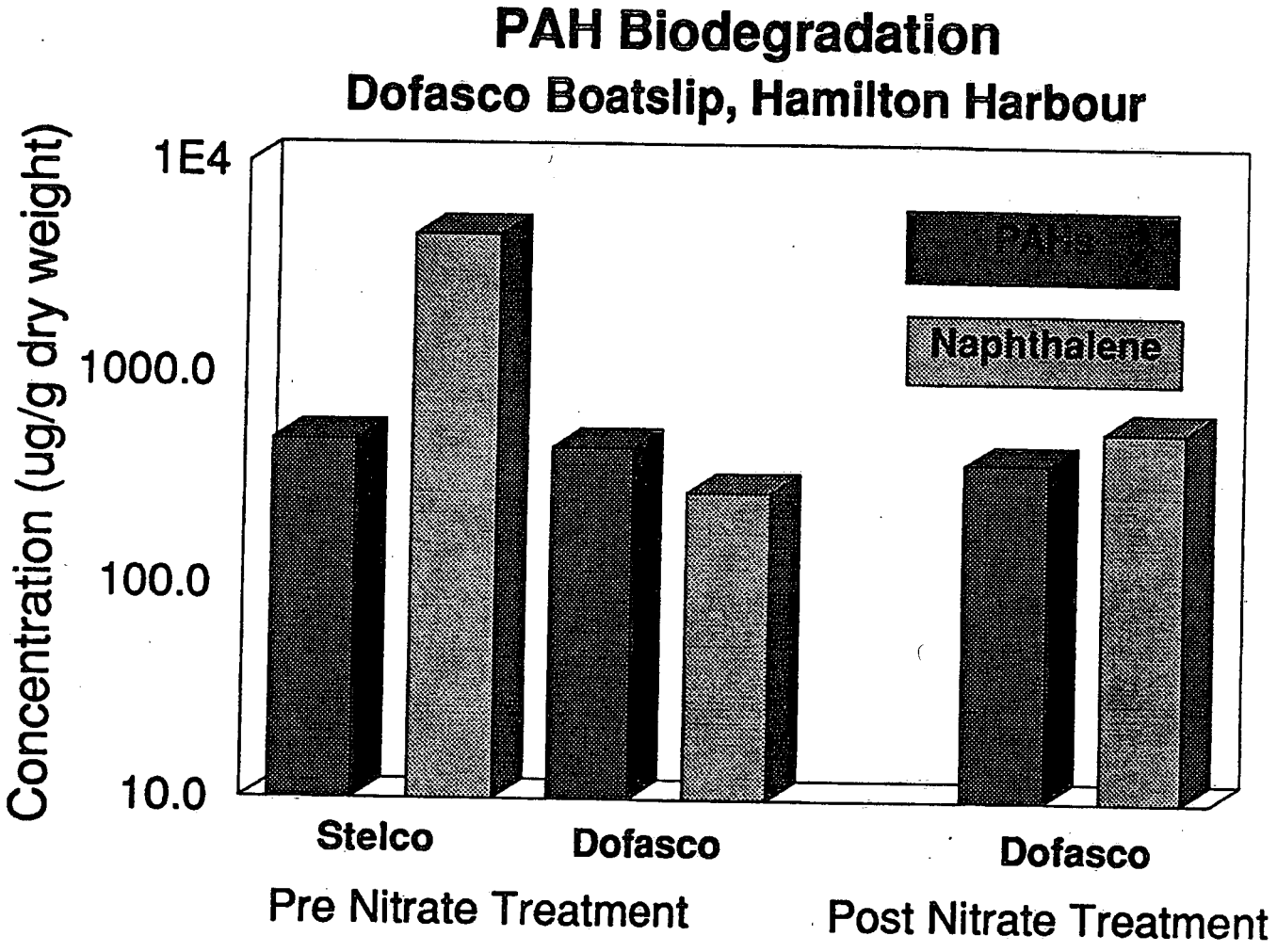

Biodegradation of Volatile Organics
Dofasco Boatslip, Hamilton Harbour
Concentration (ng/g dry weight)
160
140
120
100
80
60
40
20
0
Pre-Nitrate Treatment
Post-Nitrate Treatment
Dichloro-methane
Toluene
Ethylbenzene
m/p-Xylene
3/4-Ethyltoluene

Figure 8



Ref: Dutch Development Program Treatment Processes 1991

Figure 9


PAH Biodegradation
Dofasco Boatslip, Hamilton Harbour
Concentration (ug/g dry weight)
1E4
1000.0
100.0
10.0
PAHs
Naphthalene
Stelco
Dofasco
Dofasco
Pre Nitrate Treatment
Post Nitrate Treatment

Environment Canada Environnement Canada

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