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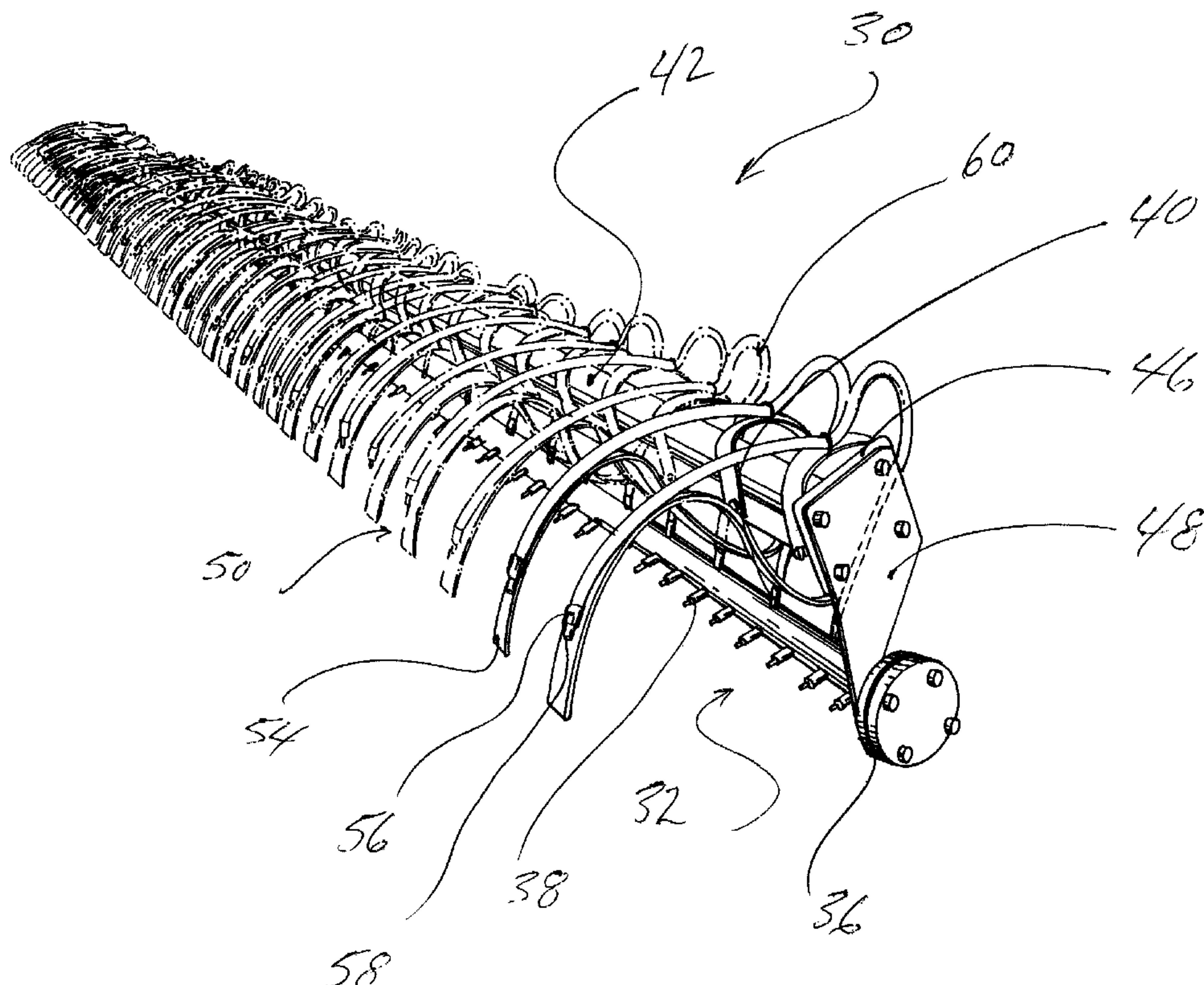
(72) Inventeurs/Inventors:
MURPHY, Tomas, CA;
SAVILE, Harry, CA

(73) Propriétaire/Owner:
HER MAJESTY THE QUEEN, IN RIGHT OF CANADA,
AS REPRESENTED BY THE MINISTER OF THE
ENVIRONMENT CANADA, CA

(74) Agent: MCFADDEN, FINCHAM

(54) Titre : METHODE ET DISPOSITIF POUR REDUIRE LA TOXICITE DE SEDIMENTS

(54) Title: SYSTEM TO REDUCE SEDIMENT TOXICITY



(57) Abrégé/Abstract:

A method and apparatus for the treatment of sediment. The apparatus provides a plurality of injection sites for injecting a biochemical oxidant into the sediment. The oxidant is useful for oxidizing a bacterial growth inhibitor to a non-inhibiting form thus permitting bacterial growth and thus greater numbers for sediment detoxification.



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ABSTRACT OF THE DISCLOSURE

A method and apparatus for the treatment of sediment. The apparatus provides a plurality of injection sites for injecting a biochemical oxidant into the sediment. The oxidant is useful for oxidizing a bacterial growth inhibitor to a non-inhibiting form thus permitting bacterial growth and thus greater numbers for sediment detoxification.

SYSTEM TO REDUCE SEDIMENT TOXICITYFIELD OF THE INVENTION

The present invention relates to a method and apparatus for the treatment of sediment and more particularly to a chemical treatment method and apparatus to effect such treatment.

BACKGROUND OF THE INVENTION

Generally speaking, most of the biodegradation studies and treatments are done in reactors (Jafvert and Rogers 1991). The largest reactor is a Dutch system where a mobile aerator moves along the treatment pond to maintain oxic conditions (Van Veen and Annokkee 1991). Other large treatments include landfarming (Van Dillen 1991) and the excavation and construction of a hill of contaminated soil with drainage tiles, nutrient dosing and sprinkler systems (Litchfield et al. 1992). These systems all require that the sediment be dredged and processed in sites which can involve the potential problems of security, cost, and public acceptance.

Some 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. Some treatments may not have provided the right environmental conditions for the microbes to completely biodegrade the organic wastes. Most of the failed bioremediation treatments in groundwater are related to either poor access to the wastes or to the blockage of the aquifer by the enhanced growth of microbes. The latter two problems do not apply to lake sediment on a macroscale; however, all sites can contain some polynuclear aromatic hydrocarbons (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).

Bioremediation of groundwater and soils is a growing industry. As long as the treatment is preceded by an analysis of the treatability and toxicity of the site, it is a promising

remedial option. Some toxins cannot be treated by biodegradation, but the cost of assessment is justifiable in that a detailed preassessment is substantially less expensive than excavation and chemical or physical treatment.

5

Bubbling the water column with oxygen has been proposed as a method of oxygenating the sediment (Murphy 1990). Some lake aeration treatments in Germany successfully oxygenated sediments but treatment with pure oxygen of some lakes in Switzerland did not oxygenate sediments (Gachter 1987). The engineering techniques are not completely developed, the treatment time may be long, and recovery difficult to predict accurately.

Further prior methods for treating sediment of sludge include the method of decontaminating wastewater sludge taught by Nicholson in U.S. Patent No. 4,781,842. Reference is made to the use of lime, cement kiln dust and lime kiln dust for treating biological sludge. The goal of the treatment is to fertilize agricultural land. The reference does not address the problem of treating sludge associated with a water body for the purpose of enhancing natural microbiological degradation.

U.S. Patent No. 5,008,020, discloses the use of a metal carbonate and a metal bicarbonate for solidifying waste material into a granular particulate form. The patentees do not discuss the merits of oxidation biodegradation inhibitors in order to effect more efficient biodegradation.

Conover, in U.S. Patent No. 5,039,427, teaches a method for removing suspended solids and to precipitate and inactivate phosphorus in lake water by adding aluminum hydroxide sulphate. The reference does not discuss oxidation of sulphide to sulphate to reduce inhibition of natural microbial biodegradation.

U.S. Patent No. 4,877,524, teaches an apparatus for treating bodies of water for correcting chemical, biological or other imbalances. The reference primarily relates to dispensing a

treatment agent within a water body, the dispensing rate being proportional to the boat speed. Both aluminum sulphate and sodium aluminate are taught as treatment material among others. There is no provision in the apparatus for injecting or otherwise contacting the sediment with biochemical oxidant and accordingly, no contemplation for enhancing the natural microbial degradation of the sediment and more particularly the toxins of the sediment.

Shuck et al. in U.S. Patent No. 4,268,398, teaches a method for rendering a sludge deposit in a waste water treatment facility into a pumpable mixture for relocation. This reference does not discuss an in-situ procedure for natural biodegradation of the sludge.

Further generally related references include U.S. Patent No. 5,055,204 and Canadian Patent Application Nos. 2,007,455 and 2,016,310

In view of the prior art, there exists a need for a sludge treatment process capable of being performed in-situ without stirring up the sediment into the water column and which permits a relatively large area to be treated quickly.

SUMMARY OF THE INVENTION

One aspect of the present invention is to provide an improved method for treating sludge and an improved apparatus for effecting the method.

In accordance with another aspect of one embodiment of the present invention, there is provided, a method of effecting natural microbial biodegradation of polynuclear aromatic hydrocarbons and petroleum hydrocarbons in sediment containing microbes and polynuclear aromatic hydrocarbons and petroleum hydrocarbons, comprising the steps of: providing a biochemical oxidant for detoxifying a microbial toxin produced during microbial biodegradation of the polynuclear aromatic hydrocarbons and petroleum hydrocarbons; contacting the sediment with the

oxidant to detoxify the toxin; and effecting microbial biodegradation of the polynuclear aromatic hydrocarbons and petroleum hydrocarbons.

5 The process of microbial decay results in the production of hydrogen sulphide. The presence of this compound generally impedes the biodegradable of polynuclear aromatic hydrocarbons and petroleum hydrocarbons. The addition of a biochemical oxidant; e.g. a bivalent alkaline earth chloride or nitrate or
10 monovalent nitrate have been found useful.

 In accordance with another aspect of the present invention there is provided a method of effecting natural microbial biodegradation of polynuclear aromatic hydrocarbons and petroleum
15 hydrocarbons in sediment containing the polynuclear aromatic hydrocarbons and petroleum hydrocarbons and microbes, comprising the steps of: providing a biochemical oxidant for oxidizing a biodegradation inhibitor produced during microbial biodegradation of the polynuclear aromatic hydrocarbons and petroleum
20 hydrocarbons; contacting the sediment with the oxidant; oxidizing the inhibitor to a non-inhibiting form; and effecting microbial biodegradation of the polynuclear aromatic hydrocarbons and petroleum hydrocarbons.

25 By oxidation of the inhibitor, substantial success was realized in the reduction of toxins in the sediment. The successful results were compounded by the fact that the sediment was contacted at a plurality of locations.

30 The overall process is continuous such that the treatment of the sludge can be effected quickly over a large area.

 Nutrients may be added with oxidant concurrently or conterminously. Further, the addition of emulsifier surfactants,
35 or other suitable treatment aids may be employed. Depending on the specific site variables, a pretreatment may be desirable in order to increase the efficiency of the procedure.

Apparatus suitable for facilitating maximum exposure of the oxidant to the sediment includes a dispensing arrangement therefore for dispensing the oxidant into the sediment in at least two locations simultaneously.

5

Thus, according to a further aspect of the present invention there is provided an apparatus suitable for treating sediment in a water body, the sediment containing chemical pollutants, comprising: a first dispensing means adapted for dispensing a treatment compound into contact with the sediment to be treated at a first level; a second dispensing means level adapted for dispensing the treatment compound within the sediment at a second level; each of the dispensing means having means for connection with a supply of the treatment compound; and support means for supporting the first dispensing means and the second dispensing means.

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A further aspect of the invention is to provide an apparatus suitable for treating sediment in a water body, the sediment containing chemical pollutants, comprising in combination: a first dispensing arrangement for dispensing a treatment compound into the sediment at a first level; a second dispensing arrangement for dispensing the treatment compound into the sediment at a second level, each the dispensing arrangement having means for connection with a supply of the treatment compound; a support frame for connecting the first dispensing arrangement and the second dispensing arrangement; and a carrier vessel for the vessel including means for connection and manipulation of the support frame.

30

Having thus generally described the invention, reference will now be made to the accompanying drawings illustrating preferred embodiments.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a perspective view of one embodiment of the apparatus of the present invention;

Figure 2 is an enlarged perspective view of one embodiment of the sediment treatment apparatus;

5 Figure 3 is a section along line 3-3 of Figure 2;

Figure 4 is an enlarged view of the mounting and fluid distribution for the sediment treatment apparatus;

10 Figure 4A is a plan view of the sediment treatment apparatus support;

Figure 4B is a schematic illustration of the apparatus in use;

15 Figure 5 is a series of graphs illustrating the concentrations of various contaminants;

Figure 6 is a schematic illustration of the test area;

20 Figure 7 is a graphic illustration of the redox potential of St. Marys River sediment cores;

25 Figure 8 is a histogram illustrating the effect of ferric chloride on sediment hydrogen sulphide for the St. Marys River treatment;

30 Figure 9 is a histogram illustrating the ATP-TOX results from Sault Ste. Marie for the first ferric chloride sediment injection;

Figure 10 is a series of histograms illustrating the sediment toxicity of photobacterium phosphoreum bioassay for data gathered at St. Marys River;

35 Figure 11 is a histogram illustrating the Daphnia magna bioassay results illustrating the average percent survival;

Figure 12 is a graph illustrating the percent mortality for the DMSO/methanol sediment extract;

5 Figure 13 is a histogram illustrating the average percent survival for Daphnia magna bioassay results for the Hamilton Harbour Stelco Hotspot site #1;

10 Figure 14 is a histogram illustrating the average percent survival for Daphnia magna bioassay results for the Hamilton Harbour Stelco Hotspot site #2;

15 Figure 15 is a histogram illustrating the average percent survival for Daphnia magna bioassay results for the Hamilton Harbour Stelco Hotspot site #3;

Figure 16 is a histogram illustrating the results of Figures 13, 14 and 15;

20 Figure 17 is an illustration of the toxicity severity of Hamilton Harbour;

Figure 18 is an illustration of the toxicity of Hamilton Harbour sediments for photobacterium;

25 Figure 19 is an illustration of the Hamilton Harbour sediment injection site;

30 Figure 20 illustrates data generated in denitrification experiments for bottle incubations;

Figure 21 illustrates data generated in denitrification experiments for 250 ml bottle incubations;

35 Figure 22 illustrates data generated in denitrification experiments for 2 L bottle incubations;

Figure 23 illustrates data generated in denitrification experiments for 250 ml bottle incubations;

5 Figure 24 illustrates data generated in denitrification experiments for 2 L bottle incubations;

Figure 25 illustrates the biodegradation of the sixteen priority pollutant polynuclear aromatic hydrocarbons;

10 Figure 26 illustrates the denitrification data comparing Hamilton Harbour Deep Basin, Stelco Hotspot and St. Marys River;

Figure 27 illustrates the effect of the nitrate treatment on the Photobacterium;

15 Figure 28 illustrates headspace GC/MS analysis for a variety of organic compounds for a control and for data gathered after nitrate treatment; and

20 Figure 29 illustrates the biodegradation of volatile toxins in the Dofasco boatslip before and after treatment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

25 Referring initially to the apparatus aspect of the present invention, Figure 1 illustrates a first embodiment of the present invention, in perspective, as situated on a carrier vessel.

30 Generally, the apparatus includes rotatable lifting apparatus 10 having a main support platform 12 mounted to the carrier vessel 14 in a known manner. Load bearing masts 16, 18 are connected to the platform 12. A winch cable system 20 includes winches 22 extends over pulleys 24 provided on the load bearing masts 16 and 18. One of the winch cables 20 includes a connecting member 26 suitable for connection with the sediment
35 treatment apparatus, generally denoted by numeral 30. A support system is provided for supporting and assisting in the

positioning of the treatment apparatus 30, and will be discussed hereinafter.

5 In one embodiment of the treatment apparatus, best illustrated in Figure 2 and 3, an elongate hollow spray bar 32 is included having opposed ends 34 (Figure 1) and 36. The spray bar 32 includes a plurality of nozzles 38 distributed along the length of bar 32 in a spaced and aligned relation. The nozzles 38 are inclined downwardly relative to a horizontal plane. A
10 second set of nozzles 40 are distributed along the length of spray bar 32 in spaced and aligned relation radially spaced from nozzles 38. Both nozzles 38 and 40 are in fluid communication with spray bar 32.

15 As is illustrated in the example, the sediment treatment apparatus 30 is composed of a plurality of connected and similar units and accordingly the description will be limited to one such unit.

20 Spaced above spray bar 32 there is provided a mounting member 42 comprising a metal tube having opposed ends 44 (Figure 1) and 46. A plurality of such members 42 are connected in end-to-end relation by suitable fasteners as illustrated. Each remote or terminal end as well as the end connection between
25 mounting members 42 includes a spacer member 48, which includes a spacer member 48, which not only spaces the members 42 from the spray bar 32, but additionally serves to impart support to the spray bar 32. Connection of spacer members 48 to member 42 and bar 32 is achieved by suitable fasteners, welding etc.

30 Each mounting member 42 includes a plurality of arcuate fingers 50 each connected thereto by bolts 52. The fingers 50 are arranged in longitudinally aligned and spaced relation. Each finger 50 subscribes to a generally sinusoidal configuration and
35 each comprises a rigid metal suitably bent into the indicated shape. The shape of each finger 50 permits resilient

flexibility. A free end 54 of each finger 50 is laterally and vertically spaced from the spray bar 32.

5 Each finger 50 includes, spaced from free end 54 thereof, a nozzle mounting 56 for mounting a nozzle 58. A conduit 60 extends between and connects nozzle 58 with nozzle 40 such that fluid communication is established.

10 Treatment fluid is distributed to each spray bar 32 by a distribution conduit 62 connected to each spray bar 32 inwardly of the end thereof by a swivel type connector 64 well known to those skilled. This is generally illustrated in Figure 4. Each conduit 62 terminates for fluid connection with a main feeder conduit 66 (Figure 1). Conduit 66 is connected to a fluid
15 treatment supply drum 68 centrally located on the carrier vessel to act as ballast. A pump (not shown) may be positioned intermediate of supply drum 68 and feeder conduit 66 or the fluid may be distributed by negative pressure.

20 Treatment fluid travelling through each spray bar 32 will be dispensed through nozzles 38 as well as through nozzles 40, all conduits being in fluid communication.

25 At least the spray bars 32 adjacent the terminal sections thereof further include frame mounts 70 for releasably coupling the treatment apparatus 30 to a frame 72.

30 Figure 4 illustrates an enlarged view of the attachment of the end of frame member 74 to spray bar 32 (removed for clarity) as is generally illustrated in Figure 1. Fastener 76 links a flange 78 on member 74 to frame mount 70. The frame 72 may include a plurality of members 74 which converge, and the member thereof will vary depending on the size of the treatment apparatus. The frame 72 permits easy manipulation of the
35 apparatus from a submerged position to a storage position, the latter position being illustrated. Frame 72 includes a

connection site 80 for connection with connecting member 26 on winch cable 20.

5 Figure 4A illustrates the hangar assembly 90 for positioning the assembly 30 into the sediment at the desired position.

10 The assembly 90 includes a main load bearing member 92 which terminates at a horizontally disposed bracket 94 for connection with spray bar 32 (not shown). Connection to spray bar 32 may be by any suitable means, e.g. clamps, bolts etc.

15 Bracket 94 and member 92 are further reinforced by braces 96 extending therebetween.

20 In order to permit treatment of sediment in a variety of situations where the depth requirement varies, load bearing member 92 may include a plurality of telescopic sections of tube 98 or may be extended by progressive manual connection of further lengths of tubing sections 98.

25 Load bearing member 92 may be pivotally connected to the load bearing masts 16 and 18, described herein previously, or may be connected directly to platform 12 for easy manipulations of member 92. The specific mounting position of member 92 will depend upon the specific parameters in the treatment area, e.g. water depth etc.

30 Generally, the tubing sections 98 may comprise rigid aluminum material or other suitable corrosion resistant materials. This material provision is additionally applicable to the overall assembly 90 and frame 72.

35 In operation, the treatment apparatus 30 is moved from the storage position shown in Figure 1 to the use position shown in Figure 4B where the apparatus is submerged below the surface of the water, W, to contact within the sediment bed, S.

In this position, both the spray bars 32 and the fingers 50 contact the sediment, S, as illustrated. The fingers 50 permit deeper penetration of the nozzles 58 and more specifically the treatment material dispensed therethrough, into contact with the sediment. The nozzles 38 dispense the treatment material in a second position spaced from that of the treatment supplied by nozzles 58. This two-point injection system has a dramatic effect on the sediment detoxification as well be evinced by the data discussed hereinafter.

The treatment apparatus 30 is dragged along the sediment bed as the carrier vessel travels the area to be treated. The arcuate fingers 50 are particularly advantageous for the sediment treatment since the same are resilient and basically unaffected by irregular bed topography, small debris etc. When encountered, the fingers 50 simply flex and return to a normal disposition as the apparatus continues to be advanced along the sediment bed. Recovery of the apparatus from the sediment may be achieved with the winch system described previously.

In preferred form, the overall length of the apparatus is eight (8) metres with the spacing between nozzles 38 and 58 being between 10 and about 20 centimetres. Such spacing permits uniform dispersion within the sediment as opposed to localized areas of treatment.

The rate at which the treatment fluid is injected into the sediment may be timed with the carrier vessel speed i.e. a higher vessel speed will require a higher rate of injection of fluid into the sediment. In an alternate embodiment, the treatment apparatus 30 and the ancillary equipment (winch, loud bearing masts etc.) as well as the submerging procedure may be effected by robotics controlled from the shore or at a point distant from the treatment area. This arrangement would reduce the exposure of human workers to the hazardous sediment material and presence around the heavy equipment.

The use of monitoring means e.g. sonar equipment, cameras ultrasonic equipment etc. are all envisioned for use with the apparatus in order to monitor gross sediment topography irregularities or obstacles with which the apparatus 30 cannot contend.

Still further, the connection points between spray bars 32 and between mounting members 42 may be hinged to permit folding of the apparatus 30. In addition, the apparatus may be telescopic.

The examples illustrated teach a two-point treatment injection system and it will be clearly understood that a multiplicity of injection points may be provided simply by, for example, the addition of a further series of fingers having a greater length than the previous series.

Having thus described the apparatus, reference will now be made to the experimental procedures and generated data.

GENERAL

EXAMPLE 1 - FERRIC CHLORIDE INJECTION

Earlier laboratory trials with Hamilton Harbour sediments indicated that the addition of iron reduced toxicity to Photobacterium phosphoreum, Daphnia magna, Salmo gairdneri, Pimephales promelas, and Hexagenia limbata. The seasonal change in sediment toxicity also seemed related to a change in redox, albeit the relationship was not firmly established. Also there was a correlation between the toxicity of the sediments to Daphnia magna and the chemical oxygen demand of the sediments. The most appropriate hypothesis to explain these observations is that much of the acute toxicity of the sediments of Hamilton Harbour was caused by reduced chemicals, probably hydrogen sulphide.

Hydrogen sulphide is very toxic. The LC_{50} for various species are: Assellus 1.07 mg/L, Crangonyx 0.84 mg/L, Gammarus

0.059 mg/L, Baetis 0.020 mg/L, Ephemera 0.361 mg/L, and Hexagenia 0.111 mg/L. Chronic analysis indicates that no-effect levels are about 10% of the LC_{50} (Oseid and Smith 1974). Although hydrogen sulphide toxicity is well known, few studies report it in
5 sediments. US EPA (1986) describe hydrogen sulphide as "ephemeral" which indicates that infrequent sampling would not measure hydrogen sulphide. Another limitation is that some professional laboratories use procedures too insensitive to detect toxic concentrations of hydrogen sulphide.

10 Studies with ^{35}S -radiolabels have measured the geochemical reactions of sediment sulphur well. For example, Nedwell (1980) determined sulphate reduction in summer is 50-100 times faster than in winter. With intensive monitoring, Ripl (1986) observed
15 large seasonal changes in sulphate; if only a few percent of the seasonal change in sulphate were converted to hydrogen sulphide, the sediments were very toxic. This simplistic assumption may underscore the ecological importance of seasonal changes in hydrogen sulphide toxicity. Ingvorsen and Jorgensen (1982)
20 observed a 20-fold seasonal change in sulphate reduction, but it was matched by seasonal changes in hydrogen sulphide flux from the sediments of 10^3 - 10^4 fold! At low rates of hydrogen sulphide production, it was mostly adsorbed to particles, but at high rates of hydrogen sulphide production, the binding sites were
25 saturated and the pulsed release of hydrogen sulphide would have killed many benthic organisms.

Similar sulphur geochemical cycling and sediment toxicity must occur in the hotspots of the Great Lakes but it is not
30 documented. Decades ago, all steel mills discharged large quantities of sulphur from several sources such as sulphur balls from the coking process or spent sulphuric acid in pickling liquor. The areas in Hamilton Harbour and the St. Marys River where these wastes would settle are anoxic and hydrogen sulphide
35 should form.

Inadequate documentation of the sulphur biochemistry could lead to misinterpretation. Hydrogen sulphide has a half life of about 19±19 h (Table 16 in Zehnder and Zinder 1980). Thus it is easy to lose the toxicity by sample handling, such as is commonly done when bubbling invertebrate bioassays with air. The reported absence of Hexagenia from the St. Marys River has been explained by correlation analysis to reflect oil and grease toxicity (St. Marys RAP 1992), but it could easily be caused by hydrogen sulphide toxicity.

Samples were collected on several trips to St. Marys River and several trips to Hamilton Harbour with Ponar (Sault) or Shipek (Hamilton) grab samplers, TechOps corers, and sediment traps. The sediment traps were deployed a metre about the sediments to determine if the sediment injection equipment resuspended sediments. In the St. Marys River, four traps were set at one upstream site and four traps were set at one site downstream of the treatment area.

All St. Marys River samples were stored in a cold room at the Great Lakes Forestry Research Centre, and processed for shipping on ice, i.e., cores were extruded there at 1 cm intervals. The Eh and pH of samples were recorded at the site. All Hamilton Harbour samples were brought back to the institute within hours of sample collection. All samples were chilled and processed quickly, i.e., all bioassays were processed within days of sample collection. Sediment samples were subsampled; half was freeze dried for metal analysis and half was frozen and retained for organic analysis.

The ATP-TOX method of Xu and Dutka (1987) was used on 10% DMSO 10% methanol elutriates. Equal volumes of sediment and DMSO were mixed together and shaken vigorously by hand for 2 minutes. The homogenized slurry was then centrifuged for 20 minutes at 10000 rpm. This system uses the measurement of ATP as indication of microbial growth. If when compared to a control, a sample

inhibits ATP production (i.e., growth), a toxic effect is assumed.

5 Daphnia magna bioassays were done on aqueous elutriates. Within two weeks of collection all samples were extracted with equal volumes of distilled water on an end-over-end shaker for 16 h. After extraction, sediment extracts were centrifuged for 20 min at 1000 g. Elutriates were centrifuged, not filtered. 10 Filtration can remove colloidal material that would not settle from disrupted sediment and that may contain toxic metallic or organic contaminants. Ten Daphnia less than 24 h old were introduced to 25 mL of test medium and placed in a 25°C incubator for 48 h. A 16 h light and 8 h dark photoperiod was used. Prior to all experiments, pH and dissolved oxygen were measured and if 15 the oxygen concentration was less than 8 mg/L, the sediment extracts were bubbled with purified air for 16 h. If more than 10% of the control Daphnia died within 48 h, the experiment was repeated.

20 Photobacterium bioassays were run on whole sediments (Brouwer et al. 1990). Dilutions for LC₅₀ analysis were done with clean sediments from an organic rich sediment from a marsh near Long Point, Lake Erie.

25 SEDIMENTS AT THE BELLEVUE PARK SITE, ST. MARYS RIVER

Unlike Hamilton Harbour, metals (Figure 5) and the 16 priority pollutant polynuclear aromatic hydrocarbons (PAHs, Table 1) are comparatively dilute at the Bellevue Park test site in the St. Marys River (Figure 6). However, sediment samples from near 30 Bellevue Park have high concentrations of oil and grease (1.4%, 1.6% and 2.4%) and wood fibres.

A high concentration of a complex PAH (retene, 2 µg/g) was found in the St. Marys River sediments. Retene can occur 35 naturally from degradation of conifers but it can also be associated with pulp and paper manufacturing. The concentrations

of many of the priority pollutant chlorinated organic compounds is near or at background levels (Tables 2 and 3).

5 Decay of the wood fibre and other wastes results in a
reducing environment as indicated by the black colour, high
ammonia (1.5-2.3 mg/L), and low redox (Figure 7). Note that the
deeper sediments are more oxic. This observation reflects the
relatively recent discharge of labile organic wastes over older
more oxic sediments. Also note that the redox of the sediments
10 changes seasonally. By November the surface sediments have
become oxygenated (Figure 7). It is a fortunate situation in
that oxidation treatment of the surface sediments could not be
compromised by diffusion of reduced materials such as hydrogen
sulphide from deeper sediments. Also the required depth of
15 treatment is only 15 cm.

Table 1

PAH Concentrations in Surficial Sediment
of Bellevue Marine Park Area

	Sample Range (ng/g)
Naphthalene-	3137 - 6878
Acenaphthylene	152 - 318
Acenaphththalene	169 - 360
Fluorene	356 - 540
Anthracene	1913 - 3425
Phenanthrene	478 - 1227
Fluoranthene	2599 - 6831
Pyrene	2021 - 5485
Chrysene	1068 - 3269
Benzo(a)anthracene	1353 - 3680
Benzo(b)fluoranthene	2004 - 2223
Benzo(k)fluoranthene	1512 - 2202
Benzo(a)pyrene	964 - 3114
Dibenzo(a,h)anthracene	275 - 1040
Indeno(1,2,3-cd)pyrene	130 - 411
Benzo(g,h,i)perylene	370 - 1214
Total PAHs	16989 - 42019

Table 2

PCB Concentrations in Surficial Sediment
of Bellevue Marine Park Area

	Sample Range (ng/g)
PCB 18	ND - 0.66
PCB 52	ND - 5.13
PCB 49	ND - 5.43
PCB 44	ND - 3.69
PCB 101	2.48 - 5.77
PCB 151	ND - 9.23
PCB 118+149	2.29 - 15.57
PCB 105	ND - 1.92
PCB 138	2.91 - 6.36
PCB 183	ND - 2.94
PCB 194	ND - 0.85
Total PCB	80.43 - 299.28

Table 3

Organic Contaminant Concentrations in Surficial Sediment
Of Bellevue Marine Park Area

	Sample Range (ng/g)		Sample Range (ng/g)
1,3 DCB	ND	Aldrin	ND
1,4 DCB	ND	OCS	ND
1,2 DCB	ND	g Chlordane	ND
HCE	ND	o,p DDE	ND
1,3,5 TCB	ND	a Endosulfan	ND
1,2,4 TCB	ND	a Chlordane	ND
1,2,3 TCB	ND	t Nonachlor	ND
1,2,3,5 TECB	ND	Dieldrin	ND
1,2,4,5 TECB	ND	p,p' DDE	1.97-3.17
1,2,3,4 TECB	ND	o,p' DDD	ND
PECB	ND	Endrin	ND
2,3,4,6 TECB	ND	B Endosulfan	ND
A BHC	1.66-4.14	p,p' DDD	1.22-3.32
HCB	ND	o,p' DDD	ND
PECA	ND	Methoxychlor	ND
Lindane	ND	Mirex	ND
Heptachlor	ND		

The highest observed concentration of hydrogen sulphide in the sediment was in June (Figure 8). By the end of August most of the hydrogen sulphide had been oxidized. The sediment treatment with ferric chloride greatly reduced the concentration of hydrogen sulphide.

The ATP-TOX bioassay indicated a seasonal change in toxicity (Figure 9) that closely matched that of the hydrogen sulphide concentration. Also, the ferric chloride treatment reduced the toxicity of the ATP-TOX bioassays in tandem with the hydrogen sulphide complexation. Photobacterium phosphoreum bioassays also indicated a seasonal change in toxicity but they were not done as intensively as the ATP-TOX bioassays (Figure 10). Daphnia magna bioassays with aqueous extracts indicated no toxicity (Figure 11 but some DMSO extracts with Daphnia could measure toxicity (Figure 12).

Two other bioassays indicated little or no toxicity. Dilution bioassays with Hexagenia (mayfly nymphs) from four field trips in 1991 (February, June, July, and August) indicated no toxicity. Bioassays with Lactuca sativa (lettuce) detected little toxicity. These latter bioassays are not sensitive to hydrogen sulphide toxicity.

The bioassay results were not as clear as visual inspection of the site was. Very few benthic invertebrates were seen; the sediments were virtually sterile to organisms. The main acute toxin is hydrogen sulphide and some laboratory bioassays cannot detect this toxin.

Three sets of Daphnia toxicity dilution experiments in Hamilton Harbour also observed a seasonal change in sediment toxicity (Figures 13, 14 and 15). Some variation exists and the trends are more obvious by looking at the average toxicity (Figure 16). In winter, these sediments have little toxicity. However, if these winter samples are purged with nitrogen, then sealed for a month to go anoxic, then bubbled with air for 2-3

h to oxygenate them, they are highly toxic. This length of oxygenation provides oxygen saturation but it is less than the half life of hydrogen sulphide oxidation (19 h).

5 By late fall, the sediment samples from the Stelco Hotspot were still highly toxic. These observations differ from the St. Marys River sediments where hydrogen sulphide toxicity was almost gone by late August. The differences in extremes of hydrogen sulphide concentrations support the hypothesis that the Stelco
10 Hotspot with 100 mg/L of hydrogen sulphide will stay toxic for much longer than the St. Marys River sediments with 4 mg/L hydrogen sulphide.

15 New toxicity maps with Daphnia magna (Figure 17) and Photobacterium phosphoreum (Figure 18) indicate much less toxicity than earlier maps (Brouwer et al. 1990). The new maps are done from analyses of surface sediment (0-1 cm), whereas the old maps were done from analyses of Ekman dredge samples (0-15 cm). In part, the surface sediments have less contaminants, but
20 the deeper sediments have less access to oxygen and anoxic decay produces hydrogen sulphide.

25 If the acute toxicity is controlled by hydrogen sulphide, then no biodegradation occurs in the deeper sediments and some occurs at a suppressed rate in the most recent sediments. The proof of this last hypothesis is found in the PAH data. The surface sediments have much less naphthalene than the deeper sediments (Tables 4 and 5). Naphthalene is biodegradable (Murphy et al. 1992). Some recovery from source control is occurring,
30 but it is slow. The rate of recovery is uncertain in the deep basin. The deeper sediments of the Stelco Hotspot, i.e., >2 cm deep are not recovering and will likely remain uninhabitable to benthos for decades.

35 Two sediment injection trials were conducted in the St. Marys River near Bellevue Park. The first trial was relatively successful but modifications were made to improve efficiency

Table 4: PAHs in Hamilton Harbour surface
sediments (0-1 cm) collected in 1991

Murphy HAMILTON HARBOUR		PAHs conc. ug/g Sediment Samples Summer 1991										pg. 1 of 3
		proc.blk	site 41	site 80	site 47	site 76	site 74	site 9	site 2			
NAPHTHALENE		<0.01	0.61	0.24	3.86	0.11	0.15	1.14	0.15			
ACENAPHTHYLENE		ND	0.12	0.02	1.27	0.02	0.04	0.20	0.03			
ACENAPHTHENE		ND	0.05	0.02	1.53	0.03	0.04	0.25	0.06			
FLUORENE		ND	0.14	0.04	2.72	0.05	0.09	0.29	0.06			
PHENANTHRENE		<0.01	1.32	0.37	22.59	0.42	0.86	1.66	0.51			
ANTHRACENE		ND	0.20	0.03	5.01	0.07	0.18	0.41	0.08			
FLUORANTHENE		<0.01	3.38	0.86	50.36	0.85	1.86	4.33	1.02			
PYRENE		<0.01	3.01	0.76	41.07	0.74	1.61	4.04	0.88			
BENZ(a)ANTHRACENE		<0.01	1.66	0.39	33.54	0.47	0.82	2.56	0.40			
CHRYSENE		<0.01	2.16	0.56	4.36	0.61	1.05	3.00	0.62			
BENZO(B)FLUORANTHENE		<0.01	6.27	0.05	57.34	0.76	1.83	0.20	0.34			
BENZO(K)FLUORANTHENE		<0.01	0.77	0.57	41.60	0.55	0.68	3.26	0.49			
BENZO(A)PYRENE		<0.01	2.40	ND	89.29	0.31	0.23	3.75	0.15			
INDENO(1,2,3-cd)PYRENE		ND	0.51	ND	179.22	0.17	ND	0.42	0.05			
DIBENZ(a,h)ANTHRACENE		ND	0.60	ND	16.85	0.13	ND	0.40	0.02			
BENZO(ghi)PERYLENE		ND	1.05	0.07	111.47	0.31	0.05	1.42	0.13			
TOTALS		<0.01	24.25	3.98	662.10	5.60	9.48	27.35	4.98			

Table 4 cont: PAHs in Hamilton Harbour surface
sediments (0-1 cm) collected in 1991

Murphy HAMILTON HARBOUR		PAHs conc. ug/g Sediment Samples Summer 1991										pg.2 of 3
		<u>site 25</u>	<u>site 15</u>	<u>site 45</u>	<u>site 9R</u>	<u>site 57</u>	<u>site 28</u>	<u>site 19</u>	<u>site 55</u>			
NAPHTHALENE		2.39	0.31	1.43	0.68	0.46	0.71	0.04	0.09			
ACENAPHTHYLENE		0.76	0.11	0.46	0.14	0.22	0.24	0.01	0.02			
ACENAPHTHENE		0.26	0.11	0.54	0.17	0.14	0.18	<0.01	0.01			
FLUORENE		0.76	0.14	0.96	0.20	0.28	0.36	0.01	0.02			
PHENANTHRENE		4.18	0.95	8.12	1.19	2.56	2.93	0.07	0.15			
ANTHRACENE		1.06	0.19	2.21	0.24	0.16	0.18	0.01	0.05			
FLUORANTHENE		17.26	2.07	11.53	3.11	4.86	5.22	0.17	0.39			
PYRENE		17.41	1.85	9.10	2.80	4.11	4.44	0.15	0.35			
BENZ(a)ANTHRACENE		15.79	1.14	4.85	1.65	2.03	2.52	0.07	0.16			
CHRYSENE		16.15	1.37	5.33	2.04	2.53	2.77	0.09	0.22			
BENZO(B)FLUORANTHENE		17.75	0.02	0.34	0.03	0.41	2.84	0.22	0.13			
BENZO(K)FLUORANTHENE		17.57	0.99	4.69	1.89	1.73	1.48	0.08	0.17			
BENZO(A)PYRENE		26.62	0.80	6.77	2.05	5.42	0.25	0.08	0.19			
INDENO(1,2,3-cd)PYRENE		6.18	0.05	0.64	0.70	0.40	ND	ND	0.01			
DIBENZ(a,h)ANTHRACENE		3.03	0.01	0.31	0.12	0.05	ND	<0.01	ND			
BENZO(ghi)PERYLENE		12.44	0.16	2.19	0.65	0.30	0.12	ND	<0.01			
TOTALS		159.60	10.26	59.47	17.67	25.64	24.26	0.98	1.96			

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Table 4 cont: PAHs in Hamilton Harbour surface
sediments (0-1 cm) collected in 1991

Murphy HAMILTON HARBOUR PAHs conc. ug/g Sediment Samples Summer 1991 pg.30f3									
	site 36	site 28R	site 48	site 29	site 53	site 37	site 61	site 61R	site 61R
NAPHTHALENE	0.83	1.00	84.82	0.41	0.36	1.17	0.65	0.84	0.84
ACENAPHTHYLENE	0.25	0.36	2.31	0.14	0.08	0.28	0.07	0.09	0.09
ACENAPHTHENE	0.17	0.20	14.24	0.10	0.06	0.18	0.16	0.21	0.21
FLUORENE	0.44	0.39	21.14	0.21	0.12	0.38	0.27	0.37	0.37
PHENANTHRENE	3.56	3.13	154.48	2.07	1.16	3.44	2.25	3.23	3.23
ANTHRACENE	1.10	1.00	56.41	0.52	0.27	0.87	0.38	0.55	0.55
FLUORANTHENE	6.76	5.79	167.90	3.77	2.21	6.28	3.20	4.72	4.72
PYRENE	5.68	4.90	139.67	3.21	1.91	5.37	2.70	3.95	3.95
BENZ(a)ANTHRACENE	3.05	3.21	90.37	1.85	0.98	3.07	1.44	2.10	2.10
CHRYSENE	3.56	3.38	80.68	2.22	1.26	3.72	1.95	2.70	2.70
BENZO(B)FLUORANTHENE	1.07	3.70	154.33	3.30	1.66	6.11	5.06	4.71	4.71
BENZO(K)FLUORANTHENE	1.76	3.25	89.25	2.33	1.08	3.69	1.51	2.33	2.33
BENZO(A)PYRENE	2.62	3.99	133.00	2.42	0.93	4.34	2.03	3.11	3.11
INDENO(1,2,3-cd)PYRENE	ND	5.97	304.70	0.92	0.21	1.24	1.16	2.92	2.92
DIBENZ(a,h)ANTHRACENE	ND	0.74	37.94	0.30	0.07	0.38	0.36	0.70	0.70
BENZO(ghi)PERYLENE	0.00	2.19	135.42	1.12	0.35	1.82	1.17	2.41	2.41
TOTALS	30.91	43.19	1,666.67	24.91	12.70	42.34	24.37	34.96	34.96

Table 5 PAHs in Ekman Dredge Samples - Stelco Hotspot

Compound	February 1990			October 1990		
	Dredge Site #1	Dredge Site #2	Dredge Site #3	Dredge Site #1	*Core Site #1	
NAPHTHALENE	2718.9	2042.1	10263.5	5457.8	2925.7	
ACENAPHTHYLENE	13.5	19.2	16.4	8.3	14.7	
ACENAPHTHENE	19.9	6.0	60.0	27.9	3.3	
FLUORENE	8.6	19.0	13.3	27.1	15.5	
PHENANTHRENE	79.6	64.7	179.0	72.8	48.5	
ANTHRACENE	24.8	22.9	53.6	25.7	17.7	
FLUORANTHENE	78.1	54.7	139.1	59.1	38.2	
PYRENE	42.9	29.2	76.3	42.6	27.6	
BENZOaANTHRACENE	41.1	24.6	59.4	20.0	12.3	
CHRYSENE	40.3	23.1	55.0	20.1	12.5	
BbFLUORANTHENE	42.0	21.0	58.1	14.5	7.2	
BkFLUORANTHENE	26.4	15.7	30.1	9.5	4.9	
BaPYRENE	38.9	20.7	49.7	12.9	6.4	
INDENOPYRENE	24.3	13.1	30.5	8.6	4.3	
DIBENZOANTHRACENE	4.6	3.1	5.9	2.5	1.6	
BENZOPERYLENE	22.0	11.1	27.6	8.1	3.6	
TOTAL (µg/g)	3225.7	2390.1	11117.6	5817.5	3143.9	

* Combined

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Table 6

Summary of Sediment Trap Data - St. Marys River Chemical Treatments

Sediment Traps (g) July 8, 1991		Sediment Traps (g) Oct 10, 1991	
Upstream	Downstream	Upstream	Downstream
0.122	0.182	0.066	0.049
0.140	0.169	0.064	0.029
0.154	0.144	0.047	0.074
0.081	0.158	0.048	0.081
0.497	0.653	0.225	0.233
0.124	0.163	0.056	0.058
	+31.4		+3.6
Total Average % Dif			
Surface Water (g/L) July 8, 1991		Surface Water (g/L) Oct 10, 1991	
Upstream	Downstream	Upstream	Downstream
0.003	0.004	0.0017	0.0015

before the second injection trial. The system, described herein previously, for injecting iron into sediments was built and tested for the first time in the St. Marys River on July 10, 1991. The system had the capacity to treat a large area; three 45-gallon barrels of ferric chloride were injected in less than an hour over an area 90 m by 12 m. The equipment was tough in that it survived bouncing over logs and other debris. In spite of minor engineering problems, the equipment worked well. The colour of the iron in the sediment cores indicated that the top 9 cm of sediments were treated. Refinements in the pumping equipment were needed before larger areas could be treated. The chemical pump required an air compressor and only large ones were available from rental agencies. A compact Honda air compressor was bought to provide more free deck space. The pore size of the nozzles was large; to pressurize the manifold to achieve equal flow through all nozzles, the flow rate of ferric chloride was higher than planned.

Divers recorded with cameras that the sediments were not resuspended into the water column. A pressure wave proceeding the injection bar raised the sediments about 20 cm, but they fell back with minimal resuspension to the upper waters. Sediment trap analysis confirms that no sediment moved to the water surface (Table 6). A large amount of gas reached the surface and small patches of oily film formed. Some macrophytes (primarily Elodea canadensis) were broken by the injection bar, but most remained intact. The sediments need to be studied in more detail but the ATP-TOX bioassay indicated a reduction in acute toxicity after the ferric chloride treatment (Figure 9).

On October 6, a second ferric chloride injection was done north of the first site to an area 200 m by 36 m. Smaller nozzles (0.031 inch diameter orifice) were used to maintain a high back pressure in the injection manifold and a constant flow through all the nozzles. The skids on the injection bar were not used so that the injection bar could penetrate deeper into the sediments. Visual observations indicated that the surface 15 cm

of sediments were treated. Observations that with the boom configuration, the boat could not move faster than 0.5 m/s or the injection manifold would rise above the sediments.

5 **EXAMPLE 2 - CALCIUM NITRATE INJECTION**

Calcium nitrate is about 100,000 times more water soluble than oxygen. The following reaction is mediated by bacteria:



10

Surface sediments (1-50 cm) from the St. Marys River were collected near Bellevue Park as illustrated in Figure 6. Surface sediments (0-15 cm) were collected from the deep basin of Hamilton Harbour as illustrated in Figure 19. Sediments were collected with either a Shipek dredge, or a Tech Ops corer. In Hamilton, samples were returned to NWRI and placed in either a fridge or 12°C incubator. In Sault Ste. Marie, samples were quickly placed in a cooler and stored in a fridge in the Great Lakes Forestry Institute. Samples were always placed in coolers and shipped quickly. Sediment cores were subdivided within 24 h. Sediment samples were placed in clean pails with lids and enough sediment was added to exclude air. Sample processing for bioassays included homogenization with larger mixer and subsequent handling in a glove box in a fumehood. Sampling of reactors was done in a glovebox after purging it with nitrogen.

25

Various bottles were tried. The first trials used 300 mL BOD bottles to incubate and measure microbial utilization of nitrate. Each sample was unique in that after opening the top, the sample was not reincubated. The microbial metabolism incubations were run using 300 mL BOD bottles with and without 100 mg N/L of calcium nitrate. The short-term experiments were successful, but the production of gas ruined longer incubations by popping the lids. Both 155 mL and 250 mL septum fitted bottles were used in subsequent trials for incubations with 500 mg/L N-NO₃. Biodegradation experiments were run in 155 mL glass bottles with serum caps and a 20 mL nitrogen headspace, with and

30

35

without 500 mg/L N calcium nitrate. The nitrogen headspace was sampled with gas tight syringes after relatively short-term incubations (2-6 weeks).

5 For all incubations, the sediments from the St. Marys River were mixed with deoxygenated water from St. Marys River and the Hamilton Harbour sediments were mixed with dechlorinated deoxygenated Burlington City water to form a 50% slurry. All the above sediments were shaken continuously on an end-over-end
10 shaker. In one trial to measure the production of ammonia, 2 L jars were used for incubations with 500 mg/L N-NO₃; these sediments were shaken once a day (except some weekends).

15 The sediment slurry was centrifuged and the supernatant was filtered and processed using an ion chromatograph to determine nitrate and sulphate concentrations. The pH of samples was measured with a pH meter. Ammonia was analyzed by colorimetric analysis (Solorzano 1969).

20 Volatile organic compounds in the headspace were measured by GC/MS in the Waste Water Treatment Centre (WTC) laboratory (Brian MacGillivray). Each assay was processed with five replicate bottle incubations and the headspace subsamples were combined. For one experiment two sets of five replicates were
25 processed to determine the analytical error; it was insignificant. Sediment samples for hydrogen sulphide analyses were frozen and delivered to Guelph Chemical Laboratories. These samples were purged with helium without any pH treatment; the hydrogen sulphide was trapped in a cold trap and injected for
30 analysis into a GC/MS.

"Oil and grease and total petroleum hydrocarbons" was measured with a derivative of the Environment Canada (1979) protocol. "Total petroleum hydrocarbon" was measured by a gas
35 chromatography method. Sodium sulphate was used to dry the samples. Dichloromethane was used to extract the samples with

10 cycles/h in a Soxhlet extractor for 8 h with a water bath at 25°C.

5 Photobacterium bioassays were run on whole sediments (Brouwer et al. 1990). Dilutions for LC₅₀ analysis were done with clean sediments from Long Point, Lake Erie.

Results

Enhancement of Microbial Metabolism

10 St. Marys River Sediments.

15 The initial laboratory reactor experiments have been successful in stimulating microbial metabolism in St. Marys River sediments with calcium nitrate. The microbial denitrification of nitrate was coupled to the rapid production of sulphate, this is illustrated in Figures 20 and 21. The production of sulphate reflects the microbial oxidation of organic sulphur, hydrogen sulphide, and perhaps elemental sulphur. The 100 mg/L N-NO₃ dose was completely denitrified (Fig. 20). The next experiment with 500 mg/L N-NO₃ resulted in incomplete denitrification of the added nitrate (Fig. 21). This sample was collected in late fall; the longer lag phase in the second experiment probably indicates that the microbes were inactive and needed more time to produce enzymes.

25 After two weeks of incubation, sediments treated with 500 mg/L N-NO₃ were given to Dr. Reynoldson (NWRI) for bioassays. They were toxic to Hexagenia. Based upon results from the second experiment (Fig. 22), these sediments had a high concentration of nitrate (>300 mg/L N-NO₃). Either the nitrate caused osmotic shock or the intense production of nitrogen gas disrupted their intestines. This experiment needs to be redone with less calcium nitrate. There would be no similar negative response in situ because no benthos would be living in sediments requiring treatment. However, this experiment does illustrate the need to balance the treatment dose to the biological oxygen demand of the sediments.

In another trial using larger containers (2 L) without continuous shaking, the utilization of nitrate was slightly slower than in Figs. 21 and 22). Since these incubations used 50% slurries, these incubations indicate that the optimal in situ does is about 350 mg/L N-NO₃. Very little ammonia was produced during these incubations (Figs. 23-24). Other short-term trials indicated that phosphorus was not limiting microbial denitrification, that addition of iron did not suppress denitrification, and that the pH did not decrease significantly. For short-term incubations, nutrients did not appear to limit microbial metabolism and pH buffering was not required.

In one year long incubations with sediments from the St. Marys River, nitrate treatment resulted in biodegradation of about 60% of the polynuclear aromatic hydrocarbons (PAHs, Figure 25). The numbers in Figure 25 refer to the molecular weight of the 16 priority pollutant polynuclear aromatic hydrocarbons. Note that the larger molecular weight compounds that can induce tumours are biodegraded as well as the smaller compounds. This observation is inconsistent with radioisotope studies done in our laboratory and in other laboratories. Smaller radiolabelled PAHs can biodegrade very quickly (within weeks). As observed in the Hamilton harbour studies, the conclusion is that very large PAHs that are too large to measure with available technology are biodegrading to produce measurable PAHs which continue to biodegrade. The rate limiting step on the treatment is the biodegradation of the large PAHs and the treated sites will require about two years for effective PAH treatment.

Hamilton Harbour

The rate of denitrification in a sediment sample from the deep basin of Hamilton Harbour was slightly slower than in a sample from the St. Marys River (Bellevue site), and much slower than in a sample from the Stelco Hotspot (Fig. 26). In the sample from the deep basin of Hamilton Harbour, the denitrification resulted in the complete elimination of toxicity to Photobacterium (Fig. 27). The incubated sample from this

Stelco Hotspot had residual hydrogen sulphide and toxicity persisted. More nitrate has been added to the Stelco Hotspot incubation and analysis will be replaced after a further six week incubation.

5

10 The oxidation of the deep basin sediments is more obvious than other sediments. These sediments were black at the start of the incubations, the control samples remained black, but the calcium nitrate treated samples turned brown. The sediments from the St. Marys River were not as black, but in long incubations (three months), the control samples turned black and the calcium nitrate samples stayed brown. The colour change reflects the change in the oxidation state of iron.

15 Another simple physical change also occurs during treatments. The control samples are very flocculant and these sediments stay in suspension for days. The treated sediments are not flocculant; these sediments precipitate within three hours after shaking. The treatments must polymerize negatively charged
20 organic colloids. This flocculation could be very useful. Colloids can contain high concentrations of contaminants and their resuspension in dredging can create problems.

25 In general, the NWRI studies are consistent with published demonstrations of biodegradation but the processes are complex and this study is not complete. Simple analyses of "oil and grease" indicate about 50% biodegradation of the organic contamination. However, "total petroleum hydrocarbon" analysis
30 indicate about 90% biodegradation of organic contamination. Some of the discrepancy is likely caused by the microbial conversion of organic contaminants into organic compounds in living cells.

35 The PAH data from headspace analysis is complex but highly encouraging. Headspace analysis of some samples indicates biodegradation of butenes, chlorobenzenes, toluene, benzene, and naphthalene at rates consistent with other studies. Other analyses indicate production of several compounds, indicating

Table 7 PAHs in solids after chemical treatment

Hamilton Harbour and Sault Ste. Marie Biodegradation study Fall 1991										
SEDIMENT ug/g	Hamilton Harbour		Hamilton Harbour		Hamilton Harbour		Sault Ste. Marie control		Sault Ste. Marie FeCl3	
	control	FeCl3	FeCl3	NO3	control	NO3	control	NO3	FeCl3	NO3
NAPHTHALENE	0.77	0.96	0.96	0.90	4.14	0.90	4.14	2.37	4.51	4.51
ACENAPHTHYLENE	0.19	0.27	0.27	0.23	0.26	0.23	0.26	0.18	0.23	0.23
ACENAPHTHENE	0.21	0.26	0.26	0.25	0.41	0.25	0.41	0.28	0.37	0.37
FLUORENE	0.50	0.67	0.67	0.52	0.64	0.52	0.64	0.45	0.56	0.56
PHENANTHRENE	3.36	4.59	4.59	4.24	4.45	4.24	4.45	3.09	4.00	4.00
ANTHRACENE	0.70	1.00	1.00	1.01	1.31	1.01	1.31	0.93	1.08	1.08
FLUORANTHENE	5.84	7.85	7.85	7.25	10.13	7.25	10.13	7.17	9.46	9.46
PYRENE	4.05	6.70	6.70	6.24	8.44	6.24	8.44	5.97	7.90	7.90
BENZ[a]ANTHRACENE	2.90	1.52	1.52	3.50	5.60	3.50	5.60	4.23	5.38	5.38
CHRYSENE	4.39	5.78	5.78	5.28	7.89	5.28	7.89	5.60	7.66	7.66
BENZO[b]FLUORANTHENE	4.92	6.05	6.05	2.77	6.38	2.77	6.38	3.76	6.68	6.68
BENZO[k]FLUORANTHENE	4.00	4.93	4.93	4.19	5.17	4.19	5.17	3.71	5.43	5.43
BENZO[a]PYRENE	1.00	5.60	5.60	7.43	7.02	7.43	7.02	6.45	7.30	7.30
INDENO[1,2,3-cd]PYRENE	3.31	1.85	1.85	0.22	2.44	0.22	2.44	0.74	3.13	3.13
DIBENZ[a,h]ANTHRACENE	1.38	1.25	1.25	0.17	1.04	0.17	1.04	0.14	1.55	1.55
BENZO[g,h,i]PERYLENE	3.23	2.15	2.15	0.96	2.64	0.96	2.64	0.88	3.22	3.22
TOTAL	40.75	51.43	51.43	45.16	67.94	45.16	67.94	45.95	68.47	68.47
RETENE	0.20	0.12	0.12	0.15	24.79	0.15	24.79	18.96	23.32	23.32

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Table 8 PAHs in water after chemical treatments

Hamilton Harbour and Sault Ste. Marie Biodegradation study Fall 1991										
SUPERNATANT ng/l	Hamilton Harbour		Hamilton Harbour		Hamilton Harbour		Sault Ste. Marie control		Sault Ste. Marie FeCl3	
	control	FeCl3	FeCl3	NO3	NO3	NO3	control	FeCl3	FeCl3	NO3
NAPHTHALENE	410.70	205.29	205.29	43.20	43.20	178.65	178.65	2076.06	1963.06	0.04
ACENAPHTHYLENE	145.07	79.12	79.12	8.40	8.40	20.00	20.00	35.76	33.89	nd
ACENAPHTHENE	247.89	71.76	71.76	nd	nd	252.16	252.16	210.61	305.28	nd
FLUORENE	301.13	155.29	155.29	28.00	28.00	178.11	178.11	274.55	256.39	nd
PHENANTHRENE	1415.49	659.71	659.71	344.40	344.40	616.22	616.22	814.30	848.31	0.03
ANTHRACENE	58.28	617.26	617.26	nd	nd	52.43	52.43	52.91	76.11	nd
FLUORANTHENE	790.99	365.88	365.88	434.08	434.08	635.57	635.57	719.52	854.81	0.02
PYRENE	444.79	99.12	99.12	109.64	109.64	413.78	413.78	332.48	467.81	0.01
BENZ[a]ANTHRACENE	45.92	16.76	16.76	22.00	22.00	78.57	78.57	45.03	85.53	0.01
CHRYSENE	108.73	61.21	61.21	84.48	84.48	147.22	147.22	93.70	164.53	0.01
BENZO[b]FLUORANTHENE	113.49	69.68	69.68	56.56	56.56	88.54	88.54	87.97	141.50	0.02
BENZO[k]FLUORANTHENE	44.76	27.47	27.47	29.76	29.76	64.95	64.95	34.70	55.81	0.01
BENZO[a]PYRENE	70.14	48.53	48.53	19.72	19.72	17.30	17.30	69.42	55.28	0.01
INDENO[1,2,3-cd]PYRENE	44.25	nd	nd	51.32	51.32	nd	nd	36.52	11.81	nd
DIBENZ[a,h]ANTHRACENE	28.68	nd	nd	7.40	7.40	nd	nd	11.00	nd	nd
BENZO[g,h,i]PERYLENE	41.69	nd	nd	22.00	22.00	nd	nd	10.18	15.00	nd
TOTAL	4312.00	2477.09	2477.09	1260.96	1260.96	2743.49	2743.49	4904.70	5335.08	0.16
RETENE	69.30	nd	nd	0.92	0.92	582.43	582.43	267.27	85.64	0.13

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cleavage of smaller molecular weight compounds from larger compounds. There are about 30 analyses as complex as Figure 28. Further synthesis is required to resolve the complexities. Note that the analyses were replicated and the analytical error was insignificant.

The PAH analysis of the solids remaining after six weeks incubation with or without calcium nitrate indicated no significant biodegradation of naphthalene or other PAHs (Table 7). Analytically, the discrepancy with headspace analysis is possible in that the headspace represents only a small fraction of the total PAHs. The headspace is in equilibrium with free, unbound, bioavailable compounds, but the particulate PAH analysis is done on samples extracted vigorously with dichloromethane in a Soxhlet apparatus. There are two hypotheses that can resolve the PAH data sets. 1) Some small compounds were being cleaved from larger compounds at similar rates that microbes were biodegrading these smaller organic compounds. 2) Only a small fraction of the PAHs are biodegradable.

Both hypotheses could be valid. Only a fraction of the total PAHs are analyzed in the routine 16 priority PAHs, no analytical techniques exist for very large molecular weight PAHs. Also for both sites there must be some PAHs locked in coal dust or other biologically inactive matrices. The interpretation would also vary between sites. For example, the proportion of PAHs in the aqueous phase in the St. Marys River incubations indicates enhanced production of naphthalene from larger compounds after the treatments (Table 8). In the aqueous phase of Hamilton Harbour incubations, the treatments appear to enhance biodegradation of naphthalene (Table 8). The uncertainties of PAH biodegradation have been resolved with longer incubations, and incubations with ^{14}C -radioactively labelled naphthalene.

Pilot-scale treatments also support the laboratory incubations. The addition of calcium nitrate to the sediments of the Dofasco Boatslip in 1992 resulted in the 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%) (Figure 29). These relatively rapid biodegradation rates are similar to those reported in laboratory studies where nitrate was added to enhance biodegradation (Hutchins 1991).

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

The biodegradation of the PAHs (polynuclear aromatic hydrocarbons), in the Dofasco boatslip was more complex. About 15% (450 $\mu\text{g/g}$, to 383 $\mu\text{g/g}$ mean of 3 samples) of 15 PAHs were biodegraded and in the process the naphthalene content increased 196% (280 $\mu\text{g/g}$ to 549 $\mu\text{g/g}$, mean of 3 samples). 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.

At first the ability of microbes to biodegrade organic wastes seemed less probable in Hamilton Harbour sediments than in sediments from the St. Marys River. Hamilton Harbour sediments have 10-100 times the concentration of metals. However, the rate of headspace naphthalene biodegradation is similar in sediments from Hamilton Harbour, St. Marys River, and samples from other sites (Heitkamp and Cerniglia 1987). Furthermore, the rates of denitrification in the St. Marys River sediments, Hamilton Harbour, and other sites in Germany (Ripl 1986) are similar. At these sites, metals do not appear to suppress microbial biodegradation. This is important in that many of the volatile organic compounds that were detected in the Hamilton Harbour Hotspot (Table 9) are biodegradable.

DISCUSSION

The oxidation of toxic hydrogen sulphide eliminates most of the acute toxicity from Hamilton Harbour and St. Marys River sediments (Murphy et al. 1992). The extreme anoxia reflected by high concentrations of hydrogen sulphide inhibits microbial biodegradation. In headspace analysis, some simple compounds like butene, naphthalene, and toluene appear to be biodegraded within weeks of nitrate addition. The biodegradation of larger non-volatile organic contaminants such as benzo(a)pyrene will be slower, albeit the published rates vary greatly. Heitkamp and Cerniglia (1987) found that naphthalene, pyrene and benzo(a)pyrene would degrade with half-lives 1.4-4.4 weeks, 38-90 weeks and 200-300 weeks, respectively. Shiaris (1989) found biodegradation turnover times of 13.2-20.1 days, 7.9-19.8 days, and 53.7-82.3 days for naphthalene, phenanthrene, and benzo(a)pyrene, respectively. Ongoing long-term bioassays in NWRI will help resolve the biodegradation of larger compounds like benzo(a)pyrene. The optimal study, however, would be the monitoring of pilot-scale applications of calcium nitrate to the sediments of as many sites as possible. Each site will be slightly different and new insights will develop from each treatment.

COMPARISON WITH FERRIC CHLORIDE TREATMENT

Because of the engineering success of the related experiments done by NWRI (Murphy et al. 1992), the calcium nitrate treatments have quickly become pilot-scale treatments. Both ferric chloride and calcium nitrate are oxidants. Ferric chloride is a weaker oxidant, albeit its reactions with metals and hydrogen sulphide are more direct and potentially useful. To achieve the equivalent oxidation potential of a 0.5% solution of calcium nitrate would require that the sediments become a 10% ferric chloride solution. This latter scenario would produce a toxic low pH that would require extensive buffering with lime. Moreover, calcium nitrate is less corrosive to equipment than ferric chloride. The chemical cost of treating the surface 15 cm of sediments with 500 mg/L N-NO₃ would cost \$2,000 to \$10,000 a hectare. The range of costs reflects the chemical oxygen. The

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Table 9

STELCO HOTSPOT SEDIMENT
ANALYSIS BY PURGE AND TRAP GC/MS

PARAMETER	ng/ml
1,1-dichloroethylene	659.2
dichloromethane	14.3
trans-1,2-dichloroethylene	11.3
1,1-dichloroethane	97.2
cis-1,2-dichloroethylene	0.0
chloroform	13.0
1,1,1-trichloroethane	0.0
tetrachloromethane	0.0
1,2-dichloroethane	18.1
benzene	831.2
trichloroethylene	0.0
1,2-dichloropropane	0.0
dibromomethane	0.0
bromodichloromethane	0.0
toluene	596.8
1,1,2-trichloroethane	0.0
tetrachloroethylene	21.6
chlorodibromomethane	0.0
1,2-dibromoethane	0.0
chlorobenzene	0.0
ethylbenzene	1348.8
m/p-xylene	3002.0
o-xylene	1225.2
styrene	274.3
cumene (isopropylbenzene)	119.3
bromoform	0.0
1,1,2,2-tetrachloroethane	5.9
propylbenzene	112.9
1,3,5-trimethylbenzene	150.8
1,2,4-trimethylbenzene	14.1
3-ethyltoluene	1050.0
4-ethyltoluene	1247.2
2-ethyltoluene	1598.0
1,3-dichlorobenzene	10.3
1,4-dichlorobenzene	0.0
1,2-dichlorobenzene	0.0
1,4-diethylbenzene	191.7
1,2-diethylbenzene	9.3
1,3-diethylbenzene	191.7
naphthalene	35920.0
hydrogen sulphide	100000.0

Table 10

CHLORINATED PHENOLS IN ST. MARYS RIVER
SEDIMENT CORE - JULY 8, 1991

SAMPLE ID (CORE DEPTH - cm)	0-1	6-7	12-14	14-16	16-18	22-24
Chlorinated Phenols (ug/kg) Dry Weight						
ortho-Chloro-phenol	*	*	*	*	*	*
meta-Chloro-phenol	*	*	*	*	*	*
para-Chloro-phenol	*	*	*	*	*	*
2,6-Chloro-phenol	ND	ND	ND	ND	ND	ND
2,4-Chloro-phenol	ND	ND	ND	ND	ND	ND
3,5-Chloro-phenol	ND	ND	ND	ND	ND	ND
2,3-Chloro-phenol	ND	ND	ND	ND	ND	ND
3,4-Chloro-phenol	ND	ND	ND	ND	ND	ND
2,4,6-Chloro-phenol	ND	ND	ND	ND	ND	ND
2,3,6-Chloro-phenol	ND	ND	ND	ND	ND	ND
2,3,5-Chloro-phenol	ND	ND	ND	ND	ND	ND
2,4,5-Chloro-phenol	ND	ND	ND	ND	ND	ND
3,4,5-Chloro-phenol	ND	ND	ND	ND	ND	ND
2,3,5,6-Chloro-phenol	ND	ND	ND	ND	ND	ND
2,3,4,5-Chloro-phenol	ND	ND	ND	ND	ND	ND
Penta-Chloro-phenol	ND	ND	ND	ND	ND	ND
4-Chloro-guaiacol	*	*	*	*	*	*
4,6-Chloro-guaiacol	ND	ND	ND	ND	ND	ND
4,5-Chloro-guaiacol	ND	ND	ND	ND	ND	ND
3,4,5-Chloro-guaiacol	ND	ND	ND	ND	ND	ND
4,5,6-Chloro-guaiacol	ND	ND	ND	ND	ND	ND
3,4,5,6-Chloro-guaiacol	ND	ND	ND	ND	ND	ND
4-Chloro-catechol	*	*	*	*	*	*
3,5-Chloro-catechol**	ND	ND	ND	ND	ND	ND
2,3,4,6-Chlorophenol**						
4,5-Chloro-catechol	ND	ND	ND	ND	ND	ND
3,4,5-Chloro-catechol	ND	ND	ND	ND	ND	ND
3,4,5,6-Chloro-catechol	ND	ND	ND	ND	ND	ND
6-Chloro-vanillin	NA	NA	NA	NA	NA	NA
5,6-Chloro-vanillin	ND	ND	ND	ND	ND	ND
Tri-chloro-syringol	ND	ND	ND	ND	ND	ND
4,5 Di-chloro-veratrole	ND	ND	ND	ND	ND	ND
3,4,5 Tri-chloro-veratrole	ND	ND	ND	ND	ND	ND
Tetra-chloro-veratrole	ND	ND	ND	ND	ND	ND
GUGICOL	*	*	*	*	*	*
CATECOL	*	*	*	*	*	*

* analysis for these compounds to follow

** these compounds coelute

ND not detected

NA not applicable

sediments of the St. Marys River and deep basin of Hamilton Harbour require less than a third of the dose required for the Stelco Hotspot. With the 8 m injection boom and ideal conditions, about four hectares a day could be treated.

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The sediments of the St. Marys River appear to be easy to treat. The acute toxicity is caused by hydrogen sulphide and it is readily oxidized by denitrification of added calcium nitrate (Murphy et al. 1992). The oxidized sediments produce no toxicity to Daphnia magna, Hexagenia limbata, Escherichia coli, or Lactuca sativa. Many chlorinated compounds often associated with pulpmill wastes were not detected (Table 10). Benzenes are detectable in these sediments and although they are carcinogens, they are biodegradable.

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The concentration of PAHs is relatively low (Table 3; Murphy et al. 1992, Table 1). The concentration of PAHs is approximately at the apparent effects threshold - the concentration where you begin to see toxic effects on the ecosystem (Long and Morgan 1990). There is no evidence that the PAHs in the sediments at the Bellevue site are a problem. Chemical data, particularly threshold concentrations, must be used cautiously. The high concentration of organic matter found in the sediments of the St. Marys River could reduce the bioavailability of PAHs as has been found at other sites (Landrum et al. 1987). As well as conducting additional chemical analyses, the endpoint of the biodegradation should be determined with bioassays. The best bioassay would be the response of the benthos in treated sediments.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of effecting natural microbial biodegradation of polynuclear aromatic hydrocarbons and petroleum hydrocarbons in sediment containing microbes and polynuclear aromatic hydrocarbons and petroleum hydrocarbons, comprising the steps of:

providing a biochemical oxidant for detoxifying a microbial toxin produced during microbial biodegradation of said polynuclear aromatic hydrocarbons and petroleum hydrocarbons;

contacting said sediment with said oxidant to detoxify said toxin; and

effecting microbial biodegradation of said polynuclear aromatic hydrocarbons and petroleum hydrocarbons.

2. The method as defined in claim 1, wherein the contacting step is a reaction step.

3. The method as defined in claim 1, wherein said oxidant comprises an alkaline earth nitrate.

4. The method as defined in claim 1, wherein said alkaline earth nitrate comprises calcium nitrate.

5. The method as defined in claim 1, further including the step of nutrifying said microbes with nutrients.

6. A method of effecting natural microbial biodegradation of polynuclear aromatic hydrocarbons and petroleum hydrocarbons in sediment containing said polynuclear aromatic hydrocarbons and petroleum hydrocarbons and microbes, comprising the steps of:

providing a biochemical oxidant for oxidizing a biodegradation inhibitor produced during microbial biodegradation of said polynuclear aromatic hydrocarbons and petroleum hydrocarbons;

contacting said sediment with said oxidant;

oxidizing said inhibitor to a non-inhibiting form; and

effecting microbial biodegradation of said polynuclear aromatic hydrocarbons and petroleum hydrocarbons.

7. The method as defined in claim 6, wherein said method is a continuous method.

8. The method as defined in claim 7, wherein the step of contacting said sediment comprises injecting said sediment with said biochemical oxidant.

9. The method as defined in claim 8, wherein said sediment is injected in at least at two different depths in said sediment.

10. A method of effecting natural microbial biodegradation of polynuclear aromatic hydrocarbons and petroleum hydrocarbons in sediment containing said polynuclear aromatic hydrocarbons and petroleum hydrocarbons and microbes, comprising the steps of:

providing a biochemical oxidant for oxidizing a sulphide biodegradation inhibitor produced during microbial biodegradation;

providing a microbial nutrient for nutrifying said microbes; injecting said oxidant and said nutrients into said sediment;

oxidizing said sulphide to a non-inhibiting sulphate;

nutrifying said microbes; and

effecting said natural microbial biodegradation of said polynuclear aromatic hydrocarbons and petroleum hydrocarbons.

11. The method as defined in claim 10, wherein said method is a continuous method.

12. The method as defined in claim 11, wherein said sediment is injected in at least two different depths.

13. The method as defined in claim 12, wherein hydrogen sulphide is oxidized.

14. A method of effecting natural microbial biodegradation of polynuclear aromatic hydrocarbons in sediment containing said polynuclear aromatic hydrocarbons and microbes, comprising the steps of:

contacting said sediment in a first contacting step with said oxidant at a first level therein;

contacting said sediment in a second contacting step with said oxidant at least at a second level in said sediment, said second level being different from said first level; and

effecting said natural microbial biodegradation of said polynuclear aromatic hydrocarbons.

15. The method as defined in claim 14, wherein said first contacting step and said second contacting step are simultaneous.

16. The method as defined in claim 15, wherein said method is continuous.

17. Use of calcium nitrate as a biochemical oxidant in the method of claims 1, 10 or 14.

18. Use of ferric chloride as a biochemical oxidant in the method of claims 1, 10 or 14.

19. An apparatus suitable for treating sediment in a water body, said sediment containing chemical pollutants, comprising:
a first dispensing means adapted for dispensing a treatment compound into contact with said sediment to be treated at a first level;

a second dispensing means adapted for dispensing said treatment compound within said sediment at a second level;

each of said dispensing means having means for connection with a supply of said treatment compound; and

support means for supporting said first dispensing means and said second dispensing means.

20. The apparatus as claimed in claim 19, wherein said apparatus further includes mounting means for mounting said apparatus to a carrier vessel.

21. The apparatus as claimed in claim 20, wherein said first dispensing means comprises a plurality of connected spray bars for spraying said treatment into said sediment.

22. The apparatus as claimed in claim 21, wherein said second dispensing means includes a plurality of finger means for supporting said second dispensing means.

23. The apparatus as claimed in claim 22, wherein said finger means comprise arcuately shaped members for penetrating said sediment.

24. The apparatus as claimed in claim 23, wherein said dispensing means comprises nozzles.

25. An apparatus suitable for treating sediment in a water body, said sediment containing chemical pollutants, comprising in combination:

- a first dispensing arrangement for dispensing a treatment compound into said sediment at a first level;

- a second dispensing arrangement for dispensing said treatment compound into said sediment at a second level, each said dispensing arrangement having means for connection with a supply of said treatment compound;

- a support frame for connecting said first dispensing arrangement and said second dispensing arrangement; and

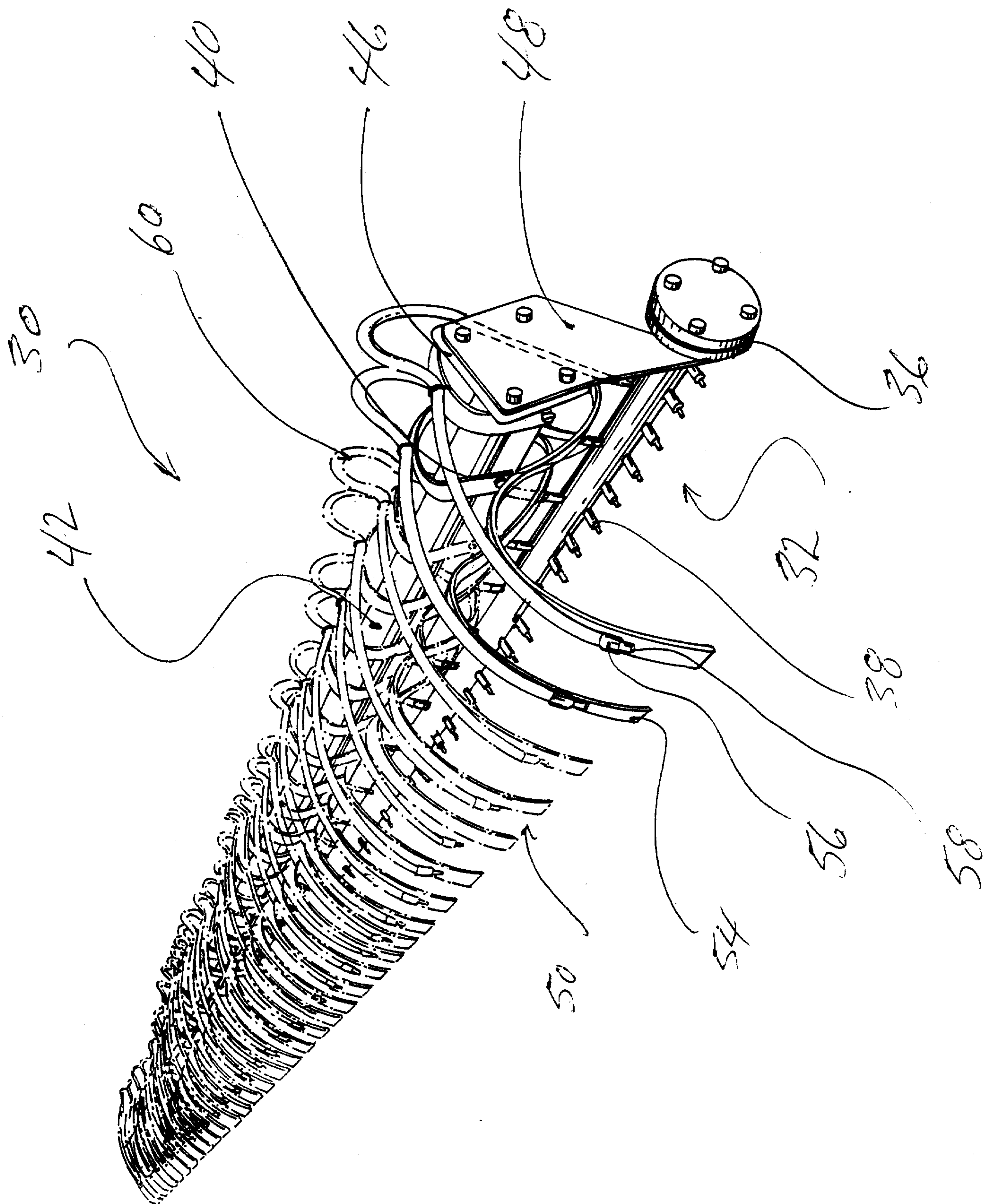
- a carrier vessel for said vessel including means for connection and manipulation of said support frame.

26. The apparatus as claimed in claim 25, wherein said first dispensing arrangement comprises an elongate spray bar.

27. The apparatus as claimed in claim 25, wherein said second dispensing arrangement includes a plurality of individual nozzles for dispensing said treatment compound.

28. The apparatus as claimed in claim 25, wherein said second dispensing arrangement further includes a plurality of fingers, each finger adapted to support and retain at least one nozzle.

29. The apparatus as claimed in claim 28, wherein said fingers comprise a resilient material.



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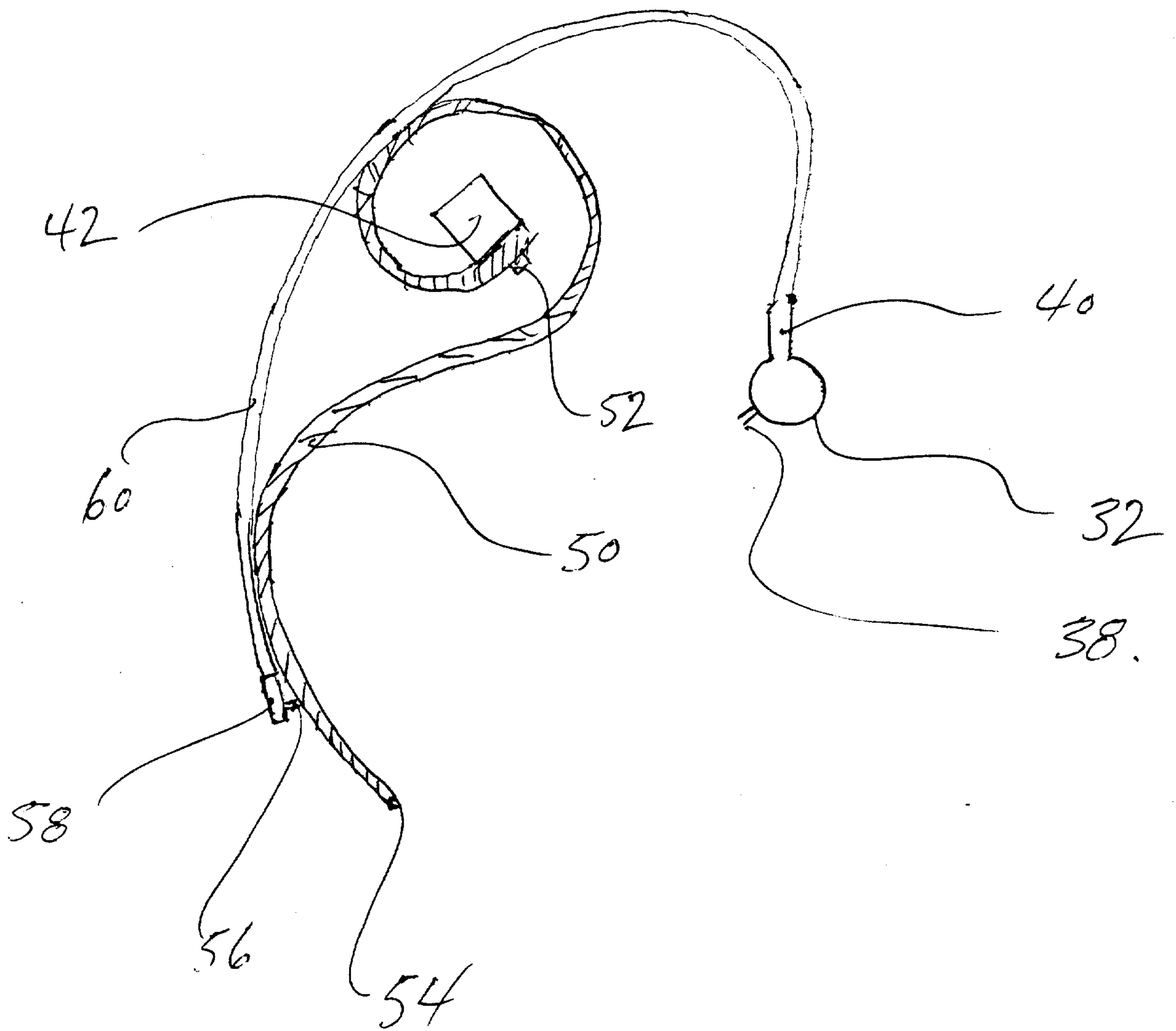
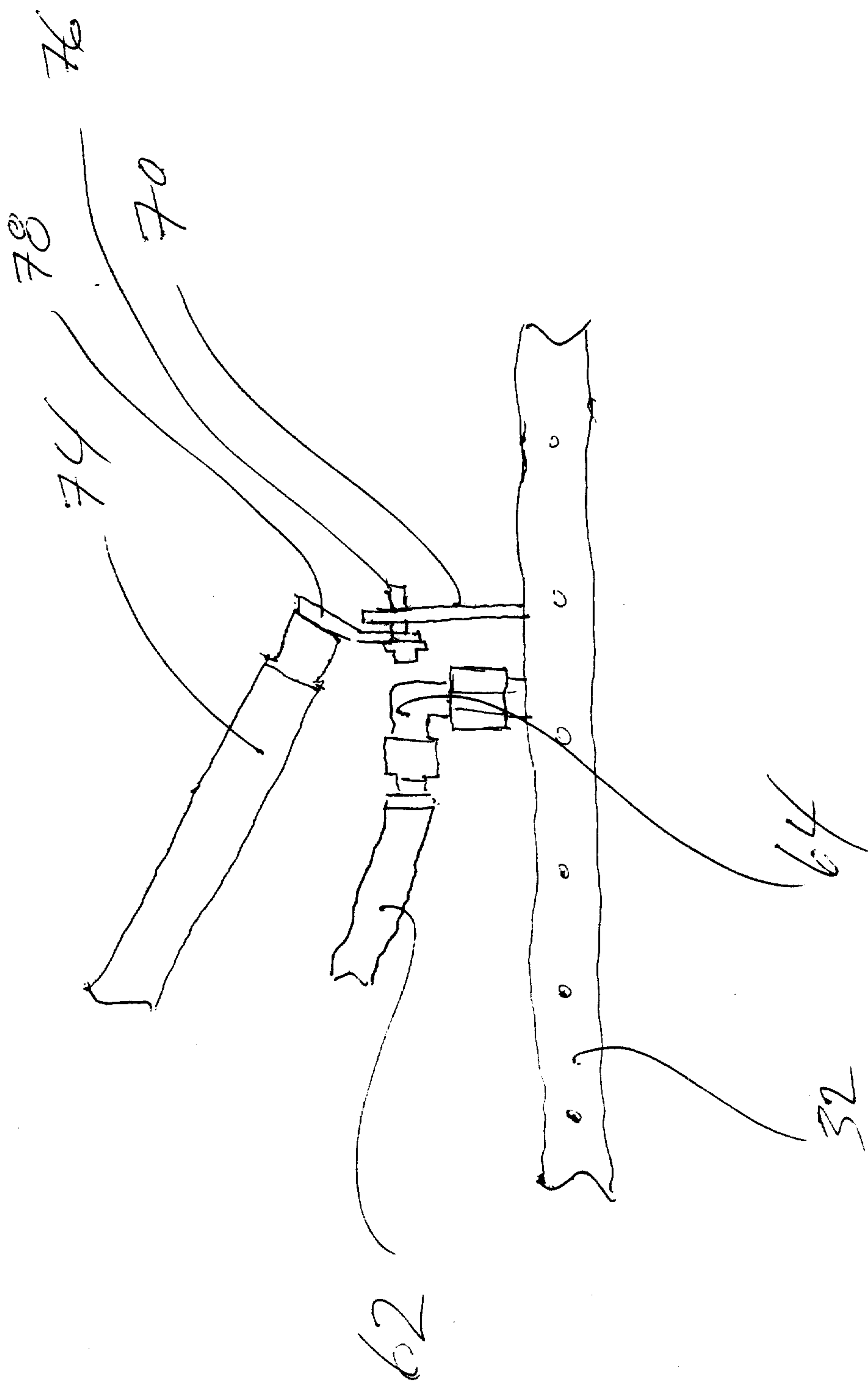
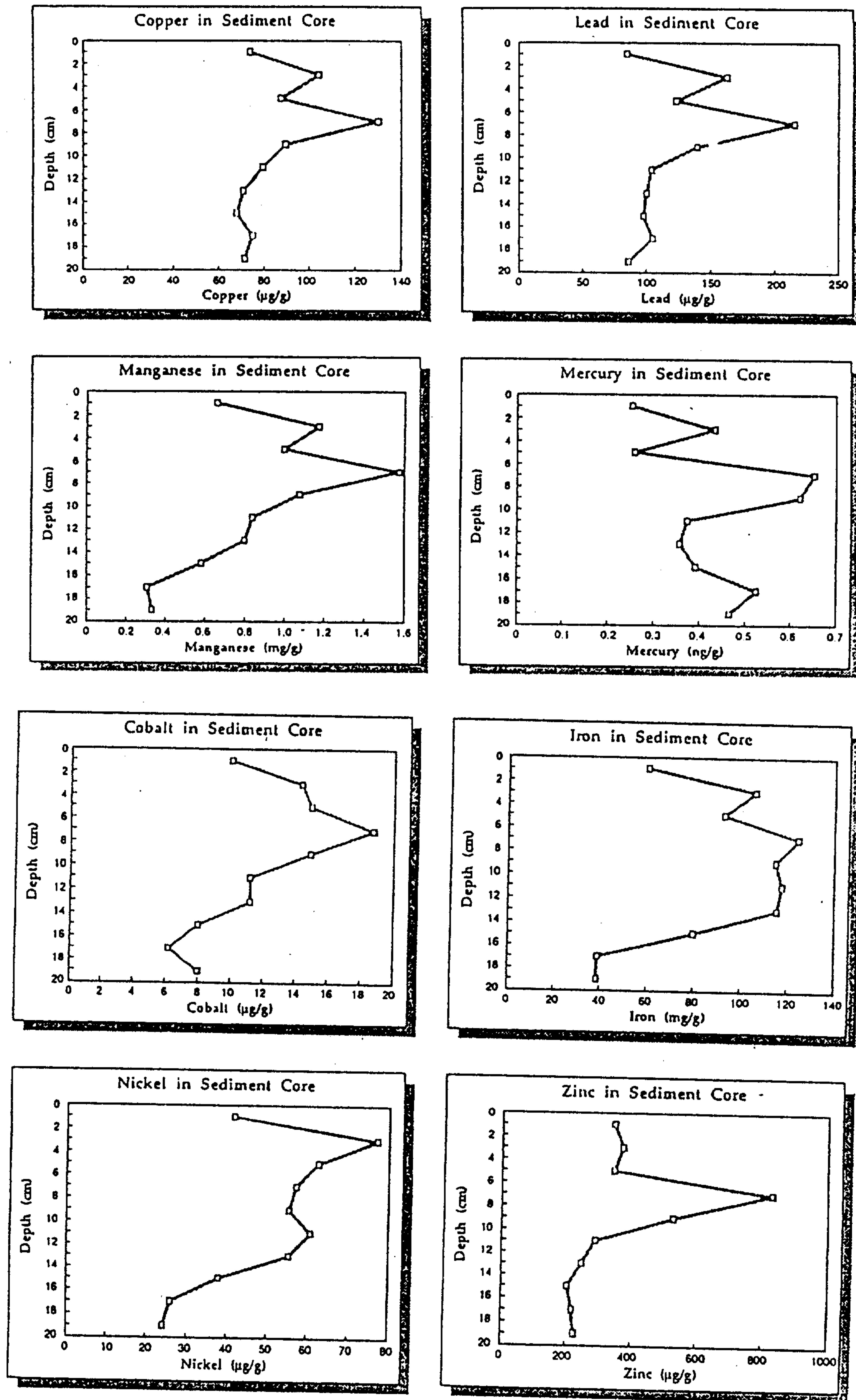


FIG. 3

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Fig. 4.





Redox Potential of St. Marys River Sediment Cores

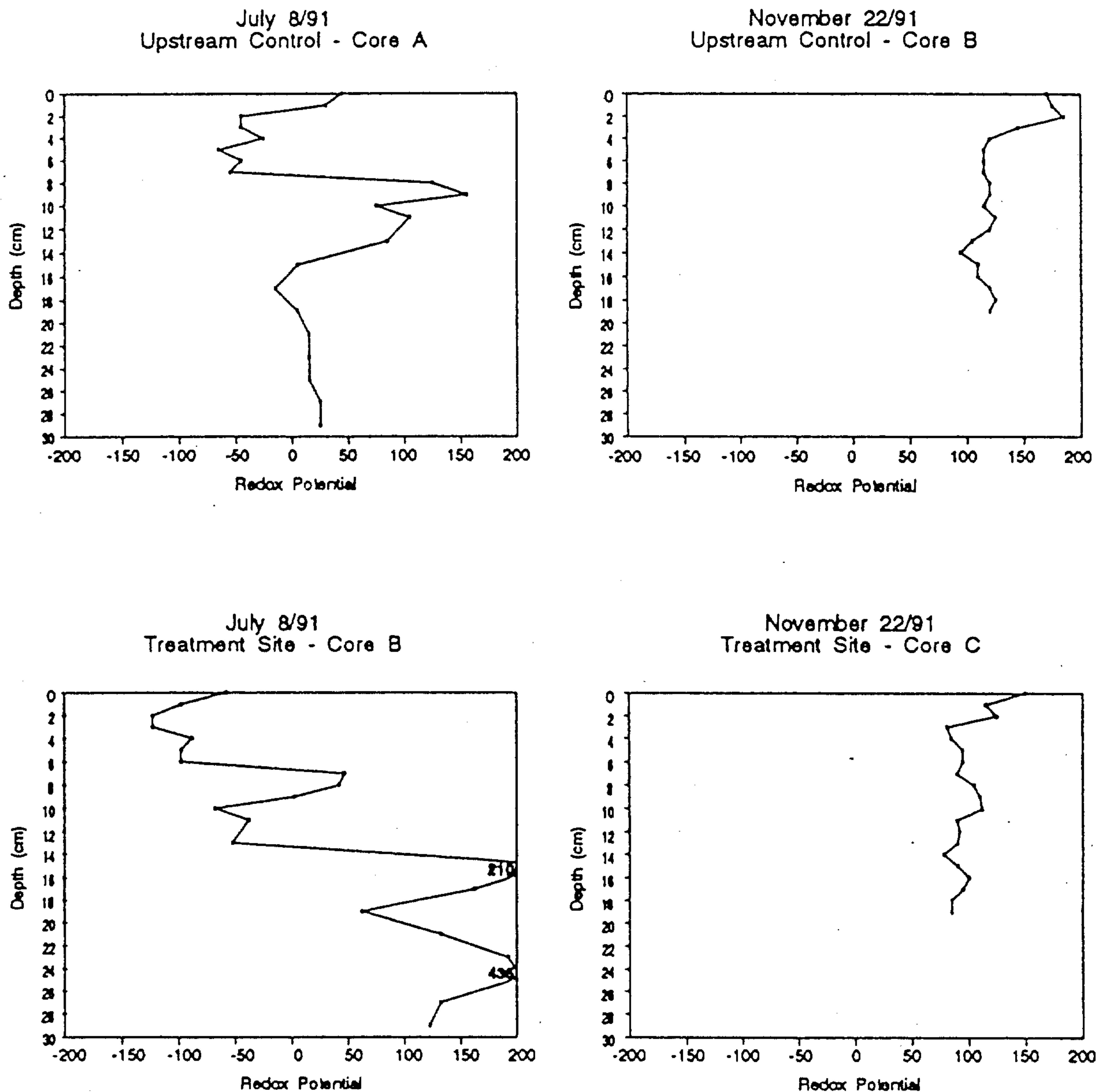


Fig. 7

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Figure 2c

Denitrification in St. Marys River Sediments

BOD bottle incubations

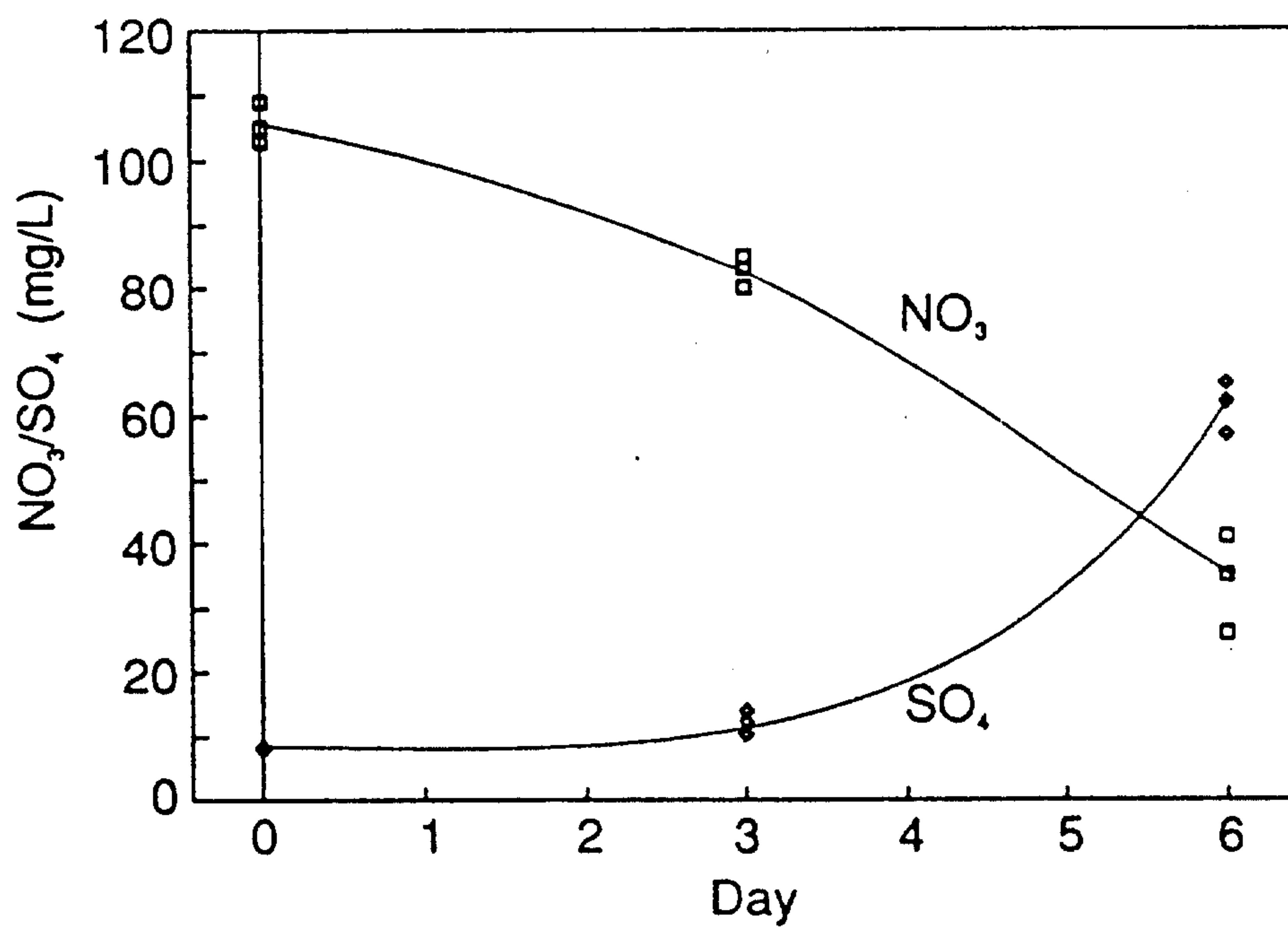


Figure 21 Denitrification in St. Marys
River Sediment- 250ml bottle incubations

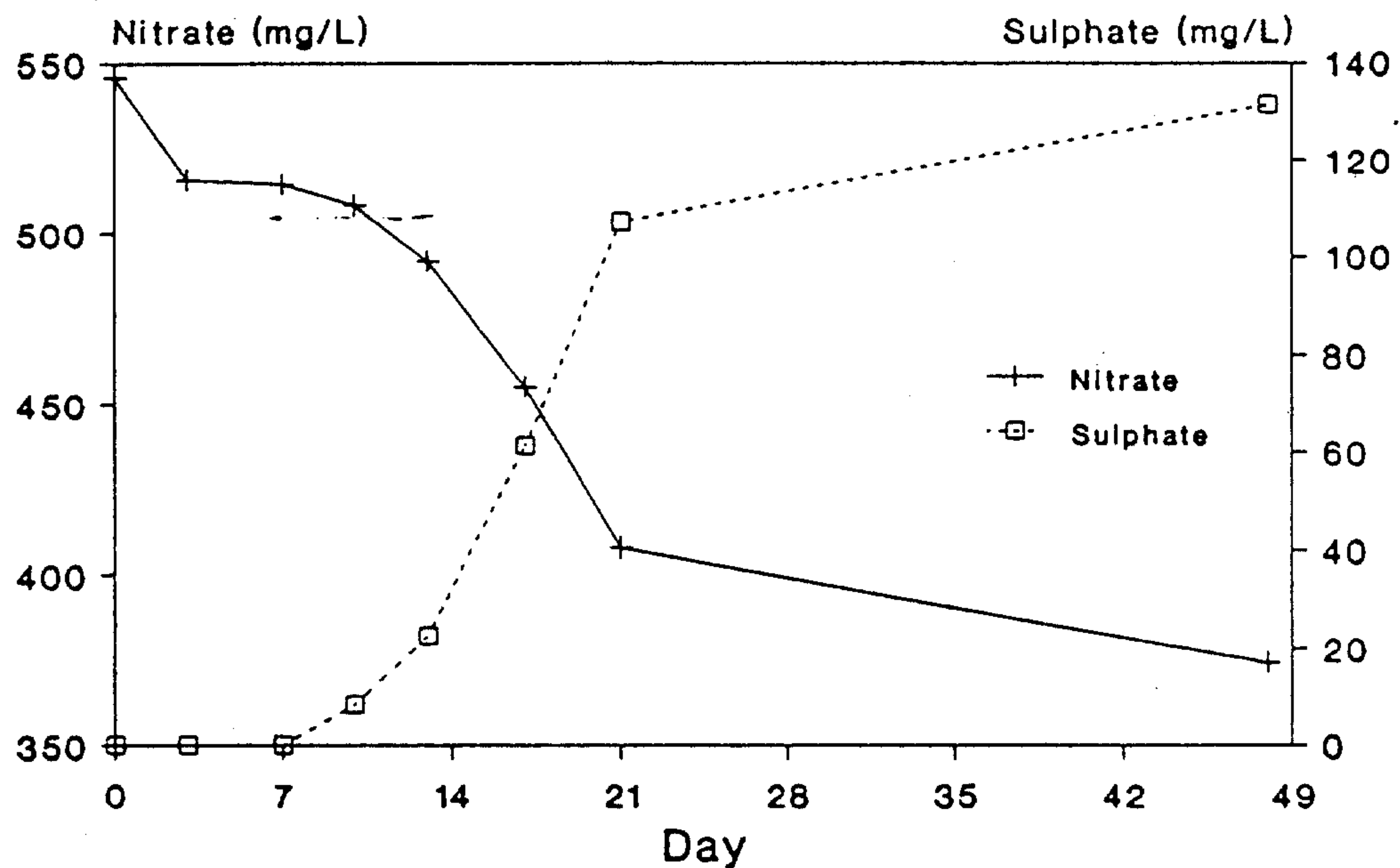


Figure 22 Denitrification in St. Marys
River Sediment - 2 L bottle incubations

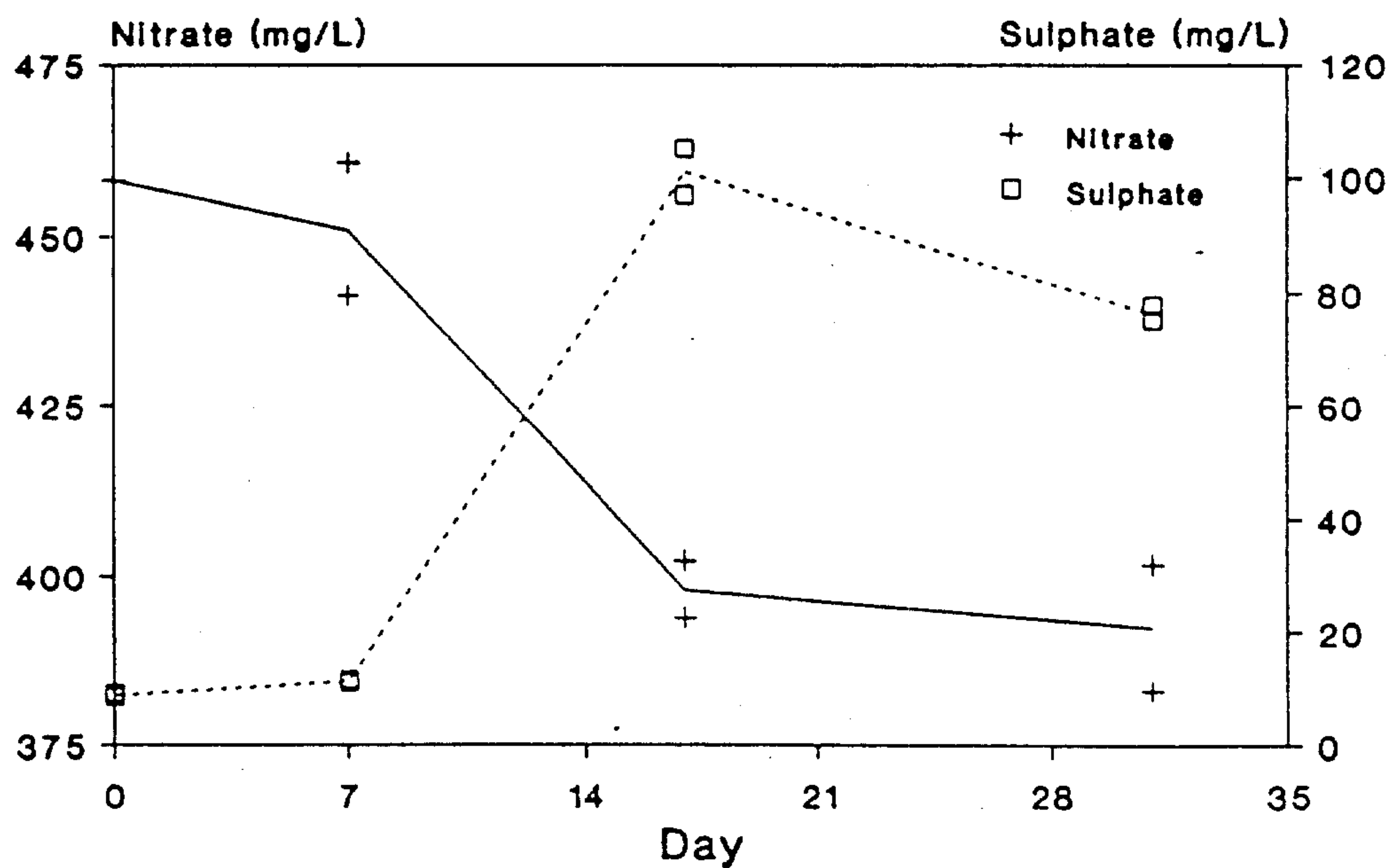


Figure 23 Denitrification of St. Marys River Sediment- 250ml bottle incubations

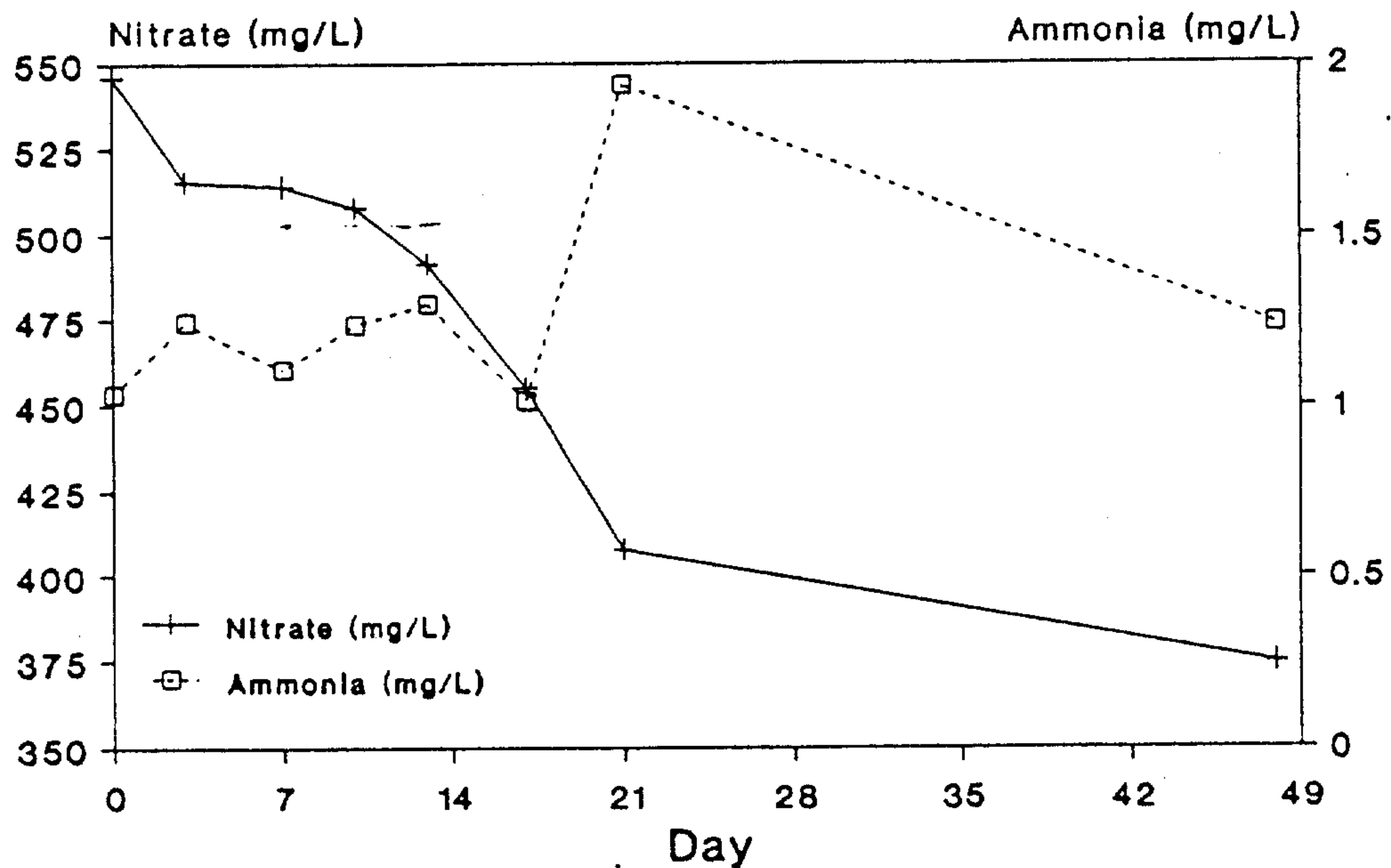
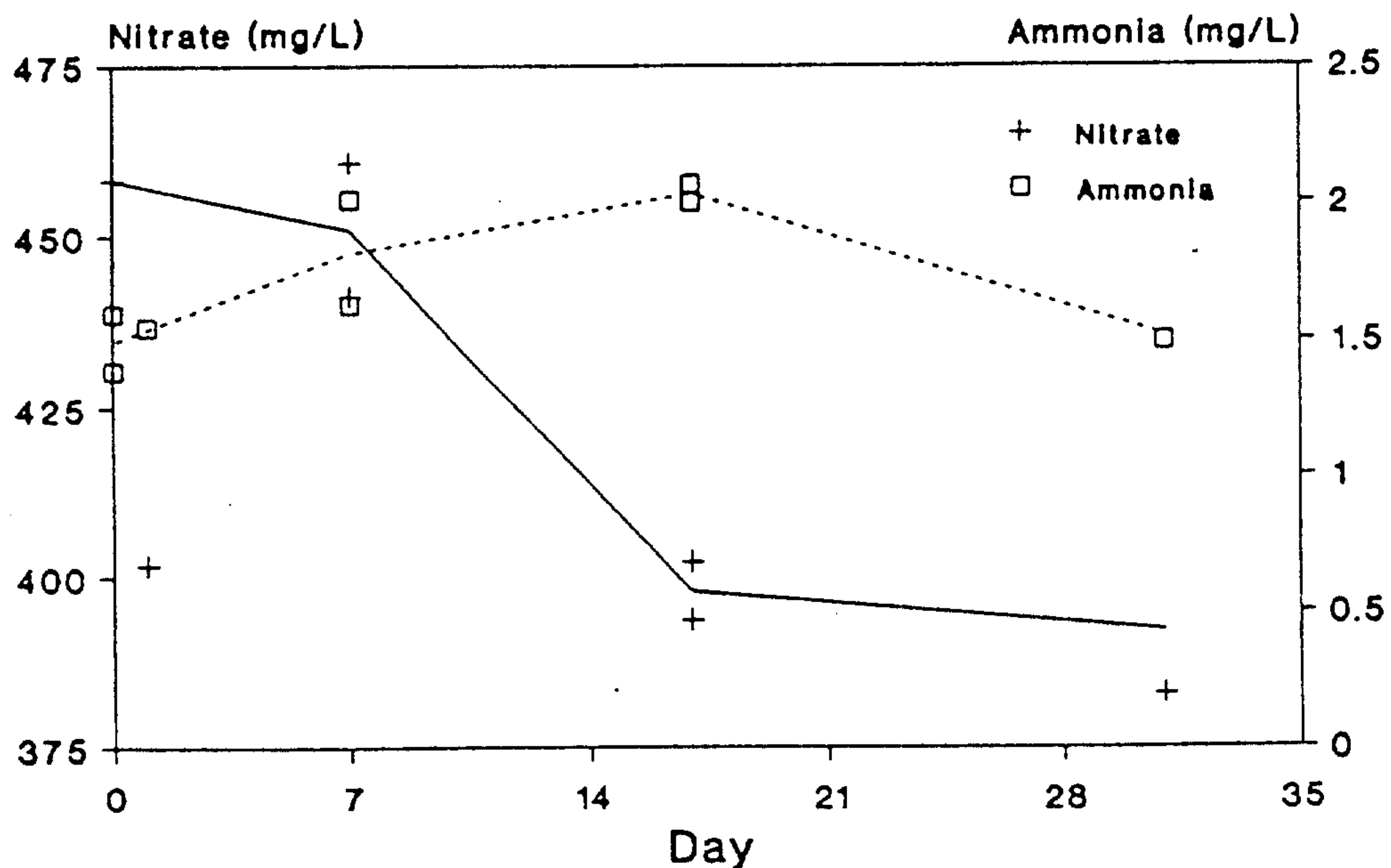


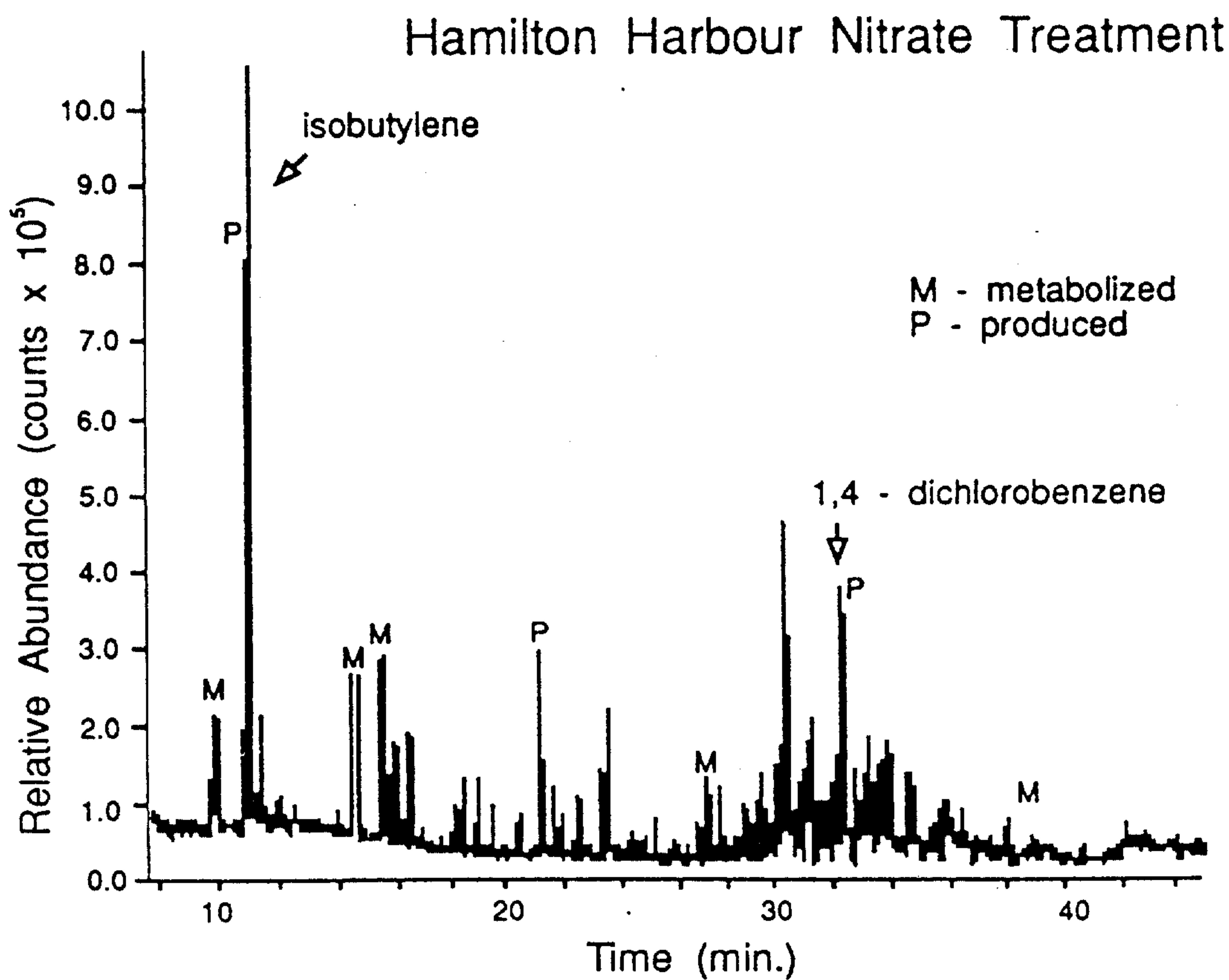
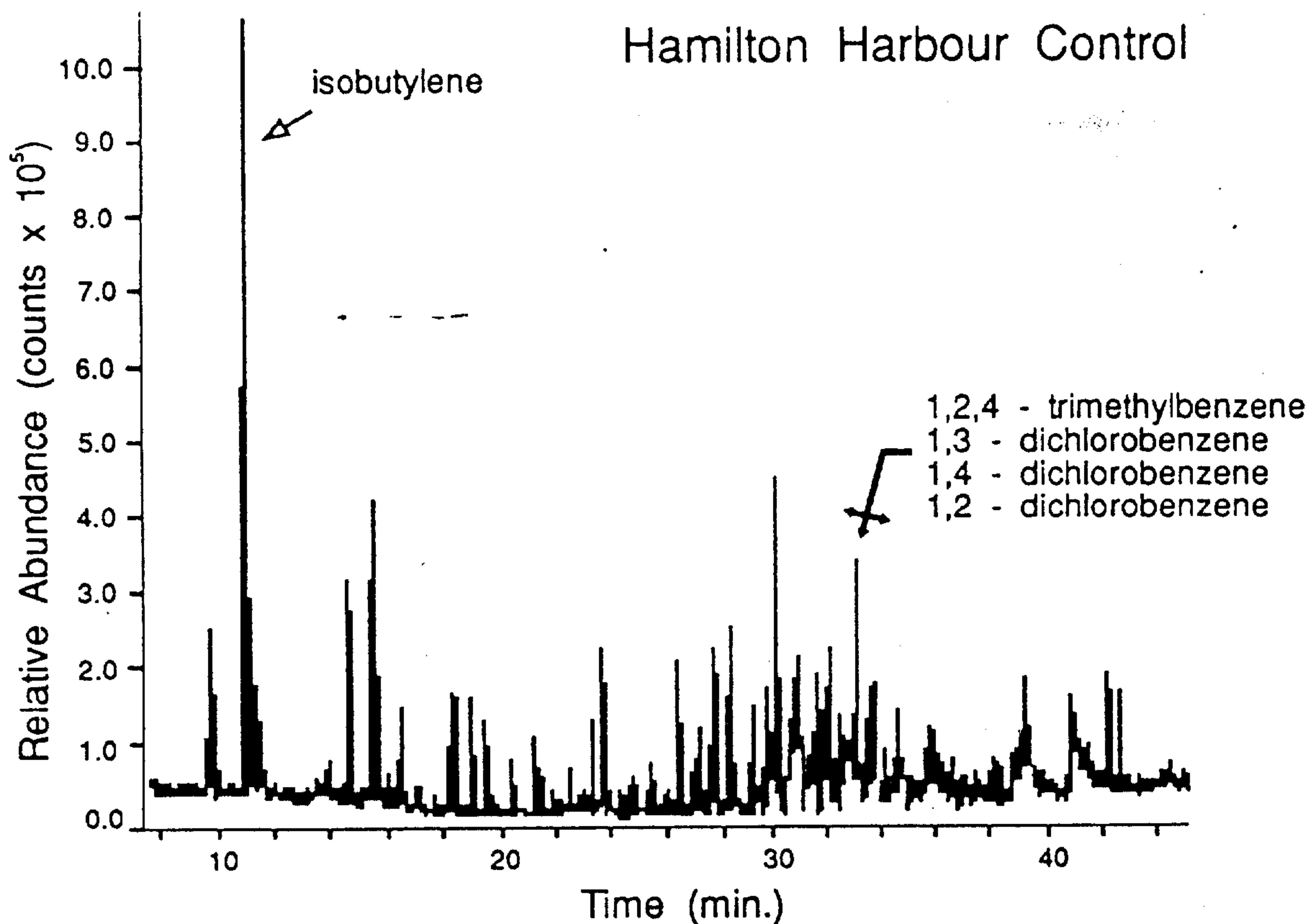
Figure 24 Denitrification in St. Marys River Sediment - 2 L bottle incubations



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Biodegradation of Organic Contaminants

Headspace GC/MS Analysis



14 Day Incubation

2099 423

UNSCANNABLE ITEM

RECEIVED WITH THIS APPLICATION

(ITEM ON THE 10TH FLOOR ZONE 5 IN THE FILE PREPARATION SECTION)

DOCUMENT REÇU AVEC CETTE DEMANDE

NE POUVANT ÊTRE BALAYÉ

(DOCUMENT AU 10 IÈME ÉTAGE AIRE 5 DANS LA SECTION DE LA
PRÉPARATION DES DOSSIERS)

