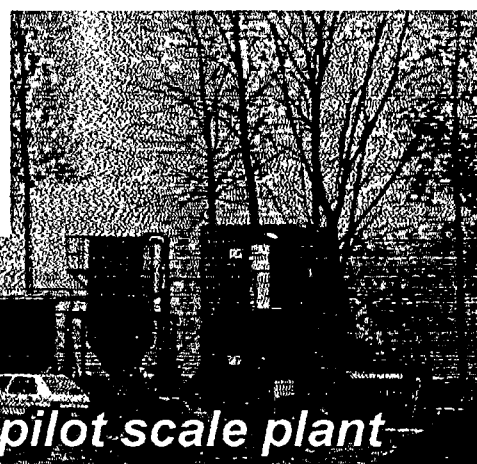


Bench Scale Demonstration of the ITORICS Process on Thunder Bay Harbour Sediment

Report Submitted to:

*Wastewater Technology Center
867, Lakeshore Road
5068 Burlington
ONTARIO Canada
L7R 4L7*



ITORICS pilot scale plant



**De Brabandere J.
Proot K.**

CONTENTS

I. GENERAL INTRODUCTION	5
A. The COSTTEP program	5
B. The Thunder Bay Harbour sediment problem.	5
C. SILT N.V. a short introduction	6
D. Treatment of sediments: general problem survey.	6
1. Behaviour of inorganic pollutants in dredged material.	6
2. Behaviour of organic pollutants in dredged material.	8
E. Bench Scale test set-up	11
1. Goal	11
2. Characterization	11
3. The inorganic part of the treatment: including a pretreatment	11
4. Organic part of the treatment	11
5. Bench scale testing of the ITORICS system: preliminary test I	11
6. Bench scale testing of the ITORICS-system: test II	12
II. PHASE 1. SEDIMENT CHARACTERIZATION	13
A. Physical analyses	13
1. Granulometry	13
2. Hydrometer test	13
3. Dry matter content	13
B. Chemical analyses	14
1. Organic matter content	14
2. Carbonate content	15
3. Acid-base titration	15
4. PAH-analysis	15
5. COD	16
6. Heavy Metal analysis	16
C. Chemical analyses according to WTC requirements	16
1. Sulphur	16
2. Heavy metals by ICP analysis, after HNO ₃ / HCl digestion	16
3. Heavy metals by ICP analysis, after HNO ₃ / HF digestion	17
4. OILS by GC VPRC 8519	17
5. Chlorophenols by GCMS VPRC 8814	17
6. Polycyclic aromatic hydrocarbons by NBS VPRC 8811	18
7. Oils and Greases by NEN 3235 9.2.2	18
8. Dry matter content NEN 5747	18
D. Discussion	18
III. BENCH SCALE TEST OF THE ITORICS SYSTEM	20
A. A.Inorganic section	20
1. Basic test	20
2. Test with different cocktails and procedures.	20
B. Organic section	21
1. Preparation of the test	21

2. Results	22
3. PAH- degradation	24
C. Bench Scale Test II	25
D. Results and Discussion	26
1. Respiration	26
2. PAH degradation	26
3. Evolution of other compounds in the ITORICS system.	30
4. WTC analyses	30
IV. ECOTOX TESTING	30
V. CONCLUSION	31
VI. ANNEXES	33
A. List of figures	34
B. Internal WTC audit report.	35

ACKNOWLEDGEMENTS

On behalf of the complete research team, which developed the ITORICS-system we would like to thank the Wastewater Technology Centre for showing us their confidence in giving us the chance to demonstrate the potential of this technology. Also we would like to thank Environment Canada's Great lakes Cleanup Fund for the financial support for this project.

We hope it may be helpfull in the clean-up of one of more sites not only in our region, but also throughout the world, and so may aid in improving our environment and this of our children.

The development of the Itorics system was co-sponsored by the Flemish governement by the Action Plan for the Development of Environmental Technologies. (Vlaams Impulsprogramma Milieutechnologie).

I. General Introduction

A. The COSTTEP program

Environment Canada's Great Lakes Cleanup Fund, one component of the federal Great Lakes Action Plan was initiated in 1991. The program focusses on Canada's 17 Areas of Concern identified by the International Joint Commission. The Cleanup Fund is designed to help meet federal commitments in the development and implementation of cleanup options. One priority of the program is to develop and demonstrate new and innovative technology on the safe removal and treatment of contaminated sediments. To evaluate sediment treatment technologies the Contaminated Sediment Treatment Technology Program (COSTTEPP) was initiated.

The mandate of COSTTEP is to foster the development and demonstration of technologies to remediate contaminated sediment and to communicate the results of the program to persons involved with Great Lakes remediation projects. Funds are provided to COSTTEP by the Cleanup Fund and are used to sponsor technology demonstration projects. Any technology is eligible for funding provided it has excellent technical merit, is innovative and has the potential to treat Great Lakes sediment in a cost-effective manner.

The program has three levels of projects which are funded: bench scale, pilot scale, and full scale. In general the program is to progress from bench through to pilot and then full scale projects. The program has been advertised nationally and internationally resulting in a very large response from technology developers and vendors. A database of technologies has been created based on the initial data submitted by these firms.

B. The Thunder Bay Harbour sediment problem.

Thunder Bay Harbour has been identified as one of the 43 Great Lake's Areas of Concern (cfr. supra). The Bay is located on the north shore of Lake Superior, Ontario. Water quality has been severely impacted, primarily as a result of historical and continuing discharges from the pulp and paper, and wood preserving industries.

Sediment within the inner Thunder Bay Harbour has been documented to contain pentachlorophenol, creosote, dioxines, furans and other toxicants. An area of severe sediment contamination, adjacent to the Northern Wood Preservers site has been selected by the COSTTEP for bench-scale sediment remediation demonstrations.

The contaminants found in the sediment originate from a number of companies. The wood preserving chemicals used historically and/or currently are chromated copper arsenate, creosote and PCP. Wastewater generated during the wood preserving operation is now treated biologically prior to discharge to the inner harbour. Surface runoff and leaching of the wood preserving chemicals from accidental spills and standard operating practises have been proposed as the most significant sources of sediment contamination immediately adjacent to the Northern Wood Preservers site.

The material used in this Bench Scale Test is derived from a number of samples taken at different locations throughout the site. The survey of the area has delineated approximately 20,000 m³ of heavily contaminated sediment. Samples from highly contaminated locations, together with samples from moderately and lightly contaminated nearby locations were collected and composited to form representative samples for the area.

C. SILT N.V. a short introduction

SILT was formed in 1988 by two parent companies which for many decades have been active in the field of (underwater) soil treatment. The companies Dredging International (DI) & Decloedt (DC) were the first companies to be confronted with the pollution of the dredged material and with international legislation on its storage. SILT N.V. mainly focuses on the treatment of silt. This is a collective name referring to heterogeneous mixtures of water and fine-grained particles, possibly in strong concentration, with their own specific physical and chemical properties.

Anno 1994 SILT is partially owned (50/50) by two holding-companies, one of which is comprised of the two original parent companies (DI-DC). The other one is a government owned holding company, particularly active in the field of environmental services. The services offered are industrial waste treatment, domestic and industrial waterpurification, composting, recycling and sludge treatment.

SILT specializes in the treatment of sludge generally produced by water production, water purification, river and sediment sanitation. Most technologies which are applicable were developed in-house. Some of the technologies however are licencies from other developers. The main activities of SILT's sludge treatment department comprise of the following:

1. Mechanical treatment
2. Physico-chemical treatment
3. Microbiological treatment
4. Recycling of sediment and sludge
5. Construction and management of disposal sites.

A last important activity of SILT is situated in the field of hydrography, directly related to activities dealing with the mapping of various parameters important for dredging activities. Both for dredging and sanitation works, the knowledge of the bottom structure is essential.

D. Treatment of sediments: general problem survey.

The treatment of contaminated sediments has been studied over the last few years. Natural dredged material has to be regarded at as a multi-component system. In general, the complexity of retention and interaction mechanisms of a pollutant with soil, sediment and the aqueous ecosystems (e.g. dredged material) is governed by a wide variety of reactions: hydrogen-bonding, ion-exchange, formation of inner- and outer sphere complexes, adsorption, etc.... Natural dredged material has to be regarded at as a multi-component system, which means that a considerable number of different equilibria are involved in the overall resulting retention reaction of one single pollutant. By disadvantaging one equilibrium, another may be advantaged and vice versa. Also phase shifting may occur. The full range of pollutants, recovered in dredged material in fact has to be divided into following 2 main categories:

- INORGANIC pollutants
- ORGANIC pollutants

1. Behaviour of inorganic pollutants in dredged material.

Inorganic pollutants have the intrinsic possibility to become critical at all time. Therefore there is a need to immobilize or to remove them from the ecosystem if possible in order to minimize future effects. Due to their possible toxicological effects the following metals are to be checked for their presence in dredged material, and this regardless whether they are present in toxic or non-toxic concentrations to man: As, Be, Cd, Cr, Co, Cu, Hg, Pb, Mn, Ni, Se,

Zn. (De Brabandere, 1991). All these metal ions may present toxicological effects to living organisms by interfering with certain biochemical reactions.

The retention mechanisms of inorganic pollutants in sediments and the form under which organic pollutants are present under naturally occurring conditions form the basis of the physico-chemical treatment techniques, which have been developed by SILT. It has been found that, for example, in the speciation of metal pollutants, the organic matter and the metal oxide fraction play a key role. Furthermore, a strong phase equilibrium exists between the solid and liquid phase. In the treatment of organic pollutants the redox potential of the sediment governs the effectiveness of the sanitation process.

The knowledge of the retention mechanisms of heavy metals in a sediment is the first important step in the development of treatment techniques. Although numerous scientific publications (Oakley e.a., 1981; Davies-Colley, 1984; Lion e.a., 1982; Verloo, 1988; etc.) already have been dedicated to this subject, still a lot remains unknown. The interaction mechanism of metals with the sediment is very complex, and a huge number of reactions and combinations are being involved. The overall resulting retention reaction for one single metal can be described by combining the interactions of this metal with the different fractions of the sediment. This is called a single component system. Describing the same retention mechanism for a complete sediment, involves the combination of various single cell retentions of a metal with a fraction of a sediment, and the cross interaction, resulting from the competition of two or more metals. The study of single component systems usually results in applying an extraction procedure to the sediment e.g. Tessier (Tessier e.a., 1979). Although some controversy about the validity of such study methods exists, it often results in the above mentioned and generally approved evidence, that particularly in the immobilization of many metal species, only 1 or 2 fractions play a key role.

A general model for the interaction of heavy metals with a sediment can be described as follows. A metal enters the complex environmental system through the aqueous phase. The chemical form in which it is present will quite rapidly become governed by the pH and oxido-reduction state of the system, together with the chemical composition of this phase. This is by the interaction with anions, hydroxides, carbonates and in particular with the solubilized organic matter. In the sediment the metal ions will also interact with the various fractions (organic matter, oxides, clay, sand...). The sediment however will compete with the aqueous phase, which results in an equilibrium state between both phases. This equilibrium is expressed with the so-called

$$K_D = \frac{[Me]_{\text{Adsorbed}}}{[Me^{z+}] \left[1 + \sum_i^{n_{OH}} \beta_n [OH]^n + \sum_i^{n_{CO_3}} \beta_n [CO_3]^n \dots + \dots \sum_i^{n_{L_1 L_2}} \beta_{nm} [L_1]^n [L_2]^m \right]}$$

K_D value.

In which:

- the nominator expresses the concentration of a particular metal in the solid phase.
- the denominator expresses the concentration of the same metal in the liquid phase. This is the summation of all chemical forms, under which the metal is present in solution.

In the case of a metal ion distribution, this constant expresses in a numerical way how strong the ion is scavenged from the aqueous towards the sediment phase. In general and under natural occurring conditions in dredged material these K_D values are typically in the order of magnitude from 10 to 10^6 for all metal ions, meaning that from 90 to 99.999 % is recovered in the sediment.

As was mentioned above a large number of equilibria are involved in the overall retention reaction in the sediment. However the most important ones are:

1. the chelation with the organic matter fraction and the sulphide complexation
2. the ionexchange in clay minerals and oxides.
3. the adsorption to organic matter, oxides and other sinks.

Not only the complexation with natural organic matter, but also the complexation with sulphide incorporated species forms an important sink for metal ions. Particularly Cd, one of the most important metal contaminants, is mainly present under a sulphide complex under reducing conditions.

When the concentration of the metals in solution is increasing, the mechanism of ion exchange becomes more important. Clay minerals for instance have reversible adsorption properties towards different cations. This is due to their specific structure and surface, which is covered with a residual usually negative net charge. The ion exchange reaction on clays is generated by the fact that cations with a different charge density compete with each other and with the hydrating ions on the surface of the clay minerals. It is generally assumed that clay minerals cannot compete with oxides and organic matter for the retention of heavy metals (Gigg, 1985). Nevertheless, these particles show a strong affinity for oxides and organic matter which in turn may adsorb or complex heavy metals. In this way clay minerals thus indirectly contribute to the immobilization of heavy metals.

Adsorption takes place when metal cations are being scavenged from the liquid phase and exchanged for protons present on the surface of metal oxides, particularly Mn, Fe and Al. These interactions are in general much weaker than ion exchange and complexation, although some metals are preferably associated with oxide fractions, e.g. Ni on MnO_2 . At high metal pollutant concentration this type of interaction will take place also on the surface of humic substances, although again the retaining strength will be smaller.

2. Behaviour of organic pollutants in dredged material.

Humic substances and related compounds recovered in sediments, comprise a large segment of the world's organic reservoir. The name "humic" is often referred to as a generic name for the total organic matter pool in soils. Humic acids are generated by biological and chemical degradation of plant and animal detritus. The so formed products tend to associate into more complex, and at the same time more stable chemical structures (Schnitzer and Khan, 1978). Due to their polyelectrolytic properties (Thurman, e.a., 1983), and their large quantities of functional groups (De Brabandere, 1989), they are able to form very strong complexes with metal ions, and with other organic compounds through hydrogen-bonding.

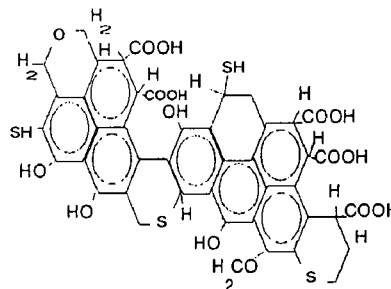


Figure a
Humic acid model

A clear distinction should be made between this type of organic matter and organic pollutants. Organic pollutants are those compounds, which are predominantly man-made, and which are interfering with biological species in an unfavourable way. However sometimes the distinction is difficult to make, as both groups of components are chemically very similar. Figure a shows a simulative structure of a humic acid.

This explains why organic pollutants are recovered in the organic matrix of a sediment. The retaining forces are controlled by strong adsorption reactions and hydrophobic interactions on the particulate organic matter. Therefore they may not be available for (biological) degrading mechanisms. This is also the main reason why various types of decontamination actions can only remove organic pollutants to a certain extent: e.g. soil flushing, bioremediation, soil washing, etc...

Inhibited diffusion of the components from within the micro-pores of the sediment, combined with a high non-polar behaviour seem to cause this persistency.

Unlike the knowledge about the mechanisms which govern the retention of heavy metals in sediments, there is still a large gap in this field about organo-pollutants.

Some degradation pathways are well known as for example these for most of the polycyclic aromatic compounds. This is shown in figure b.

This report demonstrates the possibilities of remediating Thunder Bay Harbour sediment by applying the ITORICS-system. The ITORICS-system was developed to deal with organic and inorganic contaminated sediments by combining a physico-chemical and microbiological treatment. The treatment of soils and sediments is often limited by the fact that both types of contaminants are present, requiring the application of various treatment techniques, thus increasing treatment costs. Moreover it is often seen that such different techniques are not compatible with one another.

A general flowsheet of the ITORICS-process is shown in Figure c below

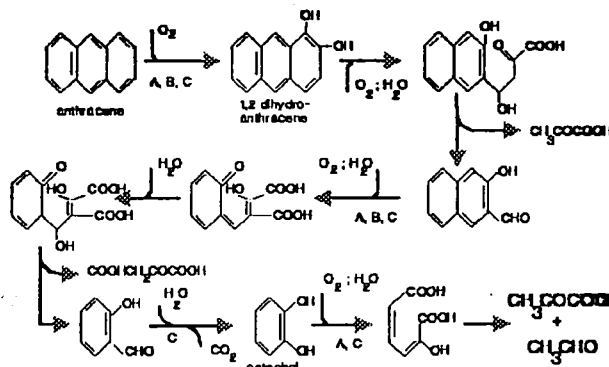
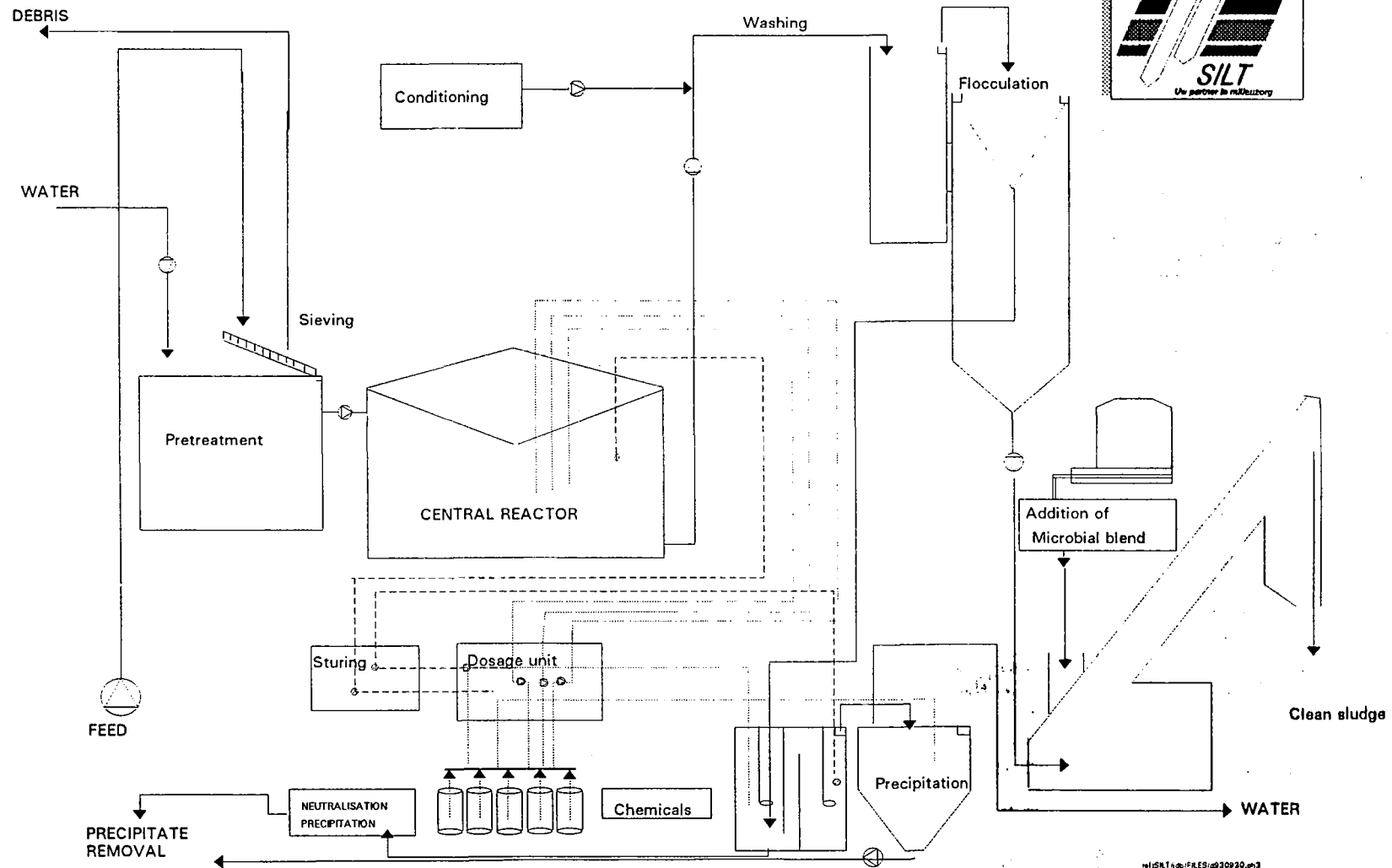


Figure b

A proposed microbial break-down pathway for anthracene.

a: Dioxygenase b: Dehydrogenase c: $\text{NADH} + \text{H}^+ = \text{NAD}^+$

Figure c: Flowscheme ITORICS-SYSTEM



E. Bench Scale test set-up

1. Goal

As explained above, the origin, the type and the composition of contaminants present in sediments limits the possibilities of dealing with those problems.

Nevertheless, in some cases a combination of techniques, dealing with both the organic and inorganic pollutants is feasible. The ITORICS system makes use of both physico-chemical, and micro biological methods. It is more cost effective, and the number of manipulations are reduced. In the case of the sediment from the Thunder Bay Harbour we are dealing with a substance which is primarily contaminated with organics from the PAH-group. Also a small contamination with heavy metal occurs, not interfering however with a possible microbial degradation. The combination technique ITORICS has been proposed to tackle the problem.

The physico-chemical treatment procedures to be applied are predetermined during a bench scale test, which is required for all new treatment projects. This is needed, as each type of sediment has a unique composition not only from contaminant point of view but also concerning the soil physical composition. During the bench scale test the sediment is characterised, and a "cocktail" is made, which must enable the removal of as much metals as possible, with as little chemicals as possible, taking into account that a post-microbiological treatment must be applicable as well.

2. Characterization

It is necessary to characterise sediments prior to treatment. This is done in a standard way. From numerous studies a method was distilled to generally characterize a sediment based on some key-analyses, for determining the process.

Characterization is done both physically and chemically. All tests are described below.

3. The inorganic part of the treatment: including a pretreatment

In this part of the bench-scale test, the sediment is being tested for removal of the heavy metal part of the contamination.

Samples of the sediment are mixed with various cocktails of chemicals in order to improve the possible extraction yield. Three different types of cocktails can be used.

The best performed technique is used to continue the bench scale test (cfr. 4)

4. Organic part of the treatment

Using a respirometer the sediment is tested separately for its ability to be treated microbiologically. This means that samples of the sediment are brought into reactor vessels. In these vessels different microbial blends are added. In addition some blank experiments are set-up in order to determine the efficiency of indigenous stimulation.

Total oxygen consumption, together with oxygen consumption rate is monitored. The vessels are closed during the tests. Sample analysis is performed at the beginning and the end of the tests.

The best performed technique is used to continue the bench scale test (cfr. step 4)

5. Bench scale testing of the ITORICS system: preliminary test I

In this step the two selected procedures are being matched with each other and combined in the ITORICS system.

Samples of the sediment are then treated accordingly, with the three major parts of the technology

1. Central reactor (metals removal and organic degradation initiation)
2. Microbial treatment
3. Post treatment of liquid phases

6. Bench scale testing of the ITORICS-system: test II

This step consists of a replication of the previous step. In this phase all parameters are also being analysed to determine the efficiency of the technology.

II. Phase 1. Sediment Characterization

A. Physical analyses

These analyses are merely performed to obtain a good impression about the properties of the material in terms of cohesivity, resistivity, viscosity and abrasivity. Those parameters are important in the treatment process for the calculation of general requirements such as energy input, type of pumps and piping, the expected velocities, etc...

1. Granulometry

The granulometry of the sample was determined by weighing an exact amount of material and executing a wet sieving on a 63 μ sieve. The total amount of material on the sieve, and the fraction smaller than 63 μ was dried.

The total mass of dry sediment was : 32.64 g

The total mass of dry sand, which remained on the sieve was 2.15 g

The same experiment was carried out in absence of organic material and carbonates. These were previously removed by standard soil chemical procedures.

The reason to determine the grain size in absence of carbonates and organic material lays in the fact that if this fraction is important enough, like in marine sediments, it can preferably be removed by mechanical action. This is more cost effective compared to a chemical extraction procedure.

Organics are removed with a peroxide digestion, whereas carbonates are removed under acidic conditions at 60° C under reflux. (cfr. infra).

The total mass of dry sediment then was: 25.474 g

The total mass of dry sand then was: 1.5 g

This gives the following result:

Granulometry	% > 63 μ		% < 63 μ	
Total sediment	6.10	6.59	93.9	93.41
Sediment without OM and CO ₃	-	5.89	-	94.11

This shows that the sediment is mostly silt and clay.

2. Hydrometer test

As a consequence to the finding that the sediment containing a large silt fraction, the size distribution of the fines was determined by a hydrometer test. The laboratory reports are shown below in annex 1 figures 1 and 2.

From these it was shown that the D₅₀ of the sediment is about 10 to 15 μ m

3. Dry matter content

The dry matter content of the native sample was found to be 44.60 % by weight.

Density

The density of the sample was measured in two ways:

1. Total sediment density by determining mass/volume ratio

Mass Sample (g)	Volume Sample (ml)	Density (g/ml)
38.593	30	1.2860
38.810	30	1.2940
38.64	30	1.2880
Mean Density		1.2890

2. Grain density

The grain density was determined by the pyknometer test. It was determined in the presence, and the absence of organic material and carbonates.

This is determined from:

- mass dry sediment: mS
- mass water + sediment: mWS
- mass water: mW

to be equal to:

$$\text{Grain Density} = \frac{mS}{(mW - mWS)} + mS$$

Grain Density in the presence of organic material and carbonates

mS (g)	mWS (g)	mW (g)	Grain Density
3.124	251.34	249.5	2.4330
3.317	251.46	249.5	2.4443
9.13	254.86	249.5	2.4218
Mean Density			2.4330

Grain Density in absence of organic material and carbonates

mS (g)	mWS (g)	mW (g)	Grain Density
9.704	255.18	249.53	2.3937
6.448	255.26	249.53	2.3723
9.13	254.86	249.53	2.4218
Mean Density			2.396

B. Chemical analyses

The analyses described below refer to SILT's own standard procedures for sediment analyses, related to the bench scale testing of the ITORICS-system. These are merely intended to be used for selecting procedures, chemicals, and sub-techniques in the treatment of the contaminants. Not all of the executed analyses can be shown for secrecy reasons.

1. Organic matter content

The organic matter content is determined by treating a known amount of sediment with 300 ml of a 30 % H₂O₂ solution, while the sample is gradually heated in a waterbath from 40 °C to 60 °C. After digestion the sample is oven dried at 105°C and the loss of weight is determined.

2. Carbonate content

The carbonate content is determined following a pretreatment of removing the organic matter, whereafter an additional treatment with HCl 0.2 N is executed. Again the loss of weight is a measure for the concentration of carbonates present in the sample.

The results are shown in following table.

Mass dry sediment (g)	Mass dry sediment after H ₂ O ₂ treatment (g)	% OM	mass dry sediment after HCl treatment (g)	% CO ₃
11.236	10.38	7.61	9.81	5.07
20.612	19.12	7.24	18.05	5.19
Mean		7.43		5.13

3. Acid-base titration

The determination of the (de)protonation reaction is a powerful tool for interpreting the acidity of the metal complexation properties of the sediment. Particularly the humic acid behaviour is very important in this respect. In addition it is a helpful tool in the determination of the total exchange capacity. The experimental setup is most important in order to exclude interfering parameters.

The titration is carried out taking into account that the adsorption of CO₂ has to be prevented. This is accomplished by operating in a completely closed vessel. For research conditions the use of N₂-atmosphere is recommended, as is working at constant temperature, and constant ionic strength. During the bench scale test we used only temperature compensation.

During the titration, small aliquots of acid and base are delivered into the titration vessel from the burets. These are connected to the titration vessel by very fine capillary tubings, that are immersed in the suspension. The titration is carried out with a completely automatised computer controlled system. Prior to use all electrodes are calibrated in 3 different buffers, till a slope of at least 98 % against ideal Nernst behaviour is obtained, meaning that a value below 58 mV/decade is rejected.

Figure 3 in the figure annex show respectively the acid and the base titration.

4. PAH-analysis

PAH analysis was performed on the Thunder Bay Harbour sediment. The exact procedure of removing the compounds from the matrix is different from most applicable methods. The reason for this is the fact that our procedure is intended to remove an amount of compounds, which is as high as possible. This enables us to calculate best yields in the treatment process afterwards.

The efficiency of the removal step lies both in the use of certain chemicals and in the physical pre-treatment of the samples. Also the samples are not dried before extraction. Using this wet method Silt often obtains recoveries, which lay from 20 to even 100 % higher than the standard methods classically used for analysis.

The samples are extracted with acetone and/or DCM, followed by a shift towards Hexane. In the next step the extractant is removed by distillation on a rotavapor. The extract is subsequently purified and if necessary concentrated whereafter it is redissolved in acetonitrile. A small aliquot of this sample is then analysed on a HPLC, with UV-fluorescence detection. Standard addition techniques are used for calibration. The samples are analysed in three-fold.

The copy of the laboratory report (fig 4 in the figure annex) shows the obtained results for the Thunder Bay Harbour samples.

5. COD

The determination of the Chemical oxygen demand was carried out by a bi-chromate digestion in the presence of H_2SO_4 - AgSO_4 , under reflux at 150 °C, followed by a back-titration with $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$

The COD was determined to be 7959.12 mg/l

6. Heavy Metal analysis

Prior to analysis the sediments are digested for at least two hours in a HCl - HNO_3 mixture under reflux. The sample is subsequently filtered. The supernatant is then analysed by AAS or ICP, depending on the availability of the equipment. (During this bench scale test AAS is being used predominantly). The heavy metals were determined in relation to the ITORICS-system. A complete analysis according WTC-requirements was performed as well (cfr. infra)

The metal content is set out below:

Compound	Heavy metal content (ppm)
Cu	25.27
Cd	1.55
Co	40.03
Cr	17.013
Zn	96.08
Ni	35.53
Pb	16.21
Fe	14011

C. Chemical analyses according to WTC requirements

According to the requirements of the contract with the WTC, the sample is also being analysed following the exact procedures requested by the WTC. This is done for reasons of enabling the comparison of results obtained with different technologies. Below are listed the results of these analyses. These were performed at the GEOS environmental laboratory, which is a governmentally approved institution for these analyses

1. Sulphur

0.19 % of dry matter content

2. Heavy metals by ICP analysis, after HNO_3 / HCl digestion

Compound	Heavy metal content (ppm)
As	6
Se	<10

3. Heavy metals by ICP analysis, after HNO₃/ HF digestion

Compound	Heavy metal content (ppm)
Ag	< 4
Sb	< 20
Th	< 20
Zn	180
Fe	52000
Cr	100
Mg	15000
Be	< 2
Cu	64
Al	54000
Ni	48
* Pb	< 100
Cd	< 2

*: Remark: the measured concentration for lead can be overestimated due to the presence of increased levels of aluminum, which interfere. This doesn't mean that the detection limit is always that high. This interference is typical for ICP analysis.

4. OILS by GC VPRC 8519

Compound	Content (ppm)
C10-C12	350
C12-C16	990
C16-C20	1000
C20-C24	980
C24-C28	550
C28-C32	430
C32-C36	290
C36-C40	180
Total	4770

5. Chlorophenols by GCMS VPRC 8814

Compound	Content (ppm)
Monochl. ph.	< 0.01
Dichl. ph.	0.09
Trichloro. ph.	0.04
Tetrachlor. ph.	0.02
Pentachlor. ph.	0.05

Chlor. ph. total	0.20
245 Trichl. ph.	<0.01

6. Polycyclic aromatic hydrocarbons by NBS VPRC 8811

Compound	Content (ppm)
Naphtalene	130
Acenaphtylene	0.3
Acenaphtene	81
Fluorene	77
Phenantrene	220
Anthracene	42
Fluoranthene	110
Pyrene	74
Benzo(a)anthracene	29
Chrysene	23
Benzo(k/b)fluoranthene	51
Benzo (a) pyrene	29
Dibenzo (ah) anthracene	<5
Benzo (ghi)perylene	13
Indeno(123cd)pyrene	21
Total PAH's	900.3

7. Oils and Greases by NEN 3235 9.2.2

6100 mg/kg (ppm)

8. Dry matter content NEN 5747

44 %

D. Discussion

The sediment from the Thunder Bay Harbour site, which we obtained to execute a bench scale test, is heavily contaminated.

The major contamination is the organic pollution with PAH's, oils and grease. The heavy metal content is slightly higher than standard levels for reference sediments, but this does not mean that an interference must be expected towards a bioremediation. For the ITORICS-system this means that the bioremediation can be executed prior to the physico-chemical treatment.

The analyses by methods specified by WTC show lower levels of PAH's compared to the data obtained from the SILT laboratory. This is as expected from the sample pretreatment, as well as from the GC compared to the HPLC analysis.

The data for heavy metal concentration show a slightly better matching except for iron and chromium, which showed a significantly higher level in the WTC analysis. The iron content is so high by either analytical method that

undesirable shifting of specification may occur during the treatment process.
It is therefore necessary to alter the process slightly.

III. Bench scale test of the Itorics system

A. A. Inorganic section

In this section the physico-chemical treatment process is optimised towards the removal of heavy metals. This involves a basic run, followed by 5 runs, during which several cocktails of chemicals are being used in various combinations of processes.

1. Basic test

In a first basic test 1 l of the sediment was diluted with water, thus obtaining a slurry with a dry matter content of 9.12 % and a pH of 6.98. This mixture was acidified with HCl 1 and 0,1 N to a pH of 1.97 and further treated according the physico-chemical procedures for about 4 hours. During a next phase an additional treatment was applied for 6 hours, in the slurry reactor.

The mixture was then allowed to settle down, after which the supernatant was decanted, and treated further with SIMAPUR to recover the removed metals.

Simapur is a specific product developed by SILT for sludge treatment. It has a high complexing capacity for heavy metals and improves filtrability. Moreover it is recycled from construction industry and is therefore relatively cheap.

The sediment was then rinsed for 12 hours, decanted and neutralised. The rinsing water was collected and treated, with SIMAPUR for metal recovery.

Results for this test are summarized in the table and figure in the laboratory report annex 1, figure 5.

From this table and figure it can be seen that most of the metals have been removed in this first run. Although the presence of metals is already low in the original sample, the removal of an easy available fraction can be executed.

All data for heavy metal contents in the table are expressed as ppm on dry weight basis.

Data for iron are not shown in the figure. In this procedure far too much iron is being extracted. In the following batch of experiments this is optimized.

2. Test with different cocktails and procedures.

Five different procedures have been selected to be tried out in this phase of the bench scale project.

The sample treatment procedure is largely the same for the different processes, as outlined hereabove for the basic sample.

The results obtained are shown hereafter in the next table and figure 6 from Annex 1.

All data regarding heavy metals are expressed in ppm.

Although the exact procedure of each individual treatment cannot be given for secrecy reasons, it can be stated that the difference between the several treatments merely lays in the type and combination of acids reagents and complexing agents used, the rotation time, the oxido reductive state of the system during the process, and the mechanical treatment, and this in order of importance.

The figure shows the overall synthesis of the heavy metal removal. Nr 1 shows the sediment at the beginning of the test, as it arrived from WTC Nr 2 and 3 are the data from the first treatment, respectively showing the data from the treated sediment and the supernatant recovered. Nr 4 and 5 are identical for treatment 2, and so on.

Again data for iron are not shown in the figure. From the table however it can be seen that the optimisation in all cases was quite successful in the fact that the iron was no longer extracted from the sediment.

The removal of the heavy metals is good for Zn, Pb, Co, Ni and Cd. A strange effect occurs with copper and chromium, which seem to be enriched during the process. This however must be regarded as an anomalous result, caused most probably by the high levels of "mobilised" iron and aluminum, interfering in the analytical procedure.

From the findings of these tests procedure 2 and 5 were selected for further investigation. After a second experiment procedure 5 was excluded from the bench scale test.

B. Organic section

Respiration tests were set-up in order to determine the biodegradation possibilities for the Thunder Bay Harbour sediment.

These tests involve the investigation towards indigenous stimulation, where the goal is to find out whether or not the sediment bacteria has the ability to degrade the organic contaminants. Moreover the residual concentration of organics is determined, once the process has stopped.

In addition the use of additional blends, which either enhance the biodegradation process, or act more as a support for increased degradation is investigated. Based on the characterization results (phase I of the bench scale test) two types of bacterial blends were selected for testing. It concerns specific strains of soil bacteria which are selected for oil, and heavy hydrocarbon degradation under aerobic conditions.

These are also compatible with the physico-chemical part of the ITORICS-system.

1. Preparation of the test

Prior to testing all reactors, as well as electrodes and other apparatus, used in the test were perfectly cleansed and subsequently sterilised. Test suspensions were made and brought into the reaction vessels. Each test was carried out in duplicate. All tests were carried out under complete aerobic conditions, in a temperature controlled environment (25 °C). All tests are carried out at a dry matter content between 5 and 20 %

The reactors were then tested to be leak proof. When all tests are cleared, the runs are started.

Samples were taken at the beginning and at the end of the runs. These are analysed for PAH's.

The following tests were run:

Test	Stimulation	Chemicals	Nr
WTCBL	Blank: Indigenous	No	1
WTCX1	X-blend	No	2
WTCX2	X-blend	Yes	3
WTCY1	Y-blend	No	4
WTCY2	Y-blend	Yes	5

The use of chemicals is intended to enhance degradation. These inducers are for instance surfactants, cofactors and adsorbers for microorganisms etc. N and P is always added to a minimum concentration to meet optimum C/N/P ratio's. These are based on findings from water purification technology.

However ratio's are different since the carbon-source to degrade is not from standard BOD-origin.

2. Results

Figures d through h show the results of the respiration. On the left axis the total accumulated oxygen consumption during the complete test is plotted as a function of time. Together with the data on COD it gives a good view on how the BOD will evolve during the break-down of the organic pollutants. On the right axis the first derivative is shown.

Both sets of data enable the technician to monitor the direction and the flow of the degradation. When the oxygen demand drops for a certain period, meaning that we obtain a plateau in the accumulation curve, some action is required, in order to enhance the degradation or to start a next phase. If no further enhancement can be induced, it means that all of the degradable Carbon has been consumed. It is the task of the technician to keep microbial activity going for as long as possible, and this at least until the degradation goal has been reached.

From the figures below it was deducted that the sediment showed a significant and quick reaction on the biostimulation after the physico-chemical treatment. During the indigenous stimulation as well as during the tests with support from external micro-organisms a smooth respiration was obtained, which was quite easy to control and to maintain.

The use of Y-type bacteria gave a somewhat slower response, particularly in the presence of additional chemicals. This is probably due to the fact that the bacteria are inhibited in the presence of the indigenous population.

Figure d: WTCBI

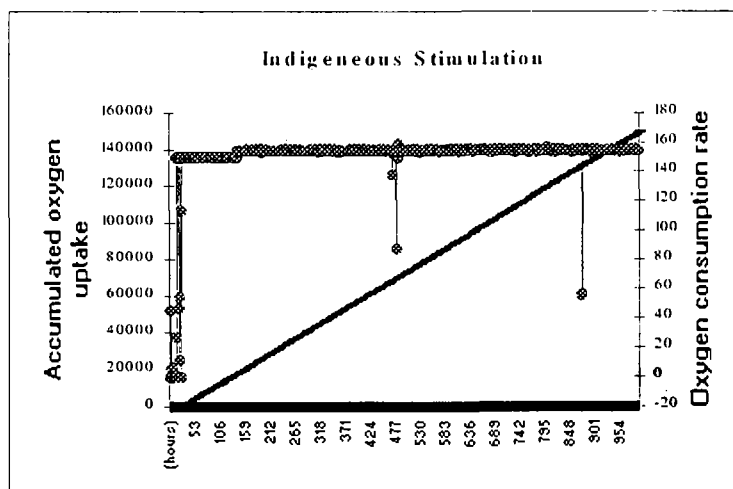


Figure e: WTCX1

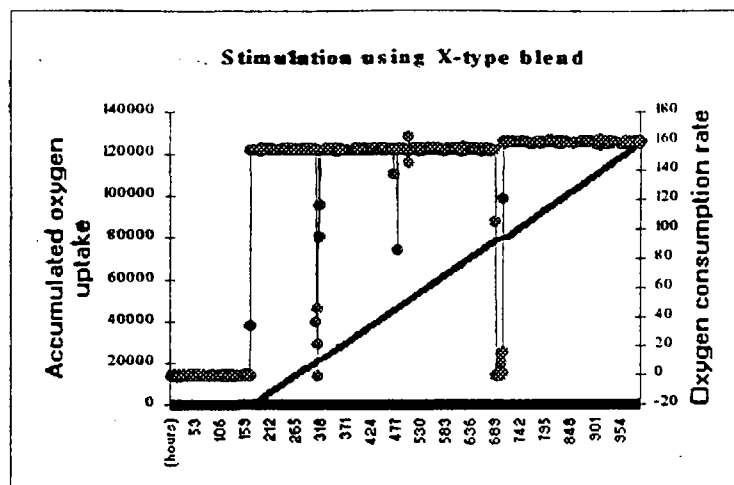


Figure f: WTCX2

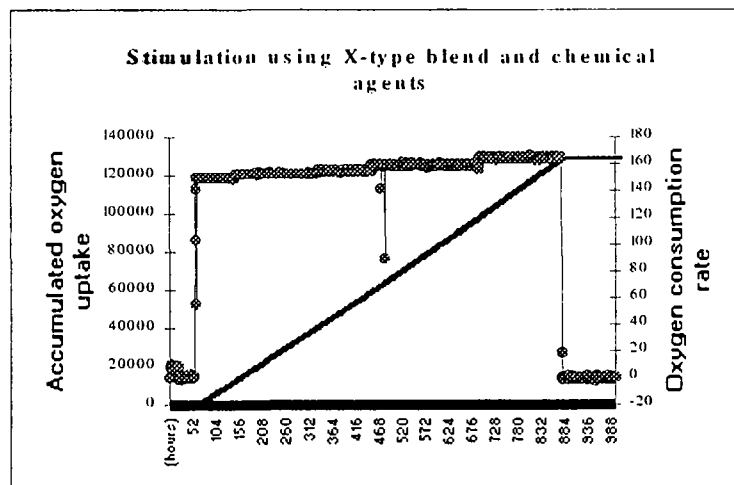


Figure g: WTCY1

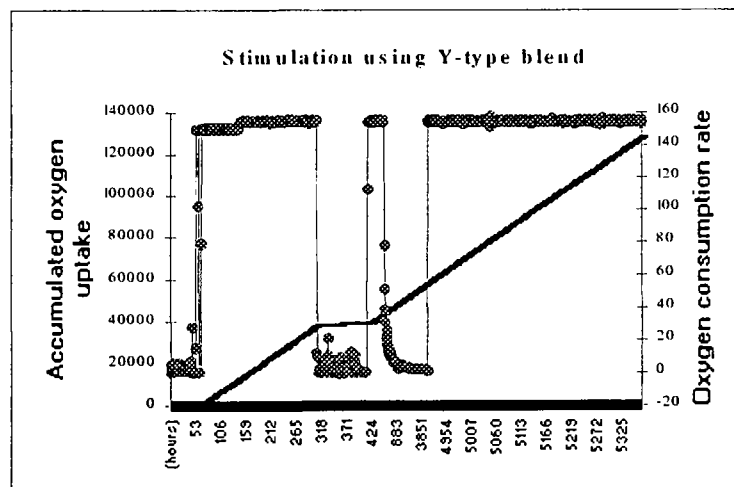
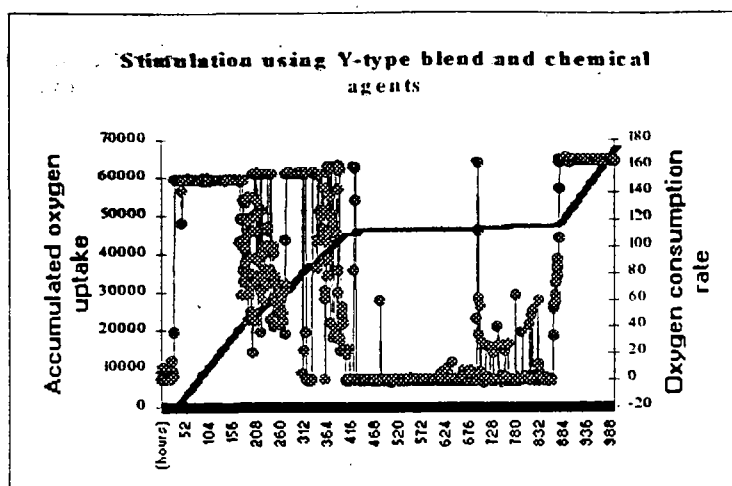


Figure h: WTCY2



3. PAH- degradation

From the respiration data it is clearly shown that the sediment has a good rehabilitation property in itself to degrade the present organic contaminants. After at least 1 day oxydation the bacterial population starts to show activity. Nevertheless from these data alone no answer can be given whether PAH are being degraded.

For all tests a similar behaviour was found, indicating the fact that the itorics system is inducing a microbial activity. The degradation however can not be drawn from these data, as it might perfectly be the case that a good respiration is merely caused by the presence of sufficient BOD, i.e. other than the organics to be degraded, in the sediment. This BOD can be degraded preferentially instead. Therefore the organic pollutant to be degraded was be monitored during the course of the degradation.

Table a:
PAH evolution during preliminary bench scale test for various treatments

PAH	nr	Concentration in ppm			
		before treatment	INDIGENEOUS Stimulation	WTCX2	WTCY2
Naphtalene	1	72.86	43.84	6.06	3.4
Acenaphtylene	2	124.89	59.22	37.72	10.5
Acenaphtene + fluorene	3 + 4	101.5	35.6	16.22	7.3
Phenantrene	5	106.98	68.3	14.93	5.2
Anthracene	6	126.96	76.5	110.01	8.4
Fluoranthene	7	264.02	98.3	82.31	50.6
Pyrene	8	90.17	83.2	35.58	20.9
Benzo(a)anthracene	9	46.75	60.4	17.09	2.9
Chrysene	10	46.94	49.5	4.27	17.3
Benzo(b)fluoranthene	11	58.09	46.83	11.46	28.9
Benzo(k)fluoranthene	12	38.26	35.58	29.07	26.5
Benzo(a)pyrene	13	58.63	54.5	30.75	14.3
Dibenzo(a,h)anthracene	14	16.52	15.8	15.97	5.2
Benzo(g,h,i)perylene	15	30.4	26.8	4.12	8.5
Indo(1,2,3)cd-pyrene	16	25.37	25.6	6.54	17.3
Total PAH's		1208.34	779.97	422.1	227.2

Results obtained during the preliminary tests are summarized in table a above. Also the laboratory reports are shown in figures 7 and 8 of Annex 1.

These data show clearly that good respiration does not necessarily result in a break-down of the desired components. The best results are obtained in the tests with the addition of Y-type blend bacteria. So the targetted PAH's are here degraded whereas in the experiment with the X-type bacteria and the indigeneous stimulation test other organics are degraded.

C. Bench Scale Test II

For the execution of the replication of the ITORICS bench scale test it was decided to use procedure 2 of the physico-chemical method in combination with the microbial stimulation procedure, using Y-type bacteria, while this gave the best results in the preliminary test phase. These were monitored for all polluting compounds.

In addition and simultaneous with to above mentioned tests procedure 2 of the physico-chemical treatment is again tested in combination with indigeneous stimulation and the X type bacteria. The tests with X and Y bacteria were carried out in the absence (index 1) and in the presence of stimulating chemicals (index 2). Finally a third consortium of microbial blend is used, which recently developed in the Itorics system. For these tests again, only the PAH-evolution is monitored.

All bench scale tests ran for more than 100 days (3 months). During the test all necessary actions were undertaken to optimize and to accelerate the degradation rate, and the degradation yield. This was based on the findings of the previous phase (cfr. sub A and B of this section)

1	INDIGENEOUS STIMULATION	Blank
2	Itorics B	WTCX1
3	Itorics C	WTCX2
4	Itorics D	WTCY1
5	Itorics E	WTCY2
6	Itorics F	WTCZ

D. Results and Discussion

1. Respiration

Annex I figure 9 show the respiration data from the various bench scale tests. The best performance was reached with the ITORICS E treatment, while second best was the indigeneous stimulation run. In both cases it was possible to maintain microbial activity without any interruption (ITORICS E) and almost no interruption (indigeneous stimulation). Also the highest oxygen consumption was obtained in these runs. As we know from the previous phase that in the case of the Y-type blend a good consumption of PAH's is realised, this may be very promising.

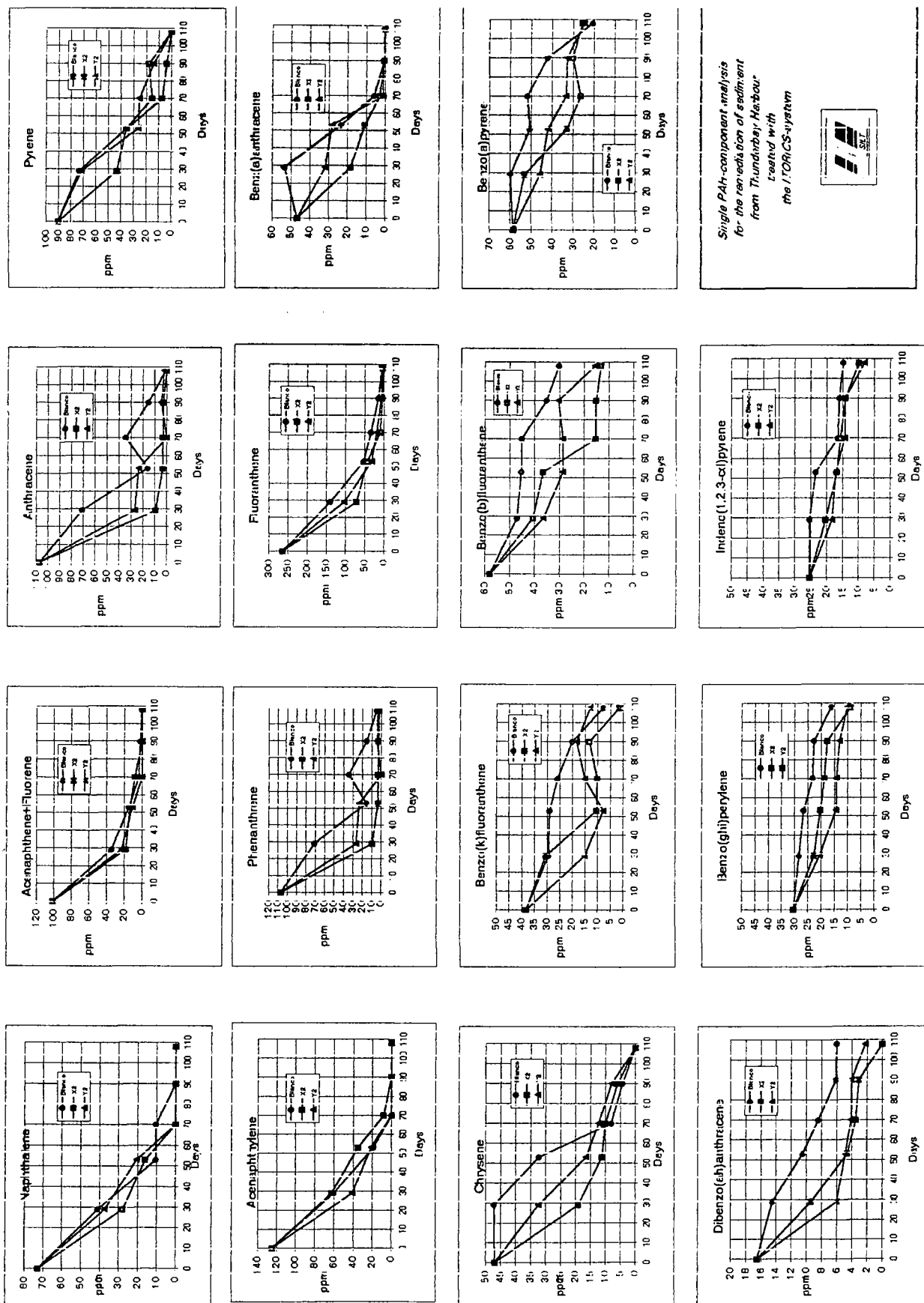
It must however be stated that although the tests were run for more than 3 months, some of the tests, and in particular the Itorics E test had not come to an end by the time the run was ended. From kinetic calculations it was found that a degradation enabling to decrease the concentration of PAH's with 50 % each 30 days could be obtained. From the starting point of 1200 ppm on average this would mean 3 months to reach a level of 150 ppm, 6 months to reach 20 ppm.

2. PAH degradation

Figures 10 through 15 from annex 1 show the results for the respective ITORICS-treatments (Blank, itorics b, c, d, e, and f). It is clear from these data that a good break-down is obtained in most bench scale tests, meaning that approximately 80 to 95 % of the total amount of PAH's have been removed after 3 months. This is of course not an end-point, as we know that in most cases the bench scale test was interrupted before a final concentration was reached.

A summary is also shown under figure i on next page.

Fig. 3



Single PAH-component analysis
for the remediation of sediment
from Thunderbay Harbour
treated with
the ITOHCS-system



The total amount of degraded PAH's is only one figure in the degradation. It is of a greater importance to look at the degradation of each individual PAH-component. Of particular interest in this matter is the evolution of the high molecular weight PAH's.

In figures 16 through 18 of annex 1, the PAH evolution from the bench scale tests which gave the best score are plotted next to the test in which we forced the indigenous stimulation to the most.

Figure j shows a summary of this figures. This is shown on next page.

In the case of the lower molecular weight PAH's (naphthalene to phenanthrene) not much difference is seen between the different treatments. We see more or less a logarithmic evolution in degradation for the three cases.

Looking at more complex PAH's like benzo(a)anthracene and chrysene a difference occurs in the lag phase of the degradation. During this first phase it is seen that particularly the indigenous stimulation test shows a certain retardation, meaning that organisms need to adapt themselves in order to attack these components. In the long run however more or less same degradation results are obtained.

Finally when one examines the behaviour of the most complex compounds like benzo(k)- and benzo(b)fluoranthene, benzo(a)pyrene. Only the final concentration, which can be obtained is no longer the same for the indigenous stimulation test, compared to the ones in which an active microbial blend is used. So here a distinct difference is made.

Another important factor is the fact that the start-off speed of the microbial activity is significantly higher in the case of using active microbial blends (lag-phase is shorter). This is significant for the treatment of the Thunder Bay Harbour sediment. A gain in treatment time may not only have important financial consequences, but also it may be necessary in the fact that treatment should be performed during a short period during summertime.

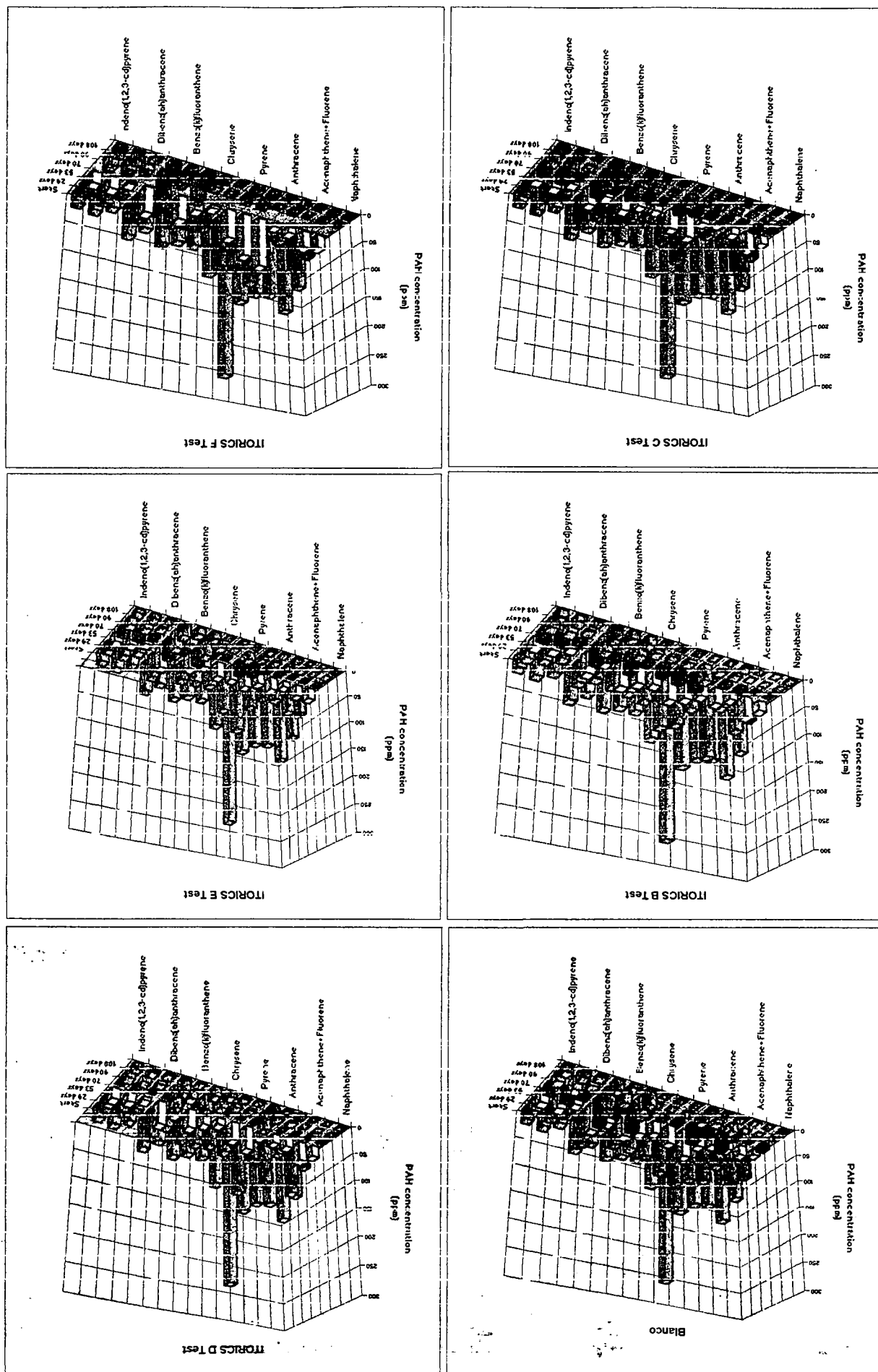


Fig. 1

3. Evolution of other compounds in the ITORICS system.

Following table shows the behaviour of the chlorophenols during the treatment. As expected no significant changes are observed. This is due to the explicite aerobic character of the process.

Compound	ITORICS E test	ITORICS blanco test (indigeneous stimulation)	Initial Content (ppm)
Monochl. ph.	<0.01	0.01	<0.01
Dichl. ph.	0.02	0.03	0.09
Trichloro. ph.	0.02	0.04	0.04
Tetrachlor. ph.	0.03	0.07	0.02
Pentachlor. ph.	0.1	0.2	0.05
Chlor. ph. total	0.17	0.35	0.20
245 Trichl. ph.	<0.01	<0.01	<0.01

4. WTC analyses

From an WTC internal audit on the same samples a breakdown efficiency was reported which varied from 80 % (Y-blended itorics test) to 89 % (indigeneous stimulation itorics test). The absolute values in PAH content reported by WTC were approximately 50 % higher than those obtained in our analyses. However the results obtained for the higher molecular weight components were in good agreement with each other.

In terms of removal of PAH's, 2 datasets are available and shown below. The audit report is available under annex b.

ITORICS PAH Removal from Thunderbay Harbour sediment

	SILT analysis		WTC audit	
	% Removal	PAH ppm	% Removal	PAH ppm
Untreated Sediment	0	1208	0	1867
ITORICS test Control (blanko)	91	107	89	207
ITORICS Y2-test	93	81.7	80	384

IV. Ecotox testing

Although this was not intended to be executed within the scope of our contract with the WTC and this bench scale test, a sample of the sediment was tested according to the procedures, which have been developed for evaluating the ITORICS-system. These are not certified tests. The test involve the investigation of the sediment on three stages in the food-chain: bacterial-test, worm-test, and plant-seed test.

The sediment showed a 3-fold positive respons to the initial Thunder Bay sediment sample. After treatment the bacterial test was still positive, whereas the worm-test and the plant-seed test showed no toxicity after the ITORICS treatment.

V. Conclusion

This bench scale test was performed on behalf of the Wastewater Technology Center Ontario Canada and was intended to test the ITORICS-system's ability to treat the Thunder Bay Harbour sediment. The Thunder Bay harbour sediment is predominantly contaminated with organic pollutants, creosote (PAH's), mineral oils, and to a smaller extent chlorophenols and heavy metals.

The focus during this bench scale test was on the treatment of PAH's, as they embody the major part of the problem. It was shown during this bench scale test that with the ITORICS-integrated system it is perfectly possible to tackle problems like the Thunder Bay harbour sediment. After a first removal of the most mobile heavy metals during a physico-chemical treatment, the sediment is capable of restoring microbial activity. It is also seen that the induction of a physico-chemical break-down is adequately followed by a further degradation by microbial activity.

This activity is largely enhanced by the use of stimulating agents. Although indigenous stimulation is well established if the system is properly optimized, the use of extra microbial blends is advisable in order to degrade the high molecular weight compounds. A significant different result is obtained between the tests in which those extra microbes are added compared to the indigenous stimulation tests.

Furthermore it is advisable to use this particular combined technique in order to speed up the lag phase at the beginning of the degradation, if this technology is to be executed on pilot or full scale.

The removal of heavy metals is largely inhibited by two factors:

1. the rather low initial concentration of metals present, and
2. the elevated iron content of the sediment.

For full scale operation it may therefore be decided not to remove the metals but directly pass on to the organic part of the ITORICS.

A major cost-factor in the treatment of sediments with the ITORICS system is time. This means the time to degrade the organics to the desired residual levels. It must however be stated that although the tests have been running for more than 3 months, the degradation is never ended by the time the bench scale test is stopped.

It is seen from the bench scale test that a half-life in the range of 20-30 days for most components is to be obtained. This means that from kinetic calculations it was found that a degradation efficiency could be obtained enabling the concentration of PAH's to decrease with 50 % each 30 days. From the starting point of 1200 ppm on average this would mean 3 months to reach a level of 150 ppm, 6 months to reach 20 ppm. Some components (e.g. fluoranthene) degrade even more rapidly upon treatment with a half-life of 15 days. Others are slower (e.g. benzo(a)pyrene) with a half-life of 60 days.

In terms of attainable levels of residual concentration it may be expected that a reduction with 90 % for the total PAH content and for the HMW-PAH's can be obtained during one season of treatment under complete aerobic conditions. The same is true for mineral oils. This means 4-5 months during summertime for the microbial treatment (ambient temperature above 15°C), plus 1 month for the physico-chemical pretreatment and 5 to 6 months for the lagooning of the treated sediment.

The unit cost for treatment for large scale operation is estimated at 6000-10000 BF per Ton sediment calculated on dry matter basis. A detailed cost estimate is to be made based on specific requirements, e.g. levels of residual concentration to be obtained.

Other components like chloro-phenols are not significantly attacked during the process. This could also not be expected from this technology, since the treatment is aerobic. From most experiences it was found that the degradation of chlorophenols require anaerobic treatment first.

VI. Annexes

A. List of figures

Figure 1 : Hydrometer test 1

Figure 2 : Hydrometer test 2

Figure 3 : Titration

Figure 4 : PAH Basic PAK analysis

Figure 5 : Basic ITORICS test

Figure 6 : Cocktail ITORICS test

Figure 7 : X₂ treatment

Figure 8 : Y₂ treatment

Figure 9 : Respiration data

Figure 10 : Blanco BST

Figure 11 : ITORICS B Test

Figure 12 : ITORICS C Test

Figure 13 : ITORICS D Test

Figure 14 : ITORICS E Test

Figure 15 : ITORICS F Test

Figure 16 : Single PAH-component degradation analysis

Naphtalene,
Acenaphthene + Fluorene,
Acenaphthylene, Phenanthrene

Figure 17 : Single PAH-component degradation analysis

Anthracene,
Pyrene,
Fluoranthene,
Benz(a)anthracene

Figure 18 : Single PAH-component degradation analysis

Chrysene,
Benzo(k)fluoranthene,
Benzo(b)fluoranthene,
Benzo(a)pyrene

Figure 19 : Single PAH-component degradation analysis

Dibenzo(ah)anthracene,
Benzo(ghi)perylene
Indeno(1,2,3-cd)pyrene

Analysis Report

SILT N.V. Laboratorium
Tijdokstraat 28
8380 ZEEBRUGGE
Tel : 050/546.144
Fax : 050/547.236



Monster ontvangen op : 14/01/94
Gevraagde analyse : Hydrometer test
Uitvoerder : Germonpre Dorine
Analyse afgewerkt op : 31-maa-94
10:51:36 AM
Totale massa v/h staal (gram) : 32.64
Dichtheid van de korrel (g/ml) : 2.4243

Grain size analysis HYDROMETERTEST				
SAMPLE Reference				
WTC Canada A In presence of OM and CO3				
Elapsed time (min)	Temperature (°C)	Hydrometer reading (gr/cm ³)	diameter (μm)	% smaller than diameter
0.5	19.5	1.0180	59	93
1	19.5	1.0160	43	83
2	19.5	1.0140	32	73
4	19.5	1.0132	23	68
8	19.5	1.0120	16	62
15	19.5	1.0105	12	54
30	19.6	1.0090	9	46
60	19.6	1.0070	6	36
90	19.6	1.0060	5	31
120	19.6	1.0055	5	28
180	19.6	1.0050	4	26
300	19.6	1.0045	3	23
390	19.6	1.0040	3	20
1440	19.6	1.0030	1	15

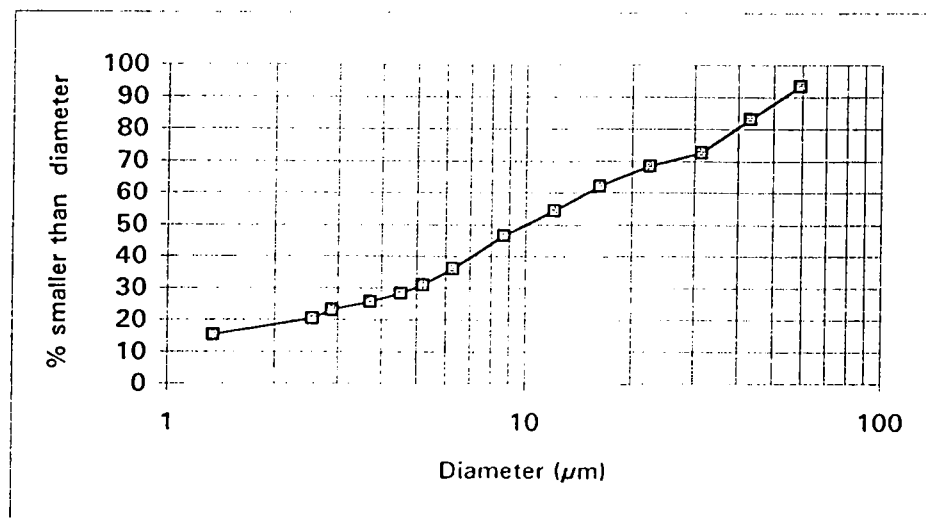


Figure 1 : Hydrometer test I

Analysis Report

SILT N.V. Laboratorium

Tijdokstraat 28

8380 ZEEBRUGGE

Tel : 050/546.144

Fax : 050/547.236



Monster ontvangen op : 14/01/94
Gevraagde analyse : Hydrometer analysis
Uitvoerder : Germonpre Dorine
Analyse afgewerkt op : 31-maa-94
 04:59:38 PM
Totale massa v/h staal (gram) : 25.479
Dichtheid van de korrel : 2.3883

Grain size analysis HYDROMETERTEST				
SAMPLE Reference				
WTC CanadaB In absence of OM and CO3				
Elapsed time (min)	Temperature (°C)	Hydrometer reading (gr/cm ³)	diameter (μm)	% smaller than diameter
0.5	19.5	1.0142	64	95
1	19.5	1.0138	45	93
2	19.5	1.0130	32	87
4	19.5	1.0120	23	80
8	19.5	1.0086	17	57
15	19.5	1.0064	13	43
30	19.6	1.0050	9	33
60	19.6	1.0038	7	25
90	19.6	1.0032	5	21
120	19.6	1.0030	5	20
180	19.6	1.0025	4	16
300	19.6	1.0022	3	14
390	19.6	1.0010	3	6
1140	19.6	1.0010	2	6

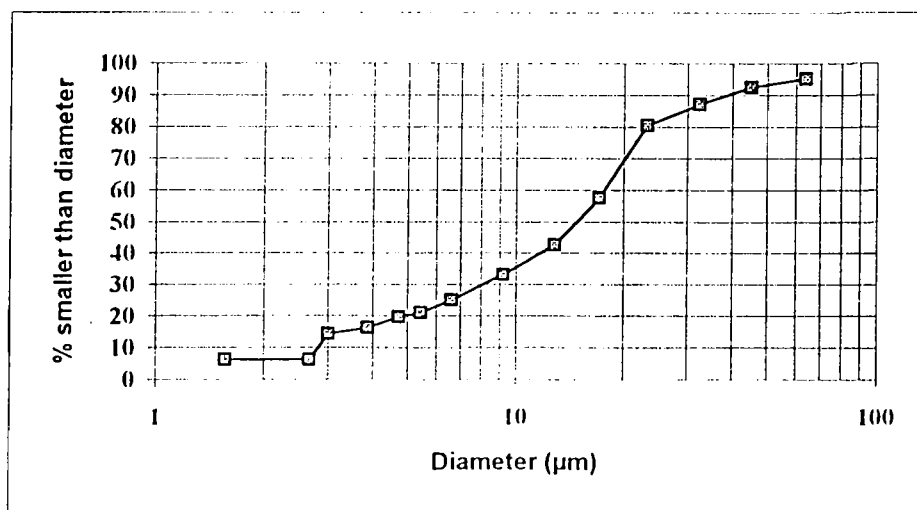


Figure 2 : Hydrometer test 2

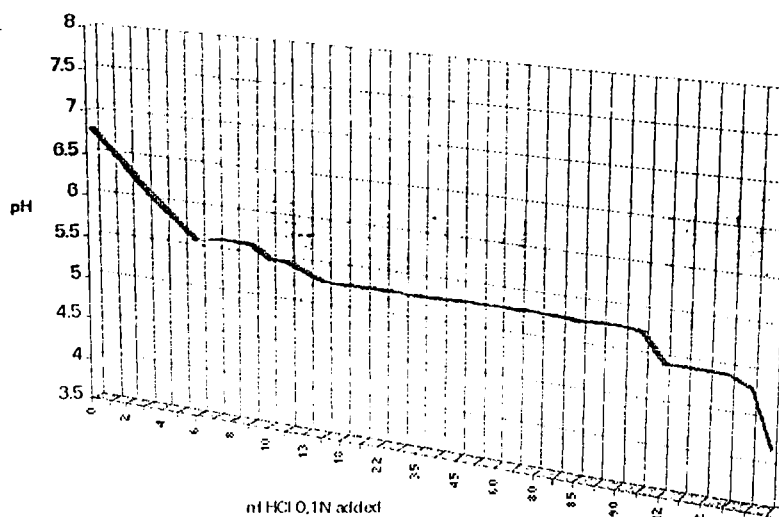


Laboratory report

WTC sample: pH titration

Date report: 15-1-94

Titration of native sediment with HCL 0,1 N



Titration of native sediment with NaOH 0,1 N

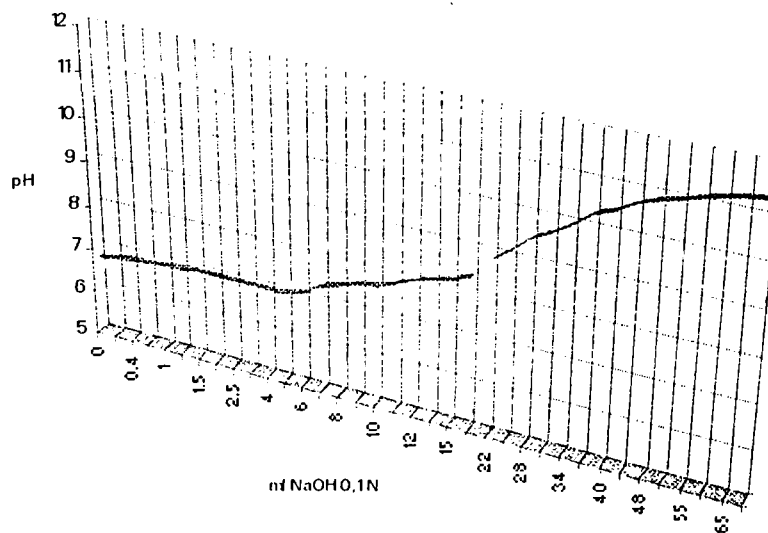


Figure 3 : Titration

Laboratory Report



PAH analysis from Thunderbay Harbour Sediment (WTC)

Referencenr SILT : E940114

Dry matter content (%) : 44,60

Date PAH analysis : 20 januari 1994

Remark: two sediment samples were treated separately

PAH	nr	Concentration in ppm	
		Extract 1	Extract 2
Naphtalene	1	67.95	72.86
Acanaphtylene	2	96.76	124.89
Acenaphtene + fluorene	3 + 4	83.5	101.5
Phenantrene	5	107.07	106.98
Anthracene	6	126.67	126.96
Fluoranthene	7	250.03	264.02
Pyrene	8	93.26	90.17
Benz(a)anthracene	9	46.93	46.75
Chrysene	10	46.34	46.94
Benz(b)fluoranthene	11	68.18	58.09
Benz(k)fluoranthene	12	35.74	38.26
Benz(a)pyrene	13	67.66	58.63
Dibenzo(a,h)anthracene	14	13.04	16.52
Benzo(g,h,i)perylene	15	24.99	30.4
Indo(1,2,3)cd-pyrene	16	28.52	25.37
Total PAH's		1156.64	1208.34

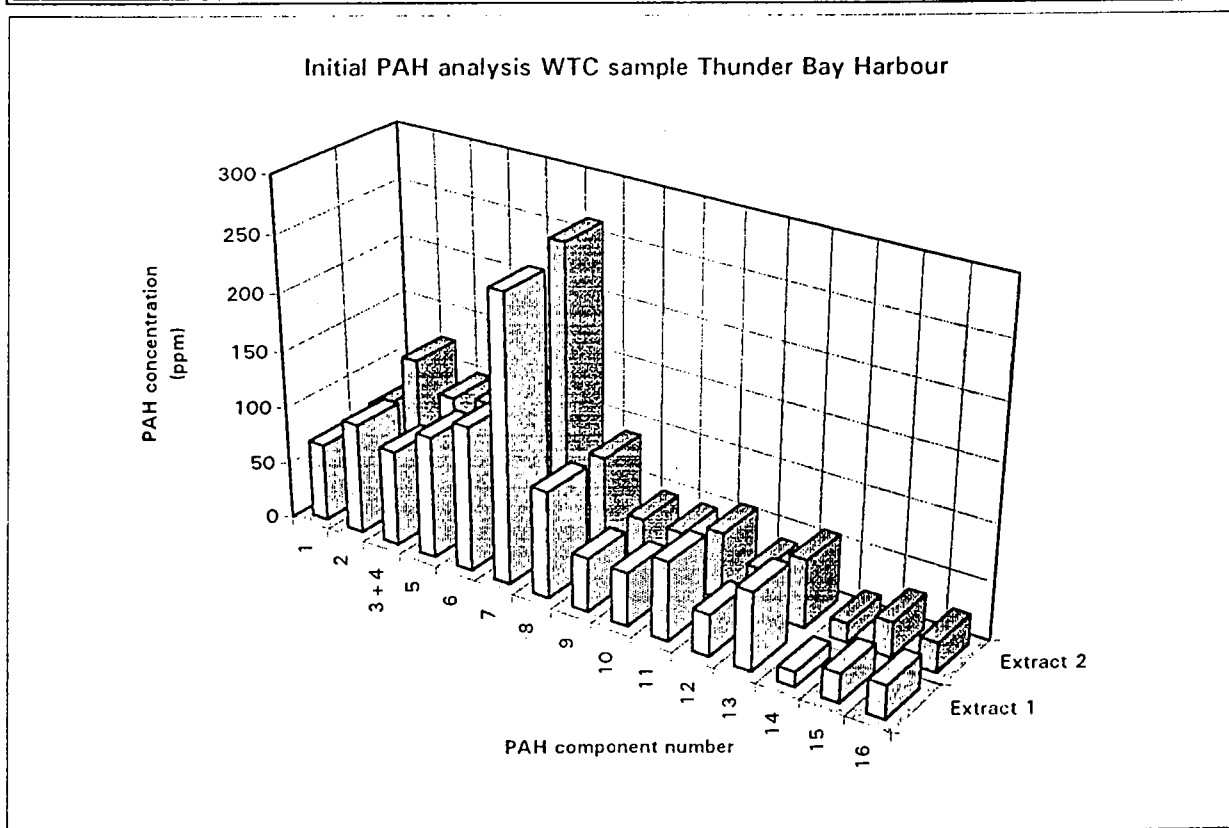
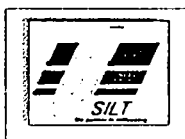


Figure 4 : PAH Basic PAK analysis



Laboratory report

WTC sample: ITORICS-Test

Physico-chemical extraction test

Date report: 23--2-94

Analysis	Sediment	Extraction step 1 sediment	Supernatant	Rinsed sediment	Rinsing water	Simapur cake	Supernatant at process end
DM %	43.52	19.03 ND		18.91 ND		9.07 ND	
pH	6.98	2.7	2.4	2.7	3.25	7.25	7.35
Cu	25.27	6.981	1.24	3.406	0.3805	95.365	0.133
Cd	1.55	4.15	1.01	0.243	0.041	1.452	0.032
Co	40.33	4.047	0.61	1.725	0.205	4.296	0.12
Cr	17.013	9.46	0.682	6.413	0.0485	3.969	0.163
Zn	96.08	37.79	9.74	19.31	3.54	91.07	0.44
Ni	35.53	6.07	1.2	5.086	0.38	9.021	0.26
Pb	16.21	7.31	1.606	5.08	0.885	8.454	0.136
Fe	14011	8194.9	710	4268.1	313	5541.5	27

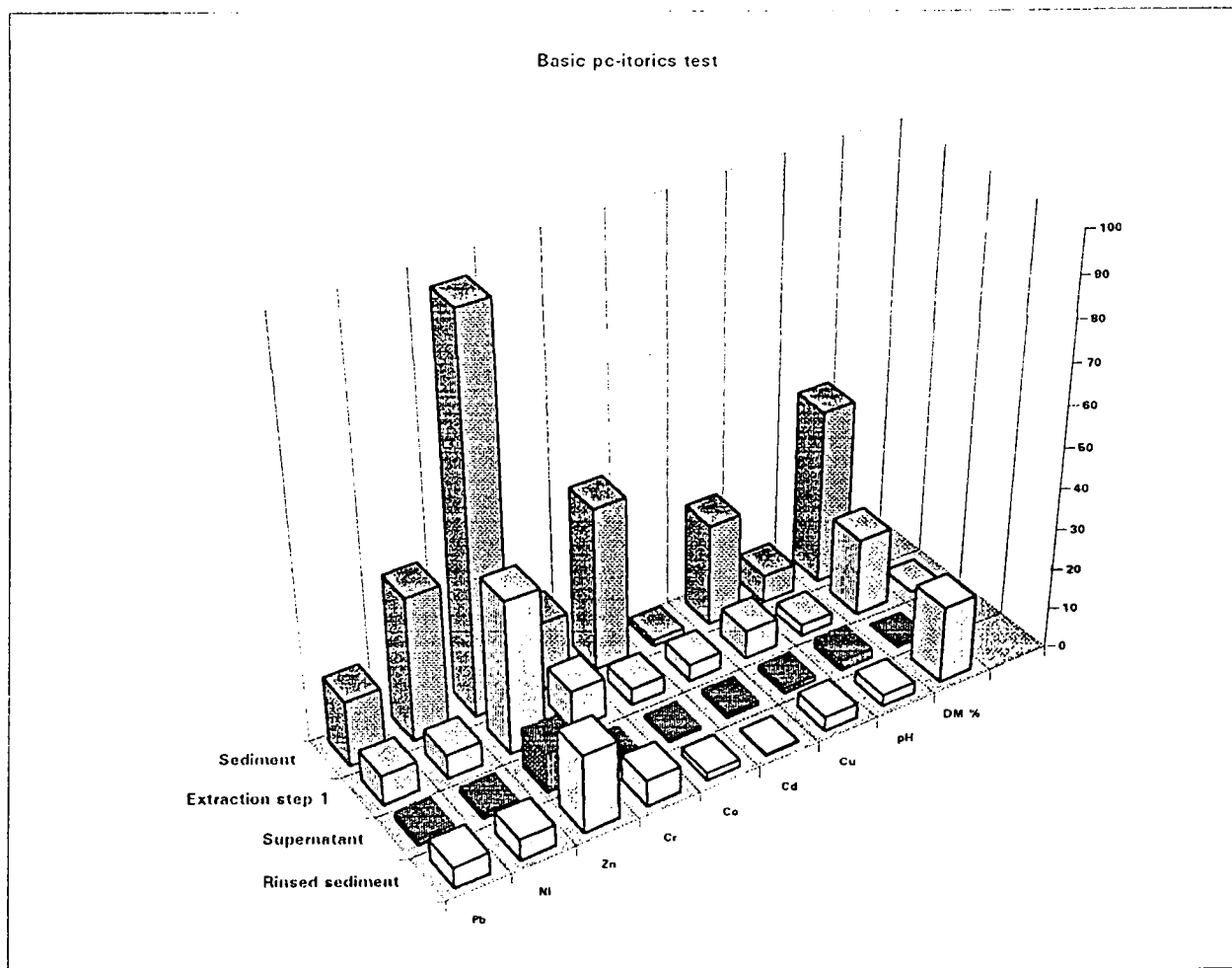


Figure 5 : Basic ITORICS test



Laboratory report

WTC sample: ITORICS-Test

Date report: 15--3-94

Sample		Nr	Zn	Pb	Co	Ni	Cu	Cd	Cr	Fe
No Treatment	Sediment	1	97.4	16.895	48.02	36.24	25.27	1.34	32.3	13160
Treatment 1	Sediment	2	40	9.63	7.15	21	57.55	0.34	50.75	16565
Treatment 2	Sediment	4	55.5	9.07	5.35	31	52.55	0.845	50.85	20220
Treatment 3	Sediment	6	64	11.248	7.925	36.5	90.85	0.903	45.63	22622.5
Treatment 4	Sediment	8	73.55	12.08	8.05	33.5	115.2	0.75	45.65	21370
Treatment 5	Sediment	10	66	5.505	6.55	30	127.45	0.79	46.6	15635
Treatment 1	Supernatant	3	1.975	0.185	0.12	1.03	0.452	0.0315	0.255	179.45
Treatment 2	Supernatant	5	2.81	0.434	0.335	1.8	0.4035	0.063	0.699	7.5
Treatment 3	Supernatant	7	3.22	0.318	0.22	1.075	1.364	0.048	0.362	123.83
Treatment 4	Supernatant	9	5.69	0.783	0.28	2.25	7.12	0.081	0.789	450.9
Treatment 5	Supernatant	11	8.08	0.471	0.425	1.55	5.185	0.07	0.756	545

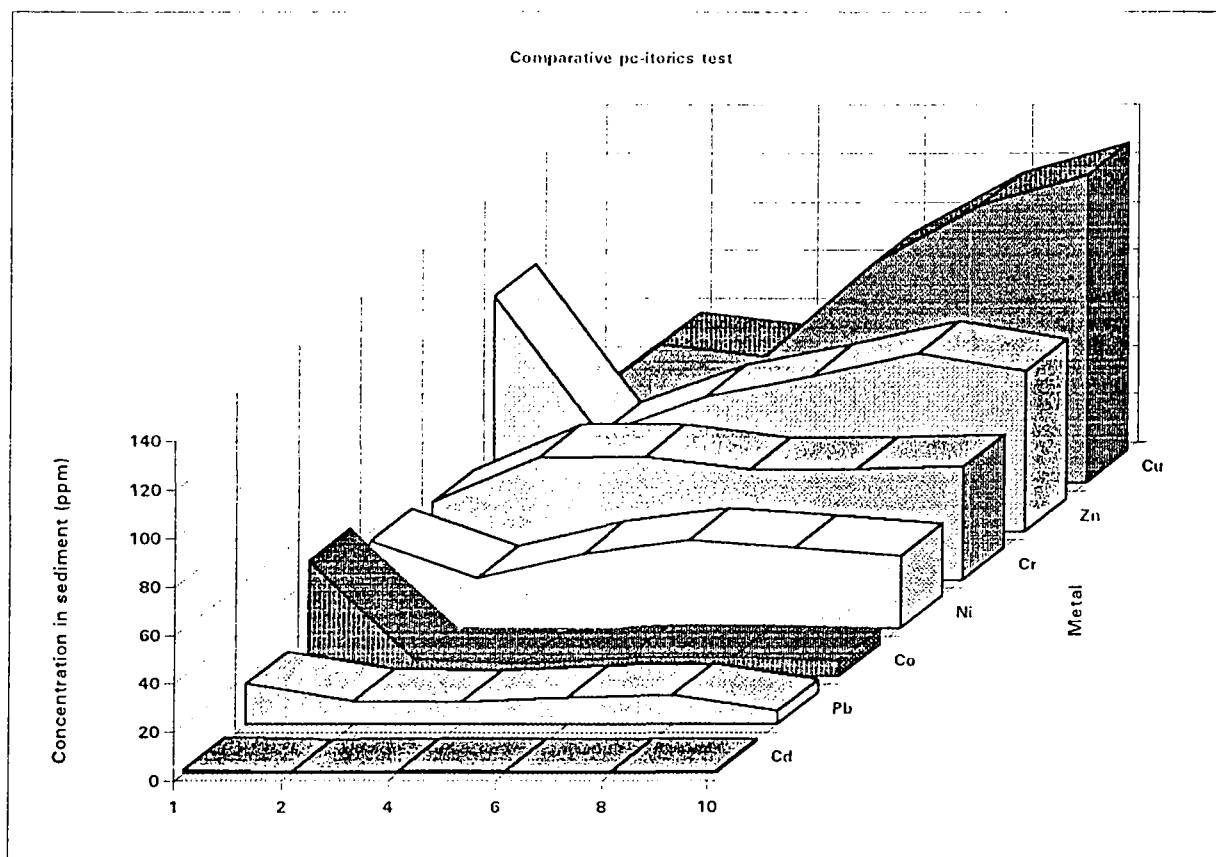


Figure 6 : Cocktail ITORICS test

Laboratory report

PAH Concentration sample (WTC) Canada



PAH concentration obtained before and after TORICS-treatment on the respirometer

WTCY2 treatment

Date bench scale test report : 24 februari 1994

PAK	nr	Concentration in ppm			
		40 days	28 days	21 days	Before treatment
Naphtalene	1	3.4	19.2	7.39	72.86
Acenaphthylene	2	10.5	18.1	28.18	124.89
Acenaphthene+fluorene	3+4	7.3	10.6	10.43	101.5
Phenanthrene	5	5.2	5.35	8.93	106.98
Anthracene	6	8.4	12.1	79.21	126.96
Fluoranthene	7	50.6	70.3	78.33	264.02
Pyrene	8	20.9	83.3	16.75	90.17
Benz(a)anthracene	9	2.9	3.18	6.73	46.75
Chrysene	10	17.3	25.9	4.09	46.94
Benz(b)fluoranthene	11	28.9	34.88	45.58	58.09
Benz(k)fluoranthene	12	26.5	33.91	37.04	38.26
Benz(a)pyrene	13	14.3	23.27	32.5	58.63
Dibenzo(a,h)anthracene	14	5.2	10.3	13.99	16.52
Benzo(g,h,i)perylene	15	8.5	15.32	18.04	30.4
Indo(1,2,3)cd-pyrene	16	17.3	15.15	24.96	25.37
Total PAH's		227.2	380.1	412.15	1208.34

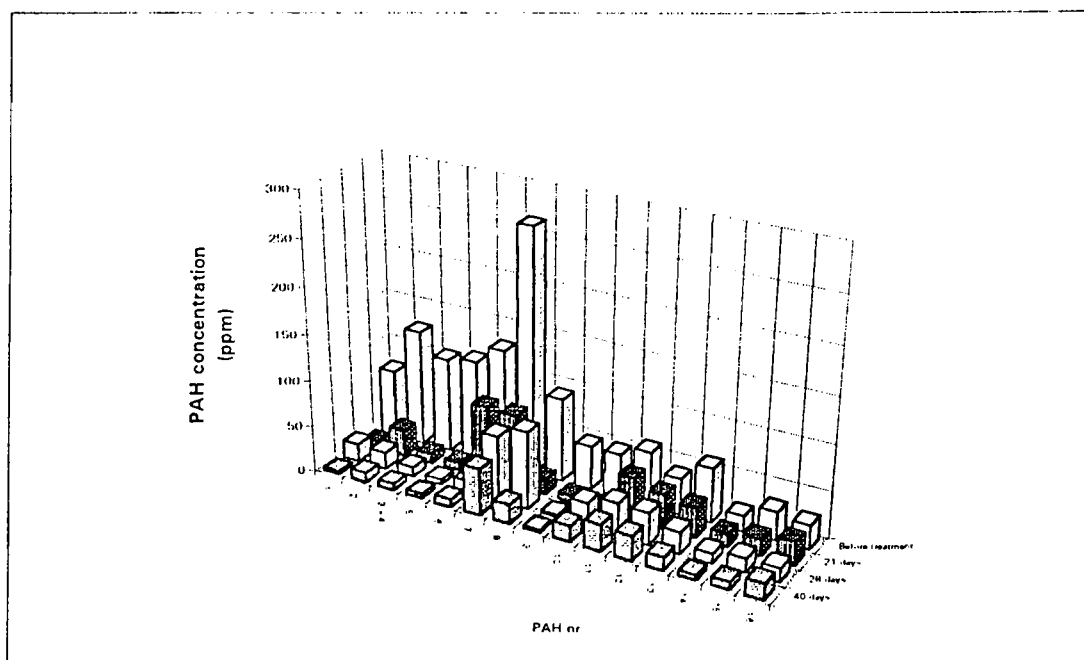


Figure 7 : X₂ treatment

Laboratory report

PAH Concentration sample (WTC) Canada



PAH concentration obtained before and after TORICS-treatment on the respirometer

WTCY2 treatment

Date bench scale test report : 24 februari 1994

PAK	nr	Concentration in ppm			
		40 days	28 days	21 days	Before treatment
Naphtalene	1	3.4	19.2	7.39	72.86
Acenaphtylene	2	10.5	18.1	28.18	124.89
Acenaphtene+fluorene	3+4	7.3	10.6	10.43	101.5
Phenantrene	5	5.2	5.35	8.93	106.98
Anthracene	6	8.4	12.1	79.21	126.96
Fluoranthene	7	50.6	70.3	78.33	264.02
Pyrene	8	20.9	83.3	16.75	90.17
Benz(a)anthracene	9	2.9	3.18	6.73	46.75
Chrysene	10	17.3	25.9	4.09	46.94
Benz(b)fluoranthene	11	28.9	34.88	45.58	58.09
Benz(k)fluoranthene	12	26.5	33.91	37.04	38.26
Benz(a)pyrene	13	14.3	23.27	32.5	58.63
Dibenzo(a,h)anthracene	14	5.2	10.3	13.99	16.52
Benzo(g,h,i)perylene	15	8.5	15.32	18.04	30.4
Indo(1,2,3)cd-pyreen	16	17.3	15.15	24.96	25.37
Total PAH's		227.2	380.1	412.15	1208.34

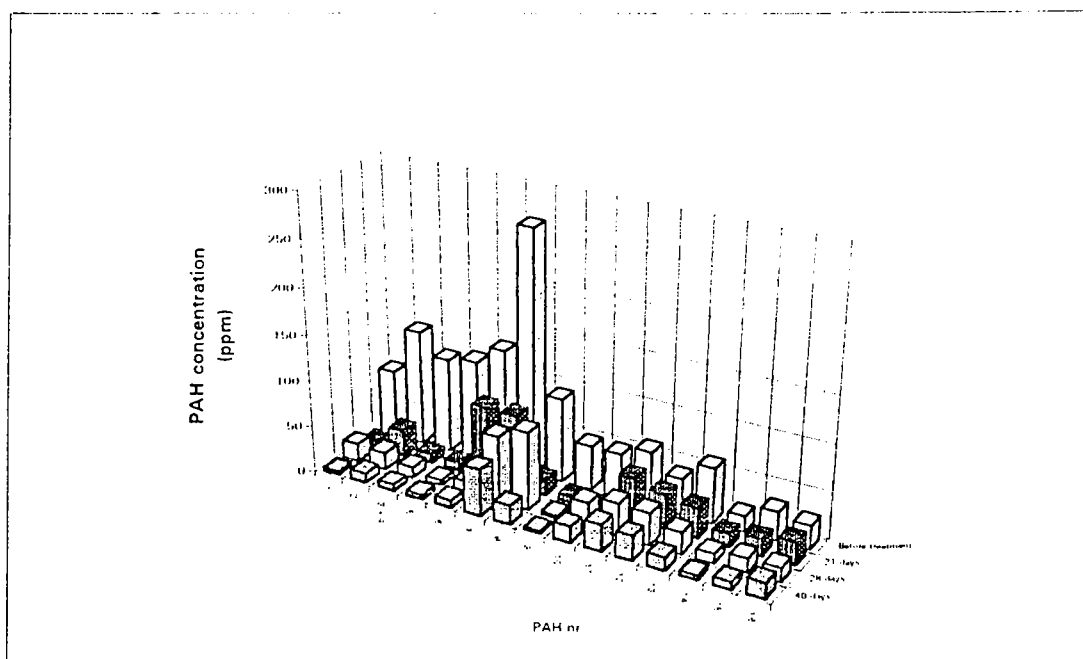
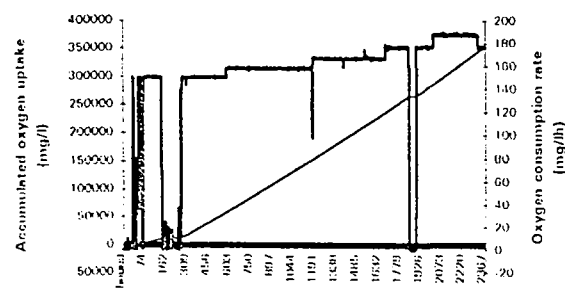


Figure 8 : Y₂ treatment

1

INDIGENEOUS Stimulation Test



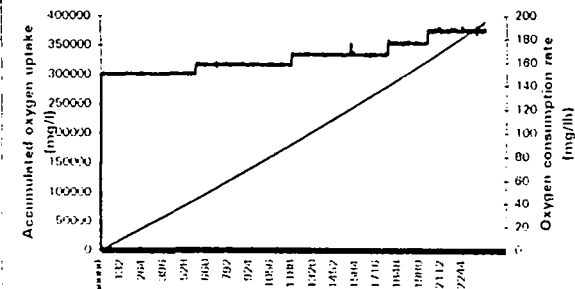
3

ITORICS C Test



5

ITORICS E Test



2

ITORICS B Test



Laboratory Report

Blanco



PAH	PAH concentration (ppm)					
	108 days	90 days	70 days	53 days	29 days	Start
Naphthalene			10.43	10.43	40.84	72.86
Acenaphthylene				18.75	60.22	124.89
Acenaphthene+Fluorene	0.35	2.01	3.72	14.91	34.72	101.5
Phenanthrene	4.74	15.46	34.57	16.08	71.09	106.98
Anthracene	0.98	8.63	15.23	25.2	76.06	126.96
Fluoranthene	4.74	14.75	34.3	52.98	139.05	264.02
Pyrene		3.59	6.89	35.25	76.43	90.17
Benz(a)anthracene	0.38	0.65	5.84	23.55	53.41	46.75
Chrysene		4.31	8.13	32.22	47.22	46.94
Benzo(b)fluoranthene	30.21	35.15	45.28	45.28	46.96	58.09
Benzo(k)fluoranthene	7.94	20.15	26.1	29.08	29.46	38.26
Benzo(a)pyrene	20.73	42.32	51.9	50.62	59.86	58.63
Dibenz(ah)anthracene	6.05	6.12	8.42	10.52	14.54	16.52
Benzo(ghi)perylene	16.26	22.76	23.32	26.62	28.3	30.4
Indeno(1,2,3-cd)pyrene	14.82	16.04	16.54	23.5	25.3	25.37
Total PAH	107.2	191.94	290.67	414.99	803.46	1208.34

Blanco

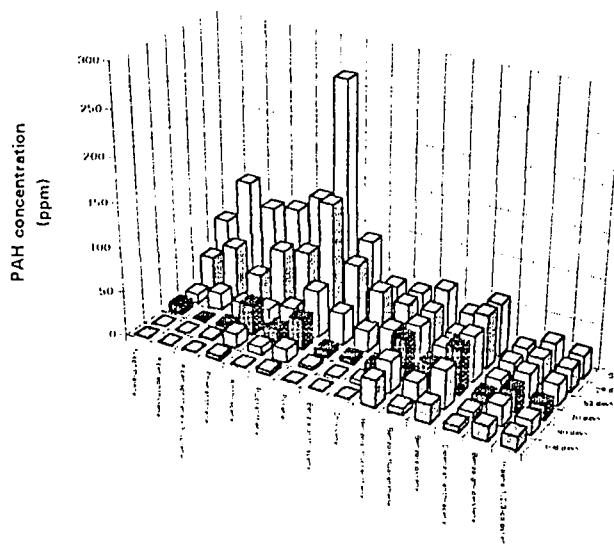


Figure 10 : Blanco BST

Laboratory report

Treatment X



PAH	PAH concentration (ppm)					
	108 days	90days	70 days	53 days	29 days	Start
Naphthalene	1.66			19.76	22.3	72.86
Acenaphthylene				38.99	51.05	124.89
Acenaphthene+Fluorene			9.04	13.25	14.53	101.5
Phenanthrene	4.76	5.02	5.62	28.95	115.11	106.98
Anthracene		5.66	3.71	22.7	32.05	126.96
Fluoranthene		30.15	32.3	36.04	69.44	264.02
Pyrene		6.65	23.8	46.05	81.4	90.17
Benz(a)anthracene	0.32	4.9	20	26.49	40.06	46.75
Chrysene		7.5	8.6	32.07	34.33	46.94
Benzo(b)fluoranthene	16.31	20.31	30.21	45.83	30.45	58.09
Benzo(k)fluoranthene	14.71	14.05	15.71	12.26	25.72	38.26
Benzo(a)pyrene	24.83	30.05	32.38	38.9	40.59	58.63
Dibenz(ah)anthracene	2.83	3.31	6.66	3.54	5.9	16.52
Benzo(ghi)perylene	12.2	15.08	15.41	15.41	16.93	30.4
Indeno(1,2,3-cd)pyrene	15.08	16.02	16.28	17.36	22.32	25.37
Total PAH	92.7	158.7	219.72	397.6	602.18	1208.34

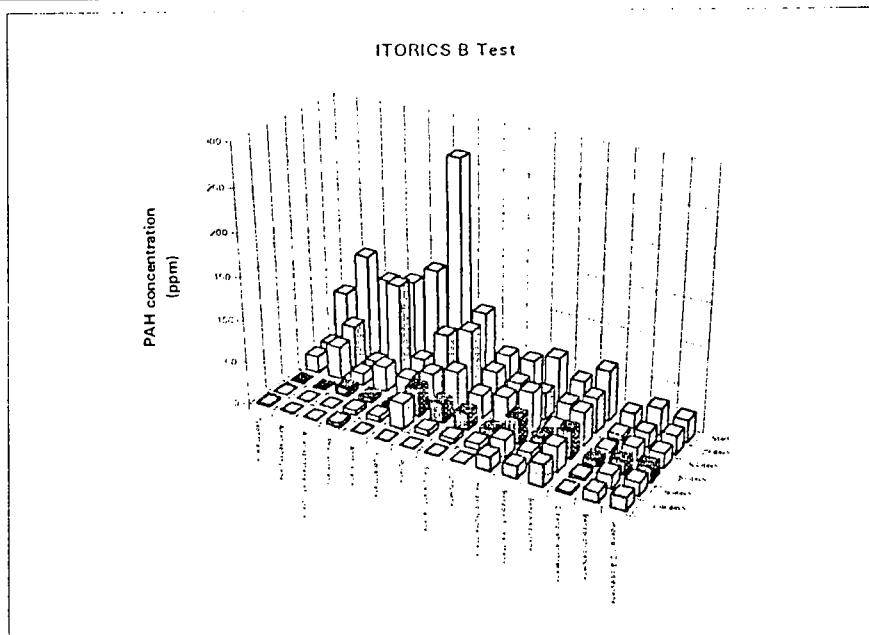


Figure 11 : ITORICS B Test

Laboratory Report

Treatment Y2



	PAH concentration (ppm)					
PAH	108 days	90 days	70 days	53 days	29 days	Start
Naphthalene				20.47	37.33	72.86
Acenaphthylene				21.26	41.18	124.89
Acenaphthene+Fluorene		2.87		10.96	23.02	101.5
Phenanthrene	3.52	4.39	2.67	23.5	26.72	106.98
Anthracene	2.06	4.05	4.08	19.27	51.62	126.96
Fluoranthene	4.12	6.59	18.84	32.5	103.23	264.02
Pyrene		14	25.42	26.45	71.48	90.17
Benz(a)anthracene	0.38	0.54	1.13	28.35	31.69	46.75
Chrysene		7.94	5.33	16.51	32.36	46.94
Benzo(b)fluoranthene	13.52	30.42	28.55	28.55	36.35	58.09
Benzo(k)fluoranthene	13.02	18.39	15.07	7.85	15.08	38.26
Benzo(a)pyrene	24.65	32.74	33.28	41.45	45.66	58.63
Dibenz(ah)anthracene	2.25	4.05	4.11	4.85	6.05	16.52
Benzo(ghi)perylene	10.23	13.11	14.27	14.37	20.48	30.4
Indeno(1,2,3-cd)pyrene	8.09	14.22	14.41	17.05	18.25	25.37
Total PAH	81.84	153.31	167.16	313.39	560.5	1208.34

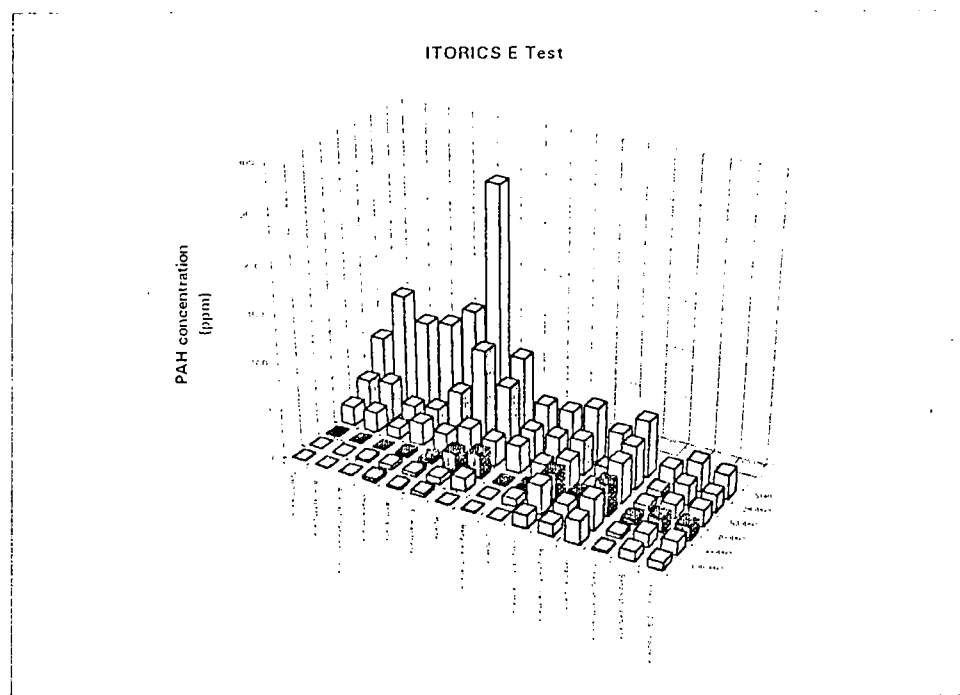


Figure 14 : ITOICS E Test

Laboratory Report

Treatment Z



PAH	PAH concentration (ppm)					
	108 days	90 days	70 days	53 days	29 days	Start
Naphthalene	1.13	3.51		24.74	24.86	72.86
Acenaphthylene	4.65	5.28		30.85	58.47	124.89
Acenaphthene+Fluorene	1.81			11.56	12.37	101.5
Phenanthrene	6.83	4.48		7.78	12.03	106.98
Anthracene	2.34	2.49		88.48	104.88	126.96
Fluoranthene	5.75	11.58		76.44	86.02	264.02
Pyrene	8.19	10.58		52.04	88.18	90.17
Benz(a)anthracene	0.88	5.07		5.71	25.92	46.75
Chrysene	4.85	5.07		18.32	30.05	46.94
Benzo(b)fluoranthene	25.18	36.08		42.77	35.94	58.09
Benzo(k)fluoranthene	14.63	16.08		10.99	22.09	38.26
Benzo(a)pyrene	32.95	42.92		46.71	45.85	58.63
Dibenz(ah)anthracene	4.43	10.33		3.97	7.37	16.52
Benzo(ghi)perylene	18.34	20		21.07	27.69	30.4
Indeno(1,2,3-cd)pyrene	14.58	20.03		20.16	20.62	25.37
Total PAH	146.54	193.5		461.59	602.34	1208.34

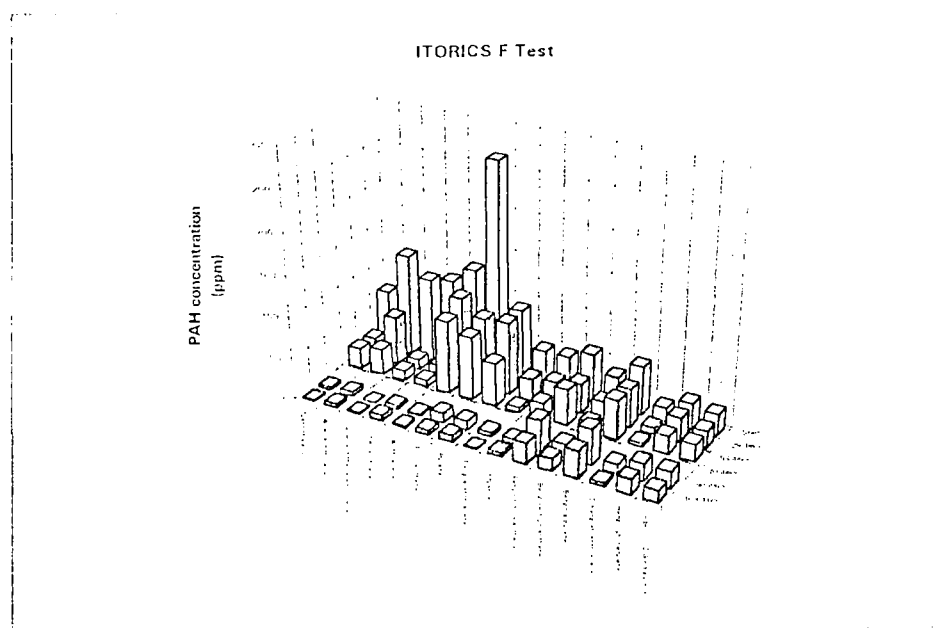


Figure 15 : ITORICS F Test

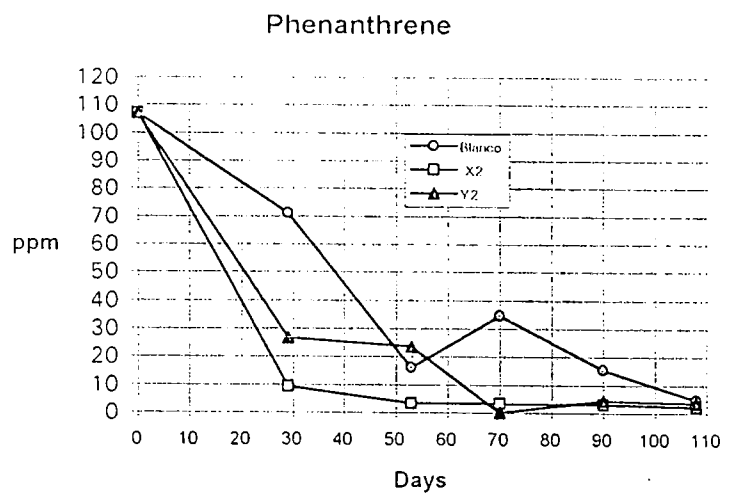
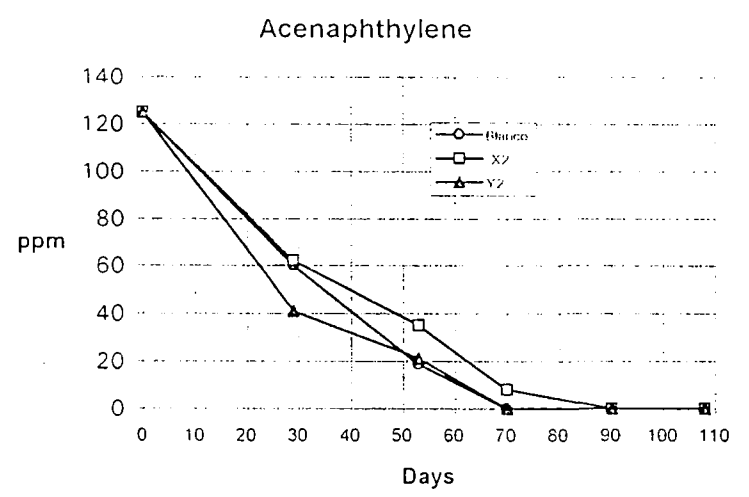
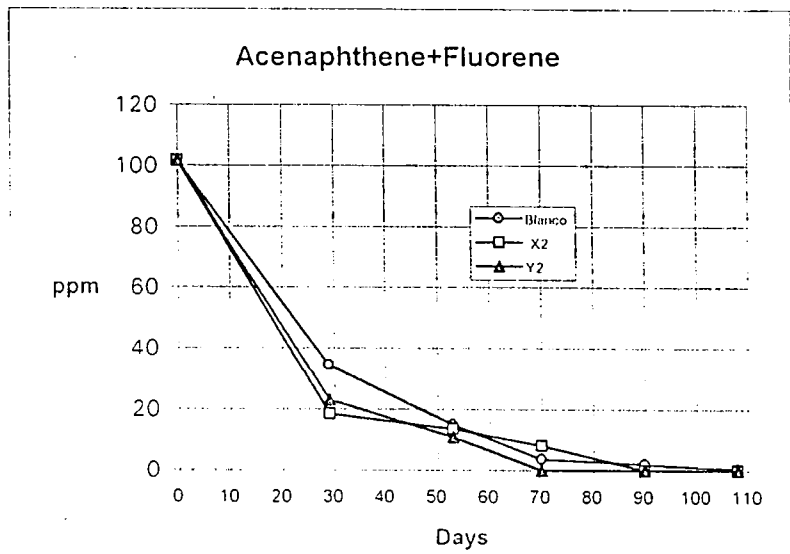
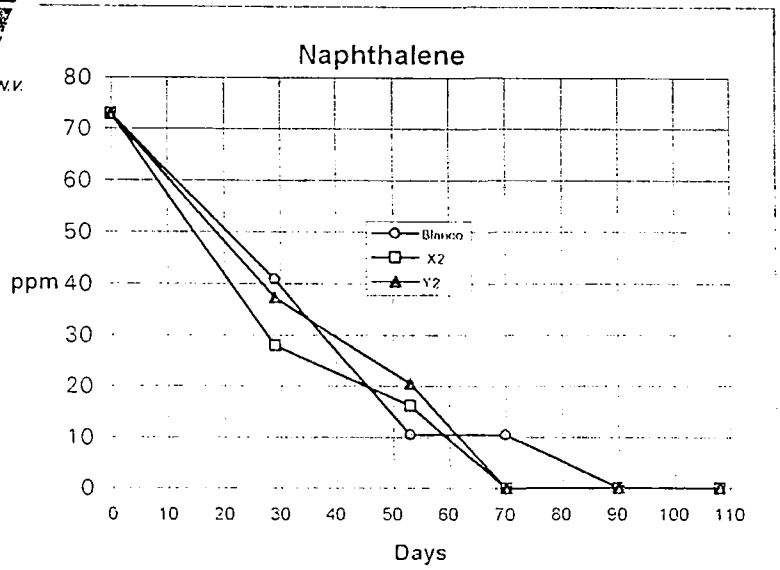


Figure 16 : Single PAH-component degradation analysis
Naphthalene, Acenaphthene+Fluorene,
Acenaphthylene, Phenanthrene

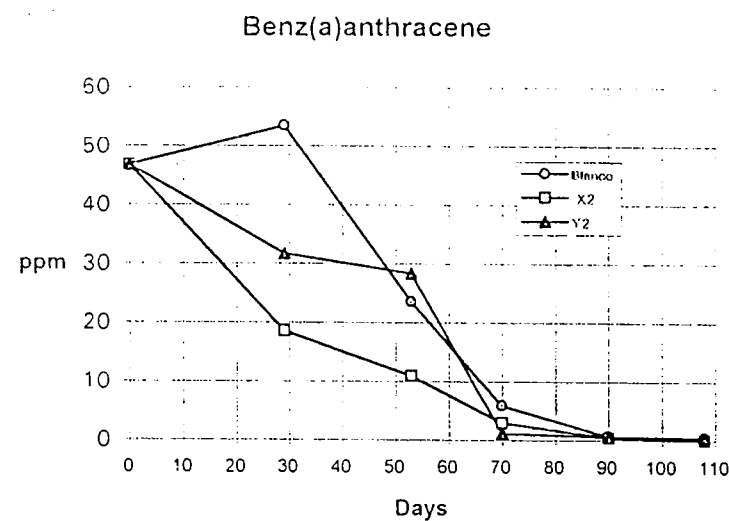
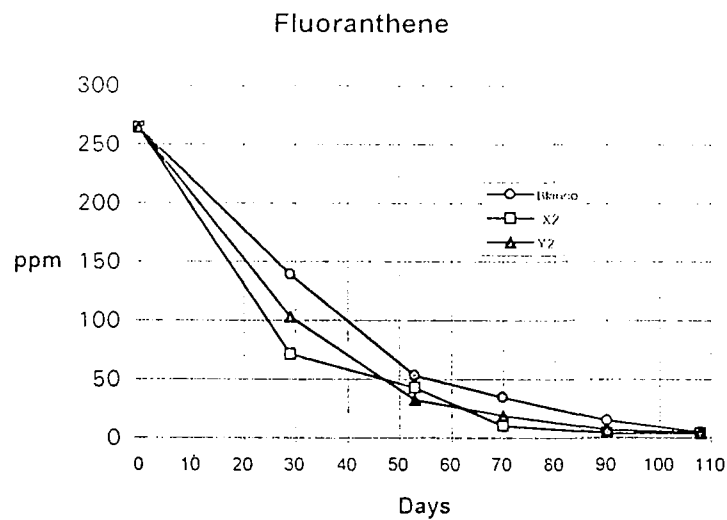
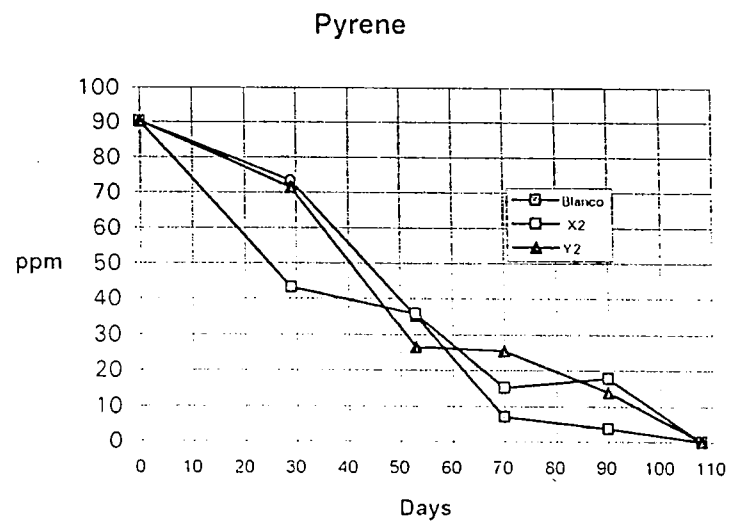
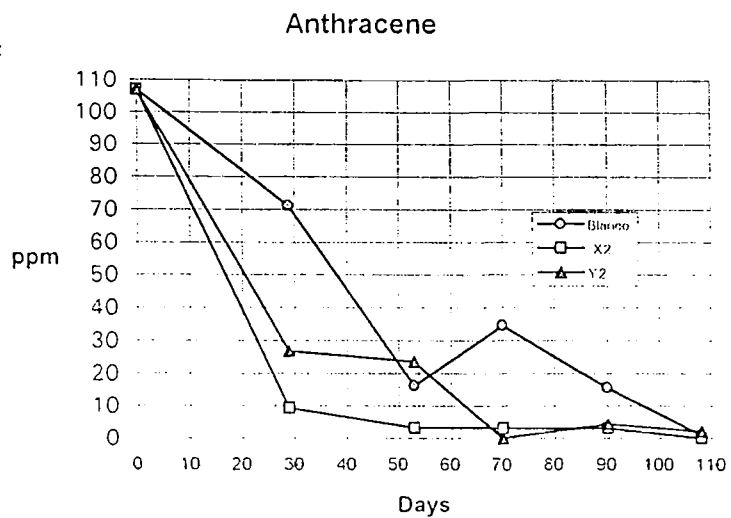


Figure 17 : Single PAH-component degradation analysis
Anthracene, Pyrene, Fluoranthene,
Benz(a)anthracene

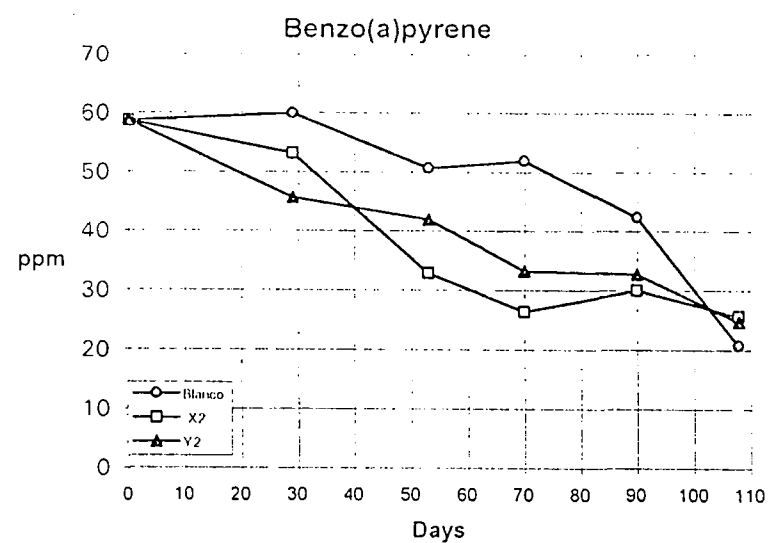
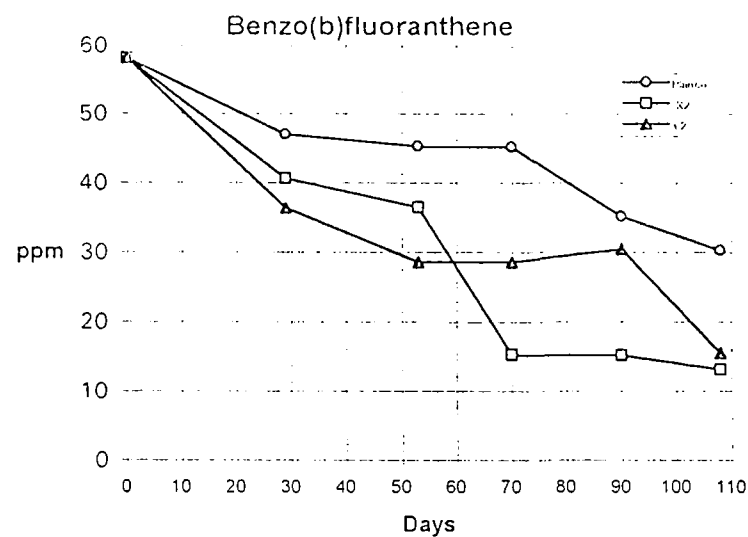
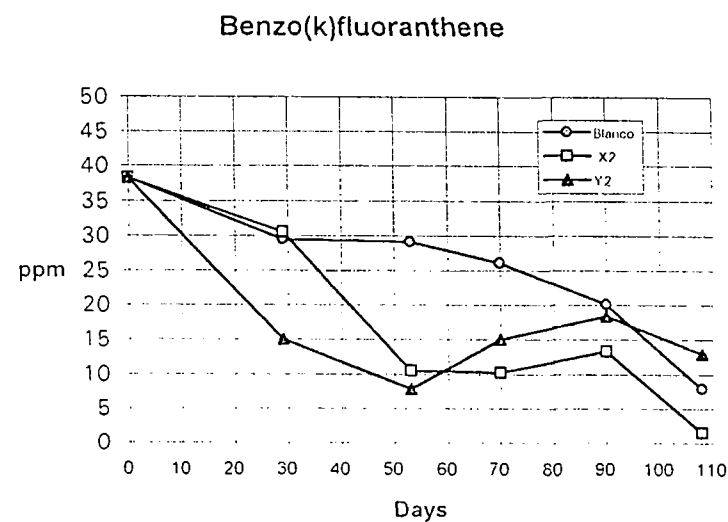
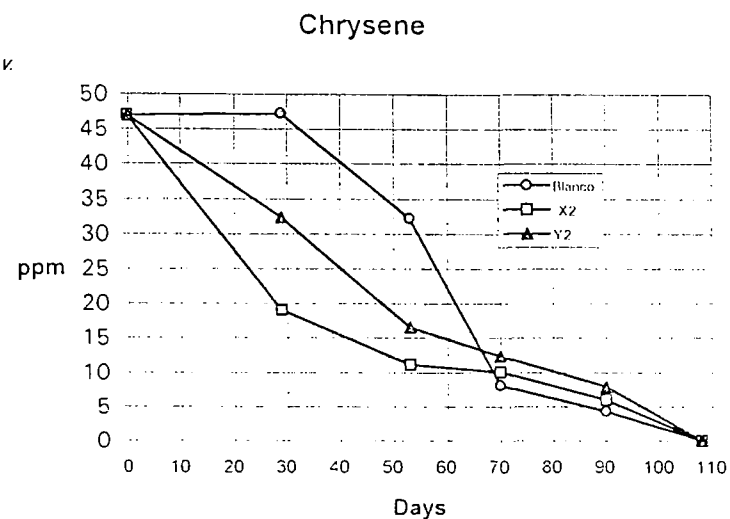


Figure 18 : Single PAH-component degradation analysis
Chrysene, Benzo(k)fluoranthene,
Benzo(b)fluoranthene, Benzo(a)pyrene

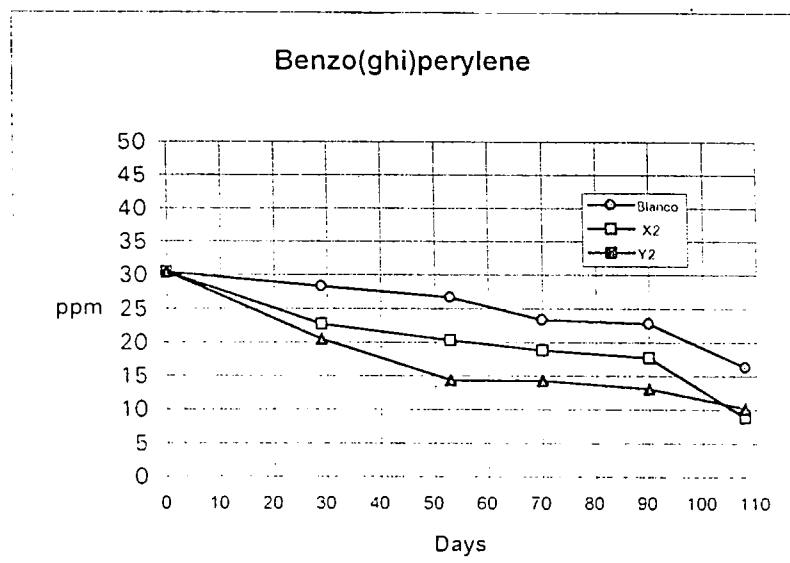
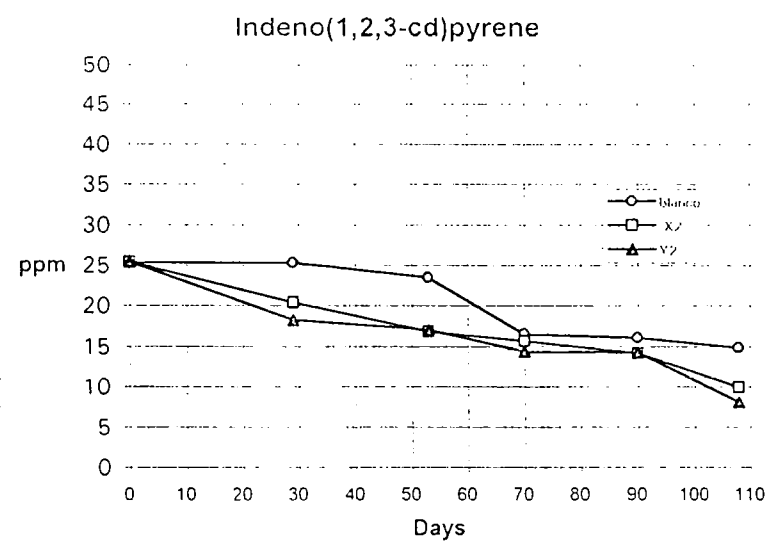
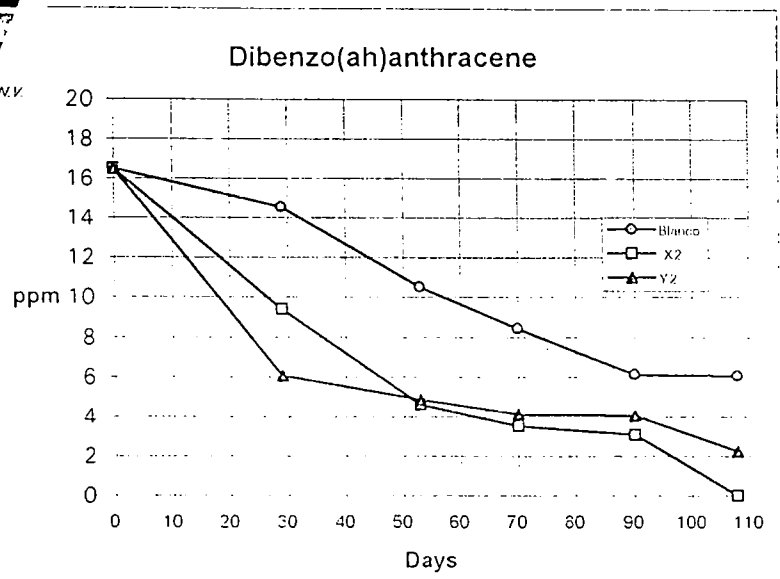


Figure 19 : Single PAH-component degradation analysis
Dibenzo(ah)anthracene,
Benzo(ghi)perylene
Indeno(1,2,3-cd)pyrene

B. Internal WTC audit report.

Wastewater Technology Centre

operated by RockCliffe Research Management Inc.

Centre Technique des Eaux Usées

dirigé par Gestion de Recherche RockCliffe Inc.

867 Lakeshore Road
P.O. Box 5068, Burlington
Ontario, Canada, L7R 4L7
☎ (905) 336-4855
Fax (905) 336-4765



File-N/Reference
Project 51895

17th April, 1995

Dr. J. De Brabandere
SILT N.V. Pre- and Post Dredging Services
Haven 1025 - Scheldedijk 30,
B-2070 Zwijndrecht, Belgium

Dear Dr. De Brabandere:

Re: SILT N.V.: ITORICS Bench-Testing with Thunder Bay Harbour Sediments

Please find the attached revised audit report for the bench testing undertaken by SILT N.V. with Thunder Bay Harbour sediments in the 1994 Fiscal year. This letter and its enclosures summarizes a comparison of WTC and SILT analytical data for organics contaminant levels in sediment samples collected from your bench-testing trials. Your final report should include both the letter and audit report. If you have any questions or concerns about this report, please feel free to contact me at your convenience.

Sincerely,

Wayne Randle
Site Remediation Division

cc Craig Wardlaw



WTC AUDIT REPORT: SILT N.V. ITORICS BENCH-SCALE TREATMENT OF THUNDER BAY HARBOUR SEDIMENTS

On July 12, 1994 six sediment samples were received at the Wastewater Technology Centre (WTC). Two of the samples were sludges which had been subjected to two separate testing scenarios, Itorics 1 & 2, respectively. A "control" sludge sample, Blanco, was also received. This sample had not been augmented with any bacterial blends, but was subjected to physico-chemical treatment. A sample of untreated sediment and liquid supernatants from the two treatments were also provided. The WTC audit involved chemical analysis of these samples for Polynuclear Aromatic Hydrocarbons (PAH's) in WTC laboratories, and a comparison of these data to the data reported by SILT in their report contained herein. The audit was based solely on the analytical data for the sludges.

Polynuclear Aromatic Hydrocarbons:

Table 1 summarizes the analytical data for the priority list of PAH compounds measured in the various sludge samples. At the WTC laboratory, each of the samples was Soxhlet extracted with acetone/hexane followed by GC/MS analysis. Overall, there was poor to fair agreement with the SILT data. The WTC data was on average 50% higher than the SILT data. However, this result is surprising since the extraction methodology(s) described in the SILT report for the PAH's analyses appeared to be at least as rigorous as those applied by the WTC laboratory. Presumably, the variability in PAH values was influenced by natural sample heterogeneity, which would have been a consideration given the nature of Thunder Bay Harbour sediment. Although not specifically listed in Table 1, the recoveries of surrogate compounds reported by the WTC laboratory were generally above 90%. Similar data was not reported for the SILT bench testing. The total PAH concentration of bulk sediment was 1867 µg/g, as measured by WTC Laboratories, compared to 1208 µg/g measured by the SILT laboratories. Results for some of the individual compounds compare very well. In particular, for the bulk (REFERENCE) sediments, where measured concentrations for the four and five-ring compounds are in very good agreement.

PARAMETER	SAMPLE CONCENTRATION AFTER 108 DAYS OF TREATMENT, µg/g dry weight basis					
	BLANCO SLUDGE		TREATMENT Y2 SLUDGE		REFERENCE (UNTREATED SEDIMENT)	
	WTC (AUDIT)	SILT	WTC (AUDIT)	SILT	WTC	SILT
Naphthalene	16.8	-	12.6	-	227	72.9
Acenaphthylene	2.21	-	2.25	-	3.19	125
Acenaphthene+Fluorene	2.37	0.35	2.09	-	134	101
Phenanthrene	9.39	4.74	6.42	3.52	500	107
Anthracene	2.38	0.98	2.14	2.06	57.5	127
Fluoranthene	6.32	4.74	7.37	4.12	306	264
Pyrene	3.76	-	155	-	222	90.2
Benz(a)anthracene	3.24	0.38	14"	0.38	83	46.7
Chrysene	1.36	-	**	-	71	46.9
Benzo(b)fluoranthene	70'	30.2	86.2'	13.5	88	58.1
Benzo(k)fluoranthene	*	7.94	*	13.0	23	38.3
Benzo(a)pyrene	28.9	20.73	40.4	24.6	62	58.6
Dibenz(ah)anthracene	7.76	6.05	7.53	2.2	18.5	16.5
Benzo(ghi)perylene	29.5	16.3	27	10.2	38	30.4
Indeno(1,2,3-cd)pyrene	23.5	14.8	21.2	8.1	34	25.4
Total PAH	207	107	384	81.7	1867	1208

Table 1. Comparison of Audit and SILT analytical data for ITORICS Treatment Bench-Testing

- sample concentration not reported * Total benzo(b) and/or (k)fluoranthene

** Total benzo(a)anthracene and/or chrysene