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PAHs AND HEAVY METALs CONTAMINATED SEDIMENT: BIOAVAILABILITY, MOBILIZATION, BIOLOGICAL AND PHISYCO-CHEMICAL TREATMENT

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Introduction

Sediment is an essential, integral and dynamic part of natural and artificial water bodies and basins (e.g. rivers, lakes, harbours), derived from the weathering and erosion of minerals, organic material and soils in upstream areas and from the erosion of banks in downstream areas.

The sediment have a fundamental ecological, social and economic value, and are one of the key components of the aquatic ecosystems supporting life and forming a variety of habitats. For centuries mankind has recognised and utilised sediments in river systems as fertiliser for farmland (e.g. the Nile in Egypt) and as a source of minerals and materials (e.g. without sediments the western part of the Netherlands should not exist).

Nowadays many hazardous chemicals are discharged in waters, some of them do not readily dissolve in water, but rather stick to solids (e.g. sediment), breaking down very slowly. Polycyclic Aromatic Hydrocarbons (PAHs) and Heavy Metals are the most common contaminants impacting sediment. At a certain level, contaminants in sediment impact the ecological or chemical water quality status complicating sediment management because of the “extra” costs for treatment (dozens times higher).

Considering the significant quantitative and qualitative problems involved, the role of sediments in aquatic environment has not yet been adequately addressed. Sediment dynamics and pollutants mobility need an interdisciplinary approach especially because:

- Sediment quality assessment is considerably more complex than water quality assessment because of the many site-specific parameters that need to be considered. The bioavailability of a contaminant, for instance, is not only species-specific but is also controlled by sediment characteristics (e.g. grain size, minerals);
- remediation techniques for contaminated sediments are generally more limited than for other solid waste. Considering world-wide dredging activities (more than 1 billion m³ year⁻¹) only a very small percentage of these materials can undergo ‘treatment’ such as solvent extraction, bioremediation, thermal desorption, that however are still not well established;
- risk assessment requires a comprehensive investigation of the behaviour, environmental stability, bioavailability and fate of pollutants in sediments.

Characterization, remediation methodologies and risk assessment should be seen within the context of Sustainable Sediment Management (SSM) and the holistic river-basin approach, as stressed in the Water Framework Directive of the European Union (EU). The goal of SSM is the central strategic objective of SedNet, Demand-Driven European Sediment Research Network, that have started its work in 2002 ending in 2006.

Observed that many issues have still to be addressed in contaminated sediment field, only a part of them were discussed in the present thesis investigating biological and physico-chemical sediment treatment technologies on sediments dredged in Italy and the Netherlands. Nevertheless the preventive application of characterization methods, as deliverable information tools, for selection of the proper treatment technologies was pointed out. Thus extraction procedures (i.e. BCR) for Heavy Metals and bioavailability studies for Heavy Metals and PAHs contaminated sediment were studied and applied. In fact the combination of the experimental results on characterization and treatment technologies should be pursued to deliver effective tools for the contaminant degradation. For instance, in thesis, a PAHs biodegradation three compartment model was proposed for landfarming PAHs contaminated sediment, based on the result of bioavailability tests.

Since up to now a common legislation on the management of the contaminated sediment has not yet been proclaimed at the EU level, an overview on the situation of several EU countries, regarding contaminated sediment legislation and remediation approaches applied, is discussed in Cap. 1. PAHs and Heavy Metals physico-chemical characteristics and their interaction with sediment are discussed in Chapter 2. In particular as established chemical protocols have been proposed to assess the total PAHs and Heavy Metals concentration in soil and sediment, the study was focused on Heavy Metals speciation and both PAHs and Heavy Metals bioavailability. Some treatment and disposal technologies for contaminated sediment are briefly discussed in Chapter 3, though several technologies, particularly referred to PAHs and Heavy Metals: Sediment Washing, Landfarming and Bioreactor are pointed out.

The contribution to the discussion about contaminated sediment, pointed out in Chapters 4, 5 and 6, is about the following topics:

- Characterization of PAHs and Heavy Metals contaminated sediment.
- Main factor (e.g. pH, E_h) affecting Heavy Metals mobilization from contaminated sediment.
- PAHs and Heavy Metals contaminated sediment bioavailability.
- Sediment washing of Heavy Metals contaminated sediment.

- Bioremediation of PAHs contaminated sediment by means of passive (Landfarming) and active (SS-SBR) technologies.
- Application of the LCA principles for the sediment treatment chains evaluation.

Heavy Metals mobilization from Sarno river contaminated sediment as a result of pH, redox potential and ionic strength modifications is presented in paragraph 5.1, whereas the effects of Heavy Metals contaminated sediment, dredged from Porto Marghera, on benthonic organisms (nematodes) is proposed in paragraph 5.2, in order to study Heavy Metals bioavailability. Sediment washing experiments on Heavy Metals contaminated sediments, dredged from Porto Marghera and Sarno river, are presented and discussed in paragraphs 5.3 and 5.4. Besides, the application of an electrochemical process to recover the chelating agents, used in the sediment washing step, is also discussed, aiming the application of an integrated cost effectiveness technologies to treat Heavy Metals contaminated sediment.

In paragraph 5.5 the results of a decennial landfarming experimental campaign on PAHs contaminated sediments, dredged by Dutch harbours, are reported. On the same sediments PAHs bioavailability studies, by means of the Tenax beads desorption, were carried out. Thus the validation and the application of a PAHs biodegradation prediction model, occurring in a PAHs contaminated sediment landfarming, based on concept of bioavailability, is proposed and discussed. PAHs contaminated sediment, dredged from Porto Marghera, treatment by means of an SS-SBR and PAHs bioavailability by means of Tenax beads desorption are reported in paragraph 5.6. Besides the Tenax desorption results were also used in the prediction model, previously proposed, to evaluate the PAHs biodegradation occurring in a landfarming treatment plant. Hence the comparison between active and passive bioremediation technologies is discussed.

Actually contaminated sediment are disposed in aquatic and subaquatic facilities. Treatment and reuse is politically encouraged, but is currently applied only at a small scale because of both the higher costs, compared to disposal, and the lack of product markets, though, in some cases, treatment and beneficial use may be a competitive alternative for confined disposal. However only the development of suitable tools, able to taking into account the life cycle of each sediment treatment chains (i.e. from cradle to grave) such as LCA, will provide the elements to compare different sediment treatment solutions. The application of the principles of the LCA to sediment treatment chains is presented in Chapter 6.

Chapter 1

1 International situation on contaminated dredged material

1.1 Introduction

The sediment that settle on the bottom of the waterways has to be removed for several reasons. Dredging consists in the sediment moving (transporting) from the bottom of the waterways to other locations. There are three types of dredging: capital, maintenance and remediation dredging. Capital dredging is mainly operated for land reclamation, maintenance dredging is mainly operated to keep waterways at a defined depth in order to ensure safe navigation, and remediation dredging is operated to solve environmental problems of contaminated sediments. Contamination mainly leads to problems in maintenance dredging because standards or regulations do not allow the free sediment disposal in the aquatic system, causing a sensible increasing of the dredging costs.

Europe-wide, the volume of dredged material is very roughly estimated at 200 million cubic metres per year. Up to now a common legislation on the management of the Dredged Material (DM) has not yet been proclaimed at the European Union level. Therefore the problem of Contaminated Dredged Material (CDM) has been also regulated in each European countries with legislations based, often, on different approaches. An overview of the DM international situation is discussed below for several European countries regarding the legislation and remediation approaches.

1.2 Netherlands

The Netherlands is a densely populated and industrialised country located in the delta of the rivers Rhine, Meuse, Ems and Scheldt, at the coast of North Sea. Each year 25-30 million m³ has to be removed albeit more than half of this amount comes from maintenance dredging of the Rotterdam harbour. The annual budget (including transport, relocation, disposal and

treatment) for dredging is on average € 130 million, of which the main part is spent on maintenance (€ 100 million year⁻¹).

Around three-quarters of dredged material is marine sediment that has been transported inland by sea currents. Actually, the 90% of the marine sediment is clean or only lightly contaminated and can be relocated back into the sea unlike. Contrary only 60% of the dredged fresh-water material can be relocated, because of both higher contamination levels and lack of space along the banks of the waterways. Thus approximately the 17.5% of the sediment dredged yearly in the NL is contaminated with organic and inorganic compounds and has to be treated.

The Dutch Soil Protection Act gives chemical criteria for both metals and organic contaminants to discriminate different levels of contamination in soils and sediments. The criteria reflect total amounts of contaminants in soil and sediments establishing 4 classes.

- Class 0 below target value clean and risks are negligible
- Class 1 Limit value: lightly contaminated
- Class 2 Test value: reference for relocation in surface water or on land
- Class 3 Intervention level: consider remediation
- Class 4 Signal value: only for heavy metals, consider remediation

Contaminant levels are normalised in order to compensate for differences in sorption characteristics between sediments. Conversion is operated referring to standard sediment with 10% organic matter and 25 % lutum (<2 micron). Normalised contaminant levels are then compared with the Dutch soil/sediment quality criteria to arrive at this classification. Following the Dutch environmental policy the order of destination preferences for DM are: relocation, direct reuse, treatment for beneficial use and at the end confined disposal.

Nevertheless the Dutch Government is putting a lot of efforts to develop suitable assessment tools, both chemical and biological, coupling the latter with the acceptable total concentration of organic and inorganic contaminants. One example is the Dutch criteria for relocation in sea, called chemical toxicity test (CTT), are based on chemical standards, bio-assays and new chemical criteria such as TBT (Stronkhorst 2003). Due to the enormous amounts of dredged material involved in relocation in sea and on land, approximately 25 million m³ year⁻¹, small changes in the regulatory framework may have large consequences for the amounts of dredged material that have to be treated or disposed.

For the dredged material that is too contaminated for relocation (3-5 million m³ year⁻¹) there are two options: treatment for beneficial use and disposal. Up to now dredged material has

been treated and re-used on a small scale only, because of higher costs of treatment compared to disposal and the problems for the public acceptance for the products of treatment. The mostly used techniques are natural dewatering or ripening ($0.7 \text{ million m}^3 \text{ year}^{-1}$) in rural areas and sand separation ($\text{m}^3 \text{ year}^{-1}$) near confined disposal facilities (CDF's). Furthermore, on a very limited scale, treatment techniques such as land farming and chemical immobilisation/stabilisation are used. Thermal immobilisation techniques to produce artificial gravel, aggregate or bricks are being considered, but not (yet) in operation.

Confined disposal in large sub-aquatic facilities is the main solution in the Netherlands for contaminated sediments that cannot be relocated. In the Netherlands extensive knowledge and experience has been gathered in the design and construction of large-scale sub-aquatic confined disposal facilities. Sub-aquatic confined disposal is considered to be an environmentally sound solution if properly designed, constructed and monitored, but a site-specific approach is necessary. Only a very small amount of dewatered dredged material is disposed in upland waste disposal sites. The largest confined disposal facility, known as the Slufter, has a design capacity of 90 million m^3 , which is mainly meant to store the contaminated dredged material from around Rotterdam. Another sub-aquatic confined disposal facility was recently constructed in the Ketelmeer (IJsseloo) with a capacity of 23 million m^3 .

1.2.1 Rotterdam harbour

In the port of Rotterdam around 20 million m^3 are dredged each year. The 90% of this material is relocated at the sea while contaminated dredged material is stored in a large confined disposal site, called the Slufter (Vellinga et al. 2003). The policy of the Rotterdam port authorities is to encourage beneficial use of the dredged material therefore since 1992 sand is separated in sedimentation basins and recently also clay is produced by natural dewatering from the dredged material. Since 2001 studies are carried out into chemical and thermal immobilisation and into the possibilities for the actual use of the dredged material. The amount of contaminated dredged material has decreased over the years due to, amongst others, the focus on the control of the initial sources of contamination by the Municipal Port Management.

1.3 Germany

In Germany (DGE 2002) about 40 to 50 million m³ of sediments have to be dredged annually for maintenance of ports and waterways, mainly in the coastal areas of the North Sea. Maintenance of the waterways is done by the Federal Waterways Administration while maintenance of the ports is done by the Federal States or Cities. Most of the above mentioned material stems from the sea and is more or less uncontaminated and can therefore be relocated. However contaminants like heavy metals, organic contaminants or TBT in the North Sea unlike to the nutrient in the Baltic Sea do not always allow their relocation into the sea.

There is no common and also no coherent German policy on DM. Germany is still working with a variety of guidelines/directives which are not nationally harmonised and limited to special areas of competence (e.g. federal waterways, harbours, Federal states). The guidelines and directives like Federal Water Act (WHG 1996), Federal Waterway Act (WStrG), Federal Soil Act (BBodSchG), Waste Management Act (KrW/AbfG 1994), HABAB - inland (HABAB 2002) and Habak - coastal (Habak 1999) have a dominant role and are the starting point in a process of national harmonisation which has started in the coastal area so far.

Hamburg and Bremen are the more active federal cities involved in the management of CDM; these cities have proposed and applied in large scale two option for the treatment of CDM as reported briefly below.

For treatment of DM Hamburg (Strom and Hafengebäude 2003) is operating the large scale METHA-plant. Its main task is to separate sand and fine-sand from silt and recovering the sand as building material and dewatering the (contaminated) silt for further beneficial use (e.g. brick production) and/or disposal. The throughput capacity is roughly 1 million m³ sediment in-situ per year corresponding to more than 500000 tons dry matter. Total investment cost was € 70 million (in the year of construction 1993). Including capital costs and expenditure for operation, maintenance and personal, the specific costs average to 15-20 €/ m³ sediment in-situ. The same task as in the METHA can be accomplished by flushing fields (for classification) and dewatering fields. Advantage are lower operating costs, disadvantages are large areas needed and dependence on climate. The pre-treated silt is mainly disposed in two specially constructed silt mounds which fulfil German criteria for landfills. Each has a capacity for ca. 20 Mio. m³ untreated sediment and will reach a final

height of 38 m above the ground. In these mounds, the separated sand is beneficially used as drainage material.

The ports of Bremen consist of the two harbour sections Bremen-City and Bremer harbour. Annually, 400000 m³ harbour sediments are dredged to maintain the water depth in the harbours of Bremen and Bremen harbour. The sediment contains organic and inorganic pollutants so that most of the dredged material it cannot be relocated into the river or the estuary. The sediment is de-watered in drainage ponds within one year and then deposited in a landfill for contaminated harbour sediments. The landfill is sealed below the dewatered sediment towards the soil and covered on the top. Both shelter systems consist of two layers, a sand to drain and a silt with a low hydraulic conductivity. Sewage water from drying the sediments in the ponds or gaining from compaction in the landfill is collected and treated before discharged into the Weser River. Treatment facilities and landfill cover an area of 127 ha and another 124 ha is needed for ecological compensation purposes. The costs for dredging and disposal of the material range due to changing amounts and various throughputs during the dewatering period between € 10 - 13 Million per year. Overall the sediment management concept in Bremen is built on three main components: First, to identify sources of pollution in the catchment-area of the Weser River and to reduce sedimentation in the harbour in order to minimise the amount of sediment which has to be managed; second to deposit the material environmental feasible (Biener et al. 1999), and third, due to the restricted capacity of the landfill different treatment techniques are investigated.

Further technologies discussed are subaqueous disposal (Jacobs and Förstner 1999), brick production (Hamer and Karius 2002), the use as containment layer in landfills (Lührte et al. 1996, Biener et al. 2003), the production of LWA (Derman and Schlieper 1999, Hamer et al. 2003) and others (Nowak and Hamer 2000).

1.4 Norway

Norway has a long coast and a lot of harbours in naturally protected sites which in many cases are situated in a fjord, however most of the rivers coming into the fjords are relatively small and the sediment transport is limited.

Nevertheless there is a strong focus on the problem of fine sediments contaminated with Heavy Metals, PCBs, PAHs, TBT and dioxins by the Norwegian Pollution Control Authority (SFT). Although less than 100000 m³ is dredged yearly to keep ports and sailing routs open

the costs for remediation in a way that restrictions on use of seafood can be removed in the fjords estimated by the SFT are between € 1.5 - 4 billions.

Since 1997 a five class system has been used in Norway to classify the environmental standard of sediments imposing remediation projects for the sediment included in the third class or worse.

In 2003 a work has started to develop a system for risk assessment of contaminated sediments. The system is a tiered approach and shown below:

- Tier 1: Simplified risk assessment using a set of background values;
- Tier 2: Calculate the site specific risk for transport to clean areas, risk for human health form consumption of seafood and risk for effect on the ecosystem;
- Tier 3: The situation is complex and special measurement has to be done to assess the risks as described in tier 2.

This system is scheduled to be finished by the end of 2005, and will replace the use of classes. Parallel to the work on the risk assessment system, regional projects to collect all available data to form the basis for giving priority between the sites has been carried out during 2003. During 2004 and 2005 the sites given priority will be subjected to risk assessment and decision made if remediation is required. Before the start of the major remediation projects there is a need to increase the knowledge of the pollution effects and to develop methods for implementing measures and new technological solutions further. The Government will use the strategy for three parallel lines of action:

- Preventing the migration of environmentally hazardous substances from contaminated sediments by ordering initiatives where such are possible with the technologies available today in areas where there is a danger of hazardous substances migrating; these include the so-called high-risk areas and ports where current operations cause daily spread of hazardous substances;
- ensuring a total regional approach to large fjords and coastal areas by drawing up county action plans;
- learning more through pilot projects, research, monitoring and the setting up of a national council to deal with sediment issues.

The general means for implementing this strategy may be as follows:

- to, where possible, impose an obligation on polluters to conduct the necessary cleanup operations;

- to make public funds available for cleanup operations in areas where it is impossible to identify those responsible for pollution or where it is not reasonable to demand that those responsible foot the entire bill;
- to assess the possibilities for introducing different payment schemes, including funds, which collect financial contributions from different polluters, and any state grants made available.

1.5 France

The yearly amount of material to be dredged for maintenance in France is estimated at about 6 million m³ for inland waterways (1.6 million m³ from national property waterways with huge operators such as French inland waterways: 700000 m³, and others as Port of Paris Authority and as National Company of Rhône). The amount is on the other hand 50 millions m³ for marine sediments obstructing ports. The six huge maritime ports authorities represent at least 50% of this annual amount.

Seventeen metropolitan commercial ports of national financial stake (Calais, Boulogne, Bayonne, Dieppe, Caen-Ouistreham, Sète, Port-la-Nouvelle, etc.), whose goods traffic is above 1 Mt or that are close by naval ports, annually dredge in addition for about 12 million m³.

The most important local dredging sites in France are:

- 10 million m³ for Port of Nantes-St Nazaire Authority (6 of which have seadisposal sites and 4 returned in suspension for the Loire's channel)
- 7 million m³ for Port of Bordeaux Authority
- 5 million m³ for Port of Rouen Authority
- 1.5 million m³ for Port of Le Havre Authority (will be 3 with *Port 2000*)
- 3 million m³ for Port of Dunkirk Authority
- only 20000 m³ for Port of Marseilles Authority

The way in which DM is managed in France is in line with international obligations resulting from the regional OSPAR Convention of September, 22th 1992 for the protection of marine natural environments of North-East Atlantic, and the world London Convention of December 29th 1972 on the prevention of marine pollution as a result of dumping waste.

In accordance with the Law N°76-599 of July, 7th 1976, authorisation is required to dump DM at sea. The procedure to obtain authorisation for dumping DM from activities — undertaken

by ports or other authorities such as municipal ones —is laid down in the French Decree N°82-842 of September, 29th 1982 taken for application and defining the procedure.

The French desired environmental standards for disposal in the sea have been legally defined recently. The interdepartmental Order dated the June, 14th 2000 precises the chemical threshold values that the dredged material to be dumped has to fulfil. This sediment quality reference table (*Référentiel RFQ*) is adapted from the work of the GEODE team (*Groupe d'Etude et d'Observation sur le Dragage et l'Environnement*; Group for Study and Observation on Dredging and Environment) that focused on 8 metallic trace elements and 7 PCBs present in the sedimentary fraction < 2mm.

If the chemical analysis results do not exceed the level N1 of the table (level without effects), the DM is acceptable for unrestricted ocean disposal. Between levels N1 and N2 (level with minor effects), complementary surveys are necessary in order to characterize and appreciate risks which sea-disposals expose natural environments.

Above N2 level (level with inauspicious effects), the dumping into sea might have an important environmental repercussion and is susceptible of prohibition if it is not proved that this solution is still the less detrimental for environment.

Presently, GEODE team and IFREMER discuss a level N3 for TBT. This level might correspond to an absolute ban for sea-disposal of CDMs. The interpretation of N2 and future N3 levels for TBT is one of the reason why CDMs extracted from French seaports have to enter land channels for valorization and disposal.

1.6 Italy

Handling of marine sediments due to dredging of ports and contaminated sites is a recurring topic of particular interest and of great social and economic importance, especially in a country with a particularly long coastline such as Italy, where many manufacturing, commercial and tourist activities are located in areas located close to the coast.

The total amount of sediment dredged annually in Italy is around 6 million of cubic meter.

Up to now it is not yet promulgated a comprehensive regulation for DM, but references to the latters have been inserted in other normative instruments regulating water supply, wastewater, solid waste, contaminated soil and groundwater etc.

In this scenario, the Central Administration follows an action line based on the following points:

- The characterization of the marine areas located in front of the contaminated sites of national interest to assess the amount and distribution of the contamination in order to identify both emergency situations with respect to all uses of the marine environment (fishery, aquaculture, bathing, recreation, etc.) and actions of remediation and environmental recovery charging ICRAM the Central Institute for scientific and technologic research applied to the sea;
- the identification of quality criteria for marine sediments and waters for the selection of the proper management options, in compliance with the principles of environmental protection and human health, similarly to what already done on land for soil, subsoil, superficial waters and ground-waters;
- the testing of treatment technologies for contaminated sediments, in order to identify environmentally sustainable management options. In general, preference will be given to biological treatments and “in situ” treatments (that do not imply removal of material), in order to minimize the impacts to the environment and in line with the technical and economic sustainability of the interventions.

The research activities already financed by the Ministry of Environment are the testing on bio-remediation techniques Bioreactors (i.e. part of this thesis was supported by the Ministry of Environment), Phytoremediation, Physical-chemical separation techniques.

The concept of sediment as “resource” instead of “waste” is slowly taking place. The Ministerial Decree of the Ministry of Environment - January 24th 1996 details the technical procedures which are necessary to obtain the authorisation for offshore dumping of dredged material and forces to execute a characterization process of the sediments that need to be dredged. In line with the international trend, the article 35 of the Legislative Decree n.258/2000 (more commonly known as Single Act on Water) establishes that offshore dumping of dredged sediments might be granted as disposal option only if it is shown that alternative management options cannot be applied.

The D.L. no. 22 of 5th February 1997 define the DM as solid waste (CER 17 05 05 and 17 05 06) that can be considered hazardous if comply with the characteristics of its attachment: H and G. Unfortunately this decree do not provide both information of the reference values of the contaminant concentration and the remediation procedures.

Additional awareness of the problem of contaminated marine areas is achieved within the legislative scenario of the Laws 426/98, 388/2000 and 179/02, and of the Ministerial Decrees 471/99 and 468/01 (“National Program of remediation and environmental recovery”). These

norms recognize the presence on the national territory of cases of contamination and establish the criteria, the procedures and the methodologies to secure, remediate and environmentally recover contaminated sites, providing intervention values for contaminant concentration in soil, subsoil, surface and ground waters in relation to different land uses. In particular, these norms identifies some highly contaminated sites (“contaminated sites of national interest”) and recognize the marine areas located in front of a contaminated site as the potential receiving body of its pollution load.

Within the national scenario, due to its peculiar fragility, Venice already developed few years ago a scientific approach in handling of (contaminated) sediments called Venice Protocol of March 1993 (tab. 1.I), that provides the environmental safety criteria for dredging, transport and disposal activities in the channels of Venice defining four sediment quality classes.

Table 1.I. Sediment classification based on the *Protocollo di Venezia*

<i>Protocollo di Venezia</i>		Classes		
		A	B	C
Hg	[mg kgTS ⁻¹]	0.5	2	10
Cd	[mg kgTS ⁻¹]	1	5	20
Pb	[mg kgTS ⁻¹]	45	100	500
As	[mg kgTS ⁻¹]	15	25	50
Cr	[mg kgTS ⁻¹]	20	100	500
Cu	[mg kgTS ⁻¹]	40	50	400
Ni	[mg kgTS ⁻¹]	45	50	150
Zn	[mg kgTS ⁻¹]	200	400	3000
Total Hydrocarbons	[mg kgTS ⁻¹]	30	500	4000
PAHs	[mg kgTS ⁻¹]	1	10	20
PCB	[mg kgTS ⁻¹]	0.01	0.2	2
Pesticides	[mg kgTS ⁻¹]	0.001	0.02	0.5

Finally, the ordinance 2002 n.3217, from the title “Disposizioni urgenti per fronteggiare l’emergenza socio-ambientale determinatasi nella Laguna d Marano Lagunare e Grado” it represents a profit tool of intervention for the individualization of DM classes of quality and accordingly the definition of their final destination. In details, Act n.3217 divides dredged sediments into four classes to which different management options are associated, as a function of the detected concentration of selected contaminants.

Particularly:

1. DM with lower concentrations of pollutants referring to the values foreseen by the column A of the Table 1 of the Protocol in Venice: for the realisation or enlargement of sandbank;
2. DM with higher concentrations of pollutants referring to the values foreseen by the column A of the Table of the Protocol in Venice and lower than the limits foreseen by the column A of the table 1 of the D.M. 471/99: for construction and the reinforcement of islands to turn into naturalistic areas;
3. DM with higher concentrations of pollutants referring to the values foreseen by the column A of the Table 1 of the D.M. 471/99 and lower than the values foreseen by the column B of the same decree: for construction of CDF and for their reinforcement;
4. DM with higher concentrations than those reported in the column B of the table 1 of the D.M. 471/99: destined in sanitary landfill respecting the laws in force.

Furthermore it establishes criteria for lateral and bottom confinement of the confined disposal facilities towards the outside environment, as a function of the quality of the sediments to be disposed:

- Lateral confinement equivalent to that offered by a layer with a minimum thickness of 50 cm and permeability coefficient $\leq 10^{-7}$ cm/s, in case the concentration of the contaminants is higher than the limit values provided in column A of the table of the Venice Protocol of 1993, but lower than the limit values provided in table 1 – column A of Annex 1 to the Ministerial Decree 471/99;
- Lateral and bottom confinement equivalent to that offered by a layer with a minimum thickness of 100 cm and permeability coefficient $\leq 10^{-7}$ cm/s, in case the concentration of the contaminants is higher than the limit values provided in table 1 – column A – of Annex 1 to the Ministerial Decree 471/99, but lower than the limit values provided in table 1 – column B - of Annex 1 to the Ministerial Decree 471/99.

In order to respect the existing legislation and simultaneously apply a strategy of saving of sources, an inertization treatment is currently applied to the dredged sediments after the drying up process in order to dispose the material of in a lower class and therefore less expensive on land waste disposal site.

1.7 Conclusion

Sediment play a very important rule both for inland and marine aquatic ecosystems. Europe-wide, 200 million cubic metres of DM are dredged per year which the 10-20 % are contaminated both with organic and inorganic compounds.

Up to now a common legislation on the management of the DM has not yet been proclaimed at the European Union level though the concept at the basis of each European country regulation is to look to the sediment as a resource and not as a waste.

The approach based on total concentrations of the main organic (PAHs, PCB, pesticides etc.) and inorganic (Heavy Metals) contaminants have been proposed in many European countries. However the researches in this field have suggested that an unique approaches based on total concentration is restrictive because small changes in the regulatory framework may have large consequences for the amounts of dredged material that have to be treated or disposed. The development of both chemical and biological assessment tools have to be pursued in order to process an integrated approach based on the latter and on total concentration.

Chapter 2

2 Organic and inorganic compounds affecting soil and sediment

2.1 Introduction

The contaminants present in soils and sediments can be the result of direct or diffuse pollutions. The typologies of pollution sources may strongly affect where and how contaminants are present on the site. Direct pollution, as in a lot of heavily polluted industrial sites, may result in presence of the neat contamination (e.g. tar-like particles or liquids), which even can be visually recognisable. In diffusely polluted areas, the contaminants are more equally distributed and are mostly not visually recognisable; their presence can be described as molecules adsorbed on or absorbed in soil and sediment. The contaminants can be introduced through air pollution, water pollution, agricultural practices or long-term use of slightly polluted sludges. Contaminants therefore can be present in soil and sediments in different physico-chemical forms, as shown in fig. 2.1 (Rulkens 1992).

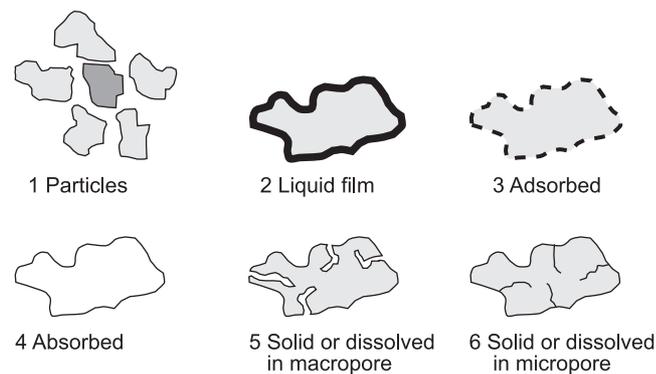


Figure 2.1. Appearance of contaminants in soil or sediment. Adapted from Rulkens (1992)

In fig. 2.1 presence of the contaminant is divided into particles, liquid film, adsorbed on or absorbed in soil aggregates, or present in large as well as in small pores.

In the following items the study of Polycyclic Aromatic Hydrocarbons and Heavy Metals chemical characteristics and their interaction with sediment have been deepened.

2.2 Polycyclic aromatic hydrocarbons

2.2.1 Physico-chemical properties

Among organic pollutants, Polycyclic Aromatic Hydrocarbons (PAHs) are perhaps the most common (Herbes 1977, Sanders et al. 1993). PAHs are a group of several hundreds substances, made up of two to six condensed benzene rings, with molecules containing only carbon and hydrogen. They cover a range of molecular weights from 128 for naphthalene (two-ring) to 276 for the six-ring compound benzo[g,h,i]perylene. In accordance with the Environmental Protection Agency (EPA) of the United States of America 17 PAHs have been listed as priority pollutants.

PAHs form during the incomplete combustion of wood, oil coal and gas, and also other organic substances (e.g. during the roasting of meat and tobacco smoking). Thus they are distributed ubiquitously in the environment. They are detected in air, in the soil, in water, in plants and also in the food.

PAHs are nonpolar, neutral and hydrophobic; the molecular weight, the vapour pressure the water solubility and the octanol partitioning coefficient (k_{ow}) of the 17 priorities PAHs are reported in tab. 2.I. PAHs sorb tightly to soil particles, especially clays, in saturates aqueous environments because of their hydrophobicity and neutrality, limiting also their bioavailability (Johnson and Ghosh 1998).

In general PAHs do not occur as single substances, but in combination and the profile of PAHs found can be indicative of certain sources (Law and Biscaya 1994). For instance the ratios of specific PAHs can be used to identify likely oil spill sources e.g. 3-ring alkylated PAHs are particularly useful for petroleum source identification (Douglas et al. 1996). Nevertheless the identification of specific PAH sources to estuarine sediments is hindered by the complexity and diversity of inputs. The dynamic nature of estuarine systems, the resuspension of bed sediments during tidal movements and the inhomogeneity of bed sediments make specific source identification difficult.

Table 2.I. EPA list PAHs physico-chemical characteristics

PAH	Molecular Weight [g mol ⁻¹]	Molecular Formula	Vapour Pressure [Pa]	Water Solubility [mg l ⁻¹]	Log K _{ow} (Log K _{oc})
Naphthalene	128.19	C ₁₀ H ₈	10 a 25°C	31.7	3.37 (3.11)
Acenaphthylene	152.20	C ₁₂ H ₈	0.12 a 25°C	16.1	4.00 (3.83)
Acenaphthene	154.21	C ₁₂ H ₁₀	1.3 10 ³ a 131.2°C	9.93	3.92 (5.38)
Fluorene	166.22	C ₁₃ H ₁₀	0.04 a 20 °C	1.98	4.18 (5.47)
Anthracene	178.23	C ₁₄ H ₁₀	3.6 10 ⁻⁴ a 25°C	0.0434	4.54 (5.76)
Phenanthrene	178.23	C ₁₄ H ₁₀	1.3 10 ³ a 118.2°C	1.29	4.57 (6.12)
Fluoranthene	202.26	C ₁₆ H ₁₀	1.23 10 ⁻³ a 25°C	0.206	5.22 (6.38)
Pyrene	202.26	C ₁₆ H ₁₀	1.19 10 ⁻² a 25°C	0.135	5.18 (6.51)
Chrysene	228.29	C ₁₈ H ₁₂	8.3 10 ⁻⁷ a 25°C	0.0016	1.64 (6.27)
Benz[a]anthracene	228.29	C ₁₈ H ₁₂	6.67 10 ⁻⁷ a 20°C	0.0094	5.91 (6.30)
Benz[a]pyrene	252.31	C ₂₀ H ₁₂	7.32 10 ⁻⁷ a 25°C	0.00162	6.04 (6.26)
Benz[b]fluoranthene	252.31	C ₂₀ H ₁₂	6.7 10 ⁻⁵ a 20°C	0.0015	5.80 (5.74)
Benz[k]fluoranthene	252.31	C ₂₀ H ₁₂	1.29 10 ⁻⁷ a 25°C	0.0008	6.00 (5.99)
Benzo[e]pyrene	252.31	C ₂₀ H ₁₂	7.6 10 ⁻⁷ a 25°C	0.004	6.21 (7.20)
Benzo[g,h,i]perylene	268.35	C ₂₁ H ₁₆	9.8 10 ⁻¹⁰ a 20°C	0.00026	6.50 (6.20)
Indeno[1,2,3-c,d]pyrene	276.33	C ₂₂ H ₁₂	9.8 10 ⁻¹⁰ a 20°C	0.00022	
Dibenzo[a,h]anthracene	278.35	C ₂₂ H ₁₄	9.8 10 ⁻¹⁰ a 20°C	0.0049	6.75 (6.52)

As it can observe from tab. 2.I the PAHs physico-chemical characteristics are quite different. In general the 2-3 rings PAHs have higher vapour pressure and for this a lower hydrofobicity. PAHs are pollutants of relevant concern especially the higher molecular weight PAHs that are recalcitrant and toxic. In fact their exposure in animals is associated with other effects including reproductive toxicity (MacKenzie and Angevine 1981), cardiovascular toxicity (Penn et al. 1981, Paigen et al. 1985), bone marrow toxicity (Legraverand et al. 1983), immune system suppression (Hardin et al. 1992), and liver toxicity (Armstrong and Bonser 1950). However, the toxic effect of most concern from exposure to PAHs is cancer. The International Agency for Research on Cancer (IARC) considers several purified PAHs and PAH derivatives to be probable (Group 2A) or possible (Group 2B) human carcinogens (IARC 1987).

2.2.2 Sediment PAHs adsorption

Adsorption, as an equilibrium process, can be considered as the presence of a contaminant on the surface of a soil particle or the surface of a soil pore, at a concentration that is in equilibrium with the concentration in the mobile pore water. The presence of a contaminant within the organic matter is instead called absorption and absorbed contaminants are in general not in equilibrium with the mobile pore water due, mainly, to the lack of direct contact.

PAHs are strongly adsorbed to the sediment organic matter (*SOM*). In an equilibrium approach the adsorption of the contaminant can be expressed with a partition coefficient (K_{oc}) between organic matter and water, expressing organic matter as organic carbon. Experimental data on adsorption of different organic contaminants in soils and sediments were collected and generalised with respect to the equilibrium sorptive behaviour of contaminants taking into account, however, only a few physical-chemical parameters, such as the octanol/water partition coefficient K_{ow} or the water solubility S (Karickhoff et al. 1979, Kooper et al. 1987, Seth et al. 1999, Xia and Pignatello 2001 and Otte et al. 2001). Nevertheless Cuypers (2001) stated that in literature presented K_{oc} values exhibit considerable variation from sorbent to sorbent varying by a factor 1-3 in magnitude.

In modelling the linear partition coefficient between soil and water (K_d) is often used, because this includes the concentration in both the pore water and the solid phase assuming that 1 g organic matter contains 0.58 g organic carbon:

$$K_d = 1000 f_{r_{oc}} K_{oc} = 580 f_{r_{om}} K_{oc} \quad (1)$$

where:

K_d = linear adsorption coefficient in $m^3 \text{ kg}^{-1}$

$f_{r_{oc}}$ = mass fraction of organic carbon in kg kg^{-1}

$f_{r_{om}}$ = mass fraction of organic matter in kg kg^{-1}

Several isotherms have been proposed to describe the organic compounds adsorption on soil and sediment though two of them are mainly applied: Langmuir and Freundlich reported in tab. 2.II.

Table 2.II. Langmuir and Freundlich adsorption models

Langmuir	$q_e = \frac{Q_a^0 \cdot b \cdot C_e}{1 + b \cdot C_e}$	q_e = Compound concentration in the solid phase C_e = Compound concentration in the liquid phase b = Links energy function Q_a^0 = Maximum adsorption
Freundlich	$q_e = K_D \cdot (C_e)^n$	q_e = Compound concentration in the solid phase C_e = Compound concentration in the liquid phase n = Links energy function K_d = Adsorption coefficient

In case of $n=1$ the Freundlich it is obtained the linear isotherms. An example of the latter is reported in fig. 2.2 for the pyrene adsorption (a) on sediment, whereas in fig. 2.2 (b) is reported the influence of organic carbon on the pyrene linear partition coefficient.

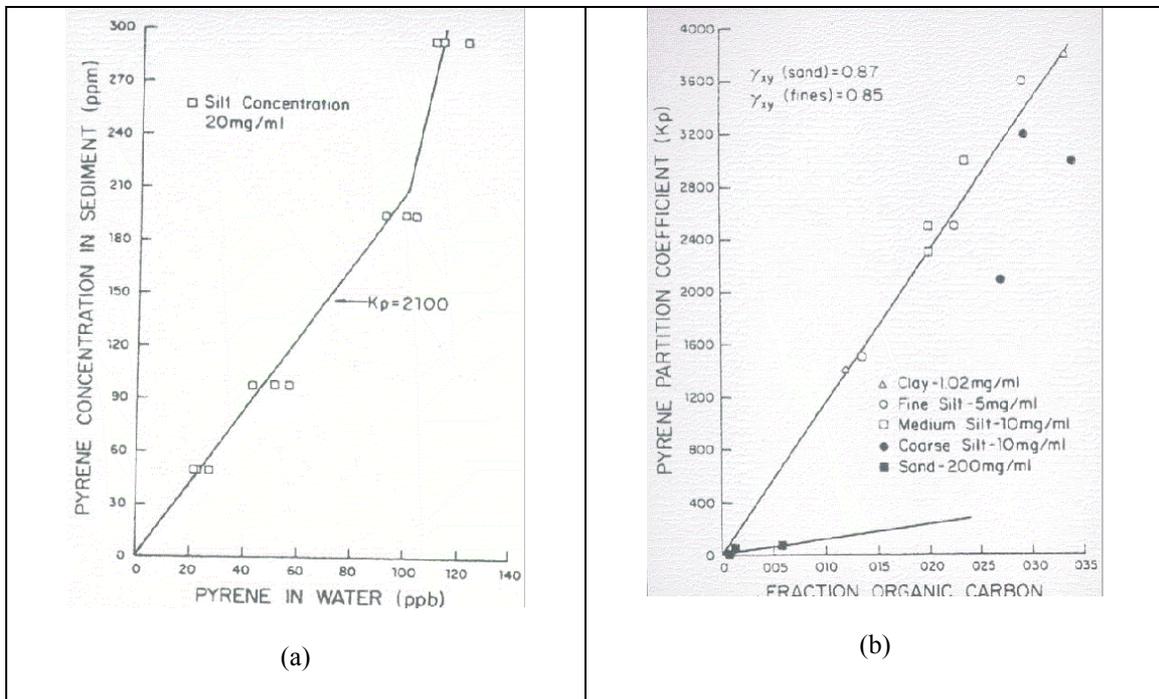


Figure 2.2. (a) Adsorption pyrene coefficient; (b) Organic carbon influence on the adsorption pyrene coefficient

Equation 1 is valid if PAHs only interact with sediment organic matter. There is, however, also an interaction with dissolved organic matter (*DOM*) mostly expressed as dissolved organic carbon (*DOC*) which is stronger for the highly insoluble PAHs (Comans et al. 2000). Also the interaction of the contaminant with *DOC* can be described with a partition coefficient between dissolved organic carbon and water: K_{oc}^{DOC} . In the expression for K_d the amount in the water phase has to be replaced by the sum of the free dissolved PAHs and the PAHs associated with the solved organic matter.

$$K_d = \frac{1000 f_{r_{oc}} K_{oc}}{[1 + f_{r_{DOC}} K_{oc}^{DOC}]} \quad (2)$$

where:

$f_{r_{DOC}}$ = mass fraction of organic carbon dissolved in water in kg kg^{-1}

K_{oc}^{DOC} = partition coefficient between *DOC* and water.

K_{oc}^{DOC} can be described by means of mathematical expression similar to the K_{oc} for solid organic matter *SOM* (Lüers and Ten Hulcher 1996, Mackay and Gschwend 2001, Laor and Rebhun 2002).

2.2.3 Sediment PAHs desorption

The desorption of organic compounds adsorbed to solid particles is fundamental in the bioremediation technologies design because it is considered that the microorganisms are able to biodegrade only dissolved compounds. Hence many investigations were carried out to study the contaminant desorption from soil and sediment aiming the formulation and validation of desorption models.

The contaminants desorption rate can be influenced by internal diffusion processes as it controls the transfer of compounds from the interior of the adsorbent to the external surfaces, and opposite. A number of chemical-kinetic and diffusion controlled models have been proposed in the literature to describe non-equilibrium sorption, varying from relatively simple first order kinetic rate equations, multi-compartment sorption, to two region transport involving contaminant exchange between mobile and relatively immobile liquid regions. The simplest one-site non-equilibrium formulation based on Fick's second diffusion and obtained regardless the shape of the sediment/soil particle or aggregate is reported below (Rolston et al. 2003):

$$\frac{\partial c}{\partial t} = k \bullet c \quad \frac{c_t}{c_0} = e^{-k \cdot t} \quad (3)$$

where:

k = first order kinetic rate constant in d^{-1}

c = contaminant concentration in the aggregate in kg m^{-3}

c_0 = sorbed concentration at $t=0$

c_t = sorbed concentration at $t=t$

The rate constant (k) in this equation has to be considered as an empirical rate constant including all physic-chemical factors (e.g. shape of the soil aggregate, moisture content, specific weight etc.).

Although k is often empirically calculated both for bioremediation and desorption experiments, the influence of the main physic-chemical factors affecting the sediment-contaminants interactions is discussed below.

The transport of a contaminant in a single aggregate, containing pores that are partially filled with water as illustrated in fig.2.3, has been described by a general diffusion equation by Rijtema et al. (1999). They included the shape of the aggregate (sphere, cylinder or plate) by the shape factor m . The diffusion equation can be solved numerically, which result an equation like 3, in which the rate constant k is expressed as:

$$k = \frac{2(m+1) D_s^w}{[\theta + \rho_s (1 - \varepsilon) K_d] r^2} \quad (4)$$

where:

θ = internal aggregate moisture content in $\text{m}^3 \text{m}^{-3}$

ε = volume fraction of total pore space in the aggregate (water and air filled) $\text{m}^3 \text{m}^{-3}$

r = distance from the surface to the centre of the aggregates in m

m = shape factor for the aggregate structure which is:

0 for plate aggregate; 1 for cylindrical aggregate; 2 for spherical aggregate

ρ_s = specific weight of the soil in kg m^{-3}

D_s^w = contaminant diffusion coefficient in sediment/soil pore water in $\text{m}^2 \text{d}^{-1}$

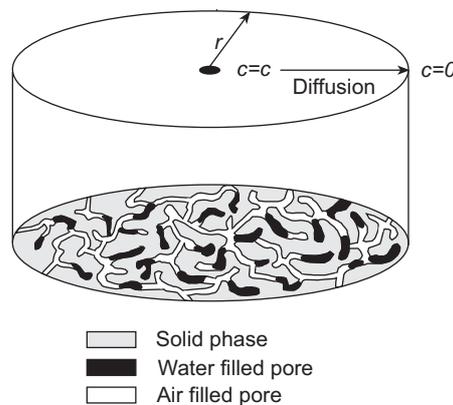


Figure 2.3. Transport of a contaminant in a single aggregate

The internal aggregate moisture content θ has to be considered in unsaturated soils as the immobile moisture fraction and depends on clay content and organic matter content. In aerobic unsaturated soils, its value varies from 0.02 in sandy soils with very low organic matter content to about 0.50 in soils rich in clay and a high content of organic matter. In sediments the moisture content will be much higher and reach values of 0.7. The contaminant diffusion coefficient in soil pore water D_s^w is still an unknown and can be approximated through the introduction of a tortuosity factor η (Equation 5):

$$D_s^w = \eta \theta D^w \quad (5)$$

The value of η depends on the clay and moisture content (Rijtema et al. 1999) while the D^w is the contaminant diffusion coefficient (Trapp and Matthies 1997) in water in $\text{m}^2 \text{d}^{-1}$ and depends on the molar mass (M).

Because all constants in the expression for the rate constant k (Equation 4) now have a physical meaning, it is possible to calculate this constant for a specific situation and to evaluate the influence of several parameters on the rate constant. In Table 2.III the effect of the association of PAHs with dissolved organic matter is presented. Column one shows the effect of ignoring the interaction of the PAH with *DOM*. In column two K_D is corrected for the interaction with *DOM* (Equation 2), and column three shows the effect of introducing a proper diffusion coefficient assumed molecular weight of 2000 for the associated *DOM* (Trapp and Matthies 1997). Other values used in tab. 2.III are reported below:

- Radius of the cylindrical content $\theta = 0.50 \text{ m}^3 \text{ m}^{-3}$
- Aggregate moisture content $\theta = 0.50 \text{ m}^3 \text{ m}^{-3}$
- Total pore space $\varepsilon = 0.55 \text{ m}^3 \text{ m}^{-3}$
- Fraction organic matter $fr_{om} = 0.05 \text{ kg kg}^{-1}$
- Fraction clay $fr_{cl} = 0.1 \text{ kg kg}^{-1}$
- Specific weight clay $\rho_{cl} = 2700 \text{ kg m}^{-3}$; specific weight sand $\rho_{sa} = 2650 \text{ kg m}^{-3}$ specific weight organic material $\rho_{om} = 1400 \text{ kg m}^{-3}$
- Dissolved organic carbon $fr_{DOC} = 10^{-4} \text{ kg dm}^{-3}$
- $K_{oc} (SOM)$ and $K_{oc} (DOM)$

Table 2.III. Calculated rate coefficients in a soil aggregate. $DOC=100 \text{ mg l}^{-1}$; $r = 10^{-5} \text{ m}$, other constants see text above

PAHs	Calculated k -values (y^{-1})		
	No interaction with DOM	Kd corrected for DOM	Diffusion coefficient for $M=2000$
Naphtalene	20	22	3.43
Acenaphtylene	6.1	9.2	1.52
Acenaphthene	5.2	7.9	1.31
Fluorene	3.0	5.9	1.00
Phenantrene	0.99	3.1	0.56
Anthracene	0.85	2.6	0.45
Fluoranthene	0.11	1.7	0.31
Pyrene	0.24	2.4	0.44
Benz[a]anthracene	0.024	1.0	0.20
Chrysene	0.028	2.5	0.51
Benz[b]fluoranthene	0.062	5.5	1.11
Benz[k]fluoranthene	0.008	1.7	0.35
Benz[a]pyrene	0.022	4.6	0.96
Dibenzo[a,h]anthracene	0.010	29	6.92
Benzo[g,h,i]perylene	0.005	1.4	0.30
Indeno[1,2,3-c,d]pyrene	0.011	20	4.68

Without the interaction with DOM , the variation in calculated rate constant k is large. Including DOM brings the values closer. As result of the higher K_{ow} values for dibenzo[a,h]anthracene and indeno[1,2,3-c,d]pyrene the calculated values for these PAHs are also larger. Including the diffusion coefficient makes the relative differences between the calculated values smaller.

Harmsen (2004) have been shown by means of desorption experiments that it is necessary to include the DOM -PAH interaction. Without including this interaction the range in calculated values is too large. In the last column also the diffusion coefficient of the associated DOM -PAH molecule is taken into account, which decreases the k -values and brings them also more together.

The effect of the aggregate radius on the rate coefficient is presented in tab. 2.IV. The same parameters as in previous example are used, including the diffusion coefficient D_s^w of the DOM -PAH molecule with a molecular weight of 2000 u.m.a.

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Table 2.IV. Calculated rate constant k for different aggregate radii. Soil properties and other used constants see text above

PAHs	Rate coefficient k in y^{-1}			
	$r = 10^{-6}$ m	$r = 10^{-5}$ m	$r = 10^{-4}$ m	$r = 10^{-3}$ m
Naphtalene	343	3.43	0.034	0.00034
Acenaphthylene	152	1.52	0.015	0.00015
Acenaphthene	131	1.31	0.013	0.00013
Fluorene	100	1.00	0.010	0.00010
Phenantrene	56	0.56	0.006	0.00006
Anthracene	45	0.45	0.005	0.00005
Fluoranthene	31	0.31	0.003	0.00003
Pyrene	44	0.44	0.004	0.00004
Benz[a]anthracene	20	0.20	0.002	0.00002
Chrysene	51	0.51	0.005	0.00005
Benz[b]fluoranthene	111	1.11	0.011	0.00011
Benz[k]fluoranthene	35	0.35	0.003	0.00003
Benz[a]pyrene	96	0.96	0.010	0.00010
Dibenzo[a,h]anthracene	692	6.92	0.069	0.00069
Benzo[g,h,i]perylene	30	0.30	0.003	0.00003
Indeno[1,2,3-c,d]pyrene	468	4.68	0.047	0.00047

Based on the results reported in tab.2.IV instantaneous desorption occurs from soil particles $< 10^{-5}$ m and desorption has to be considered as immobile in particles $>10^{-3}$ m. Two extreme situations can be present:

- Desorption can be considered as instantaneous if the rate constant is large compared with the treatment time. In a landfarm the minimum treatment time is 3 months, and then k -values larger than $20 y^{-1}$ can be considered as instantaneously (bold values).
- If the k -value is very low, the material is immobile and has to be removed from the soil through decomposition of the organic material present in the soil (bold and italic values).

Depending on the soil type (sand, peat or clay), mechanical reductions of the aggregate size to several mm can be achieved, which is not far enough to change a slow process into a fast process. Technologically this is possible in slurry reactors, but not in a landfarm though cultivation can reduce the particle size to a certain limit. However also natural processes like root activity and activity of worms can be responsible for a larger size reduction in a landfarm. Although it will take a long time before every soil particle is passed though a worm or has been penetrated by a root but there will be a positive effect of these activities on the desorption rate.

This type of modelling is very useful in understanding processes occurring in bioremediation systems as bioreactors or landfarm and can provide useful suggestions in order to improve the efficiencies of these technologies. It should, however, be realised that a real prediction of the

rate of degradation is still difficult. Several constants are not accurately known at this time. As identified before, the K_{oc} values for *DOM* and *DOC* may differ with a factor of, respectively, 3 to 6. The molar mass of *DOC* is not a specific value but a range and will differ from soil type to soil type. In a slurry reactor it may be possible to give a good estimate of the radius of soil particles present. In a landfarm in which an unsaturated soil is present it is difficult to make a good estimate of the radius of individual aggregates or the distance from an adsorbed contaminant molecule to an active micro-organism. In spite of these inaccuracies, the model is a proper tool to show the relative influence of the individual parameters.

2.2.3.1. Multi-compartment model: Influence of adsorption sites

The diffusion model described above considers a sediment/soil with constant properties of all adsorption sites (one compartment model). The resulting one-compartment first order kinetic model, gives generally poor results, because soil is an heterogeneous material consisting of many types of aggregates and within aggregates properties also differ.

To take into account these differences, all the adsorption sites are divided into several compartments grouping the adsorption sites differences; for instance the sorption to the first compartment is assumed to be instantaneously in equilibrium with the mobile pore water concentration and can be biodegraded while the sorption to the others is assumed to be more conservative.

Although two compartment models have often been described and proposed in the last years (Brusseau et al. 1991, Cornelissen et al. 1997) a three desorbing compartments have been used in this study. Assuming that no re-adsorption takes place (Cornelissen et al. 1997) the three-compartment desorption model can be described as sum of three first order decreases:

$$\frac{C_t}{C_0} = F_{fast} \cdot e^{-k_{fast} \cdot t} + F_{slow} \cdot e^{-k_{slow} \cdot t} + F_{very\ slow} \cdot e^{-k_{very\ slow} \cdot t} \quad (6)$$

where:

c_t = sediment/soil sorbed amount (mg kg⁻¹ TS) at time t (y)

c_0 = sediment/soil sorbed amount (mg kg⁻¹ TS) at time 0

F_{fast} = fraction of contaminant in fast desorbing compartment

F_{slow} = fraction of contaminant in slowly desorbing compartment

$F_{very\ slow}$ = fraction of contaminant in very slowly desorbing compartment

k_{fast} = rate constant rapid desorption (y⁻¹)

k_{slow} = rate constant slow desorption (y⁻¹)

$k_{very\ slow}$ =rate constant very slow desorption (y^{-1}).

Every first order decrease is described with two constants, the size (fraction of total amount, F) and the rate constant (k). If degradation is not possible redistribution between the different compartments takes place, which may result in decrease of the fast desorbing fraction and increase of the slow and very slow desorbing fractions. This stronger binding of contaminants to sediment or soil as effect of increasing contact time is often described as aging.

Instead of a rate constant (k), half-life time ($t_{1/2}$) is often used as a characteristic value in a first order process. Table 2.V gives half-life times and the corresponding k -values. In the fourth column of table 2.V the time necessary to reduce the compartment to 90% of its original size is given. In the last column, examples are given of the bioremediation methods that can be used within the given time frame.

Table 2.V. First order decrease expressed as half life time ($t_{1/2}$), rate constant (k), time necessary to have 90% reduction of a compartment and examples of bioremediation methods

Half life time $t_{1/2}$	Rate constant k		Time needed for 90% reduction [y]	Example of bioremediation method
	[y^{-1}]	[h^{-1}]		
1 hour	6070	0.69	0.00038	
1 day	253	2.9×10^{-2}	0.0091	
1 week	36	4.1×10^{-3}	0.064	Bioreactor
1 month	8.4	9.6×10^{-4}	0.27	
1 year	0.69	7.9×10^{-5}	3.3	Intensive landfarm
5 years	0.14	1.6×10^{-5}	17	
10 years	0.069	7.9×10^{-6}	33	Passive landfarm
20 years	0.035	3.9×10^{-6}	66	Natural attenuation

As it can be observed the bioremediation of soil/sediment contaminated with organic compounds can be pursued with “cheap” and also “cheaper” technologies having, however, the time (and space) like main constraints.

It is valuable to observe that desorption affects and limits often the biodegradation of organic compounds sorbed to soil and sediment; in this case if desorption is the explaining factor for biodegradation, this model can also be used for degradation.

2.2.4 PAHs aerobic degradation

The PAHs present in the environment have enabled the selection of several organisms able to use PAHs as substrates for their metabolic and co-metabolic reaction (Shuttleworth and

Cerniglia 1996). Bacteria, fungi, cianobacteria, algae are able to biodegrade PAHs from Naphtaleen to Benzo[a]pyreen (Cerniglia 1984). Generally the PAHs in soil and sediment can be biodegraded with different kinetics based mainly on molecular weight and number of aromatic rings; particularly the kinetics decrease increasing the MW and number of rings (Nocentini et al. 1996).

The scientific literature is plenty of studies regarding both Low Molecular Weight (LMW) and High Molecular Weight (HMW) PAHs biodegradation using: pure microorganisms culture, on single or on mixture PAHs on lab contaminated soil, sediment and water.

The co-metabolic reactions play an important rule for the PAH biodegradations; it means that the organisms is not able to use the substrate (e.g. PAHs) as carbon source but producing enzymes it provides its biodegradation (Alexander 1994).The organic aromatic compounds are biodegraded both anaerobically and aerobically, but the latter is faster and more complete. The procariots organisms, bacteria, algae and fungi have different PAHs biodegradation patterns but all use molecular oxygen (Cerniglia 1984) playing a fundamental rule in the breaking of the aromatic ring.

The different metabolic reactions for the oxidation of aromatic hydrocarbons are schematized in fig. 2.4 for the eucariots and procariots.

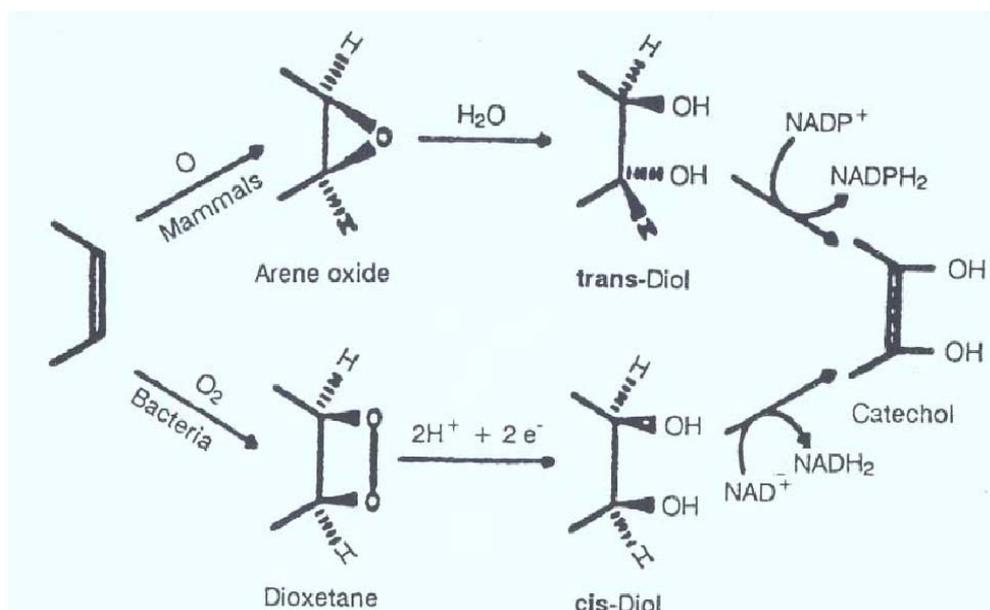


Figure 2.4. Metabolic reactions for the oxidation of aromatic hydrocarbons in eucariots e procariots

The limiting step is the initial oxidation of the aromatic ring because of its high chemical stability and low molecule reactivity (Cerniglia and Heitkamp 1989).

Fungi and algae procarriots biodegrade PAHs following the same patterns reported above (Cerniglia 1992). The fungi degradation is rather important from a toxicological point of view because is usually incomplete resulting in the formation of carcinogic and mutagenic intermediate products for the superior organisms.

The different metabolic reactions for the oxidation of PAHs are schematized in fig. 2.5 for the eucariots and procarriots.

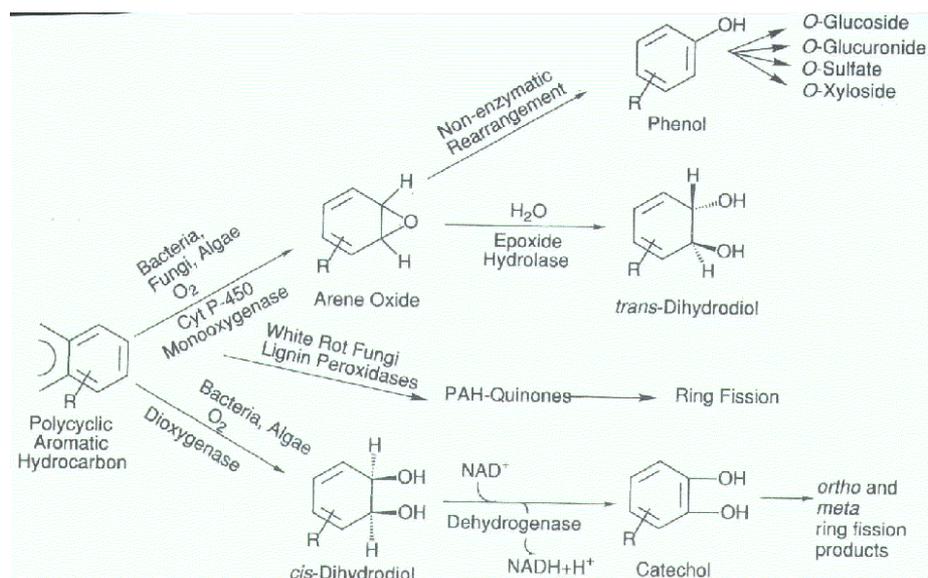


Figure 2.5. Metabolic reactions for the oxidation of PAHs in eucariots and procarriots

The microbial PAHs metabolism has been widely studied working with pure culture and single PAH on lab scale (Huddleston et al. 1986). Shabad et al. 1971 have observed that the bacteria ability to biodegrade benzo[a]pyrene increase with its initial concentration;, instead other authors have reported an inverse relation between the initial PAHs concentration and their biodegradation (Shiaris 1989). Nevertheless it seems that the initial concentration strongly influence the biodegradation efficiency.

The PAHs biodegradation in a natural environment depends both on the contaminant (i.e. concentration and number of aromatic rings) and on: salinity, pH, nutrients, temperature and contamination age (Sherril and Sayler 1982).

The salinity can influence the PAHs solubility; nevertheless whereas Shiaris (1989) and Kerr and Capone (1988) have found out a positive correlation between salinity and PAHs mineralization, Ward and Brock (1978) have observed a biodegradation decreasing in iper-saline environment. However microorganisms able to biodegrade PAHs in iper-saline (NaCl

concentration over 7.5%) environment belong to the following family *Micrococcus*, *Pseudomonas* e *Alcaligenes* (Ashoch et al. 1995).

The microorganisms generally need: pH ranging between 5.8 and 8.5 to biodegrade PAHs, but the higher efficiency occur close to the neutrality (Weissenfels et al. 1990), ratio between Carbon:Nitrogen:Phosphorus of 120:10:1 (Wilson and Jones 1993) and working temperature between 15 and 45 °C, but preferentially among 20 and 30 °C (Wilson and Jones 1993).

Several studies have showed that synthetic surfactants could improve the PAHs solubilization and consequently their biodegradation (Cox and Williams 1980). However several microorganisms living on soil and sediment contaminated with organic contaminants naturally produce biosurfactants increasing the contaminant availability for them.

Contrary very few studies have been carried out on aerobic PAHs biodegradation of natural contaminated soil or sediment. However the presence of different microorganisms as occurs in natural contaminated soil and sediment seems to play an important rule in PAHs biodegradation because involves different microorganisms able to make also the intermediate degradation.

PAHs are accumulated in sediment due to the anaerobic conditions in the sediment. By introduction of oxygen, aerobic degrading organisms are activated and start to biodegrade the contaminants. Because the contaminants have been in contact with the sediment for a long time, aging has occurs. The bio-availability (amount available for degradation) can be reduced significantly. The effect of aging is that a relatively small amount of contaminants will be degraded during the normal treatment time of the biological treatment and the necessity to enlarge the treatment time.

Two general biological degradation technologies for sediment can be distinguished:

- Treatment in reactors and basins (with active introduction of oxygen)
- Landfarming (with natural diffusion of oxygen)

2.3 Heavy Metals

2.3.1 Introduction

The term heavy metals includes elements with a specific weight higher than 5 g cm⁻³ like: Lead, Chromium, Zinc, Cadmium, Copper. An overview of the concern heavy metals affecting soil and sediment used for the experiments is reported below.

Lead: The primary industrial sources of lead (Pb) contamination include metal smelting and processing, secondary metals production, lead battery manufacturing, pigment and chemical manufacturing, and lead-contaminated wastes. Widespread contamination due to the former use of lead in gasoline is also of concern. Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and lead-metal oxyanion complexes (Smith et al. 1995).

Lead occurs most commonly with an oxidation state of 0 or +II. Pb(II) is the more common and reactive form of lead and forms mononuclear and polynuclear oxides and hydroxides. Under most conditions Pb^{2+} and lead-hydroxy complexes are the most stable forms of lead (Smith et al., 1995). Low solubility compounds are formed by complexation with inorganic (Cl^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-}) and organic ligands (humic and fulvic acids, EDTA, amino acids) (Bodek et al. 1988). Lead carbonate solids form above pH 6 and PbS is the most stable solid when high sulphide concentrations are present under reducing conditions. Most lead that is released to the environment is retained in soil and sediment (Evans 1989). The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater. The relatively volatile organo-lead compound tetramethyl lead may form in anaerobic sediments as a result of alkylation by microorganisms (Smith et al. 1995). The amount of dissolved lead in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. In surface water and ground-water systems, a significant fraction of lead is undissolved and occurs as precipitates ($PbCO_3$, Pb_2O , $Pb(OH)_2$, $PbSO_4$), sorbed ions or surface coatings on minerals, or as suspended organic matter.

Chromium: Chromium (Cr) is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$. Major sources of Cr contamination include releases from electroplating processes and the disposal of chromium containing wastes (Smith et al. 1995).

Cr(VI) is the form of chromium commonly found at contaminated sites. Chromium can also occur in the +III oxidation state, depending on pH and redox conditions. Cr (VI) is the dominant form of chromium in shallow aquifers where aerobic conditions exist. Cr(VI) can be reduced to Cr(III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions often encountered in deeper groundwater. Major Cr(VI) species include chromate (CrO_4^{2-}) and

dichromate ($\text{Cr}_2\text{O}_7^{2-}$) which precipitate readily in the presence of metal cations (especially Ba^{2+} , Pb^{2+} , and Ag^+). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Cr(III) is the dominant form of chromium at low pH (<4). Cr^{3+} forms solution complexes with NH_3 , OH^- , Cl^- , F^- , CN^- , SO_4^{2-} , and soluble organic ligands. Cr(VI) is the more toxic form of chromium and is also more mobile. Cr(III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of $\text{Cr}(\text{OH})_3(\text{s})$ (Chrotowski et al. 1991). Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater. The leachability of Cr(VI) increases as soil pH increases. Most of chromium released into natural waters is particle associated, however, and is ultimately deposited into the sediment (Smith et al. 1995).

Zinc: Zinc (Zn) does not occur naturally in elemental form. It is usually extracted from mineral ores to form zinc oxide (ZnO). The primary industrial use for Zinc is as a corrosion-resistant coating for iron or steel (Smith et al. 1995). Zinc usually occurs in the +II oxidation state and forms complexes with a number of anions, amino acids and organic acids. Zn may precipitate as $\text{Zn}(\text{OH})_2(\text{s})$, $\text{ZnCO}_3(\text{s})$, $\text{ZnS}(\text{s})$, or $\text{Zn}(\text{CN})_2(\text{s})$.

Zinc is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values. At higher pH values, zinc can form carbonate and hydroxide complexes which control zinc solubility. Zinc readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations, and may coprecipitate with hydrous oxides of iron or manganese (Smith et al. 1995).

Sorption to sediments or suspended solids, including hydrous iron and manganese oxides, clay minerals, and organic matter, is the primary fate of zinc in aquatic environments. Sorption of zinc increases as pH increases and salinity decreases.

Cadmium: Cadmium (Cd) occurs naturally in the form of CdS or CdCO_3 . Cadmium is recovered as a by-product from the mining of sulfide ores of lead, zinc and copper. Sources of cadmium contamination include plating operations and the disposal of cadmium-containing wastes (Smith et al. 1995).

The form of cadmium encountered depends on solution and soil chemistry as well as treatment of the waste prior to disposal. The most common forms of cadmium include Cd^{2+} ,

cadmium-cyanide complexes, or $\text{Cd}(\text{OH})_2$ solid sludge (Smith et al. 1995). Hydroxide ($\text{Cd}(\text{OH})_2$) and carbonate (CdCO_3) solids dominate at high pH whereas Cd^{2+} and aqueous sulfate species are the dominant forms of cadmium at lower pH (<8). Under reducing conditions when sulfur is present, the stable solid $\text{CdS}(\text{s})$ is formed. Cadmium will also precipitate in the presence of phosphate, arsenate, chromate and other anions, although solubility will vary with pH and other chemical factors.

Cadmium is relatively mobile in surface water and ground-water systems and exists primarily as hydrated ions or as complexes with humic acids and other organic ligands (Callahan et al. 1979). Under acidic conditions, cadmium may also form complexes with chloride and sulfate. Cadmium is removed from natural waters by precipitation and sorption to mineral surfaces, especially oxide minerals, at higher pH values (>pH 6). Removal by these mechanisms increases as pH increases. Sorption is also influenced by the cation exchange capacity (CEC) of clays, carbonate minerals, and organic matter present in soils and sediments. Under reducing conditions, precipitation as CdS controls the mobility of cadmium (Smith et al. 1995).

Copper: Copper (Cu) is mined as a primary ore product from copper sulfide and oxide ores. Mining activities are the major source of copper contamination in groundwater and surface waters. Other sources of copper include algicides, Chromated Copper Arsenate (CCA) pressure treated lumber, and copper pipes. Solution and soil chemistry strongly influence the speciation of copper in ground-water systems. In aerobic, sufficiently alkaline systems, CuCO_3 is the dominant soluble copper species. The cupric ion, Cu^{2+} , and hydroxide complexes, CuOH^+ and $\text{Cu}(\text{OH})_2$, are also commonly present. Copper forms strong solution complexes with humic acids. The affinity of Cu for humates increases as pH increases and ionic strength decreases. In anaerobic environments, when sulfur is present $\text{CuS}(\text{s})$ will form. Copper mobility is decreased by sorption to mineral surfaces. Cu^{2+} sorbs strongly to mineral surfaces over a wide range of pH values (Dzombak and Morel 1990).

The cupric ion (Cu^{2+}) is the most toxic species of copper. Copper toxicity has also been demonstrated for CuOH^+ and $\text{Cu}_2(\text{OH})_2^{2+}$ (LaGrega et al. 1994).

2.3.2 Heavy Metal Behaviour and Early Diagenetic Environments in Aquatic Sediments

Distribution, mobility and bioavailability of heavy metals in the environment do not simply depend on total concentrations but, critically, on their chemical and physical associations and

on transformation processes they undergo in natural systems. Heavy metals discharged into aquatic systems are mostly adsorbed on particles and finally accumulate in sediments. Gradually, contaminant potentials are formed in the sediments or in soil horizons, from which at changing chemical conditions heavy metals can be mobilized. Understanding possible mobilization effects of metals bound on solids requires detailed studies of heavy metal binding forms and how they are affected by natural environmental processes.

One of the important reactions is the mineralization of organic matter during early diagenesis of sediments, which is mainly biologically catalyzed. The commonly accepted model for decomposition of organic matter is illustrated in fig. 2.6 (Song and Muller 1999).

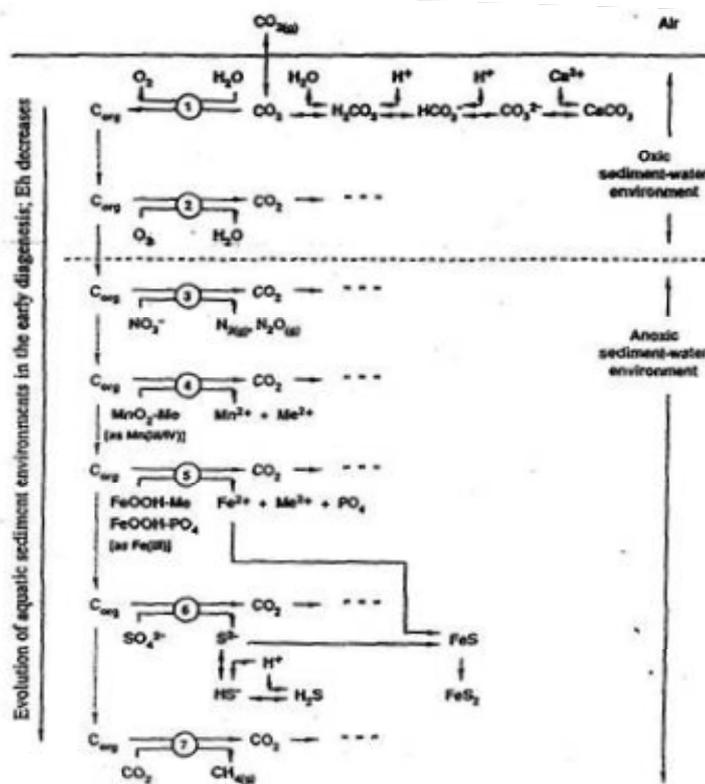
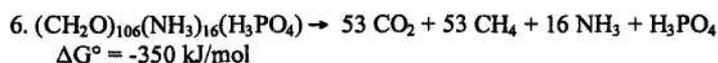
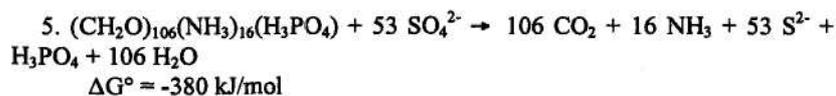
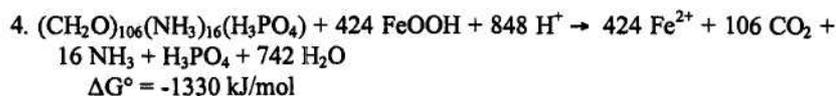
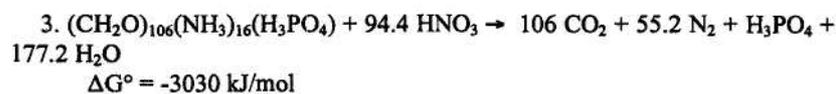
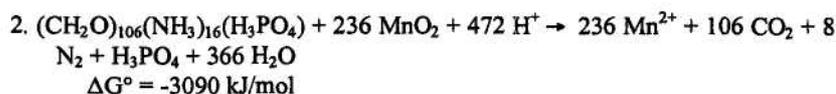
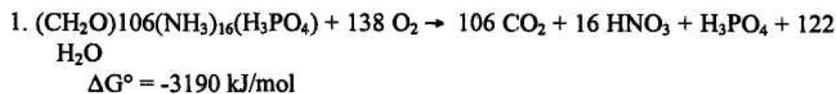


Figure 2.6. Schematic view of the early diagenesis processes

Organic matter is oxidized by the oxidant yielding the greatest free energy change per mole of organic carbon. When this oxidant is depleted, oxidation will proceed utilizing the next most efficient oxidant (Froelich et al. 1979, Berner 1980) as reported in sequence below:



In the oxic layer reaction 1 continues as long as sufficient O₂ is available for the oxidation process. In the suboxic layer MnO₂ reduction (reaction 2) and NO₃⁻ reduction (reaction 3) occur simultaneously. After consumption of NO₃⁻ and reactive MnO₂, oxidation is driven by Fe-oxide reduction (reaction 4) and SO₄²⁻ reduction (reaction 5) in the anoxic layer, and finally by methane fermentation (reaction 6). The clearest effects of early diagenesis may be observed in the pore water of sediments. Therefore, this medium is very important for the study of biological and chemical transformation processes in aquatic systems.

As the chemical environments in soils, freshwater and marine systems usually differ, varied redox reactions may dominate the decomposition of organic matter. The depth of O₂ penetration depends on its downward diffusion and consumption by aerobic decomposition of organic matter. Freshwater sediments generally have higher organic matter contents than marine sediments. This leads to rapid consumption of O₂. As a result, O₂ is depleted below a few millimetres of the sediment-water interface in freshwater sediments (Jorgensen 1983). In marine and most freshwater sediments NO₃⁻ reduction is not a dominating process because of its low concentration overlying water and pore water (Bender and Heggie 1984). In contrast, rivers draining agricultural land commonly have high NO₃⁻ concentrations, and denitrification may be an important process (Jorgensen and Sorensen 1985, Sagemann et al. 1994). Compared to methane bacteria, sulfate reducers have a higher affinity for hydrogen, acetate or methanol which can be used for SO₄²⁻ reduction. Therefore, active methane formation occurs only after the consumption of SO₄²⁻ and is spatially separated from areas of

sulfate reduction (Jorgensen 1983). In freshwater sediments SO_4^{2-} (about 0.2 mM) may be depleted rapidly because of the oxidation of organic matter, and methane formation becomes the dominating process (Mountfort and Asher 1981). Finally, seasonal temperature changes can bring about appreciable variation of biological activity and consequently have an influence on the diagenetic processes

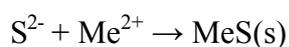
Formation of metal sulphides and other reduced components during anoxic early diagenesis is the material basis of metal release when anoxic sediments are exposed to an oxidative medium. Some mechanisms of metal sulphide formation play an important role in metal transformation during either early diagenesis or resuspension/oxidation. The following description for the formation of metal sulphides includes:

- sulphides ions combine directly with metal ions;
- metal ions replace ferrous ions in FeS;
- sulphides ions replace ligands in some metal compounds;
- formation of pyrite and its derivatives.

2.3.2.1. SO_4^{2-} reduction and direct formation of metal sulphides

Sulphate reduction in the oxidation of organic matter for normal aquatic environments is an important geochemical process. The generalized equation for recycling of organic matter occurs *via* Sulphate-reducing bacteria.

Another source of S^{2-} in sediment/water systems comes from decomposition or dissociation of organic-S. A part of the sulphides which are produced in sediments is precipitated within the reducing environment by metal ions which can directly and strongly combine with sulphides ions:

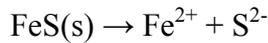


As iron is by far the most abundant metal, iron sulphides constitute the major pool of sulphur in aquatic sediments. The types of iron sulphides which are found in sediments include amorphous ferrous sulphides (FeS), mackinawite ($\text{FeS}_{0.9}$), greigite (Fe_3S_4), and pyrite (FeS_2).

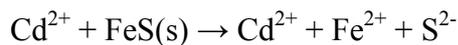
2.3.2.2. Replacement of ferrous ions in ferrous sulphides by other heavy metal ions

An important concept is the replacement of some components in anoxic aquatic sediments. It finally leads to the formation of metal sulphides as dominant metal compounds. It is one of

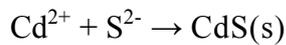
the bases of the AVS-Me extraction and relevant applications. In a typical anoxic sediment, trace metals will replace Fe(Q) and form trace metal sulphides. Di Toro et al. (1992) have described the following mechanisms. Iron mono-sulphides, FeS(s), is in equilibrium with dissolved sulphides by the reaction:



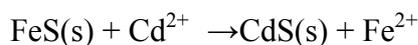
If another metal, for example cadmium, is added to the aqueous phase, the result is iron ion dissociation from FeS(s):



As the cadmium concentration increases, $[\text{Cd}^{2+}] \times [\text{S}^{2-}]$ will exceed the solubility product of cadmium sulphides and CdS(s) will start to form:



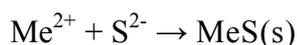
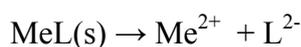
Because cadmium sulphides is more insoluble than iron monosulphides, FeS(s) should start to dissolve in response to the lowered sulphides concentration in the interstitial water. The overall reaction is:



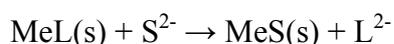
The iron in FeS(s) is replaced by cadmium to form soluble iron and solid cadmium sulphides CdS(s).

2.3.2.3. Replacement of ligands in heavy metal compounds by sulphide ions

Thermodynamic data show that metal sulphides will be the most stable in anoxic sediments. Metals in some other compounds will be gradually transformed into metal sulphides, when sulphides ion appears during sulphate reduction. This process is similar to Fe²⁺ in iron sulphides replaced by Cd²⁺ described by Di Toro et al. (1992). The processes can be expanded to other metals. The summarized expression can be written as:



The overall reaction is:



Where: L stands ligand other than S²⁻.

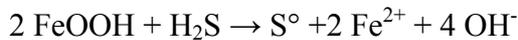
The K_{sp} of some components can be summarized in Table 2.VI where $\log K_{sp}$ of metal sulphides s, carbonates and hydroxides; $\log K_{sp}$ for metal iron-oxides from Dzombak and Morel, (1987) and the concentrations of the species used for calculations are $\text{pH}=8$; $\text{pCO}_2=10^{-3.5}$ atm; $[\text{CO}_3^{2-}]=2.51 \cdot 10^{-6}$ M; $[\text{S}^{2-}]=10^{-9}$ M.

Table 2.VI. Comparison of the K_{sp} of several heavy metals compounds

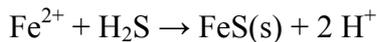
Element	Compound	$\log K_{sp}$	Required concentration, for precipitation [log C]	Log ($C_{\text{MeS}}/C_{\text{MeL}}$)
Zn	ZnCO ₃	-10.00	-4.4	-11.3
	Zn(OH) ₂	-15.52	-3.52	-12.1
	ZnS	-24.7	-15.7	
Cd	FeOCd ⁺	-0.47	-8.14	-9.86
	CdCO ₃	-13.74	-2.35	-15.65
	Cd(OH) ₂	-14.35	-18	
	CdS	-27		
Pb	FeOPb ⁺	-4.65	-7.53	-10.97
	PbCO ₃	-13.13	-3.1	-15.4
	Pb(OH) ₂	-15.1	-18.5	
	PbS	-27.5		
Cu	FeOCu ⁺	-2.89	-4.03	-23.07
	CuCO ₃	-9.63	-7.32	-19.78
	Cu(OH) ₂	-19.32	-27.1	
	CuS	-36.1	-19.75	
	Cu ₂ S	-48.5		

2.3.2.4. Pyrite formation

The amorphous ferrous sulphides is normally the first product to form. Ferrous ions are derived from iron oxide coatings on the mineral grains. Iron oxides such as goethite react chemically with H₂S present in the pore water



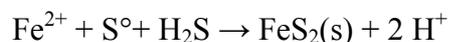
and the free ferrous ions are then precipitated with additional H₂S:



The amorphous ferrous sulphides gradually crystallizes into mackinawite. This reacts with the produced elemental sulphur to form pyrite:

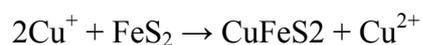


At very low H₂S levels and under slightly acidic conditions (pH < 6.5) the concentrations of ferrous and sulphides ions may not exceed the solubility product of FeS. Instead of ferrous sulphides, pyrite may then form directly by the reaction of the two ions with elemental sulphur:



Pyrite is the stable form of iron sulphides under natural reducing conditions and it is the main sink of sulphides in sediments. The rate of pyrite formation is highest in the uppermost part of the sulphides zone where the sulphate reduction rate is also highest (Jorgensen 1983).

The pyrite forms stable compounds with Metals as for instance for Cu. In a closed system containing Fe(II)/Fe(III) and Cu(I)/Cu(II) redox couples, the lack of any iron release to solution during the reaction strongly suggests that chalcopyrite formation proceeds through the reaction of pyrite with Cu(I) with the concomitant oxidation of Cu(I) to Cu(II):



Many other Cu minerals other than copper mono-sulphide (CuS) in sediments, for example, chalcocite (Cu₂S) and stannite (Cu₂FeSnS₄) have been well documented.

2.3.2.5. Heavy metals in organic matter of aquatic sediments

Organic matter of aquatic sediments originates from the remains, incompletely decomposed products and many new products during the degradation of marine and terrestrial animals and plants. Therefore metal content in organic matter depends greatly on the metal content of original bio-materials. Almost half of the several hundred known enzymes are metalloenzymes, with the metal at the catalytic (active) centre, or performing structural or ion-directing roles. Metals are found to be associated with a wide range of amino acids, proteins, and enzymes. A total of 30 elements are now believed to be essential to life. In addition to selective uptake, some metals can be taken passively, especially in an area polluted by heavy metals.

2.3.3 Mechanisms of metal remobilization from sediments

Many samples of trace metal cycles in aquatic environments have been extensively investigated (Calmano et al. 1993). Based on this study and available data from other literature, the mobilization of heavy metals in anoxic sediments can be conceptually summarized in fig. 2.7 and described as follows Metal transformation during the redox

processes forms a "metal flow" with a certain direction. O₂ is the initial motor for driving metal mobilization — "flowing" along the "orbit" (fig. 2.7).

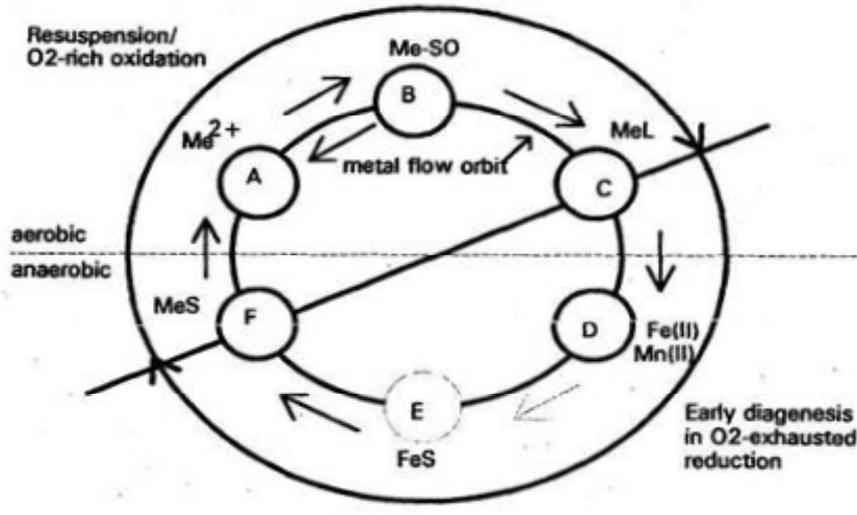


Figure 2.7. Heavy Metals flow in aquatic environment

The main parameters involved in the metal flow of anoxic sediment, reported schematically in fig. 2.7, are detailed in tab. 2.VII.

Table 2.VII. Metal flow in the oxidation reduction processes

Main process	F→ Early diagenesis O₂ exhausted stage	A→ Resuspension/ oxidation	B Redistribution
Metal form	MeS, MeS ₂ , Org-Me	Me ²⁺ , Fe(III)	Me ²⁺ , Fe(III), Me
S Form	Me-sulphides, S ²⁻ , HS ⁻ , H ₂ S	SO ₄ ²⁻	SO ₄ ²⁻
Metal energy level	Low	High	High → low
O ₂ concentration	Low or no	High	high
Thermodynamic stability for newly formed metal component	stable	unstable	unstable
Main events for metal	fixed as solid phase	Release	Scavenging
Intensity order	MeS > MeS ₂ > Org-Me	Cd>Zn>Cu>Pb Oxidation MeS > MeS ₂ > Org-Me	Pb>Cu>Zn>Cd Readsorbe on algal cell wall > Mn-oxide goethite > bentonite > quartz ion exchange adsorption/desorption strong
Chemical process	Replacement	Sulphide oxidation	Ion exchange
Typical reaction	Metal replacement	Redox	Adsorption/desorption
Metal mobility	Immobilization	Very strong	strong
Main process	C→ Transformation	D→ O₂ exhausted stage, Mn(IV), Fe(III) reduction	E SO₄²⁻ reduction
Metal form	Me, MeL, Fe(III)	Me, MeL, Fe(II)	MeS
S Form	SO ₄ ²⁻	SO ₄ ²⁻	Iron-sulphides, S ²⁻ , HS ⁻ , H ₂ S
Metal energy level	High → low	High → low	Low
O ₂ concentration	High	Low → no	no
Thermodynamic stability for newly formed metal component	Unstable → stable	Unstable → stable	stable
Main events for metal	Transformation	Fe(II), Mn(II) dissolution	FeS precipitation
Chemical process	Exchange	Fe(III), Mn(IV) reduction	Sulphide formation
Typical reaction	Solid-solid	Fe(III), Mn(IV) reduction	
Metal mobility	Strong to weak	Strong (Fe, Mn) weak (others)	Weak or none

As it can be observed mobilization of heavy metals from anoxic sediments is strongly affected by two master variables: pH and redox potential E_H . Hence processes controlling these parameters also affect the particulate heavy metal binding forms and their transformation at changing conditions.

Complexing ligands, e.g. humic and fulvic acids, nitrilotriacetate (NTA) or ethylenediaminetetraacetic acid (EDTA), may also keep metals in solution. Other factors to be considered are microbial activities and increase of ionic strength albeit solid bound metals

may be removed from particles by increasing competition with alkaline and earth alkaline cations and complexation with chloride too.

2.3.3.1. Effect of Redox potential and pH on heavy metals mobilization

To ensure the depth of rivers and navigation channels for ships to harbour access, large amounts of contaminated sediments have to be dredged. During dredging, anoxic sediments are usually re-suspended and exposed to the overlying water which is rich in dissolved oxygen. When they are removed from the bottom of the rivers and disposed on land or moved in the water body, the redox conditions are changed. Changes of the redox potential generally lead to production or consumption of hydrogen ions, respectively, and thus to a change of pH values, although in well buffered sediments, where only micro-zones or areas are affected temporarily, the changes cannot be determined directly.

In a sediment/water system the most important components producing hydrogen ions are oxidation of inorganic and organic sulfur-, nitrogen- and iron-species. They constitute the acid production capacity (APC) of the system. The most important oxidation reactions leading to a decrease of pH in low buffered sediments are listed in tab. 2.VIII (Calmano et al. 1993).

Table 2.VIII. Important acid producing oxidation reactions in aquatic systems

Element	Reaction	f
S	$\text{H}_2\text{S} + 2 \text{O}_2 = \text{SO}_4^{2-} + 2 \text{H}^+$	2
S	$\text{S}_0 + 3/2 \text{O}_2 + \text{H}_2\text{O} = \text{SO}_4^{2-} + 2 \text{H}^+$	2
S, Fe	$\text{FeS} + 9/4 \text{O}_2 + 3/2 \text{H}_2\text{O} = \text{FeOOH} + \text{SO}_4^{2-} + 2 \text{H}^+$	2
S, Fe	$\text{FeS}_2 + 15/4 \text{O}_2 + 5/2 \text{H}_2\text{O} = \text{FeOOH} + 2 \text{SO}_4^{2-} + 4 \text{H}^+$	4
Fe	$\text{Fe}^{2+} + 1/4 \text{O}_2 + 5/2 \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 2\text{H}^+$	2
N	$\text{NH}_3 + 2 \text{O}_2 = \text{NO}_3^- + \text{H}_2\text{O} + \text{H}^+$	1
N	$\text{NO}_x + 1/4 (5 - 2x)\text{O}_2 + 1/2 \text{H}_2\text{O} = \text{NO}_3^- + \text{H}^+$	1
Mn	$\text{Mn}^{2+} + 1/2 \text{O}_2 + \text{H}_2\text{O} = \text{MnO}_2 + 2\text{H}^+$	2
N organico	$\text{R-NH}_2 + 2 \text{O}_2 = \text{R-OH} + \text{NO}_3^- + \text{H}^+$	1
S organico	$\text{R-SH} + \text{H}_2\text{O} + 2 \text{O}_2 = \text{R-OH} + \text{SO}_4^{2-} + 2\text{H}^+$	2

Acidification of a sediment leads to mobilization of heavy metals both for the oxidation of sulphide-metal compounds and the adsorption competition between H^+ and Me^+ for the adsorption sites. Extent of acidification and whether heavy metals are dissolved depends on

the acid neutralization capacity (ANC). The acid neutralization capacity of a natural aquatic system is composed of the acid neutralization capacity of the solids ANC_S and that of the dissolved phase ANC_{aq} :

$$ANC = ANC_S + ANC_{aq}$$

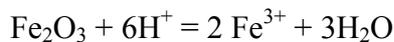
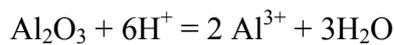
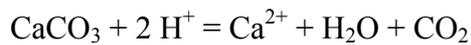
The ANC_{aq} of the dissolved phase may be described by the following equation:

$$ANC_{aq} = [HCO_3^-] + 2 [CO_3^{2-}] + 2 [S^{2-}] + [HS^-] + [NH_3] - [H^+]$$

A similar rule applies to the ANC_S of the solids at $pH > 5$:

$$ANC_S = 6 [Al_2O_3] + 2 [CaO] + 2 [MgO] + 2 [Na_2O] + 2 [K_2O] + 4 [MnO_2] + 2 [MnO] + 6 [Fe_2O_3] + 2 [FeO] - 2 [SO_4^{2-}] - 2 [P_2O_5] - [HCl]$$

In aquatic systems ANC_S is always much greater than ANC_{aq} . The most important buffer reactions taking place in sediments are :



depending mainly on the pH solution as can be observed in fig.2.8.

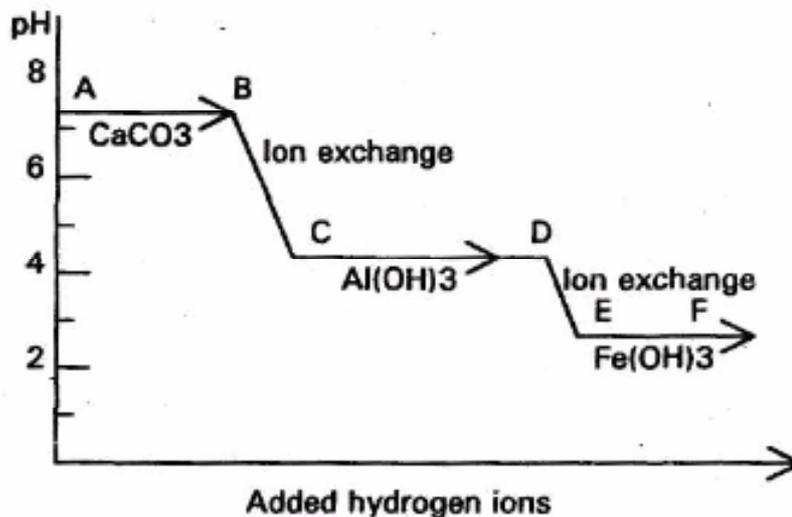


Figure 2.8. Buffering reactions compounds involved in the oxidation of anoxic sediments

From the two parameters ANC and APC an effective acid production capacity APC_{eff} can be calculated which is helpful to specify the metal remobilization potential. The APC_{eff} of a sediment suspension may be defined as:

$$APC_{\text{eff}} = V/W \cdot ([H^+]_i - [H^+]_o)$$

APC_{eff} = effective acid production capacity

V =suspension volume

W =solid mass

$[H^+]_{i,o}$ = hydrogen ions concentration before and after oxidation of the suspension

Experimental studies in a multi-chamber device and reactor cell provided information on the metal transfer between different sedimentary matrices and on interrelations between mobilization and re-adsorption mechanisms (Calmano et al. 1988). Further studies (demonstrated the role of sulfides in the large-scale changes in metal species, i.e., solid/solution interactions and bioavailability of heavy metals in aquatic systems. The combination of matrix and heavy metal data in sediments, simultaneously extracted with different reagents, can provide additional information that may be used to establish models on chemical interactions occurring under characteristic borderline conditions, with respect to sulfide, ionic strength, complexing agents and microbial activity.

2.4 Bioavailability of organic and inorganic compounds: From a conceptual to an operational definition

2.4.1 Introduction

The evaluation of the contaminated soil and sediment effects on individual species, populations, communities and ecosystems are often affected by an uncertainty in the quantification of individual species exposure (Alexander et al. 2003). Observations in laboratory and field studies have demonstrated that the responses of at-risk populations are not simply affected by the total contaminant concentration in the soil but are mainly affected by the fraction biologically available for that population at that time and soil condition (Alexander 2000).

Nevertheless administrators, stakeholders, legislator etc. are still strongly focussed on total concentrations because these endpoints have already been in use for several decades and therefore are easier to handle though it is explained that this way of thinking has often resulted in a conservative approach in exposure assessment described in regulations.

Following a request from the field of risk assessment and standard setting the Soil Communication Paper (EU 2003a) has initiated a discussion on development of European soil

strategy. In this discussion it was possible to include new developments and the Task Group on Contamination concluded that (bio) availability has to be included in the new European policy: “Policies for soil protection should be flexible and take aspects of (bio)availability into account, especially for immobile persistent chemicals (metals, PAHs).

Bioavailability is also considered, by part of the scientific community, as one of the key factors in the selection of a contaminated soil and sediment remediation strategy (Rulkens et al. 2003) because the translation of the information on bioavailability into the concept “how clean is clean” (e.g., site-specific limits for regulating the extent to what concentration of a contaminant a soil has to be cleaned up) is essential for establishing realistic risk assessments and endpoints for remediation.

The concept of bioavailability has been historically used in agriculture and agronomy (e.g. to describe the availability of nutrients and heavy metals to plants).

Unfortunately different approaches have been proposed and applied in the last years in order to define and measure bioavailability. As a result for instance a chemist can measure a chemical that he calls bioavailable, but as long as the chemical concentration has no relation to (biological) effects, it is meaningless. The same holds for a toxicologist who can measure an effect, but this effect has to be related to a chemical fraction of the total amount of the contaminant: the (bio)available fraction.

By having a common framework on bioavailability, it will be possible to introduce workable (standard) methods that can be used in soil and site assessment. Bioavailability can only become a practical tool when all risk assessors are using the same common concept and not their own specific one.

Unfortunately the concept of bioavailability have been not yet expressed (formulated) both conceptually and operationally and an open discussion is still going on in the scientific community. The NRC Committee on Bioavailability of Contaminants in Soils and Sediments (NRC Committe 2003) did not define bioavailability, but discussed ‘Bioavailability Processes’. This discussion combines the conceptual and operational definition as proposed in this chapter.

2.4.2 Conceptual and operational definition of bioavailability

A general conceptual definition of bioavailability is given in ISO/WD 11074: “Bioavailability is the degree to which chemicals present in the soil matrix may be absorbed or metabolised by human or ecological receptors or are available for interaction with biological systems”. This

definition is suitable as a conceptual definition, but has some limitations. The time factor is not clearly specified and it is not clear if there is a single degree of bioavailability or if it is dependent on the receptor or system.

Combining all approaches the following sequence is essential for the concept of availability (fig. 2.9):

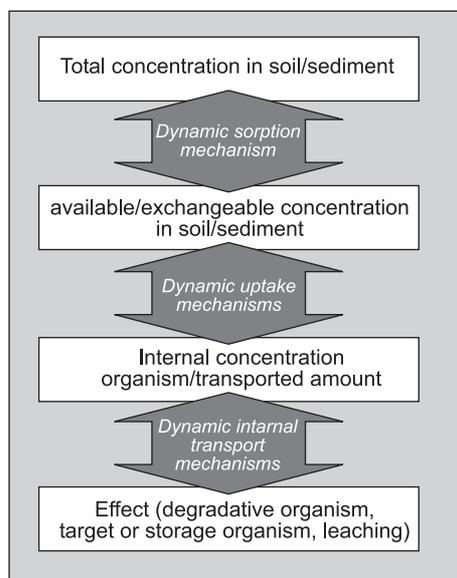


Figure 2.9. Pathways for contaminants adsorbed in soil to achieve an effect in the target organism

Because availability depends on time, it is not a fixed fraction but should be divided into more fractions or described as a continuum. The simplest approach is to define an actual available fraction, a potential available fraction, and a non-available fraction. It is important to differentiate between actual and potential availability. Actual means instantaneous uptake by or a direct effect on organisms. Measurement of the actual availability should therefore be focussed on that momentum and should not include a time dependent step. Bioavailability is the amount in the bioinfluenced zone plus the amount in instantaneous equilibrium with this zone (fig. 2.10). However, a time dependent step is always part of a method. An organism required time to take up a contaminant; and also chemical extraction procedures require a certain contact time. Depending on the organism and the method used, the amount of available contaminant will include a small or large part of the total amount (different dashed lines in fig. 2.10). The potential bioavailability is larger than the actual but their sum cannot exceed the total concentration. Potential includes the time factor and also a change in conditions of the contaminated soil or site. When circumstances change, bioavailability changes too. This can be organism-related or soil-related.

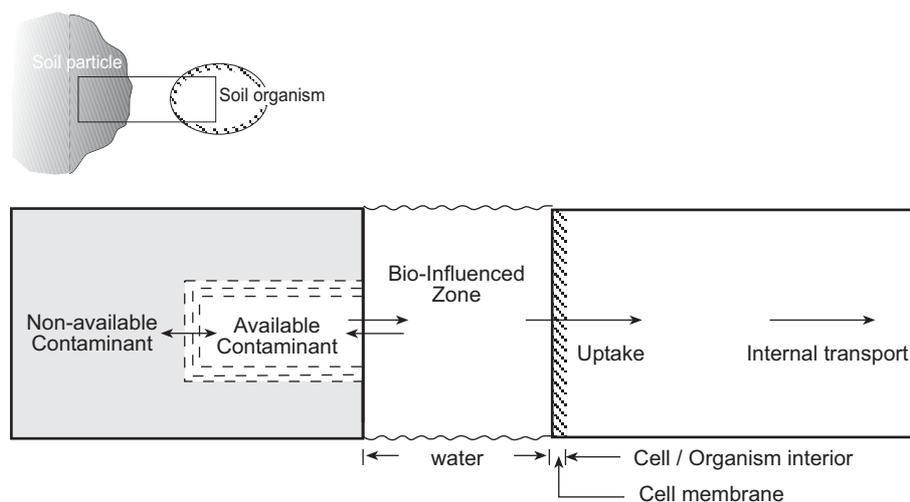


Figure 2.10. Conceptual diagram of the distribution of soil contaminants (i.e., available and non-available form), the bio-influenced zone that link soil contaminants to biological membranes and further transport in the organism. Adapted from Alexander et al. 2003

Several operational definitions can be used as for examples:

- Biodegraded using a specified method;
- Uptake by specified plants;
- Uptake by a defined organism.

Regardless of the definition, the only direct way of measuring bioavailability is through the use of a target organism ($\text{Bioavailability}_{\text{target organism}}$). This leads to an operational definition such as: “Bioavailability is the uptake (resulting in accumulation or an effect) of a component by a specified organism during a fixed period of time from the unit mass of soil involved”. However this type of testing procedure is not acceptable for use with higher organisms such as human beings. Therefore other organisms are often used to study potential effects. The number of organisms in the ecosystem is too numerous and test organisms that can be applied under laboratory conditions are often used as indices for the total ecosystem ($\text{Bioavailability}_{\text{bio}}$).

If a crucial and rate limiting process involved in the uptake of a chemical by an organism or a group of organisms in a soil can be mimicked by a chemical process, $\text{Bioavailability}_{\text{target organism}}$ can be approximated by a chemical test, in which the chemical process is allowed to work in the soil for a specified period of time. In general, since the rate of the mimicking chemical process is not the same as that of actual overall processes, the time needed to measure the bioavailability by the chemical test ($\text{Bioavailability}_{\text{chem}}$) is not the same (usually less time is necessary) to that for $\text{Bioavailability}_{\text{bio}}$. Generally, an important condition

required for $Bioavailability_{chem}$ or $Bioavailability_{bio}$ is that it is a 1:1 function of $Bioavailability_{target\ organism}$ in statistical sense:

$$Bioavailability_{target\ organism} = f(Bioavailability_{bio}) = g(Bioavailability_{chem})$$

Where f and g represent some mathematical functions. The simplest case is that both f and g are linear functions, where $Bioavailability_{target\ organism}$ is linearly correlated with $Bioavailability_{bio}$ and $Bioavailability_{chem}$.

$$Bioavailability_{target\ organism} = k_1 Bioavailability_{bio} + C_1 = k_2 Bioavailability_{chem} + C_2$$

Where k and C are constants and could be close to unity and zero, respectively, when the experimental conditions for biological tests and chemical tests are suitably adjusted.

Biological tests and chemical tests have to be considered as a tool to give indices of bioavailability for a target organism, both $Bioavailability_{bio}$ and $Bioavailability_{chem}$ should not be taken literally as ‘bioavailability’.

As a tool to predict the biodegradation, chemical measures are used, which extract a certain amount from the sediment. Because the mechanisms of these methods are understood this tool is in agreement with the conceptual definition as illustrated in fig. 2.11 (Harmsen et al. 2003).

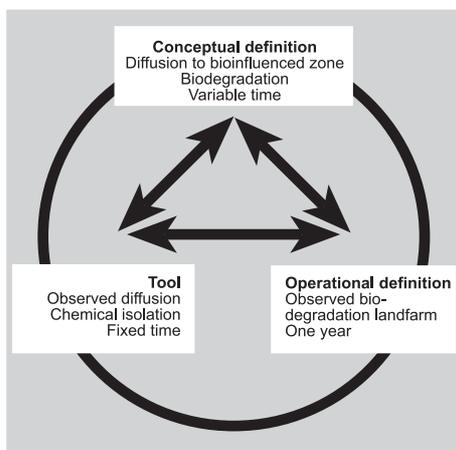


Figure 2.11. Used relations between conceptual and operational definition of bioavailability and the tool to estimate bioavailability

2.4.3 Methods for the estimation of Heavy Metals bioavailability

In general, it is recognised that metals in soil and sediment are either in the available fraction or are occluded in minerals. It is clear that some elements can be occluded within Fe or Mn oxides and become unavailable to plants, even to the extent that plants or animals grazing on those plants show deficiencies. It is known, for example, that Co is occluded within MnO_2 ,

and Ni within Fe-oxides (Tiller et al. 1969, McKenzie 1970, McLaren et al. 1985, Bruemmer et al. 1988). Cd in either oxide is poorly occluded, while Zn and Pb may be occluded to some extent (Ford et al. 1997, Bruemmer et al. 1988).

Heavy metals in soils are mainly adsorbed on those components that determine the CEC (organic matter, clay and Fe- and Al-oxides) or are present as minerals such as carbonates. In sediments they may also be present as sulphides. Adsorption onto these minerals and soil components and or precipitation is more or less reversible. To predict the solubility or phytoavailability of the element at the existing soil pH, neutral salt extractions are commonly used rather than chelating agents or acids. There are different methods available that are variations on the same principle. The dilute neutral salts (e.g. 0.01 M CaCl₂) have shown to extract amounts of Zn, Cd, or Ni proportional to plant uptake (Sauerbeck and Hein 1991, Prue et al. 1991).

Heavy metals in organisms: Smit et al. (1997) obtained a good correlation between the EC50 of the springtail *Folsomida candida* to both the CaCl₂-available and water-available extraction, both in freshly and long term polluted soil. During gut transfer in earthworms, the pH remained more or less neutral but organic matter was degraded, resulting in loss of binding sites. An extraction with buffered CaCl₂ (pH 7.2) gave a good correlation with the uptake of cadmium (Osté et al. 2001).

Some types of higher organisms ingest soil, such as grazing cattle (sheep and cows) and small children. Their digestion system is more aggressive compared to soil living organisms (low pH in the stomach, a large variety of enzymes and longer residence times in the digestive tract). This may be responsible for a higher bioavailable fraction. In fig. 2.12 are reported the heavy metals fractions available for the uptake of several testing organisms.

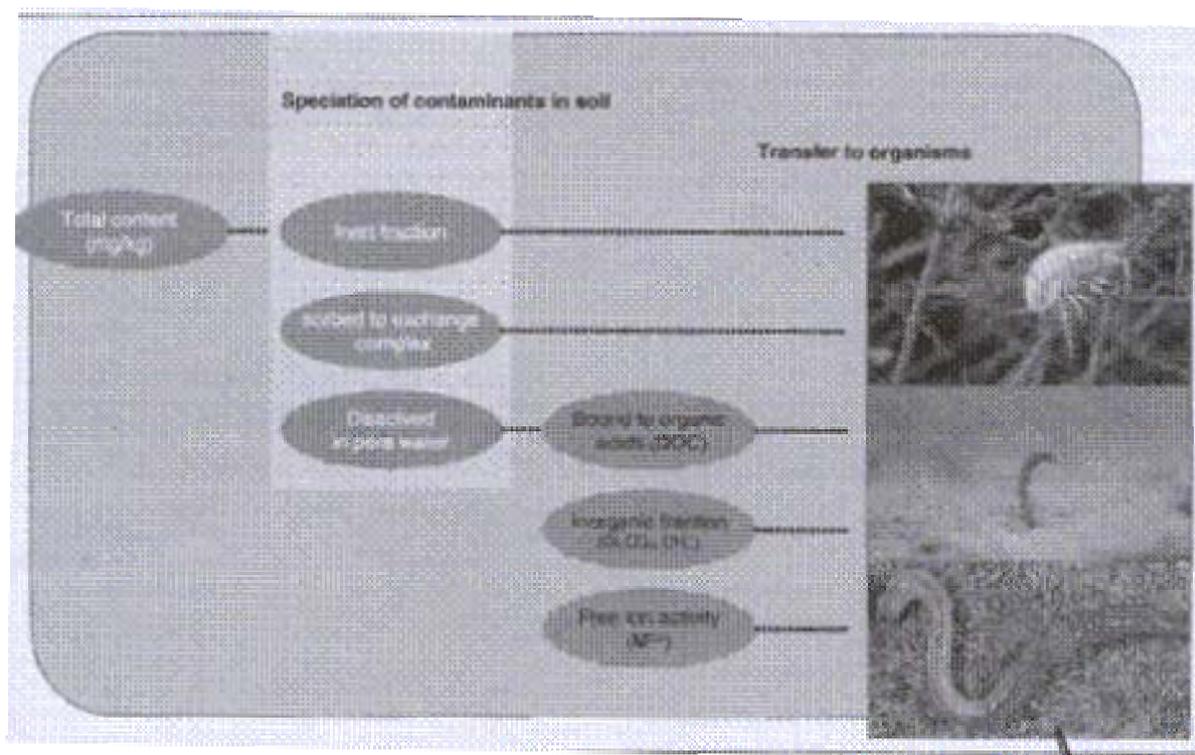


Figure 2.12. Heavy metals fractions available for the uptake of some organisms

Because soil Pb comprises significant risks to children through the soil ingestion pathway, research has been conducted to identify methods to reduce the phytoavailability and bioavailability of Pb in soils. Feeding tests showed that soils differed appreciably in the relative bioavailability of the Pb they contained (Chaney and Ryan 1994, Freeman et al. 1992, Schoof et al. 1996). The bioavailable fraction of Pb in soils can become reduced by both formation of very insoluble phosphate compounds (Ma et al. 1993, Zhang et al. 1998) and increased soil adsorption by phosphate and hydrous Fe oxide additions (Chaney and Ryan 1994, Berti and Cunningham 1997). Using these processes in remediation methods effectively reduced soil Pb bioavailability for pigs and rats (Chaney and Ryan 1994, Brown et al. 1997).

2.4.4 Methods for the estimation of Organic compounds bioavailability

Recently some new chemical methods have been described that are empirically based. Some are based upon attempts to mimic conditions of biological uptake or processes in the soil. Not all promising analytical results have yet been studied with appropriate bioassays. The following methods are described further:

- Water Based Extractions, extracting the pore water or using some extra extraction power by adding molecules (Johnson et al. 2001, van der Sloot et al. 1997) or a solid phase (Morrison et al. 2000, Tang and Alexander 1998, Cornelissen et al. 1997 and 1998) with extraction power able to "adsorb" the available contaminant solvent;
- Based Extractions with single solvents or multiple extractions. (Kelsey et al. 1997, Tang and Alexander 1998, Doddema et al. 1998, Krauss and Wilcke 2001, Jonker and Smedes 2000);
- Use of the Selective oxidation of organic matter (Weber et al. 1992, Pignatello and Xing 1996, Luthy et al. 1997, Pignatello 1998, Cuypers 2001);
- Thermal desorption to remove the more available contaminants. (Werth and Reinhard 1997, Uzigiris et al. 1995, Ghosh et al. 2001).

Because the biodegradation of PAHs has been investigated in this thesis during landfarm, the conceptual definition of bioavailability is focussed onto biodegradation:

The amount of PAHs and mineral oil that can be transported (by diffusion or physical change of the adsorption site) to a site with a degrading micro-organism in a defined time period and that can enter the bio-influenced zone of this organism.

This bioavailable amount will be biodegraded under aerobic circumstances in that period, providing there are no other limiting circumstances for degradation. Because the time period may vary, the bioavailable fraction is not a fixed amount. In addition, it is related to a specific situation. Part of the research of this thesis, in cooperation with Harmsen at the Alterra Centre (the NL), concentrates on landfarming, therefore the operational definition is defined as:

The amount that is degraded aerobically on a landfarm in one year, under Dutch climate conditions.

For the availability of PAHs, the Tenax-method gave good predictions of biodegradation. We chose the Tenax-method for the following reasons:

- The mechanism used in the Tenax-method is diffusion.
- It is possible to derive kinetic parameters from the measured results.

- The Tenax-method was already available in 1997, when Harmsen started the availability measurements on Kreekraksluizen. To be able to compare results he used the method also in following years.

Methods developed later and using other principles such as the oxidation method of Cuypers (2001) could also be used, and in that case organic matter fractions with different stabilities can explain the bioavailability mechanism. The choice of Tenax does not mean that it is the most suitable method for routine applications. That was not a part of our research. The method used supplied the necessary scientific data to get a better understanding of slow biodegradation. Which method or methods should be used as a standard method should be discussed in the ISO TC190 working group.

In this item the concept of bioavailability has been explained and defined in relation to biodegradation. It is possible to use chemical tools to predict the bioavailable (=biodegradable) fraction of PAH. These tools are used in the following chapter, for explanation of the slow degradation rates found in landfarming of contaminated sediments. It will also be discussed if the chemical tool can be correlated.

Chapter 3

3 Available Treatment Technologies

3.1 Introduction

Sediment can be considered as a sink for pollution. In a delta area new sediments are formed continuously and as long as contaminants are released into the environment, these new sediments may be polluted. Recent model studies (Kramer et al. 1997) proposed for the Netherlands have shown that if the release of the main contaminants will remain on the actual level polluted sediments are to be expected for the next hundred years, so there must become a way to handle the large amount of polluted sediments.

Different treatment and disposal technologies have been investigated and applied in order to treat contaminated sediment in the last decades. Some technologies have been adapted from other fields (e.g mining industry, soil treatment etc.), others are typical of sediment. In general sediment treatment technologies can be categorised as follows in tab. 3.I.

Table 3.I. Categorization of process options and treatment technologies for contaminated sediment

Processing Principles	Process Options (Treatment)
1. Relocation	1. Open water disposal 2. Injection dredging 3. Placement on the banks
2. Mechanical separation	1. Classification 2. Sorting
3. Dewatering	1. Evaporation 2. Mechanical dewatering
4. Contaminant separation	1. Sediment washing 2. Thermal desorption (together with thermal oxidation)
5. Contaminant destruction	1. Biological degradation (Landfarming and bioreactors) 2. Chemical oxidation 3. Thermal oxidation (together with thermal desorption)
6. Contaminant immobilisation	1. Chemical immobilisation 2. Thermal immobilisation (together with thermal desorption and oxidation)
7. Disposal	1. Sub-aquatic confined disposal 2. Upland disposal

The decision if a treatment option is technically feasible depends on different factors. The decision is not only based on the environmental condition of contaminated sediment but also on their intrinsic characteristics as: grain size, organic matter content, presence of sulphides compounds, level and type of contamination.

A brief description of the listed technologies have been reported below though in this chapter several technologies: Sediment Washing, Landfarming and Bioreactor will be pointed out.

Relocation consists into bringing back dredged sediments into the water system without any treatment. Three types of relocation are known: the Open Water Disposal, the Injection Dredging and the Placement of DM on the Banks. The open water disposal consists into dredging and dumping the sediment at another place in the water system. Hopper dredgers or other types of dredgers and additional barges are in operation for dredging, transport and relocation. Injection dredging depends on the injection of e.g. water or air into the sediment layer; the sediment is re-suspended and flushed away by the current. It can be operated in rivers or tidal zones. Placement on the bank is the use of dredged material in the same waterbeds to form and develop the embankment of rivers and ditches

Mechanical Separation is based on the principle of dividing dredged material in a fraction of coarser and finer particles or in fractions of different quality standards (e.g. different mineral fractions or different contaminated fractions). Two types of mechanical separation are known: Classification and Sorting. *Classification* depends on separation of a less contaminated coarser fraction and a more contaminated fine fraction from the original dredged material. The separation is operated to divide the grain size range of 20 – 63 μm because contaminants are very often adsorbed at the surface of the finer particles because of its higher specific surface. It can be done e.g. by sieves e.g. drum or vibration screens or hydro-cyclones. *Sorting* depends on separation into fractions of less contaminated particles and more contaminated particles or into fractions of different mineral and / or organic qualities. Separation principles depend mainly on different specific weight of the particles or on different conditions on the particle surface. Sorting can be done by upstream current-classifiers, spirals, jigs, flotation-cells or sedimentation basins.

Dewatering depends on separation of water from the solids. Two types of dewatering are known: Evaporation and the Mechanical Dewatering. *Evaporation* of water can be done by natural forces like wind and sun or technical by warming up or forming a vacuum. It can be done e.g. in dewatering fields (lagoons, ripening fields), in ovens or vacuum chambers. *Mechanical dewatering* depends on the reduction of the pore volume between the particles. It

can be done e.g. with centrifuges or presses like filter-belt-presses or membrane-chamber-filter-presses.

Contaminant Separation consists into the separation of the contaminants, mostly adsorbed on particle surface, and original mineral particles. Two types of contaminant separation are well known: Sediment washing and Thermal Desorption. *Sediment washing* depends on extraction of contaminants using acids or complexing agents. A process plant is necessary with two main parts first an extraction plant, and second a separation phase to separate solids and washing liquid. Mainly inorganic harmful substances e.g. heavy metals can be washed out. *Thermal desorption* depends on the difference of the relative volatility of the contaminants and mineral sediment particles. It is normally operated in the temperature range of about 450 °C in special ovens with an additional product gas cooling and cleaning system. Mainly organic harmful substances can be separated. Thermal desorption is always available in combination with thermal oxidation and partly with thermal immobilisation.

Contaminant destruction is based on the principle of destroying contaminant (e.g. through oxidation). Three types of contaminant destruction are known: Biological degradation, the chemical oxidation and the thermal oxidation. *Biological degradation* depends on one hand on bacteriological activities using various types of thio-bacteria to solubilise or to oxidise different types of contaminants and on the other hand the capacity of various plants e.g. willows and giant knotweed (*reynoutria sachalinense*) to collect different contaminants and stock the harmful substances in their roots and shoots and in leaves. Biological degradation can take place in technical plants using reactor tanks for lixiviation or e.g. in ripening fields (lagoons, flushing fields) that are cultivated. *Chemical oxidation* depends on addition of a chemical reactant. Mainly organic contaminants are transformed into non-toxic compounds by oxidation. *Thermal oxidation* depends on combustion of organic material at high temperatures. All types of organic material can be burned. Special combustion ovens need an additional waste gas cleaning. Thermal oxidation is always available in combination with thermal desorption and thermal immobilisation.

Contaminant immobilisation depends on stabilisation in a way that contaminants are no longer available to the environment. Two types of contaminant immobilisation are known : Chemical Immobilisation and Thermal Immobilisation. *Chemical immobilisation* is done by addition and mixing of dredged material or sediment and reactants e.g. clay, lime, cement or fly ash. After mixing there will be hydraulic-setting system and the contaminants will be bound into the matrix. Chemical immobilisation is possible in-situ as well as on land to

PAHs and Heavy Metals Contaminated Sediment: Bioavailability, Mobilization, Biological and Phisycο-Chemical Treatment

produce e.g. aggregates. *Thermal immobilisation* is done by the binding of contaminants like heavy metals in the mineral phase at high temperatures. Products of thermal immobilisation could be bricks, pellets (light weight aggregate, artificial gravel) and glass. (Mostly together with thermal oxidation).

Disposal can be conducted in *upland confined disposal* sites or in *sub-aquatic confined disposal* sites consisting in dredging the sediments placing them in a confined environment avoiding the contact with the extern.

A figure of the huger confined disposal facility located in the Port of Rotterdam and called the Slufter is reported below in fig. 3.1



Figure 3.1. Slufter with dewatering fields and sedimentation basins

3.2 Sediment Washing

3.2.1 Treatment flow chart

The basic process design of sediment washing comprises the treatment of contaminated sediment material with fresh water containing auxiliary agents and the subsequent purification and processing of exhaust air and process water solution. The contaminant fraction has either to be disposal as hazardous waste or further to be treated. The application of *on-site* chemical washing requires several as the following (fig. 3.2):

1. The material to be cleaned is *pretreated*, i.e. coarse and bulky components such as pieces of wood, broken cement, stones, etc., are removed or screened out by means of hydrocyclone processes, centrifuges or filter presses etc.
2. The pretreated solids are intensively mixed with the extraction agent for the contaminant dissolution.
3. Treated solids and extraction agents are separated by means of settling ponds, filter presses, hydrocyclones, or centrifuges, etc.
4. If needed the solids are washed once again with clean extraction agents and/or with water.
5. The extraction agent is cleaned and regenerated as the extraction agent is reused in substitution or within the fresh extraction agent.

In the following item the main part of the sediment treatment facility will be deepened.

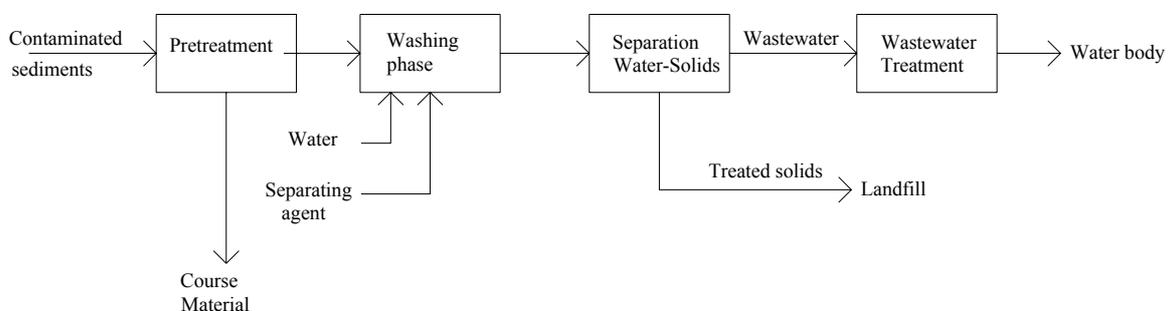


Figure 3.2. Sediment washing flow chart

3.2.2 Washing phase

3.2.2.1. Introduction

From available experiences on practiced sediment washing it is difficult to provide general rules on the extractability of specific contaminants. The treatment success is mainly dependent from the sediment properties, i.e., from the separability of a pollutants-loaded fine fraction from the widely unpolluted coarse fraction. With regard to the fact, that sediment washing procedures to a certain extent can be modified, by e.g. addition of different auxiliary substances, washing tests can be conducted systematically, adjusting to the respective contamination situation, so that eventually all pollutants can be removed. Last but not least the respective original concentrations and target limit values are decisive for a site-specific remediation success.

Sediments properties in a pedological sense influence the technological design and efficiency of washing procedures. Of particular interest are the following items:

- Grain size distribution.
- Clay fraction.
- pH-value of sediment and best pH washing operation conditions.

Actually a proportion of 30% silt and clay is often considered as an upper limit for washing processes. The clay fraction, comprising sediment constituents of smallest grain size, exhibits properties of ion exchangers and therefore the potential, to oppose pH-alterations and to bind dissolved contaminants electrochemically to the particle surface. Smaller percentages of clay constituents, on the other hand, may be indicative for a good performance of the treatment, since most contaminants are preferentially bonded to this fraction. Acidity (pH-value) of sediment determines the solubility of the contaminants and their transfer from the sediment into the washing fluid. By addition of suitable chemical reagents the pH-value can be adjusted to optimal conditions.

3.2.2.2. Extraction Agents

The dissolving of contaminants can be intensified considerably by the addition of liberation agents to the water. However, there are a series of reservations against the application of chemical liberation agents. For one, the sediment substance (particularly the organic fraction) can be deteriorated through chemical action. Also the liberation agents themselves represent a contamination and must therefore be able to be flushed out free of residues and/or to be

biologically decomposed. Despite some concerns, an increased application of chemical cleaning and liberation agents is to be reckoned with. This might be above all be necessary to also enable advance for washing of fine particles. The properties of water can be enhanced with additives including:

- *surfactants* that improve the wettability of the sediment components and improve the solubility of lipophilic impurities,
- *flotation agents* (collectors and foamers), which convert certain insoluble substances into an separable phase,
- *complexing agents* which convert heavy metals and their insoluble compounds into water soluble compounds,
- *acids or bases* for pH control which can necessary for the stability of compounds

Washing with mineral acids has been widely tested but the extraction efficiency is erratic and the cost of chemicals for acidification to pH 1 and for subsequent neutralization are usually prohibitive (Masscheleyn et al. 1996). Hydrochloric, sulfuric, and nitric acids are used in sediment remediation to extract metals; because of the good solubility of basic salts, e.g., lead and zinc, it is also possible to use treatment with sodium hydroxide (Vandevivere et al. 2001).

On the other hand, use of organic metal chelants in the wash formulation offer the advantages of high potential extraction efficiencies, homogeneous treatment of the polluted matrix, specificity for metals, and low cost because residual wastes requiring landfilling are minimized (Vandevivere et al. 2001). To keep treatment cost low, it is mandatory to recover and reuse the chelant molecules (Arevalo et al. 2002). One elegant and effective way to achieve this is by immobilizing the organic chelant on a finite-textured magnetic carrier, which is regenerated chemically (Holbein 1994, Bradbury and Scrivens 1995). Although a great number of chelants have been evaluated (Norvell 1983, Chen et al. 1995), there remains uncertainty as to the optimal choice of chelating agent(s). Factors such as degradability and residues [ethylenediamine tetraacetate (EDTA)], classification and potential adverse health effects [nitrilotriacetate (NTA)], cost, extraction efficiency (citrate and lactate), and possibility of recovering the chelant all need to be considered. A key parameter in designing a chelating based metal extraction scheme is the amount of chelant to be used. Because the main chelating agents (e.g.EDDS, EDTA, NTA etc.) are known to form 1:1 chelates with metals, the theoretical minimum chelant dosage is the one that binds the metals

stoichiometrically. Generally, however, a several fold excess of chelant is used to maximize metal extraction (Linn and Elliott 1988).

3.2.3 Regeneration of the washing solution

Due to the fact that in many cases the costs of the Mass Separating Agent (MSA) determine the economics of an extraction process, the regeneration/recycling of the MSA enables the recovery of the economic value of the extractant, the metals or both, aiming towards a closed loop operation. The selection of a proper MSA for a specific situation is determined not only by its cost but also by factors such as the nature of the solid material to treat, side reactions, stability at the operating conditions, metal speciation, feasibility of metal recovery and MSA reuse. Any attempt at minimising the costs will therefore target a reduction of the MSA demand, which is determined by:

- The consumption of acidity of the MSA by the acid neutralising capacity of the solid
- The consumption of complexing capacity (ligands) of the MSA by constituents of the solid such as iron (Fe).
- The drag-out of MSA by means of treated solid leaving the process

The regeneration technologies depends mainly on the extractant agents is being used. Regarding the complexing agents hydrometallurgical process can be used. An electrolytic cell can be implemented both for the MSA regeneration and metal recovering because of the electrodeposition (Arevalo et. al. 2002)

3.3 Landfarming

Based on research results also described in this thesis, landfarming is considered as a promising inexpensive technology (AKWA, 2001) to remediate sediments contaminated with organic compounds (e.g. PAHs, mineral oil, etc.). The application of landfarming technology changes sediment (contaminated as well as clean) into soil, which is a process that has resulted in fruitful soils in the polder areas, and has assimilated sediment from ditches to become part of the agricultural soil. Within this context, landfarming is applicable for the removal of contaminants through bioremediation of sediments and the product of landfarming, a soil, can be reused.

Sustainable landfarming can be applied to large scale polluted sites, such as military sites, old industrial areas and oil exploration sites all over the world. Especially if more intensive

cleaning technologies are too expensive for large scale pollution, sustainable treatment of the soil and area may be a solution.

3.3.1 Processes in a landfarm

Landfarming is one of the oldest bioremediation technologies (Dibble and Bartha 1979) operated spreading the soil or the sediment over the land surface adding eventually nutrients or stimulating the aeration in order to reduce the treatment time (fig. 3.3) . Landfarming of dredged sediments starts with dewatering of the sediment that allows oxygen to enter the sediment through pores in which water is replaced by air. Under aerobic circumstances biodegradation of organic contaminants like polycyclic aromatic hydrocarbons (PAHs) becomes possible. Aerobic biodegradation of contaminants in a landfarm will occur if the contaminant became bioavailable and passes the cell membrane of a micro-organism that is able to degrade the contaminant and if oxygen is present to initiate the biochemical reactions in the organism. Of course there may be other limiting circumstances including too low or too high pH, lack of nutrients, or presence of chemicals inhibiting micro-organism activity. These circumstances may make bioremediation either impossible to overcome or possible to manage, for example, by adding nutrients.

In fig. 3.3 two landfarming plants, that are the objects of part of this thesis, are reported below; the first (left) is cultivated the second (right) vegetated. It means that during the first the sediment are located in the fields and during dewatering the upper layers are mixed with the lower layers whereas during the second the mixing it is not operated, and therefore two different layer can be distinguished in the latter.



Figure 3.3. The Petroleum Harbour landfarms on Kreekraksluizen. Left the cultivated landfarm in 1995. Right the vegetated landfarm in 1997 (from Harmsen 2004)

Knowledge is used to be able to recognise the most important parameters in landfarming of sediments that have been treated in this item as the:

- Presence of contaminants in landfarmed sediment;
- Presence and activity of micro-organisms able to degrade contaminants;
- Presence of oxygen in sediment physical factors explaining the transport of oxygen.

Although the three subjects are discussed separately, they are of equal importance for landfarming. In order to achieve degradation, contaminant, oxygen and micro-organisms must be present at the same time and the same place. The result of a bioremediation process, i.e. the fraction of the contaminant degraded during a specified time, can be expressed as a summation of probabilities of each term or parameter (Harmsen et al. 1997). The fraction degraded in a volume of sediment considered can be expressed as:

$$(\text{Fraction degraded})_t = \frac{\sum_t \sum_{x,y,z} \sum_{n_c} [\text{contaminant}] \cdot [\text{micro-organism}] \cdot [\text{oxygen}]}{n_c}$$

where:

$[\text{contaminant}]$ = probability of finding the contaminant molecule on a site x,y,z per unit of time

$[\text{micro-organism}]$ = probability of finding an active degrading micro-organism on site x,y,z per unit of time

$[\text{oxygen}]$ = probability of finding oxygen on site x, y, z per unit of time

t = time elapsed after start of bioremediation in unit of time

x,y,z = co-ordinates in the volume considered

n_c = number of contaminant molecules in the volume considered

Each probability for *contaminant*, *micro-organism*, and *oxygen* terms can have the value zero or one; contaminant, micro-organisms and oxygen are present or not present.

3.3.1.1. Contaminant

Desorption and diffusion of the contaminant from a site without an active organism to a site with this organism can be described with a first order process in combination with the existence of different adsorption sites (see chapter 2). In the mathematical description of this diffusion the moisture contents and radius of the aggregate are very important parameters as the desorption rate constant is proportional to the square of the volumetric moisture content and inversely proportional to the square of the radius of the soil aggregate. At higher moisture content, higher degradation rates as result of faster desorption rates will be obtained. A high

water content, however, reduces the possibility of diffusion of oxygen and the landfarm will become anaerobic while increase of temperature has limited effect on the rate of the desorption process.

Contaminants in the water phase are not always present as individual solved molecules, but associated with dissolved organic matter. As a result, the differences in the partition coefficient of the individual contaminants become much smaller. If diffusion is the time limiting step for degradation, it is to be expected that the rate of degradation for individual PAHs becomes comparable.

Within a time frame of years, organic matter cannot be considered as a constant matrix. The rate of biodegradation of contaminants may also depend on the biodegradation of the organic matter, by which the adsorption sites are partly removed. Conversely, the organic matter may also change from a more rubber like form to a glassy form in which contaminants are more strongly absorbed (Luthy et al. 1997).

3.3.1.2. Micro-organisms

Regarding the micro-organisms it is concluded that they can be found on several places in the treated sediment (the probability of finding an active micro-organism on these places is 1). The site must be large enough to contain an organism. Not all sites are large enough, so it will be necessary that the contaminant has to diffuse to the organism. Most bacteria are present in small pores $< 1.2 \mu\text{m}$ (Hassink 1995) and the contaminant and oxygen have to diffuse to these pores.

Landfarming is a slow process, which means that the acclimation time can be ignored compared to the total process time. At the end of the landfarm period degradation will continue even below the threshold value. However, bacterial growth will stop resulting in a decreasing degrading bacterial population. The probability of finding an active organism will decrease resulting in an extra decrease of the degradation rate at lower concentration.

3.3.1.3. Oxygen

Sediments are anaerobic and after dredging they have to be transferred into an aerobic soil by dewatering and ripening. This gives physical changes in the sediment, which can be described by compaction and shrinking. The sediment becomes a soil with cracks and aggregates. The distribution and sizes of cracks and aggregates depends on the soil water potential. In the upper layer of landfarm and especially if vegetation is growing this potential is high, resulting in such a distribution that all aggregates will be aerated. At higher depths and closer to the

ground water table the aggregates are larger and diffusion of oxygen into the aggregates becomes more difficult. The aggregates will only become aerobic if the amount of oxygen diffusing into the aggregate is at least equal or larger than the amount consumed by microorganisms for degradation of organic matter. Moisture characteristics for soil can be derived from basic soil properties like clay and organic matter content and comparison with standard soils. Soil obtained after dewatering and ripening of sediments has a less compact structure compared to the standard soils.

3.3.2 Mathematical description of contaminant desorption/degradation during landfarm of contaminated sediment

The equilibrium approach is often used to describe the interactions between the organic contaminants and the solid matrix (i.e soil and sediment) aiming the contaminants partitioning between the aqueous and solid phases. However this approach is insufficient to describe the low organic chemical biodegradation rates in landfarms because of the heterogeneity of the solid matrix components. Therefore the equilibrium approach has to be coupled with a mathematical description of transport of the contaminant in soil aggregates, which introduces also the time factor.

Desorption processes, but also degradation of organic matter can be described using different desorbing or degrading fractions, expressed as fast, slow, and very slow. As mathematical description of the decrease of contaminant concentration as well as for desorption and degradation of organic matter a sum of first order decreases can be used.

Assuming that no re-adsorption takes place (Cornelissen et al. 1997) the three-compartment desorption model can be described as sum of three first order decreases:

$$\frac{C_t}{C_0} = F_{fast} \cdot e^{-k_{fast} \cdot t} + F_{slow} \cdot e^{-k_{slow} \cdot t} + F_{very\ slow} \cdot e^{-k_{very\ slow} \cdot t}$$

where:

C_t = sediment/soil sorbed amount (mg Kg⁻¹ TS) at time t (y)

C_0 = sediment/soil sorbed amount (mg Kg⁻¹ TS) at time 0

F_{fast} = fraction of contaminant in fast desorbing/degrading compartment

F_{slow} = fraction of contaminant in slowly desorbing/degrading compartment

$F_{very\ slow}$ = fraction of contaminant in very slowly desorbing/degrading compartment

k_{fast} = rate constant rapid desorption/degradation (y^{-1})

k_{slow} = rate constant slow desorption/degradation (y^{-1})

$k_{very\ slow}$ = rate constant very slow desorption/degradation (y^{-1}).

Every first order decrease is described with two constants, the size (fraction of total amount, F) and the rate constant (k). If degradation is not possible redistribution between the different compartments takes place, which may result in decrease of the fast desorbing fraction and increase of the slow and very slow desorbing fractions. This stronger binding of contaminants to sediment or soil as effect of increasing contact time is often described as aging.

The assumption that no re-adsorption takes place will be true in slurry systems with a high biological activity or in experimental systems where the desorbed contaminant is immediately taken away. In both cases the concentrations in the water phase are zero. Examples are a bioreactor or the Tenax desorption test as described in Chapter 4 and 5.

In a landfarm the desorbed contaminant is not always taken away instantaneously because of limiting as the absence of oxygen or an active degrading organism.

The duration of the period in which degradation is limited by absence of oxygen may vary depending mainly on the dewatering time. However, with thicker layers more time is necessary to have the whole layer aerated. If oxygen is absent, desorption will not lead to degradation and re-adsorption will take place.

Because of the long duration of the dewatering phase in our experiments, above considerations are not theoretical problems but reality. Fitting data in such a case with a two or three compartment model will not give proper degradation constants, in the experiments where the dewatering is a limiting step, and therefore, for these, the calculated degradation rate constant will be the result of both dewatering and degradation.

3.3.3 Perspective of landfarm

One of the result of the investigation of these unexpensive technologies is that after the treatment of contaminated sediment a residual contaminant concentration is obtained. It depends on several factors like bioavailable contaminant fraction, time etc. and often these value do not meet the regulation values. One of the hint of the application of these technologies is the use of a multifunctional approach that has conducted for instance in the

NL in the emanation of the Building Material Act (Harmsen 2004), criteria for reuse of (treated) soils and sediments as building materials that allowed higher residual concentrations. Results of remediation were no longer assessed on the basis of multifunctionality, the treated soil or sediment could also be assessed on its functionality as building material. As long as the concentration was below a set value and there was no danger for leaching, the soil or sediment could be reused. Prescribed leaching tests controlled the use of treated soil and sediment. For PAHs the consequences were considerable. Before the Building Act it was necessary to clean the soil or sediment to a residual concentration of 1 mg/kg d.m. This was a “mission impossible.” The new value of 40 mg Kg⁻¹ TS was more realistic and provided a major stimulant for the application of bioremediation.

Using these criteria, restricted use of remediated soil and sediment became possible. Cleaning by landfarming using intensive techniques became effective, and as a result bioremediation became more popular.

Many soils and sediments have PAHs-concentration levels between the reference value and the value for building material. Soils or sediments from small sites are directly, or after a short physical treatment of a few months, usable as building material. However, for diffuse polluted sites, for example, the flood plains of the River Rhine, this would not be an acceptable solution.

As mentioned previously, the application in policy of the concept of multifunctionality hampered the use of landfarming in the all European countries for a long time. Therefore, it should be realised that the development of landfarming is not only influenced by development of technology but also by target values set by the government.

3.4 Bioslurry treatment

The most widely used technologies for bioremediation of PAH contaminated soils and sediments are landfarming, bioventing, air sparging and bioslurry reactor (Hinchee et al. 1995, U.S. EPA 1990, Wilson and Jones 1993). Particularly bioslurry reactor is a biological ex-situ technology, offering optimal process control and high biodegradation rate (U.S. EPA 1990, Cesaro et al. 2003).

The bioslurry treatment (fig. 3.4) is analogous to the activated sludge system used for the wastewater treatment (Loehr 1992, Alexander 1999). The biological process is carried out in a reactor where the dredged sediments are mixed with external water. If needed, external addition of nutrients or microorganisms inoculum are provided. Solids concentration typically

ranges between 5 % and 50 %, depending on the mixing and aeration equipments and on contaminant toxicity. Bioreactors use energy for mixing and addition of oxygen. As a result they emit CO₂. Because most sediments do not contain volatile compounds, the emissions of contaminants is low. Emission of hydrogen sulphide may occur in sediments with a low pH and free hydrogen sulphide. The flow chart of a bioslurry treatment is reported in fig. 3.5.

Bioslurry treatment has been tested in different types of reactors, including: Batch System (Glaser et al 1995); Sequencing Batch Reactor (SBR) (Irvine et al. 1993); continuous-flow Completely Stirred Tank Reactor (CSTR) (Cassidy et al. 2000).

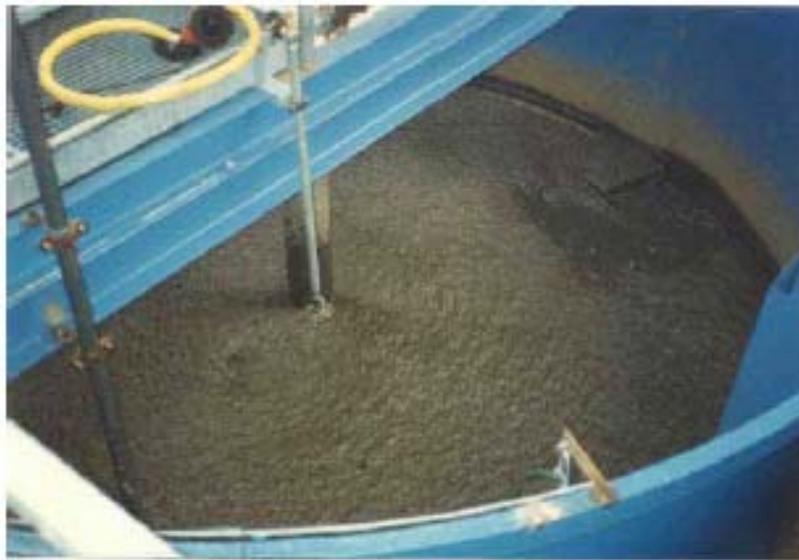


Figure 3.4. Bioreactor used for the degradation of oil and PAH in dredged material

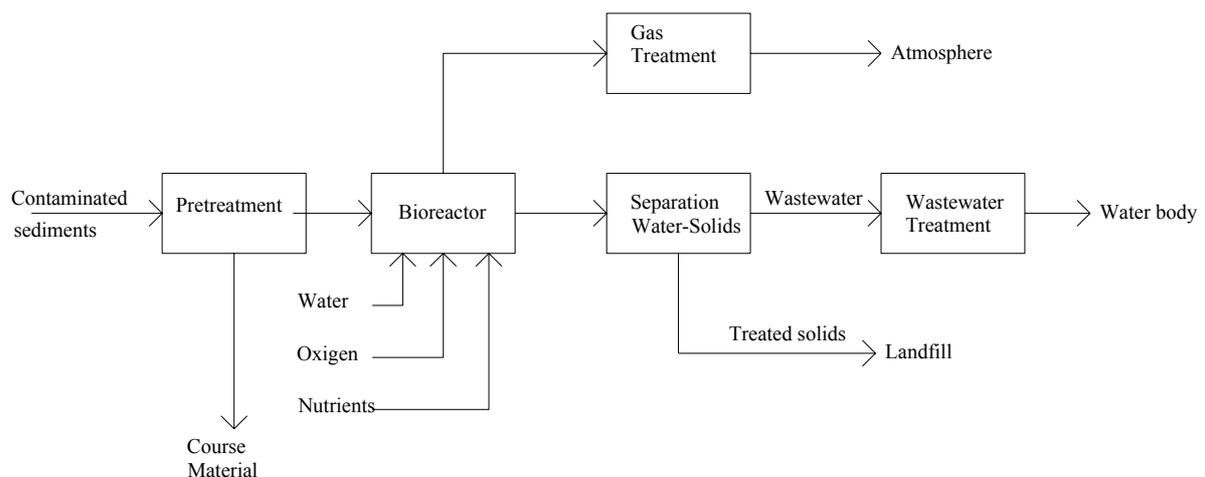


Figure 3.5. Bioslurry treatment flow chart

Irvine et al. (1993) and have compared the different bioslurry reactor configurations. The CSTR compared to Batch have guaranteed the advantage of dilution of toxic substances but a low biodegradation rates if the latter depend on contaminant (substrates) concentrations. The SBR functioning cycle includes three temporal steps: during the Fill step, the slurry is fed into the reactor; in the Reaction step the system works as a batch reactor, performing the biodegradation process; the final step consists of the extraction of a fraction of treated slurry from the reactor (Draw step) and the replacement with an equal volume of untreated slurry. The SS-SBR configuration is more flexible than CSTR regarding the contaminant flux and biomass acclimation and preservation.

Cassidy and Irvine (2001) have compared the performances of Eweis et al. (1998) SS-SBR and CSTR of two bioslurry reactors (10 % of solids) working on diesel contaminated soil practising also nutrients adding. The results have shown a higher removal efficiency (96%) of the SS-SBR than the CSTR (75 %) suggesting that the fill and draw operation selected a better biodegradable biomass. Furthermore in the SS-SBR the biosurfactants production increased diesel desorption increasing consequently its biodegradation.

Cassidy and Irvine (2001) have observed that the most important operating factors influencing the SBR removal efficiency are the hydraulic retention time (HRT), the volume of slurry replaced at the end of each cycle, the solids concentration and the mixing speed. The HRT and the volume of slurry replaced per cycle can be adjusted to face different contaminant loads to the reactor. The results have shown that increasing the solids percentage the removal efficiencies decreased contrary to Glaser et al. (1995) that found out an increasing of removal efficiencies passing from 10 to 30 % solids. Obviously from a technological perspective the highest solids percentage guarantying reliable removal efficiencies has to be pursued.

In lab scale the mixing power can also improve the removal efficiencies because reduce the aggregates particles increasing the desorption force albeit it seems to be anti-economics in a full scale.

A feasible increasing of the removal efficiencies of hydrophobic organic compounds can be achieved by means of surfactants both synthetic (Aronstein 1991) and naturally produced (Providenti et al. 1995).

A bioreactor is applicable for all types of sediments. It can be necessary to include a sieving step in order to be able to remove large particles that can block the mixing system. The contaminant amount degraded in a bioreactor can vary from 10-90% depending on many factors.

The Ecova Corporation have applied the bioslurry treatment for PAHs contaminated soil observing a very removal efficiencies of 96 % with a treatment time of 14 days. The ECOTEC company have investigated the bioslurry treatment on PAHs contaminated soil using also synthetic surfactants in order to increase PAHs desorption obtaining promising results.

A bioreactor is used for cleaning of sediments on an industrial scale. For economical reasons, the through put has to be large. Space must be present for the bioreactor and basins for the input and output of the reactor albeit the total space necessary will be limited compared to passive bioremediation technologies, but the energy input is higher. The product of a bioreactor is a dredged material with reduced contaminant content but a residual concentration will be present, which should be lower than the target concentration in order to make a reusable product. For use as soil, additional dewatering will be necessary.

3.5 Economical aspects of Sediment Washing, Landfarming and Bioreactors

Separation of clean sand from fine particles rich polluted sediment is the most used cost-effective technology though cleaning of the millions of cubic meters of polluted sediments in the coming years can only be achieved if inexpensive technologies are available. From this perspective biodegradation methods are applicable to remediate sediments contaminated with biodegradable contaminants which most important are PAHs.

The cost of a bioreactor are high ranging between 130 and 200 € m³ treated slurry , but can be reduced by up-scaling. Because of the high costs and limited result no full-scale applications have been developed yet. A bioreactor is an industrial application. Building an installation on an industrial site will not lead to problems with the public. Politically use of a bioreactor will be easily accepted providing the costs are reasonably. The limited results of a bioreactor may lead to disappointment afterwards.

The energy consumption varies from energy used in normal agricultural practice (passive landfarming) to high energy consumption in an intensive landfarm, especially if a hall is used to have a high temperature also during winter or using forced aeration. Emissions are comparable with a bioreactor. The amount of space necessary is high, and a period of at least 1-2 years is necessary (intensive landfarming) with a maximum thickness of about 1 meter. Passive landfarming may last several decades. The product varies from material in which the fast degradable contaminants are removed (intensive landfarm) to almost clean soil produced

on a passive landfarm. Thus The costs of landfarming both intensive and passive are about € 20/m³. Especially for passive landfarming the costs of the land are dominant. This can be reduced by beneficial land use, (biomass, nature development). The profit made can be subtracted from the costs. Products vary from reusable soil (building material) to clean soil. Because large areas are necessary, social support is an important issue.

Costs of sediment washing are usually in the order of 25–300 €/ton (Hazardous Waste Consultant 1996). Two companies, Biogenesis and Roy F.Weston, have combined mechanical and chemical processes for the removal of 90% of the organic compounds and 70% of the inorganic contaminants from sediments (Amiran et al. 1999). High pressure water jets are used with various surfactants, oxidizing and chelating agents. A full scale facility will be built to process 209.000m³ per year at a cost of € 40–65/m³. Large facilities with capacities greater than 380.000m³ per year would require large areas for the installation.

Chapter 4

4 Materials and Methods

4.1 Foreword

Sediments used for the experimental tests were collected from:

1. Dewatering plant Alles located in Fusina treating sediment dredged from Porto Marghera channels (Venice, Italy);
2. Sarno river (Naples, Italy);
3. Petroleum Harbour (PH) (Amsterdam, the Netherlands);
4. Wemeldinge (WEM) harbour (Wemeldinge, the Netherlands).

These sediments were used for different experimental campaign respectively:

- Factor affecting Heavy Metals (HM) mobilization from contaminated sediment using 2;
- Bioaccumulation of Cadmium in benthonic organisms using 1;
- Sediment washing of HM contaminated sediment coupled with the regeneration of the extractant agent by means of electrochemical processes using 1 and 2;
- Landfarming of PAHs contaminated sediment using 3 and 4;
- PAHs bioavailability estimation by means of Tenax beads desorption using 1, 3 and 4;
- Bioslurry treatment by means of SS-SBR reactor to treat PAHs contaminated sediment using 1;
- Respirometric tests by means of DO-stat using 1.

4.2 Experimental set up

4.2.1 Factor affecting Heavy Metals mobilization from contaminated sediment

4.2.1.1. pH stat leaching test

The amount of H^+ required, to reduce the pH, in a liquid or solid-liquid system, to a reference value is denoted Acid Neutralizing Capacity (ANC). Titration tests give information about the buffer capacity of the sediments and about redistribution of heavy metals during acidification.

The buffer capacity of the sediments has been determined using an auto titrator analyzer. The titration has been conducted leading the suspensions to different pH values (pH 2, 3, 4, and 5) by means of a 2 M nitric acid solution. In order to achieve a solid/liquid ratio of 1:10 in a 1 l glass vessel, 166 grams of wet anoxic sediments, which means 50 grams of dry matter, have been added to 384 ml of deionised water. The suspension has been stirred with a magnetic stirrer during the experiment and a pH probe has continuously recorded pH.

Samples of the suspension (15 ml) have been collected at irregular intervals (after 5 min, 1 h, 5 h, 24 h, and 48 h) and centrifuged for 10 min at 3400 rpm. The supernatant has been filtered through a 0.45 μm membrane and acidified with HNO_3 to pH 2 for the later FAAS analysis. The solid residue obtained from the sampling after 72 hours has been stored at 4 °C and afterwards has been utilized for the BCR sequential extraction.

4.2.1.2. pH and Eh effects on the mobilization of heavy metals

The test has been performed to understand the influence of the pH combined and without oxidation on the mobilization of the heavy metals. The experimental test has been performed mixing in a 1 l glass vessel 166 grams of wet anoxic sediments, which means 50 grams of dry matter, with 384 ml of a pH 2 solution prepared with deionised water and nitric acid. The solid/liquid ratio of the suspension was 1:10. Two vessels have been prepared: in the former air has been bubbled to simulate oxidation and in the latter N_2 has been bubbled to keep anoxic conditions. The suspension has been stirred with a magnetic stirrer during the experiment and pH and redox potential has been recorded continuously using different probes. Samples of the suspension (15 ml) have been collected at regular intervals (after 5 min, 1 h, 5 h, 24 h, and 48 h) and centrifuged for 10 min at 3400 rpm. The supernatant has

been filtered through a 0.45 μm membrane and acidified with a drop of concentrated HNO_3 solution to pH 2 for the later FAAS analysis.

4.2.2 Bioaccumulation of Cadmium in benthonic organisms

C. elegans is a bacterivorous nematode that develops to the adult stage through four juvenile stages separated by molts. Adult worms are about 1 to 1,5 mm in length and can be distinguished into two sexes, hermaphrodites and males. Hermaphrodites usually reproduce by self-fertilization, although they can also be fertilized by rarely occurring (<0,1%) males. The life cycle for worms grown on *Escherichia coli* is about three days at 20 °C.

When worms were needed for the test, dauer larvae were transferred on an agar plate with a fresh lawn of *E. coli*. After about three days at 20 °C a lot of gravid hermaphrodites as well as juveniles of stages 1 and 2 were found on the plates. Three tests were conducted using different weight of sediment: 5 g, 2 g, and 1 g, wet weight. The sediment was transferred into petri dishes and M9-medium (Table 2) was added to the soil in order to achieve a ratio 1: 1 between wet weight/M9-medium. Thus 5 ml of M9-medium were added to the dishes containing 5g of wet sediment, 2 ml to the dishes containing 2g of sediment and 1 ml to the dishes containing 1g of sediment. Three replicates were used for each different weight of soil and two agar plates containing *C. elegans* were used for each replicate. The worms were rinsed with M9-medium, then the suspension of worms and M9-medium were centrifuged and the supernatant discharged. This operation was repeated twice. The pellet of worms was finally transferred by pipette into the dishes containing the soil and the M9 medium. Simultaneously petri dishes containing only sediment and M9-medium (without worms) were submitted to the same procedure in order to have a blank sample.

Table 4.I. M9-medium composition

M9-medium	
Na_2HPO_4	6 gr l^{-1}
KH_2PO_4	3 gr l^{-1}
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.52 gr l^{-1}
NaCl	5 gr l^{-1}

After addition of the nematodes, both the samples with worms and without worms were kept on shaking desk at 20 °C for 24 h. At the end of the exposure time the dishes were heated

(approx. 85 °C) for 15 minutes to heat-kill the worms. This treatment results in straightened, easily visible worms.

The sediment was subsequently transferred in a centrifuge tube using approx. 15 ml of Ludox solution. The Ludox solution was obtained diluting Ludox TM 50 (colloidal silica) with distilled water in order to obtain a relative density of 1.14 gr l⁻¹, which is the same density of the *C. elegans*. After thoroughly mixing the sediment with the Ludox solution, the samples were centrifuged for 15 minutes at 3400 rpm. Nematodes were found in the supernatant that was filtered through a 5 mm membrane. An additional volume of 15 ml of Ludox solution was added to the solid residue that was resuspended by manual shaking and centrifuged once again to be sure that all the worms were extracted from the sediment. Then the filter was rinsed with distilled water and the suspension, made of worms plus distilled water, was transferred in a Petri dish. From the Petri dish the suspension was transferred again in a centrifuge tube by means of a pipette. The suspension was centrifuged for 15 min at 3600 rpm, the supernatant was discharged and the pellet was rinsed with distilled water and centrifuged once again. The supernatant was discharged. The pellet of worms obtained at the end of this procedure was given to the central lab of the TUHH. The pellet was freeze dried and digested with 1ml of HNO₃ and 0.1 ml of H₂O₂ and the suspension analysed with PE-Elan 6000 ICP-MS and PE-Optima 2000 DV OES with ICP.

4.2.3 Sediment washing of HM contaminated sediment coupled with the regeneration of the extractant agent by means of electrochemical processes

4.2.3.1. Sediment washing test

Sediment washing tests were carried out using a Jar Test (ISCO) equipped with six positions for the continuous samples mechanical mixing. The mixing rate is variable between 0-1000 rpm but was set to 150 rpm.

The experiments were carried out in 1 l vessels batchwise. The washing solutions were preliminarily prepared, and then the predetermined amount of solids was added to each solution in order to reach the fixed Total Solids (TS) percentages. The investigated percentages ranged between 2.5 and 40 % (in weight).

Both chelating agents such as: EDTA, citric and acetic acid and strong acids such as HCl, H₂SO₄ and HNO₃ were used as it detailed explained in chapter 5.

The pH effect was also investigated changing the pH of the washing solutions, before the solids addition, using HCl and Na₂SO₄ in order to reach the set pH.

The time of the sediment washing tests ranged between 72 and 500 hours as detailed in chapter 5.

4.2.3.2. Washing solution regeneration by means of electrolytic process

The electrolytic process was used in combination with EDTA extraction. The EDTA solutions after the sediment washing treatment was separated from the sediments and loaded in an electrolytic cells. The electrolytic regeneration of the extractant solution was performed batchwise in a laboratory scale divided electrolysis cell. The volume of the cathodic and anodic chambers was 50 ml each; they were divided by a cation exchange membrane NAFION* 450 (DuPont). A three dimensional cathode was used consisting of a 45x70 mm graphite plate 2 mm thick plus 35 g of a fixed bed of graphite particles with a size of 1 mm and a void fraction $e = 0.55$. The anode was a Ti/RuO₂ mesh plate (provided by DeNora Deutschland GmbH).

A flow diagram of the electrolytic regeneration process is presented in Figure 4.1. After its separation by centrifugation from the solid sample the EDTA solutions was pumped upflow through the cathodic chamber in a flow-by cell configuration, where heavy metals are reduced and deposited on the surface of the graphite. The solution is collected in a stirred vessel and recirculated through the cell. As anolyte 50 ml of a 0.2 M stagnant sulphuric acid solution were used.

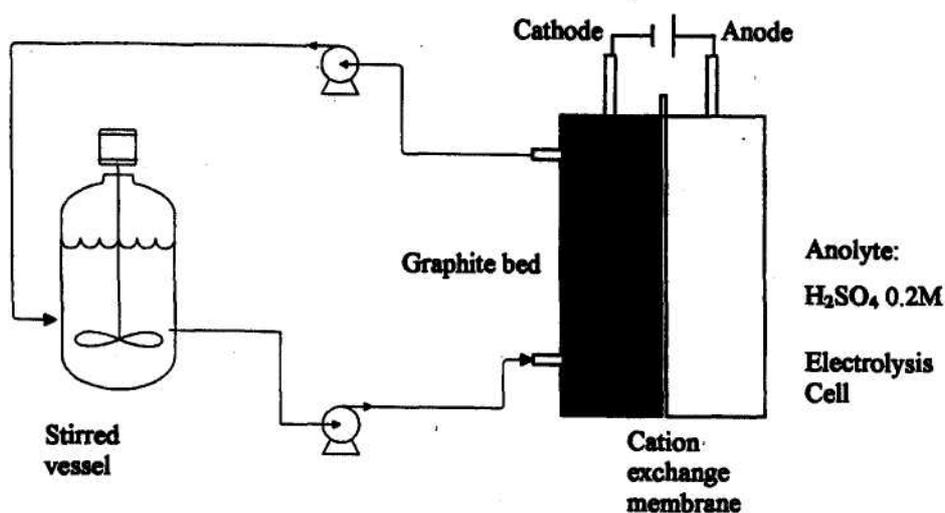


Figure 4.1. Flow diagram of the electrolytic regeneration process

4.2.4 Landfarming of PAHs contaminated sediment

Petroleum harbour (PH) in Amsterdam and Wemeldinge (WEM) harbour sediments have been landfarmed at Kreekraksluizen in the Netherlands investigating the PAHs degradation kinetics on the short and long-term. The landfarm experiments have been started in 1994 by means of proper fields of 20 x 7 m containing a sediment layer between 0.5 and 1 meter. Each field have been tooled with dewatering system in order to decrease the water sediment content.

The experiments have been carried out using intensive (cultivated) and passive (vegetated) landfarming. Intensive landfarming means cultivation by frequent tillage followed by a passive period when the tillage was not used anymore and vegetation became an important function in improvement of the soil structure and aeration. The ongoing experiments are summarized in tab. 4.II.

Table 4.II. Sediments used for PAHs contaminated sediment landfarming

	Intensive landfarming since	Passive landfarming since
PH, cultivated	1994 - 1996	1996
PH, vegetated	1994	1994
WEM, cultivated	1994 - 1996	1996
WEM, vegetated	1994	1994

PAHs of the Dutch National List (PAH-NL) were measured, including fluoreen, fenantreen, antracene, fluoranteen, pyreen, benz[a]antracene, cryseen, benzo[b]fluoranteen, benzo[k]fluoranteen, benzo[a]pyreen, benzo[g,h,i]peryleen, indeno[1,2,3-c,d]pyreen during the whole landfarms period. Naphthalene, which is also part of this list, was not measured, because of the low reliability at low concentrations. The original (fresh) PH and WEM sediments have been stored under wet anaerobic conditions in 200 l vessels from 1994. In this work the existing degradation curves (Harmsen 2004) were extended with measurements in 2004, using the same method as in the previous period.

4.2.5 PAHs bioavailability estimation by means of Tenax beads desorption

PAHs desorption sizes in both the original sediment and the sediment sampled in 2004 were determined by a two steps extraction carried out at 20 °C and at 60 °C by means of a Tenax

solid-phase extraction method (Cornelissen et al. 1997). Tenax TA (60-80 mesh; 177-250 μm), a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide, was purchased from Chrompack, The Netherlands. Before use, the Tenax TA beads were rinsed with water, acetone, and hexane (each three times, 10 mL g^{-1} of Tenax) and dried overnight at 75 °C. The desorption experiment have been carried out using a mixture of sediment (2 g dry weight), Tenax TA (1.5 g) and milli-Q water (50 mL) shaken in a 100-mL separation funnel adding also HgCl_2 (1 mg) to prevent microbial degradation (Cornelissen et a. 1998). The first desorption step have been carried out at 20 °C for 16 h in order to desorb the rapidly desorbing fraction. The Tenax (with the rapidly desorbing fraction) was separated of the water-sediment by using a separation funnel at which the Tenax sticks at the glass side. The Tenax was dried, extracted with hexane and transferred to acetonitril. After this, desorption was continued refreshing cleaned Tenax to the slurry suspension and shaking at the 60 °C for 16 hours in order to desorb the slowly desorbing fraction. The second Tenax-fraction was extracted on the same way. At the end of previous desorption tests, the slurry have been separated by the Tenax, centrifuged and extracted with acetone (25 mL) shaking for 15 min and Petroleum Ether (15 mL) shaking for 15 min. Afterwards the soil have been separated from the supernatant wherein the residual PAHs concentration have been analyzed in order to measure the very slow desorbing fraction, as described in (NEN 5771).

All analysis were carried out on HPLC which was equipped of two HPLC-pumps for an water/acetonitril gradient (Gyncotek 300 and 480, Japan), prospect for online cleanup with methanol-water (Spark, The Netherlands), reversed-phase C_{18} column (Vydac 201TP54) and a programmable fluorescence detector (Jasco 920, Japan). The data has been collected with chromatography acquiring software Atlas (Thermo Lab Systems, Greate Britain). The peaks were integrated manually and identified at retention time and using the most specified emission and excitation wavelength.

4.2.6 Bioslurry treatment by means of SS-SBR reactor

4.2.6.1. SS-SBR reactor

The study was carried out in the thermostated chamber (at 21 ± 0.3 °C) using a 8 l pyrex-made reactor with a 17.1 cm diameter and 47.0 cm height (fig. 4.2), upper closed with a stainless steel flange to ensure the seal. The reactor operating level was set at 41.0 cm (leaving 6 cm of freeboard); thus the reactor working volume was 7 l. The reactor was equipped with a DO probe (cell OX325, WTW), a pH probe (Mettler Toledo) and a magnetic

stirrer with a variable speed impeller, working at 300 rpm and placed in the flange central position.

Oxygen was supplied by an air flow of 50 N l h^{-1} and distributed through a fine bubble diffuser at the bottom of the reactor. The air flow was forced to pass through a humidifier before entering the reactor, in order to minimize evaporation.

Off gases firstly were piped to an air-cooled condenser and then collected to an amberlite resin trap (XAD2 Supelco) to catch volatile organic compounds. Peristaltic pumps (Cellai 503U) were used for fill and draw operations.

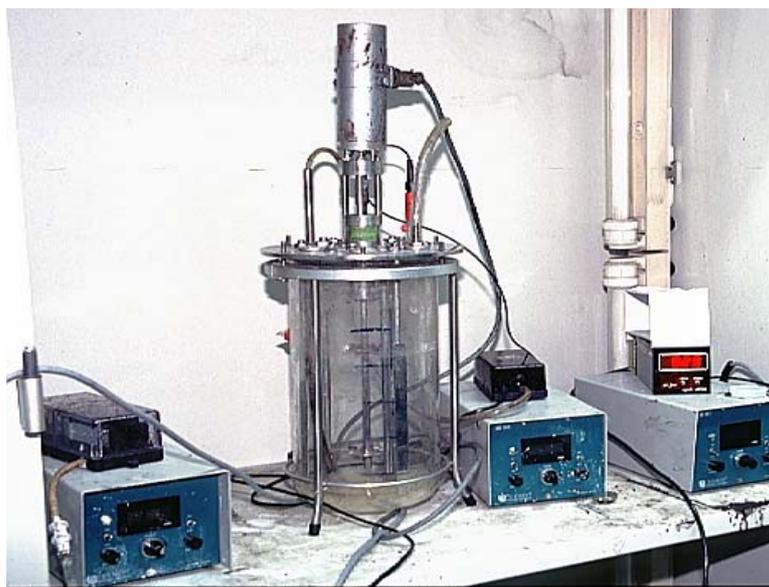


Figure 4.2. Lab-scale SS-SBR

4.2.6.2. Experimental design

The experiments were grouped into four phases with different operating conditions (tab 4.III). In all cases the times to fill and draw the lab-scale SBR were lower than 3 minutes (as a result the entire cycle length was devoted to react) and no adapted microorganisms (bioaugmentation) were added to the fed slurry to enhance the biological activity.

Table 4.III. SBR operating conditions during the four experimental Phases

Phases	Cycle Length [d]	HRT [d]	Volume replaced per cycle [l]	Number of cycles
I	14	98	1	21
II	7	70	0.7	12
III	3.5	35	0.7	16
IV (*)	3.5	35	0.7	16

(*) At the beginning of each treatment cycle of Phase IV 0.5 g of lactose were added

Phase I was aimed at starting the process and evaluating the slurry biological activity. The cycle length and HRT were set to 14 days and 98 days (corresponding to 7 cycles), respectively. The slurry volume replaced per cycle was equal to 1 l. Phase I lasted for the first 294 days, corresponding to 3 retention times, usually considered sufficient for steady state condition to be reached in bioreactors. Furthermore during Phase I, in order to detect the presence of biological activity, two carbon sources (3.65 g of glucose and 3.45 g of lactose) were added at the beginning of the two next cycles of treatment, monitoring their degradation trend.

The further three Phases were carried out to evaluate PAHs removal efficiencies and *OUR* trends in different operating conditions. In particular, during Phase II, the treatment cycle length, the HRT and the volume of slurry replaced for each cycle were adjusted to 7 days, 70 days and 0.7 l (10 % of working volume), respectively. During Phases III and IV the treatment cycle length was shortened to 3.5 days while the volume of slurry replaced for each cycle was the same as the previous Phase II. Moreover, in Phase IV, 0.5 g of lactose was added at the beginning of each treatment cycle to stimulate biosurfactant production and to provide nutrient to increase the activity of sediment microbial community.

4.2.7 Respirometric tests by means of DO-stat

DO-stat titrations were carried out by using an automated titration system, MARTINA (Multiple Analyte Reprogrammable TitratioN Analyser, Spes srl, Fabriano, Italy). The instrument scheme is plotted in fig. 4.3. This instrument allows to collect and record pH, DO, temperature and ORP data (minimum frequency 1 data/s) and to perform set-point titrations on pH and/or DO signals. pH is controlled at the user-defined set-point value by spiking NaOH or HCl diluted (0.05-0.2 M) solutions, while the DO is maintained at its set-point value by spiking a diluted (0.09-0.18 M) H₂O₂ solution.

OUR data were calculated according to the following formula:

$$\text{OUR} \left[\text{mg}_{\text{O}_2} \text{ Kg}^{-1}_{\text{slurry}} \text{ h}^{-1} \right] = r_{\text{tit}} \cdot M_{\text{H}_2\text{O}_2} \cdot 16 \cdot V_{\text{S}}^{-1} \cdot d^{-1}$$

where: r_{tit} [$\text{ml}_{\text{H}_2\text{O}_2} \text{ h}^{-1}$] is the titration rate; 16 [$\text{mg}_{\text{O}_2} \text{ mol}_{\text{H}_2\text{O}_2}^{-1}$] is the stoichiometric coefficient for H₂O₂ decomposition to oxygen (i.e.: $\text{H}_2\text{O}_2 \rightarrow 0.5\text{O}_2 + \text{H}_2\text{O}$); V_{S} is the volume of slurry [L] and d [kg L^{-1}] is the slurry density.

DO-stat titration tests were performed on 250 mL volume slurry samples collected from the SS-SBR reactor. These tests were performed averagely once a day, while tests frequency was increased to 2-3 tests per day just after the feeding phase to follow the degradation dynamics.

During DO-stat titration the slurry pH was also controlled to pH 8.3. DO set-point was chosen equal to the saturation value to avoid oxygen liquid/gas transfer. Titration tests were performed at room temperature ($T = 21 \pm 0.3$ °C).

The DO-stat technique was applied with the final scope to monitor the *OUR* trend vs. time during the treatment cycles of Phase II, III and IV in the SBR.

DO-stat titration tests were performed on 250 ml slurry samples collected from the SBR. Generally, one sample per day was taken; only during 24 hours after feeding new slurry, the number of samples per day was increased to 2 or 3 in order to better follow the *OUR* trend, excluding the first two hours to avoid chemical interferences on the measurements. During DO-stat titration DO set-point was set to the saturation value to avoid oxygen liquid/gas transfer. Titration tests were performed in the same thermostatic chamber (21 ± 0.3 °C) where the lab-scale reactor was placed.

DO-stat titrations were carried out using an automated system MARTINA (Multiple Analyte Reprogrammable TItratioN Analyser, Spes srl), which is able to collect and record pH, DO, temperature and ORP data (minimum frequency 1 per second) and convert set-point titrations into DO signals. The DO was maintained at its set-point value by spiking a diluted (0.09-0.18 M) H_2O_2 solution. *OUR* datas, related to each sample (OUR_S), were calculated according to the following formula:

$$OUR_S = r_{tit} \cdot M_{H_2O_2} \cdot 16 \cdot V_S^{-1} \cdot \rho^{-1} \quad (1)$$

where: OUR_S is expressed as $mgO_2 \text{ kg}^{-1} \text{ slurry h}^{-1}$; r_{tit} is the titration rate [$ml H_2O_2 \text{ h}^{-1}$]; $M_{H_2O_2}$ is the H_2O_2 solution molarity; 16 is the stoichiometric coefficient for H_2O_2 decomposition to oxygen [$mgO_2 \text{ molH}_2O_2^{-1}$] (i.e.: $H_2O_2 \rightarrow 0.5O_2 + H_2O$); V_S is the volume of slurry [l]; ρ is the slurry density [$kg \text{ l}^{-1}$].

For Phases III and IV, basing on data profiles, the experimental OUR_S values have been fitted with the following relationship:

$$OUR = OUR_{max} \cdot 10^{-k \cdot t} + OUR_{end} \quad (2)$$

where: OUR_{max} = maximum *OUR* value; k = kinetic constant; t = time.

This relationship hypothesises that *OUR* is the sum of two terms, related to the exogenous respiration (assumed to follow a decreasing first order kinetic) and to the endogenous respiration, respectively.

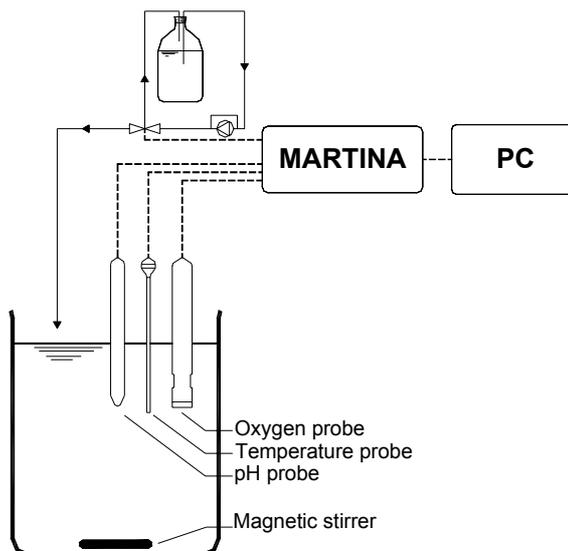


Figure 4.3. Scheme of the DO-stat

4.3 Analysis

4.3.1 Chemical Analysis

4.3.1.1. Total Heavy Metals Concentration

The total heavy metals content was determined on dried sediments using a digestion with aqua regia performed in a microwave oven. Afterwards the suspension has been centrifuged for 10 min at 3400 rpm and the supernatant has been analyzed by means of a Parkin-Elmer Zeeman/3030 Atomic Absorption Spectrophotometer (AAS), used for all the Heavy Metals determination in liquid samples.

4.3.1.2. Sequential extraction procedure (BCR)

In sequential extraction procedures various extractants are applied successively to the sediment, soil or waste material for selective leaching of the particular chemical forms of elements from samples analyzed. Each extractant is chemically more active than the previous one. The data obtained from different sequential extraction schemes are difficult to compare, since the results depend strongly on the extraction procedure used. For harmonizing different extraction schemes, a group collaborating in a Community Bureau of Reference (BCR) project proposed a three-step extraction procedure (Rauret et al 1999).

In this work an improvement of the BCR sequential extraction has been used in order to define the heavy metals distribution of the sediment samples into operationally fractions. The Sequential extraction procedure is shown in tab. 4.IV.

Table 4.IV. Sequential extraction: BCR extraction

Fraction	Extractant agent	Extracted sediment phase
Specifically sorbed; carbonate bound (Step I)	HOAc (0.11 mol l^{-1})	Bound to carbonates and adsorbed metals
Easily reducible oxides (Step II)	$\text{NH}_2\text{OH-HCl}$ (0.5 mol l^{-1})	Bound to Fe and Mn oxides
Oxidizable oxides and sulphides (Step III)	H_2O_2 (8.8 mol l^{-1}) NH_4OAc (1.0 mol l^{-1})	Bound to organic matter and sulphides

The extractable content of heavy metals has been determined using the procedure described below. The extractions have been carried out on the sediment as received in the glass bottle or on air-dried sediments. Before subsampling the sediment, the content of the bottle has been shaken manually for 3 min.

For each batch of extraction, a separate 1 g sample of the sediment has been dried in a layer of about 1 mm depth in an oven ($105 \pm 2^\circ\text{C}$) until constant mass. From this a correction “to dry mass” has been obtained which has been applied to all analytical values reported (i.e., results are quoted as amount of metal per gram of dry sediment).

Step 1. 40 ml of acetic acid 0.11 mol/l have been added to 1 gram of sediment in a 100 ml centrifuge tube, then stoppered and extracted by shaking for 16 h at $22 \pm 5^\circ\text{C}$ (overnight). Afterwards the extract has been separated from the solid residue by centrifugation at 3000 rpm for 20 min and the supernatant liquid has been decanted into a polyethylene container. The container has been stored in a refrigerator at about 4°C prior to analysis. Then the solid residue has been washed by adding 20 ml of distilled water, shaken for 15 min on the end-over-end shaker and centrifuged for 20 min at 3000 rpm after this the water has been discharged.

Step 2. 40 ml of freshly prepared hydroxylamine hydrochloride 0.5 mol l^{-1} has been added to the residue from step 1 in the centrifuge tube, then the residue has been resuspended by manual shaking, stoppered and extracted by mechanical shaking for 16 h at $22 \pm 5^\circ\text{C}$ (overnight). Afterwards the extract has been separated from the solid residue by centrifugation

at 3000 rpm for 20 min and the supernatant liquid has been decanted into a polyethylene container. The container has been stored in a refrigerator at about 4°C prior to analysis. Then the solid residue has been washed by adding 20 ml of distilled water, shaken for 15 min on the end-over-end shaker and centrifuged for 20 min at 3000 rpm after this the water has been discharged.

Step 3. 10 ml of hydrogen peroxide 8.8 mg/l has been added carefully to the residue in the centrifuge tube in small aliquots to avoid losses due to possible violent reaction. Then the vessel has been closed loosely with its cap and digested at room temperature for 1 h with occasional manual shaking. The digestion was continued for 1 h at 85±2°C in a waterbath, then the volume was reduced to less than 3 ml by further heating of the uncovered tube. A further aliquot of 10 ml of hydrogen peroxide has been added. Then the covered vessel was heated again to 85±2°C and digested for 1 h. The cover was removed and the volume of the liquid reduced to about 1 ml. Then 50 ml of ammonium acetate 1 mol l⁻¹ have been added in the cool moist residue and the tube was shaken for 16 h at 22±5°C (overnight). The extract has been separated from the solid residue by centrifugation and decantation and stored for analysis.

4.3.1.3. Bioslurry treatment

Fed and treated slurry were sampled during each treatment cycle and analysed. Total Organic Carbon was measured, on both dried (TOC_D) and filtered (0.45 µm, TOC_F) samples, using a Shimadzu TOC analyser (model VPN cph). Total and Volatile Solids (TS and VS, respectively), Total Kjeldhal Nitrogen (TKN), Total Phosphorous (P_i), Chlorides and Colony Forming Units (CFU) were measured according to Standard Methods.

The slurry fed into the reactor and the slurry drawn at the end of each cycle were analysed for PAHs determination according to the *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (EPA SW-846). Briefly, Soxhlet extraction of the organic compounds was carried out on 5-10 g dried sediments according to EPA 3540C method, silica-gel clean-up was performed on the Soxhlet extract according to EPA 3630B method, and finally the eluted fraction was analysed by GC/MS according to 8270C method using an Agilent Technologies 5973 gas-chromatograph, equipped with a 5970B mass selective detector and a 30 m x 250 µm thickness 0.25 µm, DB-5 fused silica capillary column (J&W Scientific), operating in the selected ion monitoring (SIM) mode.

4.3.1.4. Landfarming

Sediment PAHs extractions were carried out on sediment samples collected during the landfarms in Kreekraksluizen. They were performed in five fold agitation by shaking wet sediment (20 g) with Acetone (200 mL) and Petroleum Ether (100 ml) as described in NEN 5771 (1999). The with water washed petroleum ether (to remove the acetone) was evaporated to 1 mL and then dissolved in 10 mL of acetonitrile subsequently evaporated to 1 mL.

4.3.2 Phisycal analysis

4.3.2.1. Grain size ditribution

Sediments dredged were dewatered, and after removal of particles with diameter larger than 2 mm, the granule size distribution was evaluated according to the American Standard Testing Material (ASTM) D42 protocol.

4.3.2.2. Percentage loss on ignition

Loss on ignition procedure gives a crude measure of the organic content of the sediment. Generally, percentage loss on ignition values shows an inverse relationship with percentage dry weight values.

The dried (overnight at 105°C) sediment samples in crucibles are placed in the furnace and kept at 550°C for 2 hours. After 2 hours the furnace door should be opened to allow some of the heat to disperse before removing the crucibles with long-handled tongs and placing them on an asbestos mat. When they have cooled slightly they should be placed in a desiccator and allowed to cool fully before re-weighing. The percentage of the dry weight lost on ignition can then be calculated. The remaining ash sample may then be used for carbonate analysis.

4.3.2.3. Percentage carbonate content

The carbonate content of the sediment can be roughly determined by heating the sediment to 925°C. The amount of carbon dioxide lost in the process, as carbonates are converted to oxides, can be used to determine the original carbonate content of the sediment.

The weighed ash samples (see method for loss on ignition) are placed in the furnace and heated to 925°C for four hours. The furnace door is then opened to allow the heat to disperse (or left closed to cool overnight) and the crucibles removed and placed in a desiccator as described above. When cool the samples are re-weighed and the difference between the ash

weight and the weight lost at 925°C is multiplied by 1.36 (the difference between the molecular weights of CO₂ and CO₃) to derive the carbonate content which can then be expressed as a percentage of the dry weight.

Chapter 5

5 Experimental results

5.1 Heavy Metals Mobilization from Sarno River Sediment

5.1.1 Introduction

The Sarno river is in the Campania region (fig. 5.1) of Italy (of which Naples is the capital city). It rises from the slopes of Mt. Sarno and on its way to empty into the gulf of Naples. It is 24 km long, covering a river basin of 500 sq. km where 750000 inhabitants live.



Figure 5.1. Map of Sarno river

The Sarno is one of the most polluted river in Italy because of many important tannery and skins factories located along its course and large dumping of untreated agricultural and industrial waste. The Sarno river has been submitted in the last years to an intensive dredging process; thus the understanding of the sediment behaviour under changing natural conditions is an actual concern.

The present research regards the mobilization of heavy metals from Sarno river contaminated sediment as a result of pH, redox potential and ionic strength modifications and was developed in collaboration with prof. eng. Wolfgang Calmano at the Environmental Science and Technology at the Technical University of Hamburg – Harburg (Germany).

5.1.2 Experimental results

The sediments humidity content was approximately 70% and the grain size distribution have shown an high sand level (66.67%), a silt and clay contents respectively of (23.85%) and (9.40%) and a negligible gravel content.

The results for the total heavy metals and As content, referred to dry matter, are shown in tab.5.I along with the *Protocollo di Venezia* limits, while the results obtained from the loss on ignition and from the carbonate content procedures are shown in 5.II.

Table 5.I. Heavy metals and As total content in Sarno sediment

<i>Protocollo di Venezia</i>				
	Class A	Class B	Class C	Sarno river sediment
Cd [mg Kg ⁻¹ TS]	1	5	20	0.8
Cr [mg Kg ⁻¹ TS]	20	100	500	292
Cu [mg Kg ⁻¹ TS]	40	50	400	126
Ni [mg Kg ⁻¹ TS]	45	50	150	39
Pb [mg Kg ⁻¹ TS]	45	100	500	85
Zn [mg Kg ⁻¹ TS]	200	400	3000	356
As [µg Kg ⁻¹ TS]				8.8
Fe [mg Kg ⁻¹ TS]				32408

Table 5.II. Sarno sediments result of loss ignition

LOI ₅₅₀ [%]	LOI ₉₂₅ [%]	Carbonate [%]
14.7	8.3	11.3

The BCR sequential extractions were performed in different operational conditions and using both anoxic and air-dried sediments. First the extraction has been carried out on anoxic sediments but no special precaution was used for keeping anoxic conditions and air contact has been allowed. The partitioning of heavy metals in the different fractions of the anoxic sediments, obtained using the BCR sequential extraction is shown in fig. 5.2.

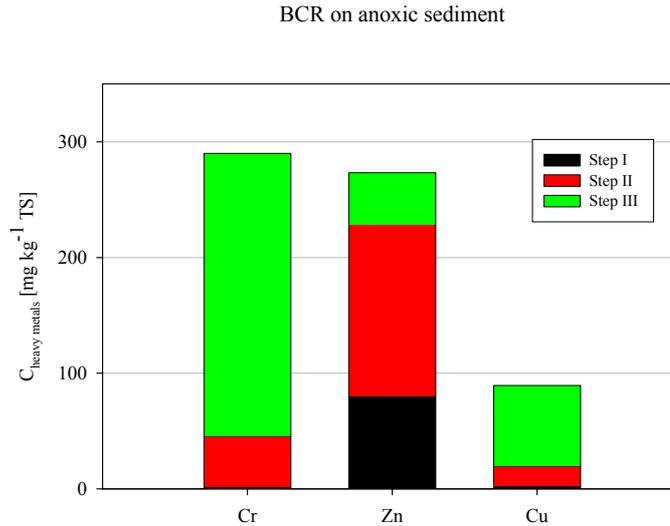


Figure 5.2. Cr, Zn and Cu partitioning. Step I: specifically adsorbed and carbonate bound; Step II: bound to Fe and Mn oxides; Step III: Bound to organic matter and sulphides

It is clear that in anoxic conditions Cr and Cu are mainly bounded with sulphides and organic matter, while Zinc is mostly related with carbonates and oxides. A great amount of Cr, more than 90%, is extracted during the three steps. On the other side more than 30% of Cu and Zn is supposed to be bounded with the residual fraction.

Then another extraction has been carried out using once again anoxic wet sediments but during the first two steps of the extraction the sediments were closed in a nitrogen glove box. Nitrogen was also bubbled into the solutions utilized in the first two steps in order to strip dissolved oxygen. It is necessary to work in an inert atmosphere in order to avoid oxidation, inducing changes in metal speciation of those suboxic and anoxic sediments.

The results obtained using the BCR extraction performed under the glove box are shown in fig. 5.3.

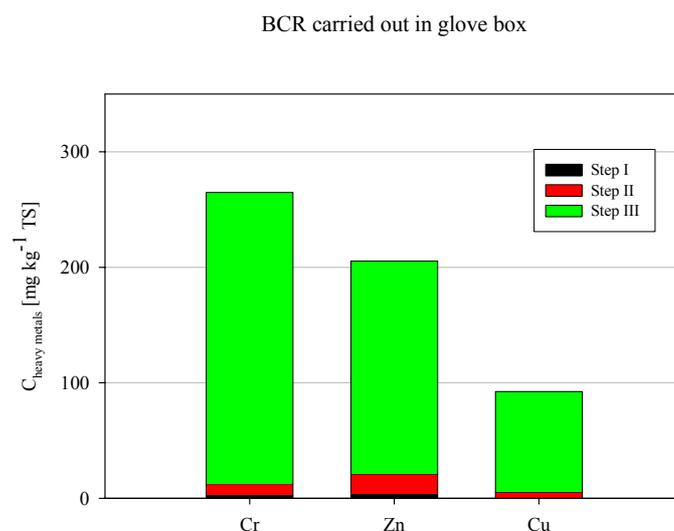


Figure 5.3. Cr, Zn and Cu partitioning Step I: specifically adsorbed and carbonate bound; Step II: bound to Fe and Mn oxides; Step III: Bound to organic matter and sulphides

Comparing the extraction performed under normal atmosphere and under glove box can be assumed that, when working with anoxic sediments within the glove box, contact with air for the first two steps has been avoided and anoxic conditions have been preserved. A sequential extraction was also carried out on air-dried sediments (fig. 5.4).

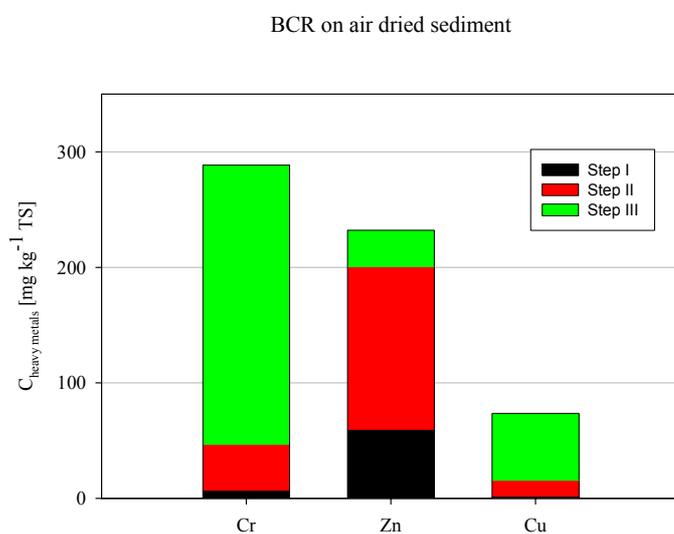


Figure 5.4. Cr, Zn and Cu partitioning. Step I: specifically adsorbed and carbonate bound; Step II: bound to Fe and Mn oxides; Step III: Bound to organic matter and sulphides

The results of the sequential extraction performed on air dried sediments are in agreement with the results obtained from the extraction performed on anoxic sediments under normal atmosphere. Thus it can be affirmed that, during the first two steps of the extraction

performed on anoxic sediments, oxidation, and consequently heavy metals redistribution occurred.

The results of the three BCR carried out respectively on anoxic, in the Glove box and on air dried sediments are reported in tab. 5.III. The values are reported in percentage, referred to the total heavy metals content reported in tab. 5.I. The residual fraction has been calculated as the difference between the sum of the heavy metals amount extracted with the three steps and the total heavy metals content.

Table 5.III. Comparison between the sequential extractions performed in normal atmosphere, within the glove box and on air dried sediments

Anoxic				
	I Step	II Step	III Step	Residual
Cr	0.5%	15.1%	83.7%	0.7%
Zn	21.1%	38.9%	11.7%	28.3%
Cu	2.0%	10.1%	42.8%	45.1%
Within glove box				
	I Step	II Step	III Step	Residual
Cr	0.9%	3.4%	86.4%	9.3%
Zn	1.2%	4.3%	48.3%	46.2%
Cu	0.0%	3.3%	53.4%	43.3%
Air dried				
	I Step	II Step	III Step	Residual
Cr	2.2%	13.8%	82.7%	1.3%
Zn	15.7%	36.9%	8.3%	39.1%
Cu	0.9%	8.9%	35.3%	54.9%

Relevant differences have been observed especially for zinc, suggesting that zinc is significantly bounded to the easily oxidisable fraction, i.e. sulphides. This result is also in agreement with the study made by Zoumis et al. (2001). This assumption can be made comparing the percentage extracted during the third step of the extraction carried out within the glove box (48.3%) and the percentage extracted during the third step of the extractions where contact with air has been allowed (11.7% for anoxic and 8.3% for air dried sediment).

On the other hand, regarding the partitioning of Cu and Cr, relevant but no substantial differences were observed. Therefore no significant redistribution occurred after oxidation, and Cr and Cu were extracted mainly during the third step of the BCR sequential extraction. This result suggested that Cr and Cu were most related to the not easily oxidisable fraction, i.e. organic matter, in agreement with the result found out by BelasoIU et al. (2001).

5.1.3 pH stat leaching test

In tab. 5.IV are reported the ANC values obtained from the titration tests. The tests have been performed leading the suspension liquid/solid to pH set values: pH 2, 3, 4 and 5.

Table 5.IV. Results obtained from the pH stat experiments

	Nitric acid 2M added [ml]	ANC [mol kg ⁻¹]
pH stat 2	150.2	6010
pH stat 3	141.9	5676
pH stat 4	109.6	4384
pH stat 5	68.8	2751

As it was expected the ANC depends on the investigated pH because at different pH occurs different buffering reactions (see fig. 2.8). Nevertheless these values are very high compared with pH stat experiments carried out by Calmano et al (1993) on Elbe river sediment.

The results for Zn, Cr and Cu mobilization in pH stat 2, pH stat 3, pH stat 4 and pH stat 5 tests are shown in fig. 5.5, 5.6 and 5.7.

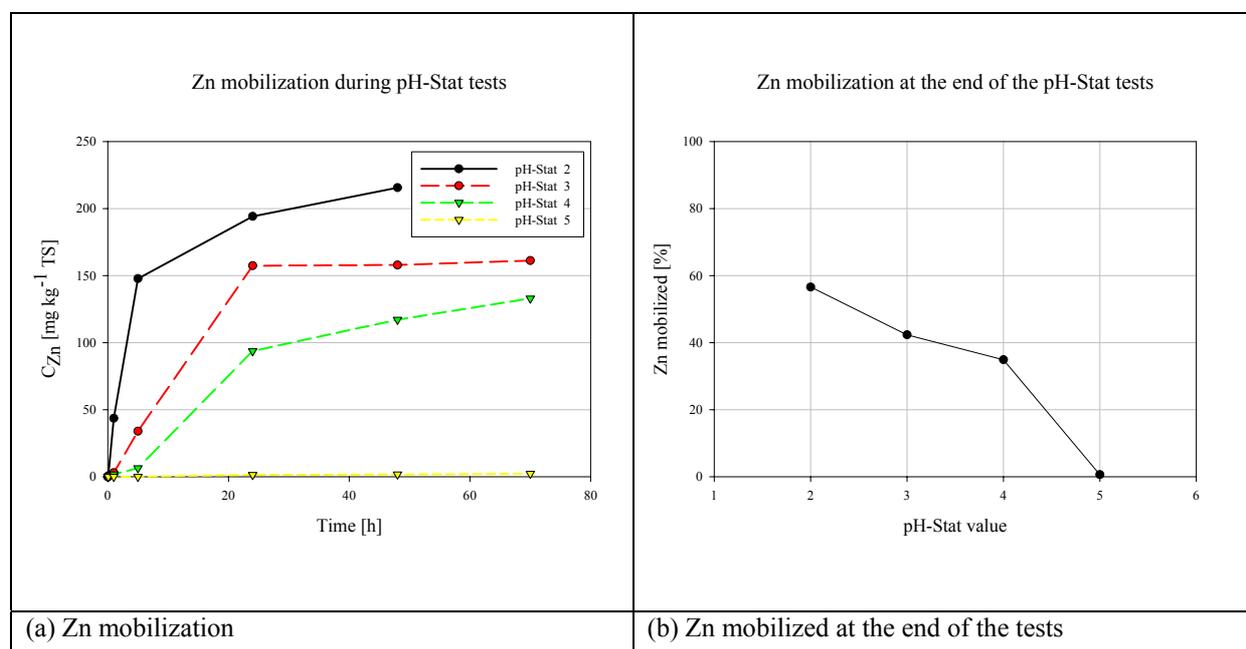


Figure 5.5. Zn release during pH stat tests (pH 2, 3, 4 and 5)

Zinc release is very high when compared with Cr and Cu release. More than 220 mg Kg⁻¹ of zinc were mobilized from Sarno sediment during the pH 2 test.

The analysis carried out on the supernatant showed a high rate of release for Zn in the first 24 hours. This high release suggests us that Zn is related to the most easily oxidisable fraction,

i.e. sulfides. An other important observation made by Kiekens 1994 is that Zn^{2+} compete with Ca^{2+} for the occupation of free adsorption sites. Thus, we can affirm that carbonates dissolution has a relevant role in Zn adsorption mechanism and the high Zn quantity released is related to desorption from exchangeable sites.

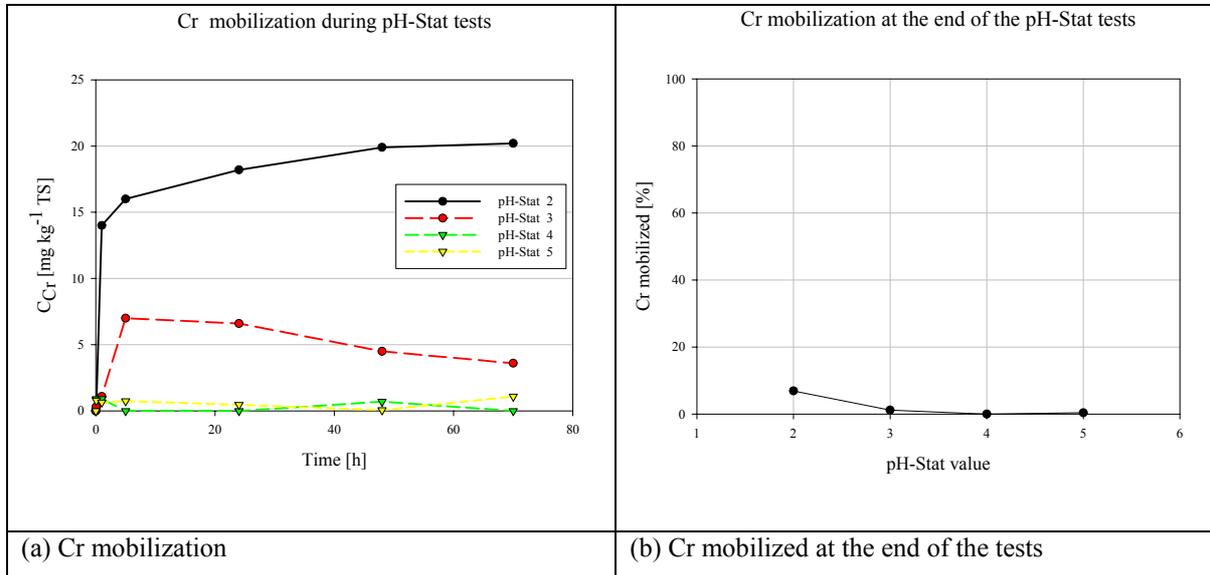


Figure 5.6. Cr release during pH stat tests (pH 2, 3, 4 and 5)

Chromium release is small if we compare the amount of chromium mobilized to the total Cr content. This behaviour is probably due to the affinity of chromium for the not easily oxidisable fraction of the sediment, i.e. organic matter.

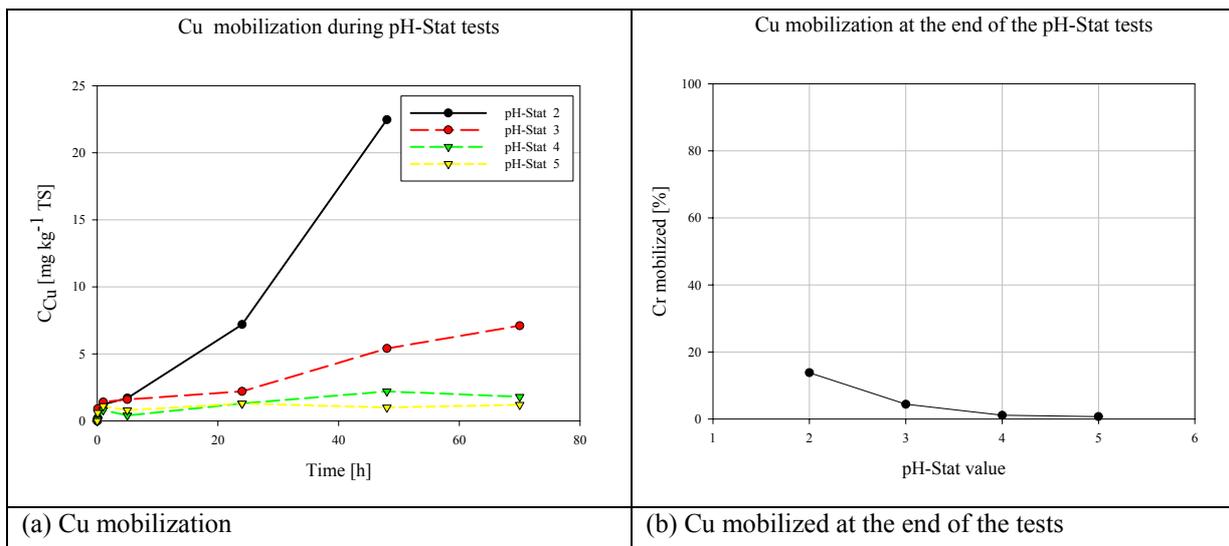


Figure 5.7. Cu release during pH stat tests(pH 2, 3, 4 and 5)

The release of Cu is slower than Cr release but after 48 hours the slope of the curve time vs mobilized Cu is still high, for the pH stat 2 test. This high slope suggests a probable further

release, but unfortunately the duration of our experiment for the pH stat 2 is only 48 hours. On the other side, has been observed (Baker 1994) that Cu is not involved in competition with other ions for adsorption. This behaviour can be assumed as one of the reasons for the low Cu release from the solid phase of the sediment.

5.1.4 pH and Eh effects on the mobilization of heavy metals

The vessel where O₂ was bubbled, resulting in a redox potential value increasing from -70 mV up to 130 mV in 48 hours. The pH value rapidly increases and after less than one hour pH 7.2 is reached and this value is kept constant until the end of the test which means that the proton introduced with the pH 2 suspension are suddenly neutralized by the sediments. This result is in agreement with the high buffering capacity of the system observed during the pH stat test. A similar behaviour was observed in the second vessel where N₂ was pumped but the pH value reached was 7.6. The redox potential recorded for the N₂-vessel is negative during the test and this result confirms that anoxic conditions has been preserved. The pH and redox potential trends for the two vessels are shown in fig. 5.8.

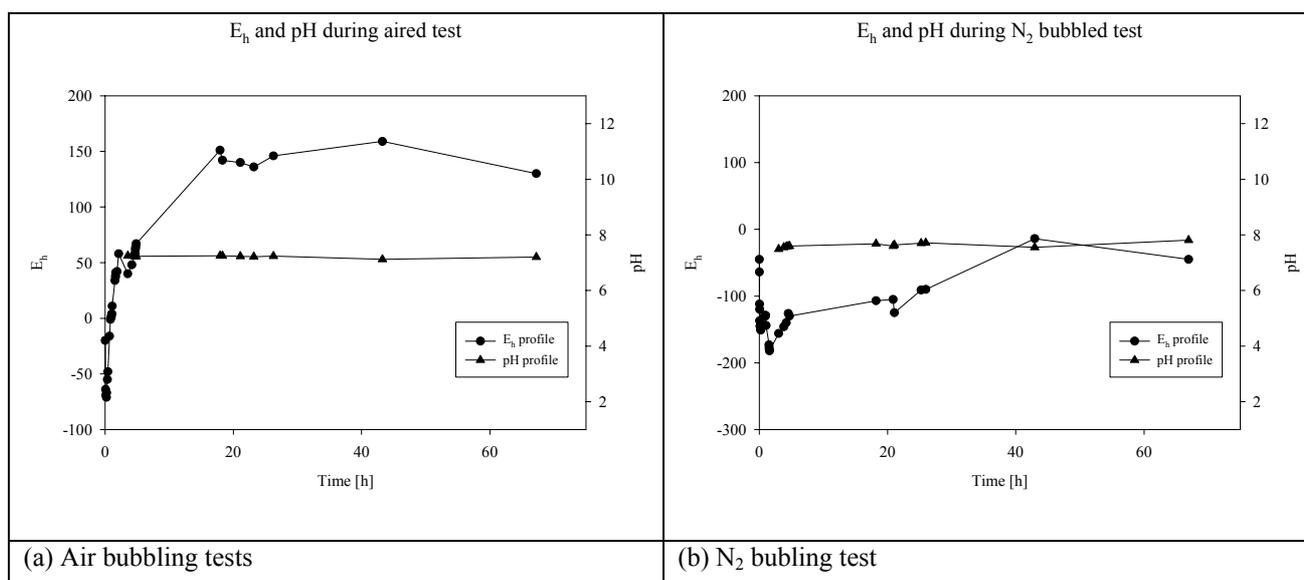


Figure 5.8. Redox potential and pH values for air-vessel (a) and N₂-vessel (b)

In these conditions no relevant heavy metals mobilization was expected to occur.

The analyses performed with the FAAS confirm this hypothesis; in fact, chromium concentrations measured was under the FAAS detection limit. Copper (a) and Zinc (b) mobilization is shown in fig. 5.9.

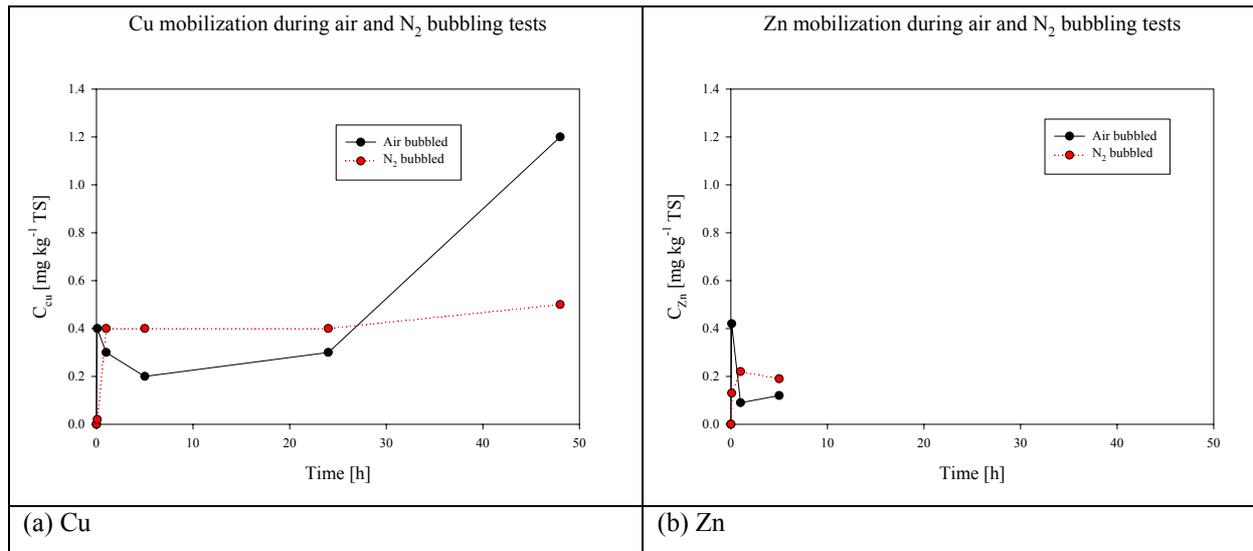


Figure 5.9. Cu and Zn release during air and nitrogen bubbling tests

It can be assumed that during 48 hours the only oxidation is not capable to determine a significant release of heavy metals from the solid phase to the aqueous phase. Only a few fraction of Cu and Zn has been released from the solid phase at the beginning of the experiment. This release can be related to the H^+ input in the system water/sediment, due to the pH 2 solution which has been mixed with the sediments. The high buffer capacity of the sediment suddenly has neutralized the acid input and no further acidification has occurred. Consequently, no further heavy metals mobilization has been observed.

A slow and little increase of Cu concentration in the aqueous phase has occurred after 24 hours, suggesting that a part of the oxidisable fraction has been oxidated and Cu related to this part has been released.

5.1.5 Conclusion

The sediment used for the mobilization experiment and dredged from the Sarno river in south part of Italy showed an high Cr, Zn and Cu level that do not meet the Italian regulations.

The BCR extractions carried out on anoxic, under glove box, and air dried showed that Cr and Cu were bounded mainly to organic matter and lightly to sulphides contrary to the Zn that was also bounded to carbonates and Fe- and Mn-hydroxides. Hence Zn was more mobilizable than Cr and Cu during pH leaching tests for all investigated pH.

Finally the Sarno river sediment showed an high Acid Neutralization Capacity mainly due to the carbonates because its flow is close to carbonates mountains. This High ANC is capable to avoid significant heavy metals release during oxidation-resuspension of the solid-liquid

PAHs and Heavy Metals Contaminated Sediment: Bioavailability, Mobilization, Biological and Phisycyco-Chemical Treatment

system. Anyway the ANC can be consumed due to periodical oxidation-reduction cycles of the sediment.

5.2 Heavy Metals Bioavailability of Porto Marghera Sediment

5.2.1 Introduction

Since the 1920's, the industrial zones of nearby Porto Marghera (fig. 5.10) have discharged both industrial chemicals and petroleum products into the water and atmosphere. Much of the growth in the industrial zone took place in the 1950's to the 1970's, with the development of chemical plants, steel works, and an oil refinery.



Figure 5.10. Venice lagoon and Porto Marghera location

Apart from the petrochemical plants, another industry carrying a strong environmental impact are the refinery stations, sited in the oldest industrial area of Porto Marghera, in which around 4 million tonnes of crude oil and semi - manufactured products are refined. Storage (around 400.000 cubic metres) and transport of the petrol products represent the most considerable risk for the environment. In the last 25 years the environmental quality of the ecosystem in the Venice lagoon is dramatically worsened e.g. decreasing of the amount and quality of fishing production reflecting in high damages for the economy of the area.

The effects on heavy metals contaminated sediment on a benthonic organisms, in order to study the heavy metals bioavailability, was investigated.

5.2.2 Experimental results

The humidity content was 35% while the total heavy metals content, referred to dry matter, are reported in tab. 5.V.

Table 5.V. Heavy metals total content in Porto Marghera sediment used for bioavailability tests

Cr [mg Kg ⁻¹ TS]	Cu [mg Kg ⁻¹ TS]	Ni [mg Kg ⁻¹ TS]	Cd [mg Kg ⁻¹ TS]	Zn [mg Kg ⁻¹ TS]
95	327	33	83	6543

More than 80 mg Kg⁻¹ TS of Cd have been detected in Fusina sediment. This value is really very high if compared with the concentrations reported within the *Protocollo di Venezia*. In fact the maximum Cd concentration that allows reuse of dredged sediments is 5 mg Kg⁻¹ TS, over this value the dredged material must be treated.

The partitioning of Cadmium in the different fractions of the sediments, obtained using the BCR sequential extraction, is shown in table 5.VI.

Table 5.VI. Sequential extraction BCR performed on Fusina sediment

BCR sequential extraction on Porto Marghera sediment	
	Cd [mg Kg ⁻¹ TS]
step I	38.5
step II	24.3
step III	4.9

Sequential extractions were also performed on the solid residue obtained at the end of the bioavailability test. Both the sediments with worms and without worms were submitted to the extraction and the results are shown in fig. 5.11.

This extraction was carried out in order to obtain information on the correlation existing between bioavailability and heavy metals fractioning in sediment.

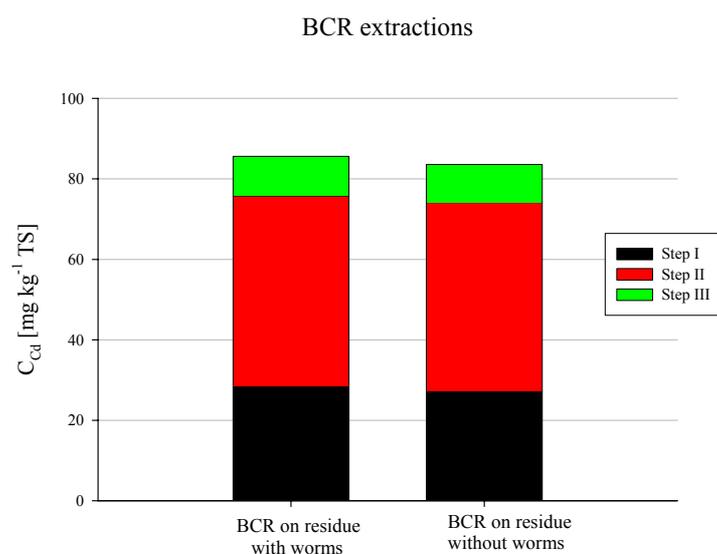


Figure 5.11. Cd partitioning. Step I: specifically adsorbed and carbonate bound; Step II: bound to Fe and Mn oxides; Step III: Bound to organic matter and sulphides

Unfortunately, the amount of Cadmium accumulated by the nematodes during the test is negligible if compared with the total amount of Cadmium measured for Porto Marghera sediments. Thus is impossible to link the bioavailable fraction of Cd to the different solid fractions composing the sediment (i.e. sulphides, iron and manganese oxides etc).

The amount of Cadmium uptaken during 24 h by the nematodes *C. elegans* is reported in tab. 5.VII. The concentrations are expressed as: mg of Cd uptake per kg of nematodes, mg of Cd uptake per kg of dried sediment and Cd uptake per total Cd content per thousand.

Table 5.VII. Cd uptake by nematodes *C. elegans*, exposure time 24 h

5 g wet weight	2 g wet weight	1 g wet weight
Cd uptake [mg Kg ⁻¹ of worms]	Cd uptake [mg Kg ⁻¹ of worms]	Cd uptake [mg Kg ⁻¹ of worms]
10.65	12	5.74
Cd uptake [mg Kg ⁻¹ TS]	Cd uptake [mg Kg ⁻¹ TS]	Cd uptake [mg Kg ⁻¹ TS]
0.0226	0.025	0.0269
Cd uptake [‰]	Cd uptake [‰]	Cd uptake [‰]
0.271	0.3	0.323

Cadmium uptake expressed in per thousand is reported in fig. 5.12.

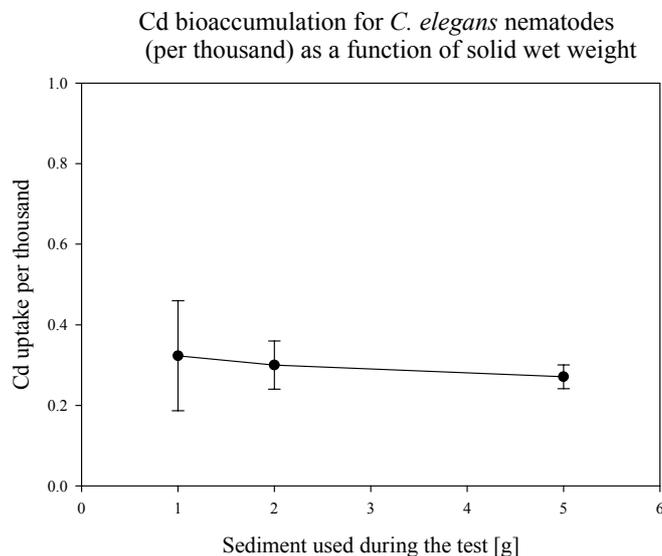


Figure 5.12. Cd uptake during 24 hours as a function of solid wet weight

Figure 5.12 shows that the amount of Cadmium uptake by nematodes is very low, when referred to the total Cd content, and is approximately 0,3 per thousand of the total content and the effect of sediment weight on the specific Cd uptake is not very recognizable. This is could due to the very high Zinc amount that can reduce cadmium uptake appreciably. However the

sediment is highly contaminated with several pollutants, and other mechanisms can act and modify the uptake of cadmium for nematodes.

On the other hand if we express this value as Cd uptake mg Kg^{-1} of worms from tab. 5.VII can be read that this value is around 10 mg Kg^{-1} of worms. Thus, if we think about this concentration as the amount of cadmium that can enter into the trophic chain, we are not allowed to neglect the environmental problem connected with biomagnification.

For an adult human being, Cd level of $50 \mu\text{g g}^{-1}$ kidney wet weight is a maximum tolerable level in order to avoid abnormal kidney function and a dietary Cd intake of $30 \mu\text{g d}^{-1}$ may result in a slight renal dysfunction in about 1% of the adult population.

Thus, even if small quantities of Cadmium enter in the food chain, the ecological risk related with the bioavailable fraction of cadmium must be taken into account.

5.2.3 Conclusions

The importance of understanding the mechanisms behind the bioaccumulation and biomagnification of toxic chemicals in biota is generally recognized among scientists. However, the mechanistic explanations for these processes are still debated, and unresolved. In this study contaminated sediment coming from Porto Marghera has been used. The amount of cadmium bioaccumulated (approximately 10 mg Kg^{-1} of worms) by the nematodes *Caenorhabditis elegans* confirms the importance of studying the possible pathways of biomagnification in the trophic chain.

On the other side, linking the bioavailable fraction of cadmium to the different solid fraction composing the sediment was not pursuable. Therefore, further studies into the dynamics of bioaccumulation under different environmental conditions, biological interactions, and at different trophic levels will ultimately improve our ability to predict and assess problems associated with bioaccumulation.

5.3 Sediment Washing on Porto Marghera Sediment

5.3.1 Introduction

This study was aimed at investigating the applicability of sediment washing treatment for the remediation of authentically heavy metals (Cd, Pb, Zn and Cu) contaminated sediments, dredged from the Porto Marghera channel (Venice, Italy) using a chelating agent: EDTA.

After having ascertained the metal partitioning in the sediments, using a selective metal extraction procedure (BCR), the effect of several operative parameters on the EDTA heavy metals extraction performances were investigated. Particularly metal extraction kinetics were evaluated varying:

- concentration of the extracting agent;
- solids percentages;
- exposure time;
- initial pH.

The sediment washing tests was performed both in a short (72 h) and long (400 h) configurations.

5.3.2 Porto Marghera sediment characterization

The sediments used for this study were a silt-clay material, with an initial humidity content of 48 %, an organic matter content of 5.5 %, and a specific weight of 1,54 gr cm⁻³.

The total heavy metals concentrations observed with the sediments dredged from Porto Marghera are reported in tab. 5.VIII.

Table 5.VIII. Heavy Metals total concentration of Porto Marghera sediment compared with the *Protocollo di Venezia* limits

<i>Protocollo di Venezia</i>				
	Class A	Class B	Class C	Porto Marghera sediment
Cd [mg Kg ⁻¹ TS]	1	5	20	13.6
Cr [mg Kg ⁻¹ TS]	20	100	500	43.5
Cu [mg Kg ⁻¹ TS]	40	50	400	200
Pb [mg Kg ⁻¹ TS]	45	100	500	244
Zn [mg Kg ⁻¹ TS]	200	400	3000	2210

Based on the HM sediment contents they can be classified, following the *Protocollo di Venezia*, as C class, and thus has to be treated.

The sequential extraction, using the BCR procedure, was performed on Porto Marghera sediments on Cd, Zn, Cu and Cr; unfortunately no BCR data are available for Pb.

The BCR sequential extraction results are reported in tab. 5.IX. along with the total concentration for the above cited HM in terms of mass (mg Kg^{-1} TS), and percentages in fig. 5.13. The residual concentration were calculated as difference between the total HM concentration and the sum of the three BCR steps.

Table 5.IX. BCR sequential extraction on Porto Marghera sediment

	Cd [mg Kg^{-1} TS]	Zn [mg Kg^{-1} TS]	Cu [mg Kg^{-1} TS]	Cr [mg Kg^{-1} TS]
I step	6.5	1442	14.1	3.6
II step	3.3	562	0.9	1.9
III step	1.9	206	82.8	1.7
Residual	1.9	0	102.2	36.3
Total	13.6	2210	200	43.5

BCR on Porto Marghera Sediment

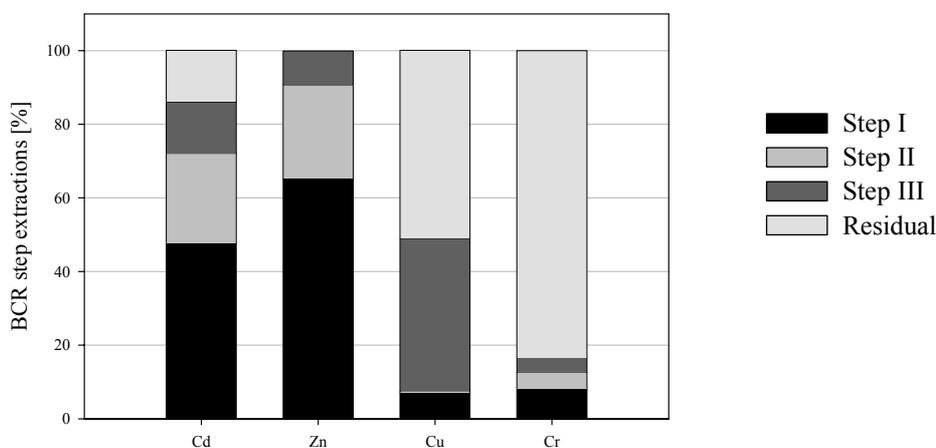
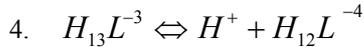
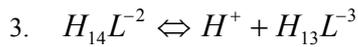
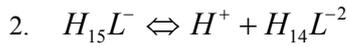
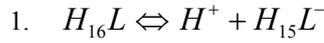


Figure 5.13. BCR on Porto Marghera sediment used during sediment washing experiments. Step I: specifically adsorbed and carbonate bound; Step II: bound to Fe and Mn oxides; Step III: Bound to organic matter and sulphides

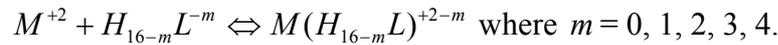
Cd is mainly bounded to carbonates (50%), but equally distributed among the other fraction with a residual concentration, that is an index of the geochemical concentration, around 15%. Zn showed a negligible residual concentration, an high fraction bounded to carbonates (60%) and Fe and Mn oxyhydroxides (20%). Cr and Cu showed a very high residual concentrations.

5.3.3 Sediment washing using EDTA

The EthyleneDiamineTetraAcetic acid (EDTA) is a weak multi-proton acid having the following molecule formula: $C_{10}H_{16}N_2O_8$. It dissolves in water through the following steps as reported below:



where L is the left molecule-part after hydrolysis ($C_{10}N_2O_8$). The heavy metals extraction from contaminated sediment occurs mainly through complexing reactions as the following:



A key parameter in sediment washing designing, based on metal extraction scheme, is the amount of chelant to be used. Because EDTA, such as other chelants (e.g. EDDS, NTA), is known to form 1:1 chelates with metals, the theoretical minimum chelant dosage is the one that binds the metals stoichiometrically. Generally, however, a several-fold excess of chelant is used to maximize metal extraction (Linn and Elliott 1988).

One pertinent issue in the choice of an adequate chelant dosage is whether all metals, including Fe and Al, should be considered in the calculation of the EDTA/Me molar ratio. This issue deserves an in-depth discussion because chelant dosage has a large impact on the economic viability of chelant-based soil and sediment remediation. The data reported by Elliott et al. (1989) suggested that Fe concentration does not need to be considered, because added EDTA removed very little Fe (12% at pH 6) compared to an 86% extraction of total Pb present. These authors explained the inert character of Fe with a fractionation analysis showing that 94% of Fe was detrital (amorphous and crystalline Fe oxide and residual fractions). It is known, indeed, that EDTA extraction of Fe present as amorphous oxyhydroxides is very slow and takes roughly 3 months before completion (Borggaard 1979). This interpretation does not, however, explain the data of Hong et al. (1993) who observed that even freshly added $Fe(NO_3)_3$ in soil had little impact on the extraction efficiency of Zn or Cu with various chelants, even though Fe had been added at a large molar excess relative to the chelant.

Considering that the sediment washing tests were carried out with different Total Solids (TS) % respectively: 2.5, 5, 10, 20, and 40 %, it means that with different solids % the heavy metals loaded to the washing reactors was not the same, different EDTA molarity was chose ranging between 0.001 to 0.05 M reporting the result of the comparison in tab. 5.X.

Table 5.X. Comparison among Σ_{HM} and EDTA molarities for the select of EDTA testing molarities

Solids (%)	Σ_{HM} [M]	EDTA/ Σ_{HM} molar ratio			
		EDTA 0.001M	EDTA 0.005 M	EDTA 0.01 M	EDTA 0.05M
2.5	0.001	1	5	10	50
5	0.002	0.5	2.5	5	25
10	0.004	0.25	1.25	2.5	12.5
20	0.008	0.125	0.625	1.25	6.25
40	0.016	0.0625	0.3125	0.625	3.125

Based on the data of tab. 5.X and considering that all the solids percentages were investigated, two EDTA solutions were tested: 0.01 and 0.05 M.

A second parameter of importance in designing chelant-based metal extraction from solids is the exposure time. Certain authors, using soils artificially contaminated in the laboratory, reported the maximum extent of metal extraction after a few hours (Peters 1999). On the other hand, authors who worked with naturally contaminated solids have usually observed that contact times of at least 24 h and up to 3-5 days were necessary to achieve maximum extraction (Rulkens et al. 1989; Samanidou and Fytianos 1990; Yu and Klarup 1994; Martin and Allen 1996).

Thus the batch tests were carried out batchwise for 72 hours, sampling 5 ml of the slurry solutions at 1, 3, 6, 24, 48, 72 h. The overall sediment washing tests carried out are reported in tab 5.XI.

Table 5.XI. Sediment washing tests carried out on Porto Marghera sediment

Solids percentage [%]	HM separating agent	HM separating agent
2.5	EDTA 0.01 M	EDTA 0.05 M
5	EDTA 0.01 M	EDTA 0.05 M
10	EDTA 0.01 M	EDTA 0.05 M
20	EDTA 0.01 M	EDTA 0.05 M
40	EDTA 0.01 M	EDTA 0.05 M

The result of the sediment washing tests carried out on Porto Marghera sediment along with the BCR sequential extractions for each Heavy Metal are reported in figg. 5.14, 5.15, 5.16 and 5.17 respectively for Cd, Pb, Zn and Cu.

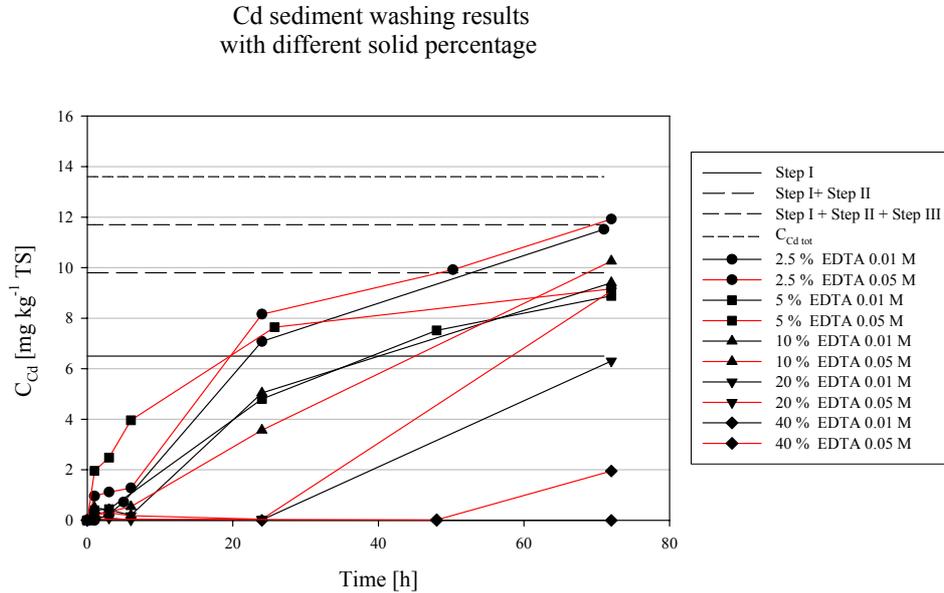


Figure 5.14. Cd sediment washing result varying EDTA molarities and solids percentages

The Cd extraction was quite high for the 2.5 and 5 % tests decreasing, as it was expected, increasing the solids percentages.

For a fixed TS percentage the Cd extraction seemed not influenced by the EDTA molarity; in fact the curves EDTA 0.01 and 0.05 M for each TS percentage are quite close each other.

The lower TS percentages tests seemed to be closer to the plateau conditions than higher TS percentage tests, however it is confirmed the days order of magnitude HM extraction (Vandevivere et al. 2001).

It can be considered that the extraction of heavy metals from contaminated solids by means of chelating agents occurs extracting the HM fractions weaker bounded to the solid matrix proceeding through the stronger bounded HM. In the case of Cd tests for 2.5, 5 and 10 % a clear change in the slope extraction profile occurred around the I BCR step Cd amount, confirming the previous observation.

The lower Cd extractions occurred for the 40 % tests; particularly a negligible extraction was observed for the test with EDTA 0.01 M while for the EDTA 0.05 M test a weak Cd extraction started in last 24 hours.

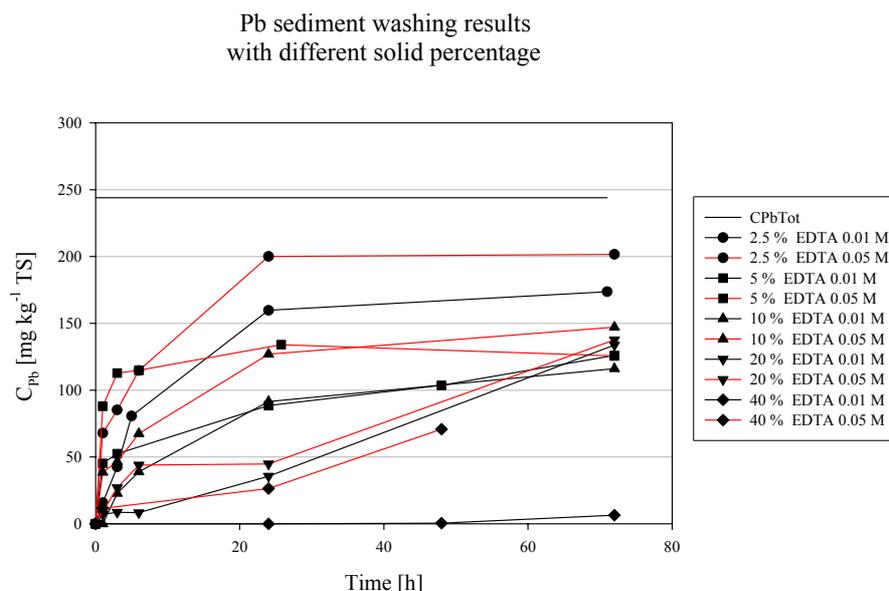


Figure 5.15. Pb sediment washing result varying EDTA molarities and solids percentages

Unlike Cd, EDTA molarities seemed to influence the Pb extractions for each TS percentage. The plateau was often reached at the end of the tests especially for the low TS tests. Unfortunately no data on BCR extractions were available, therefore consideration about the curves slope was not pursued. Also in this case the 40 % tests showed very low extractions performances.

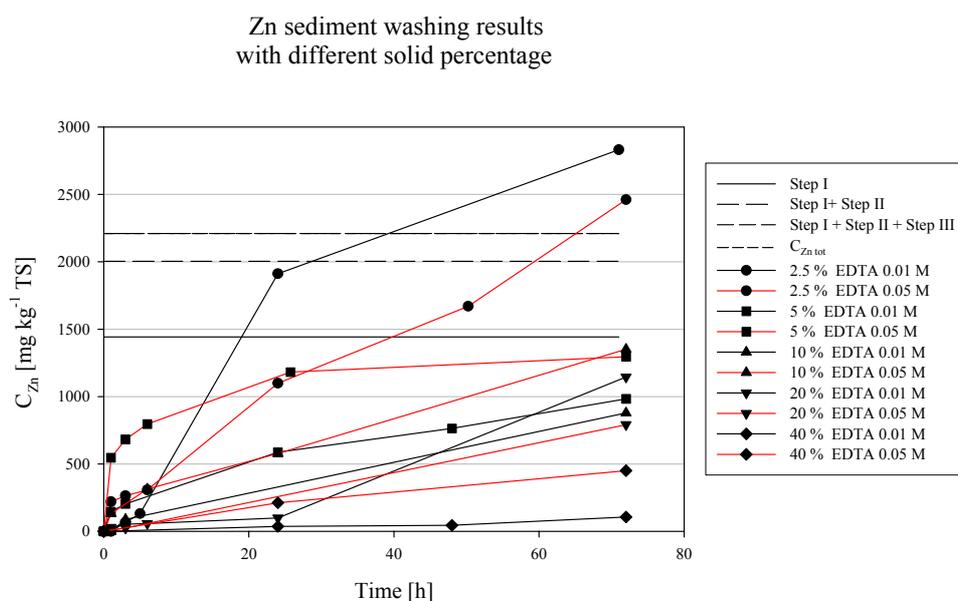


Figure 5.16. Zn sediment washing result varying EDTA molarities and solids percentages

The 2.5 % tests reached a value higher than the total Zn measured concentration, this could be due to both an heterogeneity of the sediment used during the tests but also with analytical error of the AAS. However as for Pb also for Zn many tests seemed to reach the plateau before the tests end. Despite the Zn extracted during the 2.5 % tests the others did not reached the Zn extracted with the I BCR step.

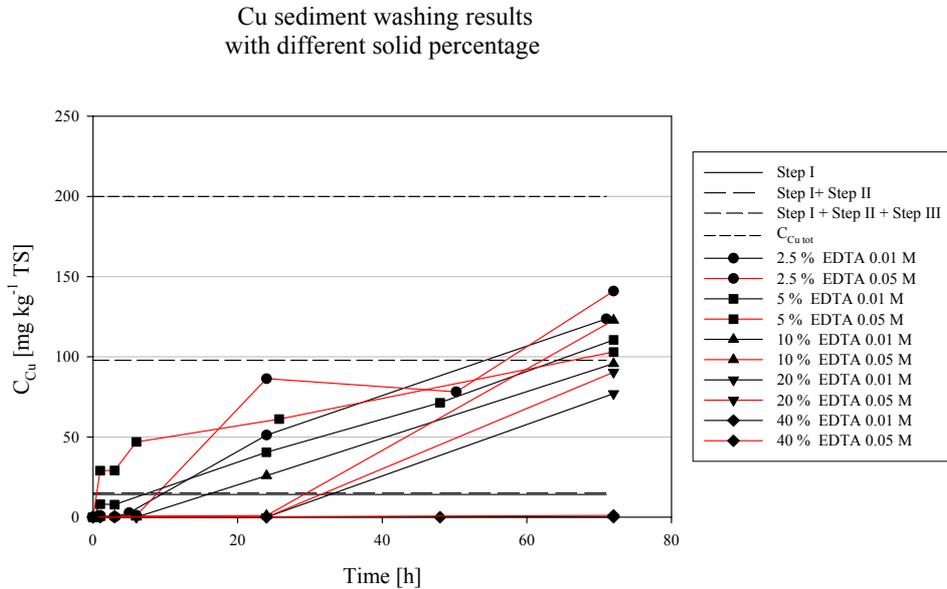


Figure 5.17. Cu sediment washing result varying EDTA molarities and solids percentages

Comparing the profile reported in fig. 5.17 with other heavy metals Cu showed a delay in the extraction beginning and thus at the end of all tests the plateau conditions were not reached.

Both for Cd, Zn and Cu increasing the TS percentages the extractions seemed to be delayed; this is could due to interference reactions that occur among EDTA and some compounds sorbed to the sediment.

The total removal efficiencies for each heavy metal, observed at the end of the sediment washing tests, are summarized in tab. 5.XII.

Table 5.XII. Total removal efficiencies of the sediment washing tests on Porto Marghera sediment

TS [%]	EDTA [M]	Removal efficiencies [%]			
		Cd	Pb	Zn	Cu
2.5	0.01	84.7	71.2	128.1	61.8
2.5	0.05	87.6	82.6	111.4	70.4
5	0.01	65.3	51.6	44.5	55.2
5	0.05	67.4	51.5	58.6	51.5
10	0.01	69.1	47.6	39.8	47.8
10	0.05	75.4	60.3	61.2	61.4
20	0.01	46.3	54.8	51.8	38.5
20	0.05	66.7	56.3	35.8	45.2
40	0.01	0.0	2.6	4.8	0.0
40	0.05	14.3	47.7	20.4	0.5

The removal efficiencies decrease with the solid percentages for all investigated heavy metals. Higher removal efficiencies were observed for EDTA 0.05 M though only for the higher solid percentages tests.

Considering only Cd all tests excluded the 40 % solids percentages and 20 % EDTA 0.01 M allowed to meet the Protocollo di Venezia limit for class B. A different situations was observed for Pb, Zn and Cu; although during the 2.5% TS tests Pb and Zn met the Class B limit of the Protocollo di Venezia, Cu did never meet this limit.

Nevertheless the respect of the normative limit on Porto Marghera sediment could be pursued with a step extractions; it means a refluxing of fresh EDTA extractive solution on the same already treated solids, as operated for Sarno sediment in the following prf.

In fig. 5.18 are reported the heavy metal removal efficiencies (%) against time for Cd, Zn, and Cu for the 2.5 % both for EDTA 0.01 M (a) and EDTA 0.05 M (b).

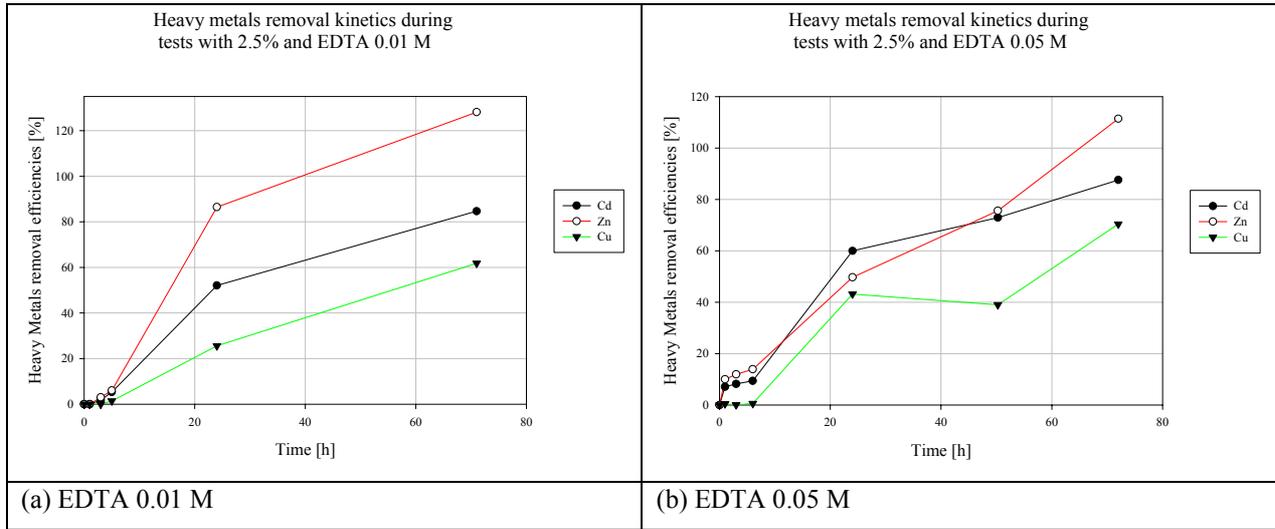


Figure 5.18. Cd, Zn and Cu removal efficiencies for the 2.5 % tests

Cd and Zn showed an higher affinity with EDTA than Cu in both tests. This result could be expected based observing (fig. 5.13) that Cd and Zn had an high I step fraction resulting an high metal amount weakly bounded to the sediment. The higher Zn than Cd removal efficiencies is probably due to the elevated Zn initial concentration.

5.3.3.1. Long sediment washing EDTA experiments

Metals present in the nondetrital fractions (exchangeable, carbonate bound, and oxidizable as organic matter) are considered easily amenable to extractive binding, whereas metals present within detrital fractions both reducible (i.e., occluded within iron-and manganese-oxyhydroxides) and residual fraction are not considered easily amenable to chelant extraction (Borggaard 1979; Elliott et al. 1989).

Since as observed by the fig. 5.14, 5.15, 5.16 and 5.17 during sediment washing tests the plateau was not always reached within the 72 hours and because very low efficiencies removal were observed during 40 % tests further two sediment experiments, as reported in tab. 5.XIII, lasting 400 h were carried out.

Table 5.XIII. Heavy Metals extracted at the end of the long EDTA experiments

Heavy Metals extracted					
TS [%]	EDTA [M]	Cd [mg kg ⁻¹ TS]	Pb [mg kg ⁻¹ TS]	Zn [mg kg ⁻¹ TS]	Cu [mg kg ⁻¹ TS]
40	0.01	0.0	81.0	797.1	0
40	0.05	10.6	183.8	1241.1	69.3

The results of the Cd, Pb, Zn and Cu of the long experiments are reported in fig. 5.19.

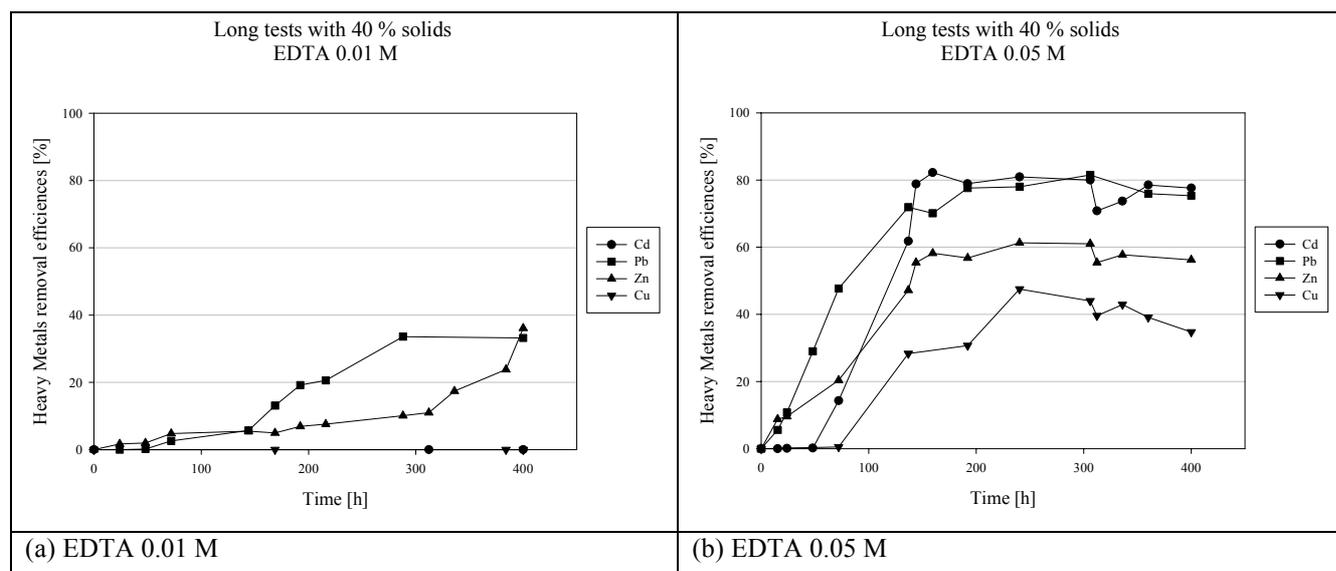


Figure 5.19. Long tests experiments with 40 % solids and EDTA 0.01M and 0.05 M for Cd, Pb, Zn and Cu.

As it can be observed in both cases for long time treatment a non negligible extraction of all HM occurred. Nevertheless lower removal efficiencies occurred in the test with EDTA 0.01 M (a); however this result could be expected based on the data reported in tab. 5.X because the $EDTA/\Sigma_{HM}$ molar ratio was < 1 . Nevertheless Zn and Pb extractions were observed confirming also the result of fig. 5.18 that shows the higher EDTA-Zn affinity during the tests on Porto Marghera sediment. The results in fig. 5.19 (b) showed that the plateaus for all investigated metals were reached around 250 h (ten days) during the 40 % tests but also that at the end of the experiments the heavy metals removal efficiencies were comparable with the lower solids percentages tests.

5.3.3.2. pH effects on Heavy Metals EDTA extractions

The pH is expected to impact chelant metal extraction in various ways, of which the most important is its great influence on the concentration of aquo metal species Me^{2+} . However when the proton concentration (H^+) increase in water several buffering reactions occur depending on the Acid Neutralization Capacity (ANC) of the system as reported in prf. 2.3.4.2. Aside from its indirect effect by means of iron interference, pH may also affect metal extraction by EDDS in various ways. First, at $pH < 5$, carbonates are completely soluble, whereby carbonate-bound metals become easily accessible to EDTA.

Thus the Ph effect on HM removal efficiencies was investigated setting the initial pH of the extractant solutions at pH 2. Six tests were carried out with 2.5, 5 and 10 % solids and both

EDTA testing concentrations. For instance the results of the tests with EDTA 0.05 M and 5% Ts are reported in fig. 5.20.

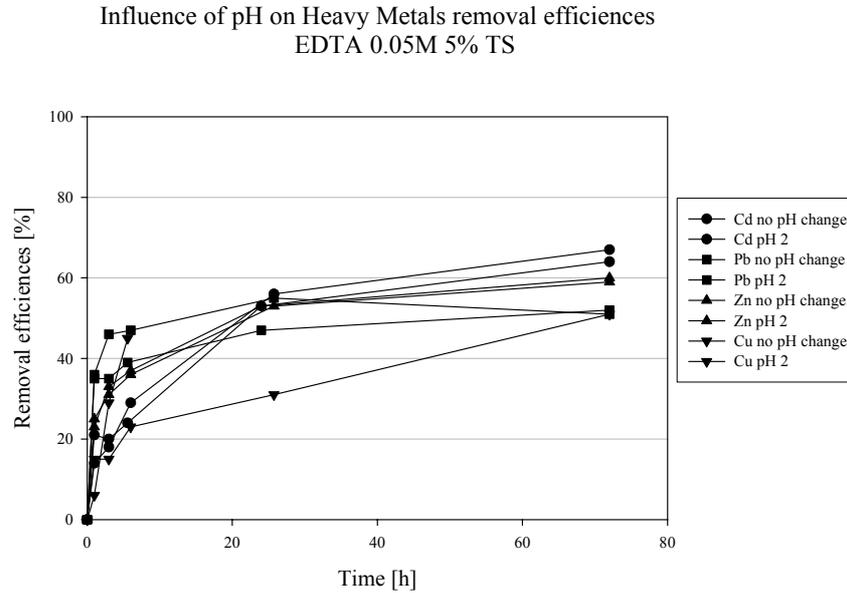


Figure 5.20. pH effect on heavy metals removal efficiencies

As it can be observed the initial H^+ concentration did not influence the HM removal efficiencies and thus it can be concluded that Porto Marghera sediment had a certain buffering capacity.

5.4 Sediment washing of Sarno river sediment coupled with the electrochemical regeneration of the extractant solution

5.4.1 Introduction

Sediment washing experiments were carried out on heavy metals contaminated sediments dredged from Sarno river (Italy), and were divided in three parts aiming respectively:

- The optimization of the sediment washing operational parameters using EDTA solutions such as. solid percentages, treatment time, initial slurry pH effect, best EDTA concentrations.
- The comparison of the EDTA heavy metals removal efficiencies with other chelating agents (i.e. citric and acetic acid) and with strong acids (i.e. Chloridic, Nitric, Sulphuric).
- The application of electrochemical process to recover EDTA solutions after sediment washing and their reuse on “fresh” contaminated sediment.

Sarno sediment were also used for the experiments reported in the prf. 5.1. It was sand-silty sediment with 50 % humidity percentage and was polluted with Cr (258 mg Kg⁻¹ TS), Pb (85 mg Kg⁻¹ TS), Zn (320 mg Kg⁻¹ TS) and Cu (163 mg Kg⁻¹ TS) in a way that did not meet the *Protocollo di Venezia* limits, consequently has to be treated.

5.4.2 Optimization of sediment washing operational parameters using EDTA

EDTA have been widely used for soil and sediment washing especially for its working versatility and relatively small environmental impacts. In this work different EDTA solutions, in a range 0.001-0.05 M, were used to investigate the influence of solid percentages (5, 10, 20 %), treatment time (up to 72 hours) and initial slurry pH (2, 3 and without changing) on Pb and Zn removal efficiencies working on heavy metals Sarno contaminated sediment.

5.4.2.1. Lead (Pb)

Exemplificative the results of EDTA 0.01 M tests are reported below in fig. 5.21 for the different operating conditions as the profile of the other experiments.

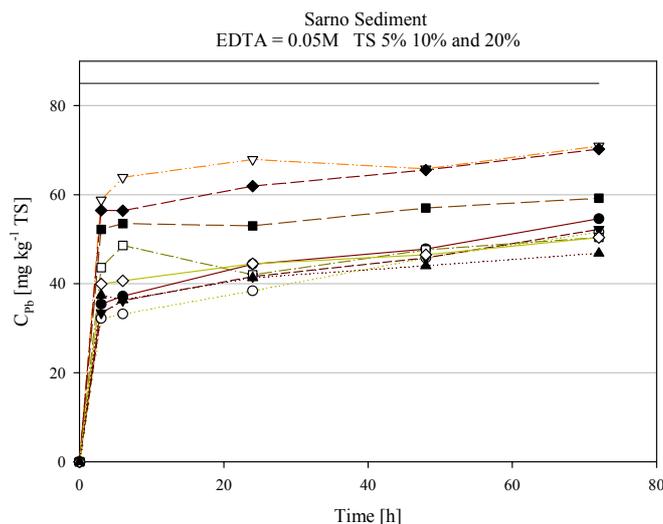


Figure 5.21. Pb extractions during EDTA 0.01 M. The solid line is the total Pb concentration

For all curves the plateau was reached within the first 24 hours confirming that heavy metals extractions by contaminated soil and sediment occur in days and not in hours.

A small increase (5 %) in the Pb extractions occurred between 24 and 72 hours. The Pb extracted ranged between 46.1 and 64.3 mg Kg⁻¹ TS, respectively during the test with 20 % without pH changing and 5 % with pH 2.

The overall results of the sediment washing experiments are reported in tab. 5.XIV grouped for solid percentages 5, 10 and 20 %.

Table 5.XIV. Pb removal efficiencies at the end of the sediment washing tests

EDTA molarity	pH	Pb extracted [mg Kg ⁻¹ TS]		
		5%	10%	20%
0.001M	2	60.4	20.0	28.3
0.001M	3	61.4	22.3	28.5
0.001M	no changes	60.6	28.3	26.0
0.005M	2	64.3	33.3	44.9
0.005M	3	60.9	29.9	42.6
0.005M	no changes	61.7	28.5	39.1
0.01M	2	64.3	61.7	56.7
0.01 M	3	60.9	58.4	49.4
0.01M	no changes	61.7	49.2	46.1
0.05M	2	72.0	68.0	67.2
0.05M	3	68.0	66.3	66.4
0.05M	no changes	68.8	66.4	61.7

The Pb extracted during the 5 % tests was comparable ranging between the 70 % and 80 % of the total amount, differently of the 10 and 20 % experiments. This is due to the fact that increasing the solid percentage in the sediment washing means an increasing of heavy metals sorbed to the solid particles loaded to the treatment system.

In fact EDTA forms ligands in a ratio 1:1 with each metal therefore the same EDTA molarities is potentially able to desorb a fixed metal amount from the solid particles. Since no removal efficiencies increasing were observed during the 5 % tests increasing the EDTA molarities it can be affirmed that residual part around 20 % is strongly bounded to the solid matrix and can not be extracted. In fact during the 10 and 20 % sediment washing test the removal efficiencies increase increasing the EDTA molarities reaching however the 80 % removal efficiencies as in the 5 % tests.

As it was expected, also based on the result reported in prf. 5.1 about the very high ANC of the Sarno sediment, the initial pH value of the slurry at the beginning of the sediment washing experiment did not influence the Pb removal efficiencies. Thus the tests with the same EDTA molarity have been averaged and reported for the three solid percentages investigated below in fig. 5.22.

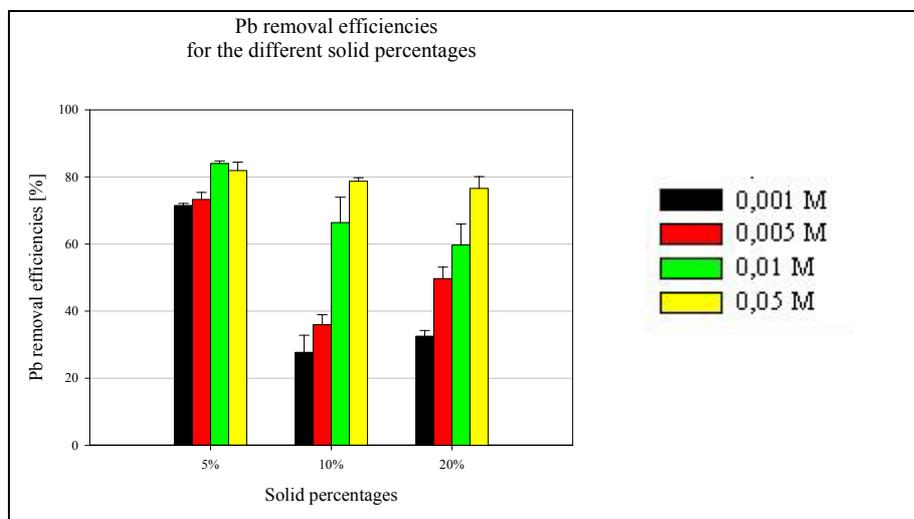


Figure 5.22. Pb sediment washing results summarized on solid percentages 5, 10 and 20 %

The EDTA molarities influenced the removal efficiencies especially for the 10 and 20 % tests but weakly for the 5 % tests. A sensible increasing (50 %) of removal efficiencies occurred in 10 and 20 % tests increasing the EDTA molarities though the maximum removal efficiencies were obtained with the 5% of solids. However the Pb removal efficiencies observed during the tests with 0.05 M EDTA seemed not influenced by the working solid percentages as in this case the chelant dosage was not limitant and adequate to extract the desorbible metals.

5.4.2.2. Zinc (Zn)

The results of EDTA 0.01 M extractions have been reported, for instance, in fig. 5.23 for the different operating conditions showing, as for Pb, that the plateau was reached within the first 24 hours.

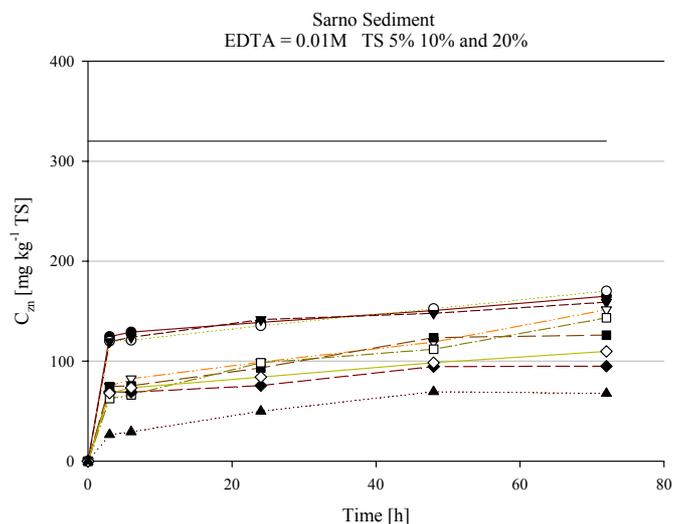


Figure 5.23. Zn extractions during EDTA 0.01 M. The solid line is the total Zn concentration

A small increase (10 %) in the Zn extraction occurred between 24 and 72 hours and the extractions were ranged between 69.3 and 169.8 mg Kg⁻¹ TS, occurred respectively during the test with 20 % without pH changing and 5 % with pH 3.

The overall results of the sediment washing experiments for Zn are reported in tab. 5.XV grouped for solid percentages 5, 10 and 20 %.

Table 5.XV. Zn removal efficiencies at the end of the sediment washing tests

EDTA molarity	pH	Zn extracted [mg Kg ⁻¹ TS]		
		5%	10%	20%
0.001M	2	144.6	78.1	106.6
0.001M	3	105.0	81.3	98.6
0.001M	no changes	99.2	70.1	122.6
0.005M	2	119.7	117.4	119.7
0.005M	3	104.3	145.9	120.0
0.005M	no changes	110.1	120.0	129.0
0.01M	2	150.7	138.2	86.7
0.01 M	3	155.2	115.2	100.2
0.01M	no changes	145.0	130.9	63.4
0.05M	2	206.1	165.8	107.8
0.05M	3	188.5	174.1	105.6
0.05M	no changes	180.2	137.3	89.0

The extractions target reached during the 5 % tests was comparable to the 10 and 20 % tests differentiating respect to the Pb data reported above. The results showed a slightly removal efficiencies increasing with EDTA molarities passing from 40 % of the 0.001 M to the 60 % of the 0.05 M during 5 % tests.

Since the very high ANC of the Sarno sediment the initial pH value did also not influence the Zn removal efficiencies, thus the tests with the same EDTA molarity have been averaged and reported for the three solid percentages investigated in fig. 5.24.

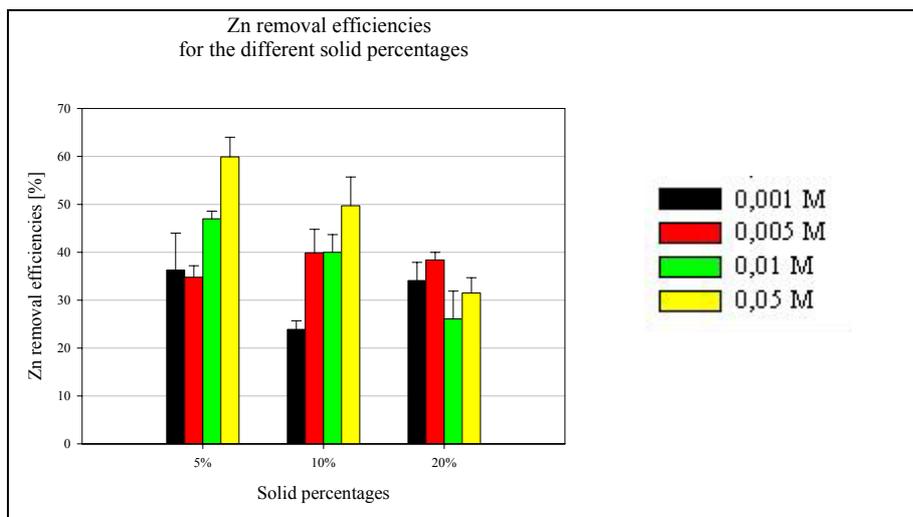


Figure 5.24. Zn sediment washing results summarised on solid percentages 5, 10 and 20 %

The Zn removal efficiencies were higher during the 5% and 10 % than 20 % tests with all EDTA molarity investigated though a small difference occurred.

5.4.3 Comparison between chelating agents and strong acids

Based on the observations reported in the previous item further sediment washing tests were carried out with 5% solid percentage testing both chelating agents and strong acids investigating Cr and Zn. Two different procedures were implemented (tab. 5.XVI); the first similar to the previous one and the latter refluxing the extractant solution (step) several times.

Table 5.XVI. Characteristics of sediment washing procedures both: Single and Step.

Sediment washing procedures					
Single		3 Steps		6 Steps	
Number of step	Treatment time [h]	Number of step	Treatment time [h]	Number of step	Treatment time [h]
I step	192 h	I step	72	I step	72
		II step	24	II step	24
		III step	24	III step	24
				IV step	24
				V step	24
				VI step	24
Total Treatment time [h]	192		120		192

The selection of a proper Mass Separating Agent (MSA) for a specific situation is determined not only by its cost but also by factors such as the nature of the solid material to treat, side reactions, stability at the operating conditions, metal speciation, feasibility of metal recovery and MSA reuse. The MSA used in the sediment washing experiments both for the Simple and Step procedures are reported in tab. 5.XVII.

Table 5.XVII. MSA used during both sediment washing procedures.

Simple procedure	Step procedure
EDTA 0.01 M	HCl 0.1 M
EDTA 0.05 M	HCl 0.5 M
Citric Acid 0.01 M	HNO ₃ 0.5 M
Citric Acid 0.05 M	HNO ₃ 1 M
Acetic acid 0.01 M	H ₂ SO ₄ 0.1 M
Acetic acid 0.05 M	H ₂ SO ₄ 0.5 M
HCl 0.5 M	H ₂ SO ₄ 1 M
H ₂ SO ₄ 0.5 M	
HNO ₃ 0.5 M	

5.4.3.1. Simple sediment washing procedure

As it was expected, based on the data reported in tab. 5.III, the chromium was strongly bounded to the sediment organic matter and thus very hardly extractable. However it was tried to use several chelating agents (i.e. EDTA, citric and acetic acid) carrying the tests for a long treatment time (192 h); nevertheless removal efficiencies lower than 10 % were observed for all chelating agents. Thus regarding Cr the results of the strong acids sediment washing

tests are reported in fig. 5.25 (a) while the Zn results in fig. 5.25 (b) along with the EDTA results.

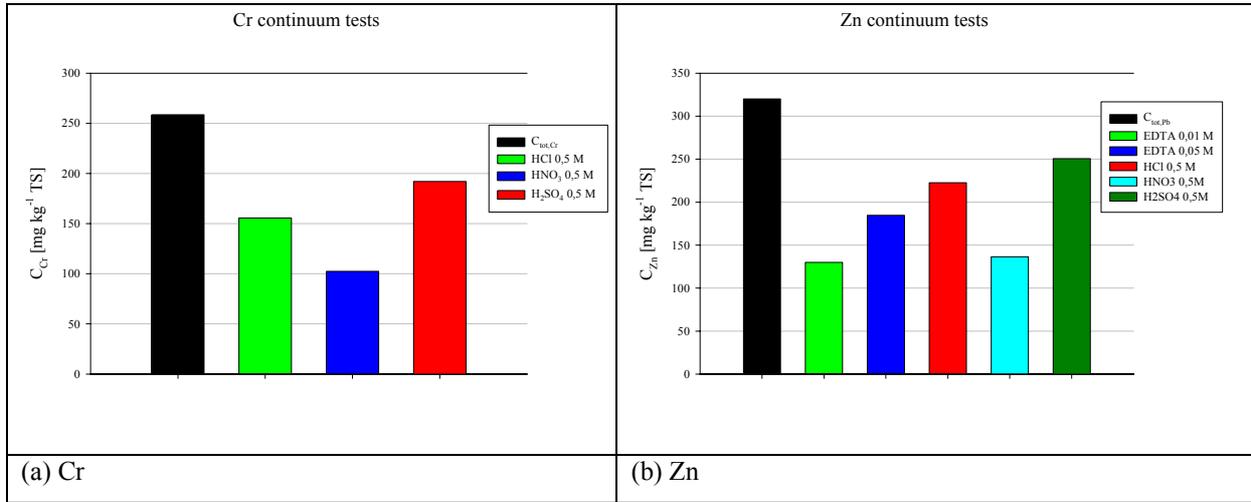


Figure 5.25. Cr and Zn sediment washing results with single extraction procedure

The higher Cr removal efficiencies, close to 70 %, was observed for sulphuric acid (H₂SO₄) while HCl and HNO₃ reached respectively the 60 and 40 %.

Citric and acetic acid did not influence Zn sediment extraction whereas removal efficiencies of 40 and 55 % were observed respectively with 0.01 M and 0.05 M EDTA. Also for Zn the highest removal efficiencies was observed for H₂SO₄ close to 75 % though comparable results were obtained for EDTA 0.05 M.

5.4.3.2. Step sediment washing procedure

The results of the Step sediment washing tests are reported in fig 5.26 for Cr (a) and Zn (b) both for the 3 and 6 steps tests.

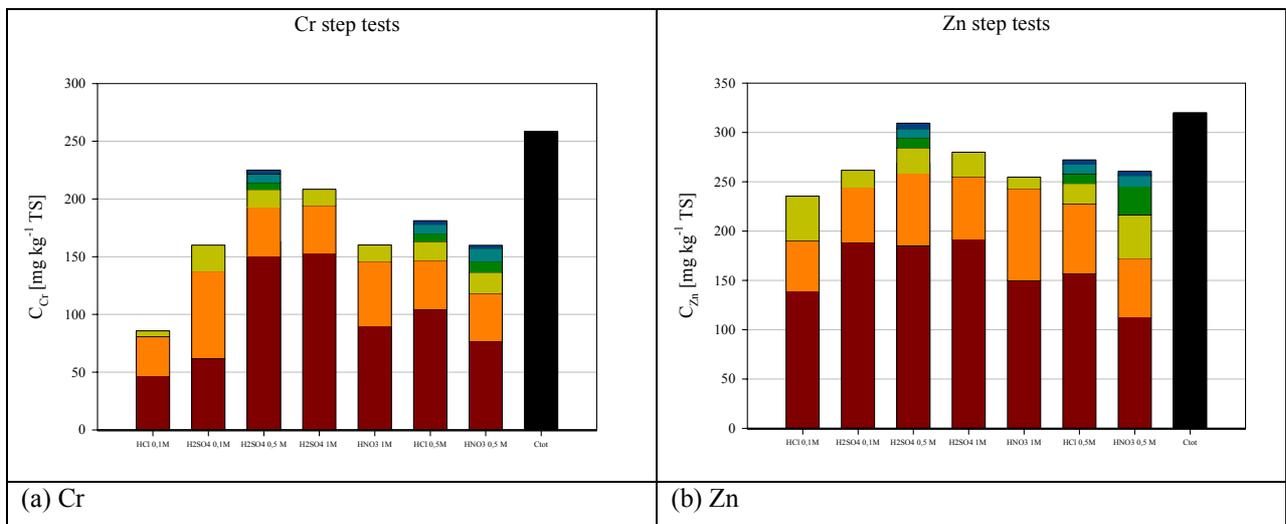


Figure 5.26. Cr and Zn sediment washing results for the Step procedure with 3 and 6 steps

As it was expected the 6 step tests achieved an higher removal efficiencies both for Cr and Zn. The removal efficiencies of each step decreased increasing the steps because the fresh extraction agent, refluxed at the beginning of each step, worked with stronger heavy metals bounded to the sediment, and thus more difficult to extract.

The comparison between the Single and Step sediment washing tests is reported below both for Cr and Zn in fig. 5.27.

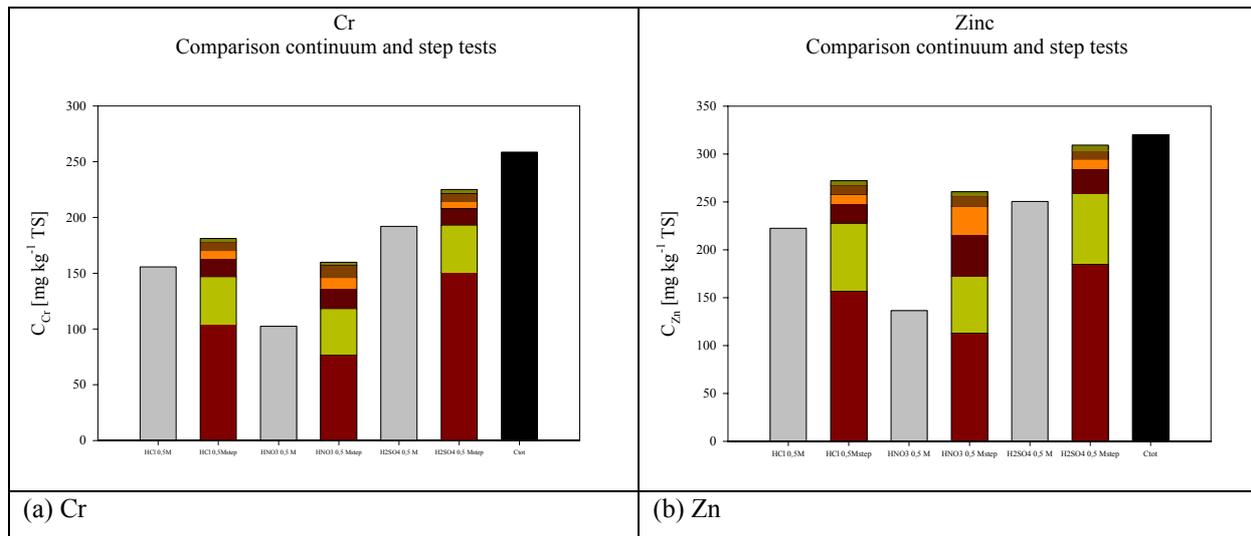


Figure 5.27. Comparison between Single and Step sediment washing procedure both for Cr and Zn

The higher Cr and Zn amounts extracted with the Single procedure is due to the fact that the tests were carried out for 192 h whereas the first step of the Step procedure lasted 72 h as it was observed that the treatment time influence the extraction albeit a fast extraction occurring within the first 24 h is followed by a slow extraction in the next hours treatment.

Consequently it can be observed that the Step procedure guaranteed an higher removal efficiencies both for Cr and Zn though the Cr and Zn extracted in each step decreased with the step increasing.

The result of the step procedure tests are reported in tab 5.XVIII both for Cr and Zn.

Table 5.XVIII. Cr and Zn removal efficiencies observed with the step procedures

	Cr [%]	Zn [%]
HCl 0.1M 3 steps	33.2	73.5
H ₂ SO ₄ 0.1M 3 steps	61.9	81.8
H ₂ SO ₄ 0.5M 6 steps	63.2	84.0
H ₂ SO ₄ 1M 3 steps	80.6	87.5
HNO ₃ 1M 3 steps	61.9	79.6
HCl 0.5M 6 steps	70.1	85.1
H ₂ SO ₄ 0.5M 6 steps	87.0	96.7
HNO ₃ 0.5M 6 steps	61.8	81.5

The removal efficiencies of the Zn were higher than the Cr for each washing solution likelihood because the Cr was stronger bounded to the solid particles.

Finally it can be observed that only the following tests met the *Protocollo di Venezia* limits: H₂SO₄ and HCl 0.5M for the Single procedure and 0.1 M, 0.5 M, and 1 M H₂SO₄, 0.5 M and 1M HNO₃, 0.5 M HCl for the Step procedure sediment washing tests.

5.4.4 Feasible application of an electrochemical process to recover EDTA solutions after sediment washing

The advantage of organic complexing agents such as EDTA over strong mineral acids are the high removal efficiencies obtained, their potential biodegradability, and the fact that they do not attack the solid matrix so aggressively. However, the costs of the agents, which depend almost linearly on the demand of the MSA, are limiting factors for their use in technical applications. Any attempt at minimising the costs will therefore target a reduction of this demand, which is determined by:

- The consumption of acidity of the MSA by the solid particles ANC;
- The consumption of complexing capacity (ligands) of the MSA by constituents of the solid such as iron (Fe).

The hypothesis of this work is that the regeneration of the MSA plays an important role in minimizing treatment costs.

The aim of this study is to determine the limitations and constraints of the sediments washing process proposed at a laboratory scale in order to evaluate both the feasibility of EDTA

regeneration by means of an electrochemical process and reuse of recovered EDTA to treat new solids following the treatment flow chart reported in fig. 5.28.

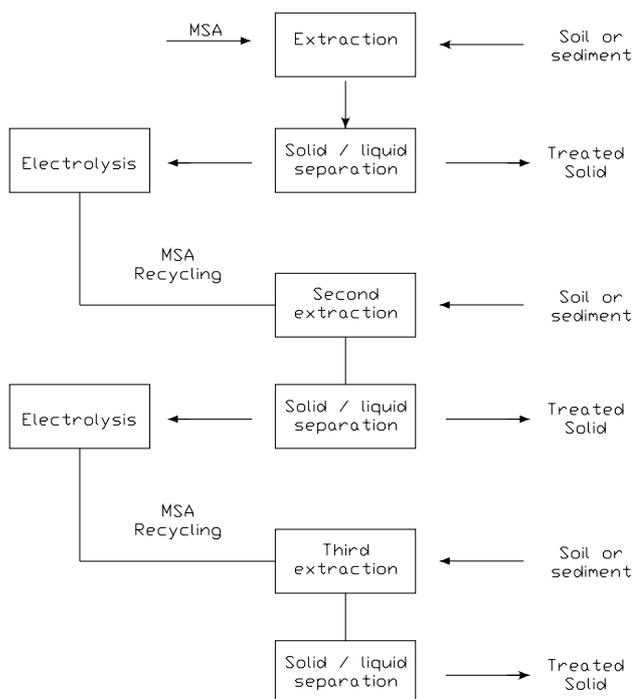


Figure 5.28. Treatment flow chart of the sediment washing system integrated with an electrochemical EDTA regeneration.

The working conditions of the electrolytic cell used is reported below in fig. 5.29.

Chapter 5. Sediment washing of Sarno river sediment coupled with the electrochemical regeneration of the extractant solution

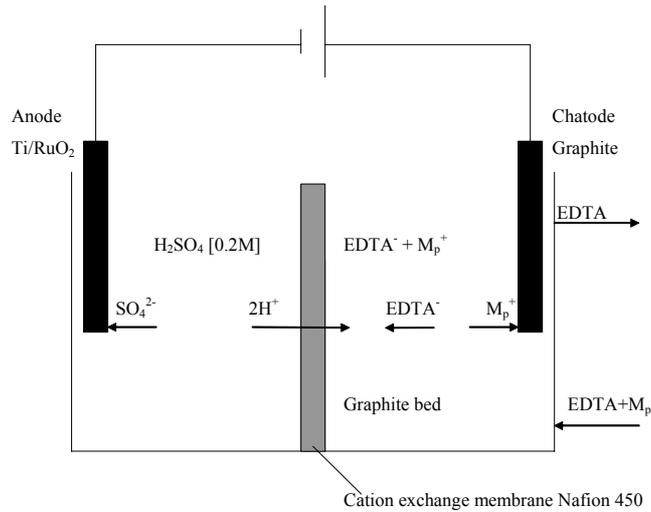


Figure 5.29. Electrolytic cell working conditions

New sediment were dredged from Sarno river and used for this purpose observing Pb and Zn total concentrations respectively of 141.8 and 320.8 mg kg⁻¹ TS.

The sediment washing experiment were carried out with 0.05 M EDTA solution, 5 % solid percentage and 120 h treatment time.

Two regeneration and three sediment washing cycles were operated with the same EDTA solution. The results of Pb (a) and Zn (b) electrolytic regeneration and the sediment washing are reported respctively in fig. 5.30 and tab.5.XIX.

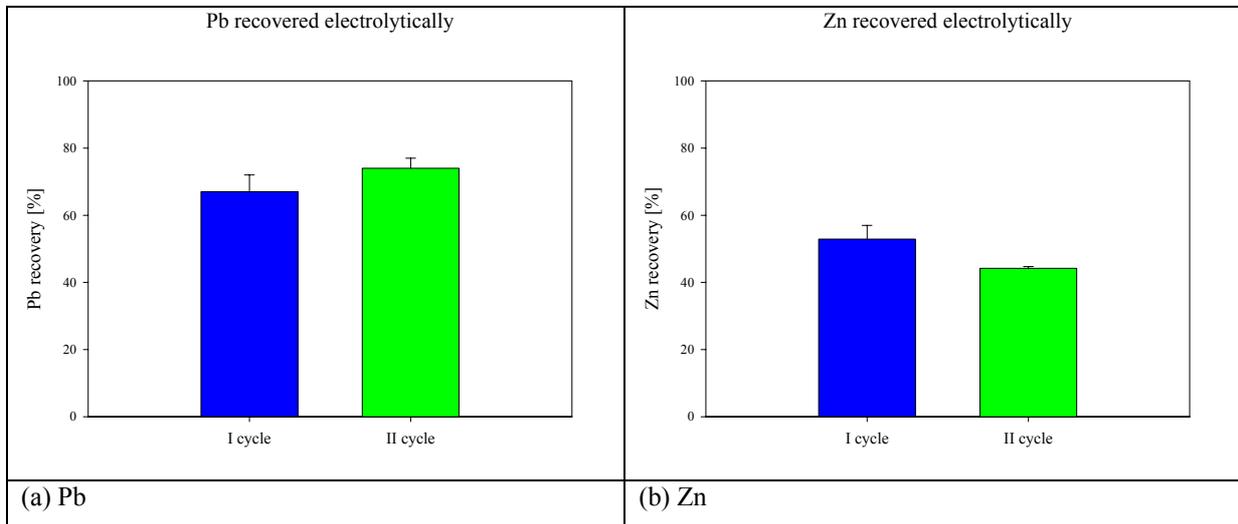


Figure 5.30. Pb and Zn recovered electrolytically

The Pb recovery was steady between the two regeneration cycles around the 65 % whereas the Zn recovered seems to be reduced increasing the recovering cycles confirming that the Heavy Metals recovery reduce trough the recovering cycles.

Table 5.XIX. MSA used during both sediment washing procedures.

	Pb		Zn	
	Removal efficiencies [%]	Residual concentration [mg kg ⁻¹ TS]	Removal efficiencies [%]	Residual concentration [mg kg ⁻¹ TS]
I cycle	87.1	11.0	46.9%	170.4
II cycles	63.3	31.2	24.3%	242.8
III cycles	58.4	35.3	20.3%	255.7

The results reported in tab. 5.XIX shows that both for Pb and Zn a decreasing in the removal efficiencies occurs trough sediment washing cycles. This result could be expected because of the electrolytic cell do not reach 100% efficiencies. However the recovered EDTA worked on new contaminated sediment both for Pb and Zn showing the suitability of an electrochemical process coupled with EDTA sediment washing as integrated process to treat Heavy Metals contaminated sediment.

5.5 Landfarming of PAHs contaminated sediment: Experiments and development of a prediction model based on PAHs bioavailability estimated by means of Tenax extraction

5.5.1 Introduction

Information on the extent to which the contaminants can be readily and/or slowly biodegraded (bioavailable for degradation) is of vital importance to decide the best option to remediate a contaminated site. As pointed out by several authors (Ogram et al. 1985) the microorganisms can probably only degrade dissolved PAHs therefore the kinetics of desorption may influence the bioavailability of the contaminants and consequently their biodegradation. There are a number of studies in which biodegradation has been compared to desorption (Fu et al. 1994, White et al. 1996, Rijnaarts et al. 1990, Carmichael et al. 1997) finding out often that desorption rates of freshly added PAHs were much larger than biodegradation rates (White et al. 1996, Carmichael et al. 1997). However Cornellissen et al. have found out a correlation between the PAHs biodegradation in bioreactors and the PAHs desorbed fraction estimated using Tenax beads extraction at 20 °C. The same research group have developed a sequential extraction by means of Tenax beads for the estimation of fast and slow desorbible PAHs fractions carrying out a sequential extractions at 20 and 60 °C.

Harmsen (2004) have attempted the comparison between the result of the PAHs Tenax beads extraction at 20 °C and the PAHs biodegradation occurred in landfarms within 1-2 years. Landfarming is one of the oldest bioremediation technologies (Dibble and Bartha 1979), operated spreading the soil or the sediment over the land surface, adding eventually nutrients or stimulating the aeration, in order to reduce the treatment time. During landfarming of sediment dewatering is the first step, and biodegradation starts as soon as aerobic conditions are obtained (Sims and Harmsen, 2001). A triphasic degradation profiles (Harmsen 2004) often occur in landfarming of sediment contaminated by organic compounds, that can be modelled by an initial phase of fast degradation (1-2 years) a slow degradation (2-10 Years) and a very slow degradation (10-40 Years).

The goal of part of the present thesis, developed in collaboration with prof. eng. Joop Harmsen at the Alterra research centre, Wageningen (the Netherlands), is to deliver an effective tool for the prediction of the PAHs biodegradation profile occurring in a landfarming treatment plant of PAHs-contaminated soil/sediments using a three compartment model based on:

- the kinetics literature data with respect to landfarm plant (Harmsen 2004);
- the results of desorption experiment by means of Tenax beads extractions for the estimation of the fast, slow and very slow desorbible fractions.

The results of a decennial landfarming experimental campaign, the Tenax desorption experiments, the validation and the application of the three compartment model have been reported below.

5.5.2 Experimental Results

5.5.2.1. Landfarming experiments

The ongoing experiments are summarized in tab. 5.XX, along with the initial PAHs and mineral oil concentration, for sediment (Petroleum Harbour and WEMeldinge) landfarmed in Kreeksluizen (the Netherlands). Twelve PAHs have been analyzed, both for the initial and landfarmed samples, according to the Dutch National List (PAH-NL) that includes: fluoreen, fenantreen, antraceen, fluoranteen, pyreen, benz[a]antraceen, cryseen, benzo[b]fluoranteen, benzo[k]fluoranteen, benzo[a]pyreen, benzo[ghi]peryleen, indeno[1,2,3-cd]pyreen.

Table 5.XX. Sediments used in this work (the average and the dev. std. have been calculated based on n=7 samples)

	Intensive landfarming since	Passive landfarming since	PAH-NL [mg kg⁻¹TS]	Mineral oil [mg kg⁻¹TS]
PH. cultivated	1994 - 1996	1996	552.1 ± 178.6	13.500
PH. vegetated		1994	552.1 ± 178.6	13.500
WEM. cultivated	1994 - 1996	1996	58.3 ± 11.7	2000
WEM. vegetated		1994	58.3 ± 11.7	2000

The PAHs are usually divided in three classes regarding the number of the rings respectively 2-3, 4 and 5-6 rings, because previous study, have pointed out similarity in the biodegradation patterns (features) of the single PAH included in each class. Thus in tab. 5.XXI are reported the three classes and the PAHs belonging to them:

Chapter 5. Landfarming of PAHs contaminated sediment: Experiments and development of a prediction model based on PAHs bioavailability estimated by means of Tenax extraction

Table 5.XXI. PAH-NL with 2-3, 4 and 5-6 rings

PAHs 2-3 RINGS		PAHs 4 RINGS		PAHs 5-6 RINGS	
1	fluoreen	4	fluoranteen	7	benzo[b]fluoranteen
2	fenantreen	5	pyreen	8	benzo[k]fluoranteen
3	antraceen	6	benz[a]antraceen	9	benzo[a]pyreen
		7	cryseen	10	Dibenzo[a,h]antracene
				11	benzo[g,h,i]peryleen
				12	indeno[1,2,3-c,d]pyreen

The result of the initial concentration for each PAH-NL both for the PH and the WEM sediment is reported below in tab.5.XXII.

Table 5.XXII. PAH-NL initial single concentration in PH and WEM sediment

PAH-NL	PH sediment		WEM sediment	
	Average [mg kg ⁻¹ TS]	Dev. Std. [mg kg ⁻¹ TS]	Average [mg kg ⁻¹ TS]	Dev. Std. [mg kg ⁻¹ TS]
fluoreen	46.2	22.9	1.6	1.1
fenantreen	143.9	54.5	7.5	3.2
antraceen	62.1	24.3	2.3	1.2
2+3 rings	252.3	52.4	11.4	3.2
fluoranteen	118.3	36.8	13.2	2.8
pyreen	69.3	19.6	8.8	1.4
benz[a]antraceen	28.0	7.9	4.3	0.6
cryseen	27.5	7.7	4.3	0.7
4 rings	243.2	43.1	30.6	4.3
benzo[b]fluoranteen	15.9	4.2	4.0	0.4
benzo[k]fluoranteen	8.8	2.1	2.0	0.2
benzo[a]pyreen	14.9	4.0	4.1	0.4
benzo[g,h,i]peryleen	7.7	1.9	2.7	0.3
indeno[1,2,3-c,d]pyreen	9.4	2.6	3.5	0.3
5-6 rings	56.7	3.8	16.4	0.9
Total PAH-NL concentration	552.1	75.8	58.3	11.7

The initial PAHs concentration of the Petroleum Harbour was 552.1 distributed with the 45.7 % for the 2-3 rings, the 44.0 % for the 4 rings and the 10.3 % for the 5-6 rings. The initial PAHs concentration of the Wemeldinge was 58.3 mg kg⁻¹ distributed with the 19.5 % for the 2-3 rings, the 52.5 % for the 4 rings and the 28.1 % for the 5-6 rings. The differences between the PH and WEM sediment were observed both for the initial PAHs concentration, that was one order of magnitude, and the distribution among the PAHs three rings classes. Whereas the

PH sediment has shown an high 2-3 and a low 5-6 rings PAHs percentages the WEM sediment has shown the opposite; as it has been observed by other authors (Giordano et al. 2005) the PAHs distribution among the rings classes can be qualitative interpreted as a sign of the contamination age. In fact, observed that the low Molecular Weight (MW) PAHs are often biodegraded faster than the high MW PAHs, high percentages of PAHs with 2-3 rings can be correlated to a young contamination while an high percentages of PAHs with 5-6 rings o an old contamination. All individual PAHs have been biodegraded in the four landfarm long-term experiments, showing that no inhibiting factors, like presence of other contaminants (e.g. heavy metals in high concentration) have been significant. However the biodegradation rates, especially during the first years, have been different in the layers of the vegetated and cultivated landfarm, explainable likelihood, with the different supply of oxygen (Harmsen 2004). As long as the presence of oxygen is the limiting factor, the degradation rate can be explained by the rate of aeration (Harmsen 2004). The landfarm biodegradation results, without limiting supply oxygen conditions, as occurred in the upper layers of vegetated landfarm of the PH and WEM sediment (fig. 5.31), are presented in this thesis. In fact in the upper layer of the vegetated landfarms, aerobic conditions were already developed during the first year, therefore the fast initial degradation occurs in these layers. In the cultivated fields more time was necessary to obtain aerobic circumstances. By cultivation the aerated upper layer was mixed again with anaerobic sediment from the lower layers and two years were necessary to obtain a field aerated over the whole depth. If it had been possible to start cultivation immediately, a higher fast degradation rate might have been obtained in the cultivated landfarm.

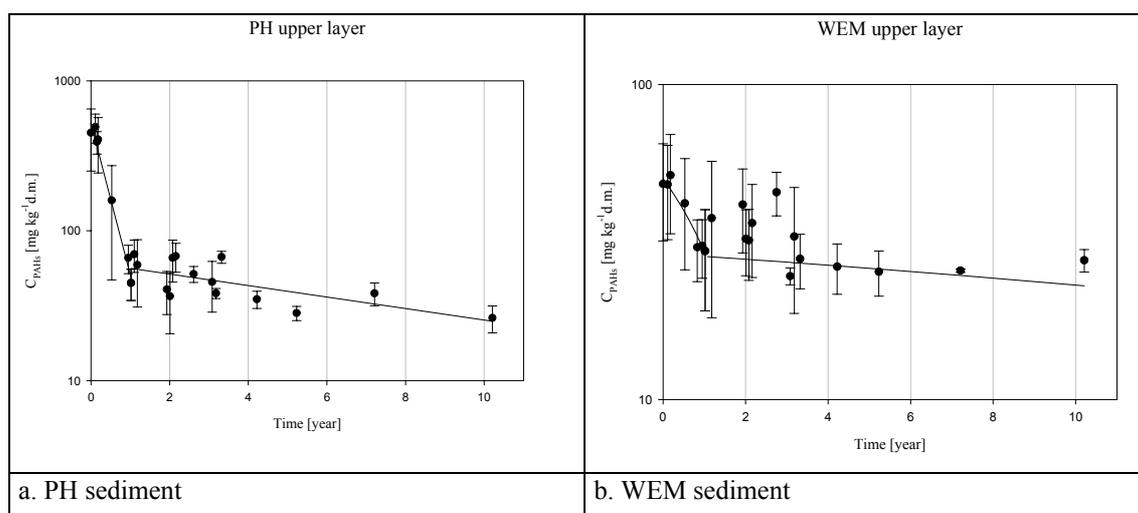


Figure 5.31. PAHs degradation profiles in the upper layers of the PH and WEM vegetated landfarm. The data, averaged on five samples, are fitted with exponential curves

Observed that similar trends were observed with the individual measured PAH, as it can be clearly observed in fig. 5.31(a) two different biodegradation trends (fast and slow) can be distinguished within the ten years. The first has been degraded in the first year while the latter between first and tenth year, therefore the data have been fitted with two exponential curves. The residual concentration present after 10 years (this was the situation in 2004) is the PAHs very slow degradable fraction. Although fast initial degradation was also expected in the WEM sediment, the fast and slow degrading fraction was more hardly distinguished because of the high data standard deviation and PAHs initial low concentration (fig. 5.31 b).

The fast degradation (within one year), slow degradation (in the following years) and residual concentration after 10 years percentages occurred in the upper layers of the PH and WEM sediment are reported in tab. 5.XXIII.

Table 5.XXIII. Single and total PAHs biodegradation percentage occurred in the PH and WEM sediment

PAH	PH sediment			WEM sediment		
	Fast [%]	Slow [%]	Residual concentration [%]	Fast [%]	Slow [%]	Residual concentration [%]
fluoreen	89.7	8.8	1.5	67.1	15.7	17.2
fenantreen	97.1	0.8	2.2	61.4	8.8	29.7
antracene	95.5	1.7	2.8	52.9	7.0	40.1
2+3 rings	94.1	3.8	2.2	60.5	10.5	29.0
fluoranteen	93.4	2.9	3.7	35.9	9.7	54.4
pyreen	90.7	5.6	3.7	28.0	21.4	50.7
benz[a]antracene	83.8	8.3	7.8	15.2	15.8	69.0
cryseen	78.4	9.2	12.4	2.4	3.1	94.6
4 rings	86.6	6.5	6.9	20.3	12.5	67.2
benzo[b]fluoranteen	57.4	29.4	13.2	8.1	29.0	62.9
benzo[k]fluoranteen	69.9	17.2	12.9	16.2	16.2	67.6
benzo[a]pyreen	55.2	28.7	16.1	16.8	16.5	66.7
benzo[g,h,i]perylene	41.2	14.2	44.6	3.7	24.5	71.8
indeno[1,2,3-c,d]pyreen	54.7	8.2	37.1	11.6	32.3	56.1
5+6 rings	55.7	19.5	24.8	11.3	23.7	65.0
Total PAH-NL	78.8	9.9	11.3	30.7	15.6	53.7

The PAHs biodegradation occurred in the WEM sediment is percentually lower than the PH sediment, probably because the PAHs initial concentration was higher in the latter and the PH sediment contained a high amount of mineral oil (13.500 mg kg⁻¹). In fact the mineral oil may act as an extractant, making the PAHs more available for biodegradation.

The PAHs biodegradation percentage after a ten year landfarming treatment have been very high for the PH sediment reaching almost the 90% and quite good for the WEM sediment reaching almost the 50%. High total biodegradation percentages have been observed for the smaller Molecular Weight (MW) PAHs compared to higher MW for the PH as well as the WEM sediment confirming the findings of several authors (Nocentini et al. 1995) regarding the PAHs biodegradation efficiency that increase decreasing the number of rings. Nevertheless it has only occurred during the fast degradation phase while it has not been observable during the slow degradation phase.

5.5.2.2. Desorption experiments using Tenax beads

Although, several biological and chemical tools (Cornelissen 1997, Reid 2000, Cuypers 2001) have been proposed in the last years in order to predict the PAHs bioavailability in soil and sediment, the Tenax beads extraction has been used in this thesis. The Tenax extraction method has been used to determine the desorbing fractions, because may be theoretically considered as a predictor of the bioavailability extent, for the reason that the Tenax beads are similar to degrading microorganisms in a way that both Tenax and microorganisms increase the sediment-water PAH concentration gradient.

A sequential PAHs extraction have been used in this thesis by means of Tenax carrying out the desorption experiments at 20 °C and then at 60 °C in order to estimate respectively the fast, slow and very slow PAHs desorbable fractions. The result of the Tenax PAHs extractions carried out on PH and WEM sediment both for fresh and 2004 samples are reported in tab. 5.XXIV.

Table 5.XXIV. Result of Tennax extraction on fresh and 2004 samples from Kreekraksluizen

Sample	PAHs desorption		
	Fast [%]	Slow [%]	Very slow [%]
PH fresh	75.9 ± 8.0	13.5 ± 4.7	10.6 ± 4.2
WEM fresh	21.5 ± 2.9	17.3 ± 1.9	61.2 ± 4.4
PH 2004 sample	3.2 ± 1.1	15.2 ± 3.2	81.6 ± 12.3
WEM 2004 sample	2.3 ± 0.8	13.8 ± 5.1	83.9 ± 15.1

The results in the first two rows of the tab. tab. 5.XXIV clearly show that the sediment used in the experimental campaign present a different desorption features, especially due to amount of the fast desorbed fractions.

The percentages of the fast and slow desorption fractions were decreased in the 2004 samples contrary to the very slow fraction, because the first, have been mainly degraded within the ten years treatment, instead of the very slow fraction that is almost completely present on the sediment at that time.

Harmsen (2004) have found out that the PAHs fast desorption available fractions measured with the Tenax-method carried out at 20°C provide a good estimate for the PAHs degradation in the following year on the landfarm. However as it has been observed (fig. 5.31) the biodegradation occurring in a PAHs contaminated sediment landfarm is quite long (dozens years) and affected by three biodegradation phases: fast, slow and very slow. Thus taking into account the results of the Tenax extractions, as reported in tab. 5.XXIV, the landfarms biodegradation has been compared with the desorption data (fig. 5.32), aiming a correlation between the PAHs fast and slow desorptions and biodegradations.

The fast desorbing fraction (20 °C) summed to the slow desorbing (60 °C) fraction of the individual PAHs in upper layer of the PH and WEM sediment versus the fraction biodegraded in ten years of landfarming are reported in fig. 5.32.

Correlation Biodegradation-Desorption

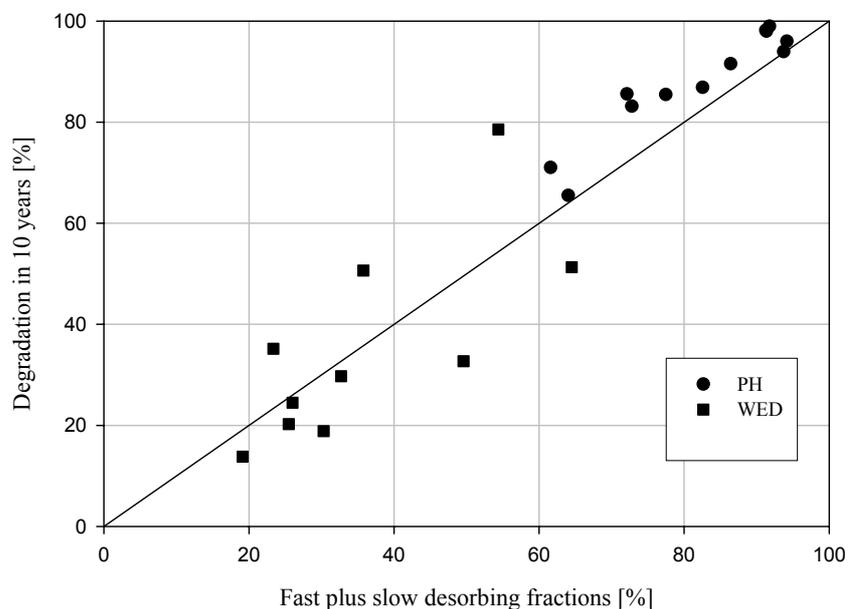


Figure 5.32. PAHs, percentage degraded on the landfarm Kreekraksluizen within tenth year versus percentage fast plus slow desorbing fraction (Tenax-measurement). The solid line is the line with slope =1

The PAHs biodegraded after ten years in the landfarm pilot plants are derived from tab. 5.XXIII, while the solid line in fig. 5.32 represents PAHs percentages degradation equal to the desorbed/bioavailable percentages (fast plus slow).

The WEM and PH results have occupied two different region of the graphic in fig. 5.32 showing a different biodegradability/desorption features. For most PAHs, the percentage of degradation is slightly larger than the percentage desorbed. This is especially true for the PH sediment, and the reason might be that a part of the very slow desorbing fraction has also been degraded during the first ten years of treatment.

As it can be observed in figure 5.32 the experimental data are close to the solid line showing a quite good correlation between the desorption fractions (fast plus slow) by means of Tenax beads technique and the biodegradation in a landfarm plant within ten years of treatment.

It is important to remark that the Tenax extraction experiment are carried out in a completely mixed system while landfarm is carried out in opened system. Thus the comparison between the desorption by means of Tenax beads and the biodegradation occurred in a landfarm treatment plant can not be based on kinetic approaches. Nevertheless it is reasonable to make the comparison, in terms of amounts (sizes), between PAHs desorbed and biodegraded.

Thus the sizes of the fast and slow desorption experiment may be considered as fast and slow bioavailable fractions that thereby may be biodegraded during the bioremediation treatment. This hypothesis can be used regardless the biodegradation time that depends mainly on the treatment system that can vary for instance by weeks for bioreactors to years for landfarming. In the case of landfarming it is reasonable to associate the fast and slow desorbing fractions estimated by means of Tenax extraction at 20 and 60 °C correspondingly to the fast and slow PAHs biodegradable fractions occurred in landfarms respectively within the first year and between the second and tenth year.

5.5.2.3. PAHs biodegradation prediction in landfarm

Degradation and desorption processes can be described with a first order kinetic model. In case various distinguishable degradable/desorbable fractions are present in the solid matrix therefore a multi compartment approach has been applied in order to model the different degradable/desorbable fractions. In this thesis a three-compartment model has been used as reported below:

$$\frac{C_t}{C_0} = F_{fast} \cdot e^{-k_{fast} \cdot t} + F_{slow} \cdot e^{-k_{slow} \cdot t} + F_{very\ slow} \cdot e^{-k_{very\ slow} \cdot t}$$

C_t = sediment/soil sorbed amount (mg/kg d.m.) at time t

C_0 = sediment/soil sorbed amount (mg/kg d.m.) at time 0

F_{fast} = rapidly bioavailable/desorbing fraction

F_{slow} = slowly bioavailable /desorbing fraction

$F_{very\ slow}$ = very slowly degrading/desorbing fraction

k_{fast} = rate constant rapid degradation/desorption (y^{-1})

k_{slow} = rate constant slow degradation/desorption (y^{-1})

$k_{very\ slow}$ = rate constant very slow degradation/desorption (y^{-1})

t = time (y)

The biodegradation rate constants (k_{fast} , k_{slow} , $k_{very\ slow}$) are independent terms depending on the treatment it is being investigating. The landfarm treatment depend on several factors as: dewatering rate, diffusion, degradation of organic matter, climate conditions. Nevertheless previous studies on landfarm have attempted to obtain the biodegradation rate constants in several operating conditions, as reported in table 5.XXV (Harmsen 2004). These values are low compared to diffusion rate constants reported for diffusion in a slurry (Cornelissen et al. 1997, Johnson et al. 2001), but the difference could be explained, as mentioned before, both by the lower moisture content and the larger particle size in a landfarm.

Table 5.XXV. Values for degradation rate constants of different fractions of contaminant (y^{-1})

	k_{fast}	k_{slow}	$k_{very\ slow}$
Landfarm, dewatered within 1 year	3.5	0.33	0.04
Surface layer passive landfarm or intensive cultivated			
Landfarm, dewatered within 3 years	0.8	0.33	0.04
Lower layer passive landfarm			
Thin layer of dredged sediment dewatered within 3 months.	9.2	0.33	0.04

The data reported in tab. 5.XXV have been obtained under Dutch climate conditions and therefore are valid for similar climate. It is valuable to remark that the presented PH and WEM landfarm results have been operated in the same conditions of the first line of table 5.XXV and therefore those biodegradation rate values have been implemented in the three

compartment model. The PH and WEM sediment have been used to parameterise the three compartment model.

5.5.2.4. Validation of the Prediction model

The results of the Tenax extraction reported in tab. 5.XXIV are used in the three compartment model as sizes of the bioavailable/biodegradable fractions as:

- Ffast=PAHs fraction extracted with Tenax at 20 °C
- Fslow= PAHs fraction extracted in the following Tenax at 60 °C
- Fvery slow= PAHs residual fraction after both Tenax extraction

The latters have been coupled with the data reported in the first line of tab. 5.XXV and both have been implemented in the three compartment model. The data obtained with the three compartment model along with the real field biodegradation data expressed in a normalized PAH-NL concentration (C_t/C_0) versus time have been plotted in fig. 5.33 and 5.34 respectively for upper layers of the PH and WEM sediment.

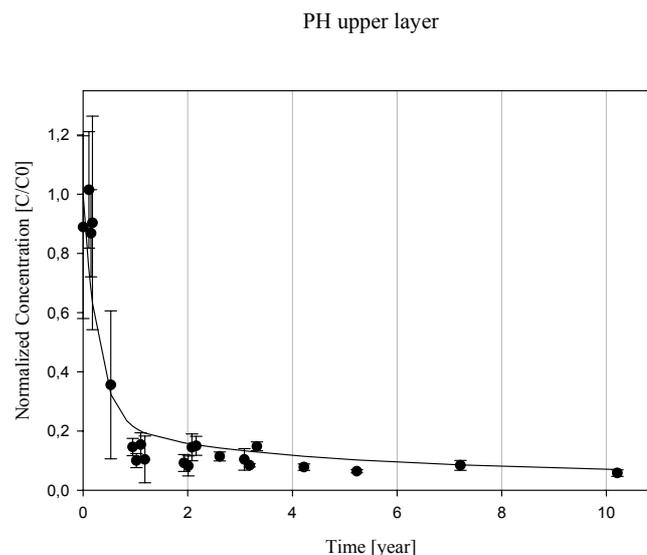


Figure 5.33. Three compartment model data coupled with the real PH biodegradation data

As it can be observed the correlation between the experimental and the model data is quite good. The experimental data are mainly below the model data especially during the slow biodegradation; this could be due to the fact that a part of the slow bioavailable fraction became “faster” bioavailable during dewatering and ripening and therefore biodegraded with an higher biodegradation rate. In this period the organic matter concentration decreased from 12 to 8% (Harmsen 2004). However the differences between the real and model data have achieved and a reliable fit after the tenth year showing a deviation lower than 5 %.

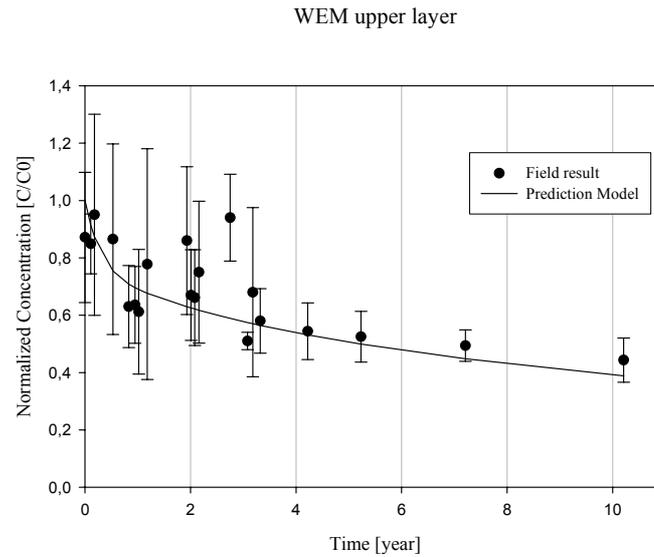


Figure 5.34. Three compartment model data coupled with the real WEM biodegradation data

The correlation of the experimental and the model data for the WEM sediment is not reliable as for the PH sediment. However it is valuable to remark that the PAHs initial concentration of the landfarmed sediment is rather different; in fact the WEM and the PH sediment have shown an initial PAHs content respectively of 62 and 538 mg kg⁻¹ TS and therefore the scattering in the measures is more influent in the WEM sediment. Nevertheless the trends of the model and the biodegradation in the fields are similar in the first part of the graphic even if the spreading of the result is quite high, though after the fifth year the scatter is less than the 15 %.

The higher PAHs concentration occurred in the WEM experiment respect to the model data could be explained by means of the changing of the organic matter that probably imply a transformation of the fast and slow fraction in the very slow fraction retarding the biodegradation. Unfortunately it was not possible to investigate the organic matter composition changing in this study within 10 years.

5.5.2.5. Application of the prediction model

The prediction model have been applied to the fresh and 2004 sampled sediments on the landfarm fields in order to predict the long term results of the landfarm.

The result of the three compartment model applied the fresh and the 2004 PH and WEM sediment based on the Tenax beads results (tab. 5.XXIV) have been reported in tab. 5.XXVI.

Table 5.XXVI. Three compartment model data based on the Tenax extraction carried out on the fresh and the 2004 sediment. The bold values are measured the others predicted

Time	PH		WEM	
	Model data on fresh sediment [mg kg ⁻¹ TS]	Model data 2004 sediment [mg kg ⁻¹ TS]	Model data on fresh sediment [mg kg ⁻¹ TS]	Model data sediment 2004 [mg kg ⁻¹ TS]
1994	535		48.3	
2004	37.4	31.0	18.8	25.7
2014	23.6	17.0	12.4	14.4
2024	15.8	11.3	8.3	9.6
2054	4.7	3.4	2.5	2.9

The predicted results on the long term are comparable and 20-30 years will be necessary to reach a target value of 10 mg kg⁻¹ while the PAHs concentration will be closer to the background value in 50 years.

The application of the prediction model have shown a good reliability of the biodegradation prediction results between the fresh and the treated sediment both for PH and WEM.

5.5.3 Conclusion

In this long-term landfarming experiment, it was possible to distinguish between different rates of degradation; a fast degradation, a slow degradation in the first period of about 10 years and a very slow degradation after the period of slow degradation. Depending on the distribution of PAHs between the different degradable fractions, therefore short and/or long periods may be necessary to reach target values set for remediation.

Tenax extractions at 20 and 60 °C on the PH and WEM sediment have been carried out in order to measure the fast and slow desorption PAHs fractions. The fast plus slow desorbed fractions by means of Tenax technique have been correlated to the extent of PAH biodegradation in a ten year landfarm showing a good correlation. The results of the tenax extraction coupled with earlier published biodegradation rate constants (k_{fast} , k_{slow} and $k_{very\ slow}$) obtained from landfarm treatment have been implemented in the three compartment model for its parameterisation.

The three compartment prediction biodegradation model have been compared with the biodegradation results of two landfarm pilot plants operated in Kreekrasluizen showing a good correlation especially for the PH sediment.

Currently, the landfarms at Kreekrasluizen are stable systems and the degradation will continue in the coming years, improving the quality of the sediment. The application of this

Chapter 5. Landfarming of PAHs contaminated sediment: Experiments and development of a prediction model based on PAHs bioavailability estimated by means of Tenax extraction

model have enabled the PAHs prediction on the long term (years-decades). The application of the three compartment model have shown that 50 years are needed for the PH and WEM sediment to reach the PAHs background value using a landfarming.

5.6 Sequencing Batch Reactor Performance Treating PAHs Contaminated Lagoon Sediment

5.6.1 Introduction

Bioslurry treatment is a biological ex-situ technology, offering optimal process control and highest biodegradation rate (USEPA 1990, Cesaro et al. 2003) among bioremediation technologies. The biological process is carried out in a reactor, where the dredged sediments are mixed with external water to make a solid-liquid suspension called: slurry. If needed, external addition of nutrients is provided. Solids concentration typically ranges between 5 % and 50 %, depending on the mixing and aeration equipments and on contaminant toxicity. Bioslurry treatment has been tested in different types of reactors, including: Batch System (Glaser et al. 1995); Sequencing Batch Reactor (SBR) (Irvine et al. 1993); continuous-flow Completely Stirred Tank Reactor (CSTR) (Cassidy et al. 2000). Recent results (Cassidy et al. 2000) have shown, at least for soil contaminated by hydrocarbons, that SBR are able to reach higher efficiencies than the other above-mentioned systems.

The SBR functioning cycle includes three temporal steps: during the Fill step, the slurry is fed into the reactor; in the Reaction step the system works as a batch reactor, performing the biodegradation process; the final step consists of the extraction of a fraction of treated slurry from the reactor (Draw step) and the replacement with an equal volume of untreated slurry.

The most important operating factors influencing the SBR removal efficiency are the hydraulic retention time (HRT), the Volume of Slurry Replaced (VSR) at the end of each cycle, the solids concentration and the mixing speed. The HRT and the volume of slurry replaced per cycle can be adjusted to face different contaminant loads to the reactor.

The sediment, dredged from Porto Marghera channels (Venice lagoon) have been used in this thesis; they have been characterized for the total PAHs content ($17.1 \text{ mg Kg TS}^{-1}$), the Total Organic Carbon, TKN, Nutrient (N and P), CFU, chlorines etc. The Venice lagoon is one of most superfund sites in Italy (listed among the main sites in needs of reclamation by the Italian Law n. 426/1998), as some lagoon areas have been used as dumping sites for urban and industrial waste since the beginning of 1900. It was estimated that $7.0 \cdot 10^6 \text{ m}^3$ of sediments must be dredged by Venice channels, whose $1.5 \cdot 10^6 \text{ m}^3$ are polluted by heavy metals, pesticides, PAHs etc. (www.port.venice.it).

The investigations, carried out with eng. Andrea Giordano at the ENEA research centre, Bologna (Italy), have regarded:

- PAHs contaminated sediment treatment by means of a lab scale (8l) SS-SBR;
- PAHs desorption by means of Tenax beads in order to estimate PAHs bioavailability.

The Tenax desorption results have been moreover used in a three compartment model to evaluate the PAHs biodegradation occurring in a landfarming treatment plant. Hence the comparison between active and passive bioremediation technologies have been discussed.

5.6.2 Experimental Results

5.6.2.1. Sediment characterisation

The granule size distribution of sediments (fig. 5.35) shows 59 % and 40 % volumetric percentages of silt and clay, respectively, with negligible sand content.

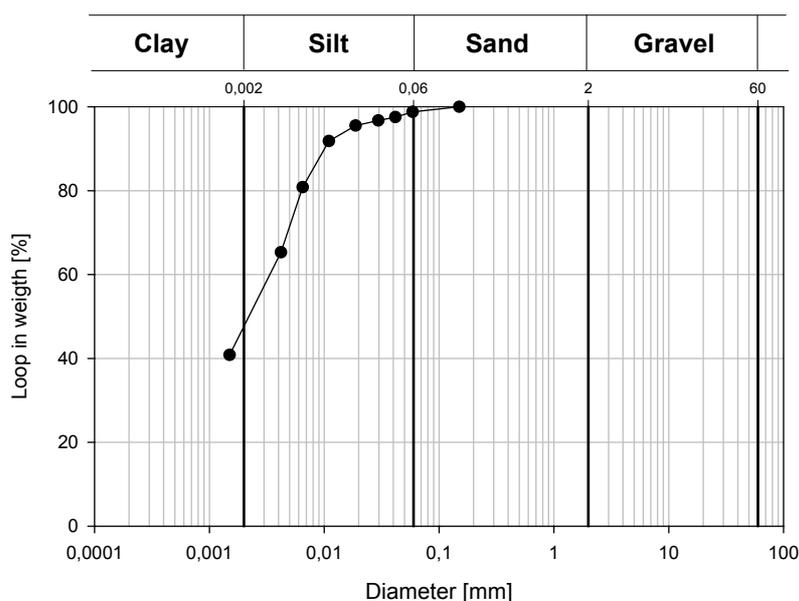


Figure 5.35. Granule size distribution curve of contaminated sediments

The sediment PAHs, TOC, TKN, Pt, Chloride, Colony Unit Formant (CFU) concentrations are listed in tab. 5.XXVII.

Table 5.XXVII. Fed slurry contaminant concentrations

Total PAH	TOC _D	TKN	P _T	Chloride	CFU
[mg kg TS ⁻¹]	[g kg TS ⁻¹]	[CFU kg TS ⁻¹]			
17.1	86.50	2.30	1.18	1.62	3.7 10 ⁷

The dredged sediments, used in this work, showed total PAHs level of 17.1 mg kg⁻¹TS, and according to the Italian law (*Protocollo di Venezia*) are classified as hazardous waste rather than a valuable solid material and then has to be treated or disposed in a confined facility.

The result of the initial concentration for the Porto Marghera sediment is reported below in tab. 5.XXVIII for each PAH of the EPA list, including: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, crysen, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, dibenzo[a,h]anthracene, indeno[1,2,3-c,d]pyrene.

Table 5.XXVIII. EPA list PAH measured in the sediment dredged from the Porto Marghera channel

PAH-EPA list	Average [mg kg⁻¹ TS]	Dev.std. [mg kg⁻¹ TS]
Naphtalene	0.41	0.1
Acenaphtylene	0.17	0.04
Acenaphthene	0.34	0.07
fluorene	0.47	0.1
phenanthrene	2.07	0.71
anthracene	0.48	0.09
2+3 rings	3.9	0.2
fluoranthene	1.92	0.49
pyrene	2.09	0.54
benz[a]anthracene	0.80	0.23
crysen	0.85	0.26
4 rings	5.7	0.4
benzo[b]fluoranthene	1.38	0.39
benzo[k]fluoranthene	1.12	0.38
benzo[a]pyrene	0.96	0.32
benzo[g,h,i]perylene	3.52	1.07
Dibenzo[a,h]anthracene	0.06	0.02
indeno[1,2,3-c,d]pyrene	0.42	0.12
5+6 rings	7.5	0.4
Total PAH-EPA list concentration	17.06	0.31

As expected, due to the aged Porto Marghera contamination, the main PAH fraction was characterised by 5-6 rings (44 %), followed by the fraction with 4 rings (33 %) and the fraction with 2-3 rings (23 %).

The PAHs contribution to the TOC was very low about 0.19 % of the Total Organic Carbon and also the ratio between TOC:TKN:P_t, well known index of the biological activity showed

a nutrients deficit respect to the reference value, used for the wastewater organic compounds biodegradation, respectively of 100:10:1.

Nevertheless the bioremediation experiments by means of the SS-SBR to treat PAHs contaminated sediment dredged from Porto Maghera channels was carried out without nutrients adding (biostimulation) and without the external microorganisms inoculum (bioaugmentation).

5.6.2.2. PAHs contaminated sediment treated by means of Sequencing Batch Reactor

The slurry (200 l) was prepared mixing sediments and tap water to reach a 10% solids concentration (weight of dry sediment/weight of slurry) and was stored at 4°C to stop the biological activity. Before feeding the slurry into the reactor, it was maintained, for about 20 min, in the thermostated chamber to restore the temperature. As it has been reported in Chapter 4 four phases have been carried out for the SS-SBR as reported in the following items.

5.6.2.2.1 Phase I

The Phase I was operated to investigate the development of endogenous microorganisms able to biodegrade TOC and especially the PAHs. It was carried out for three months with a fourteen days cycle length and a VSR of 1.0 l, resulting in a HRT of fourteen weeks.

During the first weeks of treatment the aeration was operated continuously for 12 hours and stopped for 12 hours, monitoring only the Dissolved Oxygen (DO). The DO profile, in the SS-SBR, during a treatment cycle is reported below in fig. 5.36.

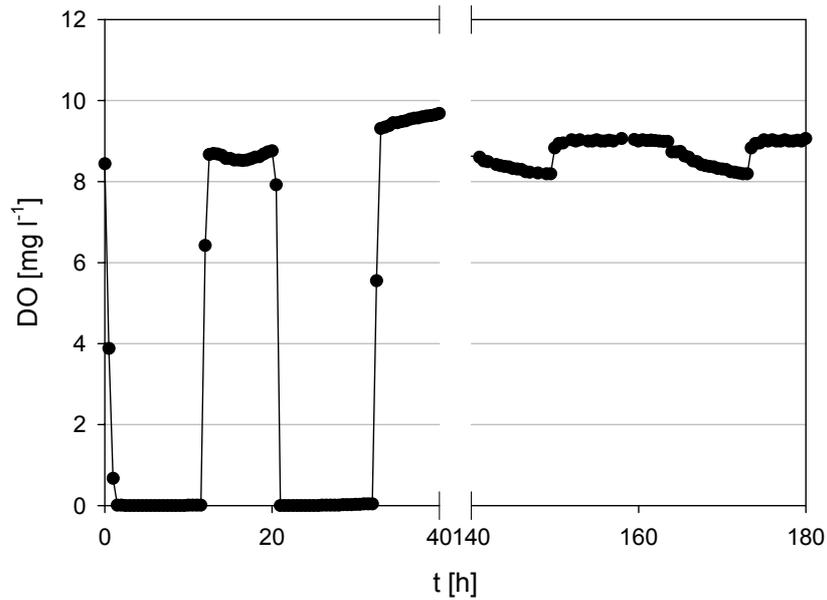


Figure 5.36. DO profile during an SS-SBR cycle treatment

As it can be observed by the figure the DO is around the saturation value during the aeration time. Contrary without the air supply two trends can be distinguished: during the first days the DO went deeply to zero when the aeration was stopped probably because there is the oxidation of the reduced compounds (e.g. sulphides) adsorbed to the sediment; however at the end of the cycle treatment a low oxygen decreasing was observed stopping the aeration.

The low oxygen demand internal to the reactor did not clearly suggest the presence of an endogenous biomass in the SS-SBR. Thus the aeration was operated continuously and exogenous organic sources: Glucose and Lactose, at the beginning of two treatment cycles, were added. The first used because it is readily biodegradable and the second in order to test the biomass ability to biodegrade a no-readily biodegradable substrate.

Figures 5.37 shows the concentrations of the externally added organic substrates (glucose and lactose) in course of time, together with the TOC_F concentrations. Both substrates were degraded before the end of the cycle (14 days), when TOC_F values lower than 35 g m^{-3} have been detected. However, whereas glucose was completely degraded in about 80 hours (less than 1/4 time of the treatment cycle length), lactose was completely degraded only at the end of the cycle (336 hours).

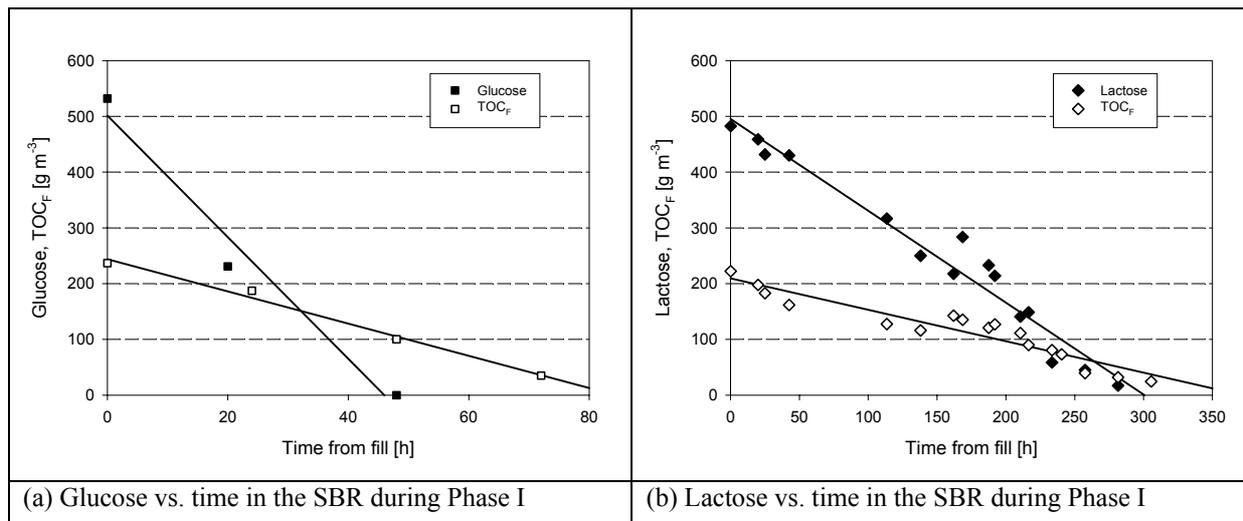


Figure 5.37. Biodegradation of the exogenous substrates added to the SS-SBR

The biodegradation of both substrates started immediately after the feeding phase, although glucose and lactose have a different biodegradability behaviour, confirming the biomass adaptation to different carbon sources.

The substrate degradation rates (calculated as the slope of the temporal depletion) were $11.10 \text{ mg l}^{-1} \text{ h}^{-1}$ and $1.64 \text{ mg l}^{-1} \text{ h}^{-1}$ for glucose and lactose, respectively. TOC_F degradation rates were $2.90 \text{ mg l}^{-1} \text{ h}^{-1}$ and $0.49 \text{ mg l}^{-1} \text{ h}^{-1}$ for glucose and lactose, respectively: the first value is five times greater than the second, according to the results obtained by Pitter and Chudoba (1990), working with activated sludge.

Hence the biomass activity on exogenous substrates were observed in the reactor, therefore the biomass ability to biodegrade endogenous substrates (TOC), and especially PAHs, was investigated, as reported below.

5.6.2.2 Phase II

The Phase I was aimed to start up the bioreactor while Phase II, III and IV were operated to investigate the PAHs biodegradation in the SS-SBR. Phase II was carried out for two months with a seven days cycle length and a VSR of 0.7 l resulting in a HRT of ten weeks.

In fig.5.38 the total PAHs profile versus time, observed in the last 6 cycles, is reported taking into account that the previous cycles were necessary to achieve the steady state conditions, usually considered equal to 3 HRT (Eweis et al. 1998).

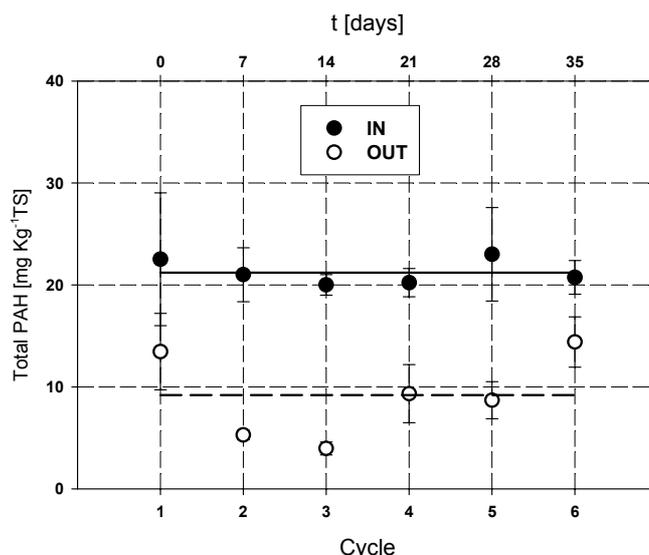


Figure 5.38. Average and standard deviation of total PAH measured in treated and untreated slurry during Phase II

The data showed a global removal efficiency of 54.4% (from about 21.2 mg kg⁻¹TS to 9.6 mg kg⁻¹TS) meeting the limit (10 mg PAHs kg⁻¹TS) imposed by the Italian law for the partial reuse of the sediment as building material. A decreasing removal efficiencies corresponding to the increase of aromatic rings was observed (tab. 5.XXIX).

Table 5.XXIX. PAH average concentrations in untreated and treated slurry during Phases II (\pm standard deviation).

Phase	Slurry	PAHs	PAHs	PAHs	PAHs
		2-3 rings [mg kg ⁻¹ TS]	4 rings [mg kg ⁻¹ TS]	5-6 rings [mg kg ⁻¹ TS]	total [mg kg ⁻¹ TS]
II	Untreated	3.71 \pm 1.12	7.18 \pm 0.45	10.26 \pm 1.70	21.16 \pm 1.20
	Treated	1.14 \pm 1.17	2.61 \pm 1.09	5.89 \pm 3.18	9.64 \pm 5.33

In fact, the concentrations of 2-3 rings PAHs in the fed and treated slurry were about 3.7 mg kg⁻¹ TS and 1.1 mg kg⁻¹ TS, respectively, with an average removal efficiency of 69.2 %. A very close result was observed on 4 rings PAHs, with a removal efficiency of 63.7 %, corresponding to initial and final concentrations of 7.2 mg kg⁻¹ TS and below 3 mg kg⁻¹ TS, respectively. Finally, PAHs with 5-6 rings, which are the main fraction, showed the lowest removal efficiency, close to 43 %, with initial and final concentrations of 10.3 mg kg⁻¹ TS and 5.9 mg kg⁻¹ TS, respectively (fig. 5.39).

The low Molecular Weight (MW) PAHs have been biodegraded with higher efficiency with respect to high MW PAHs. according to the literature data (Nocentini et al. 1996) observing

that the PAHs adsorbed to soil and sediment are biodegraded with different kinetics depending on the molecular weight and number of rings.

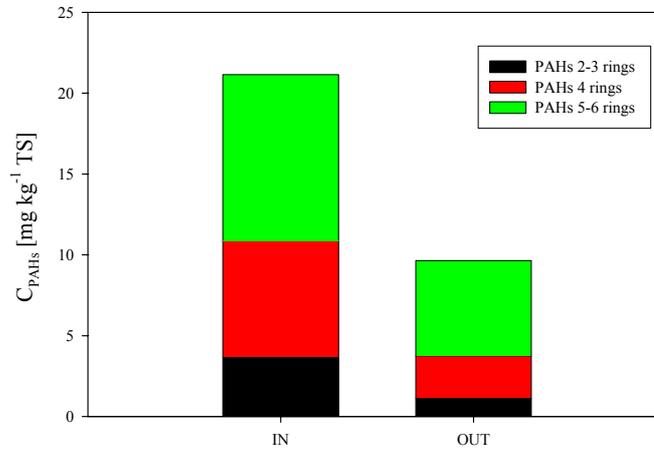


Figure 5.39. PAHs (grouped for rings number) concentrations in and out of the SS-SBR reactor during Phase II

The percentages among the three PAHs groups changes between In and OUT; in fact the PAHs with 5-6 rings increased from 46 to 59 %, 4 rings PAHs is constant while 2-3 concentration decreased from 25 to 12 %. Since the PAHs biodegradation can occur also in natural environment and observed that the biodegradation kinetics decrease increasing the PAHs rings number it is likely to find in natural environment higher percentages of PAHs with higher number of rings, as occurred for the sediment used in these experiments.

The above cited results on PAHs removal have to be attributed to the endogenous SS-SBR microbial activity since the analysis on resin trap, where off-gas reactor was collected, showed PAH concentrations below the analytical instrument detection limits, indicating negligible volatilisation and chemical reactions.

All parameters measured on fed and treated slurry during Phase II are summarised in tab. 5.XXX.

Table 5.XXX. TOC_D, CFU, TS, Ash and VS average concentrations in untreated and treated slurry during Phases II

Phase	Slurry	TOC _D [g kg ⁻¹ TS]	CFU [CFU kg ⁻¹ TS]	Total Solids %	Ash %	Volatile Solids %
II	Untreated	84.5 ± 1.7	3.7 10 ⁷	10.5 ± 1.9	7.9 ± 1.7	2.6 ± 1.5
	Treated	77.4 ± 4.0	1.2 10 ⁸	10.2 ± 0.8	8.4 ± 0.8	1.8 ± 0.6

From tab. 5.XXX a one order of magnitude increase of CFU is observed corresponding to a TOC_D decrease during each cycle equal to $6.5 \text{ g TOC}_D \text{ kg}^{-1} \text{ TS}$.

The CFU increase between the fed and treated slurry is very small if compared with a wastewater treatment but is nevertheless the index of the endogenous biomass presence confirmed also by the reduction of the TOC (8%) and the VS (30 %).

5.6.2.2.3 DO-STAT experiments during Phase II

Further investigations on biological activities of the slurry were carried out by means of a DO-stat provided by dotCOM s.r.l. As a matter of fact, during aerobic biodegradation of organic substrates oxygen is the final electron acceptor and therefore, if degradation takes place in the liquid phase, the dissolved oxygen (DO) is used up accordingly. The resulting Oxygen Uptake Rate (OUR) is therefore proportional to the degradation rate of the organic substrate.

The objective of the following experiments was therefore to measure OUR on slurry samples drawn from a SS-SBR reactor used in the bioremediation experiments.

In particular the DO-stat (standing for *static dissolved oxygen*) titration, a respirometric technique where the DO concentration in the biological sample is maintained close to a set-point value selected by the operator, was considered, using as dissolved oxygen source a diluted hydrogen peroxide solution. As a matter of fact, hydrogen peroxide is decomposed into oxygen and water by the hydroperoxidases enzymes present in most aerobic organisms. The oxygen released becomes available for microbial respiration, compensating respiratory uptake. Since DO is maintained constant, the amount of oxygen as peroxide titrated equals microbial oxygen consumption (biological oxygen demand), while the titrant flow rate is linearly proportional to the OUR of the sample. More details on DO-stat titration can be found in Young and Kuss (2000) and Rozzi et al. (in press). Up to now, this methodology has been mostly applied to assess the activity of heterotrophic and autotrophic microorganisms in activated sludge samples (Ficara et al. 2000, Rozzi et al. in press) and to assess the short term biodegradability of simple organic substrates (Ficara and Rozzi 2002).

The DO-stat technique was applied to evaluate the OUR profile in the bioslurry reactor during each cycle. Previous measurements by closed respirometry (Giordano et al. 2002) in similar experiments indicated a very high initial oxygen uptake. This phenomenon was found to be a chemical (abiotic) uptake due to reducing compounds, such as sulphides, as confirmed by addition of mercuric chloride (0.1%) to suppress biological activity. The chemical oxygen

uptake was very high (about 50 % of total oxygen demand) during the initial phase and the period of time needed to reach negligible OUR values is proportional to sediment dry matter (less than 2 hours for a 9.3% (w/w) solids concentration). Therefore, during the whole experimentation, respirometric tests were performed after 1-2 hours from the Fill phase of each cycle to avoid chemical interferences on OUR determinations.

The DO-stat technique was applied to monitor the OUR trend vs. time during the treatment cycle in the SS-SBR. Figure 5.40 reports OUR values related to these cycles. It can be observed that from an initial value of 6-8 mg_{O2} kg⁻¹ slurry h⁻¹, the OUR decreases down to a fairly constant value of about 1-1.5 mg_{O2} kg⁻¹ slurry h⁻¹, which was considered the endogenous respiration level. The latter was reached after approximately 48 h from the Fill operation.

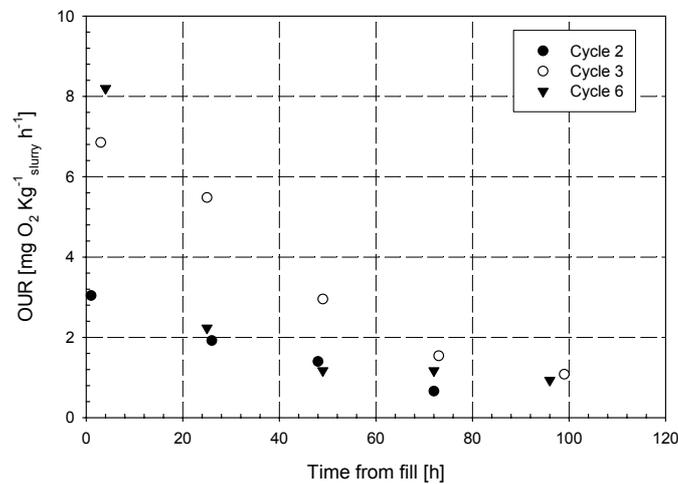


Figure 5.40. OUR vs. time during 3 SBR cycles of Phase II

These results indicated that the most exogenous activity was over after two days so the cycle length was shortened from 7 to 3.5 days.

5.6.2.2.4 Phase III

Phase III was carried out for four months with a three and half days cycle length and a VSR of 0.7 l, resulting in a HRT five weeks.

In fig. 5.41 total PAHs values vs. time in the fed and treated effluent slurry from the SBR during the last 16 cycles of Phase III are reported, taking into account that the previous cycles were necessary to achieve the steady state conditions, usually considered equal to 3 HRT (Eweis et al. 1998)

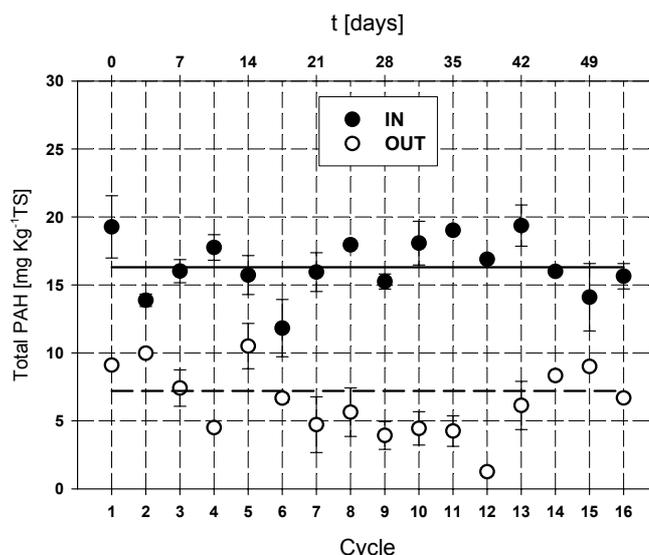


Figure 5.41. Average and standard deviation of Total PAH measured in treated and untreated slurry during Phase III

The PAH concentrations was reduced from 16.3 mg kg⁻¹ TS to 7.2 mg kg⁻¹ TS meeting the limit (10 mg PAHs kg⁻¹TS) imposed by the Italian law for the partial reuse of the sediment as building material. A decreasing removal efficiencies corresponding to the increase of aromatic rings was observed (tab. 5.XXXI).

Table 5.XXXI. PAH average concentrations in untreated and treated slurry during Phases III (\pm standard deviation).

Phase	Slurry	PAHs	PAHs	PAHs	PAHs
		2-3 rings [mg kg ⁻¹ TS]	4 rings [mg kg ⁻¹ TS]	5-6 rings [mg kg ⁻¹ TS]	total [mg kg ⁻¹ TS]
III	Untreated	3.97 \pm 0.45	5.26 \pm 0.89	7.10 \pm 1.19	16.33 \pm 1.77
	Treated	1.40 \pm 0.64	1.78 \pm 0.77	4.04 \pm 1.28	7.22 \pm 2.39

The concentrations of PAHs with 2-3 rings in the fed and treated slurry were 4.0 mg kg⁻¹ TS and 1.4 mg kg⁻¹ TS, respectively, with an average removal efficiency of 64.8 %. For 4 rings PAHs, a removal efficiency of 66.1% was obtained, from 5.3 mg kg⁻¹ TS to about 2 mg kg⁻¹ TS. Lowest removal efficiency was observed for 5-6 rings PAHs, close to 43 %, with concentrations from 7.1 mg kg⁻¹ TS to about 4 mg kg⁻¹ TS.

All parameters measured on fed and treated slurry during Phase III are summarised in tab. 5.XXXII.

Table 5.XXXII. TOC_D and CFU average concentrations in untreated and treated slurry during Phases III (± standard deviation).

Phase	Slurry	TOC _D [g kg ⁻¹ TS]	TKN [g kg ⁻¹ TS]	P tot [g kg ⁻¹ TS]	CFU [CFU kg ⁻¹ TS]	TS [%]	VS [%]
III	Untreated	86.5 ± 1.9	2.3 ± 0.3	1.2 ± 0.1	2.5 10 ⁷	9.2	2.2
	Treated	78.9 ± 1.7	2.1 ± 0.2	1.2 ± 0.0	1.9 10 ⁸	9.4	1.3

As in Phase II, a one order of magnitude CFU increase was observed and a corresponding 9% TOC_D decrease was measured.

In fig. 5.42 the OUR_S values (ranging between 9 mgO₂ kg⁻¹ slurry h⁻¹ and 2 mgO₂ kg⁻¹ slurry h⁻¹, close to the Phase II values) and the fitted OUR curve are reported.

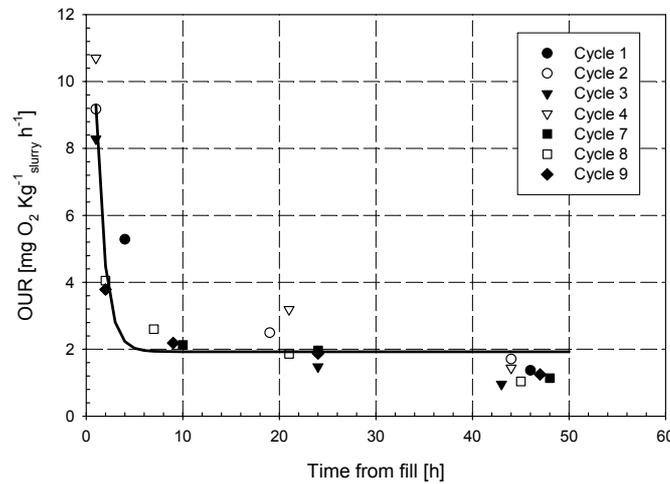


Figure 5.42. OUR vs. time during 7 SS-SBR cycles of Phase III

The parameters of relationship 2 (and the related 95 % confidence levels) were estimated using the least square error criterion ($R^2=88.3\%$) to fit the OUR_S data, obtaining:

$$OUR_{end} = 1.93 (1.44-2.41) \text{ mgO}_2 \text{ kg}^{-1} \text{ slurry h}^{-1}$$

$$OUR_{max} = 21.33 (7.75-34.92) \text{ mgO}_2 \text{ kg}^{-1} \text{ slurry h}^{-1}$$

$$k = 0.46 (0.21-0.71) \text{ h}^{-1}$$

In terms of total PAH removal efficiency, a 55.8% value has been evaluated (fig. 5.41). This result is close to those obtained during the Phase II, confirming that the length cycle shortening has no significant effect on PAHs removal because the endogenous conditions are reached before the end of the cycle length.

5.6.2.2.5 Phase IV

Phase IV was carried out for four months with a three and half days cycle length and a VSR of 0.7 l, resulting in a HRT five weeks adding 0.5 g of Lactose at the beginning of each treatment cycle.

Particularly it was investigated the Lactose effect as stimulator of biological surfactants that can influence both the efficiency removal and the treatment time. In fact previous researches have shown that both synthetic and natural surfactants (biosurfactants) can improve PAHs removal efficiencies (Aronstein et al. 1991 and Providenti et al. 1995). Further researches (Desai and Banat 1997) have demonstrated the natural biosurfactants production in the biological mineralization of hydrocarbons; these natural compounds are more biodegradable, well working with a wide range of temperature and salinity than the synthetic surfactants and less toxic than synthetic surfactants. The biosurfactants are normally produced by many microorganisms working on hydrophobic compounds (Miller et al. 1995); they stimulate the PAHs desorption make them bioavailable. The most important parameters affecting the biosurfactants production are the TOC:TKN ratio ranging between 16:1 and 18:1 and the pH 6.5-8, the oxygen content and the salinity. In a real scale Lactose could be substituted by agro-industrial or zootechnic waste having an high amount of organic matter reducing the treatment cost.

Figure 5.43 shows PAHs vs. time in the fed and treated slurry during the last 16 cycles of Phase IV.

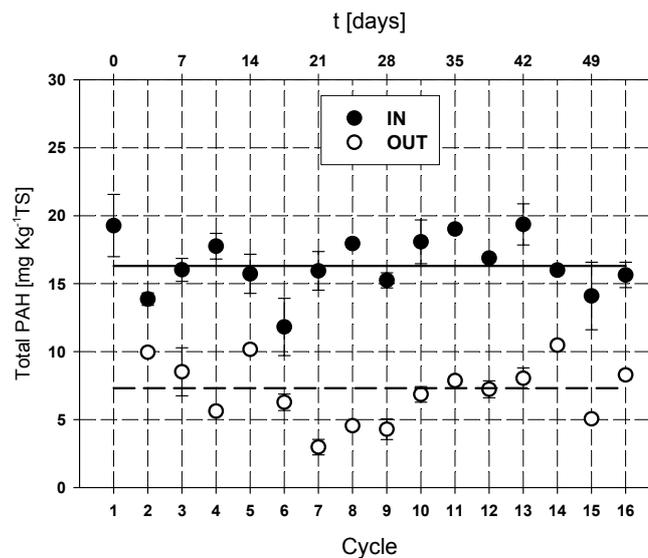


Figure 5.43. Average and standard deviation of Total PAH measured in treated and untreated slurry during Phase IV

The total PAH concentrations had just been reduced from 16.3 mg kg⁻¹ TS to 7.3 mg kg⁻¹ TS, with a 55.6 % removal efficiency close to those obtained in the previous phases: no significant enhancement of the reactor performances were observed, although the added lactose was biodegraded during each cycle.

The removal efficiencies observed for PAH with different rings are shown, whose values are equal to 69.8 %, 64.6 % and 41 % for 2-3 rings, 4 rings and 5–6 rings, respectively, whereas the related concentrations are reported in tab. 5.XXXIII.

Table 5.XXXIII. PAH average concentrations in untreated and treated slurry during Phases IV (\pm standard deviation).

Phase	Slurry	PAHs	PAHs	PAHs	PAHs
		2-3 rings [mg kg ⁻¹ TS]	4 rings [mg kg ⁻¹ TS]	5-6 rings [mg kg ⁻¹ TS]	total [mg kg ⁻¹ TS]
IV	Untreated	3.97 \pm 0.45	5.26 \pm 0.89	7.10 \pm 1.19	16.33 \pm 1.77
	Treated	1.20 \pm 0.33	1.86 \pm 0.77	4.20 \pm 1.54	7.26 \pm 2.39

All parameters measured on fed and treated slurry during Phase IV are summarised in tab. 5.XXXIV.

Table 5.XXXIV. TOC_D and CFU average concentrations in untreated and treated slurry during IV

Phase	Slurry	TOC _D	TKN	P tot	CFU
		[g kg ⁻¹ TS]	[g kg ⁻¹ TS]	[g kg ⁻¹ TS]	[CFU kg ⁻¹ TS]
IV	Untreated	86.5 \pm 1.9	2.3 \pm 0.3	1.2 \pm 0.1	2.5 10 ⁷
	Treated	81.7 \pm 1.6	2.1 \pm 0.2	1.1 \pm 0.1	4.4 10 ⁸

Once more, a CFU increase (one order of magnitude) and a TOC_D decrease were observed. The CFU increased from 2.5 10⁷ CFU KgTS⁻¹ to 4.4 10⁸ CFU KgTS⁻¹, the same order of magnitude of the Phase III without Lactose adding; thus lactose had not increased biological activity in the reactor.

In tab. tab. 5.XXXV the TS, Ash and VS in the fed and treated slurry of Phase IV are reported resulting as in the previous phases in a VS reduction.

Table 5.XXXV. TS, ash and VS average concentrations in untreated and treated slurry during Phase IV

Phase	TS	Ash	VS
	[%]	[%]	[%]
IV	9.2 \pm 1.1	6.9 \pm 1.1	2.2 \pm 1.1
	9.3 \pm 0.8	8.1 \pm 0.7	1.2 \pm 0.1

The related concentrations are listed in Table 3. OUR_S measured during Phase IV are shown in fig. 5.44.

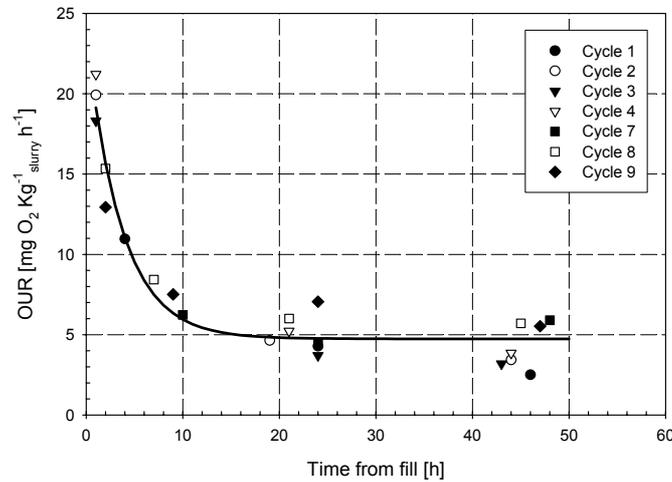


Figure 5.44. OUR vs. time during 7 SS-SBR cycles of Phase IV

The data in fig. 12 have been fitted by means of equation (2), obtaining the following parameter values and related 95% confidence levels ($R^2 = 94.7\%$):

$$OUR_{end} = 4.74 (3.98-5.50) \text{ mgO}_2 \text{ kg}^{-1} \text{ slurry h}^{-1}$$

$$OUR_{max} = 18.95 (15.85-22.06) \text{ mgO}_2 \text{ kg}^{-1} \text{ slurry h}^{-1}$$

$$k = 0.12 (0.08-0.16) \text{ h}^{-1}$$

From the initial maximum value, the OUR decreased to a fairly constant value of about 5 $\text{mgO}_2 \text{ kg}^{-1} \text{ slurry h}^{-1}$, which was assumed to be the endogenous respiration level (OUR_{end}).

As expected, the OUR_{max} and OUR_{end} were higher than the values obtained in the previous Phases since the lactose added to the SBR increased both the exogenous and endogenous oxygen uptake rates; moreover, lactose addition implies an increase of the time required to reach endogenous conditions, from about 10 h (measured in Phase III) to approximately 24 h in Phase IV.

The morphology of the microorganisms present in the sediment dredged by Porto Marghera by means of microscopy techniques resulted very difficult for the physico-chemical particles characteristics. Hence sonification was used as samples pre-treatment preliminarily fixed in paraformaldehyde at 4 % (w/v). The same samples after a dilution with PBS a saline-phosphate buffer, colored with DAPI, were observed by means of a microscopy with epifluorescent lamp. The picture of the most important microorganisms aggregates found out in the slurry drawn by the SS-SBR are reported in fig. 5.45.

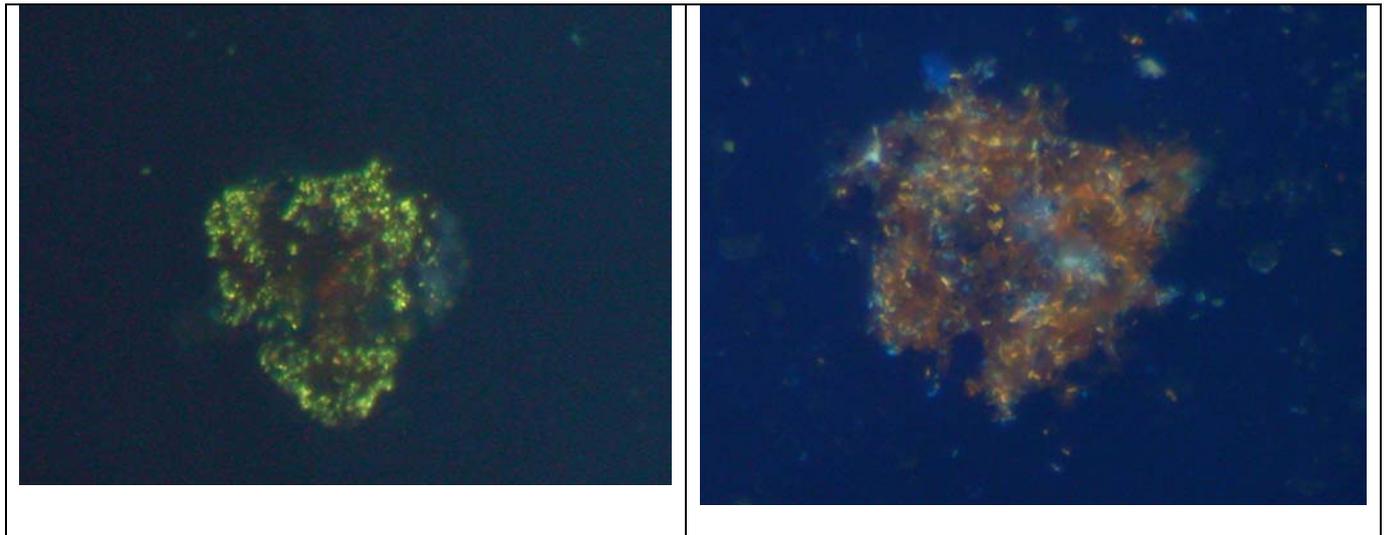


Figure 5.45. Microscopical microorganisms photo(1000X). The solid matrix is orange

Finally, the applicability of SBR biological systems to treat PAH contaminated lagoon sediments have been presented. PAH biodegradation has been tested with a lab-scale SBR operated in different conditions, obtaining an average total PAH removal efficiency close to 55 % for the different operation conditions investigated as reported in fig. 5.46.

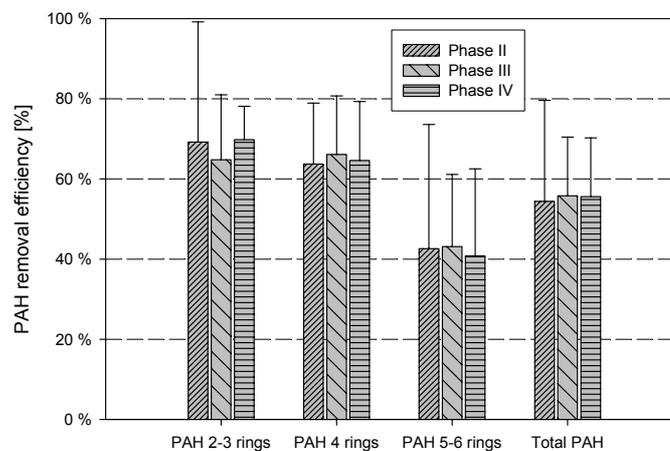


Figure 5.46. PAHs removal during Phase II, III and IV of PAHs contaminated sediment SS-SBR treatment

Finally results from this research indicate that PAH removal during bioslurry treatment is stable and not dependent on the addition of carbon source and HRT (in the range of 35-100 days). Nevertheless the presence of a PAH residual concentration met the limit (10 mg PAHs kg⁻¹TS) imposed by the Italian law (*Protocollo di Venezia*) for the partial reuse of the sediment as building material in all the experimental set-up tested.

5.6.2.3. Tenax desorption experiments

The concept of bioavailability was not well known during PAHs contaminated sediment bioremediation by means of SS-SBR. Fortunately the original sediments used in the SS-SBR experiments was stored under anaerobic conditions and still contain the original concentration of PAHs. The additional one year of ageing of the sediment will be small compared to the age of the pollution in the sediment ranging from tenths of years to more than 50 years. Thus the bioavailability estimation for the Porto Marghera sediment was pursued by means of Tenax beads extraction as explained in the previous item on Landfarming.

Tenax extractions was carried out at 20 and 60 °C in order to evaluate respectively the fast, slow and very slow PAHs bioavailable fractions. The results of the Tenax extractions for the Porto Marghera sediment have been reported below in tab. 5.XXXVI.

Table 5.XXXVI. Tenax extractions result on Porto Marghera sediment

PAHs fractions	[mg Kg TS⁻¹]	[%]
PAHs fast bioavailable	5.0 ± 0.5	26.8
PAHs slow bioavailable	3.5 ± 0.1	19.0
PAHs very slow bioavailable	10.1 ± 4.0	54.2
Total PAHs	18.6 ± 1.5	

The Tenax extraction have shown that the 45 % of the PAHs adsorbed to the sediment are fast and slow bioavailable while the 55 % is very slow available.

Cornelissen et. al. 1998, with respect to PAHs contaminated sediment, have showed that the extent of degradation in bioreactors can be roughly predicted by means of Tenax extraction at 20 °C, that estimate the PAHs rapidly desorbing fraction. They observed that rapidly desorbing PAH is preferentially degraded, probably because the slowly desorbing material is less available for the degrading microorganisms even if for most PAHs, the percentage of degradation is larger than the percentage rapidly desorbing with the ratio (PAH degradation)/(rapidly desorbing fraction) is 1.4 ± 0.5 , and the reason might be that a minor part of the slowly desorbing fraction has also been degraded during bioremediation.

The PAHs removal efficiencies obtained with the lab scale SS-SBR were close to 55 % in the three operational set up investigated showing, partially in accordance with Cornelissen et al. results, that the fast, slow a small part of very slow PAHs desorbing fractions have been probably biodegraded in a bioreactor. Unfortunately it was not possible to carry out the Tenax

extractions also on the samples drawn by the SS-SBR to investigate which changes in the desorbing fractions occur during a bioslurry treatment.

5.6.2.4. PAHs biodegradation profiles using a landfarm by means of a three compartment model

The three compartment model have been applied to the Porto Marghera sediment in order to observe the PAHs biodegradation in a passive bioremediation technology as it has been presented in the previous prf on Landfarming.

The results of the Tenax extraction reported in tab. 5.XXXVI are used in the three compartment model as sizes of the biodegradable fraction as:

- Ffast=PAHs fraction extracted with Tenax at 20 °C
- Fslow= PAHs fraction extracted in the following Tenax at 60 °C
- Fvery slow= PAHs residual fraction after both Tenax extraction

And implemented in the following three compartment model:

$$C_t = (F_{fast} \cdot e^{-k_{fast} \cdot t} + F_{slow} \cdot e^{-k_{slow} \cdot t} + F_{very\ slow} \cdot e^{-k_{very\ slow} \cdot t}) \cdot C_0$$

The PAHs biodegradation profiles have been reported below in fig. 5.47 along with the limit for the class B of the *Protocollo di Venezia*.

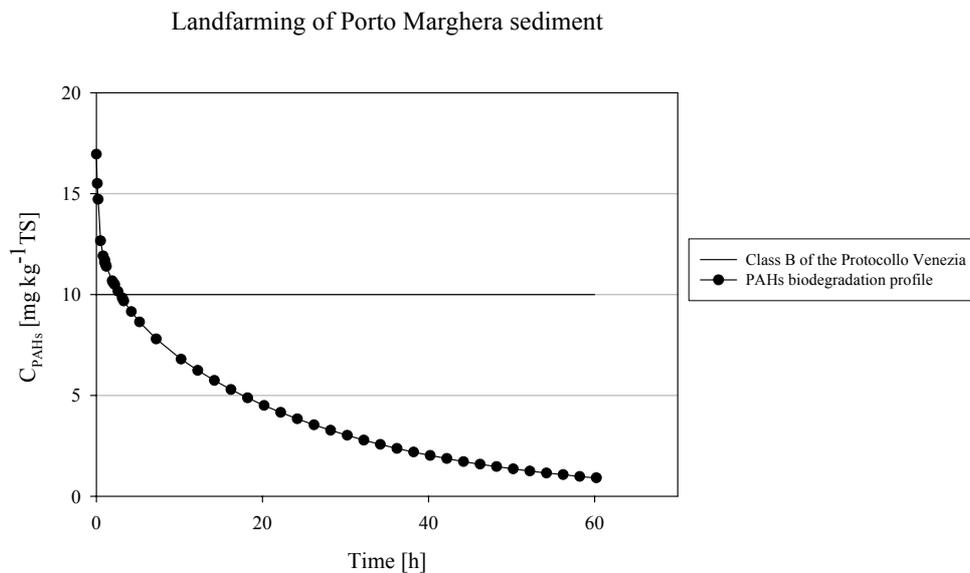


Figure 5.47. PAHs biodegradation occurring in a landfarming treatment plant obtained with the application of a three compartment model

The PAHs biodegradation profile reported in fig. 5.47 has shown that the application of a passive bioremediation system will take 10 years to reach the PAHs removal efficiencies of the SS-SBR. However the prediction model proposed above can be roughly used to estimate the number of year needed to meet the target value imposed by the regulations that respect to the Porto Marghera sediment will be between 3-4 years treatment. After this time the treated sediment will meet the target values imposed by the *Protocollo di Venezia* for the partial reuse of the solid matrix.

5.6.3 Conclusion

The applicability of a sediment slurry SBR to treat PAH contaminated lagoon sediment has been presented in this item. PAHs biodegradation has been evaluated, using a lab-scale SBR, testing several operating conditions of the reactor (e.g. HRT). Oxygen Uptake Rate, measured by DO-stat titration technique, has enabled the monitoring of the in-reactor biological activity, providing also useful information in the selection of the reactor operating conditions. *OUR* profile, modelled as the sum of two terms, related, respectively, to exogenous and endogenous respiration, could be also useful for the aeration equipment design in order to avoid air pumping (e.g. energy) waste.

A total PAH efficiency removal close to 55 % was achieved both for the long (98 days), middle (70 days) and the short (35 days) HRT of the SBR; moreover tough the addition of lactose (external carbon source) in the SBR had increased the biological activity, as clearly shown by the *OUR* tests results, no further improvement of the PAHs efficiency removal was observed.

The Tenax extractions procedure as proposed by Cornelissen et al. 1997 have been used for the same sediment to evaluate the PAHs bioavailability. The result have shown that of the total PAHs amount adsorbed to the sediment the 26.8 % is fast available the 19.0 % is slow available and the residual is very slow available.

Finally the application of the three compartment model based on the Tenax results for the prediction of the PAHs biodegradation occurring in a landfarming treatment plant have been pursued. The result have shown that 10 years landfarm treatment are necessary to reach the 55 % of PAHs removal efficiencies observed with the SS-SBR while 3-4 years are needed to meet the target value of the Italian law *Protocollo di Venezia*.

Chapter 6

6 Application of the Principles of Life Cycle Assessment to Evaluate Contaminated Sediment Treatment Chains

6.1 Introduction

Since hundreds of years sediments have been regarded as a resource normally used as soil improver, but industrialisation and emissions of contaminants due to anthropogenic activities have lead partly to the accumulation of pollutants in sediments converting them into material that has to be managed or treated in a way that risks to the environment are reduced. In order to avoid further pollution of other environmental compartments, coastal zones and locations in a river basin the decision about the management of contaminated dredged material should be based on a river basin. One mission of SedNet is to design a guidance for sustainable sediment management (SSM) on a river basin scale.

One of the aims of SedNet Work Package 4 is to derive a series of recommendations on sediment treatment processes and define a strategy to assess the treatment chains under the concept of sustainability. For this purpose a detailed description of different treatment technologies with their underlying working principle and an estimation of costs is presented in chapter 3 of this thesis.

The objective of this chapter is to define the possibilities of the application of the principles of the Life Cycle Assessment (LCA) as a tool to evaluate environmental impacts from a holistic perspective of contaminated dredged material treatment chains and to support sustainable decision making.

Environmental evaluation methods such as risk assessment (RA) of the potential environmental risks of contaminated dredged material and environmental impact assessments (EIA) to evaluate the impacts of a given project or site are well established procedures of environmental evaluation which are widely applied for decision making and have been

integrated to regulations at national and European levels (EU Directive 85/337/EEC, EU Directive 97/11/EC). While those methodologies in practice normally are focused on the evaluation of environmental issues on a plant scale (site-specific), elements of LCA can be useful to supply valuable information for process comparison and assessment not normally considered in EIAs, e.g. impacts on global, regional and local scales which would enable to account for almost all relevant effects and to perform a fair comparison.

Furthermore this chapter aims to introduce a system-oriented perspective to the way of assessing contaminated sediment treatment chains in order to complement the parcelled site-specific environmental information that is considered along with economic and social criteria in decision-making procedures.

This topic was developed in collaboration with prof. eng. Wolfgang Calmano and eng. Eduardo Arevalo at the Environmental Science and Technology at the Technical University of Hamburg – Harburg (Germany) for the Sednet Work Package 4.

6.2 Sustainability and life cycle thinking methodologies to evaluate processes for treating contaminated dredged sediment

The concept of sustainable development implies that human activities and industrial systems must be designed in a way that the possibilities of future generations to meet their needs must not be compromised by today's practices (WCED 1987). Sustainability sets the challenge to use existing or develop processes and implement them in a way that they are economically feasible, environmentally friendly along the complete chain of processes on a local but also global scales, and acceptable by stakeholders and society in general. Additionally, it implies the application of assessment strategies for process evaluation according to such criteria.

The implementation of the elements of sustainability requires the involvement of different sectors on local as well as regional and global scales, e.g. governments, local authorities, the public and stakeholders, and has implications in temporal and spatial dimensions. An example of efforts to promote the involvement of the public in environmental issues of concern is exemplified in the new EU-Directive to improve public participation in environmental impact assessments (SEA). The notion of sustainability supposes that environmental and social criteria have to be incorporated along with economic criteria in the

management structure of processes, and on the other hand in all the steps of the treatment process chains.

The efficiency of a remediation process is normally related to its ability to remove or immobilise the initial load of contaminants or secure the dredged material at reasonable costs. In terms of the spatial scale this means that the environmental criteria in treatment and remediation processes are viewed from a site specific (or problem specific) perspective considering only the pollutants of concern in a given situation, the local legal framework, public acceptance usually under strong economic constraints. This situation in many cases lead to a parcelled view of environmental issues where decision makers do not consider all consequences that could occur outside their area of responsibility resulting in sub-optimal allocation of resources and end-of-pipe type decisions.

Besides costs and environmental criteria, an important point to be considered is that the decision about remediation or treatment is also influenced by strong pressure from the public and stakeholders or from the willingness to avoid such pressure. In fact public acceptance plays an important role in decision-making processes. The problem is that in general quantification of social issues remains a difficult task due to the lack of science based methods to quantify them. Furthermore, one problem is that public interest and perception might change quickly due to specific events, e.g. catastrophes. It is also a fact that regulations to deal with contaminated sediments are usually managed locally, and fragmented legislation adds complexity to the task of managing contaminated sediments on a river basin scale (Förstner 2002). To tackle the problem of decision-making under the notion of sustainability in this context of temporal and high spatial variability, as it is the case in Europe, tools are needed that provide transparency to decision-making procedures under such complex boundary conditions.

The afore mentioned considerations give insight regarding the complexity of trying to include economic, environmental and social criteria on decision making procedures regarding treatment technologies. As Thöming (2002) points out the inclusion of sustainability elements into practice means the inclusion of a “multidimensional space of parameters rather than clearly defined targets” of treatment and remediation processes.

The inclusion of environmental criteria requires suitable assessment tools to identify and quantify the whole range of impacts that a treatment chain can cause on the environment. This means that traditional site-specific assessment approaches have to be expanded to include a comprehensive assessment over the complete process chain, i.e. *life-cycle*; from extraction of

resources from nature to the final steps of disposal of waste streams including long term effects.

A life-cycle thinking approach gives the decision-maker a broader view of the problem and the possibility to make strategic decisions regarding environmental issues from a system-wide standpoint. As schematically presented in fig. 6.1, life-cycle thinking moves away from the philosophy of end-of-pipe measures and even goes a step further than pollution prevention strategies in the sense that it introduces a holistic way of thinking not on a process- but on a system-level. It is not a reactive approach towards regulations but a pro-active one, because it is oriented to the analysis of the process life-cycle to identify potentials for process improvement protecting environmental assets for which no criteria such as threshold values exist. It represents a step towards more sustainable ways in dealing with treatment and remediation processes.

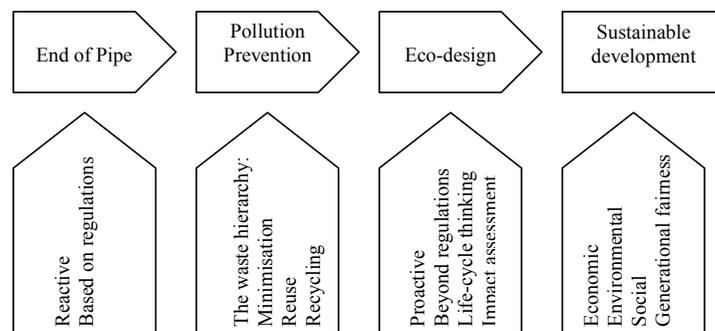


Figure 6.1. Evolution of environmental issues from a treatment perspective (adapted from Mihelcic et al., 2003)

This way of thinking should be also applied to contaminated dredged material management strategies. In the context of contaminated dredged material treatment an approach based on life-cycle thinking enables a fair process comparison because of the inclusion of the whole system and the interactions between the life-cycle stages. Not only impacts due to the technology under consideration are quantified but also indirect effects in activities carried out elsewhere, i.e. effects due to consumption of energy and raw materials, emissions along the complete life-cycle until disposal. By this way a picture of material and energy flows is drawn in order to improve integration of process chains and take into account both distant effects of local actions and local effects to distant actions. For instance, when comparing a number of dredged sediment treatment processes feasible in a given situation as shown in chapter 3 it could be possible that the alternatives considered, while achieving the treatment targets to protect the local environment, cause greatly different indirect impacts along the process life-

cycle. Only if these aspects are taken into account a fair comparison of treatment chains can be performed.

The need to include the elements of LCA to enable a sustainability oriented approach has been recognized in previous years. For instance the Aquatic Sediment Expert Centre in the Netherlands, AKWA, conducted a study about the economic and environmental implications of treatment of contaminated dredged sediments for defining a government position regarding this issue. A LCA based approach was employed to quantify part of the environmental indicators for the comparison of processes (AKWA 2000).

6.3 The Life-Cycle Assessment

The inclusion of environmental criteria in process assessment remains a complex problem for which suitable tools have to be developed and adapted to decision-making procedures.

Among the approaches based on life-cycle thinking, the Life Cycle Assessment (LCA) is an environmental assessment tool that enables the quantification of environmental burdens and their potential impacts over the complete life-cycle of process systems, i.e. “from cradle to grave”. It evaluates the environmental performance of the system and enables coupling the system material and energy balances to environmental impacts.

Although the principles of LCA date back to the 1970s and were mostly related to an efficient use of energy in process engineering, LCA has gained wider application in the 1990s due to the transparency and standardisation of its methodology (EN ISO 14040, ISO/DIS 14042, ISO/FDIS 14041, ISO/CD 14043). LCA has been mostly applied for the assessment of products, services and processes. It finds also applications in the phases of process selection, design and optimisation (Azapagic and Clift 1999). LCA can be used as a tool in strategic environmental impact assessment (EIA) (Tukker 1999). Traditionally EIA and LCA were regarded to be incompatible as the former is normally regarded as a site-specific study at a process level while the latter has been considered typically as global or location independent assessment. Nevertheless it has been shown that even both approaches have their origins in different scientific communities and are often used in different contexts. The elements of LCA supply valuable information for process comparison to complement tools in EIA and risk assessment (Tukker 1999). Conversely, also assessment tools in LCA can be complemented with other environmental assessment tools not normally applied in LCA to enhance its capabilities, reduce uncertainty of results and expand the scope of the assessment.

Such synergy between process assessment tools enables the application of elements of LCA to evaluate dredged sediment treatment chains as part of a holistic assessment approach.

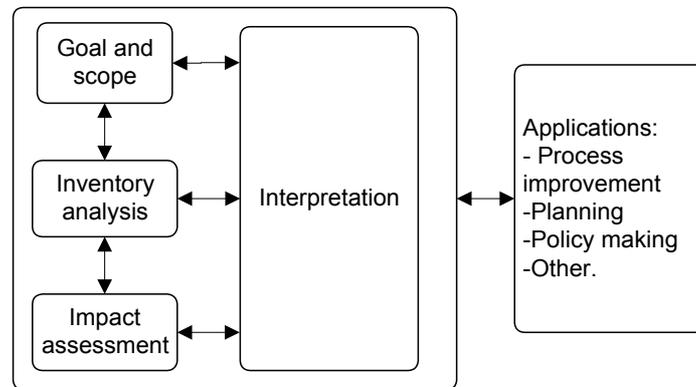


Figure 6.2. Phases of the Life-Cycle Assessment (EN ISO 14040)

The phases of the standard LCA methodology are presented in fig. 6.2. The phase of goal and scope definition requires defining the system to be studied, i.e., its boundaries, function, processes to be included, etc. In the inventory phase the material and energy balances of the process life-cycle is calculated. The conversion of mass and energy flows into potential environmental impacts is performed in the impact assessment step. In the interpretation phase findings of the inventory and impact assessment are evaluated to draw conclusions to support decision-making. The LCA methodology has been documented in the ISO 14040-14043 standards, which provide the basis for conducting and critically reviewing such studies.

LCA has been traditionally oriented towards the following objectives (Azapagic and Clift 1999):

- a) The identification of the steps of a process that could be improved in terms of their environmental performance;
- b) providing information in terms of environmental performance to help decision-makers to choose between different processes or locations;
- c) defining relevant environmental indicators to evaluate processes;
- d) product marketing, e.g., eco-labelling, product declaration, etc.

Due to the historical development of the methodology, industry had taken a leading role in the implementation of LCA for analysing product chains, marketing strategies, process assessment/optimisation and product design. Since the 1990s a new paradigm for technology assessment has been adopted and initiatives were undertaken by industry and the public sector that make use of the principles of LCA pursuing the following aims:

- a) to support the environmental assessment of processes from a cross-media approach, that is, targeting to protect all environmental compartments;
- b) to identify and quantify environmental indicators for decision-making to introduce them into new environmental policies or to promote discussion about environmental problems;

The strengths of LCA are the calculation of impacts out of the complete material and energy balances, its well structured standardised methodology, the consideration of the complete life-cycle of a process and its compatibility with decision-support schemes. Nevertheless, due to the complexity of process life-cycles a comprehensive LCA study is a very resource intensive process. To interpret LCA results and transfer them into a decision-making scheme, which is indeed the ultimate goal of an LCA study, several stakeholders must be involved actively. These are part of the operational limitations for the application of the standard LCA methodology into assessment approaches of treatment chains.

Attempts have been made to streamline the LCA methodology and to improve its applicability. In many cases a compromise between the strengths and limitations of LCA has derived in life-cycle thinking approaches in which the data intensity and time requirements of the study are greatly reduced by applying generic data from databases for non-critical processes in the life-cycle in order to improve its operational cost effectiveness and achieve a rapid and effective implementation (Breedveld 2001, Graedel 1998).

6.4 On the potential uses of Life-Cycle approaches to assess dredged treatment chains – a perspective

So far the case has been made for life-cycle-thinking as a comprehensive way of mapping environmental impacts of a process along its entire life and its potential to complement site-specific environmental assessment tools to provide information when deciding among alternative treatment chains. Although the need of applying life-cycle thinking to evaluate the environmental aspects of sediment treatment chains has been recognised in former years (Stokman and Bruggeman 1995), the application of a Life-Cycle (LC) based approach to sediment treatment chains is by no means straightforward, mainly due to the diversity of sediment treatment processes [ref. Chapter 3], the different possible scenarios resulting from each of them, the difficulty to quantify their impacts along the complete life-cycle and including long term effects.

In order to apply a LC based methodology to dredged sediment treatment chains the following aspects should be taken into account:

- a) Holistic thinking: inclusion of indirect impacts.

In contrast to accounting for environmental impacts on a plant level or site-specific scale, an approach based on life-cycle thinking enables the identification of treatment technologies which produce increased impacts on the whole life-cycle in order to reduce the risk of “exporting” a problem from a local to a regional or global scale and to account for indirect effects associated to dredged sediment treatment chains. Furthermore, the possibility of selecting a technology that reduces a particular pollutant in a location but increases the emission of this or other pollutant elsewhere in the life-cycle could be avoided (Azapagic 1999).

- b) System definition and long term effects.

As mentioned before in this chapter the prerequisite to perform an assessment of dredged sediment treatment chains based on a life-cycle thinking is the extension of the system boundaries to include impacts caused not only in the treatment process itself but also along the life-cycle of the process system. This implies the inclusion of activities that occur upstream the treatment chain, i.e. extraction, production and consumption of resources, and to follow the products until the end of their life-cycle including the evaluation of long term effects of the management option applied, i.e. confined disposal facilities, disposal on land, beneficial use, etc.

In a LCA based methodology different choices can be made when defining the system to be studied, and these choices inevitably determine the results and validity of the conclusions. The system boundaries should be chosen according to the purpose of the study, nevertheless this is not a straightforward task as one could initially think. For instance, when comparing disposal of sediments with brick-making with contaminated dredged material at a plant level, it is clear that brick making is more intensive in energetic resources. A holistic way of thinking should include the interactions with surrounding systems; e.g. bricks produced out of dredged material not only save natural resources by substituting natural clay with sediment but it must be considered that the bricks produced could replace bricks produced elsewhere in a region. When the picture is viewed from a holistic perspective, possible effects on a region can be identified which are otherwise difficult to assess from a plant level. System definition plays a significant role when trying to compare options such as treatment and beneficial use with disposal techniques from a holistic perspective. In the former cases impacts are strongly

related to material and energy consumption, while for the latter space demand, monitoring and risks to the surrounding environment and groundwater over time are key environmental aspects.

Another example of how the selection of system boundaries influence the outcome of an LCA-based study is for instance the decision to exclude dredging operations from the system boundaries. For the case of highly contaminated sediments, dredging activities are expected to cause higher environmental impacts which should not be neglected.

Because impact assessment methods normally applied in LCA have been historically developed for the assessment of production processes, they are suitable to assess dredged sediment remediation chains like treatment and processing for beneficial use. For the case of management options such as disposal, in which risks are relevant over long periods of time, additional tools are required, e.g. site specific information, monitoring and the generation of models that are able to reflect the potential impacts to the surrounding environment and long term effects.

The definition of system boundaries and time frame in the context of life-cycle thinking for sediment treatment chains is also congruent with the holistic way of thinking at a river basin scale discussed within SedNet. For instance the Conceptual Basin Model approach proposed to support river-basin management aims to coordinate parcelled sediment assessment into a holistic river basin management strategy (Heise 2003, Apitz and Power 2003). It provides a system-wide perspective to define basin objectives, set priorities on management actions in order to make strategic decisions taking the “big picture” into account. This would provide the basis for a better allocation of resources in the river basin and better targeting of management actions by means of cost-benefit analyses (Apitz and Power 2003). Similarly, life-cycle thinking provides the frame for a system-oriented approach to the assessment of dredged sediment treatment chains. It would enable strategic decisions regarding the most suitable treatment option and consider not only their feasibility to meet site-specific environmental criteria such as threshold levels of contaminants but also its implications on local, regional and global scales.

c) Quantification of relevant life-cycle indicators.

Table 6.I summarises some of the impact categories considered in life cycle assessment studies. For the case of dredged sediment treatment chains, the most relevant environmental impacts that potentially could be caused can be classified as follows:

- Impacts related to inputs to the life-cycle: for instance, depletion of abiotic resources, i.e. energy and raw materials; demand of space for disposal or ripening.
- Impacts related to outputs and emissions: effects of toxic substances in the dredged material potentially contributing to human or eco-toxicity; release of pollutants to nearby environment due to activities as relocation or even upland or sub-aquatic disposal; emissions of global or regional relevance that occur over the process life-cycle, e.g. global warming, acidification mostly related to the consumption of energy, transport and raw materials.

Table 6.I. Impact categories used in life cycle assessment studies

Input/Output related	Impact category	Spatial scale of effects
Input related	Depletion of abiotic resources, e.g. energy carriers for fuel, electricity production, minerals, raw materials, etc.	Global
	Depletion of biotic resources, e.g. wood, fishery, etc.	Global, regional
	Land demand, land competition and landscape transformation.	Regional, local.
Output related	Climate change, e.g. gaseous emissions responsible for global warming.	Global
	Depletion of ozone layer	Global
	Human toxicity	Regional, local
	Eco-toxicity, e.g. toxic emissions to the different environmental compartments (air, water bodies, soils and sediments).	Regional, local
	Acidification	Regional
	Eutrophication, i.e. enrichment of nutrients in water bodies which affect the structure and function of aquatic eco-systems	Regional, local
	Noise	Site specific
	<i>Waste heat</i>	Site specific

The structure of impact assessment in LCA normally relies on models that enable the quantification of impacts of materials and energy balances and relates them to a functional unit. Traditionally in LCA methods have been applied to account for *potential* environmental impacts, in particular for input related impact categories and impacts due to emissions of global or regional relevance, e.g. climate change, acidification, etc.

The assessment of emissions of toxic substances in LCA is subjected to large uncertainties that could undermine the ability of LCA to assess sediment treatment chains. This is due to the difficulty to model the mechanisms by which toxic substances could cause an effect on the environment (Schulze et al. 2001, Tukker 1998). For instance, multimedia fate and transport

models are commonly used. Nevertheless, the inclusion of environmental processes such as bioaccumulation, biomagnification, diffusive transport, degradation, etc. is difficult. Furthermore, there is uncertainty and lack of reliable data about physical-chemical and ecotoxicological data of the properties of more than 100 000 chemicals used in industry, many of which can end up accumulating in sediments as they act as sinks of pollutants. Information about distribution coefficients, bio-concentration factors, degradation rates in water, air, sediment and soil, diffusion rates between compartments, (from water column to sediments, or volatilization, etc) are lacking for most substances, and in many cases parameters calculated from generic estimates which introduce additional uncertainties to the results produced.

Due to the uncertainties in models applied in impact assessment of toxic emissions in LCA, this step can only be regarded as deriving *directional* indicators based on an inventory of contaminants and their concentrations (Tukker 1998, Potting and Hauschild 1997). This is an initial step of a long term process and as models are refined and methods improved the quality of the information that LCA delivers will be improved to the same extent. In Europe the new mechanism for control of chemicals, the Registration, Evaluation and Authorisation of CHemicals (REACH) will provide data on the long run which reduce the uncertainty of such toxicity assessment models. Nevertheless, due to diffuse sources of pollution, from a cost effective view it is unrealistic to determine complete inventories of all contaminants possibly present in dredged material. This is why methods such as biological effect-based assessment (BEBA) relying on bioassays are powerful tools to account for toxic effects, synergistic effects, and bioavailability that cannot be determined with methods based on chemical concentration inventories as in impact assessment in LCA (Tukker 1998). The integration of effect-oriented approaches based on bioassays into life-cycle impact assessment of toxic emissions is a step that would improve the ability of LCA to support the selection of a sediment treatment chain.

d) Sustainable decision-making and the life-cycle assessment.

Decision-making under the notion of sustainability is a complex problem where multiple criteria accounting for environmental, economic and social factors have to be considered. This task is seldom straightforward because of the different nature of information involved to select among dredged material management options. Therefore, tools to support the decision-maker become more necessary. Among such tools Multiple-Criteria Decision Analysis

(MCDA) enables breaking down complex problems into their main factors and a systematic elicitation of preferences within a structured framework to support decision-making.

As an assessment tool LCA should be seen in a broader context, as a tool that provides environmental information for decision-making procedures. By definition LCA considers only environmental issues. Economic and social aspects are not part of LCA. LCA is also able to provide part of the relevant environmental information needed for decision making. Figure 6.3 illustrates a possible role that LCA can play in order to supply information to complement other assessment methodologies, to account for all relevant environmental criteria needed to select and to compare dredged sediment treatment chains.

The contribution of an LCA approach to sustainable decision-making is not only limited to the quantification of usually neglected environmental impacts but also to the structure of the decision-making scheme itself. As LCA normally deals with multiple environmental criteria its framework to support decision-making regarding environmental issues is compatible with MCDA tools and can also benefit from them (Seppälä et al. 2002).

Tools such as the Analytical Hierarchy Process (AHP) (Saaty 1996) enable a structured way of elicitation of weights among the relevant criteria, i.e. economic, environmental and social.

The implementation of such tools would help the decision maker to improve the quality of the resulting decisions and to make the decision-making process more transparent. It would increase the decision-makers' understanding of the problem and enable to combine globally relevant issues with site-specific information, to assign preferences and to make compromises between the different criteria in a transparent way.

LCA and MCDA tools provide a framework to support decision-making but at the end it is the decision-maker who sets the preferences of the different criteria. Such preferences depend on site specific conditions e.g. regulations, space availability for disposal of sediments, budgets, etc. So it must be clear that even for similar problems the outcome of the decision-making process will vary depending on the boundary conditions. Nevertheless the way to reach such decisions could be reviewed and critically evaluated in an easier way.

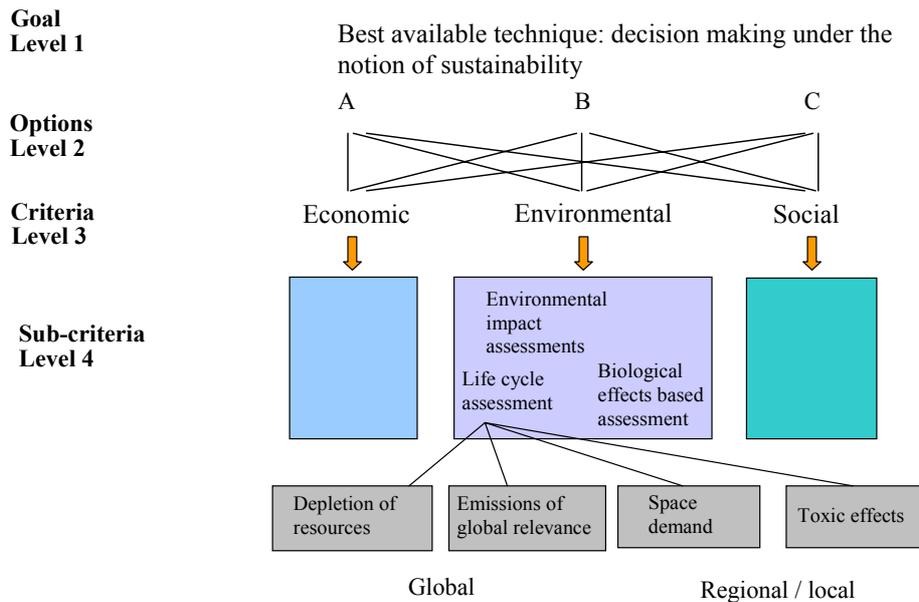


Figure 6.3. Hierarchical representation a decision-making problem considering economic, environmental, social criteria and the contribution of a LCA approach

6.5 Application of the principles of LCA to assess dredged sediment treatment chains

Up to now comparisons among different technologies are based on site-specific criteria as process efficiency, feasible budgets, space demand/availability and market availability. The best technology is the one that better satisfy such criteria. Life cycle thinking introduces a new point of view in the comparison of the different technology analyzing the environmental performance of the process in a long term perspective along the all life cycle. The analysis of the environmental performance of treatments chains for contaminated sediments must evaluate the complete set of impacts, considering all relevant processes causing effects including those at the other locations. Furthermore, links and interactions with other systems, indirect environmental impacts related to auxiliary material use, water and energy consumptions (i.e. electricity and heat) and waste production must be taken into account.

The application of the principles of LCA to contaminated dredged sediment treatment chains is illustrated by means of two examples as shown in fig. 6.4:

1. Mechanical sand separation and dewatering process combined with reuse of sand fraction and silt fraction disposal.
2. Mechanical sand separation and dewatering process combined production of bricks out of the silt fraction.

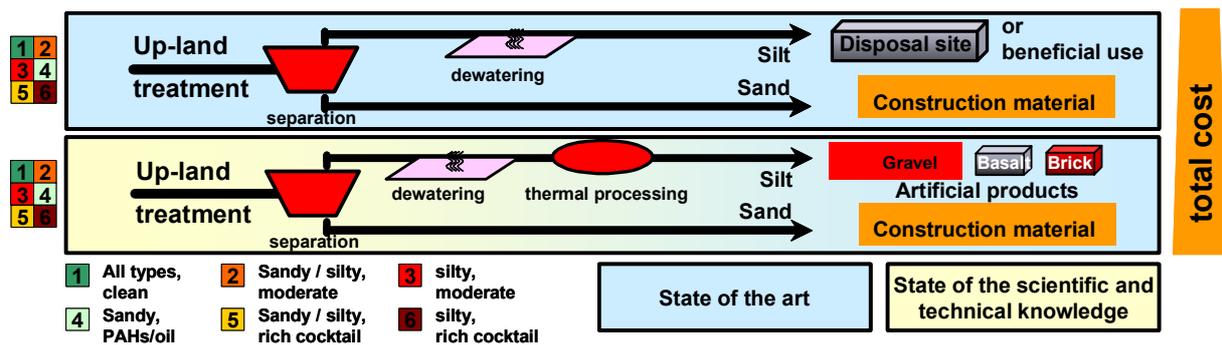


Figure 6.4. Sediment treatment chain used for the LCA application (AKWA 2000)

The objective of this section is to illustrate with two treatment chains for contaminated sediment the kind of information that can be gained by using a life-cycle thinking approach and to give an insight about what could it be useful for in terms of a limited set of impact categories. It is not within the scope of this work to perform a complete LCA study on the two treatment chains detailed above but to assess them in terms of depletion of resources, demand of space and impacts due to global warming and acidification (see tab. 6.I). Due to the limitations in data availability important impact categories listed in tab. 6.I such as eco-toxicity will not be included in the study.

6.5.1 Treatment chain 1: Mechanical sand separation and dewatering process combined with reuse of sand fraction and disposal of the silt fraction

The mechanical sand separation and dewatering sediment treatment chain is applied with the following objectives:

- Separation of sand and silt to decrease the amount of highly contaminated sediments to be disposed (saving disposal capacity);
- To decrease the potential impacts to the environment due to pollutants in sediments by confinement of the silt fraction (reduction of potential mobilization effects).

An example of mechanical sand separation process is the *MEchanical Treatment of HARbour sediment (METHA)* in the Port of Hamburg. The process consists of rotary screens to remove coarse material, hydrocyclones and fluidized bed classifiers to separate sand from silt, lamellar thickeners and screen belt press to dewater the silt fraction. A detailed explanation of

the process as well as the flow diagram can be found elsewhere (Detzner et al. 1998, Detzner et al. 2005).

The goal of this section is to evaluate the performance of the process along the life-cycle in terms of the following factors, i.e. stressors:

- Energy consumption.
- Raw material consumption.
- Transport of sediment fractions.
- Space demand for disposal of silt.

The definition of the system boundaries is schematically presented in Figure 6.5. There also an overview about the structure of the system of study is given along with the most important material and energy flows. As stated in the previous section the definition of the system boundaries plays a significant role on the outcome of the study, it is clear that a comprehensive assessment of the process life-cycle should not omit relevant operations, e.g. dredging operations, waste water treatment or disposal of the contaminated silt fraction.

For the purpose of this example the focus of the study is the evaluation of the performance of the mechanical separation process in terms of consumption of resources (energy and materials), transport and space demand; and not to perform a complete LCA including all possible environmental issues associated to the treatment chain. Due lack of information, it was neither possible to include all processes of the treatment chain nor to consider the impacts of the contaminated material before and after the treatment. In this sense the results of this environmental assessment are incomplete and therefore should be taken with caution.

The definition of the system boundaries shown in fig. 6.5 implies that the following operations were not considered as being part of the system:

- a. Dredging operations. Environmental impacts due to dredging of sediments, e.g. remobilisation of contaminants, are not considered in the assessment, nor materials, energy consumption, transport or emissions during dredging.
- b. Waste water treatment . Impacts due to material and energy consumption and due to the discharge of treated waste water and solids are not included
- c. Disposal of the contaminated silt fraction. Potential impacts due to disposal of the silt fraction are not considered.
- d. Production and maintenance of capital goods.
- e. Disposal of coarse material separated from the sediment.

PAHs and Heavy Metals Contaminated Sediment: Bioavailability, Mobilization, Biological and Phisycy-Chemical Treatment

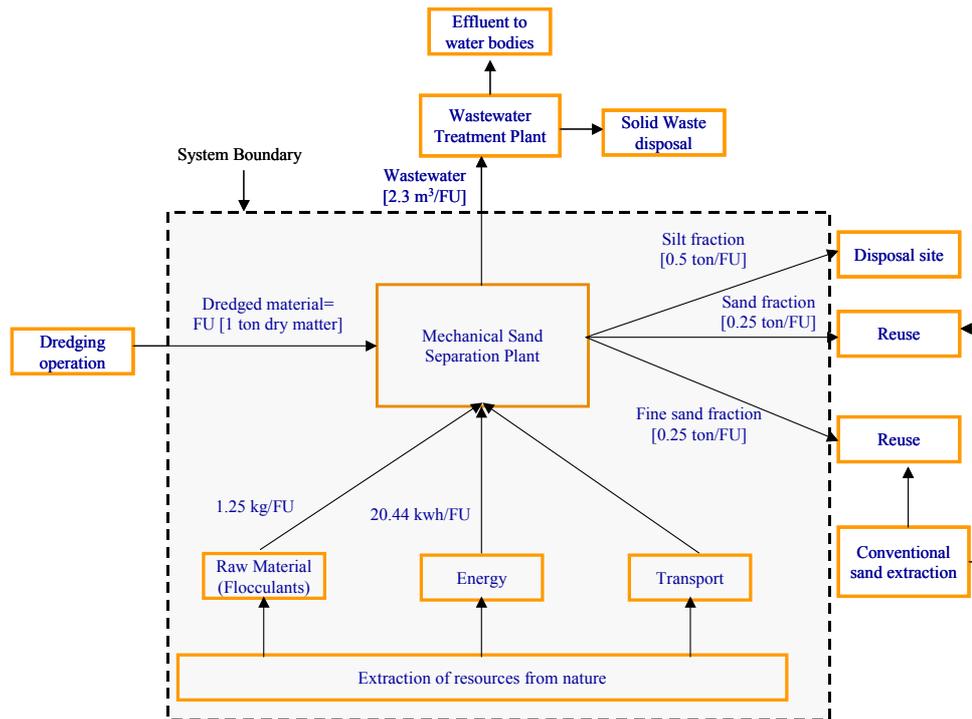


Figure 6.5. System boundaries of the Mechanical Sand Separation and dewatering process combined with reuse of sand fraction and silt fraction disposal

The *functional unit* (FU) to which all process streams will be related is 1 ton of dry matter with 50 % by weight of silt and clay entering the separation process. The main components of the process life-cycle are presented in fig. 6.6.

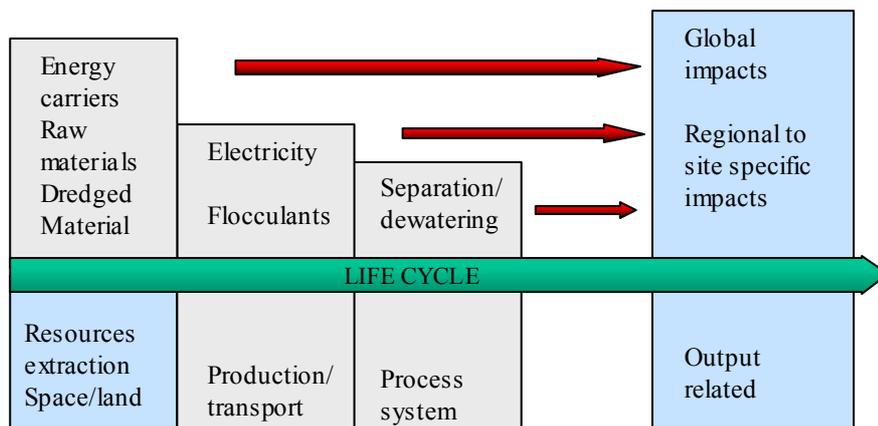


Figure 6.6. Life-cycle components of the mechanical sand separation and dewatering process

The initial sediment composition is assumed as 50 % of silt and 50 % of sand. The fractions separated in the plant are summarised in tab. 6.II.

Table 6.II. Composition of the original dredged material

Fraction	Size	Percentage [%]	Destination
Silt	< 20 μm	50	Disposal
Fine sand	< 63 μm	25	Reuse
Sand	> 63 μm	25	Reuse
Coarse material		Negligible	--

The technical data to calculate environmental impacts according to the stressors mentioned above are summarised below.

- Energy consumption. Comprises the electricity for operating the process units (hydrocyclones, screen belt press, etc). The total energy consumption of the process is 20.44 kWh / FU.
- Raw material consumption. Is associated to the consumption of flocculants in the sedimentation and screen belt press to dewater the silt. It is estimated to be 1.25 kg / FU.
- Transport. Includes the transport of the sediment fractions to their final destination. The sand and fine sand fractions are assumed to meet the requirements for being reused as building material (Detzner et al. 1998). 40 % of the sand is assumed to be transported 2 km to the silt fraction disposal site and used instead of natural sand for a separating and drainage layer. It is assumed that the 60 % of the sand fraction and 100 % of the fine sand fraction are transported to 10 km from the separation plant to be reused as a building material.
- Space demand for the disposal of silt fraction. The space demand for the disposal site is an important issue because as pointed out above, one of the aims of this technology is the reduction of sediment sent to the disposal site. The silt fraction is disposed in silt hills (Detzner et al. 2005). The disposal site is assumed to be located at 2 km from the separation plant. The contaminated silt is landfilled with sand used as drainage material in ratio 5 to 1 (personal communication by Mr Detzner, 2004). For the functional unit (FU=1 ton dry matter entering the plant), 500 kg of silt is separated (0.25 m^3 assuming a density of 2000 kg m^{-3} for a water content of 50%) and 100 kg of sand (0.05 m^3 assuming a density of 2000 kg m^{-3} for a water content of 50%). Therefore, the total space consumption in the disposal site can be estimated to be about $0.3 \text{ m}^3/\text{FU}$.

The disposal site which includes systems for leachate control, collection and treatment is not within the system boundaries. A more detailed description of the disposal site is described in Detzner et al. 1998 and Detzner et al. 2005.

For the life-cycle inventory, the calculation of emissions due to transport operations, energy production and raw material production were performed using the databases detailed in tab. 6.III.

Table 6.III. Data sources employed for the life-cycle inventory

	Category of data	Type of data	Database / Source
Land transport, truck	Transportation	Average	BUWAL 250, 1998
Flocculants	Basic chemicals	Average	BUWAL 250, 1998
Electricity West Germany	Energy system		BUWAL 250, 1998
Mechanical sand separation	Process	1 site	METHA process, annual report 2002

The impact categories were selected for the impact assessment step (LCIA) to evaluate the environmental performance of the process in terms of the stressors chosen. The impact categories chosen can be divided in two main groups:

- a) Input related categories
 - i. Depletion of abiotic resources (DAR): accounts for the consumption of materials, fuels for energy productions, e.g. electricity, heat.
 - ii. Demand of space.
- b) Output related categories
 - i. Global warming (GW)
 - ii. Acidification (A).

The first categories account for the resources potentially consumed while the others are indices of the potential impacts due to emissions. The categories and models to be implemented in the impact assessment step are summarised in tab 6.IV. The impact categories whether input or output related have a differentiated spatial relevance, e.g. of global, regional or local relevance which is also detailed in tab 6.IV.

Table 6.IV. Impact categories and models applied for the LCIA

Impact category	Spatial scope	Characterisation factor/ Model	Impact category unit per FU
Depletion of abiotic resources	Global	Depletion of abiotic resources potential (ADP): Reserves and reserves production ratio (Guinee 1995)	Expressed in MJ of fossil energy
Space demand	Local	Volume of fractions disposed	m ³
Global warming	Global	Global warming potentials (GWP): calculated for a time horizon of 100 yrs (Houghton et al.1994 and 1995)	kg CO ₂ equivalents
Acidification	Regional /local	Acidification potential (Hauschild and Wenzel 1998)	kg SO ₂ equivalents

With the previous information a LCA model was created in SimaPro v.5.1. This model enables the quantification and the contribution of the life cycle stages among the impacts categories. The results of impact assessment of the stressors “Energy consumption”, “Transport” and “Raw material consumption” are reported in fig. 6.7.

The separation of sand and fine sand by the process for reuse as construction material means that it could replace an equivalent amount of sand extracted by conventional processes, e.g. surface mining. In fig. 6.7, besides the impact calculations for the stressors afore mentioned, the scenario where impacts are avoided by the replacement of sand as construction material, and its transport to the construction site (assumed distance: 5 km) is presented as “Avoided impacts due to sand and fine sand reuse”.

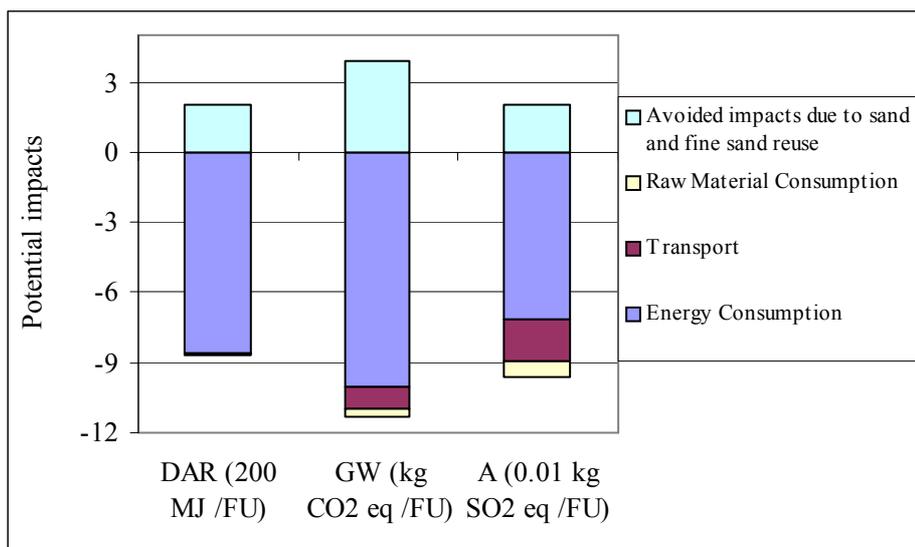


Figure 6.7. Impact assessment results for the mechanical sand separation and dewatering process and for the scenario of replacement of conventionally extracted sand (DAR: depletion of abiotic resources, GW: global warming, A: acidification)

In fig. 6.7 each bar represents the result of each impact categories considered, i.e. depletion of abiotic resources, global warming and acidification for the defined stressors along the life-cycle. The impacts of the treatment chain are presented in the negative region of the vertical axis. In the positive region the quantification of impacts avoided due to sand and fine sand reuse is shown. From the information presented in fig. 6.7 it is possible to evaluate which stressor is the main contributor in each impact category in terms of absolute value. The contribution expressed on percentage of the total impact score is presented in fig. 6.8.

As expected, from the stressors considered the one causing higher impacts in the three impact categories is energy consumption, i.e. electricity of which up to 60% is produced out of fossil sources (coal, lignite, oil, etc.). This fact is reflected in the contribution to global warming and acidification which show a similar tendency as depletion of abiotic resources.

Figure 6.8 shows that the impacts avoided by separating sand and fine sand and reusing it are estimated to be between 20 to 35% of the total impacts associated to the treatment chain. This information is normally not taken into account when evaluating a process on a plant-level. Hence, it is an important information that gives a clearer picture of potential benefits and implications of the process from a system-wide perspective.

As mentioned before in this example neither the assessment of toxic substances in the silt fraction nor the fate of those pollutants in the disposal site have been considered. The lack of data on the fate of toxic substances in the disposal site limits the use of an LCA approach to evaluate toxic impacts; to perform such assessment site-specific investigations are needed.

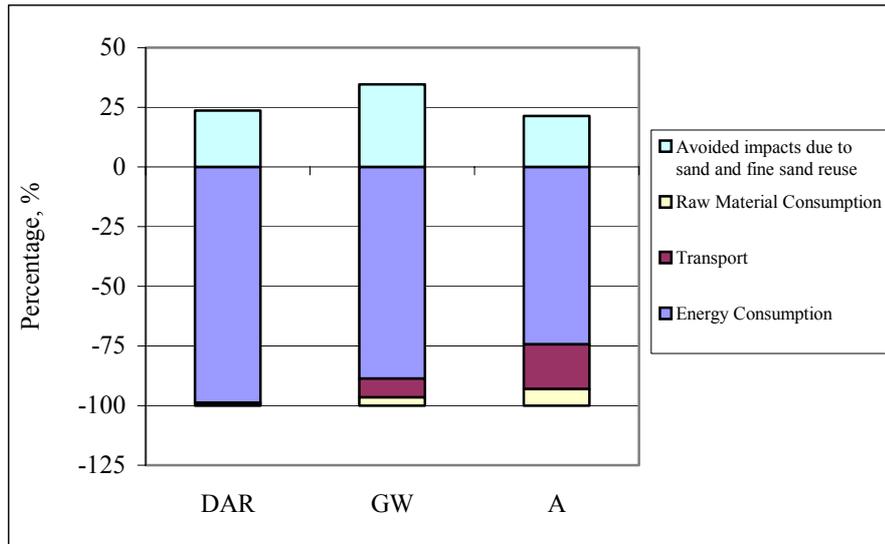


Figure 6.8. Contribution in percentage of the stressors to the impact categories (DAR: depletion of abiotic resources, GW: global warming, A: acidification)

The information in fig. 6.7 and 6.8 show the environmental impacts of operations such as transport or the environmental benefits of reusing the sand produced in the plant. This approach also can be useful to evaluate different scenarios of the operations involved in the process. For instance to calculate impacts due to transport operations for different destinations of the material to be reused or disposed. Furthermore, to assess the operations with higher contributions to the impact categories in order to optimise the steps where improvements will have higher effect on the environmental performance of the process.

6.5.2 Treatment chain 2: Mechanical sand separation and dewatering process combined bricks making

In the second example a thermal process to produce commercial bricks using the silt fraction after sand separation and dewatering process is evaluated. The description of the treatment chain is performed in chapter 4 of Bortone (2005), so it will not be explained in detail here. The aim of the process is:

- Production of bricks using 67% of sediment silt fraction and 33% of natural clay.
- Thermal treatment and immobilization of contaminants in the solid matrix.
- To avoid the disposal of the silt fraction in order to eliminate the demand of space for disposal.

The sediment treatment chain described above is applied in Hamburg by HZG-Hanseaten-Stein Ziegelei GmbH, that has succeeded in developing a process for manufacturing high

value ceramic building materials, e.g. wall bricks, building bricks, cobblestones (Öko-Institut 1996).

The sediment silt fraction is separated from the sandy fraction by the process described in section 6.5.1. The operation units of the brick making process consists of pre-drying of sediment silt fraction; mixing of the silt with natural clay; shaping, drying and firing of the bricks (personal communication Ulbricht, 2004)

As in section 6.5.1 the goal is to evaluate the performance of the life-cycle in terms of a limited number of stressors, being the following:

- Energy consumption.
- Raw material consumption.
- Space demand.

The system boundaries are presented in fig. 6.9 along with the most important material and energy flows while fig. 6.10 shows the main components of the process life-cycle. In this example the focus will be put on the mechanical sand separation process and the production of bricks out of the resulting silt fraction. As in the previous section the objective is not to perform a complete LCA but to evaluate the performance of the in terms of impacts due to consumption of energetic resources, materials and transport operations.

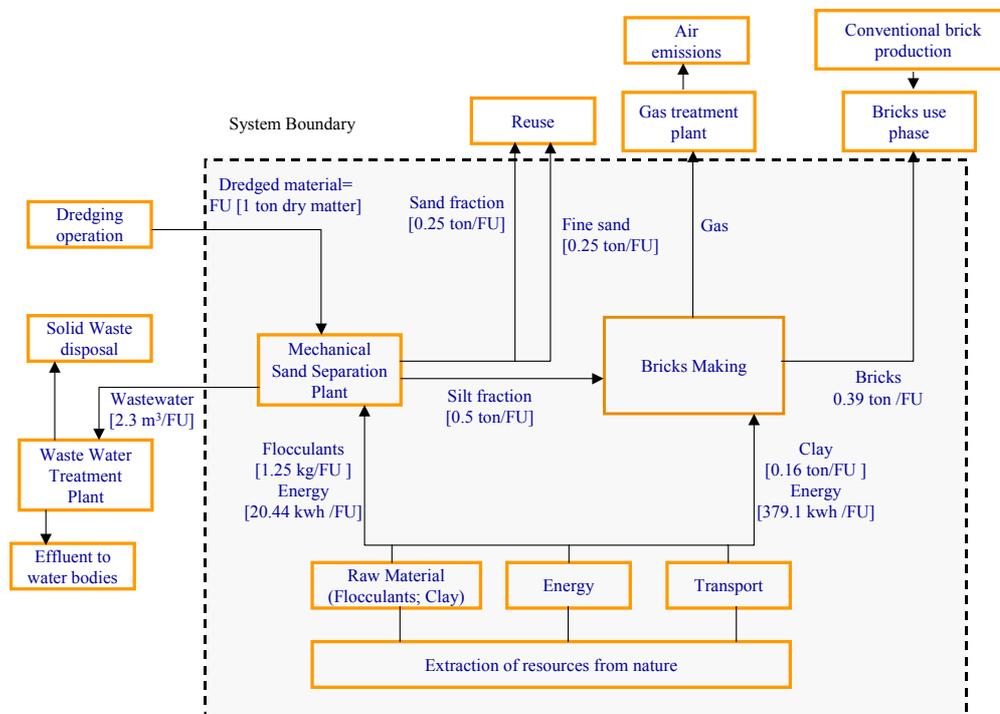


Figure 6.9. System boundaries of Mechanical sand separation and dewatering process combined brick making

The operations that are not considered as being part of the system of study are:

- Dredging operations
- Waste water treatment
- Gas treatment in the brick making process.
- Production and maintenance of capital goods.
- The use phase of the bricks produced and their disposal after use.

The functional unit (FU) to which all process streams are related is 1 ton of dry matter entering the separation and dewatering process with 50 % of silt and clay which is used to produce 0.39 ton of bricks per FU.

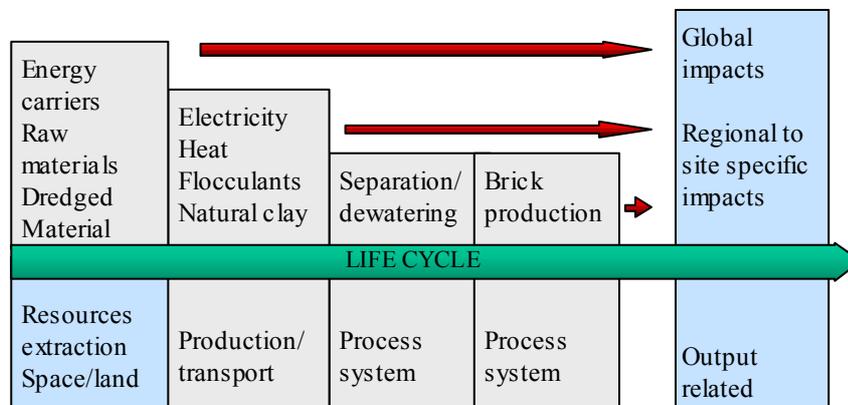


Figure 6.10. Life-cycle components of the mechanical sand separation with dewatering process combined with brick making

For this example, the factors considered to evaluate the performance of the process are:

- Energy consumption. Comprises the electricity and heat needed to operate sand separation and the brick making processes. The total electricity demand of the separation process is 20.44 kWh/FU and 58.40 kWh/FU for brick making. The heat energy, used in the brick production, is 565.94 kWh/FU.
- Raw material consumption. It includes flocculants for the sand separation process (1.25 kg/FU) and natural clay to be mixed with the sediment silt fraction. The demand of natural clay is 265 kg/FU.
- Transport. It includes the transport of sand and fine sand fractions from the separation process (reused as building material) and bricks. All those materials are assumed to be used at 10 km from the production process.

Table 6.V summarises the sources to calculate the emissions of all the processes included in the system. The same impact categories as in section 6.5.1 were considered and a LCA model developed in SimaPro v.5.1 was used for the calculations.

Table 6.V. Data sources employed for the life-cycle inventory.

	Category of data	Type of data	Database / Source.
Land transport, truck	Transportation	Average	BUWAL 250
Flocculants	Basic chemicals	Average	BUWAL 250
Energy production	Energy system	Average	BUWAL 250
Electricity mix Germany	Energy system		VDEW
Mechanical sand separation	Process	1 site	METHA
Bricks factory	Process	1 site	HZG

Similarly to section 6.5.1 the results of the impact assessment was calculated for the stressors considered for the same impact categories as in section 6.5.1, i.e. depletion of abiotic resources, global warming and acidification. The results are presented in fig. 6.11 as impact scores and fig. 6.12 as the relative contribution of the stressors in each impact category . Additionally, two scenarios calculating the “avoided impacts” due to the replacement of sand as construction material and bricks produced by conventional process were performed and shown in fig. 6.11 and 6.12 as “Avoided impacts due to sand and fine sand reuse” and “Avoided impacts due to the replacement of bricks from conventional process”.

The information for calculating the impacts due to the conventional brick making process out of natural clay was taken from the eco-inventories prepared by the Öko-Institut 1996. The consumption of energy to produce a ton of bricks by the conventional process is approximately 1310 MJ of heat produced out of natural gas combustion, 150 MJ electricity, that is, 511 MJ/FU and 59 MJ/FU respectively.

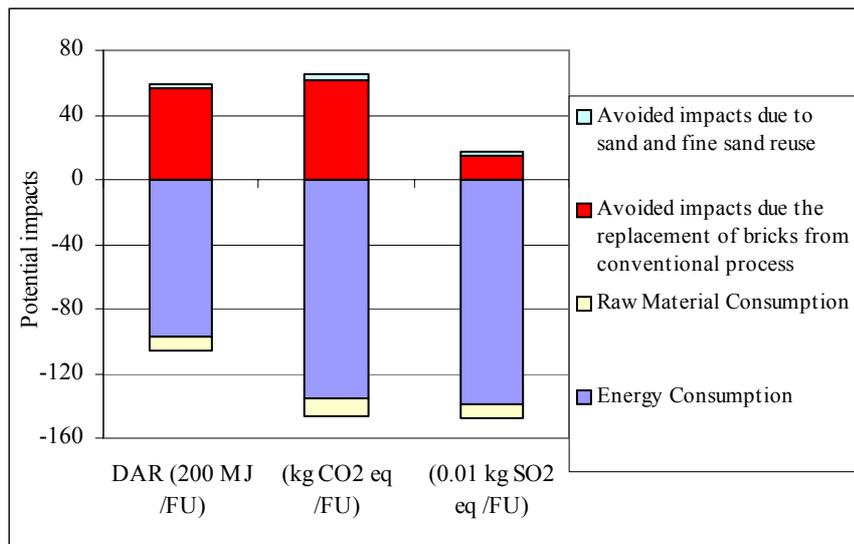


Figure 6.11. Impact assessment results for the mechanical sand separation and dewatering process and for the scenario of replacement conventional bricks in treatment chain 2 (DAR: depletion of abiotic resources, GW: global warming, A: acidification)

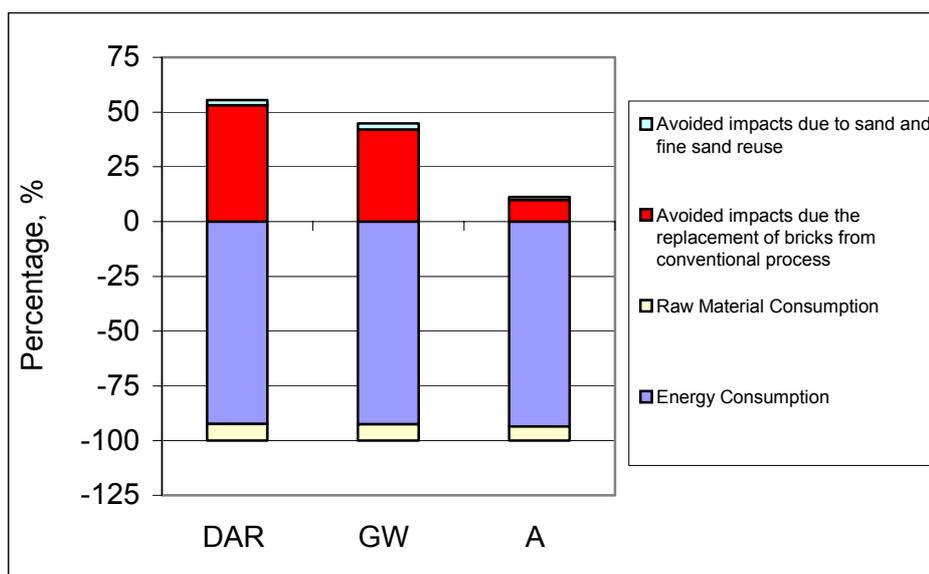


Figure 6.12. Contribution in percentage of the stressors to the impact categories in treatment chain 2 (DAR: depletion of abiotic resources, GW: global warming, A: acidification)

As brick production is a highly energy intensive process, the results show that energy consumption is the main stressor in the process life-cycle for the three impact categories presented, while impacts due to transport operations produce negligible impacts and thus are not presented in figures 6.11 and 6.12.

A more detailed comparison of the impacts to produce 0.39 t of bricks by means treatment chain 2 with impacts due to conventional production of bricks using clay as raw material is

presented in fig. 6.13 for depletion of abiotic resources. The score of treatment chain 2 (negative region of the vertical axis) is higher than the ones occurring at conventional brick-making processes due to the additional energy needed in the pre-drying of the silt fraction entering the plant with higher water contents.

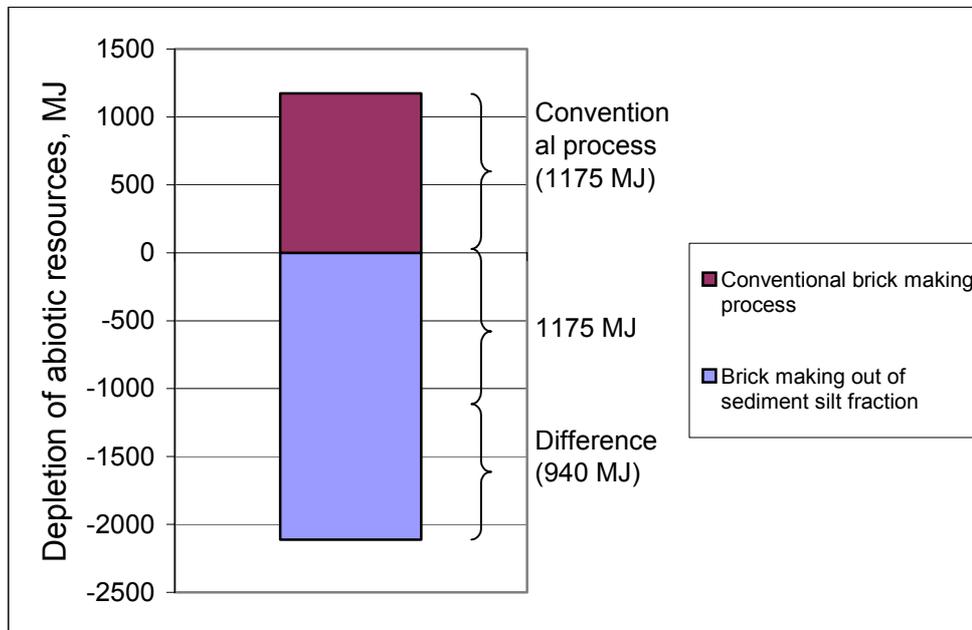


Figure 6.13. Depletion of abiotic resources to produce 0.39 ton bricks by means of a conventional brick manufacturing process and by treatment chain 2

As in section 6.5.1 the LCA based approach enables to take into potential benefits of applying treatment chain 2 which do not occur at the level of the plant. For instance from fig. 6.13 it can be observed that although the production of bricks by treatment chain 2 is more resource consuming than a conventional brick making process (with a difference in DAR in the range of 940 MJ), benefits of applying treatment chain 2 in case of successful commercialisation of the bricks produced are the avoidance of the disposal of the silt fraction coming from the mechanical sand separation process, the reduction of environmental risks by thermal treatment and immobilization of contaminants and the reduction of consumption of natural clay as a natural resource.

6.6 Conclusion

The aim of this simplified LCA study was to illustrate by means of two examples the application of the life cycle thinking to the assessment of treatment chains for contaminated dredged material and how it can be useful to evaluate them from a system perspective.

The examples presented in sections 6.5.1 and 6.5.2 were performed with a limited set of data and are short from being a comprehensive LCA study. The environmental performance of the treatment chains was evaluated with respect to a limited set of criteria, representing mostly consumption of raw materials, energetic resources, space demand, etc. Due to lack of data, it was not possible to include in the analysis important aspects such as impacts due to toxic substances in the sediment. Such issues should be considered if a comprehensive assessment and process comparison is intended. It is clear that the outcome of such a study is dependant on the assumptions initially made, system boundaries considered and data availability.

By means of LCA benefits and impacts not considered in site-specific assessment schemes and which occur at other locations can be evaluated in a systematic way. For instance the benefits (in terms of decreased environmental risks and space for disposal) of processing contaminated sediments to produce bricks can be quantified and evaluated against the higher energy demand of brick making, as shown in figures fig. 6.11 and 6.12.

For the case of treatment chains which produce value added products out of sediment, e.g. bricks, LCA can also give valuable insight regarding the relation of the process to conventional production processes. For example fig. 6.13 shows that brick making out of sediment is more resources consuming than conventional processes (approx. 940 MJ more per 0.4 ton of bricks produced). Nevertheless this can be seen as the additional energy needed in order to save space for disposal and reduce the risks owing to the pollutants thermally decomposed and immobilised during the brick making process. This kind of studies can help decision-makers to better understand the benefits and drawbacks of replacing conventional products by providing a system wide perspective to the analysis.

Finally, it must be considered that LCA is a tool to support decision-making regarding environmental issues associated to process systems. As decision-making in sediment management are subjected to strong site-specific constraints which differ in every location, e.g. at locations where space for disposal is limited, treatment of contaminated dredged material is more likely to be conducted; LCA can provide transparency to the way environmental criteria are valuated. Different scenarios can be analysed using different boundary conditions to give deeper insights about environmental implications when comparing alternative processes, e.g. impacts due to transport can be evaluated for different locations of the treatment process and transport distances, or the relative importance of criteria such as demand of space for disposal with respect to consumption of energetic resources for treatment.

6.7 Outlook

An LCA study can cover part of the environmental aspects related to the assessment of sediment treatment chains. Along with risk assessment and environmental impact assessment tools it can provide the necessary information to evaluate and compare sediment treatment chains.

LCA is a tool that is in line with sustainability oriented thinking and as discussed previously, the system wide perspective of process assessment in LCA is compatible with the holistic sediment management approach on a river basin scale. The implementation of a life cycle thinking approach in a sustainability oriented scheme is not straightforward though.

As a first step decision-makers, port managers and environmental administrations should recognise the need to introduce life cycle thinking into the assessment schemes of contaminated sediment treatment chains. This implies that not only willingness but also resources have to be committed to conduct LCA-based studies. Then the results produced have to be critically evaluated, integrated with other environmental information derived from other tools, economic analysis and socio-economic criteria and opportunities to improve the outcome of the decision-making process have to be identified. This is an iterative process that on the long run enables to gain a more comprehensive insight regarding environmental aspects from a system-wide perspective providing environmental information about the relation of sediment treatment chains with other systems outside the area of responsibility of decision-makers.

Conclusion

The present thesis dealt with characterization, remediation and assessment of contaminated sediments, both experimentally and analytically. The first part was aimed to better understand the mobilization, bioavailability, biological and physico-chemical treatment of both PAHs and Heavy Metals contaminated sediment, attempting the prediction of sediment treatment performances based on the information delivered by sediment characterization (e.g. bioavailability). The latter consisted in the application of the Life Cycle Assessment (LCA) procedure as a tool for the evaluation and comparison of sediment treatment chains.

Heavy metals bioavailability was investigated on Porto Marghera sediment, testing a new procedure using *Caenorhabditis elegans*, benthonic worm belonging to the nematodes family, as target organism. The Cd bioavailable fraction was around 0.3‰, only apparently very low. In fact considering that the Cd bioaccumulated was approximately 10 mg Kg⁻¹ of worms and for an adult human being Cd a maximum tolerable level is 50 µg g⁻¹ wet weight, it can be observed that this amount was not negligible. Nevertheless this study is still continuing in order to deliver a reliable tool to be inserted in the legislation for risk assessment evaluation of heavy metals contaminated sediment.

Mobilization of heavy metals was investigated using Sarno river sediment. The BCR extractions carried out in “anoxic”, “under glove box”, and “air dried” conditions enabled the characterization of the main heavy metals bindings. Afterwards the effect of H⁺ and dissolved O₂ was investigated showing an high Acid Neutralization Capacity (ANC) of the Sarno river sediment, mainly due to carbonates. This high ANC is capable to avoid significant heavy metals release both during sediment oxidation-resuspension and during treatment (e.g. sediment washing).

The BCR and ANC evaluations were also used for the sediment washing experiments carried out both on Porto Marghera and Sarno river sediments. Porto Marghera sediment was used to study the operational parameters influencing sediment washing such as solid percentages, treatment time, initial slurry pH effect using EDTA as heavy metals as Mass Separating Agent (MSA). The results showed a decreasing in the removal efficiencies increasing the solid percentages. Nevertheless, when EDTA/ΣHM molar ratio was not a limiting factor, increasing the time treatment comparable heavy metals removal efficiencies were observed

also for the higher solid percentages tests. Sediment washing tests on Sarno river sediment were carried out both with chelating agents and with strong acids because of the very high Sarno sediment ANC. However the main bottleneck of sediment washing is the MSA costs that can be reduced recovering the MSA. An integrated technologies coupling sediment washing and an electrochemical mass separating agent regeneration for heavy metals contaminated sediment was tested showing very promising results both in terms of recovery of the extractant solution and heavy metals extraction effectiveness of the recovered MSA.

One of the aim of the present thesis was to deliver effective tools for the prediction of sediment treatment technologies as developed for PAHs contaminated sediment landfarming. Based on the data of a decennial landfarming campaign on PAHs contaminated sediment PAHs landfarming biodegradation was compared with PAHs bioavailable fractions evaluated with Tenax beads extraction, obtaining a good correlation. Thus a three compartment model based on biodegradation rate constants (k_{fast} , k_{slow} and $k_{very\ slow}$) of contaminated sediment landfarms and Tenax beads extraction was parameterise in order to deliver the PAHs biodegradation profile occurring in a landfarming. The applicability of a sediment slurry SBR to treat PAHs contaminated lagoon sediment, dredged from Porto Marghera, was investigated for different operating conditions (e.g. HRT). A total PAH efficiency removal close to 55 % was achieved both for the long (98 days), middle (70 days) and the short (35 days) HRT of the SBR. The Tenax beads extractions procedure was also used to evaluate the PAHs bioavailability, compared with the biodegradation occurred in a bioslurry treatment. Finally the application of the three compartment model based on the Tenax results for the prediction of the PAHs biodegradation occurring in a landfarming treatment plant was also pursued. The result have shown that 10 years landfarm treatment are necessary to reach the 55 % of PAHs removal efficiencies observed with the SS-SBR while 3-4 years are needed to meet the target value fixed for the Venice lagoon (*Protocollo di Venezia*).

LCA, risk assessment and environmental impact assessment can provide the necessary information to evaluate and compare sediment treatment chains. The LCA procedure was performed on two sediment treatment chains because it can peculiarly deliver information on benefits and impacts not considered in site-specific assessment schemes and which occur at other locations in a systematic way. For instance the benefits (in terms of decreased environmental risks and space for disposal) of processing contaminated sediments to produce bricks can be quantified and evaluated against the higher energy demand of brick making. For the case of treatment chains which produce value added products out of sediment, e.g. bricks,

LCA can also give valuable insight regarding the relation of the process to conventional production processes. For example although brick making out of sediment is more resources consuming than conventional processes (approx. 940 MJ more per 0.4 ton of bricks produced) the additional energy needed can be seen as space saved for disposal and risks reducing due to the pollutants thermally decomposed and immobilised during the brick making process. This kind of studies can help decision-makers to better understand the benefits and drawbacks of replacing conventional products by providing a system wide perspective to the analysis.

The present thesis have dealt with a relatively “young” subject: Contaminated Sediment investigating characterization, remediation and assessment. Although there is still much to work on this subject, the information delivered in this thesis aim both the development of a proper legislation on contaminated sediment based on: total contaminant concentration along with risk assessment and reliable and suitable contaminated sediment treatment technologies.

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