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REMEDIATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN MARINE SEDIMENTS: SOIL WASHING AND FENTON OXIDATION

PhD Thesis

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants of relevant environmental interest due to: i) their persistence, ii) their continuous production and immission in the environment and iii) their toxic, mutagenic and carcinogenic properties. Sediments contaminated with PAHs represent dangerous reservoirs of these pollutants for the overlying seawater, the marine ecosystem and ultimately the human health due to the potential release consequent to unpredictable variations of chemical-physical properties of the environment. In order to reduce the effect of pollutants on the environment, different remediation techniques are applied in relation to: i) the modes and extension of the contamination, ii) the properties of pollutants, iii) the destination of use of the sites, and iv) an ensemble of economic considerations related to the importance of the areas.

In this study two chemical remediation techniques, “soil washing” and Fenton oxidation, are examined by a theoretical and experimental approach, in order to evaluate their potential application to polluted marine sediments.

Five samples were selected for the experiments, from sediments of two highly polluted areas of the southern coast of Italy (the Naples’s harbour and the industrial area of Bagnoli) in order to represent a wide spectrum of PAHs concentrations and physical characteristics (grain size, content of organic carbon, black carbon, etc.), functional to extend the results of the remediation techniques to a broad range of real situations.

A preliminary analysis of the PAHs distribution in the different sediment grain size fractions has evidenced a unhomogeneous and unexpected behaviour with the highest concentrations associated to the larger fractions ($\phi > 250 \mu\text{m}$). These results suggested the application of the remediation techniques to the whole samples without “a priori” exclusion of any grain size fraction of sediments.

The efficiency of the remediation technique applied to the studied marine sediments demonstrated to be strictly related to a complex interplay of factors related to the chemical-physical properties of the different PAH congeners and of the sediments. In particular, the desorption behaviour of the single PAH congeners appeared directly ruled by the interaction of PAH with sedimentary organic matter and with clay-minerals.

An excellent correlation between total organic carbon present in the sediments and the concentration of the single PAH congeners, clearly evidenced by the results of multivariate statistical analysis of the whole dataset, suggested that the PAH hydrophobicity and the distribution pattern of PAHs in the sediments (mainly related to the different local sources and transport mechanisms), are the two main parameters to consider for a comprehensive understanding of the behaviour of PAH during the different steps of remediation.

Direct comparison of all the experiments clearly indicate that soil washing with humic acid (HA) for 24h at temperature of 60°C. and soil washing with HA for 24h represent the best techniques of remediation of PAHs for studied sediments

The efficiency of remediation is estimated of ~60% for sample with high content of sand by application of soil washing with HA for 24h. An evident primary effect of clay minerals on the PAHs desorption from sediments is evidenced by a first order linear correlation observed between the percentage of release of total PAHs estimated after soil washing, and silt/clay content with an estimated lack of ~10% of PAH desorption efficiency for a ~8% /11% of silt/clay content.

During soil washing experiment, the desorption of single PAH congeners appear to directly depend on the hydrophobic character of the single PAH thus suggesting a strong tendency of PAHs in partitioning into a pseudo-micellar phase which is clearly explained by the estimated linear correlation between the coefficients of water-micelle partitioning and the coefficient of water-octanol partitioning of the single PAHs congeners.

The experiments of Fenton oxidation demonstrated that the removal of PAHs from sediment depends on the PAHs reactivity in relation to their ionisation potential and consequently to the capability of PAHs to be chemically oxidized. Evident difference in terms of PAHs removal from sediment were correlated to different concentrations of H_2O_2 and times of addition of it to the mixture.

Application of isotope tracing techniques (by spiking of ^{13}C pyrene) to verify the dynamics of the oxidation processes after the Fenton oxidation of PAH in Humic acid solution, suggested a potential kinetic fractionation of $^{13}\text{C}_3$ pyrene related to differential reactivity of the hydroxyl radicals on carbon tied at different locations on the PAH benzene rings. In particular, at the end of the oxidation process, $^{13}\text{C}_3$ pyrene seems to lose its aromatic character.

The ensemble of results of soil washing and Fenton oxidation carried out on the studied samples, indicated that PAHs were not completely and definitely eliminated from the sediments thus suggesting that these two chemical treatments have restrictive capacity to degrade this class of hydrophobic contaminants in sediments. In particular, it is evident that the release of sediment-bound PAH to the aqueous phase results in a initial period of fast deliver, followed by a period of slower release of contaminants from the sediments.

A further investigation of the desorption rate of PAHs related to the different physical and chemical properties of the sediments and the diffusion through organic matter, with different aging should provide more definitive information for an adequate evaluation of potential risk associated to the incomplete remediation and prediction of the effects of the detained sediment-bound PAH.

ABSTRACT

Gli idrocarburi policiclici aromatici (IPA) rappresentano una classe di inquinanti organici di rilevante importanza ambientale in relazione: i) alla loro persistenza nell'ambiente, ii) alla loro continua produzione ed immisione e iii) alle loro proprietà mutagene e cancerogene. I sedimenti contaminati da IPA rappresentano una pericolosa riserva di questi inquinanti per la colonna d'acqua, per l'ecosistema marino e infine per la salute umana a causa del possibile rilascio causato dalle imprevedibili variazioni delle proprietà chimico fisiche dell'ambiente. Per ridurre gli effetti di tali inquinanti sull' ambiente, differenti tecniche di decontaminazione vengono generalmente applicate in relazione: i) alle modalità e all'estensione della contaminazione, ii) alle proprietà degli inquinanti, iii) alla destinazione d'uso del sito, e iv) ad un insieme di considerazioni economiche relative all'area di interesse.

In questo studio sono esaminate due tecniche di decontaminazione: il "soil washing" e l'ossidazione chimica tramite il reagente di Fenton. L' approccio utilizzato è sia teorico che sperimentale, ed è finalizzato alla valutazione delle potenziali applicazioni su sedimenti marini contaminati.

Gli esperimenti sono stati eseguiti su cinque campioni di sedimento marino prelevati in due aree fortemente inquinate della costa meridionale italiana (il porto di Napoli e l'area industriale di Bagnoli) al fine di rappresentare un ampio spettro di concentrazioni di IPA e caratteristiche fisiche (granulometria, contenuto di carbonio organico, black carbon etc.), utili ad estendere i risultati delle tecniche di decontaminazione applicate ad un ampio range di situazioni reali.

L' analisi preliminare della distribuzione degli IPA nelle differenti frazioni granulometriche ha evidenziato un disomogeneo ed inatteso comportamento, con i più alti valori di concentrazione associati alle frazioni più grossolane ($\phi > 250$ nm). Questi risultati suggeriscono che le tecniche di decontaminazione devono essere effettuate su tutto il sedimento senza una aprioristica esclusione di una o più frazioni granulometriche.

L'efficienza delle tecniche di decontaminazione applicate ai sedimenti marini presi in esame, dimostrano che esse sono relazionate ad una complessità di fattori riguardanti le proprietà chimico-fisiche dei singoli congeneri di IPA e dei sedimenti. In particolare, il desorbimento dei singoli congeneri di IPA sembra dipendere direttamente dalle interazioni degli IPA con la materia organica e con la frazione più fine contenuta nei sedimenti.

Un' eccellente correlazione tra carbonio organico totale presente nei sedimenti e la concentrazione dei singoli congeneri di IPA, chiaramente evidenziata dai risultati dell'analisi

statistica multivariata dell'intero dataset, suggeriscono che l'idrofobicità degli IPA e il pattern di distribuzione degli stessi microinquinanti nei sedimenti (frutto delle differenti sorgenti di inquinamento e dei meccanismi di trasporto), sono i due principali parametri utili per comprendere le modalità dei desorbimento dei singoli congeneri durante i differenti steps di decontaminazione.

Attraverso un confronto diretto di tutti gli esperimenti di decontaminazione è stato possibile osservare che il "soil wahing" con acidi umici (AU) effettuato per 24 ore a 60°C e il "soil washing" con AU effettuato per 24 ore a temperatura ambiente rappresentano le migliori condizioni per la decontaminazione da IPA tramite le tecniche utilizzate.

Durante gli esperimenti di "soil washing", il desorbimento dei singoli congeneri di IPA appare dipendere direttamente dal carattere idrofobico dei singoli IPA suggerendo una forte tendenza degli IPA a ripartirsi nella fase "pseudomicellare" come è chiaramente espresso dalla correlazione lineare tra i coefficienti di ripartizione acqua-micella e acqua- ottanolo dei singoli congeneri di IPA:

Gli esperimenti di ossidazione chimica attraverso il reagente di Fenton dimostrano che la rimozione degli IPA dal sedimento dipende dalla reattività dei singoli congeneri in relazione al loro potenziale di ionizzazione e conseguentemente alla loro tendenza ad essere ossidati. Evidenti differenze di rimozione degli IPA dal sedimento sono strettamente correlate alle differenti concentrazioni del perossido di idrogeno e ai tempi di aggiunta di questo alla miscela.

L'applicazione di tecniche isotopiche con utilizzo di un tracciante marcato ($^{13}\text{C}_3$ pirene) ha permesso di verificare le dinamiche dopo l'ossidazione chimica degli IPA in una soluzione di acidi umici, suggerendo effetti di frazionamento cinetico del $^{13}\text{C}_3$ pirene relativamente alla diversa reattività dell'idrossi radicale verso gli atomi di carboni localizzati in diverse posizioni dell'anello aromatico. Alla fine del processo di ossidazione il $^{13}\text{C}_3$ pirene sembra perdere il suo carattere aromatico e trasformarsi in una molecola a 3 atomi di carbonio.

I risultati del "soil washing" e dell'ossidazione chimica mediante reagente di Fenton effettuati sui sedimenti presi in esame mostrano che gli IPA non vengono completamente eliminati dai sedimenti e che questi due trattamenti chimici hanno limitate capacità di eliminare completamente contaminati idrofobici dai sedimenti. In particolare, è evidente che il rilascio di IPA, fortemente legati al sedimento, nella fase acquosa è frutto di un iniziale periodo di rapido rilascio seguito da un periodo di un più lento trasferimento dal sedimento.

Un'ulteriore ricerca sulle cinetiche di rilascio degli IPA dal sedimento, in relazione alle differenti proprietà chimico-fisiche di quest'ultimo e alla velocità di diffusione attraverso la

materia organica, potrebbe consentire di valutare il potenziale rischio associato alla incompleta degradazione dei microinquinanti considerati e a predire gli effetti di quella frazione di IPA fortemente trattenuta dal sedimento.

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Chapter I

INTRODUCTION

I. 1. Polycyclic aromatic hydrocarbons in the marine environment

Marine sediments belonging to urbanized as well as industrialized coastal areas are considered sinks and reservoirs for various kinds of organic and inorganic contaminants. They represent final receptors of wastewater from agricultural, urban and industrial stream discharges. From the other hand, these sediments represent dangerous potential secondary reservoirs of pollutants for the overlying seawater, for the marine ecosystem and human health due to the potential release of contaminants in relation to unpredictable variations of chemical-physical properties of the environmental system. Contaminated sediments can have an impact on the aquatic life by making areas uninhabitable for benthic organisms, affecting fish and wildlife, inducing effects of bioaccumulation and biomagnification of contaminants in the food chain (e.g., Pfitezenmeyer, 1975; Reinharz, 1981), etc. Documented adverse ecological effects induced by contaminated sediments include fit rot, increase of tumor frequency, and scarce reproductive efficiency in fish as well as decreased biodiversity in the aquatic ecosystems (e.g., Baumann, 1987). Contaminated sediments can also pose a threat to human health when pollutants in sediments bioaccumulate in edible aquatic organisms (Baumann, 1987; Puget Sound Estuary program, 1998). While sediment contamination has been recognized as a serious problem, a limited success has been demonstrated in managing it. One reason is the general lack of specific and comprehensive sediment quality guidelines appropriately to define what levels of the various pollutants present in the marine sediments really cause adverse ecological and human health effects (actually only a preliminary list of priority pollutants, with related toxic concentration levels, was proposed by the EPA's contaminated sediment Management strategy, 1998). Moreover, the total concentration of single contaminants can be of interest, but generally it overestimates the concentration that may be associated to an actual risk (Sehlin, 2004).

An evaluation of the bioavailable fraction of the pollutant present in the environment may represent a more appropriate measure of its dangerous effects of the environment. In the marine sediments, the availability of pollutants depends on different chemical and physical parameters: hydrophobicity, content of organic matter, the contact time between the

contaminant and the sediment, temperature, pH, etc. Therefore, to evaluate the potential risk associated to contaminated marine sediments, it is necessary to assess the effective fraction of a chemical that can be taken up or biotransformed by living organisms, the so-called bioavailability (Semple et al., 2003). According to the theory of the equilibrium partitioning (Dituro et al., 1991) the toxicity of organic contaminants for sediment-dwelling organisms can be quantitatively determined by evaluating how the pollutants are distributed among sediments, water and organisms. In particular, for organisms living at the water/rock interface, the toxicity of the sediments appears directly related to the amount of unbound organic pollutants dissolved in the sediment porewaters.

In the last years, a huge international effort (e.g., Demars et al., 1995) was devoted to the definition of appropriate and efficient protocols for “clean up” of marine sediments characterized by high levels of pollutants, toxic for the human health and the marine ecosystem. Three different conceptual approaches to the “remediation” of contaminated sediments/soils are generally considered: “removal” (the pollutants are removed from the contaminated sites), “treatment” (the pollutants are transformed in non-toxic or less-toxic chemicals), “keep” (the pollutants are left in the contaminated sites avoiding potential diffusion or contact with the human population and/or the ecosystem).

The remediation activity can be carried out by *in situ* or *ex situ* approaches through physical, chemical and biological treatments, depending on the typology and extension of the contamination. Moreover, the choice of different remediation technologies generally depends on: i) modes and extension of the contamination, ii) the properties of pollutants, iii) destination of use of the considered site, iv) economical considerations, etc.

A number of researches (Cerniglia, 1992, 1995; Juhasz et al., 2000; Johnsen et al. 2000) explored the efficiency of different kinds of microorganisms to degrade organic contaminants (bioremediation) as an environmentally friendly and economical technique for decontamination of polluted soils/sediments. However, several problems seem hardly to limit the versatility of this approach for efficient decontamination of polluted soils/sediments: i) the search of adequate microbial strains generally characterized by restrict and specific chemical-physical exigences for different kind of contamination, ii) the high chemico-physical variability of the soils/sediments which directly influences and limits the microbial activity and synthesis, iii) the recalcitrance of pollutants to biodegradation (an example is represented by PAHs with more of 4 rings, (Wilson and Jones, 1993; Lundstedt, 2003), iv) the formation of metabolites which may be more toxic than the parent contaminant (Boopathy, 2000), etc.

An efficient and relatively inexpensive alternative to the bioremediation is represented by the technique of chemical remediation related to the so-called “soil washing” (Conte et al., 2005) and Fenton oxidation (Kawara et al., 1995; Nam et al., 2001; Watts et al., 2002). Particularly, soil washing consists in using natural (Humic acids, HA) and/or synthetic (*e.g.*, Triton X-100) surfactants to increase the solubility of recalcitrant organic contaminants present in the solid phase and thus favouring their removal. On the other hand, Fenton oxidation involves the introduction of a strong oxidant into the sediments, the hydroxyl radicals ($\cdot\text{OH}$) formed by Fe(II)-catalyzed decomposition of hydrogen peroxide, to “burn” the organic contaminants and reduce them to CO_2 and H_2O .

The main aim of this research is a detailed investigation of the kinetic and thermodynamic processes related to the soil washing and Fenton oxidation techniques on an ensemble of marine sediments highly contaminated by polycyclic aromatic hydrocarbons (PAHs). PAHs are persistent organic pollutants of relevant environmental interest due to: i) their persistence, ii) their continuous production and immission in the environment, iii) their toxic, mutagenic and carcinogenic effects (Delistraty, 1997).

The research is developed through a number of experiments designed to verify the role of different chemico-physical parameters (grain size, total organic carbon and black carbon contents, different PAH concentrations) on the different steps of desorbing/oxidation of PAHs from marine sediments.

A preliminary characterization of the studied samples in terms of PAHs distribution, granulometric features as well as organic carbon contents and then, in terms of potential sources of the PAHs, was carried out. Then, a detailed analysis of the role played by different physical parameters (grain size, total organic carbon, black carbon, distribution, etc.) on the distribution of the different PAH congeners present in the samples was performed.

Based on such a kind of information, a detailed kinetic study of the PAHs desorption processes was carried out comparing the results relative to the different remediation treatments. In particular, the desorption behaviour of single PAH congeners was carefully investigated, studying: i) the interaction of each PAH with sedimentary organic matter (SOM), ii) the solubilization of PAHs by micelle-surfactants and iii) the role of organic matter and clay minerals on PAH desorption. Finally the amount of black carbon was measured because it is known to strongly sorb PAH molecules and the effects of solid-water partitioning related to hydrophobic organic pollutants in terms of reduction of their bioavailability in sediments (Elmqvist, 2007).

A last group of experiments consisted in using an isotope tracer ($^{13}\text{C}_3$ pyrene) to verify the dynamics of the oxidation processes and to trace the formation of potential intermediate oxidation molecules after Fenton application on PAH molecules in HA solution.

All the experiments were carried out on marine sediments collected from two highly polluted areas of the southern Italy: the harbour of Naples and the industrialised area of Bagnoli. Detailed geochemical monitoring of the two areas carried out during the last four years, and partially involving the work of this research, allowed an appropriate selection of samples useful to accurately test the results of the different experiments in a wide range of environmental conditions.

In the following Chapter, a short presentation will be provided on: i) the state of the art about the different approaches currently usual for remediation of soils/sediments contaminated by organic compounds, ii) a detailed description of the most relevant chemical-physical features and toxicity of PAHs (the class of contaminants considered in this research work), iii) a synthetic view of chemico-physical properties and sources of black carbon in marine sediments, iv) a description of the recent results obtained by application of bioremediation technologies with the relative limits in terms of efficiency, v) description of the different reagents used for the chemical approach used in this research. A final paragraph is dedicated to the presentation of the technique of isotope tracing used to verify the dynamic of Fenton oxidation and the efficiency of soil washing.

I.2. Soil washing and geooxidation: state of the art

In the USA and Europe, the costs for soils/sediments remediation generally exceed the net economic value of the land, and often threaten responsible companies with bankruptcy. Given this perspective it is not surprising that scientists and engineers are firstly trying to evaluate what is the real risk associated with a contaminated site through a study of bioavailability and toxicity of pollutants. Moreover, they have tried to develop novel remediation technologies that show a considerable promise from a technical and economic perspectives (US EPA 1998, 1999).

In situ remediation is one novel class of technologies which do not imply the removal of contaminated sediments. One of the techniques of in situ remediation is represented by the bioremediation which enables permanent elimination of pollutants at low cost. However, this approach is limited by the correct selection of active microbes, the appropriate sediment condition for microbial activity, the recalcitrance of pollutants to biodegradation, and the formation of metabolites which may be more toxic than parent contaminant (Boopathy, 2000).

Among other techniques, soil washing and Fenton oxidation seem to represent a valid and relatively inexpensive alternative for remediation of marine sediments. However, each decontamination technique, including soil washing and Fenton oxidation, shows limitations and therefore investigation is currently needed to develop more appropriate and reliable applications (e.g., Conte et al. 2005; Georgi et al., 2007).

In this study the application of soil washing and Fenton oxidation to remediate contaminated marine sediments, are examined in order to evaluate their potential application to marine sediments. Soil washing was realized through the action of HA as surfactants (Conte et al., 2005).

Humic substances (HS) are usually chosen for remediation technologies because of their irregular and heterogeneous structure (Hayes et al., 1989) that give them resistance to biodegradation (McCarty and Rice, 1991). Infact, the recalcitrant nature of humics is of practical relevance particularly when the objective is to develop soil/aquifer remediation technologies on a predicted reactive matrix that is not consumed by microorganisms during remediation. Humics can: i) be oxidized by strong oxidants, ii) act as reducing agents, iii) take part in protolytic ion exchange and complexation reactions, iv) participate in donor-acceptor interactions (Clapp et al., 1996). Hence, HS can interact practically with all chemicals released in the environment. In particular, HS are known: i) to form stable complexes with heavy metals (Weber 1988; Varshal et al., 1993; Benedetti et al., 1996; Linnik et al., 1986; Croué et al., 2003), ii) to interact with hydrophobic organic compounds (Gauthier et al., 1987; McCarthy et al., 1985; Gevaio et al., 2000; Kristoffer et al., 2002), iii) to produce charge-transfer complexes (Muller-Wegener et al., 1980; Senesi et al., 1982), iv) to act as electron shuttles (Lovley et al., 1996, 1999), v) to mediate redox reactions of transition metals (Gu and Chen 2003), chlorinated and nitrated hydrocarbons (Bradley et al., 1998; Tranyek et al., 1989), vi) to adsorb onto mineral surface (Murphy et al., 1992; Vermeer et al., 1998), vii) and to influence the interface distribution of contaminants (Laird et al., 1994; Murphy et al., 1995). Finally, HS can strengthen the resistance of living organisms against non-specific stress factors (Khristeva 1970; Nardi et al., 2002). Moreover, the advantage of humic matter application as detoxifying agents for remediation purposes resides in: i) a lack of danger of secondary pollution of contaminated sites, ii) a detoxifying impact on the hydrophobic contaminants due to the presence in their structure of a hydrophobic components responsible for the increase of solubility of organic pollutants, contiguous to hydrophilic domains where biological availability may favour the biodegrading biomass in proximity of organic pollutants and, thereby enhancing the results of biodegradation (Fava and Piccolo, 2001) iii)

a direct beneficial effect on the biotic community living in the contaminated sites (Fava and Piccolo, 2001). However, new researchers are necessary to define the kinetics, stability and longevity of humic complexes and/or adducts with organic chemicals and heavy metals.

Fenton's reagent is often used to treat wastewaters from various industrial activities (Kuo, 1992; Schulte et al., 1995; Wanpeng et al., 1996; Lin and Lo, 1997; Kang and Hwang, 2000). It can also be applied for the remediation of contaminated solid matrices, such as soils, sediments or sludges (Muhranta and Viikari, 1993; Kawahara et al., 1995; Martens and Frankenberger, 1995; Watts and Dilly, 1996; EPA, 1998; Watts et al., 1999; Nam et al., 2001; Lee et al., 2002; Neyens et al., 2002; Watts et al., 2002; Neyens and Baeyens, 2003). Fenton oxidation is a process that can be used in combination with bioremediation techniques, as a pre-treatment for the oxidation of PAHs to more biodegradable compounds. The application of Fenton process for remediation of marine sediments is limited because it is not a selective process; infact, hydroxyl radicals can react with organic and inorganic pollutants (Neyens et al., 2003; Pignatello et al., 2006), as well as with sedimentary organic matter (SOM) and with itself. SOM has been found to consume and compete for the oxidant during Fenton reaction, and as a result, the content and structure of the SOM might vary after Fenton oxidation (Gates et al., 1995). The variation in the content and structure of the SOM seems to strongly influence its sorption/desorption effects on for PAHs. Besides, there are very limited studies regarding the charge of SOM and the following effects on sorption and desorption characteristic to PAHs after Fenton oxidation (Sun et al., 2007). Moreover, Fenton reagent should provide a total mineralization of the contaminants in carbon dioxide and water; preliminary results by Lundstedt (2003) seem to indicate that application of Fenton oxidation to contaminated soils/sediments may produce a variety of temporary intermediates and compounds that may be resistant to further degradation and be more toxic for the environment than the parent PAHs. For this reason, a detailed study of the degradation and transformation of PAH during the oxidation process, in terms of characterization and evaluation of toxicity of oxy-PAHs and possible intermediates formed during the reactions, is necessary for final application of this technique to real situation. Finally, the pH optimum for Fenton oxidation is usually reported in the acidic range near pH= 3 (Pignatello et al., 2006). Marine sediments possess a high buffer capacity; therefore, the necessity to acidify the reaction medium limits the applicability of Fenton process in the real marine environment. The main reason of the low reactivity at circumneutral pH is the precipitation of Fe(III) as hydrous oxyhydroxides $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ which inhibits the recycling of Fe(III)/Fe(II). In order to keep the iron solution, the use of synthetic chelators such as aminopolycarboxylates, polyhydroxy aromatics and N-

heterocyclic carboxylates in modified Fenton systems has been studied (Sun et al., 1992; Sun et al., 1992). In particular, Georgi et al. (2007) proposed the application of humic acid as iron chelator in modified Fenton system. The chelating agent EDTA is routinely used in modified Fenton system. The main disadvantages of EDTA is that it is persistent and it may enhance the mobilization of heavy and radioactive metals (Oviedo and Rodriguez, 2003).

I.3. Polycyclic aromatic hydrocarbons: a synthetic overview

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic contaminants with stable chemical structure and high hydrophobic behaviour. They are composed by two or more benzene rings and contain only carbon and hydrogen atoms. However, alkyl- substituted PAHs, heterocyclic PAHs containing nitrogen, sulphur and oxygen, and oxidation products of PAHs, including PAH ketones, PAH quinones, and hydroxylated PAHs are often grouped together with the unsubstituted PAHs and are then referred as polycyclic aromatic compounds (PACs) (Connell, 1997).

PAHs occur in the environment due to natural events for instance related to effects of forest fires, and/or to anthropogenic processes, generally related to urban and industrial activities. In the marine environment (seawater and sediments), they can be transported by the atmosphere emission or by river drainages and are rapidly sorbed onto sediment particles (Karickhoff, 1980). Sorption proportionally increases with the number of benzene rings of the PAH molecules due to their increasing lipophilicity (Bossert et al., 1986; Sims et al., 1983). PAHs derive from classically three different kinds of processes: petrogenic, pyrolytic and diagenetic. The group of petrogenic PAHs mainly consist of two- and three parental rings and methylated compounds and a low concentration of congeners with a high number of rings (Bjorseth and Ramdahl, 1983; Pruell and Quinn, 1988; Vazquez-Duhalt, 1989; Latimer et al., 1990; O'Malley, 1994). They are formed during oil production and attributed both to the aromatization of multi-rings biological compounds and fusion of smaller hydrocarbon fragments into new aromatic structures (e.g. Radke, 1987; Neilson and Hynning, 1998; Simoneit, 1998). The group of pyrolytic PAHs consists of four and five-rings PAHs that are formed by burial maturation of sedimentary organic matter leading to oil and coal formation and that are generally burned. The incomplete combustion at high temperature ($> 400^{\circ}\text{C}$) generates four- and five-rings PAHs and/or two and three rings PAHs, depending on: i) the original unburned matter, ii) the environmental conditions of the pyrolysis processes related for instance to the temperature of heats, potential absence of oxygen, etc. and iii) kinetic factors (Abrajano et al., 2003). The pyrolytic process is characterised by radical reactions

where organic compounds are cracked to smaller unstable molecules and then their fragment fused into larger and more stable aromatic structures (Abrajano et al., 2003).

PAHs of diagenetic origin are formed by short-term degradation of biogenic precursors (Soclo et al., 2000).

Depending on their structure, PAHs exhibit different chemical behaviour in the marine sediments. For instance, due to the larger number of benzene rings, pyrogenic PAHs are thermodynamically more stable than the petrogenic ones, they appear more hydrophobic and strongly adsorbed on the marine sediments.

The US-Environmental Protection Agency has classified 16 congeners of PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene) as hazardous compounds and divided them into human carcinogenic and non carcinogenic congeners. The two and three rings PAHs are non-carcinogenic while several of the four, five and six rings PAHs have evidenced cancerogenous effects. In particular, the four rings PAHs, chrysene and benzo(a)anthracene, the five rings PAHs benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and dibenzo(a,h)anthracene and the six ring PAH indeno(1,2,3-cd)pyrene are potential carcinogenic PAHs, with benzo(a)pyrene representing the most carcinogenic among all the different congeners (NTP, 2005). The European Community and Italian Legislation (DM 152/06) have adopted the USA-EPA classification of the sixteen priority PAH congeners and inserted the analysis of these compounds as necessary for an appropriate definition of the state of contamination of the marine environment (in its different compartment). The main chemical properties of the 16 priority US-EPA congeners are reported in Tab. 1.

	Number of rings	Molecular weight	Aqueous	Vapor press.	Log K _{ow}	Log K _{oc}
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			solubility (mg/l)	(Pa)		
Naphthalene	2	128	31	1.0×10^{-2}	3.37	1.30×10^4
Acenaphthylene	3	152	16	9.0×10^{-1}	4.00	2.50×10^3
Acenaphthene	3	154	3.8	3.0×10^{-1}	3.92	4.60×10^3
Fluorene	3	166	1.9	9.0×10^{-2}	4.18	
Phenanthrene	3	178	1.1	2.0×10^{-2}	4.57	1.40×10^4
Anthracene	3	178	0.045	1.0×10^{-3}	4.54	1.40×10^4
Pyrene	4	202	0.13	6.0×10^{-4}	5.18	3.80×10^4
Fluoranthene	4	202	0.26	1.2×10^{-4}	5.22	3.80×10^4
Benzo(a)anthracene	4	228	0.011	2.8×10^{-5}	5.91	1.38×10^6
Crysene	5	228	0.006	5.7×10^{-7}	5.91	2.00×10^5
Benzo(b)fluoranthene	5	252	0.0015	-	5.80	5.50×10^5
Benzo(k)fluoranthene	5	252	0.0008	5.2×10^{-8}	6.00	5.50×10^5
Benzo(a)pyrene	6	252	0.0038	7.0×10^{-7}	5.91	5.50×10^6
Dibenzo(a,h)anthracene	6	278	0.0006	3.7×10^{-10}	6.75	3.30×10^6
Indeno(1,2,3-cd)pyrene	6	276	0.00019	-	6.50	1.60×10^6
Benzo(g,h,i)perylene	6	276	0.00026	1.4×10^{-8}	6.50	1.60×10^6

Tab. 1. Some chemical proprieties of the 16 priority US-EPA PAH congeners (from Mackay *et al.*, 1992). Log K_{ow} and Log K_d are respectively the octanol-water and soild-water partition coefficients.

I.4. Toxic effects of PAHs.

PAHs have been shown to damage DNA and cause mutations, which in some cases may produce cancer. PAHs require activation of electrophilic metabolites to exert their mutagenic or carcinogenic effects (Xue et al., 2005). There are three principal pathways currently proposed for metabolic activation of PAHs: the pathway via “bay region” dihydrodiol epoxide by cytochrome P450 enzymes (CYPs) (Hall and Graver, 1990; Harvey, 1994), the pathway via radical cation by one-electron oxidation (Cavalieri and Rogan 1992, 1995), and the ortho-quinone pathway by dihydrodiol dehydrogenase (DD) (Penning et al. 1996, 1999). The first metabolic activation pathway involves three enzyme-mediated reactions: i) oxidation of the double bond catalyzed by CYPs to unstable arene oxides, ii) hydrolysis of the arene oxides by microsomal epoxide hydrolase to trans dihydrodiols, iii) a second CYP-catalyzed oxidation at the double bond adjacent to the diol-epoxides. This pathway can lead to sterically hindred bay or fjord region diol-epoxides that are electrophiles capable of binding to DNA, while some of the diol-epoxide stereoisomers of PAHs are found to be ultimate carcinogens. For the “bay region” diol-epoxide of PAH the major adducts have been found to result from bonding between the benzylic carbon of the epoxide and the exocyclic amino groups of dGuo and dAdo residues in the DNA (Dipple, 1994). Radical cation pathway consists of the formation of radical cation of PAHs by removal of one electron from π electron system of the molecule through one electron oxidation. The radical cations are electrophilic in nature, capable of

interacting with nucleophilic centers in DNA. A relatively low ionization potential, a favourable charge location in the PAH radical cation makes this intermediate specifically and efficiently reactive toward nucleophiles and an optimal geometric configuration that facilitates covalent binding with nucleophilic centers in cellular macromolecule like DNA. (Cavalieri and Rogan, 1992). Activation through PAH-o-quinone consists of the formation of o-quinone by dihydrodiol dehydrogenases (DD)- catalyzed oxidation (Penning et al. 1996, 1999). Under physiological conditions, the DD enzyme competes with P450 to oxidize the non-K-region diol, a proximate carcinogenic metabolic of PAH but not the K-region diol. The mechanism of this NADP⁺- dependent oxidation involves the initial formation of a ketol that spontaneously rearranges to form a cathecol by the activation of DD followed by autoxidation of the unstable cathecol to o-quinone. PAH-o-quinone are reactive 1,4 Micheal addition acceptors having the potential to form various DNA adduct. All of the metabolic activation pathways may contribute to PAHs-induced carcinogenesis. The relative significance of each mechanism depends on the chemical/biological characteristics of each individual compound, the animal species, the tumor site, level of expression of the activation enzymes involved and so forth (Xue et al. 2005).

I.5. Bioremediation: a synthesis on the state of the art

According to the view of Johnsen et al. (2000), the degradation of PAHs by microbial activity occurs through three different functions: i) assimilative biodegradation that yields carbon and energy for degrading organism and assisting the mineralization of the compounds or part of them, ii) intracellular detoxification processes where the purpose is to make the PAHs water-soluble as pre-requisite for excretion of the compounds, iii) co-metabolism by degradation of PAHs without generation of energy and carbon useful for the metabolism of the cell. Co-metabolism is defined as a non specific enzymatic reaction, with a substrate competing with the structurally similar primary substrate for the enzyme's active site (Johnsen et al., 2000).

The bacterial degradation of PAHs generally begins with a dioxygenase attack on one of the aromatic rings to form a cis-dihydrodiol, which is subsequently dehydrated to cathecol. Cathecol is a key intermediate from which ring cleavage can occur. The aromatic ring is cleaved between the hydroxyl groups (ortho fission) or adjacent to one of the hydroxyl groups (meta fission). Succesive rings degradation may then occur, ultimately degrading the compounds to molecules that can enter the central metabolic pathways of the bacteria (Cerniglia, 1992, 1995). The rates, metabolic pathways, enzymatic regulation and genetic

regulation of 3-rings PAHs have been well documented (Evans et al. 1995; Kiyoara and Nagao, 1978; Monna et al. 1993; Grifoll et al.1995). Instead, until recently, there has been a paucity of information on the bacterial efficiency for degradation of larger, more recalcitrant, high molecular weight PAHs containing four or more fused benzene rings (Juhasz et al. 2000). Many high molecular weight PAHs, such as benzo(a)pyrene are degraded with difficulty or not at all. Low water solubility, high resonance energy, and toxicity (Cerniglia 1992) of this high molecular weight PAHs represent only some of the known characteristic that render the bioremediation approach unefficient for decontamination of environments polluted by high molecular weight PAHs.

I.6. Black carbon

The term black carbon (BC) is used to describe relatively inert carbon particles originating from incomplete combustion of organic compounds. It is ubiquitous in nature and mainly consist of carbon atoms (Goldberg, 1985). The carbon-based fuel carbons that produce these type of particles can broadly be separated into: i) solid materials such as coal, charcoal, wood grass, leaves, ii) fluid materials such as oil, gasoline, diesel and iii) gaseous material. The most prominent BC sources are natural wild-fires and anthropogenic combustion within major cities. There, vehicles and domestic home heating are primary BC sources. The BC may also emitted from fossil fuel combustion in urban areas. BC is not a specific chemical compound with well-defined characteristics, but can be associated to a final product of different processe according to the “combustion continuum model” of Hedges et al., 2000 and Masiello, 2004. Depending on factors such as fuel material, oxygen flow, temperature of the fire and formation phase, the BC particle will have different physical and chemical properties (Fig. 1). In particular, char is the residual phase left after combustion. These particles are larger than the soot ones and are formed at lower temperature. It means that the source material is not fully destroyed and some morphological features can be retained. The diameter of char particles generally ranges from 1 to 100 μm . Soot on the other hand, is formed in the gas-phase, resulting in smaller sized primary particles (30-40 nm), aggregated into micron-sized clusters and generally having surface areas of 100 m^2g^{-1} .

Soot consists of sub-micron particles formed at high temperature from the condensation of hydrocarbons in the gas-phase. This condensation is followed by stacking of aromatic layer, which conglomerate into grape-like structures and leading to BC particles constituting of a randomly ordered inner core and a more crystallized outer shell (Ishiguro et al., 1997; Stanmore et al., 20001).

	Slightly charred biomass	char	charcoal	soot	graphite
Origin	pyrogenic				geological
Formation T	low	→ high			high T,P
Formation phase	Solid residual-phase		gas-phase condensate		
Particle size	mm and larger	mm to submicron		submicron	
Reactivity	high	← low			low
O/C	high	← low			low

Fig. 1. Physical and chemical properties of BC

The soot spherules are joined together by shared carbon deposits to form loose aggregates of 0.1 to 1 μm size. The soot particles are covered with a thin oily film, which condenses on the particle when the temperature decreases further away from the combustion flame (Hamins, 1993). BC in water and sediment is considered directly influence the solid-water partitioning of hydrophobic pollutants and potentially reducing the bioavailability.

I.7. Chemical approaches to the remediation of marine sediments contaminated by PAHs: the reagents

I.7.1. The surfactants: natural and synthetic

Surfactants are water-soluble, surface-active compounds characterized by a hydrophobic portion tied to a hydrophilic or water soluble functional group. They can be grouped according to the charge present in the hydrophilic portion of the molecule (after dissociation in the aqueous solution) in four different categories:

- anionic surfactants;
- non-ionic surfactants;
- cationic surfactants;
- ampholytic surfactants.

Different classes of surfactants are employed for soil washing remediation depending on the nature of the contaminants (Conte et al., 2005). Generally, compared to ionic surfactants,

non-ionic ones have a greater solubilization power for organic contaminants and generally show higher remediation efficiency (Zhou and Zhu, 2006).

The surfactants enhance the remediation of contaminated sediments by increasing the aqueous-phase concentration of the organic contaminant via “micelle solubilization” (Kile and Chiou 1989; Edwards et al., 1991; Diallo et al., 1994; Jafvert et al., 1994; Pennell et al., 1997) and the mobilization of organic contaminants from the solid to the aqueous phase (Deitsch and Smith, 1995; Yeom et al., 1996; Johson et al., 1999). It improves the availability of the organic compounds for successive treatments such as bioremediation and/or phytoremediation (Bury and Miller, 1993; Tsomides et al., 1995; Guha and Jeffe, 1996). Thus, surfactant represent intermediate systems for efficient desorption of organics from soils/sediments that then can be metabolized/oxydized by different bio/chemical/physical treatments.

The most important parameter useful to define of the capability of the surfactants to desorb organic pollutants from contaminated soils/sediments is the surfactant Critical Micelle Concentration (CMC) that is defined as the concentration of the surfactants at which the thermodynamics of the surfactant-solvent system favour the formation of micelles in turns defined as an aggregation of the surface-active molecule into clusters with the hydrophobic groups located at the centre of the clusters and the hydrophilic head groups directed towards the solvent (Haigh, 1996; Li and Chen, 2002). At low concentration, the molecules of surfactants exist as monomers and chains of hydrocarbons and disrupt the normal hydrogen binding of the surrounding. The resultant high entropy “structured water” which surrounds the chains increases the free energy that can be minimised if the hydrocarbon chains are partially or totally removed from contact with water, either by adsorption or absorption on organic matter. At high concentration of surfactants the system’s free energy can also be reduced by the formation of micelles. At concentration higher than the CMC, surfactants have the ability to solubilise significantly more of a hydrophobic organic compound than would dissolve in water alone (Haigh, 1996). The surfactant’s hydrophilic parts are directed towards the water molecule while the hydrophobic part interacts with the hydrophobic contaminant. The process of incorporation of hydrophobic compound in the micelles is termed solubilization.

Among non-ionic surfactants, Triton X-100 and HA have the highest capacity of solubilization (Conte et al., 2005).

Triton X-100 is a non-ionic surfactant which has a hydrophilic polyethylene oxide group (on average 9.5 ethylene oxide units) and a hydrocarbon lipophilic or hydrophobic group that is constituted by a 4-(1,1,3,3-tetramethylbutyl)-phenyl group (Fig. 2). Data reported by

Conte et al. (2005) indicated a high efficiency of this surfactant in removing significant amounts of pollutants from highly contaminated solid matrix.

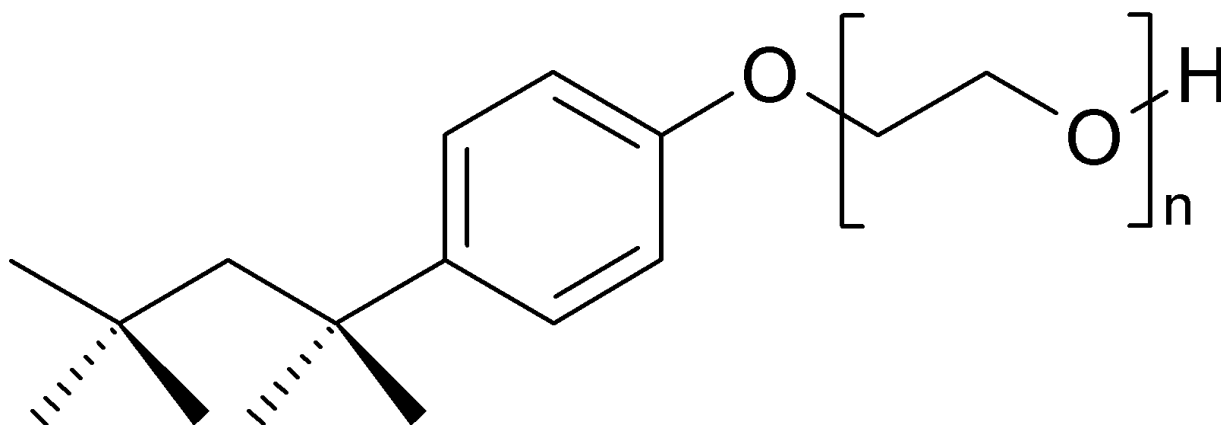


Fig. 2. The chemical structure of Triton X-100 ($n = 9-10$)

HA are a fraction of Humic Substance together with fulvic acids (FA) and humin.

Humic substances, natural organic substances that are ubiquitous in water, soils and sediments, are of paramount importance in sustaining plant growth and controlling both the fate of environment pollutants and the biogeochemistry of organic carbon (OC) in the global ecosystem (Piccolo, 1996). Most of the difficulties encountered in chemically defining the structure and reactivity of HS derive from their large chemical heterogeneity and geographical variability. Piccolo (2001) reported that HS are supramolecular assemblages of relatively small heterogeneous molecules of various origins that are not associated by covalent bonds but are stabilized only by weak forces such as dispersive hydrophobic interactions (van der Waals, π - π , and CH- π bondings) and hydrogen bonds, the latter progressively more important at low pH values. Hydrophilic and hydrophobic domains of humic molecules can be contiguous to or contained in each other and, in hydration water, form apparently large molecular associations. In humic supramolecular organisations, the intermolecular forces determine the conformational structure of HS and the complexities of the multiple noncovalent interactions control their environment reactivity. In solution, HS can vary their conformational structures in which the hydrophilic groups are located at the interface of the humic substances solution, whereas the hydrophobic portions of the molecule are likely to arrange themselves in the interior of the macromolecule (Barak and Chen, 1992). This new arrangement of the conformational structure of HS (pseudo-micelles) favour the repartition of

the apolar contaminants into the hydrophobic domains present in the supra-molecular structure (Piccolo, 2001). Due to their different interaction for organic compounds and trace metals, they have a special relevance for many geochemical processes, the mobility and bioavailability of pollutants and micronutrient in the marine environment and can find special application as immobilisers of contaminants for remediation purposes (e.g., Conte et al. 2001).

HAs can be obtained at relatively low cost by alkaline extraction of peat, lignite or leonardite and thus are commercially available on a large scale. The HAs are composed by associations of predominantly hydrophobic compounds (polymethylenic chains, fatty acids, steroid compounds) that are stabilized at neutral pH by hydrophobic dispersive forces (van der Waals, π - π , and CH- π bondings) (Piccolo, 2001). They can be structurally described as a ligands with a variety of different functional groups useful to bind organics in a number of ways.

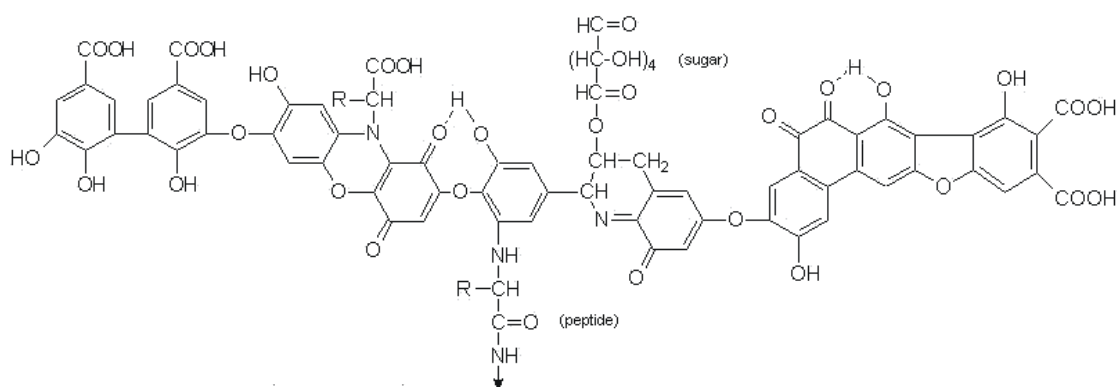
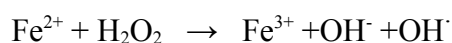


Fig. 3. Model structure of HA (Stevenson, 1982)

1.7.2. The Fenton reagent

Oxidative chemicals are considered useful tools to destroy or convert organics, such as PAHs, to non-toxic or less hazardous compounds, or to intermediates that can be further degraded by microorganisms (Hamby, 1996). One of the most used oxidant agent for remedial purpose is the Fenton reagent (Saxe et al., 2000, Foltron et al., 2004; Georgi et al., 2006, Jonsoon et al., 2007) that consists of hydrogen peroxide in combination with ferrous iron (Fe^{2+}) which produce hydroxyl radicals ($\cdot\text{OH}$) in aqueous solution (Walling, 1975):

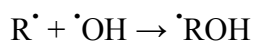
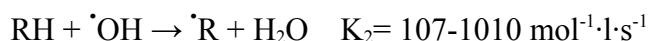


$$K_1=53-76 \text{ mol}^{-1}\cdot\text{l}\cdot\text{sec}^{-1}$$

The standard oxidation potential (in Volts) of the hydroxyl radicals is the highest (2.8V) than those of the other typical oxidants used in or formed for this purpose as sulphate radical (2.5V); ozone (2.1V), sodium persulfate (2.0V), hydrogen peroxide (1.8V) and oxygen (1.2V).

At pH 2-3, precipitation of iron salt is prevented while at higher pH values, iron precipitation has to be inhibited by complexation with, for example, addition of ethylene-diammino-tetraacetic-acid (EDTA). EDTA decreases the redox potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$, thus favouring the Fe^{2+} oxidation and the $\cdot\text{OH}$ formation.

The formed hydroxyl radical degrade organic compound either by hydrogen extraction and/or by hydroxyl addition:



Usually, the disappearance of the organic substrate follows a pseudo first order kinetic law, the $\cdot\text{OH}$ concentration being considered as a constant (due to its high reactivity).

The hydroxyl radicals react with aromatic compound at near diffusion-controlled rates (i.e., $k_{\cdot\text{OH}} > 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$) (Haag and Yao, 1992) by extracting hydrogen atoms or by addition to double bonds (Legrini et al. 1993; Güsten et al., 1995; Sabljic and Peijnenburg, 2000). Thus, the oxidation is no selective and any oxidizable material will react with the hydroxyl radical. The final result of the oxidation process should be the total mineralization of the organic contaminants in carbon dioxide and water. In reality, when applied to sediments polluted by PAHs, the oxidation appears generally incomplete (Lundstedt, 2003) with formation of products that may be potentially more toxic or mutagenic than their parent molecules (Møller et al., 1985; Fernandez et al., 1992; Mallakin et al., 1999). The reaction pathways are very complexes and numerous intermediates seem to be formed. The intermediates formed during Fenton oxidation of PAHs have not been thoroughly investigated, but results reported by Beltran et al., (1998), Rivas et al., (2000), Lee et al., (1998, 2001) and Lee and Hosomi, (2001) indicate that the products are similar to the compounds formed during ozonization and UV-degradation of PAHs (Kochany and Maguire, 1994; Mallakin et al., 1999). In particular,

oxygenated PAHs (oxy-PAHs) such as ketones, quinones, appear to be important oxidation products (Lundstedt et al., 2006).

I.8. Isotope Geochemistry

Radioactive (unstable) isotopes are nuclides that spontaneously disintegrate over time to form other isotopes. During the disintegration, radioactive isotopes emit alpha or beta particles and sometimes also gamma rays. Stable isotopes are nuclides that do not appear to decay to other isotopes on geologic time scale, but may themselves be product by of radioactive isotopes.

For nuclides of low atomic mass, the greatest stability is achieved when the number of neutrons and protons are approximately equal ($N=Z$); these are the so-called stable isotopes. However, as the atomic mass increases, the stable neutron/proton ratio increases until $N/Z=1.5$.

The stable isotope compositions of low mass elements such as oxygen, hydrogen, carbon, nitrogen, and sulphur are normally reported as δ values. δ values are reported in units of parts per thousand (‰) relative to a standard of known composition. δ values are calculated by the equation:

$$\delta \text{ (in ‰)} = (R_x/R_s - 1) \cdot 1000$$

where R denotes the ratio of the heavy to light isotope in the sample (R_x) and standard (R_s), respectively.

The isotopic compositions of samples analyzed by mass spectrometers are usually reported relative to some international reference standards. Reference standards are available for calibration purposes from either the National Institute of Standards and Technology (NIST) or the International Atomic Energy Agency (IAEA). The δ value of the reference standard is defined to be 0‰. $\delta^{13}\text{C}$ values for carbonates and for organic matter are generally reported versus VPDB standard.

At the isotopic equilibrium the ratio of different isotopes, in each compound, is constant at a particular temperature. During equilibrium reactions, the heavier isotope generally preferentially accumulates in the species or compound with the higher oxidation state. Among different phases of the same compound or different species of the same element, the more dense the material, the more it tends to be enriched in the heavier isotope. During phase changes, the ratio of heavy to light isotopes in the molecules of the two phases changes. This phenomenon is called isotopic fractionation process. The fractionation associated with the

equilibrium exchange reaction between two substances A and B can be expressed by use of the isotopic fractionation factor α .

$$\alpha_{A-B} = R_A/R_B$$

where R is the ratio of the heavier to the lighter isotope in the compound A and B.

In systems out chemical and isotopic equilibrium, reaction rates are dependent on the ratio of the masses of the isotopes and their vibrational energies, and therefore isotope fractionation is primarily ruled kinetic effects. The magnitude of the kinetic isotope fractionation depends on the reaction rate, and the relative bond energies involved with different reactions. Bonds between the lighter isotopes are broken more easily than equivalent bonds of heavier isotopes. The light isotopes react faster and became concentrated in the products, causing the residual reactants to become enriched in the heavy isotopes.

Rayleigh equation, typically used to describe the mass balance evolution of distillation processes, is an exponential relation that describes the partitioning of isotopes between two reservoir as one reservoir decreases in size. The equations can be used to describe an isotope fractionation process if: (1) the material is continuously removed from mixed system containing molecules of two or more isotopic species; (2) the fractionation accompanying the removal process at any instance is described by the fractionation factor α , and (3) α does not change during the process. Under these conditions, the evaluation of the isotopic composition in the residual material can be described by the following equation:

$$(R/R_0) = (X_1/X_{1^0})^{\alpha-1}$$

Where R= ratio of the isotopes in the reactant, R_0 = initial isotope ratio, X_1 = the concentration or amount of the more abundant isotope and X_{1^0} = initial concentration.

Because the concentration of $X_1 \gg H_h, X_1$ is approximately equal to the amount of original material in the phase. Hence, if $f = X_1/X_{1^0}$ = fraction of material remaining, then:

$$R = R_0 f^{(\alpha-1)}$$

Rayleigh fractionation should only be used for chemically open systems where the isotopic species removed at every instant is in thermodynamic and isotopic equilibrium with those remaining in the system at the moment of removal (Kendall and Caldwell, 1998).

Chapter II

MATERIAL AND METHODS

II.1. A short overview of the sampling sites

The studied marine sediment samples were collected from the areas of the Naples harbour and the industrial plant of Bagnoli which represent two highly polluted marine areas of the southern coast of Italy. The Naples's harbour receives municipal discharges (either untreated or with only primary treatment) a urban center of ~1.5 million people. In addition, it is receptor of multiple industrial (petroleum refineries, metallurgy, cement and food production), port activities (shipbuilding, good stocking, commercial and tourist transactions), commercial discharges, and urban wastewaters. A detailed geochemical characterization and monitoring of the sediments of the harbour of Naples carried out during years 2003-2005 allowed one to carefully select, for this research work, a group of sediment samples characterized by a large spectrum of chemical-physical features and PAHs contamination.

The industrialized area of Bagnoli was the center of one of the greatest takeovers of the south of Italy, in particular one of the steel mill of the ILVA was active until the beginning of the 1900, and definitively closed in the '90s. As a result of these industrial activities, the Bagnoli area is characterized by high concentration of inorganic and organic contaminants such as reported by the results of geochemical monitoring carried out in this area since year 2002 (De Pippo et al., 2002).

II.2. Sampling of marine sediments

The location of the studied samples is shown in Fig. 4.

Surficial sediments (0-20 cm) were collected using a vibro-corer with an inner diameter of 10 cm, and 6 m long. Samples were immediately homogenized with a plastic spoon after collection, placed into pre-cleaned high-density polyethylene (HDPE) bottles for chemical analyses and stored at -18°C.

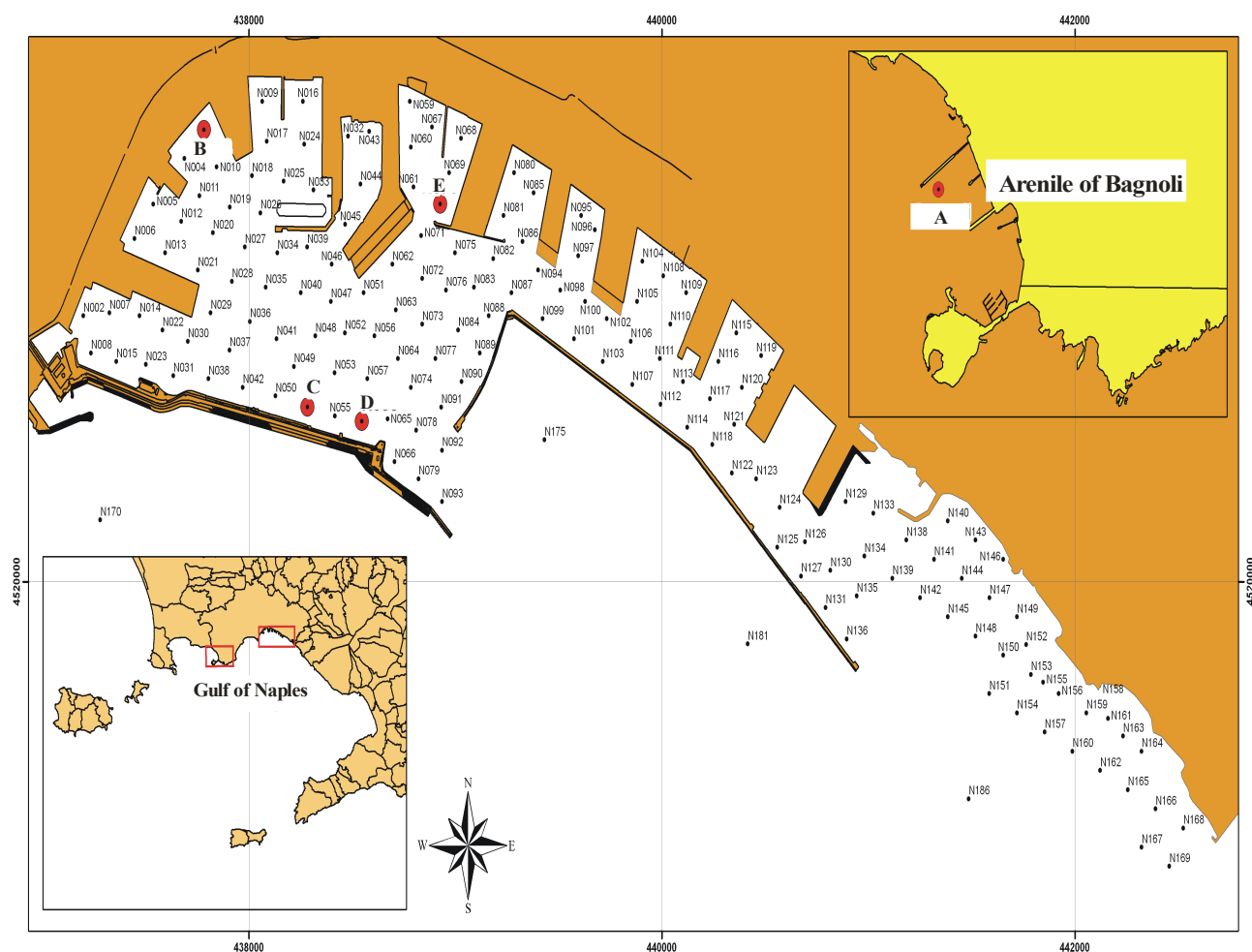


Fig. 4. Location map of the studied samples. samples B,C,D and E from the Naples's harbour, sample A from the "Arenile of Bagnoli"

II.3. Analytical methods for PAHs measurements

The quantitative analysis of PAH of in the studied sediments was carried out following four steps:

- i) pretreatment, ii) extraction, iii) clean up, iv) GC-MS analysis.

II.3.1. Pre-treatment

Sample were air dried to facilitate the subsequent griding and to increase the contact between the sediment and the organic solvent used for extraction in order to favour the extractability of the analytes. Drying was carried out at low temperature (35°C) to avoid the volatilization of the analytes. After drying the samples were ground in a mortar (at $\phi < 2$ mm) to increase the homogeneity of the sample and to increase the extractability of the analytes by enhancing the exposed surface area of the particles.

II.3.2. Extraction by Accelerated Solvent Extraction (ASE)

PAHs were extracted from sediments by a Dionex ASE which utilizes organic solvent at elevated temperature and pressure. The sample (~2g of sediment mixed with ~2g of diatomaceous earth) was loaded into the extraction cell, and placed into the oven of the extraction system. Solvent was pumped from the solvent bottle into the cell, which was then pressurized and heated. Solvent was collected in a vial and the sample was flushed with fresh solvent. Finally, the sample was purged with suitable gas (N₂) to recover the last solvent residues.

The ASE program for PAHs extraction is:

Pressure: 1500 psi;

Temperature: 113°C;

Static time: 5min.;

Flush volume: 60%;

Static cycle: 1.

Solvent utilized for the extraction was hexane/acetone 80:20 v/v. Hexane has the capacity to form weak bond (Van der Waals interaction) with PAHs while acetone favours the interaction between hexane and the analytes avoiding formation of emulsions with residual water.

The recovery of PAHs was estimated by spiking a mixture of six deuterated PAHs on the sediments before extraction. The solution of deuterated PAH included: acenaphthene d-10, fluoranthene d-10, phenanthrene d-10, benzo(a)anthracene d-12, benzo(a)pyrene d-12, dibenzo(a,h)anthracene d-12.

II.3.3. Clean up

After the extraction, the mixture was diluted fifty times and then 1 ml of it concentrated under N₂ flux and re-dissolved in 0.5 ml of cyclohexane. The solution was purified by solid phase extraction (SPE) containing 2g of silica, activated with 25 ml of hexane. Initially columns were eluted with 10 ml of hexane to eliminate aliphatic compounds present in the silica column. Then PAHs were eluted with 20 ml of cyclohexane: acetone 70:30. The eluted was dried under N₂ flux and re-dissolved with 400µl solution of two deuterated PAHs (acenaphthylene d-8 and chrysene d-12). The concentration of individual PAH molecules was determined by gas chromatography with mass spectrometric detection.

(GC/MS). Dilution of final solutions and the clean up allowed to efficiently reduce the effects of the interferences during PAHs analysis.

II.3.4. GC-MS analysis

All the gas-mass analyse were performed by a Thermo Fisher DSQ-Trace GC-MS. An analytical column (95% dimethyl 5% phenil-polisilossano) 30m x 0.25mm x 0.25 μ m was used to separate PAH molecules. The temperature program was the following: 80°C held for 1.5 min; to 200 °C at a 15°C/min then to 305°C at a 7°C/min; isothermal for 10 min. The injection volume was 1 μ l in splitless mode. Operative conditions were: ion source 280°C, inlet 250°C and carrier gas He 1.2 ml/min. PAH molecules (Tab. 2) were identified by their GC-retetion time in comparison with reference compounds and literature data. However, for more reliable identification, the retetion time data were complemented with mass spectral data obtained by MS NIST library. The mass spectrometer operated at an EI of 70 eV .After the identification of PAH molecules, mass spectrometer was operated in selective ion monitoring (SIM) mode to increase the sensibility and accuracy of the instrument. Laboratory quality control procedures included analyses of blanks and reference material used for quality control (BCR-535). Instrument stability and response was checked using NIST standard solutions. Estimated recovery for each analyte ranged between 94% and 107%. Accuracy was estimated to be better than $\pm 10\%$ for each single analyte. Riproducibility estimated on triplicate samples was $\geq 90\%$. The limit of detection was estimated ≥ 5 ng/g for each PAHs.

The highly complex matrix characteristic of the studied samples required a previous dilution ($\sim 1/50$) to ensure an accurate determination of the single analytes. The effects of diluition, were evaluated on the basis of multiple tests carried out on the certified BCR 535 reference material and on the studied samples. An example of the effects of diluition on the chromatograms of sample A are reported in Fig. 5 and Fig. 6. As an example in the inside graphs, the signal-noise ratio for Cry-d₁₂ shows an evident changes between 64 to 642, associated to a variation of the area between 148445 to 254607. The estimated difference in the internal standard quantification produced an inaccuracy of the final measuring of the PAH congeners with respect to the diluited (1/50) solution in a range of 70-150%. All the analysed samples were diluited 50 times before final quantitative analysis in GC-MS.

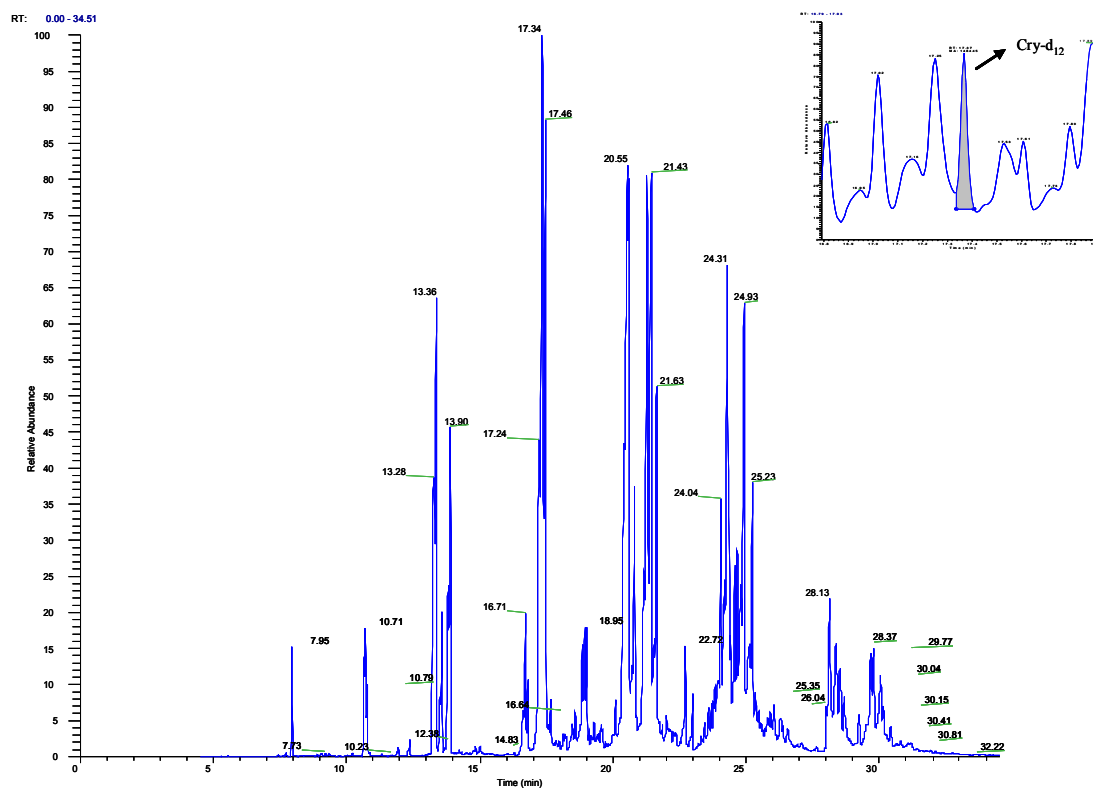


Fig. 5. Chromatogram of sample A before dilution.

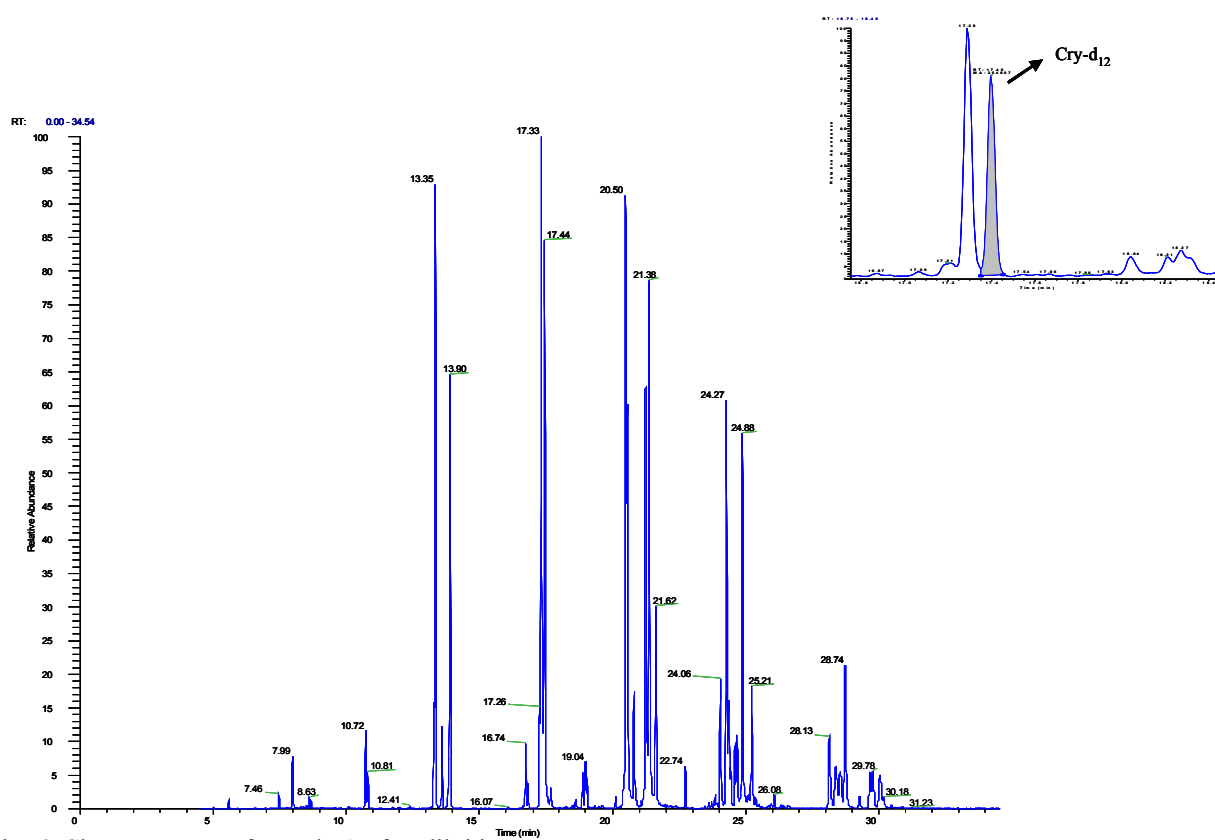


Fig. 6. Chromatogram of sample A after dilution.

	Retention time
Naphthalene	5.61
Acenaphthylene d-8	7.98
Acenaphthylene	8.00
Acenaphthene d-10	8.34
Acenaphthene	8.36
Fluorene	9.09
Phenanthrene d-10	10.71
Phenanthrene	10.75
Anthracene	10.84
Fluoranthene d-10	13.33
Fluoranthene	13.38
Pyrene	13.93
Benzo(a)anthracene	17.35
Benzo(a)anthracene d-12	17.29
Crysene	17.47
Crysene d-12	17.40
Benzo(b)fluoranthene	20.54
Benzo(k)fluoranthene	20.59
Benzo(a)pyrene	21.29
Benzo(a)pyrene d-12	21.35
Benzo(e)pyrene	21.41
Indeno(1,2,3-cd)pyrene	24.31
Dibenzo(a,h)anthracene d12	24.31
Dibenzo(a,h)anthracene	24.39
Benzo(g,h,i)perylene	24.93

Tab. 2. PAH congeners analysed by GC-MS and relative retention time

II.4. Analysis of Total Organic Carbon (TOC)

About 15 mg of sediments were treated with a solution of HCl 10% and dried at 65°C in order to eliminate the contribution of CaCO₃ present in the samples. TOC in the samples was analyzed by an Element Analyzer (Thermo Electron Flash EA1112). Duplication of an aliquot of samples produced a reproducibility values < ±5%. Reference standard was cyclohexanone (N:C 20.14%:51.79%). External standard calibration was utilized to quantify the amount of total organic carbon in the samples.

II.5. Grain size analysis

Samples for grain size analysis were treated with H₂O₂, then washed and dried at 40°C. Fine size fraction (silt and clay, <63 µm) was analysed by laser particle-size analyzer. The results are expressed in % as the ratio between mineralogic fraction and weigh of total sample. The Shepard (1954) grain size classification was used.

II.6. PAHs extraction from different grain size fractions

About 100g of sediments were suspended in 150 ml of water and sonicated with a Lindsonic ISCO sonicator. A frequency of 50 Hz was applied for 20 minutes to the soil suspension. After sonification, the suspension was filtered through sieves of different size: $\phi > 1000 \mu\text{m}$; $1000 < \phi < 500 \mu\text{m}$; $500 < \phi < 250 \mu\text{m}$; $250 < \phi < 125 \mu\text{m}$; $125 < \phi < 90 \mu\text{m}$; $90 < \phi < 63 \mu\text{m}$; $\phi < 63 \mu\text{m}$. Every mineralogic fraction is washed with distilled water and dried at 35°C and finally analysed for PAHs.

II.7. Humic Acid extraction

Humic acids were isolated from a North Dakota Leonardite (Mammoth, Chem. Co., Houston, Texas), and purified as reported by Piccolo et al. (2002). The HAs were then suspended in distilled water and titrated to pH 7 by an automatic titrator (VIT 909 Videotitrator, Copenhagen) with a 0.1 M NaOH solution under N₂ stream. The resulting sodium-humate was then filtered through a Millipore 0.45 µm membrane and “freeze-dried”.

II.8. Iron analysis

Iron concentrations in the samples were measured by inductively coupled plasma atomic absorption (ICP-AES) using a Varian Vista MPX, after total digestion of sediments with a HNO₃:HCl:HF = 3:1:1 acid mixture using a microwave oven (CEM Mars 5 equipment) at controlled pressure and temperature (step 1: 300 psi, 165°C, 900W power for 10 min; step 2: 300 psi, 165°C, 900W power for 5 min) followed by a final step (step 3: 100 psi, 165°C, 600W power for 10 min) with boric acid.

II.9. Stable isotope analysis

Stable isotopes were measured by an isotope ratio mass spectrometer. Sample preparation involves the production of pure gas from solely the compound of interest, chromatographic purification of the gas, introduction into the mass spectrometer, ionization to produce positively charged species, dispersion of different masses in a magnetic field, impact of different masses on different collector cups, and measurement of the ratios.

The $\delta^{13}\text{C}$ was determined directly on bulk powdered samples and weighted in tin capsules. The $\delta^{13}\text{C}$ of TOC fraction was determined by a Thermo Electron Flash EA 1112 elemental coupled to the isotope ratio mass spectrometer (IRMS) Thermo Electron Delta Plus XP. Isotopic ratios were expressed in the usual δ -notation in parts per mil (‰). For carbon, the international reference standard is the VPBD. Data quality control was checked by running an internal standard each six samples. For $\delta^{13}\text{C}$ analyser the sediments were weighted (2-5mg) and the carbonate fraction was eliminated after treatment with 1M HCl directly in silver capsules and then dried (60°C) in a oven of lab and analyser. Samples were run with blank cups and known urea standards in order to correct for the C associated with tin cups and calibrate for elemental analysis. Standards were prepared by weighing (from 0.5 to 2 mg) of analytical grade urea ($\text{CH}_4\text{N}_2\text{O}$ mw=60, C=20% N=46%). Data quality control was checked by running a reference standard (urea) after every six samples.

II.10. Chemical remediation: the experiments

II.10.1. Soil washing

About 10g of sediment were suspended in 100 ml of each “soil washing” solution and shaken for 24h (or 48h) in a rotary shaker at 10 rpm. All the suspensions were centrifuged in glass tubes at 10,000 rpm for 15 min in order to separate solid residues from washing solutions. The solid residues were dried at 35°C and then their PAHs concentrations measured. In some cases, soil washing was repeated two times on the same sample (double soil washing). Solutions used for soil washing were: 1) humic acid solution: 1g HAs in 100 ml H_2O ; 2) 0.4% Triton X-100 in humic acid solution; 3) 1%Triton X-100 in humic acid solution. The concentration of humic acid solution was reported to represent the critical micelle concentration of HAs (Guetzloff and Rice, 1994).

II.10.2. Fenton oxidation

About 5g of sediment were suspended in 50 ml of water, and then reacted with a total of 6.25 ml of 1% (or 30%) H_2O_2 and 6.25 ml of Fe^{2+} /EDTA solution ($[\text{Fe(II)}]=0.3\text{M}$; $\text{Fe(II)/EDTA}1:1$), with peroxide added at increments of 1.56 ml about 30s (or 15min) after the initial iron addition. The mixture was shaken for 24h in a rotatory shaker at 10 rpm. The suspension was centrifuged in a glass tube at 10,000 rpm for 15 min in order to separate solid residues from washing solution. The solid residues were dried at 35°C and the amount of PAHs measured

II.10.3. Analysis of black carbon

About 5g of sediment (fraction $\phi < 63\mu\text{m}$) were suspended in a solution of CeCl (32g CeCl in 40ml H_2O_2) with $\rho = 1.8\text{g/l}$ and centrifugated in a glass tube at 2000 rpm for 10 min in order to separate solid residues from aqueous solution. The supernatant contains black carbon particles which were left extol and filtered. After filtration the supernatant was washed with distilled water to eliminate trace of CeCl, and then dried at 35°C . The solid residue obtained after centrifugation was washed with distilled water to eliminate trace of CeCl and dried at 35°C . The amount of PAHs were measured only in the solid residue because the amount of black carbon was too limited ($< 0.6\%$ of the total organic carbon) to allow PAHs extraction.

II.10.4. Extraction of PAHs from HA surfactant solution

Two solutions of PAH congeners (containing 93 ng of Phe; 94 ng of An, B(a)a and B(a)p; 92 ng of Py; 95 ng of Cry, B(b)f, B(k+j)f and Ind; 188 ng of Flu; 189 ng of D(a,h)a and B(g,h,i)p) were spiked into two HA solutions (containing 0.25g of HA) and shaken for 24h. Then the two spiked solutions (α and β) were air dried and then PAHs were extracted by ASE using two different temperatures: 113°C and 150°C , respectively.

II.10.5. Soil washing solution with $^{13}\text{C}_3$ pyrene spikes

About 20g of $^{13}\text{C}_3$ Pyrene were spiked in 2.5g of sediment. After about 1 month, the sediment was suspended in 25ml of HA solution (0.25g HAs in 25 ml H_2O) and shaken for 24h in a rotatory shaker at 10 rpm. Then, the suspension was centrifuged in glass tubes at 10,000 rpm for 15 min in order to separate solid residue from the washing solution. The latter was dried at 35°C and the solid residue was analysed in IRMS.

II.10.6. Fenton oxidation of $^{13}\text{C}_3$ pyrene spiked in HA solution

About 20g of $^{13}\text{C}_3$ pyrene were spiked in a HA solution (0.25g HAs in 25 ml H_2O) and shaken for 24h. After shaking, the solution was reacted with a total of 0.78 ml of 1% (or 30%) H_2O_2 and 3.12 ml of Fe^{2+} /EDTA solution ($[\text{Fe(II)}] = 0.3\text{M}$; $\text{Fe(II)}/\text{EDTA} 1:1$), with peroxide being added at increments of 0.195 ml increments, 30s after the initial iron addition. The suspension was centrifuged in a glass tube at 10,000 rpm for 15 min in order to separate the solid residue from the liquid phase. The liquid phase was dried at 35°C and the solid residue analysed in IRMS.

Chapter III

RESULTS

III.1. Physical properties of the studied samples.

All the experiments were carried out on five selected surface (depth of 0-20 cm) marine sedimentary samples, we labelled from A to E which were collected from the Bagnoli area (A) and the harbour of Naples (B to E) (Tab. 3, Fig. 3).

Sample	Depth (cm)	Long (degree)	Lat (degree)
A	0-20	11.539240	45.111860
B	0-20	14.261944	40.842902
C	0-20	14.267983	40.834202
D	0-20	14.271119	40.833772
E	0-20	14.275539	40.840646

Tab. 3. Depth, longitude and latitude of the studied samples

The results from the project of environmental monitoring of the Naples's harbour area (Sprovieri et al., 2007) indicated that total concentrations of PAHs in those sediments varied between 0.01 and 25.98 mg/kg as shown in Fig. 7.

The samples selected for this research were collected in order to represent a large spectrum of PAHs distribution and physical characteristics of sediments, useful to extend the results to a wide range of real situations.

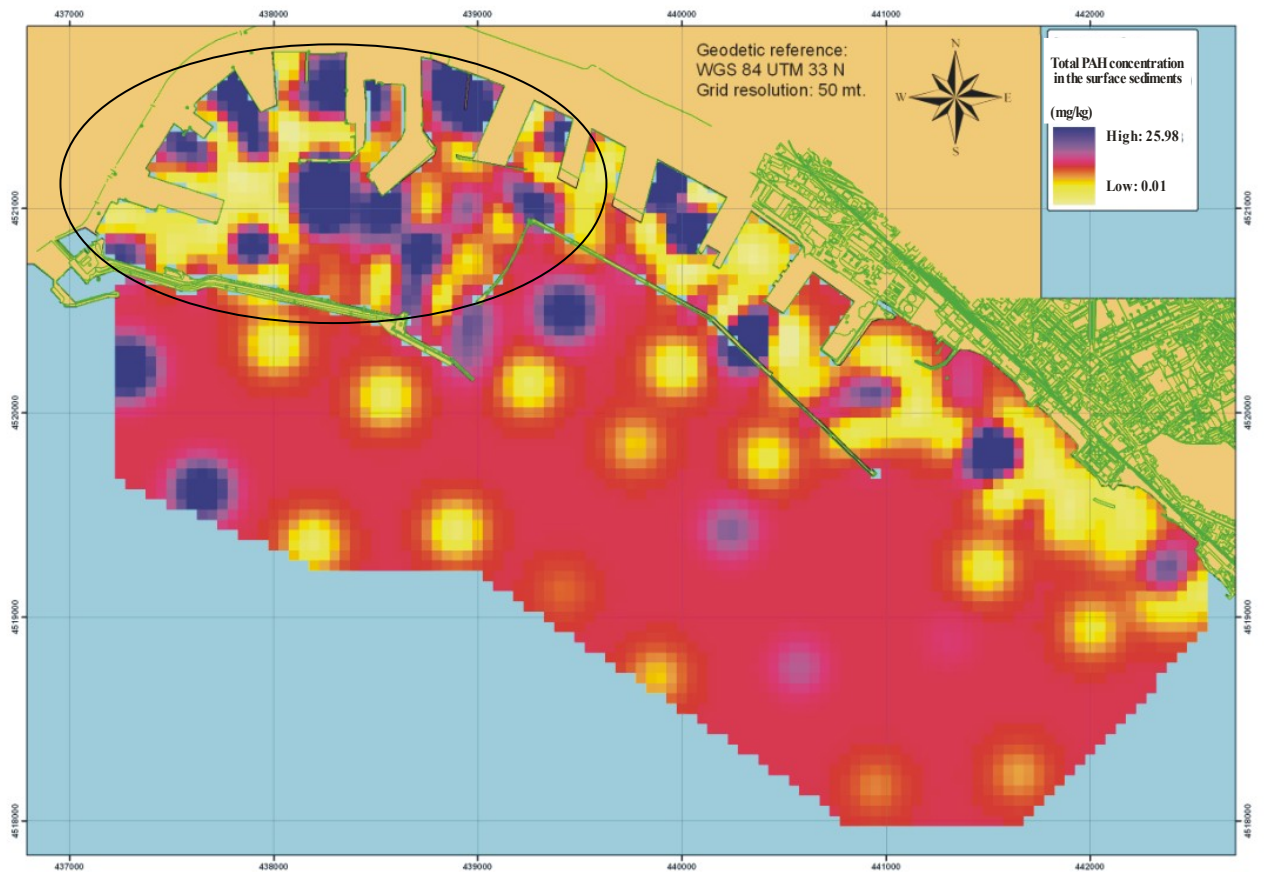


Fig. 7. Map of distribution of the Σ PAHs concentrations in the Naples's harbour. Circle indicates the area where the samples for this research were collected.

Grain size and TOC of the studied samples are reported in Tab.4.

Sample	Gravel %	Sand %	Silt %	Clay %	TOC %
A	16.8	78.7	3.7	0.7	2.00
B	13.7	54.6	24.9	6.7	0.58
C	27.3	22.5	40.5	9.7	1.23
D	20.7	14.1	53.6	11.6	1.34
E	0	17.3	70.5	12.2	1.23

Tab.4. Grain size and TOC distribution in the studied samples

The percentage of silt and clay increases from sample A to E mirroring a proportional decrease of sand, from percentages of 78.7 to 14.1%.

A refined grain size analysis for the coarser fraction is reported in Tab. 5 where seven classes of ϕ were distinguished.

	$\phi > 1000$ %	$1000 < \phi < 500$ %	$500 < \phi < 250$ %	$250 < \phi < 125$ %	$125 < \phi < 90$ %	$90 < \phi < 63$ %	$\phi < 63$ %
A	0.48	1.10	5.90	51.00	15.00	7.00	2.30
B	2.60	2.17	3.90	19.77	19.74	19.89	12.70
C	2.00	1.61	3.60	6.99	2.92	6.06	50.00
D	0.17	0.22	0.30	1.11	1.40	8.50	67.00
E	0.02	0.17	0.80	8.50	8.2	12.20	64.00

Tab. 5. Percentage of the different grain size fractions . ϕ is in μm

For all samples, the percentage of grain size with $\phi > 250 \mu\text{m}$ is very low (generally lower than 5.90%). A high percentage (51%) in the fraction $250 < \phi < 125 \mu\text{m}$ is present only in the sample A. Sample B is characterized by high percentage values ($\sim 19\%$) of the three fraction $250 < \phi < 125 \mu\text{m}$, $125 < \phi < 90 \mu\text{m}$, $90 < \phi < 63 \mu\text{m}$ while silt is predominant in sample C, D and E (ranging from 50 and 60%).

Percentage of TOC in sample A is about 2%, decreasing to values of about 1.2-1.3% in samples C, D and E. Sample B shows the lowest TOC percentage with an estimated value of $\sim 0.6\%$.

A C/N ratio > 20 was estimated for the samples C and D, while sample E showed a C/N ~ 17 . Sample B showed the percentage of nitrogen was under the detection limit of the instrument and then the C/N ratio was not calculated. The map of C/N ratio of Naples's harbour shows higher values in the nord-west area where the samples used in this research were collected (Fig. 8).

The C/N value of sample A was assumed > 20 as estimated for the entire Gulf of Pozzuoli by Damiani et al. (2004).

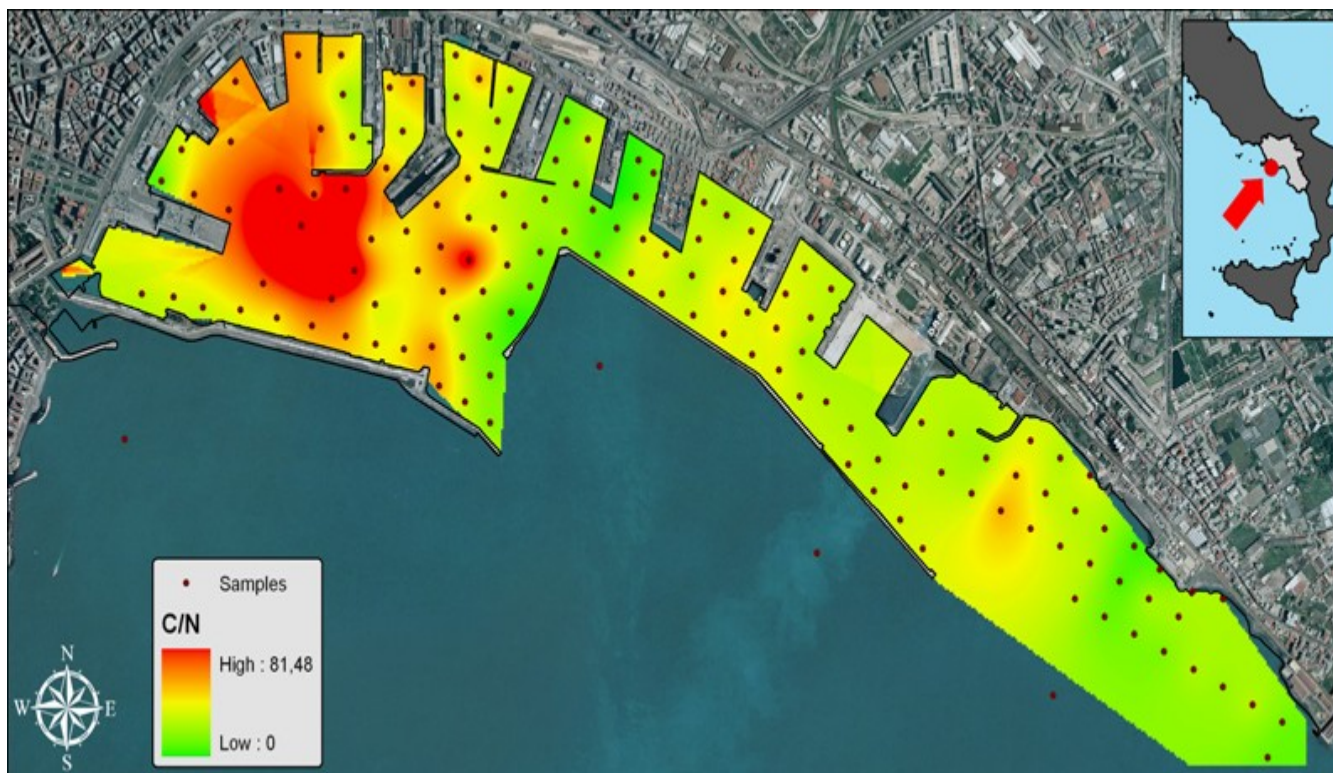


Fig. 8. Map of distribution of C/N ratio in the Naples's harbour

III.2. Concentration of PAHs in the studied samples

Only the PAHs indicated by the US-EPA Clear Water Act as priority ones were analysed; phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Py), benzo(a)anthracene (B(a)a), crysene (Cry), benzo(b)fluoranthene (B(b)f), benzo(k+j)fluoranthene (B(k+j)f), benzo(a)pyrene (B(a)p), benzo(e)pyrene (B(e)p), indeno(1,2,3-cd)pyrene (Ind), dibenzo(a,h)anthracene (D(a,h)a) and benzo(g,h,i)perylene, (B(g,h,i)p). Naphtalene, acenaphthylene, acenaphtene and fluorene were not monitored in this study due to their high vapour pressure and associated scarce recovery.

The concentrations of the total PAHs (Σ PAH) and the singular analysed congeners are reported in Tab. 6 for the five studied samples.

Sample	Phe mg·kg ⁻¹	An mg·kg ⁻¹	Flu mg·kg ⁻¹	Py mg·kg ⁻¹	B(a)a mg·kg ⁻¹	Cry mg·kg ⁻¹	B(b)f mg·kg ⁻¹	B(k+j)f mg·kg ⁻¹	B(a)p mg·kg ⁻¹	B(e)p mg·kg ⁻¹	Ind mg·kg ⁻¹	D(a,h)a mg·kg ⁻¹	B(g,h,i)p mg·kg ⁻¹	Σ PAH mg·kg ⁻¹
A	6.28	3.38	19.91	12.21	7.25	8.23	6.99	3.47	5.84	7.84	7.19	1.32	7.53	97.90
B	1.30	0.35	1.19	1.09	0.61	0.85	0.58	0.29	0.45	0.50	0.42	0.14	0.39	8.16
C	3.98	3.22	4.39	3.57	2.78	3.35	7.73	4.14	4.81	7.44	3.59	1.73	3.74	54.47
D	1.77	4.15	1.94	1.77	1.48	1.87	4.40	2.29	3.13	6.38	3.34	0.63	3.74	36.91
E	0.55	0.59	0.27	0.64	0.46	0.55	0.84	0.26	0.35	0.40	0.52	0.63	0.59	6.65

Tab. 6. Concentration of ΣPAHs and single congeners for the five samples

The sample A shows the highest value of ΣPAH ($97.90 \text{ mg}\cdot\text{kg}^{-1}$) with a predominance of Flu ($19.91 \text{ mg}\cdot\text{kg}^{-1}$) and Py ($12.21 \text{ mg}\cdot\text{kg}^{-1}$). The samples B and E have the lowest ΣPAH (8.16 and $6.65 \text{ mg}\cdot\text{kg}^{-1}$, respectively) with a predominance of Phe ($1.30 \text{ mg}\cdot\text{kg}^{-1}$), Flu ($1.19 \text{ mg}\cdot\text{kg}^{-1}$) and Py ($1.09 \text{ mg}\cdot\text{kg}^{-1}$) in sample B, and of B(b)f ($0.84 \text{ mg}\cdot\text{kg}^{-1}$) in sample E. The samples C and D have ΣPAH of 54.47 and $36.91 \text{ mg}\cdot\text{kg}^{-1}$, respectively with a predominance of B(b)f ($7.73 \text{ mg}\cdot\text{kg}^{-1}$) and B(e)p ($7.44 \text{ mg}\cdot\text{kg}^{-1}$) in sample C and of B(e)p ($6.38 \text{ mg}\cdot\text{kg}^{-1}$) in sample D.

The distribution of PAHs in the different classes of grain size is reported in Fig. 9. The highest values of ΣPAH are generally present in the coarser fractions ($\phi > 1000 \text{ }\mu\text{m}$, $1000 < \phi < 500 \text{ }\mu\text{m}$, and $500 < \phi < 250 \text{ }\mu\text{m}$). In particular the samples A, D and E have the highest ΣPAH content in the fraction $\phi > 1000 \text{ }\mu\text{m}$, while the samples B and C have higher PAH contents in the fraction $1000 < \phi < 500 \text{ }\mu\text{m}$.

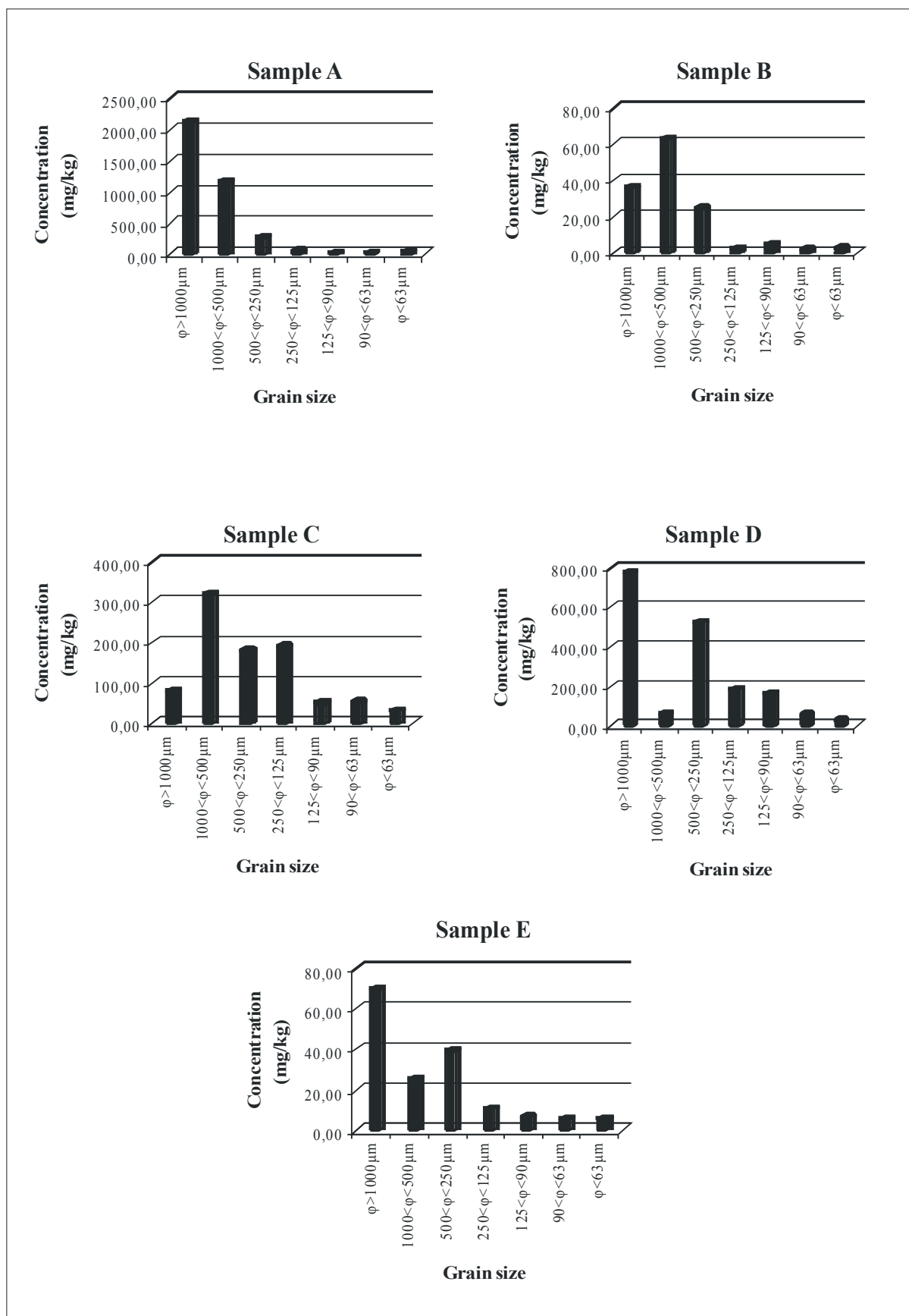


Fig. 9. Concentration of ΣPAHs measured in the different classes of grain size

As for the distribution of Σ PAHs, in all the studied samples, the concentration of the single PAH congeners are generally higher in the coarser fraction and decrease in the finer components (Fig. 10 to Fig. 14). This is particularly evident in the sample A, characterised by a large difference between the concentration values of PAH congeners in the two fraction, $\phi > 1000 \mu\text{m}$ and $1000 < \phi < 500 \mu\text{m}$, and those measured in the finer fraction. This difference is less evident in samples B, C and D and it appears irrelevant in sample E.

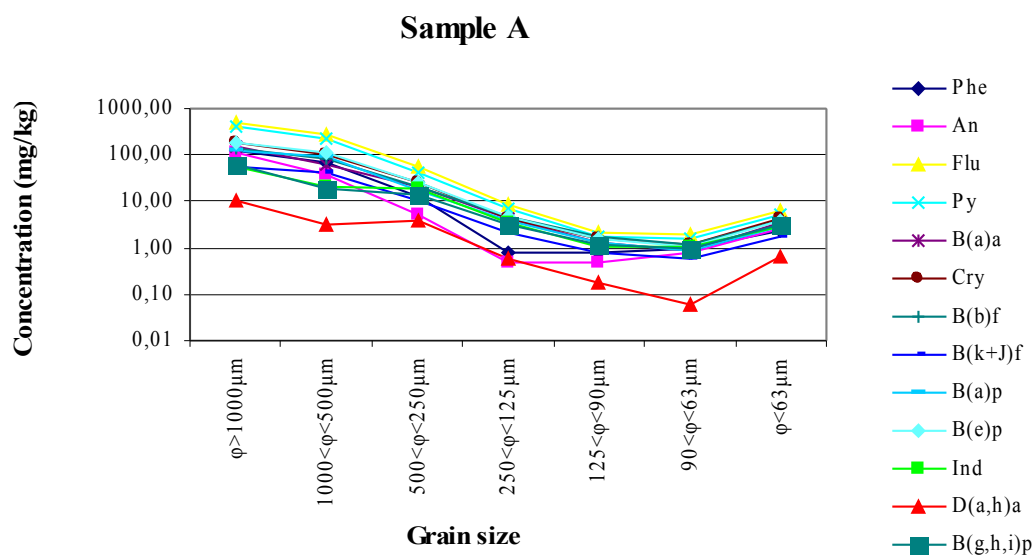


Fig. 10. Concentration values of the single PAH congeners in the different size fractions of sample A

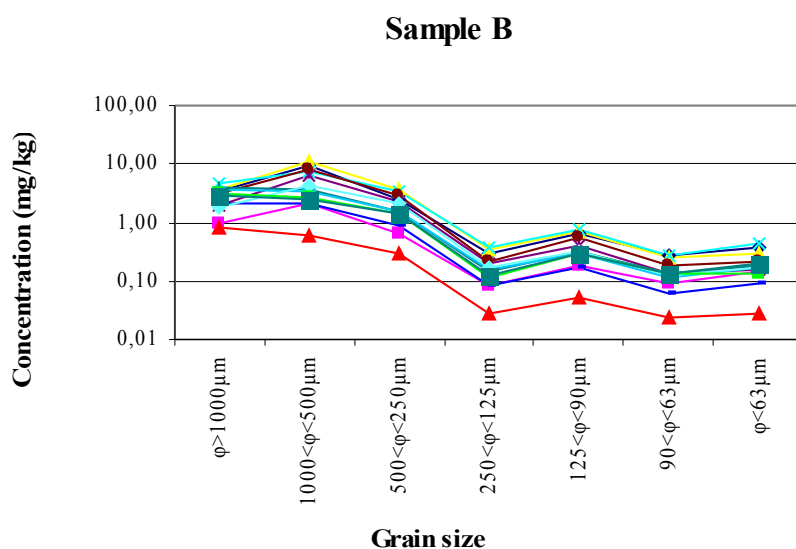


Fig. 11. Concentration values of the single PAH congeners in the different size fractions of sample B

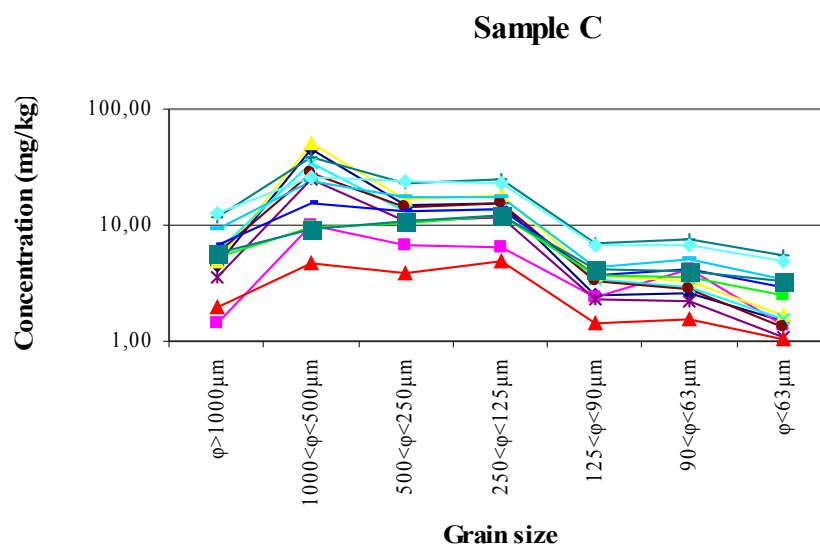


Fig. 12. Concentration values of the single PAH congeners in the different size fractions of sample C

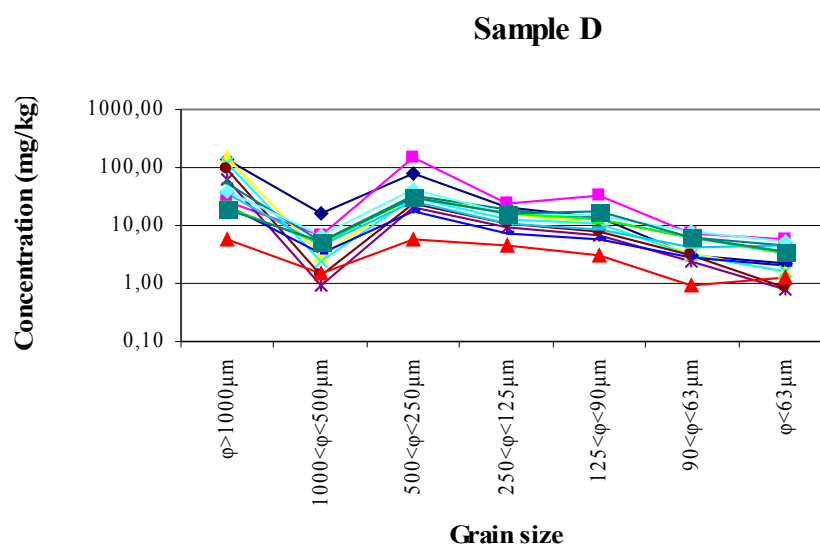


Fig. 13. Concentration values of the single PAH congeners in the different size fractions of sample D

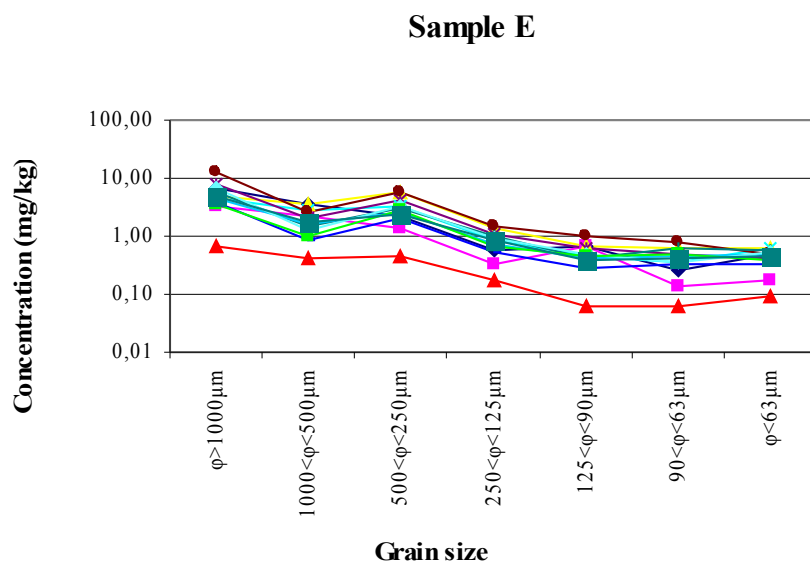


Fig. 14. Concentration values of the single PAH congeners in the different size fractions of sample E

III.3 Results of the remediation experiments

A complete outlook of the different remediation experiments carried out during this research is reported in Tab. 7.

N° of experiment	Chemical treatments	Label	Treated sample
1	Washing with HA for 24h	W (24h)	A,B,C,D,E
2	Washing with HA for 48h	W (48h)	A
3	Double washing with HA for 24h	WW	A
4	Washing with HA for 24h at 60°C	W (60°C,24h)	A
5	Washing with HA solution containing 0.4% of Triton X-100 (24h).	W+Tx (0.4%) [24h]	A
6	Fenton oxidation (1% H ₂ O ₂ , t=15min)	Fe (1%,15min)	A
7	Fenton oxidation (30% H ₂ O ₂ , t=30s)	Fe(1%,30s)	A
8	Fenton oxidation (30% H ₂ O ₂ , t=15min)	Fe(30%,15min)	A
9	Washing with HA 24h and successive Fenton oxidation (1% H ₂ O ₂ , t=15 min)	W+Fe (1%,15min)	A
10	Fenton oxidation (1% H ₂ O ₂ , t=15min) and successive washing with HA (24 h).	Fe(1%,15min)+W	A
11	Washing with HA solution containing 1% Triton X-100 (24h).	W+Tx(1%)[24h]	E
12	Washing with HA at basic pH (24h)	Wbasic	E
13	Fenton oxidation (30% H ₂ O ₂ , t=30s)	Fe(30%,30s)	E

Tab. 7. Scheme of the experiments carried out in this research work

All the samples were washed with a solution of HA for 24h, as reported by Conte et al. (2005). The samples A and E, representing the two end-members for grain size distribution, were selected for application of a wide spectrum of soil washing and Fenton oxidation experiments. In particular, a series of modified soil washing experiments were applied to sample A in order to verify which treatment was the most effective.

On the other hand, due to the verified low percentage of desorption (~6%) after soil washing with HA (24h), sample E was subjected to stronger treatments with addition of Triton X-100 in a high pH solution to favour the solubilization both of the HAs and PAHs.

The oxidation with Fenton reagent was carried out on samples A and E as reported in Saxe et al. (2000) using EDTA at neutral pH. In particular, on sample A, a series of oxidations with Fenton reagent were carried out using variable concentrations of H_2O_2 and times of addition to the mixture.

On the sample E, the oxidation was carried out using directly high concentration of H_2O_2 (30%) after verifying the low percentage of desorption obtained by all the soil washing treatments.

Soil washing with a successive Fenton oxidation step, and viceversa, was carried out only on the sample A.

III.3.1. Soil washing with humic acid for 24h

Concentrations of Σ PAHs in all the samples after soil washing with HA for 24h are: 38.20 $mgkg^{-1}$ (sample A), 5.33 $mgkg^{-1}$ (sample B), 41.00 $mgkg^{-1}$ (sample C), 33.50 $mgkg^{-1}$ (sample D), 6.23 $mgkg^{-1}$ (sample E). Thus, the estimated remediation ranging between 6 and 60%. A direct comparison of the concentration values of the singular PAH molecules before (Tab. 6) and after (Tab. 8) soil washing with HA clearly shows an evident difference in the behaviour of different congeners with increasing coarser character of the grain size (Fig. 15 to Fig. 19).

However, some exceptions are represented by the following cases: the percentage of desorption of An in sample C (62.20%) and in sample E (60.54%) is higher than in sample B (41.90%) in which the amount of sand is higher; the percentage of desorption of B(a)a in sample C (30.18%) is higher than in sample B (15.88%); the percentage of desorption of Cry is ~27% in sample B and C and 16.20% in sample E in turns characterised by a higher percentage of desorption of Cry in sample D (9.21%).

Tab. 8. Concentration values of ΣPAHs and each single congener for the five samples after soil washing

Sample	Phe mg·kg⁻¹	An mg·kg⁻¹	Flu mg·kg⁻¹	Py mg·kg⁻¹	B(a)a mg·kg⁻¹	Cry mg·kg⁻¹	B(b)f mg·kg⁻¹	B(k+j)f mg·kg⁻¹	B(a)p mg·kg⁻¹	B(e)p mg·kg⁻¹	Ind mg·kg⁻¹	D(a,h)a mg·kg⁻¹	B(g,h,i)p mg·kg⁻¹	Σ PAH mg·kg⁻¹
A	0.25	0.08	8.09	6.24	3.01	3.39	3.25	1.36	2.98	3.84	2.89	0.21	2.64	38.20
B	0.55	0.21	0.81	0.73	0.52	0.62	0.32	0.19	0.32	0.42	0.30	0.06	0.30	5.33
C	2.79	1.20	3.39	3.19	1.94	2.42	6.51	2.88	3.82	5.46	2.89	1.01	3.50	41.00
D	1.77	4.15	1.91	1.67	1.33	1.70	4.18	1.97	2.15	5.15	3.34	0.62	3.55	33.50
E	0.54	0.23	0.79	0.65	0.53	0.46	0.66	0.30	0.50	0.52	0.45	0.09	0.50	6.23

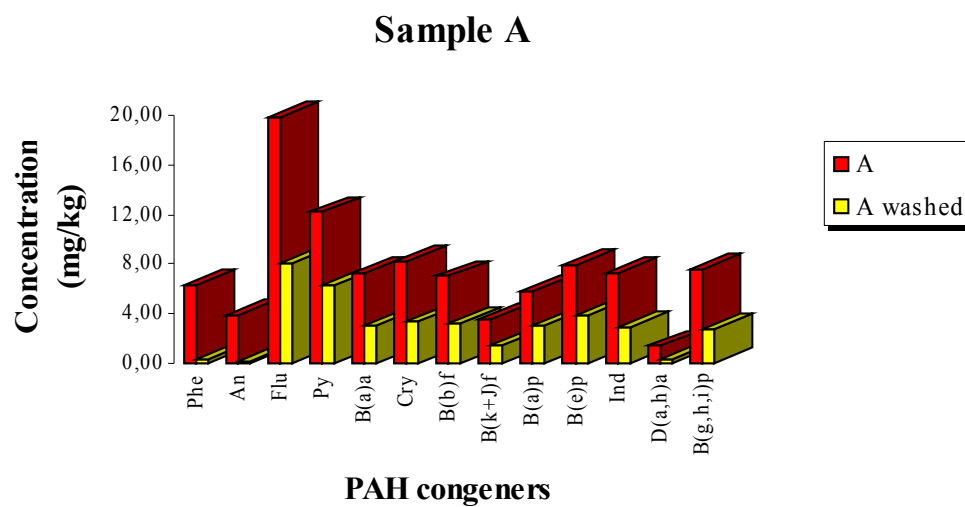


Fig. 15. Concentration values of PAH congeners in the sample A before (red) and after (yellow) soil washing

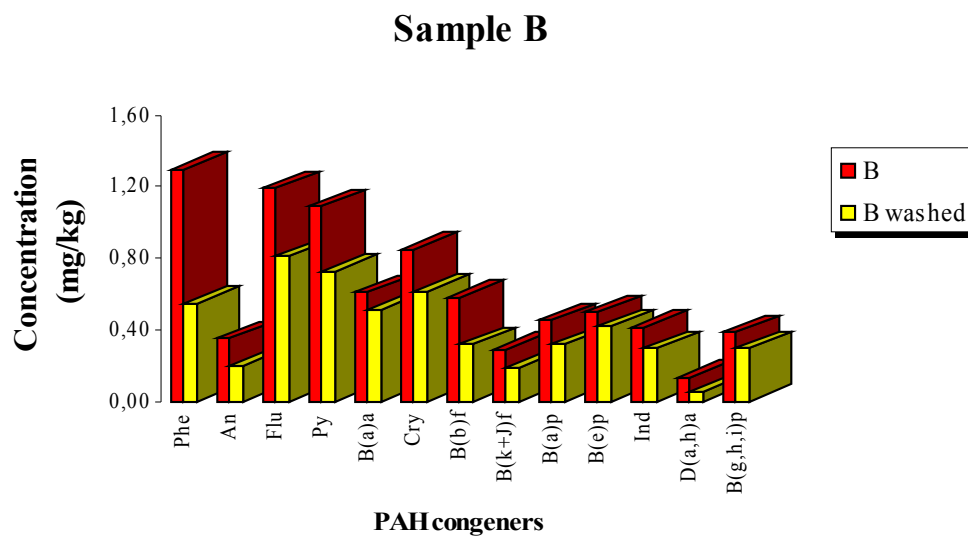


Fig. 16. Concentration values of PAH congeners in the sample B before (red) and after (yellow) soil washing

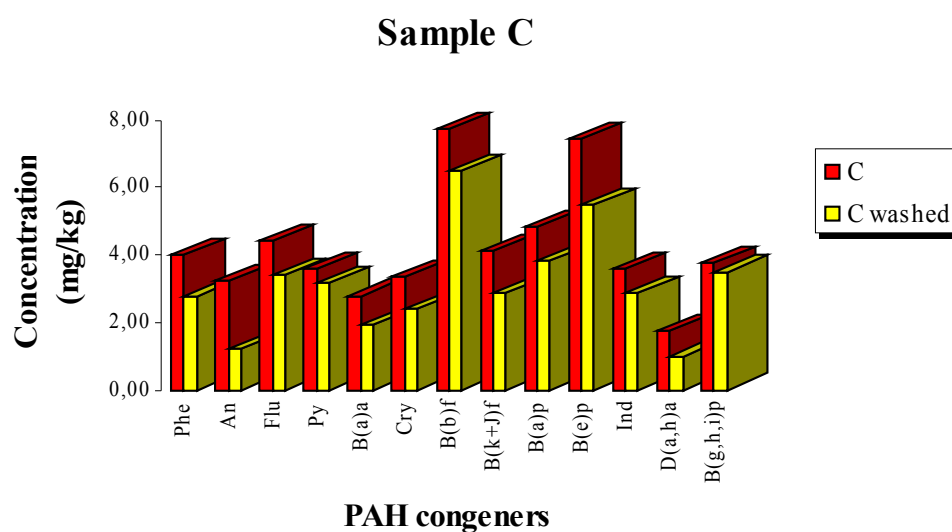


Fig. 17. Concentration values of PAH congeners in the sample C before (red) and after (yellow) soil washing

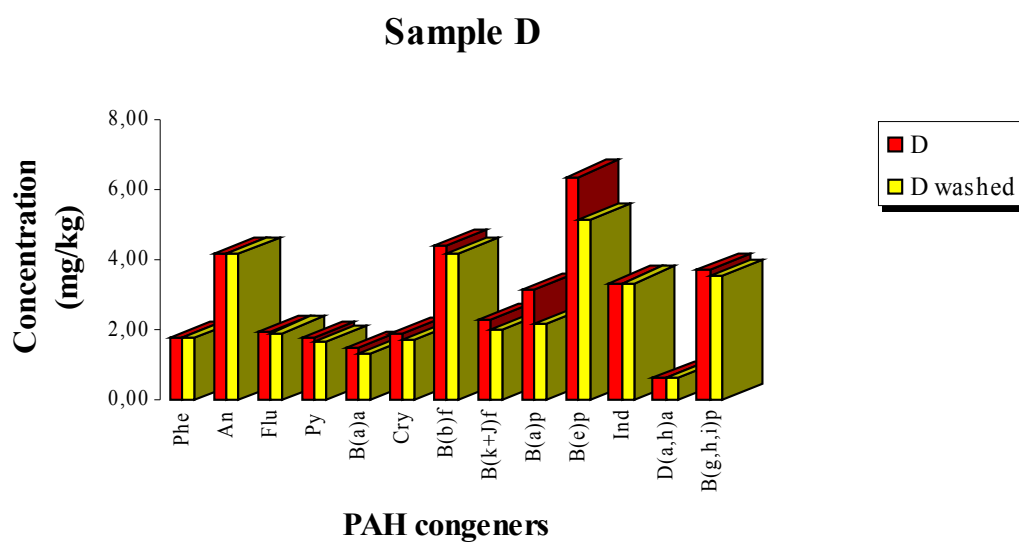


Fig. 18. Concentration values of PAH congeners in the sample D before (red) and after (yellow) soil washing

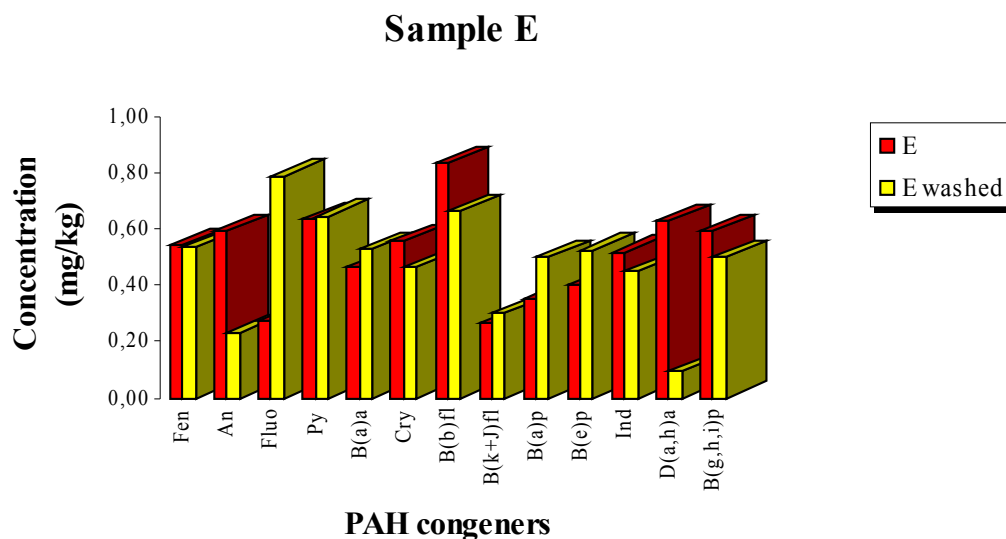


Fig. 19. Concentration values of PAH congeners in the sample E before (red) and after (yellow) soil washing

Moreover, the percentage of desorption of B(b)f in sample E (20.77%) is higher than in sample D (4.90%); the percentage of desorption of B(a)p (31.37%) in sample D is higher than in sample B and C (15.88% and 20.49%, respectively); the percentage of desorption of Ind in sample E (13.23%) is higher than in sample D (0.09%); the percentage of desorption of D(a,h)a in the sample E (84.91%) is higher than in sample B, C and D (59.26, 41.82, 1.60%, respectively) while this value is similar to the percentage of desorption of D(a,h)a in sample A (84.51%). Finally the percentage of desorption of B(g,h,i)p in sample E (15.18%) is higher than in sample D (5.09%). A peculiar result refers to the negative values of the percentage of desorption estimated for Flu, Py, B(a)p, B(k+j)f, B(a)p and B(e)p in the sample E (Tab. 9).

Sample	Phe %	An %	Flu %	Py %	B(a)a %	Cry %	B(b)f %	B(k+j)f %	B(a)p %	B(e)p %	Ind %	D(a,h)a %	B(g,h,i)p %	Σ PAH %
A	95.9	97.97	59.36	48.90	58.49	58.86	53.59	60.95	49.01	50.99	59.88	84.51	64.97	60.98
B	57.51	41.90	31.81	33.25	15.88	27.50	44.88	33.43	29.42	15.45	29.25	59.26	22.76	34.68
C	29.98	62.59	22.80	10.79	30.18	27.85	15.88	30.40	20.49	26.56	19.38	41.82	6.49	24.73
D	0.21	0.02	1.47	5.51	10.41	9.21	4.90	13.94	31.37	19.23	0.09	1.60	5.09	9.23
E	1.64	60.54	-188.88	-1.36	-14.36	16.20	20.77	-14.73	-40.70	-31.08	13.23	84.91	15.18	6.31

Tab. 9. Percentage of desorption of PAH congeners in the studied samples

In all samples, except in the sample D, Phe and D(a,h)a show the highest percentage of desorption compared to the other PAH congeners while An is characterized by high values of desorption percentage in sample A (~97%) and B (~41%) (Fig. 20).

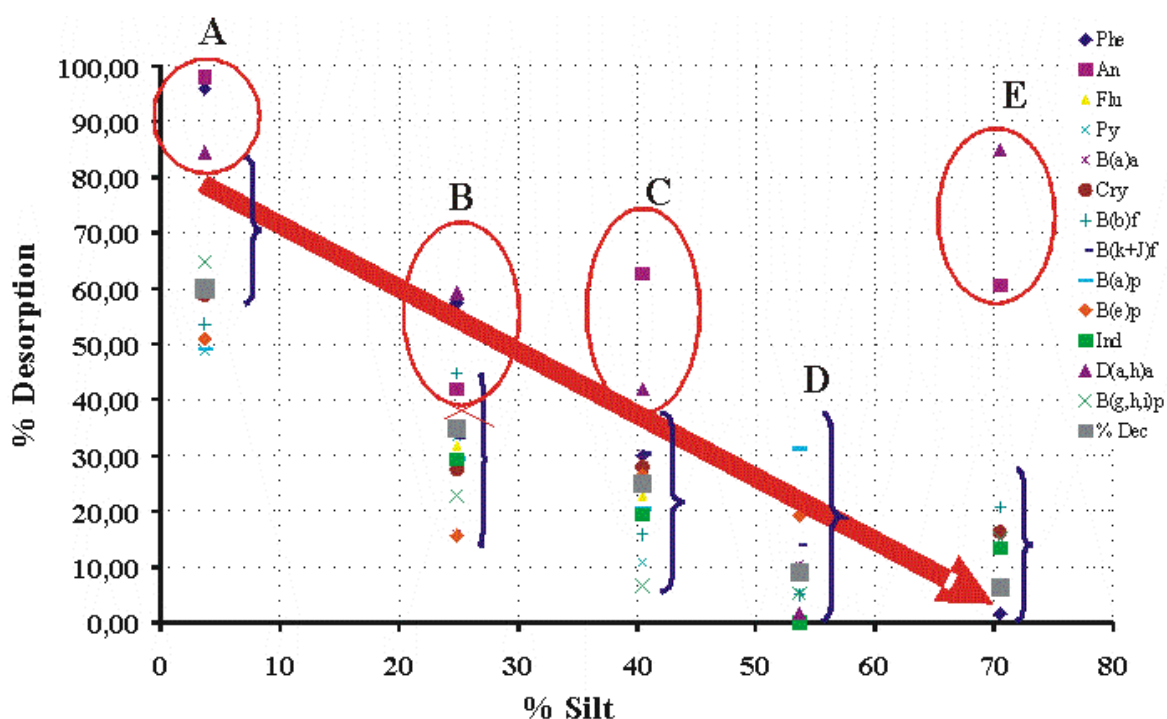


Fig. 20. Percentage of desorption vs percentage of silt for the single PAH congeners

Estimated percentage of Σ PAHs desorbed after soil washing with HA for 24h is: ~60% in sample A, ~35% in sample B, ~25% in sample C, ~9% in sample D and ~6% in sample E. A first order linear correlation is shown in Fig. 21 and Fig. 22 where a decreasing efficiency in soil washing remediation with increasing silt/clay content is evident. A coarse estimate indicates a lack of efficiency of about 10% at an increasing content of ~8 % of silt and 11% of clay in the sediment.

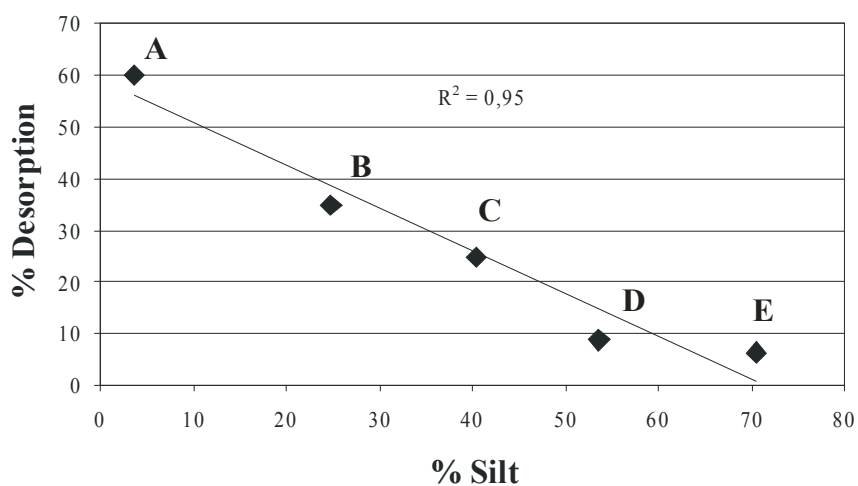


Fig. 21. First order correlation obtained plotting the percentage of desorption of PAHs vs the percentage of silt present in the samples

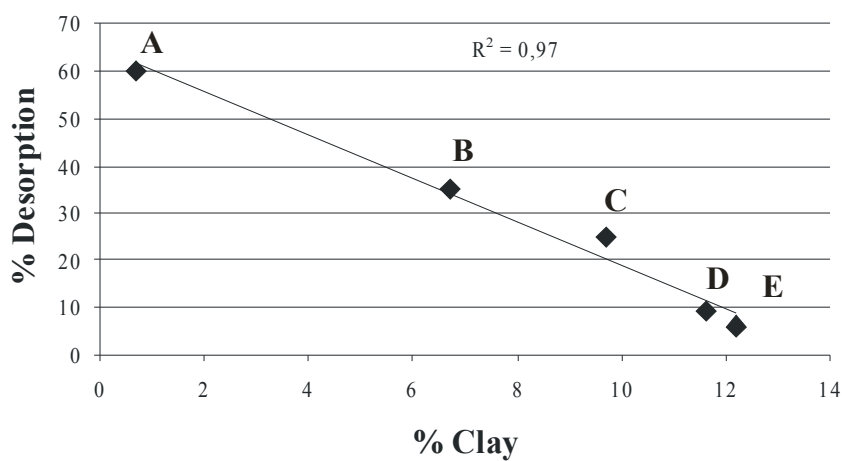


Fig. 22. First order correlation obtained plotting the percentage of desorption of PAHs vs the percentage of clay

III.3.2. Results of experiments 1 to 10 (sample A)

Results for the different experiments carried out on sample A are reported in Fig. 23.

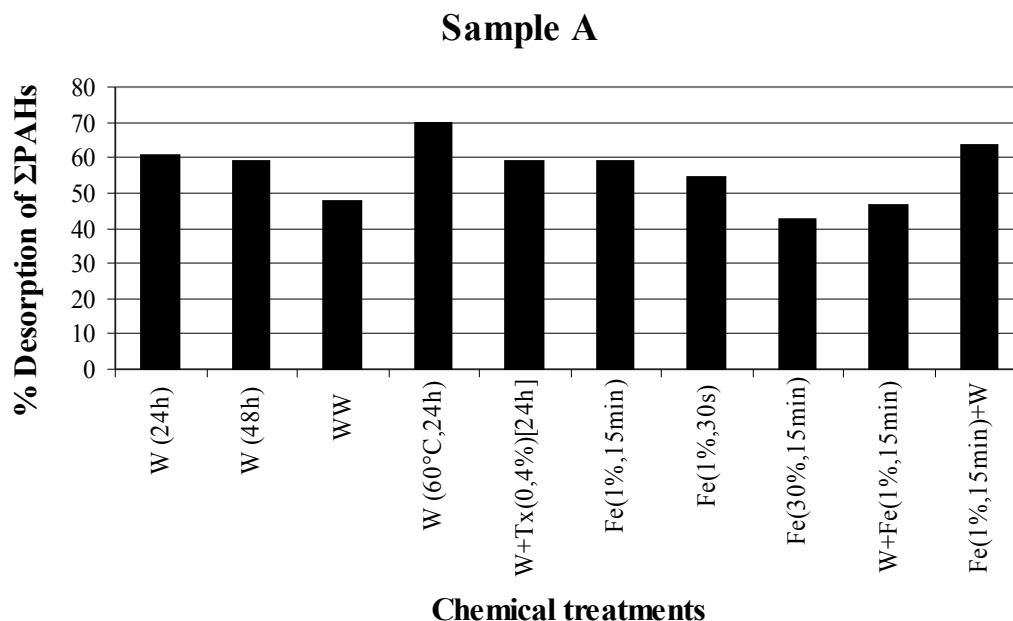


Fig. 23. Results of soil washing and Fenton reagent experiments carried on sample A

The percentage of desorption after soil washing with HA is ~ 60%, both for treatments at 24h and 48h (W(24h) and W(48h)). It increases (~70%) if the treatment is carried out at 60°C (W(60°C, 24h)), while decreases (~47%) if the sediment is washed two times with HA solution (WW) or if it is washed with HA solution containing mixed surfactants (~59% in W+Tx(0.4%)[24h]). The percentage of desorption obtained by application of Fenton oxidation (Fe(1%, 30s)) is ~59% and it varies using different concentration of H₂O₂ and varying the time of the addition of hydrogen peroxide to the mixture (54% in Fe(1%, 30s) and 42% in Fe(30%, 15min). The percentage of desorption in the integrated processes is ~ 46% in the experiment W+Fe(1%, 15min) and 63% in the experiment Fe(1, 15min)+W. The concentration values of the different PAH congeners and ΣPAHs in sample A after different experiments are reported in Tab. 10.

Chemical treatments	Phe mg·kg⁻¹	An mg·kg⁻¹	Flu mg·kg⁻¹	Py mg·kg⁻¹	B(a)a mg·kg⁻¹	Cry mg·kg⁻¹	B(b)f mg·kg⁻¹	B(k+j)f mg·kg⁻¹	B(a)p mg·kg⁻¹	B(e)p mg·kg⁻¹	Ind mg·kg⁻¹	D(a,h)a mg·kg⁻¹	B(g,h,i)p mg·kg⁻¹	ΣPAHs mg·kg⁻¹
W (24h)	0.25	0.08	8.09	6.24	3.01	3.39	3.25	1.36	2.98	3.84	2.89	0.21	2.64	38.20
W (48h)	0.12	1.17	8.56	6.40	3.41	4.49	3.37	1.41	2.87	3.78	2.14	0.28	1.97	39.37
WW	1.22	0.82	7.02	4.57	4.84	5.41	6.21	3.19	4.76	6.19	3.50	0.61	2.81	51.15
W (60°C, 24h)	0.10	0.13	4.45	3.03	2.57	3.11	3.51	1.33	2.62	3.11	2.72	0.51	2.36	29.56
W+Tx(0.4%)[24h]	0.58	0.17	7.67	5.32	3.41	3.36	4.51	1.78	3.42	4.25	2.80	0.42	2.51	40.18
Fe(1%,15min)	0.92	0.80	8.76	5.55	3.40	4.02	3.24	1.63	2.28	3.58	2.89	0.35	2.56	39.37
Fe(1%,30s)	0.14	0.26	6.88	5.65	3.39	4.68	5.33	2.37	3.92	4.16	3.78	0.72	3.32	44.62
Fe(30%,15min)	0.19	0.19	10.46	8.14	4.74	5.71	5.77	2.83	4.46	5.86	4.01	0.65	3.42	56.44
W+Fe(1%,30s)	1.36	1.22	7.96	5.02	5.46	6.73	4.53	2.32	3.23	4.83	4.76	0.59	4.40	52.41
F+W (24h)	0.22	0.24	6.54	5.26	3.03	3.48	3.63	1.91	2.73	3.33	2.42	0.62	2.17	35.60

Tab. 10. Concentration of PAH congeners and ΣPAHs after soil washing and Fenton oxidation for sample A

In all experiments, the histograms related to percentages of desorption of the single PAH congeners (Fig. 24 to Fig. 26) show the highest values of desorption for 3-rings PAHs while PAHs with 4 and 5 rings have similar lower values. D(a,h)a shows, together with 6-rings PAHs, the highest values of percentage of desorption among all the PAHs with high molecular weight.

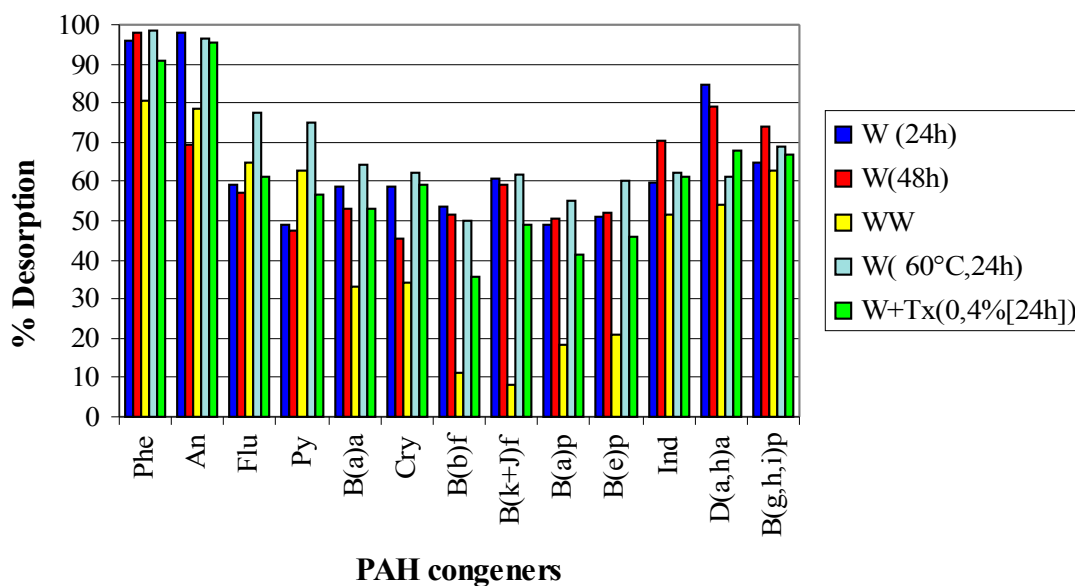


Fig. 24. Comparison among the percentages of desorption of single PAH congeners after W(24h), W(48h), WW, W(60°C,24h) and W+Tx(0.4[24h]) experiments.

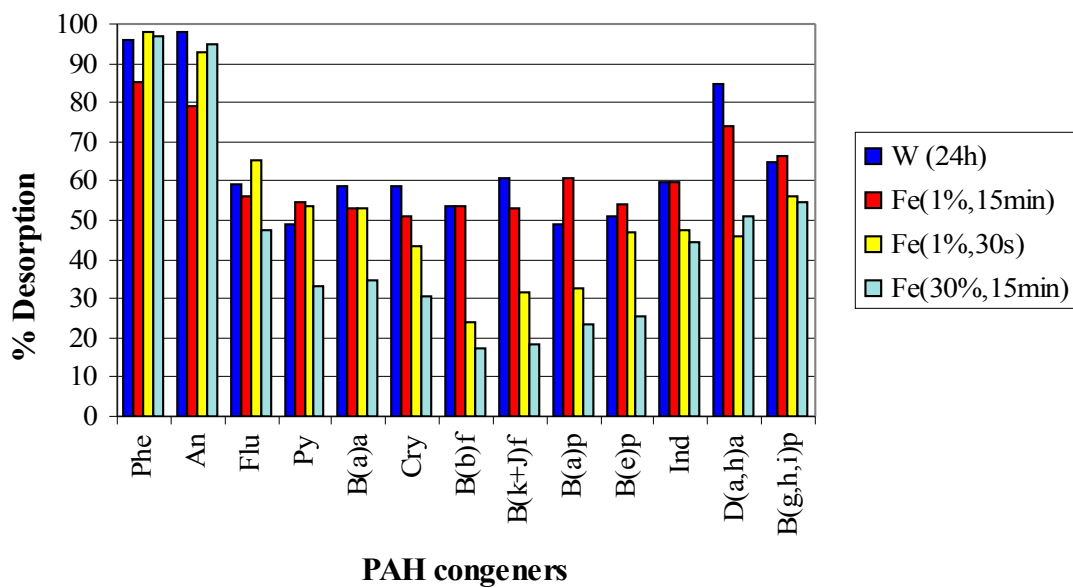


Fig. 25. Comparison among the percentages of desorption of single PAH congeners after W(24h), and Fenton oxidation (Fe(1%,15min), Fe(1%,30s), Fe(30%,15min)) experiments

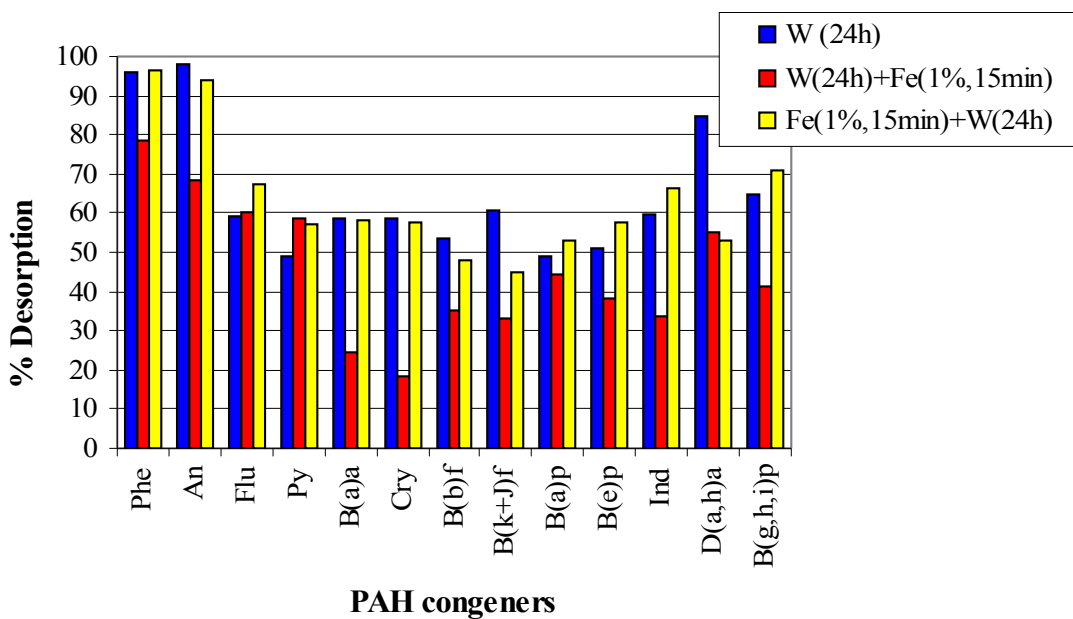


Fig. 26. Comparison among the percentages of desorption of single PAH congeners after W(24h), and the integrate process (W(24h)+Fe(1%,15min), Fe(1%,15min)+W(24h))

III.3.3. Results of experiments 1 and 11 to 13(sample E)

A complete view of the results related to the obtained remediation for the different experiments carried out on the sample E is reported in Fig. 27.

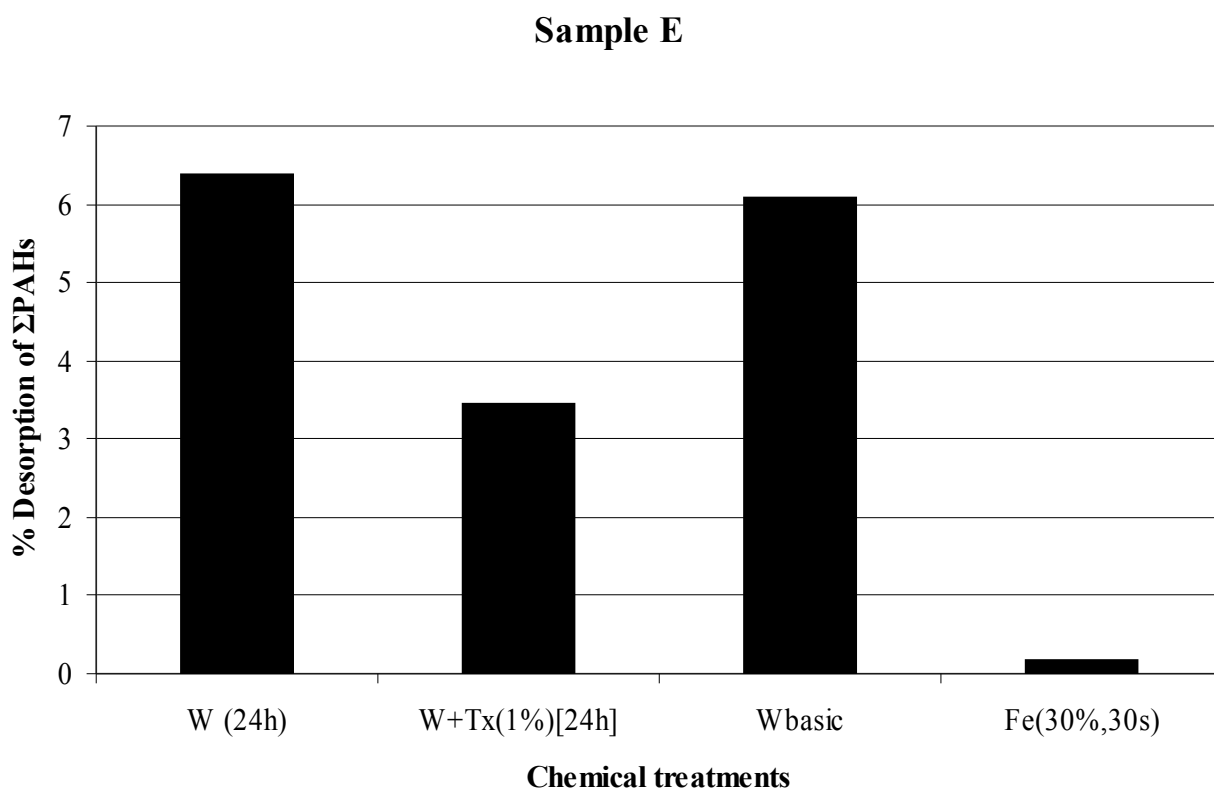


Fig. 27. Results of soil washing and Fenton reagent experiments carried on sample E

The concentration values of the PAH congeners after soil washing and Fenton oxidation on the sample E are reported in Tab. 11:

Chemical treatments	Phe mg·kg ⁻¹	An mg·kg ⁻¹	Flu mg·kg ⁻¹	Py mg·kg ⁻¹	B(a)a mg·kg ⁻¹	Cry mg·kg ⁻¹	B(b)f mg·kg ⁻¹	B(k+j)f mg·kg ⁻¹	B(a)p mg·kg ⁻¹	B(e)p mg·kg ⁻¹	Ind mg·kg ⁻¹	D(a,h)a mg·kg ⁻¹	B(g,h,i)p mg·kg ⁻¹	ΣPAHs mg·kg ⁻¹
W(24h)	0.54	0.23	0.79	0.65	0.53	0.46	0.66	0.30	0.50	0.52	0.45	0.09	0.50	6.23
W+Tx(1%)[24h]	0.44	0.22	0.70	0.57	0.57	0.67	0.77	0.34	0.57	0.63	0.45	0.09	0.41	6.43
Wbasic	0.50	0.20	0.75	0.65	0.50	0.48	0.69	0.39	0.50	0.49	0.46	0.10	0.54	6.25
Fe(30%,30s)	0.10	0.08	0.95	0.67	0.47	0.56	0.81	0.45	0.45	0.63	0.65	0.20	0.60	6.64

Tab. 11. Concentration of PAH congeners after soil washing and Fenton oxidation of sample E

III.4. Effects of PAHs desorption from the different grain size fractions

The desorption of PAHs measured from the different grain size fractions characterising the marine sediments was carefully investigated on sample C, characterized by 50% of $\phi < 63 \mu\text{m}$ and 50% of coarser grain size (of which $\sim 22\%$, sand). This grain size distribution renders this sample an intermediate between the others ones. The different response of grain size fractions to effects of desorption were tested only by application of soil washing with HA for 24h. The results shown in Fig. 28 to 31 evidence the percentage of desorption for 3-rings, 4-rings, 5-rings and 6-rings PAH molecules in the fraction $\phi > 1000$, $1000 < \phi < 500$, $500 < \phi < 250$, $250 < \phi < 125$, $125 < \phi < 90$, $90 < \phi < 63$, and $\phi < 63 \mu\text{m}$. The behaviour of single PAH congeners appears comparable to those with the same number of rings. In particular, for PAHs with 3-rings the percentage of desorption is higher than in the coarser fraction while PAHs with 4-rings present higher percentage of desorption in the size fractions $\phi > 1000 \mu\text{m}$ and $250 < \phi < 125 \mu\text{m}$. PAHs with more than 4-rings present the highest percentage of desorption in the fraction $250 < \phi < 125 \mu\text{m}$.

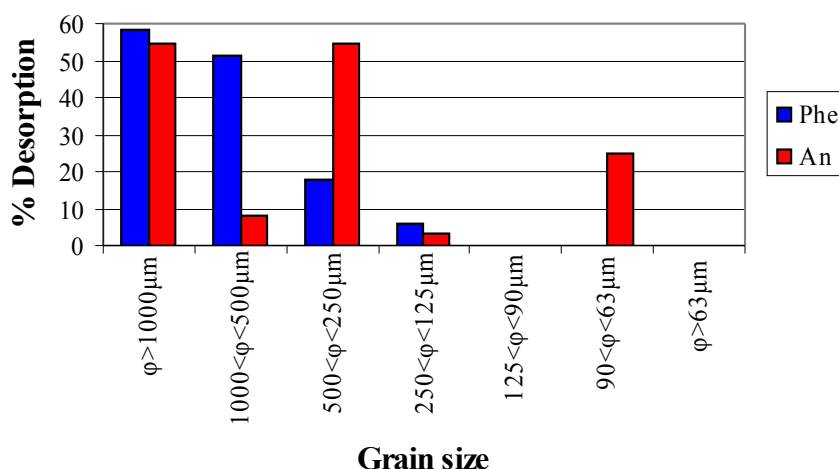


Fig. 28. Percentage of desorption of 3-rings PAHs in the different grain size fractions

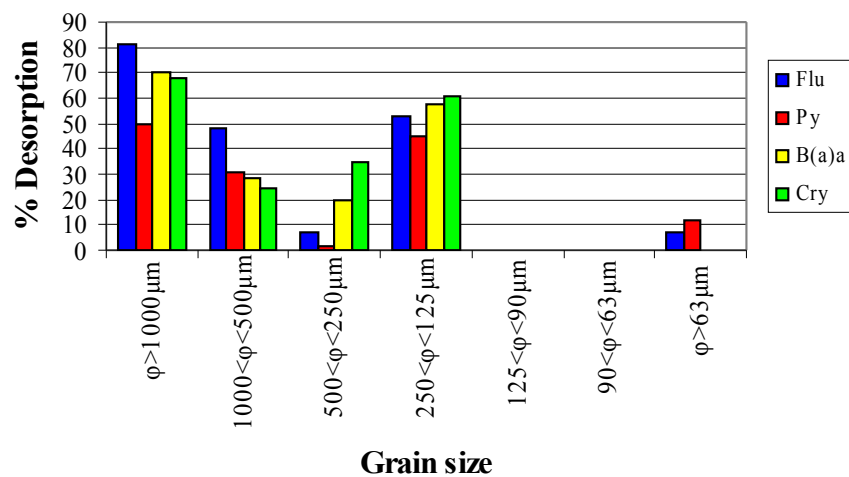


Fig. 29. Percentage of desorption 4-rings PAHs in the different grain size fractions

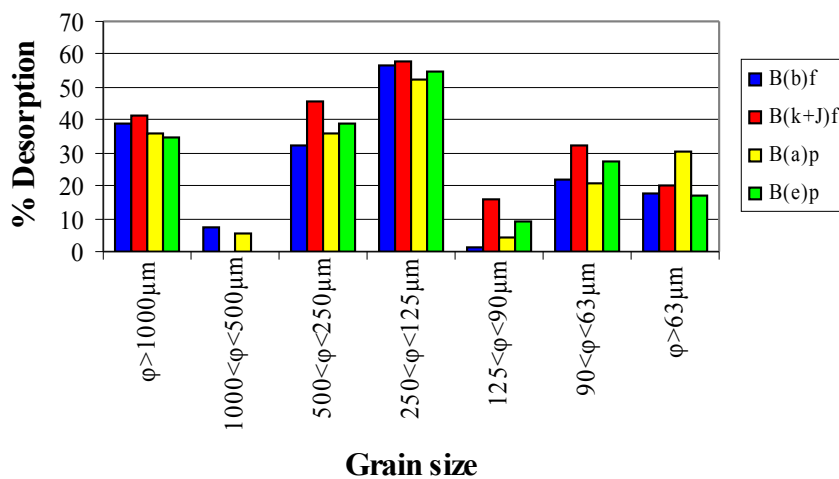


Fig. 30. Percentage of desorption of 5-rings PAHs in the different grain size fractions

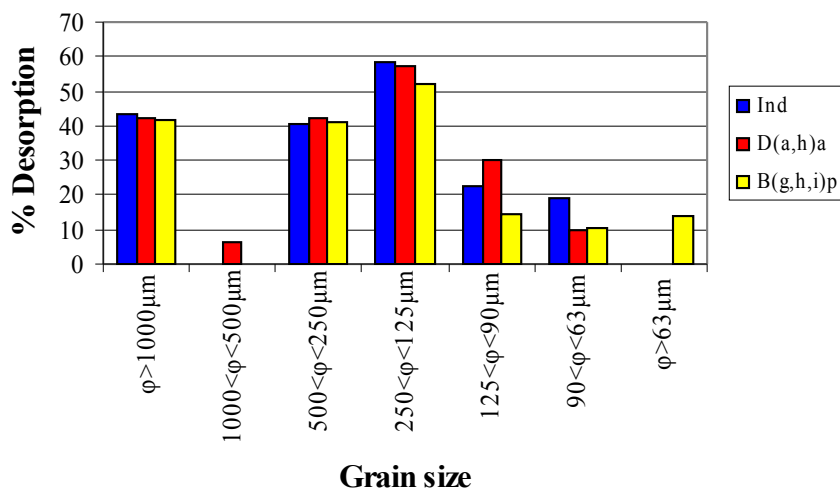


Fig. 31. Percentage of desorption of 6-rings PAHs in the different grain size fractions

III.5. Extraction of PAHs from HA

The recovery of the single PAHs congeners extracted by ASE at 113°C and 150°C after spiking in a HA solution are reported in Tab. 12.

Temp. of extraction	Phe %	An %	Flu %	Py %	B(a)a %	Cry %	B(b)f %	B(k)f %	B(a)p %	Ind %	D(a,h)a %	B(g,h,i)p %
113°C	58	31	51	54	49	53	75	25	5	44	34	25
150°C	86	46	60	57	54	50	56	19	25	31	36	23

Tab. 12. Recovery of PAH congeners extracted by ASE from HA solution

Phe, An, Flu and B(a)p show higher recovery values extracted at 150°C. PAHs with 5 and 6 rings show very low values of recovery in both extraction methods.

III.6. PAHs content in the black carbon particles

The analysis of BC content in the sample C provided a value of ~0.3% in weight. The concentration of PAH congeners in the size fraction $\phi < 63 \mu\text{m}$ in sample C was analyzed before and after removal of black carbon (Fig. 32).

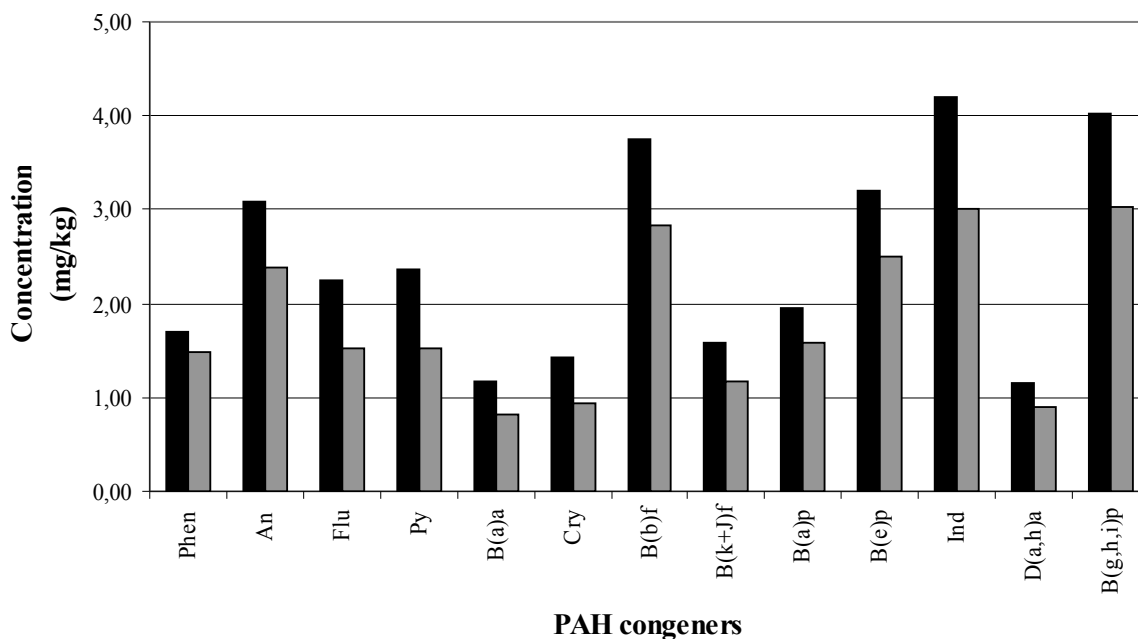


Fig. 32. Concentration of PAH congeners in sample C before (black) and after (gray) BC removal

A relevant decrease of ~26% of Σ PAH concentration was observed after BC removal. Moreover, the percentages of single PAH congeners associated with BC in the sediments are reported in Tab. 13.

Phe %	An %	Flu %	Py %	B(a)p %	Cry %	B(b)f %	B(k+j) f %	B(a)p %	B(e)p %	Ind %	D(a,h)a %	B(g,h,i)p %
13	23	32	35	30	35	25	27	19	22	28	21	25

Tab. 13. Percentage of PAH congeners removed with BC

Percentages of PAH congeners removed with BC vary between ~10 and ~35%. The highest values are observed for Flu, Py, B(a)a and Cry (~ 30-35%).

III.7. Isotope experiments

III.7.1. Isotope tracing during soil washing experiments

In order to calculate the extraction capacity of the HA solution on PAHs, a simple first-order mass balance equation was applied to the two cases. The mass balance is expressed by the following equation:

$$(1-x) \delta_{ws} + x \delta_{py} = \delta_{mixture} \quad (1)$$

where x and δ_{mixture} represent, the mass fraction of the spiked $^{13}\text{C}_3$ pyrene and the isotope composition of the carbon measured in the liquid phase after soil washing, δ_{ws} is the isotopic composition of carbon measured in the liquid phase after soil washing of unspiked samples, and δ_{py} represents the isotope composition of the pure $^{13}\text{C}_3$ pyrene spike, calculated according to the equation:

$$\delta_{\text{py}} = \{ [(^{13}\text{C}/^{12}\text{C})_{\text{py}} / (^{13}\text{C}/^{12}\text{C})_{\text{std}}] - 1 \} \cdot 1000 = \{ [(3/13)/0.01123] - 1 \} \cdot 1000$$

expressed in ‰ units and where $(^{13}\text{C}/^{12}\text{C})_{\text{std}}$ represents the isotope composition of the VPDB international isotope standard. Final δ_{py} value is 19549‰.

Sample	$\delta^{13}\text{C}_{\text{L}}$	$\delta^{13}\text{C}_{\text{Lspike}}$	Extraction capacity of soil washing
A	-24,12 ‰	-22.40‰	~85%
E	-24.80‰	-24.80‰	~24%

Tab. 14. Isotope composition of carbon in the liquid phase after soil washing with and without the a previously spike on $^{13}\text{C}_3$ pyrene and relative extraction capacity of soil washing

The isotope composition of carbon in the liquid phase after soil washing ($\delta^{13}\text{C}_{\text{L}}$) measured in samples A and E were -24,12 ‰ and -24.80‰, respectively. Isotope composition of carbon dissolved in the liquid phase, after washing of the same sediments previously spiked by 20µg $^{13}\text{C}_3$ pyrene ($\delta^{13}\text{C}_{\text{Lspike}}$) were -22.40‰ and -24.80‰, for sample A and E, respectively. Results obtained for the two samples provide a final extraction capacity of soil washing of ~85% and ~24% for samples A and E, respectively.

III.7.2. Isotope tracing for the Fenton oxidation experiment

The dynamics of Fenton oxidation and the formation of potential oxidation products were investigated by means of spiking with $^{13}\text{C}_3$ pyrene in a HA solution. In particular, Fenton oxidation ($\text{Fe}^{2+}/\text{EDTA}/\text{H}_2\text{O}_2$) of $^{13}\text{C}_3$ pyrene dissolved in a HA solution was investigated by isotope tracing. The isotope composition of carbon in that solution was -25.96‰. Unspiked Fenton oxidation carried out on a HA solution produced an isotope composition of -29.70‰.

Solving of mass balance equation (1) provided unexpected $^{13}\text{C}_3$ pyrene recovery of ~237%. This result directly suggests an effect of kinetic fractionation of the $^{13}\text{C}_3$ pyrene due to a potential oxidation of original PAHs.

Moreover an increase of H_2O_2 concentration, four times the initial concentration values, caused a change of isotope composition of -26.79‰.

Chapter IV

DISCUSSION

IV.1. Introduction

In this chapter the ensemble of the obtained results will be interpreted at the light of the most recent theoretical approaches in order to: i) characterize the potential sources of PAHs in the studied marine sediments on the basis of diagnostic isomer ratios, ii) analyse the desorption effect of the single PAH congeners from sediments and their partitioning between water and surfactant micelles, iii) investigate the kinetic mechanisms involved in the PAH desorption from sediments, iv) show the best strategy of remediation after comparing the values of Σ PAHs desorption using the different chemical approaches, v) evidence the role of organic matter and clay fractions on the PAH desorption, and vi) trace the products of Fenton oxidation by means of the results of techniques.

IV.2. Sources of PAHs in studied samples

The sources of the PAHs in the marine sediments are simply divided in three main categories: petrogenic, pyrogenic and biogenic, on the basis of diagnostic mass ratios and/or predominance of different PAHs congeners (e.g., Boehm et al., 1998a,b; Burns et al., 1997; Page et al., 1999).

The higher concentration values of PAHs with more 4-rings measured in the studied samples (Tab. 6) suggest that PAH sources may be represented by processes of coke oven, production by the electric arc furnace and heavy oil combustion (Yang et al. 1998). Main indicators of PAHs from industrial stacks are B(a)a, D(a,h)a, B(a)P and B(e)p while An is classical tracer of contamination by cement plant (Yang et al., 1998). PAHs from processes of industrial waste incinerators are generally Ind and Cry while PAHs produced by diesel and gasoline-powered vehicles are mainly represented by lower molecular weight PAHs such as Flu (Yang et al., 1998).

An efficient method to discriminate the source of PAHs in contaminated marine sediments is based on the calculation of PAH isomer ratios according to: i) the different thermodynamic stability of congeners, ii) the composition of different PAH sources, and iii) the changes in PAHs abundances (e.g., Yunker et al., 1996, 1999). Basically, PAHs generated by combustion and/or anthropogenic inputs are characterized by an increase in the proportion of the less stable “kinetic” PAH isomers relative to the more stable “thermodynamic” ones (Yunker and Macdonald, 1995). The relative stability of PAHs has been evaluated from the

relative heat of formation calculated using the AM1 and PCMODEL methods as reported in Yunker et al. (2002).

As an example, the isomers with 202 mass (typically Flu and Py) have a large range of stability and are good indicators of thermodynamic vs. kinetic processes (for instance petroleum versus combustion processes). Phe (mass 178) and An (mass 178) are commonly used to distinguish between combustion and petroleum sources (e.g., Gschwend and Hites, 1981; Budzinski et al., 1997; Soclo et al., 2000). An/(An+Phe) ratio lower than 0.10 is usually taken as an indication of unburned petroleum, while ratio higher than the 0.10 indicates a dominance of combustion effect (Budzinski et al., 1997). A Flu/(Flu+Py) ratio of 0.50 is usually defined as the petroleum/combustion transition point (Budzinski et al., 1997), but in practice this boundary appears to be less definitive than the 0.10 ratio of An/(An+Phe). The Flu/(Flu+Py) ratio is below 0.50 in kerosene, grass, most coal and wood combustion samples and creosote, but is below 0.40-0.50 for gasoline, diesel, fuel oil and crude oil combustion and emission from cars and diesel trucks. PAHs of molecular masses 228 (B(a)a and Cry) and 276 (Ind and Bg,h,p) are less frequently used as PAH source indicators and few information have been established for their interpretation (e.g., Gogou et al., 1996; Yunker et al., 1996, 1999). Higher mass PAHs usually are minor contributors to refined petroleum products (William et al., 1986; Wang et al., 1999a,b) and are generally present in significant amounts only in higher fractions such as asphalt (Readman et al., 2002) and possibly in bitumen or coal (Yunker et al., 1996, 2002). A B(a)/(B(a)+Cry) ratio over 0.50 has been taken to indicate combustion while a ratio below 0.50 has been attributed to low temperature diagenesis (Soclo et al., 2000).

Three distribution maps of the selected PAH isomers for the harbour of Naples based on the analysis of about 150 surface sample collected during the geochemical monitoring program of 2004 and measured in this work, are reported in Fig. 33 to Fig. 35. These maps allow a general vision of the pollution sources of PAHs present in the sediments of the harbour of Naples. The maps show a prevalence of PAHs with a pyrolytic origin (An/An+Phe >0.1; Flu/Flu+Py >0.5, and B(a)/B(a)+Cry >0.35) and limited areas (primarily localized along the coast) characterized by PAHs of petrogenic origin (An/An+Phe <0.1; Flu/Flu+Py <0.4, and B(a)/B(a)+Cry <0.20).

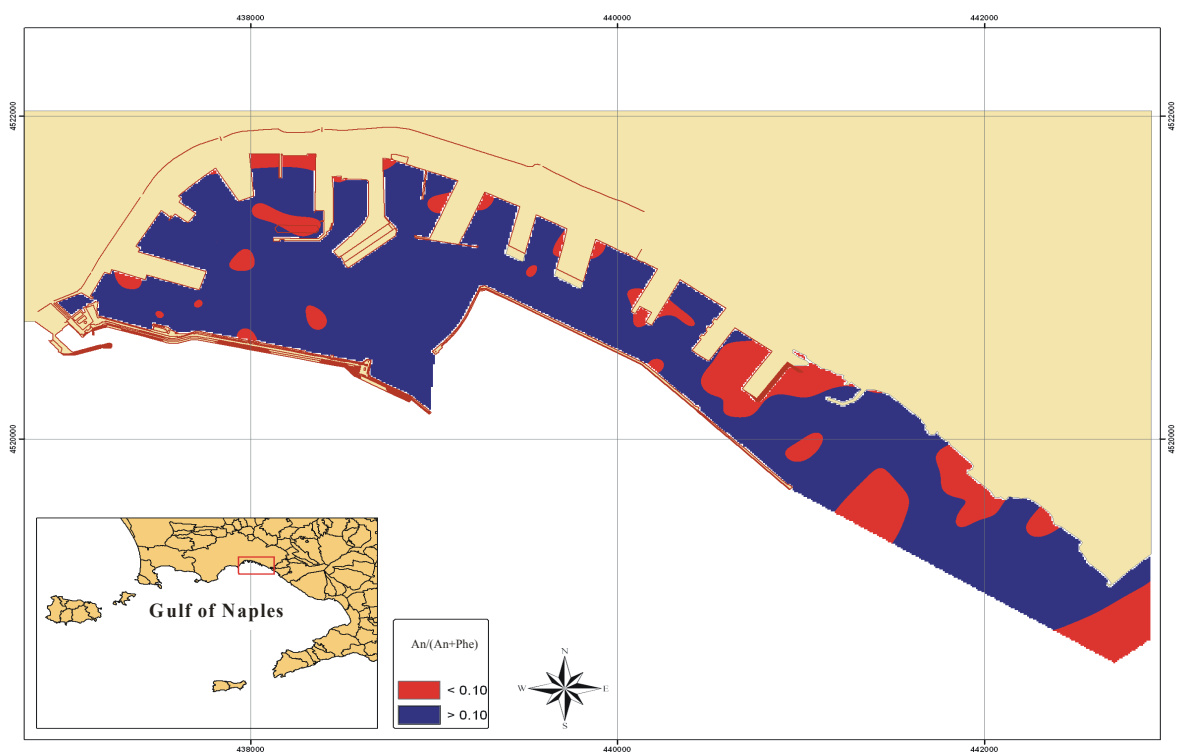


Fig. 33. Distribution map of An/(An+Phe) isomer ratios in the harbour of Naples

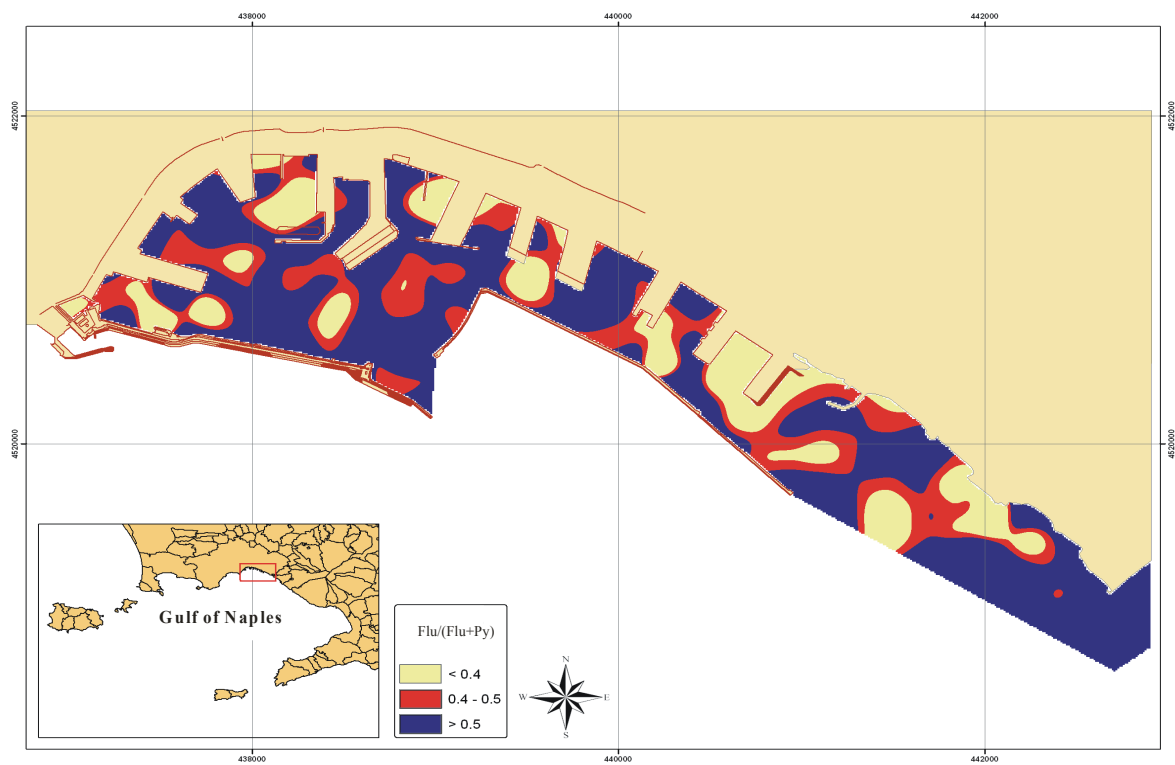


Fig. 34. Distribution map of Flu/(Flu+Py) isomer ratios in the harbour of Naples

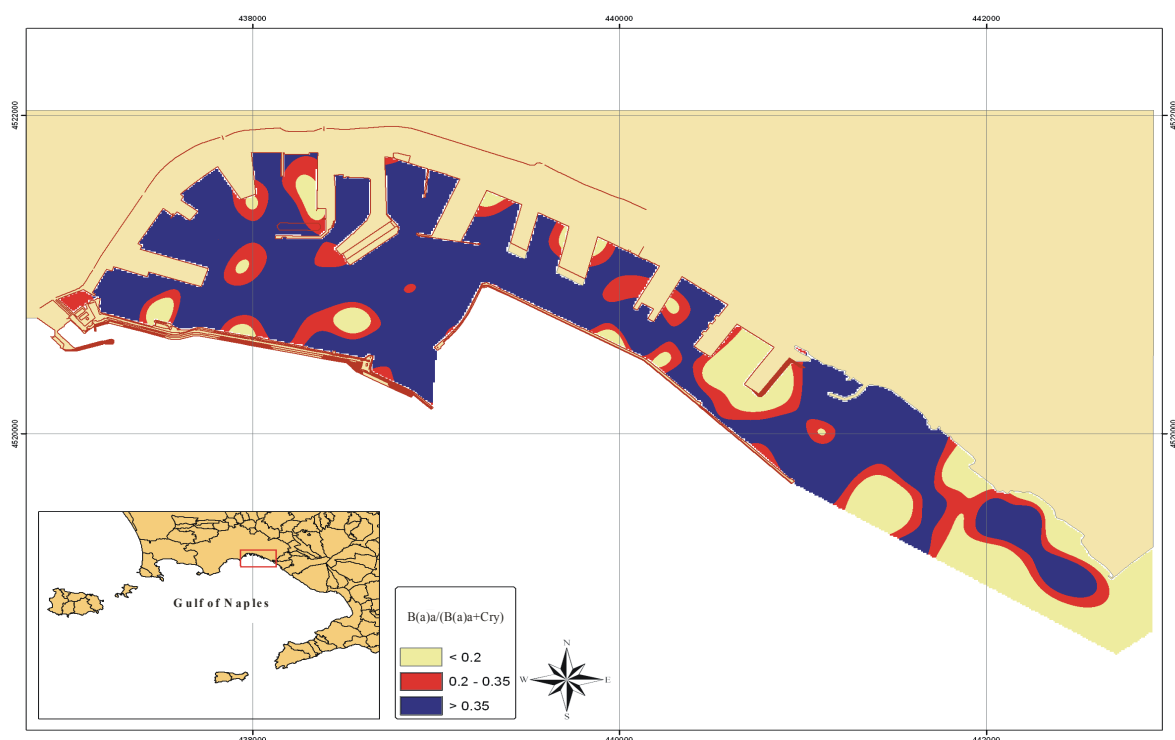


Fig. 35. Distribution map of Ba(a)/(B(a)a+Cry) isomer ratios in the harbour of Naples

A synthesis of the isomer ratios measured in the five studied samples used for remediation experiments of this work, is reported in Tab. 14.

Sample	An/(An+Phe)	Flu/(Flu+Py)	B(a)a/(B(a)a+Cry)
A	0.38	0.62	0.47
B	0.21	0.52	0.42
C	0.45	0.55	0.45
D	0.70	0.52	0.44
E	0.52	0.30	0.46

Tab. 15. PAH isomer ratios calculated for the studied samples

These results clearly indicate a pyrolytic origin for the PAHs present in the studied samples. In particular, the PAH isomer ratios measured in the five samples, are typical of sources characterized by processes of combustion of coal at high temperature. A classical process is that related to the carbonization of bituminous coal to form creosote (Goyette and Books, 1998) that produce PAH ratios similar to those of coal tar or coal combustion (Yunker et al. 2002).

IV.3. PAHs distribution in different grain size classes

The general vision about washing processes applied to soils/sediments contaminated by organic and inorganic contaminants considers, as essential first step for choosing the most efficient cleaning procedures, the physical separation of the contaminated soils/sediments in different grain size classes: the coarser fraction, with an assumed low contamination and the finer fraction, generally considered the preferential site of contamination (e.g., Werther et al., 2001). The main objective of such an approach is to significantly reduce the volumes of the washing surfactants and simultaneously to improve the results of the decontamination.

The results of PAHs distribution in the sediments studied in this research suggest (Fig. 9) an unpredicted relationship with the different grain size fractions present in the samples. Actually, the highest concentrations of Σ PAHs, and the singular PAH congeners, are generally associated to the larger fractions ($\phi > 250 \mu\text{m}$), while silt and clay ($< 63 \mu\text{m}$) are generally less enriched in PAHs. These results appear to be conflicting with the general vision which considers the fine particles (with their high specific surface) to have a significantly higher content of pollutants (e.g., Maruya et al., 1996). Based on the assumption that the contamination is located on the surface of the particles, the specific surface area S_v is dependent on the particle diameter d_p (when spherical particles are assumed) as given by the equation: $S_v = 6/d_p$. This equation indicates that a significant increase of the specific surface area corresponds to a decreasing particle diameter. Therefore, the high specific surface area of the fine grain size is considered a key factor to account for the high potential contamination effect on the smaller grain size particles. Additionally, the accumulation of contaminants in the fine fraction is enhanced by the presence of humic matter that coats the surfaces of fine particles and that results in an effect of stronger bonding for organic pollutants.

An appropriate interpretation of the results obtained in this research work calls for an alternative hypothesis. In particular, detailed studies carried out by Wilichowski (2001) on the particle size effects on the distribution of pollutants in soils, demonstrated that PAHs are not only necessarily sorbed on fine particles surface but they may form tar particulates with diameters of several hundred of microns that finally produce high contents of PAHs in the coarser grain size fraction. A similar behaviour seems to be reflected in the distribution of PAHs in the studied samples. Moreover, the analysis of organic carbon content in the different grain size fractions of sample A, has evidenced higher values associated to the coarser fractions (12.40%, 9.44%, 11.45%, 2.88%, 1.90%, 0.47%, 1.06% respectively for $\phi > 1000$, $1000 < \phi < 500$, $500 < \phi < 250$, $125 < \phi < 90$, $90 < \phi < 63$, $\phi < 63 \mu\text{m}$) thus suggesting that the content of organic matter in the different grain size fractions is an important factor of regulation of PAHs in the sediments. However, a more detailed interpretation on the

characteristic of the organic matter is needed for definitive considerations since its origins and maturities may have different PAH sorption effects. For example, particulate organic matter of charcoal, plant detritus and coal particles have a sorbing capacity of PAHs higher than organic matter associated with clay minerals (Wang et al., 2001).

As a direct consequence of this part of the investigation, it can be generalized that it is absolutely a priority to clearly define, for different real environmental situations, the different distribution of PAHs in the grain size classes characterising the sediments in order to define the most appropriate strategy for remediation. In particular, due to the highly unhomogeneous distribution of PAH recorded in the different size fractions of the studied samples, the claimed first step of physical separation did not appeared, appropriate to increase the cleaning efficiency. Washing of the whole sediments is certainly the best solution for application of the remediation techniques to soils/sediments with heterogeneous distribution of contaminants in the different grain size classes.

IV.4. Desorption of the single PAH congeners from sediments

IV.4.1. Interaction of PAHs with sedimentary organic matter

Humic substances (HS) account for about 50 to 80% of the organic carbon in soils, natural waters and marine sediments (Aiken et al., 1985; Orlov et al., 1990; Thurman, 1985). In particular, HS in marine sediments originate from two different sources: organic matter from aquatic organisms living in the marine ecosystem (autochthonous) and organic matter is transferred to estuary from surroundings soils and streams (allochthonous) (Pineiro et al., 2006). Terrigenous organic matter can be identified in marine sediments by its high organic carbon content and correspondingly high carbon:nitrogen (C/N) ratio (Faganeli et al., 1988). Infact, the C/N ratio of organic matter in sediments has been frequently used as an indicator of terrigenous inputs to the marine sediments (Pocklington and Leonard, 1979). Basically, a C/N atomic ratio >20 is considered to indicate an enrichment of organic C over N from land-derived organic matter (Scheffer and Schachtschnabel, 1984), while a C/N ≤ 10 indicates an autochthonous marine origin (Parsons, 1975). Land plants and marine algae differ in their C/N ratios; marine algae, due to their enrichment in protein and absence of cellulose, have a C/N ratio of 15 and greater (Meyers, 1997).

The map of distribution of C/N generated for the sediments of the harbour of Naples (Fig. 8) based on the results obtained by 150 surface sediments homogeneously distributed within the area, evidenced a prevalence of organic matter of terrigenous origin, primarily evident in the area where the five samples used for the remediation experiments, were

collected. In particular, the studied samples C and D are characterized by a C/N ratio >20, while sample E has a C/N ratio ~17 indicating a mix of terrigenous and marine organic matter. On the other hand, a clear terrigenous origin for the organic matter can be associated to sample A collected in Bagnoli area characterized by a C/N>20 (Damiani et al., 1987).

A clear attribution of the origin of organic matter present in the sediments represents an essential starting point parameter to hypothesize their molecular structure and the consequent interactions with PAHs.

A master tool for analysis of the molecular structure of humic substances in soil and sediments is generally carried out by Solid State Carbon-13 Nuclear Magnetic Resonance Spectroscopy (CPMAS ^{13}C -NMR) (Wilson et al., 1987; Arshad and Schnitzer, 1989; Amalfitano et al., 1992, 1995; Knicker and Ludemann, 1996; Zech and Guggenberger, 1996; Piccolo and Conte, 1997). Such an analytical approach requires a C/Fe ratio in the sediments >1 in order to obtain a reliable quantitative spectrum, since the presence of paramagnetic ions, such as Fe^{3+} , in soil/sediment samples shortens the relaxation times of proton nuclei in the rotating frame ($T_{1\rho}\text{H}$) causing a loss of signal of carbon nuclei (Wilson 1987). Also, Pfeffer et al. (1988) proved that Fe^{3+} affects mainly the cross-polarization and the proton relaxation times of high hydrophilic humic matter. Although initially planned for this research, unfortunately, the samples studied in this research evidenced a C/Fe ratio <1 (0.0003, 0.0001, 0.0002, 0.0003 and 0.0004 for the samples A, B, C, D and E, respectively) also after treatment with a solution of 10% HF used to remove Fe^{3+} from sediments, (C/Fe = 0.0024, 0.0044, 0.0038, 0.0028 and 0.0097 for samples A, B, C, D and E respectively).

However, regarding HS, recent studies have clearly evidenced significant differences in the bulk molecular characteristics of organic matter extracted from soils and sediments (e.g. Fookien and Liebezeit, 2000). In particular, CPMAS ^{13}C -NMR spectrum of marine derived HAs is characterized by chemical shift values, diagnostic of proteins, carbohydrates, lipids and lignin-derived phenols (Sardessai et al., 1997) and showing a lower degree of aromaticity when compared to terrestrial HA, basically constituted by functional groups of lignin phenols (Ertel, 1984). Acquisition of ^1H NMR spectra of bulk HA isolated from lignite, (Piccolo et al., 2002) indicated chemical shifts diagnostic of alkyl component, olefinic compounds, oxygenated systems, aromatic and heterocyclic components characterising that component of organic matter. Moreover, Piccolo et al. (1998) analysing the structural characteristic of HA in soils, observed that the conformational arrangement of humic materials (either by themselves or in interaction with clay minerals) may play a considerable role in controlling the adsorption and desorption of organic pollutants in soils. In particular, the aromatic groups

appeared to contribute to the binding of organic pollutants at humic substances less than the aliphatic groups. In fact, the less flexible conformation conferred to humic materials by a large content of aromatic rings may lead to an organic pollutants adsorption that is limited to only the surface of the humic molecular aggregate, thereby enhancing the ability of the pollutants to desorb in water (Piccolo et al., 1998).

In the studied samples, an evident binding affinity between HA and PAHs is clearly evidenced by the results of the Principal Component Analysis (PCA), performed using the available data set of the 13 PAH congeners, %TOC, silt and clay contents. Statistical results evidence an excellent correlation between %TOC (roughly assumed to reflect the content of HS) and the concentration of the single PAH congeners (Fig. 36). Moreover, increasing the number of benzene rings of the different PAH congeners, generally considered an adequate indicator of hydrophobicity of the same organics, does not appear necessarily correspond to a proportional correlation with TOC. In particular, the relative lower correlation of D(a,h)a with TOC seems to suggest a limited interaction of D(a,h)a with humics when compared to that expected between humics and the other 5-rings PAHs, although the log K_{ow} value of D(a,h)a is the highest (6.75) among the other PAHs. It follows that the hydrophobicity may not represent the only parameter to explain the interactions of PAH molecules with sedimentary organic matter. Conversely an important factor ruling the distribution of PAHs in the sediments might be represented by the different original sources and transport mechanisms of pollutants in the studied marine environment, that may selectively influence the distribution pattern of the different congeners. On the other hand, the variable hydrophobicity character (Tab. 14) of the single PAH congeners seems well explain the high percentage of desorption observed for Phe and An in all the studied samples with low values of log K_{ow} (4.57 and 4.54, respectively) directly responsible of the lower binding affinity for humics. Conversely, 4, 5 and 6-rings PAHs with higher log K_{ow} values when compared to those of 3-rings PAHs, show higher binding affinities for humics and consequently are characterized by potential lower values of the percentage of desorption. However, the small changes measured in the percentage of desorption among 4, 5 and 6-rings PAHs (Tab. 9) in all studied samples again suggest an important influence of different sources and or transport mechanisms of PAHs on the final measured results of PAH desorption.

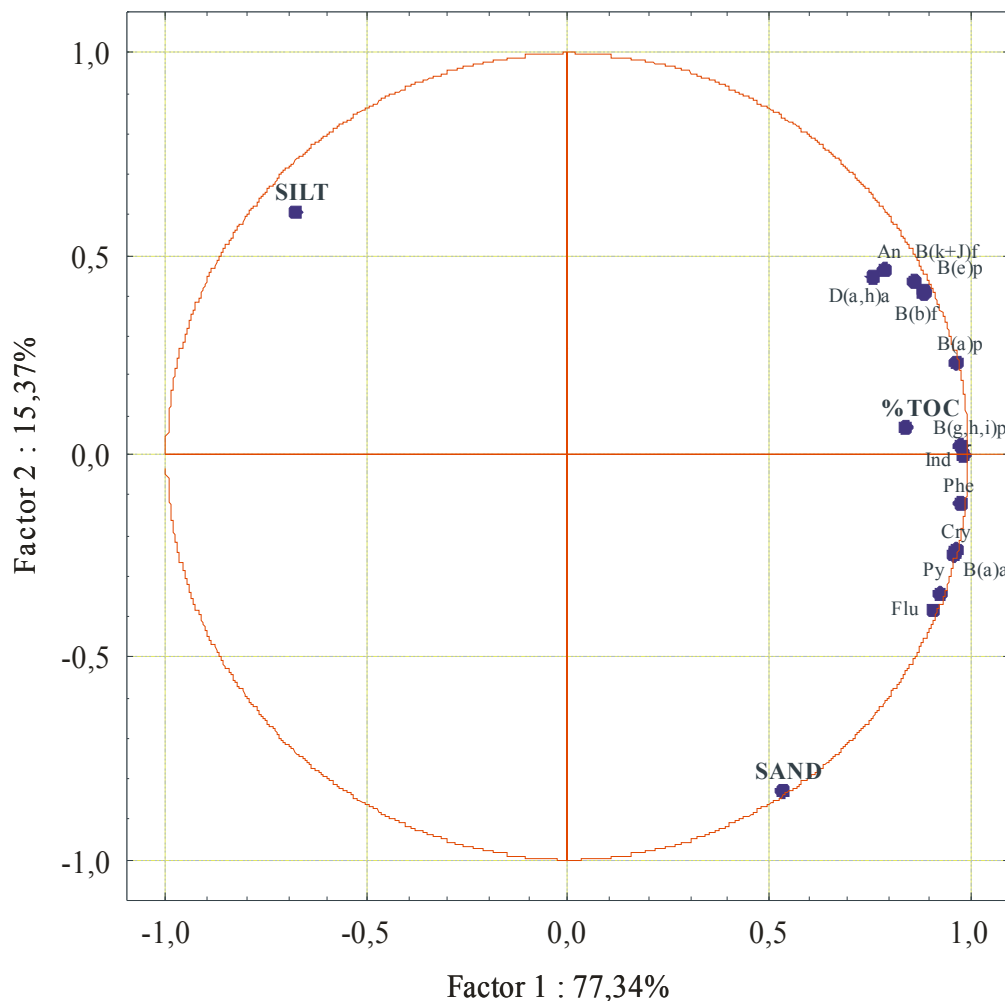


Fig. 36. Principal Component Analysis (PCA) performed using the variables: concentrations of the 13 PAH congeners, %TOC, silt and clay contents and on all the studied samples.

IV.4.2. Effects of solubilization of PAHs by interaction with surfactants

To study the effects of solubilization of PAHs by interaction with surfactants, the experiment of soil washing with HA for 24 h applied on sample A is taken into account.

The concentration of HA in the solution used to “wash” the sediments was 10g/l, reported as the pseudo critical micelle concentration (CMC) for HAs (Guetzloff and Rice, 1994). The pseudo-micelle-water partitioning coefficient (K_{mc} , $l \cdot mol^{-1}$) can be used to quantify the solubilization capacity of the HAs. Infact, K_{mc} indicates the partitioning of organic solutes between the surfactant pseudo-micelles and the water phase according to the equation: $K_{mc} = S_{mc}/S_w C_{mc}$ (Almgren et al., 1979; Jafvert et al., 1994).

In the equation, S_{mc} and S_w are the concentrations of solute in the pseudo-micelles and in the water phase and C_{mc} is the concentration of the surfactant in pseudo-micellar form. For HA, C_{mc} can be estimated as a mass concentration of HA in solution expressed on an organic carbon basis ($kg \cdot C \cdot l^{-1}$). Generally, S_w is estimated as the solubility of the compound in pure

water (Luning Prak and Pritchard, 2002; Zhou and Zhu, 2006). Therefore, the concentration of each PAH congener in the pseudo-micelles was calculated according to the equation:

$$S_{mc} = [PAH]_{des} - S_w$$

where $[PAH]_{des}$ is the initial concentration (before the pseudo-micelle-solubilisation) of the PAH congener in the aqueous phase and it is expressed:

$$[PAH]_{des} = C_s^o - C_s$$

C_s^o and C_s are the concentrations of each PAH congener in the sediment before and after soil washing.

The estimated values of K_{mc} for the single PAH congeners in HA for the sample A, are reported in Tab. 15.

PAH congener	Log K_{mc} ($l \cdot kg^{-1} \cdot C^{-1}$)
An	3.09
Fuo	2.77
Py	2.78
B(a)a	3.80
Cry	4.12
B(b)	3.91
B(a)p	4.09
B(e)p	3.79
D(a,h)a	4.49
Ind	5.57
B(g,h,i)p	5.49

Tab. 16. Values of log K_{mc} calculated for single PAH congeners of sample A

Values of K_{mc} previously calculated for PAHs vary between 10^2 and $10^6 l \cdot kg^{-1} \cdot C^{-1}$ (Gauthier et al., 1987; McCarthy et al., 1985; Jones et al., 1999; Schlautman et al., 1993; Chin et al., 1997). Generally, largest values (10^5 - $10^6 l \cdot kg^{-1} \cdot C^{-1}$) were calculated for PAHs having more than four rings in their structure (McCarthy et al., 1989; Morehead et al., 1986). Compared to the values reported in the literature, the K_{mc} estimated in this work (Tab. 15) appear absolutely comparable.

A linear correlation can be observed plotting the values of log K_{mc} versus log K_{ow} for the single PAH congeners (Fig. 37).

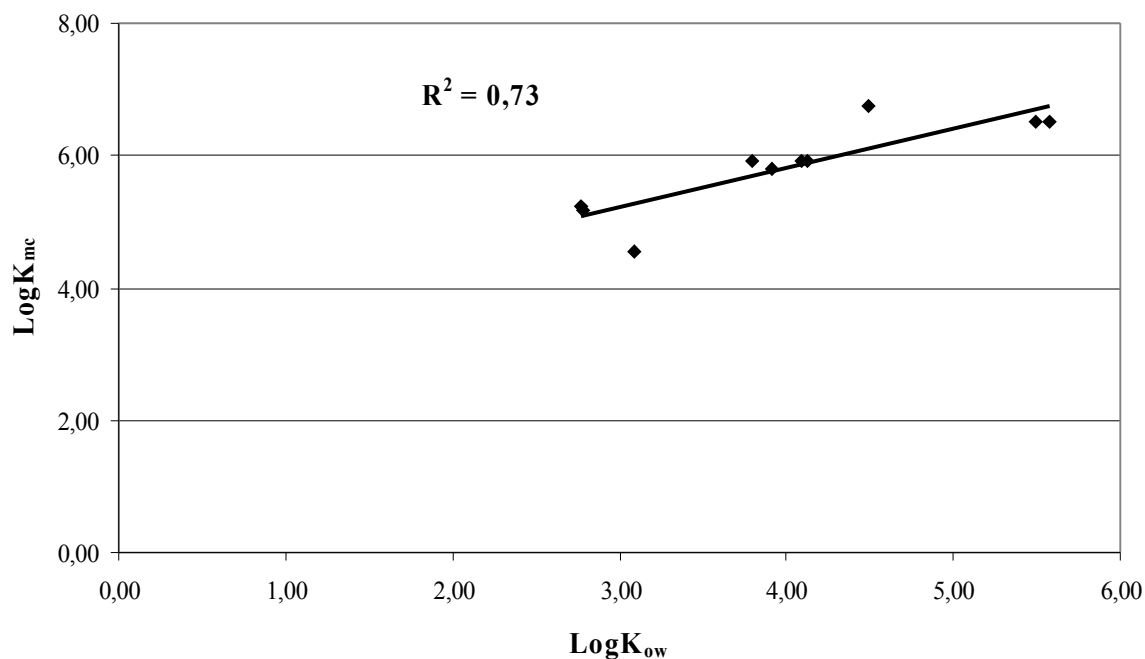


Fig. 37. Scatter plot log K_{mc} vs log K_{ow} calculated for the single PAH congeners reported in Tab. 15

This correlation suggests that the solubilisation of PAHs in the studied samples is favoured by the stronger interactions between PAHs, especially the congeners with more than 4-rings, and the surfactants since HA result more accessible for the incorporation of hydrophobic compounds compared to when they are dissolved in water (Rav-Acha et al., 1992). However, Zhou et al. (2005) have found for a mixture of non-ionic surfactants, a better linear relationship ($R^2 = 0.99$) between K_{mc} and K_{ow} suggesting that the larger K_{ow} of the particular hydrophobic solubilizate correspond to the greater tendency it possess in partitioning into the micellar phase.

The less evident linear relationship between K_{mc} and K_{ow} obtained in this research may be related to the differences measured in the initial concentrations (before micelle-solubilisation) of the PAH congeners. For example, the value of log K_{mc} of Cry is higher than that of B(a)a although they have the same value of log K_{ow} . The initial higher concentration of Cry (0.48 $\mu\text{g/ml}$) with respect to B(a)a (0.42 $\mu\text{g/ml}$) may have contributed to mask the potential log K_{mc} / log K_{ow} correlation. Moreover, Ind shows the highest value of log K_{mc} , although D(a,h)a has the highest value of log K_{ow} again, the initial concentration of Ind (0.43 $\mu\text{g/ml}$), higher than that of D(a,h)a (0.11 $\mu\text{g/ml}$) seems to strongly influence the repartition between water and pseudo-micelle of HA.

A further demonstration of the different binding affinity between PAHs and pseudo-micelles of HA, is represented by the different pattern of recovery of the single PAH congeners after extraction from the dissolved HAs at different temperatures (113°C and 150°C). Actually, at higher temperature, 5 and 6-rings PAHs evidenced a very low recovery suggesting a higher binding affinity for HA with respect to the 3 and 4-rings PAHs.

IV.4.3. Temperature effect on PAH solubilization

According to Yeom et al., (1996), Yeom and Ghosh, (1998), Zhou and Rhue, (2000), the process of solubilization depends on different variables: the type and dose of surfactants, hydrophobicity of PAHs, surfactant-sediment interaction, time of contact of contaminants and sediment. Moreover, solubilization increases with the temperature since the solutions of non-ionic surfactant solution tend to enhance the aggregation numbers and/or sizes of the micelles (Rosen, 1989) thus favouring the desorption of PAHs from the sediments. This was observed during the W(60°C,24h) experiment where the percentage of desorption was ~10% higher than that observed during the other soil washing treatments.

However, the potential effect of the increasing temperature on the diffusivity of the compounds through macromolecular organic matter or through intraparticle pores characterized by hydrophobic wall coating (Cussel et al., 1995; TenHusscher et al., 1996) and notoriously ruled by the well known Arrhenius's equation $D = D_0 e^{-E_a/RT}$ (Cussel et al. 1995; TenHusscher et al. 1996; Pilorz et al., 1999) cannot be excluded and further research is needed to discriminate the contribution of the two thermodynamic processes to the overall desorption effects.

IV.4.4 Effect of mixed surfactant solutions on PAHs solubilization

A further factor contributing to the solubilization of PAHs from sediments, tested by the set of experiments carried out during this research is related to the effect of mixed surfactant solutions such as documented by Zhu and Chiuo, (2001) and Zhu and Feng, (2003) that seems to induce an effect of solubilization of PAHs substantially different from that verified using single surfactants. The estimated differences are generally attributed to specific interactions of complex synergistic/antagonist effects between the surfactants present in the solution (Zhu and Feng, 2003; Zhang et al. 2006). The observed decrease of ~2-3% of PAH desorption in sample A (Fig. 22) and in sample E (Fig. 26) after washing with the mixed surfactant solutions (HA and Triton X-100) seems to suggest a proportional antagonist interaction

between HA and Triton X-100. Such a kind of effects appears more evident in the sample E where the higher (1%) concentration of Triton X-100 in the mixed solution was present.

IV.4.5. Kinetic of PAH desorption

Both the patterns of desorption shown for the different PAH congeners, and the comparable percentage of desorption obtained with the different experiments (Tab.7) suggest a common effect of detachment from the sediment as an obligated step in the remediation process.

The micelle-solubilization and the oxidation process decrease the concentration of PAHs in the water phase causing a shift of the equilibrium of the sediment-water system inducing an increase of PAHs concentrations in water and therefore inducing a more efficient desorption of PAHs from sediments.

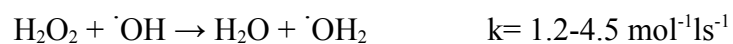
It follows that kinetic factors have also to be taken into account to explain time and efficiency of PAH desorption from marine sediments. Infact, surfactants enhance the rate of PAH solubilization through two main mechanisms: 1) micellar solubilization and 2) sorption and inclusion of the surfactant molecules within the sediments inducing swelling of sediments and increasing matrix diffusivity of PAHs (Yeom et al., 1996).

From the other hand, application of Fenton reagent allows PAHs oxidation only when they are desorbed from the solid phase because in the water phase PAHs are able to react with hydroxyl radicals generated in aqueous solution (Sedlak and Andren, 1994; Watts et al., 1999). Hydroxyl radicals are known to react with aromatic compounds at rates approaching those of the diffusion (Haag et al., 1992). However, the rate of PAHs degradation depends on the reactivity of PAH molecule. In particular, higher value of ionisation potential (IP-HOMO) correspond to higher reactivity towards hydroxyl radicals (Zander, 1983).

Results from experiments Fe (1%, 15 min), Fe (1%, 30s), Fe (30%, 15 min), show that D(a,h)a, B(a)p B(e)p and 6-rings PAH are more efficiently removed with respect to the other PAH congeners, although characterized by a lower log K_{ow} , possibly because of their higher values of the ionisation potential (Fig. 38). However, although the ionisation potential of An is higher than that of Phe, the desorption of Phe was higher again possibly due to the different sources and transport mechanisms of PAHs in the studied system, and because of significant inhomogenities in the chemical composition of the sedimentary organic matter.

Moreover, comparing the values of percentage of desorption obtained as a result of Fenton oxidation experiments, we can observe that the removal of PAH from sediment was dependent on the concentration of H_2O_2 and the time of addition of it to the mixture. In

particular, PAH destruction was greater when the hydrogen peroxide was added in four smaller doses (1%) and in longer times (15 min.) after the addition of iron. It meant that the most relevant quenchers in our reaction solution were H₂O₂:



However, the decrease of PAH desorption after W+Fe(1%, 15 min) treatment showed that also HA in the reaction can be considered a significant quencher.

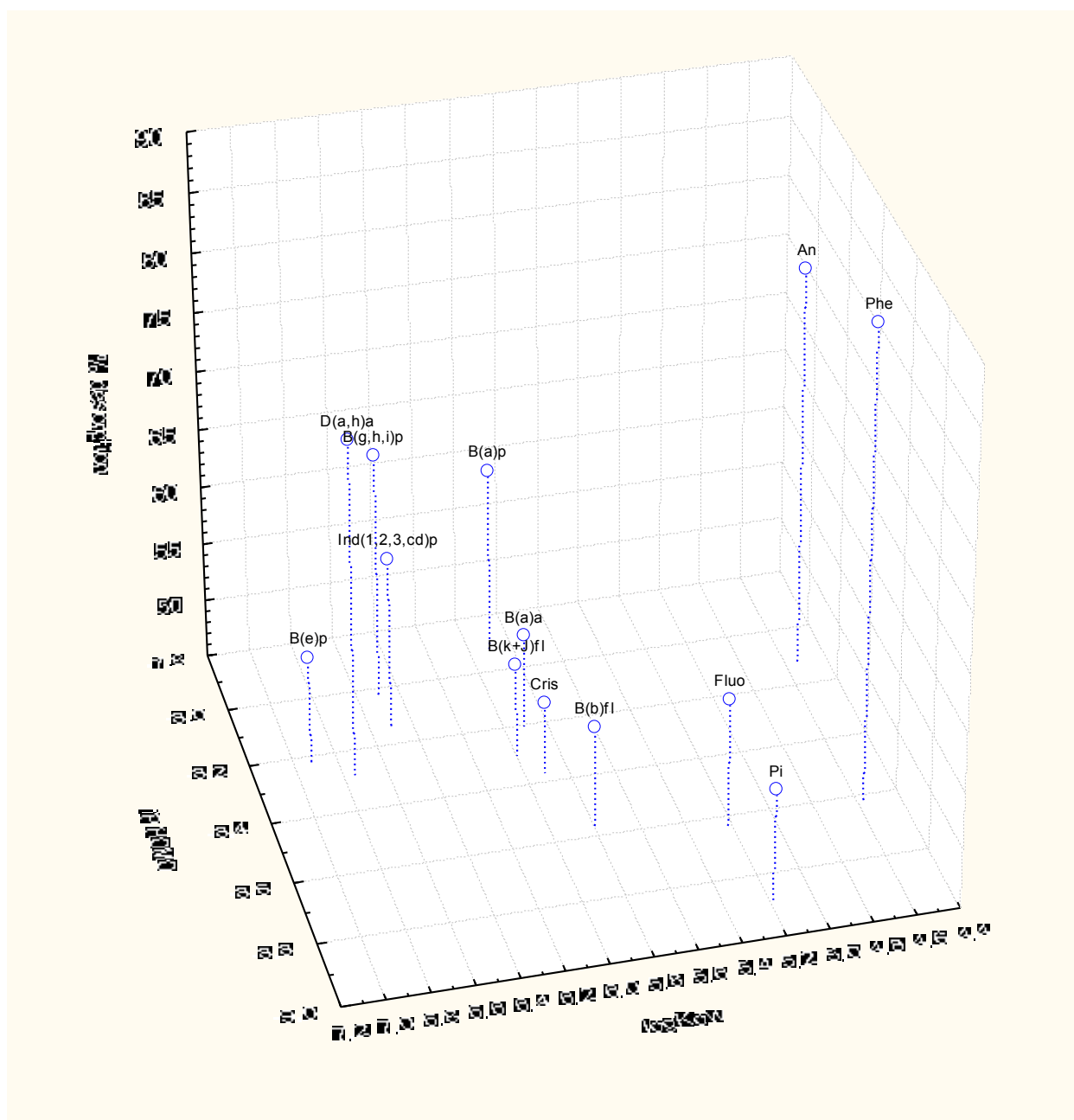


Fig. 38. Influence of log K_{ow} and HOMO energy (IP_HOMO) values on PAH desorption following Fenton treatment.

IV.4.6. Technical consideration on PAH removal capacity of soil washing and Fenton oxidation

In this paragraph I will synthesize the most relevant results in terms of technical aspects, obtained by application of soil washing and Fenton oxidation techniques. In particular the ensemble of the performed experiments demonstrated that the higher value of PAH desorption (~70%) are obtained through washing of sediments proportionally to the content of coarser grain size by application of humic acid solution at temperatures of 60°C and by soil washing for 24h of sediments at room temperature (~60%).

The results achieved by double washing of sediments with HA for 24h show a lower efficiency in Σ PAH removal (~47%) possibly due to the presence of a residue of surfactant, containing desorbed PAHs, after the washing.

Application of soil washing, with mixed surfactant solutions does not apparently increase significantly the effects of desorption of PAHs from sediment. Moreover, since synthetic surfactant such as Triton X-100, have toxic effects on microorganisms (e.g., Allen 1999), application of such a surfactants for remediation technologies appears not appropriate.

Fenton oxidation experiments showed any capacity for PAH removal but lower than that resulting from application of soil washing. Actually, the highest value of PAH desorption, after Fenton oxidation, obtained with experiment Fe(1%, 30s) with lower concentrations of H_2O_2 appears ideal to minimize the quenching effect of H_2O_2 .

Finally, combination of soil washing and Fenton oxidation did not favour any significant Σ PAHs removal from sediments. Conversely, results from experiment W+Fe(1%, 15 min) showed a percentage of decontamination lower (46%) than that of Fe(1%, 15 min)+W, possibly to again attribute to the the presence of residues of surfactants, with desorbed PAHs, after washing.

Samples with high content of silt (for instance, sample E) the efficiency of remediation reduces to very low values (~6%).

The highest value of PAH desorption (6.37%) is obtained after soil washing with HA for 24h. A basic pH, useful to favour the solubilization of HAs and avoiding their potential adsorption on sediments, didn't favour any increase of PAH removal from the sediment.

Using of a mixed surfactant solutions produces a decrease of ~3% of PAH desorption from this fine sediments, while the application of Fenton oxidation again appeared to provide a limited contribution to the effects of remediation.

IV.5. The role of organic matter and clay minerals on PAH desorption

IV.5.1. Geosorbent organic matter

The results of soil washing and Fenton oxidation carried out on the studied samples, showed that PAH were not definitely eliminated from the sediments. The release of sediment-bond PAH from solid to the aqueous phase typically results in an initial period of rapid release, followed by a slower loss of contaminants (Guerin et al., 1997; Loehr et al., 1996). These differences in the rate of release are generally attributed to presence of two principal types of organic domains in sedimentary organic matter (SOM) (LeBoeuf and Weber, 1997 and Xing and Pignatello, 1997): i) a high amorphous one (rubbery domain) where sorption of organic compounds can be considered a linear, fast, and completely reversible process and ii) a relatively condensed one (glass domain) where sorption is generally nonlinear, slow and “hysteretic” (Weber et al. 1999). This dual model of reactive domain was developed to explain the non-linearity and hysteresis of the sorption of organic compounds onto organic matter in soils/sediments (Karickhoff et al., 1979; Celis et al., 1998; Weber et al., 1998; Spurlock et al., 1994; Chiou et al., 2000).

In a number of studies (Pignatello et al., 1996; LeBoeuf et al., 1997; Huang et al., 1997) the two SOM domains have been linked to two thermodynamic states of synthetic organic polymers, known to exhibit two main forms of mechanical behaviour, depending on whether they exist in so-called “glassy” or “rubbery” thermodynamic states (LeBoeuf and Weber, 1997). In particular, glassy polymers are differentiated from rubbery polymers by their hard, rigid, glass-like structures at room temperature. Rubbery polymers are soft and flexible at room temperature. The flexible nature of rubbery polymers can be attributed to long-range (multi-molecular) motions of polymer chains not fully present in the glassy structure. By heating a glassy polymer above room temperature (120°C) results in its transition to rubbery-like behaviour (LeBoeuf and Weber, 1997). Cooling a rubbery polymer results in less long-range molecular motion, and consequent polymer stiffness and rigidity. The temperature at which increased molecular motions leads to rubbery behaviour is referred to as glass transition temperature, T_g (LeBoeuf and Weber 1997). The rubbery domain of SOM is primarily characterized by oxygen-functional groups such as carbohydrates and carboxyl acids while glassy domain is characterized by aromatic and aliphatic oxygen-free functional groups (e.g. kerogen) (Weber et al. 1999). Humic substances enriched with glassy rigid domains have the highest sorption affinity for organic pollutants and provide the slowest desorption kinetics, or the highest retardation of the organics.

Based on this theoretical approach, the fraction of PAHs that remained in the studied sediments after the remediation treatments may be represented by that part strongly bound to the SOM and subjected to a lower diffusion through the organic matrix. Observing the different behaviour of PAH desorption from different size fractions of sample C, after soil washing with HA for 24h, it is possible to identify the two domains of SOM. The two domains of SOM were investigated through desorption experiments carried out on the different size fractions of the sample C. A hypothetical prevalence of glassy domain may be associated with SOM present in the size fractions $1000 < \Phi < 500 \mu\text{m}$, $125 < \Phi < 90 \mu\text{m}$ and $90 < \Phi < 63 \mu\text{m}$ since the percentage of desorption of PAH congeners were lower than those observed in the other fractions. Instead, a hypothetical prevalence of rubbery domain may be associated with SOM in the size fractions $\Phi > 1000 \mu\text{m}$ and $250 < \Phi < 125 \mu\text{m}$ since they showed the highest percentage of desorption (except for 3-rings PAHs). The prevalence of glassy and rubbery domain depends on the origin and maturities of the organic matter. As diagenetic effects increase, SOM tends to become chemically more reduced and physically more condensed.

However, the desorption of PAHs from sediments depends not only on physical and chemical properties of sediments but also on PAH properties. Infact the desorption behaviour of PAHs with the same number of rings is similar in a particular size fraction (Fig. 28 to Fig. 31). This indicates that organic material may have a similar affinity for PAHs with the same number of rings.

A further investigations of the kinetic of PAH desorption from the two organic domains of SOM will allow to understand the mobility and the availability of PAHs after remediation treatment, thus predicting the risk to humans and the environment.

IV.5.2. The role of the Black carbon (BC) in the processes of PAH desorption

PAHs sorbed on coal particles are associated with high desorption activation energies (115-139 kJ/mol) and associated extremely slow desorption rates (estimated around 10^{-17} - $10^{-19} \text{ cm}^2\text{s}^{-1}$) and limited availability at environment temperatures (Gosh et al., 2001; Talley et al., 2002).

These characteristics are attributed to the strong π - π electrodynamic interactions (Sakurovs, 1998) between PAH molecules present within the coal matrix and the coal macromolecules such as well evidenced by nuclear magnetic resonance studies (Sakurovs, 1998). In particular, sorption of PAH on coal-derived particles is expected to resemble polymer sorption due to the physical structure of coal, which is described as a porous

macromolecular gel (Gorbaty ,1994) that swells on interaction with solvent (Larsen et al., 1990) and shows a glass transition temperature of about 325 °C (Nishioka et al., 1990). Although based on results obtained only on the sample C where BC content ranged around 0.3% of the total sediment weight but with an associated content of about 26% of total PAHs, 15-20% of 3-ring PAHs, 30% of 4-ring and 20% of 5 and 6-rings PAHs, it has been reasonable do not exclude additional separation processes useful to remove BC from the sediments.

IV.5.3. Influence of silt/clay on PAH desorption

Results relative to the experiments of soil washing with HA for 24h (Tab. 9), show that the percentages of desorption of PAH from the studied sediments are significantly influenced by the silt/clay contents in the samples. The first order linear correlation between silt/clay and percentage of PAH desorption (Fig. 21) allows to approximate a lack of ~10% of PAH desorption efficiency related to an increase of ~ 8% /11% of silt/clay content. A relevant interaction between PAH and clay minerals may explain the observed anticorrelation between silt and percentage of desorption for different PAH congeners clearly evidenced by the Principal Component Analysis performed using a data set of variables composed of the percentage of desorption of the 13 PAH congeners, the %TOC, the silt and clay contents and applied to the all studied samples (Fig. 39).

Such an efficient interaction was attributed (Zhu et al, 2004) to the cation π -bonding (bond formed between π electrons of organics and cation). The magnitude of the enthalpy values of these interactions (approximately 20 kcal/mol) is approximately one-fifth that of a covalent bond but about five times stronger than a hydrogen bond (Dougherty and Taufefer, 1990; Kumpf and Dougherty, 1993; Gokel et al., 2001). Based on the reported value of enthalpy, the interactions of PAHs with clay minerals are stronger than those with humic acids (Hwang et al., 2004). Because clay minerals accumulate cations at the mineral-water interface, the formation of cation- π interactions between PAHs and exchangeable cations may effect PAH sorption to the mineral surface. Zhu et al. (2004) observed that stronger sorption and a more significant upward-curving isotherms are related to soft cations relative to hard cations (e.g., $\text{Ag}^+ \gg \text{Cs}^+ > \text{Na}^+$) and π donators relative to non π donators (e.g. phenanthrene $\gg$ 1,2,4,5- tetrachlorobenzene). Several models were implemented to describe the driving forces for sorption of non-ionic-organics (NOCs) such as PAHs, by mineral surfaces. For instance, NOCs sorption to hydrated mineral surfaces has been ascribed to

“hydrophobic effect” whereby sorption is controlled by a combination of relatively small van der Waals forces and substantial entropic differences (Tanford, 1980; Israelacvili, 1985).

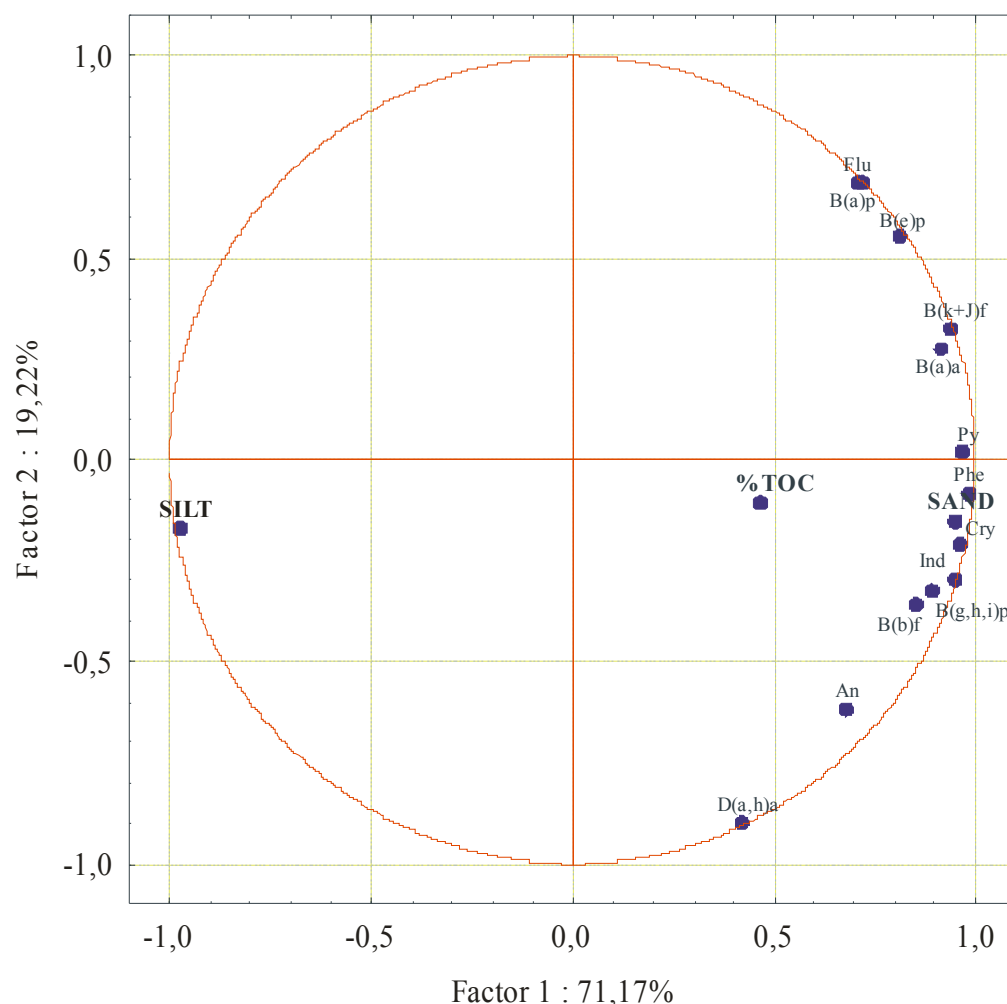


Fig. 39. Principal Component Analysis (PCA) performed using a data set of variables composed of the percentage of desorption of 13 PAH congeners, %TOC, silt and clay contents and applied to the all studied samples: an anticorrelation is evidenced between silt and the percentage of PAH congeners

Hydrophobic effects were also used to explain observed correlations between the logarithms of K_d values and PAH aqueous activity coefficient (Schwarzenbach and Westall, 1981; Mader et al. 1997). The generally accepted theory related to an entropic-driven sorption mechanism, implies that chemical bonds formed between mineral surfaces and PAH are weak (or nonexistent) and do not contribute significantly to the enthalpy change (ΔH) and the Gibbs free energy change (ΔG) of the reaction. If this mechanism were true, PAHs sorption would not be affected by the type of exchangeable cation or the mineral surface chemistry for a given PAH as observed by Zhu et al. (2004) and, in our studies, the desorption of PAH would

not be significantly affected by silt/clay content. Therefore, according to the latter authors, the best conceptual mechanistic model of PAH sorption to mineral surfaces is one that combines the enthalpic effects due to the formation of specific interaction between exchangeable cations on the mineral surface and the PAH molecules with the influence of entropy on PAH activity coefficients.

A further complex interaction of PAH bond to humic matter associated with mineral surfaces may directly influence the desorption of PAH congeners as suggested by the different values of percentage of desorption (Tab.9) obtained by samples containing the same amount of total organic carbon (Tab. 4). However, the capacity of sorption of organic matter depends not only on the quality, but also the quantity of the organic material present in the sediments. Actually, as reported by Murphy et al. (1990), the distribution of hydroxyl sites on the clay surface, which represent points of attachment for carboxyl groups of humic substances, affect the interfacial configuration of the humic coating possibly altering the size or accessibility of the hydrophobic domain. This could mean that mineral-HA complex are less accessible for incorporation of hydrophobic compound (Laor et al., 1998); and/or, if HA has already incorporated PAHs before its adsorption to clay minerals, the interaction of HA-PAH complex with the mineral can alter the size of HA in such way that the desorption of PAHs might become more complicated.

IV.6. Isotope experiments

IV.6.1. Isotope tracing during soil washing experiment

The results of soil washing experiments carried out by $^{13}\text{C}_3$ pyrene stable isotope spiking of the sediment samples A and E, confirm the different efficiency of soil washing desorbing of PAHs from sediments with very different contents of fine grain size that strongly drives the desorbing effects of PAHs from the solid phase. However, the results clearly appear sufficiently different from the percentage of desorption measured for pyrene during the experiment 1 (W(24h)) applied to the same samples. The most plausible explanation for such a result may be related to the kinetic of adsorbing effects of spiked PAH on the sediments (only 1 month). A relatively limited interaction with all the organic/inorganic components constituting the sediment may have provided a more efficient capacity of release of the added $^{13}\text{C}_3$ pyrene from the solid phase after soil washing treatment once compared to the extraction of more mature organics from the original samples.

IV.6.2. Fenton oxidation

The oxidation agent utilized for PAH oxidation in HA solution was hydrogen peroxide in combination with iron (Fe^{2+}) which produce hydroxyl radicals in a reaction commonly known as Fenton's reaction. The chemical oxidation method is non-selective, which means that any oxidizable material could react with the oxidizing agent ($\cdot\text{OH}$). In particular, hydrogen peroxide itself acts as a quencher of $\cdot\text{OH}$. Most studies report the existence of an optimum H_2O_2 concentration for the degradation of organic compounds by means of the catalytic Fenton process (e.g., Saxe et al., 2000). Moreover, Lindsey and Tarr (2000) found a decrease in the rate of various aromatic compounds by Fenton reaction (pH=2.5) when fulvic and humic acid in concentration of 5-30 mg/l were added. Infact, humic substances react with $\cdot\text{OH}$ resulting in bleaching, mineralization and production of low molecular-weight acids as formic, acetic, malonic and oxalic acid (Goldstone et al., 2002). The relative rate of the reactions of $\cdot\text{OH}$ with the quenchers (H_2O_2 and HA), present in a system can be estimated according to the following equation (Georgi et al., 2007):

$$v_n/v_m = k_{n,\text{OH}} \cdot c_n / k_{m,\text{OH}} \cdot c_m$$

where v_n and v_m are the rates of the reactions of the species n and m with $\cdot\text{OH}$, $k_{n,\text{OH}}$ and $k_{m,\text{OH}}$ are the second-order-rate constants of these reactions and c_n and c_m are the local concentrations of these species in the environment of the $\cdot\text{OH}$ radicals. Georgi et al. (2007) estimated that in a solution containing 65 mM H_2O_2 the quenching of $\cdot\text{OH}$ by HA is negligible compared to that by H_2O_2 when the HA concentration is low ($v_{\text{H}_2\text{O}_2}/v_{\text{DOC}} \approx 20$ at $c_{\text{HA}} = 10$ mg/l), whereas the quenching ratio increases to values of $v_{\text{H}_2\text{O}_2}/v_{\text{DOC}} \approx 4$ and 2 at HA concentrations of 50 or 100 mg/l, respectively.

However, HAs can have a positive effect on the oxidation reaction because the formation of HA-Fe(II) complexes would become important for catalytic Fenton systems in case of strong inhibiting effects (Georgi et al., 2007). Infact, different types of Fe(III)-HA complexes can be formed depending on the concentration ratio of iron and HA in solution due

to the competition of different functional groups of the HA in the binding of iron. If these functional groups simultaneously facilitate Fe(III) reduction, the reaction would be accelerated with increasing HA concentration until all of the Fe (III) is bound to this type of functional groups.

In our studies, $^{13}\text{C}_3$ Pyrene was used as isotope tracing to understand the oxidation of a PAH molecule in humic acid solution. Isotopic composition value measured for the mixture HA/ $^{13}\text{C}_3$ pyrene/ Fe^{2+} /EDTA/ H_2O_2 was -25.96 ‰ while the assumed value of the mixture in absence of H_2O_2 , of -28.66‰. This variation of ~3‰ suggests a potential kinetic effect generally characterized by the classic Rayleigh equation. If we assume that only HAs and EDTA were oxidized by $\cdot\text{OH}$ radicals, the obtained final isotope composition may be attributed to an oxidation of HAs and EDTA of ~85%. This would imply an oxidation of ~50% of HAs. If this was true, we should observe that the original brown colour of HA solution turned in yellow tone during the reaction (Georgi et al., 2007). Instead the colour remained brown during all the reaction thus showing that HAs were not transformed at all.

Consequently, $^{13}\text{C}_3$ pyrene represent the last candidate for the oxidation by $\cdot\text{OH}$ radicals.

An increase of H_2O_2 concentration (4 times the initial value) in the $^{13}\text{C}_3$ Pyrene spiked humic acid solution caused a decrease of isotope composition of carbon of ~1‰ suggesting a quenching effect of $\cdot\text{OH}$ radicals by H_2O_2 .

IV.6.3. Reactivity of PAHs and oxidation products of $^{13}\text{C}_3$ pyrene after Fenton oxidation

The electron distribution over the PAH molecule determines the position of the atoms most reactive. The localization energy is the energy difference between the aromatic molecule and σ -complex intermediate that is formed after the attack of a nucleophile, electrophile or radical. The term σ -complex is used to describe an intermediate in which the carbon at the site of substitution is bonded to both the nucleophile (or electrophile or radical) and hydrogen that is displaced. Localization energy is reflected by a number of reactivity indices one of the which is the Dewar's reactivity number (N_u) (Dewar, 1952). This number reflects the localization energy and the reactivity at certain position of the aromatic compound. Smaller values of N_u correspond to a lower activation energy and therefore to a greater reaction rate in that particular position. Benzene has high values of N_u therefore it is considered the least

reactive species. PAHs are generally more reactive than benzene because the activation energy for formation of the σ -complex is lower than benzene because more of initial resonance stabilization is retained in intermediates than have a fused benzene ring.

The localization energy concept may be helpful in clarifying the mechanism of PAH-degradation and PAH-derivate formation. In particular, for a pyrene molecule, a higher reactivity is expected for the position 1 and position 10 ($N_u = 1.51$ and 1.68 respectively, comparing to position 2 ($N_u = 2.31$)) (Lundstedt, 2003).

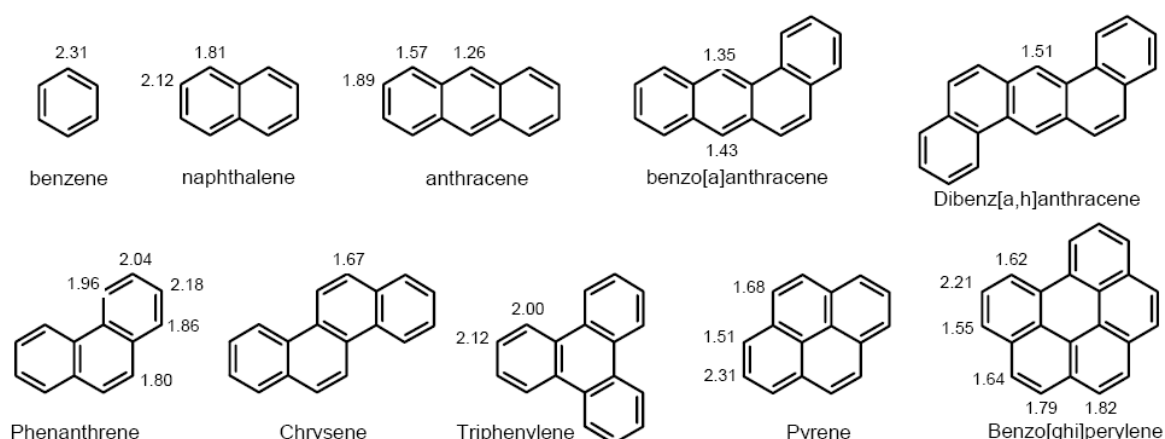


Fig. 40. Electron localization energy for benzene and selected PAHs, based on the work of Zander 1979

Lundsted et al. (2006), reported that during chemical reactions, PAHs didn't lose their aromatic character because a considerable amount of energy is required to change an aromatic compound into a non aromatic compound, so the dead-end products appears to be primarily carbonyl compounds, such as ketones, quinones, dicarboxylic acid anhydrides and coumarins, while carboxylic acids and phenols seems to be more easily degraded or transformed. In particular they identified the 4-oxapyrene as oxy-PAH formed after Fenton oxidation enhanced by ethanol pre-treatment.

However, in the presented experiments, the observed isotope fractionation may be directly related to a differential reactivity of the hydroxyl radicals on carbon tied at different locations and the PAH benzene rings. In particular, partial oxidation of $^{13}\text{C}_3$ pyrene to 4-oxapyrene should produce a final $\delta^{13}\text{C}$ value for the mixture of -28.78‰ . Only the lost of the aromatic character of the PAH molecules, with formation of compounds with 7 carbon atoms with 3 ^{13}C may produce an isotope fractionation of the some order of magnitude than that measured in the presented experiments ($\sim 4\text{‰}$). This preliminary results suggest that during

Fenton oxidation, PAHs are not completely oxidized in CO_2 and H_2O_2 , but that they lose their aromatic character forming organic molecules with a reduced number of carbon atoms.

Chapter V

CONCLUSIONS AND FUTURE PERSPECTIVES

The ensemble of experiments of chemical remediation carried out on a group of real samples (marine sediments) provided a new and broad spectrum of data useful to better understand the chemical-physical behaviour of PAHs (in particular the 16 USA-EPA priority ones) in the marine environment and the different interactions with sediments necessary to efficiently calibrate different approaches to decontamination.

The main results achieved from this research work can be synthesized in the following points:

- Analysis on the distribution of PAHs in the different grain size fractions of the studied marine sediments provided a clear evidence of unexpected behaviour of this class of contaminants in relation to the particle size distribution with accumulation of the organics (and of all the single congeners) in the larger components of samples. This suggest that the classical “a priori” approach of a selective application of remediation techniques to the finer grain size of samples may result deeply uncorrected and confusing for appropriate interpretations of the final effects of organic pollutants removal.
- The distribution patterns of PAHs in the marine sediments, in terms of potential sources and transport mechanisms, investigated on the basis of the differential physical behaviour of the various congeners, demonstrated a key element for a comprehensive understanding of the results of remediation techniques applied to the samples. In particular, a clear pyrolytic origin for PAHs was identified for the studied samples. Moreover, the higher concentration values of PAHs, with more 4-rings measured in the studied samples suggest that PAH sources may be mainly related to activities involving use of coke oven, electric arc furnace, heavy oil combustion and industrial stacks.

- A comprehensive comparison of the efficiency of Σ PAHs desorption shows that the best results achieved by soil washing with HA for 24h at temperature of 60°C. Moreover, the simple soil washing with HA for 24h can be also considered as an optimum strategy of sediment remediation.
Fenton oxidation generally shows an efficiency of PAH removal lower than that observed after in soil washing experiments due possibly to the unspecificity of hydroxyl radicals.
- The efficiency of is estimated of ~60% for sample with high content of sand soil washing with HA for 24h. A primary role played by the content of clay minerals in the sediments on the desorption effects of PAHs was clearly evidenced by a first order linear correlation between the percentage of desorption of total PAHs estimated after soil washing, and silt/clay abundance with an estimated lack of ~10% of PAH desorption efficiency with an increase of ~8% /11% of silt/clay content.
- Differential hydrophobicity features of the various PAHs and their relation with humic substances present in the sediments demonstrated essential parameters influencing the distribution of contaminants in the sediment and their potential release under “soil washing” application.
- The desorption efficiency of the single PAH congeners appeared to directly depend on the hydrophobic character of the single PAH suggesting a high tendency of PAHs in partitioning into a pseudo-micellar phase. This is well-expressed by the linear correlation between the calculated coefficients of water-micelle partitioning and the coefficient of water-octanol partitioning of the single PAH congeners.
- The experiments of Fenton oxidation demonstrated that the removal of PAHs from sediments depends on the PAHs reactivity in relation to their ionisation potential and consequently to the capability of PAHs to be chemically oxidized. Evident difference in terms of PAHs removal from sediment were correlated to different concentrations of H₂O₂ and times of addition of it to the mixture. In particular, PAHs oxidation was greater when the hydrogen peroxide was added in four smaller doses (1%) and in

longer times (15 min.) after the addition of iron. Finally, clear evidence indicates that the most relevant quenchers in the reactions was H_2O_2 .

- The ensemble of results of soil washing and Fenton oxidation demonstrated that PAHs cannot be definitely eliminated from the sediments (the maximum value of remediation efficiency was ~60% for the more sandy samples) and therefore these two chemical approaches show a relatively limited capacity to degrade hydrophobic contaminants mainly in sediments with high content of silt. It follows that application of this kind of remediation techniques calls for appropriate monitoring of the decontaminated sediments in order to verify potential slow desorption of stay-bound PAH and transferring to the environment.
- Isotope tracing experiments demonstrated were extremely useful to confirm the different efficiency of soil washing and desorbing of PAHs from sediments with different grain size distribution. The recovery of the isotope tracer ($^{13}\text{C}_3$ pyrene) in the liquid phase after the soil washing of sandy sample was higher than that of silty samples. The differences in calculated recovery may be due to the techniques of spiking which not efficiently reproduced natural sorbing conditions of organics onto sediments. Preliminary results on Fenton oxidation carried out on an isotope tracer ($^{13}\text{C}_3$ pyrene) suggested a potential kinetic fractionation of $^{13}\text{C}_3$ pyrene related to a differential reactivity of the hydroxyl radicals on carbon tied at different locations and the PAH benzene rings. The potential product of $^{13}\text{C}_3$ pyrene oxidation seems to be a compound with 7 carbon atoms with 3 ^{13}C .

Based on the obtained results it emerges a clear need for a better understanding of the supramolecular behaviour of HS that may favour PAHs biodegradation. In fact the presence of hydrophobic components responsible for increase solubility of PAHs is contiguous to hydrophilic domains where is particularly favoured a biological lability that directly control the efficiency of biodegradation. Moreover, the verified incomplete degradation of PAHs after Fenton oxidation and the potential production of toxic intermediates that may be resistant to further degradation, calls for a detailed study of the transformation of the PAH congeners during the process and is absolutely demands an opportune transferring of the studied remediation approaches to the commercial “world”.

The influence of Fenton oxidation on the composition of the sedimentary organic matter and the consequent change of its sorption and desorption on PAHs need to be deeply investigated because of the potential influence on the accumulation and mobility effects of hydrophobic contaminants in the sediments.

Finally, a more definitive study of the desorption rate of PAHs, in the different physical and chemical condition of the sediments and of the effects of diffusion of PAHs through the organic matter characterised by different aging, will provide an appropriate evaluation of the risk associated to the slow release of strong-bond contaminants remained in the sediments after the application of soil washing and Fenton techniques.

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