JYVÄSKYLÄ STUDIES IN BIOLOGICAL AND ENVIRONMENTAL SCIENCE

99

Tarja Hyötyläinen

Assessment of Ecotoxicological Effects of Creosote-Contaminated Lake Sediment and its Remediation

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UNIVERSITY OF JYVÄSKYLÄ

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ABSTRACT

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There is an urgent need to develop accurate methods to identify risks associated with contaminated sediments and complex mixtures. Biological and chemical assessment of the adjacent environment can be considered an integral component of the remediation plan for any site heavily contaminated. An investigation was therefore conducted to identify any ecotoxicological risk associated with the creosote-contaminated sediment of Lake Jämsänvesi, in Central Finland and its remediation. Creosote is a widely used wood preservative containing about 85 % polycyclic aromatic hydrocarbons (PAHs) with various hydrophobicities.

Desorption studies showed the resuspension of sediment spread toxic contaminants from sediment to the water layer - also in high mixing ratios. The elutriates contained high molecular weight PAHs and part of these are also carcinogenic compounds. The elutriates of the contaminated sediment were also toxic to photoluminescence bacteria (*Vibrio fischeri*) and waterfleas (*Daphnia magna*). Thus, the toxicity of elutriate in contaminated sediment increased when the elutriate contained a high total PAH concentration. The oligochaetes (*Lumbriculus variegatus*) accumulated PAHs from contaminated sediment. This suggested the bioavailability of PAHs from Lake Jämsänvesi to the benthic food chain, potentially resulting to the exposure and responses of fish (*Onchorhynchus mykiss*) characteristic to PAHs. The same PAHs were present in the mussel (*Anodonta anatina*) tissue and in settled particulate material during the remediation of Lake Jämsänvesi by capping. Remediation of Lake Jämsänvesi creosote-contaminated sediment may have also spread the contaminated material from the sediment to the water layer. Risk assessment and evaluation of remediation strategies at contaminated sites require estimation on both the total amounts of contaminants present and their potential for release from sediments to be evaluated.

Key words: Creosote; elutriate; PAH; remediation; risk assessment; sediment; toxicity.

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CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following articles and manuscript, which are referred to in the text by their Roman numerals. I have planned the works with professor Aimo Oikari, and performed a significant proportion of the exprimental work and writing of the papers I-VI.

I Hyötyläinen T. & Oikari A. 1999. The toxicity and concentrations of PAHs in creosote-contaminated lake sediment. Chemosphere 38: 1135 – 1144.

II Hyötyläinen T. & Oikari A. 1999. Assessment of toxicity hazards of dredged lake sediment contaminated by creosote. The Science of the Total Environment. 243/244: 97 –105.

III Hyötyläinen T. & Oikari A. 2001. Desorption of PAHs from creosote-contaminated and PAH-spiked sediment to lake water. Environmental Pollution (submitted).

IV Hyötyläinen T. & Oikari A. 1999. Assessment of the bioactivity of creosote-contaminated sediment by liver biotransformation system of rainbow trout. Ecotoxicology and Environmental Safety 44: 253 – 258.

V Hyötyläinen T. & Oikari A. 2001. Bioaccumulation of PAHs from creosote-contaminated sediment in a laboratory-exposed freshwater oligochaete, *Lumbriculus variegatus*. Manuscript.

VI Hyötyläinen T., Karels A. & Oikari A. 2001. Biological and chemical assessment of remediation actions with caged mussels (*Anodonta anatina)* at a creosote-contaminated lake sediment site. Water Research (submitted).

ABBREVIATIONS

PAH	polycyclic aromatic hydrocarbon
Ace	acenaphthene
Acy	acenaphtylene
An	anthracene
B(a)An	benzo(a)anthracene
B(b)F	benzo(b)fluoranthene
B(k)F	benzo(k)fluoranthene
B(a)P	benzo(a)pyrene
Cry	chrysene
dB(a,h)An	dibenzo(a,h)anthracene
dB(g,h,i)P	dibenzo(g,h,i)perylene
F	fluoranthene
Fl	fluorene
I(cd)Pyr	indeno(1,2,3-cd)pyrene
Nap	napthalene
Ph	phenanthrene
Pyr	pyrene

BNF	β-naftoflavone
CYP 1A1	cytochrome P450 1A1
dw	dry weight
EROD	7-ethoxyresorufin O-deethylase
1-OH pyrene	1-hydroxy pyrene
ISTD	internal standard
nd	not detected
OC	organic carbon
OM	organic matter
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibezo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
PMS	postmitochondrial supernatant
RA_{PAH}	relative amount of PAH compounds
RDE	relative toxic emission yield
RTE	relative toxic emission
SFS	synchronous fluorescence spectrometry
SPM	settled particulate material
TOC	total organic carbon
TU	toxic unit
ww	wet weight

1 INTRODUCTION

1.1 Occurrence and properties of PAHs

Ever since its isolation from coal tar in 1932 (Cook et al. 1933), the model polycyclic hydrocarbon, benzo(a)pyrene, B(a)P, has been widely studied as an environmental chemical carcinogen (Black et al. 1988, Sikka et al. 1990, Steward et al. 1991, Chin & Gschwend 1992, Kantoniemi et al. 1996, Rocca et al. 1996, Bestari et al. 1998; Table 1). Creosote is composed of approximately 85 % polycyclic aromatic hydrocarbons (PAHs), 10 % phenolic compounds, and 5 % N-, S-, and O- heterocyclics. PAHs are composed of hydrogen and carbon atoms arranged in two or more benzene rings. The aromatic system of a polycyclic aromatic compound must also contain atoms with p orbitals available for bonding, and the entire aromatic ring system must be planar. As the molecular weight of these compounds increases, their solubility in lipids increases and their resistance to oxidation and reduction decreases (Eisler 1987). Higher molecular weight PAHs such as fluoranthene (F), pyrene (Pyr), 2,3-benzo(b)fluorene, chrysene (Cry) and benzo(a)pyrene (B(a)P) represent the type of compounds that tend to accumulate in aquatic life exposed to them in the environment (Mueller et al. 1989). PAHs are also strongly adsorbed to particles and accumulate in the sediments.

Polycyclic aromatic hydrocarbons are widely distributed in the environment. Many of these high -boiling point, fat-soluble compounds are markedly carcinogenic to human beings, as well as other animals. PAHs are typically released to the atmosphere from the combustion of fuels, traffic, forest fires, burning coal refuse banks, and coke production (Crosby 1998). For example, U.S. tap water contains up to 24 ng/l total PAHs, urban runoff up to 10 µg/l of individual congeners, and 15 – 62 mg/kg of highly carcinogenic benzo(b)phenanthrene was found in urban soil (Crosby 1998).

The desorption from sediment to water, apart from water solubility, is also related to some structural and physicochemical properties of PAHs (molecular weight, molecular area, octanol/water partition coefficient K_{OW}, Narbonne et

al. 1999). Hattum et al. (1998) grouped PAHs according to the octanol-water partition coefficient (log K_{OW}) as follows:

I Nap, Acy, Ace, F, Ph, An $\log K_{OW} < 4.6$

II Fl, Pyr ,B(a)An ,Cry, B(b)F, B(k)F, B(a)P $4.6 < \log K_{OW} < 6.1$

III I(123-cd)P, dB(ah)An, B(g,h,i)P $6.1 < \log K_{OW} < 7.1$

Hydrophobic and lipophilic chemicals may easily penetrate through the lipophilic membranes of organisms, accumulate in tissues and may be directly toxic to benthic biota. Persistent chemicals may move up the food chain and even be subject to biomagnification (Biddinger & Gloss 1984, Kay 1984). The PAHs are readily metabolized by vertebrates (Varanasi et al. 1989, Smeets et al. 1999) and the metabolic products can be mutagens (Shugart 1997) and carcinogens. Conjugated metabolites are more water-soluble and can be excreted by the animal. Most species of aquatic organisms will rapidly accumulate PAHs from their surrounding environment, but will also metabolize quite rapidly according to species-specific metabolizing factors. Furthermore, it is evident that potentially toxic intermediates are produced in fishes [e.g. catfish (*Ictalurus punctatus*), common carp (*Cyprinus carpio*), Reichert et al. 1985, Steward et al. 1991, Bristol 1994, Kane & McElroy 1996].

TABLE 1 PAHs of mussel tissues, sediments and water samples analyzed (Kauss and Hamdy 1991). Abbrevations of the complete names and information on mutagenic and carcinogenic properties are also included.

Compound	Abbreviation	Mutagenicity	Carcinogencity
Napthalene	Nap	-	-
Acenaphthylene	Acy	-	-
Acenaphthene	Ace	+	-
Fluorene	Fl	-	-
Phenanthrene	Ph	-	-
Anthracene	An	-	-
Fluoranthene	F		-
Pyrene	Pyr	-	-
Benzo(a)anthracene	B(a)An	+	+
Chrysene	Cry	+	±
Benzo(b)fluoranthene	B(b)F		++
Benzo(k)fluoranthene	B(k)F		-
Benzo(a)pyrene	B(a)Pyr	+	+++
Indeno(1,2,3-cd) pyrene	I(c,d)Pyr		+
Dibenzo(a,h) anthracene	dB(a,h)An	+	+++
Dibenzo(g,h,i) perylene	dB(g,h,I)P		-

Notes 1)Information on mutagenic and carcinogenic properties is from Verschueren (1983); Oehme (1985); from the U.S. National Academy of Sciences, reported in National Research Council (1983) and from Kauss & Hamdy (1991). 2) Carcinogencity ranking is '-', not carcinogenic; '±', uncertain or weakly carcinogenic; '+', carcinogenic; '++', '+++', strongly carcinogenic.

1.2 Ecotoxicological risk assessment

The marketing and use of creosote and preparations containing creosote, as well as creosote-treated wood, is regulated by EU Directive 94/60/EC. Classification in regard to the carcinogenicity of creosote is based on the B(a)P content, the PAH chosen as a marker for the classification of coal tar-derived mixtures. The carcinogenic risk of exposure (determined using male mice exposed to two different preparations of coal tar) is considered linearly dose-response so that each exposure is also associated with a certain risk even at low doses. The Finnish government ruled on the use of creosote and creosote treated wood on 18th December 1992 (according to the Chemical Act, 744/89). Wood treatment is prohibited, if the creosote contains more than 0.005 -% by weight of B(a)P or more than 3 -% by weight of water extracted phenols. This decision came into force on 20th June 1996 (Haavisto & Kivelä-Ikonen 1995).

Ecological risk assessment (procedure ERA) is the practice of determining the nature and likelihood of effects of our actions on animals, plants, and the environment. ERA is characterized by a standard logical structure, or paradigm. This structure, derived from human health risk assessment (HHRA), has been modified for ecological systems (Suter 1993, Fig. 1).

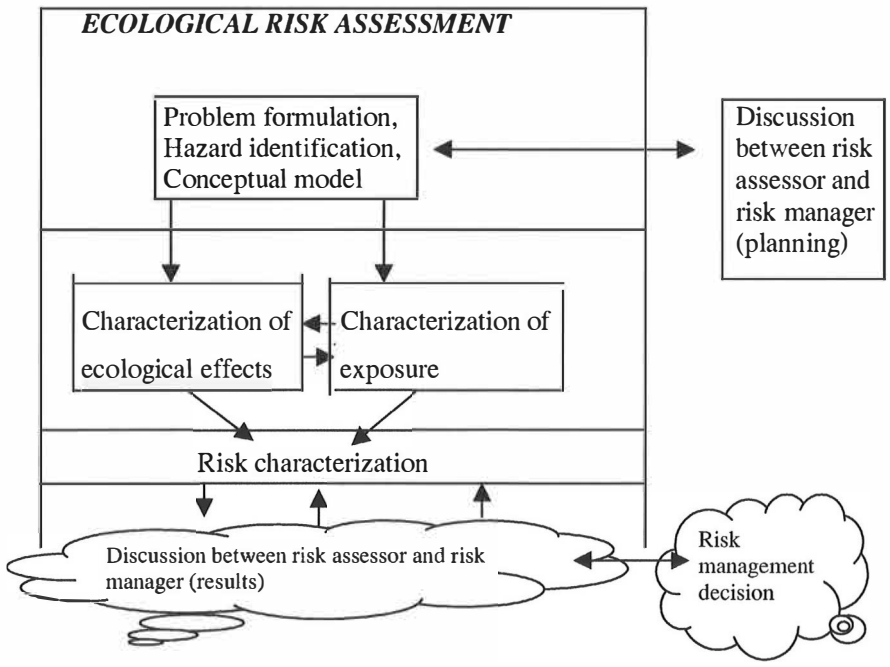


FIGURE 1 The U.S. Environmental Protection Agency risk assessment procedure (Suter 1993).

The framework for ecological risk assessment, or ecorisk framework, provides a process for analyzing stressors and effects, characterizing risks, and examining the consequences of risk management decisions. The premise of the ecorisk

approach is that adverse ecological effects occur as a result of exposure to one or more stressors (USEPA 1992, USEPA 1998).

Generally, the risk assessment is based on the chemical analysis of contaminants and community alteration in Finland. However, ecological risk assessment, particularly toxicity assessment, is anticipated to be applied more in the future in Finland (Vuori 1999).

The most integral assessment system (not as yet well-known in Finland) for contaminated sediments is the Triad approach: sediment chemistry analyses measure contamination, laboratory toxicity tests measure effects under standardised conditions (experimentation), and assessment by observation of resident community alteration (benthic fauna) measures field conditions (Ingersol et al. 1995, Chapman et al. 1991). This concept uses the complementarity of the different components. The Triad approach can be very useful for assessing the quality of sediments and for ranking contaminated sediments. An integral assessment is necessary because our understanding of cause and effect in determining environmental quality is incomplete.

1.3 Induction of CYP1A by PAHs and determination of metabolites of PAHs

Exposure to many PAHs, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) results in the induction of a specific form(s) of cytochrome (CYP1A) that catalyzes aryl hydrocarbon hydroxylase (AHH) and ethoxyresorufin O-deethyltion (EROD) activities (Black et al. 1988, Buhler & Williams 1988, Van Veld et al. 1990, Schoor et al. 1991). The maximum induction of CYP1A was about 200 pmol/mg/min for rainbow trout exposed to refinery effluent (approximately 10 to 100 fold increasing EROD activity) in the Mackenzie River, USA (Parrott & Tillitt 1997). The reactions catalyzed by cytochrome P450-dependent mixed function oxygenases (MFOs) result in the insertion of one oxygen atom from dioxygen to a substrate molecule, increasing its hydrosolubility and facilitating its elimination from the body. Liver EROD activity in fish has been found to be a very sensitive biomarker, responding to a wide range of PAH concentrations under different exposure conditions (Livingstone et al. 2000).

The bile of PAH-exposed fish contains a multitude of oxygenated PAH derivatives, excreted for the most part as glucuronide, sulfate, or glutathion conjugates. Analytical protocols for the determination of PAH metabolites in fish bile, representing an exposure to ambient PAHs, were developed by Krahn & coworkers (1987). 1-hydroxy pyrene (1-OH pyrene), the main metabolite of pyrene, accounts for a large percentage of the total PAH metabolite profile in the bile of fish exposed to a PAH mixture like creosote. 1-OH pyrene is easily quantified in fish bile by synchronous fluorescence spectrometry (SFS; Ariese et al. 1993, Lin et al. 1994). Synchronous fluorescence spectrometry, with its excellent sensitivity, has provided a useful analytical tool for monitoring many

trace organic compounds (Vo-Dinh 1978, Omland et al. 1996). The PAH-metabolite determination is very specific: exposure to other xenobiotics, like PCBs or dioxins (PCDDs, PCDFs), will not interfere with the measurement. Compounds that could possibly interfere with the analysis are other conjugates of the same metabolite, like sulfates, conjugates of 4-hydroxy pyrene, conjugated metabolites of alkylated pyrenes or partly saturated metabolites of larger PAHs in which a pyrene-type of chromophore has remained, such as 7,8,9,10-tetrahydroxy tetrahydro B(a)P (Ariese et al. 1993).

1.4 Oligochaetes and mussels as indicators of PAH exposure

Biological and chemical monitoring of the adjacent environment can be considered an integral component of the remediation plan for any site heavily contaminated by hazardous chemicals. Standard bioaccumulation experiments provide information on the potential of organisms to accumulate sediment associated contaminants (Rand & Petrocelli 1985). *Lumbriculus variegatus* is one of the proposed test organisms for bioaccumulation experiments (ASTM 1997, Leppänen & Kukkonen 1998). Oligochaetes act as do terrestrial earthworms, mixing the surface layers of sediment. They have been shown to uniformly mix surface layers and play a major role in the cycling of metals and organics out of the sediments (Burton 1991). Hydrophobic (lipophilic) chemicals can easily penetrate through the lipophilic membranes of organisms, accumulate in tissues, and may be directly toxic to benthic biota.

Duck mussels take up PAHs by the filtration of water and particulates in it, e.g. may derive from turbated bottom surface sediment (Baumard et al. 1998). Higher molecular weight PAHs, such as fluoranthene (F), pyrene (Pyr), chrysene (Cry) and benzo(a)pyrene (B(a)P), represent the type of compounds that tend to accumulate during environmental exposure. According to Kauss & Hamdy (1991), 25 PAH-compounds were identified in the surficial sediment in River St. Mary. As many as of these PAHs can be monitored within a three-week exposure period by caged mussels (the main compounds were phenanthrene, fluoranthene and pyrene) in studies at a PAH-contaminated river site.

1.5 The photobacterium and waterflea biotests

The majority of laboratories using the bioluminescence photobacterium test use commercial preparations. The method has been standardized for water samples (ISO 1998) and the correlation of Microtox with higher organisms has been suggested (Steinberrg et al. 1995) but the validity and meaning of interspecies correlations (particularly with Microtox) is quite dubious, except for broad-brush approaches. Initially the protocols were developed for waste water and

effluent monitoring (Bulich et al. 1981). Toxicity testing with *Vibrio fischeri* is now widely used. The bacterial luminescent pathway is a branch of the electron-transport chain, the luminescent measurement assess the flow of electrons in the respiratory chain and the metabolic state of the cell (Hastings 1978). New applications of luminescent bacteria include specific compound biosensors which can detect chemicals at sub toxic concentrations. These are not naturally bioluminescent bacteria, but they have been constructed by recombinant DNA technology (for review see Lappalainen 2001).

The sensitivity of organisms to the toxic properties of a substance may vary considerably from one species to another, owing to differences in their metabolism and the nature of their habitats (ISO 1989). Species that do reside in the sediment for part of their life cycle are useful in assessments on sediment. Though, *Daphnia magna* is planktonic, they spend an extensive amount of time feeding on the sediment surface. *D.magna*'s relative sensitivity to a wide variety of contaminants in whole-sediment interstitial water, elutriate, and suspended-sediment assays is well established (Nebeker et al. 1984, ASTM 1993).
The advantages and disadvantages of the biotests were compared as follows:

TABLE 2 Summary of biotests in the original publications I-VI with discription of advantages and disadvantages of the biotests.

Biotest	Exposure time	Advantages	Disadvantages/limitations
i.p. exposure (rainbow trout, EROD)	96 h	quite rapid experiment, specified dose, rainbow trout is a sensitive species	not always correspond to real situation in the environment.
Oligochaete (*Lumbriculus variegatus*) experiment	28 days	easily cultured in the laboratory, easily handled, environment realism	large number of individuals in the experiment
Photobacterium (*Vibrio fischeri*) test	5, 15, 30 min	very rapid, replicable, sensitive indicators, inexpensive,	not dark/coloured samples
Waterflea (*Daphnia magna*) test	24 h	rapid, ease of culture and handling, relative sensitivity, replicable	sometimes reproduction problems, not necessarily representative of pelagic *cladocerans*
Mussel (*Anodonta anatina*) experiment (VI)	10 months	sensitive indicators, ease of handling "in situ" experiment	reproducibility of experiment may be difficult

1.6 Sediment remediation techniques

1.6.1 Dredging

Dredging is a process of excavating sediment from a waterway, often involving transportation of the excavated dredged material to another site. Because sediments are the ultimate reservoir for many contaminants, sediments may be the subject of environmental concern (SETAC 1997). The dredging techniques may be divided into two categories: mechanical and hydraulic dredging. During mechanical dredging, the sediments are physically lifted from the bottom by a mechanical process. Mechanically dredged material is typically placed in barges and transported to the disposal area (Miller & Dorkin 1998). During hydraulic dredging, the bottom material is fluidized, lifted via a pipeline by a centrifugal pump, and transported as a slurry. Material dredged by hopper dredges is also considered hydraulic dredging because of the fluidization process required to lift the material into the hoppers (Miller & Dorkin 1998). Hydraulically dredged material is typically transported via a pipeline to the disposal site and discharged with large amounts of entrained water. For both cases of hydraulic dredges (pipeline and hopper), the less dense material is more susceptible to stripping and creates a flatter feature covering a larger area of the bottom (Miller & Dorkin 1998).

The choice of dredging method depends greatly on the circumstances. When planning the removal of the sediment, the following factors should be considered: mapping of the problem area, the physical and chemical quality of the sediment, the removal depth of the sediment, environmental effects of the removal of the sediment, the dumping area of the sediment, and the location of the subject (Fig. 2, Suter 1993).

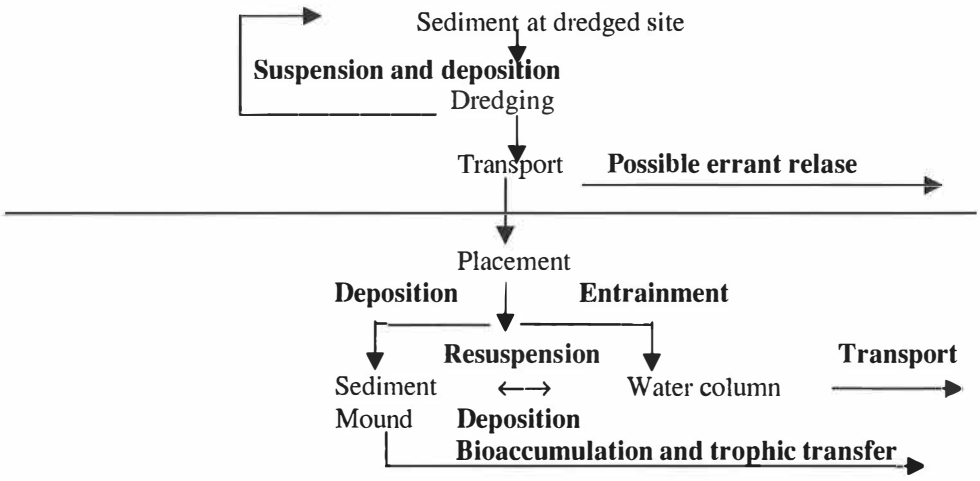


FIGURE 2 Possible exposure pathways during dredging and dredged material placement at an aquatic site (Suter 1993).

While dredging is often necessary for navigational reasons in many harbors, it may not be the best method for remediating contaminated sediments. For example, during the Hamilton Harbor project, suspended sediments appeared to flow away from the clamshell dredge (EPA 1998, Table 3). In Zierikee Harbour located in the Netherlands, it was observed that after dredging, the top sediment layer was more contaminated than before dredging. A Dutch review identified this as a common result of dredging (Anon. 1991).

1.6.2 Capping

In-situ capping is a form of containment in place. *In-situ* capping (ISC) refers to the placement of a covering or cap over an in-situ deposit of contaminated sediment. The cap may be composed of clean sediments, sand or gravel, or it may involve a more complex design with geotextile, liners and multiple layers. A variation on ISC could involve the removal of contaminated sediments to some depth, followed by capping of the remaining sediments *in-situ* (Tuchman 1998).

An example of remediation by dredging and capping is the creosote-contaminated bottom area in Våna in central Sweden. The contaminated area was discovered in 1987. The impregnation plant operated between the years 1953 – 1967. During this period about 14, 000 – 15, 000 tons of creosote was used. The contaminated sediments were two meters deep at maximum. Dredging by digging caused vigorous mixing of the sediment and a large amount of creosote spread from the sediment into the water layer. To prevent the contamination spreading in this way, the dredged and undredged contaminated sediment areas were covered by a filter textile and gravel layer (approx. 60 cm). Some PAHs were detected in the water during the covering work, but the spreading of PAHs was remarkably minimal compared to during the dredging operation (IVO 1996).

1.6.3 Biological treatment

Biological treatment is one of the remediation alternatives. Traditionally, bioremediation has been conducted by optimizing the activity of degradative bacteria already present in the environment, by adding suitable nutrients and by improving other physico-chemical conditions. Alternatively, suitable bacteria have been introduced to the contaminated material and, in a smaller number of instances, reactors have been used whereby the microbial activity takes place in a specially designed vessel under ideal conditions (Holdroyd & Caunt 1995). For a mixture of compounds to be degraded biologically under field conditions, several basic criteria must be met (Mueller et al. 1989). Firstly, an appropriate microbial community possessing the requisite catabolic ability must be present. As is the case with many other xenobiotics, the ability to degrade unique carbon sources is often associated with prior adaptive exposure of microbial communities to the chemical or to similar chemicals. Secondly, the bioavailability of the potential substrate must be considered along with the requirement for organism-substrate interaction. Lastly, environmental

parameters such as temperature, redox potential, oxygen and nutrient availability, and moisture must be conductive to the growth of the requisite organism(s) (Mueller et al. 1989). The biodegradation of small molecular weight PAHs such as naphthalene is relatively rapid. The biological transformation of 3-ring PAHs such as acenaphthene, anthracene, and phenanthrene is usually slower. Microorganisms that are capable of transforming higher molecular weight PAHs such as benzo(a)anthracene, benzo(a)pyrene, fluoranthene and pyrene have also been found (Mueller et al. 1989). A variety of microorganisms have been found to possess the ability to degrade PAHs, viz. bacteria of the genera *Aeromonas*, *Alcaligenes*, *Beijerinkia*, *Cyanobacter*, *Flavobacterium*, *Micrococcus*, *Mycobacterium*, *Nocardia*, *Pseudomonas*, *Vibrio*, and the fungus *Phanerochaete chrysosporium* (Mueller et al. 1989, Geiselbrecht et al. 1996, Romero et al. 1998).

In situ treatment of contaminated sediments has long been considered a possible cost-effective and ecological treatment option, but little has been done to investigate this (Table 3). In general, using in situ treatment appears to be less expensive than ex situ treatment or the disposal of contaminated sediment (Murphy et al. 1995).

1.6.4 Remediation alternatives for Lake Jämsänvesi

In the current work the five possible remediation alternative estimates were advanced for dealing with the creosote-contaminated sediment in Lake Jämsänvesi (I-VI). These were (Keto 1996) a) dry digging in summer, b) dry digging in winter, c) suction dredging, d) suction dredging and thick filling and e) thick filling. Excavator-dredging was also a possible alternative in Jämsänvesi. All the remediation alternatives may cause the resuspension of sediment in the water column. The post treatment alternatives of the dredged masses were the following: a) composting, b) a special landfill and c) burning in a mass burning line (power burning). The IVO company (1996) made the report on the possible remediation alternatives for Lake Jämsänvesi.

The five possible remediation alternatives and their total cost estimates for creosote-contaminated sediment were as follows (Keto 1996):

a) dry digging in summer	approx. FIM 3, 710, 000 – 4, 380, 000
b) dry digging in winter	approx. FIM 3, 910, 000 – 4, 630, 000
c) suction dredging	approx. FIM 3, 390, 000 – 5, 160, 000
d) thick filling	approx. FIM 1, 700, 000

The post treatment alternatives for the dredged materials were the following:

a) composting	approx. FIM 2, 230, 000 – 2, 850, 000
b) the special landfill	approx. FIM 2, 400, 000
c) burning in a mass burning line (power burning)	approx. FIM 3, 000,000 approx. FIM. 11, 000, 000

The IVO company proposed remediation of the contaminated sediment by thick filling and the Central Finland Environment Center accepted this proposal. IVO obtained a permit for the remediation from the Water Rights Court in 1998. The

remediation of Lake Jämsänvesi creosote-contaminated sediment was accomplished in 1998 and 1999. I enquired about the total cost of the remediation from Fortum, but the information was not available at the time this thesis was written.

The advantages and disadvantages of the different remediation methods are described below:

TABLE 3 Examples of the advantages and risks of different remediation methods.

Remediation Method	Advantages	Disadventages/ Risks	References (Project Location)
Dredging a)mechanical	cost-effective simple	resuspension of contaminated sediment, contaminants spread to water layer, transporting contaminant sediments can result in losses	EPA 1998 (Hamilton Harbor and St. Mary's River, Canada)
b)hydraulical	more efficient then mechanical dredging, avoid partly disturbances	some contaminants spread to water, transporting contaminant sediments can result in losses, expensive	EPA 1999 (Fox River, US)
Capping	sediments left in place, cost-effective	contaminated material may be "puffed", uncertainty of cover	EPA 1999 (Great Lakes, US)
Biological treatment	cost-effective, ecological, reduction in the need for handling sediments, reduction in the volatilization and irretrivable loss to the atmosphere of contaminants that are brought to the surface treatment permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances	little to investigate, treatment efficiency of in situ treatment is almost always less than ex situ	EPA 1990 EPA 1993 (Hudson River,US Fox River, US)

2 OBJECTIVES

The aim of this work was to identify the possible ecotoxicological risks of creosote-contaminated sediment and its remediation to the lake ecosystem and to relate this information to the presence and fate of PAH compounds from the sediment to the water column.

The main objectives of this work were:

1. To determine the PAH concentration of creosote which describes the toxicity of the sediment (I).
2. To provide information on the sediment/water ratios which generate the highest amount of PAH concentrations due to release from the sediment to water (II, III). The contaminants may be spread from the sediment to the water layer during normal resuspension of sediment and during remediation operations e.g. dredging and capping.
3. To determine the elutriates of creosote-contaminated sediment which are toxic to photoluminescent bacteria (*Vibrio fischeri*) and waterfleas (*Daphnia magna)* and to identify the possible risk of creosote-contaminated sediment by bacteria and waterflea tests (I, II)
4. To study the bioaccumulation of PAHs from creosote-contaminated sediment by laboratory-exposed oligochaetes (*Lumbriculus variegatus*, V)
5. To evaluate the doses of PAHs of creosote which induce CYP1A1 (EROD) activity in the liver of rainbow trout (*Onchorhynchus mykiss*, IV)
6. To assess the spread of PAHs from creosote-contaminated sediment by caged mussels (*Anodonta anatina*) and accumulation of settled particulate material in collectors during the remediation by capping (VI)
7. To assess the possible ecotoxicological risk of the remediation operation for contaminated sediment to the adjacent environment (VI)

3 MATERIALS AND METHODS

3.1 The case site in Lake Jämsänvesi

Lake Jämsänvesi, located in the municipality of Petäjävesi approx. 35 km west of Jyväskylä in Finland, has been contaminated by earlier use of creosote. A creosote impregnation plant (owned by the IVO company), which was in operation for 20 years up to 1976, contaminated part of the bottom sediments of Lake Jämsänvesi. The Central Finland Regional Environment Centre studied sediment samples near the one-time impregnation plant in 1993 to assess the remediation needs of the sediment. Based on this preliminary information, showing that the area of the contaminated sediment was approximately 6700 - 7600 m^2 and the thickness was 0.1 –0.25 m, our first set of sediment samples were collected around the most contaminated site suggested. The sediment samples were collected at 16 sites in Lake Jämsänvesi for our studies (I). The sampling sites ranged from supposedly heavily contaminated to background areas. The IVO company proposed the remediation of the contaminated sediment by thick filling, a proposal that was accepted by the Central Finland Environment Center. IVO obtained a permit for the remediation from the Water Rights Court in 1998. The mussels and settled particulate material (SPM) collectors were deployed in the lake at the same time as the remediation operation was started (Fig. 3, 4). The remediation of creosote-contaminated sediment was accomplished in 1998 and 1999. Contaminated sediment in Lake Jämsänvesi was covered by a filter geotextile (polypropylene), gravel and sand (about 1 - 1.5 m) which were spread out on the ice (thick capping) and then sunk onto the bottom of the lake when the ice melted in May 1999 (Fig. 4, 5).

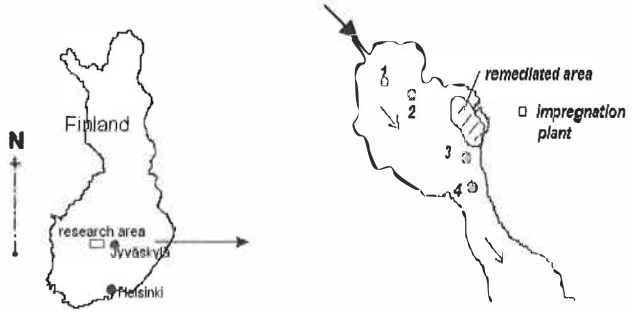


FIGURE 3 Location of mussel cages and SPM collectors in Sites 1, 2, 3 and 4. The arrows indicate the gross direction of water currents (VI).

The history of sediment contamination and operation in Lake Jämsänvesi between the years 1950 and 1999 is as follows:

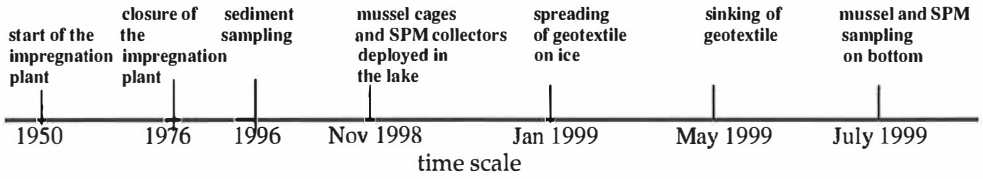


FIGURE 4 The time segment of the sampling and remediation operation (in 1950–1999), SPM = settled particulate material.

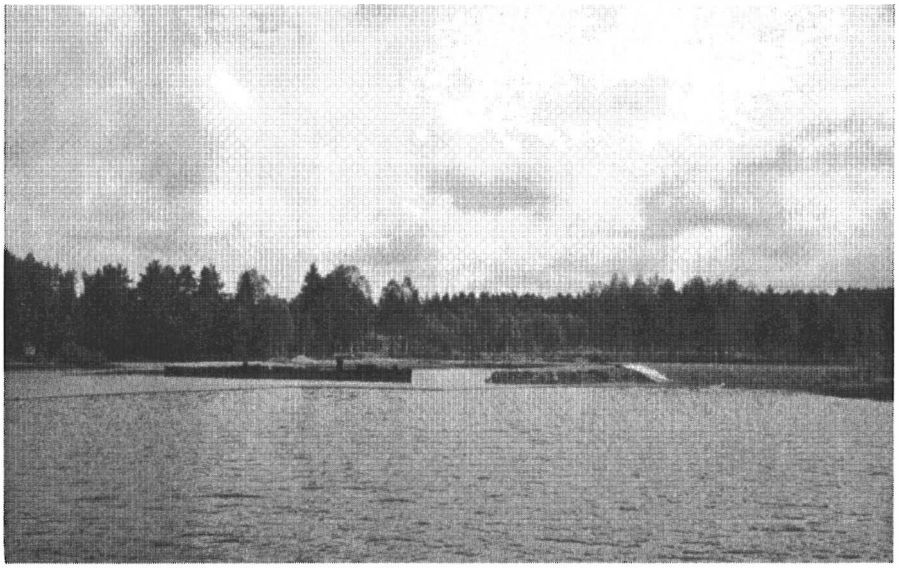


FIGURE 5 The Lake area contaminated by creosote and remediated in Lake Jämsänvesi, Central Finland.

3.2 Sampling and preparation of samples

Sediment samples were collected Lake Jämsänvesi by Kajak-Brinkhurst corer (I). The Kajak-Brinkhurst corer is suitable for sampling soft, fine-grained sediments. The weight of this device was about 9 kg and the lead weight was 7 kg. The core tube size was 5 cm I.D,. with a length of 50 – 100 cm (Mudroch & Azcue 1995). The sampling sites ranged from most heavily contaminated to background areas. The samples were divided into three layers (0-10 cm, 10-20 cm and 20-30 cm). After transfer to glass jars, the atmosphere in the sample jars was replaced by nitrogen in the laboratory and stored at 4 °C. Next day, sediment solids and porewater were separated by centrifuging. Whole sediment and pore water samples were then stored at –20 °C until the time of the analyses (I). The pristine reference sediment (0-10 cm) was collected in oligotrophic Lake Palosjärvi (Toivakka, 40 km SE from Jyväskylä) from a depth of approx. 1m.

The mussels and settled particulate material collectors (SPM) were taken to Lake Jämsänvesi at the same time as the remedation operation was started in November 1998 (Fig. 3). Two reference sites (Sites 1 and 2) were located upstream. Collectors at Sites 3 and 4 were located downstream. The Site 3 collector was situated near the highest creosote-contaminated site that was eventually capped (Fig. 3). The samples were stored at 4 °C in the laboratory. Two days later sedimented solids and water were separated by centrifuging. SPM and water samples were stored at –20 °C until the time of the chemical analyses. Some of the water samples were stored for two weeks at 4 °C for toxicity tests (Burton, 1992, ASTM, 1994). Further details of the analyses of the PAHs in sediment, SPM, oligochaete and mussel tissues in the original papers I-VI (Fig. 6, Table 4).

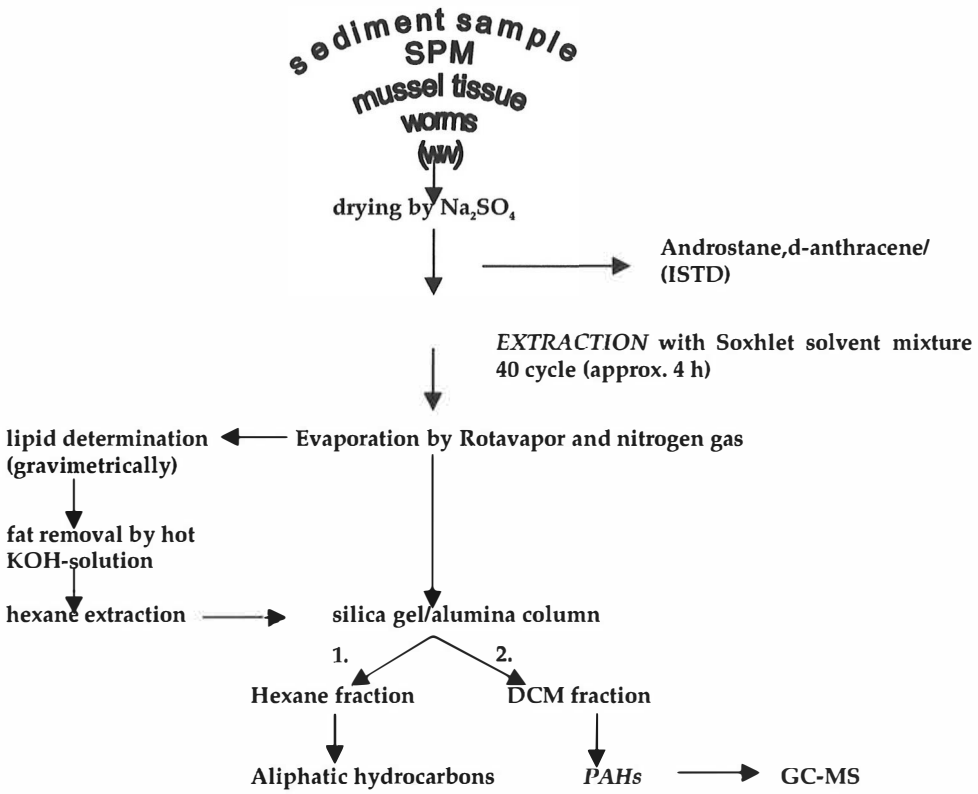


FIGURE 6 Analytical procedure for the isolation and quantitation of PAHs from whole sediment, SPM, oligochaetes and mussel tissue.

The interpolated map was made according to the PAH concentrations of Lake Jämsänvesi sediment by kriging method. It is a method estimating the value of a spatially distributed variable at a given point from known adjacent values while applying the interdependence expressed in the variogram. The kriging involves the construction of a weighted moving average equation including knowledge of the spatial covariance between the estimation point and sample points within the range of interaction. While other linear unbiased estimators exist, the kriging method as a minimum variance estimator minimizes the variance of the estimation errors (Cressie 1993, Soimasuo 1997, Suutari et al. 1999).

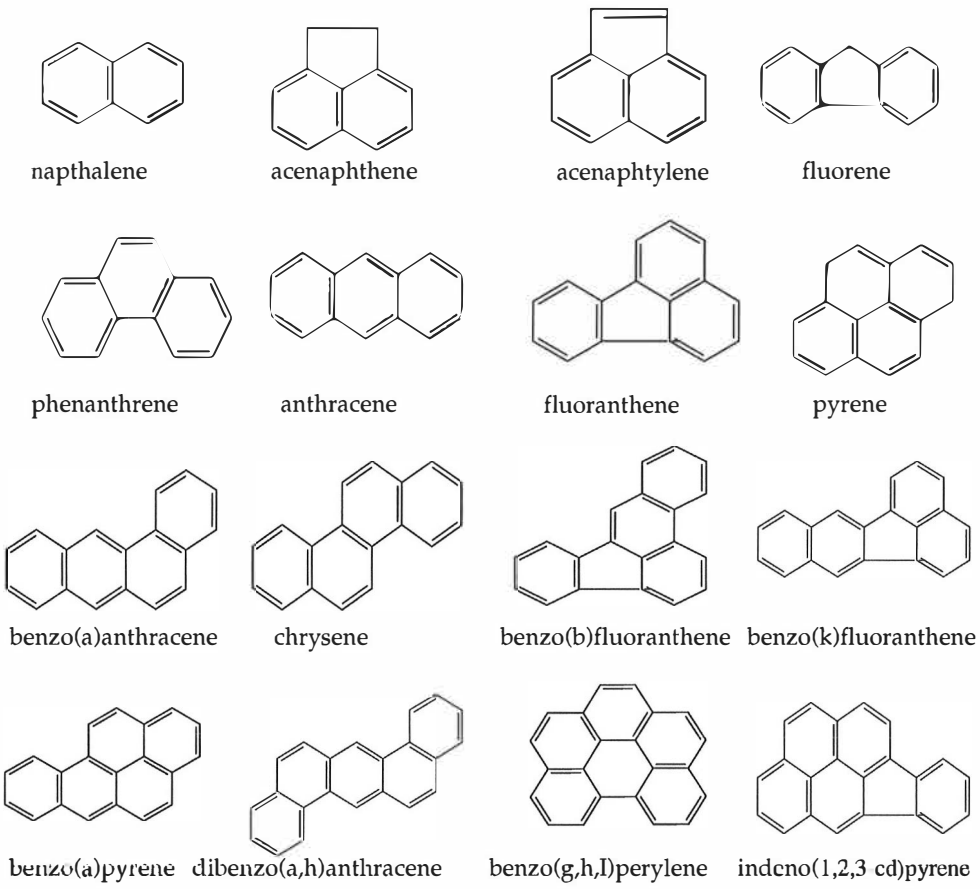


FIGURE 7 Structures of the compounds studied.

3.2.1 Desorption experiments (II, III)

We have studied the desorption of PAHs from creosote-contaminated sediment, PAH mixture spiked sediment and settled particulate material. The elutriates of sediment and settled particulate material were prepared as follows: wet, well settled material (approx. 10 g) was mixed with artificial lake water (artificial lake water = distilled water and salt solution: 8 mM $CaCl_2$, 20 mM $MgSO_4$, $NaHCO_3$, 3 mM KCl in the ratios 1:1, 1:2, 1:4, 1:8, 1:16, 1:24, 1:32, 1:64, 1:96, 1:128, 1:256 (v/v) (10 ml, 20 ml, 40 ml, 80 ml, 160 ml, 240ml, 320 ml, 640 ml, 960ml, 1280 ml and 2560 ml). Three replicate experiments were carried out for each ratio. The mixture was agitated on a mechanical shaker for one hour at room temperature and then allowed to settle down at 4 °C. Water samples (50 ml) were taken at 24 h, 120 h and 500 h. The sediment – water slurries were mixed between the sampling. Elutriates were stored at 4 °C until the time of the analyses (Hill et al. 1993, ASTM 1994, II, III). The extraction of PAHs in

elutriates was modified from earlier methods Haddock et al. 1983, Lee et al. 1987, Spørstol et al. 1983, Paasivirta et al. 1989, Simpson et al. 1995, I, II, III).

3.2.2 Treatment of the oligochaetes, mussels and rainbow trout (IV – VI)

The sediments for the bioaccumulation experiments of oligochaetes were Lake Jämsänvesi creosote-contaminated (total PAHs 3.3 mg/g dw, I) sediment and synthetic sediment. For both sediments there were three replicate beakers.

The sediment was placed in a 2-l Pyrex beaker and artificial freshwater was added on top, after which the mixture was aerated overnight. The 28- d exposures were initiated by placing animals (100 oligochaetes/beacker) in a beaker containing 250 ml sediment (ww) and 1 l artificial lake water with aeration (Fig. 8). The test was conducted at 20 ± 2 °C in a 8 : 16 light/dark cycle. Oligochaetes were not fed during the experiment. Water renewal was carried out after one week. After sieving the oligochaetes from the sediments, these were placed in clean artifical freshwater for 6 hours to purge their gut.

The wet worms (approx. 100 worms) were dried at 70 °C for 2 h and then at 35 °C for 8 h before extraction in a Soxhlet-apparatus. After the addition of an internal standard the sample was extracted with a hexane-acetone mixture (Raccanelli et al. 1994, I). The fat of the oligochaetes was removed in a similar way to the fat of mussels (VI). The solvent mixture, containing PAHs, was evaporated gently to dryness with a nitrogen gas stream. Then the residue was dissolved with hexane and analysed by an MS-GC-system (V).

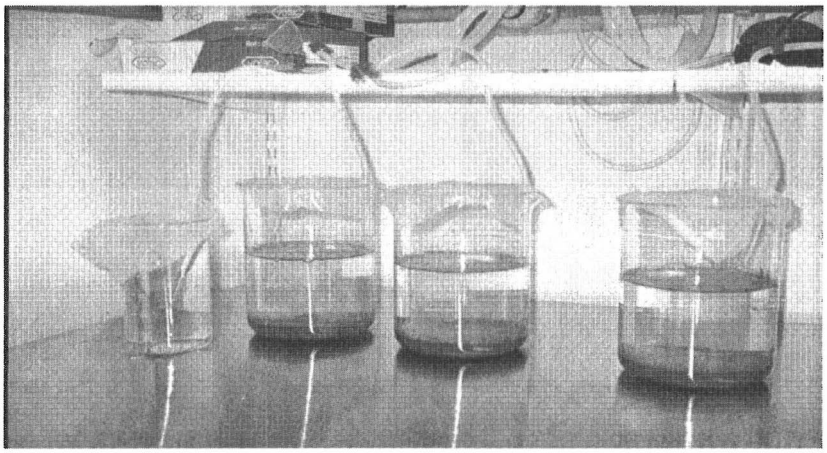


FIGURE 8 The oligochaetes were exposured to the creosote-contaminated sediment in a laboratory experiment. The 28 d exposures were started by placing worms (100 oligochaetes/Pyrex beaker) in a beaker containing 250 ml sediment (ww) and 1 l artificial lake water with aeration (V).

Mussels (15 mussel/site) were exposed for ten months in the lake (from November 1998) in the 250-liter cages. The cages were submerged on the bottom at a depth of 3 – 6 m. Two reference sites (Sites 1 and 2) were located upstream. The Site 3 cage was situated downstream, near the highest creosote-

contaminated site that was eventually capped (see Fig. 3). The mussels were transported to the laboratory in water from the exposure site, and kept in this lake water (10 ± 2 °C), with aeration, until they were dissected the next day.

In the laboratory, closed mussels were weighed, the shell length was measured and the shells were opened. Once the water inside the shells had run off, the soft tissue was weighed and kept –20°C for the analysis. The adductor muscles (from mussels of Sites 3 and 4) were dissected for glycogen and protein analyses and kept at –85 °C. Further details of the analysis of mussels in the original paper VI.

The juvenile rainbow trout (50 - 190 g) came from Hanka-Taimen Oy (in Hankasalmi, about 40 km north-east of Jyväskylä). The fish were acclimated in water at 12 °C for 30 days. The light cycle was 12 h on, 12 h off. The fish were fed twice a day (about 1 % of weight of fish per day) and feeding was stopped two days before the start of the exposure. The fish (n=6/group) were anesthetized and then injected intraperitoneally (three doses per exctract) with sediment/creosote extracts dissolved in olive oil. The fish were killed 96 h after the single injection. Liver and bile samples were taken from the fish. Samples were stored in liquid nitrogen until analysis (IV).

For PMS the liver (about 50 mg) was blotted dry with adsorbent paper, weighed and homogenized for 10 cycles in the centrifuge tube with a Teflon pestle. The homogenate was centrifuged at 9000 x g for 20 min at 2 °C (Hodson et al. 1992, Martel et al. 1994). The PMS was carefully removed, frozen in liquid nitrogen and stored at -80°C before the EROD analysis (IV). PMS were prepared according to Burke et al. (1985).

3.3 Concentration determinations and toxicity tests

3.3.1 GC-MS- and SFS-analysis

An EPA standard mixture was used in gas chromatographic (GC) analyses (16 PAH compounds) and the PAH compounds were additionally identified by mass spectrometry (Hewlet Packard 5973, mass selective detector). The limits of determination were 0.2 µg/g (dw) for Nap, Acy, Ace, Fl, Ph, An, F, Pyr, B(a)An, Cry, B(b)F, B(k)F, B(a)Pyr, I(c,d)Pyr, dB(a,h)An, dB(g,h,I)P. The carrier gas was helium at a flow rate of 1 ml/min, the injector and detector temperatures being 250°C and 350°C, respectively. The column was a 25-m long fused silica column with a 0.32-mm inner diameter coated with SE-54 (film thickness 0.25 µm). The column temperature was raised from 50°C (maintained for 1 min) to 290°C at a rate of 10°C/min and held there for 5 min. Besides using a known EPA standard mixture

[16 PAH compounds, Total PAHs = Σ 16 PAHs = napthalene(Nap), acenaphtylene(Acy), acenaphthene(Ace), fluorene(Fl), phenanthrene(Ph), anthracene(An), fluoranthene(F), pyrene(Pyr), benzo(a)anthrcene(B(a)An), chrysene(Cry), benzo(b)fluoranthene(B(b)F),

benzo(k)fluoranthene(B(k)F), benzo(a)pyrene(B(a)Pyr), indeno(1,2,3cd)pyrene(I(c,d)Pyr), dibenzo(a,h)anthracene(dB(a,h)An), dibenzo(g,h,i)perylene(dB(g,h,i)P)],
the PAH compounds were additionally identified by mass spectrometry (Hewlet Packard 5973, mass selective detector; I, II, III, V, VI).
The bile concentration of PAH metabolites in creosote-exposed trout was measured using SFS, which preferentially detects hydroxylated pyrene chromophores (pyrene-type metabolites, IV). The bile samples were treated in two ways. Firstly the samples were diluted with distilled water 1 : 500 v/v (Ariese et al. 1993). In the second technique free 1-hydroxy pyrene was quantitatively extracted with n-hexane. SFS spectra were measured using a Perkin Elmer LS50B spectrofluorometer. The instrument was set for a synchronous scan with the following parameters: wavelength difference of 37 nm, slitwidths of 2.5 nm for excitation and 5 nm for emission, a scan range of 300 to 450 nm, and a scanning speed of 240 nm/min. Further details of SFS measurement are presented in Paper IV.

3.3.2 Bioluminescence inhibition and waterflea EC_{50}-tests

Acute toxicity of porewater samples and elutriates was assayed by its ability to decrease bioluminescence (Bio-Orbit 1257 Luminometer). The assay dilutions of pore waters were 45.5, 22.8, 11.4 and 5.7 % (diluted with 2 % NaCl). The dilutions were inoculated with photoluminescent bacteria (*Vibrio fischeri*) and incubated at 15°C for 5, 15 and 30 min before the reading of the light emitted (Ankley et al. 1989, Springer & Bazarow 1993, Hauser et al. 1997). EC_{50} values were obtained using the Biotox programme of the Bio-Orbit company (Turku, Finland, I, II).

Acute toxicity (immobilization) of elutriates and porewaters to *Daphnia magna* was determined as described in ISO 1989 (Barry 1996). Animals studied were less than 24 h old. Artifical fresh water used as the diluent was prepared by adding stock solutions (calcium chloride solution 11.8 g/l, magnesium sulfate solution 4.9 g/l, sodium bicarbonate solution 2.6 g/l and potassium chloride solution 0.2 g/l), 25 ml each, to 900 ml deionized water. First, a preliminary test (the dilution series 10, 30, 40, 50, 60, 70, 80, 90 %) was carried out on each porewater and elutriate, followed by the definitive test on samples that revealed some toxicity. The dilution series contained seven concentrations, with two replicates for each. Additionally, each series contained a control (dilution water only). EC_{50}-values (24 and 48 h) were determined using graphic and probit methods by counting immobilized animals (ISO 1989, Pastorok et al. 1994, I, II).

3.3.3 EROD activity of rainbow trout liver

Hepatic biotransformation activity, 7-ethoxyresorufin O-deethylase (EROD), was measured from the postmitochondrial supernatant (PMS) fraction at 20°C fluorometrically according to Burke et al. (1985), adapted for the microplate format (Labsystems Ascent microplate fluorometer). Microsomes (200 µg protein well $^{-1}$) were incubated in 100 mM potassium phosphate buffer of pH 8, 2.5 µM ethoxyresorufin (Sigma Chemical Co.), and 0.5 mM NADPH (Sigma Chemical Co.) in a final volume of 200 µl (in preliminary test). Fluorescence (excitation 530 nm, emission 584 nm) was recorded at 30 s intervals for 4 min at 20°C. This EROD assay was also adapted for the microplate format (Labsystems Reader MF).

3.3.4 Protein- and glycogen analysis

The glycogen content of the adductor muscle was determined by digesting a sample (approx. 30 mg) of unthawed tissues in 30 % KOH for 30 min at 95°C. Glycogen was then precipitated by 96 % ethanol (700 µl), sedimented by centrifugation, and hydrolysed with 1 M HCl in 2 h at 95 °C. Free glucose in the solution was measured by the GOD-Perid method (Mäkelä 1995, VI). Since the recovery percentage of glycogen was 83 – 90 %, it can be concluded that the analytical method was suitable for glycogen determination.

Protein content was determined by the Folin method (Lowry et al. 1951, IV, VI) with bovine serum albumin as a standard (Bio-Rad Protein Assay Kit). The Hepes buffer (pH 7.5, 750 µl) was added to the adductor mussel and then the sample was homogenized in a glass tube with an Ultra Turrax (about 3 min).

TABLE 4 Summary of the methods and the studied samples in the original publications I-VI and the relevant literature.

	I	II	III	IV	V	VI
Method	GC-FID waterflea & photoluminescent bacteria tests	GC-FID waterflea & photoluminescent bacteria tests	GC-FID photoluminescent bacteria test	fluorometer (EROD) SFS	GC-MS	GC-MS photoluminescent bacteria test, fluorometer
Studied Samples	Site 13 contaminated sediment (0-10,10-20, 20-30cm) elutriates of Site 13 sediment	Site 13 contaminated sediment and its elutriates (1:1-1:128, desorption experiments)	Site 13 elutriates (1:1-1:256), water inside Site 3 collector (desorption experiments)	liver and bile samples of rainbow trout (i.p. exposure), extracts of Site 13 contaminated sediment, creosote spiked sediment and their elutriates	worms, Site 13 contaminated sediment (bioaccumulation experiment in laboratory)	mussels, settled particulate, material (SPM), water inside Site 3 collector (bioaccumulation experiment in situ)
Ref.	Paasivirta et al. 1981 Spørstol et al. 1983, Lee et al. 1987, Winger et al. 1993 Raccanelli et al. 1994, Carr et al. 1996, Chen et al. 1997	Kalf et al. 1997, Sved & Van Veld 1997, Padma et al. 1998	McGroddy et al. 1996 Latimer et al. 1999 Narbonne et al. 1999 Narbonne et al. 1999	Bristol 1993 Ariese et al. 1993 Lewis et al. 1997	Landrum 1989 ASTM 1997 Brunson et al. 1998, Leppänen et al. 1999	Herve et al. 1988 Kauss & Hamdy 1991 Baumard et al. 1998

4 RESULTS AND DISCUSSION

4.1 Sediment risk assessment

4.1.1 Distribution of PAHs in the lake sediment

The concentrations of PAHs in sediments were higher in the surface layer (0-10 cm) than in deeper layers (10-30 cm). The highest total PAH concentration in the whole sediment was 3.3 mg/g dw in the Site 13 sediment (Fig. 9, I). Although, acenaphthene (60 mg/g dw), phenanthrene (60 mg/g dw) and fluorene (40 mg/g dw) were the main compounds in the commercial creosote product, they did not predominate in the sediment. Most sediment samples contained anthracene and fluoranthene and PAHs with four to six rings. Every surface layer of the sediments contained benzo(a)pyrene. Creosote was spread nonhomogenously on the bottom of Lake Jämsänvesi (I). The profiles of PAHs in the surface sediments (0-10 cm) of Sites 7, 13 and 15 were not identical (I). The stable PAHs with four to six rings accumulated in the sediment and it is possible that a proportion of PAHs with two to three rings volatilized or biodegraded (I).

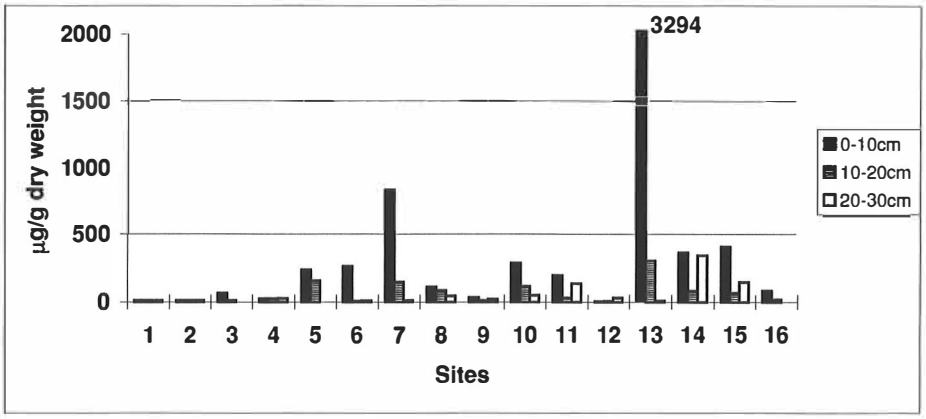


FIGURE 9 Total PAH-concentrations (µg/g dry weight) of the creosote-contaminated sediment from Sites 1 - 16, at different depths in Lake Jämsänvesi. Sites 1 – 4 were located upstream (I). For the location of the sampled sites, see map in Fig. 10.

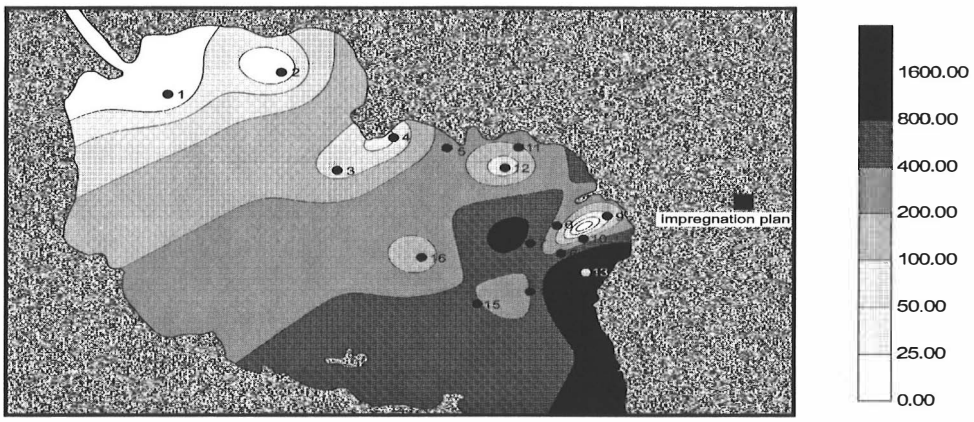


FIGURE 10 The interpolated map of the spreading of PAHs (µg/g dw) at a depth of 0–10 cm in Lake Jämsänvesi (Sites 1 – 16).

The spreading of PAH compounds in Lake Jämsänvesi can be assessed by the aid of the interpolated map (Kriging method, Fig. 10). The highest creosote-contaminated site was around Site 13 (total PAH concentration ≥ 1600 µg/g dw). Total PAH concentrations were 100 – 200 µg/g dw in Sites 2 – 3 about 600 - 800 m from the most contaminated area. There is a small island in the middle of Sites 6, 9 and 10 (according to the interpolated map there is an uncontaminated area). Since there were no sampling sites downstream, the idea that the most contaminated area lay downstream seems erroneous (Fig 10). Numerous contaminated sediments have been studied over the world (Burton 1991, Adams et al. 1992, Bristol 1993, Padma et al. 1998). Among others, Kauss & Hamdy (1991) have studied the PAH-contaminated sediments of the St. Mary's River, Canada. Inputs of contaminants from paper mills, shipping and

power generation have degraded water and sediment quality in the St. Mary's River. The highest total PAH concentration was 711 µg/g dw in surficial sediments (Kauss & Hamdy 1991); this was only fifth of the PAH concentration of the highest contaminated Lake Jämsänvesi sediment (I).

The same PAHs as those present in Lake Jämsänvesi sediment were identified from many PAH contaminated river sediments in the USA (Table 5).

TABLE 5 Examples for comparsion of PAH concentrations at different depths in the contaminated sediments.

Case site	layer (cm)	total PAH-concentration (mg/g dw)
Black River,US (EPA, 2000)	0-10	**0.04-0.050** (Ph,B(a)An,B(a)P,I(1,2,3-cd)P)
	10-60	**0.003** (Ph, B(a)An, B(a)P,I(1,2,3-cd)P)
	60-120	**0.0008** (Ph, B(a)An, B(a)P,I(1,2,3-cd)P)
Detroit River,US (Pranckevicius& Kisuse, 1989)	0-10	**600** (Nap,Ace,Acy,Fl,Ph,An,F,Pyr,Cry B(a)An, B(k)F,B(a)P,I(1,2,3-cd)P,dB(g,h,I)P)
Lackawanna & Union Canals,US (Rockwell et al. 1984)	0-10	**392** (Nap,Ace,Acy,Fl,Ph,F,Pyr, B(a)An, B(k)F,B(a)P,I(1,2,3-cd)P,dB(g,h,I)P)
Buffalo Rivers,US (Niagara River Toxics Committee, 1984)	0-10	**285** (Nap,Ace,Acy,Fl,Ph,F,Pyr,B(a)An, B(k)F,B(a)P)
This study Site 13	0-10	**3.3** (Nap,Ace,Acy,Fl,An,B(k)F,B(a)P,I(1,2,3-cd)P,dB(g,h,i)P)
	10-20	**0.3** (B(a)P)
	20-30	**0.008** (Ph)

4.1.2 Desorption of PAHs from sediment to water

The US-EPA method determines the bioactivity of slurried supernatant composed of sediment and water (1 : 4; v/v). In our study the highest total PAH concentration was about 2 mg/l in the elutriate (of ratios 1:1 to 1 : 4) of the surface layer (0-10 cm) prepared from the sediment at Site 13 (Fig. 10, I). In contaminated coastal areas and harbours, concentrations of total PAH may rise to 505 µg/l in water and 232 mg/kg dry weight in sediments (Menzie et al. 1992). According to this study the total PAH concentration of elutriate of Site 13 sediment was about four times higher than Menzie et al. (1992) reported.

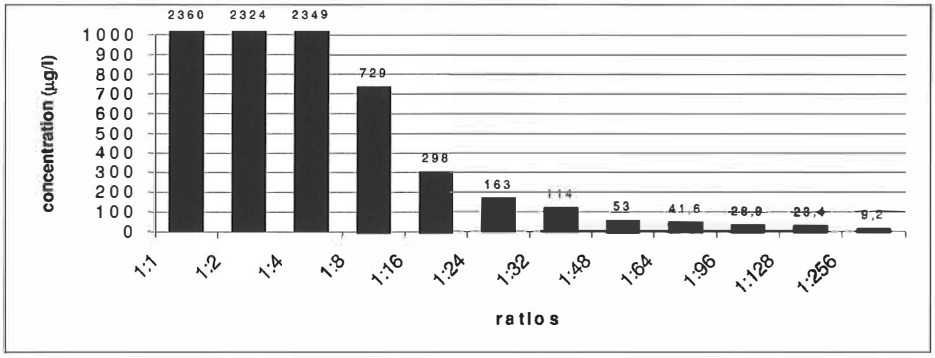


FIGURE 11 The concentrations of the total PAHs (µg/l) in the elutriates of the creosote-contaminated Site 13 sediment of ratios from 1:1 to 1:256 in the 500 h desorption experiment.

In the Lake Jämsänvesi the highest total PAH concentrations of elutriates of the creosote-contaminated sediment were in the ratios 1:1, 1:2 and 1:4 in the 24 h, 120 h and 500 h desorption experiments (Fig. 11, III). The relative amount (RA_{PAH}) describes how much PAHs are moved from sediment to water column. RA_{PAH} of desorbed values were calculated by means of the total PAH-concentrations of elutriates (µg/l) and the water volume (l) of mixing ratios (II). The relative desorption efficiency (RDE) values were calculated by means of the total PAH-concentrations of elutriates and the mixing ratios, the value 1.00 given for the ratio 1:1 (II). The relative amount of total PAHs of elutriates of creosote-contaminated sediment was between 2.4 and 9.4 and the desorption efficiency values varied from 1.00 to 4.00 (Fig. 12, III). The highest RDE-value was in the ratio 1:4, but it was remarkable that the RDE-value in the mixing ratio 1:256 was the same as in the ratio 1:1 (Fig. 12, III).

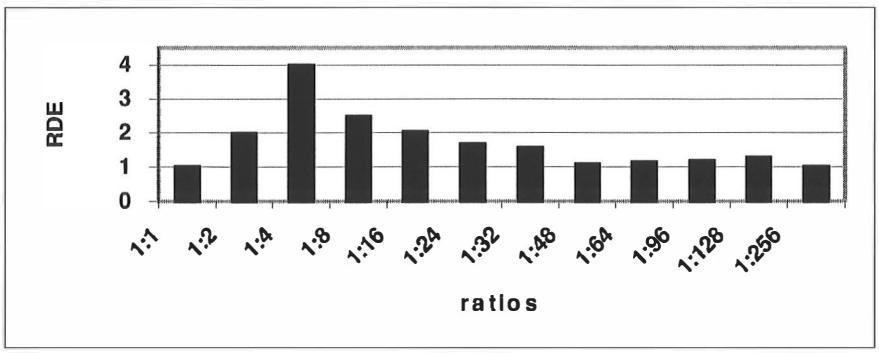
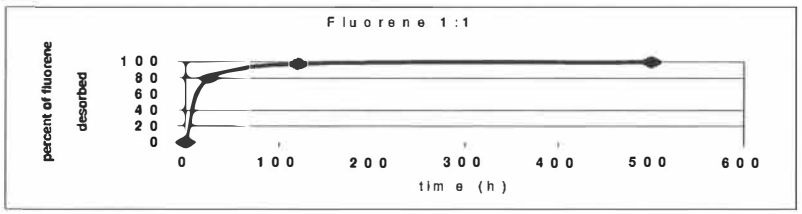


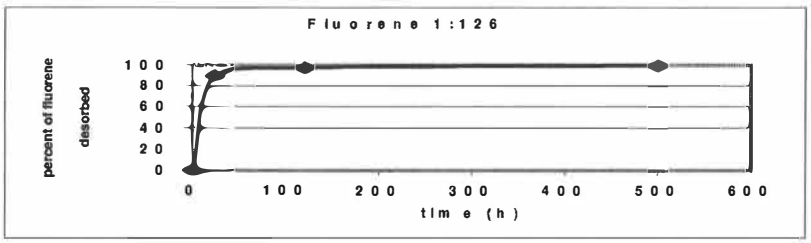
FIGURE 12 The relative desorption efficiency values of total PAHs of elutriates of creosote-contaminated sediment (Site 13) in ratios of from 1:1 to 1:256 in the 500h desorption experiment (III).

It appeared that a steady state of main individual PAHs - fluorene, B(k)F and dB(g,h,I)P - were achieved within a 120 h desorption time (Fig. 13,a-d). The fluorene and phenanthrene concentrations were the highest in the elutriates of spiked sediment (300 and 3000 μg/g dw). Half of the fluorene and B(k)F desorbed within 13 h in the 1:1, 1:24 and 1:128 sediment-water mixing ratios (Fig. 13). Half of the dB(g,h,I)P desorbed in the ratio 1:1 within 8 h (Fig. 13,e), whereas in the ratio 1:24 it took 61 h (III).

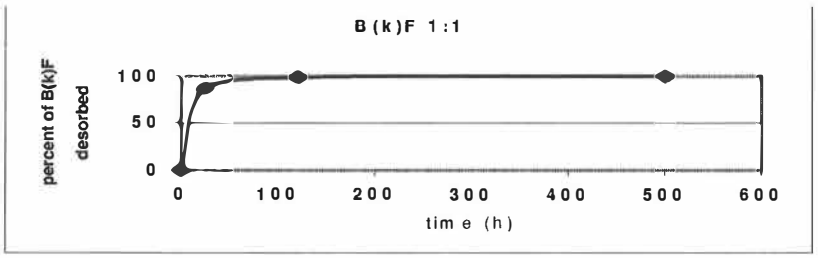
a)



b)



c)



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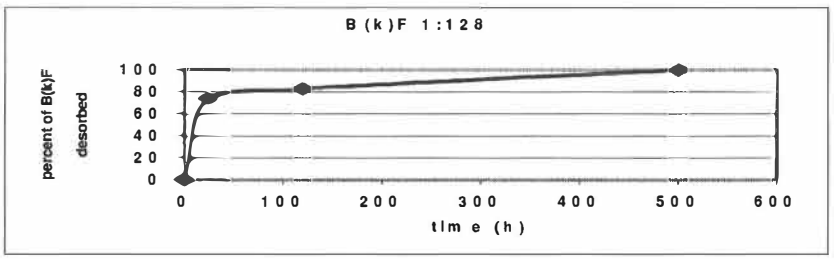

e)

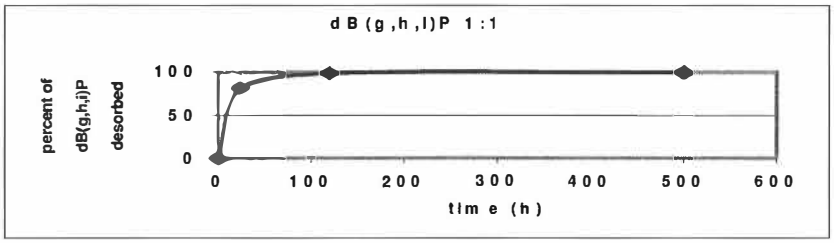

FIGURE 13 Desorption times (h) of three main PAH compounds in the creosote-contaminated lake sediment (L. Jämsänvesi) at two mixing ratios with water, 1:1 and 1:128 (a-e, III).

It can be seen that PAHs were more easily dissoluted to water from creosote-contaminated sediment than PAHs from spiked sediment. This study is important for predicting the environmental mobility and bioavailability of the PAHs from contaminated sediment to the water layer (II, III).

As the water-to-oil ratio increases, the concentration of these compounds and the total water soluble fraction (WSF) decreases, and the less soluble compounds in the oil make up a larger portion of the WSF (Shiu et al. 1990). Majanen et al. (1984) described this behaviour as a "depletion effect": the oil becomes depleted of water soluble material as the water-to-oil ratio increases, thus causing the apparent "solubility" to fall. Increasing concentration of dissolved organic carbon (OC) generally led to decreasing bioavailability of organic contaminants (Haitzer et al. 1998). According to Simpson et al. 1996 a correlation between PAH levels (in surficial sediments in Kitimat Harbor, Canada) and sediment organic carbon was observed. However, this was only significant for highly contaminated (approx. 10 mg/g dw) sites in the harbor. Creosote-contaminated sediments can continue to act as a source of pollution for many years, because natural and anthropogenic disturbances may redissolve or resuspend sediment-associated contaminants (Padma et al. 1998).

Environmental quality objectives (EQOs) for water, soil, and sediment have been derived for PAHs. In the Netherlands EQOs constitutes an important instrument in the effects-oriented environmental policy of the Dutch Ministry of the Environment (Kalf et al. 1997). Importantly, EQOs are based on scientifically derived risk limits: maximum permissible concentrations (MPC) and negligible concentration (NC) (Kalf et al. 1997). Kalf et al. (1997) have derived the following MPCs for water and sediment:

TABLE 6 MPC-values for PAHs in water and sediment (Kalf et al. 1997).

Compound	(MPCs for) water (µg/l)	(MCPs for) sediment (mg/kg)
naphthalene	1.2	0.14
anthracene	0.07	0.12
phenanthrene	0.30	0.51
fluoranthene	0.30	2.6
benzo(a)anthracene	0.01	0.36
chrysene	0.34	10.7
benzo(k)fluoranthene	0.04	2.4
benzo(a)pyrene	0.05	2.7
benzo(ghi)perylene	0.03	7.5
indeno(1,2,3-cd)pyrene	0.04	5.9

When the concentrations of PAHs in the creosote-contaminated sediment and elutriate of Lake Jämsänvesi are compared with MCPs (Table 6) for water and sediment, I can conclude that part of the sediment is so highly contaminated by creosote that an obvious ecotoxicity risk follows. The elutriate of the highest creosote-contaminated Site 13 in the Lake Jämsänvesi sediment contained about a 30 times higher benzo(a)pyrene concentration than the MPCs for water. More specifically, also the concentration of benzo(a)pyrene in contaminated sediment was over one hundred times higher than the MPC presented in Table 2.

4.1.3 The toxicity of elutriate by photoluminescence bacteria (*Vibrio fischeri*) and waterfleas (*Daphnia magna*)

The elutriate and porewater of the most creosote-contaminated sediment (Site 13) and the elutriates of ratios 1:1, 1:2 and 1:4 of sediment Site 13 and water were the most toxic to bacteria (EC_{50}= 4.5 – 9.3 % by volume) but not as toxic to the waterfleas (EC_{50} = 21 – 22.9 %, Fig 14, 15, I, II). It is possible that some individual PAH-compounds primarily contributed to the toxic effects to bacteria. When the total PAH-concentration of elutriates remained below 0.7 µg/l (dw), the elutriates were nontoxic (I). Unpredictably, the elutriate of the mixing ratio 1:32 was more toxic than the elutriate of the ratio 1:16 in the bacterial test (Fig. 14). The EC_{50}-value of ratio 1:128 was very high (41 %) in the bacteria test. The toxicity of the elutriates of ratios 1:1, 1:2 and 1:4 were approximately equally toxic to waterfleas (EC_{50} = 21 – 23 %), but the elutriates of ratios 1:8, 1:16 and 1:32 were fairly similar in waterflea tests (EC_{50} = 40.5 – 50.4, Fig. 15).

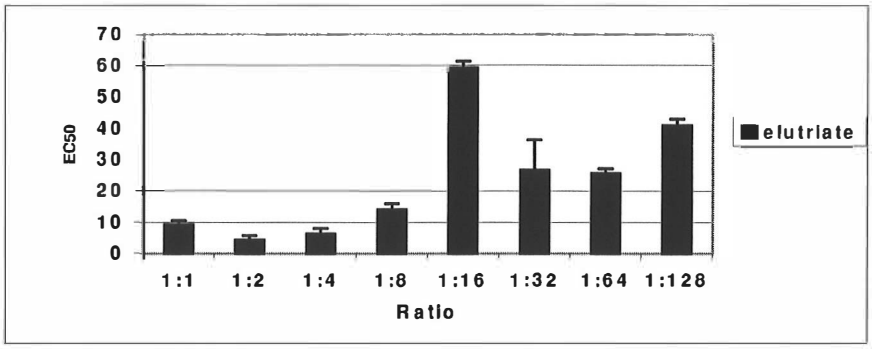

FIGURE 14 The EC_{50}-values (mean ± standard deviation) of bacterial photoluminescence of elutriates at different mixing ratios of sediment (Site 13) and water (II).

Harkey et al. (1994) have studied porewaters and the elutriates of the sediments. The benzo(a) pyrene concentration of whole sediment was 0.27 – 80.9 ng/g d.w., while porewater contained 0.004 – 0.913 ng B(a)P/ml and (1:4 v/v) elutriate 0.001 – 0.262 ng B(a)P/ml. Porewater had about a four times higher benzo(a)pyrene concentration than elutriate. As expected, the porewater was thus more concentrated in this sense than the elutriate. Carr & Chapman (1992) and Liβ & Ahlf (1997) assumed that porewater and elutriate toxicity tests are sensitive for determining the acceptability of dredged material for open ocean disposal. My studies support that assumption (I, II). The elutriates of mixing ratios 1:1, 1:2 and 1:4 (EC_{50}=4.5 – 9.3 %) were very similar to the porewater (EC_{50} = 5.8 %) in the most contaminated sediment site (I). Thus, it can be assumed that the elutriates of ratios 1:1, 1:2 and 1:4 reveal a sediment toxicity similar to that of porewater (I).

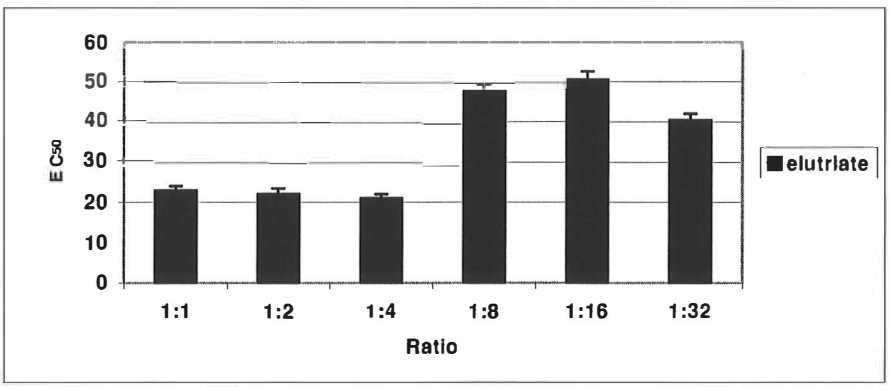

FIGURE 15 EC_{50}- values (mean ± standard deviation) of the elutriates at different mixing ratios of sediment (Site 13) and water as determined from the waterflea (*Daphnia magna*, II)

According to Padma et al. (1998), the LC_{50}-value for napthalene exposed *Daphnia magna* waterfleas was 24.1 mg/l in 48-h test. In *Daphnia pulex* test, LC_{50}-values were 0.1 mg/l for phenanthrene (48h), 0.01 mg/l for benzo(a)anthracene (96h) and 0.05 mg/l for benzo(a)pyrene (96h). Our studies revealed that the EC_{50} -value for the highest creosote-contaminated elutriate of ratio 1:4 exposed waterfleas was about 20 % for in 24-h and 48-h tests.

Toxic unit (TU) describes the toxicity of chemical mixtures or wastewaters. 1 TU equals the concentration that kill the animals by 50 % (photoluminesecent bacterias and *Daphnia magna* waterfleas in my studies, II). The highest toxic unit values (TU) of elutriates were in the ratios 1:1, 1:2 and 1:4 (TU = 10.8 –22.2) in the bacteria and waterflea tests (TU = 4.4 – 4.8, II). The TU-value of the elutriate of the ratio 1:2, based on bacteria bioassay, was the highest (TU=22.2). The TU-values (2.0 - 4.8) of the elutriates were quite high in the waterflea tests. For comparison, the highest TU-values of resin acids in waste waters from a pulp and paper mill have ranged between 1.25 and 1.75 (Petänen & Oikari 1987). The relative toxic emission (RTE) is the yield value that describes the potential to released of water amount to toxicity (TU x mixing ratio). The relative toxic emission yield values were calculated by means of TU-values of the elutriates and mixing ratios The RTE yield values describe toxic emissions in diluting volumes. The highest values in the bacteria test were in the ratios 1:32, 1:64 and 1:128 (II). When the amount of water per solid unit increases, the relative toxic emission yield level also increases.

4.1.4 Assessing the bioaccumulation of PAHs from creosote-contaminated sediment to oligochaetes (*Lumbriculus variegatus*)

In uncontaminated control sediments the worms were vertically distributed throughout the whole sediment (with depth approximately 20 mm). On the contrary, the animals in creosote-contaminated sediment did not burrow normally (with depth approximately 5 mm). They remained in a group on the surface sediment for about four days and then they burrowed into the surface. After exposure the color of the worms was paler than of worms in clean sediment. (V).

The water for the oligochaete experiment contained only fluorene and B(k)F. The PAH concentration of fluorene was 50.5 µg/l and that of B(k)F 55.7 µg/l after a one-week exposure. The total PAH concentration of the one-week waters was 106 µg/l and of two-, three- and four week combined waters was 157 µg/l (V).

The sediment used for this study was the most contaminated sediment in Lake Jämsänvesi. Before the exposure the total PAH concentration of Lake Jämsänvesi creosote-contaminated sediment was 3059 µg/g dw, decreasing to about one third of the intial total PAH concentration in the 28- d experiment (Table 7). The total PAH concentration of worms was 3311 µg/g dw and the main individual PAH compound was B(k)F (Fig. 16).

TABLE 7 The PAH concentrations (mean ± SD, µg/g dw, n=3) in Site 13 creosote-contaminated sediment before and after 28-d exposures (V). Δ% = the change of PAH-concentrations in the sediment before and after exposure,

Compound	Before	After	Δ%
Fl	403 ± 10	276 ± 2.9	68
An	714 ± 12	205 ± 5.7	29
B(k)F	1150± 20	400 ± 9.5	35
B(a)P	338 ± 7.8	114 ± 3.6	34
I(c,d)Pyr	34.8 ± 3.3	19.0 ± 1.6	55
dB(g,h,I)P	419 ± 6.9	189 ± 5.9	45
Total PAHs	3059	1206	

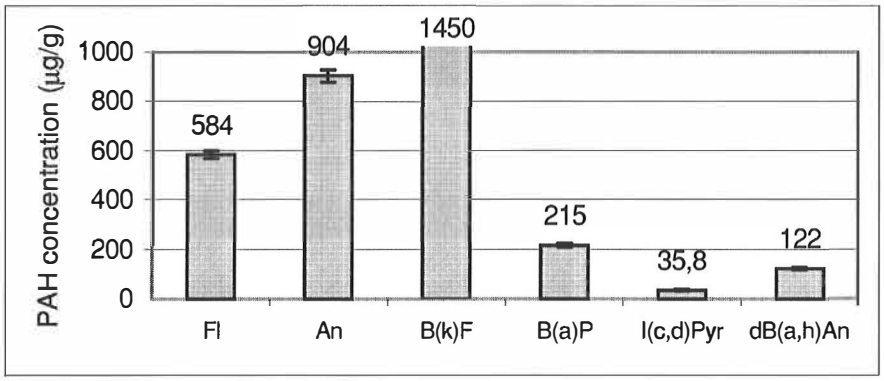

FIGURE 16 The PAH concentrations (mean ± SD, n=3 experiments) of oligochaetes exposed to creosote-contaminated sediment (µg/g dw) for 28 d exposure.

TABLE 8 Biota-sediment accumulation factors of individual PAHs in the 28 d oligochaete experiments.

Compound	BSAF
Fl	5.74
An	5.48
B(k)F	5.17
B(a)P	2.68
I(c,d)Pyr	4.46
dB(g,h,I)P	1.24

Several investigators have conducted bioaccumulation studies with *L.variegatus* using either field-collected or laboratory-spiked sediments (Schuytema et al. 1988, Nebker et al. 1984, Ankley et al. 1992, Brunson et al. 1998, Landrum et al. 1989). Biota-sediment-accumulation factors (BSAFs) were determined from levels in sediments (organic matter, OM) and oligochaete tissues (lipid weight, LW, V, VI, Van der Oost *et al.*, 1996, Brunson *et al.*, 1998). BSAFs in the present

study were typically greater than Ankley et al. (1992, 0.17-2.26). Our results agree with Landrum's (1989) findings. In this study BSAF values varied between 1.24 and 5.74 (Table 8, V). It appears that the PAH compounds were accumulated by the worms.

4.1.5 Toxicity of extracts of creosote-contaminated sediment to juvenile rainbow trout (IV)

Compared to vehicle controls and pristine reference sediment extract (average EROD activity 0.9 – 1.3 pmol/min/mg PMS protein), the extract of creosote-contaminated sediment from Lake Jämsänvesi induced EROD activity up to 20 – 30 times with a dose of 100 mg/kg (mg total PAHs / kg fish, Table 9, IV). The measurement of EROD -activity in the PMS-fraction proved a practical analytical method and this was fairly rapid for a large series.

TABLE 9 The activity (pmol/min/PMS mg protein) of hepatic 7-ethoxyresorufin O-deethylase (EROD) in juvenile rainbow trout exposed to different doses of extracts from creosote-contaminated sediments (n = 6, IV).

Sample	Dose of total PAH (mg/kg)	EROD (pmol/min/mg prot.)
Controls:		
Olive oil		1.3 ± 0.30
L. Palosjärvi		0.9 ± 0.29
BNF	100	20.1 ± 3.93
Creosote	100	54.7± 12.8
Extracts:		
13(0-10 cm)	1	0.81 ± 0.14
	50	2.1 ± 0.65
	100	27.2 ± 8.10
13(10-30 cm)	3.25	2.1 ± 0.65
	6.5	2.7 ± 1.10
	13	3.6 ± 1.00
CSS	1	0.98 ± 0.30
	50	2.2 ± 0.72
	100	42.5 ± 11.8

13 (0-10 cm) = the extract of creosote-contaminated sediment at Site 13 (see Fig 10) at a depth of 0–10 cm, doses of total PAHs/fish were 1, 50 and 100 mg/kg, 13(10-30 cm) = the extract of sediment Site 13 at a depth of 10–30 cm, doses of 3.25, 6.5 and 13 mg/kg, CSS = the extract of creosote-spiked sediment, BNF = β-naftoflavone, positive control; olive oil and sediment of Lake Palosjärvi = negative controls (Paper IV).

Many studies have shown that basal enzymatic activities and the inducibility of the hepatic microsomal monooxygenase system can vary considerably among fish species. Species differences in the background levels of cytochrome P-450 and enzyme inducibility by PAHs among fishes have been documented (Stegeman et al. 1997). Whyte et al. (2000) have studied EROD activity in creosote-exposed rainbow trout. Their findings support the results of this thesis. PAHs played a role in elevating EROD activity in the creosote-exposed trout. According to Basu et al. (2001) the exposure to individual PAH, benzo(k)fluoranthene, caused concentration-dependent increases in EROD

activity in trout, relative to acetone carrier controls, which averaged 0.65 pmol/mg/min. Thus, exposure to PAHs (both single ones and mixtures) caused significant CYP1A induction in trout, as measured by EROD activity (Basu et al. 2001).

The 1-OH pyrene concentration (metabolite of PAHs) equivalents of the hexane extracted bile was similar to that measured in the unextracted biles (r = 0.999, IV). Thus, due to simplicity, the direct SFS scan method for bile samples diluted with deionized water is preferable. The highest 1-OH pyrene equivalent concentration (190 ng/ml bile, not extracted) was found in fish exposed to the extract of creosote-contaminated sediment from Site 13, depth 0-10 cm (dose 100 mg/kg in fish), with quite high EROD-activity (27 pmol/min/mg prot) but not the highest measured in trout. Overall, the dose-response ratio was weak. The bile of fish exposed to olive oil and the sediment of Lake Palosjärvi contained below 10 ng/ml of 1-OH-pyrene. The 1-OH pyrene concentration was only 20 ng/ml in the bile of fish exposed to extract of creosote-spiked sediment (CSS exposed fish). The sediment sample itself from Site 13 did not contain pyrene (I). Thus the concentration of 1-OH pyrene could not be explained by the pyrene concentration of the sample (IV). The SFS-spectrum of the bile and that of the 1-OH pyrene standard are identical (Fig. 17). We can thus conclude that the bile sample contained 1-OH pyrene (IV).

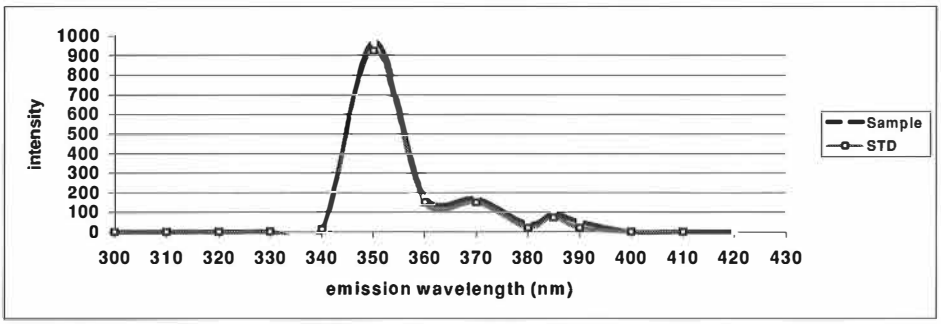

FIGURE 17 A representative SFS-spectrum of the bile from rainbow trout exposed i.p. to an extract of Lake Jämsänvesi creosote-contaminated sediment (Site 13, depth 0-10 cm) and the SFS-spectrum of the 1-OH pyrene standard (180 ng/ml, IV).

According to Lin et al. (1994) the concentration of PAH metabolites in the bile of the brown bullhead (*Ictalurus nebulosus*) was related to hepatic EROD activity. Malins et al. (1987) and Stein et al. (1992) reported similar findings in benthic fish from Puget Sound, USA.

4.2 Assessment of possible ecotoxicological risks caused by remediation of contaminated sediment

4.2.1 Assessing the effects of capping of creosote-contaminated sediment by settled particulate material (SPM)

The total PAH concentration of Site 3 SPM was 176.8 µg/g dw and the main PAH compound was phenanthrene (45.4 µg/g dw, Table 10). The total PAH concentration of water inside the Site 3 collector was 68.7 µg/l and the main PAH compound was also phenanthrene (35.5 µg/). The highest total PAH concentration was found in the elutriate of SPM in the ratio 1:1 and the main PAH compound was B(a)An. The total PAH concentration of the elutriate of ratio 1:1 (63.8 µg/l, Table 11) was almost as high as PAH concentration in the water of the sediment collector (69 µg/l, VI). It appears that the Site 3 SPM was eluted inside the collector, mimicking the mixing ratio 1:1 (III, VI).

TABLE 10 The concentrations (µg/g dry weight) of the individual PAHs of the settled particulate material accumulated by the collectors kept for ten months at Sites 1, 2, 3 and 4 (see Fig 3). The limit of detection denoted by nd was 0.1 µg/g (dw, VI).

Compound	Site 1	Site2	Site3	Site4
Ace	nd	10.3	21.5	2.36
Fl	nd	nd	6.00	nd
Ph	6.00	17.0	45.4	3.20
An	nd	4.70	30.4	nd
F	7.60	9.00	26.0	nd
Pyr	nd	nd	18.7	nd
B(a)An	nd	nd	22.0	2.67
Cry	nd	2.60	4.60	5.10
B(a)P	nd	2.00	2.21	2.18
Total PAHs	13.6	45.6	176.8	15.5

TABLE 11 The concentrations of total PAHs (µg/l) in the elutriates from the settled particulate material of Site 3. SPM : water ratios from 1:1 to 1:16 were studied.

	ratio				
compound (µg/l)	1:1	1:2	1:4	1:8	1:16
total PAHs	63.8	53.2	50.1	20.7	6.46

The elutriates of Site 3 SPM in the ratios 1:1, 1:2 and 1:4 were toxic to bacteria photoluminescence (Fig. 18), whereas the elutriates of ratios of from 1:24 to 1:256 not containing PAHs (i.e. concentrations lying below the detection limit) were not toxic.

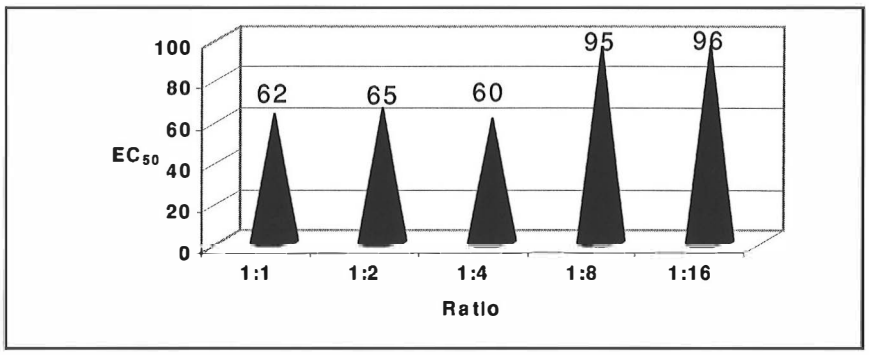

FIGURE 18 The EC_{50}-values (%) of elutriates of the settled particulate material (SPM) provided a measure of bacterial photoluminescence inhibition. The SPM was collected from Site 3 nearest the remediated site. Several wet SPM : water ratios of from 1:1 to 1:16 were tested. All other ratios, from 1:24 to 1:256, proved not to be toxic (≥ 100%, VI).

4.2.2 Exposure of mussels (*Anodonta anatina*) during the remediation by capping

To understand the PAH distribution in mussel tissues, it is necessary to compare the mussel PAH burden with the PAH content of the sediment in the polluted area of the lake. It appears that PAH compounds occurred round the remediated site in Lake Jämsänvesi. Several PAHs accumulated in the mussel tissue. The PAHs may have been taken up by filtration from the water column, or the accumulation might have come from the sediment. There could also be combined accumulation from both the water and the sediment. The PAH profiles of mussel tissues and SPM are quite similar. According to Marvin et al. (1995), the similarities in the PAH profiles in extracts of mussels, amphipods and sediment can provide evidence for a common source of contaminants.

The highest PAH concentrations were found in the mussels of Site 3 (Fig. 19, VI), which were located nearest to the remediated area (see Fig. 3). This possibly revealed an increased exposure of animals to PAHs due to the remediation activities, although no conclusive evidence exists, owing to the PAH contamination of the topmost sediment (I) also being the highest at that location. In our study the BSAFs for mussels ranged from 0.79 to 1.23 for acenaphthene, phenanthrene, anthracene, fluorene and pyrene. The BSAF for benzo(a)anthracene was the highest (1.45, Fig. 20). According to Brunson et al. (1998), -the BSAFs for PAHs were within the range of about 1.0 to 2.6 for oligochaete. Lee (1992) has also reported BSAFs for some PAHs. The BSAF for B(a)An was 0.97 for the mussels in the laboratory test.

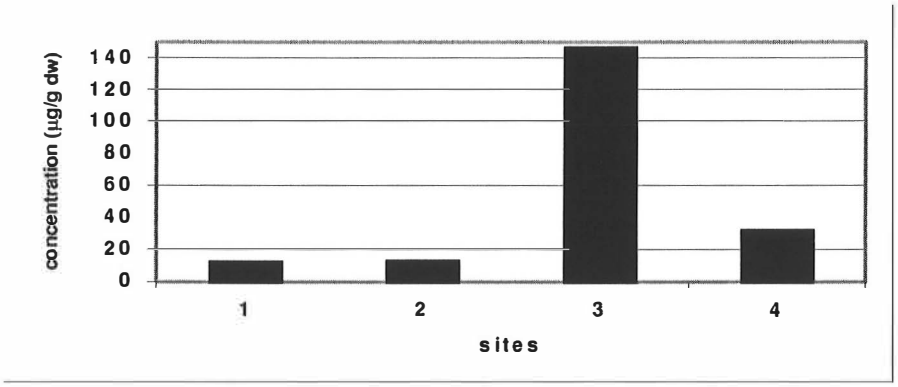

FIGURE 19 Whole body PAH concentrations (µg/g dw) in the mussel of exposure Sites 1, 2, 3 and 4 (Fig. 3). The mussels were caged for ten months. The lipid of mussel tissue extract was removed with concentrated KOH-solution (VI).

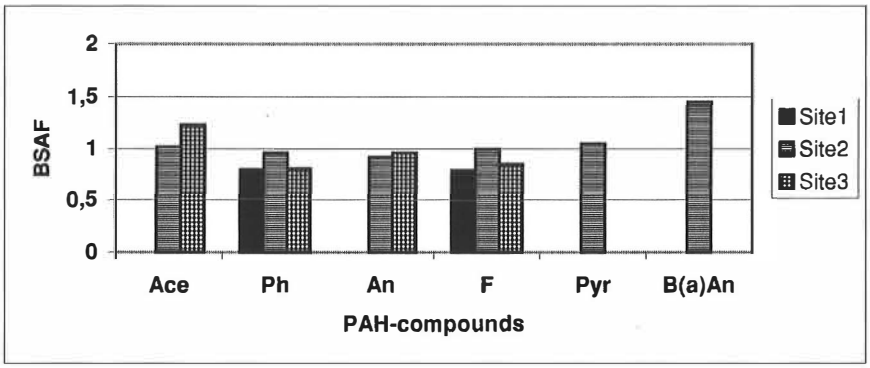

FIGURE 20 Biota-accumulation factors (BSAFs) of some individual PAHs of duck mussels from Sites 1, 2 and 3 (see Fig 3, VI).

Moreover, the water inside the shells of these Site 3 mussels exhibited the highest photoluminescent inhibition by bacteria (*Vibrio fisheri*) (EC_{50}=55.5 ± 3). The EC_{50}-value of water in Site 3 mussels was 68 ± 4. Water in mussels at Sites 1 and 4 was not toxic to bacteria (VI).

Glycogen is an energy storage polysaccharide occuring in the liver and muscles of most animals (Ioan et al. 1999). Its content in muscle can be an important bioenergetic prerequisite. Glycogen stores form an important metabolic fuel for a variety of cell types (Hardin & Roberts 1997). In the present work we applied glycogen analyzed from the adductor muscle of duck mussel as a bioenergetic marker of the possible long-term effect related to exposure to a creosote-contaminated sediment site and the remediation effects of the contaminated area to the caged mussels. The glycogen concentration of the adductor muscle was 8.4 ± 2.3 mg/g (ww, mean ± S.D.) in Site 3 mussels (n=9) and 12.4 ± 2.7 mg/g in Site 4 mussels (n=9). Glycogen and protein analyses of the adductor muscle of mussels served as biomarkers of possible long-term

physiological effects on the body condition of animals. The glycogen concentration of the adductor muscle (n=9) was 13.7 ± 1.4 mg/g in reference Site 1 and - 12.5 ± 1.1mg/g in reference Site 2. Protein concentrations of the adductor muscles of mussels at Site 3 were 20.7 ± 1.4 mg/g (ww, n=9) and 32.0 ± 1.2 mg/g (ww) in mussels at Site 4 (n=9). Protein concentration in the adductor muscles of mussels was 34.8 mg/g ± 1.7 in Site 1 and 31.4 mg/g ± 1.9 in Site 2 (VI). A statistical difference of < 0.05 was obtained between the glycogen concentrations of mussels in Sites 3 and 4. Therefore, the low glycogen and protein concentrations of adductor muscle of mussels in Site 3 might have been caused by stress induced by PAH-contaminated sediment (VI).

The same PAHs were dominated in the mussel tissue and in SPM. The "site 3" water inside the collector also contained same PAHs than mussel tissue and SPM. This suggested bioavailability of PAHs from Lake Jämsänvesi for the benthic animals possibly after the remediation by capping.

5 CONCLUSIONS

The focus of the present study was a) to identify the ecotoxicological effects of creosote-contaminated sediment and b) to assess the possible risks of remediation of contaminated sediment to the adjacent environment. The main conclusions are the following:

1. This study shows that resuspension spread toxic contaminants from sediment to the water layer (II, III). Relative desorption efficiency values were of the same order of magnitude in different sediment/water mixing ratios (1:1 – 1:256). Hence, the contaminants also spread in broad mixing ratios (II, III).
2. It appeared that a steady state was achieved in terms of the main individual PAHs - fluorene, B(k)F and dB(g,h,I)P within a 120- h desorption time. Half of fluorene and B(k)F desorbed within 13 h in sediment/water mixing ratios of 1:1, 1:24 and 1:128. Correspondingly, dB(g,h,I)P desorbed in the ratio 1:1 within 8 h, whereas in the ratio 1:24 it took approx. 60 h (III). It was also observed that PAHs were transferred more easily from creosote-contaminated sediment than from PAH-spiked sediment to water (III)
3. The elutriates of creosote-contaminated sediment in Lake Jämsänvesi were toxic to photoluminescent bacteria and waterfleas (I, II)
4. This study also confirmed the marked ability of benthic worms to accumulate and retain PAHs from creosote-contaminated sediment (V). Biota-sediment-accumulation factors for PAHs varied between 1.2 to 5.7 in the oligochaete experiments (V).
5. The extract of creosote-contaminated sediment induced EROD-activity at doses higher than 50 mg/kg (IV). Thus, the toxic contaminants can pose a threat to aquatic life.
6. We can assume that PAHs accumulated in the mussels during the capping operation, this was associated with the agitation of contaminated sediment (VI).
7. Capping, in terms of releasable PAHs may be a better alternative than the conventional dredging of sediment but, nevertheless, creosote remains in the sediment under the cover. The capping material, such as geotextile,

decays in the course of time (in less than 100 years in a dumping area). If this happens, the creosote may contaminate the other capping materials (gravel and soil) and it may then spread into the environment. Thus, I recommend that the Lake Jämsänvesi sediment and water quality be monitored by chemical analysis and toxicity tests in the future.

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YHTEENVETO (Résumé on Finnish)

Kreosootilla saastuneen järvisedimentin ekotoksikologisen riskin ja kunnostuksen arvionti

Saastuneiden sedimenttien riskin tunnistamismenetelmien kehittäminen on muodostunut erittäin tärkeäksi asiaksi nykypäivänä. Saastuneita sedimenttialueita on ympäri maailmaa, mm. useiden satama-alueiden järven/meren pohjat ovat hyvin saastuneita. Oikean kunnostusvaihtoehdon valitseminen on hyvin tärkeää saasteiden leviämisen kannalta. Kivihiiliöljyn tislauksessa syntyvä kreosootti on hyvin laajasti käytetty puunsuojauskemikaali. Kreosootti sisältää jopa 85 % polysyklisiä aromaattisia hiilivetyjä (PAH) sekä muita hydrofobisia yhdisteitä. PAHit ovat mm. lipofiilisia ja hydrofobisia sekä sitoutuvat nopeasti kiintoainekseen ja näinollen kertyvät sedimentteihin sekä eliöihin/eläimiin, josta ne voivat levitä myös muualle ympäristöön ja jopa ihmisiin.

Tutkimuskohteena on ollut Jämsänveden kreosootilla saastunut sedimenttialue Keski-Suomessa. Tutkimuksen tavoitteet olivat seuraavat: (1) tunnistaa kreosootin sisältämät PAH-yhdisteet ja määrittää niiden pitoisuudet sedimentissä ja sen elutriaatissa (sedimentin vesiuute), (2) tutkia missä sedimentin ja veden sekoitussuhteessa vapautuu eniten PAH-yhdisteitä sedimentistä veteen (desorptiokokeet), (3) arvioida kreosootilla saastuneen sedimentin elutriaattien potentiaalista toksisuutta valobakteeri (*Vibrio fischeri*)- ja vesikirpputestien (*Daphnia magna*) avulla, (4) tutkia PAH-yhdisteiden kerääntymistä sedimentistä pohjamatoihin pitkäaikaisella laboratorioaltistuksella, (5) arvioida kreosootilla saastuneen sedimentin ja sen elutriaattien toksisuutta kirjolohen poikasilla sekä (6) arvioida simpukoiden ja keräimiin laskeutuneen materiaalin (SPM) avulla saastuneen alueen peittämisen aiheuttamia mahdollisia riskejä. Tutkimustulosten avulla voidaan arvioida, minkälaisia vaikutuksia saastuneella sedimentillä (esim. resuspensiolla) on muuhun ympäristöön ja aiheuttaako saastuneen sedimentin kunnostus ekotoksikologisen riskin ympäristölle.

Tutkimus osoitti, että kontaminantit leviävät saastuneesta sedimentistä vesikerrokseen myös suurissa sedimentin ja veden sekoitussuhteissa. Suhteellisen desorption tehokkuus (RDE) arvot olivat sedimentin ja veden suhteilla 1:1 – 1:256 (v/v) välillä 1,00 – 3,98. Huomioon otettavaa on, että laimeimmilla sekoitussuhteilla (1:64 – 1:256) on lähes saman suuruiset RDE-arvot kuin väkevillä sekoitussuhteilla. Elutriaatit, jotka sisälsivat suurimmat pitoisuudet PAH-yhdisteitä olivat myös eniten toksisia bakteereille ja vesikirpuille. Kreosootilla saastuneimmasta sedimentistä valmistetut elutriaatit olivat eniten toksisia bakteereille (EC_{50} = 4,5 – 9,3 %) sedimentin ja veden sekoitussuhteen ollessa 1:1, 1:2 ja 1:4 (v/v).

Harvasukamadolla (*L. variegatus*) tehdyissä laboratorioaltistuksissa (28 vrk) todettiin PAH-yhdisteiden kertyvän matoihin. BSAF-arvot olivat yksittäisillä PAH-yhdisteillä välillä 1,2 – 5,7. Altistuksen alkaessa havaittiin madoilla epänormaalia kaivautumiskäyttäytymistä (normaalisti kaivautuvat koko sedi-

menttiin). Madot olivat ryhmässä sedimentin pinnalla n. neljän vuorokauden ajan, jonka jälkeen ne kaivautuivat sedimentin pintakerrokseen. Matojen väri oli myös huomattavasti vaaleampi kuin kontrollimadoilla.

Kreosootilla saastuneen sedimentin uutteella (> 50 mg/kg = mg kokonais-PAH pitoisuus/ kg kalaa) altistettujen kirjolohien maksan 7-etoksiresorufiini O-de-etylaasin (EROD) aktiivisuus kasvoi 20 – 30 kertaiseksi verrattaessa kontrollikalojen EROD-aktiivisuuteen. Tutkimuksen mukaan toksisuusvaikutukset olivat huomattavat, kun kokonais-PAH pitoisuus oli n. 3 mg/g (dw) kalassa.

Simpukoihin kertyi PAH-yhdisteitä kreosootilla saastuneen alueen peittämisen aikana, ja samoja PAH-yhdisteitä havaittiin myös SPM-näytteissä. On mahdollista, että kunnostuksen aikana, kun peittomateriaali vajosi saastuneen alueen päälle, tapahtui kreosootin "pöllähdys", jolloin saastunutta sedimenttiä levisi myös kunnostusalueen ympärille.

Tutkimustulosten perusteella voidaan olettaa suuren vesimäärän vapauttavan toksisia ja akkumuloituvia yhdisteitä saastuneesta sedimentistä veteen. Kontaminoituneen sedimentin kunnostuksen mahdollisesti aiheuttamat ekotoksikologiset riskit on aina huomioitava kunnostusvaihtoehtoa valittaessa. Tutkimuksessa todettiin, että rasvaliukoiset PAH-yhdisteet kertyvät sekä simpukoihin että matoihin ja leviävät vesistössä muualle ympäristöön, mahdollisesti jopa ravintoketjun päähän.

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I

The toxicity and concentrations of PAHs in creosote-contaminated sediment lake sediment

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II

Assessment of toxicity of hazards of dredged lake sediment contaminated by creosote

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III

Desorption of PAHs from creosote-contaminated and PAH-spiked sediment to water

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Environmental Pollution (submitted)

DESORPTION OF PAHs FROM CREOSOTE-CONTAMINATED AND PAH-SPIKED SEDIMENT TO LAKE WATER

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) were measured in laboratory desorption experiments using an authentic sediment from a creosote-contaminated sediment lake site, settled particulate material (SPM) collected subsequent to physical remediation action, and spiked sediment containing known mixture of individual PAH-compounds (fluorene, anthracene, phenanthrene, fluoranthene, benzo(k)fluoranthene). The purpose of the experiments was to identify possible risks of contaminated sediment as such and subsequent to the remediation actions to the adjacent environment. In order to assess the total emission from the sediment material, a wide range of suspension (sediment/water) ratios (from 1:1 to 1: 256 v/v) were monitored. The highest total PAH concentration in the elutriate of the creosote-contaminated sediment was 2360 µg/l in ratio 1:1 observed after 500 h desorption. The PAH concentrations in elutriates of spiked sediments were lower than PAH concentrations in elutriates of the creosote-contaminated sediment. Fluorene, B(k)F and dB(g,h,I)P were the main PAH compounds in elutriates. The time for half amount of major PAH compounds to desorb from its sample matrix varied from 8 to 61 hours. It appeared not to directly depend on the chemical or the mixing ratio. The acute toxicity of elutriates made of SPM, as well as the water inside the SPM collector, was measured by bioluminescence inhibition test (*Vibrio fischeri*). The elutriates of ratios 1:1, 1:2 and 1:4 of SPM were most toxic (EC_{50} –values were between 60 and 65 vol-%). The water inside the collector was also toxic to photoluminencent bacteria (EC_{50} was 60 vol- %). Risk assessment of the remediation strategies for contaminated sites require that both the total amounts of contaminants present in the sediment and their potential for release from this matrix are evaluated.

Keywords: PAH, creosote, desorption, elutriate, sediment

1 INTRODUCTION

Harbours, marinas, oil refinery recipints and waters adjacent to creosote impregnation plants commonly reside sediment sites contaminated by polyaromatic hydrocarbons, PAHs (Mcgroddy & Farrington 1995, Ghosh et al. 2000). According to Villholth (1999) a relatively large number of creosote waste sites from previous gas works, asphalt factories, and wood preservation industries have been identified in Denmark. Under several occasions, e.g. dredging, dumping and remediation by a physical measure like site capping, the contaminated sediment resuspend to the ambient water phase (Jarvis et al. 1996, Latimer et al. 1999).

Related to various time scales, the partitioning or dissolution behaviour of PAHs into water is of considerable intrest and concern, especially from a toxicity viewpoint (Shiu et al. 1990). The concentrations of the various soluble components in the water depends, however, on several factors, like the composition of the oil, temperature, water salinity, and the ratio of the volumes of water and oil which are brought into contact (Shiu et al. 1988). At high ratios, the organic liquid may become substantially depleted of the more soluble components (Shiu et al. 1988). According to Shiu et al. (1990) the concentration of the water soluble fraction (WSF) decreases when the water-to-oil ratio increases and, more importantly the composition of the WSF changes as the ratio changes. The concentrations of the less soluble compounds, such as highly alkylated benzenes and naphthalenes, is far less dependent upon the water-to-oil ratio than the more soluble compounds. Their concentration remains relatively constant over the range of water-to–oil ratios tested while the concentration of the more soluble compounds increases dramatically. Therefore, the presence of these less soluble compounds becomes more important as the ratio is increased. Desorption of hydrophobic organic compounds (HOC) from sediments and soils have often been observed to take place in two stages: a rapid one followed by a stage of much slower release. Rapidly released fraction has been considered available for biodegradation and toxic response (Hulscher et al. 1999, Ghosh et al. 2000).

Creosote-contaminated sediments may continue to act as a source of pollution for many years, because natural and anthropogenic perturbatios may redissolve or resuspend sediment associated contaminants (Padma et al. 1998). We have earlier investigated an such case site in Finland (Lake Jämsänvesi), and identified ecotoxicological risk which may become actual due to planned remediation measures (Hyötyläinen & Oikari 1999a,b,c, Hyötyläinen et al. 2001).

In order to affirm the reproducibility and precisity of effects anticipated, in the previous study on elutriates of sediments, total PAH-concentration (Hyötyläinen & Oikari 1999b) a further investigation was necessary. In previous studies the sediment/water mixing ratios were between 1:1 and 1:128 (Hyötyläinen & Oikari 1999b). The dominant PAHs released from sediment

were fluoranthene, B(k)F and dB(g,h,I)P. The total PAH-concentration in elutriates in ratios from 1:1 to 1:4 was as high as 2.3 mg/l. One of the goals in this study was to enlarge the mixing ratio from 1:128 to 1:256. Even the high sediment/water mixing ratio (1:256) may evoke increased ecotoxicological risk for ambient environment. The remediation of contaminated Lake Jämsänvesi sediment by capping made addition research necessary.

2 MATERIALS AND METHODS

2.1 The study site

The sediment site is locating in Lake Jämsänvesi, Central Finland (Hyötyläinen and Oikari 1999a). A creosote impregnation plant was operating in 1956 – 1976 ca. 250 m uphill contaminating the sediment by its runoffs (Figure 1.). Particulate material (SPM) collectors were deployed to the lake at the same time as the remedation operation by capping was started in November 1998. The most creosote-contaminated sediment "site 13" from the remediated area, settled particulate material from "site 3" and creosote-spiked uncontaminated sediment (Fig. 1) were the source of samples used in the desorption experiments.

FIGURE 1.

We have compared the desorption of PAHs of creosote oil contaminated sediment to PAH mixture spiked sediment. An apparent steady state was reached for several individual PAHs. For those compounds an estimate was derived to describe time needed for 50 % desorbed time.

2.2. Preparation of synthetic sediment and elutriates, and spiking of sediment by PAH-mixture

Synthetic sediment was formulated from washed sand [fine (0.05 – 0.2 mm) and medium (0.3 – 0.6 mm) sand (ratio 2:1)], kaolin and organic matter (Lake Palosjärvi sediment, OC = 23%, Walsh et al. 1991, Harrahy & Clements, 1997). The mixture was mixed for 1 h on rolling mill. The synthetic sediment formed contained 5 % organic matter (dry weight). The sediment was aged for 5 days before spiking at 4 °C.

Uncontaminated Lake Palosjärvi sediment (Toivakka, 40 km SE from Jyväskylä) was spiked by the individual PAHs. Spiked sediments were prepared as follows: (a) the uncontaminated wet synthetic sediment was mixed with artificial lake water [distilled water and salt solution (8 mM $CaCl_2$, 20 mM $MgSO_4$, $NaHCO_3$, 3 mM KCl, pH = 7)] (sediment + water, 1 + 2 v/v) (b) while mixed continuously, the carrier-containing PAH-mixture (300 µg/g dw and 3000 µg/g dw, Table 1) was added gradually to the slurry during one hour at room temperature, and (c) and further mixed for 24 hour at 4 °C. (d) The

sediment-water slurry was let to equilibrate at 4 °C for 28 days, and (e) water layer and sediment were separated by decanting (Hill et al. 1993, Hyötyläinen & Oikari 1999b).

TABLE 1.

A mixture of PAHs with various hydrophobicites containing the main PAH-compounds simulated the composition of PAHs in creosote-contaminated Lake Jämsänvesi sediment (Table 1).

The elutriates of settled particulate material (SPM), "site 13" sediment and PAHs-spiked sediment were prepared as follows: wet well-settled material (10 g) was mixed with artificial lake water in ratios 1:1, 1:2, 1:4, 1:8, 1:16, 1:24, 1:32, 1:64, 1:96, 1:128, 1:256 (v/v) (10 ml, 20 ml, 40 ml, 80 ml, 160 ml, 240ml, 320 ml, 640 ml, 960ml, 1280 ml and 2560 ml). Three replicate experiments were done from each ratio. The mixture was agitated on a mechanical shaker for one hour at room temperature and then let to settle down at 4 °C. Water samples (50 ml) were taken from "site 13" sediment and PAHs-spiked sediment mixtures in 24 h, 120 h and 500 h. Water samples of SPM mixture were taken after 24 h. The sediment – water slurries were mixed between the sampling. Elutriates were stored at 4 °C until time of analyses (Hill et al. 1993, ASTM 1994, Hyötyläinen & Oikari 1999b).

2.3 Chemical analysis of elutriates

The extraction of PAHs of elutriates was modified from earlier methods (Lee et al. 1987, Spørstol et al. 1983, Simpson et al. 1995). After addition of the internal standard (d-anthracene), the elutriates (50 ml) were extracted with 15 ml of hexane (three sequential extractions of 15 ml) in separatory funnel (Hyötyläinen & Oikari 1999a,b). The extract was first concentrated to about 5 ml by Rotavapor and transferred to Kimax-tube, and further evaporated gently to dryness with nitrogen gas flow. The residue was finally dissolved in 200 µl of hexane for GC-MS analysis (Hyötyläinen & Oikari, 1999). EPA PAH-standard (16 PAHs) was used for analysis, described as follows:

Total PAHs = Σ 16 PAHs = napthalene(Nap), acenaphtylene(Acy), acenaphthene(Ace), fluorene,(Fl), phenanthrene(Ph), anthracene(An), fluoranthene(F), pyrene(Pyr), benzo(a)anthrcene(B(a)An), chrysene(Cry), benzo(b)fluoranthene(B(b)F), benzo(k)fluoranthene(B(k)F), benzo(a)pyrene (B(a)Pyr), indeno(1,2,3cd)pyrene(I(c,d)Pyr), dibenzo(a,h)anthracene(dB(a,h)An), dibenzo(g,h,i)perylene(dB(g,h,i)P)

The relative amount (RA_{PAH}) of desorbed values were calculated by means of the total PAH-concentrations of elutriates (mg/l) and the water volume (l) of mixing ratios (Hyötyläinen & Oikari, 1999b):

$$RA_{PAH} = \textit{total PAHs mg/l x volume (l)}$$

The relative desorption efficiency (RDE) values were calculated by means of the total PAH-concentrations of elutriates and the mixing ratios, the value 1.00 given for the ratio 1:1 (Hyötyläinen & Oikari 1999b).

2.4 Bioluminescence inhibition

The toxicity of elutriates from ratios 1:1 to 1:256 of "site 3" SPM and water inside the collector were also studied. Acute toxicity of elutriates of SPM and water inside the collectors from "sites 1, 2, 3 and 4" were measured by photoluminescent bacteria (*Vibrio fischeri*; Bio-Orbit 1257 Luminometer). The assay is relatively sensitive to many common aquatic contaminants and has been used to assess the toxicity of a variety of aqueous samples including surface waters and different types of sediment extracts (Ankley et al. 1989). The freezed bacteria were activated by 2 % NaCl. The assay dilutions of elutriates were 45.5, 22.8, 11.4 and 5.7 % and osmotically adjusted with 2 % NaCl. The responsivity of bacteria was tested with zinc sulfate ($ZnSO_4$) as the positive control. Dilutions were inoculated with bacteria and incubated at 15 °C for 15 min before reading the light emitted (Ankley et al. 1989, Hyötyläinen & Oikari 1999a,b). Two replicates were made per sample. EC_{50} values (effective concentration that reduce bioluminenscence by 50 %) were obtained by Biotox-programme of Bio-Orbit company.

Toxic unit (TU) describtion was used to quentify toxic emission of samples. 1 TU equals the concentration that decreases luminescence by 50 %. TU values for the elutriates were calculated by the following formula (Bervoets et al., 1996, Hyötyläinen and Oikari, 1999b):

$$TU = 100\ \% \ / \ EC_{50}$$

The relative toxic emission (RTE) is the yield that describes the potential of water amount a release toxicity (TU x mixing ratio), calculated by means of TU-values of elutriates and mixing ratios (Hyötyläinen & Oikari 1999b).

3 RESULTS

3.1. The PAH-concentrations in elutriates of SPM and effect of suspension ratio

While measuring various ratios the highest total PAH-concentration was in elutriate of SPM of ratio 1:1. The main PAH-compound was B(a)An (Table 2). No PAHs was detectable (< 2 µg/l) in elutriates of ratios from 1: 24 to 1:256.

TABLE 2.

Total PAHs in the elutriate of "site 13" creosote-contaminated sediment (Hyötyläinen & Oikari 1999a) in ratio 1:256 was about 9 µg/l, whereas in

elutriate of PAH-spiked sediment in ratio 1:256 were not detectable (Tables 3 and 4).

TABLE 3.

TABLE 4.

FIGURE 2.

Half of desorption of PAHs was also determinated. It is presumable in calculation, that 100 % of PAHs desorbed in 500 h. It appeared that a steady state of main individual PAHs - fluorene, B(k)F and dB(g,h,I)P - was achieved within 500 h desorption time (Fig. 2), though no accurate description on time needed for 50 % desorption was possible to estimate. Approximately, however, somewhat faster, 50 % of fluorene ("site 13" elutriate) in ratio 1:1 was desorbed within 13 h, in ratios 1:24 and 1:128 within 10 h. Half of B(k)F ("site 13" elutriate) in ratio 1:1 desorbed within 8 h, in ratios 1:24 and 1:128 within 11 h experiment. For dB(g,h,I)P ("site 13") in ratio 1:1 the corresbonding rate was 8 h, but in ratio 1:24 much longer, 61 h (Table 5). 50 % of fluorene and fluoranthene (elutriate of PAHs spiked sediment) in ratios 1:1 and 1:24 were desorbed in 13 h, whereas B(k)F in ratio 1:1 in 32 h. In all, therefore, was no K_{ow} -values connection to 50 % desorption of PAHs at the same mixing ratio.

TABLE 5.

TABLE 6.

TABLE 7

The relative amount (RA) values of total PAHs of elutriates of creosote-contaminated sediment were between 2.4 to 9.4 and the desorption efficiency (RDE) values varied from 1.00 to 4.00 (Table 6). In spiked sediment (3000 μg/g) RA-values of total PAHs of elutriates were between 1.97 and 8.14 and RDE-values varied from 1.00 to 3.82 (Table 7).

3.2 Toxicity of SPM elutriates and water inside the SPM collectors

The elutriates of "site 3" SPM in ratios 1:1, 1:2 and 1:4 were toxic to bacterial photoluminescence (Fig. 3), whereas the elutriates of ratios from 1:24 to 1:256 not containing PAHs (i.e. concentrations were below detection limit) were not toxic.

FIGURE 4.

The water inside the collector at "site 3" was most toxic (EC_{50} = 60 %) to bacteria, whereas EC_{50} –values of water inside collectors at "sites 1 and 2" were 80 and 96 % (Fig. 4).

TABLE 8.

Toxic unit values (TU) were between 1.0 and 1.7. TU- values for water inside the collectors were 1.0 and 1.3 in upstream "sites 1 and 2", 1.7 and 1.4 in downstream "sites 3 and 4". Relative toxic emission (RTE) yield values varied from 1.6 to 16 for elutriates of SPM in ratios from 1:1 to 1:16 (Table 8).

4 DISCUSSION

4.1 Desorption of PAH compounds from sediment materials

The total PAH-concentration of elutriate of "site 3" SPM at ratio 1:1 (64 µg/l, Table 2) was equal with that of water of "site 3" SPM collector (69 µg/l, Hyötyläinen et al. 2001). The total PAH-concentrations of water inside "sites 1, 2 and 4" collectors were between 7.7 and 15.3 µg/ (Hyötyläinen et al. 2001). It seems that "site 3" SPM was eluted in side the collector, mimiking mixing ratio 1:1. Because organic carbon (OC) contents of "site 13" creosote-contaminated sediment and that of "site 3" SPM were about same (4.8 and 5.5 %), the elutriate represented well the tendency for desorption of PAHs inconnection of a remediation operation.

According to prevoius work the total PAH-concentration of "site 3" SPM was 177 µg/g dw, the main compound being phenanthrene (45 µg/g dw, Hyötyläinen et al. 2001), similar to the water inside collector (36 µg/l, Hyötyläinen et al. 2001). However, the water inside collector also contained the high molecular weight PAHs, such as benzo(a)anthracene (B(a)An), chrysene (Cry) and benzo(a)pyrene (B(a)P, about 5 µg/l). The main individual PAHs of elutriates of "site 3" SPM in ratios from 1:1 to 1:4 were phenanthrene and B(a)An. The individual PAHs of "site 3" SPM were quite similar to those of PAHs in remediated area (like "site 13"). What has to be taken into consideration here is that sediment around the remediated area contained the same PAHs as in "site 3" SPM. Thus, it is difficult to prove the origins of PAHs in "site 3" SPM.

It is observed that PAHs were transferred easier from creosote "oily" sediment than PAH-spiked sediment to water. Total PAH-concentrations of elutriates of creosote-contaminated sediment (3300 mg/g dw, Hyötyläinen & Oikari 1999a) were higher then elutriates in PAH spiked sediment (total 3000 µg/g dw), the highest total PAH-concentrations were in elutriates in ratios 1:1, 1:2 and 1:4 after 500 h desorption (Tables 3 and 4). 50 % desorption of most individual PAHs (from "site 13" sediment and PAHs-spiked sediment) and in ratios from 1:1 to 1:256 were desorbed within 13 h. However, for B(k)F (from

spiked sediment) in ratio 1:1 the rate was 32 h and desorption of dB(g,h,I)P ("site 13" sediment) in ratio 1:24 was even 61 h. Fluorene, B(k)F and dB(g,h,I)P were the main PAH-compounds of elutriates of "site 13" sediment in 24 h, 120 h and 500 h experiments. Fluorene and phenanthrene concentrations were the highest in the elutriates of spiked sediment (300 and 3000 μg/g dw). B(k)F-concentrations were higher in elutriates of creosote-contaminated sediment then in elutriates of spiked sediment (3000 μg/g dw). For example the concentration of B(k)F of elutriate of creosote-contaminated sediment (in ratio 1:1 within 500 h) was almost two times higher then in elutriate of spiked sediment. The elutriates of "site 13" creosote-contaminated sediment of ratios from 1:1 to 1:128 contained B(k)F in proportion the elutriate of spiked sediment contained B(k)F only in ratios from 1:1 to 1:24 in 500 h experiment. The PAH-profiles of elutriates of creosote-contaminated sediment from ratios 1:1 to 1:4 were quite same in all three time period.

The more soluble compounds present in the oil are the dominant WSF components, and total WSF concentration is fairly high. As the water-to-oil ratio increases, the concentration of these compounds and total WSF concentration decreases, and the less soluble compounds in the oil make up a larger portion of WSF (Shiu et al. 1990). Majanen et al. (1984) described this behaviour as a "depletion effect": the oil became depleted of water soluble material as the water-to-oil ratio increased, thus causing the apparent "solubility" to fall.

It was suggested that understanding the determinants of desorption from sediment matrix gives useful information regarding to ecotoxicological consequences due to physical remediation measure like capping. According to Narbonne et al. (1999) a rapid transfer to the water was observed within the 4 h for B(a)P and within 24 h for other PAHs. According to our study the 50 % major PAHs (fluorene, B(k)F and dB(g,h,I)P were largely transferred to the water within 13 h. However, desorption rate depended on the sediment and water mixing ratio, e.g. desorption of dB(g,h,I)P in mixing ratio 1:24 was 61 h. In the present study the full transfer to the water layer was observed within 120 h for fluorene, B(k)F and dB(g,h,I)P in ratio 1:1 (Fig. 2). It was apparent that, when mixing ratio increases, the desorption time of high molecular weight PAHs (log K_{ow} > 6.2) also increased (Fig. 3). According to Narbonne et al. (1999) the order of increasing rates of transfer from sediment was Pyr (K_{ow}=5.2) < Ant (K_{ow}=4.54) < Ph (K_{ow}=4.46). Mcgroddy et al. (1996) noted that petroleum-derived PAH-compounds are be present in the sediment pore waters as freely dissolved compounds as well as associated with pore water organic colloids sediment resuspension events as well as active bioturbation could result in the rapid transport of these compounds to the overlying water column. It is important to take into account the effect of water-to-oil volume ratio when preparing elutriate, especially for bioassay purposes (Shiu et al. 1990). According to Latimer et al. (1999) the desorption rates are dependent on the particle /floc size and density distributions, the type of water, the amount of organic carbon in the sediments, the time of adsorption before desorption,

and the chemical partition coefficient. In the previous study the most RA- and RDE-values were the same order (RDEs varied from 1.00 to 10) then RA- and RDE-values (1.00 – 4.00) in the present study (Table 6).

Creosote-contaminated sites are potential risks also for groudwater. At these sites, high molecular weight PAHs have been detected downstream of creosote-contaminated sources even at concentrations exceeding solubilities. Rather similarly high molecular weight PAHs, such as B(k)F, B(a)P and dB(g,h,I)P, were detectable in the water extracts of the contaminated sediment from Lake Jämsänvesi. Because the PAHs are hydrophobic by nature, the affinity of PAHs to the colloids is anticipated to increase with increasing molecular weight (and K_{ow}) of PAHs, facilitated even more by increasing organic carbon content of the elutriates (Villholth 1999). A mixture of PAHs with various hydrophobicites containing the main PAH-compounds simulated the composition of PAHs in creosote-contaminated Lake Jämsänvesi sediment (Table 1). Octanol water partition coefficient (K_{ow}) has been widely used to correlate environmental partitioning phenomena such as bioconcentration and sorption. Data for quantities are regarded essential in any assessment or prediction of environmental fate of chemical substances (Mackay et al. 1980).

4.2 Toxicity of SPM water extracts

In our previous work on the elutriates, prepared from sediment (now under the area remediated by capping "site 13") with the PAH-concentration 19 times higher than the "site 3" SPM now, were all toxic to bacteria at ratios from 1:1 to 1:128 (Hyötyläinen & Oikari, 1999b).

The EC_{50}-value of "site 3" water inside the collector was most toxic (EC_{50} = 60.2 $\pm$ 1.8, Figure 4) in the bacterial test, actually of the same order as EC_{50}-values of elutriates of "site 3" SPM, at ratios 1:1, 1:2 and 1:4. Toxic unit value was the highest in elutriate of "site 3" SPM in ratio 1:4, whereas the highest relative toxic emission yield was in elutriate in ratio 1:16. This establish that contaminats can also spread in wide sediment-water mixing ratios. We assume that elutriate ratios 1:1, 1:2 and 1:4 describe the toxicity of water due to the physical remediation operations (e.g. dredging, capping) of the most contaminated sediment site. This assumption is supported by largely nontoxic waters in SPM-collectors more upstream to the remediated site.

5 CONCLUSSION

It was observed that PAHs are spread to water from creosote-contaminated sediment, much like from sediment spiked PAHs. Relative desorption efficiency values were same order in differ sediment-water mixing ratios, thus the contaminants spread also in wide mixing ratios. This study predicts the

environmental mobility and bioavailability of the PAHs from contaminated sediment which is caused by remediation by some physical technique or normal resuspension of a sediment around the remediated area.

6 ACKNOWLEDGEMENTS

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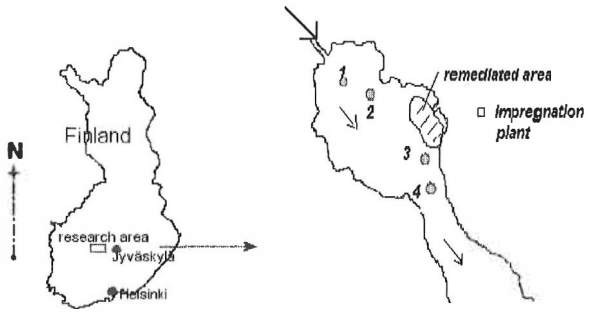

FIGURE 1 The study area in the Lake Jämsänvesi, Central Finland and the location of SPM collectors at "sites 1, 2 (apparent upstream) 3 and 4" (downstram) and the area remediated by capping.

TABLE 1 Nominal concentrations (µg/g dw) of PAHs in two theoretical sediments spiked by known PAH mixture. The contact time was 28 days at 4 °C. Octanol-water partition coefficients (log K_{ow}) for PAHs are also presented (Miller et al. 1985).

individual PAH	log K_{ow}	Level 1	Level 2
fluorene	4.38	61.8	574.4
anthracene	4.54	60.5	633.0
phenanthrene	4.57	52.9	574.3
fluoranthene	5.22	65.7	627.8
benzo(k)fluoranthene	6.04	59.1	590.5
total PAHs (5)	300	3000	

TABLE 2 The concentrations of PAHs (µg/l) in the elutriates from the settled particulate material of "site 3" after one hour mixing time. SPM : water ratios from 1:1 to 1:16 were studied. For the abbreviation of compounds, see the section of Materials and Methods.

compound (µg/l)	1:1	1:2	1:4	1:8	1:16
Fl	2.00	nd	nd	nd	nd
Ph	22.1	30.0	29.6	nd	2.46
An	2.94	4.80	10.0	nd	nd
Pyr	5.02	nd	nd	nd	nd
B(a)An	27.7	18.4	10.5	20.7	4.00
Cry	nd	nd	nd	nd	nd
B(a)P	4.00	nd	nd	nd	nd
Total PAHs	63.8	53.2	50.1	20.7	6.46

limit of determination was 2 µg/l for Fl, Ph, An, Pyr, B(a)An,Cry, B(a)P

TABLE 3 Elutio of total concentration of PAHs (Fl, Ph, An, F, B(a)An, Cry, B(k)F, B(a)P, dB(g,h,I)P) with time at 12 sediment: water mixing ratios (1:1–1:256). Total PAH concentrations (µg/l) in the elutriates of the creosote-contaminated "site 13" sediment of ratios from 1:1 to 1:256 in 24, 120 and 500h desorption test.

Mixing ratio (vol/vol, ww)	Desorption time (h)		
	24	120	500
1:1	1693 ± 25	2315 ± 35	2360 ±30
1:2	1626 ± 22	2278 ± 38	2324 ± 35
1:4	1640 ± 27	2286 ± 32	2349 ± 32
1:8	434 ± 12	687 ± 15	729 ± 16
1:16	145 ± 8.0	255 ± 11	298 ± 13
1:24	104 ± 7.5	148 ± 9.8	163 ± 11
1:32	80.1 ± 4.8	94.8 ± 7.9	114 ± 10
1:48	41.8 ± 2.9	47.1 ± 3.1	53.0 ± 4.1
1:64	35.5 ± 2.8	40.3 ± 2.9	41.6 ± 3.1
1:96	23.3 ±.1.9	28.2± 2.0	28.9 ± 2.4
1:128	19.4 ± 2.6	21.4 ± 1.4	23.4 ± 2.1
1:256	6.79 ± 0.8	8.11 ± 1.1	9.20 ± 1.3

TABLE 4 Elutio of total concentration of PAHs (Fl, Ph, An, F, B(a)An, Cry, B(k)F, B(a)P, dB(g,h,I)P) with time at 12 sediment: water mixing ratios (1:1–1:256). The concentrations of the total PAHs (µg/l) in the elutriates of the PAH spiked (c 1 = 300 and c 2 = 3000 µg/g dw) sediment of ratios from 1:1 to 1:96 in 24, 120h and 500h desorption test. No PAHs were detected in ratio 1:256.

Mixing ratio (vol/vol, ww)	Desorption time (h)		
	24	120	500
1:1 c1	71.1 ± 6.7	85.9 ± 6.8	98.8 ± 7.0
c2	1443 ± 14	1849 ± 15	1968 ± 16
1:2 c1	61.5 ± 4.6	82.9 ± 5.9	92.3 ± 6.1
c2	1431 ± 12	1776 ± 15	1863 ± 14
1:4 c1	68.4 ± 4.9	85.2 ± 6.0	94.7 ± 7.1
c2	1411 ± 11	1792 ± 14	1882 ± 17
1:8 c1	24.1 ± 2.8	40.9 ± 3.8	51.5 ± 4.3
c2	749 ± 8.9	975 ± 9.9	1018 ± 10
1:16 c1	5.10 ± 0.7	13.7 ± 2.1	18.1 ± 3.4
c2	254 ± 9.0	311 ± 5.9	326 ± 6.0
1:24 c1	nd	10.8 ± 1.8	14.8 ± 2.1
c2	91.6 ± 8.4	113 ± 3.9	125 ± 4.0
1:32 c1	nd	nd	10.0 ± 2.0
c2	30.8 ± 4.9	38.8 ± 3.2	47.0 ± 3.6
1:48 c1	nd	nd	6.95 ± 0.9
c2	8.70 ± 0.6	12.3 + 1.0	19.0 ± 1.8
1:64 c1	nd	nd	nd
c2	5.85 ± 0.4	7.80 + 0.4	7.90 ± 0.7
1:96 c1	nd	nd	nd
c2	5.00± 0.5	7.00 ± 0.3	7.50 ± 0.5
1:128c1	nd	nd	nd
c2	nd	6.50 + 0.2	6.90 ± 0.3
1:256c1	nd	nd	nd
c2	nd	nd	nd

totalPAHs=fluorene(Fl), phenanthrene(Ph), anthracene(An), fluoranthene(F), benzo(a)anthrcene(B(a)An), chrysene(Cry), benzo(k)fluoranthene(B(k)F), benzo(a)pyrene(B(a)Pyr), dibenzo(g,h,I)perylene(dB(g,h,I)P, limit of determination was 5 µg/l

TABLE 5. Half desorption times (h) of three main PAH compounds in the creosote-contaminated lake sediment (Lake Jämsänvesi) at three mixing ratios with water (1:1, 1:24, 1:128). The elutriate of ratio 1:128 not contained dB(g,h,I)P.

compound	ratio (v/v)	half time (h)
Fl	1:1	13
	1:24	10
	1:128	10
B(k)F	1:1	8
	1:24	11
	1:128	11
dB(d,g,I)P	1:1	8
	1:24	61

TABLE 6. The relative amount (RA_{PAH} = total PAH concentration of the elutriate x mixing ratio) and relative desorption efficiency values (RDE) of total PAHs in elutriate of creosote-contaminated sediment ("site 13") in ratios from 1:1 to 1:256 in 500h desorption experiment. The RDE-values were calculated thus the value 1.00 given for the ratio 1:1.

Elutriate of sediment:water ratio (v/v)	RA_{PAH} (mg)	RDE
1:1	2.36	1.00
1:2	4.65	1.97
1:4	9.40	3.98
1:8	5.83	2.47
1:16	4.77	2.02
1:24	3.91	1.66
1:32	3.65	1.55
1:48	2.54	1.08
1:64	2.66	1.13
1:96	2.77	1.17
1:128	3.00	1.27
1:256	2.36	1.00

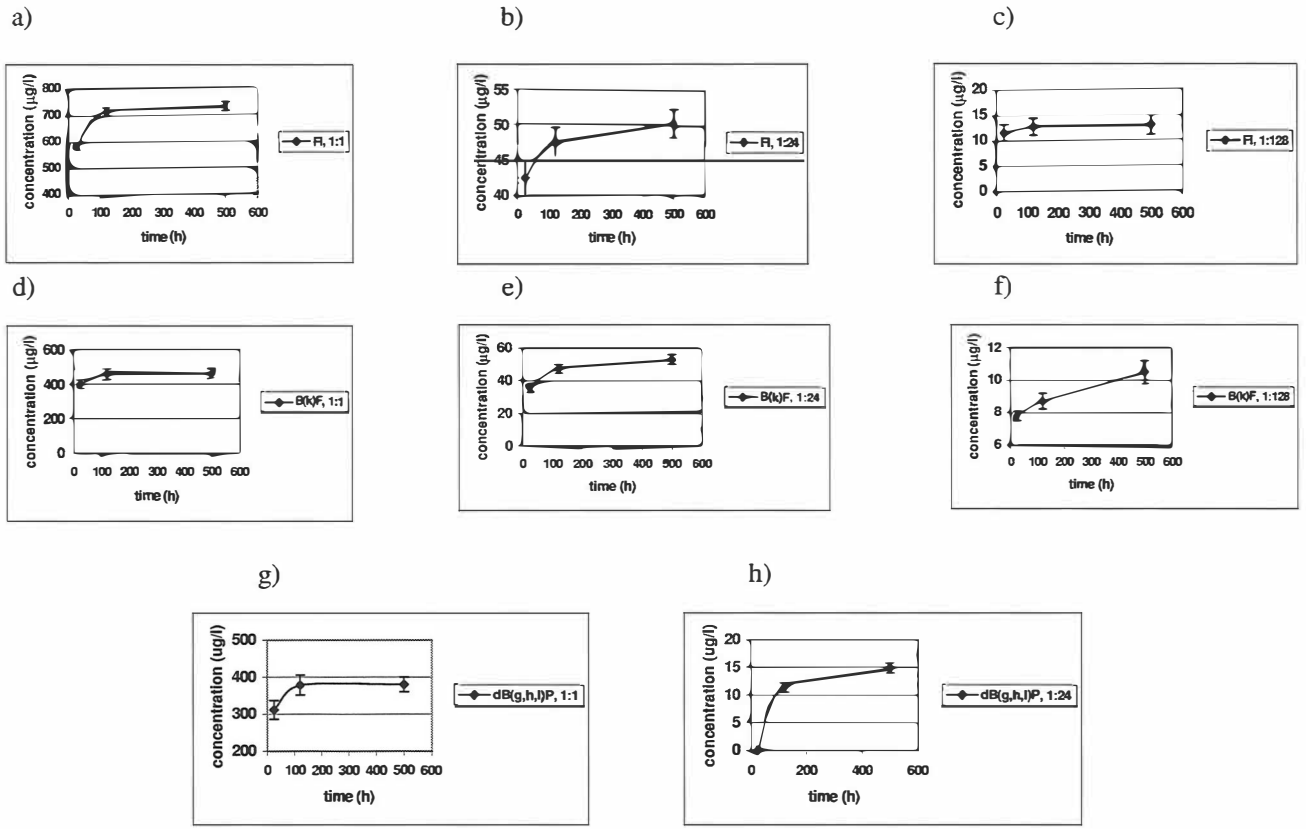

FIGURE 2 Desorption kinetics of main PAH-compounds (fluorene, benzo(k)fluoranthene and dibenzo(g,h,I)perylene) desorbed from creosote-contaminated sediment to water. Three sediment : water mixing ratios 1:1, 1:24 and 1:128 were studied. In the elutriate of ratio 1 : 128 not detected dB(g,h,I)P.

TABLE 7 The relative amount (RA_{PAH} = total PAH-concentration of the elutriates x mixing ratio) and relative desorption efficiency values (RDE) of total PAHs extracted by water in elutriate of PAH-spiked sediment (c1 = 300 µg/g dw, c2 = 3000 µg/g dw) in ratios from 1:1 to 1:256.

Elutriate sediment:water ratio (v/v)	RA_{PAH}(mg) c1	c2	RDE c1	c2
1:1	0.10	1.97	1.00	1.00
1:2	0.18	3.73	1.80	1.89
1:4	0.38	7.53	3.80	3.82
1:8	0.41	8.14	4.10	4.13
1:16	0.29	5.22	2.90	2.65
1:24	0.36	3.00	3.60	1.52
1:32	0.32	1.50	3.20	0.76
1:48	0.33	0.91	3.30	0.46
1:64	nd	0.51	nd	0.26
1:96	nd	0.72	nd	0.37
1:128	nd	0.88	nd	0.45
1:256	nd	nd	nd	nd

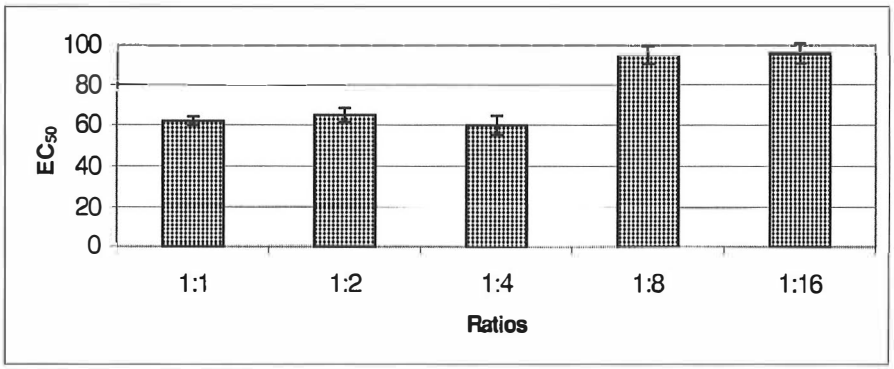

FIGURE 3 Toxicity (bioluminescence inhibition) of elutriates of settled particulate material (SPM) in SPM-collectors at the nearest site "downstream" (site 3) from the remediated sediment area of Lake Jämsänvesi. Elutriates of SPM were made for one hour at different mixing ratios. Mixing ratios from 1:24 to 1:256 were nontoxic (EC_{50} > 100 % vol).

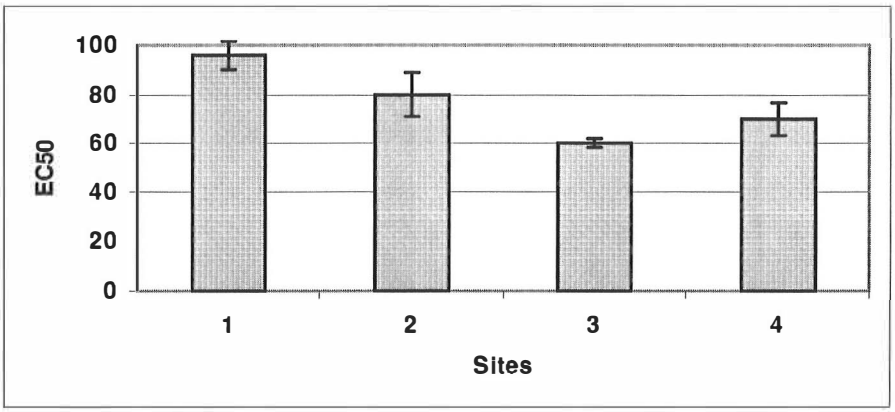

FIGURE 4 The EC_{50}-values (mean ± standard deviation) of the water inside the SPM-collectors for the "sites 1, 2, 3 and 4" measured as bacterial photoluminescence, see Fig. 1.

TABLE 8 Toxic unit (TU) values and the relative toxic emission yield (RTE) values for the elutriates of SPM from ratios 1:1 to 1:16.

elutriate of sediment:water ratio (v/v)	TU	RTE
1:1	1.6	1.6
1:2	1.5	3.0
1:4	1.7	6.8
1:8	1.1	8.8
1:16	1.0	16.0

IV

Assessment of the bioactivity of creosote-contaminated sediment by liver biotransformation system of rainbow trout

Hyötyläinen T. & Oikari A. 1999

Ecotoxicology and Environmental Safety 44: 253-258

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V

Biaccumulation of PAHs from creosote-contaminated sediment in a laboratory-exposed freshwater oligochaete, *Lumbriculus variegatus*

Hyötyläinen T. & Oikari A.

Manuscript

https://doi.org/10.1016/j.chemosphere.2004.05.001

VI

Biological and chemical assessment of remediation actions with caged mussels *(Anodonta anatina)* at a creosote-contaminated lake sediment site

Hyötyläinen T., Karels A. & Oikari A.

Water Research (submitted)

https://doi.org/10.1016/S0043-1354(02)00156-2