

IS THE ECOLOGICAL RISK OF CONTAMINATED SEDIMENTS BEING OVERESTIMATED BY CURRENT RISK ASSESSMENT PRACTICES? AN ILLUSTRATION USING NORWEGIAN HARBOURS

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Introduction

Ecological risk of contaminated sediments in both North America and Europe has traditionally been assessed by analysing the total contents of contaminants in sediments and comparing these to numerical sediment quality guidelines (SQGs).^{1,2} However, the assumptions used in the derivation of SQGs have been challenged as the generic solid-water distribution ratios used to determine SQGs can be underestimated by up to a factor of 1000. This underestimation follows from studies on strong sorption and consequent limited bioavailability of hydrophobic organic compounds (HOCs) in sediments and is caused by strong binding to ubiquitous anthropogenic carbonaceous particles.³⁻⁹

Thus, the SQGs presented in risk assessment frameworks can be overly conservative. The result is that SQGs may be used inappropriately such that contaminated sites could be erroneously prioritised for remediation. This unnecessary conservativeness can be avoided by using alternative approaches to the existing risk assessment framework which can estimate the bioavailable fraction: (i) the rapidly desorbing contaminant fraction using infinite-sink extraction methods, as well as (ii) freely dissolved concentrations using passive samplers.

In order to illustrate the assessment of actual risk, a case study comparing field-aged harbour sediments from Oslo, Drammen, Bergen and Tromsø was employed to represent a realistic risk assessment scenario of polycyclic aromatic hydrocarbons (PAHs) as model contaminants.

Materials and Methods

Sediment Sampling and Characterisation: Sediments were collected from four Norwegian harbours: Oslo (OS), Drammen (DR), Bergen (BG) and Tromsø (TR) (Figure 1) as described in Oen et al.¹⁰ These sediments are all PAH contaminated as a result of urban runoff, municipal wastewater discharges, shipping activities as well as historic industrial activities. Black carbon (BC; soot and charcoal) contents were determined by combustion at 375 °C followed by acidification.

Rapidly Desorbing Fraction: Desorption kinetics were determined by means of the Tenax solid-phase extraction method where Tenax serves as an infinite sink to all desorbed PAHs.^{11,12} Details are described by Oen et al.¹³

Freely Dissolved Concentrations: A slightly modified version of the Polyoxymethylene-Solid Phase Extraction (POM-SPE) method¹⁴ was employed where a POM-water-sediment system is shaken until equilibrium is reached. After the equilibrium time, the POM strips were analysed for PAH contents.¹⁵ Freely dissolved concentrations ($C_{w,free}$) were determined from the PAH contents in the POM, using concentration-independent POM-water distribution ratios, K_{POM} .

Results and Discussion

Sediment contamination investigations are usually the result of sampling in the surface sediment with subsequent chemical analysis of the total concentrations which are thereafter compared to SQGs. For HOCs, this comparison provides an indication of potential risk. Table 1 illustrates the potential risk of phenanthrene and benzo[a]pyrene for the four Norwegian harbour sediments investigated. As shown in the table, all values of the total concentrations exceed the SQGs.

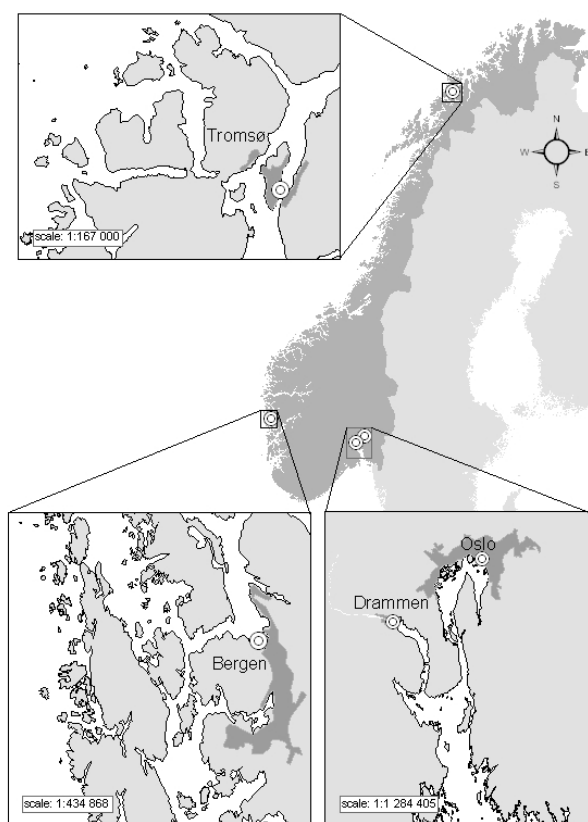


Figure 1. Map showing the location of the sampling sites in four Norwegian harbours.

Table 1. Sediment quality guidelines (SQGs) and the available concentrations calculated for phenanthrene and benzo[a]pyrene in Oslo (OS), Bergen (BG) and Tromsø (TR) sediment samples based on the total concentration in the sediment (C_s) and the rapidly desorbing fraction (F_{rapid}).

Sediment	SQG ($\mu\text{g}/\text{kg dw}$)	C_s^{13} ($\mu\text{g}/\text{kg dw}$)	F_{rapid}^{13} (%)	$C_{s,\text{available}}$ ($\mu\text{g}/\text{kg dw}$)
Phenanthrene	543 ^a			
OS		570	1.4	8
BG		4,600	2	92
TR		770	1	8
Benzo[a]pyrene	33 ^a			
OS		1,400	7	98
BG		6,900	2	138
TR		570	7	40

^aPresented SQG values are based on ecological risk and not human risk.¹⁶

Risk assessment based on Tenax extractions: The rapidly desorbing contaminant fraction extracted by Tenax has been shown to correlate well with bioavailability.¹⁶⁻¹⁸ In order to assess risk, the absolute magnitude of the bioavailable fraction or the available concentration ($C_{s,available}$) must be addressed. Values of $C_{s,available}$ can be obtained by either multiplying F_{rapid} with the PAH concentration in the sediment sample²⁰⁻²¹ or by measuring the amount extracted by Tenax in a "one-point" Tenax extraction.²² Table 1 presents the available concentrations for phenanthrene and benzo[a]pyrene in Oslo (OS), Bergen (BG) and Tromsø (TR) harbour sediment samples. The available concentrations should be compared to SQGs in order to assess actual risk (Table 1). For the studied sediments, all three harbour sediments show that the available concentrations for phenanthrene are below the SQG for this compound. On the other hand, the available concentrations for all of the sediments exceed the SQG for benzo[a]pyrene by a factor of 1.5-4. However, this represents an improvement over using the total sediment concentrations which were 20-200 times over the SQG value for benzo[a]pyrene. Thus, the uncertainty in risk assessments is reduced by using the rapidly desorbing fractions to correct for generic solid-water partition ratios.

Risk assessment based on freely dissolved concentrations: In the scientific literature there is a recommendation to directly measure freely dissolved concentrations in the sediment pore water or the aqueous environment using passive samplers and compare these values to aquatic toxicity data.²³⁻²⁵ For example, in the Norwegian Sediment Risk Assessment Guidelines¹⁶ the 5% Effect Concentration (EC5) is considered as an acceptable aqueous concentration for the protection of 95% of the ecological population. This EC5 value represents the toxicity-based water quality criteria (WQC) (Table 2). The WQC for each compound can subsequently be compared to measured values of $C_{w,free}$ as shown in Table 2 which reports $C_{w,free}$ values for phenanthrene and benzo[a]pyrene as determined by Cornelissen et al. (2006) for the four harbour sediments using the POM equilibrium extraction method. According to this comparison, the measurements of $C_{w,free}$ for phenanthrene were 1-3 orders of magnitude less than the WQC in all sediment samples. The measurements of $C_{w,free}$ for benzo[a]pyrene were less than the WQC for all sediments except the BG sediment sample. However, even for the OS and TR sediments samples, these $C_{w,free}$ were only just below the WQC which brings up another complex issue of interpreting results that are close to stringent cut-off values like WQC. Although this will not be further dealt with, it is something that should be kept in mind and can be overcome with assessments which use several lines-of-evidence.

Table 5. Water quality criteria (WQC) and freely dissolved concentrations ($C_{w,free}$) measured for phenanthrene and benzo[a]pyrene in Oslo (OS), Drammen, (DR), Bergen (BG) and Tromsø (TR) sediment samples.

Sediment	WQC ¹⁶ (ng/l)	$C_{w,free}$ ¹⁵ (ng/l)
Phenanthrene	3,200	
OS		16.8
DR		3.8
BG		128
TR		59
Benzo[a]pyrene	5	
OS		3.3
DR		0.33
BG		9.8
TR		2.8

Implications for risk assessment: Infinite-sink extraction methods like the Tenax method are advantageous as the available concentration can be calculated using the rapidly desorbing fraction, which can be determined within one day. However, such methods still utilise generic solid-water distribution ratios. Equilibrium extraction methods using passive samplers are probably advantageous because very low aqueous concentrations can be detected and they are simple, reproducible and inexpensive. Furthermore, they can be easily deployed in the

field. These methods have also been found to successfully measure freely dissolved concentrations of polychlorinated biphenyls and dioxins.

The future of conducting an ecological risk assessment lies in the ability of risk assessment strategies to account for bioavailability at an earlier phase in the assessment. This can effectively be accomplished by utilising passive samplers to measure freely dissolved concentrations (which can inexpensively and easily be conducted on several samples) in combination with toxicity and bioaccumulation studies on selected samples and organisms of interest to calibrate and verify the solid-phase extraction results. Including freely dissolved concentrations together with toxicological and biological assessments improves the current risk assessment framework and increases confidence in risk-based decisions regarding the allocation of resources for remediation efforts.

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