A SENSITIVE METHOD FOR DETECTION AND QUANTIFICATION OF PCB LEAKAGE FROM CONTAMINATED SITES TO SEA

Voie ØA, Johnsen A, Rossland HK, Longva KS

Norwegian Defence Research Establishment, Division Protection, P.O. Box 25, NO-2027 Kjeller, Norway

Introduction

The quantification of emissions of PCB from contaminated lands to sea is crucial for carrying out risk assessment and remediation action planning. However, such emissions are difficult to monitor and quantification is currently based on crude mathematical models that can bring along a great deal of uncertainty. Semipermeable membrane devices (SPMDs) have been proven useful for pollution monitoring, and for locating point sources.[1] An advantageous feature of this type of sampling is that low concentrations of PCBs can be detected. Another method that allows measurement of low concentrations of PCBs in water is a high-volume water sampling system.[2] The current study aims to monitor the leakage in a way that produces more exact results by introducing a physical barrier in the water just outside the contaminated site. The role of the physical barrier (a plastic fabric from the surface to the seabed) is to prohibit diffusion and dilution of the PCBs from the leakage with the surrounding seawater. Hence, water samples can be taken inside and outside the physical barrier and the concentrations of PCBs can be compared. If a leakage from the contaminated site is present, one should expect that the water samples taken from the water body inside the physical barrier have a higher concentration of PCBs than water samples taken outside of the barrier. The method was tested in connection with a larger investigation at the old demolished docks at the submarine pen in Laksevåg, Bergen.

Methods and Materials

The site of investigation is an old submarine pen constructed during World War II in Laksevåg, Bergen. After the war, three of the six docks were demolished. The other three docks are still in use. The demolished docks were filled with filling compounds that might contain PCBs. Currently there is a parking area covering most of the demolished docks. In spite of the filling compounds the tidal water seems to pass into the demolished docks. The Norwegian pollution control authority suspects that the submarine pen contributes to the high concentrations of PCBs that have been measured in the fjord sediments near by. A waterproof plastic fabric was arranged outside one of the demolished docks, attached to buoys at the surface and sandbags at the seabed (Fig. 1 and 2). The barrier was arranged in such a way that water was not allowed flowing through gaps or large holes. However, the nature of the area makes it hard to eliminate this possibility. Two weeks after the establishment of the barrier, water samples were taken. The water samples were taken by two methods; by a high-volume water sampling system, and by SPMDs. The high-volume water sampling system consists of a pump, a filter (1.0 µm cartridge filter from Millipore) and a XAD-2 column. The filter collects particle bound PCBs, while the XAD-2 column adsorb PCBs dissolved in the water. Water samples (500 l) were taken inside and outside the physical barrier shown in Figure 1 and 2. The XAD-2 samples were analysed by a congener specific method using dichloromethane extraction, cleanup with sulphuric acid and gel permeation chromatography (GPC) and analysis by GC/ECD. The filters were analysed in a similar way except for using heptane as an extraction medium. The SPMDs were supplied by Expometer AB, Sweden and were of a low-density polyethylene, layflat tubing, filled with triolein as described by Huckins et al, 2003.[3] The SPMDs were placed in their respective stainless steel cages and lowered down in the water column to tree meter below the water surface. Two SPMDs were deployed inside the physical barrier and three were deployed outside as shown in Figure 1. The SPMDs were analysed by a congener-specific method using solvent extraction, sulphuric acid cleanup and analysis by GC/ECD. The samples were analysed for PCB_7 (Seven Dutch) (#28, #52, #101, #118, #138, #153 and #180).

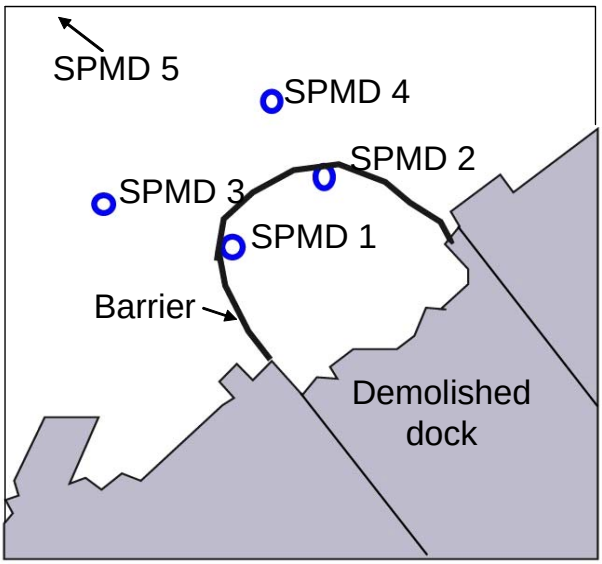

Fig. 1. Illustration showing the localization of SPMDs, and the physical barrier (black line), outside one of the demolished docks. SPMD 5 was a reference sampling station located about 2 km away from the site.

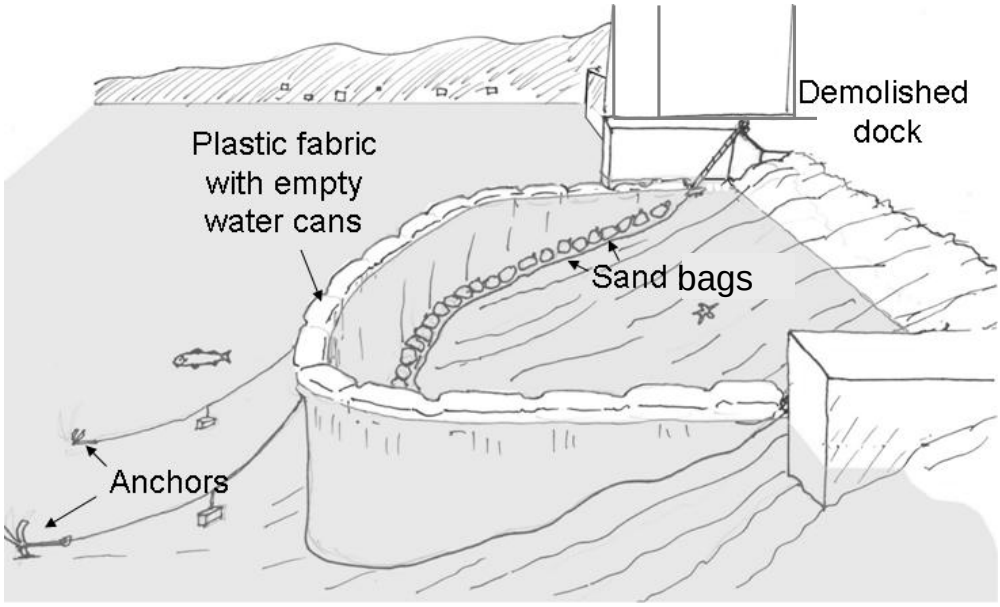

Fig. 2. Drawing of the physical barrier arranged outside one of the demolished docks (Drawing: Ø.A. Voie)

Results and Discussion

The water samples taken by the high-volume water sampling system revealed a higher concentration of PCBs inside the barrier than in the water outside the barrier (Table 1). The reference station was located 2 km away from the submarine pen. The reference station had about the same concentration as the station right outside the barrier. This indicates that PCBs have accumulated inside the barrier increasing the concentration by ~ 60 % in a period of 14 days.

Sample	#28 ng/l	#52 ng/l	#101 ng/l	#118 ng/l	#138 ng/l	#153 ng/l	#180 ng/l	PCB_7 ng/l
Reference	0,01	0,09	0,04	0,06	0,08	0,06	0,03	0,37
Outside barrier	0,13	0,17	0,01	0,04	0,04	0,03	< 0,01	0,42
Inside barrier	0,27	0,16	0,07	0,11	0,18	0,11	0,05	0,95

Table 1 Concentration of PCBs in water samples taken by a high-volume water sampling system.

The accumulated amount of PCBs in the SPMDs is shown in Table 1. The concentration of PCB_7 in the SPMDs 3, 4 and 5 (reference station), that were localized outside the physical barrier was 0.21, 0.29, and 0.18 ng/l respectively calculated from an extraction rate of 1.4 l/day (estimated). The concentration of PCB_7 in the SPMDs 1 and 2 that were localized inside the physical barrier was 0.99 and 0.70 ng/l. These results suggest a leakage from the demolished dock to the sea, increasing the concentration of PCBsin water by 60 – 80 % in a period of 14 days.

SPMDs	#28 ng	#52 ng	#101 ng	#118 ng	#138 ng	#153 ng	#180 ng	PCB_7 ng	PCB_7 ng/l
1	0,5	2,4	2,8	3,1	5,1	4,2	1,3	19,4	0,99
2	0,5	2,3	2,3	2,1	3,1	2,8	0,6	13,7	0,70
3	0,4	1,6	0,9	0,3	0,4	0,4	0,1	4,1	0,21
4	0,9	1,9	0,8	0,5	0,9	0,6	< 0,1	5,6	0,29
5	0,3	1,0	0,7	< 0,1	0,8	0,6	0,1	3,6	0,18

Table 1 Accumulated PCBs in the SPMDs and concentration in the water calculated from an extraction rate of 1.4 l/day.

Assuming that there is no dilution of the water inside the barrier, and estimating the volume inside the barrier to 975 000 l, and that the water concentration is increased by 0.55 ng/l gives a leakage rate of 38 µg/day. This is considered to be a rate of little environmental concern and indicates that the submarine pen site is no worse than other diffuse sources of PCBs in Bergen that are emitted to the fjord by the drainage water. Since the seabed under the barrier consisted of stones and concrete blocks, it is reason to believe that small gaps between the barrier and the bedside lead to an exchange of water from the outside of the barrier. To eliminate this uncertainty, tracers should be added inside the barrier in order to measure the dilution factor. This will possibly be carried out in the near future.

References

1. Sanchez-Hernandez JC, Borghini F, Corral A, Grimalt JO. *J Environ Mod* 2004; 6(11): 919
2. Suarez MP, Rifai HS, Palachek R, Dean K, Koenig L. *Chemosphere* 2006; 62(3): 417.
3. Huckins JN, Manuweera GK, Petty JD, Mackay D, Lebo JA. *Environ Sci Technol* 1993; 2489.