

### ABSTRACT

The Vefsn fjord in Northern Norway has received discharges containing polycyclic aromatic hydrocarbons (PAHs) for many years, in particular from smelting processes at Elkem Aluminium Mosjøen. Measurements of the availability of PAHs in sediments collected at 3 different points along the Vefsn fjord were made using silicone rubber passive samplers. The results were compared to direct measurements of the accumulation of PAHs by the marine polychaete, *Nereis virens* experimentally exposed to the contaminated sediments. The sediments were dominated by the 4- (~ 32%), 5- (~ 40%) and 6- (~ 20%) ring PAHs, which is typical of sediments from around aluminium smelters. The 4 to 6-ring compounds accounted for 93, 96 and 85 % of the PAH concentration in *N. virens* with a higher dominance of the 4 ring compounds (69%) at station 1 while the 5- and 6-ring PAHs dominated at stations 3 and 8 (~ 43% each). Biota sediment accumulation factors measured ranged from 0.01 to 4.6 kg oc per kg lipid with median values of 0.06, 0.04 and 0.01 kg oc per kg lipid at sampling station 1, 3 and 8 respectively. BSAFs calculated from pore water concentrations agreed better to those measured from the concentrations in the worms, than the theoretical BSAF value of ~ 1.



Fig 1: Sediment sampling stations within the Vefsn Fjord, 2006. Samples for this study were collected only at S1, S3 and S8. The Elkem Aluminium Smelting Co. is upstream of station 1 (S1). Sediment grab inset of map

### INTRODUCTION

Persistent organic pollutants (POPs) with low water solubility like the PAHs have been shown to partition into particulates and accumulate in sediment (deBruyn and Gobas, 2004) from where they can be bioaccumulated by benthic organisms. The exchange or uptake into the organism is mainly via direct absorption of compounds in the water phase or indirectly from those adsorbed on the small grain size fraction of particles through the digestive system (Baumard *et al.*, 1998). Thus environmental concentrations are relevant in assessing the risks of contamination by POPs. There have been a few studies in recent times that aimed to look at the relationship between bioaccumulation and aqueous (free dissolved) water concentrations (Cornelissen *et al.*, 2006 and Oen *et al.*, 2006). The availability of PAHs in 3 contaminated marine sediments (from the Vefsn fjord, Norway, Fig 1) to a marine polychaete (*Nereis virens*, a ragworm) was therefore studied and the obtained results related to pore water concentrations from the application of the silicone rubber passive samplers to the same contaminated sediments.

### EXPERIMENTAL METHODS

#### Sediment Analyses

PAHs were extracted by sonication of sediment in DCM and methanol. The halogenated solvent was dried over Na<sub>2</sub>SO<sub>4</sub>, solvent exchanged into iso-hexane and reduced to a small volume. Separation of aromatic and aliphatics was by normal phase isocratic HPLC, followed by quantification using GC-MSD.

Total organic carbon (TOC), particle size distributions and water content were determined by standard methods.

#### Accumulation and determination of PAHs in *Nereis virens*

*N. virens* were acclimated for 8 days in constant temperature (CT) room, and then held for 15 days in 1L glass beakers containing test sediments (Fig 2). Worms were removed, cleaned and homogenised before analysis for PAHs by saponification in methanolic sodium hydroxide solution, followed by separation of aromatic and aliphatics by normal phase isocratic HPLC and quantification of 2- to 6-ring parent and alkylated PAHs by GC-MSD (Webster *et al.*, 2007).

#### Pore water concentrations

Sediment pore water concentrations, C<sub>pw</sub> (Fig 3) were determined as described in Yates *et al.* (2007)

All Analytical methods for sediment and biota are accredited at FRS to ISO17025.



Fig 2: Experimental set-up showing exposure of *N. virens* to test sediments.

### RESULTS AND DISCUSSION

The sediments were dominated by the 4- to 6-ring PAHs (~ 95 % at each station) which is typical of sediments from around aluminium smelters and this was similarly reflected in the body burdens of the worms, Fig 3, (93, 96 and 85 % at station 1, 3 and 8 respectively). However, the pore water concentrations determined using the silicone rubber sampler was dominated by the 4-ring PAHs with the 2- to 4-ring PAHs cumulatively accounting for ~ 96 % at each station.

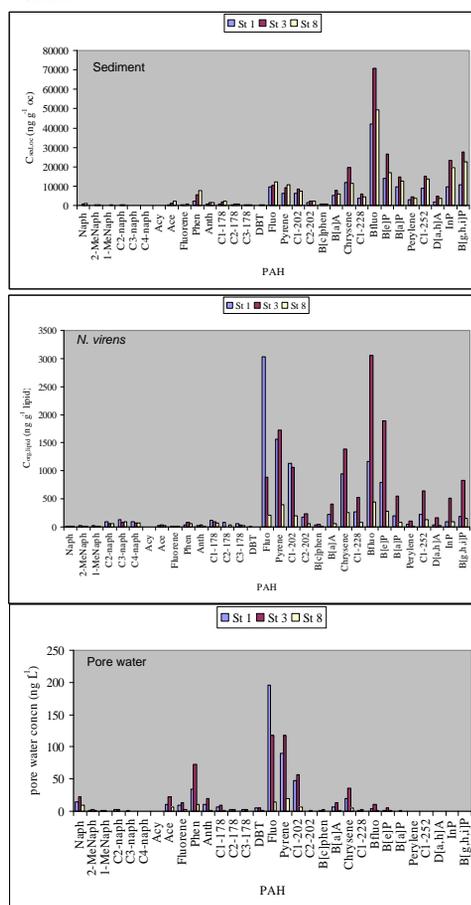


Fig 3: PAH concentrations in sediment samples (C<sub>sed,oc</sub>; top panel) and worms (C<sub>org,lipid</sub>; middle panel expressed as means of triplicate exposures) exposed to respective sediment. Pore water concentrations (ng L<sup>-1</sup>) determined using a silicone rubber sampler (bottom panel)

Biota-Sediment Accumulation Factors (BSAF) were calculated using equation 1 for the individual PAHs and sediments:

$$BSAF = \left( C_{org,lipid} / C_{sed,oc} \right) \quad (1)$$

Measured BSAFs (using Eq. 1) ranged from 0.01 to 4.6 kg oc per kg lipid with median values as 0.06, 0.04 and 0.01 kg oc/kg lipid at stations 1, 3 and 8 respectively. These are shown in Fig 4 for the individual PAHs and were a factor of 1 to 227 below the theoretical BSAF (~1) based on total sediment concentrations (Di Toro *et al.*, 1991). Measured BSAF was progressively lower in the heavier PAHs

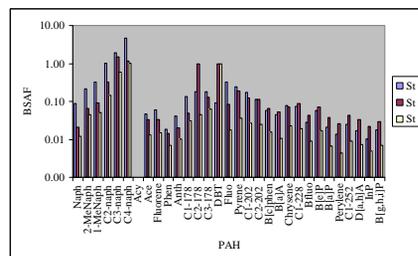


Fig 4: Measured BSAF for individual PAHs using the equation 1 above.

Measured C<sub>org,lip</sub> were also compared (Fig 5) to predicted C<sub>org,lip</sub>, estimated from log BCF = log K<sub>ow</sub> - 0.60 (EC TGD, 2003) and C<sub>pw</sub> using equation 2. The values found showed good agreement apart from the naphthalenes.

$$C_{org,lip} = BCF \cdot C_{pw} \quad (2)$$

BCF is the bioconcentration factor

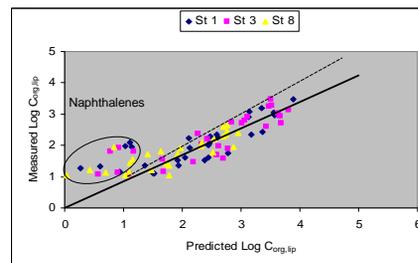


Fig 5: Measured log C<sub>org,lip</sub> versus predicted C<sub>org,lip</sub>. Naphthalenes deviated as observed in Fig 4. Drawn solid line is the observed relationship (Y=0.85X; r<sup>2</sup> = 0.78), while the broken line represents the expected 1:1 relationship.

### CONCLUSION

Equilibrium partition models based on pore water concentrations measured with silicone rubber samplers are better predictors of bioaccumulation in polychaetes than the sediment-organic carbon normalised concentrations.

### REFERENCES

- Baumard, P., Budzinski, H., and Garrigues, P. (1998) *Environ. Toxicol. Chem.*, Vol. 17, 765-766
- Cornelissen, G., Breedveld, G. D., Næs, K. O., Oen, A. M. P., and Ruus, A. (2006) *Environ. Toxicol. Chem.*, Vol. 25, 2349- 2355
- deBruyn, A. M. H., and Gobas, F. A. P. C. (2004) *Ecological Modelling*, Vol. 179, 405-416
- Di Toro, D. M., Zarba, C. S., Hansen, D. J., Berry, W. J., Swartz, R. C., Cowan, C. E., Pavlou, S. P., Allen, H. E., Thomas, N. A., and Paquin, P. R., (1991) *Environ. Toxicol. Chem.*, Vol. 10, 1541-1583
- EC Technical Guidance Document on Risk Assessment, Part III, EUR 20418 EN13, European Chemicals Bureau, 2003.
- Oen, A. M. P., Schaanning, M., Ruus, A., Cornelissen, G., Källqvist, T., and Breedveld, G. D. (2006) *Chemosphere*, Vol. 64, 1412-1420
- Webster, L., Russell, M., Phillips, L., McIntosh, A., Walsham P., Packer, G., Dalgarno, E. McKenzie, M., and Moffat C. (2007) *J. Environ. Monit.*, Vol. 9, 616-629
- Yates, K., Davies, I. M., L. Webster, L., Pollard, P., Lawton, L., and Moffat, C. F. (2007) ICES Annual Science Conference, Helsinki, Finland, September 17-21, 2007

The Authors would like to acknowledge Kristoffer Næs and his colleagues from NIVA for the opportunity to join them on the Field sampling aboard the *Fangst Molde*.