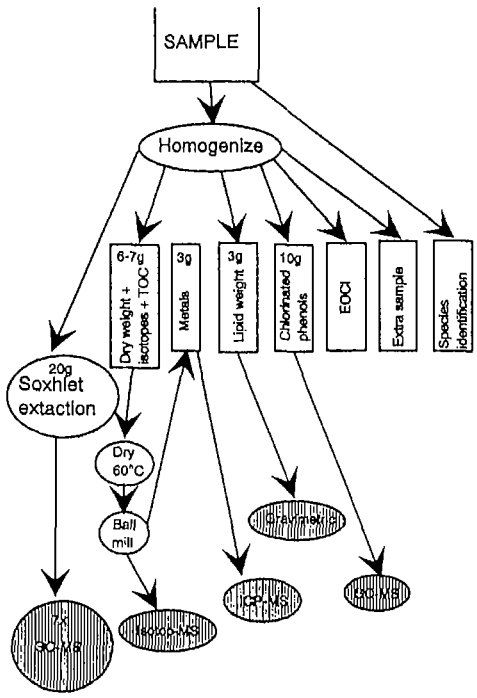
Multi-residue Analytical Method Including Planar PCB,Dioxins and other Organic Contaminants for Marine Samples.

Bergqvist P.-A.[1], Bandh C.[2,3], Broman D.[2], Ishaq R.[2,3], Lundgren K.[1], Näf C.[2], Pettersen H.[2,3], Rappe C.[1], Rolff C.[2], Strandberg B.[1], Zebühr Y.[3] and Zook D. R.[1],
[1]Institute of Environmental Chemistry, Umeå University, S-901 87 Umeå, Sweden.
[2]Aquatic Chemical Ecotoxikology, Department of Zoology, Stockholm University, S-106 91 Stockholm, Sweden.
[3]Department of Analytical Chemistry, Stockholm University, S-106 91 Stockholm, Sweden.

The "Gulf of Bothnia Year 1991" is a coordinated multidisciplinary project including over 100 subprojects initiated via a Swedish-Finnish cooperative for marine samples collected in 1991. One important aspect has been to study the accumulation and distribution of xenobiotic compounds in the Gulf of Bothnia food web. Two particular food chains and some additional species were selected for representation of organisms distributed throughout the entire gulf. Of two pelagic and six coastal locations, all but two have been suggested to be "non-contaminated" areas. The objective of this paper is to describe the sample handling and analytical method under development for this project and to give some results obtained from the validation study on selected samples. The sample handling strategies are given in Figure 1.



In some cases it is relatively easy to get large samples from the marine environment (e.g. sediment, seal tissue) but often the sample availability is very restricted (e.g. plankton, certain crustaceans). In this project several different species are to be studied, and often the quantity of available sample is limited. Since comparisons between compounds is of value for both discussions concerning differences in trophic levels and geographical variations, most of the target compounds are to be analysed from the same sample cleanup as efficiently as possible. For detection limit reasons the splitting of samples is avoided as much as possible. All organic target compounds, except phenolic compounds, are analysed in different fractions from the same original extract. Phenolic compounds, metals, extractable organic halogen and nitrogen and carbon isotopes are analysed from different subsamples.
Samples included in the Gulf of Bothnia project consist of organisms and other material from pelagic, benthic, and littoral food chains. The pelagic food chain sam-

ples include settling particulate matter, phytoplankton, zooplankton, mysids (*Mysis sp.*), and herring (*Clupea harengus*). The benthic food chain consists of surface sediment, settling particulate matter, isopods (*Saduria entomon*), amphipods (*Monoporeia affinis*), Fourhorn Sculpin (*Cottus quadricornis*); Perch (*Perca fluviatilis*) and juvenile Goosander (*Mergus merganser*). The organisms selected in this study provides the opportunity to study differences in profiles and patterns between species, locals, and compounds. The contaminant patterns observed should be representative for the given sampling area because these species has a limited migratory behaviour.

All samples are Soxhlet (Dean Stark) extracted with toluene followed by extraction with a mixture of acetone/hexane. The sample are spiked with more than 20 labeled standards before extraction. Lipid and water content is measured after each extraction. A separate subsample is extracted with acetone/hexane and hexane/diethylether for common lipid determination. To achieve good detection limits for all target compounds relatively large samples must be extracted thus giving large lipid extracts. A nondestructive reduction of the fat was employed including dialyses membranes with cyclopentane as the solvent as described earlier[1,2]. Lipid reduction of more than 99% can be achieved with as large lipid samples as 20g in one step.

After lipid reduction a 10% subsample was taken out for florisil separation (modification of Muir *et al.*)[3]. The separation was performed on a 10g florisil 1%(w/w) water deactivated column giving 4 fractions. The 90% subsample was fractionated on HPLC Amino column giving three fractions according to previously described method[4]. Fraction one is discharged and fraction three is used for the analyses of three- and up benzene ring polycyclic aromatic hydrocarbons. Fraction two is further fractionated on a HPLC carbon column (PX-21 carbon)[4]. After fractionation 10 injections on different mass spectrometer systems will be carried out. For organic contaminants 6 injections are performed on HRGC/LRMS and 2 injections on HRGC/HRMS. For analysing metals an ICP-MS will be used and for nitrogen and carbon isotopes a Isotope-MS.

The sediment and crustacean (monoporeia) samples were both sampled north of Gävle on the Swedish east coast. In table 1, 2, and 3 (below) some data on 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), planar- and monoortho polychlorinated biphenyls (PCB), polychlorinated dibenzothiophenes (PCDTs) and alkylated dibenzofurans (R-PCDFs) will be presented. A 42 gram dry weight (84 gram wet weight) sediment sample was extracted and the monoporeia sample was 106 gram (wet weight) containing 6.88 g soxhlet extracted lipids.

Table 1. Concentration of PCDDs and PCDFs in sediment and monoporeia. The results are given in pg/g dry weight and pg/g lipid weight respectively. The recovery for ^{13}C-labeled PCDDs and PCDFs was over 70%.

Sample type	Sediment	Monoporeia
2,3,7,8-TCDF	5.0	60
2,3,7,8-TCDD	1.1	11
1,2,3,7,8-PeCDF	2.1	25
2,3,4,7,8-PeCDF	3.6	48
1,2,3,7,8-PeCDD	1.1	10
1,2,3,4,7,9/1,2,3,4,7,8-HxCDF	2.0	7.7
1,2,3,6,7,8-HxCDF	1.6	6.3
1,2,3,7,8,9-HxCDF	<0.3	<3
2,3,4,6,7,8-HxCDF	1.6	3.8
1,2,3,4,7,8-HxCDD	0.40	<1.5
1,2,3,6,7,8-HxCDD	4.5	16
1,2,3,7,8,9-HxCDD	<0.4	<1.5

Table 1. (cont.)

1,2,3,4,6,7,8-HpCDF	95	64
1,2,3,4,7,8,9-HpCDF	2.6	<9.6
1,2,3,4,6,7,8-HpCDD	17	36
OCDF	12	<18
OCDD	15	42
N-TEQ	6pg/g	50pg/g

Table 2. Concentration of PCB target compounds in sediment and monoporeia. The results are given in ng/g dry weight and ng/g lipid respectively.

Sample type	Sediment	Monoporeia
PCB #77	0.020	1.1
PCB #126	0.004	0.9
PCB #169	0.001	0.6
PCB #105	0.17	5.4
PCB #118	0.50	18
PCB #101	0.24	21
PCB #153	0.52	60
N-TEQ (PCB #77, #126, #169)	0.4pg/g	100pg/g

Table 3. Concentration of other xenobiotic compounds in sediment and monoporeia. The results are given in ng/g dry weight and ng/g lipid respectively.

Sample type	Sediment	Monoporeia
o,p-DDD	0.016	2.2
p,p-DDD	0.028	1.6
o,p-DDT	0.017	0.060
p,p-DDT	0.19	0.86
o,p-DDE	ND	0.91
p,p-DDE	0.78	24
Trans-chlordane	0.005	0.69
Cis-chlordane	0.013	3.2
Trans-nonachlor	0.034	1.6
Cis-nonachlor	0.005	0.40
Heptachlorepoxide	0.008	1.2
Dieldrin	0.079	7.6

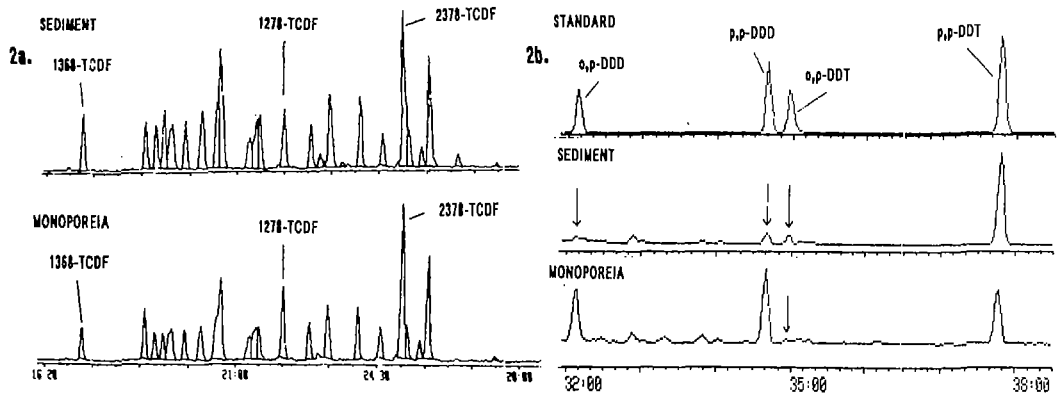
Table 4. Concentrations of PAH in sediment and Monoporeia. The results are given in ng/g dry weight and ng/g lipid weight respectively. Recovery of D_{10}-Pyrene and D_{12}-Chrysene was between 80% and 97%.

Sample type	Sediment	Monoporeia
Phenanthrene	59	50
3-methylphenanthrene	7	15
1-methylphenanthrene	8	14
Flouranthene	120	600
Pyrene	69	650
Benzo(ghi)Flouranthene	18	190

Table 4 cont.

Cyclopenta(cd)Pyrene	2	19
Benz(a)Anthracene	41	82
Chrysene/Triphenylene	98	510
Benzo(j+k)Flouranthene	270	410
Benzo(e)Pyrene	100	250
Benzo(a)Pyrene	55	60
Perylene	34	14
Indeno(1,2,3-cd)Pyrene	150	27
Benzo(ghi)Pyrene	62	27
Coronene	21	<2

The concentrations and patterns are similar between sediment and monoporeia. In figure 2a selected ion recording (SIR) chromatograms for tetrachlorinated dibenzofurans (m/z 306) show striking similarities, the same is observed for nonplanar PCBs (not shown). However apparent differences can also be seen, especially for metabolized DDT compounds shown in Figure 2b.



References

1 Bergqvist P-A, Strandberg B, Hjelt M, Rappe C. Nondestructive steps for the lipid reduction in PCDD and PCDF analyses. *Organohalogen compounds 2: Short papers presented at DIOXIN' 90.* Eds. O. Hutzinger and H. Fiedler. Ecoinforma press, Bayreught, FRG,1990

2 Huckins JN, Tubergen MW, Lebo JA,Gale RW, Schwartz TR. Polymeric film dialyses in organic solvent media for cleanup of organic contaminants. *J - Assoc Off Anal Chem* 1990;73:290-3.

3 Muir DCG, Norstrom RJ, Simon M. Organochlorine contaminants in Arctic marine food chains: accumulation of specific PCB congeners and chlordane-related compounds. *Environ Sci Technol* 1988;22:1071-9.

4 Zebühr Y, Näf C, Broman D, Lexén K, Colmsjö A, Östman C. Sampling techniques and clean up procedures for some complex environmental samples with respect to PCDDs and PCDFs and other organic contaminants. *Chemosphere* 1989;19:39-44

5 Lundgren K, Bergqvist P-A, Haglund P, Rappe C. Separation of polychlorinated polycyclic aromatic pollutants on a HPLC carbon column. Abstract submitted to Dioxin '92 meeting in Tampere, Finland.