NATUR
VÅRDS
VERKET

Forskningsprogram

SNAP ■ **REPROSA**□**E** **FLIPP** Inriktning: Ekonomis□ka styrmedel
Inriktning: Informationssystem oc□h
indikatorer IPP

Projekttitel (svensk): Gas-fas provtagning av luftföroreningar med SPMD diffusionsteknik för beskriva koncentration och toxicitet av lipofila ämnen i långtidsprover

Projekttitel (engelsk): Gas-phase sampling of air pollution with diffusive SPMD technique for describin concentrations and toxicity of long term average lipophilic samples.

Huvudsökande

Efternamn: Bergqvist	Förnamn:Per-Anders	Födelseår:195	Kvinna □ Man ■
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Medsökande

Efternamn, förnamn, tjänst, organisation, institution:		
Telefon:	E-post:	Kvinna □ Man □

Sammanfattning på **svenska** strukturerad enligt följande: 1) Projektets betydelse för programm
2) Miljörelevans och förväntad betydelse för miljöpolitiken 3) Mål och hypotes 4) Metodik oc
genomförande
5) Kommunikationsinsatser i relation till programmet:

Detta projekt avser att validera en provtagningsutrustning som kan beskriva lipofila luftföroreningar i gasfas inom ett exponeringsområde med betydligt tätare povtagning. Man ka då undvika de stora extrapoleringar som för närvarande används när enstaka högvolymsprovta representerar hela städer och stora (ej provtagna) tidsintervall. En enkel provtagningsteknik (SPMD) som bygger på diffusionsprovtagning föreslås. Koncentrerade extrakt från provtagare vilket normalt motsvarar mer än 200m^3 luft kan renframställas och användas i toxicitetstester i olika system. Detta sammantaget gör att man kan beskriva concentration och risker från luft vi olika tidsperioder och olika mindre områden i en stad. Tidigare har detta baserats på ffa partikl innehåll av luftföroreningar.
Möjligen har betydelsen av gasfasen av dessa lipofila ämnen underskattats enär kinetiken för a desorbera ämnen från partiklar är relativt långsam i miljön. Den direkt bioupptagbara fraktione är den som befinner sig i gasfas. Möjligen skall partikelgränsvärden kompletteras med gasfasvärden av även de ämnen som tidigare betraktats som partikelbundna.
Genom att validera SPMD provtagaren även vid kallt klimat (minus-grader) och att genomföra relevanta toxicitetstester (in vitro och carcinogenitetstest) kan kunskapsbasen för risker med exponering av luftföroreningar i gasfas enkelt studeras. Detta bör samordnas med annan verksamhet inom programmet så att mostvarande områden och effektparametrar studeras.
Kalibreringen av SPMD genomförs vid kontrollerade pumpförsök där samma luft tempereras t olika temperaturer och upptagskoefficienterna beräknas. Toxiciteten beräknas genom att beskr responsen per provtagen dag av det erhållna extraktet.
Genom deltagande i konferenser och publisering av erhållna resultat skall samhället informera
Inom programmet vill vi stimulera till en diskussion om biotillgängligheten av ämnen som framför allt är partikelbundna i luften. Ytor och partiklar spelar stor roll vid luftexponering, me kinetiken för desorption måste också vägas in.

	År 2004	År 2005
Summa sökta med per år i kr:	400.400	392.600

Sökta projektmedel fördelade på kostnadsslag	År 2004 (k	År 2005 (k
Personalkostnad inkl. soc. avgifter * 50% tjänst	180.000	180.000
Övriga omkostn exkl moms (förbrukningsmtrl, analyser, resor etc)** Experimentuppsättning frysutrustning mm Provtagningsutrustning, SPMD, Hi-Vol mm Standards Analysinstrument, lösningsmedel mm Resor vid provtagning Tox tester Adm kostnader, papper, telefon mm Publisering	 38.000 20.000 10.000 30.000 15.000 12.000 3.000	 20.000 30.000 15.000 35.000 12.000 10.000
Delsumma av ovanstående poster:	308.000	302.000
Förvaltningspåslag: ......30..... %	92.400	90.600
Totalsumma per år: (införs sid. 1):	400.400	392.600

*) Specificera namn, tjänst **) Specificera

Samtliga övriga miljörelaterade projekt för vilka de sökande har beviljats anslag eller söker anslag för 2004-2006. OBS Även EU-finansiering.

Projekttitel	Finansiär	Tidsperiod	Sökt kr	Beviljat kr

Miljörelaterade projekt för vilka sökande har beviljats anslag för 2000-2003
OBS Även EU-finansiering

Projekttitel	Finansiär	Tidsperiod	Beviljat Kr
The presence and risk of nitro-polycyclic aromatic hydrocarbons (nitro-PAHs)	EU FP4 INCO	-2002	900.000

Datum och sökandes underskrift, vilken samtidigt ger Naturvårdsverket tillåtelse att publicera sökandes namn på sin webbplats:	Datum och underskrift av prefekt eller motsvarande med namnförtydligande:

Gas-phase sampling of air pollution with diffusive SPMD technique for describing concentrations and toxicity of long term average lipophilic samples.

Objectives

To validate an SPMD air sampler for lipophilic organic compounds in gas-phase to be used in quantitative sampling on a local and regional scale. Time-weighted average concentrations of the pollutants can be compard with the particle-phase concentrations and the discussion on desorption kinetics and bioavaibility of air pollutants can be initiated. The average concentrations of air pollutants can then be extracted and used in toxicity tests. The test systems has to be harmonized with current tests performed in the program.

The goal is to have a quantitative sampler, which works in Swedish cold climates and accurately describes the gas-phase exposure and air toxicity. This should be simple to perform and have a good surface coverage as well as time coverage.

Background

Passive diffusive sampling have predominantly been an area for sampling of gaseous compounds in air, where first samplers were developed in the late 60ies, such as the well known Palmes tube for NO2 in air. The high diffusion rate of gaseous compounds in air makes diffusion an attractive sampling technique, as the sampling rate can be up to several litres per hour for a well designed passive sampler. The theoretical basis of uptake dynamics of gasses in air is now pretty well understood, as this relies basically on diffusion theory, and diffusion of gasses is reasonably simple to model compared to molecules in fluids. Samplers are cheap and easy to manufacture and avoids the need for expensive field sampling equipment (pumps, sample changers etc.).

Diffusive samplers have been used for integrative measurements of several air pollutants in indoor environments as well as ambient, outdoor environments ranging from remote areas to urban areas. The advantages of a diffusive sampling technique is that it does not require maintenance or electricity, has a long operating time and therefore can be used to determine time-weighted average (TWA) concentrations. In a semipermeable membrane device (SPMD), diffusive sampling is achieved by physical absorption in a membrane, or diffusion through the membrane, and absorption into triolein (a neutral lipid found in most aquatic organisms). The sampling rate, R_S, is affected by the physicochemical properties of the compound sampled, the design of sampler and the environmental conditions. Temperature and biofouling has an effect on the SPMD sampling in water as well. Both temperature and wind-speed are expected to affect the SPMD sampling in air in a similar way as in water whereas the effect of biofouling is expected to be negligible. One way to reduce the effects of environmental variables during SPMD sampling in air, is to protect the SPMDs from direct exposure to e.g. wind.

In water the R_S of SPMD is generally calibrated at given temperatures prior to use, as was made by Huckins. To our knowledge, the calibration data of SPMDs in air is limited to one study by Ockenden et al. that reported field-calibrated R_S of six PCBs and another study by Shoeib and Harner suggesting R_S for a number of PCBs, and SPMDs have mostly been used to compare the between-site differences in the amounts absorbed by the SPMD.

When the SPMDs are calibrated prior to use, many different exposure situations, and a number of compounds have to be tested. Huckins et al. proposed the use of performance reference compounds, PRCs, to calibrate the SPMDs *in situ* and thereby assess the actual sampling conditions. PRCs are compounds which are not naturally occurring in the environment, have moderate to high log K_{OA} values, and are added to the lipid-phase of the SPMDs prior to use. The theory of the PRC approach is that the release rates of these compounds are related to the uptake rates of the native compounds sampled.

International connection

Environmental chemistry in Umeå has established a bilateral cooperation with Environmental Engineering at Kaunas University in Lithuania. This department (Dr. Linas Kliucininkas) was earlier responsible for implementing the air monitoring structure, evaluation and running the instruments for Kaunas city. Today the department is working with city air pollution e.g. BTEX and PAH and connect the results with city planning tools.

The cooperation is establishment of PhD-sandwish program, where PhD-students from Kaunas spend 4-6 month per year at Umeå University cooperating with researchers and PhD-students at both departments. The present application will utilize this coopoeration and one PhD-sandwish student (Ms Aurelija Cicenaite) should be directly involved.

The international group of scientists working with research regarding diffusive SPMD air sampling are not large today but growing. The applicant has close contact with James Huckins and Jim Petty at USGS in USA, Kees Booij in Holland, Jochen Müller in Australia, Tom Harner in Canada and Kevin Jones in Great Britain. Per-Anders Bergqvist is also the initiator and in Scientific commite of 1st European SPMD workshop 2002 and 1st International passive sampling workshop and symposium, April 2004.

Theory

The principle of diffusive sampling relies on the formation of a steady state concentration gradient and diffusion controlled mass transport, which is described by the flux of molecules (dm/dt) over the concentration gradient (dC/dz) by Fick's 1st law of diffusion in eq 1.

$$Flux = \frac{dm}{A \cdot dt} = - \cdot D \frac{dC}{dz} \qquad (1)$$

The concentration (Co) of ions outside the sampler may be estimated by integrating eq 1, forming eq 2 for time integrated mass uptake (m(t)). The terms L, D and A are constants: the diffusion coefficient (D, cm2 sec-1 specific to each metal ion), the length (L, cm) and cross section area (A, cm2) of the diffusion membrane.

$$m(t) = (Co - Ci) \cdot t \cdot D \cdot \frac{A}{L} \qquad (2)$$

where the uptake is proportional to the difference between the outside and inside concentration of the compound (Co – Ci) over the diffusive membrane used in the sampler. If the sampler absorbent is an efficient sink for ions (i.e. the concentration of ions at the absorbent surface approximates zero (Ci~0) and no back diffusion occurs), the Ci term is zero or close to that, so that the basic expression for diffusive sampling reduces to eq 3 where we solve eq 2 for concentration:

$$Co = \frac{x}{t} \cdot \frac{L}{DA} \qquad (3)$$

The L term in eq 2 and 3 must be expanded summing up the total length of the diffusion layer, i.e. the thickness of the gel membrane (G), the filter (f) and the diffusive boundary layer (δ) forming eq 4. The DA/L term in eq 2 represents the uptake rate factor (cm3 sec-1). For ions with typical D values of 5E-6 cm2 sec-1 uptake rates are in the order of ~0.5 ml per h or ~12 ml per 24h at 25 oC (using the typical dimensions of the sampler: A=3.14 cm2 and L=G+f+δ =1020 µm). The uptake rate is not a sampling rate in the sense normally thought of, but the volume of water "diffusively emptied" of ions per time unit.

Time averaged concentration $$Co = \frac{m}{t} \cdot \frac{(G + f + \delta)}{DA} \qquad (4)$$

Diffusion coefficients depend on temperature (T) and viscosity (η) and adjustments of D are done by the Stokes-Einstein equation (eq 5

Stokes-Einstein correction of D $$\frac{D_t \eta_t}{T_t} = \frac{D_O \eta_O}{T_O} \qquad (5)$$

Method

Sampling method

The SPMD sampling is easy to perform. The membranes are deployed in the air at a height of 2-3 meter. Measurements of temperature, wind speed, wind direction, humidity and pressure can be done simultaneously with continuous measures. For the membrane sampling no electricity or maintenance are needed during the whole sampling period. This opens the possibility to deploy samplers at several locations in the investigation area instead one expensive sampling station representing a large area. SPMD sampling retains gas phase concentrations, which is more readily available for uptake into organisms during the exposure. The TWA-value (time-weighted average) also describes a long-term exposure, which is achieved by this diffusive sampling method. In figure 1 the deployment device is shown. The sampling continues for typically 2-3 weeks and then the membranes are stored in freezer until extraction and analysis which can be postponed several years if necessary. The sampler is currently used in cooperation with YMK, Göteborg University in the Hagfors study.
Field sampling periods in this study should be coordinated in time with other activities in the program in order to obtain comparison data for both chemistry and for health effects. This has previously been discussed with Dr. Bertil Forsberg at Umeå University.

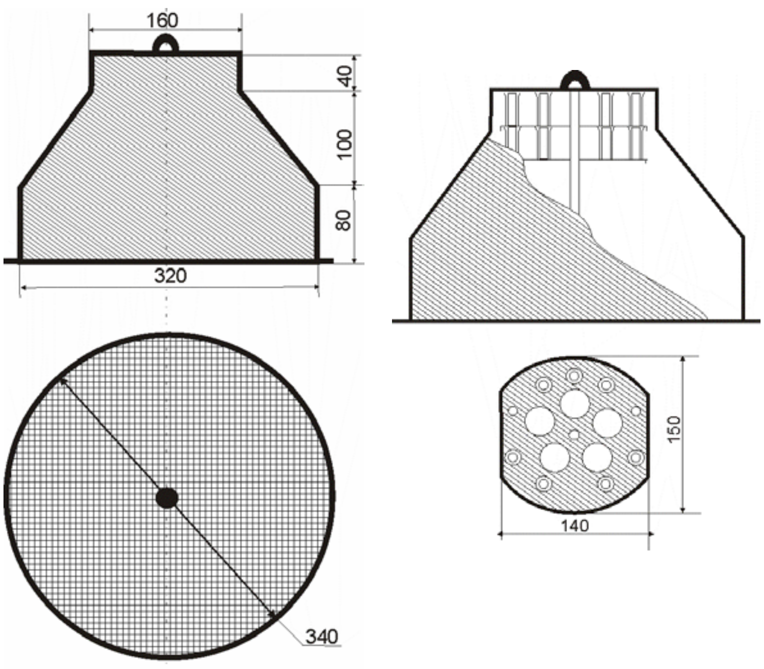

Figure 1. Deployment device for SPMD membrane sampling in air where the SPMD is deployed on the spider is shown in bottom right drawing.

Cold climate (below zero) sampling

In this study a method validation is suggested for calibrating the SPMD sampler for cold (freezing) conditions. This has not been performed earlier and are of great importance for allowing quantitative samplings year-around in Sweden. Many specific sources is increasing during winter (biofuel, automobile exhaust etc.) and the Swedish situation is serious due to both effluents and to exposure during winter situations.
The quantitative sampling rates, which are described above) can be studied by an experimental setup where polluted cold air is pumped into cooling tanks (calibrated freezers) at different temperatures. The same polluted air should be used simultaneously in this investigation. Smaller than standard size SPMDs can be used for allowing less air to be cooled to the different temperatures (-20, -10, 0, +4). During this investigation performance reference compounds (PRCs) should be used. A parallel sampling with high-volume gas sampler can be performed at the same site. By this experimental setup

the K_{SPMD-a} constant can be calculated and then the K_e value can be estimated by using the results from PRC measurements.

<u>Analysis</u>

The analysis of accumulated compounds in the membrane is usually performed with HPLC or GC methods. Below is an example of an earlier performed pilot study in Lithuania which we did 2002. The gas phase concentration of polycyclic aromatic compounds (PAHs) and alkylated PAHs were analysed by GC/MS. In figure 2 are the results from city air at four sites presented. The five- and six-ringed PAH are of course low in gas-phase concentration, but it is possible to measure them. Since the gas-phase is readily exposing humans (no desorption from carbon particles is needed) this fraction can be of great interest. In figure 3 is the composition of alkyl-PAH compared with PAH compounds at different distances from a refinery, which in this case serve as an example of different pollution source of PAH compounds. The alkylated PAH is closely related to petrogenic effluents. The ratio for R-PAH is decreasing with distance from the petrogenic pollution source. In another study we have analyzed reten, which is a marker for biofuel burning.

In this study we plan to use both HPLC and GC/MS analysis dependent on the question. When PRCs are used GC/MS is the most suitable analytical method, since we added deuterated PAH as PRC into the membrane. In the same study we plan to analyze for polychlorinated biphenyls and some oil products. Many lipophilic compounds can thus not be analyzed, since we do not know the composition. In that case the use of toxicity tests for identifying which air sample is contaminated can be of great importance.

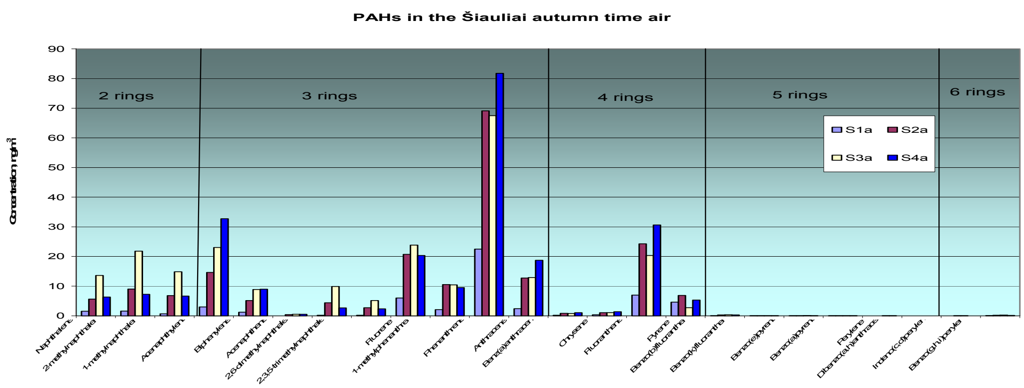

Figure 2. PAH concentrations in Šiauliai autumn period.
S – Šiauliai city; number with letters (for e.g. S1) – sampling place number; a – autumn period;

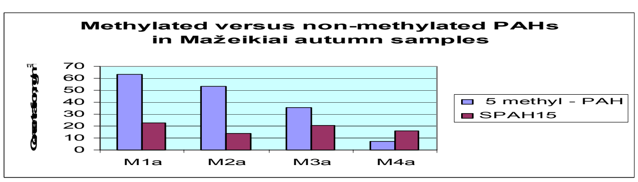

Figure 3. Comparison of methylated and unsubstituted PAHs in Mažeikiai autumn sampling sites. SPAH15 = ΣPAH_{15} (EPA PAH_{16} without naphthalene)
M – Mažeikiai oil refinery; number with letters (for e.g. M1) – sampling place number; a – autumn period

<u>Extracts for toxicity testing</u>

The extracts are based on lipophilic extraction of accumulated compounds in the SPMD during the whole sampling period. After extraction the extract can be transferred to a suitable carrier to be used directly in the selected toxicity test. If a cleaner extract is necessary, gel permeation chromatography is efficient and this extract is transferred to the carrier solvent and applied to the test system. DMSO, acetone and peanut oil is commonly used carriers, depending on test system. Not all gas-phase compounds is sampled nor are they extracted and retained in the test extract, but the method is developed for retaining the most bioconcentrable compounds from air.

Toxicity testing

- *In vitro* test system to be decided.
- Mutagenicity test (Ames test or Mutatox® or UMU-test or...)

For performing the toxicity test several different methods of administering the extracts can be found in the literature. The applicant has previously used Microtox, Daphnia, fish egg injections and cell cultures for describing the toxicity of extracts from water sampling. In this project a discussion with the program board is suitable to use similar test system as other groups do in the program.

Deliverables

- An understanding of diffusive air sampling with SPMD in cold climate.
- An understanding of performance reference compounds (PRCs) in passive sampling devices.
- Provide extracts of gaseous air pollutants for *in vitro* toxicity testing.
- Describe relative toxicity (from *in vitro* toxicity testing) of air sampled as exposure to time weighted average concentrations during several weeks at selected locations.
- Sampling rates and equilibrium between SPMD and air (R_s and $K_{SPMD\text{-}a}$) of gaseous PAH, PCB and other organic compounds.
- Validate a quantitative tool for TWA sampling of gaseous liphophilic pollutants which is simple to use, for describing exposure differences in a geographic area.

Information

We intend to publish results in peer reviewed international journals and present results at conferences. Provide the community with SPMD sampling rates (R_s) at lower temperatures to add to existing database which is covering higher temperatures (8-26ºC).
Give one basis for discussion at seminars on the comparable relevance of particle-bound and gaseous pollutant exposures to human and other organisms.

Timeplan

	Spring 2004	Autumn 2004	Spring 2005	Autumn 2005
Develop exposure chamber	x			
Sampling cold temperature		x		
Analysis of samples		x	x	
Field sampling			x	
Prep. of extracts		x	x	
Toxicity testing			x	x
PRC eval.			x	x
Litterature search	x	x	x	x
Report & publ.			x	x

CURRICULUM VITAE

Name: Per-Anders Bergqvist, Place of birth: Härnösand, Sweden
Natl. Nr.: 560324-7874 Marital status: Single

Education and work

1977-1981 Batchelor degree in chemistry with environmental chemistry and occupational hygiene, Umeå Universitet

19980612 Dissertation at Institute of Environmental Chemistry, Umeå Universitet
Ph.D. in Environmental Chemistry, Umeå Universitet

19991101-20011231 Director of undergraduate studies at Umeå school of the Environment, resercher and lecturer at Center for Interdisciplinary studies, Umeå Universitet. Director of Baltic University Program in Sweden until 2001-12-31

2002-07-01- Resercher and lecturer at Institute of Environmental Chemistry 100%

International work

1981 Columbia National Fisheries Contaminant Research Centre. Fish and Wildlife Service. USA. 3 month.
1983 Canadian Wildlife Service, Pesticide Research center. 2 månader. Consultant for developing semiautomatic cleanup method for the analysis of dioxins and other persistant organic pollutants.
1995 och 1997 Teaching at Czeck republic environmental ministry about pollutants and the environmental effects.
1998 Consultant for Vattenfall in connection to SwePol Link.

Ph.D. Per-Anders Bergqvist have been working with organic analytical chemistry in relation to environmental questions and xenobiotic compounds since 1980. The title of the Thesis was “Analysis and bioaccumulation of dioxins”. Have been leading some large projects as "Bioaccumulation and effects of extracts of naturally occurring xenobiotic compounds added to fish food." Which included 10 research groups, "Use of SPMD as an environmental sampling tool for lipophilic compounds." and "Accumulation and distribution of xenobiotic compounds in the Gulf of Bothnia." which has up to now resulted in 5 Ph.D. thesis’s.
Main interest during last years have been directed towards methods to expose organisms and *in vitro* tests with natural extracts from food sources, air, water and soil. Also studies of bioaccumulative compounds in the environment and the leachate of these compounds from different types of landfills and sediments utilizing integrative sampling methods as SPMD (for lipophilic compounds) and DGT (for metals). During the years he has developed several analytical methods for organic pollutants.

Teaching

He have been part time teaching at Organic Chemistry department (6 years), Environmental Protection and Public Health institute (19 years), Center for Interdisciplinary studies (9 years), Intstitute of Environmental Chemistry (13 years), Umeå Universitet as well as several other courses at Umeå University and Swedish agricultural university. Mainly courses in Environmental questions and sustainable development. During the year 2000 and 2001 he was on temporaty leave for fulfilling the position of Director of studies at Umeå school of the environment.

<u>Supervisor for project thesis 10p (more than 20)</u>
<u>Supervisor for master thesis D20p (more than 15)</u>

Participation in scientific conferences

1981 First specimen banking conference in Saarbrücken.
………………………………………..
2003 2nd Swedish-Norwegian Environmental Chemistry Winter meeting, Storlien, Sweden *
2004 1nd International Passive sampling Workshop and symposium *¥

2004 14th SETAC Europe in Prague, Czeck Republic ¥

* Organizer ¥ Scientific commite

Publications: More than 100 publications. See a selection below.

1. Bergqvist, P.-A. and Strandberg, L. Organiska miljögifter i mark och luftprover från omgivningarna runt Borlänge och SSAB under juni 1997 med SPMD-teknik. 1-12. 10-10-1997. Umeå, Institute of Environmental Chemistry. (GENERIC)
   Ref Type: Report

2. Strandberg B, Wågman N, Bergqvist P-A, Haglund P, Rappe C: Semipermeable membrane devices as passive samplers to determine organochlorine pollutants in compost. Environ.Sci.Technol. 1997; 31: 2960-2965.

3. Bergqvist P-A, Strandberg B, Ekelund R, Rappe C, Granmo Å: Temporal monitoring of organochlorine compounds in sea water by semipermeable membranes following a flooding episode in western Europe. 1998; (Environmental Science & Technolgy)

4. Bergqvist P-A, Strandberg B, Rappe C: Lipid removal with semipermeable membranes (SPMs) during chemical analysis of large samples. 1998; (Chemosphere)

5. Bergqvist, P.-A. and Strandberg, L. Mikrotox-toxicitet i vattenprover tagna i Umeälven i september 1996 med SPMD-teknik. 1-4. 1-1-1998. Umeå, Institute of Environmental Chemistry. (GENERIC)
   Ref Type: Report

6. Strandberg B, Bergqvist P-A, Rappe C: Dialysis with semipermeable membranes as an efficient lipid removal method in the analysis of bioaccumulative chemicals. Anal.Chem. 1998;

7. Norrgren L, Pettersson U, Örn S and Bergqvist PA (2000) Environmental monitoring of the Kafue River located in the copperbelt, Zambia. Arch. Env. Con. Tox. 38 334-341

8. Strandberg B, Bergqvist P-A, Rappe C: Dialysis with semipermeable membranes as an efficient lipid removal method in the analysis of bioaccumulative chemicals. Anal.Chem. 1998;

9. Oanh NTK, Bengtsson BE, Reutergardh LB, Hoa DT, Bergqvist PA, Broman D, Zebuhr Y Persistent organochlorines in the effluents from a chlorine-bleached kraft integrated pulp and paper mill in southeast Asia ARCHIVES OF ENVIRONMENTAL CONTAMINATION AND TOXICOLOGY 37 (3): 303-309 OCT 1999

10. Granmo Å, Ekelund R, Berggren M, Brorström-Lunden E, Bergqvist P-A. Temporal trend of organochlorine marine pollution indicated by concentrations in mussels, semipermeable membrane devices and sediment. Environ. Sci. Technol. 2000, 34, 3323-3329

11. Strandberg B, Bandh C, van Bavel B, Bergqvist PA, Broman D, Ishaq R, Naf C, Rappe C Organochlorine compounds in the Gulf of Bothnia: sediment and benthic species CHEMOSPHERE 2000, 40 (9-11): 1205-1211

12. Lindström A, Buerge IJ, Poiger T, Bergqvist P-A, Müller M and Buser H-R. Occurence and environmental behaviour of the bactericide Triclosan and its methyl derivative in surface water and in wastewater. Environ. Sci. Technol. 2002. 36, 2322-2329.

13. Poiger T, Lindstrom A, Buerge IJ, Buser HR, Bergqvist PA, Muller MD Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater CHIMIA 57 (1-2): 26-29 2003

14. Söderström H and Bergqvist P-A. Polycyclic aromatic hydrocarbons (PAHs) in a Semiaquatic Plant and Semipermeable membrane devices exposed to air in Thailand. . Environ. Sci. Technol. 2003 37 (1): 47-52

15. Söderström H and Bergqvist P-A. The effects of wind on diffusive sampling in air using Semipermeable Membrane Devices with Performance Reference Compounds. Submitted 2003

16. Söderström H and Bergqvist P-A. Semipermeable membrane devices exposed to different wind-speeds *in situ* calibrated by performance reference compounds. Submitted 2003