



UNIVERSITY OF NOVI SAD
FACULTY OF TECHNICAL SCIENCES „MIHAILO PUPIN“
ZRENJANIN, REPUBLIC OF SERBIA
in cooperation with
POLITEHNICA UNIVERSITY,
TIMISOARA, ROMANIA

PROCEEDINGS



2nd INTERNATIONAL CONFERENCE

„ECOLOGY OF URBAN AREAS 2012“

Zrenjanin, October 15th, 2012
Serbia



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II International Conference
„ECOLOGY OF URBAN AREAS 2012“

P R O C E E D I N G S

Ečka - Zrenjanin, Hunting Manor
15th October 2012

Organizer:

University of Novi Sad, Faculty of Technical Sciences "Mihajlo Pupin", Zrenjanin, Republic of Serbia

Co-organizer:

Politehnica University, Timisoara, Romania

Publisher:

University of Novi Sad, Faculty of Technical Sciences "Mihajlo Pupin"
Djure Djakovica bb, Zrenjanin, Republic of Serbia

For publisher:

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The Conference is supported by the Ministry of Education and Science of Republic of Serbia; Ministry of Environment, Mining and Spatial Planning of Republic of Serbia; Ministry of Economy and Regional Development of Republic of Serbia; Serbian Chamber of Commerce; Provincial Secretariat for Science and Technological Development; Provincial Secretariat for Protection of Environment and Sustainable Development.

ISBN 978-86-7672-172-6

CIP – Каталогизacija у публикацији
Библиотека Матице српске, Нови Сад

502.22:711.4(082)

INTERNATIONAL Conference "Ecology of Urban Areas 2012" (2; 2012; Ечка)

Proceedings [Elektronski izvor]/II International Conference "Ecology of Urban Areas 2012", Ечка – Zrenjanin, 15th October 2012; [organizers Faculty of Technical Sciences "Mihajlo Pupin", Zrenjanin and Politehnica University, Timisoara]. – Zrenjanin : Faculty of Technical Sciences "Mihajlo Pupin", 2012. - 1 elektronski opticki disk (CD-ROM): tekst; 12 cm

Str. 5: Introduction/Vjekoslav Sajfert. - Bibliografija

ISBN 978-86-7672-172-6

а) Урбана екологија - Зборници
COBISS.SR-ID 274586119

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INTRODUCTION

Science has a very important role in raising awareness of the importance of responsible use of natural resources and environmental protection. We, as scientists and individuals, should have a mission to find new ways for prevention of damage caused by rising levels of pollution, nuclear waste, depletion of non-renewable natural resources and to find a balance between rapid scientific and technological progress, on one hand, and protection of environment and health, on the other.

The Faculty of Technical Sciences “Mihajlo Pupin“ from Zrenjanin, as a part of the University of Novi Sad, in cooperation with the Politechnica University from Timisoara, Romania, has organized the Second International Conference “Ecology of Urban Areas 2012” (URBANECO 2012).

The conference is organized bearing in mind the importance of the ecological aspect in the sustainability of urban areas and its activities are aimed at the presentation of issues related to protection and development of urban areas in the region and beyond.

It aims to enable and expand regional and international cooperation between the University of Novi Sad and other educational institutions and businesses, especially the Politechnica University from Timisoara, thus increasing the level of professional and scientific activities at the Faculty of Technical Sciences “Mihajlo Pupin“ from Zrenjanin. We wish to engage research capacities in the region to solve the problems of protection of urban environment, to enhance the level of research in this area, and the interest of the economy for the introduction of new technologies.

The indirect aim of the project is the promotion of the Faculty of Technical Sciences from Zrenjanin as one of the bearers of economic and social development in the Banat region.

The aims of the International Conference “Ecology of Urban Areas 2012” are in full accordance with the priorities of the adopted Strategy for Sustainable Development as well as the Scientific and Technological Development Strategy of the Republic of Serbia.

Topics which will be dealt with at this year's conference are: Air quality, Management of solid urban waste, Water quality in urban areas (ground water, drinking water, waste water and facilities), System of ecological management (ISO 14000), Economics of sustainable development of urban areas, Noise and vibrations in urban areas, Electro and electro- magnetic pollution in urban areas, Climate changes and urban pollution, Transfer stations in the system of management of solid communal waste, Spatial planning and greening in urban areas, Development of urban ecology through educative and information activities, ICT in the ecology of urban areas, Accidents in urban areas, Environmental aspects of traffic in urban areas, Impact of agricultural activities to urban area and Public health and the ecology of urban areas.

We would like to express our gratitude to the Ministry of Environment, Mining and Spatial Planning of Serbia, the Ministry of Education and Science of Serbia, the Ministry of Economy and Regional Development of Serbia, Serbian Chamber of Commerce, Provincial Department of Science and Technology and Provincial Secretariat for Environmental Protection and Sustainable Development.

Finally, we wish to thank all the authors of papers and participants in the Conference in hope that we will continue our cooperation successfully in the future and that each new year will bring better ideas and solutions to help raise awareness of the responsibility we hold today for the well-being of future generations.

President of the Organizing Committee
Ph.D Vjekoslav Sajfert

Zrenjanin, October 2012.

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**II International Conference
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**METHODS USING PASSIVE SAMPLING TECHNIQUES IN
SEDIMENT**

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ABSTRACT

Sampling is the most important step of any analytical procedure. Errors committed at this stage cannot be corrected later during the analysis. There is a different specific methods, which depend on the nature of the analyte and their concentration levels. Solutions for this situation are methods of passive sampling and extraction of analytes, which involve measurement of the concentration of any analyte as a weighted average over the sampling and/or extraction time. The concentration of the analyte is integrated over the whole exposure time, making such a method immune to accidental, extreme variations of pollutant concentrations. Information obtained in this way is a suitable means of obtaining a long-term overview of pollutant levels in a environmental compartments. Techniques like Solid Phase Micro Extraction (SPME), Low Density Polyethylene- (LDPE), Silicon rubber- (PDMS) and POM- Solid Phase Extraction are applied to determine the pore water concentrations. TENAX extractions are used to estimate the available fraction, and In-vitro Passive Sampling (IVPS) gives an estimate of both pore water and available concentrations. Consequently, the partition coefficients of the compounds of interest for the available fraction in the sediment the are determined as well. The availability concept and how the different methods contribute to obtaining information on availability for uptake are discussed.

Key words: *passive sampling , sediment, SPME, TENAX, POM, PDMS, LDPE, IVPS.*

INTRODUCTION

Historically, environmental monitoring programs have tended to focus on organic chemicals, particularly those that are known to resist degradation, bioaccumulate in the fatty tissues of organisms, and have a known adverse toxicological effect.

Recently, it has been recognized that risks to aquatic and terrestrial organisms, including humans, are not limited to chemicals fitting the classical POP definition. An examination of the complex mixtures of chemicals present in natural water reveals the presence of organic chemicals covering a wide range of water solubilities and environmental half-lives. Many of these chemicals have been termed —emerging contaminants by the scientific community.

The first step in understanding the potential biological impact of ECs in the environment is to identify and quantify the types of ECs that are present. To do so, innovative sampling methodologies need to be coupled with analytical techniques which can confirm the identity of targeted and unknown chemicals at trace concentrations in complex environmental samples. (David A. Alvarez et.al. 2004)

The risk presented by hydrophobic ECs accumulated in sediment is not necessarily reflected by the concentration of the contaminants in the sediment, but rather by what can be released from the sediment to the water phase. The freely dissolved concentration in the water phase plays a key role in the uptake route for organisms, and exchange between the various compartments in the aqueous system (Foppe Smedes, 2007).

Partition coefficients can be applied to calculate freely dissolved concentrations from concentrations measured in sediment. Partition coefficients describe the ratio between the freely dissolved concentration in water phase and another environmental compartment (e.g. sediment) at equilibrium. For the sediment, the relevant constant is the sediment-water partition coefficient (K_{SED}).

For this purpose passive sampling has been introduced in several forms for the measuring of free dissolved concentrations (Mayer et al., 2003). In passive sampling, a reference phase (e.g. polyoxymethylate (POM) (Jonker and Koelmans 2001), polydimethylsiloxane (PDMS) (Mayer et al. 2000a and 2000b; Heringa and Hermens 2003) low density polyethylene (LDPE) (Müller et al., 2001; Booij et al. 2003) or TENAX (Cornelissen 1999, Ten Hulscher 2005) is introduced in a water/sediment suspension and shaken for an extended period of time. The sediment releases contaminants that are taken up by the reference phase. From the uptake, either the free dissolved concentration after equilibrium is estimated, or some measure of the releasable fraction is obtained (TENAX). These are both relevant for describing the risk of sediment contamination (Reichenberg and Mayer 2006). This paper describes the different passive sampling methods available for estimation of freely dissolved pore water concentrations of hydrophobic organic contaminants (Foppe Smedes, 2007).

SAMPLING METHODS

Development of a Sampling Plan

Obtaining a sample of the matrix of biotic and nonbiotic is an often-overlooked but vital component of any environmental monitoring program. Failure to properly collect a sample can invalidate any results subsequently obtained. The sample should be representative of the original environmental matrix (air, water, sediment, biota, etc.) and be free of any contamination arising during sample collection and transport to the analytical facility. The collection of a representative sample starts in the office or laboratory with the training of personnel and formulation of a sampling plan, moves to the field for the actual sampling, and ends with the shipment of the sample to the laboratory (David A. Alvarez et al. 2008).

A successful sampling strategy must begin with a thorough plan and established protocols. Areas of questions which need to be addressed while planning the sampling trip include: 1) selection of the sampling method to obtain a representative sample, 2) determination of the sample quantity needed to meet the minimum quantitation limits of the analytical method, 3) identification of quality control (QC) measures to be taken to address any bias introduced by the sample collection, 4) identification of safety measures that need to be taken, and 5) determination of sampling objectives. The study plan must define the chemicals to be assayed in the sample and sample size requirements of the analytical methods. Different extraction and processing procedures may be needed to isolate targeted chemical classes from each other and potential interferences, resulting in larger sample size requirements.

The field log should include sample collection procedures, location of the sampling sites on maps, global positioning system (GPS) coordinates or other data to identify the site(s), date and time samples were collected, types of QC that were used, and names of the personnel involved in the sample collection. Additional information on weather conditions during sampling, visible point sources of contamination and surrounding land use can be useful during the final interpretation of the data. Photographs of the sampling sites are often helpful.

Regardless of the type of sample matrix method used, issues of sample preservation, storage conditions and time, and shipping methods must be resolved. Samples should be collected with equipment made of stainless steel, aluminum, glass, or fluorocarbon polymers. Materials made of polyethylene, rubber, Tygon®, or other plastics should be avoided due to the potential for these materials to absorb or desorb targeted chemicals from/into the collected sample. Since plasticizers and flame retardants are commonly targeted ECs, plastics should not be used as they may contain high levels of these chemicals from the manufacturing process. To prevent alteration, samples are shipped

chilled (<4-6 °C) via overnight carrier to the laboratory and if ECs are potentially sensitive to UV radiation, amber bottles are used to prevent photodegradation. (David A. Alvarez et.al. 2004)

Time-Integrated Sampling Techniques

Passive sampling is based on free flow of analyte molecules from the sampled medium to a collecting medium as a result of a difference in chemical potentials. It can be used for the determination of both inorganic and organic compounds in a variety of matrices, including air, water and soil. The devices used for passive sampling are usually based on diffusion through a well-defined diffusion barrier or permeation through a membrane. Living organisms can also be used as passive samplers. In most cases, passive sampling vastly simplifies sampling and sample preparation, eliminates power requirements, and significantly reduces the costs of analysis. The technique is particularly suited to the determination of time-weighted average concentrations. (Tadeusz Górecki et.al., 2002)

Time-weighted average (TWA) concentrations of chemicals are commonly used to determine exposure, they are a fundamental part of an ecological risk assessment process for chemical stressors (Huckins et al., 2006). Since grab samples only represent the concentration of chemicals at the instant of sampling, TWA exposure is difficult to accurately estimate even with repetitive sampling. Episodic events are often missed with routine grab sampling schedules. In addition, the detection of trace concentrations of ECs can be problematic as standard methods are designed to handle small (<5 L) volumes of water. Passive sampling devices provide an alternative to grab sampling, overcoming many of the inherent limitations of those traditional techniques (David A. Alvarez et.al. 2004).

Integrative or equilibrium passive samplers can be used depending on their design, the exposure time in the field, and the properties of the targeted chemicals. Integrative samplers are characterized by having an infinite sink for the retention of sampled chemicals, providing a higher degree of assurance that episodic changes of chemical concentrations in the water will not be missed. The use of an integrative sampler is essential for the determination of TWA. (David A. Alvarez et.al. 2008).

PASSIVE SAMPLING METHODS

TENAX

About 1 g (dry weight) sediment is mixed with 50-100 ml water and shaken with the 1-1.5 g of pre-extracted TENAX for a selected time (Cornelissen et al., 2001). The pores of TENAX contain air which makes it float on water and can therefore be easily separated from the sediment suspension. Depending on the exposure time, different releasable fractions are extracted from the sediment; a rapidly desorbed fraction is considered to be extracted after 6 hours, a less available fraction after 24 hours, and a very slow fraction after 10-24 days (Noort et al., 2003). Since TENAX behaves as an infinite sink, i.e. the TENAX-water partition coefficients are infinitely large compared to the sediment-water coefficient, the results do not give information on the freely dissolved concentrations. By assuming that the rapidly desorbed amount ($C_{SED-RAP}$) represents the concentration bound to the regular organic matter (f_{OC}), this concentration can be combined with a generic value for K_{OC} for organic matter to calculate to a kind of estimate for the freely dissolve concentration (C_w) (1).

$$C_w = \frac{C_{SED-RAP}}{f_{OC} \cdot K_{OC}} \quad (1)$$

As the uncertainty of KOC is generally large, the values obtained for CW also will have large uncertainty (Foppe Smedes, 2007).

POM, PDMS and LDPE

The exposure procedure for reference phases other than TENAX is quite similar. A known mass of the reference phase is exposed to a sediment suspension while shaking. The shaking time is selected such

that equilibrium is obtained, typically 20–40 days. Using the reference phase-water partition coefficient (K_{SW}), an estimate of the freely dissolved concentration in the pore water is obtained (2).

$$C_w = \frac{C_s}{K_{SW}} \quad (2)$$

It should be noted that during the exposure period, the concentration in the sediment has decreased as a certain fraction of the contaminants accumulates in the reference phase. This fraction can be small, as in solid phase micro extraction (SPME) where only up to 1 μ l PDMS is used in combination with ~30g of sediment, or large as the solid phase extraction (SPE-POM) method described by Jonker and Koelmans (2001) where POM was exposed to almost equal amounts of sediment. In the latter situation, a considerable depletion of the contaminants in the sediment, compared to the initial conditions, may occur. Authors often correct for this by calculating a partition coefficient (K_{SED}) from the C_w obtained and the residual concentration in the sediment and use this, with the unaffected concentration in the sediment, to calculate the C_w in the unaffected situation. This extrapolation assumes a linear relationship between C_{SED} and C_w that passes through the origin, which is not necessarily an accurate reflection of the true situation (Foppe Smedes, 2007).

IVPS

In Vitro Passive Sampling (IVPS) uses PDMS and is in practical sense applied in a similar way as described above. However, the approach is different and may result in definition of a sorption isotherm, without assuming that the isotherm has any particular shape. In IVPS, the PDMS is coated on the wall of glass bottles and exposed to sediment suspensions in series of different ratios between Sediment and PDMS. A large amount of sediment with a small amount of PDMS will most closely reflect the original situation and lead to only a small decrease in C_{SED} and the estimate of C_w is almost unaffected by the experimental procedure.

Combination with data from exposures at intermediate ratios allows a sorption isotherm to be constructed. The remaining sediment concentration for each exposure ratio is calculated by subtracting the total amount in the exposed sediment by the amount that was accumulated in the PDMS. The isotherms obtained generally look like those depicted in Fig. 1. The x-axis represents the C_{SED} after exposure and the y-axis the C_w calculated from the concentration measure in the PDMS for each specific exposure ratio. Each point represents a different exposure ratio. Curve A shows a linear isotherm of a compound that follows ideal partitioning behavior. The inverse of the slope of the isotherm equals the partition coefficient. Line B shows a steep decrease in C_w for only a limited decrease in C_{SED} . The left part of curve B therefore represents a much higher partition coefficient than the right part.

Extrapolation of a straight line fitted through the points in case B intercepts the x-axis, and on the left side indicates the concentration that is limited or not available for exchange with the water phase. The portion of C_{SED} to the right from the intercept is probably held following the normal partitioning with regular organic matter (Foppe Smedes, 2007).

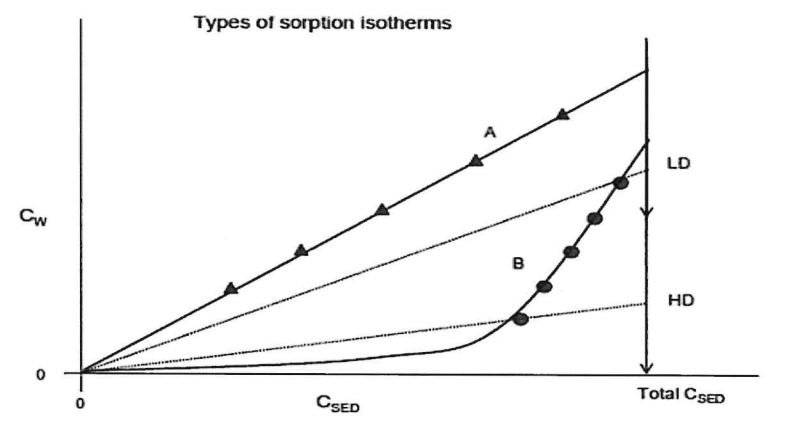


Figure 1. Sorption isotherms as observed by IVPS. On the x-axis, the concentration in the sediment (residual after exposure) is plotted (x axis) and on the y-axis the freely dissolved concentration calculated from the concentration in the PDMS. (A): linear isotherm and (B): non-linear isotherm. The line on the right side in the graph represents the total concentration in the sediment measured by a total extraction method, for example soxhlet extraction or accelerated solvent extraction (Foppe Smedes, 2007)

SUMMARY

Despite its relatively long history, passive sampling is still developing. It has many significant advantages, including simplicity, low cost, no need for expensive and sometimes complicated equipment, no power requirements, unattended operation, and the ability to produce accurate results. There are also some limitations that may sometimes be difficult to overcome, probably the most important of which is the possible effect of environmental conditions (such as temperature, air movement, and humidity) on the analyte uptake. Despite such concerns, many users find passive sampling an attractive alternative to more established sampling procedures.

Passive sampling methods like SPME, TENAX, POM, PDMS, LDPE, IVPS are used most often for the determination of concentrations, when the response time of the samplers is dictated by the length of the period studied. Once the measurement session is completed, however, passive sampling very often significantly simplifies further steps in the analytical procedure, as it generally combines sampling and sample preconcentration into a single step. Thus, with a few exceptions, passive sampling shortens the time between sample collection and analysis, improving the response time of the entire system.

Using passive sampling methods, the concentration of pharmaceuticals (caffeine) and pesticide (methomyl) have been monitored. The research is in the progress.

ACKNOWLEDGMENT

This research was supported by the Ministry of Education and Science, Republic of Serbia (III46009 and TR34014).

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