

Water sampling techniques for continuous monitoring of pesticides in water

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SUMMARY

Good ecological and chemical status of water represents the most important aim of the Water Framework Directive 2000/60/EC, which implies respect of water quality standards at the level of entire river basin (2008/105/EC and 2013/39/EC). This especially refers to the control of pesticide residues in surface waters. In order to achieve the set goals, a continuous monitoring program that should provide a comprehensive and interrelated overview of water status should be implemented. However, it demands the use of appropriate analysis techniques. Until now, the procedure for sampling and quantification of residual pesticide quantities in aquatic environment was based on the use of traditional sampling techniques that imply periodical collecting of individual samples. However, this type of sampling provides only a snapshot of the situation in regard to the presence of pollutants in water. As an alternative, the technique of passive sampling of pollutants in water, including pesticides has been introduced. Different samplers are available for pesticide sampling in surface water, depending on compounds. The technique itself is based on keeping a device in water over a longer period of time which varies from several days to several weeks, depending on the kind of compound. In this manner, the average concentrations of pollutants dissolved in water during a time period (time-weighted average concentrations, TWA) are obtained, which enables monitoring of trends in areal and seasonal variations. The use of these techniques also leads to an increase in sensitivity of analytical methods, considering that pre-concentration of analytes takes place within the sorption medium. However, the use of these techniques for determination of pesticide concentrations in real water environments requires calibration studies for the estimation of sampling rates (R_s). R_s is a volume of water per time, calculated as the product of overall mass transfer coefficient and area of the receiving phase exposed to the external environment, and it is substance specific.

Keywords: Pesticide residues; Water sampling; Monitoring; Sampling techniques

INTRODUCTION

“What is rare is expensive. Water, as the most important thing in the world, on the contrary, has no price.” (Plato, 427-347 BC)

From being a substance that is taken for granted, water has become a strategic natural resource of the highest importance in the 21st century. Water is a renewable resource that circulates in nature, passing through cycles of exploitation, use and discharge, and turning to atmospheric and then liquid water again. However, water changes during circulation, mostly negatively, by washing away various harmful substances and pollutants of biological, chemical or radiological origin. Given that human species and all life on our planet have depended directly on water quantity and quality, preservation of the remaining clean waters and pollution reduction during exploitation processes have become the basic goals.

Despite its significance, water is the least safeguarded and managed resource in the world (Fakayode, 2005), and due to different human activities, it is at the same time the most endangered basic natural resource. Endangerment of aquatic ecosystems by human activities taking place in catchment areas is more and more evident and more widespread, and agriculture has a special impact on water quality, preservation of water resources and the environment. The presence of organic contaminants in the environment has recently become a great concern, focusing on pesticides as emerging contaminants. Agricultural activity is the main pathway through which pesticides enter the aquatic environment. Besides its direct impact on the amount of available water, through consumption for irrigation purposes, agriculture also significantly affects the quality of water. Specifically, intensive agricultural production demands ever increasing applications of agrochemicals (pesticides and fertilizers), which lead to their accumulation in water. Runoff over fields, spray drift and infiltration caused by precipitation are the major causes of the presence of these agrochemicals in surface and ground waters, and as a consequence, residues of some harmful pesticides can be detected in water samples. Pesticide pollution can be not only problematic in terms of human health, but of endangerment of aquatic organisms as well. Therefore, it is necessary to control the presence of pollutants in aquatic ecosystems, devoting special attention to pesticide residues in surface waters.

In order to achieve this, it is necessary to implement a continuous monitoring program which should provide a comprehensive and interrelated overview of water status (WFD Guidance WG 2.7), which requires the application of appropriate sampling and determination techniques.

LEGAL FRAMEWORK FOR WATER PROTECTION IN THE EU AND SERBIA

Since the year 2000, water pollution and protection have been regulated in the European Union by the Water Framework Directive (WFD). The EU Directive 2000/60/EC installed a framework for the protection of aquatic environments and established a strategy against chemical pollution of water bodies. This directive represents a completely new approach to protection of aquatic ecosystems, it includes all water categories and all previous laws have now been incorporated in a single one. In addition, the directive regulates water use, it prevents pollution, protects waterways and enables fulfillment of international commitments relating to the presence of toxic substances in water.

Initially, the basic goal of the WFD was to ensure good chemical and ecological status of waters in the EU territory until December 2015, which was a precondition for sustainable development and use of water resources. However, due to weak realization of the set goals, the deadline has been extended to 2021. At the same time, the most important demands of the Directive are: a reduction in primary emission of pollutants and elimination of priority hazardous substances from aquatic ecosystems.

Additionally, the WFD obliges the EU Member States to identify pollutants of water basins as pollutants of national interest and to prescribe appropriate quality standards. After this, it is necessary to implement a continuous monitoring of surface water programs in order to identify a wide spectrum of pollutants, so as to assess the risks and take appropriate steps in time.

The establishment of a continuous monitoring program is also an obligation of candidate countries for EU membership. For surface waters, this protection is partly achieved by the daughter Directive 2008/105/EC through identification of a list of priority substances in the field of water policy, comprising 33 compounds, including 12 pesticides: alachlor, atrazine, simazine, isoproturon, trifluralin, diuron, chlorfenvinfos, chlorpyrifos, cyclodiene pesticides (aldrin, dieldrin, endrin, isodrin), DDT and endosulphan. The Directive also defines a list of substances that are subjected to review, including the pesticides bentazone, glyphosate, quinoxifen, mecoprop and dicophol. The Directive for the first time set Environmental Quality Standards (EQS) for priority substances in the EU.

The EU Water Framework Directive 2013/39/EC was introduced in August 2013, amending the EU Directives 2000/60/EC and 2008/105/EC. According to the latest one, priority substances comprise 45 pollutants, including 23 pesticides (herbicides: alachlor, atrazine, simazine, isoproturon, trifluralin, diuron, bentazone, glyphosate, mecoprop, alconifen, bifenox, terbutryn, cybutryne;

insecticides – chlorpheninfos, chlorpyrifos, ciclodien pesticides (aldrin, dieldrin, endrin, isodrin), DDT, endosulphan, dicofol, cypermethrin and dichlorvos; and the fungicide quinoxyfen).

Additionally, under Decision (EU) 2015/495, the European Commission introduced a new Watch List that requires monitoring of substances that might pose a risk at the EU level for which monitoring data have not yet been sufficient to confirm risks. Pesticides that are included on that list are oxadiazon, methidathion and neonicotinoids.

In addition to the EU WFD, a list of non-regulated environmental contaminants with potentially harmful effects, such as agrochemicals, pharmaceuticals, personal care products, industrial substance, etc., has been defined by NORMAN (a network of reference laboratories, research centers, and related organizations for monitoring of emerging environmental substances). NORMAN was founded in September 2005 and has been financially supported by the European Commission as a FP6 project. Since 2009, NORMAN network has become a permanent self-sustaining network (<http://www.norman-network.net>). The NORMAN list of substances ranks the frequency of their occurrence in the environment based on their toxicity and intensity of use, and includes over 700 substances.

In the NORMAN scheme, none of the substances is discarded from prioritization because of a lack of monitoring or toxicity data (Vrana et al., 2016).

According to FAO research, Serbia is on the 47th position among 180 world countries regarding the quantity and quality of its water resources, which means that we neither belong to a group of countries poor in water, nor to those rich in that resource as it was believed in previous decades. Similar to other developing countries, Serbia also treats these reserves in a quite non-economic and non-ecological manner. In our country, water protection and water pollution have been regulated by the Water Act in 2010 (Zakon o vodama, 2010), i.e. by the amended versions of 2012 and 2016, while the limit values for priority and priority hazardous substances in surface waters have been determined by the “Regulation on limit values for priority and priority hazardous substances that pollute surface waters and deadlines for their achievement” (Uredba, 2014). The current regulation has been harmonized with the WFD 2008/105/EC.

SAMPLING TECHNIQUES

Permanent monitoring of water resources is necessary in order to prevent water contamination and negative impact on the environment and various organisms. It implies a series of long-term standardized measurements, aiming to

define the status and changes in water quality and sediment for the purpose of collecting quantitative and qualitative data (distribution of pollutants, emission and immersion of pollutants, pollution sources, transport of pollutants, determination of concentrations at certain measuring points, etc.). It consists of a series of successive observations of environmental elements in space and time (Munn, 1973).

In order to achieve all that, it is necessary to use appropriate techniques for water sampling and analysis of pollutants. The use of extraction and analysis techniques is defined by the EU Directive 2009/90/EC and includes the application of standard methods, i.e. those validated in compliance with the standard ISO17025, and limits of quantification (LOQ) <30% EQS. However, the question of appropriate sampling techniques has also arisen. While the focus of research in recent years has been on the development of new and more sensitive analytical instruments and methods, less attention was paid to the development of appropriate sampling techniques.

So far, surface water sampling for determination of pesticide residues has been based on the application of traditional techniques (Lazić et al., 2010; Lazić et al., 2013; Grahovac et al., 2013). It implies periodical taking of a single sample or use of an autosampler to form a composite sample. However, both of these methods have a number of shortcomings. Primarily, they provide only temporary overview of pollutants present in water, and give inappropriate information on the variability of their concentrations. Also, they demand large amounts of water for determination of compounds present at low concentrations and the use of highly sensitive equipment during instrumental analysis. Another very important weakness is that it makes more difficult the registration of temporal oscillations in water contamination levels, as well as extreme and accidental emission incidences.

In an absence of time-integrated measurements, the precise time of oscillations in degrees of environmental contamination are difficult to register, as well as extreme episodic emission events. The problem refers in particular to polar substances. The retention time of hydrophilic components in aqueous media is shorter than the retention time of hydrophobic organic compounds.

There are two options for overcoming the listed shortcomings - it is possible to increase the frequency of individual sampling or to use automatic on-line monitoring systems. However, both options are expensive and rather impractical for realization in actual environmental conditions, as they are labor consuming, and their results depend largely on the choice of locality for sampling, etc. As a possibility for overcoming these

deficiencies, techniques of passive sampling of pollutants in all surface waters, including of pesticides, have recently been developed (ISO 5667-23:2011).

PASSIVE SAMPLING TECHNIQUES

Passive sampling is an up-to-date technique for time-integrated measurements of pollutants present in aquatic environments. Since the 1970s, this sampling method has been used for assessment of air quality and exposure of working areas to potentially hazardous air pollutants (Vojinović-Miloradov et al., 2014). However, passive sampling techniques suitable for monitoring of water, soil and sediment quality are still being developed.

Some of the significant advantages of passive sampling techniques are certainly their low price, possibility of multiple uses, and simple construction and handling. These techniques are based on the accumulation of analytes of interest in a sorption material within a passive sampling device, which occurs due to a difference in chemical potential gradients.

One of the most frequently used methods for measuring concentration of analytes is solid phase extraction (SPE) with different copolymers as sorbents (e.g. Oasis HLB) (Teijon et al., 2010). Additionally, polydimethylsiloxane (PDMS) is also reliably used as a material for analytes extraction from water samples, and the solid phase microextraction (SPME) technique. Depending on the kind of compound, different devices are available for pollutant sampling in surface waters – the SPMD (semipermeable membrane device), PDMS (polydimethylsiloxane), LDPE (low density polyethylene), MESCO (membrane enclosed sorptive coating), DGT (diffusive gradient in thin-films), Chemcatcher, POCIS (polar organic chemical integrative sampler) (Figure 1).

To enable separation of a compound of interest out of a sorbent to the greatest possible extent, methanol and a mixture of dichloromethane and acetonitrile are used as eluents (Sun et al., 2008) or a mixture of acetone and methanol. One of the most important procedures that precede extraction is the adding of isotopically labeled internal standard to the sample (Loos et al., 2010).



Figure 1. Passive sampling devices

(Originals: <http://www.est-lab.com/spmd.php>; <http://www.dgtresearch.com/product-category/research/>; <http://www.port.ac.uk/research/chemcatcher/research/>; http://www.mestech.ie/wp-content/uploads/2015/06/IMG_7703.jpg)

The uptake of analytes depends on several factors, such as the physicochemical properties of compounds, properties of the receiving phase, water properties, environmental parameters, such as temperature, pH and salinity, biofouling, water turbulence and flow, etc. (Vrana et al., 2005).

When it comes to using passive pesticide sampling in surface waters, POCIS, SPMD and Chemcatcher® samplers have been successfully used for determination of TWA concentrations of pesticides (Schafer et al., 2008; Alvarez et al., 2005, 2007; Arditoglou & Voutsas, 2008) in various aquatic environments (wastewater effluents, streams, lakes, rivers, and coastal waters).

The working principle of passive samplers is based on placing a sampler in water for a longer period of time, varying from several days to several weeks. The time period depends primarily on the kind of compound that is the subject of research. Data on average concentrations of pollutants dissolved in water during a defined time period (time-weighted average concentrations, TWA) are obtained this way, which enables monitoring of trends in spatial and seasonal variations.

Determination of sampling rate, R_s

In order to implement the passive sampling technique under real environmental conditions, it is necessary to determine the value of the sampling rate (R_s). The R_s can be described as the number of liters of water per day that are sampled 'through' the sampler over an exposure time. The value of R_s is specific for each compound and it is necessary to determine it for each analyte separately and under given conditions.

So far, the available R_s data are mainly those from the WFD list of priority pollutants and they have been obtained by laboratory or *in-situ* calibration of devices for passive sampling and refer to a smaller number of pesticides.

Calibration procedure implies an exposure of passive sampling devices to water spiked with corresponding concentrations of studied compounds. Over a certain period of time, lasting mostly 2–4 weeks, samples are removed from water at regular time intervals. After that, compounds accumulated in the sampler's medium are separated by extraction and then quantified by a specified analytical procedure using an appropriate chromatographic method (Šunjka et al., 2016a, 2016b).

Accumulation of compounds in a passive sampler occurs according to the first order kinetic and includes a linear (stage 1), curvilinear (stage 2) and equilibrium

(stage 3) phases (Alvarez et al., 2004). Passive samplers work at the linear phase. In that phase, the adsorbent can be assumed to be an infinite sink (Alvarez et al., 2004), which makes an estimation of the TWA concentration possible for a specific period of time (Alvarez et al., 2004) (Figure 2). Moreover, for this purpose a linear regression model with zero intercept has often been used (Mazzella et al., 2007; Arditoglou & Voutsas, 2008).

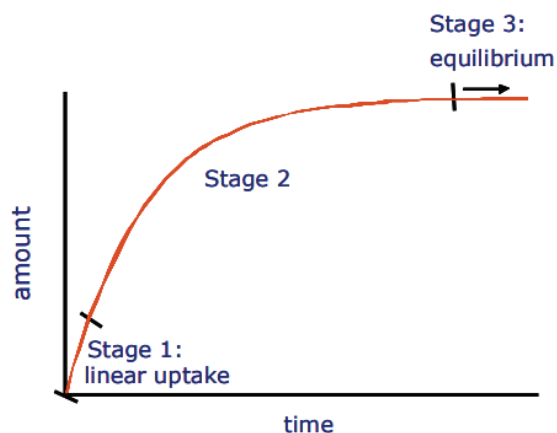


Figure 2. Uptake kinetics in a partition passive sampler (Smedes et al., 2010)

So far, calibration experiments in laboratories have been mainly conducted in static systems (Hernando et al., 2005; Mazzella et al., 2007, 2010; Lissalde et al., 2011) or in static systems under stirring conditions (Alvarez et al., 2004, 2007; Thomatou et al., 2011).

The experiments provided a basis for sampler exposure to water spiked with the analyte of interest in the restricted space of a closed container. However, such a way of R_s determination does not include the influence of the parameters of exposure media.

Simulation of real environmental conditions is possible by using constant flow of a river-like water system. Such a system includes the impact of different environmental parameters in a laboratory calibration experiment, and as such has been applied only in several studies (Harman et al., 2009; Mazzella et al., 2007).

Performance reference compounds (PRCs)

As explained already, environmental conditions have a significant impact on the R_s value of each compound. In order to correct this impact, performance reference compounds (PRCs) have been recently used for R_s assessments and correction of laboratory-derived sampling rates (Mazzella et al., 2010). The PRCs are

non-interfering compounds that are not found in environmental waters (such as deuterated compounds) (Alvarez et al., 2007). The procedure is based on adding PRCs to the sampling device during construction, and their release into the surrounding water during experiment.

The values obtained during such experiments are used for calculation of a correction factor (elimination of constant rate, k_c), in order to compensate environmental impact and, therefore, to provide better estimation of TWA water concentrations.

Determination of pesticide contents

Finally, the last phase in the application of passive samplers for determination of pesticides in surface water is their quantification. After their removal from water and extraction, the present compounds need to be measured by an appropriate analytical method. Having in mind that pre-concentration of analytes runs inside the sorption medium, the use of passive samplers leads to an increase in sensitivity of analytical methods.

High performance liquid chromatography (HPLC) with UV and DAD detectors, suitable for water soluble and thermally labile pesticides, is used most frequently (Šunjka et al., 2013; Grahovac et al., 2013). The HPLC coupled with mass spectrometry (MS or MS/MS) has been proven as a powerful tool for pesticide residues determination in environmental samples, due to their high sensitivity and high degree of selectivity (de Lafontaine et al., 2014). On the other hand, thermally stable pesticides are commonly analyzed by gas chromatography with electron capture detector (ECD) (Lazić et al., 2011), or coupled with mass spectrometry (MS, MS/MS).

PROVISIONAL CONCLUSION

Considering all facts presented here, the use of passive sampling techniques for determination of pesticides concentrations, as well as other pollutants, in surface waters represents one of the most acceptable techniques for time integrated measurements. Besides, the pre-concentration step enables the application of more analytical techniques. Finally, validation of the passive sampling method is essential for attracting broader acceptance for the technology in regulatory programs (Vrana et al., 2005), which would enable application of passive sampling methods for monitoring organic chemicals within the WFD.

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Tehnike uzorkovanja vode u cilju kontinuiranog praćenja sadržaja pesticida

REZIME

Postizanje dobrog ekološkog i hemijskog statusa voda predstavlja najvažniji cilj okvirne direktive 2000/60/EC, što podrazumeva poštovanje standarda kvaliteta voda na nivou celog sliva (2008/105/EC i 2013/39/EC). Ovo se, između ostalog, odnosi i na kontrolu prisustva ostataka pesticida u površinskim vodama. Da bi se ovo postiglo, neophodno je sprovođenje kontinuiranog monitoring programa koji treba da obezbedi sveobuhvatan i međusobno povezan pregled statusa voda, što zahteva primenu odgovarajućih tehnika analize. Do sada, procedura za uzorkovanje i kvantifikaciju rezidualnih količina pesticida u vodenoj sredini bazirala se na primeni tradicionalnih tehnika uzorkovanja, koje podrazumevaju periodična uzimanja pojedinačnih uzoraka. Međutim, ovakav tip uzorkovanja pruža samo trenutnu sliku stanja u pogledu prisustva polutanata u vodi. Da bi se prevazišli nedostaci, moguće je povećati frekvenciju pojedinačnih uzorkovanja ili koristiti automatske, on-line, monitoring sisteme. Oba ova rešenja su izuzetno skupa i nepraktična; podrazumevaju dugotrajan proces rada, izbor odgovarajućeg lokaliteta, itd. U novije vreme, kao alternativa, u primenu se uvodi tehnika pasivnog uzorkovanja polutanata u vodi, uključujući pesticide. Ovu savremenu tehniku, pored jednostavnosti konstrukcije i rukovanja, karakteriše niska cena i mogućnost višestruke upotrebe.

U osnovi tehnike je akumuliranje analita u odgovarajućem sorpcionom materijalu unutar uređaja za pasivno uzorkovanje. Zavisno od vrste jedinjenja, za uzorkovanje pesticida u površinskim vodama dostupni su različiti uzorkivači. Sama tehnika zasniva se na postavljanju uređaja u vodenu sredinu u dužem vremenskom periodu, koji varira od nekoliko dana do više nedelja, zavisno od vrste jedinjenja. Na ovaj način se kao rezultat dobijaju prosečne koncentracije polutanata rastvorenih u vodi tokom određenog vremenskog perioda (time-weighted average concentrations, TWA), što omogućava praćenje trenda prostornih i sezonskih varijacija. Takođe, primena ovih tehnika dovodi do porasta osetljivosti analitičkih metoda, imajući u vidu da se unutar sorpcionog medijuma odvija prekoncentrovanje analita. Međutim, da bi tehnika bila primenjena za određivanje koncentracije pesticida u realnim uslovima vodene sredine, neophodno je odrediti vrednost stope uzorkovanja (R_s), specifične za svako jedinjenje. R_s se dobija laboratorijskom ili *in-situ* kalibracijom uređaja za pasivno uzorkovanje.

Ključne reči: Ostaci pesticide; Uzorkovanje vode; Monitoring; Tehnike uzorkovanja