

Pravdepodobnosť výskytu budúcich záplav je založená na opise využitia územia a opise povodní, ku ktorým došlo v minulosti, najmä ich počtosti a dosiahnutého stupňa povodňovej aktivity [3]. Treba vyzdvihnúť, že v takomto rozsahu, ako je prezentované v príspevku, povodne ešte zaznamenané neboli. Veľkým technickým prínosom bolo využitie GIS systémov pre spracovanie údajov a tvorbu výstupov. Slovenský vodohospodársky podnik, š. p., má za povinnosť podľa smernice Európskeho parlamentu a rady 2007/60/ES o hodnotení a manažmente povodňových rizík, zabezpečiť mapy povodňového ohrozenia a mapy povodňového rizika do roku 2013. Do doby ich spracovania sú výsledky tejto úlohy užitočným podkladom pri hodnotení rizikových oblastí a vyjadrovacej činnosti SVP.

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AGRICULTURAL CHEMICALS OF EMERGING CONCERN IN THE VOJVODINA REGION

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ABSTRACT

Modern agriculture is extremely dependant on pesticides. Designed to kill targeted pests, they are often harmful to humans and other species. Methomyl is a broad spectrum carbamate insecticide. It belongs to the group of pesticides that show neurotoxic effect, given the fact that it is a cholinesterase inhibitor. By inhibiting the cholinesterase activity, methomyl interrupts the hydrolysis of the neurotransmitter acetylcholine into choline and acetic acid, a reaction necessary to allow a cholinergic neuron to return to its resting state after activation. The presence of methomyl has been registered in many locations due to its wide applications. Regulations relating to the use of methomyl have been changing over the years from its introduction in 1966. Clinical studies showed potential adverse effect on animal and human health. Therefore, legal changes regarding the use of this pesticide took place during the last decade of XX century. Based on specific chemical properties, persistence, toxicity and bioaccumulation, methomyl is classified in NORMAN list of emerging substances. The paper presents the results of preliminary screening of methomyl residues in surface soil layers in Vojvodina as a typical agricultural area.

Keywords: Emerging substances, Residues, Screening

INTRODUCTION

Economy in the Vojvodina region is based on the abundant wealth of the fertile arable land, which makes 84% of its total area. The fertility of this soil is further enhanced by an irrigation network; around 0.5 million hectares, out of 1.78 million, of arable land is drained. Therefore, the quality of surface and groundwater is one of the most important challenges of our time. The risk of drinking water sources contamination could have adverse effect to public health. Contamination of drinking water is derived from the pollutants from the surface water, agriculture and urban waste water, and industrial plants located near the water sources. One of the biggest rivers in Vojvodina is the river Danube, that is contaminated by non-treatment waste and municipal wastewater discharged directly into Danube.

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Emerging substances, EmS, represent a specific group of the mainly synthesized compounds identified as pollutants, primarily detected in surface waters of large river basins, groundwater, lakes and other water bodies. Emerging substances are generated from the industrial, pharmaceutical, chemical and agricultural activities, inadequate deposit of waste (wild landfills), as well as from every other human activity. EmS are freely inserted through the waste water directly into natural recipient and then they spread to all parts of the environment. EmS residues are detected in water, soil, air and sediment, river silt and other abiotic and biotic matrices. Concentration levels and routine monitoring of emerging substances are not defined by legal regulations at the EU level, while the transport, ecotoxicity and the fate of EmS are still unknown and are in the research stage. EmS are found at very low concentrations in magnitude of ppb, ppt and lower. For many years, EmS are present in the natural recipients, and are transported and distributed in surface water and soil, and evaporate into the atmosphere. EmS are active substances in a number of commercial products and are present in everyday life for many years. At the beginning of 21st century, they were recognized and detected as potentially hazardous and highly toxic agents with cancerogenic, mutagenic and teratogenic effects. What makes EmS so significant and emerging is that their toxicity doesn't decrease with lowering the dose of the chemical. As these substances are with emerging properties, there is no maximum allowed concentration. The relationship between low doses and risk is often not linear. Toxicologists now believe that constant exposure to toxins at very low levels have more adverse effects on homeostasis than very high or mid-level exposure.

A large number of chemicals, primarily organic and less of inorganic origin are in the group of emerging substances and contribute to "improving" the quality of life, development and the progress of society, but, as the controversy, they also contribute to contamination of water, air, soil, biosystems and humans. The constant presence in the soil and surface water, as well as their migration in groundwater bodies and the possibility of their input directly to the sources of drinking water is the primary and dominant way of transport and entry of EmS in the human body.

PESTICIDES AS EMERGING SUBSTANCES

Modern agriculture is extremely dependent on pesticides. Pesticides is the common name for all the compounds that are produced for the use in agriculture in order to prevent or limit the harmful effects of biological species such as insects, rodents, inducers of plant diseases, undesirable plant species (weeds) and others. The harm that these pesticides sometimes do is not entirely accidental: designed to kill targeted pests, they are often harmful to humans, other species and environment. A lot of synthetic substances which can be found in food, environment - soil, air, water, and in everyday products are proven to have toxic effect on biosystem. Current research classifies certain pesticides in the group of emerging substances included in the NORMAN list (Network of reference laboratories for monitoring of emerging environmental pollutants).

Methomyl (S-methyl-N-([methylcarbamoyl]-oxy)thioacetimidate) is a polar pesticide from the family of carbamate pesticides, and an emerging substance on the current NORMAN list. Synthesized by the US Company "DuPont", in cooperation with the US Environmental Protection Agency, methomyl was first used in 1966. as insecticide in the commercial cultivation of chrysanthemum. Soon, methomyl began to be applied more often as a pest control, and as of that time, it became part of the protective treatment from most crops. Methomyl belongs to a group of neurotoxins since it works as an inhibitor of the enzyme cholinesterase, essential for the normal function of the nervous system. Cholinesterase is a family of enzymes that catalyze the hydrolysis of the neurotransmitter acetylcholine into

choline and acetic acid, a reaction necessary to allow a cholinergic neuron to return to its resting state after activation. Methomyl interrupts that reaction, suppresses the action of the cholinesterase enzyme which may lead to different adverse effects on living organisms.

The most common ways in which methomyl enters surface and ground water are spraying pesticides in and outside of the planned area and its diffusion in aquatic systems, water outflow followed by erosion and accidental leakages. Small but constant amounts of pesticide dispers through the environmental media, but accidental events during which a large concentration of methomyl are released into the environment are not uncommon.

The use of methomyl is starting to be reduced, after a number of clinical studies on animals which have proven its adverse effects on the health of living organisms as well as the human. Significant changes to regulatory requirements that define the application of methomyl have taken place during the last decade of XX century. The European Union (Commission Regulation (EC) No 1097/2009) defined the maximum allowed concentrations of methomyl residues, depending on type of matrix, which range from 0.02 to 10mg/kg.

The latest studies unexpectedly revealed a negative effect of very low doses, in contrary to earlier belief that background levels were safe to the environment. The adverse effect of EmS in magnitude of nano concentrations and lower, require the shift in the traditional thinking of contamination and initiate the creation of new environmental approach.

MATERIALS AND METHODS

The aim of this study was the preliminary screening for the presence of polar pesticide methomyl, as an emergent substance, in surface layers of soil in Vojvodina region. The selected sampling sites were located in areas near the arable land and animal husbandry. Soil sampling was performed at four different locations (L1, L2, L3, L4) in the vicinity of livestock farms in the agricultural and high-populated areas of Vojvodina. Sampling and preparation of surface soil layer samples were carried out according to standard procedure. Given that the quantitative analysis of target polar organic compounds require selective and sensitive detection of a wide range of concentrations, high performance liquid chromatography with mass detector (HPLC-MS) was used to determine the concentration levels of methomyl.

RESULTS AND DISCUSSION

Soil sampling, using standard procedure, was performed at four different sites and 43 samples of surface soil layers were collected. At the L1 site, a total of 14 soil samples were collected. Results of quantitative analysis showed that in 7 out of 14 samples, concentration levels of methomyl were below the limit of detection (<0.01 mg/kg). Concentration levels of methomyl residues in the remaining 7 samples are graphically shown in figure 1. The maximum concentration of polar pesticides in surface soil layers measured on this site was 0.027 mg/kg. At the site L2, a total of 17 soil samples were collected. In ten analyzed samples, methomyl was below the limit of detection (<0.01 mg/kg), whereas the concentrations detected in the remaining 7 soil samples are shown in figure 1. The maximum concentration value of methomyl measured at this sampling site was 0.07 mg/kg. On remaining two sites, L3 and L4, methomyl concentration levels were below detection limits.

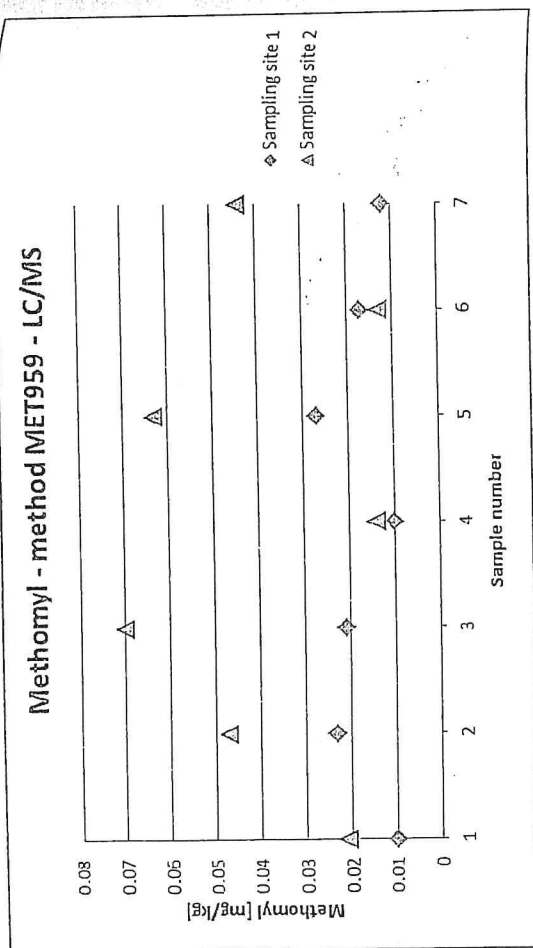


Figure 1. Methomyl concentration levels in surface soil layers

CONCLUSIONS

Based on preliminary screening results of methomyl presence in the surface layers of soil on 4 different sites in Vojvodina, the measured pesticide residues were present in large number of samples obtained in 2 out of 4 observed localities. Qualitative and quantitative analysis of polar organic pesticides in soil of Vojvodina region are in agreement with those obtained in other agricultural regions of Europe. In order to draw valid conclusions about the seasonal and spatial variations of concentration levels of pesticide methomyl in Vojvodina, it is necessary to implement complex and multidimensional sampling campaign.

It is necessary to point out that the transport and fate of methomyl, as well as its ecotoxicological effects are still largely unknown. A particular problem with this emerging polar pesticide is the lack of relevant toxicological studies that would provide the necessary information on the mechanisms of its chronic, low-dose, effect on humans and other living organisms. Since the relevant risk assessment for the most EmS cannot be established with sufficient certainty, the traditional approach to management of emerging substances must be modified.

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