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DETERMINATIONS CONCERNING THE PRESENCE OF ORGANIC MICROPOLLUTANTS IN WATER SOURCES AS A RESULT OF ECONOMIC ACTIVITY

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Key words: *micropollutants, economic activity, pesticides*

INTRODUCTION

The harmonious development of the complex ecosystem which forms the biosphere is closely related to environmental factors. The balanced relations within a biom undergo important changes under the influence of natural and/or anthropogenic factors. In case preventive and monitoring measures are not implemented according to a plan, the economic activity of an area results in environmental damage. The presence of the organic micropollutants in both surface and subterraneous waters is one of the inevitable effects the economic activity has on environment [4]**.**

The term "micropollutants" refers to organic compounds, persistent in the environment, able to resist bio-degradation and decomposing. They can accumulate in the environment, as they are present in food supplies and human tissues posing a true risk on human health. For example, dioxin accumulates in the food chain, acrylamide forms in products during high- temperature cooking processes, such as oil frying or may occur in waste, a case in which it may fix on various fruits and vegetables easily making their way into the human body [3].

Organic micropollutants are frequently used in obtaining biocidal products. These are highly used in various domains such as: food industry, cosmetics, paints and lacquers, in agriculture – in pesticides, insecticides and the herbicides used for pest and disease control. The use of micropollutants as well as of the all persistent organic pollutants has grown exponentially due to technical progress and especially to the lack of awareness and the danger these chemicals pose to human health and environment [1].

In normal conditions of use, these products are not expected to undergo harmful effects to human and animal bodies. In reality, such chemicals enter the group of highly potential substances which lead to disorders and cause serious illnesses as well as cancer. The present paper analyses the way in which the economic activities in Bacău County pollute with organic micro-pollutants the water resources in Siret hydrographic basin. We made use of the gas chromatography as a method of determination. The conclusions drawn at the end of the analysis highlight the degree of danger that occurs in the case of uncontrolled/ unmonitored downstream and/or overflowed technological processes.

MATERIALS AND METHODS

There is a large range of methods which can be used in order to identify organic micropollutants. The most suitable ones include cromatography and spectrophotometry as they are far more selective and accurately than others. A major part of the carrier gas or of the eluent, such as: helium, nitrogen or argon, is sent to the chromatography column while the pressure with which it enters the column (1-3atm) is adjusted with the help of a reducer; the other part is transmitted directly to the detector. The carrier gas must not contain traces of water, oxygen or carbon dioxide as it may adversely affect the stationary phase. Thus, on the gas trace, drying filters are inserted in order to reduce the oxygen. Column chromatography is placed in an oven fitted on the outside with a device for introducing the sample and, on the inside with an electric heating device. After leaving the column, the carrier gas together with its separate components, enters in the measuring cell of the detector where the corresponding electrical signals are obtained and recorded.

The detector is an analytical instrument in itself which, with a high response, has the role of quickly sensing the components of the sample under analysis. The most used detectors are: the thermal conductivity detector, the flame ionization detector with photoionization and electron capture.

Using the equipments and the methodology presented above, we passed to determining the impact the economic activities have on the water quality within Siret basin, the area related to the Water Management System in Bacău, in terms of loading with organic micropollutants. It should be noted that Siret River Basin is divided into four areas of territorial water management such as: SGA Suceava, SGA Neamț, SGA Bacău and SGA Vrancea.

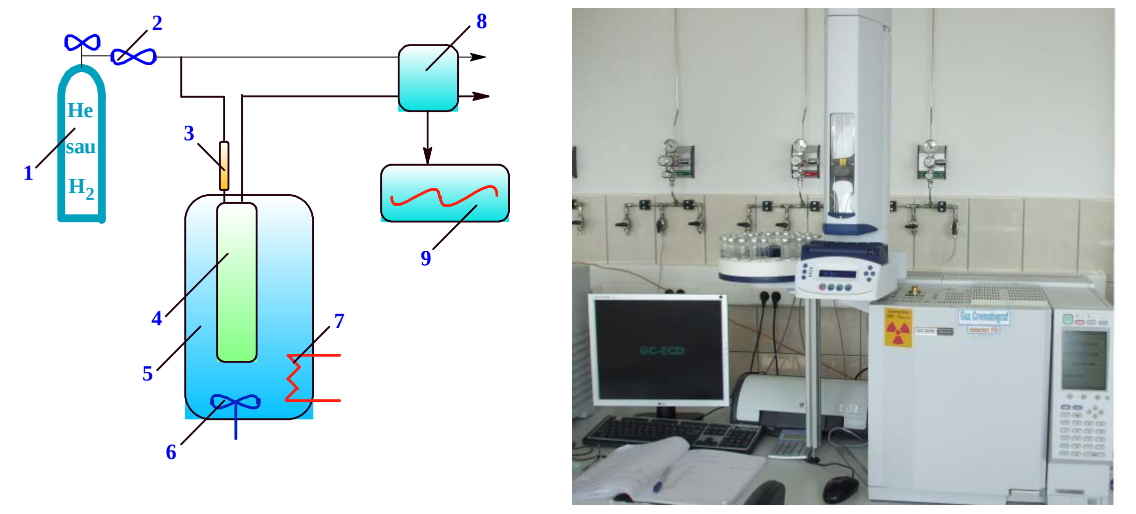

Fig. 1. Overview and schematic drawing for gas-chromatograph
1 – pressure cylinder; 2 – reducer; 3 – microsirynge; 4 – chromatographic column; 5 – cabinet dryer/thermostatic oven; 6 – fan; 7 – heating resistance; 8 – detector; 9 – recorder

RESULTS AND DISCUSSIONS

In order to determine the impact the economic activities in Bacău have on water quality, water samples from Drăgeşti (samples taken from Siret River) had to be taken, before the Hydroelectric power plant of Galbeni, from the downstream of SC Amurco Letea SRL and from Letea paper factory draining out.

The samples were taken in January and May and their comparison led to some conclusions viewing the water quality evolution. It must be stated that, at the time of the survey, the Amurco society and Letea factory were functioning within normal parameters.

The first two sampling points, Drăgeşti and Galbeni, allowed us to determine the impact the agricultural activities have upon the surface water quality while the last sampling points, allowed us to determine the impact of the industrial activities within Bacău.

The chromatogram obtained in the case of Drăgăneşti sampling point revealed the identification of about 25 components, of which, the highest concentrations were registered in the case of pesticides and insecticides, which contained semi-volatile chlorinated organic compounds. As figure 2 emphasises, Drăgăneşti water source contains organochlorine pesticide residues, as well as semi-volatile organic compounds from the class of chlorobenzene.

A series of organochlorine pesticide residues and semi-volatile organic compounds from the class of chlorobenzene were identified.

The maximum concentration was exceeded at all the substances identified.

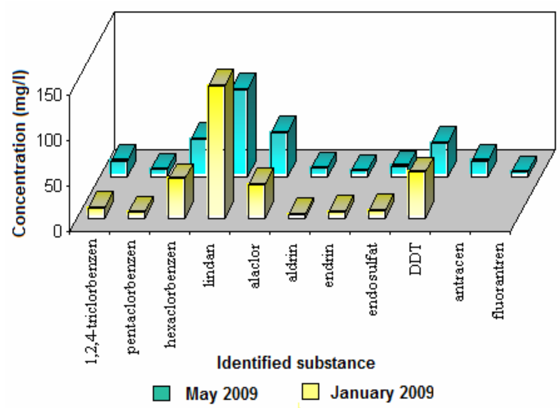

Fig. 2. Variations in the concentration of the substances identified by gas chromatography in Drăgeşti water source

The class of chlorobenzene registered the highest percentage, determining the presence of lindane, alachlor and organochlorine pesticides from the DDT class. According to STAS 1342-91 the permissible concentration of each pesticide is 0,1μg/l and for the the sum of all parts is 0,5 μg/l.

The simple presence of pesticide changes the water quality as pesticides are substances with a pronounced biological activity and toxic properties, a reason for which they are considered extremely dangerous for both flora and fauna as well as for the human body. As it is well known, the pesticides usually deposit in the fatty tissues of the living organisms through water, food and air, leading to the emergence of acute and chronic effects which consist in imbalances in the immune system, the endocrine and reproductive systems, producing genotoxicity ailments and cancer. terrestrial and aquatic systems.

The water pollution registered at Drăgeşti source is unquestionably the result of soil treatment with pesticides. The rainfall on these soils as well as the water from irrigation engages the pesticides and residues contained in these substances, then the water loaded with these substances, gets to Drăgeşti source causing the phenomena of pollution.

According to figure number 3, in the case of Galbeni water samples, there were identified hydrocarbons, organophosphate pesticides and fungicides; the maximum concentration allowed for all the pollutants identified within the water was exceeded.

The polycyclic hydrocarbons, pesticides and fungicides which pollute the water source in Galbeni derive from agricultural activities and domestic discharges. These substances exert a pronounced toxic action on both flora and living organisms. The polycyclic hydrocarbons are modifying the organoleptic indices, modification which leads to predictable ecological imbalances. Polycyclic hydrocarbons are lighter than water forming a layer at its surface which blocks the process of oxygenation. The effect of these substances manifests its toxicity by affecting the cardiovascular and nervous systems and by producing changes in the blood components being labelled as carcinogenic substances with a broad effect.

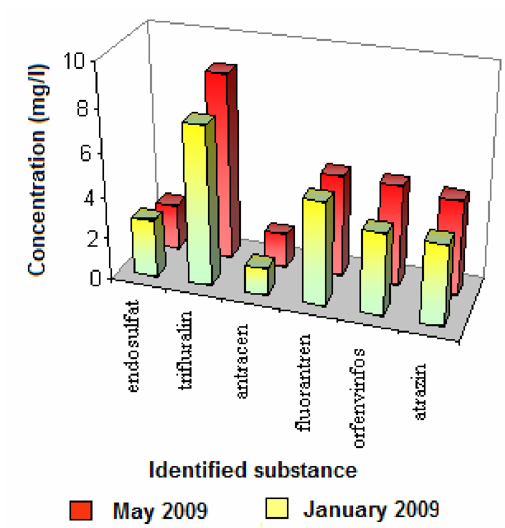

Fig. 3. The concentration of substances identified by gas chromatography in Galbeni water source

The two water sources presented are surface waters whose pollution derives mainly from agricultural activities and domestic discharges.

The chromatography in the case of Letea water supply outlet (figure 4) listed approximately 19 components from which, the highest concentrations recorded semi-volatile organic chlorinated compounds, substances used in the manufacture of paper and organochlorine pesticides.

The maximum admitted concentration was exceeded in the following cases: 1,2,4-trichlorobenzene, 1,2,3- trichlorobenzene and hexachloro-benzene of the semi-volatile organic compounds, respectively lindane and alachlor from the class of organochlorurate pesticide class. The presence of these substances in water can be detected through taste and smell and leads to carcinogenic effects on human health.

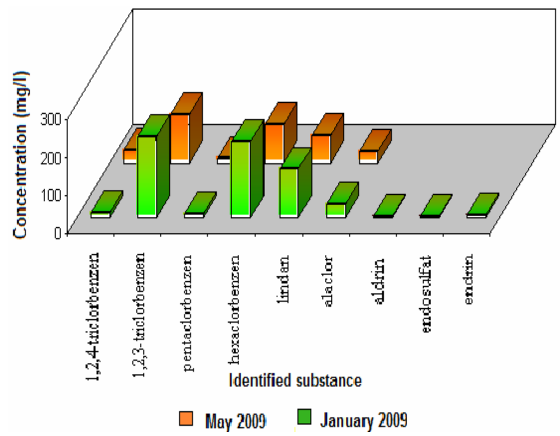

Fig. 4. The concentration of substances identified by gas chromatography at the discharges within Letea outlet source

Analysing the figure, one can observe the overflow of the maximum concentration admitted which is far more pronounced in January than in May. This is due to the industrial wastewaters discharged in January, which were in a large quantity and presented a higher load with pollutants.

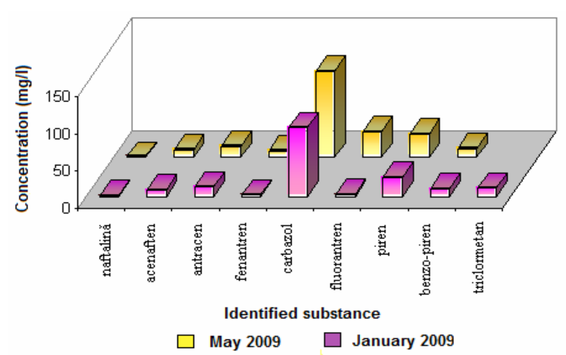

Fig. 5. The concentration of substances identified by gas chromatography in the case of Amurco downstream source

In the case of the samples taken from Amurco downstream, figure 5, there were 22 chemical components identified. The highest concentrations were recorded in the case of polycyclic hydrocarbons; the maximum permissible concentrations being exceeded in the case of the following chemicals: anthracene, carbazole, fluoranthene and respectively, pyrene. A higher concentration of these substances registered in May. The pollution of this water source recorded due to the fact that the wastewater discharged in this source comes from S.C. Amurco S.R.L., famous for producing chemical fertilizers. The wastewaters resulting from the manufacturing processes contain toxic residues in a significant concentration.

Figures 6 to 11 emphasize a comparative study between the shifting concentrations of substances for all water sources analyzed. The water sources Galbeni, Drăgeşti and Letea were compared in terms of existing pesticides, substances of interest for the three cases presented. Water samples were taken at an interval of six days and recorded particularly in January and May.

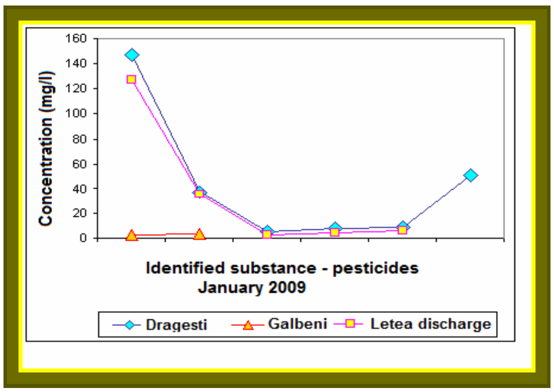

Figure 6. Variation of pesticide concentration in January for the analysed water sources

The experimental data presented in figures 6 and 7 shows that Drăgeşti water source presents a powerful load with pesticides compared to Galbeni, the phenomena of pollution maintains high over a larger period of time.

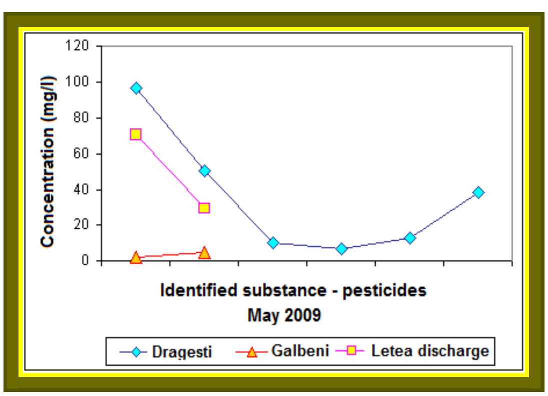

Figure 7. Variation of pesticide concentration in May for the water sources analysed

One can notice the same pesticide load both in January and in May – only that the presence of the same pesticides was a little reduced. The Letea outlet source presented a strong pesticide load in January, while in May, the load of pollutant pesticides decreased. In May, only two substances from the class of organochlorine pesticides were identified, namely lindane and alachlor, while their concentration in water was lower. However, Galbeni water source presented a lower pesticide load throughout the period analyzed. The presence in water of two other pesticides whose concentration, lesser as compared to other analysed sources was also signalled.

The conclusions that result from this comparative study are:

- The wastewaters discharged by Letea during peak production period (the end of December and the beginning of January) determine a powerful change of the water quality. The charging curve with pesticides follows the production flow of the factory. Although in May the recorded values are lower, the charging curve has the same aspect in both months starting from a maximum, decreasing towards the middle, and increasing towards the end of the month. The measurements recommended point to changing the manufacturing technology and the development of a performing treatment plant.
- The large amount of pesticides used in Drăgesti area are heavily polluting Siret river, exceeding the maximum values recorded at the water discharge within Letea source. The leaks generated by rain and irrigation, washing the agricultural land are extremely dangerous and can be compared with the wastewaters discharge. Control measurements viewing the amount of pesticides used together with determining the degree of groundwater pollution through soil contamination are a necessity.
- Having a reduced load of pesticides, the samples taken from Galbeni In the case of reduced loads from the pesticide group with a lower occurrence, samples taken from Galbeni still highlight the exceeding limits and thus, the measurements recommended above are also necessary.

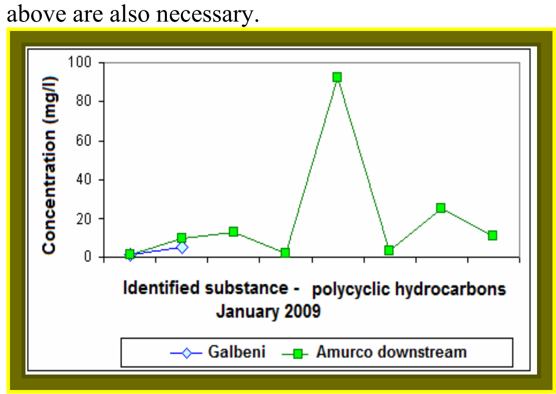

Figure 8. The variation of polycyclic hydrocarbons during January, for the water sources under analysis

Figures 8 and 9 emphasize the variation of polycyclic hydrocarbons concentration for three sources of water analysed, sources in which the presence of these substances has been signalled.

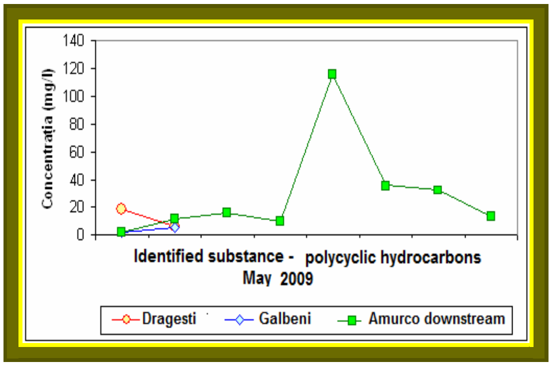

Figure 9. The variation of polycyclic hydrocarbons during May, for the water sources under analysis

The analysis clearly showed that the Amurco downstream presented the most powerful load throughout the study. Within Galbeni source, there were identified only two polycyclic hydrocarbon substances, but their concentration is reduced throughout the period taken into analysis.

Drăgeşti water source emphasised a load with polycyclic hydrocarbons only in May, their concentration in water being reduced.

The results of these comparative studies highlight the dangers of wastewaters discharged by the Amurco, the chemical fertilizers manufacturer. The waters are discharged carrying a high load of polycyclic hydrocarbons in a concentration far beyond the admissible limit. The treatments applied to agricultural fields also exceed the permitted limit although they manifest over a short period of time.

Semi-volatile organic chlorinated compounds (figures 10 and 11) were identified only within Drăgeşti source and Letea downstream.

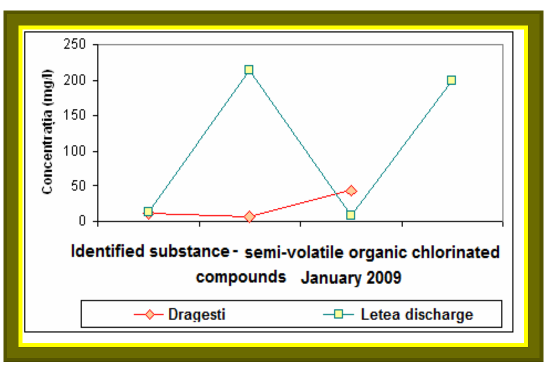

Figure 10. Variations in the concentration of semi-volatile organic substances in January, for the water sources under analysis

The concentration of these substances in water is higher in Letea downstream compared to the one within Drăgeşti source. This difference can be attributed to the fact that Drăgeşti source is surface water while Letea downstream is industrial water which attributes the latter a larger the load with pollutant substances. Nevertheless, both sources exceed the permitted limit.

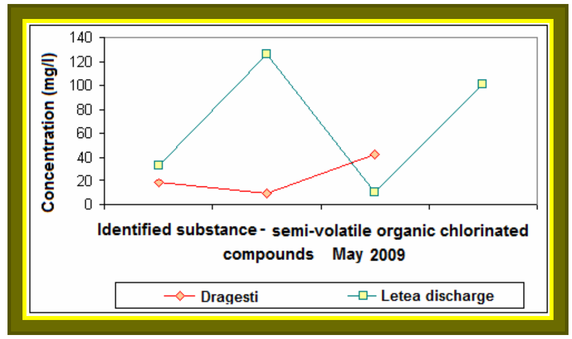

Figure 11. Variations in the semi concentration of organic matter in May, for the water sources under analysis

CONCLUSIONS

At the level of the year 2009, the monitoring of the surface waters within Siret River basin from the corresponding sector of SGA Bacău, highlighted the fact that these waters are polluted with organic substances, of which, the most commonly encountered substances are: nitrates and nitrites, pesticides, organochlorine and organophosphate, volatile organic compounds (chlorides, sulphur compounds), semi-volatile organic chlorinated polycyclic aromatic hydrocarbons (PAH), herbicides and fungicides, heavy metals (manganese and chromium) in some areas that exceed the maximum permitted concentration of the standard imposed by STAS 1342/91 /the report viewing the environmental status.

From the collected data one can conclude that the analysed water sources present a higher concentration of pollutant agents from the most toxically ones, respectively organochlorine pesticides, polycyclic hydrocarbons and organic semi-volatile chlorinated compounds, most substances with harmful and long term effects on the flora and living organisms. It results that such water sources are not indicated for use as drinking water even after chemical treatment.

Chemical industries pose a powerful source of environmental pollution due to the outdated technologies they use. The most recommended solution in the case of pollution produced by industrial wastewaters discharge is to bring technological processes up to date. Recent researches have emphasised the existence of specific processes that reduce the occurrence of organic mocropollutants in surface waters. Thus, the ozone proves very efficient in the case of large class of pesticides especially used in combination with carbon activated filters [2].

In the case of agricultural pollution, the studies carried up to present have shown that, depending on the treatments applied to crops, the agricultural pollution can be more powerful than the one produced by industrial processes [5].

ABSTRACT

The article concentrates on the researches conducted in the case of four surface water sources. In order to emphasize the impact the economic activity of the area has on water quality, we propose to determine the level of organic micropollutants identified within the water. The samples of water for the analysis were taken in 2009, during January and May, and for the analysis we chose to use the method of gas chromatography due to its accuracy.

Two of the water sources under analysis allowed us to determine the impact the agricultural activities can have upon the surface water quality. Thus, within the water samples taken from Galbeni and Dragesti, the analysis has identified the existence of polycyclic hydrocarbons, organophosphoric pesticides and fungicides in different concentrations. Excessive treatment of soil, followed by the leakage of rain water and irrigation from these surfaces, leads these substances within Siret basin damaging the water and causing a powerful pollution.

Viewing the research of industrial activity impact, there were taken water samples from the downstream of two companies with different fields of activity, such as S.C. Amurco, a manufacturer of chemical fertilizers and SC Letea, a pulp and paper factory. In the case of water samples within Letea source, the chromatographic analysis identified components of which the highest concentrations were recorded in the case of semi-volatile organic chlorinated compounds, substances used in paper manufacturing and also in the case of organochlorine pesticides.

In the case of the water sample taken within Amurco downstream, the highest concentrations were recorded in the case of polycyclic hydrocarbons, while the maximum legal concentration was exceeded in the case of anthracene, carbazole, fluoranthene and pyrene.

Protecting the water quality water sources requires taking the following measures: monitoring and controlling the treatments applied to crops, developing the manufacturing technology and the existence of better cleaning stations.

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