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APPEARANCE OF WATER MICROPOLLUTANTS IN WATER AS EFFECTS OF EXTREME METEOROLOGICAL EVENTS

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ABSTRACT. The objective of the present study is to obtain data on micropollutants sources present in surface and drinking water after extreme meteorological events in Romanian regions. The analyses were performed on water samples collected from potable water sources using GC/MS method after LL extraction. Were detected and discussed anthropogenic compounds from following compound groups: lubricant and plastic additives and hydrocarbons. The compound identification was done based on mass spectra obtained by electron impact ionisation in full scan mode.

Key words: *emerging contaminants, extreme events, lubricant additives, mineral oils*.

INTRODUCTION

Human activity is causing the atmospheric accumulation of greenhouse gases, increasing temperatures, and producing changes in the hydrologic cycle (Louis et al., 2008)

These climatologic changes, contribute to a wide variety of effects, including direct effects on temperature and climatologic instability, such as heatwaves, drought, and increased frequency and severity of extreme precipitation events (Yeomona et al., 2017; WHO 2011; FCM 2004; Alderman et al., 2012).

By studies of the environmental events a real relationship was observed between extreme rainfall and elevated concentration of different organic pollutants. Heavy rainfall events are characterized by high volumes of water, increased flow rates, and, consequently, more significant run-off transportation of suspended solids and possibly chemical and biological substances. The quality of water resources (surface water and groundwater) can be severely impacted, and the quality of the associated drinking water may also be degraded. Flooding is a seriously contaminant transfer mechanism to river catchments (Bei et al., 2016; Corada-Fernandez et al., 2017; Roig et al., 2011).

Human activity continues to add an increasing variety of organic compounds into the environment or has changed the ratios and amounts of naturally compounds. Both anthropogenic and naturally occurring compounds are found mixed together in recent environmental samples and several of these compounds may be used as tracers to study natural processes affecting the fate and effects of chemical contaminants in water.

The occurrence of pollutants in streams resulting from surface runoff, from agricultural and industrial fields has been documented in several studies (Rasmussen, 2011). Because of the hydrodynamic situation during the meteorological event, sedimentation and resuspension phenomena can be considered negligible (Ciaponi et al., 2002). Furthermore, surface runoff has often been emphasised as important entry routes chemicals to streams having a potential impact on drinking water sources. The quantity of anthropogenic compounds released into environment and their potential adverse effects to environmental and human health represent major challenges in the scientific community. For that reason, developments in instrumentation and methods are increasing towards the study the structure and quantity of the compounds present in environmental matrices. In respect to this, one of priorities is to determine the environmental distribution of organic pollutants in the surface waters.

The objective of the present study is to obtain data on micropollutants sources present in surface and drinking water after extreme meteorological events in Romanian regions. The results of micropollutants detection in a potable water source are presented. The analyses were performed using GC/MS method after LL extraction. The compound identification was done based on mass spectra obtained by Electron Impact Ionisation in full scan mode. The results are discussed in connection to main families of compounds with high potential for entering in the surface water in flood condition (Cavestri, 1997; ATC 2007; AccuStandard, 2013*).*

EXPERIMENTAL

Study area

Sampling site was a drinking water well from north region of Transylvania (Romania) at few days after a flood caused of a very abundantly rain (60 l/m^2), in the summer of the 2016. The well is very common source of potable water in this region. Climatic conditions are temperate and average annual precipitation is about of 635 mm. Main of the total area is used for agricultural activity. Dominating crop types are cereals followed by grasslands and maize.

Instruments

The compounds concentration were performed by extraction liquid-liquid (LL) using hexane as solvent after acidulation at pH 2 and filtrated (Glass filter of 0.47 um). Analysis was carried out using a gas chromatography – mass spectrometer (Polaris, Thermo-electron Corporation, USA). The chromatographic separation was

accomplished by an HP-5MS column (l = 30m, d_i = 0.25 mm) with helium as carrier gas at a flow rate of 1.5 mL/min. The GC oven temperature was programmed from 90 ^{0}C (hold 1 min) to 120 ^{0}C (at 20 ^{0}C/min, then to 300 ^{0}C (hold 10 min) at 4 ^{0}C/min. The injection port temperature was set at 250 ^{0}C. Mass spectrometric analysis was performed by MS operating in electron impact (EI) mode at 70 eV and with the ion source temperature at 250 ^{0}C. The mass spectra were obtained in full scan mode in the range 50-650 Daltons.

RESULTS AND DISCUSSION

The composition of surface and underground waters depends strong of natural factors. The early studies conducted in different countries show that storm water runoff from roadways and also from other areas (car parks, service stations etc.) are highly contaminated and have a negative impact on receivers (Papiri et al., 2008). Characteristic of pollutants transported, varies with runoff volumes, water levels and weather conditions (Pizarro et al., 2007).

The pollutants identified in this study are from family of plastic additives (AccuStandard, 2013) and lubricant additives (ATC, 2007). The compounds separation is shown in the figure 1 and figure 2. The identification of compounds from family of lubricant antioxidants is presented in table 1.

Table 1. *Identification of compound from figure 1*

No	Molecular Weight	Name	Compound family
1	236	3,3-dimethyl-1,1-diphenyl-1-butene	Lubricant additives
2	268	2-t-Butyl-4-methyl-6-(amethylbenzyl)phenol	
3	268	2-t-Butyl-4-(dimethylbenzyl)phenol	
4	324	4,6-Bis-(t-butyl)-2(dimethylbenzyl)phenol	
5	248	3,5-di-t-Butyl-4-hydroxyacetophenone	
6	324	2,6-Bis(t-butyl)-4-(dimethylbenzyl)phenol	
7	330	2,4-Bis(dimethylbenzyl)phenol	
8	386	2,4-bis(dimethylbenzyl)-6-t-butylpenol	
9	448	2,4,6-Tri(dimethylbenzyl)phenol	

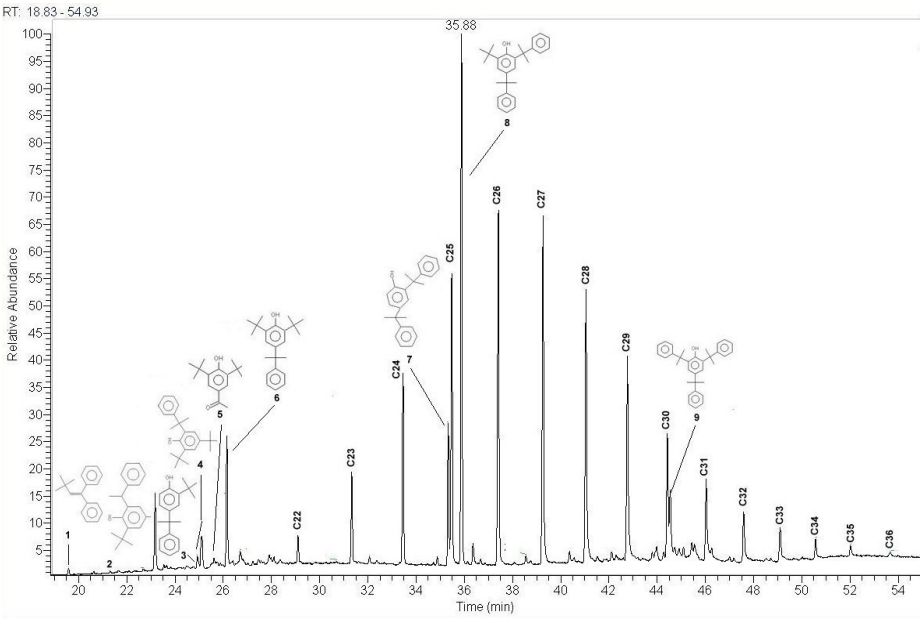

Fig. 1. *GC/MS chromatogram of the well water sample. Peak 1-9 are identified in Table 1. The peaks C_{22}-C_{36} are the hydrocarbons with the number of carbons in the range 22-36*

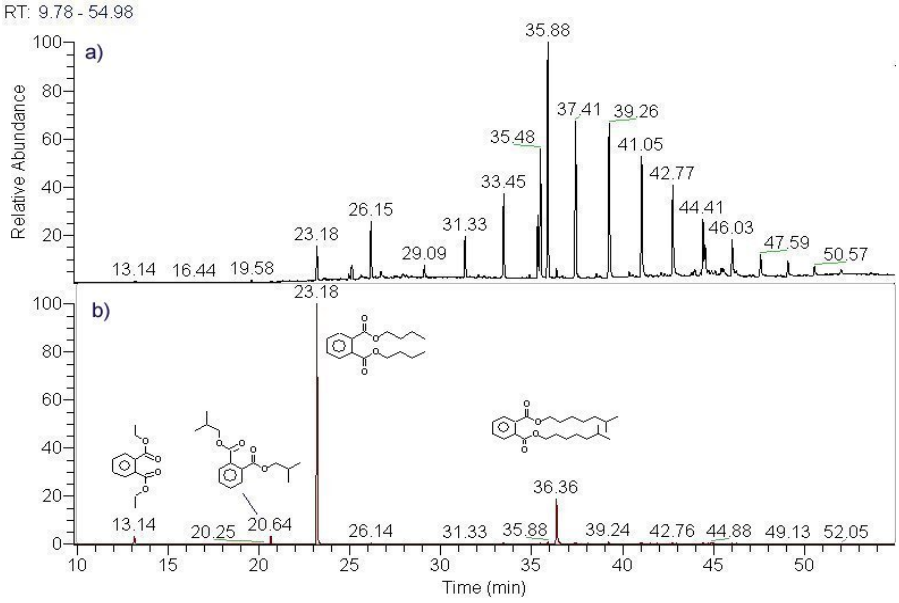

Fig. 2. *Detection of plastic additive (plasticizers) in studied water sample; a) TIC chromatogram; b) Characteristic ion chromatogram to m/z 149: Diethylphtalate (t=13.14), Diisobutylphtalate (t=20.64), Dibutylphtalate (t=23.18), Diisooctylphtalate (t=36.36).*

Plastics and other polymeric materials have become indispensable in our everyday lives. Although they offer many benefits, hazardous chemicals may be present in these materials. These hazardous materials can be introduced either intentionally as additives, or unintentionally as pollutants (AccuStandard, 2013). Therefore the plastic materials can be a significant source for new and emerging pollutants. The plastic additives are used for production of plastics with particular application as: Medical Devices, Food Packaging, Pharmaceutical Packaging, Toys, Wire and Cable, etc. Plastic additive are of following types:

a) Antioxidants work to slow down the oxidation cycle, usually by scavenging free radicals. (organophosphites, sterically hindered phenols, amines, and thioesters);

b) Accelerators (promoters) are additives that accelerate or speed up the chemical reaction or the curing of the polymers into the final plastic;

c) Antifoaming agents act to stop foaming during processing. Antifoaming agents typically work by reducing surface tension breaking up the foam;

d) Antidegradants include a broad category of additives used in compounding to slow deterioration that can occur due to oxidation, ozone or light;

e) Antiozonants are materials added to plastics to slow the deterioration of the finished product that occurs from exposure to ozone;

e) Blowing agents are sometimes also called chemical foaming agents. They are used to release gas into the plastic or resin. Blowing agents can be used to reduce weight, improve softness, provide insulation, add shock absorption properties or add resilience in the final product;

f) Coupling agents promote the physical or chemical interaction with the polymer;

g) Crosslinking is the polymerization reaction that branches out from the main molecular chain forming a network pattern of chemical bonds;

h) Crosslinking adds desirable properties such as: solidity, elasticity, impermeability to gases, and better electrical insulation;

i) Flame retardants are added to inhibit ignition or the flammability of the end-use product. Flame retardants generally function by inhibiting the mechanisms of burning;

j) A plasticizer is a compound added to a material, usually a plastic, to make it flexible, resilient and easier to handle. Plasticizers are major components in plastics that determine the physical properties of polymer products;

k) Biphenols are endocrine disrupters that exhibit hormone-like properties. This raises concerns about their use in polycarbonate based household products as well as medical devices;

l) Processing aids are compounding materials that improve the processing of polymers. (Reducing powder consumption during mixing, promoting compound fusion, adding lubrication, improving knitting);

m) Retarders are used to delay the onset of crosslinking and can be used to allow for longer processing times. They are also used to reduce scorching;

n) UV stabilizers, or light absorbers, act to protect the plastic against UV or sunlight damage such as discoloration, cracking, brittleness, or other loss of desirable physical properties;

o) Dyes and colorant products are one of the largest categories of plastic additives and are also used in textiles, leather goods, food and personal care products.

The petroleum additive industry is developing technologies and materials for the supply of service products for engines and motor vehicles, in cooperation with the petroleum and automotive industries, amongst others. While the activities of the industry are very well known on oil industry is very little public literature available. As a result, it is a need to know more about oil industry and particularly its impact on the environment (ATC, 2007).

The lubricant additives are produced with following purposes: friction reduction, corrosion protection, heat transfer, operating at extremes of temperature, engine seals protection, suspension of crankcase oil contaminants and viscosity regulators.Main chemical families of lubricant additives are (Yeomana et al., 2017):

a) Sterically hindered phenols;
b) Hindered Diphenylamines;
c) Zinc dithiophosphates (ZDDPs);
d) Phosphorus compounds;
e) Polysiloxanes.

CONCLUSIONS

Heavy rainfall events, impact drastic the quality of the surface water and water resource used for drinking-water.

The study of water sample collected from a drinking water well shows the presence of lubricants additives and plastic additives as pollutants. The presence of emerging pollutants in drinking water source is the result of agricultural, urban and industrial activities in the basin jointly with extreme rainfall.

This study focuses in an important aspect of the EU planning approach (regarding water quality and changes on water directives) due to extreme events. Implementation of suitable monitoring tools and procedures must to be planned with a view to a better knowledge of water-quality variation for a complete risk assessment and management program.

The increasing pollution by meteorological events leads to conclusion that for o good water management, the development of decision-support systems (DSSs) could be very advantageous in cases of extreme rainfall events. Finally, to respond and to react adequately to the crisis, analytical data need to be transferred to water managers for relevant, accurate decision making. DSSs represent the solution of the future, and are beginning to be employed in the drinking-water supply sector.

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