

## Monitoring priority/priority dangerous substances in the Someș-Tisa River Basin. Results and interpretation

<sup>1</sup>Giana Popa, <sup>2</sup>Viorica Coșier

<sup>1</sup>Someș Tisa Water Division – Romanian Water National Administration; <sup>2</sup>University of Agricultural Sciences and Veterinary Medicine, Cluj-Napoca, Romania, EU;  
Corresponding author: Giana Popa, giana.popa@dast.rowater.ro

**Abstract.** Ensuring the quality management of the water source in the hydrographic basin Someș-Tisa, in the acceptance of the Water Framework Directive 2000/60/EC, to reach to the good ecological status, involves the establishment of integrated monitoring and of some action plans for those sources that generate priority/priority dangerous substances (list I/ list II) in order to eliminate/decrease the pollution of the aquatic environment. The results of the monitoring put into light the areas of industrial/human activity generating chemical compounds under the incidence of EU Directive 2006/11/EC, replacing EU Directive 76/464/EC (the pollution due to discharges of dangerous substances in aquatic environment), as well as the level of pollution induced by them. From the analysis of the data base, the constitution at the level of the hydrographic basin Someș-Tisa, realized in concordance with the requirements of the legislation in the area of the management of the water source, the way of action and the measures needed to reach the level of compliance with the terms established in the Position Document between Romania and European Commission about Chapter 22 - Environment was adopted. The concreting of the diligences to comply with the EU Directive 2006/11/EC shall be realized in the report to elaborate at the end of the period of transition for the substances from List I (31.12.2009), as well as by applying the Management Plan of Someș-Tisa River Basin.

**Key Words:** dangerous substances, monitoring, action plans, evaluation.

**Résumé.** Dans l'acceptation de la Directive Cadre Eau 2000/60/EC en vue d'atteindre un bon état écologique, pour assurer le management qualitatif de la ressource d'eau du bassin hydrographique Someș Tisa il est nécessaire qu'on établisse un monitoring intégré et un plan d'action aux sources qui génèrent des substances prioritaires et prioritairement dangereuses (liste I/ lista II) dans le but d'éliminer/de réduire la pollution du milieu aquatique. Les résultats du monitoring ont mis en évidence les domaines d'activité industriels/humains générateurs de composés chimiques trouvés sous l'incidence de la Directive UE 2006/11/EC qui remplacent la Directive 76/464/EC concernant la pollution causée par les substances dangereuses déchargées dans le milieu aquatique, de même que le niveau de pollution que ces substances produisent. L'analyse de la base des données constituée au niveau du bassin hydrographique Someș Tisa, réalisée en concordance avec les exigences de la législation du domaine du management des ressources d'eau, a également démontré la manière d'agir et les mesures nécessaires pour atteindre le niveau de conformité aux termes établis par le Document de Position conclu entre la Roumanie et CE relatif au Chapitre 22 Milieu. Les démarches pour se conformer à la Directive 2006/11/EC seront concrétisées par le rapport élaboré à la fin de la période de transition pour les substances de la liste I (31.12.2009), et par la mise en pratique du Projet de Management du bassin hydrographique Someș Tisa.

**Mots-Clés:** substances dangereuses, monitoring, plans d'action, evaluation.

**Rezumat.** Asigurarea managementului calitativ al resursei de apă din bazinul hidrografic Someș Tisa, în accepțiunea Directivei Cadru 2000/60/CE, pentru atingerea stării ecologice bune, implică stabilirea unui monitoring corect și a unor planuri de acțiune acelor surse care generează substanțe prioritare/prioritar periculoase (lista I/ lista II) în scopul eliminării/ reducerii poluării mediului acvatic. Rezultatele monitoringului au pus în evidență domeniile de activitate industriale/umane generatoare de compuși chimici aflați sub incidența 2006/11/EC, care înlocuiește Directiva UE 76/464/CE precum și nivelul de poluare indus de acestea. De asemenea, din analiza bazei de date constituită la nivelul bazinului hidrografic Someș Tisa, realizată în concordanță cu cerințele legislației din domeniul managementului resursei de apă, s-a stabilit modul de acțiune și măsurile necesare atingerii nivelului de conformare la termenele stabilite prin Documentul de Poziție încheiat între România și CE referitor la Capitolul 22 Mediu. Concretizarea demersurilor pentru conformare pe Directiva 2006/11/EC se va realiza prin raportul ce se va elabora la sfârșitul perioadei de tranziție pentru substanțele din lista I (31.12.2009), precum și prin punerea în aplicare a Planului de Management al bazinului hidrografic Someș Tisa.

**Cuvinte cheie:** substanțe periculoase, monitoring, planuri de acțiune, evaluare.

**Introduction.** The community strategy regarding the prevention of pollution of the aquatic environment is relieved in the content of the Water Framework Directive, in art. 16, establishing and stating new procedures of identification of the chemical substances, as well as the development of a plan of measures needed to comply with. In this context, the European Parliament and Commission adopted Decision 2455/2001/EC establishing the list of priority substances in the area of water policy, realizing in the same time the amendment of the Directive 2000/60/EC<sup>1</sup>. This decision realizes the identification of those priority dangerous substances representing a significant risk for the aquatic environment and confer the priority to the actions of elimination/reduction of them<sup>2</sup>.

The Directive 76/464/EC<sup>3</sup> regarding the discharge of the dangerous substances in the aquatic environment was one of the first related directives that were adopted, which proposed ambitious goals for the regeneration of the aquatic potential affected by the multitude of chemical substances discharged, resulting from the anthropic activities, by the introduction of the concept of substances from List I and List II, that shall be eliminated/reduced.

For Romania, as a member state of the European Union, the negotiations for Chapter 22 – Environment from December of 2004, aimed at the Plan of Implementation of the Directive 76/464/EC and subsequent directives, including, along with the transposition of the Acquis Communautaire in the Romanian Legislation (Law of Waters No. 107/1996<sup>4</sup> with subsequent amendments and changes), time schedules and phases, including financing strategies and plans of securing the public and private investments, in infrastructure and technology, in order to decrease the global and cross border pollution (Șerban 2004).

A data base of monitoring dangerous substances existing at the level of Somes Tisa Water Division, gives many possibilities to value different degrees of implementation of EU Directive 76/464/EC, to establish the areas specifics and accomplish adequate programs of measures, so this document will distinguish those aspects.

**Context and Monitoring.** In this context, considering the prime inventory of polluters discharging dangerous substances (List I) in the surface waters, realized in the year 2002 in accordance with the Government's Resolution 118/2002, as well as the screening of the pollution sources with substances priority dangerous (List II) resulted from different types of activities realized in May of 2003, Romania asked for a period of transition until December 31, 2009 for the following substances from the List I: hexachlorobenzene, hexachlorobutadiene, 1,2 dichlorethane, trichlorethylene and trichlorobenzene in the case of 21 industrial units, cadmium and mercury, in the case of 27 industrial units and linden in the case of three industrial units. For the substances priority dangerous from the List II the programs of pollution decrease shall develop no later than five years after these were established.

In order to achieve the commitments taken in order to comply with this EU Directive, the monitoring program of the surface resource focused on the composition of the dangerous substances, respectively on adopting programs of measures to reach the target goals.

To apply integrated management of water resources concept is meaning to combine the usage water problems with those concerning natural ecosystems protection. (Jula & Șerban 2001)

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<sup>1</sup> Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, Official Journal of the European Communities, L 327/1, 22.12.2000.

<sup>2</sup> Data from <http://ec.europa.eu/environment/water/water-framework>

<sup>3</sup> Directive 76/464/EC about the pollution due to discharges of dangerous substances in aquatic environment, published in the Official Journal OJ L 129, 18/05/1976 P. 0023 - 0029.

<sup>4</sup> Law of Waters No. 107/1996 with subsequent amendments and changes, of the Romanian Parliament, published in Official Monitor 244, 8.10.1996

So, the water resources system (Koudstaal et al 1992) formed on natural water resources system and water management infrastructure, assure goods and services for water users, in the same time assure the conservation of aquatic ecosystems.

For the hydrographic basin Someș-Tisa the monitoring of the dangerous substances from the surface resource has developed since the year 2000 for the heavy metals, and since the year 2005 for the organic micro polluters. Similarly, there are measures of the pollution level of the sediments with heavy metals in certain sections executed in the same period (natural lakes, filling lakes).

The estimate about surface water quality was accomplish by legislation norm and monitoring data existent. So, in the year 2003, the general qualitative situation was established upon the basis of a legal norm (Order 1146/2002<sup>5</sup>, STAS 4704/1988<sup>6</sup>) that classifies the water flows on quality categories, after the quality and quantity monitoring ensured for the 1681 km from the hydrographic basin Someș – Crasna and the 505 km from the hydrographic basin Tisa, evidencing the existence of 933 km in the 2<sup>nd</sup> category, 938 km in the 3<sup>rd</sup> category, 167 km in the 4<sup>th</sup> category and 147 km as "degraded". In the "degraded" category of the water flows, were included those where quality the monitoring recorded in the group of "heavy metals" exceedings of the maximum accepted limits for the surface waters, that is: the rivers of Lapuș and Săsar (the hydrographic basin Someș Crasna), the rivers Vișeu, Cisla, Turt (the hydrographic basin Tisa) (see diagram in Figure 1).

Stare calitativa retea hidrografica - 2003

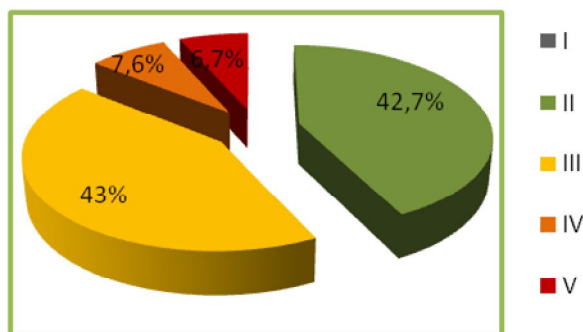


Figure 1. The qualitative state of the hydrographic network, 2003 (I-V – water quality classes)

In the year 2006, by promulgation of Order of the Ministry of Environment and Waters Management 161/2006<sup>7</sup>, was introduced in the specific Romanian legislation, the notion of "ecological situation" of the water bodies, who is actually, the target objective of the Framework Directive, when there are set five chemical quality class situations for the rivers, and natural lakes, partial using the biological qualitative elements.

This norm isn't totally agree with the stipulations of Water Framework Directive, but in the first part of 2009, ICIM București has elaborated the national methodology for quality status evaluation (rivers and lackes), in according to WFD. At this moment, is unrolling the testing/application of the methodology at the level of Someș Tisa river basin.

It was also established that, where the chemical pollution is responsible for the degradation of the ecological situation, the pollutant or pollutants with chemicals that represent the cause of the degradation shall be determined in order to act upon the concentration of the pollutant for the decrease of the impact underlined by the quality standard.

<sup>5</sup> Order of the Ministry of Environment and Waters Management 1146/2002, concerning of reference objectives for surface water quality clasification, published on Official Monitor 197, 27.03.2003;

<sup>6</sup> STAS 4706/1988, surface waters and quality technical conditions, of the Romanian Government;

<sup>7</sup> Order of the Ministry of Environment and Waters Management 161/2006 about surface water quality clasification to establish water body ecological status, published on Official Monitor 511, 13.06.2006;

It was also established that, where the chemical pollution is responsible for the degradation of the ecological situation, the pollutant or pollutants with chemicals that represent the cause of the degradation shall be determined in order to act upon the concentration of the pollutant for the decrease of the impact underlined by the quality standard.

**Stare calitativa retea hidrografica - 2008**

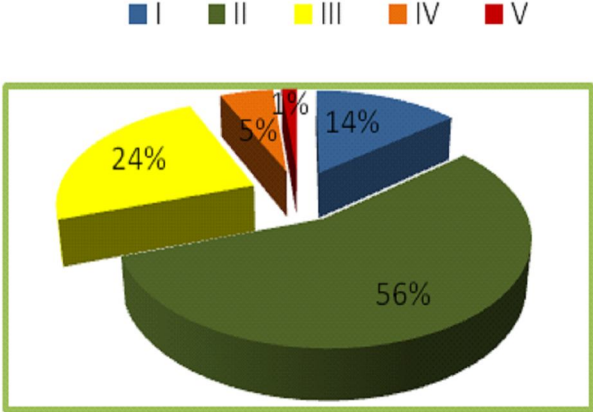


Figure 2. The qualitative state of the hydrographic network, 2008 (I-V – water quality classes)



Figure 3. The map of surface waters compared to their ecological situation, 2008, Someș Tisa River Basin

Considering the newly created conditions, the latter data of the quality monitoring from the year 2008, applied to the hydrographic network (extended, as compared to the year 2003) if 1818 km from the hydrographic basin Someș Crasna and 569 km from the hydrographic basin Tisa, noted the following qualitative situation, this time interpreted

function of the physicochemical and biological: 334 km 1<sup>st</sup> quality class, 1329 km 2<sup>nd</sup> quality class, 565 km 3<sup>rd</sup> quality class, 124 km 4<sup>th</sup> quality class, and 35 km lower quality class (map in Figure 3 and diagram in Figure 2). The same areas which were identified in the year 2003 out of the quality limits remain as areas with problems; however their area decreased.

**Results and Discussion.** In a comparative analysis of the two diagrams, it results that in the interval 2003-2008, the level of pollution of the surface resource decreased, on one side, consequence of the desistance/ decrease of the impacting industrial activities (metallurgy, pharmaceutical, cellulose and paper, mining), on the other hand, due to the appliance of the programs meant to improve the purification processes, especially in the area represented by human agglomerations. We can appreciate that, until now, for the decrease of the pollution in the hydrographic basin Someş-Tisa works representing 10% of the investing necessary of EUR 734.75 million planned for human agglomeration, and a small percent of the investing needed planned for the industry, of about EUR 74,511 million were realized. We must specify that the investment effort for the industry is 69.2% allocated for the works of securing and purifying the mining sites, which represent one of the most serious environment issues, and 26.38% are anticipated for works of technology upgrades and rehabilitation in the industry of cellulose and paper (incident to the IPPC Directive). For implementation the stipulations of Directive 76/464/EC are necessary about 2 thousand million euro (Serban & Galie 2006).

From the point of view of the monitoring of the priority/ priority dangerous substances the qualitative situation of the hydrographic network in the year 2008 noted four zones with higher risk of pollution with dangerous substances, respectively the areas of Baia Borsa, Baia Mare, Cavnic and Turt, where the anthropic mining activity generated serious influences on the environment, corroborated with the existing natural ground natural existent, rich in heavy metals (see Table 1).

Tabelul 1

Area	River	Chemical substances ( $\mu\text{g/l}$ )			
		Cu	Zn	Pb	Cd
Baia Borsa (1)	Cisla, subbasin Tisa	210.4	1305.3	156	65
Baia Mare (2)	Firiza Basin Somes	144.2	400.9	142.4	62
	Sasar, downstream Baia Mare, Basin Somes	71.8	870	-	-
	Ilba, right affluent of river Somes	257	16245	157	84
Cavnic (3)	Cavnic, affluent of r.Lăpuş	59.3	370.9	-	23
Turt (4)	Turt, subbasin Tisa	-	1061	26.06	5

The evaluation of the risk of failure to reach the good status for water bodies take into account the criteria for the identification of pressures and the criteria for the impact evaluation. (Serban & Galie 2006). The analyze was made considering:

- pollution with organic substances;
- pollution with nutrients;
- pollution with priority substances / dangerous substances
- hydromorphological alterations

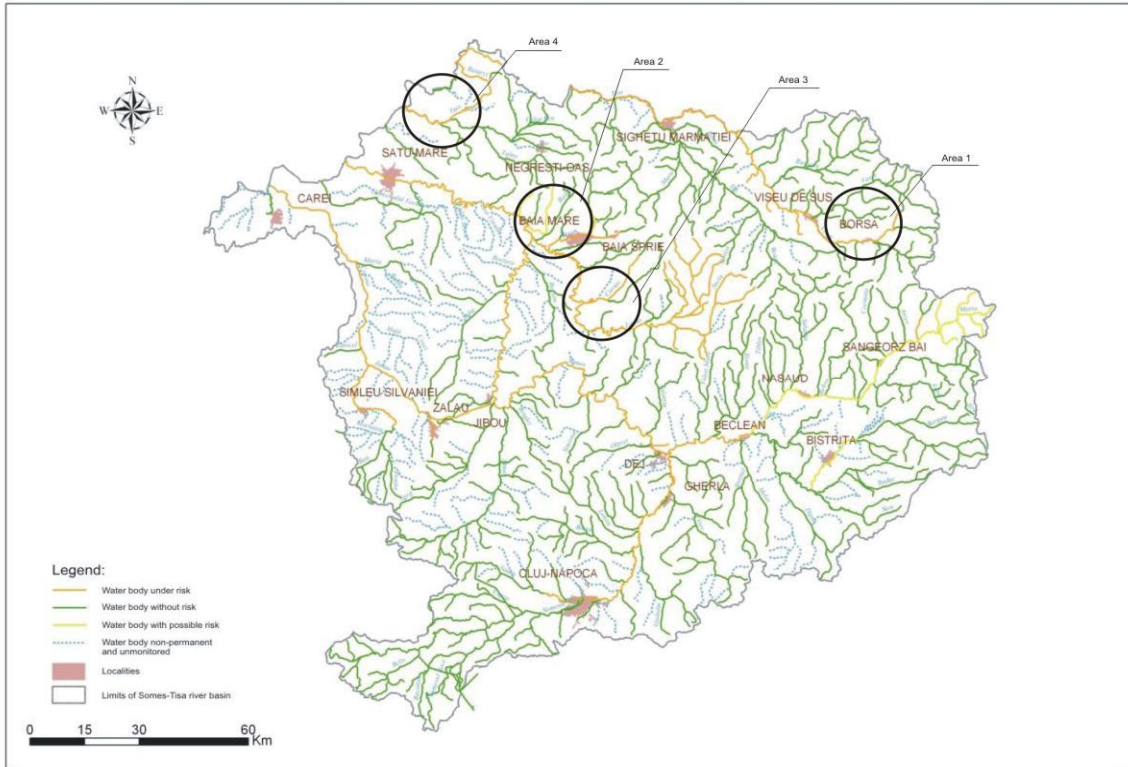


Figure 4. Map showing the water bodies under the risk in 2008, Someș Tisa River Basin. Yellow colour marked those water bodies who are affected by pollution with dangerous substances (heavy metals) and showing the 4 principal areas affected.

The river segments affected by the priority dangerous substances pollution (List II) were identified, consequent to the existence of the not purified stores of household waste in the area near the water flows, without ensuring the soil protection conditions (r. Zapodie, affl. Someș Mic), or discharges of household sewage waters, not properly purified, from industrial activities under the incidence of IPPC Directive – manufacturing of cellulose and paper and waste processing (r. Someș, at Dej) and urban management activities (r. Crasna).

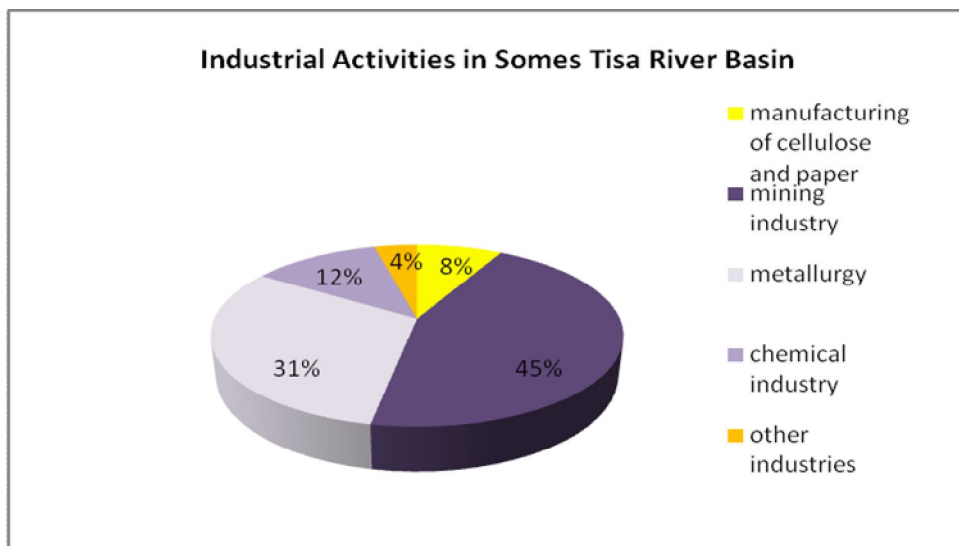


Figure 5. Repartition of industrial activities on domaines, in 2008

Most important industrial activity is representing by mining activities, about 45%, who's generating important quantities of pollutants in surface resources, as heavy metals.

The evaluation of the industrial activity at the level of the hydrographic basin Someş-Tisa, in accordance with the Directive 76/464/EC, and later with the Directive 2006/11/EC<sup>8</sup>, stipulating the re-launching of the protection of the aquatic environment, by applying specific measures, leading to the progressive decrease of the discharges, issues and losses of priority/priority dangerous substances in the water resources, included all the water sources suspected to generate this class of substances, being realized function of the type of activity, raw materials used in the processes, anthropic activity, and risk for accidental pollution, especially by the sensibility of the outlets in the impact zones.

In the hydrographic basin Someş-Tisa, the industry with a major impact on the environment factors, submitted to the incidences of the EU Directives regarding the Integrated Control of Pollution (Directive 96/61/EC<sup>9</sup> - IPPC), the discharge of the priority/priority dangerous substances in the aquatic environment (Directive 76/464/EC), storing dangerous waste (Directive 1999/31/EC<sup>10</sup>), is represented by the activity of extraction of the non-ferrous ore, metallurgy, manufacturing of cellulose and paper, chemical industry, their zonal distribution and weigh being represented in the diagram.

From this areas of activities, a number of 27 economic units required and obtained the period of transition until December 31, 2009 for the Directive 76/464/EC, in order to eliminate/decrease the discharges in the surface resource of the substances from List I (heavy metals, organic micro polluters). For the compliance, since the year 2005, plans of action were elaborated, including measures related to the monitoring for the substances from List I, correlated with the implementation of elimination/reduction methods of them from the discharges. Consequent to the appliance of these plans, 12% of the units terminated the works, by the decrease of the listed substances charge, 17% of them are developing these plans, 20% are promoting large breadth works for the conservation of the mining sites, 34% are executing the improvement of the purification processes, and 17% stopped the activity totally, or reallocated the activity in complying locations. Decreases of the charges were generally noted, however not substantial, for cadmium being recorded a decrease by 114,163 kg in 2008 as compared to 2007.

The monitoring of the substances from List I was applied in those domains of activity which were suspected for generating this class of chemical compounds in the effluents. In an unjustified manner, chloroform CHCl<sub>3</sub> was identified (its discharge limit in the surface resource is 0), in activities not specific to it, as a consequence of using their own technological processes, of water treated with liquid chlorine, for disinfecting purposes, collected from the urban centralized system. By applying the procedure of automatic dosing of chlorine for the disinfection of water and the compliance with the stipulations of Directive 98/83/EC<sup>11</sup> regarding the quality of water destined to the human consumption, the regional operator of the public services of water supply decreased the concentration of chloroform in the network, and even in the effluents.

As for the manufacturing of cellulose and paper, a domain of activity under the incidence of Directive 76/464/EC, it generated in the surface resource chloroform, due to the appliance of the whitening procedure of the cellulose paste with gaseous chlorine, chlorine dioxide and sodium hypochlorite. In the context of obtaining the period of transition until 2015 stated in the Directive 96/61/EC, a limitation of the emissions in the surface resource was accepted, conditioned by paying the priority to the investments in technology by applying the Best Available Technologies (BAT).

<sup>8</sup> Directive 2006/11/EC, replace Directive 76/464/EC about the plollution due to discharges of dangerous substances in aquatic environment, published in the Official Journal OJ L 318(17), 17.11.2006;

<sup>9</sup> Directive 96/61/EC concerning integrated pollution prevention and control, published in the Official Journal, OJ L 257, 10.10.1996;

<sup>10</sup> Directive 1999/31/EC on the landfill of waste, published in the Official Journal OJ L 182, 16.07.1999;

<sup>11</sup> Directive 98/83/EC, on the quality of water intendedfor human consumption (DWD - The Drinking Water Directive), published in the Official Journal OJ L 330, 5.12.1998;

The monitoring of the substances from the List II identified in the effluents discharged in the surface resource substances priority dangerous from the group of heavy metals represented by zinc, copper, nickel, lead, respectively the group of the organic micro pollutants represented by benzene, toluene, benz(a)pirene, benz(b+k)fluoranthene, phenanthrene, naphthalene, anthracene, cyanides. A number of 28 industrial units entered in a monitoring program, between that being identified a number of five with organic micro pollutants emissions in the pharmaceutical, textile industry, railway activity, a number of 10 with combined emissions of heavy metals and organic micro pollutants in the metallurgic, cellulose and paper, energetic industry, and respectively 13 with emissions of heavy metals preponderantly in the mining, metallurgic industry. Likewise were aimed the animal breeding and urban used waters purification activities, characterized by ammonium/azotates emissions, and respectively chrome, nickel, copper, cyanides, polycyclic aromatic hydrocarbures (PAH).

All the emissions are regulated by water management permits, establishing the conditions of discharge in the aquatic environment and the maximum admitted limits, in accordance with the aquis communautaire, adopted by the Romanian legislation.

The programs of implemented measures for compliance are in different phases of achievement, however, every year the emissions of pollutants in the surface resource are decreasing, therefore in the year 2008 compared to 2007, for the lead the discharged quantity decreased by 2441 kg, for the nickel it decreased by 188,8 kg, for the chrome it decreased by 113,8 kg, and for the zinc it decreased by 390 kg.

As for the monitored organic micro pollutants in the effluents of the industrial or human activities, the identified concentrations were measured in micrograms, which were generally under the detection limits of the homologated measuring devices, their variation being dictated by the raw materials or the profile of activity, so that, until now, we appreciate that the surface resource is not affected by this class of compounds.

**Conclusions.** The evaluation of the qualitative situation of the hydrographic network in the hydrographic area Someş-Tisa was realized in accordance with the specific legislation, stipulating the interpretation of the data depending on the specific indicators groups for assessing the chemical situation, as well as partial of the biological elements, the general physicochemical conditions and specific pollutants for establishing the ecological situation. The assessed chemical situation is relevant only in the conditions of the superposition of the database regarding the specific monitoring and that related to the monitoring of the priority/ priority dangerous substances, relieving the areas affected by on-spot and/or diffuse impact generated by human activity, for the latter investigation and establishing the plans of measures needed to decrease pollution.

In December of 2008, the European Commission adopted the Directive 2008/105/EC<sup>12</sup>, establishing the ecological quality standards (EQS) for the priority dangerous substances, that must be achieved in the surface water until 2015, in order to ensure the good chemical situation of the surface waters. The Directive imposes the progressive decrease of the issues, losses and discharges for all the priority substances, elimination or stopping issues, losses, and discharges for the priority dangerous substances. This shall be adopted in the Romanian legislation until July 13, 2010, when its stipulations must be enforced.

For the compliance with the Water Framework Directive (WFD), it is compulsory to establish the quality standards for the specific pollutants in each hydrographic basin, identified in concordance with the stipulations of this directive, and acts for the purpose to reach the compliant chemical quality, as part of the ecological situation, in the year 2015.

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<sup>12</sup> Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council OJ L 348, 24.12.2008;



For reaching the compliance, a program of measures for each basin is being elaborated, within the Basin Management Plan, till the end of 2009, which shall become operational until 2012. In this respect, the long term monitoring shall be applied, for a number of 33 priority substances included in Appendix I of the EQS Directive, which tend to accumulate in the in sediment and/or biota, paying a particular attention to the substances: anthracene, brominated dipheniloxye, cadmium, chloralcanes, Di(2-ethylhexyl) phthalate, fluoranthenes, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclohexane, lead, mercury, pentachlorobenzene, PAHs, and measures shall be adopted to decrease the accumulated concentrations in the sediment and/or relevant in biota.

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Authors:

Giana Popa, Romanian Water National Administration, Someș Tisa Water Division, Inspection Departament, Cluj Napoca, Romania, EU, 17 Vanatorului street, 400213, e-mail:giana.popa@dast.rowater.ro

Viorica Coșier, University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca, Faculty of Animal Husbandry, Department of Biotechnologies, Cluj-Napoca, Romania, EU, Calea Mănăștur 3-5, 400372, e-mail:viorica.cosier@gmail.com

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