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Trajectory of inorganic contaminants in river systems in the mining areas of northwestern Romania – Satu Mare County

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Abstract. Traditional mining operations have not taken into consideration long-term negative impact on the environment, because in the beginning of these activities, there were no regulations or standards to guide these works and neither concepts of regeneration and restoration of affected sites have not existed. The disturbance of surface and groundwater resources has resulted in a number of serious environmental issues, such as acid mine drainages, erosion/sedimentation, contamination of groundwater and surface water, chemical agents and air pollution. Now, beyond their damaging impact on the environment, the abandoned mine sites register several serious threats to public health and safety. One of many problems that can may be present at an abandoned mine area near the human settlements is the drinking water supplies contaminated due to pollution with heavy metals or with chemical agents used in mining process. This issue is present in northwestern Romania due to the mining activity which dates back to the second half of the eighteenth century. This paper presents the simulation of the trajectory of the inorganic pollutants (Cd, Pb, Zn, Cu and Cr) in surface waters for a period of four years (2011-2014) which is essential to control the contaminants, because they are non-decaying substances. The simulation has generated charts highlighting the evolution of heavy metals on horizontal and vertical direction along the riverbed Socea on an area of 3 km. The Socea Valley is situated in the Tarna-Mare village, Satu Mare County.
Key Words: inorganic contaminants, mining area, surface water, environmental issues.

Introduction. The aquatic systems of "river" type are an important component for life, work and human development. Bringing and maintaining water quality in good condition is the primary aim of the Water Framework Directive 2000/60/EC, approved by the European Commission.

Recent studies from around the world have shown the long-term negative impact of wastewater discharges from abandoned mines, e.g. in the England and Wales up to 6% of the rivers are affected (Jones et al 2013). This is mainly due to the limited perimeter between the surface water and mining activities. The mining operations need to use water as a power source and for ore processing (Bird et al 2010; Coulthard & Macklin 2003). The metals which reached into the surface water can be transported by it which flow through areas with human settlements, both as metal in solution and metal adsorbed to suspended solids (Pintilie et al 2007).

A current example is the Philippines where mining is practiced both on a small scale and artisanal for subsistence level or as a business and established mining companies. Here it was estimated that 75% are in subsistence mining, 15% are small individual or family businesses and the last 10% are established commercial mining firms (Buot et al 2014).

In Romania the available water resources are strongly influenced both quantitatively and qualitatively due to human activities, both industrial and agricultural (Mocanu & Fodor 2011).

The essential parameter regarding the river pollution is the spatial and temporal variation of concentration of the pollutant in the water. Recently, both the water resource agencies and the consulting engineers have expressed the need for water quality estimation at a certain point and time by the input of pollutants in water resource. Due to the complexity of the process, it is often difficult to predict the extent and impact of the contamination.

Because loadings degrade the water quality, the behavior of heavy metals in environment depends on their inherent chemical properties. These contaminants can be divided into different categories according to their dissolved form and redox status. One category of metals like copper, cadmium, lead, nickel and zinc form free or complex cations when are dissolved in water, e.g. Cu^{2-} or CuCl. The other category, the soluble complexes are formed with negatively charged ions such as chlorine. Metals also tend to form poorly soluble sulphides under chemically reducing conditions. The differences between groups of metals have important consequences for the partitioning of the metals among several dissolved and particulate phases (Loucks et al 2005).

The fate of heavy metals in a water system is determined primarily by partitioning in water and particulate matter (including phytoplankton) and by transport. The partitioning divides the total amount of a pollutant into a dissolved fraction and several adsorbed fractions. The fractions of a metal that are adsorbed onto particulate matter are influenced by all the processes that affect particulate matter, such as settling and resuspension. The partitioning is described by sorption to particulates, precipitation in minerals and complexation in solution. Sorption can be described as an equilibrium process (equilibrium partitioning) or as the resultant of slow adsorption and desorption reactions (kinetic formulations) (Loucks et al 2005; Chaabelasru et al 2014; Martin & McCutcheon 1998).

The soluble metal concentration is determined on the basis of the relevant solubility product. The excess metal is stored in a precipitated metal fraction. Sorption and precipitation affect the dissolved metal concentration in different ways. Both the adsorbed and dissolved fractions increase the total concentration as long as no solubility product is exceeded. When it is, precipitation occurs (Loucks et al 2005; Chaabelasru et al 2014; Martin & McCutcheon 1998; Coulthard & Macklin 2003; Kachiashvili et al 2007; Borah & Bera 2003).

In general, the behavior of metals in natural waters depends on substrate sediment composition, suspended sediment composition, and water chemistry. Human activity promotes the accumulation of contaminated sediments in water courses. These activities sometimes indirectly increase the amounts of heavy metals released into the environment by natural processes. Immediately after entering into surface waters, heavy metals deposition occurs on the bottom of aquatic areas (streams, sediments, lakes, estuaries) (Pintilie et al 2007).

Rivers passing through industrial and mining areas transporting metals, partly as metal in solution and partly as metal adsorbed to suspended material. Aquatic organisms may be adversely affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry composition in the surface water system (Pintilie et al 2007).

Given those, for the sake of current and future generations, there is a need to safeguard the purity and quantity of water against irresponsible mineral development that can increase the contamination and sedimentation loads. This irresponsibility can lead to a reduced quantity of available water (Adetunde et al 2014).

The main objective of this study was to assess the load of certain heavy metals (Cd, Pb, Zn, Cu and Cr) in surface water located near an abandoned mining area (Socea mining area, Tarna Mare village, Satu-Mare County) for over 20 years and to show the differences between the four years of monitoring 2011-2014.

Material and Method

Study site. The study area is in the northwestern Romania, specifically in Satu Mare County, village Tarna Mare (Oaş Land - traditional area in the field of mining) as depicted in Figure 1. The area has a temperate continental climate, moderated with slightly more warm summers and winters milder than generally in the rest of the country. The average annual temperature at the foothills of Oaş-Gutâi Mountains is 8^{o}C (Karácsonyi 1995).

Tarna Mare is the most northern commune of Satu Mare county, located in the foothills of Oaş Mountains, at a distance of 60 km north-east of the county, DN19 route, 1C and DJ109M. It has borders with Ukraine and a border crossing point, but it is not in operation. The village is situated on the Tarna River (www.tarnamare.ro).

Both qualitatively and quantitatively aspects of the Tarna River through the Socea Valley near to abandoned mining area were evaluated. Socea Valley is an important source of drinking water, so its pollution presents a risk to human health. Tarna River is the Tisza River tributary with catchment areas > 1.000 km^{2}. The latter collects water from rivers in the northwestern Romania and then flows entering into the Danube near Titel, Serbia. The area chosen for study being near the Ukraine border is considered to be an environmental concern because the pollutants can spread beyond the borders of Romania through surface water and can have serious consequences.

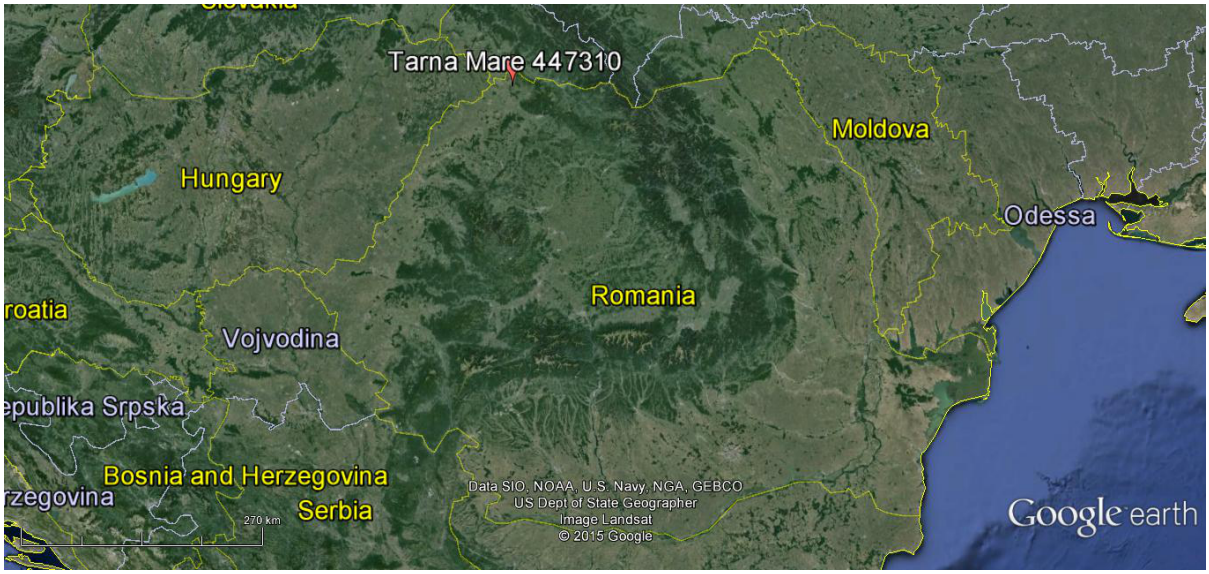

Figure 1. Study location map (45°35'21.10" N : 24°28'02.29" E - GPS coordinates).

Sample collection and handling. This part in environmental study and monitoring is very important because any error created cannot be rectified even by a perfect analytical procedure and technique.

Sample collection took place from 15-20 August each year, during four years (2011-2014). Sampling points are along the Socea Valley from the upstream to the downstream and in all campaigns they were collected from the same location (middle of the valley) at a depth of 10 cm below the surface water (Figure 2). During the sampling phase, the weather reports and river aspects were different.

Samples from Socea Valley were taken near the roads publicly available in accordance with local regulations. The field sampling did not involve endangered or protected species. Stream water samples were collected in metal-free 2L polypropylene recipients and tightly cap immediately after sampling. Water pH was measured during each water collection. Water samples were stored at 4^{o}C in a car cooling box until performing the laboratory analysis (such the degradation or alteration of the sample is minimized) and replicates were run within 4 to 6 weeks. Samples were not acidified in the field.

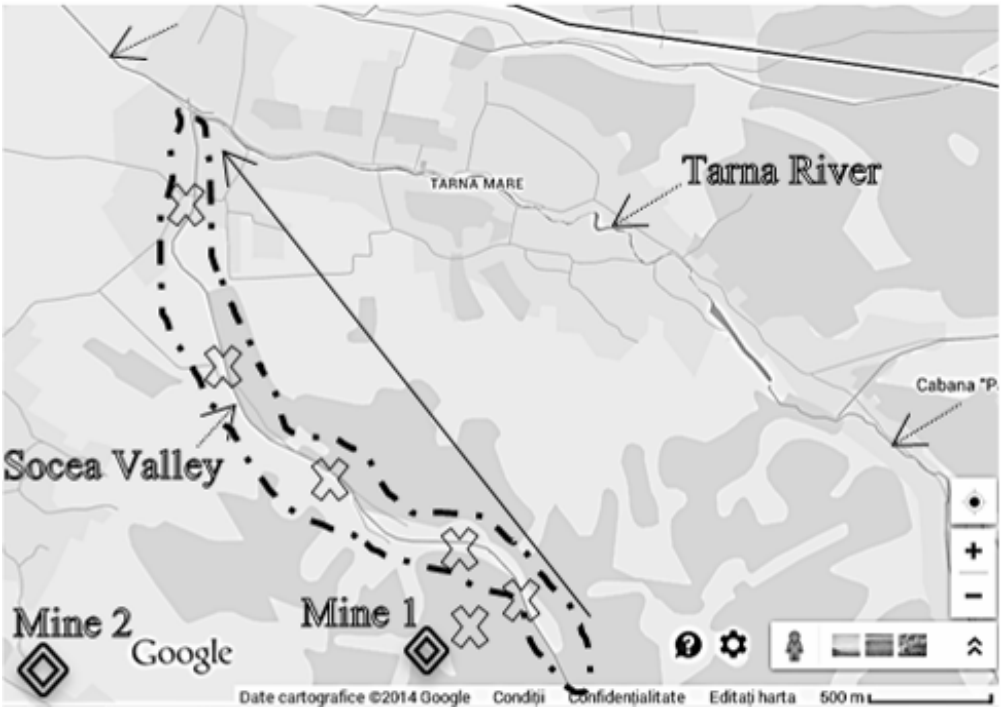

Figure 2. Sampling location map – sampling points on Socea Valley (Google Earth 2014).

Sample analysis The chemical analyses were performed in the laboratory within the National Institute for Research and Development in Environmental Protection – INCDPM, Bucharest. The samples were acidified in the laboratory with nitric acid to pH < 2 and after 16 hours (to allow the adsorbed metals to re-dissolve) were analyzed. Then they were digested according to SR EN ISO 15587-2:2003 Water quality - Digestion for the determination of selected elements in water - Part 2: Nitric acid digestion. An Atomic Absorption Spectrometer (A.A.S.) was used for measurements of metals (cadmium, lead, zinc, copper and chromium) concentrations in the water samples collected according to the procedure described by the Varian manufacturer.

Results and Discussion. Following the laboratory analysis of samples taken in each August from 2011 to 2014 was found significantly exceeded the limit values of concentration of the cadmium and zinc according to the order established by Order 161/2006 – a Romanian guideline. To control the contamination along the riverbed Socea on an area of 3 km near the point source (abandoned mines site) was simulated the metals trajectory by charts with data obtained at the time of sampling (Figure 3).

The valley watershed is a simple but dynamic system. Because of this we have not used a complex numerical model to simulate the temporal variation of concentration of heavy metals discharged into the riverine system. It is assumed that the metals are distributed homogeneously in the water column. The metals from the analyzed samples can exist in either a dissolved form or adsorbed to solid particles. Water flows into the water column at a volumetric flow rate Q, with a total metal concentration Ct. It is assumed that the water flows through the water column element at the same rate and at the same concentration as in the whole water column.

In order to simulate the behavior of the system, the representations are solved using the Excel software and considering the initial conditions (height of water column = 0.5 m; volume of water column V = 10 m^3; water velocity, vs m day^{-1} = 0.1).

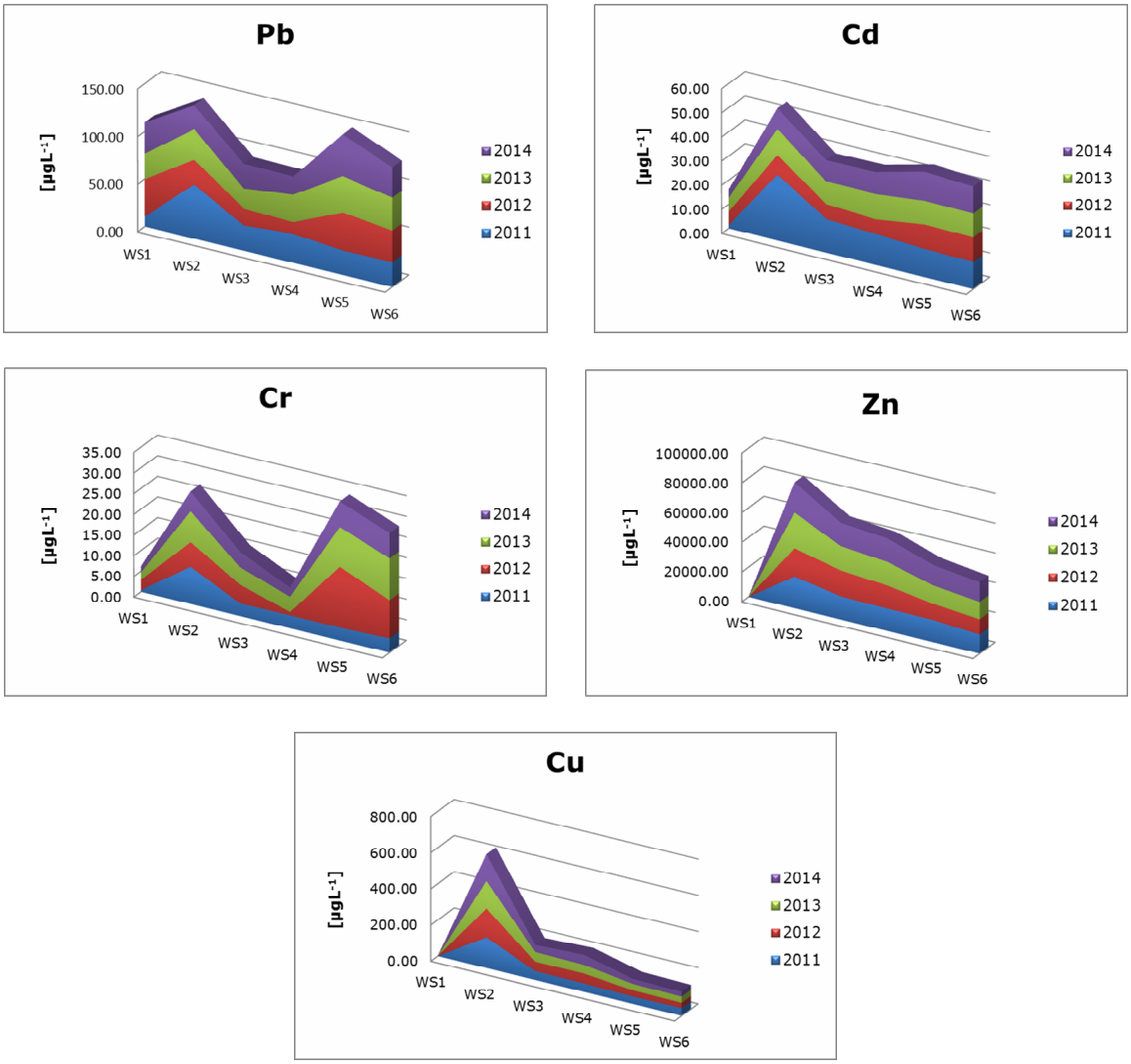

Figure 3. Metals dispersion in surface water according to the obtained results during four years.

Metals accumulate continuously in the water column during the monitoring period (48 months), due to continuous discharges originated from the source (Figure 4). The maximum concentrations are reached close to the discharge point. After that, the concentration remains almost constant, even when the water flow rate drops to 70% of its initial value.

Therefore, the metals values ranged between: Pb = 10.50–57.00 µg L^{-1}, Cd = 1.40–27.35 µg L^{-1}, Cr = 0.40–14.71 µg L^{-1}, Zn = 19.23–24073.40 µgL^{-1}, and Cu = 0.55–169.55 µg L^{-1}. The values were found along the river course within the period of study. The concentration distribution for Pb and Cr in the study area showed is irregular, except the first year (2011). This irregularity, in general, is influenced by meteorological parameters (such as rainfall and temperature), metals deposition and bioaccumulation process of metals in aquatic organisms.

To achieve the graph of annual metal loading the entire period 2011-2014 as 100% was considered (Figure 4).

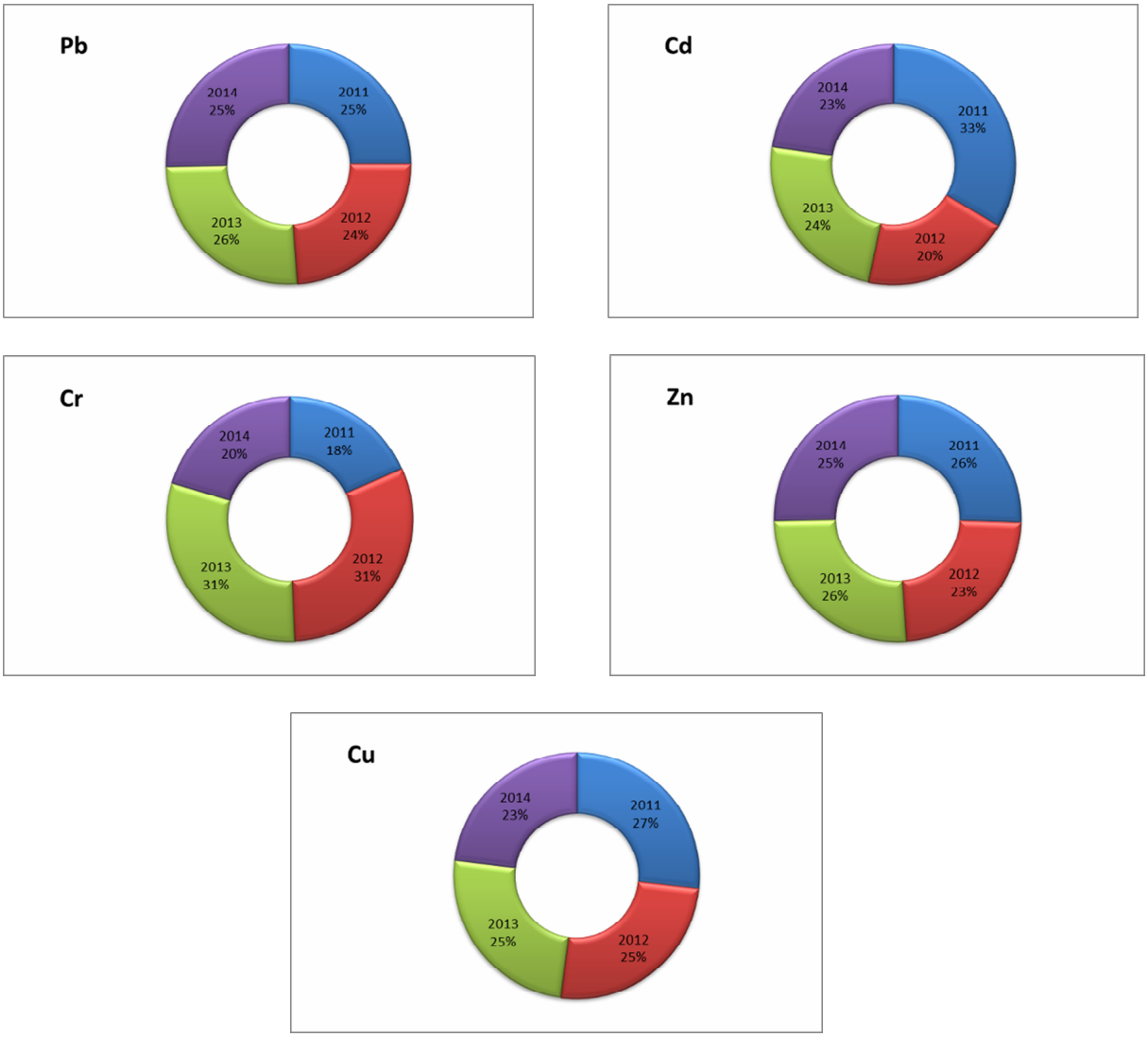

Figure 4. Annual load of metals in the aquatic environment as a percentage.

It is noticed that between annual discharges there are no significant differences. The loads constantly occur in surface water maintaining the level of pollution.

In general, due to relatively of small depths of water courses, the vertical turbulent diffusion effects manifest only over a relatively short distance downstream of the pollutant source (vertical concentration distribution becomes uniform rapidly) (Petrescu & Sumbasacu 2010), but in this case the high loads contradict. The surface water has small depths until flows into Tarna Mare River and along its watercourse in samples were maintained high concentrations of metals during the monitored period.

Peak pollutant concentrations and loads occurred during storms in this natural river basin because the rainfall collects higher quantity of metals in the surface water originating from the pollution source. For aquatic ecosystems the critical limits of Pb and Cd are related to ecotoxicological effects (De Vries et al 2005).

As expected, the high metal concentrations obtained persist today and tomorrow unfortunately in Socea Valley due to the historical pollution source - here the mining activities dates before the Second World War.

In recent years the monitoring efforts made by several agencies near to the study location reflect a special interest for controlling the metals dispersion into the environment from the source point because they are non-decaying substances. A common approach to controlling point source discharges is to impose standards specifying maximum allowable pollutant loads or concentrations in their effluents. But this is often done in ways that are not economically efficient or even environmentally

effective. In general, effluent standards content do not take into account the particular assimilative capacities of the receiving water body.

Conclusions. This paper has shown that the Socea riverbed is severely contaminated with heavy metals (Cd, Pb, Zn, Cu and Cr) and they continue to spread beyond the study area. This is a pointer to the fact that there is an irregular discharge of contaminated effluent into the natural receptor – Socea Valley. Limited data obtained and presented here can be considered a huge step for future detailed studies regarding environmental protection in this area.

Further studies should be performed in the future for an advanced investigation including the water/air temperature, rainfall and the influence of wind intensities and direction and in a larger study area.

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