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Cover 1: *Taxodium distichium* with *Tillandsia usneoides* (moss).
Photo: Graeme Mattews

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CONTENTS – SOMMAIRE – CONTENIDO – CUPRINS

STUDIA UBB AMBIENTUM, LXV, 1, 2020, pp. 5-11
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CURRENT URBAN CO_2 CONCENTRATION IN DIFFERENT PLACES IN CLUJ-NAPOCA TOWN

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ABSTRACT. CO_2 enrichment in the atmosphere through quantify of urban emissions remains a challenge. It is a directly links between urban CO_2, CO_2 emission in the cities and the urban form, functions, and climate. Has been measured the current CO_2 concentration in two different important road nodes connected by an important road artery; one located at a higher altitude–Zorilor-Calea Turzii and the other at low altitude Cipariu-Calea Turzii. Also, current urban CO_2 concentration on different road in Cluj-Napoca town is presented. Following the idea of low carbon city, such relationship have important implication in re-organization of cities, modeling of activities, technologies, setting the direction on certain major road or bypass road. The measurement has happened between June-July 2019. Additionally the correlation with number and type of autos was done. With this study we try to create a better understanding on implication of the spatial form in low carbon urban development.

Key words: *urban CO_2, emission CO_2, low carbon, CO_2 monitoring*

AIMS AND BACKGROUND

At the urban scale, the sources of CO_2 can be attributed to the combustion of fossil fuels for heating, ventilation, and air conditioning (HVAC), transportation, industrial processes and power generation (Kennedy et al., 2009; Mitchell et al., 2018) along with biological sources, namely soil, plant and human respiration; CO_2 is also taken up by photosynthesis.

Air pollutant emission from transport are a main contributor to air quality problems in Europe and not only, (California Clean Air, EPA Doket, NHTSA.Docket 2016; EEA Report 2018).

Emission of particulate matter (PM), nitrogen oxides (NOx) unburnt hydrocarbons (HC) and carbon monoxide (CO) are regulated in the EU. In 2016, road transport contributed nearly 21% of the EU's total emission of carbon dioxide –the main greenhouse gas. On 17 April 2019, the European Parliament and the Council adopted Regulation (EU) 2019/631 setting new CO_2 emission standards for cars and vans. The new regulation will apply from 1 January 2020. EU legislation requires Member States to ensure that relevant information is provided to consumers, including label showing a car's fuel efficiency and CO_2 emissions.

EXPERIMENTAL

Telaire 7001 CO_2 Monitor has been used to measure the all (CO_2) concentrations. At the same time the temperature of air, humidity and wind rate have been registered. All these parameters were necessary to estimate the air quality into the town (Haiduc et al., 2005; Beldean-Galea et al., 2007[a,b]).

Procedure: Monitoring of CO_2 concentration was done in the morning and after the lunch, in the same day, in different road nodes, but also in other different days at the same time. In the end, the average for each point was done and the value up to limit accepted was represented.

Google map and Google Earth program were necessary for placing the measurement point on the map. Statistical program used was excel and origin 7.0.

RESULTS AND DISCUSSIONS

The values recorded on the same day for two important roundabouts in Cluj-Napoca: Cipariu and Zorilor, we can say that a lower temperature, while higher humidity influences the atmospheric concentration of CO_2. Thus relating to a value of 500 ppm limit, the excess is an increase of about 7.8% for values in the Cipariu roundabout (table 1) and figure 1.

Table 1. *Temperature, humidity, atmospheric pressure and CO2 concentrations recorded on the same day in two major roundabouts in Cluj-Napoca, Zorilor and Cipariu*

Date	Temperature (°C)	Humidity (%)	Atmospheric pressure (mb)	Wind (Km/h)	CO_2 concentrations (ppm)
28.06.2019 At noon, Zorilor	25.5	64	1015	15	483
28.06.2019 In the morning, Cipariu	23.9	68	1015	15	539

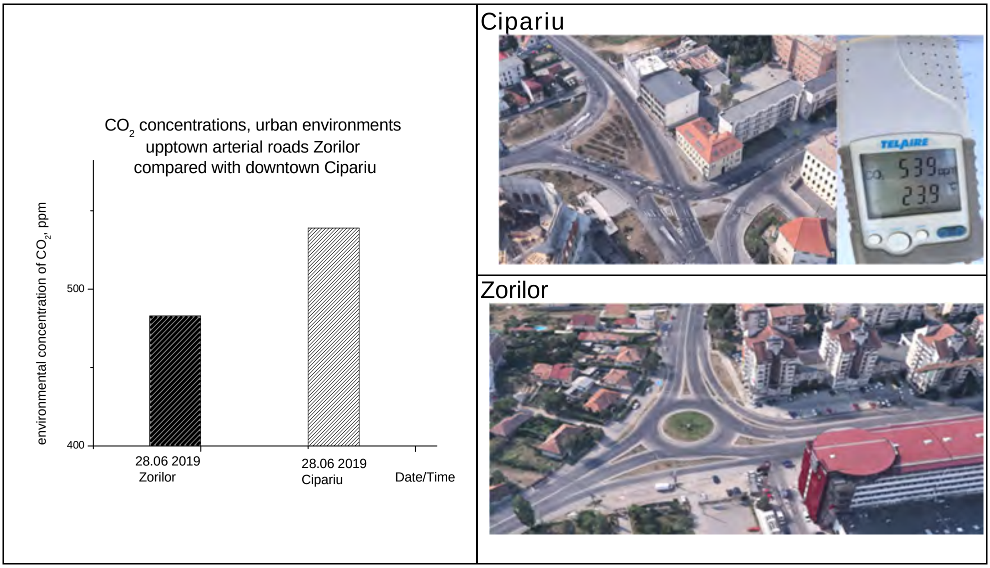


Fig. 1. *Monitoring CO_2 concentration in Cipariu Square roundabout, up to Calea Turzii street, Cluj-Napoca and Zorilor roundabout, near UTCN*

When CO_2 concentration measurement was performed in the same roundabout – Zorilor, at noon, on two different days - late June and early July, even with some difference of about 7.8°C temperature, 6% of humidity and 6 mb pressure, obtained values were less the reference numeral 500 ppm (table 2, figure 2).

CO_2 concentration measurements were made again in the same day, within a range of 3 hours around noon on different roads. It is worth mentioning the fact that the measurements were recorded in the car with the windows open. Even so, all the values were 500 ppm under the mark (figure 3).

Table 2. *Temperature, humidity, atmospheric pressure and concentrations of CO_2 recorded on two different days, at noon on the Zorilor roundabout*

Date	Temperature (ºC)	Humidity (%)	Atmospheric pressure (mb)	Wind (Km/h)	CO_2 concentrations (ppm)
28.06.2019 At noon, Zorilor	25.5	64	1015	15	483
01.07.2019 At noon, Zorilor	33.3	50	1021	8	477

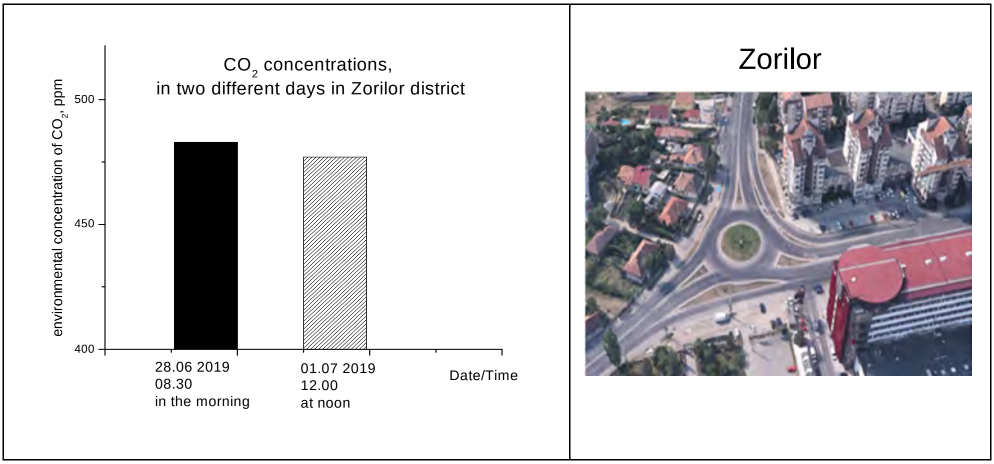
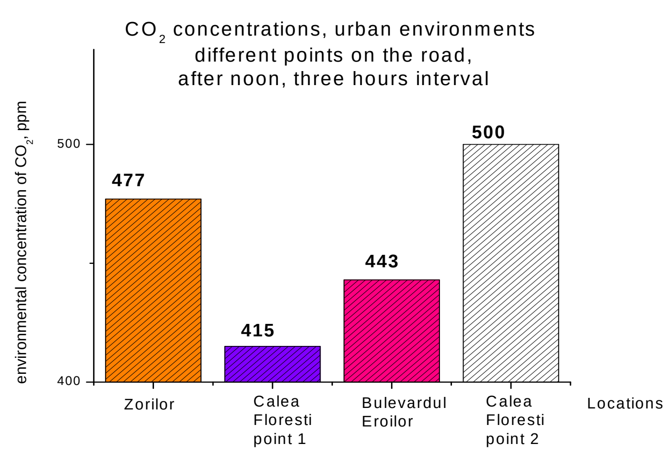


Fig. 2. *CO_2 measurement in UTC Zorilor roundabout (morning and noon)*

The highest concentrations of CO_2's, was also seen in the afternoon, in downtown, near crosswalks.

Map and figure 4 presents suggestive locations and magnitude recorded on hot-spots. The surplus was observed between 55.8% and were within 2%.

Measurement of CO_2 corresponds to monitoring of air quality and the final target is the reduction of greenhouse gases. Estimating weight also means polluting sources to quantify CO_2 emissions from fossil sources, customized by region. The CO_2 in the atmosphere corresponds to the exchange of CO_2 between tanks. If CO_2 is absorbed by plants during photosynthesis is greatest during periods of plant growth, his release back into the atmosphere will be even greater as amplitudidea process of breathing will be higher (includes both the processes of decay, rotting matter wood and the breathing metabolic



Obsevation: There were no significant differences recorded in different locations on main arteries in Cluj.

Fig. 3. *CO_2 concentration in different places in city, when the measurement has been made from the inside of car while driving*

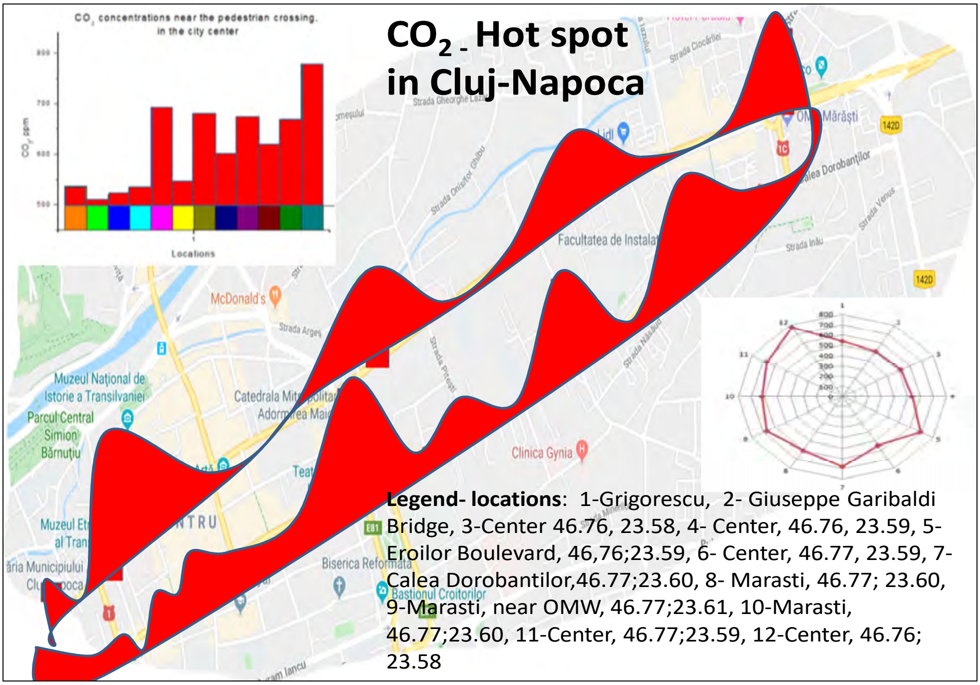


Fig. 4. *CO_2 - Hot spot in Cluj-Napoca*

green plants. CT 2017 version Carnegie-Ames Stanford Approach (CASA) calculates flows global carbon equivalent CO_2 stream, taking into account climate models coordinated by biophysical processes and difference normalized index of vegetation NDVI - based on satellite observations. Net primary production, NPP and heterotrophic respiration, RH, will thus be simulated for each cell in terrestrial broadcast, which is a difference between charges with NPP photosynthetic carbon (coarse primary - Production GPP) and carbon released by same plant due to “maintain breathing” or just breathing autotrophic $R_{A.}$

The difference between Net primary production, NPP and carbon released CO_2 R_H characterized net exchange of an ecosystem, NEE.

CarbonTracker CT2017 CT 2017 also takes into account emissions from fossil fuels, taking into account both the diurnal variability and weekly variability time (Gately and Hutyra, 2017; 2018).

Considering the low vegetation existing downtown, figure 4, according to image taken from Google Earth, one can conclude that in that short measure when weather changes were insignificant surpluses recorded were due to strict emissions from transport.

CONCLUSIONS

The registered values in Cluj-Napoca center, near the road nodes was up to 500 ppm, considered the normal value limit. All these suggested the used terms of urban thermal island or urban hot spots. Time analysis of these emissions associated with changing transport patterns could influence urbanization process thus favoring suburban development areas. A solution of hot spots should be recorded and the construction of a metropolitan belt.

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LAND-USE INFLUENCE ON HYPORHEIC BIOTA FROM MEDITERRANEAN STREAMS IN CENTRAL SPAIN

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ABSTRACT. Detailed knowledge of hyporheic zone (HZ) biota response to change in land use is crucial for understanding the ecohydrological functioning of communities within the river corridors. This paper investigates the response of hyporheic crustacean communities in relation to spatial heterogeneity in water conditions under changes in land use of the alluvial floodplain of the Jarama basin in central Spain. The study is conducted in four streams of the basin under distinct local land-use and water resource protection conditions: i) preserved forested natural sites at river headwaters where critical river ecosystem processes were unaltered or less altered by human activities, and ii) sites with different degrees of anthropogenic impact from agriculture and urban/ industrial activities in the lowland. The results indicate that streams draining forest and semi-natural areas were characterized by cold and pristine hyporheic waters and crustaceans' communities harbor a well-developed stygobite fraction. Conversely, intensive agricultural practices in the lowland cause nutrient enrichment of hyporheic waters. Thus, this type of land use increases the diversity and abundance of non-stygobites, whereas the abundance of stygobites is decreased. Mixed activities, industrial and urban development and agricultural cause an extreme decline of the crustacean community and/or species loss due to a combined effect of increase of nitrites, ammonia, trace metals and volatile organic compounds, and a deleterious decline of dissolved oxygen reaching hypoxic and/or anoxic hyporheic water conditions. The combined information of spatial variability of hyporheic biota has the potential to improve the understanding of impacts caused by changes in land-uses on HZ water conditions.

Key words: *land-use, hyporheic zone, crustacean, river management, Spain.*

INTRODUCTION

The hyporheic zone (HZ), located at the interface between surface and groundwater and plays a significant role as ecosystem service provider for river ecosystems (Boulton, 2008). This zone is an important component of river ecosystems controlling the water exchanges between surface and groundwater and ensures the cycling of carbon, energy, and nutrients and provides a habitat for benthic and hyporheic invertebrates (Danielopol, 1989; Dole-Olivier et al., 2009; Iepure et al., 2013). Furthermore, it serves as buffer and bioremediation zone for distinct pollutants mainly organics (Dole-Olivier et al., 2009). If changes in land use occur in alluvial plains, the hyporheic habitat may undergo severe disturbance reflected in loss of ecosystem services (Boulton, 1997, 1998; Hancock, 2002). This occurs via direct contamination of the surface/hyporheic waters or by polluted groundwater discharge in stream bed sediments (Conant et al., 2004; Chapman et al., 2007; Kalbus et al., 2007, 2009) by loading suspended sediments (Kuhnle et al., 2001), phosphorous (Cooke and Prepas, 1998), organic matter (Strayer et al., 2003) and trace metals (Mösslacher, 1988; Plénet et al., 1995; Moldovan et al., 2011; Iepure et al., 2013). In addition, overexploitation in the alluvial plain causes a disruption of hydrological exchange pathways between surface, groundwater, and the riparian zone of river ecosystems (Ward et al., 1998; Gibert et al., 1990; Tockner et al., 2000). Overall, the alteration of both river channels and their alluvial plain functionality endorses changes of the main functional role of the hyporheic zone of rivers: to warrant a good quality and 'health' for lotic ecosystems (Boulton et al., 2010).

The water quality in river ecosystems impacts the hyporheic community composition and the abundance of different groundwater dwellers (Dole-Olivier et al., 2009). Recent exhaustive studies in remote lotic ecosystems have shown that increasing agricultural practices (i.e. pasture, logging), intensive deforestation and rivers channel alterations cause a decline in hyporheos diversity and/or abundance (Gibert, 1991; Gibert et al., 1995; Notenboom et al., 1994; Boulton et al., 1998; Mösslacher and Notenboom, 1999; Illyová et al., 2011; Di Lorenzo and Galassi, 2013). They also revealed that the strong modification of alluvial floodplains for agricultural purposes causes a decline of obligate groundwater species (stygobites) that are mainly present in pristine streams draining native forested areas (Boulton et al., 1998). Intensive urban industrial activities also contribute to the impairment of hyporheic waters (especially with trace metals and volatile organic compounds) that will promote a reduction in groundwater communities' diversity further (Mösslacher, 1988; Plénet and

Gibert, 1994; Gibert et al., 1995; Plénet, 1995; Plénet et al., 1995, 1996; Claret et al., 1999; Marmonier et al., 2000; Iepure and Selescu, 2009; Steube et al., 2012; Iepure et al., 2013).

The Jarama basin located in central Spain (a tributary of the river Tajo from northwest) has an extended alluvial floodplain and has a great economic significance for agriculture and industry (Bastida, 2009). The basin has been subject to a variety of land-use changes during the last century (Llamas, 2007). After '30 almost all headwaters streams of the basin were affected by geomorphological changes trough construction of large dams, or the channelization of rivers for flow regulation purposes. This has altered the downstream flows and discharges and has changed the erosion processes and sedimentary dynamics of their tributaries. During the '50 the alluvial floodplains were prone to alterations from the primary use of soil for forestry and rural shifted to agricultural and industrial purposes (Vizcaíno et al., 2003; Llamas, 2007). Furthermore, the intensive industrialization in the 50' in the region caused an increase of urban development, an extension of residential areas and of large-scale industrial and commercial areas, and an enhanced infrastructure for transport (Alcolea and Garcia Alvarado, 2006).

Nowadays, the main pressures that pose risks to the Jarama basin occur in the lowland alluvial floodplain and stem from both industry and agricultural practices (Bastida, 2009). River water is directly affected by emissions from wastewater treatment plants (WWTPs) (approx. 5000) that process the water discharged from large urbanizations and the metropolitan area of Madrid (with > 6.5 mil. inhabitants) and from industrial plants. Besides a large number of contaminants from industry (i.e. trace metals, hydrocarbours and volatile organic compounds) or contaminants emerged from personal care products and micro drugs (recently detected for > 80 groups of such products) (Martínez-Bueno et al., 2010; Hernando et al., 2011) alters the rivers water quality and their associated aquifers.

The intensive practice of gravel extractions (for conglomerates or mining) puts additional pressure on alluvial aquifers and triggers large fluctuations (± 3 m) of the shallow aquifers (Llamas, 2007; Bastida, 2009). These practices also cause a direct impact on discharge of river channels by removing water and in-stream sediments. 2/3 of a total of 50 gravel bar extractions in the Madrid area in 2003 were located in the Jarama River only (Blanco-Garcıa et al., 2004). Moreover, some of them have changed their initial exploitation locations leaving a large number of scattered gravel pits and residual lagoons, which were left with minimal or inadequate management and restoration measurements (Martínez-Pérez and Sastre, 1999). Additional risks upon the river-alluvial aquifer system are also triggered by intensive groundwater withdrawal for irrigation and illegal aquifers exploitation (Bastida, 2009).

These long-term and persistent activities in the Jarama river and the alluvial floodplain sum up to a mosaic of different land-use terrains which nowadays alternate from pristine areas at the headwaters to areas with mixed anthropogenic activities from agriculture and industry in the lowlands (Bastida, 2009). They affect the river ecosystems further, by changing the water quality at both the surface and the hyporheic zone, and with negative consequences for the surface and subterranean aquatic life (Camargo and Jimenez, 2007; Camargo et al., 2011; Iepure et al., 2013). The ecological response of benthic (Camargo and Jimenez, 2007; Camargo et al., 2011; Rasines, 2011) and hyporheic invertebrates (Iepure et al., 2013) to changes in physico-chemical conditions of the waters at local level is well known and clearly reflects a decline of populations diversity and abundance with decrease of water condition in the lowland.

The present study aims at the quantification of the response of hyporheos diversity and ecological community structures to alterations in hyporheic river water conditions linked to land-uses changes at local (habitat) and regional (hydrographic basin) scales in the Jarama basin alluvial floodplain (central Spain). Our main goal was to evaluate which type of land use affects the hyporheic environmental conditions and hyporheic crustacean communities the most. To achieve this goal, we conducted an intensive field-survey in the hyporheic zone of the main Jarama channel and three main tributaries. Here we tracked changes in the structure of hyporheic crustacean assemblage and water physico-chemical features associated with distinct types of land-use: 1) undisturbed sites at headwaters (forested and semi-natural zones) and 2) perturbed areas in the lowland (agricultural, urban and industrial development). We start from the hypothesis that intensive and mixed land-uses within the alluvial floodplain of the basin will reduce the diversity and abundance of hyporheos and will change the ecological structure of the crustacean community (stygobite vs. non-stygobite species). Due to the scattered pattern of regional faunal composition and the restricted geographic distribution of some hyporeobiotic taxa we hypothesize that the observed responses might vary between distinct rivers.

MATERIAL AND METHODS

Location of the investigation area

The Jarama catchment is the largest discharge basin of Tajo River (6,000 km^2) and drains several rivers crossing the Madrid and Guadalajara provinces from central Spain (figure 1). Jarama River and three tributaries

(Manzanares, Henares and Tajuña) were considered for the present study. The landscape is characterised by higher slope at the headwaters (maximum of 28.5%) and moderate slope in the lowland (maximum of 7.68%). The natural flow regime of the investigated rivers is by groundwater discharge in-stream bed sediments and rainwater (Fennessy, 1982).

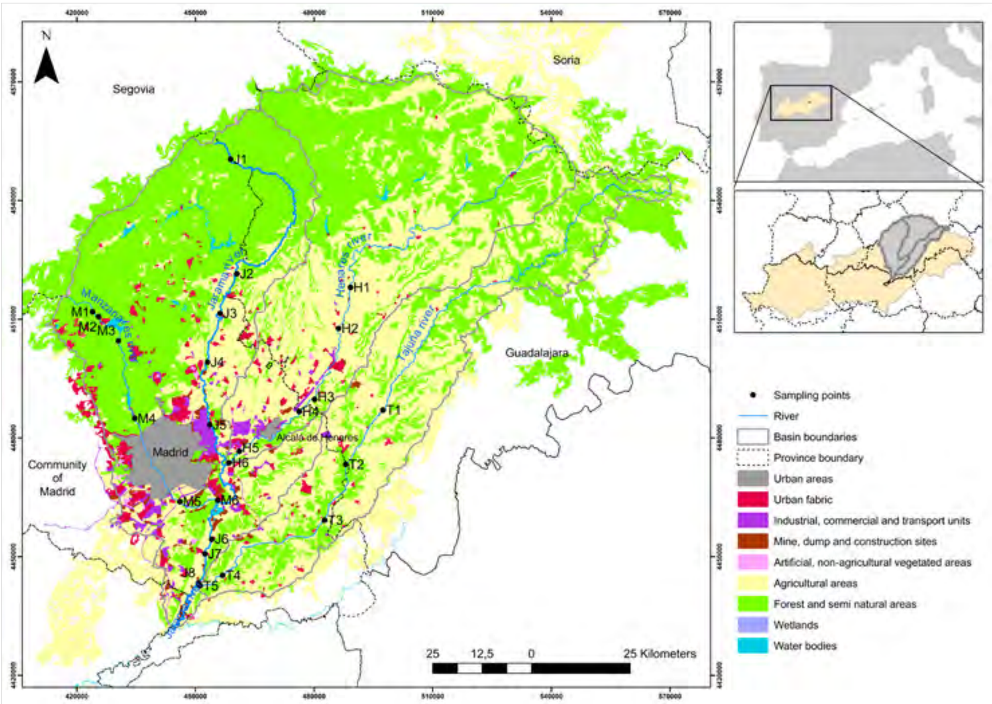


Fig. 1. *Location of the hyporheic sampling sites in the Jarama basin (central Spain)*

The climate in the region is Mediterranean with hot (average temperature in the hottest month >22°C) and warm summers (average temperature in the hottest month < or equal to 22°C, and with four months or more with average temperature >10°C) and relatively dry winters (AEMET, 2011). The rainfall in the region is low with a mean annual precipitation averages between 400 mm and 500 mm/yr (AEMET, data for the last 10 years), which causes a high variability of river discharges throughout the year (www.chtajo.es).

The river processes and associated ecosystems at the headwaters of the Jarama River and the Manzanares River are unaltered by human activities and consist of semi-natural zones of uncultivated lands and forests.

These areas are protected by national legislation, i.e. they are located in the national park of Sierra de Rincon and the Biosphere Reserve Cuenca Alta de Manzanares. Both streams in the upper parts flows through hilly slopes and semi-natural forests dominated by *Populus nigra*, *Salix* spp., *Fraxinus angustifolia*, *Quercus pyrenaica*, *Betula pendula*, *Frangula alnus* and *Crataegus monogyna* (Almodóvar et al., 2006).

The mid- and lower courses of the investigated rivers are characterised by distinct human activities of diverse intensity (e.g. agricultural and urban development) (Bastida 2009). The agricultural land use areas are represented by arable land (permanent irrigated land and rice fields), permanent crops (vineyards, fruit trees and berry plantations and olive groves), pasture and heterogeneous agricultural cultures (annual crops associated with permanent crops, complex cultivation patterns, land principally occupied by agriculture with significant areas of natural vegetation) (see figure 1 for specific location of the sites and Appendix 1). Artificial surfaces are present in urban and rural areas, where a mixture of activities can be found: urban fabrics, and industrial, commercial and transport units (road and rail networks and associated land, airports); mine, dump and construction areas and artificial, non-agricultural and vegetated areas (with green urban areas and sport and leisure facilities).

Within the lowland courses, the riparian zone is well-developed at specific sites as leisure parks (mainly in the Henares and Jarama Rivers). The vegetation is dominated by *Populus nigra*, *Salix* sp., *Rosa canina*, and/or is mixed with hydrophilic plants, shrubs, grasses, and emergent plants.

The Madrid community established a legal framework to protect seven sites from the Jarama and Henares Rivers through Nature 2000 Network (Boletín Official de la Comunidad de Madrid, 2011). Additionally, some sectors of the Manzanares and Jarama Rivers downstream Madrid were subject to punctual restorations and are protected through natural parks (Parque Regional del Sur-Este).

Sampling design and land-use types classification

The survey was conducted in spring 2011 (March-April) during high flow at 25 sampling sites in the Jarama River and the three tributaries (figure 1). The sampling sites were selected according to land-use heterogeneity: 1) forested areas, 2) agricultural crops and 3) artificial surfaces with urban and intensive industrial development (table 1). For all streams there are distinct land uses to various extents present in the area adjacent to the sampling points (figure 1). However, in some cases the crops or artificial surfaces do not reach the stream edge due to the presence of a riparian zone or leisure parks.

A geographical information system (GIS) (ArcGIS 9.3, ESRI) was used to quantify the land cover/use at each sampling point. The information's were based on the 2006 Corine Land cover data set derived from satellite images produced by Landsat TM (1990), Landsat7 (2000) and SPOT4 (2006) (table 1). A buffer polygon with a diameter of 500 m was placed around the study site, and the percentage of each type of land use present in this area was calculated (Appendix 1). We used actual aerial photography and Google Maps for a verification of the Corine Land cover classification nearby our 25 measurement sites. In 10% of the cases we had to conduct minor corrections. At each site we appraise the abundant type of vegetation. This serves as surrogate to infer the development of the according riparian corridor.

The distance of each site to the headwaters was considered to establish if spatial patterns of species distribution (abundance/diversity) are natural or induced by anthropogenic activity.

Table 1. *Land use codes for the selected 25 sampled sites in the Jarama basin (central Spain)*

Land Covers used in this study	Classes	Code
Artificial surfaces	Urban fabrics	Urb
	Industrial commercial and transport units	Ictu
	Mine dump and construction sites	Mdcs
Agricultural areas	Arable land	Ar
	Heterogeneous agricultural areas	Haa
Forested areas	Forest	F
	Scrubs and/or herbaceous vegetation associations	Shva
	Open spaces with little or no vegetation	Osv

Environmental variables

Temperature (°C), dissolved oxygen (in % and mg/l), electrical conductivity (µS/cm) and pH were measured *in situ* by means of field sensors in triplicates samples from the river and hyporheic zone. No a-priori treatment was applied to water samples that were transported to the laboratory and were stored refrigerated (4ºC) before the analyses. Water samples were analysed for 27 quantitative chemical variables (Iepure et al., 2013).

The particle size from hyporheic was determined using the standard protocol and described in Iepure et al. (2013). Four sediment size categories were identified at each hyporheic site and categorized as: silt/clay (< 63 µm), fine sand (63-250 µm), medium coarse sand (250 µm-1 mm) and coarse sand (1-2 mm).

Hyporheic faunal sampling

A perforated steel pipe with 2-3 cm in diameter and 1.5 m in length, and with 10 cm with holes of 0.5 mm diameter at one end was installed at a depth of 20-40 cm in-stream river bed sediments of unconsolidated detrital deposits represented by a mixture of non-homogeneous fine sand, boulders, and stones. The interstitial material (water, sediment, and fauna) was sampled by pumping 12 l using a Bou-Rouch sampler (Bou and Rouch, 1967; Malard et al., 2002). The macroinvertebrates and meiofauna was sieved trough a 63 μm mesh net, together with the water and sediments. Three faunal replicates in the hyporheic habitat per each sampling site have been collected at each site (about 0.5-1.0 m distance). The fauna samples were preserved in the field in 96% ethanol, then stored in the laboratory at 4°C and kept until laboratory analyses.

The hyporheos was pre-sorted into major taxonomic groups under a 20-40 x magnification and then counted. Cyclopoids, harpacticoids, and ostracods were identified to the lowest taxonomic level (Meisch, 2000; Dussard and Defaye, 2006). Amphipods, isopods and syncarids were identified at family level, whereas other metazoan where just counted.

The crustacean species were classified according to their ecological preferences: in stygobites - obligate groundwater species (s) and non-stygobites - commonly found in groundwater (ns) as stygophiles (species able to survive temporary in subsurface) and stygoxenes (species accidentally drifted from the surface habitats) (Stoch and Galassi, 2010).

Data analysis and statistics

For multivariate statistical analysis of the environmental hyporheic water conditions, we pooled the triplicates in a single data set. Most of the variables do not show a normal distribution, and they were log-normalized (log 10 (x+1)) before any further statistical analyses. A principal component analysis (PCA) of the covariance matrix of the following attributes was performed: two groups of geographical variables (elevation and slope); water environmental data e.g. nitrites, nitrates, phosphates, non-purgeable organic carbon (NPOC), non-purgeable total organic carbon (NTOC), inorganic carbon (IC), total carbon (TC), trace metals (Cu, Zn, Ni, Mn, Pb, Cd), volatile organic compounds (VOCs) and endosulfan sulphate. The PCA directions thus indicate common environmental conditions. Loadings over 0.4 were considered significant (Hair et al., 1987) and hence only these parameters were retained. The resulting ordination was evaluated in agreement with land use data by labelling sites regarding the highest % of use (i.e. artificial surface/ agricultural use/forest). The analysis was performed with the PAST software.

The changes in community structure pattern of hyporheic crustaceans were evaluated by quantifying total crustacean abundance (total number per site) and diversity (Shannon index, H') using the subprogram DIVERSE of the PRIMER v.6 package software (Clarke and Gorley, 2006; Clarke and Warwick, 2006). These indexes are generally used to identify the environmental stress. Additional estimation of stygobites (H'_s) and non-stygobites diversity (H'_{ns}) was assessed for each site in order to use their bio-indicative status for water disturbance in hyporheic communities.

A one-way analysis of variance (one-way ANOVA) was computed on biotic and abiotic data to test whether there are significant differences among and within the sites using PAST software. Multivariate analyses were furthermore applied to depict the pattern of physico-chemical variables and crustacean's attributes (abundance and H') among the sites. Canonical analysis of principal components (CAP) based on square root transformation for the abundance of biota was performed using subprogram PERMANOVA+ Ltd, 2009 of PRIMER v. 6 (Clarke and Warwick, 2006). In figure 3b, CAP axes 1 and 2 and overlaying vectors indicating Pearson correlation between species (only species with correlation > 0.4 were considered) is illustrated. Furthermore, the SIMPER routine was used to estimate the contribution of each species to characterize the hyporheic waters under the influences of distinct land use types.

A regression tree analysis (Berk, 2008) was additionally completed to determine if certain environmental, geographical parameters (e.g. elevation or slope) and water physico-chemical features are important for the prediction of abundance and diversities (H', H's and H'_{ns}) of hyporheic crustacean communities. This method does not need the specification of the link function between predictors and response (e.g. linear or polynomial) and is thus suitable for the assessment of their rather complex and unknown relationships. In a second step, we linked the environmental parameters from each site with the associated type of land cover (e.g. % of forests and semi-natural areas) and land use (e.g. % of arable land, urban fabrics, industrial commercial and transport units; and mine dump and construction sites) and could thus relate land cover and land use types to the response of biotic component. The regression tree analysis was performed with the r part package of the software R (R Development Core Team, 2013).

RESULTS

Land-use pattern

The spatial arrangement and percentage of forests and semi-natural areas, agriculture and artificial surfaces varied considerably among streams at the selected scale (Table 1). It showed that the Jarama and Manzanares headwaters sites had > 80% forest and < 20% agriculture and/or artificial surfaces within the 500 m round buffer zone. The lowland sites are governed by agricultural practices with > 60% arable crops and the rest of lands is fragmented between several urban activities (up to 34% of urban fabrics, industrial commercial and transport, mine dump) and forested riparian zones (up to 30%). Within Tajuña and Henares Rivers all investigated sites were entirely dominated by agricultural practices (Appendix 1). At five sites scrub and/or herbaceous vegetation associations (< 31%) and urban fabrics (< 16%) are recognized. Within the lowland of the Jarama basin, the artificial surfaces with urban fabrics are identified at ten nearby sites and attain almost 35% (Appendix 1).

Environmental condition of the hyporheic waters

The physical variables showed to vary in relation to the site location and to the land-cover/use patterns (see Iepure et al., 2013). The percentage of medium pebbles and coarse gravel (> 0.5 mm) is higher at forested sites. Sand particles (0.05-0.1 mm) increase at sites governed by agricultural land-use and are slightly negatively related with elevation ($r=-0.47$, $p<0.05$) and slope ($r=-0.41$, $p<0.05$).

Temperature shows the highest variability among sites. Mean hyporheic temperature decreases with increasing altitude ($r=-0.75$, $n=25$, $p<0.005$) indicating that forested and semi-natural headwaters were on average the coldest habitats (< 12.03°C). In contrast the warmest sites and more stable at the time of sampling (approximately 15.9°C on average) were located in the lowland where agricultural and urban land-use governs. Maximum temperatures in the lowland were mainly observed at sites without a riparian zone or with high discharge and low water flow (Appendix 1).

Dissolved oxygen (DO) exceeds 9 mg/l at forested sites and slightly decreases with increasing percentage of agricultural land use (~ 7.2 mg/l). Dissolved oxygen exceptionally decreases to hypoxia (< 3 mg/l) at sites located in agricultural areas and/or intensive urban development areas (e.g. urban fabrics, industrial commercial and transport units and/or mine dumps). The total carbon (TOC) is significantly lower at forested sites (2.7-3.77 mg/l) and increase consistently where agricultural practices dominate (18.2 mg/l on average) (Iepure et al., 2013).

The chemical response of hyporheic waters was also related to land cover and land use patterns. The specific conductivity (EC) varies among sites from < 470 $\mu S/cm^{-1}$ in forested and semi-natural areas up to > 2700 $\mu S/cm^{-1}$ in agricultural areas and artificial surfaces (Appendix 1). EC was strongly positively related to the majority of cations and anions and negatively related to elevation. Trace metals highly varied among sites with high concentrations for Mn (0.9 – 3.28 μg/l) and Zn (0.02-0.26 μg/l) in sites located downstream industrial and urban development areas. Similarly, VOCs are higher at these sites and attain 3,462.6 μg/l. Endosulfan sulphates appears locally at agricultural governed sites and exceeds 40 ppm (Iepure et al., 2013).

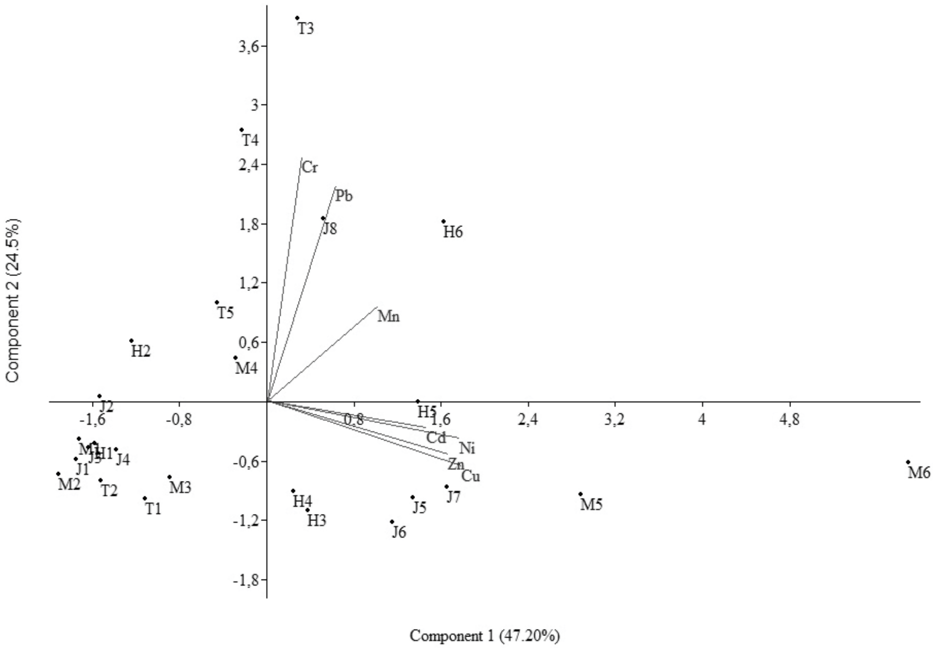


Fig. 2. *Principal component analysis (PCA) ordination plot showing sampling sites distribution based on trace metals concentration in hyporheic waters.*

The distribution pattern of the sites in the PCA ordination reflects the distinct type of land-uses around a hyporheic site. PCA analysis (based on covariance matrix) indicates a strong separation along the first axis (99.83% of the variance) of the hyporheic waters located in areas of mixed agricultural/ artificial surfaces (figure 2). Elevation and slope have high positive loadings for this PC, whereas IC, Ni, Zn, Cu, Pb and VOCs have high negative loadings. These variables are presumed to be key benchmarks to classify the sites. The second axis (0.10%) separates mainly sites governed by agricultural practices. For the second PC axis, slope, NPOC, TOC and TC have high loadings.

Hyporheic crustacean assemblage structure among sites and environmental conditions

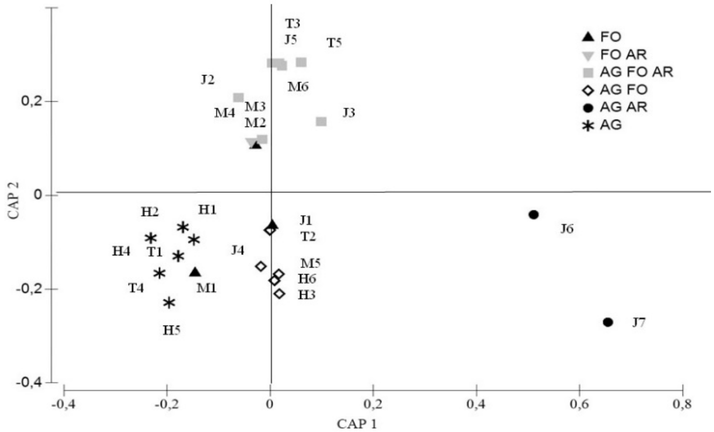
There was a marked distinction between hyporheic crustacean taxonomic compositions among the sites. The most common crustacean taxa across all sites were: ostracods (36% of total abundance), cyclopoids (27%), harpacticoids (26%) followed by the rest of the groups in < 5% (cladoceran, calanoids, sincarids amphipods and isopods). The rarest crustaceans were calandoids, sincarids and isopods (in 1% of the sites). Of the 42 species identified in total 19 taxa occurred in one sample and the rest in more than two. Only nine locations host stygobites whereas the rest contain exclusively non-stygobites. Hyporheic crustacean abundance varied among sites from complete absence to > 2000 specimens/site (table 2).

Table 2. *Pearson correlation coefficients between physico-chemical parameters and biota (with bold p < 0.005 and (p < 0.01; H'- Shannon Wienner, H'$_{s}$ – stygobites diversity, H'$_{ns}$ – non-stygobites diversity)*

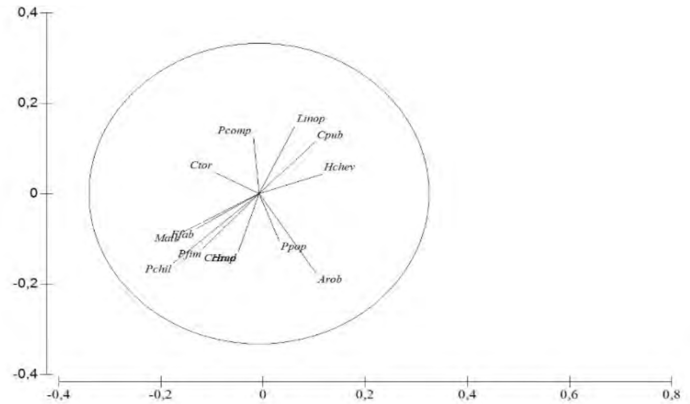
Axis	Eigenvalue	Cumulative percent
1	301763,3	99.83
2	30.94	0.10
Variables	Factor 1	Factor 2
Elevation (m asl)	1	-0.0007
Slope (%)	**0.59**	**0.80**
log NPOC	0.001	0.45
log TOC	0.0004	0.44
log TC	-0.21	**0.54**
log IC	**-0.73**	-0.08
log Ni	**-0.58**	-0.085
log Cu	-0.43(	-0.10
log Zn	**-0.51**	-0.004
log Pb	-0.46(	-0.12
log VOC	**-0.62**	-0.13

Faunal data have been classified in multidimensional space using CAP analysis to maximize differences between the groups of sites governed by distinct land uses. CAP results (figure 3a) indicate a similar distribution of the sites with respect to the pattern of hyporheic crustacean assemblage composition as the PCA chart based on environmental data (figure 2). The first CAP axis (95.3%) indicates a separation of the hyporheic waters with medium (right upwards) or low diversity (right downwards) of hyporheic crustaceans (figure 3a). These sites are associated with high levels of ammonia (up to

13.64 µg/l) and trace metals (Cu, Cd, Zn, Ni and Mn). The second axis markedly separates highly diverse hyporheic communities (left downwards) with nitrate level of 22 µg/l from the sites less diverse and exposed to elevated concentrations of TC and Cr (left upwards) (figure 3 a).



3a



3b

Fig. 3 (a). *Canonical Analysis of Principal Coordinates (CAP) showing sites distribution based on species presence in hyporheic waters (symbols are land-uses types: grey squares – arable land/forest; black triangle – forest; grey triangle – forest/arable land; rhombus – scrubs and herbaceous vegetation/arable land/forest; black dots - scrubs and herbaceous vegetation/arable land; stars – arable land);*
(b) – *Vectors pointing species based on Pearson correlation (Ostracoda: Linop – Limnocythere inopinata, Cpub – Cypris pubera, Hchev – Herpetocypris chevreuxi, Hrep – Herpetocypris reptans, Ffab – Fabaeformiscandona faba, Ctor – Cyprideis torrosa, Pcomp – Pseudocandona compressa; Cyclopoida: Arob – Acanthocyclops robustus*, Ppop – *Paracyclops poppei*, Pfim – *Paracyclopc fimbriatus*, Pchil – *Paracyclops chiltoni*, Malb – *Macrocyclops albidus*)

Species showing a high correlation with the first two axes are those identified by the SIMPER analysis as characterizing particular sites with similar types of land use (figure 3b). The ostracods *Fabaeformiscandona fabaeformis* and *Herpetocypris reptans* and the cyclopoids crustaceans *Macrocyclops albidus*, *Paracyclops fimbriatus* and *P. chiltoni* were primarily confined to sites governed by agriculture practices. All these species are non-stygobites with large ecological valence. The cluster of non-stygobites species formed by *Limnocythere inopinata*, *Cypris pubera* (ostracods) and *Acanthocyclops robustus* (cyclopoid) was most highly related to sites governed by mixed land use types (especially agricultural and artificial surfaces). A group of typical hyporheos with mixed ecology are highly correlated with forested areas, e.g. *Pseudocandona eremita* (stygobite) and *Cryptocandona vavrai*, *Pseudocandona albicans*, *P. compressa* gr. (non-stygobites). There are few shared species between the forested and less forested sites and only two are stygobites (*Acanthocyclops* sp. new and *Darwinula stevensoni*) whereas the majority of species which occur at sites with distinct land use types are cosmopolitan species, which are tolerant to various environmental conditions, e.g. *Diacyclops languidoides* s.l., *Paracyclops poppei* and *Pseudocandona albicans*.

Hyporheic crustacean pattern land-use predictors

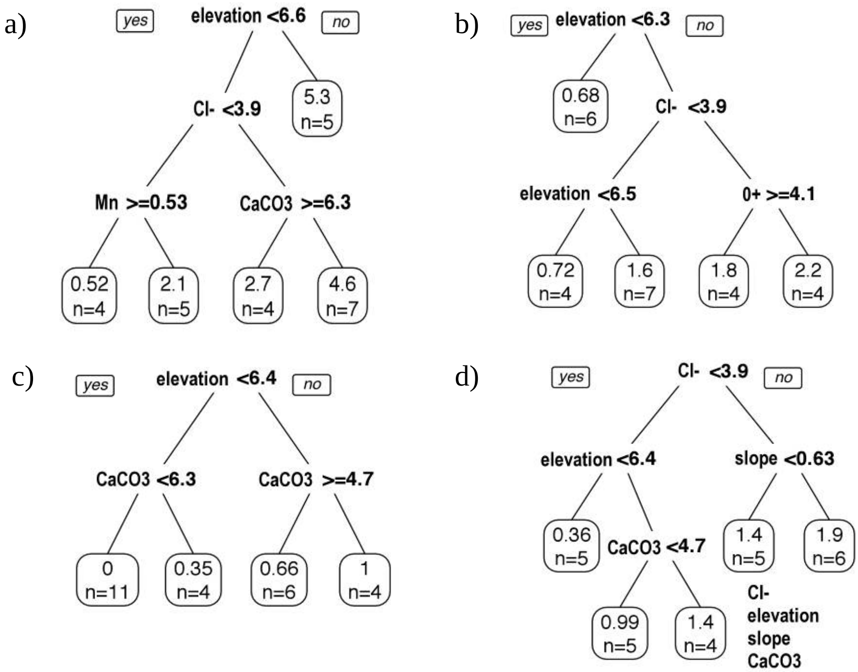


Fig. 4. *Regression trees **a**) total abundance of hyporheic crustaceans; **b**) Species diversity (H'); **c**) Stygobites diversty (H'$_S$); **d**) Non-stygobites diversity (H'$_{ns}$)*

The one-way ANOVA does not indicate significant differences between the sites in terms of abundance and diversity (H') ($F=2.75$, $p<0.1$), whereas significant differences have been found when the ecological community structure is considered (stygobite vs. non-stygobite) ($F=21.38$, $p<0.0002$). The most important predictors for the total abundance were primarily elevation (ANOVA analysis, significance level 0.1) and secondly TC, which are both associated with forested areas (figure 4). The Pearson correlation returns similar results and indicates a slightly positive correlation of hyporheos abundance with elevation and, a negative correlation with temperature, NO_2^- and Ni (at 0.01 significance level) (table 3).

Table 3. *Pearson correlation coefficients between physico-chemical parameters and biota (with bold p < 0.005 and * p < 0.01; H'- Shannon Wienner, H'_s – stygobites diversity, H'_{ns} – non-stygobites diversity)*

Variables	Unit	Crustacean density (individ./ sample)	*H'*	H'_S	H'_{NS}
Elevation	m	0,36	0,31	**0,56**	0,09
Slope	%	0,06	0,31	0,47*	0,15
Temperature	° C	-0,18	-0,19	**-0,50**	0,01
Dissolved oxygen	%	0,43*	**0,69**	0,38	**0,64**
NO^{2-}	mg/l	-0,41*	-0,45*	-0,35	-0,38
NO_3^-	mg/l	0,13	0,12	-0,15	0,23
NH_4^+	mg/l	-0,49*	**-0,69**	-0,39	**-0,63**
NPOC	mg/l	-0,02	0,13	0,27	0,04
TOC	mg/l	-0,02	0,10	0,26	0,01
TC	mg/l	-0,08	-0,03	-0,02	0,00
IC	mg/l	-0,09	-0,15	-0,46*	0,10
Cr^-	mg/l	0,07	-0,01	-0,02	0,05
Mn^-	mg/l	-0,28	**-0,50**	-0,29	-0,43*
Ni^-	mg/l	**-0,63**	**-0,59**	**-0,50**	-0,46*
Cu^-	mg/l	-0,33	-0,40*	-0,31	-0,34
Zn^-	mg/l	-0,32	-0,26	-0,44*	-0,13
Cd^-	mg/l	-0,35	-0,40*	-0,17	-0,38
Pb^-	mg/l	0,05	0,09	-0,16	0,20
VOCs	mg/l	-0,38	**-0,54**	**-0,54**	-0,39
Endosulfan sulfate	mg/l	0,33	0,38	0,22	0,41*
% Agricultural areas & forest and seminatural areas		89(16-138)	7 (5-9)	2(0-4)	5.66(3-7)
% Agricultural areas & forest and semi-natural areas & artificial surfaces		361.2(1-2700)	3(2-4)	2(0-3)	2.4(1-4)
% Agricultural areas & artificial surfaces		32.16(0-129)	0.5(0-1)	0	1(0.1)

River ecosystems draining non-irrigated and permanently irrigated croplands were characterized by relatively well-developed sclerophylluous vegetation in the riparian zone of the selected sampling sites and they display furthermore a high species diversity mainly non-stygobites (table 3). However, ANOVA (linear regression) finds no significant predictor for total species diversity (H') but the exploratory analysis suggests a link in polynomial form of second order for TOC and elevation, and a linear relation for carbonates (figure 5). The Pearson correlation indicates a positive correlation of the diversity of non-stygobite species with dissolved oxygen, and a negative correlation with NO_2^- and NH_4^+ (table 3).

The stygobite diversity (H') decreases in sites with a low percentage of forest and/or riparian zone development. The ANOVA determines as best predictors for the diversity of stygobites, elevation ($p<0.01$, the higher the altitude, the higher the H'_s) and temperature ($p<0.05$, the lower the temperature the higher the H'_s).

Furthermore, regression tree analysis has been performed to confirm these results by allowing for non-linear relationships, which are most probably present in the data. Due to the limited number of available data, the minimum number in a node is restricted to 4 and the minimum number to split is 6. Thus, prediction trees with 4-5 terminal nodes are produced (figure 4). The few data available causes the regression tree analysis results not to be significant. However, they give valuable insight in the process dynamics and serve thus for interpretation purposes. As depicted in figure 4 a) and b), elevation shows to be a good classifier for species diversity and abundance in general. Moreover, elevation is as well the most important variable to determine stygobite and non-stygobite diversity (see figure 4c) and d). Slope is also an important classification variable to predict non-stygobites diversity. Thus, results are in line with the ANOVA and Pearson correlation assessment.

The regression tree analysis serves also to classify and predict species abundance and diversity (figure 6), even with a quantitative error approximation. It shows that, except for stygobite diversity (figure 6 c), the model estimates the observations reasonably well (small differences between the observations (black circles) and regression tree node values (black dots) are envisaged), given the few data available. It also shows that medium Cl^- values (~ 60 mg/l) causes a high total (H') and non-stygobites (H'ns) species diversity, and total abundance and a high $CaCO_3$ value (> 150 mg/l) causes high diversity rates of stygobites.

Some of the site classes (see x axes) show a clear correspondence to land use types (figure 3a). For all four response variables (abundance, H', H'_s/H'_{ns}), the sites dominated by agricultural activities are put in different classes than the forest dominated sites. Moreover, the class with highest stygobite diversity is forest dominated sites, whereas the class with highest non-stygobite diversity comprises sites dominated by agricultural practices. This confirms our theses on the influences that land use types on the species diversity and especially of stygobites have.

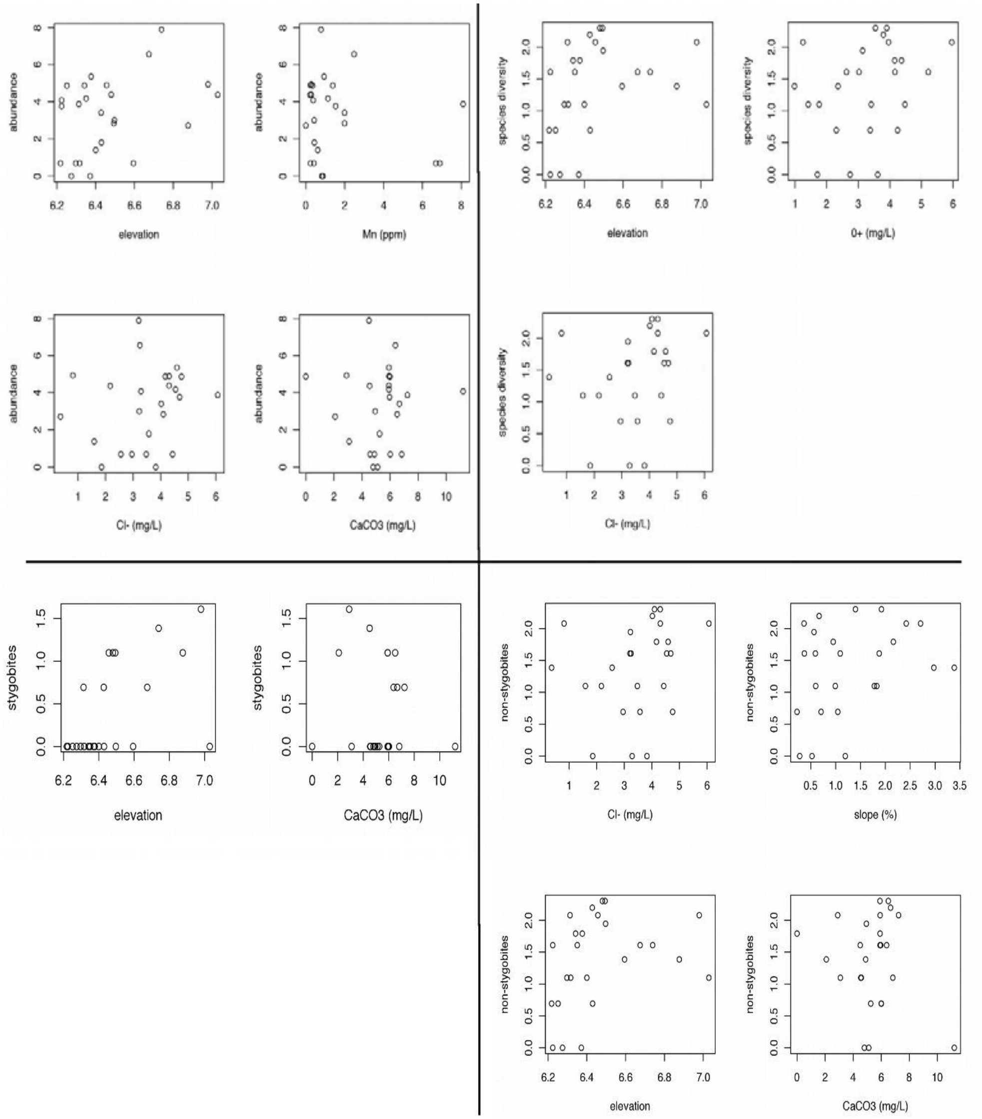


Fig. 5. *Scatterplots of abundance, species diversity, stygobites and non-stygobites versus their respective best predictors (according to ANOVA).*

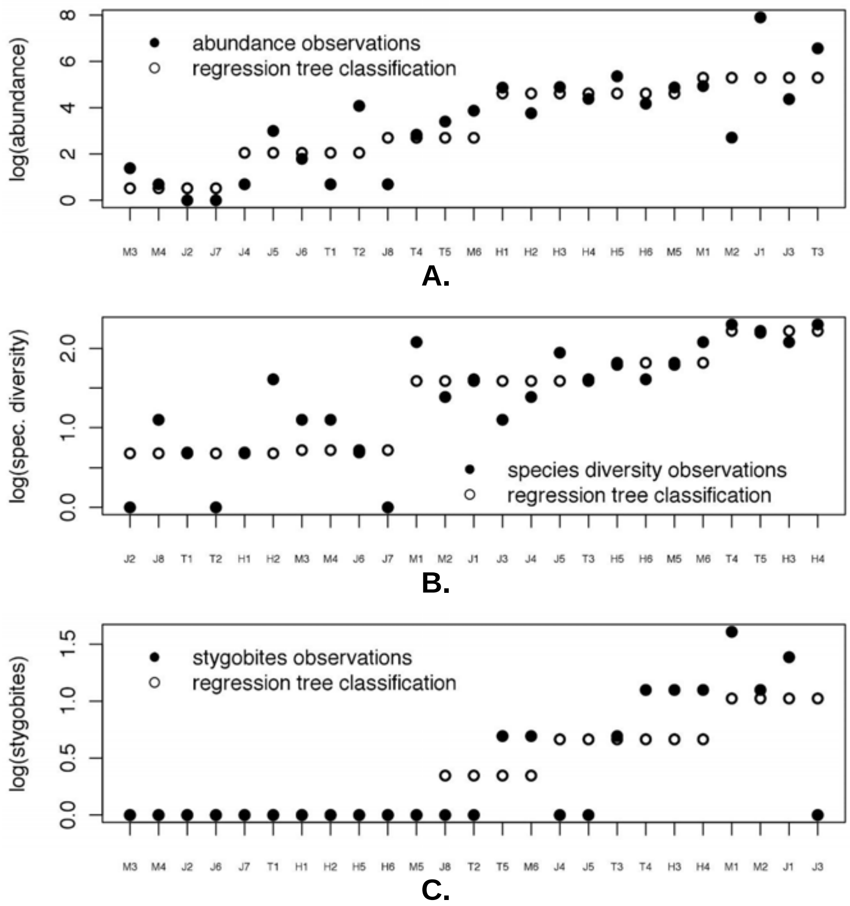


Fig. 6. *Regression tree classifications: **a**) Total hyporheic abundance; **b**) Species diversity (H'); **c**) Stygobites diversity (H'$_s$); **d**) Non-stygobites diversity (H'$_{ns}$)*

DISCUSSIONS

Environmental water conditions differences among hyporheic waters

Results from our study of the hyporheic zone of four streams in the Jarama basin (central Spain) indicate significant changes of physico-chemical properties of hyporheic water, which are associated with physico-geographical features (e.g. elevation and slope) and land use types at local scale in the river watersheds.

The patterns of sediment deposition vary from site to site. However, an increase of fine sands (0.63 mm) from the forested headwaters to the lowlands with intensive land-use for agriculture is observed. The hyporheic waters of the Manzanares and Jarama sites located at high elevations are dominated by medium pebbles and coarse gravel. The mean substratum of fine particle size was inversely related to altitude indicating that this fraction is associated with agricultural practices around sites (cf. Lenat et al., 1981; Richard et al., 1996).

Past studies reveal a direct relationship between the large amount of fine sediments and the lowering of the dissolved oxygen in the hyporheic zone (Poole and Stewart, 1976; Strommer and Smock, 1989; Bretschko, 1994). Our results do not indicate a significant connection at the time of sampling. However, dissolved oxygen content tends to decrease from the headwaters to the lowlands (see Iepure et al., 2013). Hyporheic waters from the forested sites display remarkably high oxygenated waters (> 9 mg/l). Less oxygenated hyporheic waters are associated with sites located in the lowland. Here artificial surfaces and especially industrial and urban activities dominate the land use. Although a longer residence time of water has been proved to partially explain the variation of dissolved oxygen in hyporheic waters (Findlay, 1995), the used natural tracers (conductivity, Br^- and Cl^-) found this pattern at eight sites only.

Intensive land-use for agricultural practice in the lowland of the Jarama basin lead to an increase of nitrates and phosphates in the hyporheic waters of all sites. However, the concentrations do not exceed the established standard limits for surface and ground water according to the Water Framework (WFD 2000/60/EC) and Groundwater Directives (2006/118/EC) (< 50 mg/l). Endosulfan sulphate presence is mainly associated with the presence of agricultural activities at specific sites in the mid-courses of Tajuña and Henares (table 2). According to both directives, endosulfan sulphate is a prohibited substance in water bodies since 1999 however it might be still used punctually in the Jarama basin and not at a larger scale.

The physico-chemistry of hyporheic water declines progressively and accumulates trace metals and VOCs due to changes in land use and growing artificial surfaces and industrial development. Trace metals like Cu, Cd, Zn, Pb, Mn and Ni exceed the standards limits in hyporheic waters at sites where industrial practices are present and located downstream the Madrid metropolitan, industrial polls and large residential urbanizations (i.e. Paracuellos de Jarama, Azuqueca de Henares and Alcala de Henares) (Iepure et al., 2013). Previous investigations indicate that some trace metals are accumulating in the riverbed sediments from the Jarama basin from where they are most probably remobilised into the interstitial hyporheic water (Arauzo et al., 2003).

Differences in hyporheic crustaceans and land-use predictors

The comparison of catchment characteristics and nearby land-use practices (within a 500-m buffer) has revealed the impact of land use on hyporheic water quality and biotic crustacean communities in the Jarama basin. In accordance with these results, we identified three groups of hyporheic communities that differed in crustacean abundance and diversity, but also in the proportion of stygobites/non-stygobites taxa present (according to water conditions): 1) forested sites with medium abundance and species diversity (H') dominated by stygobite species; 2) agricultural sites with high diversity and abundance, and communities conquered by non-stygobites; 3) sites with mixed agricultural and industrial activities with low diversity and abundance and/or loss of crustaceans.

Forested hyporheic waters harbor the richest crustacean communities and crustaceans such are cyclopoids, harpacticoids, ostracods and calanoids which are the most abundant species. Except the later epigean taxa, whose presence is evidently influenced by the site location downstream of a large artificial lake (Santillana reservoir), the other taxa are typically common hyporheos. Results from the regression tree analysis also indicate that the abundance and high stygobites diversity are predicted by a high percentage of forests at headwater sites. The diversity of stygobites is significantly correlated with high levels of dissolved oxygen and with low temperatures of the hyporheic waters. Forested sites are also characterized by oligotrophic hyporheic waters. Species associated with forested sites are obligate subterranean dwellers (stygobites), i.e. *Parastenocaris* n. sp. 1, *Parastenocaris* n. sp. 2, *Acanthocyclops* sp. 1, *Pseudocandona eremita* gr. and *Darwinula stevensoni*. Boulton (1997) found somewhat similar results in five New Zeeland streams where in-stream draining native forests harbored a diverse and mixt benthic with few apparently hyporheic taxa. We suggest that the high diversity and abundance of stygobites at the forested sites indicate that hyporheic zone is sufficiently developed and provide conditions to support subterranean dwellers populations.

Generally, stygobites are ground water–adapted species and their presence in the hyporheic ecotone zone commonly provides information on water conditions. The diversity of stygobites in the Jarama basin was negatively related to specific industrial contaminants present in the lowlands (e.g. NO_2^-, Ni and VOCs), where land use types are associated with continuous and/or discontinuous urban fabrics. Due to their restricted requirements and being influenced by water physico-chemistry settings (Maurice and Bloomfield, 2012), stygobites may play an important role as forthcoming ecosystem service providers for subsurface water conditions (Tomlinson et al., 2007; Griebler et al., 2010; Iepure et al., 2013).

The hyporheic waters exposed to agricultural practices in the Jarama basin lowland display a large amount of nutrients, as indicates the enrichment of total carbon (TC), inorganic carbon (IC) and nutrient content in form of nitrates which are higher at sites exposed to agriculture than at forested sites (see Iepure et al., 2013). Consequently, the hyporheic crustaceans develop a highly diverse community formed by a mixture of species with distinct ecological traits. The regression tree analysis supports these observations and indicates that the abundance and non-stygoxene diversity might be predicted by the agricultural land use practices. Our results are consistent with previous studies reporting that land-cover is a good predictor for in-stream nutrients (Omernik, 1976; Johnson et al., 1997) and that agricultural activities cause an augmentation of diversity in hyporheic faunal assemblage as results of nutrient enrichment (Boulton et al., 2008).

Non-stygobite species in hyporheic waters, which are exposed to agricultural practices, prevail upon stygobites, but this observed pattern is likely due to an increase of in-stream productivity. Sufficient nutrients in the hyporheic zone support the development of a large array of non-stygobite taxa, but also favor the invasion of benthic species like *Paracyclops chiltoni* and *P. imminutus*. The stygobites *Acanthocylops* sp. 1 and *Darwinula stenvensoni* are also present however, they appear in low density. We suggest that the reduction or in some cases disappearance of the stygobites fraction at agricultural sites might be due to cumulative factors such as the enrichment of water organic content and the competitiveness of the non-stygobites. Our statement agrees with other studies showing that stygobionts are more sensitive to organic contamination and stygoxenes replaced them (Notenboom et al., 1994; Malard et al., 1994; Di Lorenzo & Galassi, 2013).

Our survey also indicates that the presence of riparian vegetation in riverbanks with mixed land use may contribute to an increased diversification of non-stygobites hyporheos. An example is two sites of the Henares River, which are located close to residential urbanization but surrounded by leisure parks (downstream of Alcala de Henares city). Here the classification of the land cover/use indicates primarily agricultural practices with non-irrigated and permanently irrigated crops, and secondarily natural grasslands and sclerophyllous vegetation and industrial & commercial units (Appendix 1). It is worth mentioning, that nitrites and nitrates are missing from the two Henares sites, whereas they were present in the hyporheic sites of both Rivers Henares and Tajuña with no riparian zone. This fact may suggest the significant contribution of the riverine vegetation to guaranteeing effective processes of denitrification and nitrification, which consequently lead to a local improvement of the hyporheic habitat quality. The relationship between riparian vegetation and water quality is well known. However, most studies were oriented on benthic habitats and macroinvertebrates (Peterjohn and Correl, 1984). Previous recent assessment of macroinvertebrate associations and benthic habitats at these sites indicate a slight enhancement of the surface water quality and an increase of the diversity of benthic macroinvertebrates (Rasines-Ladero, 2011; Fuentes-Alvarez, 2011).

Multiple land-use practices with intense urban and industrial activities cause a reduction of hyporheic crustacean richness with a complete loss of crustaceans at some sites indicating water conditions impoverishment. Here only the non-stygobite *Acanthocyclops robustus* were collected during our survey, which have been most probably drifted from the upstream sites. Particularly, the interactive effects of trace metals, ammonia and VOCs exceeding the standard limits for surface waters (cf. EU-WFD (2000) combined with a lowering of dissolved oxygen down to hypoxia (< 3 mg/l) were detrimental for the hyporheic crustaceans. The univariate ANOVA analysis also indicates that hyporheos crustacean diversity (H') is mainly affected by nitrites, ammonia, Ni and VOCs.

Integrating the hyporheic zone in the management of river ecosystems

The HZ of river ecosystems can provide unique habitat for in-stream invertebrates and refugee for benthic species when surface water conditions decline. Previous studies show the significance of the in-stream biota and the hyporheic zone in ensuring a good functionality of the stream ecosystems as a whole (Boulton et al., 2010). They also show the linkage between the hyporheic zone and the associated alluvial plain of which alteration cause changes in water conditions, sediments deposition in riverbeds and modification in surface/groundwater exchanges to mention few that alter the structuring of hyporheic biota.

Additional conservation of the riparian zone connected with the main channel is also of huge wealth in ensuring a good functionality of the hyporheic water flow and quality and consequently safeguarding the hyporheic communities. Previous researches (Ward, 1989; Tockner et al., 1999; Ward et al., 1999) indicate that the alpha-diversity of macroinvertebrates and biomass increases at moderate connectivity of the riparian zone with the rivers channel, which is likely to occur for hyporheic biota as well.

It is also suggested that for a successful rehabilitation of rivers ecosystems or sectors affected by distinct disturbances a comprehensive understanding and recognition of the hyporheic zone ecology and its capacity to get recovered is required that is often misleading (Danielopol, 1989; Ward et al., 2001; Boulton, 2007; Boulton et al., 2010). For example, the time required for hyporheic biota to recover after persistent disturbances of their habitats is generally high (> 10 years) (Wallace, 1990; Dole-Olivier et al., 2000) and highly depends on the attainment of relatively stable levels of environmental conditions that includes best practices to recover the surface water quality. A more holistic view of river restoration management is compulsory to protect both surface and subsurface associated ecosystems (Boulton et al., 2003; Strayer, 2006; Strayer and Dudgeon, 2010). The large plethora of organisms that have been proved to represent efficient service providers for the subsurface ecosystems they belong should be highly considered in management decisions about river water resource development in the area. In these regards, empirical studies of the transitional surface/ground waters at distinct spatial scales from remote regions are of huge wealth.

CONCLUSIONS

The differences among the investigated hyporheic zone of the Jarama basin in central Spain indicate the consequences of distinct practices occurring in the alluvial floodplain have on the hyporheic zone and selected crustaceans. This study showed important differences in hyporheic waters environmental conditions regarding nutrients (expressed as TOC, NPOC, TC, IC and nitrates) and urban/industrial contaminants (Cu, Zn, Ni, Mn, Pb and VOCs) associated with the land cover and use in the alluvial plain of the Jarama basin. We could also link the land cover and land use types to hyporheic crustacean patterns of the distribution, diversity, and the ecological structure of hyporheic populations. Despite the well-known spatial patchy distribution of hyporheic biota our observations indicate that they are subject to changes significantly, especially in configuration of the communities' ecological structure, when alterations in the associated alluvial aquifer occur.

There was significant evidence that the high overall diversity of hyporheic crustacean communities is linked to agricultural land use, whereas stygobites presence is mainly related to pristine and cold hyporheic waters from forested areas of the investigated Mediterranean rivers. However, we are still lacking the information on changes in hyporheic biota related to the temporal dynamics of land use that impair the prediction of the future impact on this biota by increasing human pressures in the area.

Investigating the effects of land-use at distinct spatial and temporal scales will be critical for a comprehensive understanding and the prediction of the hyporheic community structure in a catchment. Sensitivity tests of certain hyporheos to distinct types of contaminants would also enhance their effective use as bioindicators of the decline of subsurface waters caused by changes in land uses within the alluvial floodplain.

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Appendix 1.

Environmental conditions of the 25 sampled sites from the Jarama basin (central Spain) by means of physico-chemistry and land use variables. Physico-chemistry: Conduc (water conductivity in μS/cm^{-1}); temperature (°C), pH, dissolved oxygen, (mg/l) and NO_3^- (nitrate) (mg/l), PO_4^{2-} (phosphates) (mg/l). Land use: Urb (Urban fabrics), Ictu (Industrial commercial and transport units), Mdcs (Mine dump and construction sites), Ar (Arable land), Haa (heterogeneous agricultural areas), F (forest), Shva (Scrubs and/or herbaceous vegetation associations), Osv (Open spaces with little or no vegetation).

							Hyporheic water physico-chemistry						Land use cover (%)							
River unit		Codes	Elevation (m)	Distance to the headwaters (km)	Slope (%)	EC (μs/l)	Temp.	pH	DO (mg/l)	NO_3^- (mg/l)	NPOC (mg/l)	NO_3 (mg/l)	Urb	Ictu	Mdcs	Ar	Haa	F	Shva	Osv
Jarama River	Hayedo de Montejo	J1	1128	5	4.92	2,10	10,20	6,76	9,50	2,25	2,68	2,25	0.0	0.0	0.0	0.0	0.0	42.20	57.81	0.0
	Torremocha de Jarama	J2	730	30	18.6	246,67	13,70	7,76	10,54	0,54	1,37	0,54	20.49	0.0	0.0	0.0	0.0	14.04	9.13	56.33
	Talamanca de Jarama	J3	662	50	0,76	366,33	17,80	8,07	9,48	1,00	1,44	1,00	0.0	0.0	0.0	0.0	0.0	100	0.0	0.0
	Fuente el Saz	J4	619	58	1,84	366,00	17,50	7,81	8,49	2,75	2,51	2,75	0.0	13.94	0.0	17.59	0.0	18.47	50	0.0
	Paracuellos de Jarama	J5	584	72	0,69	448,00	15,00	7,44	2,29	0,00	7,64	0,00	0.0	0.0	0.0	81.33	0.0	0.0	18.67	0.0
	San Fernando de Henares	J6	584	86	0,82	484,33	14,73	7,77	2,41	3,13	3,55	3,13	21.23	0.0	3.23	12.98	0.0	0.0	62.57	0.0
	San Martin de la Vega	J7	542	110	1,03	811,00	19,33	7,58	5,93	5,71	3,17	5,71	0.0	0.0	0.0	0.0	0.0	42.4	56.6	0.0
	Titulcia 1	J8	551	119	0,32	1569,67	17,20	6,93	0,88	0,77	10,94	0,77	8.25	0.0	0.0	50.32	0.0	9.69	0.0	0.0
Manzanares River	Manzanares el Real 1	M1	1073	5	14,25	19,67	8,00	6,99	9,15	1,57	1,98	1,57	18.77	0.0	0.0	42.04	0.0	39.18	0.0	32.40
	Manzanares el Real 2	M2	968	6	28,55	8,33	5,90	8,27	10,63	0,25	759,58	0,25	0.0	0.0	0.0	37.47	0.0	61.95	0.58	0.0

River unit		Codes	Elevation (m)	Distance to the headwaters (km)	Slope (%)	EC (µs/l)	Hyporheic water physico-chemistry						Land use cover (%)							
							Temp.	pH	DO (mg/l)	NO_3^- (mg/l)	NPOC (mg/l)	NO_3 (mg/l)	Urb	Ictu	Mdcs	Ar	Haa	F	Shva	Osv
	Puente Medieval	M3	844	11	1,98	113,17	16,17	5,23	6,47	0,34	3,63	0,34	34.11	10.36	0.0	37.00	0.0	0.0	18.53	0.0
	El Pardo	M4	601	28	1,7	430,00	12,90	4,65	2,77	1,59	15,31	1,59	3.75	0.0	0.0	96.25	0.0	0.0	0.0	0.0
	Perales del Rio	M5	553	40	5,22	1268,33	18,37	7,19	2,95	5,38	5,26	5,38	0.20	0.0	0.0	99.80	0.0	0.0	0.0	0.0
	Rivas-Vaciamadrid	M6	530	54	2,3	2744,67	17,70	7,13	2,81	0,00	12,05	0,00	0.30	0.0	0.0	55.50	0.0	0.0	24.21	0.0
Tajuña River	Armuña de Tajuña	T1	791	85	5,53	552,00	12,40	5,28	7,84	8,14	1,17	8,14	0.0	0.0	0.0	28.92	71.08	0.0	0.0	0.0
	Loranca de Tajuña	T2	660	97	5,83	1279,67	12,90	7,78	8,79	6,63	1,55	6,63	0.0	0.0	0.0	98.14	0.0	0.0	31.86	0.0
	Carabaña-Orusco	T3	618	121	0,95	1076,00	16,33	8,06	9,21	9,18	24,41	9,18	16.89	0.0	0.0	62.72	11.74	0.0	8.65	0.0
	San Galindo - Chinchon	T4	518	144	0,25	1384,33	12,57	8,03	10,46	22,36	1,86	22,36	0.0	0.0	0.0	97.12	2.88	0.0	0.0	0.0
	Titulcia 2	T5	551	154	0,45	1490,67	18,33	8,01	9,32	5,95	11,00	5,95	0.84	0.0	0.0	89.16	0.0	0.0	0.0	0.0
Henares River	Heras de Ayuso	H1	636	62	10,24	999,67	13,93	7,94	8,30	0,00	23,96	0,00	0.0	0.0	0.0	79.29	0.0	0.0	0.0	0.0
	Fontanar	H2	651	72	3,05	1066,33	15,10	8,02	9,71	2,86	35,82	2,86	0.0	0.0	0.0	100	0.0	0.0	0.0	0.0
	Azuqueca de Henares	H3	587	88	7,68	937,33	16,30	7,73	8,74	5,51	3,15	5,51	0.0	0.0	0.0	11.92	0.0	0.0	25.18	0.0
	Los Santos de la Humosa	H4	572	98	0,81	883,00	13,73	7,41	5,07	5,24	2,59	5,24	0.0	0.0	0.0	80.43	0.0	0.0	0.0	0.0
	Torejon de Ardoz	H5	567	125	1,59	983,00	17,30	7,88	9,04	0,00	38,34	0,00	0.0	7.27	0.0	92.73	0.0	0.0	0.0	0.0
	Mejorada del Campo	H6	551	131	0,44	1838,67	15,03	7,20	11,56	0,00	107,46	0,00	0.0	0.0	0.0	80.11	0.0	0.0	19.87	0.0

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EVALUATION OF GROUNDWATER QUALITY FOR DRINKING AND IRRIGATION BY CALCULATING SPECIFIC QUALITY INDEXES. CASE STUDY: BAIA MARE MINING AREA, ROMANIA

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ABSTRACT. Baia Mare region is one of the most polluted areas from our country due to extraction and processing of ores with high content of Cd, Cu, Pb, Zn and precious metals. The main objectives of the present study were: to assess the groundwater quality by determine the physico-chemical parameters values, dissolved ions and heavy metal concentration and to evaluate if those groundwater sources can be used for irrigation and drinking purposes by calculating 10 specific quality indexes.

A total of 70 groundwater samples were collected from 14 private wells and springs from Baia Mare and surrounding areas (November 2013 and December 2013, June 2014, September 2014 and December 2014).

In situ a portable multiparameter WTW Inolab 320i respectively a portable turbidimeter were used to determine the physico-chemical parameters like: pH, ORP, EC, TDS, DO, salinity and turbidity.

The dissolved ions (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were analysed in laboratory by using an ion chromatograph IC DIONEX 1500. An atomic absorption spectrometer ZEENIT 700 was used to determine the heavy metals concentrations like: Cd, Fe, Mn, Ni, Pb and Zn.

After calculating the specific quality indexes (WQI, MI, HPI, PI, SAR, % Na, SSP, MH, MR and KR), the obtained results indicated that the majority of the investigated water sources are not recommended for drinking and most of them are suitable to be used only like irrigation waters.

Key words: *Baia Mare, mining area, groundwater, specific quality indexes, irrigation, drinking.*

INTRODUCTION

Unfortunately, the mining activities have an important impact on water quality even if the mining practice has improved in recent years.

STUDY AREA

Baia Mare town is the residence of Maramureș County and it is an important urban center from the North-West part of the country.

The town is located in the Baia Mare depression, on the middle course of the Săsar River, at the foot of the Gutâi Mountains.

The most important mining centers of Maramureș County are located in the territories surrounding the city of Baia Mare.

Baia Mare region is known not only for its underground riches, but also for the fact that is one of the most pollution areas from our country due to extraction and processing of ores with high content of Cd, Cu, Pb, Zn and precious metals (Filip, 2008).

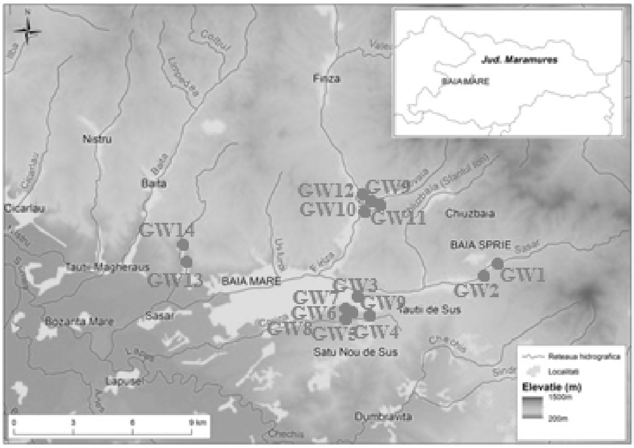

Fig. 1. *Study area (Baia Mare mining area) with sampling points*

AIMS AND OBJECTIVES

The present study aimed to investigate the groundwater quality, from Baia Mare mining area, for drinking and irrigation purposes by calculating specific quality index.

A total of 70 groundwater samples were collected from 14 private wells and springs from Baia Mare and surrounding areas (November 2013 and December 2013, June 2014, September 2014 and December 2014).

MATERIALS AND METHODS

In situ a portable multiparameter WTW Inolab 320i respectively a portable turbidimeter were used to determine the physico-chemical parameters like: pH, ORP, EC, TDS, DO, salinity and turbidity.

The dissolved ions (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were analysed in laboratory by using an ion chromatograph IC DIONEX 1500. An atomic absorption spectrometer ZEENIT 700 are used to determine the heavy metals concentrations like: Cd, Fe, Mn, Ni, Pb and Zn.

Water Quality Index (WQI)

Using water quality index (**WQI**), a single value can be obtained to expresses the general quality of the surface/groundwater source, based on several quality parameters.

There are three steps in order to calculate WQI (Ramakrishnaiah et al., 2009; Ravikumar 2013):

1. A weight (*w_i*) has to be assigned to each of the chemical parameters: 5 which is the highest weight has to be assigned to the most important parameter regarding its impact on human health or water quality and 2 has to be assigned to non-dangerous parameters.
2. Relative weight (*Wi*) of each parameter has to be calculate using the following equation:

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \qquad (1)$$

Where: W_i is the relative weight, w_i is the weight of each parameter and *n* is the number of parameters.

3. For each parameter has to be calculated a quality rating scale (q_i) by dividing its concentration in each water sample by its standard according and multiplied the result by 100:

$$q_i=\frac{C_i}{S_i} \times 100 \qquad (2)$$

Where: qi is the quality rating, C_i = concentration of each chemical parameter in each water sample in mg/L, S_i = maximum concentration limit (Low 456/2002 regarding drinking water quality).

In order to calculate the **WQI** the water quality sub-index (SI_i) has to be determined:

$$SI_i = W_i * qi \qquad (3) \qquad ; \qquad WQI = \sum SI\ i \qquad (4)$$

Table 1. *Water quality based on WQI values (Ramakrishnaiah et al., 2009; Ravikumar, 2013)*

WQI values	Water quality
WQI < 50	Excellent
50 < WQI < 100	Good
100 < WQI < 200	Moderate
200 < WQI < 300	Poor
WQI > 300	Unsuitable for drinking

Metal Index (MI)

Using MI we can classify the quality of the water body, in terms of heavy metal contamination. MI was calculated using the following formula:

$$MI = \sum_{i=1}^{n} \frac{C_i}{(MAC)_i} \qquad (5)$$

Where: C_i = the concentration of metal taken into account; MAC = maximum concentration level for the parameter taken into account.

If the MI value is higher than 1 then the warning threshold has been exceeded (Bakan et al., 2010; Goher et al., 2014).

Heavy Metal Pollution Index (HPI)

The heavy metal pollution index is used to indicate the influence of a cumulative number of heavy metals on the overall water quality. The index was developed in 1996 (Mohan et al., 1996) in order to assess the quality of drinking water. Over time, various researchers (Edet and Offiong, 2002; Nasrabadi, 2015; Tiwari et al., 2015; Yang et al., 2015) have adapted the heavy metal pollution index to determine the quality of different types of water.

The heavy metal pollution index is calculated using the following formulas:

Weight of each heavy metal taken into account:

$$W_i = \frac{k}{S_i} \qquad (6)$$

Where: k = constant *of* proportionality (k=1); S_i = the legalized value for the heavy metal taken into account.

Quality assessment for each heavy metal considered:

$$Q_i = 100 * \frac{C_i}{S_i} \qquad (7)$$

Where: C_i= heavy metal concentration taken into account (µg/L); S_i= the legalized value for the heavy metal taken into account.

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \qquad (8)$$

The sign (-) indicates the numerical difference between two values, this must be ignored. The critical value of the HPI is 100, above this value the water source is considered unsuitable for the purposes for which we intend to use it (Yang et al., 2015).

In the present study, in order to calculate the HPI, all the heavy metals investigated and detected in the monitored water sources were taken into account.

Pollution Index, PI

PI is based on the calculation of each metal and its classification into five quality classes (Table 2). In the present study **PI** was calculated for all investigated heavy metals (Fe, Zn, Cr, Cd, Mn, Ni, Pb). **PI** is calculated using the following formula:

$$PI = \frac{\sqrt{\left[\left(\frac{C_i}{S_i}\right)^2_{max} + \left(\frac{C_i}{S_i}\right)^2_{min}\right]}}{2} \qquad (9)$$

Where: C_i = the concentration of metal taken into account; S_i = maximum concentration level for the parameter taken into account (Caeiro et al., 2005; Bakan et al., 2010; Goher et al., 2014).

Table 2. *Water classification based on PI values (Bakan et al., 2010; Goher et al., 2014)*

Class	Values	Status
1	< 1	no effect
2	1-2	slightly affected
3	2-3	moderately affected
4	3-5	strongly affected
5	>5	seriously affected

Sodium Adsorption Ratio (SAR)

In order to calculate sodium adsorption ratio (**SAR**) we used the sodium, calcium and magnesium concentrations (where all ionic concentrations are expressed in milli equivalent per liter) using the following equation (Harront et al., 1983; Sisir and Anindita, 2012).

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \qquad (10)$$

Table 3. *Water classification based on SAR values (Sudhakar and Narsimha, 2013)*

SAR values	Status
SAR < 10	Excellent
10 < SAR < 18	Good
18 < SAR < 26	Doubtful
SAR > 26	Unsuitable

Kelley Ratio (KR)

The Kelley index indicates whether the investigated water sources can be used for agricultural purposes (Ravikumar and Somashekar 2011).

The Kelley index was calculated using the following calculation formula:

$$KR = \frac{Na^{+}}{Ca^{2+} + Mg^{2+}} \qquad (11)$$

The ionic concentrations are expressed in mEq / L (Reddy, 2013)

Sodium Percentage (%Na)

%Na was calculated using the equation (12). The ionic concentrations are expressed in mEq / L (Roşu et al., 2014).

$$\%\ Na = \frac{(Na^{+} + K^{+}) * 100}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \qquad (12)$$

Table 4. *Water classification based on % Na values (Wilcox, 1995)*

% Na values	Status
< 20	Excellent
20 - 40	Good
40 - 60	Permissible
60 - 80	Doutful
> 80	Unsuitable

Magnesium Ratio (MR)

Based on the Mg/Ca ratio, the investigated water sources can be classified as recommended for use in agriculture.

Table 5. *Water classification based on MR values (Ravikumar and Somashekar, 2011)*

Magnesium Ratio value	Status
< 1.5	Excellent
1.5 - 3	Moderate
> 3	Unsafe

Soluble Sodium Percentage (SSP)

SSP was calculated using the formula (13). The ionic concentrations are expressed in mEq/L (Ravikumar and Somashekar, 2011).

$$\text{SSP} = \frac{Na^{+}}{Na^{+}+Ca^{2+}+Mg^{2+}} * 100 \qquad (13)$$

Table 6. *Water classification based on SSP values (Le Breton and Berg, 1965)*

SSP value	Status
0 - 20	Excellent
20 - 40	Good
40 - 60	Permissible
60 - 80	Doubtful
80 - 100	Unsuitable

„Magnesium hazard” (MH)

MH was calculated using the equation (14). The ionic concentrations are expressed in mEq/L.

$$\text{MH} = \frac{Mg^{2+} * 100}{Ca^{2+}+Mg^{2+}} \qquad (14)$$

If the "magnesium hazard" index exceeds 50%, it is considered that the use of that water source will increase the alkalinity of the soil, affecting the crops growth (Ravikumar and Somashekar, 2011; Sudhakar and Narsimha, 2013).

RESULTS AND DISCUSSIONS

As can be seen in figure 2, two groundwater samples (14 %) are not suitable for drinking. GW3 was collected from a private well which is very close to Tautii de Sus tailing pond and GW9 was collected from a private well as well, but this downstream of Herja Mine, near Herja creek.

If we are taking into account only the concentration of heavy metals, due to high values 71 % of groundwater samples are not suitables for drinking (figure 3), because HPI > 100. GW9 was collected from a private well, near Herja creek and has the higher value.

Regarding the MI all the groundwater samples exceeded the warning thresdold, are not recommended to be used as drinking water sources (figure 4), because MI > 1.

As can be seen in figure 5, regarding PI for Pb non of the ground water samples are seriously affected, because PI < 1. If we take into consideration the PI for Zn – only GW9 is strongly affected, PI for Ni – GW1, GW3, GW7, GW9, GW10, GW11, GW12 and GW13 are moderately affected, PI for Mn – GW2, GW3 and GW13 are seriously afected; PI for Fe – GW2, GW3, GW10, GW11 and GW13 are seriously afected and PI for Cd – only GW9 is seriously afected (figure 4).

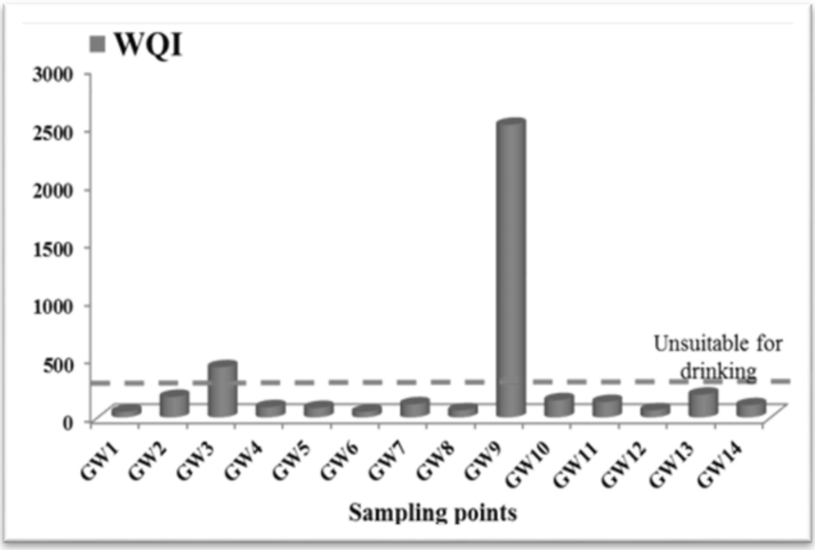

Fig. 2. *Water Quality Index values, depending on the sampling point*

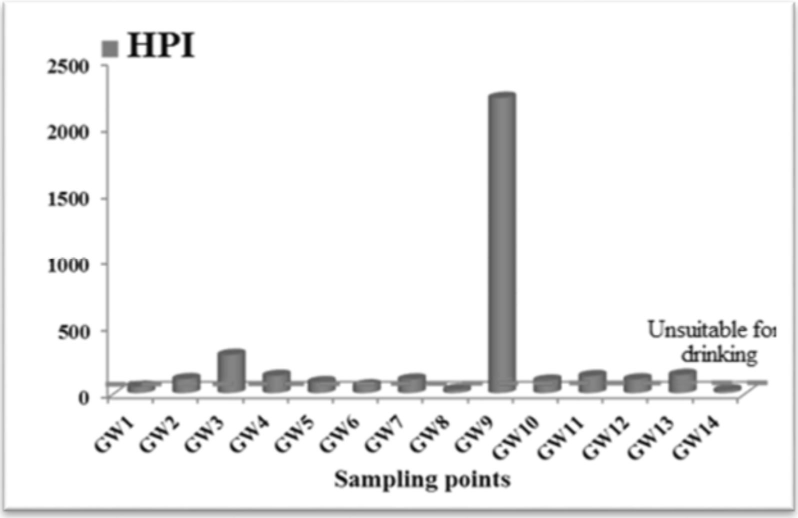

Fig. 3. *Heavy Metal Pollution Index values, depending on the sampling point*

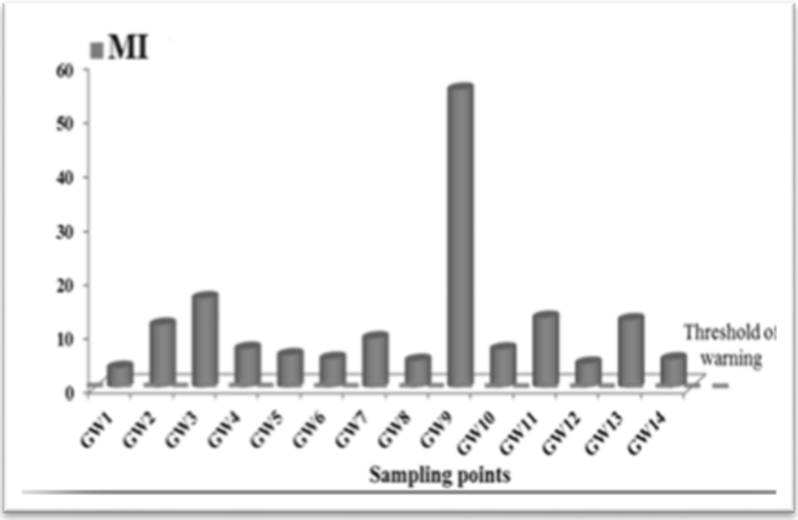

Fig. 4. *Metal Index values, depending on the sampling point*

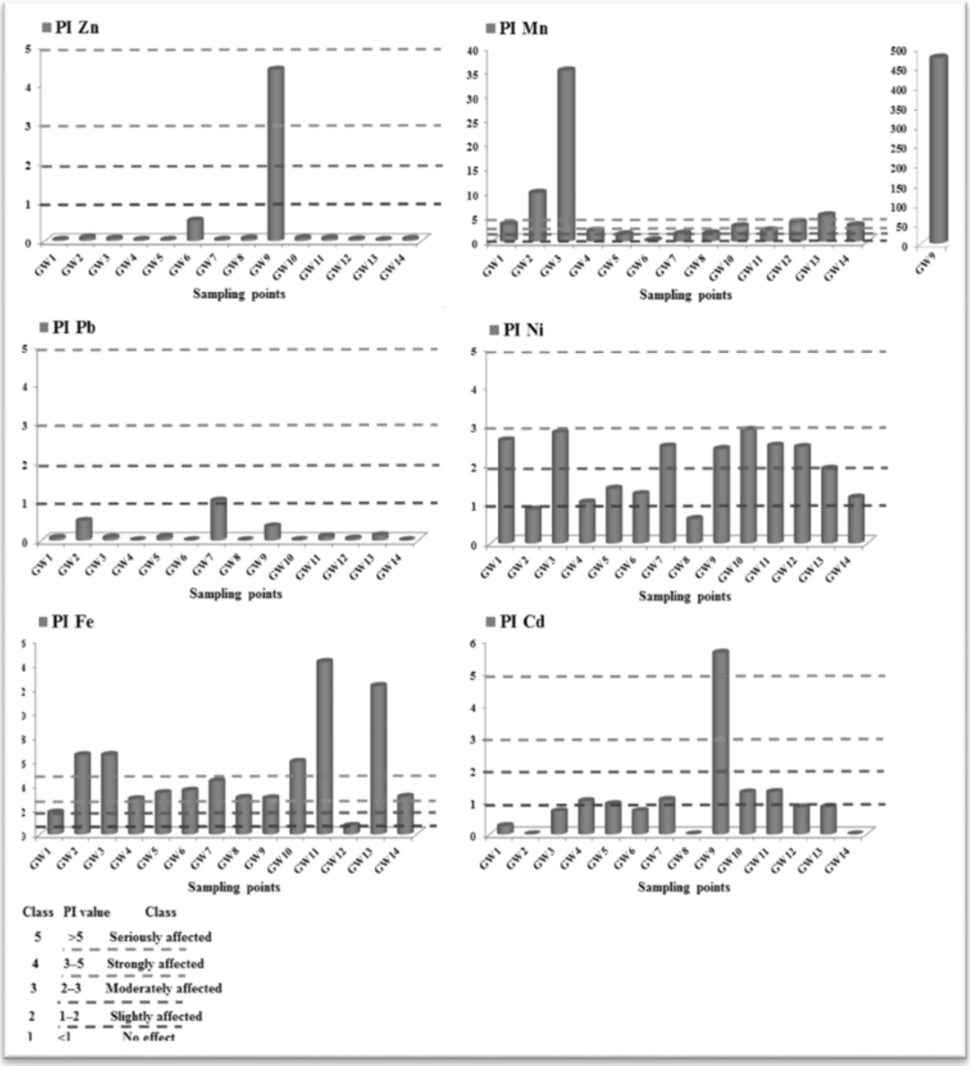

Fig. 5. ***P**ollution **I**ndex (PI) values, depending on the sampling point*

Irrigation

Six specific quality indexes were calculated in order to evaluate if those groundwater sources can be used for irrigation (KR, %Na, MR, MH, SSP and SAR).

Regarding **K**elley **R**atio (Fig. 6) only one groundwater sample (GW13) is not suitable for irrigation, this sample being collected from a pomp downstream of Herja Mine.

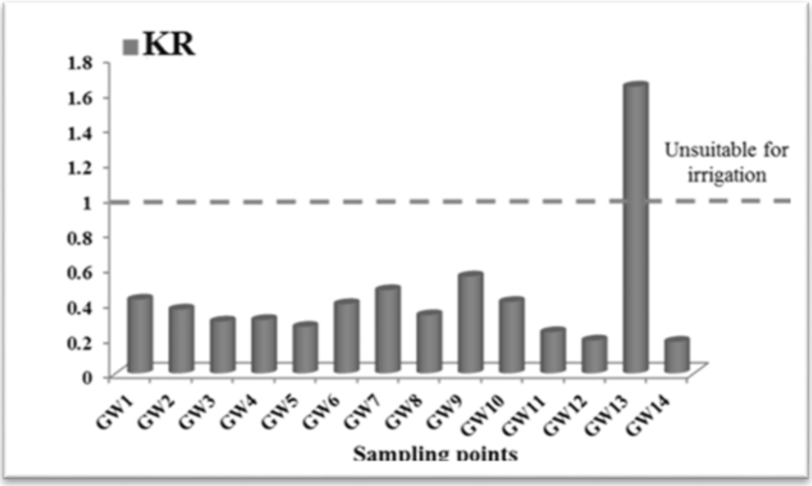

Fig. 6. ***K**elley **R**atio values, depending on the sampling point*

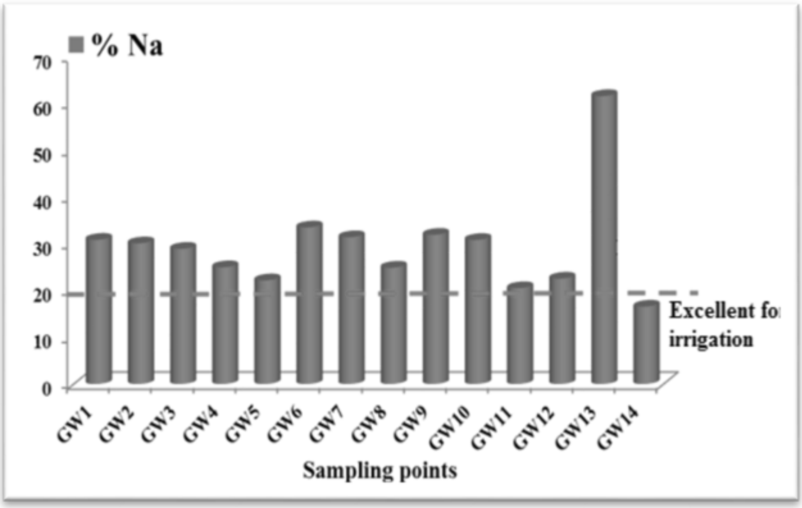

Fig. 7. *Sodium Percentage values, depending on the sampling point*

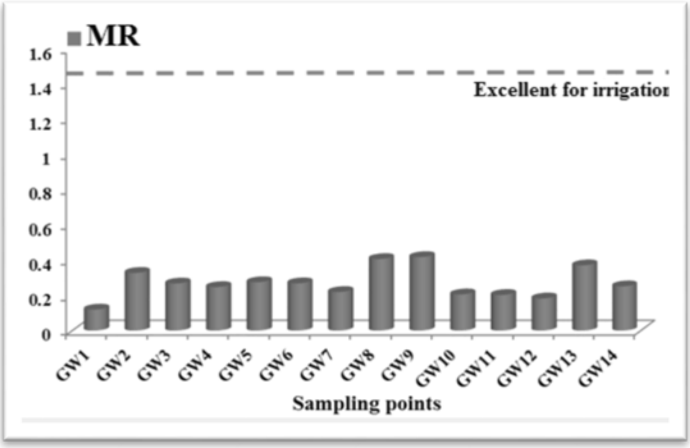

Fig. 8. ***M**agnesium **R**atio values, depending on the sampling point*

In terms of Sodium Percentage (figure 7) only one groundwater samples belong to excellent category, GW14.

Magnesium Ratio (**MR**) and Magnesium Hazard (**MH**) values indicates that all groundwater samples belong to excellent category, this is due to the fact that in order to calculate this index is necessary only the magnesium and calcium concentration (figure 8 and figure 9).

Taking into consideration the **S**oluble **S**odium **P**ercentage (**SSP**) and **S**odium **A**dsorption **R**atio (**SAR**) none of the groundwater samples belong to unsuitable for irrigation category (figure 10 and figure 11).

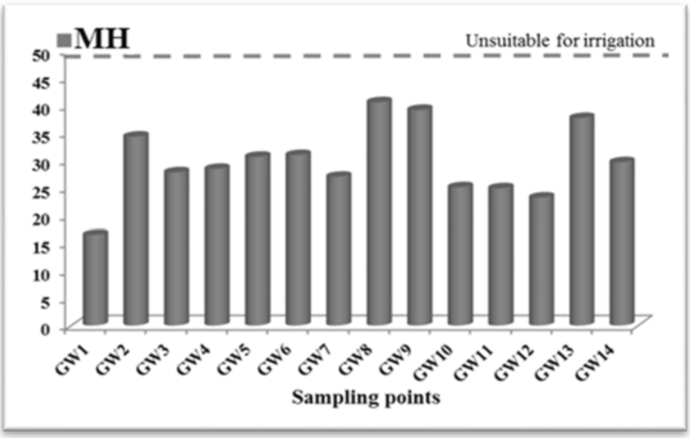

Fig. 9. ***M**agnesium **H**azard values, depending on the sampling point*

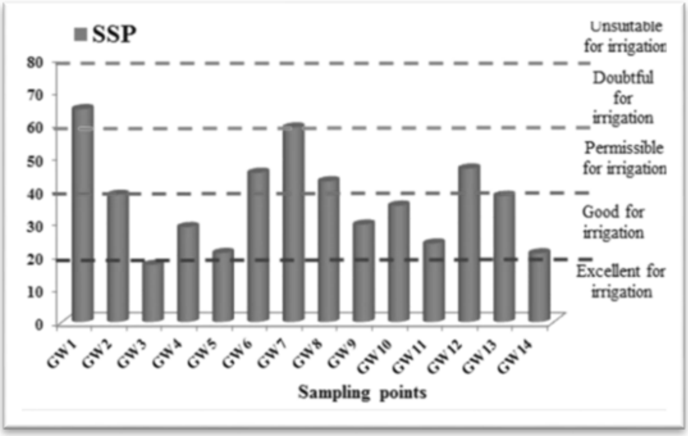

Fig. 10. ***S****oluble* ***S****odium* ***P****ercentage values, depending on the sampling point*

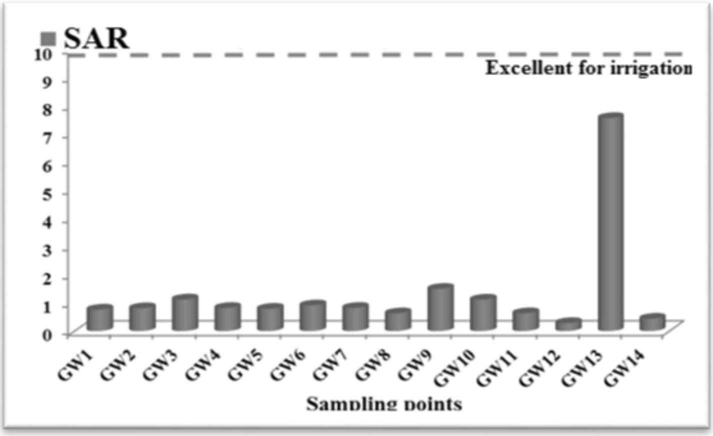

Fig. 11. ***S****odium* ***A****dsorption* ***R****atio values, depending on the sampling point*

CONCLUSIONS

The investigated groundwater samples proved to be high polluted with manganese, iron and nickel, these are not recommended to be used like drinking waters. By calculating **WQI**, **HPI** and **MI** it can be seen that the sampling point GW9, which is a private well, is the most polluted. It may be due to the fact that this well is located downstream of Herja Mine, and near the Herja creek where all mine waters are discharged.

After calculating **KR**, **SSP**, **%Na**, **SAR**, **MR** and **MH** it can be concluded that almost all groundwater samples can be used like irrigation water, a special attention should be paid to GW13 sampling point, due to its high sodium content it cannot be used as a reliable source of irrigation.

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CONDUCTOMETRIC TESTS AND TOTAL CHROMIUM LEACHABILITY IN AQUEOUS SOLUTION, FROM TANNED LEATHER WASTE

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ABSTRACT. Tanning is the most important operation in leather processing, which turned the leather into a non-putrefying material. Tanning may be carried out with chromium salts (III) or with a variety of other tanning agents. In present days, tanning with chromium salts (III) is the most widely used technique in industrial processing of leather, almost 90 % of leather goods being processed by this method.

Taking into account the fact that the wastes from the leather and fur industry are framed by Commission Decision 532/2000 under code 04 01 08 (non hazardous), this study aim's to analyze the leachability of total chromium from tanned and dyed leather waste originated from leather processing industries, in order to establish the environmental risks of them. Leachability tests, conductometric tests and determination of the refractive index were carried for three types of tanned leather waste (G-gray, Bn-brown, Bk-black), at different temperatures.

The results shown that the values for the total chromium in leachate were higher than the maximum allowed concentration for the hazardous waste (MAC = 70 mg/kg). The leachability of total chromium increased at low temperatures (5-13°C) and at high temperatures (40-60°C).

In Romania an important amount of tanned leather waste reaches the municipal landfills. These results indicate that the leather waste can be disposed *only in special landfills for hazardous waste.*

Key words: *chromium, leather, waste, leachate, conductometric tests*

INTRODUCTION

Waste represents a particular challenge due to: the increasing quantities and types that by degradation and infestation represent a threat to the natural environment and human health, and also because of the important raw materials quantities that can be recovered and returned to the economic cycle. Leather industry has always been one of the most important industries of the European economy (Vișan et al., 2002). Worldwide, the largest amount of generated waste in the leather processing is in Asia (without China) and China (see figure 1). Generally it can be observed that the waste amounts generated in Asia (excluding China) and the Western Europe are approximately equal, specifying that it represents about half of the total waste worldwide generated.

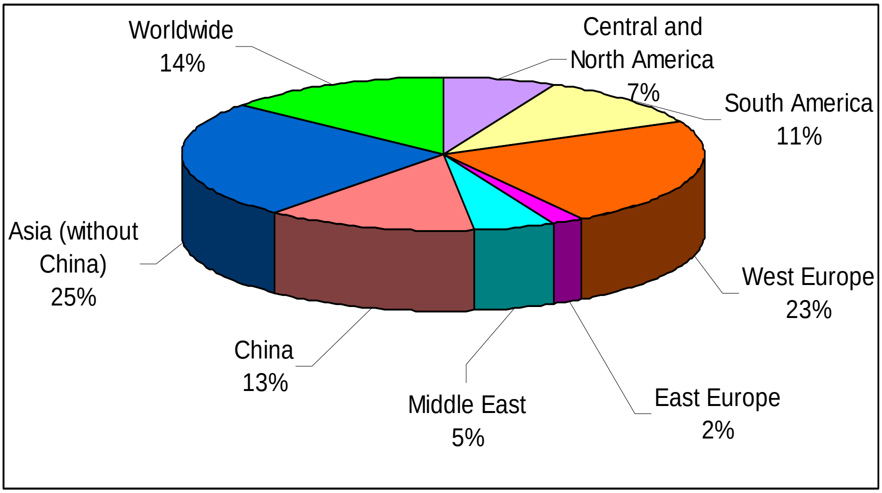

Fig. 1. *The worldwide waste quantity generated in the leather processing process (CTC, 2000)*

From figure 1 it can be observed large differences between the generated waste from Western Europe and Asia (excluding China), and the rest of the world. The largest quantities, 25% belong to Asia (without China) and the lowest amounts are recorded to Eastern Europe at a rate of 2%. Asia together with Western Europe, with a share of 61%, is generating more than half of the generated worldwide waste.

The main goal in the leather industry is the production of the leather products, this sector representing 41% of all industrial uses for this material. In this context, Romania had an important tradition in leather processing and still has it.

The leather industry is using only 80% of the rawhide material, the rest of 20% representing the processing waste. A proportion of 25% of the rawhide represents the final product, 70% is represented by the solid waste, and 5% by the residual water. By tanning, from 1,000 kg of leather is obtained 600 to 700 kg of solid waste and 40-50 m^3 of wastewater (Vișan et al., 2002). Approximately 70% of the waste is recovered and for the rest are studying utilization possibilities (Vişan et al., 2002). In Romania, the total rawhide amount annually processed, about 11,000 tons of waste, is structured as follows: 5,500 tons / year of raw-hide waste; 3,500 tons / year of tanned and unfinished leather waste; 1,800 tons / year of tanned and finished leather waste; 200 tons / year of leather fur waste (Vișan et al., 2002).

The processed leather waste has a major impact on the environment because of the contained substances, mostly heavy metals. It is very important to not discard the processed leather waste in nature or to store it in open dump landfills; it is indicated to manage it properly through recycling and recovery thereof or by storage in compliant landfills. The open dump landfills, generally, due to lack of facilities and poor exploitation, generate impact and risk to the environment and public health. The main impacts and risks are: the changes in landscape and visual discomfort, air pollution, surface water pollution, changes in soil fertility and biocenosis composition of the neighboring land (Lixandru, 1999; Popița et al., 2013).Therefore, the waste from tanneries must be handled and stored so as to avoid leakage, odor problems and air emissions (BAT, 2013).

In the tannery process, generally, as tanning agent are used trivalent chromium (Cr III) compounds. But, some leather products may contain traces of hexavalent chromium (Cr VI), which is considered prioritary / hazardous substance (Directive 60, 2000; Directive 105, 2008; Regulation 1272, 2008). In tanning process, only Cr (III) compounds are used, but it may be possible sources of Cr (VI) as a contaminant: after UV exposure (at over 80°C) the fat-liquoring acids is possibly to lead to the oxidation of Cr (III); the formation of Cr (VI) may result in the process of the storage of fat-liquored leather at 35% humidity (Kolomaznik et al., 2008). Also, in the shoe production, the use of alkaline glues may contribute to the formation of Cr (VI) (Kolomaznik et al., 2008).

The oxidation of Cr (III) to Cr (VI), in basic solutions, occurs easily with the use of peroxides and hypochlorite. The oxidation of Cr (III) to Cr (VI), in acid solutions, occurs with the use of sulfuric acid. The oxidation occurs after the following equations (Eq. 1 and 2):

For an alkali medium:

$$2Cr_2O_3 + 8OH^- + 3O_2 \rightarrow 4CrO_4^{2-} + 4H_2O \quad (1)$$

For an acid medium:

$$2Cr_2O_3 + 3O_2 + 2H_2O \rightarrow 2Cr_2O_7^{2-} + 4H^+ \quad (2)$$

(Kolomaznik et al., 2008)

Cr (VI) usually exists in the form of $H_2Cr_2O_7$ and its salts and in the form of $Cr_2O_7^{2-}$. Both anions CrO_4^{2-} and $Cr_2O_7^{2-}$ are water soluble and their formation is pH dependent. Above pH=7 predominates the Cr (III) and below pH=6 predominates Cr (VI) (Frey and McGuire, 2004; Gode, 2007).

In case of the open dump landfills, it can occurs that the acid rain leach the Cr (III) compounds from the landfilled leather waste and the soluble salts can reach underground water sources and surface water streams. The underground water could reach a treatment water plant, where in the process of the sterilization of drinking water under strong oxidation conditions by ozone or by hypochlorite, the Cr (III) is converted into Cr (VI). The reaction with magnesium and calcium ions present in drinking water and generate magnesium and calcium chromate or dichromate salts which are carcinogenic. In this respect the calcium and magnesium chromate and dichromate salts which are elements presents in soil and drinking water, were classified as carcinogenic compounds (Kirk, 1992).

Leather processing generates substantial amounts of solid and liquid waste (skins, grease, dust, manure, sludge). In the literature, there are numerous studies (Yilmaz et al., 2007; Alptekin et. al., 2012; Nogueira et. al., 2011; Famielec and Wieczorek-Ciurowa, 2011) on tanned leather waste treatment for recycling and recovery. Most of these studies are related to the extraction of chromium from the waste to be reused in the tanning process (Yilmaz et al., 2007).

For leather processing, the reference documents for best available techniques (BAT - Best Available Techniques) are covered by the Directive 2010/75/EC (Directive 75, 2010). In the European legislation, as well as in the Romanian one, the waste from the leather industry, fur and textiles are listed and coded under Chapter 04 “Wastes from the leather, fur and textile industries” (Decision 532, 2000; GD 856, 2002).

It must be noticed that the leather waste, containing chromium salts isn’t framed as hazardous waste; this waste is coded at code 04 01 08: “waste tanned leather (blue sheeting, shavings, cutting, buffing dust) containing Chromium”. Only the codes marked with an asterisk (*) are considered as a hazardous waste (Decision 532, 2000; GD 856, 2002).

In this respect the present study mainly aims to analyze the leaching of the total chromium from leather waste originated from leather processing industry and comparing with the Maximum Allowed Concentration from leaching waste legislation. Also we determinate the conductometric parameters (pH, TDS, EC, salinity) in order to monitor the behavior of leather waste in the environment.

MATERIALS AND METHODS

In this study was used tanned leather waste from a shoe factory, which has been tested in different conditions of temperature and over different periods of time, to observe the leachability of the total chromium. We have used three different types of waste leather with different colors and textures (figure 2).

a b c

Fig. 2. *Waste leather type black-**Bk** (a), waste leather type brown-**Bn** (b) and waste leather type gray-**G** (c)*

Conductometric tests, the refractive index determination and leachability tests for total chromium were made for each type of waste leather for 5 days at 4 different temperatures: 5-13°C (outside temperature at the determination moment), 22-25°C (indoor temperature), 30-40°C and 40-60°C.

Conductometric tests (pH, total dissolved solids - TDS, electrical conductivity - EC, salinity) were performed with a portable multiparameter WTW Multi 350i. The refractive index was determinate with a digital refractometer Reichert AR 200. The total chromium concentration was analyzed with an Atomic Absorption Spectrometer (AAS) ZEEnit 700 (Analytic Jena) by flame absorption.

Leather waste was collected from a shoe factory, from the leather waste bins located inside of the company's perimeter. These wastes were taught to a sanitation company to transport them to the municipal open dump landfill waste. Leather waste was sorted by colors and/or different textures. For this study, were chosen three types of waste leather with different colors and textures to track the behavior, over time, of certain parameters in the leachate, in order to evidence if the different pigments influence the chromium leachability. The cutting step of the chosen leather waste types was made using mechanical shears by cutting small pieces with the length and width of about 1 cm.

In order to perform the leachability study was chosen, in accordance with the OM 95, 2005 (2 L/kg), the ratio scrap leather waste/distilled water and leather waste + sand/distilled water (OM 95, 2005). The vessels were filled with distilled water in which was immersed the leather waste and were subjected to various temperature conditions for 8 hours/day, 5 days, for each sample. Conductometric tests were carried out daily, at the temperatures presented above, after the 8 hours period accomplished.

After the completion of the conductometric experiment, the 2 phases (liquid/solid) were separated, the leachate was collected, acidified with concentrated nitric acid (HNO_3) to a pH = 2 and filtered in order to analyze the concentration of the total chromium.

The analysis of the total chromium from the leachate was performed by using the Atomic Absorption Spectrometry ZEEnit 700 (Analytic Jena) by flame atomic absorption method.

RESULTS AND DISCUSSIONS

The results showed a correlation between the total chromium concentration in the leachate, and the changes of the conductometric measured parameters during the analysis time (5 days) and the different temperatures.

The conductometric parameters determination

Conductometric tests (pH, TDS, EC and salinity determination) and the refractive index determination were made for three types of waste leather (**G**-gray, **Bn**-brown, **Bk**-black) for 5 days at 4 different temperatures: 5-13°C (outside temperature at the determination moment), 22-25°C (indoor temperature), 30-40°C and 40-60°C.

In figure 3 is presented the pH variation for the three waste leather types (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature.

From figure 3 it can be seen that the samples with leather brown waste **Bn** had a basic pH=7-8, at all temperatures, which slowly decrease or remain constant during the analysis period of 5 days.

Note that the blank had a pH = 5.2. The samples **G** and **Bk** were acidic at a pH=3-4 and remained acidic with slow modifications during the analysis period of 5 days.

The EC (electroconductivity) variation for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature is presented in figure 4.

The figure 4 show that the **Bk** type of waste leather had the highest values at high temperatures (40-60°C), but also at outside indoor and 30-40°C temperatures. The **Bn** type had the highest values at temperatures of 30-40°C and also at indoor temperatures. As can be seen the **Bn** type values are lower at higher temperatures than at indoor temperatures. The **G** type had the lowest values at all temperatures.

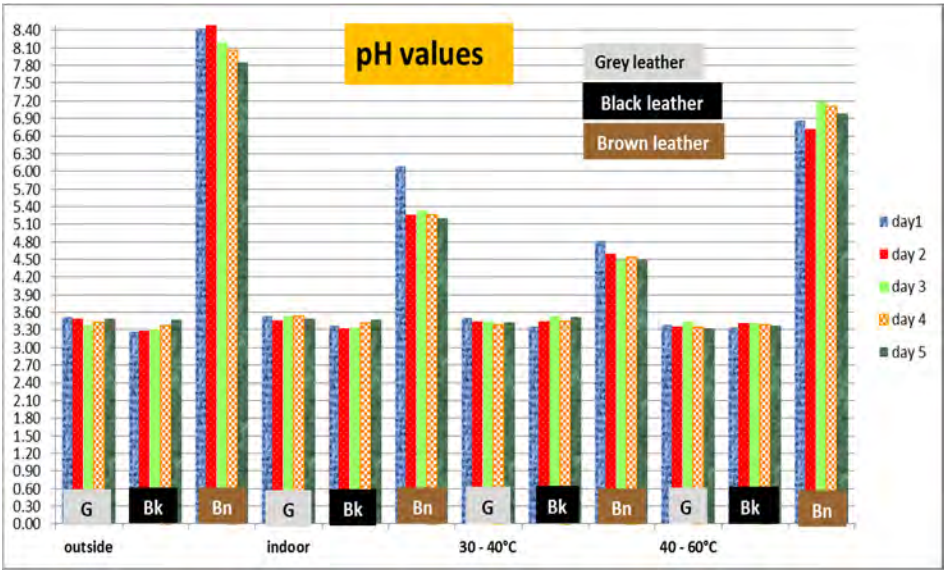

Fig. 3. *The pH variation for the three waste leather type (gray G, black Bk and brown Bn), depending on analysis time and temperature*

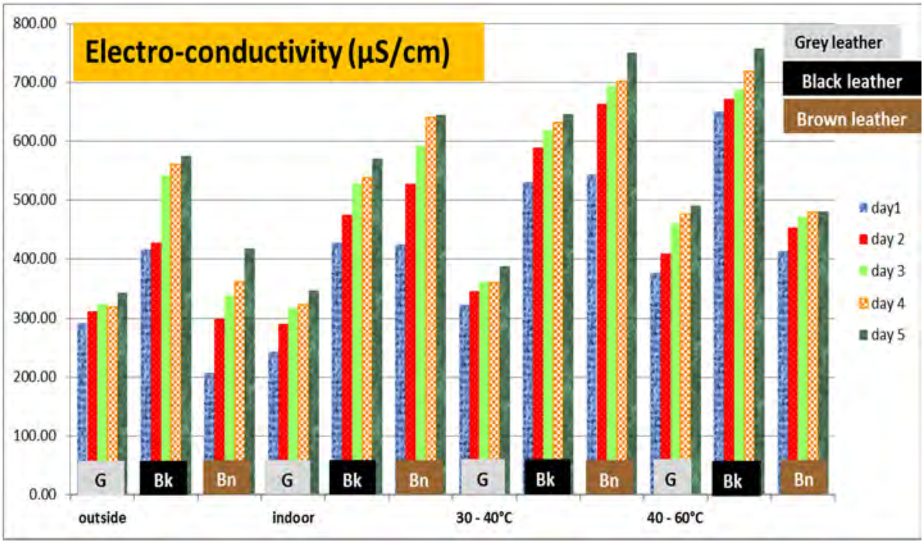

Fig. 4. *The EC variation for the for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature*

TDS variation for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature is presented in figure 5.

Figure 5 show, as in the case of EC, that the waste leather type **Bk** had the highest values at the highest temperature (40-60°C). The **G** type had the lowest values at all temperatures. During the 5 days, all the waste leather types presented increases, proportional with the analysis time. Note that the **Bk** type had higher values at outside temperatures and indoor temperature, in contrast with the other types of waste leather **G** and **Bn**. That means that the temperature is an important factor in the leaching waste leather process. High levels of TDS in water can indicate the presence of a wide range of pollutants.

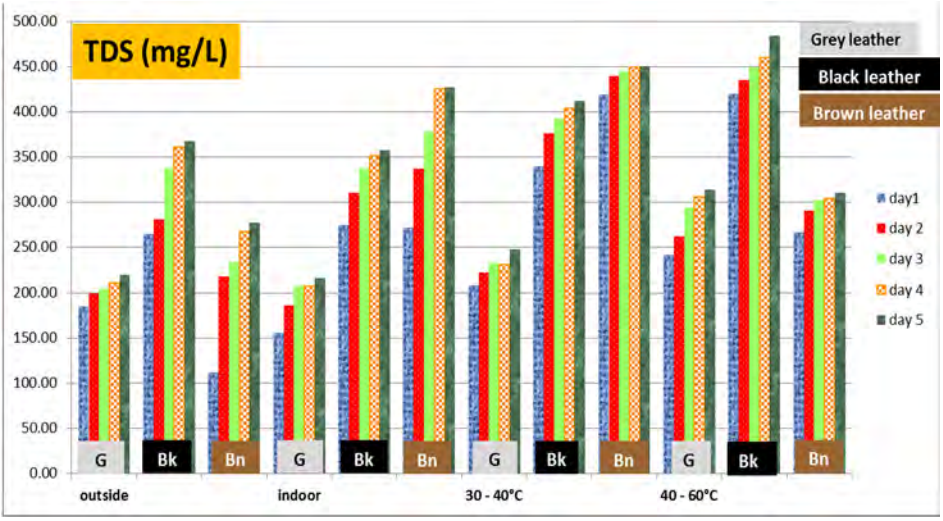

Fig. 5.*TDS variation for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature*

Figure 6 offers information about the salinity variation for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature.

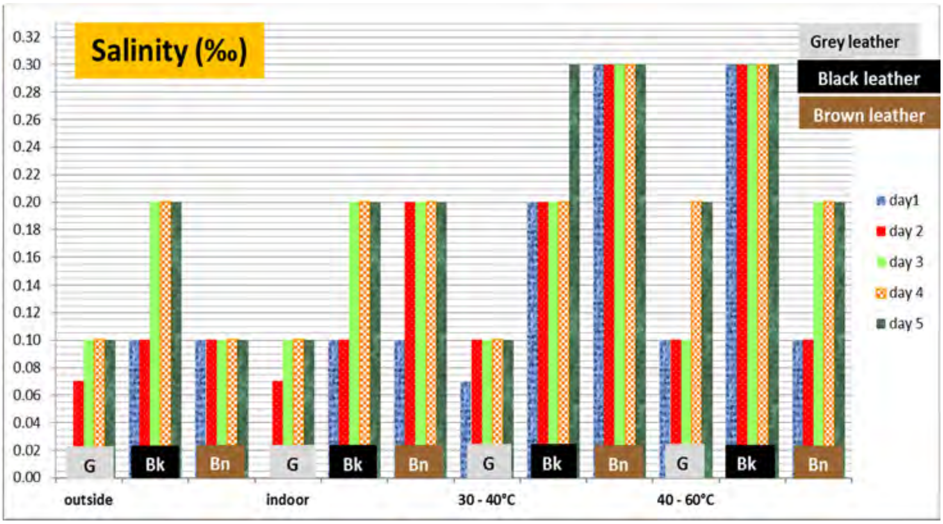

Fig. 6. *Salinity variation for the for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature*

As can be seen in figure 6, the **Bk** type of waste leather had the highest values at high temperatures (40-60°C), but also at outside indoor and 30-40°C temperatures. The **Bn** type had the highest values at temperatures of 30-40°C and the **G** type had the lowest values at all temperatures. It can be observed that the salinity generally had a gradual increase grows after the first day of experiment. The increasing of salinity was pronounced at low temperatures.

Figure 7 represents the refractive index variation for for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature.

From figure 7 it can be seen that the refractive index increased proportional with the analysis time and has the highest values at outdoor temperatures, for all types of leather. The highest values belong to the **G** waste leather type. The refractive index decreased with the increasing of the temperature. The higher was the refractive index; the cleanest was the water in which the leather was immersed. This is related with the lowest values of the **G** type for the: salinity, TDS and EC values.

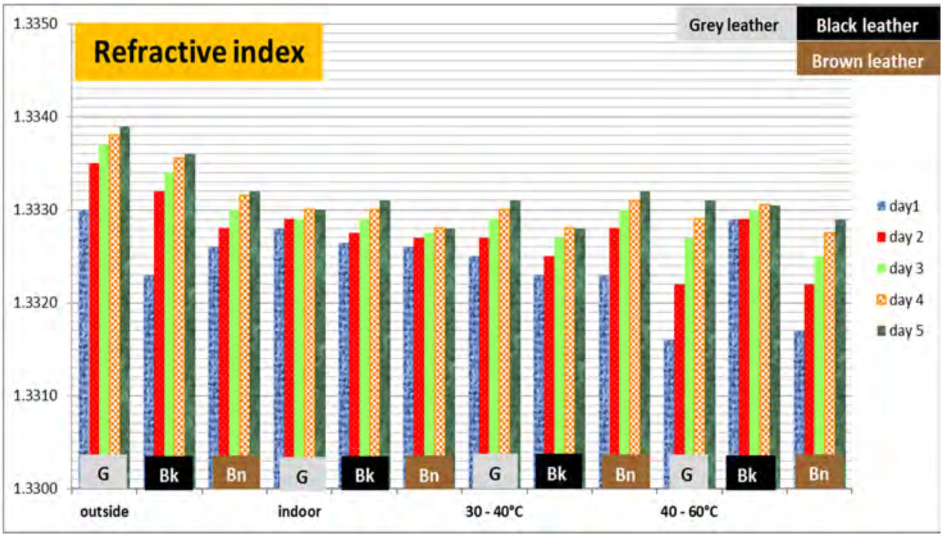

Fig. 7. *Refractive index variation for the for the three waste leather type (gray-**G**, black-**Bk** and brown-**Bn**), depending on analysis time and temperature*

Total chromium analysis

The total chromium concentration was analysed from the leachate of the three types of leather waste: gray-**G**, brown-**Bn** and black-**Bk**.

Figure 8 presents the values of the total chromium concentration in the leachate for the three types of leather waste.

From figure 8, it can be seen that all the samples at all the temperatures range, shown a significant increase of the total chromium concentration in leachate, over the maximum allowed concentration MAC = 70 mg/kg (OM 95, 2005, table 4.1 hazardous waste leachability). That means that the samples are characterized by a hazardous character and represents a serious problem for the environment.

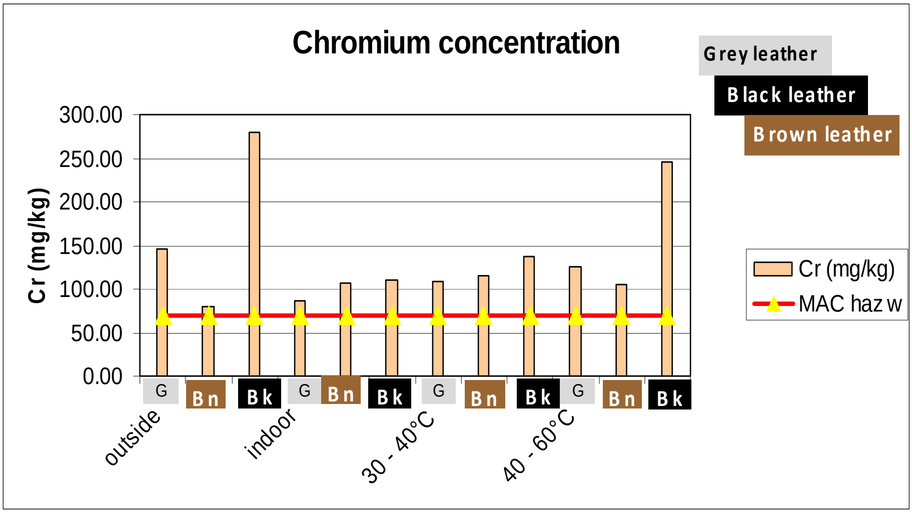

Fig. 8. *The total chromium concentration in the leachate for the for the three types of leather waste: gray-**G**, brown-**Bn** and black-**Bk***

In this respect the **Bk** type had the highest values at outside temperatures, followed by the values at temperatures between 40-60°C. It is interesting to note that for the total chromium concentration increases above the MAC not only at outside-low temperatures, but also at temperatures higher than 40°C. This behavior may be characteristic for this type of leather waste if reach on the open dump landfills and leach in natural condition (winter and summer temperatures). In contrast with other analyzed leather waste types (gray, brown), the total chromium concentration in leachate are much higher for black leather waste, probably resulting due to the absorbed chromium salts in the tanning process. The **G** type had the following highest values after the **Bk** type at the same range of temperatures (low and high).

It can be seen a closely correlation between the pH range (figure 3) and the total chromium concentration values. The **Bk** and **G** types had acidic pH (3-3.5) at outside and high temperatures (40-60°C) and the total chromium values were higher than for the **Bn** type which had a basic pH range (7-8.5) at the same temperatures. If we correlate the obtained values with the pH dependence of the chromium species, Cr (III) and Cr (VI), we can conclude that the **Bk** and **G** type may contain mainly Cr (VI) compounds and the **Bn** type may contain mainly Cr (III) salts.

It is very known that a particular importance has the speciation between the Cr (III) and Cr (VI), because of the carcinogenic action of the Cr (VI) compounds. The Cr (III) and Cr (VI) compounds are accessible to the population due to their presence in many consumer products. The primary ways for exposure are: inhalation, ingestion in the case of Cr (III) and absorption through the skin in case of Cr (VI). The higher solubility and the reaction with cell membrane of the Cr (VI) compounds, than the Cr (III) compounds represent a problem for the human health (Kolomaznik et al., 2008).

CONCLUSIONS

The experimental results obtained from the conductometric tests and analysis of the total chromium concentration highlighted the following:

- The present study shows a strong link between the conductometric tests (pH, EC, TDS, salinity, refractive index) performed for three different types of tanned leather wastes (**G**-gray, **Bn** -brown and **Bk**-black), with the analysis time and the temperature.
- Each type of leather waste had a different behavior depending on temperature and analysis time, maybe because of the different composition with substances, originated from the tanning process (the tanning being done differently according to the leather color and texture).
- The **Bk** type presented the following: an acidic pH ranged between 3-3.5, for all temperatures; higher TDS and EC values at higher temperatures (both 40-60°C and 30-40°C), at ouside temperatures had the highest values in contrast with the other two types **G** and **Bn**; highest values for salinity at highest temperatures (40-60°C), at ouside temperatures had the highest values in contrast with the other two types **G** and **Bn;** the refractive index had higher values for the outside temperatures which for the conductometric parameters valuest were lower and the lower values for the highest temperature range at higher values of the conductometric parameters.

- The **Bn** type presented the following: a basic pH ranged between 7-8.5, for all temperatures; higher TDS and EC values at high temperatures (30-40°C), at ouside temperatures had low values in contrast with the other two types **G** and **Bk**; highest values for salinity at high temperatures (30-40°C), at ouside temperatures had the low values as the **G** type in contrast with **Bk** type**;** the refractive index had higher values for the outside temperatures which for the conductometric parameters valuest were lower and the lower values for the highest temperature range at higher values of the conductometric parameters.
- The **G** type presented the following: an acidic pH ranged between 3-3.5, for all temperatures; lowest TDS and EC values at all temperatures; lowest values for salinity at all temperatures**;** the refractive index had higher values for the outside temperatures which for the conductometric parameters valuest were lower and the lower values for the highest temperature range at higher values of the conductometric parameters.
- Total chromium concentration in the leachate for all three types of leather waste exceeded the MAC for hazardous waste leachability (OM 95, 2005, table 4.1 hazardous waste leachability).
- The **Bk** type had the highest values for the total chromium concentration at outside temperatures and at the highest temperature (40-60°C), followed by the **G** type which had high values at outside temperatures.
- The tanned leather waste is framed in the specific legislation as a non-hazardous waste at code 04 01 08: "waste tanned leather (blue sheeting, shavings, cutting, buffing dust) containing Chromium", but it should be considered as a hazardous waste, as regards the behavior in aqueous solution, under different conditions of temperature.
- The tanned leather waste cannot be landfilled in municipal landfills, due to the higher concentration of total chromium in leachate.

Because of the higher values of the total chromium analyzed concentration, a particular importance has the speciation between the Cr (III) and Cr (VI), because it is known that the Cr (VI) compounds have carcinogenic action. In this respect further studies regarding the speciation will be developed.

In conclusion is necessary to find new recycling methods for the tanned leather waste, because it requires landfilling in special authorized landfills for hazardous waste.

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GROUNDWATER QUALITY IN TWO RURAL COMMUNITIES FROM CLUJ AND BISTRIȚA-NĂSĂUD COUNTIES – ROMANIA

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ABSTRACT. In Romania, there are rural areas where the access to safe drinking water sources is still an unsolved issue. The main objective of the present study was to assess the quality of several underground drinking water sources from two rural communities from Romania and to evaluate the suitability of using those water sources in drinking and agricultural purposes. The investigated parameters were: pH, redox potential (E_h), electrical conductivity (EC), total dissolved solids (TDS), salinity, dissolved ions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{-3}, SO_4^{-2}, Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and metals (Fe, Zn, Cr, Cu, Cd, Ni, Pb and Mn). The analyses indicated high levels of sulphates (up to 353.2 mg/l) in the wells from Cluj County and high concentrations of nitrates (up to 111.4 mg/l) and nitrites (up to 1.49 mg/l) in the wells from Bistrița-Năsăud County, these parameters frequently exceeded the safely limits imposed by national and international legislation. The levels of the other investigated parameters were generally below the maximum limits imposed by national and international legislation. Based on the sodium adsorption ratio, sodium percentage and magnesium adsorption ratio values, most of the investigated water sources can be safely used in agriculture purposes.

Key words: *rural communities, drinking water quality, water quality index, sodium adsorption ratio, sodium percentage*, *magnesium adsorption ratio*

INTRODUCTION

The access to safe drinking water supply in rural areas is an important national goal in many developing countries. Drinking water sources are susceptible to chemical, physical or biological contamination, depending on the geological conditions, agricultural, industrial, or other man-made activities. According to the European Commission, the groundwater pollution represents the most serious problem of the EU water resources policy (Llamas, 2004). As a consequence, in the new EU Water Framework Directive enacted in December 2000, great attention has been paid to the groundwater quality. In Romania, there are rural areas where the access to safe drinking water sources is still an unsolved issue. In many rural areas from Romania, the underground water is the only source of drinking water. As a consequence, the investigation of the underground water quality has a major importance. The main objectives of the present study were: (1) to investigate several physico-chemical (pH, redox potential, electrical conductivity, total dissolved solids, salinity) and chemical water quality parameters (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Fe, Zn, Cr, Cu, Cd, Ni, Pb and Mn) in 16 private wells from two rural areas located in Cluj County (Fizeșu Gherlii) and Bistrița-Năsăud County (Mărișelu); (2) to assess the monthly fluctuations of the quality parameters; (3) to evaluate the water quality by calculating the water quality index (WQI); and (4) to assess the suitability of using the water sources for agricultural purposes, by calculating specific indices.

MATERIALS AND METHODS

Sampling and processing

For the present study, a total of 48 samples were collected from 16 private wells from Fizeșu Gherlii village (Cluj County) and Mărișelu village (Bistrița-Năsăud County). The samples were collected during three campaigns, in November 2017, December 2017 and January 2018 (Roșu et al., 2018).

Fizeşu Gherlii is a commune in Cluj County, Romania. It lies between 47°01′41″ north latitudes and 23°59′16″ east longitudes, at an altitude of 265 m and it is composed of four villages: Bonț, Fizeșu Gherlii, Nicula and Săcălaia. The total surface is of 67.12 km², and it has a population of 2,631 inhabitants (according to the 2011 census), with a density of 39.51 inhabitants/km².

Mărișelu is a commune in Bistrița-Năsăud County, Romania. It lies between 47°01′46″ north latitudes and 24°29′39″ east longitudes, at an altitude of 357 m and it is composed of seven villages: Bârla, Domnești, Jeica, Măgurele, Mărișelu, Nețeni and Sântioana. The total surface is of 71.68 km², and it has a population of 2,383 inhabitants (according to the 2011 census), with a density of 33.24 inhabitants/km².

The analysed physico-chemical parameters were: pH, redox potential (E_h), electrical conductivity (EC), total dissolved solids (TDS) and salinity.

They were measured *in situ* using a portable multiparameter (WTW inolab 350i). The sampling and processing procedures were performed according to standard protocols (EN 25667-2; EN ISO 5667-3). The water samples were collected in polyethylene bottles and were filtered *in situ* using 0.45 µm syringe filters. The water samples used for metals analysis were acidified to a pH ≈ 2 (with HNO_3 65%). The samples were then transported to the laboratory, stored at dark and 4ºC, and analyzed within 48 hours from sampling. The dissolved ions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were analyzed by ion chromatography, using an IC1500 Dionex system. The total amount of heavy metals (Fe, Mn, Zn, Cu, Cd, Cr, Pb and Ni) were analyzed by atomic absorption spectrometry (AAS), using an AAS system ZeeNIT 700 (Analytik Jena) equipped with air-acetylene flame and graphite furnace.

Water quality index (WQI)

WQI was developed by Horton (1965) in United States by selecting the most commonly used water quality parameters like dissolved oxygen (DO), pH, coliforms, specific conductance, alkalinity, chloride, etc. and has been widely applied and accepted in many countries. Furthermore, new models for WQI, similar to Horton's index, have been developed by different scientific researcher groups.

In the present study, WQI was calculated based on fifteen parameters: pH, EC, TDS, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, Fe, Zn, Ni and Mn, using the equations 1 – 3 (Thakov et al., 2011; Yogendra and Puttaiah, 2008; Srinivas et al., 2011):

$$\mathrm{WQI} = \frac{\sum_{i=1}^{n} q_i \cdot W_i}{\sum_{i=1}^{n} W_i} \quad (1)\ ; \quad W_i = \frac{k}{S_i} \quad (2)\ ; \quad q_i = \frac{V_a - V_i}{S_i - V_i} \cdot 100 \quad (3)$$

where, W_i is the weightage factor; k is the proportionality constant (k = 1); S_i is the standard value of the ith water quality parameter; n is the total number of water quality parameters; q_i is the quality rating for the ith water quality parameter; V_a is the value of the ith water quality parameter determinate in laboratory, V_i is the ideal value of the ith water quality parameter obtained from standard tables (V_i for pH = 7 and for the other parameter the V_i = 0) (Srinivas et al., 2011).

Possibility of using water sources for agricultural purposes

In order to assess the possibility of using the investigated water sources in agricultural purposes, three indices were calculated: the sodium adsorption ratio (**SAR**) (equation 4), the sodium percentage (**SP**) (equation 5) and magnesium adsorption ratio (**MAR**) (equation 6). SAR, is a parameter which influences the infiltration rate of water and it was calculated based on the sodium, calcium and magnesium concentrations (expressed in milliequivalent per liter) (Harront et al., 1983; WHO, 1984; WHO, 1989; BC Health Act Safe Drinking Water Regulation, 2001).

$$SAR = \frac{\mathrm{Na^+}}{\sqrt{\frac{\mathrm{Ca^{2+}+Mg^{2+}}}{2}}} \quad (4); \qquad \mathrm{SP} = \frac{\mathrm{Na^+ + K^+}}{\mathrm{Ca^{2+}+Mg^{2+}+ Na^+ + K^+}} \cdot 100 \quad (5);$$

$$MAR = \frac{Mg^{2+}}{Ca^{2+}+Mg^{2+}} \cdot 100 \quad (6)$$

Based on the sodium, calcium, magnesium and potassium concentrations (expressed in milliequivalent per liter), the SP was calculated (Kelly, 1940; Wilcox, 1958), while the magnesium adsorption ratio was calculated using the magnesium and calcium content (expressed in milliequivalent per liter) (Paliwal, 1972).

RESULTS AND DISCUSSIONS

Physico-chemical and chemical parameters

The values of the investigated physico-chemical and chemical parameters are presented in Fig.1 and Fig. 2. The water samples proved to be neutral to slightly basic, having the pH within the permissible limits (6.5 – 9.5) set by the Romanian legislation (Drinking water law 458/2002). The redox potential had negative values (-14 – -85.4 mV) indicating the presence of anaerobic redox potential and reducing conditions in the aquifer. The redox potential was within the WHO (World Health Organization) and US-EPA (United States – Environmental Protection Agency) recommendation (-100 – +100 mV) for drinking water (US EPA, 1991; WHO, 1984; WHO, 2008). The analyzed waters had a low electrical conductivity, between 358 – 1,317 µS/cm, being lower than the limit (2,500 µS/cm) imposed by national legislation (Drinking water law 458/2002). The EC level was slightly higher in the water sampled from Cluj County (Fizeșu Gherlii) than those from Bistrița-Năsăud County (Mărișelu) (figure 1). The low level of EC, TDS (233 – 762 mg/l) and salinity (0.1 – 0.6‰) reflect the relatively low content of dissolved salts for the analysed drinking water sources.

The water samples had a low level of F^- (0.01 – 0.93 mg/l) and Cl^- (7.3 – 107.4 mg/l), being within the national permissible limits (1.2 mg/l and 250 mg/l) (Roșu et al., 2018). With the exception of one well from Cluj County

(Fizeșu Gherlii), the Na^+ content was considerably lower than the national limit (200 mg/l) (figure 1). The content of Mg^{2+} (11.0 – 49.1 mg/l) and Ca^{2+} (17.8 – 235.3 mg/l) were, with one exception, within the recommendations (50 mg/l and 200 mg/l) of international forums (BC Health Act Safe Drinking Water Regulation–Canada and World Health Organization, 2001; WHO, 1984; WHO, 2008; Roșu et al., 2018). Calcium and magnesium are two important macroelements for human body, and the Ca/Mg ratio has a great importance in drinking water. An optimal value for this ratio is 2:1, offering greater protection against cardiovascular disease (Feru, 2012). In the present study, the Ca/Mg ratio ranged between 0.9 and 9.6. In addition, high contents of calcium and magnesium increase the water hardness.

The analysed water sources proved to have a considerably high level of K^+, especially those from Cluj County (Fizeșu Gherlii) (4.1 – 303.3 mg/l), exceeding the limit (10 mg/l) recommended by the international forums (BC Health Act Safe Drinking Water Regulation–Canada and World Health Organization, 2001; WHO, 1984; WHO, 2008). It is possible that such high potassium level could be a consequence of the hydrogeological features of the two aquifers, but further investigations should be performed on this topic. There are studies (Diaconu et al., 2005) which indicated that the intake of high levels of sodium and potassium via water and food ingestion can be associated with increased incidence of hypertension. The optimal Na/K ratio is 3:1 (Feru, 2012). In the analysed water samples, the Na/K ratio was relatively low, ranging between 0.1 and 5.4, being generally below the optimal value.

Some of the investigated water sources proved to be contaminated with NO_2^- (0.08 – 1.49 mg/l), NO_3^- (0.7 – 111.4 mg/l) and SO_4^{2-} (17.5 – 353.2 mg/l), exceeding the limits imposed by national and international legislation (0.5 mg/l, 50 mg/l and 250 mg/l). The residents who use those water sources for drinking, cooking, recreational or agricultural purposes, should be informed in order to stop or restrict as much as possible the usage of those water sources, because of the possible negative impact on their health. The presence of high levels of SO_4^{2-} in some of the investigated wells can be a consequence of the presence of anthropogenic sources such as the application of fertilizers on cultivated lands (Khan et al., 2012). The ingestion of high levels of sulphates through drinking water may cause heath effect such as laxative action (WHO, 1996). The high level of NO_3^- and NO_2^- from some of the investigated wells can be a consequence of over-application of fertilizers, sewage disposal, or manure applications in the vicinity of the wells (Chowdary et al., 2005; Liu et al., 2005; Khan et al., 2012). Nitrites are classified as toxic to human body, and the exposure to high levels of NO_3^- and NO_2^- via water ingestion can lead to seriously health problems like methemoglobinemia (blue baby syndrome) (Gupta et al., 2000).

By comparing the two areas, the waters sampled from Cluj County (Fizeșu Gherlii) had a higher content of F^-, Na^+, SO_4^{2-}, K^+ than the water sources from Bistrița-Năsăud County (Mărișelu).

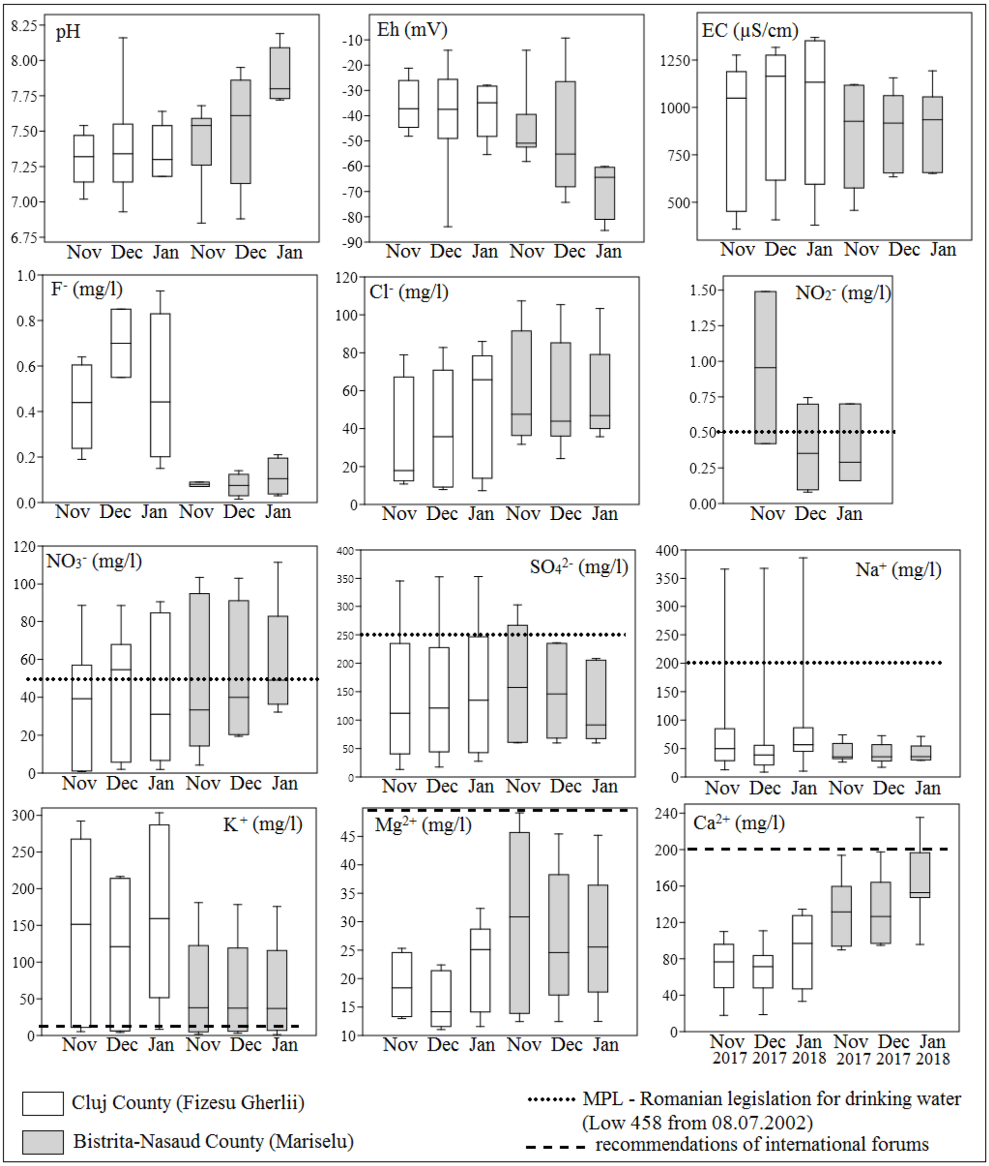

Fig. 1. *Monthly fluctuations of analysed physico-chemical parameters and dissolved ions*

The water sources proved to have low levels of metals, the presence of Cd, Cr, Pb, Cu, was not detected in any of the analysed water samples, while the content of Zn (0.001 – 0.092 mg/l), Fe (0.09 – 0.16 m/l) and Ni (0.005 – 0.019 mg/l) were within the national limits (5 mg/l for Zn, 0.2 mg/l for Fe and 0.02 mg/l for Ni) (Fig. 2). The level of Ni in some wells from Bistrița-Năsăud County (Mărișelu) should be carefully monitored because it is close to the maximum permissible limits. The continuous exposure to Ni via water ingestion could be a risk factor for resident's health, considering that Ni is classified as human carcinogenic. Manganese (0.02 – 0.09 mg/l) was detected only in two wells from Bistrița-Năsăud County (Mărișelu), exceeding in one water sources the national limit (0.05 mg/l).

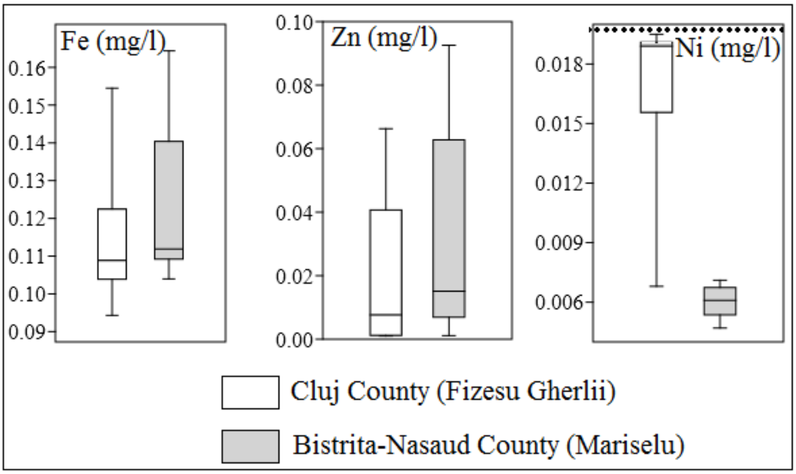

Fig. 2. *Metal content in the analysed water samples*

Generally, the chemical quality parameters presented low fluctuations during the three months of monitoring indicating a good hydrochemical stability of aquifers.

Water quality index

In order to evaluate the overall quality of the investigated drinking water sources, the **WQI** was calculated. The results are shown in figure 3.

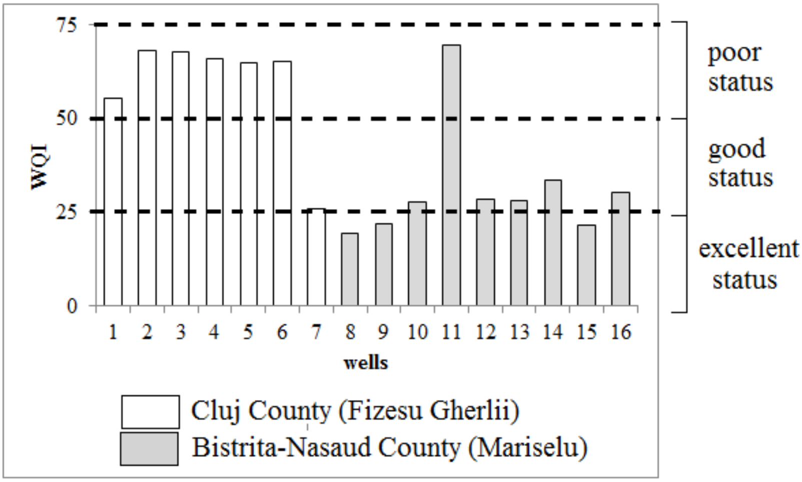

Fig. 3. *Water quality index for the investigated water sources*

Based on **WQI**, one of the wells from Fizeșu Gherlii (sample 7) (figure 3) can be classified as good water quality, while the other wells from the area, are classified as poor quality (because of the high levels of K^+, SO_4^{2-}, NO_3^-, NO_2^- and Ni). Three of the wells from Mărișelu (8, 9 and 15) had an excellent status and four of the wells (10, 12, 13, 14 and 16) had a good status being suitable for drinking purposes. Only one of the wells from Mărișelu area (11) had a poor water quality status (because of the high level of manganese which exceeded the permissible limits). The **WQI** values indicated that the waters sampled from Cluj County (Fizeșu Gherlii) had an inferior quality than those from Bistrița-Năsăud County (Mărișelu) (figure 3).

Possibility of using water sources for agricultural purposes

The content of sodium, potassium, calcium and magnesium are important factors in irrigation water quality assessment. Considering the high content of these elements in some of the investigated water sources, three indices were calculated (sodium adsorption ratio - **SAR**, sodium percentage - **SP** and magnesium adsorption ratio - **MAR**) in order to evaluate the suitability of using those water sources in agricultural purposes (figure 4).

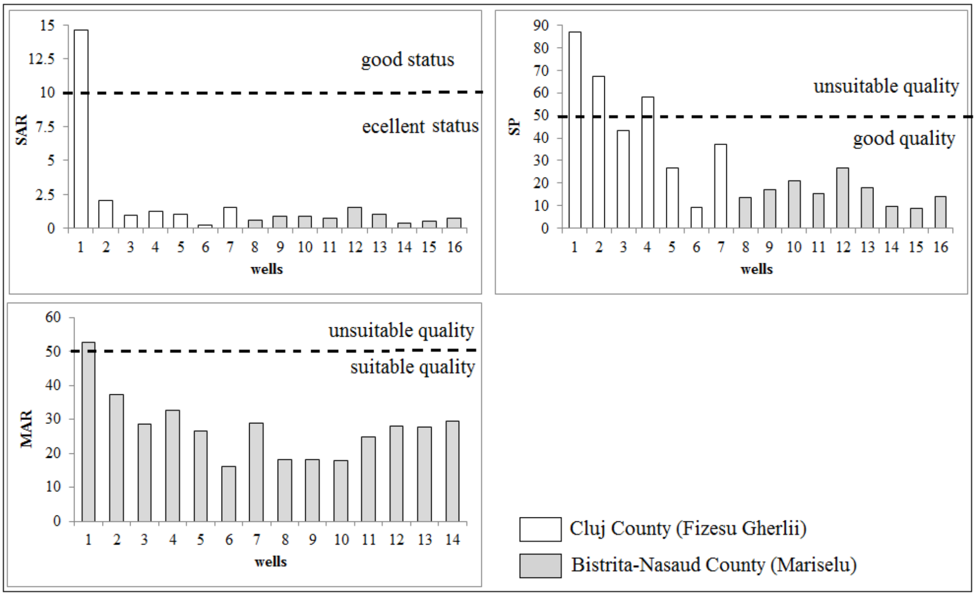

Fig. 4. *Water suitability for agricultural usages based on specific indices*

SAR ranged between 0.2 and 14.6, being below 10, with the exception of one well from Cluj County (Fizeșu Gherlii) (figure 4). If the **SAR** level is below 10, it is considered that the water has an excellent status and can be safely used in irrigations. With the exception of three wells from Fizeșu Gherlii, the level of **SP** was lower than 50%, which indicates a good water quality, being suitable for irrigations purposes. With the exception of one well from Fizeșu Gherlii, the analysed water sources had the **MAR** index below 50, indicating that their quality is suitable for agricultural usages.

Based on the **SAR**, **SP** and **MAR** values, it results that most of the investigated water sources can be safely used in agriculture purposes.

CONCLUSION

The results of the present study showed that there were identified several water sources, where the chemical quality parameter were within the permissible limits, and these waters can be safely used as drinking water sources. On the other hand, there were water sources where the content of NO_2^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+} and Mn exceeded the recommendations on national and international forums. The residents who use those water sources for drinking, cooking, recreational or agricultural purposes, should be informed in order to stop or restrict as much as possible the usage of those water sources, because of the possible negative impact on their health.

Generally, the chemical quality parameters presented low fluctuations during the three months of motorisation indicating a good hydrochemical stability of aquifers.

Based on **WQI**, most of the water sources from Cluj County (Fizeșu Gherlii) can be classified as poor quality, while the majority of water sources from Bistrița-Năsăud County (Mărișelu) belong to excellent to good quality class.

Based on the **SAR**, **SP** and **MAR** indices, it results that most of the investigated water sources had an excellent/good quality and they can be safely used in agriculture purposes.

The results have an important practical implication for rural communities in the areas as population has low information on the quality of their drinking water.

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SOMEȘUL MIC RIVER (CLUJ COUNTY, ROMANIA) WATER QUALITY ASSESSMENT UNDER ANTHROPOGENIC IMPACT

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ABSTRACT. The quality of surface waters has an important role in the environmental context. Someșul Mic river quality, in the studied area, is influenced by the pollution resulted from Florești locality and Cluj-Napoca city. Were collected and analyzed 28 water samples from the course of the river, on a distance of 20 km crossing Cluj-Napoca city. The studied physico-chemical parameters were: pH, redox potential (Eh), electrical conductivity (EC), total dissolved solids (TDS) and salinity, using a WTW 350i multiparameter. The anions (F^-, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}) and cations content (Li^+, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) were analyzed using a IC 1500 Dionex Ion Cromatograph. The sampling was realized in two campaigns: Octomber 2018 and February 2019. According to the analyzed parameters, the quality of Someșul Mic River, in the investigated area, corresponds to a moderated water quality index (WQI = 64.94). In the investigated collection points, in three cases were identified high concentrations of nitrates (NO_3^-), above 5 mg/l. For most of the investigated parameters, the values measured in autumn 2018 were higher than those from spring 2019, one cause might be represented by the precipitations before October 2018, which brought a load of chemicals and contributed mainly to the higher nitrate values. The values of the analyzed parameters in spring 2019 tend to show an increasing trend from upstream to downstream.

Key words: *surface water, pollution, water quality, water quality index, Someşul Mic*

INTRODUCTION

The aim of the study is to follow the evolution over time of the water quality in correlation with the anthropogenic factor around the studied area. Through this study we propose an evaluation of the water quality in the

Someșul Mic River under the action of anthropogenic impact. Thus we want to monitor water quality (depending on the analyzed parameters) in correlation with the development of human society along the river course. Șomeșul Mic River crosses Cluj-Napoca city, which extends in the Someşului Mic Corridor, at the contact of three large geographical units: the Transylvanian Plain, the Someşan Plateau and the Apuseni Mountains, at an average altitude of 360 m (Stoian, 2011), which leads to a great influence of anthropogenic impact on water quality.

Because the city of Cluj-Napoca developed along the Someșul Mic, this river strongly feels the influence of the anthropic factor. Due to the agriculture that is practiced on some lands upstream, the pesticides and fertilizers used (nitrites / nitrates) end up being discharged into the waters of Someșul Mic River after the washing of agricultural lands by rainfalls. Also another important role is played by industrial discharges, so that these anthropogenic actions lead to the degradation of surface water quality, an effect that will affect the well-being of the municipal population.

The Someșul Mic River is located in the Someș river basin, which has an area of 15,740 km^2. Somesul Mic is the most important tributary formed by the union of Someșul Cald and Someșul Rece. The surface occupied by the hydrographic basin of the studied river is 3773 km^2, having a length of 178 km and an average annual flow of 14.5 m^3/s in Cluj-Napoca. Someşul Mic river has his origins in the Apuseni Mountains, mountains with many smooth peaks, only a few of them higher, of which the peak Vlădeasa (height 1836 m) located at the border of the basin, is the second highest in the Western Carpathians (Iordan, 2014).

The upper basin of Someşul Mic includes 5 larger accumulation lakes (Fântânele, Tarniţa, Someşul Cald, Gilău, Someşul Rece I, the last with a catchment role) whose total volume represents 72.0% of the total volume of accumulations in the Someş basin (464.32 million m^3) (Şerban et al., 2010).

In the municipality of Cluj-Napoca and the localities of Gilău, Floresti, Săvădisla and Baciu domestic and industrial wastewaters are collected in the sewerage network with a length of 516.5 km, and discharged into the river Someşul Mic after their treatment in the Someseni treatment plant. In general, the wastewater discharged into the Someşul Mic River falls within the maximum limits allowed by the regulatory acts except for the nitrogen indicator (R.S.M.C, 2011).

The number of the studies conducted in this area is limited, and only a few follow the parameters investigated in this paper, forwards are mentioned some of them: Luca et al. (2006) studied the aspects regarding the pollution and protection of surface waters in the Someș basin; Moldovan et al. (2009) studied the environmental exposure to perfumes and medicines from Șomesul

Mic, before and after the modernization of the water treatment plant; Perșoiu and Rădoane (2011) investigated the spatial and temporal responses of the Someşu Mic River to natural and anthropogenic controls over the past 150 years; Iepure et al. (2014), make an ecological assessment of water quality in relation to hydrogeology in the asphalt urban aquifer: Someșul Mic; the study conducted by Ani et al. (2014) “Dynamic Simulation of Someș River Pollution Using MATLAB and COMSOL Models” implements a new approach to provide the possibility to use the parameter-dependent space of the river based on analytical models; the study conducted by Voicu and Bretcan (2014) aims to solve the problem related to the impact of fish migration on the Șomesul Mic (“Solution for fish migration on the Someșul Mic river upstream - downstream of Mănăștur dam in Cluj-Napoca”); Cîmpean (2018) conducted the “Taxonomic and ecological study on the communities of aquatic mites (*Acari, Hydrachnidia*) in the drainage basin of Someșul Mic river and their role as indicators of water quality, the parameters studied in this case were only those of a physico-chemical nature (pH, conductivity and dissolved oxygen); the study of Barhoumi et al. (2019), investigates the levels of trace metals and organic pollutants in the surface sediments of Someșul Mic River.

STUDY AREA

Cluj-Napoca is a metropolitan city in the northwest of Romania, located in the central part of Transylvania at a latitude and longitude of 46°46' N, 23° 6' E, with an area of about 179.5 km^2 at about 410 m above sea level.

Along the Someșul Mic watercourse, 28 sampling points (see figure 1) have been established, taking into consideration the possible pressure points due to the impact of the urban wastewater discharge, the possible diffuse pressures generated by different plants located in the industrial area of the city and the use of chemical fertilizers in agriculture. The sampling was done along the course of Someșul Mic River, starting from the dam situated in Floresti locality (upstream) and ending with the bridge on Radu Tudoran Street (Cluj-Napoca). The first series of samples were taken at the end of October 2018, and the second series at the beginning of April 2019 (from the same sampling points, accordingly with the geographical coordinates). We chose these months of the year to be able to observe the changes in the quality of Someșul Mic river in 2 different periods, a cold period with low temperatures and in a warmer period.

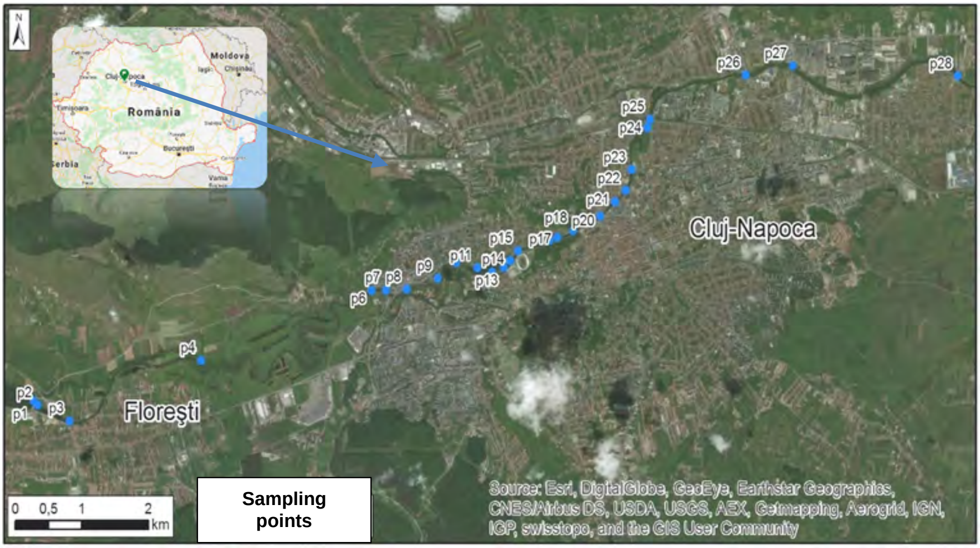


Fig. 1. *Water sampling points (Someșul Mic River)*

MATERIALS AND METHODS

The water samples were collected and processed according to the standard procedure imposed by international protocols ISO 5567-2 and ISO 5667-3.

The samples were collected in 0.5 l clean polyethylene containers, and before sampling, the bottles were rinsed with sampled water, labelled. After introducing the water samples into the container, the air was completely removed from it and transported to the laboratory (during this time the samples were stored in the refrigerator at 4°C) within 12 hours and analysed in a timely manner, without the need for preservation. For ion analysis, the samples were filtered with a millipore filter (0.45 µm) and diluted according to the conductivity of the samples (to be below 100 µS/cm^2).

During the sampling period the meteorological conditions were as follows:

- First campaign (at the end of October 2018) there was heavy rainfall with a temperature of about 8-10 °C.

- Second campaign - ambient temperatures of 21 ℃, without precipitation.

The following parameters were studied:

- pH, temperature, redox potential (Eh), electrical conductivity (EC), total dissolved solids (TDS), salinity (S), and the following ions: sodium, lithium, ammonium, potassium, magnesium, calcium, fluorides, chlorides, nitrites, bromides, nitrates, phosphates and sulphates).

The main physico-chemical parameters of the water were determined using a WTW 350i Multiparameter. The pH was determined according to SR ISO 10523: 2009. pH measurement is of great importance because a pH low or above 9 has toxic effects on aquatic organisms. This parameter is the most important to evaluate the corrosive properties of an aquatic environment.

For the determination of cations and anions, Ion Chromatograph DIONEX ICS 1500 was used, once the mechanical filtration phase of the samples was completed and the dilution (using ultrapure water, of 18 MΩ.cm).

For the evaluation of the Someșul Mic river quality was calculated the Water Quality Index (WQI), the evaluation using integrated indices, can be a complex process, and includes a significant number of parameters. This contribute with different pressure on surface water quality (Bharti and Katyal, 2011; Teodorof et al., 2016).

In this study we used the Canadian method for calculating the water quality index for the Someșul Mic river, whose empirical equation and description is detailed in a previous study (Martonoș et al., 2018).

RESULTS AND DISCUSSIONS

In figure 2 are illustrated the differences in pH along the investigated points, in the first campaign the pH was influenced by the abundant rainfall of that period, as can be observed variations in the pH values. The electrical conductivity in the second campaign (2019) was much lower (average value: 92.25 µS/cm), comparative to 2018 campaign (average value: 145.55 µS/cm), observing major differences in certain collection points. The TDS values in 2019 were smaller than those registered in 2018 (see figure 3), these values and the variation registered in 2018 being influenced by the rainwater discharged into Somesul Mic river, this adding different contaminants in certain investigated points.

The obtained concentrations of Mg^{2+} (2018 average value (a.v.) = 3.50 mg/l, 2019 a.v. = 3.30 mg/l), Ca^{2+} (2018 a.v. = 27.06 mg/l, 2019 a.v. = 17.85 mg/l), K^{+} (2018 a.v. = 0.88 mg/l, 2019 a.v. = 0.88 mg/l), Na^{+} (2018 a.v. = 6.22 mg/l, 2019 a.v. = 5.12 mg/l), classifies this river, in the studied points, in class I of quality accordingly to Order 161/2006. The changes in the concentrations of cations are due to heavy rainfall in October 2018, comparative to April 2019, which changed the chemical composition of the water, and the variations in concentrations recorded along the Someșul Mic River are due to occasional discharges of wastewater. The course of the river suffers modifications in its route through the city of Cluj-Napoca (as can be observed for example also in the case of Ca^{2+}, in figure 4).

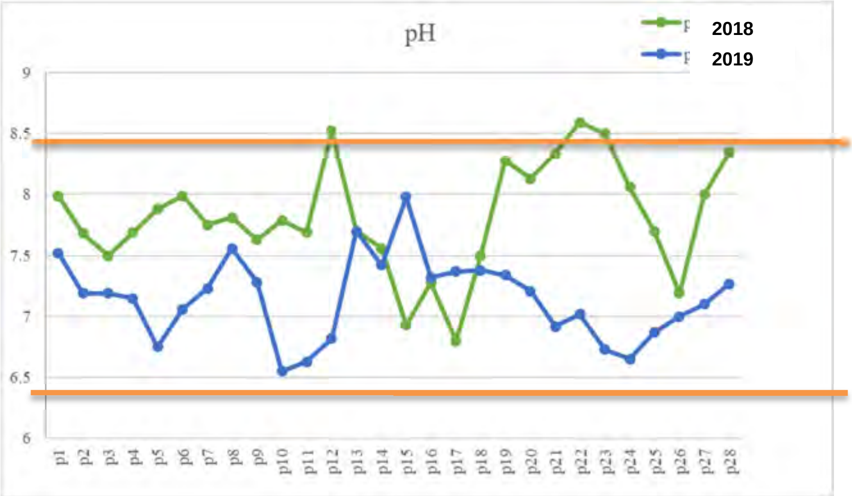


Fig. 2. *pH variation on Someșul Mic River (through Cluj-Napoca)*

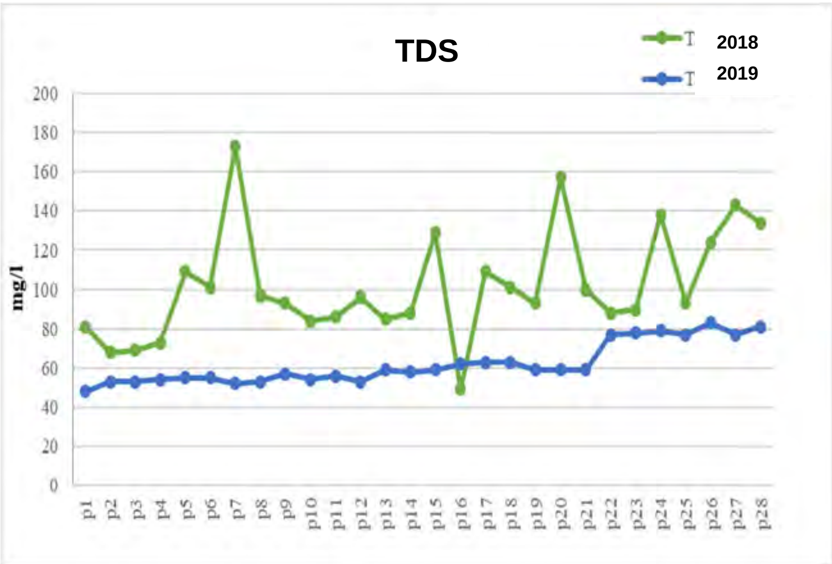


Fig. 3. *TDS variation on Someșul Mic River (through Cluj-Napoca)*

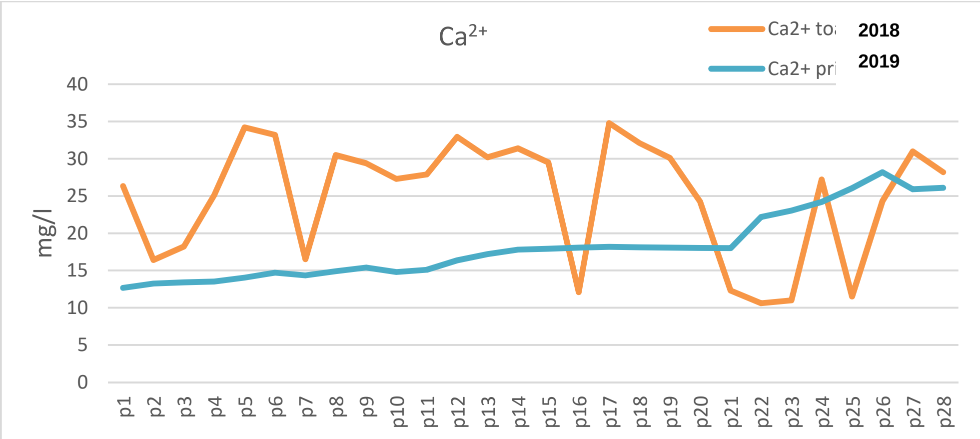
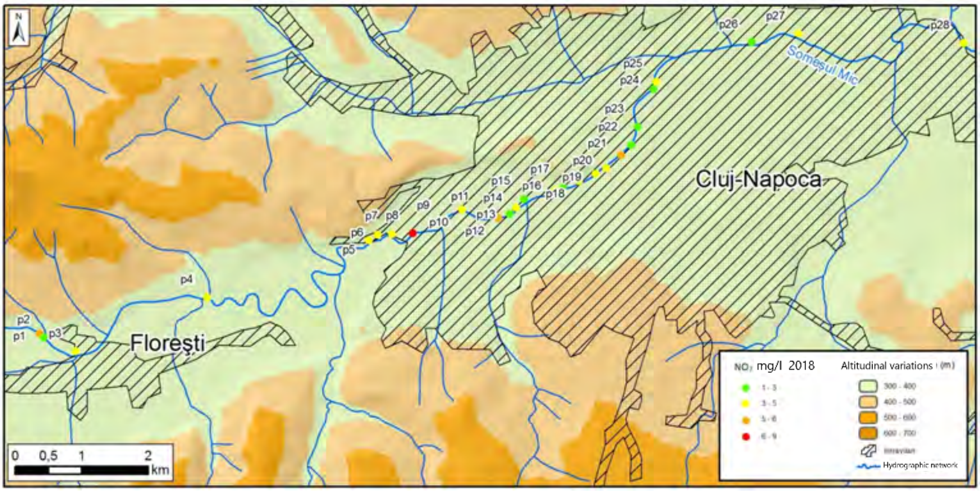


Fig. 4. *Ca^{2+} variation on Someșul Mic River (through Cluj-Napoca)*

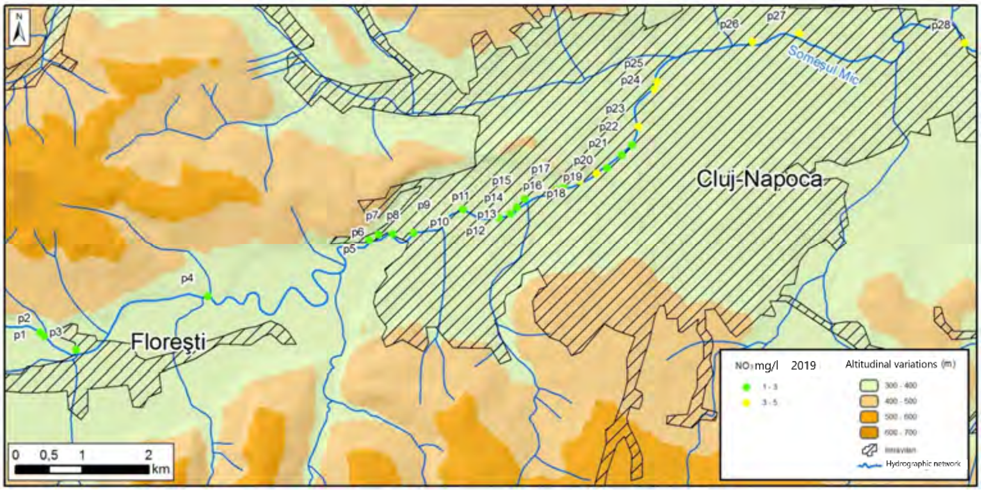
At the level of anions, we could observe the same variations as in the case of cations, with higher values recorded in the case of nitrates (see figure 5 a, b). The average values of SO_4^{2-} are the following: 12.98 mg/l (2018) and 12.6 mg/l (2019), classifying this part of the river in class I of quality accordingly this parameter. The concentrations of Cl^- varied between 3.02 mg/l – 27.21 mg/l, with an average value of 6.28 mg/l in 2018 and between 3.25-6.5 mg/l in 2019, with an average value of 4.9 mg/l. NO_2^- were identified only in 3 sampling points, with the following values: 1.34 mg/l (P7), 0.86 mg/l (P11), 0.90 mg/l (P20) in the 2018 campaign, in the 2019 campaign the concentration of nitrites was below the detection limit. The values recorded in the first campaign classify the river on those points in class V of quality (according Order 161/2006).

The algorithm for selecting the parameters taken into account to calculate WQI is based on the centralization of the results in each sampling point and the classification in classes according to Order 161/2006. The average value was calculated for the analyzed items and were selected the most significant parameters (those regulated by the national legislation). The average values were compared with the maximum allowed concentration (MAC) for class II (Order 161/2006). Applying the equation mentioned in methodology, we observed that for the analyzed parameters were identified 19 exceeding's of the MAC (according to class II – Order 161/2006); the nitrites and nitrates, recorded exceedances of MAC at the average values measured on Someșul Mic River.

The obtained value for WQI is 64.94, which shows that the degree of pollution of the Someșul Mic River is moderate.



A



B

Fig. 5. *Concentration of nitrates along Someșul Mic River, in the investigated points (A-2018, B-2019)*

CONCLUSIONS

At the majority of the investigated parameters the obtained values were included in quality class I (for surface waters), in the case of pH only in two from the 28 sampling points the upper limit of 8.5 was insignificantly exceeded, in P12 with a value of 8.52 and in P22 with a value of 8.59.

In the collection point P7 was registered a value of 1.34 mg/l (4 times higher than the MAC for quality class V) for nitrites, and for chlorides a value of 27.21 mg, which includes this point in quality class II regarding the chlorides concentration.

Nitrates registered high values in 14 collection points out of 28, in these points the value exceeding the MAC for quality class II (according to order 161/2006), of 3 mg/l.

The significant variations of the investigated parameters along the river in autumn 2018, is possibly due to precipitation, which brought a load of chemicals, and contributed to higher levels of nitrates and nitrites.

For most parameters, the values measured in autumn 2018 were higher than those measured in spring 2019.

The values of the parameters analyzed in spring 2019 tend to show an increasing trend from upstream to downstream, this makes us conclude that Cluj-Napoca city influence the quality of Someșul Mic River, this being polluted on its route through the city, from different anthropic sources (agricultural lands near the water course on which chemicals are used, industrial waters, pluvial waters and other punctual sources).

The quality index shows us a moderate pollution of the Someșul Mic River (from the point of view of the analyzed parameters).

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