

Ecological Survey of Padiş Area, Romania

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Abstract

A couple of stream water samples from the Padiş tourist area (Romania) were analyzed using the chemical methods stipulated in the Romanian Pharmacopoeia in order to establish their content of heavy metals and other ions, both cations and anions. Additionally, the samples were investigated using microwave plasma – atomic emission spectrometry (MP-AES) to quantify specific elements, namely aluminium, barium, cobalt, chromium, copper, manganese, molybdenum, nickel, lead, strontium and zinc. The cation levels found were compared with the Romanian and international standards regarding surface and drinking water quality.

Introduction

The Padiş tourist area is located in the Apuseni Mountains (Western Carpathians, Romania), more precisely in the Bihor Mountains on the west-southwestern slope of Măgura Vânăță Peak (highest altitude: 1641 m). It is placed at the eastern edge of a karst plateau which is developed on an area of about 10 km², at an altitude of around 1300 m, with frequent sinkholes (dolines), uvalas and caves [1].

The hydrographic minibasins are developed on top of the Permo-Mesozoic (sandstones and conglomerates) and the Pannonian Quaternary deposits (sands, gravels and clays). The ponors are located at the lithological contact between the Mesozoic (Anisian) dolomites and the Quaternary deposits, composed of sands, gravels, and clays. The hydrography is characterized by short segments (within 3 km) of epigenous permanent streams (except during extreme drought) which drains the southwestern side of Măgura Vânăță Peak. These streams are focusing towards the many insurgency points (sinkholes) found at the contact between the karstifiable and the non-karstifiable rocks, located in some sinkholes on the plateau (e.g., Trânghești Ponor). The flow rates are between 1-2 L/s at baseflow and 0.5 m³/s at spring floods. The area is wooded with spruce forests (*Picea abies*) and bilberry (*Vaccinium*) which grow on brown acid soils and andosols [1].

Two stream water samples were collected from the Padiş area, one upstream from the main settlement while the other downstream, the two points being separated by a distance of about 1 km. Samples were collected August 2, 2015, at noon. Weather was generally stable

prior and during the sampling, with temperature minima around 8.8°C during the night.

Experimental

The geographic coordinates and altitudes were established using a Magellan Meridian Platinum Mapping GPS receiver, while air temperature and pressure were recorded with a portable weather station.

The sample temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS) were registered with a portable Hanna HI 98130 Combo pH&EC measuring device. The levels of nitrite and sulfate were estimated *in situ* using Merck test strips (Merckoquant® Nitrit-Test and Merckoquant® Sulfat-Test).

The heavy metal content of solutions may change between sampling and analysis due to adsorption effects on the container walls or by contamination due to extraction of heavy metals already contained in the material of the storage units. To prevent these contaminations thoroughly cleaned plastic recipients were used, taking some special precautions. Thus, the recipients were prepared in the laboratory by protracted soaking with 2M nitric acid followed by rinsing with double distilled water. They were also conditioned *in situ* with several aliquots of the water to be sampled. After completing this protocol a volume of 350 mL of water was collected. Also, to avoid the loss of elements by adsorption on the wall of the storage recipients, the samples were stabilized by acidification to pH~1 by adding 20 mL of 2 mol L⁻¹ aqueous nitric acid. All glassware needed for analysis was washed with 2 mol L⁻¹ aqueous nitric acid and thoroughly rinsed with double distilled water just prior of being used [2,3,4].

Preliminary analyses were performed on filtrated samples the day after they were collected according to the general procedures stated by the Romanian Pharmacopoeia (10th edition). A blank solution (350 mL double-distilled water with 20 mL 2 mol L⁻¹ aqueous nitric acid) was also prepared in an identical plastic container and tested for comparison. The following aqueous reagents were used: Nessler's reagent (a mixture of potassium tetraiodomercurate(II), K₂HgI₄, and potassium hydroxide, KOH) for ammonium, sodium hypophosphite (NaH₂PO₂) in hydrochloric acid (HCl) for arsenic, ammonium oxalate ((NH₄)₂C₂O₄) for calcium, silver(I) nitrate (AgNO₃) for chloride, potassium hexacyanoferrate(II) (K₄[Fe(CN)₆]) for iron, sodium sulfide (Na₂S) for heavy metals (e.g., lead) and barium chloride (BaCl₂) for sulfates. The chemical reactions that use these reagents are stated to have the following detection limits: 0.3 ppm for ammonium, 1 ppm for arsenic, 3.5 ppm for calcium, 0.5 ppm for chlorides, 0.5 ppm for iron, 0.5 ppm for lead and 3 ppm for sulfates [2]. The presence of reducing organic substances was tested using one drop of 0.02 mol L⁻¹ KMnO₄ and two drops of 98% H₂SO₄ for 10 mL of sample, followed by heating on the water bath.

For MP-AES an Agilent 4100 with web-integrated Agilent MP Expert software was used. The instrument was adjusted using as calibration standard the provided Wavelength Calibration Concentrate for ICP-OES & MP-AES (Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, Zn 50 mg/L, K 500 mg/L). The following wavelengths (in nm) were measured: Al 394.401, Ba 455.403, Co 340.512, Cr 425.433, Cu 324.754, Mn 403.076, Mo 379.825, Ni 305.082, Pb 368.346, Sr 421.552 and Zn 213.857.

Results and discussion

The surroundings of the sampling sites are illustrated in Figure 1, while the measured sample and environment parameters are given in Tables 1 and 2.



Figure 1. The sampling sites for sample 1 (top) and sample 2 (bottom)

Table 1. Environment and sample parameters

Parameter	Sample 1	Sample 2
<i>Latitude</i>	46°35'52''N	46°35'49''N
<i>Longitude</i>	022°44'14''E	022°43'50''E
<i>Altitude (m)</i>	1321	1282
<i>Air temperature (°C)</i>	19.6	22.4
<i>Air pressure</i>	657.9	658.8
<i>Sample temperature</i>	12.1	15.5
<i>pH</i>	5.8	5.3
<i>EC (mS/cm)</i>	0.00	0.00
<i>TDS (ppt)</i>	0.00	0.00

Table 2. MP-AES cation levels

Sample	<i>Al</i>	<i>Ba</i>	<i>Co</i>	<i>Cr</i>	<i>Cu</i>	<i>Mn</i>	<i>Mo</i>	<i>Ni</i>	<i>Pb</i>	<i>Sr</i>	<i>Zn</i>
1	0.08	0.10	0.00	0.00	0.03	0.04	0.01	0.00	0.00	0.00	0.00
2	0.12	0.10	0.00	0.00	0.05	0.04	0.01	0.00	0.00	0.00	0.01

The ammonium, arsenic, calcium, chloride (also bromide and iodide), iron, heavy metals (i.e., lead), nitrite and sulfate chemical test all gave negative results, an observation also supported by the low conductivity value, which was under the sensibility of the measuring instrument. The only MP-AES detected cations were aluminium, barium, copper

and manganese at low levels, and possibly traces of molybdenum and zinc. A small increase was detected for aluminium and copper in the second sample when compared with the first sample. Also, the pH value dropped by half of a unit, resulting in an increase of acidity for the second sample. The level of reducing organic substances also increased for the second sample.

The pH is below the required minimum value of 6.5 for drinking and surface water, according to both the EU [5] and Romanian [6,7] standards (the WHO [8] standards state no guideline regarding the pH). The measured cation levels are within the imposed limits for drinking water. Also, according to both measured samples, this mountain stream could be included in class I of surface water quality, except for the measured barium and copper levels which place it in class II or III [7].

Conclusion

A negligible increase in the levels of aluminium and copper was observed after the passing of the river through the Padiş settlement. Also, both the acidity and the level of reducing organic substances increase in the same direction, which could relate to natural causes (the acidic soils in the area) or, possibly, to the anthropic activity in the settlement (grazing, logging, and tourism).

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