Experimental geochemical mapping of Slovenia by spring water sampling

Nataša Kukar[1], Simon Pirc[1] & Robert Šajn[2]

[1]Faculty of Natural Sciences and Engineering, Department of Geology, University of Ljubljana, Aškerčeva 12, SI - 1000 Ljubljana, Slovenia;
E-mail: natasa.kukar@ntfgeo.uni-lj.si and simon.pirc@ntfgeo.uni-lj.si
[2]Geological Survey of Slovenia, Dimičeva 14, SI - 1000 Ljubljana, Slovenia;
E-mail: robert.sajn@geo-zs.si

Abstract: In the study 149 groundwater samples were systematically collected on the national territory of Slovenia in order to establish the distribution of their properties and compare them with world averages. The associations between 50 most reliably determined properties were studied by the R mode factor analysis, and six factors that account for more than 63 % of total variance were extracted and preliminarily interpreted.

Key words: hydrogeochemistry, spring water, Slovenian averages, factor analysis

Introduction

The goal of the study was to sample systematically on the national territory of Slovenia the groundwaters as they are discharged at springs, and to construct on these basis experimental geochemical maps. The study is related to geochemical mapping as practiced in many countries, and to the research performed for the future geochemical map of the world (IUGS Task Group on Global Geochemical Baselines).

Sampling and analysis of groundwater was done according to the standards and recommendations of the IGCP 360 Project (Foregs, 1997) and the hydrogeologic practices (Kranjc et al., 1985) according to an analysis of variance based sampling design.
Analysis of variance was applied for statistically assessing the spatial character of areal geochemical trends, and the quality of performed chemical determinations. For sampling the national territory of Slovenia, an hierarchic unbalanced statistical model of analysis of variance was used that permits a representative quantitative geochemical estimate on the basis of relatively few samples (Pirc et al., 1991). The design was shaped in the way to partition the geographic variance to four levels that correspond to sampling cell grids of 25 × 25 km, 5 × 5 km, 1 × 1 km and 200 × 200 m (Pirc, 1993). For application of the design, the country was covered by a square sampling grid of 29 sampling cells of 25 × 25 km (Pirc, 1993). In the reported study, three more cells were added: one in the north, in the south, and in the east part of the country.

Scientific paper

Sampling was performed in summer 1997, always at least 4 days after rain. The water flux was in the range from 0.1 to 10 l/s which assures the hydrodynamic stability and comparability (HEISE, 1984). At each spring, the streaming water was sampled, and special care consecrated to avoiding contamination (JURANJI, 1998). The water sample for determination of cations and trace elements was filtered by the Sartorius 0.45 μm nitrate-cellulose filter and acidified to pH 2 by adding a drop of Merck superpure (61 %) nitric acid. For anions, water was filtered but not acidified. In the field, temperature, conductivity and pH were measured, and various descriptive data on the locality recorded in the sampling protocol (JURANJI, 1998). The concentrations of cations Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}, and total concentrations of Ag, Al, As, Au, Ba, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, I, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, Os, Pb, Pd, Pr, Pt, Rb, Re, Ru, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr were determined by ICP-MS (ACTLABS, 1997). Alkalinity was determined titrimetrically (SNELL & ETTRE, 1974), and also anions SO_4^{2-}, NO_3^{-} and Cl^{-} (EKAR, 1997). Accuracy of analysis was controlled with reference materials SRM 1643d and SRM 1643c, and precision (of analysis plus sampling and handling) by analysis of variance on the basis of the 19 replicated samples.

The associations between 50 most reliably determined variables (47 elements, conductance, temperature, and pH) were studied by the R mode factor analysis (JURANJI, 1999). By the six-factor solution after Varimax rotation, more than 63 % of information, carried by 47 elements (all 50 variables without conductance, temperature, and pH) was explained.

RESULTS AND DISCUSSION

With respect to the world averages, the spring waters in Slovenia have higher means of Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^{-}, Eu, Mn, Ni, Sc, Sr, Ti and U, about equal Na^{+}, Ag, Ba, Cd, Co, Li, Rb and Se, and lower K^{+}, Cl^{-}, Si, Al, As, Ce, Cr, Cu, Fe, Ga, J, La, Mo, Nd, Pb, Sb, Sn, Th, V, Zn and Y. The analysis of variance permitted to assess the existence of significant geochemical trends for measured chemical properties.

The R-mode factor analysis shows that the areal geochemistry of Slovenia's groundwaters can be summarized by six factors that account together for 63 % of the total variance in data. The three strong factors account together for 47 % of the total variance, each of them for more than 13 %. The other three factors are weak, together they explain 16 % of the total variance. Factor 1 (18 % of total variance) groups loadings of nine rare earth elements (Ce, Dy, Gd, La, Nd, Pr, Sm, Y and Yb) and Al, Fe, Mn and Th, factor 3 (16 %) the alkali elements Na^{+} and K^{+}, Ba, Br, Eu, Li, Rb, Sc, Se, Si, Sr and NO_3^{-} and Cl^{-} as anions, and factor 2 (13 %) the earth alkalies Ca^{2+} and Mg^{2+}, Ti and U, HCO_3^{-}, SO_4^{2-} and Cl^{-} as anions and Co, Re, Mo and Sr. The factors 4 and 5 are weak, their patterns are local, and both

contain elements typical for environmental pollution: factor 4 (7 %) Zn, Cu, Pb, Cd, Ni, Sb and Fe, and factor 5 (5 %) V, As and Mo. Factor 6 loaded by Cr and Yb explains only 4 % of total variation but its pattern is regional.

Conclusions

The general conclusion of the study is the confirmation of the spring water as an appropriate sampling medium for geochemical mapping of territories as this investigated according to the applied methodology. The produced experimental maps furnished a wealth of information on geochemistry of spring waters in Slovenia as well as predictions on the feasibility of the elemental maps based on denser sample spacing.

Five meaningful hydrogeochemical associations were established by factor analysis, and the scale and stability of their areal distributions across Slovenia assessed by analysis of variance. Three strong associations, one of rare earth elements, the other of alkali metals, chloride and nitrate, and the third of earth alkali metals, hydrocarbonate, sulfate and chloride, have wide scale more or less stable regional patterns. Two weaker hydrogeochemical associations, one of heavy metals, and the other of V, As and Mo, have local variability only, and the trends they show on maps are not stable. The interpretation of areal distributions of individual elements and of their associations in spring waters with respect to geology, hydrology and relief will require more additional study.

Acknowledgements

This work was financially supported by the Slovenian Ministry of Education, Science and Sports.

References

Actlabs (1997): Fee schedule, effective February 1997. Activation Laboratories Ltd., 21 p., Ancaster.

Ekar, I. (1997): verbal communication.

Foregs (1997): *Geochemical Mapping Field Manual*, Draft Version, 32 p.

Heise, E. (1984): Hydrogeology of Karstic Terrains. *International Contributions to Hydrogeology,* 264 p., Hannover.

Juranji, N. (1998): *Geokemično kartiranje Slovenije z vodo izvirov*, diplomsko delo. Univerza v Ljubljani, Naravoslovnotehniška fakulteta, Oddelek za geologijo, 117 p., Ljubljana.

Juranji, N., Pirc, S., Šajn, R., Brenčič, M. (1999): Mapping Slovenia with water sampled at springs. *RMZ – Materials and Geoenvironment*, Vol.46, No.3, p. 515 – 529, Ljubljana.

Kranjc, S. (1985): *Kataster vodnih virov R Slovenije, letno poročilo s prilogo Splošna navodila za odvzem in izvedbo vzorčenja*. Arhiv IGGG, 57 p., Ljubljana.

PIRC, S. (1993): *Regional Geochemical Surveys of Carbonate Rocks*, Final Report No. JF 881-0. Institute of Geology, University in Ljubljana, 30 p., Ljubljana.

PIRC, S. (1991): Geochemical Mapping of Carbonate Terrains. *Transactions of the Institution of Mining and Metallurgy*, Vol. 100, May-August, p. B74-B87.

SNELL, F. D. & ETTRE, L. S. (1974): *Encyclopedia of Industrial Chemical Analysis*, 19. Wiley-Interscience, 795 p., New York.