

ABSTRACT

Karst is a distinctive landscape with specific surface morphologies and underground water drainage systems created by the fast dissolution of the rock. Worldwide, it accounts for around 20% of the dry surface (excluding that part of the Earth covered by ice caps). Carbonate karst alone extends over around 10-15% of the continental ice free area, and provides water supply for approximately one fourth of the world's population. A complex system of chemical equilibria between different forms of inorganic carbon in the rock, percolating water and in the gas phase plays an important role in the genesis of karst features. The main aim of this thesis is to contribute to a better understanding of the inorganic carbon path inside a limestone massif. This is achieved by identifying the functional compartments and mechanisms for its transport and by quantifying the different fluxes, assessing their relative contributions and their seasonal variations.

The studied site, Bijambare protected area, is located around 25 km north of Sarajevo, and encompasses 490 hectares of coniferous forest and meadows as well as several karst features. The region has an average elevation of 900-950 m, temperature of 6.2°C and precipitation of 917 mm year⁻¹. Several parameters have been monitored at Srednja Bijambarska cave (a show cave and the longest speleological object in the area) in the scope of this study. Temperature, relative humidity, pressure, air velocity, carbon dioxide and radon concentration have been measured in the cave atmosphere while physical-chemical analyses have been conducted on the percolating water including determination of flow rate, calcium and magnesium concentration, alkalinity, pH, temperature and specific electric conductivity. Calcite deposition rates on glass plates left under three cave drip sites have been calculated by repeated measurements of plate weight.

Carbon dioxide in the cave air, originated by degassing from percolating water, is transported between underground passages by advection and then released to the external atmosphere. Temporal variations of the carbon dioxide (CO₂) concentration are controlled by switching between the ventilation regimes, driven by outside temperature changes. A regression model with a simple perfectly mixed volume applied to a cave sector ("Music hall") resulted in an estimate of ventilation rates between 0.02 h⁻¹ to 0.54 h⁻¹. Carbon dioxide input per plan surface unit is estimated by

the model at around $50 \times 10^{-6} \text{ m h}^{-1}$ during the winter season, to more than $1000 \times 10^{-6} \text{ m h}^{-1}$ during the first temperature falls at the end of summer ($0.62 \mu\text{mol m}^{-2} \text{ s}^{-1}$ and $12.40 \mu\text{mol m}^{-2} \text{ s}^{-1}$ at normal conditions respectively). These values have been found to be related to the cave ventilation rate and dependent on the availability of CO_2 in the surrounding environment. For airflow close to zero, the values of CO_2 input per plan surface are in the order of a few units $\times 10^{-6} \text{ m h}^{-1}$. The anthropogenic contribution from cave visitors has been calculated, based on two experiments, at between $0.35 \text{ LCO}_2 \text{ min}^{-1} \text{ person}^{-1}$ and $0.45 \text{ LCO}_2 \text{ min}^{-1} \text{ person}^{-1}$. 10 kg of carbon dioxide was released into the cave environment during a short experiment with detailed monitored conditions. Several assumptions, hypothesis and results obtained from previously described modelling of carbon dioxide concentration natural variations have been confirmed.

Drip water at three sites appears to have originated from a parent solution with an equilibrium carbon dioxide partial pressure ranging between 15000 ppm and 26000 ppm. A large part of the observed variability in drip water composition is explained by different stage of degassing. Water composition analyses at several cave pools confirm that drip water rapidly achieves equilibrium with the cave atmosphere following impact on the stalagmite apex, while calcite oversaturation is retained longer. The difference of DIC between the solution entering and leaving the cave represents the total inorganic carbon lost by degassing into cave atmosphere and precipitation of calcite. The DIC concentrations have been converted into fluxes per unit of surface using an average effective infiltration of 497 mm year^{-1} . The resulting flux of carbon dioxide degassing from drip water is in the range $0.03\text{-}0.06 \mu\text{mol m}^{-2} \text{ s}^{-1}$. These values are similar to the results estimated by modelling of carbon dioxide variations in the cave atmosphere.

Calcite precipitation rates on glass tablets located under three drip sites have been recorded monthly for around one year. Recorded rates range from 0.2 to 4.7 mg d^{-1} . Results are compared with several potential predictors including external temperature, rainfall, drip rate and composition. Differences between sites have been found to be correlated mainly to drip flow rate, while only within one site correlation with calcium concentration is significant. Theoretical predicted values overestimate experimental values on average by a factor two, and fail to predict the observed correlation with drip

rate. It is therefore proposed to modify the standard theory by considering an effective drip rate lower than measured drip rate by a factor Φ_l . This factor accounts for drip water by-passing the glass tablet due to drop splashing. Best fit of experimental data is obtained when about 99.9% of water is considered to be ejected during drop impingement. The order of magnitude is confirmed by additional laboratory experiment and comparison with literature data.

A preliminary investigation of the carbon stable isotopic composition of the DIC from drip water samples show similar results from two campaigns realized during summer and winter respectively. The calcite deposited over glass tablets left in place almost one year under the same drip sites returns $\delta^{13}\text{C}$ values around 1.5 ‰ higher than in the drip water DIC. $^{13}\text{C}/^{12}\text{C}$ ratio in cave air is significantly different during winter and summer sampling campaign, due to the different cave ventilation conditions. A simple mass balance of the cave system applied to carbon dioxide and carbon isotopes predicts that cave air isotopic composition is a linear function of the inverse of carbon dioxide concentration (Keeling's plot). Observed summer and winter $\delta^{13}\text{C}$ values can be explained by an ideal mixing between a typical canopy air and a pure carbon dioxide source (degassing) with average $\delta^{13}\text{C}$ of -16.2 ‰.

KEY WORDS

INORGANIC CARBON BALANCE, CARBON DIOXIDE, KARST, CAVE