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Extended Abstracts

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Ewa Kmiecik**



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title: **Evaluation of the accuracy of determination of the chemical denudation in the Biały Potok Watershed, using numerical geochemical modeling**

author(s): **Marzena Szostakiewicz**
University of Warsaw, Faculty of Geology, Poland,
marzena.szostakiewicz@uw.edu.pl

Jerzy J. Małecki
University of Warsaw, Faculty of Geology, Poland, jerzy.malecki@uw.edu.pl

Marek Matyjasik
Weber State University, Department of Geosciences, United States,
mmatyjasik@weber.edu

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INTRODUCTION

Chemical denudation, understood as a set of processes that lead to the removal the rock material dissolved in water from the land masses, is one of the components of the chemical elements cycle in nature which significantly influences chemical composition of surface water and groundwater in the zone of hypergenesis. Chemical denudation is also one of the processes actively reshaping the Earth's surface, and understanding of these processes (dissolution-transport-deposition) allows to determine the nature of this mechanism and rates of the present geomorphic processes (Pulina, 1992, 1999; Manecki et al, 1994; Langmuir, 1997; Faure, 1998; Kehew, 2001).

Processes occurring in the phreatic zone have not been typically considered in quantitative evaluation methods of chemical denudation. These methods use the "black box" model. They estimate chemical denudation, without including processes occurring in the phreatic zone, based on recharging and discharging water chemistry and flow volumes (Pulina, 1999; Zambo, Ford, 1997; Andrejchuk, 2000; Bouchard, Jolicoeur, 2002; Hodson et al., 2002).

A new approach which uses a numerical, and includes processes occurring in the phreatic zone, allows to evaluate how these processes affect the chemical denudation (Małeck, Szostakiewicz, 2004, 2006, 2008; Szostakiewicz, Małeck, 2006).

FIELD EXPERIMENTAL STUDY AREA

This research has been conducted in the drainage basin of the Biały Potok, located south of town of Zakopane, within the West Tatra Mountains. The experimental field area is mainly composed of carbonate sediments – dolomites and limestone from the Triassic Lower Regle Series (Fig. 1).

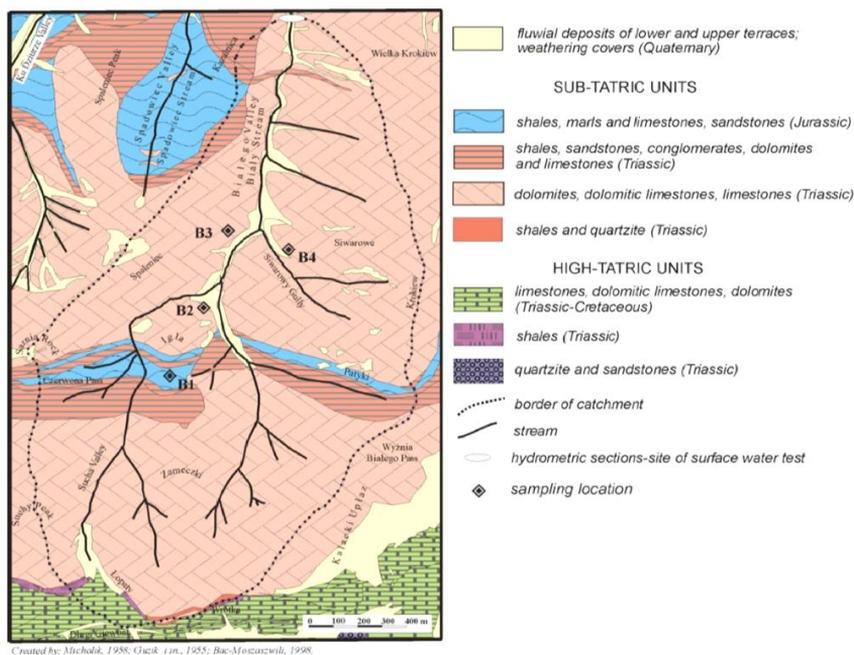


Figure 1. Geology of the experimental field area.

Dolomite and calcite are dominant minerals in the series. Clastic rocks mainly composed of quartz, calcite and dolomite occur locally. Minor amounts of clay minerals (mainly illite), plagioclase feldspar, iron and manganese oxides and silica occur infrequently. Pyrite accumulations in calcite veins also occur (Turnau- Morawska, 1953; Pawlikowski et al., 1997). Groundwater in the Biały Potok drainage basin are recharged from the infiltrating atmospheric precipitation, and they are discharged by streams and springs. Multi-year water budget from this area indicates that there are no lateral flows from and to this drainage basin resulting in deficits or surpluses. If lateral flows existed, they would add or remove unknown amounts of chemical load, making close to impossible evaluation of chemical denudation.

Surface waters and groundwater in the Biały Potok drainage basin are weakly alkaline and their total dissolved solids (TDS) between 200 and 300 mg/L. They have intermediate hardness (using classification of Pazdro, Kozerski, 1990), with significant dominance of the carbonate hardness, which is associated with lithology of the drainage basin rocks. Values of the oxidizing-reducing potential (300-400 mV) indicate oxidizing conditions in the aquifer. This range of Eh values accompanied with pH ranging from 7,5 to 8,1, is characteristic for groundwater in the active chemical transfer zone in carbonate rocks regolith (Macioszczyk, Dobrzynski, 2002). Calcium, magnesium and bicarbonate ions dominate in surface waters and groundwater. They are $\text{HCO}_3\text{-Ca-Mg}$ type according to Szukariew-Prikłonski classification.

QUANTITATIVE EVALUATION OF CHEMICAL DENUDATION

Quantitative determination of chemical denudation requires information about discharging flow from the experimental field area and the mass dissolved in this flow. Quarterly monitoring of physico-chemical properties of atmospheric precipitation, surface waters and groundwater, including temperature, pH, redox, electric conductivity and chemical composition, has been conducted in years 2008-2009 in the Biały Potok drainage basin in order to collect this information. Concentration of major ions and of iron, manganese, aluminum, and silica has been determined in water samples. Automatic flow measurements in the hydrometric profile characterizing the total discharge from the drainage basin, was conducted every 30 minutes, which allowed evaluation of the surface water flow in the basin. Field and laboratory data collected, and mineral composition of the dominant sediments in the studied drainage basin, were used in geochemical modeling.

Conceptualization and simplification of hydrodynamic and hydrochemical conditions comprised the first phase of the modeling. There are several simultaneous processes in the aquifer, which interactions are difficult to present in numerical modeling. Therefore, numerical models do not perfectly reflect the real conditions. The following assumptions were used in modeling:

- Groundwater recharge is exclusively from infiltration, and discharge occurs only in surface water flows and springs.
- Lateral inflows and outflows are insignificant based on the determined water budget in the drainage basin.
- Chemical composition of groundwater and surface waters is affected by chemical composition of atmospheric precipitation, evapotranspiration, physico-chemical properties of aqueous solutions, and dissolution and precipitation of minerals.

- Dissolution of carbonates occurs in the open system with unlimited access to carbon dioxide and its constant partial pressure. This assumption was considered appropriate based on the partial pressure of carbon dioxide determined in groundwater. Determined logarithms of partial pressure ranging from -1,5 to -2,5 are characteristic for groundwaters where calcite dissolution occurs in open systems (Appelo, Postma, 1993).
- Feldspars do not precipitate from surface water and groundwater, and clay minerals form as products of their weathering (Allen, 2000).
- It was assumed that aqueous solution is in the quasi-equilibrium with the solid and gas phases, characterized by saturation indexes with respect to minerals occurring in the drainage basin.
- Anthropogenic factors influencing physico-chemical properties of surface waters and groundwater were neglected.

The authors understand that assumptions used simplify the natural hydrochemical system, however they do not significantly compromise the validity of the results.

In the next phase, a modeling program, which allows numerical modeling reflecting hydrogeochemical processes occurring in the study area, was selected. Program PHREEQC v.2.11 with compatible thermodynamic data base phreeq.dat was selected. This program allows to: characterize aqueous solution, perform forward and reverse modeling, consider temperature effects in the infiltrating water, and increase of concentration caused by evapotranspiration. This geochemical modeling program is also most frequently used and verified in the world (Macioszczyk, Witczak, 1999; Parkhurst, Appelo, 1999; Ženisova et al., 2002; Ozdemir, Nalbantcilar, 2002; Lachmar et al., 2006; Demirel, Cuneit 2006).

Supporting reverse models were prepared in the following phase which allowed to identify which minerals were likely to dissolve or precipitate in the aquifer water.

Physico-chemical parameters of water samples and mineral composition of the sediments in the Biały Potok drainage basin, were used as input data in the reverse model. The models were constructed based on physico-chemical properties and ionic composition of waters that were in contact in conceptual hydrologic cycle.

The output results from the reverse models were consequently used in forward models. Atmospheric precipitation water equilibrated with respect to carbon dioxide was used as the input aqueous solution. Evaporation and temperature changes along the infiltration path were used in addition to dissolution and precipitation reactions in forward models.

The results of the modeling were verified by comparing them to field and laboratory measurements. The level of agreement exceeded 95% (Tab. 1).

Table 1. Verification example of the forward geochemical modeling (November 2008).

Atmospheric precipitation water				Water sample - surface water				Error*
		 Dissolved Phase		Simulated physico-chemical parameters		Observed physico-chemical parameters		
	mol/L		mol/L		mol/L		mol/L	%
Na	1.96E-05	Calcite	2.86E-05	Na	3.27E-05	Na	3.26E-05	-0.06
K	4.86E-06	Dolomite	3.78E-04	K	8.32E-06	K	8.44E-06	0.75
Ca	1.37E-04	CO ₂ (g)	7.36E-04	Ca	8.03E-04	Ca	8.21E-04	1.10
Mg	6.17E-06	Potassium feldspar	6.42E-06	Mg	5.73E-04	Mg	5.78E-04	0.45
Fe	5.37E-08	Albite	1.39E-05	Fe	5.39E-08	Fe	5.37E-08	-0.11
Mn	9.10E-09	Hematite	1.14E-08	Mn	1.81E-08	Mn	1.82E-08	0.44
Al	1.89E-06	Piroluzite	2.93E-09	Al	3.76E-07	Al	3.71E-07	-0.67
SiO ₂	8.32E-07	Siderite	4.95E-09	SiO ₂	1.68E-05	SiO ₂	1.68E-05	0.06
Cl	6.60E-05	Precipitated Phase		Cl	8.14E-05	Cl	8.18E-05	0.25
SO ₄	2.60E-05	Halite	1.17E-05	SO ₄	2.64E-05	SO ₄	2.60E-05	-0.78
HCO ₃	2.98E-04	Gypsum	8.40E-06	HCO ₃	2.86E-03	HCO ₃	2.79E-03	-1.36
		Illite	9.56E-06					
pH	6.93	SiO ₂ (a)	1.72E-05	pH	8.09	pH	8.08	
pe	7.42			pe	5.95	pe	5.95	

Calculated as (observed data-simulated data)/(observed data+simulated data)*100%

Mass transfer obtained from forward modeling allowed to determine potential amounts of dissolved and precipitated mineral phases in the study area. Dissolved masses of specific minerals and their densities determined in geochemical forward model were used to calculate (Eq. 1) the total volume of dissolved minerals in unit solution volume.

$$d = \sum_{j=1}^n \frac{m_j}{\zeta_j} \quad (1)$$

Where:

d — total volume of dissolved minerals in unit solution volume (Allen, 2000)

m_j — mineral j dissolved mass in unit solution volume [g/dm³]

ζ_j — mineral density [g/dm³]

These data combined with the measured flow volumes in the drainage basin and the drainage basin surface area (calculated using program ArcView GIS 9.3) were used to quantitative estimation of chemical denudation in the experimental study area. The study period was divided onto time intervals because of temporal fluctuations in flow volumes and total volumes of dissolved minerals (Fig. 2).

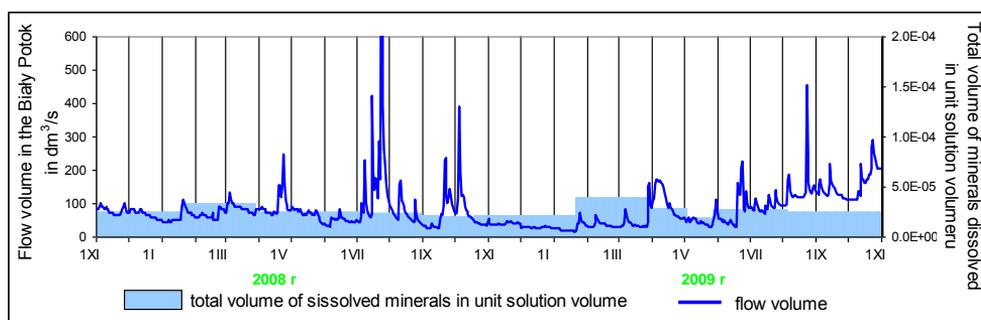


Figure 2. Discretization of the flow volume in the Biały Potok and total volume of dissolved minerals.

Average arithmetic values were used for flow volumes and total volume of dissolved minerals in each of the time intervals. Chemical denudation was therefore calculated from equation 2.

$$D_{ch} = \frac{\sum_{i=1}^n Q_i \cdot \Delta t_i \cdot d_i}{\sum_{i=1}^n \Delta t_i} \cdot P^{-1} \cdot 0,365 \quad (2)$$

where:

D_{ch} — chemical denudation [$m^3/km^2 \cdot year$]

P — basin surface area [km^2]

Q_i — total discharge flow in a time interval Δt_i [dm^3/day]

d_i — total volume of minerals dissolved in a given time interval Δt_i in a unit solution volume (Allen, 2000)

Δt_i — time interval used [days]

Obtained results were compared with chemical denudation values in the study area for the same time intervals calculated frequently used hydrologic equation by Pulina (1999), eq. 3.

$$D_{ch} = \alpha \cdot \frac{\Delta T \cdot Q}{P} \quad (3)$$

where:

D_{ch} — chemical denudation [$m^3/km^2 \cdot year$]

α — proportionality coefficient (Numerical coefficient alpha depends on density of soluble rocks. It allows to use the same dimensions in the equation 3. Value of 12.6 is assumed for carbonates, sulfates, and chlorides) (Allen, 2000)

$\Delta T = T - T_a$, where ΔT — total dissolved solids, resulting from mineral dissolution in karstified study area [mg/dm^3], T — amount of dissolved salts in discharging water leaving the karstified drainage basin [mg/dm^3]

Q — average annual outflow from a karstified drainage basin or study area [m^3/s]

P — the real surface area of the karstified basin or study area [km^2]

Values of chemical denudation in the Biały Potok drainage basin calculated using the new method described in this paper based on results of geochemical modeling (Eq. 2) are significantly lower than those calculated using hydrologic method (Eq. 3, Fig. 3).

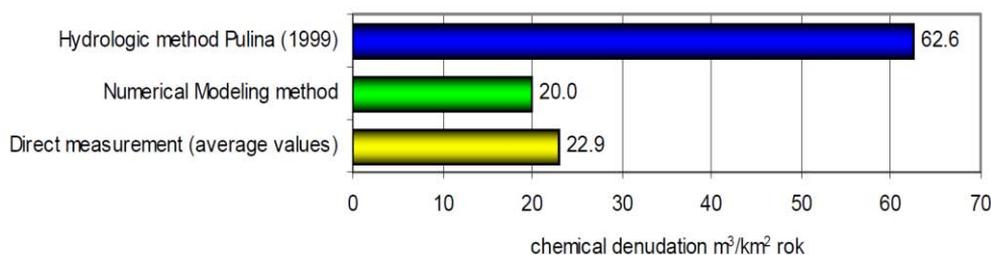


Figure 3. Comparison between different methods of estimation of chemical denudation in the Biały Potok drainage basin.

VERIFICATION OF CHEMICAL DENUDATION RESULTS

Results of estimated chemical denudation using both methods, the hydrologic approach and the numerical modeling approach, significantly vary from each other. In order to establish validity of both methods, the direct verification method was used.

Qualitative verification was based on observation of weathering alterations in thin sections, cut from rocks comprising the experimental field area and buried in the aquifer. Open thin sections were photographed and their mineralogical and petrographic composition was characterized in optical microscope in passing light. These thin sections were then placed in the aquifer where they were exposed to weathering processes. They were recovered after 1.5 year from the aquifer and their mineralogical and petrographic composition was examined again. Thin sections from two rocks characteristic for the Biały Potok drainage basin were examined: dolomites outcropping over more than 90% of the study area (sample B4) and clastic rocks (quartz sandstone, sample B1) exposed in the central part of the study area (Fig. 1). Time interval of reaction of 1.5 year appeared to be too short to result in changes significant enough to be observed in optical passing light microscope.

Similar studies were simultaneously conducted in two other experimental field stations: the Suchy Potok drainage basin (Podhale Region) composed mainly of sandstones and shales, and the Macelowy Potok drainage basin (Pieniny Klippen Belt) composed of both sandstones and shales as well as carbonates. In thin sections from Globo-trunkana limestone collected in the Macelowy Potok drainage basin, that were exposed in the aquifer to weathering conditions, significant weathering alterations were observed. Zones filled with calcite, mainly microfossils (planktonic foraminifera from Globotruncana genus), became recrystallized, forming a series of finer crystals or losing entirely its crystalline nature. Previously clearly seen microfossils became barely visible (Fig. 4).

Initial observations, despite a very short sample exposure time to weathering, are in agreement with results of geochemical modeling. They confirm a hypothesis that mainly carbonates, especially calcite, undergo denudation processes in the studied drainage basins.

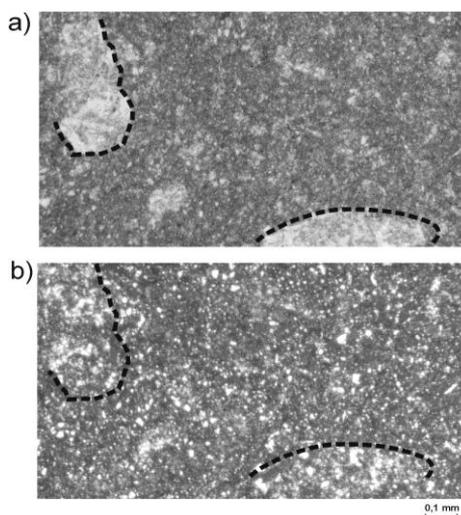


Figure 4. Weathering in Globotruncana limestones: Photograph taken before the sample was exposed to weathering Photograph taken after the sample has been exposed to weathering for 1.5 year.

The second phase of verification of the new quantitative method based on numerical modeling was direct measurement of the dissolved rock mass. In order to accomplish goal, discs of diameter 5 cm and height of 2 cm, and weight ca 100 g, were cut from the rocks comprising the study area. They were then placed on the ground surface exposed to atmospheric precipitation and buried in the vadose zone of the aquifer in the study areas. These discs were accurately weighted before and after exposure to weathering processes. To avoid weight differences caused by varied sample moisture content, all samples were first over dried at temperature 105°C during 24 hours, and then cooled down to the room temperature in exicators (Matsukura et al. 2001). Temperature of 105°C allows to remove water molecules not attached to the mineral lattice in the studied rocks, and simultaneously not causing disintegration of minerals comprising the aquifer material, such as carbonates, which would alter its natural solubility.

Based on the discs evaluation, it was observed that rock discs placed on the ground surface and in direct contact with atmospheric precipitation, underwent more intense weathering than the rock disc buried in the aquifer (Fig. 5). It agrees with the modeling analysis results, indicating much greater potential mineral dissolution in atmospheric precipitation water than in water infiltrating through the vadose zone.

The results of the modeling were also verified by comparing them with the rates of chemical denudation calculated from empirical equations. Direct chemical denudation measurement method was used to accomplish this goal (Kotarba 1972; Thorn et al., 2002). In this method, the lost mass from the rock discs, is divided by the rock density and presented relative to the sample surface area.

The calculated results of chemical denudation in the studied drainage basin using the direct method are consistent with the values determined from numerical modeling and significantly lower than the results obtained using the hydrologic approach (Fig. 3). In views of the authors, it confirms validity of the analysis based on the numerical modeling.

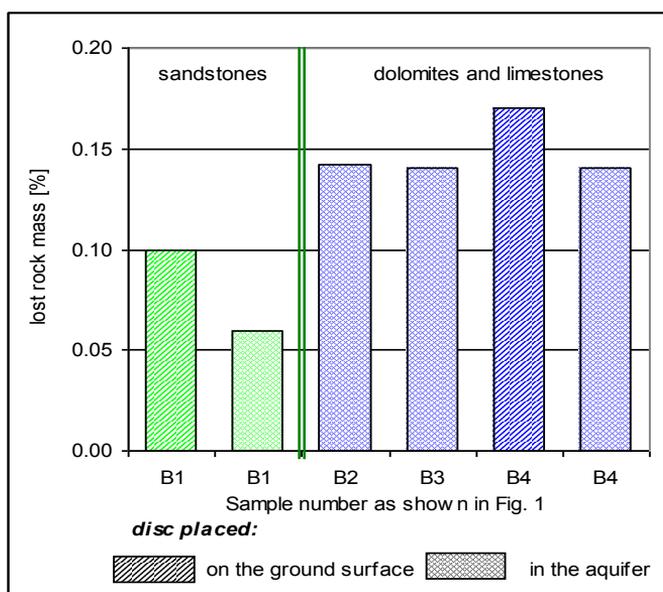


Figure 5. Average mass loss of the rock core discs.

The hydrological approach computations lead to excessive values. The differences between the values calculated using the hydrologic approach and the numerical modeling results from not considering the following factors in the hydrologic approach:

- Contribution of carbon dioxide in carbonate dissolution. This factor significantly affects chemical denudation in the study area, as the Biały Potok drainage basin is mainly composed of carbonates.
- Field evaporation, resulting in increased concentration of elements dissolved in atmospheric precipitation water.
- Variability in density and solubility of minerals, parameters required to correct assessment of the removed rock volume.

In conclusions, empirical studies of denudation processes conducted in the studied drainage basin (qualitative and quantitative) confirm validity of the results obtained from numerical modeling. Rates of chemical denudation determined previously from the hydrologic approach are significantly higher than from numerical modeling. Thus, commonly used hydrologic methods, might lead to underestimation of the karst massive morphology, by as much as 30%.

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