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CHEMICAL DENUDATION AS A GEOMORPHIC PROCESS

ABSTRACT: GAMS I., *Chemical denudation as a geomorphic process.* (IT ISSN 0391-9838, 1998).

In the paper the discrepancy between a significant part (one-fifth to one-sixth) of solutes in total river load and the insignificant percentage of solutional landforms identified in geomorphology is treated. The abundance of data on chemical denudation in the predominant impermeable carbonates on the southern border of the Pannonian basin shows that solution is also the prevailing process there, but local erosion and soil denudation prevent the formation of proper solutional features. The solution of the noncarbonatic sediments is almost overlooked in geomorphogenetics.

The second reason for the discrepancy is that geomorphology had identified landforms before sufficient knowledge on solutes accumulation. Some mesaurements of water chemistry have shown the solution to be an additional process, not only in blind valleys and allogenic caves, but also in through valleys previously regarded as solely erosional or/and glacial landforms.

KEY WORDS: Chemical denudation, Solutional landforms, Pannonian basin.

RIASSUNTO: GAMS L., *La dissoluzione chimica come processo geomorfico.* (IT ISSN 0391-9838, 1998).

Nell'articolo si tratta della discrepanza fra la realtà dell'esistenza di una parte significativa (da 1/5 a 1/6) di sostanze disciolte sul totale del carico dei fiumi e la insignificante percentuale di forme dovute ai processi di dissoluzione identificate in geomorfologia. L'abbondanza di dati sulla denudazione chimica nei carbonati impermeabili al bordo meridionale del Bacino Pannonico mostra che la dissoluzione è il principale processo geomorfologico, ma l'erosione e il denudamento del suolo prevengono la formazione di forme proprie da dissoluzione. La dissoluzione dei sedimenti diversi dai carbonati è forse sovrastimata in geomorfologia.

La seconda ragione della discrepanza, cui si è accennato all'inizio, è che la scienza geomorfologica ha identificato le forme del paesaggio prima di aver avuto una conoscenza di base sufficiente sull'accumulo dei prodotti della dissoluzione. Alcune misure idrochimiche hanno mostrato invece che la dissoluzione può essere un processo aggiuntivo agli altri, non soltanto nelle valli cieche o nelle grotte, ma anche nelle valli trasversali in precedenza interpretate come esclusivamente dovute a erosioni o ai processi glaciali.

TERMINI CHIAVE: Dissoluzione chimica, Forme di dissoluzione, Bacino Pannnico.

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KARST MORPHOLOGY

Since the 1950s, detailed and systematic measurements of so-called chemical denudation (also called solutinal denudation, chemical erosion, corrosion) have been performed in karst areas. At first, chemical erosion seemed easier to detect than other processes. It is necessary to estabilish the average «minirelisation» of water in a river, multiply its weight by discharge and then distribute the calculated solute load over the river basin. Discharge is usually expressed in $l/km^2/sec$ as reported by national or regional hydrological service. Solutes are given in mg/l and tonnes per sq km in one year, or in mm in thousand years. There are many formulae for calculation (reviewed by Ford & Williams, 1989, pp. 106-109).

Thirty years ago chemical denudation was studied in the 23 river basins of the Slovenian Dinaric and Alpine karst built of permeable limestone and dolomite (Gams, 1962, 1967, 1972, 1982). It was found that, besides lithology, runoff is the most important factor - as opposed to air temperature as claimed in many contemporary texbooks. This contradicts the supposition that there was a greater chemical solution in warmer Tertiary climates than at present in the temperate zone, assumed only on the basis of higher temperatures. The same study found no correlation between chemical denudation expressed in $m^3/km^2/y$ of dissolved limestone and dolomite and the stage of karstification expressed in percentage of karst depressions on the surface (Gams, 1966, 1980). Almost the same rate of chemical denudation as in limestone and dolomite was found for «fluviokarsts» built of dolomite (with nearly one half in $MgCO_3$), virtually free of karst depressions. In one such river basin (Temenica river, Slovenia) solute amounts slightly exceed suspended load (Šali, 1969). In a nearby larger river (Krha), draining mostly limestone areas, solute transport greatly exceeds that of solids. This applies to chemical erosion in areas built of impermeable and partially carbonatic marls, sandstones, and other non-consolidated sediments of flysch and molasse type outside of the Dinarids.

Corbel (1959), the first geomorphologist to conduct systematic mesaurements of water hardness on a global scale, attributed river solute load to limestone and dolomitic areas in the river basin only, thus excluding the area of impermeable sediments. If the latter are calcareous or partially calcareous, this pratice is unjustified. For instance, in the river basins ot the Una, Vrbas, Bosna and Neretva with a considerable part in the impermeable carbonatic sediments, chemical erosion expressed in tones per km^2 is similar to chemical erosion in the proper karst areas with the same runoff (Gams, 1972).

That highlights the problem of depth of solution front of permeable rock in karst. If on impermeable carbonatic sediments the chemical erosion stands close to that on karst proper (in reality, water hardness is more reduced at high water level), in karst areas the bulk of solution must occur near the surface. In reality, in permeable carbonatic sediments the corrosion (solutional) front rearches down to the first fissure or cavern in which CO_2 concentration in the air is below that in the soil percolated by the same water. It is at this depth that the deposition of flowstone begins because CO_2 pressures in water there are in disequilibrium with that in the air. The depth of the solutional front is thus dependent on the grade of aerated fissures functioning as water conduits. Under rock surfaces in the Julian Alps this depth exceeds 1,000 m. In the middle and lower karst areas covered by soil mantle the bulk of solution occurs close to the surface. The estimation of recent rate of surface lowering on the basis of measured chemical erosion in river basins in covered karst is therefore reasonable (Gams, 1980). Water hardness in colder climates (Pleistocene) was lower, the solution front lower, but runoff relatively higher.

These findings have also been confirmed by systematic measurement of dissolved river load in small tributaries in different, homogeneous lithological units in Serbia, carried out in the well-equipped Laboratorium of the Geographical Faculty (Manojlović, 1992a, 1992b, 1994). In rivers draining a limestone area as an average mineralisation was found to be 280 mg/l, and in rivers draining impermeable Neogene sediments, almost 500 mg $CaCO_3$/l (Manojlović, 1992a, p. 11). Elswhere greatest chemical erosion is found in rivers draining impermeable gypsum and salts (see Ford & Williams, 1989, 114-120).

It is difficult to obtain the exact portion of the nondenudational river load contributed by solutes in rainwater. Stations for the solute minerals in precipitations are usually located in towns and their values are too high for these purposes. As a case study the only station in a large unpopulated and wooded area in Slovenia (Mašun) was selected for analysis and two-year seasonal hydrochemical measurements and the runoff records for the rivers Mirna (run-off 518 mm, precipitation 1186 mm) and Pesnica (run-off 330 mm, precipitation 987 mm) of the Slovene Hydrological Service (Onesnaženost zraka... 1995, p. 32) were used. In both river basins impermeable carbonates predominate and in the Pesnica basin karst is virtually absent. In the Mirna, in the Dinarids, the noncarbonatic component is 9 per cent and in the Pesnica 13.8 per cent. Total hardness amounts in the first river 238 mg and in the second 250 mg $CaCO_3$+ $MgCO_3$ per litre. The nondenudational input by rainwater is given as a percentage of the dissolved minerals in the rivers (table 1).

TABLE 1 - Solute input from rainwater

	Ca	*Mg*	*Na*	*Cl*	*SO_4*	*HCO*
Global *	2.5	1.5	53	72	19	57
Mirna	0.7	0,7	9.8	18	12	2.7
Pesnica	1.8	1.1	7.1	41	27	2.3

* According to Summerfiel, 1991, p. 382.

Discharge, distance to the seashore (Na, Cl) and lithology must have an important role in the rate of nondenudational solution. If carbonates prevail, the nondenudational input is small in comparison to other findings (Summerfield, 1991, p. 382). Manojlovic & Živković (1994, p. 17) consider that nondenudational load in Eastern Serbian limestone areas with discharges over 15 l/s contributes 15 per cent, and in areas with a lower runoff and noncarbonatic sediments, especially in lowlands, over 50 per cent. In basins of shists, red sandstone, gneiss and at 4-5 l/s/km^2 of runoff, in exceptionally exceeds 100 per cent. In Russia this percentage is in general 14.4 per cent (cited in Manojlović, 1994, p. 19), while on global scale (Summerfield, 1991) it is 15 per cent (In Eastern Serbia, seriuos air pollution is caused by mining in Borovo and in the vicinity of Belgrade).

On the southwestern border of the Pannonian basin, in the Dinarids and the Eastern Alps, runoff is much higher than the global average (locally up to 80 l/km^2). Moreover, permeable and impermeable carbonates are far more common here. Therefore, chemical erosion is also higher. In the Slovene Karst areas the modest general mineralisation of rivers (ca 160-220 mg/$CaCO_3$+ $MgCO_3$/l is mostly due to large discharges. It is much higher in Eastern Serbia, where annual precipitation is usually bellow 800 mm. Depending on the rock chemistry and runoff in the Carpathian-Balkan Mountains in Serbia, the weight of solutes in rivers draining granite areas is 269 mg, from gabbro 282, andesite 322-381, quartz 145, gneiss 118, loess 495, and limestone 275-288 mg/l. (Manojlović, 1992, p. 82). Abstracting the nondenudational part of the river load, chemical erosion in shists, red sandstones and gneisses, depending on runoff, ranges between 4 and 53 t/km^2 annually; in the limestone area with 20 l/s of runoff, it is 167 t/km^2/y, which is 59 m^3 of $CaCO_3$ m^3/km^2/y. A specific removal of dissolved minerals in andesites and andesitic tuff was 49.7-76.6 t/km^2/y. With reduction of this value for the nondenudation part (HCO_3) the chemical denudation of the rock is 18.8-35.4 t/km^2/y. For this process an disintegration of 85.5 to 160.9 m^3/km^2/y occurs (Manojlović, 1994, p. 37). In Negeone marine sediments in East Serbia the chemical erosion is 53 t/km^2/y (runoff 4 l/s/km^2/y) and the disposition of solutes by precipitation and man ranges between 17 and 35 t/km^2/y (average 22,3 t/km^2/y - Manojlovic & Živković, 1994, p. 20). The nondenudational inputs comprise in East Serbian river basins between 15 and 77 per cent of total chemical denudation (*ibid.*, p. 17).

The Danube basin comprises a large part of the Alps and Dinarides, both permeable and impermeable carbonates. Therefore, the non-solutional chemical load in the river is smaller than globally postulated by Summerfield (1991).

GLOBAL CHEMICAL EROSION

The systematic measurement of constituents of load transported in the greatest rivers in the world, along with measurements of discharge, is largely performed by national and regional hydrological services, and has only recently been used for geomorphogenetic research (Ljvovič, 1974; Meybeck, 1983, Summerfield, 1991). The inaccuracy of data on chemical denudation and of river load is generally emphasised (Ford, Williams, 1989, pp. 104-120). In Summerfield's diagrams (1991, pp. 385 and 387) the mean value of the layer removed by solution for the 32-35 listed river basins, which comprise some 53.14 million km^2 (almost half of the earth's surface), is 10.3 mm per thousand years and 268 mm of runoff annually. This is equal to 10.3 m over one million years, and 247 m thick layer in the 24 million year period of the Miocene, Pliocene and Quaternary. On the southern border of the Pannonian basin this layer is manifold thicker (with hypothetically the same chemical erosion as at present).

High precipitation, mostly in monsoon regions, and mountainous relief give rise to the highest chemical denudation in the river basins of Southeast Asia (Brahmaputra: 34 mm, Yangtze: 37 mm and Ganges: 22). They contrast with the very low solutional load in rivers in semiarid regions (Rio Grande: 3 mm, Chari: 2 mm, Murray: 2 mm, Orange: 3 mm, Nile: 2 mm). But it is not clear why the solution rate in eg. the mountainous river basins of the Kolyma (111 mm of runoff) is only 2 mm. From experience in the Alps the reason was found in the (mainly) rocky rather than wooded surfaces. The river basins in largely forested areas in the temperate regions of Europe and North America have above average solutions at middle runoff (Danube: 16 mm, Volga: 13 mm, Mackenzie: 10 mm, St. Lawrence: 12 mm). Alone in the mountainous part of the Amazon river basin the chemical denudation of 13 mm in 1,000 years cannot be explained in this way.

These anomalies can partially be explained by biochemical solution closely related to annual biomass production and plant associations (the highest in humid [sub]tropical forests, followed by temperate forests - Birot, 1965). The annual consumption of CaO is, eg. in the USA, in fir forests 89 kg, in beech forests 78 kg, in oak forests 64 kg, in pine forests 55 kg/hectare (Lutz & Chandler, 1962, pp. 66, 100-101). It is equivalent to 8.9, 7.8, 6.4 and 5.5 tonnes or 5.5-8.9 t/km^2/y. The yearly decomposition of plant material, along with formation of humus and complex organic acids, adds Ca and Mg to the soil in amounts of 5-52 t/km^2/y (Manojlović, 1992, p. 111).

In the Istrian peninsula (Northwestern Dinarids, submediterranean climate with 700-1200 mm precipitation), in the litter (leaves, needles etc.) of spruce forests there is 1860 kg/ha CaO, MgO, P_2O_5 and K_2O (Martinović & Cestar, 1987, p. 128). Plants are providing the necessary solutes via their roots, especially the smaller roots, the lengths of which are measured in hundred metres per plant. Following decay of organic matter, the minerals are used by new plants and the rest washed into the river. The suspended river load also contains organic matter which consists of considerable amounts of dissolved minerals. therefore, total suspension load cannot automatically be added to solid denudation as it is often the case in geomorphological studies.

Regarding solution mostly a biochemical and pedological process, the distribution of chemical denudation in the world can be additionally explained by the annual production of organic substances and, more precisely, by the annual amount of dead vegetation. Accordin to Schmithüsen (1976, p. 78-79), the highest amount of dead substance is found in the monson climate of Asia, in the southeastern USA and Canada, as well in temperate zones with wet growing season in the northern hemisphere of Eurasia, and also in the Siberian taiga, where the solute amounts are higher than those estimated from runoff. Warm and temperate wetlands have the highest annual production of biomass. This is why the relatively high chemical denudation in some river basins with extensive wetlands (according to Summerfield, 1991, p. 385: Amazon: 13 mm, Orinoco: 13 mm, Lena: 9 mm, Mississippi: 9 mm, St. Lawrence: 12 mm, Mekong: 20 mm) can be explained. The role of biosolution can account for the small variation in chemical denudation on permeable and impermeable carbonates and the exeptionally low solution in the humic, long-frozen soils of Alpine mountains. In permanently wet soils the highest solution rate was found in an investigation by standard limestone tablets in Slovenia (Gams, 1985).

CHEMICAL PROCESSES IN GEOMORPHIC EVOLUTION

Karst areas comprise 7-10 per cent of the Eart's land surface (Ford & Williams, 1989, p. 6). Even in the classic karst (Kras) north of the Bay of Trieste, closed depressions account for less than 10 per cent of the surface. Larger closed depressions and larger caves develop mostly through locally accelerated solution in contact karst (Gams, 1995) or through neotectonics. In highly permeable sediments without surface flow (according to Šušteršič's, 1996, pure karst model) and without soil denudation, depressions do not usually occur. Although in «fluviokarst» solution is nearly equal to other processes, they are exceptional there, and in calcareous impermeable sediments they are entirely absent. Textbooks claim that karst is the only relief type where solution has an important role. If a karst landscape is defined as an assemblage of characteristic features (closed depressions in temperate and elevations in the humid tropics), the real solutional area should be limited only to few percentages of the total surface. This is in marked contradiction with the mentioned estimate, i.e. that solutes in total global river transport take up one-fifth or one-sixth.

Why is there such a difference? The first reason is the poor capability of the solution process for the generation of autonomous landforms. In geomorphic evolution solution is subordinate to other processes which prevent it from developing its own forms or mask them (especially through soil denudation and soil creep). The second reason is the general opinion that, on impermeable sediments, the solution is automatically excluded. Tests of solution in rapidly dissolving sediments in much wider section of valleys between two gorges are rare, since the whole topography is thought to be erosional (as in the case of younger impermeable sediments filing poljes). Special solutional landforms are not known even from hot and humid climates where, according to some geomorphologists, the chemical weathering of noncalcerous rocks is an important geomorphic process controlled by soils and climate change. Even in many karst areas of the Dinarids and the Alps solutional landforms are not conspicuous. Their prekarst forms as karst levels, pediplains, valleys etc. are inherited in the present relief from the prekarstic nondenudational landforms as evenly distributed solution lowers the surface evenly (in the conditions of the so-called pure karst model - Šušteršič, 1996). For this reason, in addition to solution, other important processes in recent karst formation are presumed. According to recent findings, if «eroded» upper sediments were built of impermeable calcareous sediment, they would be removed mainly by solution. Moreover, it is also responsable for the removal of a considerable part of some noncalcareous sediments (peridotite, sienite, granodiorite, andesite, gabbro, gneiss, amfibolite and eclogite with 3-12 per cent of CaO and 2-34 per cent of MgO used by plant roots).

The mentioned discrepancy between solution as shown by solutes in river load and solutional landforms on a global scale challenges geomorphologists. By measuring the increase of water hardness during river flow on limestone surfaces, by exposing limestone tablets in rivers in through valleys, and in sinking rivers in ponor caves, it has so far been possible to provide evidence that solution as an important additional process in forming through valleys, blind valleys and caves with sinking rivers (Gams, 1994).

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