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# The mechanisms of dissolved solids transport in flysch drainage basins

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ABSTRACT The transformation of precipitation input into runoff is accompanied by a continuous change in the chemical properties of water involved in the water circulation cycle. These range from slightly acid precipitation water, through neutral stream water to alkaline underground waters. The relationship between discharge and total dissolved solids concentration conforms to a curved regression equation, in the form $y = a^x - b$. Changes in total dissolved solids concentrations follow a certain pattern which is controlled by the smallest drainage basin areas and their relation to the trunk stream. The nature of relationships that approximate spatial variation in chemical denudation parameters for a small drainage basin reflects the distinct differences existing between symmetrical and asymmetrical drainage basins. The variations in unit chemical denudation rates with increasing basin area can be expressed by a hyperbolic equation, in the form $y = (ax - b)/x$.

*Le mécanisme de transport des matières dissoutes dans un bassin versant de flysch*

RESUME Au cours de la transformation des précipitations au écoulement les paramètres chimiques des eaux en circulation se modifient. En commençant par des eaux de pluie très acides on aboutit à des eaux neutres de rivière et enfin à des eaux souterraines alcalines. La relation entre le débit et la concentration des matières dissoutes peut-être estimée par l'equation de régression curviligne du type $y = a^x - b$. La concentration en matières dissoutes dépend de l'étendue des bassins versants partiels et de leurs position par rapport aux cours d'eau principaux. Dans le petit bassin versant on a déterminé la différenciation du caractère de la relation concernant la régularité de la différenciation spatiale du paramètre de la dénudation chimique entre le bassin symétrique et asymétrique. La relation de l'érosion calculée pour un $km^2$ avec l'accroissement du surface du bassin versant peut-être estimée par l'équation de l'hyperbole: $y = (ax - b)/x$.

## INTRODUCTION

Basic data on dissolved solids transport have been collected by the author since 1969 at the Research Station of the Department of Geomorphology and Hydrology, Institute of Geography and Spatial Organization, Polish Academy of Sciences, which is located at Frycowa in the Western Carpathians. The study area is a typical flysch drainage basin of medium size (239 $km^2$, 280-1084 m a.s.l.). It is drained by the Kamienica Nawojowska, together with its tributaries of the Kryściów stream (7.03 $km^2$), Homerka stream (19.6 $km^2$), and Bącza stream (3.9 $km^2$). Unmetalled roads, a Holocene gully and areas close to the main water course, which are drained by sheet flow and are being studied on a 0.26 $km^2$ experimental slope (Froehlich, 1979), also contribute runoff and dissolved material to the main stream. The study area is in mountains of intermediate height and exhibits moderate and high relief, which in turn is related to the lithology of flysch strata including sandstones, conglomerates, shales and marl. Variations in the physical and chemical parameters of both bedrock and waste sheets reflect the vertical zonation of landforms (Starkel, 1972).

The present study is designed to investigate the mechanisms of dissolved solids transport in flysch drainage basins of varying size by determining the quantitative relationships between hydrologic and transport parameters.

## CHEMICAL PARAMETERS OF WATERS CIRCULATING IN A FLYSCH DRAINAGE BASIN

The determination of spatial variation in the intensity of chemical denudation requires knowledge of the chemical parameters of waters involved in the processes which transform precipitation input into runoff. The intensity of leaching of the substratum depends mainly on the aggressiveness of circulating waters, i.e. on the hydrogen ion activity (pH), whereas the oxidization and reduction properties of solutes are expressed by the redox potential. In the Carpathian flysch basins, pH values for different water types vary between 3 and 8.5, and the corresponding redox potentials lie in the range of -50 to +280 mV (Pasternak, 1968; Maultz, 1972; Froehlich, 1975, 1982). The latter parameter is lowest in spring, but increases in summer and autumn.

The relationship between hydrogen ion activity and redox potential is described by a straight-line equation, which has a high correlation coefficient (Fig.1). High values of acidity (3-5 pH units) and redox potential (>150 mV) are characteristic of precipitation and sheet flow. Although these waters are highly aggressive, their impact on the substratum is of a very short duration, and infiltrating waters show only a slight trend towards neutrality. The ground surface provides the upper limit to this transformation, and the lower limit is the water table which is either stable or migrates during the year and becomes perched in the waste mantle (Froehlich, 1982). Below this limit, only reduction reactions are taking place. The chemical activity of surface runoff and groundwater combine to determine the properties of stream waters, which exhibit pH values between 7.2 and 8.5 during the year. Channel waters are therefore

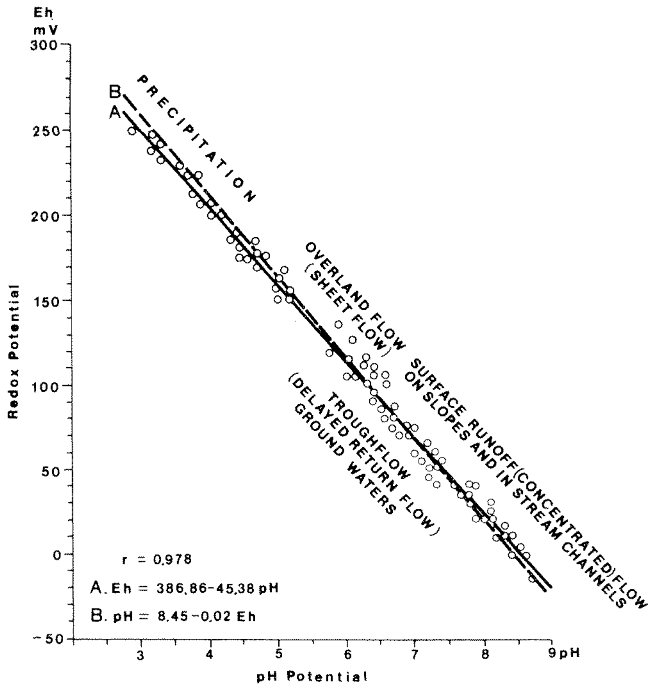


*FIG.1 Relationship between redox potential (EH) and hydrogen ion activity (pH) for various types of water circulating in the Homerka drainage basin.*

slightly aggressive, but because of a buffer effect, no dissolution occurs in the channel (Kotarba, 1972). The transformation of precipitation input into runoff is thus accompanied by a continuous change in the chemical parameters of waters involved in the water cycle. These range from highly acid precipitation water, through neutral stream water to alkaline groundwater. A corresponding change takes place in chemical reactions which vary from oxidization to reduction types. It appears that both the intensity and trend of leaching processes depend upon the relative importance of the different sources of runoff.

An increase in dissolved solids concentration occurs through the mechanisms of water circulation. The relationship between specific conductance and total dissolved solids concentration for various types of water is approximated by a straight-line equation, which has a high correlation coefficient (Fig.2). Concentrations of the major ions contributed by the substratum are proportional to dissolved solids concentrations and specific conductance (cf. Hem, 1970; Walling, 1974). Relationships between major ion concentrations and total dissolved solids concentration assume the form of a straight line and are associated with correlation coefficients in the range 0.72-0.99 (Fig.3). The low correlation coefficient for $SO_4^{2-}$ ions can be ascribed to the influence of biochemical processes and sewage. It is possible, using these relationships, to evaluate the composition of the total dissolved solids load and to quantify the ratios of individual ions.

## RELATIONSHIPS BETWEEN DISSOLVED SOLIDS CONCENTRATIONS AND STREAM DISCHARGE IN DRAINAGE BASINS OF DIFFERENT SIZES

The relationship between total dissolved solids (TDS) concentration and discharge assumes the form of a hysteretic loop varying in shape during each high stage event (Fig.4). Each loop consists of two distinct limbs corresponding to the rising and the falling stage

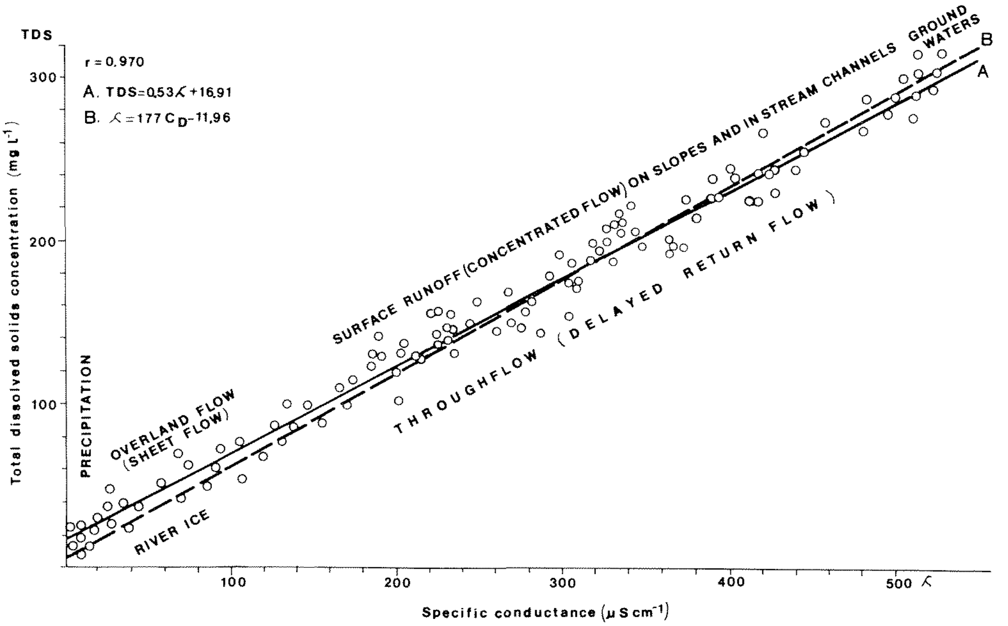


*FIG.2 Relationship between TDS concentration and specific conductance (λ) for various types of water circulating in the Homerka drainage basin.*

(cf. Walling & Webb, 1980). Minimum concentrations are associated with the peak flows (Fig.5), and this also applies to high stages that have several peaks. Each peak is associated with the generation of another loop. After the peak, the plot of rising solute concentration is the hysteretic reflection of the discharge recession curve.

During the year, minimum dissolved solids concentrations are associated with high flows generated by snowmelt. Stream water is diluted by the melting of ice covers in the channel. Since freezing is accompanied by the precipitation of some salts, dissolved solids concentrations are significantly lower in these meltwaters. The high proportion of sheet flow in peak discharges may also account for low concentrations. Snowmelt waters and overland flow on slopes are marked by low dissolved solids concentrations (Fig.2). In floods generated by rainfall, TDS concentrations depend upon the type of rainfall. TDS concentrations are higher in floods produced by throughfall during prolonged rainfall than in flash floods. Throughflow is marked by high concentrations (Welc, 1978; Froehlich, 1982). The initial phases of floods generated by rainfall are accompanied by a decline of concentrations, caused by channel precipitation together with sheet flow and linear flow from contributing areas close to the water course. TDS concentrations in these waters are low. In general, a series of closely spaced and similar high discharges exhibits progressively lower TDS concentrations, and this

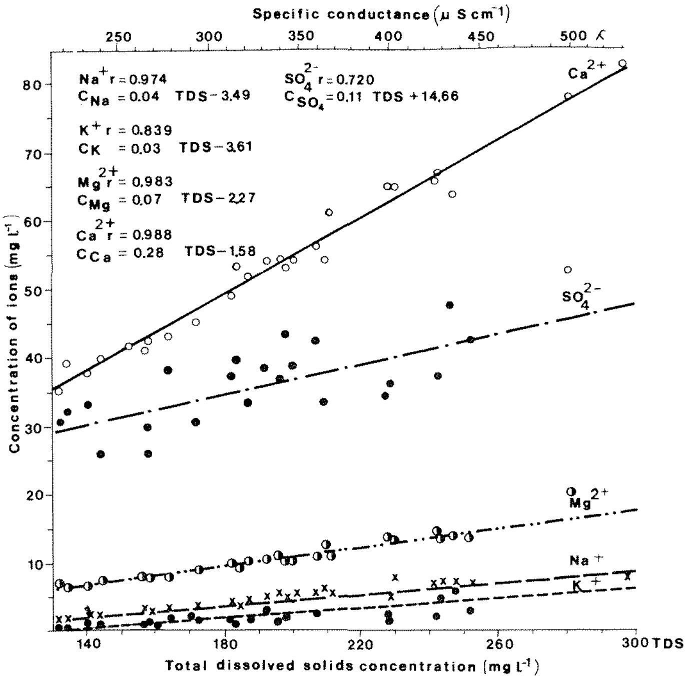


*FIG.3 Relationships between major ion concentrations (C) and TDS concentration for waters from the Homerka drainage basin.*

feature reflects a temporary exhaustion of soluble salts which are supplied from the same sources during the sequence of events. This tendency of falling concentrations is interrupted either by a longer flood-free interval or by the occurrence of another flood type, and the process of solute leaching is clearly time-dependent.

In the flysch drainage basins, the relationship between TDS concentration and discharge conforms best to a curved-line equation (Froehlich, 1982) in the form:

$$y = a^x - b \qquad (1)$$

Three sections can be distinguished in this relationship (Fig.6). The first, which has the highest gradient, corresponds to low flows and the transition to mean annual discharge. The high concentrations associated with this range of flows are controlled by the duration and depth of water circulation, and from a hydrochemical viewpoint runoff in this phase is "saturated". The second section of the relationship relates to a range of flows between mean annual discharges and the onset of high discharges. It exhibits a characteristic bend

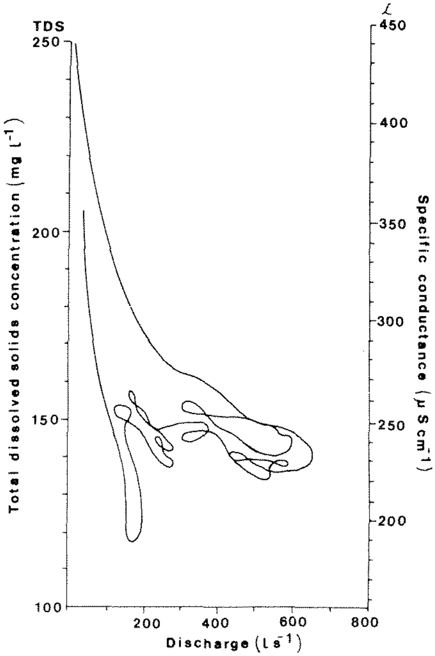


*FIG.4 Relationship between TDS concentration and discharge for the Bącza stream during the rain-generated flood of 17-22 August 1978.*

and represents a transitional phase when solutes are being supplied by the delayed circulation and by throughflow and overland flow. The longest section of the concentration-discharge relationship (Fig.6) corresponds to the whole range of high flows and has a low gradient.

In Fig.7, the relationship:

$$\mathrm{TDS} = f(Q) \tag{2}$$

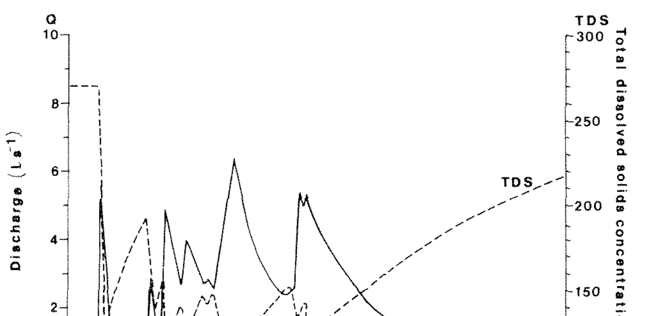


*FIG.5 Discharge (Q) and TDS concentration for the Bącza stream during the rain-generated flood of 17-22 August 1978.*

plots as a series of straight, sub-parallel lines for the heterogeneous Kamienica Nawojowska drainage basin and its tributaries. The Kamienica Nawojowska River plots in the highest position on the graph, whereas tributary basins of varying size plot at successively lower positions. This hierarchical organization of the drainage basins shows that changes in TDS concentrations follow a certain pattern which is controlled by the area of the tributary basin and its relation to the trunk stream. In the latter case, solutes

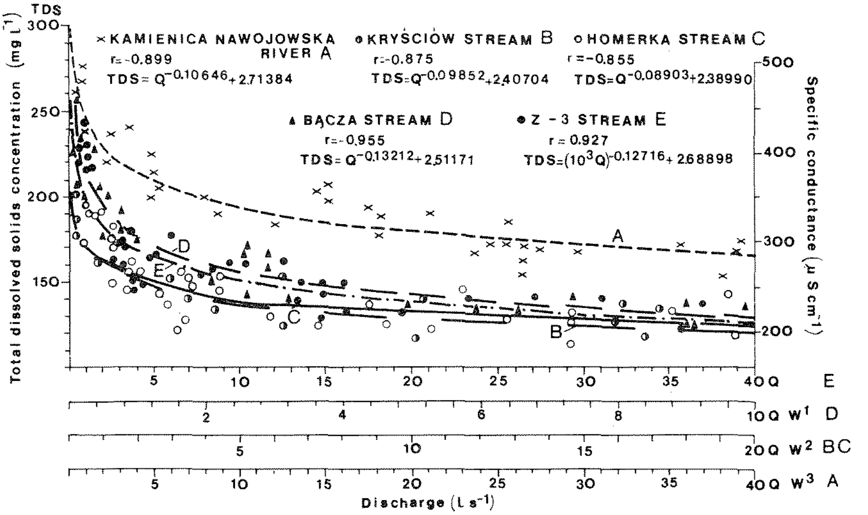


*FIG.6 Relationships between TDS concentration and discharge (Q) for the Kamienica Nawojowska basin (E refers to a small stream draining a Holocene gully on the experimental slope).*

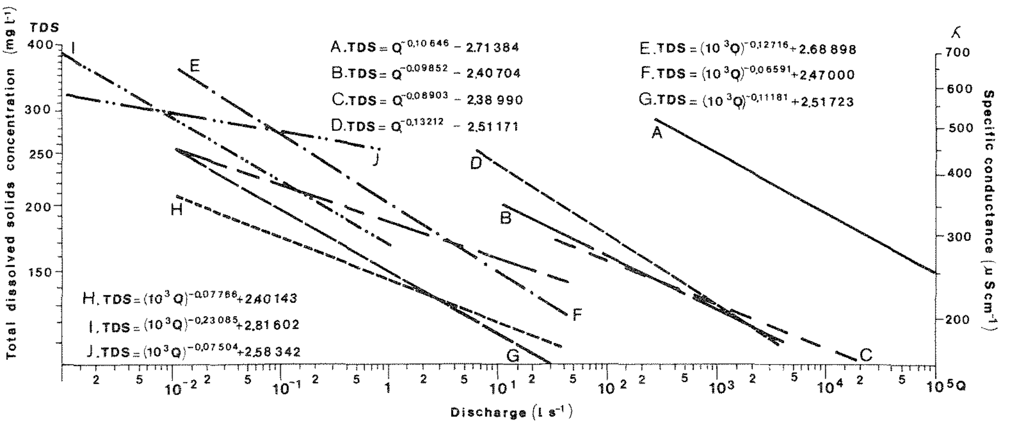


*FIG.7 Relationships between TDS concentration and discharge (Q) for the study basins (A) Kamienica Nawojowska, (B) Kryściów, (C) Homerka, (D) Bącza, (E) small stream draining a Holocene gully on the experimental slope, (F), (G), (H) unmetalled roads, (I) spring on the experimental slope, (J) spring in the Bącza valley floor.*

supplied from alluvial valley fills elevate dissolved concentrations. In narrow valleys, groundwater comes into contact with those flowing downslope, and this provides a primary source of dissolved solids. For this reason, the increase of TDS concentrations with increasing basin area is inversely proportional to specific runoff values (Froehlich & Słupik, 1980).

## VARIATIONS IN DISSOLVED SOLIDS TRANSPORT WITH INCREASING STREAM LENGTH

In order to evaluate the representativeness of results obtained from a hydrometric station located at the lower end of a drainage basin, it is necessary to investigate how dissolved solids transport varies in a downstream direction with increasing basin area (Froehlich & Słupik, 1980). *TDS concentrations generally rise along the Carpathian* rivers and rivulets in a downstream direction from spring sources, and this trend is clearly illustrated by the Kamienica Nawojowska River, together with its tributaries (Fig.8). The gradient of the

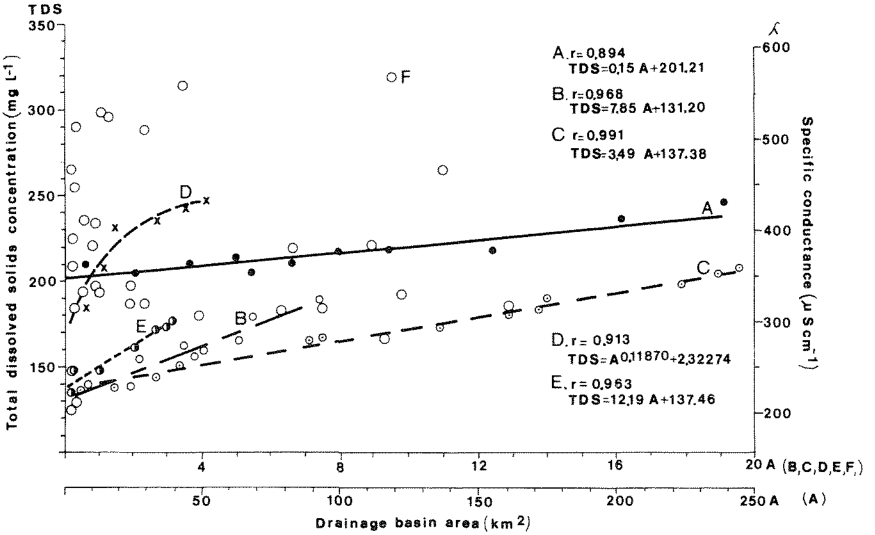


*FIG.8 Relationships between TDS concentration and basin area in channels of the study streams (A) Kamienica Nawojowska, (B) Kryściów, (C) Homerka, (D) Bącza, (E) Sucha Kamionka, (F) tributaries of the Kamienica Nawojowska, Homerka and Bącza.*

downstream increase in TDS concentrations is similar for drainage basins of varying size, and in small tributaries, concentrations rise along shorter flowpaths than in the larger drainage basins. This downstream trend mainly reflects lithological variations, to which the other environmental components that influence the water cycle are related (Froehlich & Słupik, 1980). In the study basins, the relationship between TDS concentration and drainage area (stream length) is approximated by a straight-line equation, with the exception of the asymmetrical Bącza drainage basin, where a curved-line relationship was found to be more appropriate (Fig.8). The terms "symmetrical" and "asymmetrical" are applied here to drainage basins, with axes crossed by the boundaries of morphogenic belts at right angles and oblique angles respectively.

The downstream increase in stream discharge and dissolved solids load is proportional to the increase in basin area. The relationship between TDS load and drainage basin area is approximated by a straight-line equation for the Homerka drainage basin (Fig.9), and by a curved-line equation for the asymmetrical Bącza drainage basin.

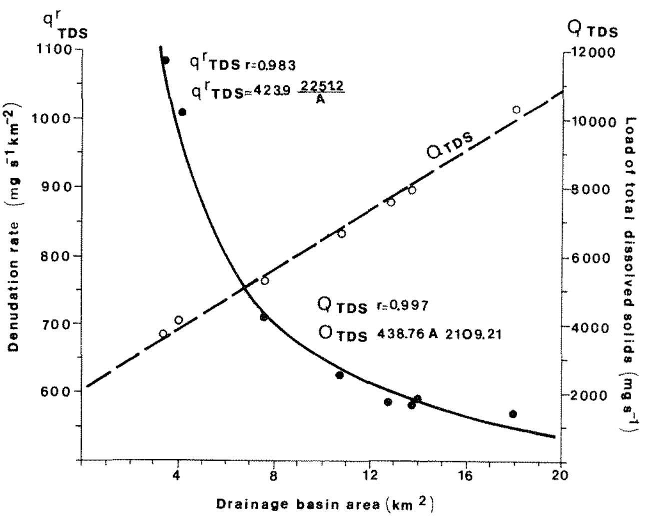


*FIG.9 Variation of TDS load and an index of chemical denudation rate with drainage basin area in the Homerka stream.*

In contrast, the relationship between an index of chemical denudation per unit area and drainage basin size is best expressed by a hyperbolic equation (Fig.9) of the form:

$$y = (ax - b)/x \qquad (3)$$

It is therefore clearly apparent that chemical denudation rates will vary with the location of the monitoring site in the drainage basin, and this fact must be borne in mind when extrapolating the results of measurements obtained from a single hydrometric section to the whole drainage basin.

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