Dissolved Loads of Rivers and Surface Water Quantity/Quality Relationships
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Dissolved loads in streams and rivers — discharge and seasonally related variations

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ABSTRACT Basins of various sizes have been compared to examine behaviour patterns of chemical and hydrological parameters under different geological and climatic conditions. Data from small forested basins up to 1 km^2, middle sized river systems up to 10 000 km^2, and several stations on the River Rhine below Lake Constance were used. Basins were investigated with varying degrees of sampling intensity, depending on size and the immediate aims of the particular study. In general the major physical parameters were recorded continuously, and chemical parameters were determined for continuous composite samples from large basins. Frequent grab samples were taken in smaller basins. The basic sampling regime permitted the examination of annual periodicity in fluctuations. The variance of dissolved loads in streams and rivers is markedly reduced when data evaluation includes consideration of the annual cyclic pattern. In the present study this behaviour has been identified for a number of parameters, and annual patterns are similar for small and large basins. The recognition of basin-independent patterns aids comparison of data from basins varying in size and other characteristics.

La matiére dissoute dans les ruisseaux et rivières - ses variations liées aux débits et aux saisons

RESUME Le but de cette étude est d'examiner le comportement des paramètres chimiques et hydrologiques pour différentes conditions de la géologie et du climat des bassins versants. Des bassins de caractères très variés ont été comparés: petits bassins boisés, d'environ 1 km^2, bassins de grandeur moyenne, moins de 10 000 km^2, ainsi que plusieurs stations sur le Rhin en aval du lac de Constance. Les échantillons ont été pris avec une fréquence variée et en rapport avec le but particulier de l'étude. En général la majorité des paramètres physiques ont été observés en continu. Pour les paramètres chimiques l'échantillonnage était continu et mélangé pour les grands bassins tandis que dans les petits bassins de fréquents échantillons instantanés ont été pris. Le régime des mesures permettait donc en plus des paramètres usuels d'examiner la périodicité annuelle des fluctuations. Cette étude a démontré que la variance des charges dissoutes dans les ruisseaux et rivières est considérablement réduite quand on tient compte du comportement cyclique annuel dans l'évaluation des données. Ceci a permis de montrer que pour de nombreux paramètres la structure de leur évolution était très semblable tant pour les petits que pour les grands bassins étudiés. Cette constatation constitue une aide importante dans la comparaison des données provenant de bassins de grandeur et autres caractéristiques différentes.

INTRODUCTION

Examination of the mechanisms by which weathering, erosion and various anthropogenic activities influence river loads and a quantitive assessment of the contributions from these sources require measurements of dissolved and suspended material transport. The growing need for such information, which has been spurred on by man's increasing impact upon river systems and the necessity of maintaining water quality, has vastly expanded the study of river loads. However, it is often not possible to extrapolate results from one basin to another, or even to compare data within different parts of a single basin, because of contrasting basin characteristics and also the different techniques of water sampling used. Contributing to this difficulty has been a lack of knowledge on general mechanisms of behaviour, which could aid in comparative studies. Part of the difficulty in obtaining information on these mechanisms has stemmed from the type of data evaluation employed. In order to condense and obtain an overview of large data sets collected from automatic sampling equipment, summary statistics are often calculated. Such an approach, however, involves loss of information pertinent to the study of the mechanisms which influence the behaviour of river loads. After data condensation, the factors which contribute to deviations about an average value may no longer be identifiable, and this disadvantage of statistical analysis is often neglected.

In the present study the emphasis is placed on investigating the basic *behavioural* mechanisms affecting several load parameters. The approach to data evaluation is different to that employed in studies of a statistical nature, and the aim of the investigation is to make the data collected in one basin more comparable with, and valid to, studies in other basins of similar or different size.

METHODOLOGY

General methods of estimating dissolved loads

Continuous information on dissolved load via records of flow *and* concentration is available only in rare cases. In order to compensate for the lack of data on concentration, a number of methods have been used to make estimates on a continuous basis (e.g. Davis & Zobrist, 1978; Feller & Kimmins 1979; Hall, 1970, 1971; Johnson *et al.*, 1969; Johnson & Swank, 1973; Johnson, 1979; Keller, 1979). Concentrations in grab samples are often correlated with streamflow, but the resulting regression equations are mostly nonlinear, and extrapolation to unsampled high flow levels may cause considerable uncertainty in the estimate. In addition, scatter due to the influence of factors other than streamflow reduces the accuracy of the estimate. Under such conditions, load estimates for long periods may be more reliable than for short periods. Methods based on continuous records of parameters other than streamflow are therefore of interest, and electrical conductance and temperature, which are easy to monitor, have been used to esimate mineral concentrations in small streams (Keller, 1970). In many cases such estimates were markedly better than the simple flow related regression estimates.

Technically demanding, but more appropriate for accurate load estimates, is the use of a flow-proportional composite sampling scheme. A recent installation in a small research basin (Keller & Strobel, 1982), which is based on weekly sampling, allows a preliminary comparison with simpler sampling methods. First results indicate that load estimates based on flow-proportional sampling are slightly lower than those based on regression with flow. The choice of the method to calculate dissolved loads depends on the aim of the study. For forecasting purposes, a method linked to the easily measured parameter of runoff and its relation to the dissolved load is desirable. However, monitoring designed to investigate the functioning of a stream or river system often employs a flow-proportional sampling scheme. The investigation of processes is also aided by measurements of other environmental parameters (e.g. temperature).

Sampling methods

Depending on the goals of the various individual projects, different sampling methods have been employed. Where more than one method was used in the same project, a comparison was made to detect possible differences in the information collected. At stations on larger rivers samples were collected continuously on a flow-proportional basis. The sampling period was generally one week, during which 1.5-3 l were accumulated from the individual 1-2 ml samples taken every few minutes. From the sampling device, the water sample flows through a tube directly to glass bottles stored in a refrigerator at 4°C. For certain studies, parallel samples were taken for heavy metal analysis, and the bottles for these contained acid for preservation. In small basins, grab sampling was used with the exception of one basin where a flow-proportional sampler has been recently installed.

Data evaluation

The information obtained from a data set is *not* independent of the evaluation method used. This has been particularly evident in the evaluation of data obtained in surface water studies, and for comparative purposes, a short overview of the most commonly used methods and the type of information they provide is given here.

Time course This is frequently the first step in plotting data, since changes in concentration as a function of time can give an indication of possible patterns in the parameter being examined. An asymmetrical sinusoidal behaviour is often observed but without correlation to the corresponding changes in waterflow, it is not apparent whether changes in concentration are related to different discharge levels, different inputs or other factors.

Average values These have the advantages of being simple and providing a rapid overview of large amounts of data. However, average values do not provide information on fluctuations, nor do they indicate if the statistic is actually representative of the system.

Cumulative distribution curves Information on the frequency of occurrence of values over the entire range observed is provided by the construction of these curves. However, this technique does not set changes in the magnitude and distribution of concentrations into the context of corresponding flow variations, and again it is not possible to determine the influence of discharge, load fluctuations or other influences on concentration values.

Correlation analysis This approach simultaneously accomplishes data reduction and gives an indication of the interdependence, though not necessarily the direction of causation, between two parameters. A strong correlation between parameters may imply similar sources or other related factors, which deserve further examination. However, if the relationship between parameters is affected by seasonal factors (e.g. temperature) there may be no detectable correlation over the period of an entire year.

Factor analysis This technique groups those parameters which have related behaviour (Davis & Zobrist, 1978) and can indicate in one analysis which factors, in addition to flow, influence concentration. If the factor scores for individual sampling dates are obtained from the analysis, the effects of seasonal changes may also be investigated.

The waterflow (Q)-concentration (c) diagram This enables the influence of flow on concentration to be directly visualized (Manczak & Florczyk, 1971). Using this relationship for regression analysis makes the tacit assumption that the independent variable (Q) exerts the main influence upon the dependent variable (c). However, if other factors play a role, there may be considerable variation in concentration which can lead to difficulties in interpretation of the relationship between Q and c (Fig.1(a)).

The flow-concentration-time (Q-c-t) diagram This "three-dimensional" relationship allows the concentration to be examined as a function of flow during the course of time, and different concentrations, related to the same discharge level occurring at different times of the year, can be readily identified. Figure 1(b) plots the data in Fig.1(a) as a moving average over four consecutive values on a Q-c-t diagram, which reveals a very marked cyclic variation in concentration with little deviation from this pattern. This indicates that the observed variation was in fact not due to random factors, but those associated with an annual periodicity. This approach has been used

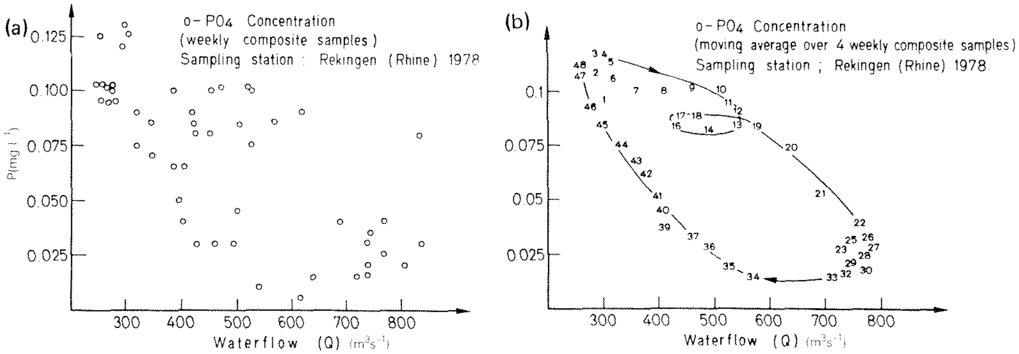

FIG.1 Concentration of o-PO_4 plotted (a) as a function of flow and (b) on a Q-c-t diagram (point 1 represents average of weeks 1-4, point 2 represents average of weeks 2-5, etc).

in the present study to investigate the behaviour of various parameters and their controlling factors in basins of difference size.

RESULTS AND INTERPRETATIONS

The study basins can be roughly divided into the three categories of small forested basins, with drainage area up to 1 km^2 and flow up to ∿ 3 m^3s^{-1}; middle sized river systems, with drainage area up to *c.* 10 000 km^2 and flow up to ∿ 400 m^3s^{-1}; and several stations along the Rhine, with flow up to ∿ 2500 m^3s^{-1}. Figure 2 shows the location of the small research basins and the stations on the main rivers in Switzerland. The characteristics of the small basins (Keller & Strobel, 1982) are given in Table 1. The differences between the categories of study basin include not only size but also a number of other factors and, in particular, the influence of anthropogenic loadings. Furthermore, the different groups have been studied for different purposes, and sampling of larger river systems, in general, has been dictated by the goals of quality standards and load trend

TABLE 1 Selected characteristics of six small hydrological research basins in the Alptal, Switzerland

	Basin:					
	3	*4*	*5*	*7*	*8*	*10*
Size (ha)	*155*	*93*	*108*	*52*	*94*	*64*
Exposure	*ESE*	*ESE*	*E*	*WNW*	*WNW*	*W*
Mean slope (%)	*41*	*27*	*39*	*65*	*38*	*30*
Forest cover (%)	*63*	*19*	*38*	*93*	*60*	*39*
Wetland (%)	*25*	*24*	*20*	*4*	*40*	*61*
Alpine pasture (%)	*12*	*57*	*42*	*3*	*-*	*-*
In operation (from-till)	*68-*	*72-*	*71-74*	*69-75*	*71-77*	*77-*

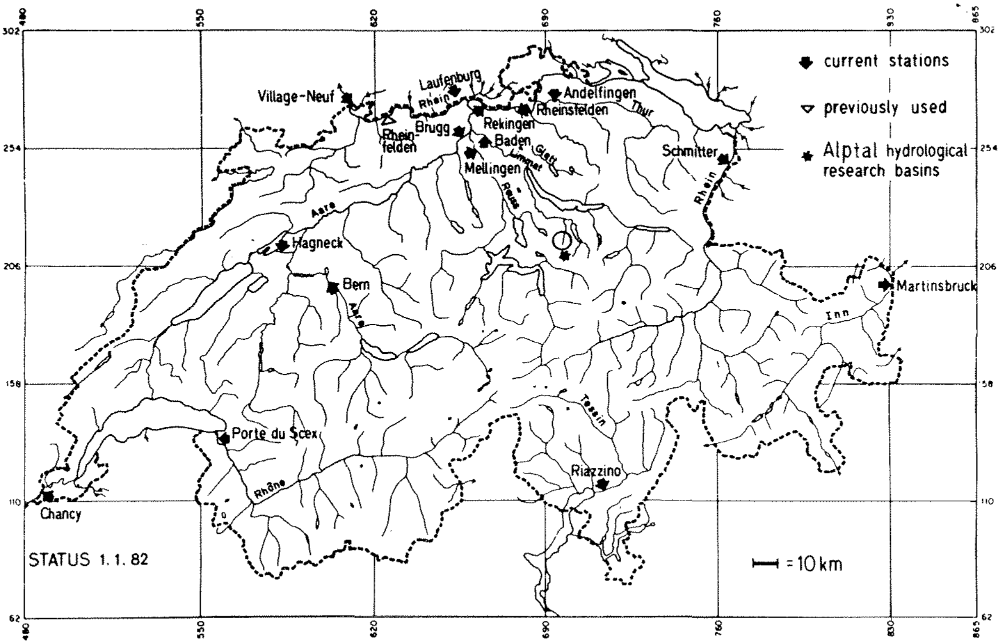

FIG.2 Location of small basin research areas and sampling stations on major Swiss rivers. (The stations indicated are part of the Swiss NADUF-Program, a national programme for long-term river studies. Selected stations are used in the present study).

analysis. Nevertheless, the type of data collected in these studies is compatible with that of the smaller basins and allows interpretation beyond these specific goals. Data analysis for large rivers has also been carried out with emphasis on quality standards, and for this purpose the role of flow as a dilution factor has been basic to data evaluation. However, construction of Q-c-t diagrams has shown that other major factors affect the behaviour of particular load or concentration parameters and cause significant variation at a particular discharge level. In general, a cyclic behaviour of concentration has been observed very clearly in larger river systems for a number of nutrients (Figs 1(b) and 3(a)) and geochemical components (Fig.3(b),5). This effect is enhanced at stations below lakes, because of the annual periodicity in stagnation and mixing of lake waters.

A cyclic behaviour can also be characteristic of the relationship between precipitation and streamflow within a basin, and Fig.4 reveals three main phases in a particular cycle. In winter, there is considerable variation in precipitation (snow) with little change in streamflow; during snowmelt, high flow results from little or no precipitation; and then a transition leads to summer and autumn conditions with obvious evapotranspiration losses. This pattern reveals an underlying seasonal influence on the varying contribution of water from rain, snowmelt and groundwater during the course of the year. Since each of these water types has a markedly different range of concentrations for geochemical components, it may be

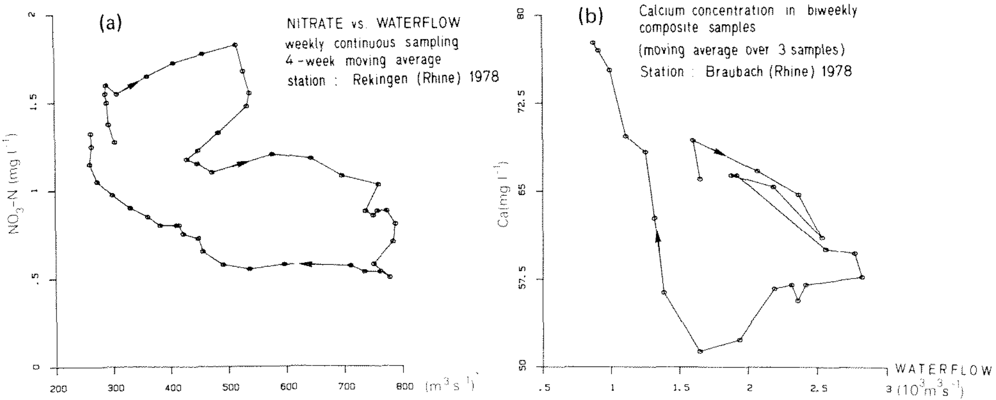

FIG.3 Concentration of (a) nitrate and (b) calcium as a function of flow.

considered a logical consequence that cyclic behaviour will also characterize the concentration of most geochemical components found in stream water. One exception is the case of sulphate, which may remain quite constant during the year. In some instances this may reflect similar sulphate concentrations in surface flow and groundwater, so that a change in source does not cause a change in concentration.

In a small basin with a significant snow contribution, the cyclic behaviour of geochemical components appears particularly affected by the melt runoff in spring, which leads to a much lower mineral content than at other times of the year when groundwater contributes a higher proportion of streamflow. This effect is also apparent in the pattern of electrical conductance (Fig.5) which reflects the different mineral content of water and thus of its source.

The relationship of load to flow (Fig.6) reveals a flattening of the cyclic pattern compared with that of concentration. The general trend is nevertheless visible, and in this small basin the sodium load

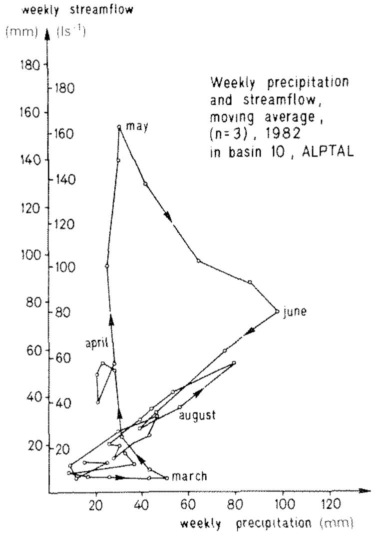

FIG.4 Relationship between precipitation and flow.

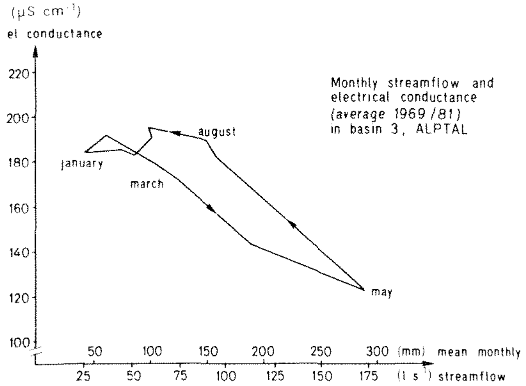

FIG.5 Electrical conductance as function of flow.

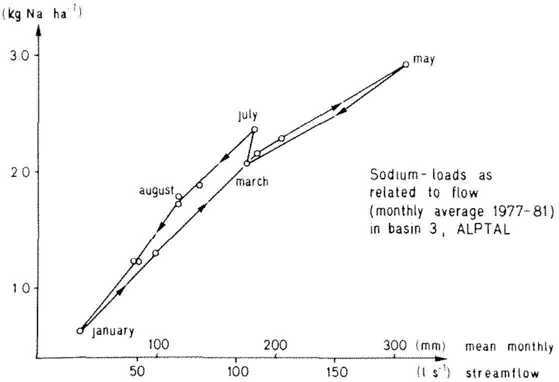

FIG.6 Sodium load as function of flow.

is lower in the spring months with melt runoff, than at the same flow levels later in the year.

Water temperature is another factor characterized by cyclic behaviour, and since it can influence solute levels, for example through the rate of nutrient consumption or the effect upon steady-state concentration, variations in water temperature may also contribute to the observed cyclic pattern of concentration. Figure 7 shows for two stations that flows of the same magnitude can have very different temperatures. Although the two basins are very different, their cyclic patterns of water temperature are very similar. It has long been observed that, in general, both temperature and flow exhibit a sinusoidal pattern in their annual fluctuations, with periodicities which are slightly out of phase, and the method of plotting adopted in Fig.7 makes this hysteresis very clear. Biological reactions, in particular, are expected to be affected by temperature, and marked differences in nitrate concentrations at the same flow level during spring and autumn (Fig.3(a)) may partly reflect temperature dependent contrasts in biological activity. Direct examination of the relationship between nitrate concentration and water temperature, reveals a strong correlation for both small and large basins (Fig.8). Very little fluctuation is apparent in this relationship for the large river, even during several years with

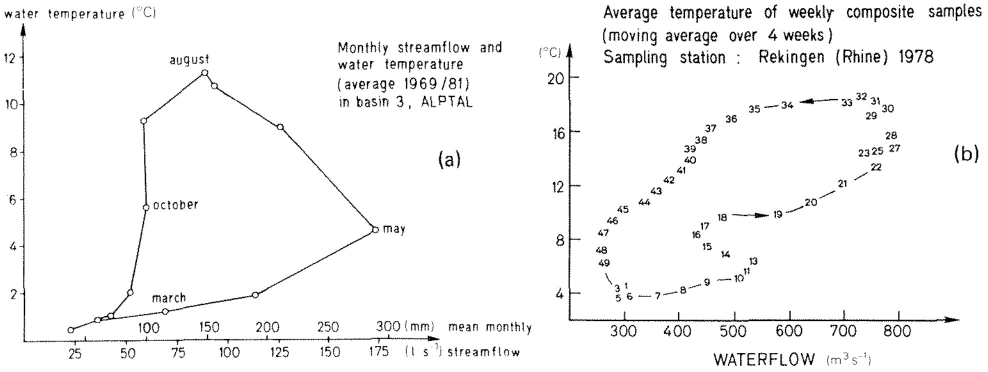

FIG.7 Relationship between water temperature and flow in (a) small and (b) large drainage basins.

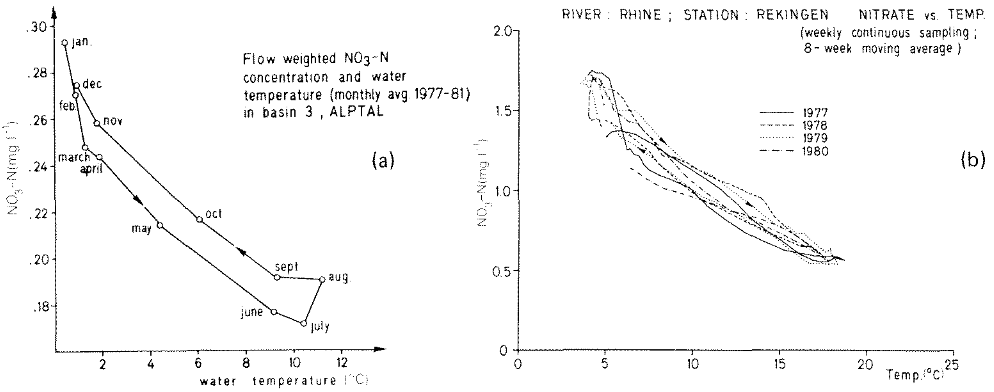

FIG.8 Concentration of nitrate as a function of temperature in (a) a small research basin and (b) a large river over four consecutive years.

varying flow patterns (Fig.8(b)).

In a small basin, nutrient loads show a partially reversed behaviour pattern compared to geochemical loads. Nutrient loads in summer and autumn reflect the occurrence of low concentrations and are considerably lower than those of spring (Fig.9), whereas the geochemical components have low loads during the spring period. The trend of nutrient loads appears to be related to an increase in biological uptake, especially by plants during the vegetation period. In waters of large basins which receive discharges from water treatment plants or are loaded with nutrients in other ways, there may be sufficient biological activity to affect nutrient consumption and to lower concentration.

The strong effect of temperature can be particularly important to the assessment of water quality since it is apparent from this study, that a reduction in the nutrient load can arise through increased biological consumption at higher temperatures. Furthermore, biomass may be precipitated out, which changes the amount of particulate matter present and, for example, influences the total-phosphorus content. Clearly, assessment of water quality must take into consideration the annual periodicity of concentration and load

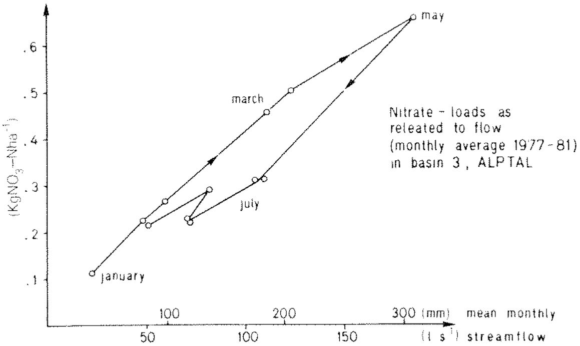

FIG.9 Nitrate load as function of flow.

behaviour, which further implies the need for sampling at various times of the year as well as at different levels of flow.

CONCLUSIONS AND FURTHER RESEARCH

A comparison of various basins has revealed that behaviour patterns of selected chemical and hydrological parameters are independent of basin size, and detection of these patterns aids in the extrapolation of data from one basin to another. Cyclical patterns of change was the main behaviour observed in the study basins. The driving mechanism was considered to be the same in small and large areas and is related to seasonal changes which are themselves of a cyclic nature (Davis, 1980).

Based on these observations, additional studies are being carried out in selected experimental basins. The aim of the work is to obtain a quantitative estimate of the water being contributed from various sources (melt runoff, surface and groundwater) during the course of the year. The effect of different hydrological regimes upon parameter behaviour is also being examined as part of a study of the River Rhine. Between Lake Constance and the Dutch border, the Rhine changes from a water course, which is supplied mainly from lake water and has high flow in summer as a result of snowmelt, to a river, which has high flow in winter due to the influence of surface runoff. Tracing this spatial and temporal change will provide further insights into the sources which contribute to runoff and how they vary both with geological and hydrological conditions and throughout the year.

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