Integrated Modelling of Runoff, Alkalinity, and pH on a Daily Basis

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Based on the experience from runoff and groundwater recharge simulation a model system has been developed for terrestrial, hydrochemical, and hydrological simulations. The system emphasizes the role of temporary or long term storage in the aquifers of a basin and, separately, accounts for each rainfall or snowmelt event from its entrance into the ground until mixing in the river system. The model is primarily intended for simulation of natural short term variations in alkalinity and pH in running waters. The hydrochemical processes are modelled in a semi-empirical way without assumption of complete hydrochemichal mass-balance. In the paper a brief hydrochemical background is given, and a model with two alternative hydrochemical sub-structures is described. Examples of daily simulations of runoff alkalinity and pH from three different basins are given.

Introduction

The use of conceptual runoff models has so far, with few exceptions, been restricted to water quantity problems. The main reason for this is the well founded uncertainty among the modellers as concerns the physical relevance of their models. As a matter of fact it has been shown that model structures of great diversity can produce almost identical runoff simulations. Terrestrial water quality modelling requires models with a more advanced description of the transport phenomena from rainfall or snowmelt to runoff in a river. The models must then not

only be based on a sound description of the runoff generation process at a point, they also have to account for the variability of these processes in the basin.

In 1982 work started at SMHI to develop a model for terrestrial water quality problems. The background is the experience from the HBV-model for runoff simulation (Bergström and Forsman 1973) and its later modification for groundwater applications (Bergström and Sandberg 1983).

The primary objective of the work is to develop a model for simulation of short term natural variations in pH in a stream, caused by variable contributions from shallow acid groundwater with short residence time and deeper groundwater of high alkalinity. No attempt is made to model the long term acidfication of the system or the effect of variations in the atmospheric deposition.

Modelling Philosophy

Christophersen and Wright (1981) applied the Birkenes-Model to acidified waters in Norway, and Grip used the same model in one small research basin in Sweden (Grip 1982). Further attempts to model the impact of acid rain on the hydrological system have been made by Schnoor, Palmer, and Glass (1984) and Chen et al. (1984). These applications represent a range of relatively sophisticated chemical model structures imposed on simplified hydrological ones.

Knowing that the residence-time and the geochemical environment of water is of dominating importance for the hydrochemical response of a basin, we decided to start with a rather advanced, distributed model structure for the water balance in combination with simplified semi-empirical, hydrochemical subroutines. The strive towards simplicity has made it necessary to accept a certain amount of empiricism in the work, which means that some model parameters will have to be estimated by calibration. This calibration is combined with a sensitivity analysis in order to check the impact of each parameter on the simulation.

The empirical approach also means that no attempt is made to model the complete budget of the major ions in the system. We concentrate on simulation of some selected hydrochemical properties. In this paper, the selection is pH and alkalinity in the running water.

In most conceptual runoff models the residence time of water is of little interest if only the hydrograph is reproduced with acceptable precision. The response function is therefore not feasible for hydrochemical applications, unless complete mixing can be assumed. Our approach has been to avoid this assumption by keeping track of the volume and hydrochemical status of each pulse of snowmelt or rainfall through the whole model system. This is actually the origin of the name we chose, the PULSE model.

Initial model runs soon revealed that the model would be very sensitive to the water balance simulation. In order to avoid confusion as to whether the hydro-

chemical simulation suffered from poor agreement between computed and observed runoff, it was decided to update the water balance part of the model prior to the simulation of hydrochemistry. After the water balance model had been calibrated to optimum parameter values, the updating was performed by adjustments of the meteorological input data on some strategic dates.

The Water Balance Model

The hydrological snow accumulation and melt routine of the water balance model is identical to that of the HBV-model (Bergström 1975), and so is the modelling of the unsaturated zone with the only exception that capillary rise from the saturated to the unsaturated zone is considered.

The saturated zone is modelled according to the modifications introduced when applying the HBV-model to groundwater observations (Bergström and Sandberg 1983). This means that there is no limiting percolation capacity within the time step (24 hours), and quicker runoff can only occur when the groundwater level is high.

In the saturated zone, each pulse of snowmelt or rainfall is treated individually without mixing. These pulses are the basic framework for the hydrochemical subroutines.

Each pulse drains individually by a recession coefficient which is specific for its level in the saturated zone as illustrated in Fig. 1. The effect of this method is that
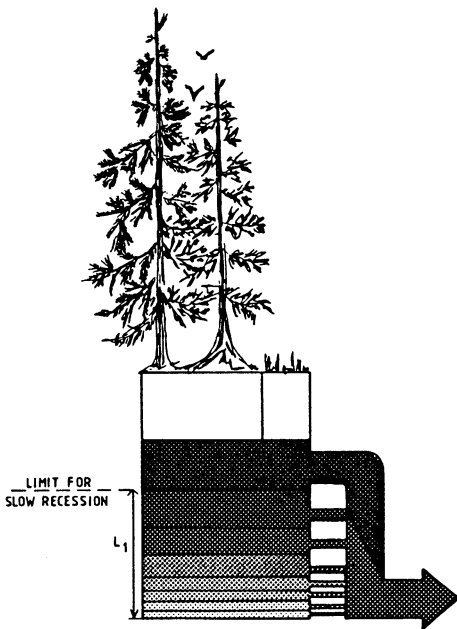

LIMIT FOR
SLOW RECESSION

L_1

Fig. 1.
Schematic presentation of the final drainage routine of an aquifer in the PULSE-model with individual recession of each pulse.

1) Esker aquifer with high storage capacity.
2) Till aquifer with intermediate storage capacity.
3) Till aquifer with high groundwater levels and low storage capacity.
4) Exposed bedrock or thin soil cover with low storage capacity.
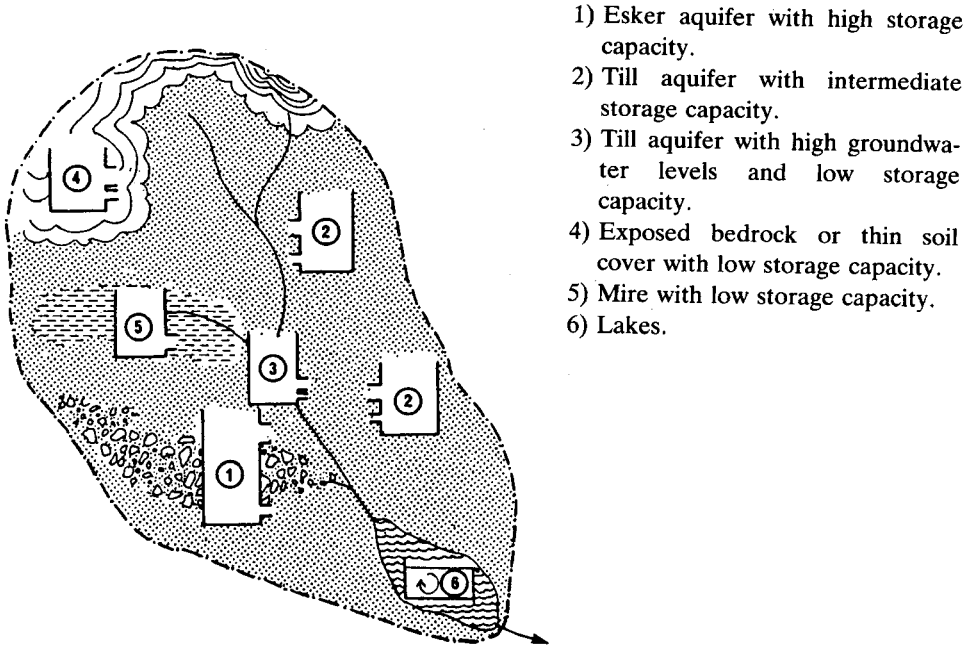5) Mire with low storage capacity.
6) Lakes.

Fig. 2. Principal description of a possible classification of aquifers in the PULSE-model. In this example the figures have the above representation.

the age of a pulse will increase with increasing depth in the aquifer and that the volume of water in each pulse will decrease exponentially with time. Shallow groundwater will further drain faster than deeper groundwater and thus dominate during a flood event.

The process described above refers to one single aquifer. The type of drainage basin, which we intend to model, consists of a large number of aquifers with variable storage characteristics, all linked together in a complex mosaic. We have therefore introduced a classification of aquifers by distribution of the threshold value L_1 (Fig. 1) of the saturated zone. The interpretation is that high values of L_1 are representing aquifers of high storage capacity, for example glaciofluvial deposits. Intermediate L_1 values represent most of the till aquifers, and low L_1 values are representative for thin soil covers, svamp areas, and areas with a groundwater table near the ground surface. The idea is illustrated in Fig. 2.

The present computer code admits the use of 6 classes of aquifers. Extensive test-runs have shown that only little is gained, if the number is increased to the cost of increasing computer time and memory requirements. It is, however, possible that the degree of distribution will have to be increased when the model is applied to larger and more heterogeneous basins. So far the areal extent of

various classes of aquifers in a basin have been identified from inspections of maps only.

The lakes in the basins are modelled separately by a single linear reservoir, if they are of significant volume. Even small water bodies can be very important for the response of the model during a low flow period. This makes the depth of the lakes and important factor, which unfortunately often has to be estimated in a rather crude manner.

Hydrochemical Model Procedures

In the model no account is taken for the acidity of the precipitation, except for the direct precipitation on water surfaces. Instead it is assumed that the water composition will be adjusted by cation exchange in the humic layer, and that a considerable water exchange occurs as the water passes through the unsaturated zone. This will level out the effect of temporary variations in the composition of the precipitation and also the variations in the dry deposition. The pH-value in the humic layer in podzolic soils is lower than in the precipitation, often below pH 4 in non-calcareous areas (SNV 1981), and in the model an average, fixed, pH-value is used for the water passing through the organic horizon.

As the water percolates through the soil, the pH-value will successively rise due to cation exchange and weathering processes. Cation exchange is a rapid process compared to weathering. As the hydrogen ion concentration increases, some of the hydrogen ions will substitute base cations, primarily calcium and magnesium on the soil particles. In this way the pH of the leachate will be kept up and the water will have an increased content of calcium and magnesium ions. As the model is only intended for the simulation of short-term variations no account has been taken for the possible long-term depletion of base cations in the soil.

In general the neutralization due to weathering is most intensive when the water is most acid. In the model the rate of neutralization is therefore successively lowered with residence time.

The weathering is further enhanced by the high content of carbon dioxide in the soil atmosphere. The carbon dioxide, originating mainly from the decay of organic matter in the soil, can be dissolved in the soil water giving carbonic acid. Carbonic acid is consumed in the weathering reactions and bicarbonate ions and base cations are produced. The seasonal variation of carbon dioxide in the soil atmosphere is the justification for the introduction of a seasonal variation in the neutralization procedure of the model.

The acid neutralizing capacity of a water is usually determined as alkalinity by acidimetric titration to a pH-value of 5.4. In most natural waters the alkalinity is determined primarily by the carbonate system
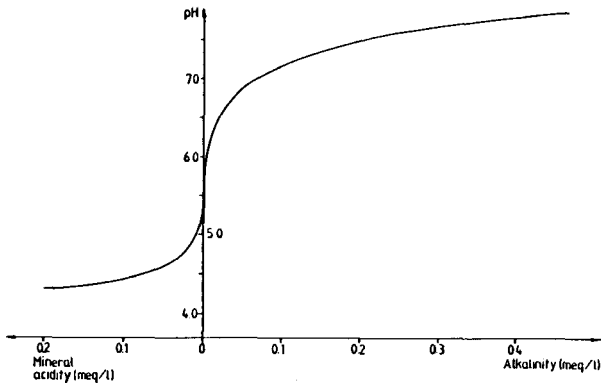
Fig. 3. Principal sketch of the relation between modelled alkalinity/acidity and pH at the outlet of a basin as modelled by the PULSE-model.

$$\texttt{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

The partial pressure of carbon dioxide determines the concentration of the carbonate species at different pH-levels and therefore also the pH-alkalinity relationship. Below the titration endpoint hydrogen ions become more important than the bicarbonate and negative values for the alkalinity, mineral acidity, results. For the low pH-values it is necessary to include the contribution to the mineral acidity caused by the hydrolysis of aluminium.

In coloured waters, i.e. in the two southern test areas, probably also organic acids should be considered (see for example Henriksen and Seip 1980). This contribution is at present ignored due to lack of information on organic carbon.

Alkalinity is a capacity variable which easily can be used for calculating the effect of mixing of waters, and it is not influenced by changes in carbon dioxide pressure. It is therefore the basis for the hydrochemical subroutines with a fixed curve relating alkalinity to pH as a final step in the model (Fig. 3). In this way even small amounts of deeper groundwater with high alkalinity can give a substantial increase in the pH when the waters mix in the river system.

Two fundamentally different model aproaches to neutralization of the system have been attempted. One is based on the concept of residence time of each pulse of snowmelt or rain and is named PULSE-1; the other, PULSE-2, is based on the level of each pulse or on the geochemical environment, from which it is drained. In both model versions, each pulse of rain or snowmelt is given a constant initial acidity or alkalinity, ALK_{min} (corresponding to a fixed pH-value), as it enters into the ground.

PULSE-1

In the PULSE-1 version, the residence time in the saturated zone of the model is governing neutralization of the pulse according to Eq. (1)

$$\text{ALK}(t) = \text{ALK}(t-1) + C_1\,(\text{ALK}(\infty) - \text{ALK}(t-1)) \qquad (1)$$

where

$\quad$ ALK(t) $\;-$ computed alkalinity (or acidity, if negative) at time t,
$\quad$ ALK(∞)$-$ maximum modelled alkalinity ($t \rightarrow \infty$),
$\quad C_1 \qquad -$ empirical coefficient.

The CO_2-pressure in the soil has a seasonal co-variation with humidity and temperature. This effect on weathering mechanisms in the ground is accounted for by linking the C_1 coefficient to the computed actual evapotranspiration according to Eq. (2)

$$C_1(t) = C_0 + \frac{Ea(t)}{Ep_{max}}\,C_2 \qquad (2)$$

where

$\quad C_1(t) \quad -$ value of C_1 at time t
$\quad C_0 \qquad -$ minimum value of C_1 (in winter)
$\quad C_2 \qquad -$ maximum increase of C_1 (in summer)
$\quad Ea(t) \quad -$ actual computed evapotranspiration at time t
$\quad Ep_{max} \;-$ maximum mean monthly potential evapotranspiration in a year (normally June).

Eqs. (1) and (2) mean that the alkalinity of a given pulse of snowmelt or rain will approach ALK(∞) exponentially as long as the water remains in the modelled aquifer.

This procedure, in combination with the water balance model, will produce runoff water of a higher acidity during a flow situation than during a dry spell. Neutralization will be slower in winter than in summer, as the value of C_1 is lower. The model will thus give more acid runoff in winter than in summer, provided all other hydrological conditions are identical.

The concept of residence time of the model has to be interpreted with care, since we only consider water stored from full saturation down to field capacity. If harder bounded water in the saturated zone is considered, the residence time will, of course, be longer. It is our belief, however, that this discrepancy is accounted for implicitly by the calibration of C_0 and C_2, but it leads to the consequence that the physical meaning of these two parameters is somewhat diffuse.

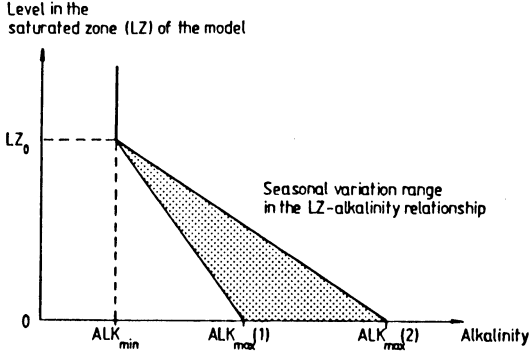Level in the
saturated zone (LZ) of the model

Fig. 4. Principal relationship between the level (LZ) and alkalinity/acidity in the saturated
zone of the PULSE-2 model.

PULSE-2

The PULSE-2 version is based on the assumption that the passage through the
unsaturated zone is more important for neutralization than is the residence time in
the saturated zone.

Instead of using the model residence time as driving variable for neutralization,
the PULSE-2 version uses the location or depth in the model aquifer, from where
the water drains, as an indication of alkalinity/acidity according to Fig. 4. As
indicated in the figure, a seasonal component of the rate of weathering, again
governed by the computed actual evaporation is included in the model, so that the
maximum alkalinity in an aquifer is $ALK_{max}(1)$ in winter and $ALK_{max}(2)$ in
summer.

The variation between these is expressed by

$$ALK_{max}(t) = ALK_{max}(1) + \frac{Ea(t)}{Ep_{max}} (ALK_{max}(2) - ALK_{max}(1)) \qquad (3)$$

where

$ALK_{max}(t)$ – maximum alkalinity in the bottom of the model aquifer at time t,
$ALK_{max}(1)$ – maximum alkalinity in the bottom of the model aquifer in winter
$\qquad\qquad (Ea(t) = 0)$,
$ALK_{max}(2)$ – maximum alkalinity in the bottom of the model aquifer in summer
$\qquad\qquad (Ea(t) = Ep_{max})$,
$Ea(t)$ $\qquad$ – actual computed evapotranspiration at time t,
Ep_{max} $\qquad$ – maximum mean monthly potential evapotranspiration in a year
$\qquad\qquad$ (normally June).

Because of the strong correlation between modelled residence time and modelled

location, the PULSE-1 and PULSE-2 approaches result in very similar dynamics of the hydrochemical output of the system. The applications will, however, show some significant differences under certain hydrological conditions, in particular when a flow starts after a long dry period. Both models have four main coefficients to calibrate in the hydrochemical substructure, C_0, C_2, ALK_{min}, and $ALK(\infty)$ in PULSE-1, and LZ_0, ALK_{min}, $ALK_{max}(1)$, and $ALK_{max}(2)$ in PULSE-2.

Both PULSE-1 and 2 model acidity or alkalinity in the water that leaves various types of aquifers. Down the river system these contributions are added up, and a mixed alkalinity is computed. The pH-value of rainfall on the lakes is transformed into acidity and is thus the only direct effect, in the model, of short-term variations in atmospheric fallout. Finally the alkalinity or acidity at the outlet of a basin is transformed to pH according to the relation in Fig. 3. This means that the model will produce daily computations of runoff, alkalinity and pH simultaneously.

Basins for Model Verification

Three test basins have so far been used for verification of the model. Their locations are shown in Fig. 5, and basin characteristics are given in Table 1.

The basins were chosen for being fairly well documented with hydrological and hydrochemical records of acceptable sampling frequency, and for having different pH-ranges.

The topography in the two southern test areas is rather even, while the northern area is situated in the high mountains. There are only small parts of exposed

Table 1 – Characteristics of the basins for model verification.

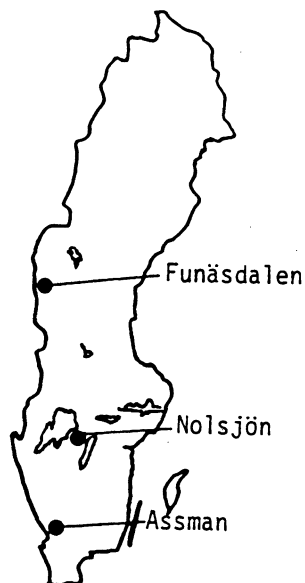|	Nolsjön	Assman	Funäs-dalen
Drainage area (km^2)	18.2	55	340
Lakes (%)	1.5	1.5	0.9
Mire (%)	14	65	2
Arable land (%)	4	–	–
Elevation range (m.a.s.l.)	125-175	150-200	550-1600
Area above timberline (%)	–	–	50
Predominant vegetation cover (below timberline)	Coniferous forest	Coniferous forest	Coniferous forest
Predominant soil cover	Till	Till and peat	Till
No. precipitation stations	2	4	2
No. air temperature stations	1	2	1
pH-range in runoff	4.3-5.8	4.3-7.1	6.3-8.0

Fig. 5. Geographical location of the test basins.

bedrock within the test areas. In the Nolsjön and Assman areas weathering resistant granites and gneisses dominates. In Funäsdalen the bedrock, consisting of schists and also some limestone, is more easily weathered.

Data Base

The model is run on a daily basis with daily totals of precipitation and daily mean air temperature as input together with monthly standard values (30 years means) of potential evapotranspiration (Wallén 1966).

Verification is an essential part of model development, in particular if the model includes parameters which have to be estimated by calibration. It was therefore decided, parallel to the modelling work, to increase the hydrochemical sampling frequency in the Nolsjön research basin from one sample per month to one sample per week or day depending on the hydrological situation.

pH of precipitation, which in the model has direct effect on the lakes only, are normally from monthly total precipitation observations. For the intense period in the Nolsjön basin higher resolution in time is used.

As the model is calibrated and updated against runoff data, these may therefore, to some extent, be considered as input to the hydrochemical simulations.

Sampling of pH-data is a critical procedure. Differences are often observed, if the samples are analyzed in field or in a laboratory, or if the analyses routines are
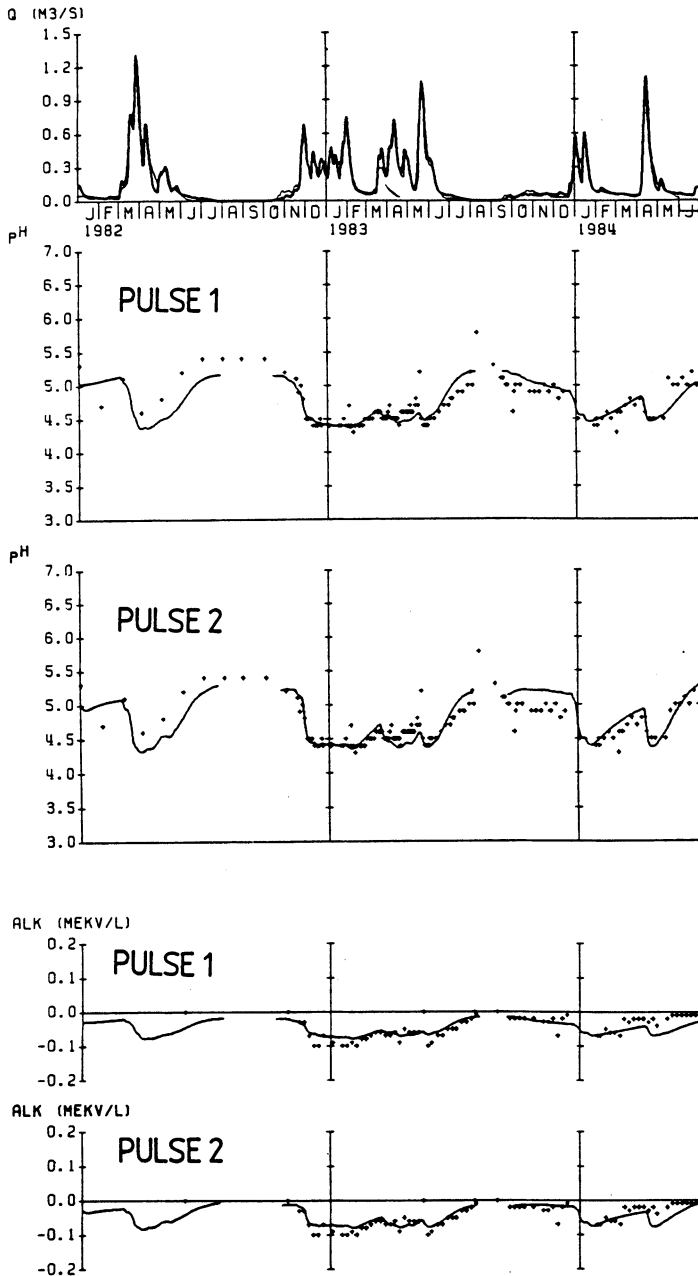
Fig. 6. Simulation of runoff (updated), alkalinity, and pH by the PULSE-1 and PULSE-2 models in the Nolsjön basin. Calibration period. (Thick line = computed runoff, thin line = observed runoff, dots = observed hydrochemistry.)
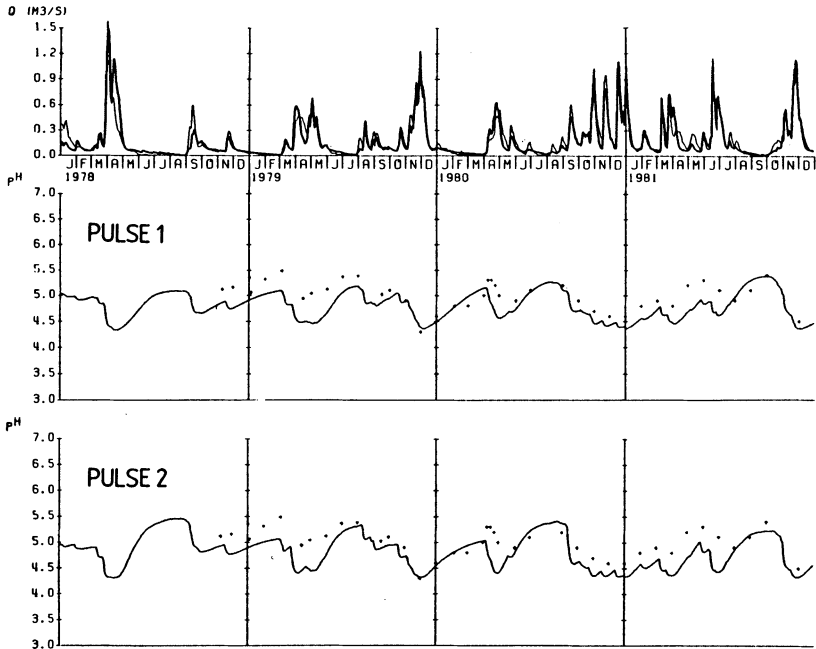
Fig. 7. Simulation of runoff (updated) and pH by the PULSE-1 and Pulse-2 models in the Nolsjön basin. Independent test period. (Thick line = computed runoff, thin line = observed runoff, dots ≡ observed hydrochemistry.)

modified during the period of observation. We have tried to keep the routines unchanged rather than to use the most appropriate method in order to maintain a homogeneous record. This means that the water has been analyzed in laboratory. Comparisons with field measurements in the Nolsjön basin show a systematic deviation in the order of 0.2 pH units. Deviations of this type can be accounted for by a shift in the pH-alkalinity relationship in the hydrochemical subroutine of the model, if a disagreement is obvious.

Results from the Nolsjön Basin

The two model versions were calibrated for the intensively monitored period in the Nolsjön basin. The resulting curves of updated runoff, alkalinity/acidity, and pH are shown in Fig. 6. The corresponding curves for the less frequently sampled test period are shown in Fig. 7. As can be seen, the general behaviour of PULSE-1 and PULSE-2 are similar. As the models are calibrated by a manual procedure based on visual inspection of the graphs, some of the differences between the model versions can, of course, be attributed to inconsistent calibration.
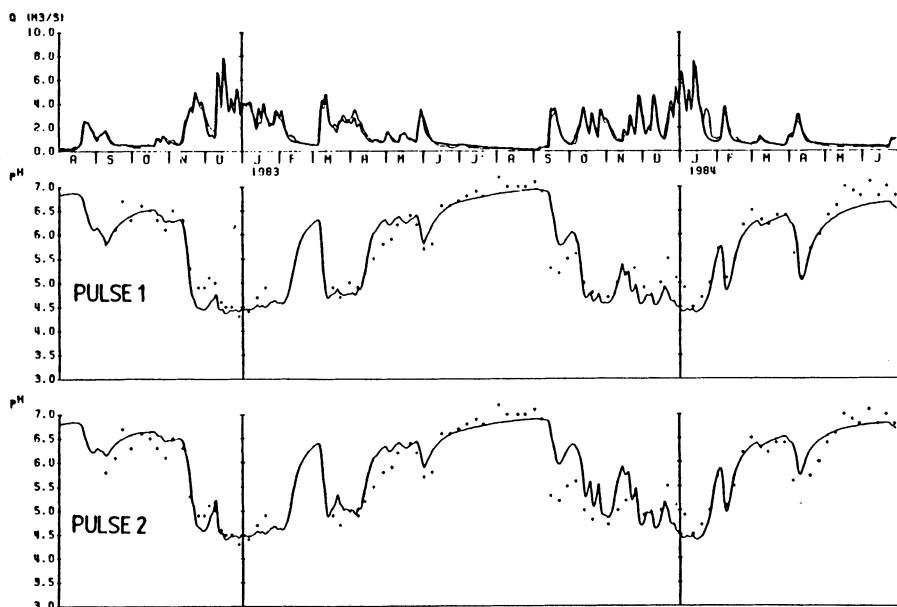
Fig. 8. Simulation of runoff (updated) and pH by the PULSE-1 and PULSE-2 models in the Asmann basin. Calibration period. (Thick line ≡ computed runoff, thin line ≡ observed runoff, dots ≡ observed hydrochemistry.)

Results from the Assman Basin

The data records for the Assman basin were not considered long enough for split-sample calibration, and no data were available on alkalinity/acidity. In Fig. 8 is therefore only shown a calibration period of updated runoff and pH for the two model versions. As in the Nolsjön basin, there is little difference between the general behaviour of the two models.

Results from the Funäsdalen Basin

As in the Assman basin, no verification against measured alkalinity/acidity was made in Funäsdalen. Data for the period 1974-1982 were used for calibration of the models, and the years 1967-1973 were used as independent test periods. The three last years of the test period are shown in Fig. 9.

In the Funäsdalen basin, the difference between the two model versions showed up more clearly than in Nolsjön and Assman. In particular during the midwinter melt period in 1973 the PULSE-1 simulation collapses due to the complete replacement of water in the model aquifers.
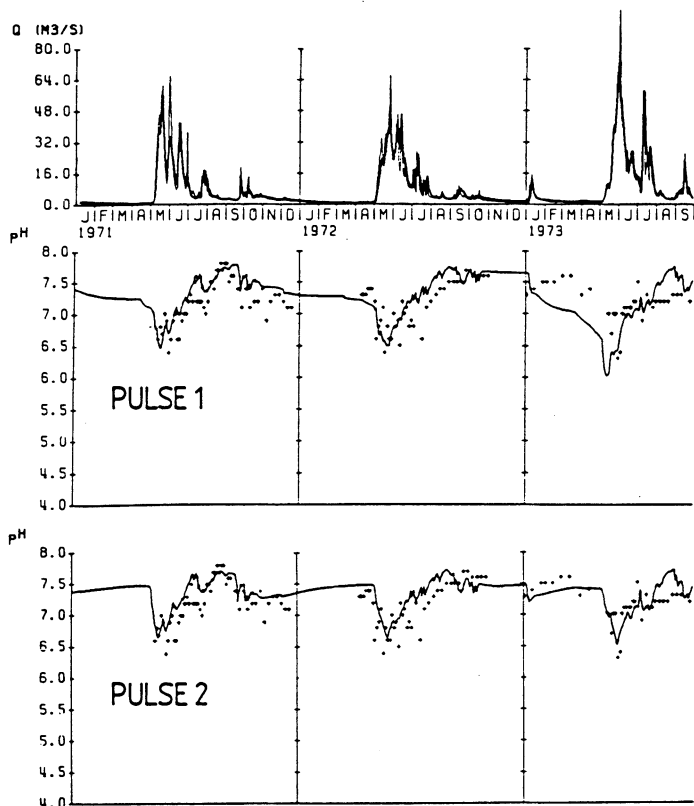
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Fig. 9. Simulation of runoff (updated) and pH by the PULSE-1 and PULSE-2 models in the Funäsdalen basin. Part of the independent test period. (Thick line = computed runoff, thin line = observed runoff, dots = observed hydrochemistry.)

Sensitivity of the Models

In addition to the model parameters of the water balance model the hydrochemical substructures of PULSE-1 and PULSE-2 have four parameters to calibrate. Some of these show strong interaction with each other, but they also interact with the water balance parameters. As a matter of fact, we have experienced that changes of the water balance parameters, which have negligible effect on the simulated runoff, may strongly effect the simulated alkalinity and pH. The effect of changes in the water balance parameters can often be compensated for by recalibration of the hydrochemical parameters. Against this background it is important to consider the hydrochemical parameters as truly empirical and specific for each water balance calibration, and much more experience from different basins is needed until any attempt to generalize them can be made.

Discussion and Conclusions

The results by the two models have shown that a major part of the natural short term variability of pH in running water can be explained by temporary variations in the hydrological situation. The dynamics of the models are governed by simplified hydrochemical subroutines with a few coefficients which are found by model calibration for a given basin. This means that the models can be used as a reference in order to detect long term changes in the acid status of a river from short term natural variations. Due to the simplified hydrochemical assumptions, in particular in the unsaturated zone, and since no hydrochemical mass-balance is considered, they are not feasable for prediction of effects of changes in the acid load on a basin. They are therefore not directly comparable with the models by for example Christophersen and Wright (1982) or Chen et al. (1984). On the other hand the PULSE-model approach can be used in a large variety of rivers, if only hydrological data and pH are available.

The results of hydrochemical models of this type are very sensitive to the calibration of the water balance model. This means that the empirical hydrochemical coefficients of the model also are compensating for incomplete hydrological descriptions of the system and therefore are very difficult to generalize. This further means that at present a record on hydrological and hydrochemical data is essential for parameter estimation. In the future independent assessments of the hydrochemical model parameters is an important task.

The applications of the PULSE-1 and PULSE-2 concepts show great similarities due to the strong correlation between model residence-time and modelled location of each pulse of snowmelt or rainfall. We feel that PULSE-2 is more geochemically realistic. It also performs better under some well specified conditions. Therefore this version, or a combination of the two, will probably be the basis for future research and applications.

The seasonal variation of the neutralization of acid rain has been the subject of intense discussions within the group. We have so far accepted the hypothesis that it can be explained by seasonal variations in the CO_2-pressure of the soil atmosphere, but there may be other explanations. One is limnological processes, as all basins have lakes. The modelling of a small basin without lakes or rivers has high priority in future work.

man basin by Ingvar Nilsson at the Halmstad municipality.

All other data are from the official networks of the SMHI. The project has been financed jointly by the Swedish National Environment Protection Board, the Swedish Natural Science Research Council and the SMHI.

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