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A HYDROGEOLOGICAL STUDY IN THE BASIN OF GULP CREEK A RECONNAISSANCE IN A SMALL CATCHMENT AREA

PART 3: CHEMISTRY OF SURFACE AND GROUND WATER

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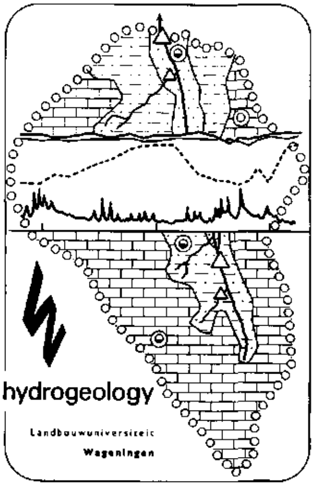

CIP-gegevens

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ABSTRACT

This paper discusses the chemistry of surface and ground water in the basin of Gulp creek. It is the fourth of a series of reports dealing with the results of hydrogeological studies carried out within the framework of a trainingproject for students of the Agricultural University of Wageningen; the study area is located in the southeastern part of the Netherlands and adjacent Belgium.

Primarily, the composition of the natural water in relation to the lithology has been studied; in this way the adverse effects on natural water composition by activities of man can be detected.

During the extended period of sampling, between 1975 and 1985, the effects of temporal variations in water composition and their meaning and significance in terms of aquifer characteristics could be recognized. The temporal variations illustrate the normal seasonal effects as well as the behaviour of the aquifer system during and after a period of severe drought (1975 and 1976). The variations in concentration and flux of individual ions made it possible to distinguish the dynamic interrelationship between the flow types and flow routes of the water passing through the basin. During the wet season interflow along the hillslopes was found to be important in flushing pollutants (e.g. nitrate) out of the regolith towards the stream.

A new rectangular diagram was introduced and was found most useful for plotting several entire water analyses; it is easy to read and it shows proportional as well as absolute values.

1 INTRODUCTION

The Gulp basin forms part of a dissected plateau landscape, that is located in the southeastern part of the Netherlands and adjacent Belgium. Gulp creek is a tributary of the river Geul, which in its turn debouches into the Meuse river (Fig. 1). Geologically, the area of investigation is situated near the northern margin of the Ardennes upland, where the Hercynian fold belt dips into the subsoil beneath a subhorizontal cover that consists of mainly Upper-Cretaceous

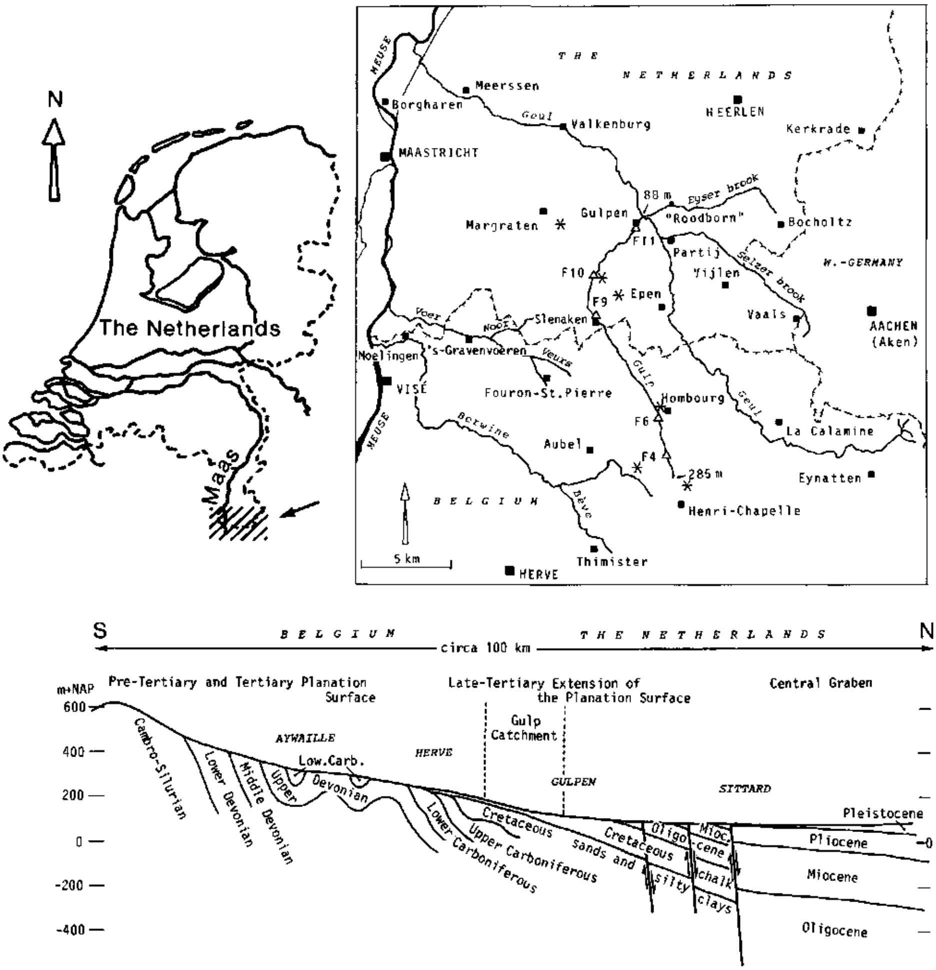

FIG. 1. Location of the study area with surroundings and some gauging sites for discharge (△) and for precipitation (✳); the S to N longitudinal profile depicts the geological situation.

deposits. The consolidated Paleozoic rocks thus underlie the basin and are considered to form the impermeable base of the groundwater flow system in the overlying formations. This paper expands upon three earlier reports to which reference is recommended (Nota and van de Weerd, 1978, 1980; Nota and Bakker, 1983); it discusses the relations between water chemistry, basin geology and flow systems.

The water samples were analyzed for calcium, magnesium, sodium, potassium, bicarbonate, carbonate, sulfate, chloride, nitrate and for non ionized silica (H_4SiO_4). The pH, the specific conductivity (Ec) and the temperature were measured in the field as well as in the laboratory. Chemical equilibrium calculations were made on the analytical data or on the mean values, leading to a.o. theoretical pH values. Precipitation was measured with the aid of a pluviograph and samples for chemical analysis were taken at regular intervals.

The analytic procedures adopted were the following:
for Ca^{2+}, Mg^{2+} – atomic absorption; for Na^+, K^+ – atomic emission; for HCO_3^-, CO_3^{2-} – colorimetric titration; for SO_4^{2-}, Cl^- and NO_3^- – ion chromatography; for H_4SiO_4 – spectrophotometry. The analyses have been carried out in the chemistry laboratory of the Department of Soil Science of the Agricultural University of Wageningen. Throughout this report chemical compositions of the water are given as millimoles per litre, or as milligrams per litre (mg/l); for ionic species millimoles refer to millimoles of unit charge – formerly denoted as milliequivalents.

During the period of sampling – between 1975 and 1985 – some 1000 samples of surface water and ground water have been analyzed. Surface water and ground water were sampled at standard locations every month and every second month respectively. The samples were stored in 500 ml polyethylene bottles filled to the top; a few drops of chloroform were added as growth inhibitor to prevent algal and microbial growth within the bottle. During transportation from the field to the laboratory – a distance of about 200 kms – the samples were kept in a cool box. The laboratory analysis started in the morning of the day after sampling.

It is known that water from samples collected from ground water or obtained from springs or surface water becomes unstable in as much as the solubility of carbon dioxide changes with temperature and pressure and because the water sample is no longer in contact with its hydrogeological environment (Davis and de Wiest, 1967; Wallick, 1977). In order to evaluate the probable magnitude of such changes, a number of selected samples were analyzed in the field as well as in the laboratory. The samples were collected through the four seasons of the year, in October, December, March and June. The samples were analyzed in the field for pH, temperature, conductivity, HCO_3^- and CO_3^{2-}.

In the laboratory these samples were analyzed for Ca^{2+}, HCO_3^- and CO_3^{2-}; Ca^{2+} was also determined from an acidified sample. In all cases analyses were carried out on filtered samples as well as non-filtered samples. Some of the test samples were also analysed after having been vigorously stirred for some hours.

Altogether, the result of this comparative investigation was that the differences between the outcome of the various analytical procedures were only small and not significant. Differences between field pH values and laboratory values were not consistent, usually not more than 0.2 pH unit and often practically the same value was found. Conductivity differences were in most cases not more than about 30 μS/cm. Calcium determinations showed deviations of about 2%, while bicarbonate and carbonate differ about 1 to 2% respectively. Within the scope of this study these data were considered to indicate that no major changes in sample composition have occurred between the field and the laboratory before the samples were analyzed. It did appear however, that the time between collection and subsequent laboratory analysis should be as short as possible to minimize the effect of processes that can alter the original state of chemical equilibrium.

2 FRAMEWORK AND CLIMATE

The *Gulp basin* is one of the stream networks that drain the dissected plateau landscape in the southeastern part of the Netherlands. This catchment was selected for a hydrogeological study primarily to serve as a training facility for students and secondly to obtain an insight into the major characteristics of the water movement through a dissected plateau with pronounced relief which consists of a relatively permeable Upper-Cretaceous sequence underlain by an impermeable base of Paleozoic bedrock.

The total surface area of the basin of Gulp creek is about 4600 ha, the length of the valley is approximately 18 km, while the maximum width between the topographic divides is about 4 km. The cross profile of the valley is asymmetrical (Figs. 2 and 3). The steepness of the eastern slope amounts to about 17%, while the more gentle western slope averages 5%. Permanent pasture covers 90% of the area. The catchment begins as a dry valley at about 357 m above sea level, just north of Henri-Chapelle in Belgium and carries surface water as a perennial stream from around 285 m. The average discharge in the upper reach measured at gauging station F6 (730 ha) near Hombourg amounts to 40 l/s., the average discharge for 1981 and 1982, measured at F11 in the village of Gulpen (the Netherlands, not far from the point where Gulp creek joins the Geul) was found to be about 500 l/s.

The geological framework, depicted in Fig. 2, shows that the contiguous catchments of the *Geul* and *Berwine* have different stream networks, are more deeply incised and have cut into the Paleozoic bedrock over large areas; in general the *Gulp* stream has incised only the subhorizontal Upper-Cretaceous formations that cover discordantly the folded Paleozoic basement. The Upper-Cretaceous formations overlying the rocks of Paleozoic age are composed of a sequence of fine grained sands, silty clay and chalk. Tilting and faulting as a result of uneven Cenozoic uplifting and the evolution of the valley of the Meuse River have largely controlled the development of the various tributary drainage systems. The differences in basin geology are well reflected in the chemistry of their surface waters (Table 1). The Gulp stream carries higher concentrations of calcium, bicarbonate and silica (Fig. 4), whereas the Geul and Berwine samples show higher sulfate and magnesium values. Although a part of the dissolved constituents may be derived from non-lithologic sources, generally, these differences can be regarded as a result of differences in composition of the rocks through which the waters in the various catchments move.

The Gulp stream network typically reflects a catchment area, in which chalk is the dominant rock type that is drained, whereas the composition of the Berwine and Geul samples reflects also the contribution of extensive outcrops of Paleozoic sandstones and shales, as well as some dolomites in particular for the Geul catchment. Near-surface coalmining activities from earlier days still affect the streamwater of the Berwine that thus has become contaminated with

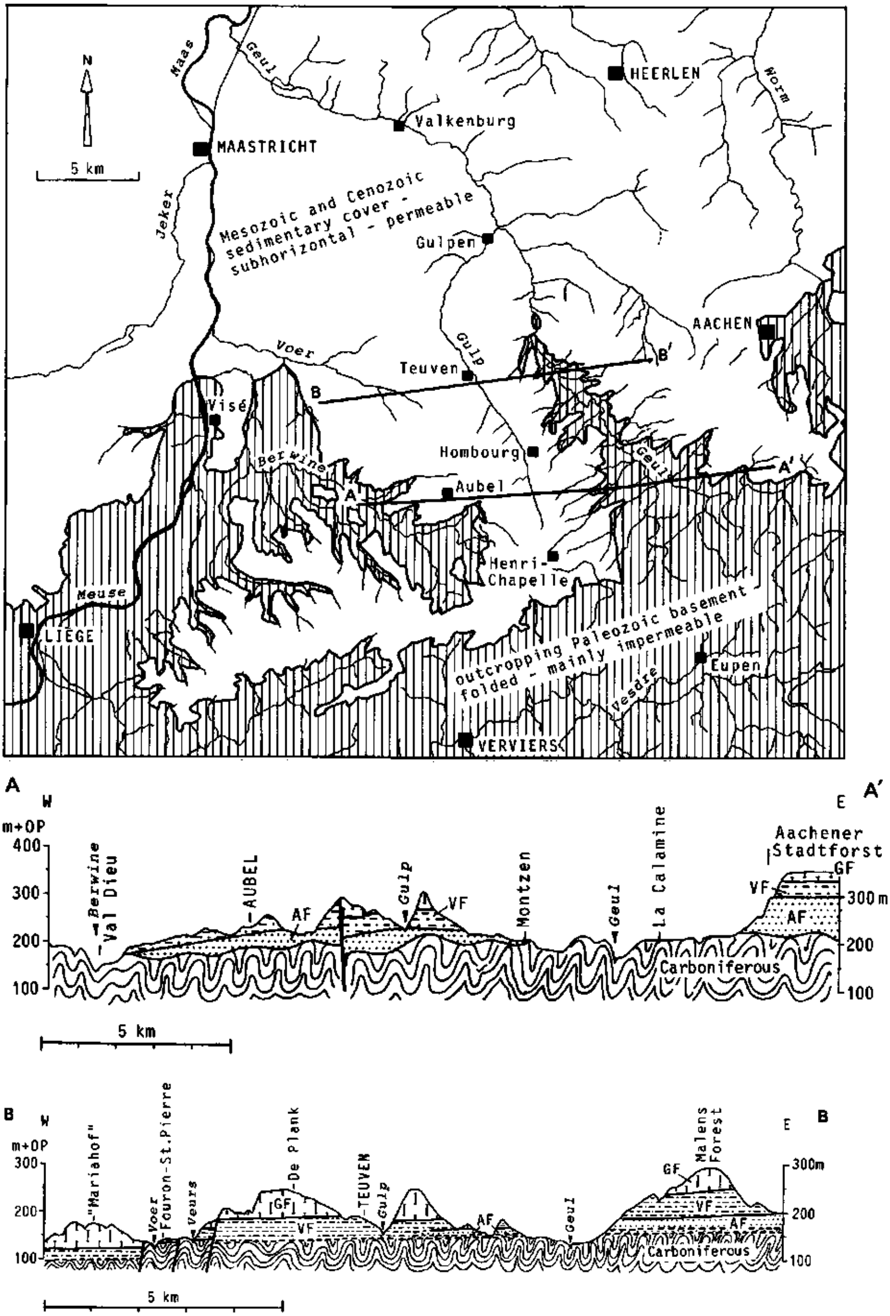

FIG. 2. Geological framework of the Gulp basin and surroundings. For stratigraphic legend see figure 3.
GF = Gulpen Formation, VF = Vaals Formation, AF = Aken Formation, OP = Ostende Peil.

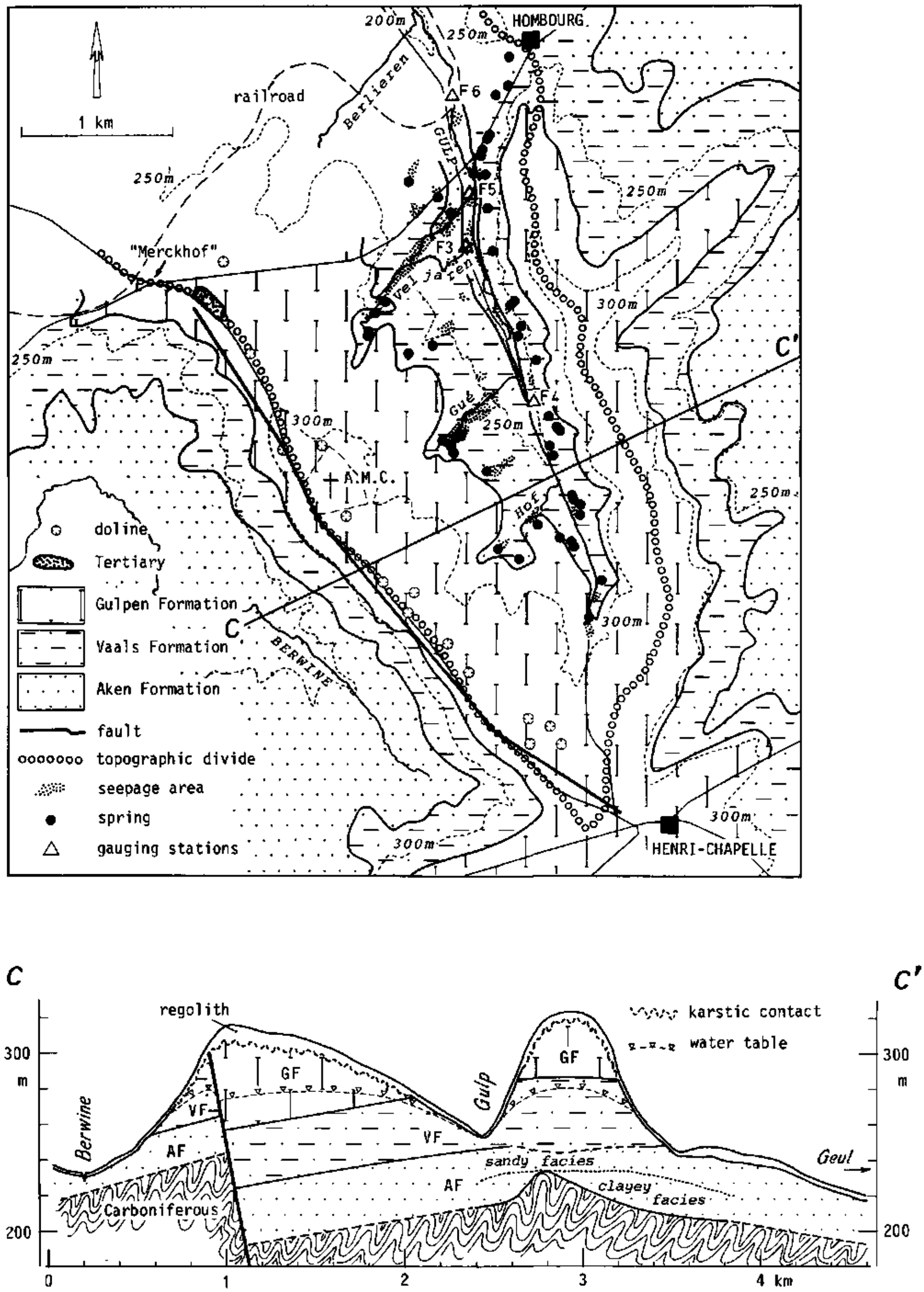

FIG. 3. Map and cross section to show the general hydrogeological conditions in the southernmost part of the Gulp basin.

Table 1. Mean chemical composition of surface waters from Geul, Gulp and Berwine stream networks in mg/l.*

Location	Ca^{2+}	Mg^{2+}	Na^+	K^+	$HCO_3^- + CO_3^{2-}$	SO_4^{2+}	Cl^-	NO_3^-	H_4SiO_4	pH	Ec 25°	TDS
Gulp at Gulpen	112	4	8	4	279	45	18	21	37	7.6	612	528
Berwine at Moelingen	99	10	30	6	232	110	26	24	20	7.5	719	557
Geul at Partij	82	12	12	5	221	53	19	24	20	7.5	570	448
Geul at Meerssen	96	9	17	5	257	50	27	20	28	7.2	646	509

* Period of sampling: Febr. '80 – Oct. '84; number of samples per site: 28, taken every second month; total dissolved solids reported are the sum of the constituents analyzed.

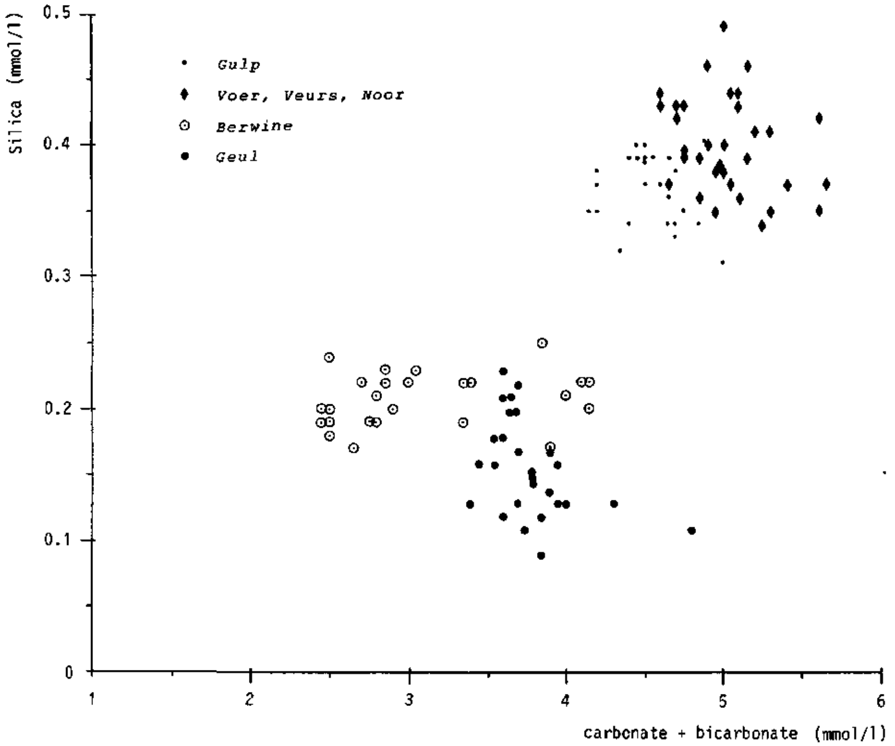

Fig. 4. Relations between the concentrations of silica and bicarbonate + carbonate – a comparison between the surface waters of the Gulp and some adjacent streams (see Fig. 1). Concentrations refer to millimoles of unit charge.

water having sulfate concentrations between 200 and 400 mg/l; other sources of contamination (e.g. road salting and abattoirs) probably account for the elevated sodium levels.

The properties of the *Gulp catchment* in relation to the passage of water through it have been discussed in earlier reports. It was shown that the gross lithology of the formations underlying the catchment is favourable for local recharge and ground-water storage. Hydrographs of outflow indicate that baseflow comprises some 70% of the total discharge. The topographic divide was found not to be congruent with the ground-water divide (see Fig. 3). Substantial ground-water loss was found to occur along a fault zone that practically coincides with the southwestern edge of the catchment; on the other hand the regional 1-2 per cent northwesterly dip of the geological formations in the study area, may cause some minor ground-water contribution from outside the basin along the eastern border of the catchment. Since interbasin flow is a major factor in the study area, problems exist in defining catchment boundaries. Precipitation, however, is presumed to be the major source of the water eventually discharged into the stream network.

According to Köppen's classification the climate in the region can be described as temperate rainy, moist in all seasons. The precipitation averages some 800 mm. Rainfall intensity is highest in summer; during a thunderstorm 19.5

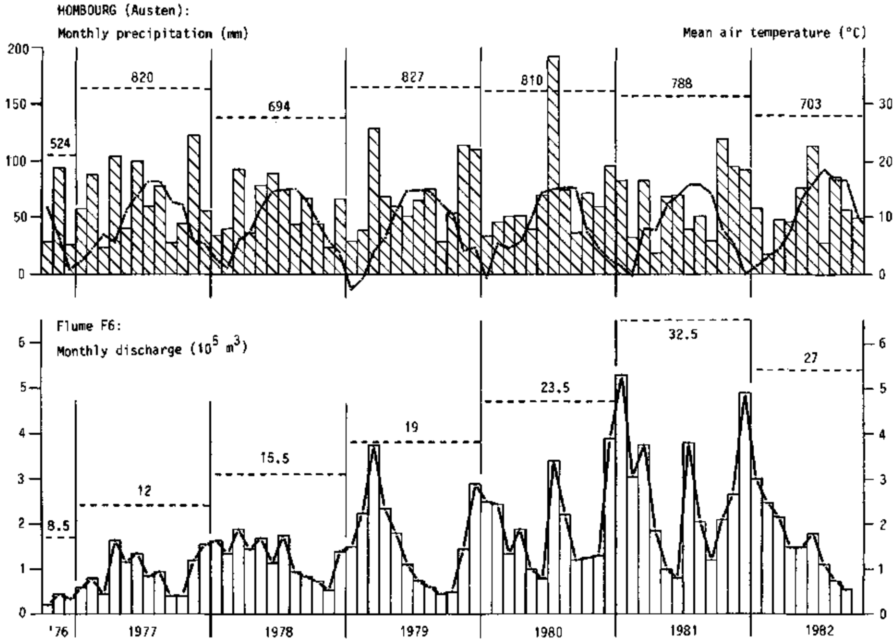

FIG. 5. Monthly precipitation (block plot) and air temperature (line plot) for the hydrogeologic field station at Hombourg (Austen) – monthly discharge recorded at station F6 near Hombourg. Annual precipitation and discharge are also indicated.

mm per hour has been measured. During the winter precipitation intensities are lower and average between 1 and 3 mm per hour. Figure 5 presents precipitation and temperature data from Hombourg (location Austen). Comparative measurements have shown that the pluviograph readings may be up to 15 per cent lower than the values obtained with standard rain gauges.

Chemical characteristics of the precipitation have been monitored from May 1981 through January 1984 to appreciate the input of it in the load of dissolved solids eventually discharged through the basin. Six sampling sites have been selected according to a pattern that would reveal north to south as well as plateau and valley differences (Fig. 1); precipitation samples were collected over approximately 3-week periods.

The results presented in table 2 show the weighted average values for the whole area (1, 2 and 3), for the northern and southern sites (4 and 5) and for the plateau and valley locations (6 and 7), respectively. Covering the main points from table 2, the precipitation may be considered to be composed (on a molecular basis) of mainly ammonium sulfate (about 50%) and calcium nitrate (about 25%) admixed with about 12 per cent of NaCl and 6 per cent of H^+. The source of these dissolved ions is not known with certainty, but it is commonly accepted that they originate mainly from nearby extensive industrial complexes, situated to the northwest and west of the area of study; ammonium is expected to originate also from air sprayed manure, used as fertilizer.

Another notable feature is, that, except for Na^+ and Cl^-, all constituents differentiate significantly from N to S, the northern sites roughly featuring a 20% higher concentration. The relatively high concentrations of calcium and its clear gradient from N to S appear to originate from air-bôrne chalk and cement, derived from the extensive cement industries located some 20 km to the northwest and west of the study area. In contrast to the N to S differentiation found, plateau and valley sites only show minor variations.

The total of dissolved solids in precipitation averages 16–20 mg/l. A compari-

TABLE 2. Weighted average composition and mean other parameter values of precipitation in the Gulp catchment; see text.*

Location	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	H^+	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	pH	Ec	Q
	57.0	10.2	27.6	4.6	110	28.1	15.4	36.6	130	62.3	4.55	45.4	799
(2)	12.0	2.1	5.8	1.0	23.2	5.9	3.2	7.5	26.6	12.8	4.55	45.4	799
(3)	1.14	.12	.641	.18	1.98	.03	.94	1.30	6.23	3.90	4.55	45.4	799
(4)	1.41	.14	.64	.23	2.22	.02	1.20	1.35	6.80	4.25	4.63	47.6	821
(5)	.94	.11	.63	.15	1.80	.03	.74	1.26	5.78	3.58	4.50	43.8	781
(6)	1.13	.13	.63	.17	2.09	.03	.88	1.32	6.43	3.82	4.55	46.5	788
(7)	1.16	.12	.64	.20	1.84	.03	1.02	1.27	5.95	3.93	4.55	44.1	810

* Concentrations are given in real $mmol/m^3$ (1), in equivalent percentages (2) and in mg/l (3-7); Ec is the specific electrical conductivity in $\mu S/cm$ at 25 °C; Q is precipitation in mm/year.

son with the total dissolved solids found in surface and ground-water samples (Table 1) shows that concentrations are about 20 to 30 times higher. For certain ions, e.g. calcium and bicarbonate, the solutes are hundreds of times more concentrated. It is thus clear that further investigation of the relationship between the natural water and the lithology of the basin is needed.

3 LITHOLOGY AND PERMEABILITY

The Upper-Cretaceous sequence that immediately overlies the Paleozoic bedrock forms the greater part of the framework through which ground water moves from its recharge area on the plateau towards the discharge zones in the valley and further towards the north. To evaluate the relationship between the water composition and the lithology in the catchment, a number of selected rock samples have been analyzed for their mineralogical and chemical characteristics using X-ray diffraction and X-ray fluorescence spectrometry. Stratigraphically, the Upper-Cretaceous sequence can be subdivided into Aken, Vaals and Gulpen formations (Fig. 3).

The AKEN FORMATION consists of non-indurated pyritiferous clays and silty clays in the lower part of the series and of light coloured fine-grained well sorted quartz sands (Md values between 150-200 microns) in the upper part. The Aken sands consist of some 97% quartz and contain pyrite at certain levels; the thickness of the formation measures some 35 m. Field measurements (kD-values) have indicated that the permeability for the well sorted sands ranges between 6 and 8 m/day.

The VAALS FORMATION, overlying the Aken Formation, is about 40 m thick. Generally it consists of silty clay and clayey silt with glauconite; at certain levels the clayey facies is interbedded with consolidated fine-grained sandstone layers (thicknesses of 10-20 cm) that are fractured. In this sequence quartz and clay minerals are predominant while calcite and pyrite are accessories. The coarser fractions consist mainly of quartz with glauconite, feldspar, muscovite and some calcite. The clay fraction is mainly montmorillonite with mica, glauconite and illite. The consolidated sandstone layers are cemented with silica while calcite and pyrite are lacking. The permeability of the fractured sandstones has been evaluated by pumping tests over a section of several metres of alternating silty clays and interbedded sandstones; kD-values of some 40 m^2/day indicate that the individual fractured layers have permeabilities between 20 and 50 m/day.

The GULPEN FORMATION is a light coloured fine-grained fairly homogeneous chalk with joints and fissures in places; its thickness measures approximately 40 m. The chalk consists of nearly 90% calcite and the remaining 10% is largely quartz with some potash feldspar, kaolinite and glauconite. The limestone is soft, poorly bedded and silifications are rare. Pumping tests of wells have given k-values between 15 and 18 m/day; however, the large variations that can be expected in the chalk and that have been experienced, make it reasonable to estimate the average permeability between 0,5 and 10 m/day.

The REGOLITH overlying the various geological formations discussed above forms a blanket of variable thickness. It is usually less than 2 m thick on the steeper eastern slope and thicker on the more gentle western slope. The composition of the regolith varies greatly from one place to another; in most cases it is composed of an admixture of chert nodules, clay size material and loess. The compositional relationship with the underlying formations can be recognized in most cases. The clay fraction of samples from the plateau shows an abundance of kaolinite with mica and chlorite, while samples down the slope are characterized by a predominance of montmorillonite; the coarser fractions contain chert fragments, potash feldspar, glauconite and mica; calcite and pyrite occur locally. Measurements have shown that the regolith is sufficiently permeable to permit infiltration. The saturated vertical permeability for the upper 50 cm was found to range between approximately 0.50 and 4.00 m/day, this being dependent to a large degree upon the frequency of the bioturbations.

4 WATER CHEMISTRY

As water moves through a catchment its chemical composition approaches equilibrium with its environment. Naturally, the quantity and type of dissolved constituents in ground water for the most part depend on the chemical and physical properties of the matrix rocks and on the underground residence time of the water. A diversity of human activities such as agricultural uses, disposal of wastes and acid precipitation do modify the natural water quality. Generally, in the study area, the chemical type of ground-water, however, remains a function of the interaction between the water and the geological framework.

Given the three aspects of the region that control the hydrogeological environment, namely (1) location and topography with pronounced relief, (2) geology, including the physical and chemical properties of the rocks and (3) climatic characteristics with enough precipitation, the study area as a whole may be considered as an area of hydraulic recharge. The ground-water circulation through the unconfined and relatively shallow aquifer system is sufficiently rapid (Nota and Bakker, 1983) to neglect the influence of any fossil water on the present water composition.

The ground-water samples have been obtained mainly from domestic dug wells with diameters usually of approximately 80 cm. Depth to ground water varies from 3 to 60 metres. The shallow wells are located in the valley and on the valley slopes, the deeper wells on the plateaus. Some of the wells have been abandoned and in most cases well logs or drilling records are not available. Since the primary purpose of this study is to determine the main chemical characteristics of the water with special reference to the interrelationship between surface water and ground water, not much attention has been paid to variations between individual samples because many unknowns (insufficient data from well logs) still exist among the factors controlling them. Hence the interpretation of the water chemistry will be on an areal rather than on a local scale.

The *ground-water samples* from the catchment generally contain between 300 and 600 mg/l of total dissolved solids (TDS); the *surface water samples* average some 500 mg/l. TDS values vary with time and location in the flow system (Table 3).

The pH values for ground water range between approximately 6.1 and 7.5, for surface water between 7.5 and 8.1; calcium and bicarbonate are the dominant ions. Comparison of these measured concentrations with calculated pH values (page 3) gives Saturation Index (SI) values, the distribution of which is plotted in figure 6. Negative SI values indicate that the actual pH is less than the theoretically derived pH value, rendering the water undersaturated with respect to $CaCO_3$ or, as it is commonly called then, agressive. On the other hand, positive SI values point to a state of supersaturation. Figure 6 suggests a common subsaturated nature of the ground waters as compared with a more saturated habitus of the surface waters.

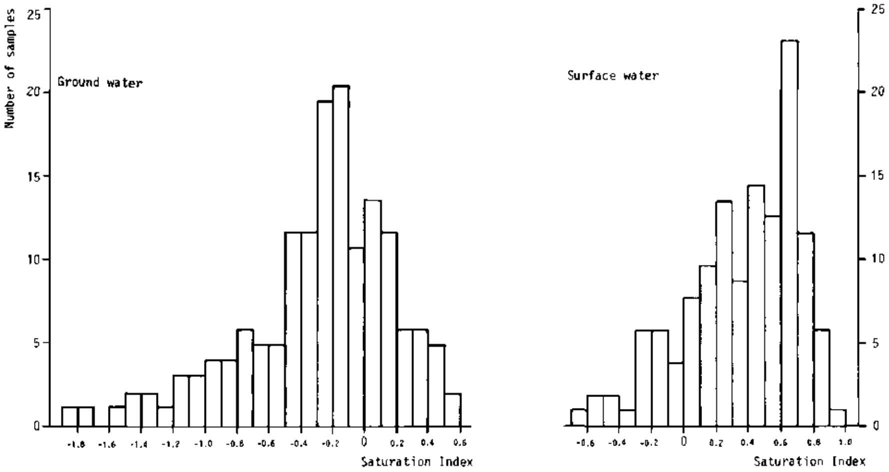

FIG. 6. Saturation index (SI) values from ground water and surface water samples of the Gulp basin. Frequency diagrams indicate a common subsaturated nature of the ground waters as compared with a more saturated state of the surface waters.

Dissolved solids in *precipitation* during the extended period of sampling (1975-1985) average 16.6 mg/l and vary from 6 to 41 mg/l. The pH varies from 3.7 to 6.9 and averages 4.7. For details on the precipitation data the reader is referred to page 10 and table 2.

The Upper-Cretaceous sequence through which the ground water moves is not homogeneous but an unconfined multiple layer aquifer composed of geological formations with different lithologies, viz. the chalk from the Gulpen Formation, the clayey silts and silty clays with glauconite and some pyrite of the Vaals Formation and the fine-grained well sorted quartz sands of the Aken Formation respectively. Differences found for samples from ground-water wells are primarily related to the geological formations (Table 3). It is obvious, that the easily soluble calcareous deposits furnish the major portion of the soluble constituents in the Gulp basin.

4.1 RELATIONSHIP BETWEEN GROUND WATER AND SURFACE WATER – RELATION TO LITHOLOGY.

Though there exists a certain degree of water pollution in the study area (see below) these modifications in the water quality are generally only local and such that the circulation system of the natural water can be recognized. A definite distinction between *lithologic* and *non-lithologic* sources of the dissolved constituents in water can not be made however. For example the calcium may be derived from limestone, but also from fertilizers; the sulfate may come from solution of sulfate minerals, from oxidation of pyrite and marcasite but also from fertilizers; atmospheric chloride usually is a significant factor influencing

TABLE 3. Average dissolved constituents in water samples from the Gulp basin (mg/l).

	Ca^{2+}	Mg^{2+}	$Na^+ + K^+$	$HCO_3^- + CO_3^{2-}$	SO_4^{2-}	Cl^-	H_4SiO_4	pH range	TDS	number of samples
Ground water Gulpen Formation	133	2	7	315	29	24	34	6.7-7.5	544	140
Ground water Vaals Formation	74	6	21	121	71	29	32	6.1-7.1	354	70
Ground water Aken Formation	62	4	14	98	51	27	30	6.1	286	35
Water from springs	118	2	6	313	28	16	39	6.9-7.1	522	190
Surface water	114	3	12	289	45	17	31	7.5-8.1	511	190
Precipitation	1.1	0.1	0.6	1.3	6.2	1.1	–	3.7-6.9	16.6	241

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the anion content, but also animal wastes may serve as sources of chloride.

This complexity might somewhat obscure the relative importance of factors controlling the chemical evolution of the water. However, the main features of the relationship between natural ground water and surface water can be obtained, albeit on an areal rather than on a local scale. The interpretation of these features is based primarily on the characteristic relations between the *major ions* in the natural water. Fortheron in the text entire analyses including the elements of water pollution will be given in a special diagram.

A widely used technique to describe the water composition is to express the analyses in terms of cationic and anionic components in two separate triangles. These diagrams, however, only give relative compositions of the various constituents.

Therefore, these mass diagrams should be considered in connection with concentration differences, because otherwise the interpretation can be misleading. Furthermore, it should be emphasized that the usual ground water-surface water system is too complex and sampling technique and treatment too uncertain to justify *an exacting interpretation* (cf. Hem, 1970). For, the present water composition is the outcome of the manifold interaction between many variables; to mention only a few: dry and wet atmospheric deposition, geogenetic (natural) water, land use, wastes, fertilizers and dilution processes. Water chemistry relationships usually constitute supporting evidence regarding the interpretation of the circulation system of the natural water, but most certainly need other bases of support as field evidence.

The diagrams in figure 7 show the relative amounts of the *major* dissolved constituents in ground water, spring water and surface water. The chemical composition of the *ground-water* samples shows that generally the water in the catchment is of the calcium-bicarbonate type. The spread of the composition in the ground-water samples is related to the location of the water wells in different geological formations.

The composition of the water samples from the Gulpen Formation (GF) shows a fairly limited spread and indicate they are typical calcium-bicarbonate waters. The calcium contents average 130 mg/l, the bicarbonate content 310 mg/l; typical chalk waters contain about 15 to 30 mg/l sulfate (Table 3). The wells in the Gulpen Formation are located on the high land and their depths vary usually between 20 and 50 m.

Water from the underlying Vaals Formation (VF) is collected from wells successively downslope from those of the Gulpen Formation. Trilinear positions show trends away from the calcium and bicarbonate corners, towards the sodium + potassium and sulfate corners, respectively; calcium remains dominant however. Sulfate mostly varies here between 40 and 60%. The calcium content averages 75 mg/l, the bicarbonate content is about 120 mg/l, while the sulfate content averages some 70 mg/l; the sulfate concentrations have been found to vary widely in some of the wells however (Fig. 15). The wells are shallow and their depths rarely exceed 5 metres. The relative amounts of the major dissolved constituents in water samples from the Aken Formation (AF) are situated at

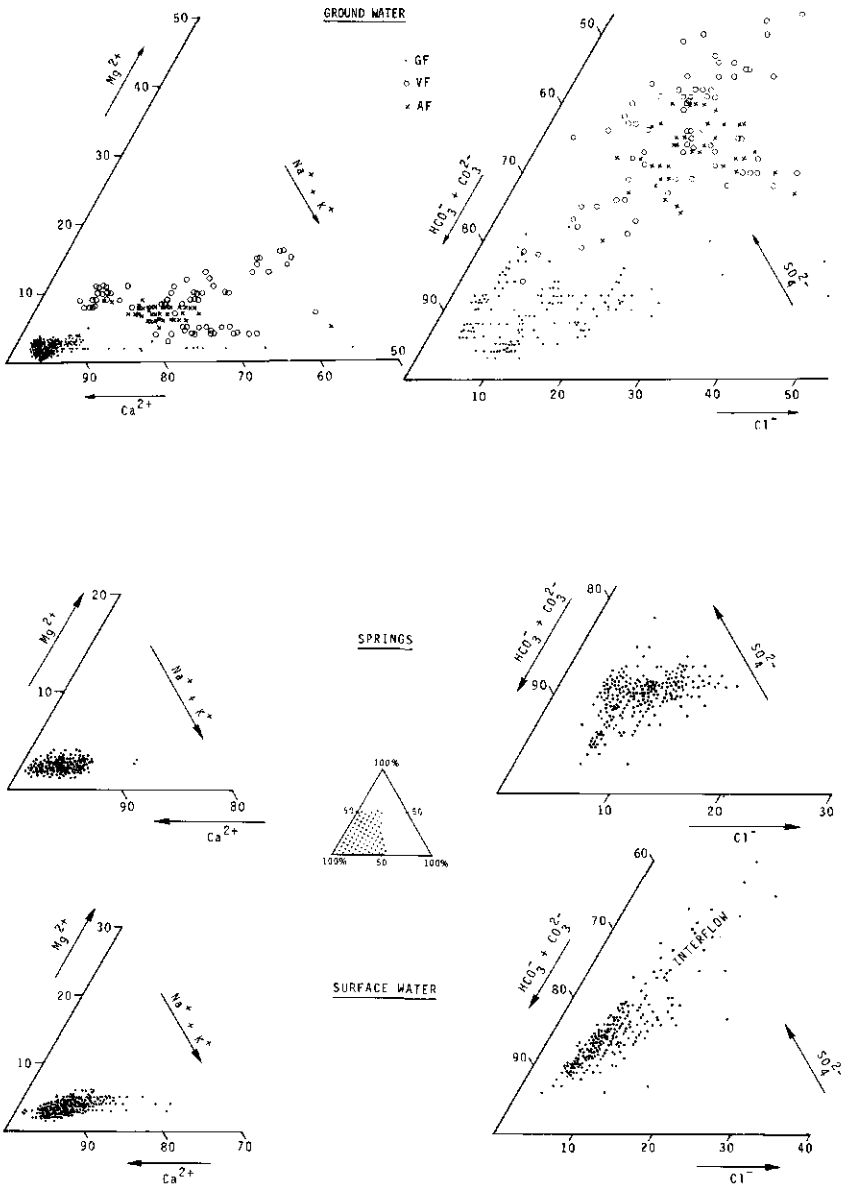

FIG. 7. Trilinear diagrams based on equivalent percentages to show the relative amounts of the major dissolved constituents in ground water, spring water and surface water; see text.GF = Gulpen formation; VF = Vaals Formation; AF = Aken Formation.

more or less intermediate positions between those of the Gulpen and Vaals Formations. The concentrations of the various dissolved solid species are lower than those from the overlying Vaals and Gulpen Formations; the calcium content averages 60 mg/l, the bicarbonate content is about 100 mg/l and the sulfate content occurs in concentrations that average 50 mg/l. The wells are shallow and, here again, rarely exceed depths of more than 5 m.

Ground-water outflow into the valley occurs through springs and seepages near the permeability break between the Gulpen and Vaals Formations, but also through springs and seepages that issue through fractured consolidated sandstones that are intercalated between low permeable silty clays of the Vaals Formation. The analysis of the spring waters clearly shows (Fig. 7) that they originate mainly from the drainage of the chalk waters of the Gulpen Formation. The contents for calcium amount to 120 mg/l, for bicarbonate to 310 mg/l while the sulfate content is around 25 mg/l.

The close relationship between the chemical composition of the spring waters and the surface water is supported by the fact that baseflow comprises approximately 70% of the total discharge in the catchment; this means that the discharge of Gulp creek is largely sustained by the drainage of the chalk water. It is worth noticing, that a number of samples of surface water (Fig. 7) show trends towards the sulfate corner. A closer examination of these analyses reveals that these samples have been obtained during the wet season when subsurface runoff, viz. interflow (Kirkby, 1979) is an important flow route of water passing through the basin (see below); it has been shown that (polluted) sulfate waters of hillslope origin are superimposed on (natural) bicarbonate baseflow waters (Nota and Bakker, 1983). In times of baseflow only, the chemical composition of the surface water is very much like that of the chalk waters. The occurrence of the Aken Formation is limited to the central part of the upper reach of the valley, approximately between F4 and F6; hence its contribution to the baseflow is only of local importance, as is shown in figure 8 (see also Nota and van de Weerd, 1978; Fig. 7).

It is obvious that the drain function of the fractured sandtones interbedded in the Vaals Formation is very crucial for the ground-water circulation in the catchment. A few particulars may be given. Albers (1976) made a detailed study on the fine stratigraphy and facies analyses of the Vaals Formation (Lower Campanian) in the area of Aachen and adjacent Limburg and Belgium. The framework of the complicated sedimentary sequence has been interpreted as a (lagoonal) shallow water facies with little tidal effects and deposition of sand-silt and silty-clay deposits. It was found that during accumulation a number of regressive and transgressive phases took place as a result of climatic changes and/or epirogenetic events. The complicated sedimentary sequence thus developed, shows a number of continuous sand layers ('horizonts'), formed during a transgressive phase) alternating with gully sands and adjoining shelf muds (silty clays) accumulated during regressive phases; the sequence was found to be fining-upward and – westward (Felder, 1975).

The chemical analyses of the water samples give evidence that the sedimentary structure of the Vaals Formation acts as an effective system to drain the ground water of the overlying Gulpen chalk. The continuous fine-sand layers ('horizonts')

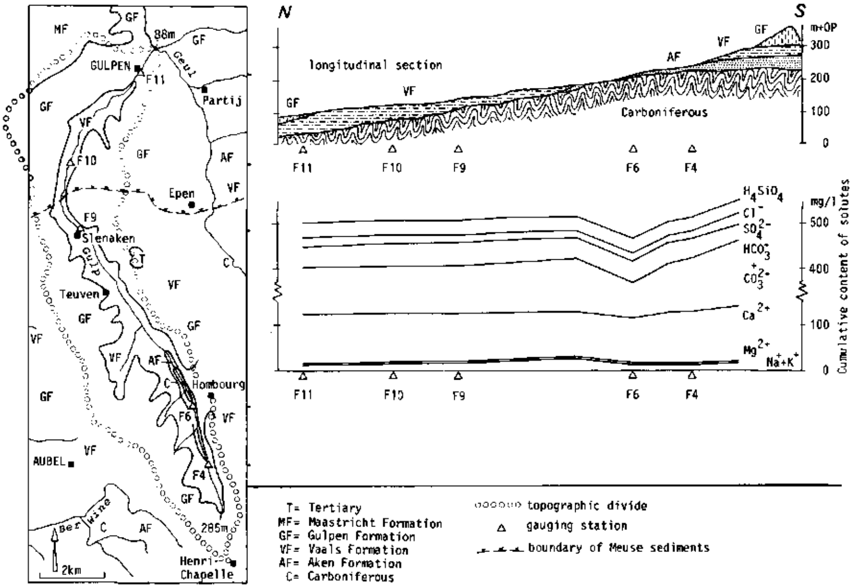

FIG. 8. Average surface water composition (grand means) along Gulp creek – note the distinct local influence of the Aken Formation near stations F4 and F6.

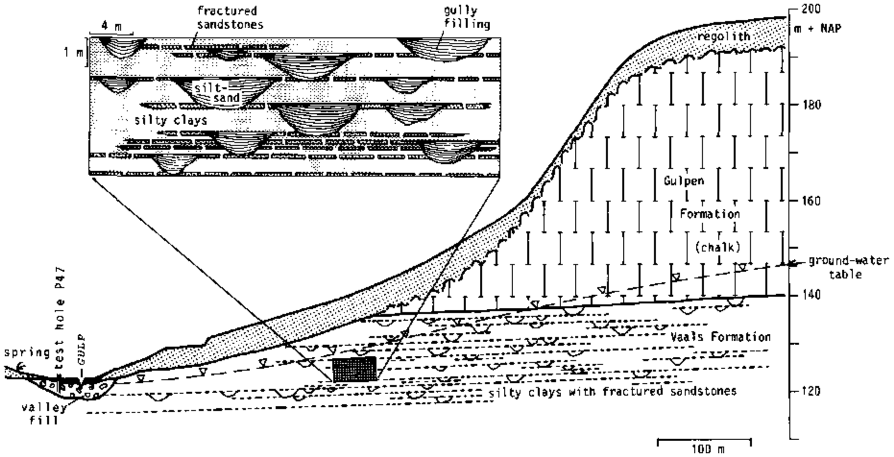

FIG. 9. Simplified diagram to illustrate the vertical hydraulic interconnection between the Gulpen Formation and the Vaals Formation; the sedimentary structure of the Vaals Formation makes its drain function possible (see text).

have become fractured and are considered now to act as the main passages of the drain system through which the ground-water movement is mainly lateral (measurements have shown hydraulic conductivities of 20-50 m/day); on the other hand the gully fillings make the vertical interconnections. Figure 9 gives a simplified illustration of the supposed ground-water flow pattern. Thus there exists a multiple layer unconfined aquifer system with hydraulic continuity in the vertical direction. In the main, however, the Vaals Formation has to be re-

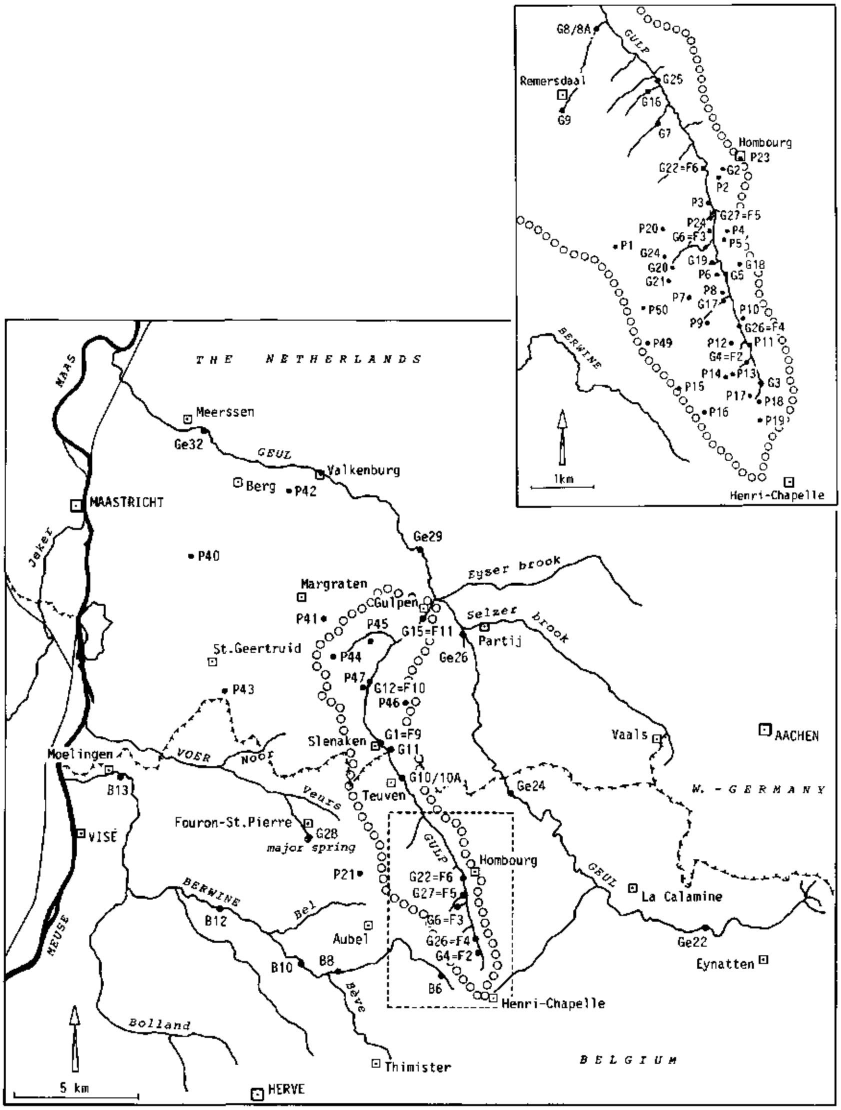

FIG. 10. Location of sampling sites for ground water (P) and for surface water (G for Gulp, Ge for Geul, and B for Berwine series).

garded as a unit of low permeability and the ground water in the silty clay facies thus moves only very slow and does not play an active part in the hydrologic cycle in the catchment (Table 3).

4.2 WATER QUALITY IN RELATION TO ACTIVITIES OF MAN

The foregoing discussion aimed to delineate the genetic evolution of the *natural water* based on evidence from the geologic environment; eventually the ground-water movement, its outflow and its relationship to the surface water have been revealed.

Trilinear diagrams as used above are less suitable for a representation of the entire analysis of water samples, since the variation of only a limited number of variables can be shown and absolute values are not given. For that reason the authors developed a new type of diagram showing the *entire analysis* of the water samples including proportional and absolute values. The rectangular diagram shown in figures 11-13 proved to be most useful. In this diagram* the horizontal coordinate accomodates the cumulative molar percentages of the ionic constituents, while on the vertical axis the samples have been plotted according to their total ionic concentrations. Unlike the Schoeller diagram it uses linear instead of logarithmic scales and the cumulative percentages of each analysis lies on a single straight horizontal line. The vertical axis acts as a reference and dispersing coordinate and this means that also any other value such as TDS, Ec or characteristic components such as bicarbonate, nitrate, sulfate or the pH could be selected. As an example figure 11 shows the manner of plotting of the water samples from table 4 into this rectangular diagram; the position of each sample on the vertical axis is determined by its total ionic concentration. The left hand part of the diagram refers to the cumulative proportions of the cations of sodium, potassium, magnesium and calcium respectively; accordingly in the right hand side part bicarbonate (+ carbonate), sulfate and chloride ions are given. Thus the major ions occupy the central part of the diagram, while the remaining ions take positions along the flanks of it. Cation deficiences are exceptions and show up in the diagram as deviations from the central 50% position; anion deficiencies are more common and fill up to the 100% position at the extreme right of the diagram; according to the available analyses they usually refer to nitrate.

This type of diagram has several advantages (1) it is easy to read; (2) it gives proportional as well as absolute values; (3) the diagram is easily computerizable; (4) it offers possibilities for classification and quick comparison of many analytical data at a time; in addition it may present the adverse effects of human activities on natural water quality.

It is most convenient to plot the obvious pollutants such as sodium (e.g. from

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* This type of graphic representation is primarily based on a rectangular diagram proposed by Doeglas (1960) for the classification of sediments and soils.

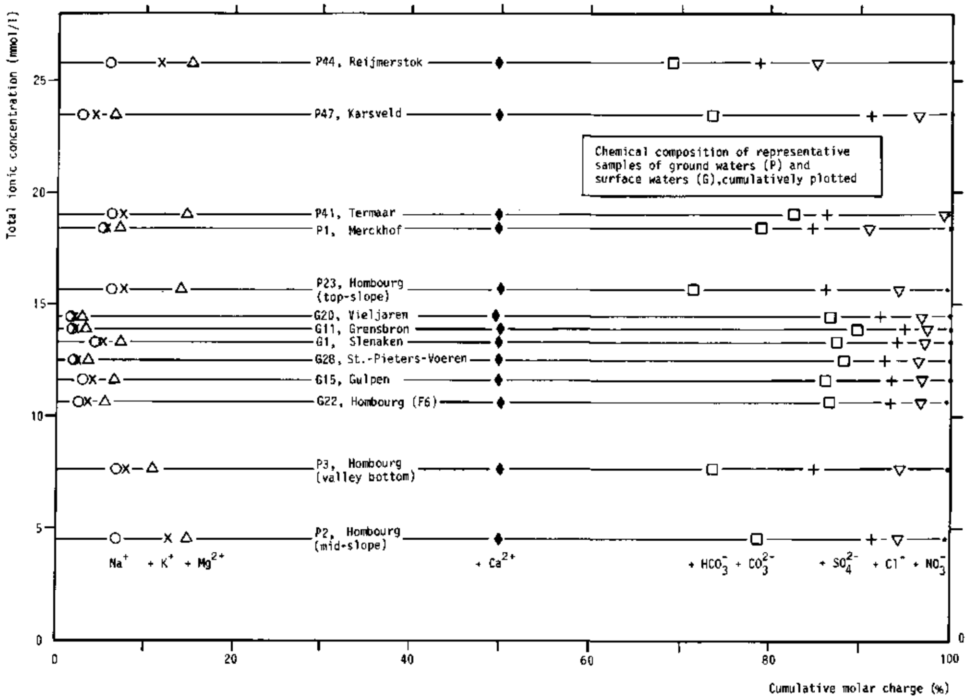

FIG. 11. Rectangular diagram for plotting the water composition, of the type proposed in this study. Each analysis is represented on a straight horizontal line; its vertical position in the diagram is plotted according to the total ionic concentration. As an example the water samples from Table 4 have been plotted; for further details see text.

TABLE 4. Chemical composition of representative samples of ground waters (P) and surface waters (G); values in mmol/l, sum of ions and cations and of ion deficiencies are also indicated.

	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	HCO$_3^-$ +CO$_3^{2-}$	SO$_4^{2-}$	Cl$^-$	NO$_3^-$	sum	Δ
P1	0.48	0.05	0.31	8.32	5.31	1.06	1.15	1.68	18.40	+0.04
P2	0.31	0.27	0.09	1.60	1.30	0.58	0.13	0.24	4.54	−0.02
P3	0.52	0.07	0.24	3.00	1.81	0.86	0.73	0.41	7.66	−0.02
P23	0.95	0.23	1.00	5.65	3.35	2.31	1.26	0.85	15.66	−0.06
P41	1.15	0.27	1.36	6.71	6.18	0.72	2.48	0.08	19.04	−0.06
P44	1.31	1.70	0.90	8.92	4.88	2.53	1.64	3.84	25.78	+0.06
P47	0.63	0.34	0.52	10.20	5.48	4.16	1.25	0.83	23.44	+0.03
G1	0.57	0.11	0.28	5.68	4.98	0.89	0.40	0.39	13.32	+0.02
G11	0.23	0.02	0.20	6.51	5.52	0.73	0.34	0.37	13.92	0
G15	0.33	0.11	0.31	5.05	4.20	0.86	0.38	0.38	11.64	+0.02
G20	0.21	0.02	0.16	6.76	5.28	0.81	0.67	0.46	14.44	+0.07
G22	0.25	0.12	0.20	4.74	3.88	0.72	0.36	0.31	10.62	−0.04
G28	0.23	0.03	0.17	5.81	4.77	0.57	0.46	0.46	12.52	0

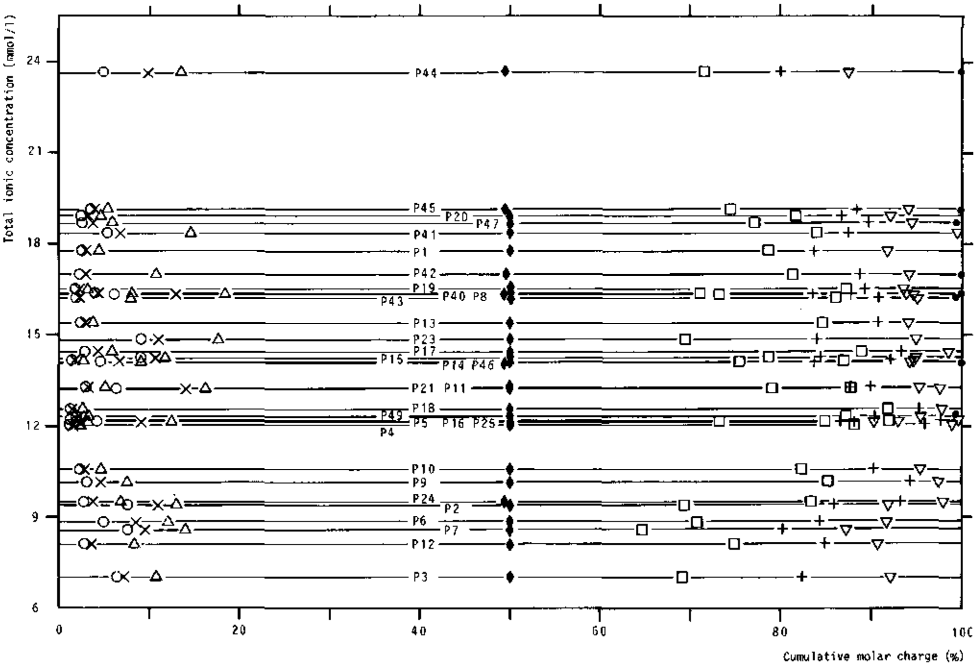

FIG. 12. Ground-water samples from the Gulp basin (grand mean values). Note the large spread of the total ionic concentrations, the large variations in composition and the degree of pollution (see text and also figure 13). Symbols used for the ions are the same as in figure 11.

road salting) and nitrate (e.g. from agricultural activities) respectively at the extreme left and right hand side of the solute distribution. Hence degradation of the natural water quality is manifest in particular at the extreme ends of the diagram; it is clear, that the activities of man can adversely affect the entire solute distribution.

The diagrams in figures 12 and 13 show the analyses of ground water and of spring and surface water respectively. A comparison between the ground-water samples from the wells (Fig. 12) and the samples from spring water and surface water (Fig. 13) shows two striking differences: (1) a large spreading along the vertical axis for the samples from the wells (total concentrations between approximately 7,5 and 24 mmol/l) versus a rather narrow range (between approximately 10 and 14 mmol/l) for the spring water and surface water samples and (2) a near absent or low degree of pollution for surface- and spring waters, while the well samples are more affected, in some cases severely. Stated in other words, these diagrams clearly mark the difference between the ill-defined or 'poorly sorted' character of the ground-water samples against the 'well sorted' and clearly defined character of the spring and surface waters. The large spread of the ground-water samples reflects their specific relationship with the various geological formations (Table 3) and the – sometimes severe – effects of pollution; the much more uniform surface and spring waters reflect their relation with

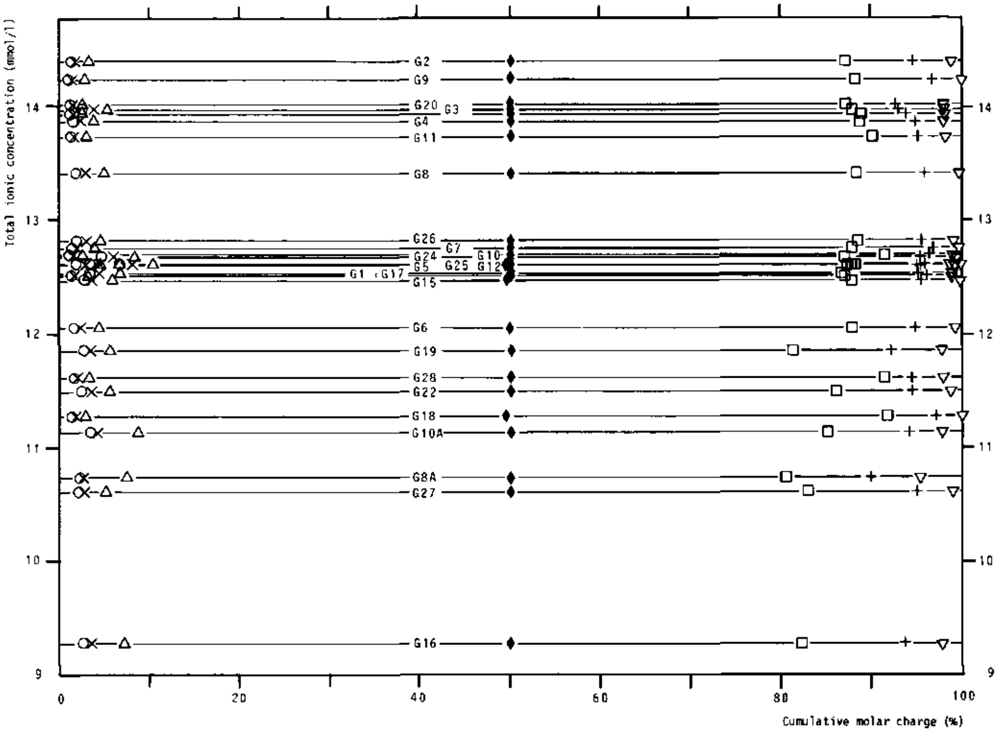

FIG. 13. Surface and spring water from the Gulp basin (grand mean values). Note the well marked differences compared with the ground-water samples; the surface and spring waters are more uniform and less polluted (see text). For symbols of the ions see figure 11.

the mobile chalk waters, outlined earlier in this report (see page 15).

It is evident that the concentration of human activities around wells in rural areas are causes and sources of pollution. This is demonstrated in figure 14 that shows the geometry of the nitrate distribution in wells in the study area. The nitrate pollution is concentrated around the hamlets, where most of the wells are found. It thus suggests that the low degree of pollution of the surface waters is effected mainly by dilution of polluted water with predominant masses of unpolluted water.

The ground water appears to be only locally polluted. Many of the dug wells have their base in the low permeable and sorptive silty clays of the Vaals Formation, which means that dispersion of the pollutants is relatively slow and over a restricted area. Moreover, weathering processes in the glauconitic and pyritiferous silty clays, combined with a long residence time, may contribute to denitrification. Spring waters have been found to be essentially unaffected, but the proximity of a spring to a local source of pollution (e.g. intensively manured cornfields) can cause its degradation, in particular when the area contributing water to the spring is restricted.

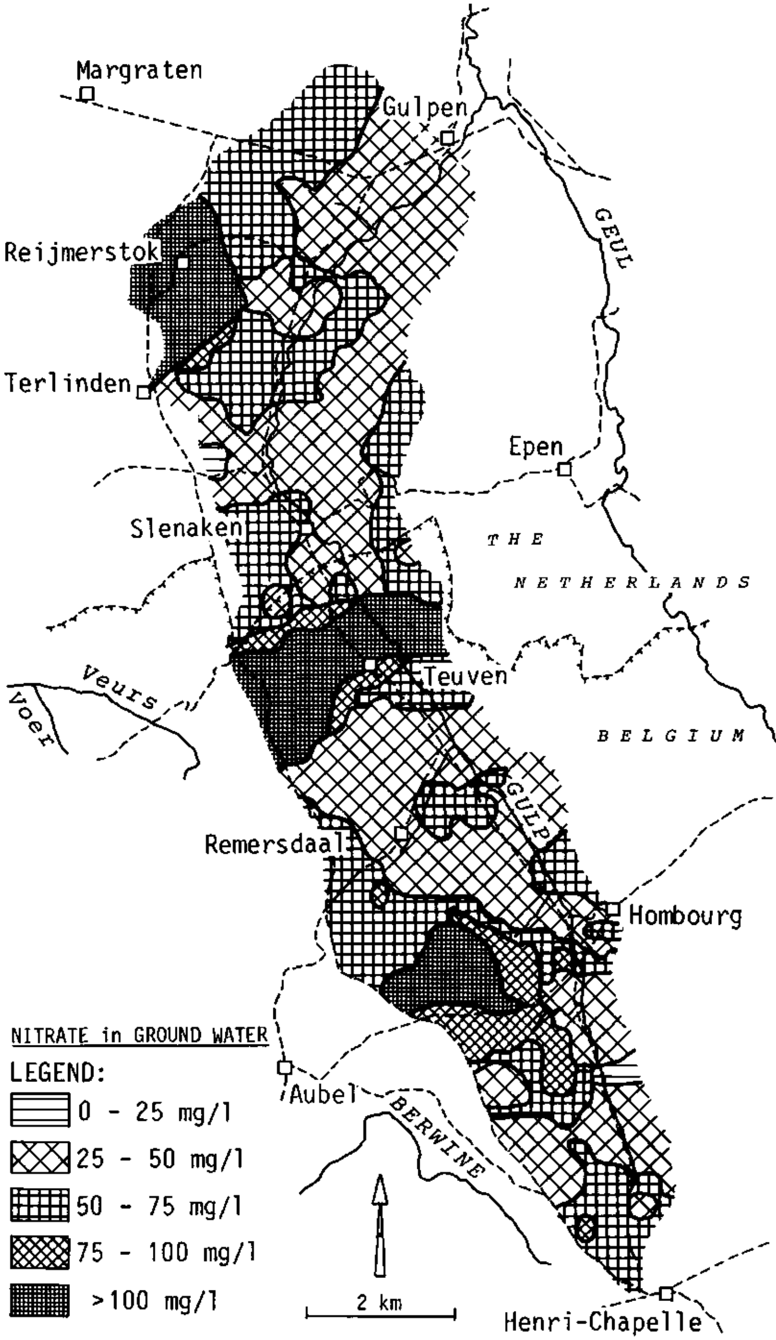

FIG. 14. Generalized geometry of the nitrate pollution of ground water in the Gulp area. Note that the highest nitrate concentrations occur near the hamlets.

4.3 TEMPORAL VARIATIONS IN WATER QUALITY

The chemical characteristics of the water from the catchment discussed in the previous sections mainly deal with the *average water composition* in the basin. Concentrations of the dissolved constituents, however, vary with time and from place to place.

Among others, the chemical composition of the water will be determined by flow type and the flow route of the water. Thus, for ground water, place and depth in the ground-water body, for surface water, the relative amounts of the baseflow and hillslope waters are the determining factors. The interrelationship is dynamic; it varies with time. Drainage basin characteristics, such as relief, rock type, regolith, vegetation cover, land use and position of the hydrologic base will determine the variety of flow routes and water quality. It is obvious that the Gulpen chalk, that is fissured and karstified in places and the typical sedimentary structure of the Vaals Formation with the fractured sandstones, will cause the basin of the Gulp to be drained, at least in part, through zones of preferential ground-water flow. Given the pronounced relief in the study area, subsurface runoff, viz. interflow can be expected to be an important feature along the hillslopes. Furthermore, the varying depth of the hydrologic base of the system can force the ground water to outflow at places where the basement is at or very near the surface.

4.3.1. Ground water

Eight wells have been selected to show the kind and frequency of the temporal variations of ground-water composition (Fig. 15). The well sites have been selected according to a simplified threefold division of the basin into uplands (plateaus), valley sides and valley bottom. For convenience a model is shown in figure 16, in which among others, the type location of the selected wells, represented in figure 15, has been depicted. The pattern of ground-water flow as indicated, is based on water table measurements in available dug wells, observation wells, springs etc.; further on field evidence, the knowledge of the hydrogeological framework and on available hydrochemical data. The model does not pretend to explain in detail all the differences between individual samples and their temporal variations, but it gives schematically an indication of the major trends of flow routes and sources that affect the chemical composition of the water that is transmitted through the basin.

The data from figures 15 and 16 should be read together. Given the geologic framework and the simplified threefold division of the basin into plateaus, valley sides and valley bottom, the plateau wells are in the chalk of the Gulpen Formation, the wells on the valley sides generally are in the silty clays of the Vaals Formation, while the wells in the valley are either in the Vaals Formation, in the fine grained sands of the Aken Formation, or in the deposits of the valley fill. The characteristics of these various wells will be discussed in the following.

1) Plateau wells drain chalk water and their depths vary usually between 20

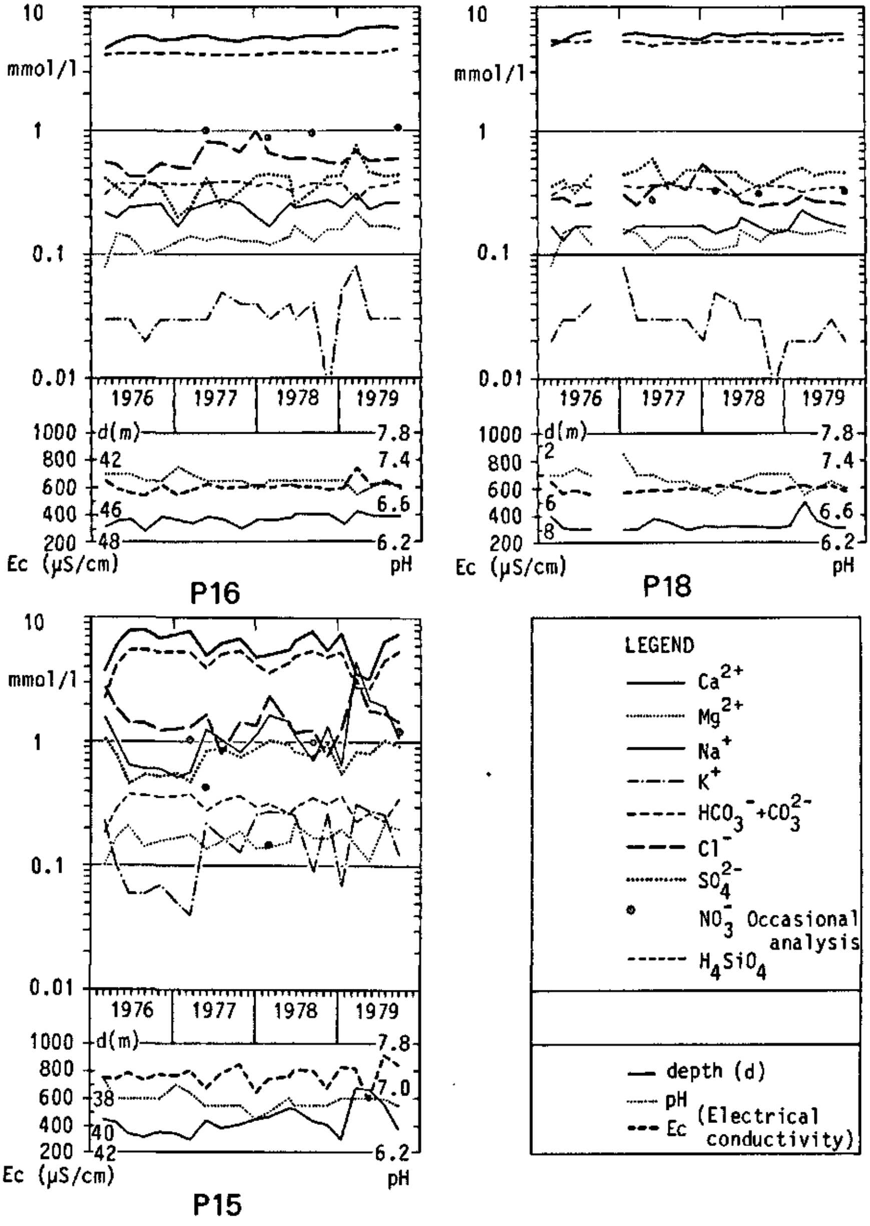

FIG. 15a. Temporal variations in the chemical composition of ground water from wells on the plateaus. For explanation see text. The depth refers to the water table level below surface. Concentrations refer to millimoles of unit charge.

and 50 m; three wells have been selected to describe the ground-water conditions on the highland viz. P16, P18 and P15. Their locations are shown in figure 10.

P16 and P18 are wells selected to approximate the average conditions in the ground-water body under the plateau – P16 is located on top of the plateau and P18 is situated along the plateau edge. P16 is a domestic dug well with a depth of about 46 m and is still in use; P18 is located at the entrance of an abandonned infiltration gallery, formerly belonging to the waterworks of the city of Aubel, and the depth of the water table at the sampling site is about 8 metres below the surface.

Graphically (Fig. 15a), both waters are characterized by a clear threefold partition of the diagram. The top part of the diagrams (ranging between 1 and 10 mmol/l) shows the dominance of calcium and bicarbonate ions with values between around 6 and 4 mmol/l respectively – the central part (with values between 0.1 and 1 mmol/l) is occupied by chloride, silica, sulfate, sodium and magnesium, while the bottom part (0.01-0.1 mmol/l) shows a very irregular course for potassium.

Altogether the temporal variations are fairly small and only are manifest in the central and lower parts of the diagram. The variations for chloride and sulfate are the most pronounced, more or less co-vary and appear to be seasonal. The sulfate concentration is of a low level (Table 3). While chloride is primarily atmospheric in origin, sulfate certainly has also a lithologic source (Nota and Bakker, 1983).

The differences between the chloride and sulfate concentration for P16 and P18 are related to well depth (chalk wells sometimes are dug into the Vaals Formation to enlarge the reservoir capacity of the well), road salting and agricultural activities. The sodium pattern for P16 most probably is affected by road salting of a nearby main road. Silica (H_4SiO_4) remains practically stable at values between 0.3 and 0.4 mmol/l. The concentrations of magnesium are low; unlike the variations of chloride and sulfate, concentrations decrease with increasing precipitation; generally, however, there is a slight increase through the years, which suggests that its main source is from fertilizers, but this cannot be confirmed, sofar. As mentioned above, the potassium concentration is low and its pattern is very irregular; the fluctations are considered to be connected with agricultural activities and its easy adsorption by clays. Unlike P16 and P18, well P15 does not meet average ground-water conditions. P15 is located practically on top of a fault zone, along which a series of more or less linearly arranged dolines occur. The ground-water table fluctuates widely and often independently from observation wells not far apart. Increased fracture density and zones of increased permeability do occur in the vicinity of the fault (Nota and van de Weerd, 1978, 1980). It is considered that these peculiar hydrogeological conditions account for the deviating behaviour of this well. Chemical variations are much more pronounced and also affect calcium and bicarbonate, that show even higher concentrations than the waters from P16 and P18. Higher concentrations are also found for chloride, sulfate and sodium. It is assumed that the higher fracture density in this zone causes a higher vulnerability of the well for human activities such as agriculture, road salting etc.

Because nitrate analyses have not been incorporated in the standard series

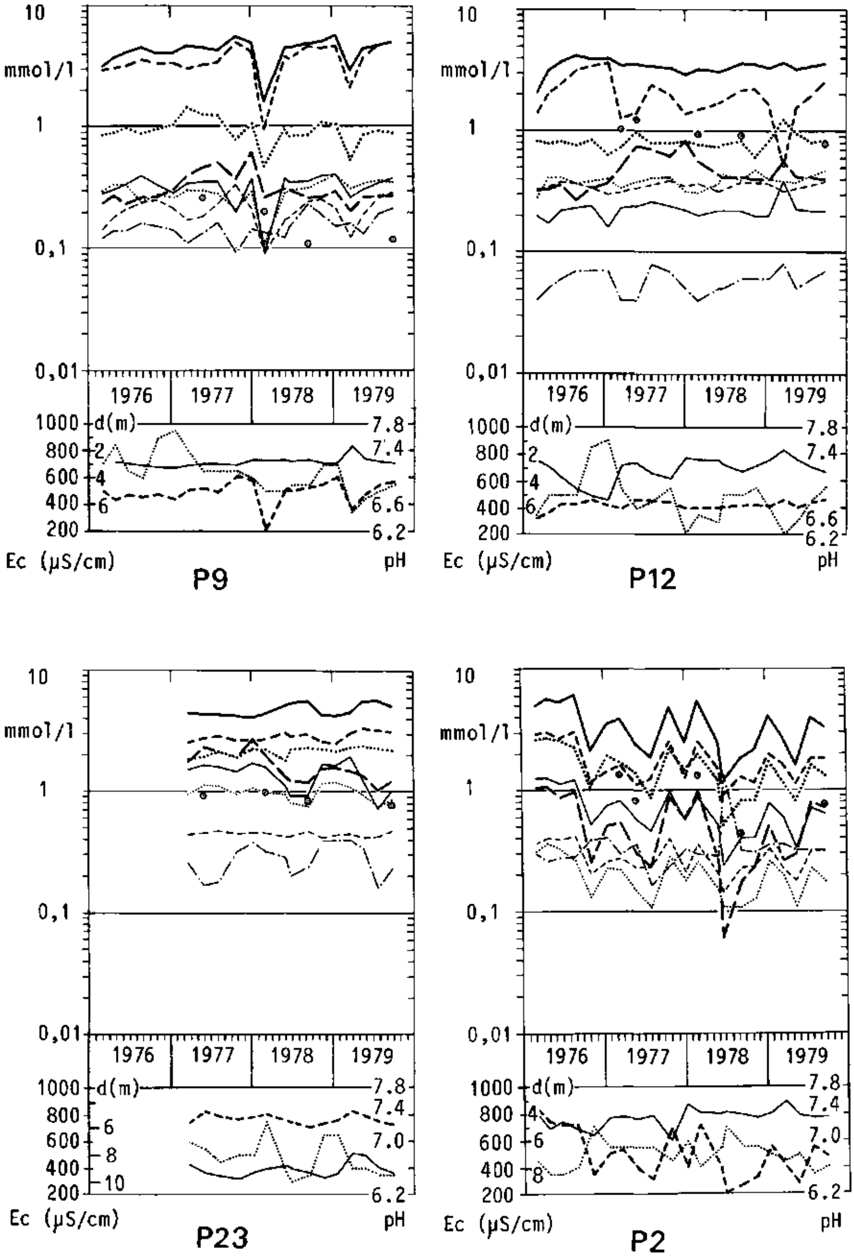

FIG. 15b. Temporal variations in the chemical composition of ground water from wells along the valley slopes. Concentrations refer to millimoles of unit charge.

from the beginning, only separate values are represented in the diagrams. Further it should be noted that the ground-water table fluctuations manifest for P15 and P16 are not really natural, since these wells are still in use and will be affected by pumping.

2) The wells along the valley sides are shallow, their depths rarely exceed 5 m and they are employed for domestic use or for livestock; they are dug wells that extend a few metres below the water table into the silty clays of the Vaals Formation and usually have penetrated through interbedded fractured sandstones.

Previous discussions (Nota and Bakker, 1983) indicated that the water circulation in the silty clays is too sluggish to play an active part in the hydrolic cycle in the catchment and that the interbedded fractured sandstones act as drains for the outflow of ground water, mainly from the overlying Gulpen chalk; further, that subsurface runoff along the valley slopes is substantial. Thus it can be expected that the wells along the valley sides have mixed waters that have different flow sources. P9, P12, P23 and P2 have been chosen to describe the major characteristics of the ground water along the valley slopes (Fig. 15b). P9 and P12 are located along the western slope in pasture, while P23 and P2 are situated near the village of Hombourg.

P9 and P12 are representatives of the more or less 'pure members' of these wells. The waters still show a clear partition of their diagrams with Ca^{2+} and HCO_3^- as the dominant ions; the concentrations of these ions, however, are a little lower when compared with those of the plateau wells. In contrast, sulfate is the major anion among the remaining ions; this higher sulfate level is typical for wells dug into the Vaals Formation (Table 3); the source of the sulfate is considered twofold (1) from the interaction (following oxidation) with pyritiferous sediments and (2) from subsurface runoff of polluted waters along the valley slopes.

A notable difference with the diagrams of the plateau wells is the pronounced temporal variation of bicarbonate and calcium (in particular for P9). These variations are considered to result from the varying quantities of interflow water that are superimposed upon the baseflow chalk waters. Frequent fluctations of the ground-water level and quick responses after rainfall (measured with the aid of float recorders, that were installed in some of the wells) provided supporting evidence for the passage of additional water as interflow along the valley slopes. The diverging pattern of calcium, bicarbonate and sulfate in well P12 must be attributed to local application of Ca^{2+} and SO_4^{2-} containing fertilizers around well P12; the nitrate level is also higher. Differences in land use as well as differences in the composition viz. permeability of the regolith, thus account for the local variations in quality and quantity of the interflow waters.

As was mentioned above, wells P23 and P2 are located in or nearby the village of Hombourg – P23 is located on a higher position (upslope), while P2 is situated downslope from the centre of the village. Most striking are the elevated and relatively high values of the constituents that 'normally' occupy the central part of the diagram (range between 0.1 – 1 mmol/l).

It is assumed that this feature is closely associated with a variety of human activities in and near the village. As stated previously these waters also ought

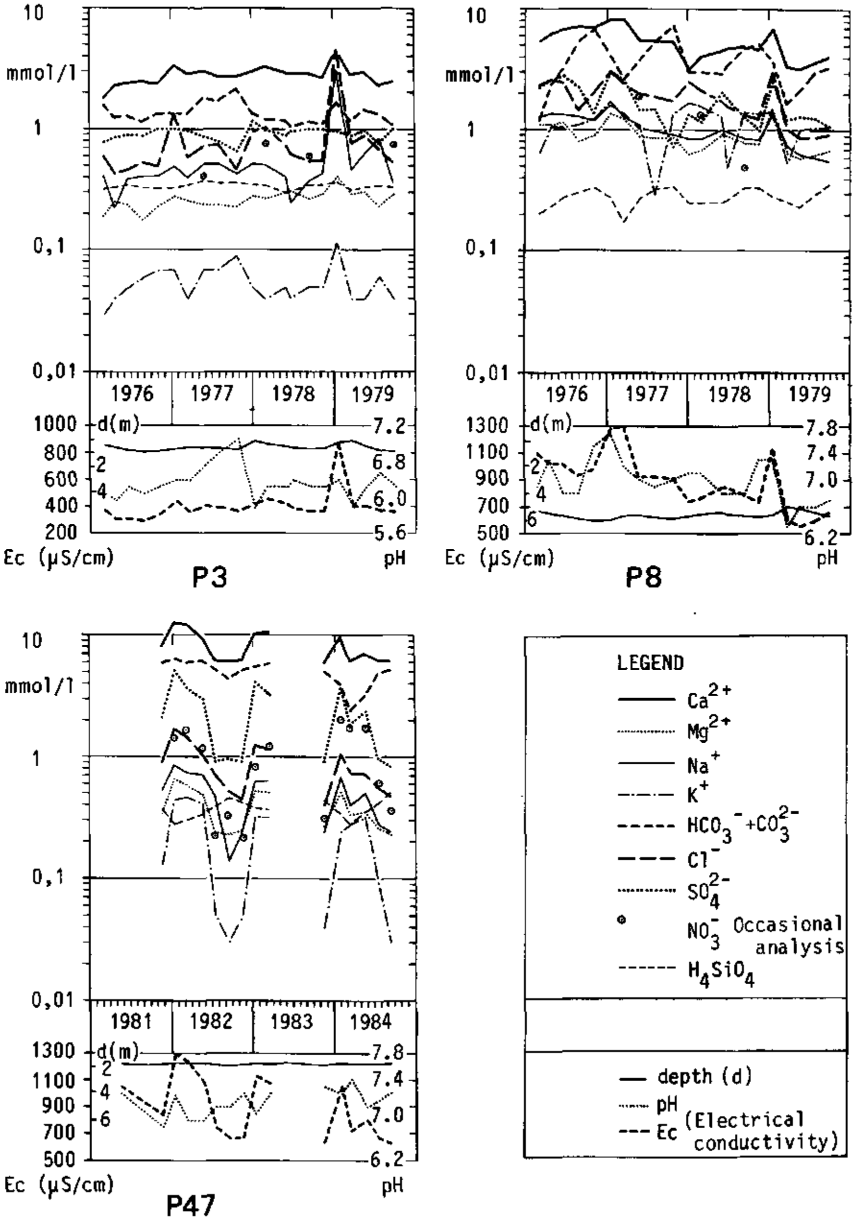

FIG. 15c. Temporal variations in the chemical composition of ground water from wells in the zone of the valley bottom. Concentrations refer to millimoles of unit charge.

to be considered largely as chalk waters intermixed with varying amounts of interflow water; *interflow water that varies greatly with place and time.*

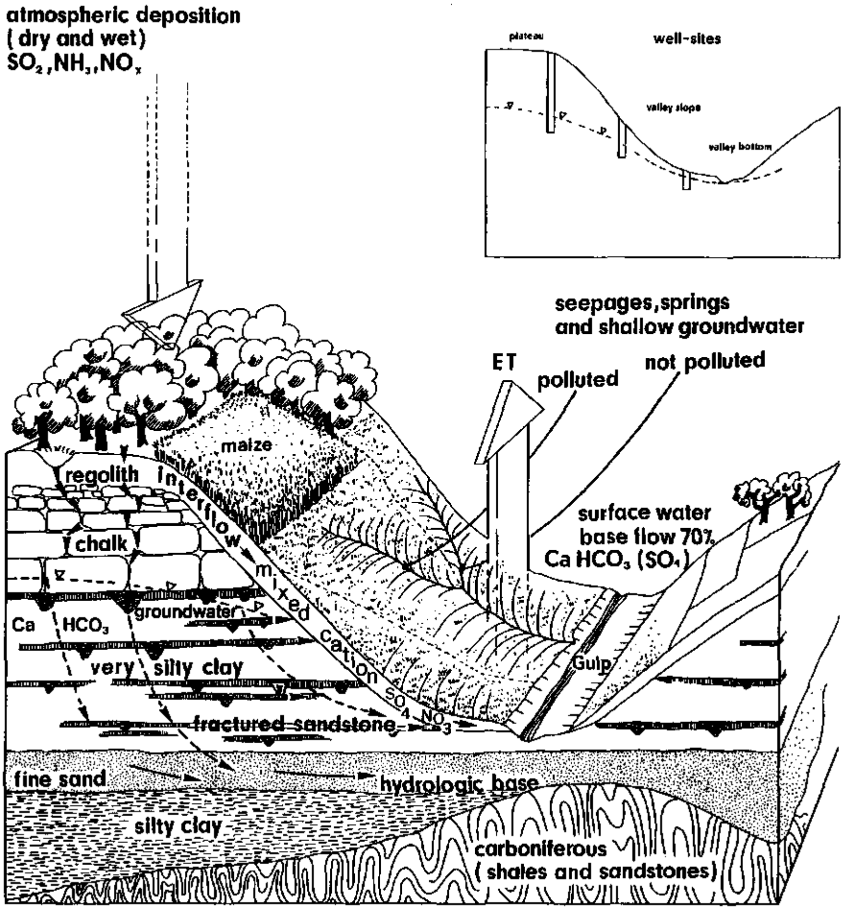

FIG. 16. Block diagram to show the manner by which water is transmitted through the basin. Flow routes and sources that affect the chemical composition of the water are indicated as well as the type location of the selected wells described in the text.

3) The wells in the zone of the valley bottom have depths that range between 1 and 6 metres. P3 and P8 (near Hombourg) and the test hole P47 (at Karsveld, halfway between Slenaken and Gulpen) have been selected to illustrate temporal variations of ground-water composition in this zone (Fig. 15c). P8 is located near the outer edge of the valley bottom. The uppermost well section cuts through the Vaals Formation before the water table is struck in the underlying Aken Formation; it is an abandoned well for livestock near a farm. The compositional fluctuations are very pronounced; the concentrations are distinctly higher than the average ground-water concentrations of the Aken Formation (Table 3). Ec values over 1000 µS/cm have been measured and it is not surprising

that many of the ions that normally occupy the central part of the diagram have shifted towards the upper part of it. The increased concentrations of the constituents are artificially induced and most probably are derived from animal wastes or fertilizers. Sources and causes for ground-water pollution are all around near the well site, particularly since the well is not properly protected against pollution. The fluctuations are seasonal and related to hillslope processes as described in previous paragraphs.

Well P3 is a domestic dug well, excavated into the Aken Formation and located in the central part of the valley bottom. The well is installed in the basement of a private house near a road crossing for through traffic. The diagram of P3 is markedly different from that of P8: the concentrations are lower and unlike P8, it conforms to the average character of ground water from the Aken Formation (Table 3). The major deviations concern sodium and chloride ions (and that of calcium to a lesser extent). Their fluctuations are attributed to the application of deicing salts in winter. Given the location of the well site in the centre of the basin, on the lower slope of the valley and in a hamlet, its fairly unpolluted character is surprising. It is considered that the local hydrogeologic situation between the stream gauging stations F4 and F6 should be taken into account (Fig. 8; see also Nota and van de Weerd 1978, Figs. 7 and 8). The emergence of the Paleozoic impermeable basement in this section, forming a subsurface restriction, forces ground water to the surface. This rising ground water contributes to an approximately 40 per cent extra discharge at station F6. It is assumed that the emerging ground water together with the intergranular filtration and dispersion through the well-sorted fine grained sands of the Aken Formation causes a dilution and thus a decrease of the concentration of available pollutants.

The test hole P47, located at Karsveld, penetrates into a residual gravel layer underneath the present alluvial valley fill; the thickness of the gravel layer is not more than 2 metres. Location and framework of the site have been indicated in figure 9. Although its position in the central part of the valley bottom is similar to that of P3, the temporal variations of the water composition at P47 are strikingly different. There is ground-water discharge (seepage and springs) into the valley bottom that orginates from the valley sides. Unfortunately, the record of the water composition is not continuous; it gives, however, enough information to characterize the temporal variations at the site of the test hole. The very pronounced seasonal variations and the abnormal high concentrations of all the measured constituents (except silica) are most striking. It is assumed that the seasonal variations are caused by the varying amounts of polluted interflow water from the valley sides. It is obvious that the gravel layer is not efficient to attenuate the polluted ground water. Agricultural activities from nearby are considered to affect the groundwater quality, thus causing high TDS values; particularly high nitrate, sulfate and calcium ion concentrations occur.

4.3.2. *Surface water*

Seasonal variations of precipitation, ground-water table level and stream discharge are depicted in figure 17; their marked interrelationship indicates that

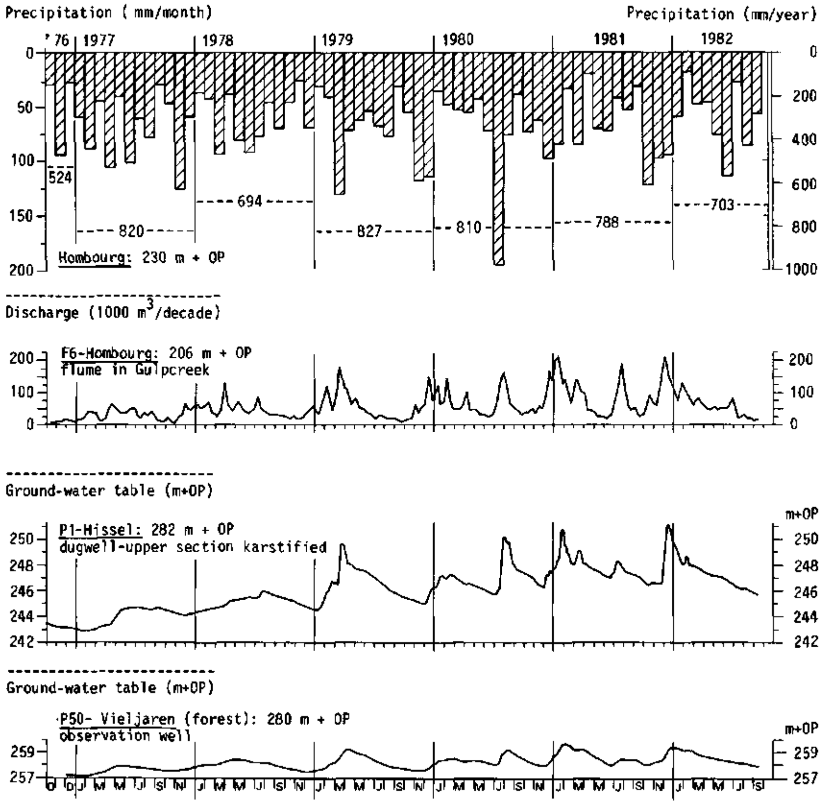

FIG. 17. Temporal variations of precipitation, stream discharge and ground-water table in the catchment of Gulp creek; the marked interrelationships substantiate the stabilizing influence of ground-water storage on the streamflow.

the gross lithology of the formations underlying the Gulp catchment favours deep percolation and ground-water storage.

Thus baseflow amounting approximately 70% of the total discharge largely controls the outflow of water through the basin. Foregoing discussions on the water chemistry have shown that the discharge of the Gulp stream is largely sustained by the drainage of the chalk water from the Gulpen Formation and that, consequently, calcium and bicarbonate are by far the dominant ions carried in solution. As is shown in figure 18 approximately 75% of the dissolved load consists of bicarbonate (+ carbonate) and calcium, whereas sulfate (8 – 12%) and silica (6 – 7%) are third and fourth in abundance. It is obvious from the *flux diagram* that the load being transported is closely related with the stream discharge. This means for instance, that in August 1977 a total dissolved load of about 53 g/s was carried off through F9, whereas during the hump in April 1979 the load approximated some 195 g/s; during that period (April 1979) about

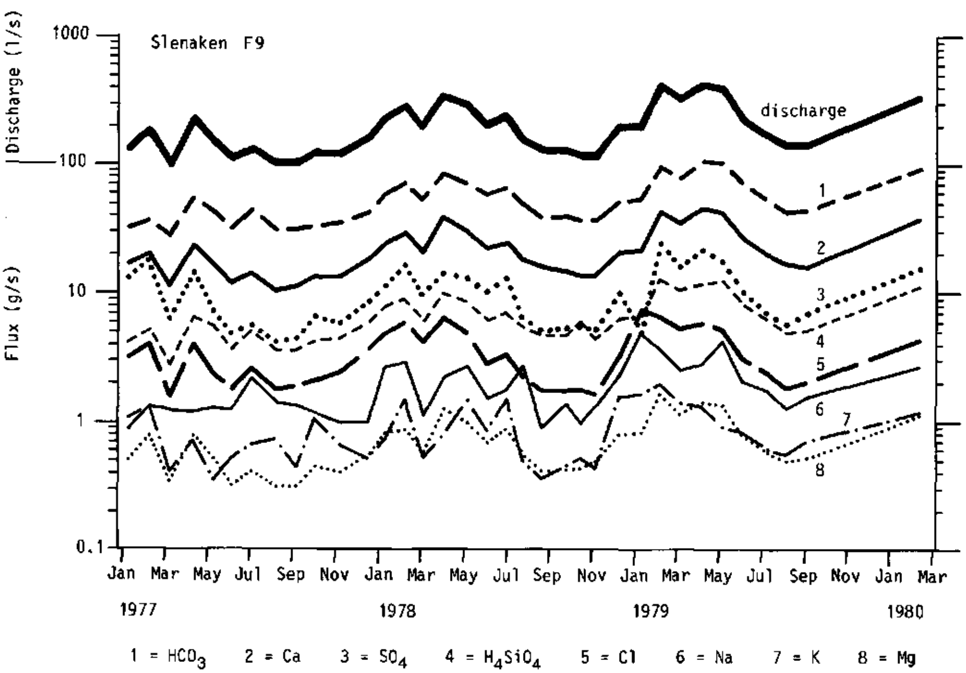

FIG. 18. Flux diagram to show temporal variations in the quantity and composition of the dissolved load that is carried off through the Gulp stream at Slenaken (station F9); the topmost curve represents the simplified discharge hydrograph at the moment of sampling.

100 g HCO^-_3 (+ CO_3^{2-}), 46 g Ca^{2+}, 22 g SO_4^{2-}, 12 g H_4SiO_4, 6 g Cl^- and 3g Na^+ were transported per second (Fig. 18). Using a factor of 0.82 to convert HCO_3 into $CaCO_3$ (Hem, 1970) the Gulp stream carried a total amount of some 1850 tons of calcium carbonate solute through the gauching station F9 at Slenaken during the year 1979. For Gulpen, at the stream gauching station F11, these figures amount to approximately 1900 ton/year for 1976 (annual precipitation at Hombourg 524 mm) and to about 3400 ton/year for 1984 (annual precipita-tion at Hombourg 926 mm). Obviously, the rate of chemical denudation is proportional to the amount of precipitation. As a consequence the collapse of dolines in the area of study (Nota and van de Weerd, 1978) can be expected to occur mostly after and during longer periods of abundant precipitation when there is also the added overweight of the regolith on top of solution cavities in the underlying chalk.

The storage capacity of the aquifer system on the one hand (its porosity, thickness and extension) and the moderate permeability on the other hand, cause the system generally to exert a stabilizing influence on the composition and amount of water that is released into the Gulp stream, despite the pronounced relief of the landscape. Its peculiar character is well illustrated in figure 19 (see also under framework, page 5). The Gulp catchment tends to be relatively con-

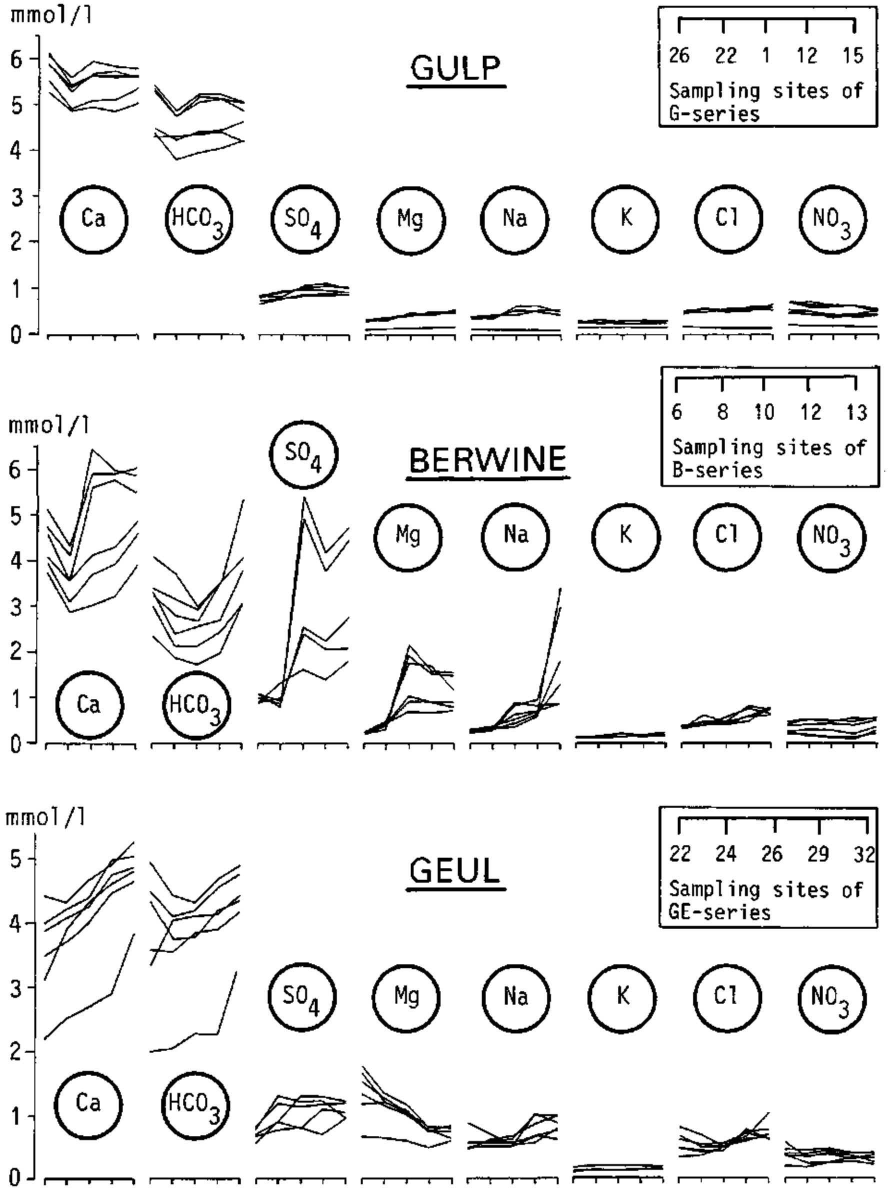

FIG. 19. A comparison of seasonal variations of surface water composition (year: 1980) between the Gulp and the adjacent Berwine and Geul systems. For location of sampling sites see figure 10. Separate plotted lines give the variation in ionic concentrations along the stream per sampling date (samples have been taken every second month). Concentrations refer to millimoles of unit charge.

stant throughout the year whereas the Berwine in particular is very variable. Approximately 52% of the catchment of the Berwine is underlain by fairly impermeable paleozoic sandstones and shales (Nota and van de Weerd, in preparation). The inability of the precipitation to infiltrate to any depth over large areas, causes the general lack of a substantial ground-water storage in the catchment. Its flow is sustained by minor baseflow contributions from chalk waters that originate from the edges of the catchment, from a plateau remnant in the southwest (Fig. 2) and further mainly from shallow surficial (regolith) deposits overlying the paleozoic bedrock. The behaviour of the Geul system lies somewhere between that of the Gulp and the Berwine catchments. Its upstream part is comparable to that of the Berwine system, whereas the lower courses are very much like that of the Gulp catchment (the major tributary of the Geul stream). The differences between the seasonal variations of surface water composition for the three catchments thus apparently refer to differences in rock type and aquifer systems.

Unusual climatic variations such as periods of drought offer a special opportunity to detect the behaviour of the aquifer system in other than usual seasonal circumstances. The period of drought that occurred over large parts of Western Europe in 1975 and 1976 revealed the way in which ground water is released from the present multiple aquifer system during periods of depleted ground-water storage. Ground-water levels and stream discharge decreased significantly and were extremely low during 1976 (Fig. 17). Changes in concentrations reveal these peculiarities better than fluxes and restricted parts of the catchment may afford detailing phenomena better than the whole Gulp area.

The data of figure 20 show the relation between stream discharge and water composition in the Veljaren area near Hombourg; it is a seepage area and a number of springs issue near the contact zone between the Gulpen and Vaals Formation (Figs. 3, 8 and 10). The Veljaren tributary area (between F4 and F6) has been chosen because in that section of the Gulp catchment all the members of the hydrostratigraphic sequence, viz. the Gulpen- Vaals- and Aken Formations are involved, while the impermeable Paleozoic base is near the surface, thus forcing the outflowing water to pass largely through the nearby gauching stations F3 (G6), F5 (G27) and F6 (G22).

G20 represents one of the springs that feed the Veljaren tributary. Downstream it divides into two separate branches G6 and G27, of which the individual behaviour will be discussed. The stream hydrograph of G6 is presented in figure 20, that of G27 is not given, but it is similar.

Some relevant chemical parameters, such as the pH, and the concentrations of bicarbonate (+ carbonate) and sulfate have been plotted as time trends over the periods October 1975 through October 1979.

The nearly constant chemical composition of the springwater (G20 is sampled at the point of discharge) contrasts with the strongly varying surface water (G6 and G27). It is notable that pH values of G20 are constant around 7 which is distinctly lower than the values for surface water at G6 and G27 that approach values between 7,5-8,0; the higher CO_2 pressure in the emerging ground water accounts for this feature, while in the surface waters the hydrogen ion concentration has been lowered through degassing.

Actually, the contribution of solutes from each of the members of the multiple aquifer system can be recognized. G20 shows that the water issued from the Gulpen Formation has a bicarbonate concentration between 5 and 6 mmol/l, while the sulfate concentration approximates 1 mmol/l. The surface water passing through G6 is a mixture of this chalk water with varying amounts of water from interflow origin. The normal seasonal variations for G6 are well illustrated in figure 20. The varying concentrations of bicarbonate, being lower in winter,

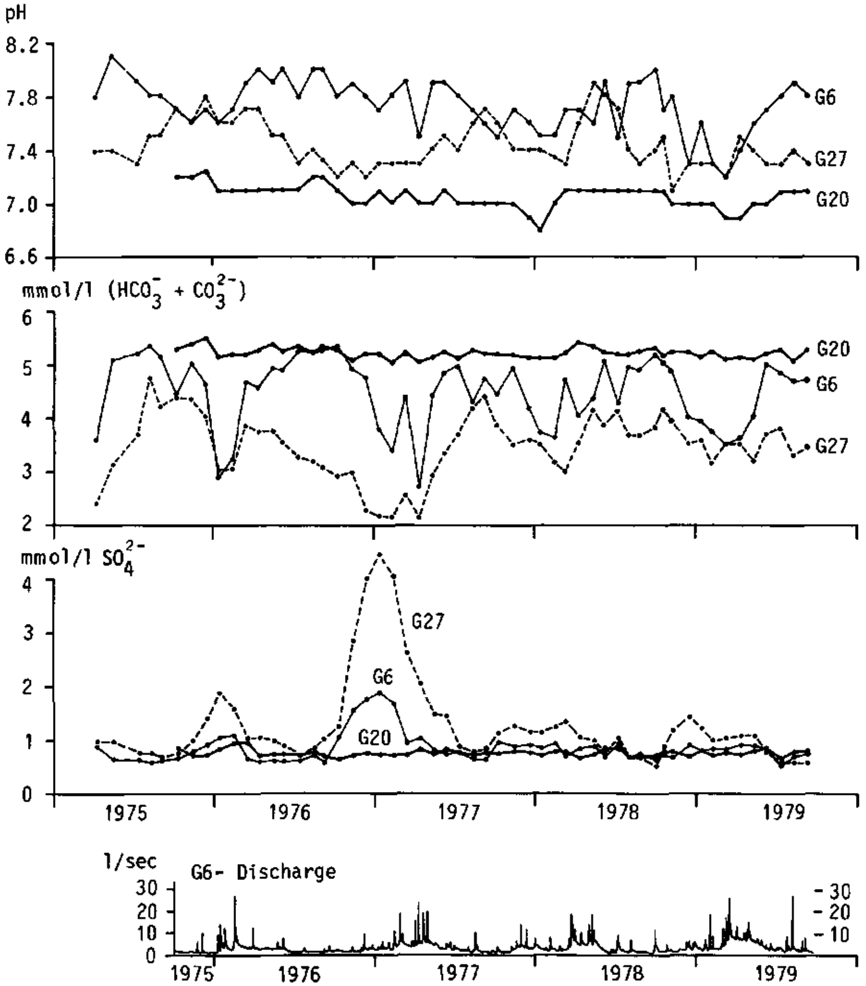

FIG. 20. The behaviour of the present multiple aquifer system under unusual climatic conditions at the Veljaren area near Hombourg – showing pronounced chemical variations in water composition during and after the period of drought in 1975–1976; G20 is a spring, feeding the two separate branches G 6 and G 27; for explanation see text. Concentrations refer to millimoles of unit charge.

approach baseflow composition at the end of the summer. The hump in the sulfate concentration for G6 occurred from November 1976 to March 1977 – the wet season that followed upon the period of drought in 1976. As was described earlier (Nota and Bakker, 1983) the unusually high sulfate concentration at G6 largely resulted from the oxydation of the sulfides in the pyritiferous sediments of the Vaals Formation during the decline of the watertable in the period of drought in 1975 and 1976. These layers, rich in sulfates, were flushed during the following wet season and this water contributed to the stream as subsurface (interflow) water, superimposed on the bicarbonate baseflow water. G27 measures the discharge from the second branch in the Veljaren area. Before this water reaches the gauge, the stream has drained a seepage area where the Aken Formation is in the subsoil (Fig. 3). During the conditions of a declined groundwater table, a considerable quantity of hydrogen and sulfate ions, resulting from the oxidation of sulfides that occur in the Aken Formation, was produced. Consequently an extra flux of sulfate ions was carried off in the surface water during the following rainy period. The very pronounced sulfate peak for G27 coincides with a decrease of the HCO^-_3 concentration.

The above observations thus confirm that sulfate is brought into the catchment water not only from polluted precipitation but also from the aquifer system (Tables 2 and 3).

The temporal variations of the *concentration* of the dissolved solids over the period 1975 through 1979 are presented for two gauge sites – F6 (Hombourg) and F11 (Gulpen). These data (figure 21) are largely self explanatory and summarize much of the foregoing discussions.

A few comments may be given:

- The seasonal variations of what are by far the major ions, calcium and bicarbonate, are relatively low and thus confirm the drainage behaviour of a permeable catchment of which the baseflow portion is high;
- sulfate and silica are the third and fourth ranked solutes being released from the aquifer;
- silica in particular, with only minor variations, reflects its character as a baseflow component and shows a trend similar to calcium and bicarbonate;
- sulfate ion concentrations exceed average values during rainy periods after exceptional drought; concentration peaks are most pronounced when close to the source area of pyritic oxydation (between F4 and F6). An appropriate lowering of the bicarbonate concentrations occurs;
- the concentrations of K, Na, Mg and Cl ions generally are low, show frequent seasonal variations, and thus do not reflect baseflow characteristics; their source is primarily not lithologic but atmospheric (chloride), from road salting (sodium and chloride, 1979) or fertilizers (K and Mg ions).

Nitrate analyses that have been carried out from samples taken regularly between January 1980 and October 1984 show very pronounced seasonal variations. During periods of baseflow (Fig. 22) nitrate concentrations are lowest and vary between 10 and 15 mg/l; peak concentrations (between about 30 and 34 mg/l) occur during flood water periods, usually during the wet season between

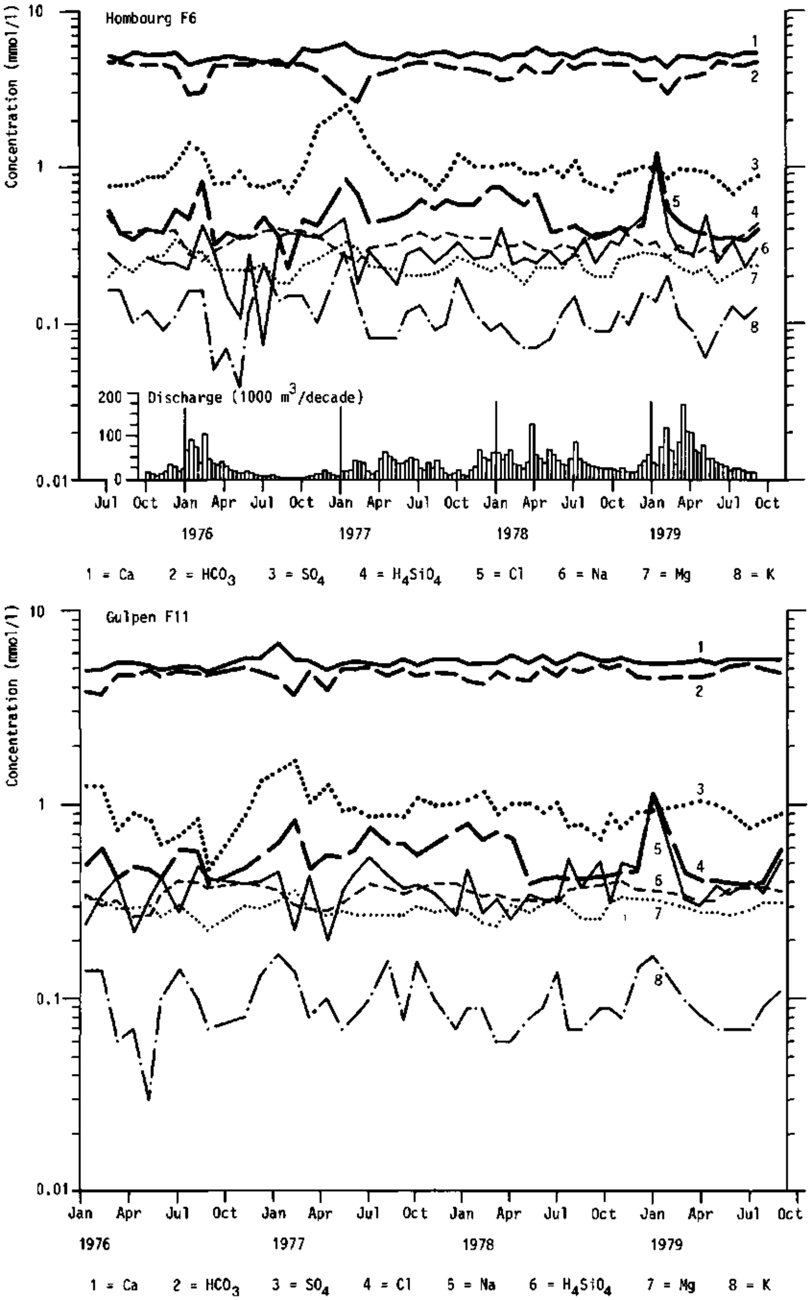

FIG. 21. Temporal variations over the period 1976 through 1979 in the concentrations of the dissolved constituents at stations F6 (Hombourg) and F11 (Gulpen); see text. Concentrations refer to millimoles of unit charge. The discharge hydrograph of F11 is not given, but it is similar to that of F6.

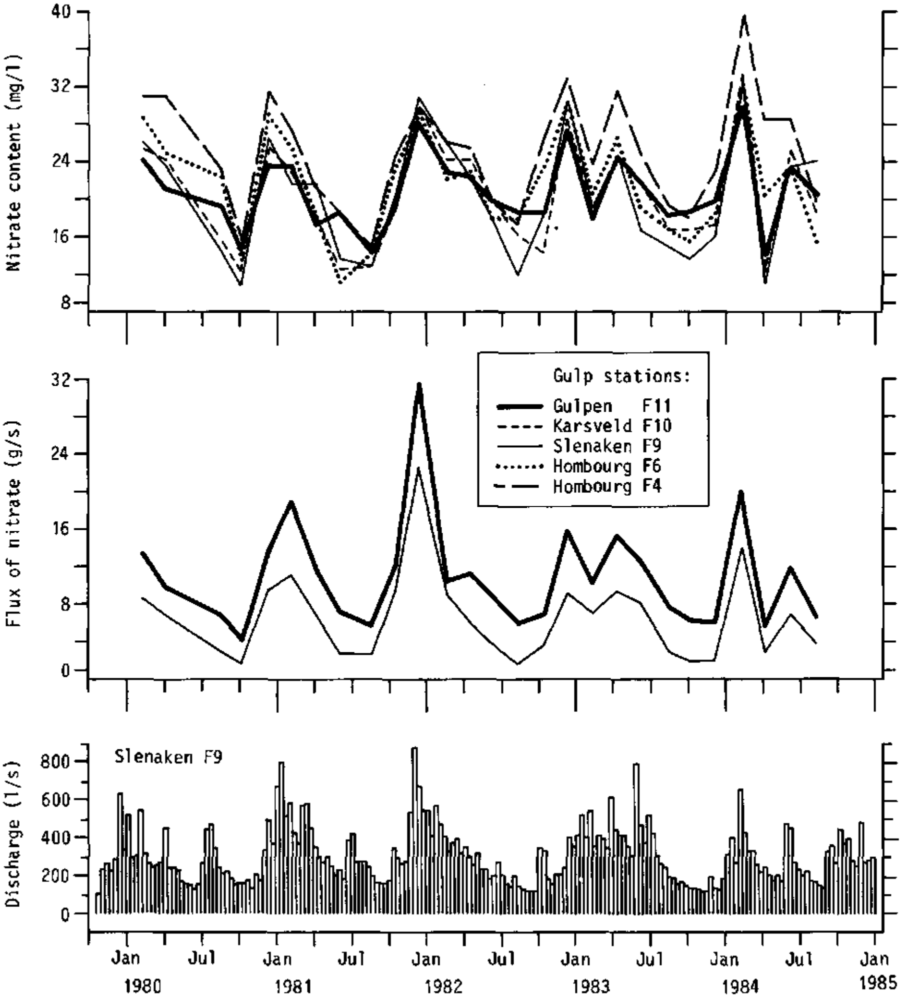

FIG. 22a. Variation of nitrate content for five gauging stations along the Gulp creek. Note that peak concentrations occur during periods of high flows. The discharge hydrograph of station F9 is given as a reference.

FIG. 22b. Flux diagrams of nitrate for stations F9 (Slenaken) and F11 (Gulpen). During the period recorded (4½ years) an average flux of 23 kg/hr NO^-_3 was carried through F9, while 39 kg/hr NO^-_3 had passed through F11.

November and April. These seasonal differences indicate that the degree of pollution of the baseflow waters is still low, while during the period of peak flow, when interflow is an important agent, hillslope subsurface water flushes nitrate from the toplayers (regolith) towards the valley, thus increasing substantially the pollution of the stream water. According to the available data there is a slight increase in the maximum nitrate values over the period of investigation.

5 SUMMARY AND CONCLUSIONS

This report deals with the study and interpretation of the chemical composition of ground water and surface water in the basin of the Gulp stream. Primarily, the relation of the water composition to the lithology has been studied to detect the dynamic interrelationship between surface and ground water; this approach proved also most helpful for finding the sources and routes of contaminants. The study of the temporal variations of water composition made it possible to identify different flow routes of the water passing through the basin and to understand the behaviour of the aquifer system under varying conditions.

An investigation was made of a relatively small catchment (4600 ha), in one of the stream networks that drain the dissected plateau in the southeastern part of the Netherlands (Fig. 1); this type of catchment was selected because a drainage basin of this size is most suitable in which to study the dynamic relationships.

For the readers' convenience much of the foregoing discussion has been depicted in the form of figures and tables. This information is largely self-explanatory and, if necessary, readers will find comments in the text. In order to avoid large scale repetition, only the major results will be summarized in the following:

1. The aquifer system of the Gulp catchment is a multiple layer Mesozoic sequence of which the chalk of the Gulpen Formation, forming the top layer, is most important for the storage and release of ground water.
2. The water composition of the Gulp basin is different from the adjacent Geul and Berwine networks (Table 1). The differences are primarily related to the geological framework (Fig. 2) and are also influenced by the activities of man. Comparison of the seasonal variations of the surface water shows that the ground-water storage capacity of the Gulp catchment exerts a stabilizing influence on the water composition (Fig. 19).
3. The dissolved load of the Gulp stream mainly consists of calcium and bicarbonate (about 75%), sulfate (8-12%) and silica (6-7%); flux diagrams (Fig. 18) show that in general the total dissolved load carried from the catchment is proportionally related to the discharge of the stream: in 1976 (precipitation 524 mm) the total of 1900 tons of calcium carbonate were removed through gauge site F11 (Gulpen); in 1981 (precipitation 788 mm) 3500 tons were carried off.
4. The overall permeability of the Gulp catchment is well illustrated by the relationship between the chemical composition of the ground water and the surface water (Fig. 7 and Table 3); baseflow comprises a good 70% of the total stream discharge and is largely sustained by the drainage of the chalk waters from the Gulpen Formation. The ground water of the Vaals Formation does not contribute substantially to the stream and that of the Aken Formation is only of local importance. Most of the ground water flowing out into the valley, discharges along two separate preferential routes – (a) through seepages and springs near the permeability break between the Gulpen chalk

and the silty clays of the Vaals Formation and – (b) through fractured sandstones interbedded in the Vaals Formation (Fig. 9). Groundwater escapes from the catchment along its southwestern boundary through a karstified fault zone (Fig. 3).

5. Plateau wells in the chalk generally show fairly regular concentrations over time (Figs. 15 and 16), but the concentration of ions may be elevated and variations get more irregular when the wells are under the influence of karstifications that affect the regolith. Temporal variations of the water composition are most pronounced for wells located along the valley slopes and in the zone of the valley bottom: subsurface flow, viz. interflow is considered to be the determining factor.
6. Subsurface flow along the valley slopes is an important agent in flushing pollutants downslope towards the surface streams. Observations in abandoned shallow dug wells indicate that the processes occur over a depth of several (2-5) metres. These processes prevent further percolation of a substantial part of the pollutants and thus affect the nutrient cycle. Temporal variations of nitrate concentrations and fluxes give clear evidence of this (Fig. 22). Observations in the surroundings have shown the occurrence of pseudokarstic features developed by throughflow (piping, tunnel erosion) in the regolith overlying the Vaals Formation.
7. The low degree of pollution, e.g. of nitrates, in surface waters as compared with severely contaminated ground water at a number of well sites is very striking. It is considered to be the result of dilution by deeper ground water and may also be associated with assimilation processes in the surface stream.
8. Although agriculture in the Belgian part of the Gulp catchment is less intensive than in the Dutch part, the flux of nitrate in the stream that crosses the border, is (in absolute as well as in relative terms) higher than the amount which is added to the Gulp stream in the Netherlands (Fig. 22b).
9. Shallow wells along the valley slope and in the valley bottom were found to be very vulnerable to pollution in catchments with pronounced relief. This phenomenon should be taken into consideration when plans are made to develop wells for local use in urban areas (Shallow Well Programs).

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