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Soil-Water Interactions [and Discussion]

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Soil–water interactions

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The composition of water flowing through and out of soils and rocks reflects the composition of the material that it has passed through. The chemical processes involved are mainly relatively rapid cation exchange reactions with soil colloidal materials, and slow acid hydrolysis reactions which decompose primary minerals. Examples are given of the results of these processes during flow through acid podzolic soils into surface waters. This pattern is modified during periods of high water discharge. The proportion of flow that takes different routes through the land surface, and the contact time with soil or rock, are then important for water composition. Sources of acidity can be generated within soil, when chemically reduced material in anaerobic environments is exposed to air by changes in the soil water regime. It is suggested that only detailed soil–water investigations in the field can satisfactorily explain lake and stream water composition at any specific site.

INTRODUCTION

The composition of atmospheric deposition may change by interaction with vegetation, as described earlier in this symposium. Percolating water may then pass over or through soil and permeable rock, where the possibility exists for more extensive alteration of its composition, with corresponding changes in the soil. Water then continues its passage into the surface drainage system of streams, lakes and rivers. The composition of the water entering streams or lakes is therefore determined by the interplay of two main factors: the composition of the soil and rock components of the land surface, and the hydrological pathway of percolating water through the land surface. The large number of options inherent in these two factors ensures that a wide variety of conditions may occur in nature. This overview outlines the processes involved and the results that they produce in certain prescribed circumstances. This allows reasonable predictions to be made for many type situations, which are confirmed by observations reported in the literature. A number of uncertainties still remain, and it is suggested that these can only be resolved by careful experimentation in the field.

It seems worthwhile to illustrate processes by using simplified quantitative data, in spite of the large variations that occur in nature. A suggested 'composition standard' for a solution percolating into soil in areas severely impacted by acid deposition, is given in table 1. This omits nitrate because it is usually small and variable in amount in northern Europe, but it is important if it occurs at the time of year when it is not taken up by vegetation, such as during snowmelt in spring. The amounts of sodium chloride indicate maritime influence, and it is frequently assumed that both of these ions interact little with the soil–rock system.

TABLE 1. EXAMPLE OF ACID RAIN COMPOSITION

percolation at surface/(mm a^{-1})		1000		
concentration of percolate/(meq l^{-1})	H^+	0.10	SO_4^{2-}	0.25
	$(Ca, Mg)^{2+}$	0.15	Cl^-	0.20
	Na^+	0.20		
addition from percolate/(eq m^{-2} a^{-1})	H^+	0.10	SO_4^{2-}	0.25
	$(Ca, Mg)^{2+}$	0.15	Cl^-	0.20
	Na^+	0.20		

INTERACTIONS OF ACID WATERS WITH SOILS: GENERAL PRINCIPLES

Cation exchange reactions

Many experiments with leaching columns on soil material have shown that cation exchange processes operate both rapidly and quantitatively. The adsorption of hydrogen ions by non-calcareous soils can be represented by the reaction

$$\text{soil Ca} + 2H^+ \rightleftharpoons \text{soil } H_2 + Ca^{2+}, \tag{1}$$

for which the 'equivalent fraction selectivity coefficient' (Helfferich 1967) reduces to:

$$K^1 = \frac{(q_H)^2}{q_{Ca}\, q_0} \frac{a_{Ca}}{(a_H)^2} = QS. \tag{2}$$

Where Q and S represent a surface and a solution component respectively, q = the surface adsorbed ions in meq kg^{-1}, q_0 = the cation exchange capacity of the soil, and a = ion activities in solution, mol kg^{-1}. Equation (2) rearranges to:

$$\tfrac{1}{2}\lg (K^1/Q) = \text{pH} - \tfrac{1}{2}\text{pCa} \tag{3}$$

thus defining the solution component. Ion exchange can only occur when excess salt is present so that the charge balance in solution must be maintained.

$$2m_{Ca^{2+}} + m_{H^+} = 2m_{A^{2-}} + m_{A^-},$$

where m refers to concentrations in mol kg^{-1}, and A^- and A^{2-} to monovalent and divalent anions respectively. This emphasizes the apparently paradoxical importance of the presence of anions for cation exchange reactions, otherwise there are no diffusible cations in solution to exchange. The selectivity coefficient K^1 is not a constant over the whole exchange isotherm, but (2) and (3) indicate the direction of the reaction and the position of equilibrium. The solution component $\text{pH} - \tfrac{1}{2}\text{pCa}$, known also as the lime potential, is readily determined for soils and waters; the Ca term is taken to include Mg ions also. Because pH varies over a much greater range (3.5–6.5) than does $\tfrac{1}{2}$pCa (1.2–1.7), a direct comparison of pH between soil solutions and influent solutions gives an approximate indication of expected reactions.

Concentration effects

For reaction of acid water to occur with soil, there must be considerable disequilibrium between their initial hydrogen ion concentrations. The greater the disequilibrium the more rapid the reaction, and an equivalent amount of $(Ca, Mg)^{2+}$ cations are displaced by a given amount of strong acid. Thus hydrogen ion *concentration* as reflected in pH, or better $\text{pH} - \tfrac{1}{2}\text{pCa}$, is the only determinant of reaction. The volume of water in which a given acid deposition is dissolved, is therefore also important. Figure 1 shows the different effects of the standard acid deposition of 0.1 eq m^{-2} a^{-1} given in table 1, when deposited in extremes of 400 mm and 5000 mm of rainfall, giving mean pH values of approximately 3.6 and 4.7 respectively. The extent of reaction with soils of a given pH is indicated approximately by the horizontal lines of the diagram. The more dilute rain will not affect the soil of pH 4.7, in spite of containing the same total amount of strong acid as the more concentrated rain. On the other hand, both solutions would have equal effect on soils of pH between 5.5 and 6.0, for both would react strongly with the soil and the whole of the 0.1 eq m^{-2} would be adsorbed; here the *amount* of acid is important. For soil at pH 3.6, the dilute rain will be acidified by the soil, but the concentrated rain will have no effect.

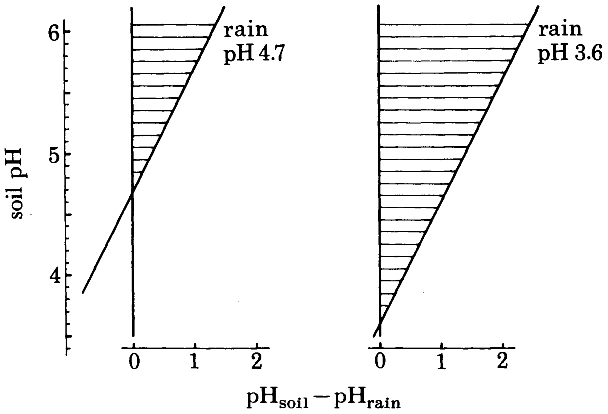

FIGURE 1. Diagram to illustrate the effect of concentration and amount of acid on its reaction with soil. 0.1 eq m^{-2} a^{-1} of acid deposited by 400 mm rainfall would give a mean pH of 3.6, and when deposited by 5000 mm rainfall would give a mean pH of 4.7. The horizontal lines indicate the extent of disequilibrium between rain and soil. Provided disequilibrium occurs, reaction with soil is equivalent to the amount of acid deposited.

Changes expected in soil

Accelerated acidification of soil by acid deposition at a distance from point sources is by its nature extremely difficult to detect. It can only be a slow, long-term process, and it is difficult to separate natural acidification processes from the extra anthropogenic airborne burden. The evidence of Butzke (1981) seems to indicate detectable changes in poorly buffered forest soils in Germany, but a similar picture documented by Troedsson (1980) in Sweden shows a strong correlation between the age of forests and the decrease in pH of the soil A_0 horizon.

We can, however, calculate the effect of our standard acid input on a non-calcareous loam soil of pH 6 of moderate buffer capacity and exchangeable $(Ca, Mg)^{2+} \approx 100$ meq kg^{-1}, typical of much agricultural land in the cool moist temperate zone. The acid input from the polluted rain will leach approximately 50% of the exchangeable (Ca, Mg) from a 10 cm depth of soil in about 50 years, leaving the soil with pH ≈ 5. This assumes that the soil contains no weatherable minerals (see below) or other acid-consuming mechanisms to replace this base cation loss. The effluent would have pH ≈ 6, but would have higher concentrations of (Ca, Mg) than the incoming water, because of natural bicarbonate leaching, as in table 2.

Many sandy soils have much lower cation exchange capacities and exchangeable (Ca, Mg) contents than this example, and would be expected to acidify correspondingly more quickly. It is likely, however, that semi-natural sandy soils have acidified naturally long ago, and if the soils are managed for agriculture they would be regularly limed so that no damage can occur.

Table 2. Reaction with topsoil pH 6

	inflow	meq l^{-1}	soil	meq kg^{-1}	outflow	meq l^{-1}
ion composition	H^+	0.10	exch. (Ca, Mg)	100	H^+	0.001
	$(Ca, Mg)^{2+}$	0.15	total acidity	100	$(Ca, Mg)^{2+}$	0.35
	SO_4^{2-}	0.25			SO_4^{2-}	0.25
					HCO_3^-	0.10
pH	4.0		6.0		6.0	

10 cm depth of soil becomes 50% decalcified, to pH 5, in 50 years.

An indication of the change produced by a given acid input is given by the *buffer capacity* of the soil, defined by $\beta = \Delta AB/\Delta pH$, the input of acid or base required to produce a given change in pH. The cation exchange capacity (which is routinely measured on soil survey samples) is often taken as a good indication of buffer capacity (McFee 1980), or the buffer capacity can be directly measured in the laboratory. Neither of these measurements takes account of slow changes in the soil that can adsorb acid, such as penetration to the interior of clay layers, or the weathering of primary minerals that the soil contains, and these processes will be important in the response of soils to acid inputs over a number of years.

Interactions with strongly acid soils

Percolation through podzolic soils and peats

The typical natural or semi-natural soils of the cool moist temperate zone are podzols, peaty podzols and peats (spodosols and histosols), and these support mainly forest or heath vegetation. A simplified representation of the chemical features of one such soil is given in table 3. Very acid surface humic horizons, and pale coloured leached A horizons, overlie somewhat less acid B horizons, which are strongly coloured by coatings of iron hydroxides and, or, humus precipitated after moving from the upper horizons. These grade into the C horizons, which are typically weathering tills, moraines or rotting country rocks.

The humic surface layers may have pH ≈ 3.5, exchangeable $(Ca, Mg)^{2+} \approx 10$ meq kg^{-1}, but total acidity (to pH 8) up to 1000 meq kg^{-1}. The low pH and high exchange capacity of these humic layers causes water flowing through them to reflect their composition: the acid humic horizons adsorb $(Ca, Mg)^{2+}$ from the water and release H^+, so that the pH of the percolate is lowered to about 3.6 (table 4). Experiments with peat in leaching columns shows that acid humus does not appear to adsorb Na^+ in exchange for H^+, the preferential adsorption of Ca^{2+} being enhanced by organic complexing, which does not affect Na^+.

The reactions that occur in the mainly mineral B horizons depend on whether or not anion adsorption occurs. The dominant exchangeable cation of podzol B horizons is Al^{3+}, with only small amounts of $(Ca, Mg)^{2+}$ (table 3). The anion concentration of the solution is the critical variable, because the cation concentration must be equivalent to it. The main cations in the system are Al^{3+} and H^+, with small amounts of $(Ca, Mg)^{2+}$ and Na^+, and their solution concentrations are determined by the proportions of each present, and the strength of their bonding to the mineral surface which is reflected in selectivity coefficients for exchange. At pH ≈ 4.5, Al^{3+} concentrations in equilibrium with mineral subsoils were higher than H^+ concentrations, 0.50 and 0.03 meq l^{-1} respectively, for soils studied by Bache (1974). The

TABLE 3. SOME CHEMICAL DATA OF TYPICAL PODZOL SOIL HORIZONS

			exchangeable cations meq kg^{-1}	
		soil pH	$(Ca, Mg)^{2+}$	Al^{3+}
humic horizons	F–H	3.5	10	5
bleached horizons	A	3.8	1	8
enriched horizons	B	4.5	0.5	15
parent material	C	6.0	—	—

TABLE 4. CHANGE IN WATER COMPOSITION BY INTERACTION WITH CERTAIN HORIZONS OF A PODZOL SOIL PROFILE

		H	(Ca, Mg)	Al	Na	SO_4	Cl	HCO_3
stage, soil horizon	pH				meq l^{-1}			
inflow	4.0	0.10	0.15	—	0.20	0.25	0.20	—
humic horizons	3.5							
exch. (Ca, Mg) = 10 meq kg^{-1}								
exch. acidity = 1000 meq kg^{-1}								
intermediate 1	3.6	0.25	—	—	0.20	0.25	0.20	—
B horizon	4.5							
exch. (Ca, Mg) = 0.5 meq kg^{-1}								
exch. Al = 15 meq kg^{-1}								
total acidity = 50 meq kg^{-1}								
intermediate 2a (no SO_4 adsorption)	4.5	0.03	—	0.22	0.20	0.25	0.20	—
intermediate 2b (SO_4 adsorption)	4.5	0.03	—	0.07	0.20	0.10	0.20	—
C horizon decomposing minerals	6.0							
outflow	6.0	0.001	0.30		0.25	0.20	0.20	0.15

solution in equilibrium with this horizon, and that flowing from it, will therefore be dominated by Al^{3+} and its hydrolysis products. A small adsorption of Na^+ is likely to occur here, to give an approximate ion balance as in table 4. If the sesquioxide content of the B horizon is sufficient for SO_4^{2-} adsorption to be complete, perhaps forming basic aluminium sulphate (Nordstrom 1982), the salt concentration will be reduced, but SO_4^{2-} is unlikely to be completely adsorbed. Even if SO_4^{2-} was completely adsorbed, Al^{3+} would still leach from these horizons with Cl^- or NO_3^- anions. In this sense Cl^- is not unimportant, although it does not interact specifically with soils. Nitrate only occurs in subsoils under unusual conditions, such as the removal of vegetation or the sudden rewetting of dry soils, because it is normally taken up by vegetation in the upper horizons. When it does leach through, however, it is strongly associated with Al mobility in B horizons.

Primary mineral decomposition in soils

The normal flow of water through a podzolic soil takes it into a C horizon of rotting rock or glacial moraine that usually contains at least the vestiges of some primary minerals in various states of decomposition.

Primary minerals may occur as discrete fragments in soils, or in more massive conglomerations as components of rocks. Their decomposition following exposure to the moisture, chemical and temperature conditions at the surface of the earth is usually termed ‘weathering’. Although water is the primary chemical agent of decomposition, simple solution accounts for very little mineral breakdown, and acid hydrolysis is the main process involved (table 5). Carbonic acid is the most important acid, dissolved CO_2 in equilibrium with air giving a pH of 5.6 and a total $(CO_2 + HCO_3^-)$ concentration of 10^{-5} M at 25 °C.

TABLE 5. DECOMPOSITION OF PRIMARY MINERALS

processes	
simple solution	
acid hydrolysis	
carbonic acid	$H_2O + CO_2 \rightarrow H^+ + HCO_3^-$
humus acids	$(R.COOH)_n$, $(COOH)_2$
mineral acids	HNO_3, H_2SO_4
oxidation	$Fe^{2+} \rightarrow Fe^{3+}$
	$S^{2-} \rightarrow SO_4^{2-}$
examples	
calcite	$CaCO_3 \xrightarrow{2H^+} Ca^{2+} + H_2CO_3$
anorthite	$CaAl_2Si_2O_8 \xrightarrow{2H^+} Ca^{2+} + Al_2(OH)_4Si_2O_5$
olivine	$(Fe, Mg)_2SiO_4 \xrightarrow{2H^+} Mg^{2+} + Fe(OH)_3 + Si(OH)_4$

Higher partial pressures of CO_2 are experienced in organic topsoil horizons, where decomposing plant and animal remains and the slow oxidative decomposition of humus also produces both organic acids and simple mineral acids. While many of the organic products may be ephemeral, soluble polycarboxylic acids ('fulvic acids') are sufficiently persistent and in high enough concentration to be important, and oxalic acid excreted by lichens, $(COOH)_2$, is an important decomposition agent on bare rock surfaces (Wilson *et al.* 1981).

If calcite occurs in soils or rocks, it rapidly neutralizes any percolating acid and the pH of the solution rises above 7. Feldspars, micas and ferromagnesian minerals decompose in natural acids, but at very different rates depending on their crystal structure and composition (Berner 1978) and the accessibility of percolating water to the decomposing mineral. Plagioclase feldspars (Ca, Na) decompose more rapidly than orthoclase (K) and the oxidation $Fe^{II} \rightarrow Fe^{III}$ assists the decomposition of minerals such as biotite, hornblende and olivine. These processes all consume acid, and they occur at faster rates as the pH drops (Helgeson 1971) and as the particle size of the minerals decreases. The base cations (Ca^{2+}, Mg^{2+}) are leached mainly as bicarbonate salts and the pH of the medium rises to near 7. Quartz (SiO_2) is a major constituent of granites and gneisses, but is extremely stable and is virtually unweatherable. Some sandstones may be composed almost entirely of quartz, and having no decomposable minerals they will have virtually no capacity to neutralize either natural or anthropogenic acid.

These mineral weathering and decomposition reactions normally neutralize all natural or anthropogenic acid, so that in water flowing from the base horizons of podzolic soils, even on granitic rocks, the anions are leached as Ca, Mg and Na salts together with bicarbonate in solutions of pH 6–7. The composition of stream water from a selection of rocks, including 'acidic' ones (that is, high in SiO_2), is given in table 6. Provided rocks contain weatherable minerals, there is abundant capacity to neutralize acidity (Bache 1983). Water draining from deeper fluvioglacial deposits around some acid Swedish lakes showed these features (Hultberg & Johansson 1981).

Table 6. Stream water composition from various sources

rock	source	pH	(Ca, Mg)	M^+	SO_4	Cl	HCO_3	SiO_2
			meq l^{-1}					mmol l^{-1}
quartz diorite	(1)	6.2	0.22	0.16	0.02	0.01	0.33	0.03
pelitic schist	(2)	6.6	0.16	0.10	0.10	0.06	0.11	0.15
mixed schists	(3)	4.9	0.11	0.05	0.13	0.02	0.02	0.08
granite	(4)	6.4	0.25	0.24	0.14	0.17	0.17	0.14
calcareous sandstone	(1)	8.0	0.89	0.07	0.20	0.01	1.20	0.08

(1) Garrels & Mackenzie (1967); (2) Bricker *et al.* (1967); (3) Likens *et al.* (1977); (4) Reid *et al.* (1981).

Hydrologic pathways through land surfaces, and their effects

Outline of the main water flow patterns

The simple percolation of water in a mainly vertical direction down a soil profile, and its flow along a rock surface issuing into a lake or stream, as described in the previous section, contributes to the *base flow* of streams when light rain is falling (figure 2*a*). This pattern of water flow ensures almost complete neutralization of acids by soils and rocks, and gives stream water of relatively high pH.

Continuous heavy rain may produce quite a different pattern of water movement in some catchments, as illustrated by the sharp hydrograph peak, decaying exponentially with time, for the upper basin shown in figure 3. Three major processes contribute to this hydrograph peak (Dunne 1978). Percolation of rain into soil rapidly re-charges soil moisture and quickly saturates the deeper soil horizons which have relatively low porosity, and later the surface horizons with higher porosity may also become saturated. Saturated pore space generates *subsurface flow* (or throughflow) laterally down the hill slope. Upper soil layers have the highest porosity, and in a study on glacial till in Sweden subsurface flow occurred mainly in the top 50 cm of the soil profile where the hydraulic conductivity was $> 10^{-5}$ m s^{-1}, but was almost negligible in lower horizons (Lundin 1982).

As more soil becomes saturated, the water table appears at the surface in hollows and depressions or emerges as a spring line. Flow then occurs over the land surface much faster than within soil, and this tends to be most common at the base of slopes. In heavy storms, overland flow is the main source of most of the water contributing to the sharp hydrograph peak. Its major component is *return flow* consisting of water that has initially entered the soil on high land, and has returned to the surface at lower levels. *Direct precipitation* onto saturated areas also contributes to saturated overland flow.

The lower basin hydrograph depicted in figure 3 is quite different, and this pattern of flow is found on topography with gentle straight slopes, and deep soils that have a high water storage capacity, so that they rarely saturate to the surface, even during storms. Here most of the water moves by subsurface flow.

Two special cases need to be mentioned, that are important for acid rain considerations. *Bare rock surfaces* occur particularly in Scandanavia and in North America, because of erosion of the weathering skin on the rock from which soil is formed. The erosion may be natural, or accelerated because of changes in vegetation, which exposes soil to rain wash and frost heaving. Obviously rainfall runs rapidly off the bare rock, but still normally passes through some rotting rock, soil or peat on the lower part of slopes before entering streams or lakes. *Pipe flow* is

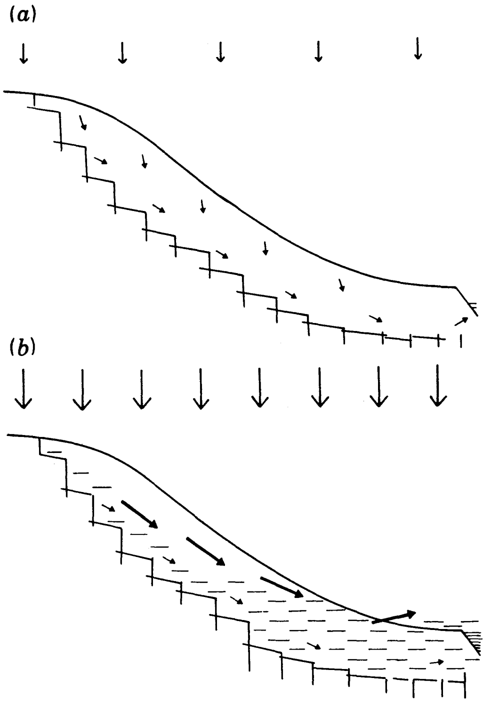

FIGURE 2. Diagrams to illustrate hydrology on hillslope soils. (*a*) Light rain produces base flow to streams. (*b*) Heavy rain produces throughflow and return overland flow.

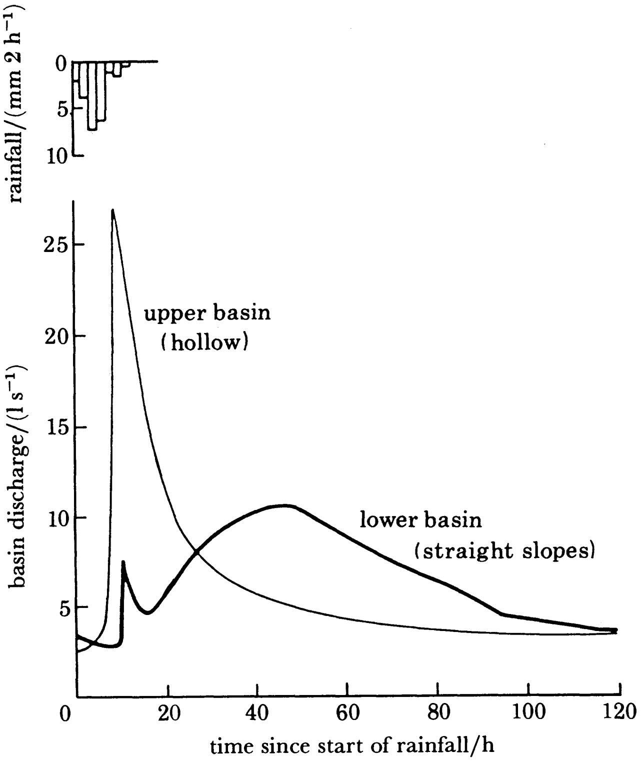

FIGURE 3. Storm hydrographs from an upper basin and a lower basin (both 0.1 km²) of a catchment in Somerset. From Dunne (1978). (Reproduced with permission.)

concentrated rapid subsurface flow of water in natural channels. These channels are particularly prevalent in peat lands, but may occur anywhere owing to subsurface erosion or solution, or to animal or large root channels.

Distribution of flow in space and time

The aspects of the hydrological pathways that are of most importance for acid deposition effects are (i) the proportion of flow that takes different routes through the land surface, and (ii) contact time with soil or rock. The latter can be expressed in terms of residence time distribution or transit time distribution functions, and although these have been worked out and demonstrated in simple experimental systems (Himmelblau & Bischoff 1968), little work has been done in the field because of the obvious practical difficulties. It is clear, however, that a very wide range of distributions can operate.

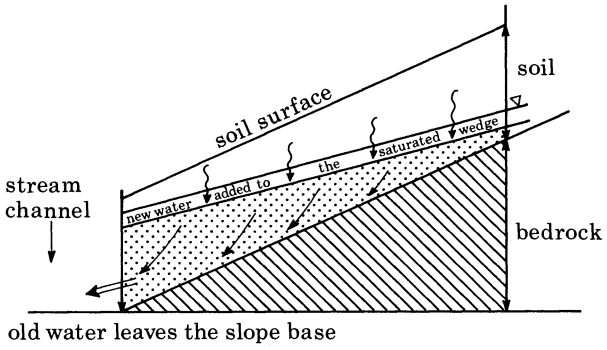

FIGURE 4. Displacement of a wedge of 'old' water from groundwater storage by recent rainfall. From Anderson & Burt (1982). (Reproduced with permission.)

The storm hydrograph peak in figure 3 shows that a large volume of water enters the stream within hours of the storm beginning. What this does not show, is where that water comes from and how long it took to get to the stream.

The indications from both hydrological and chemical studies of a Somerset catchment are that 'new' water displaced 'old' water from a saturated wedge, as shown schematically in figure 4 (Anderson & Burt 1982). This has also been demonstrated by using tritium as tracer for water in simulated storms, which showed that the tagged water moves downward as a distinguishable water mass, between the older rainwater below and the younger rainwater above (Dunne 1978). The precise pattern of flow must, however, depend on the porosity and conductivity of the soil horizons, but if most of the hydrograph peak flow is return flow, as is normally though to be the case (Dunne 1978), the water may still have been flowing through soil and rock for a considerable time. Chemical tracing techniques, or observations of the chemical composition of waters, are needed to answer these questions, but the data available are limited.

Oxygen isotope ratios were used by Rodhe (1981) to show that normally 75–86% of the runoff into the Lake Gårdsjö catchment, Sweden, is from groundwater discharging close to the stream, and that even in times of intense snowmelt or heavy rain, 66–80% of the runoff comes from groundwater discharge. The use of tritium for tracing water movement in the same catchment showed longer residence times (10–30 d) than might have been expected, particularly in view of groundwater level measurements which fluctuated rapidly during stormflow discharges (Nilsson 1981).

Because rain normally has much lower concentrations of solutes than soil or groundwater, the comparison of the specific conductance of streams during stormflows with those of rainfall and throughflow can in principle indicate the proportions of water coming from different sources, by means of a chemical mixing model. In its simplest form this can be expressed as

$$Q_T C_T = Q_1 C_1 + Q_2 C_2,$$

where Q indicates the water flux and C its concentration, for two different water sources 1 and 2, and for the combined totals T (Pilgrim *et al.* 1979). Anderson & Burt (1982) found only a little difference between two water sources for a small catchment on Old Red Sandstone, and concluded that although a chemical mixing model may give generally useful conclusions, it cannot predict complex runoff in detail. Reid *et al.* (1981) measured the concentrations of a number of ions during a storm event. Figure 5, taken from their work, shows not only a massive dilution of bicarbonate, which was accompanied by a pH drop of from 7 to 5, in storm water from a $41\ \mathrm{km}^3$ catchment, but also an increase in the output of total organic carbon. The authors attribute this behaviour to the storm flow being mainly through the upper (acidic organic) horizons of the soils, whereas the base flow passes through the lower mineral horizons.

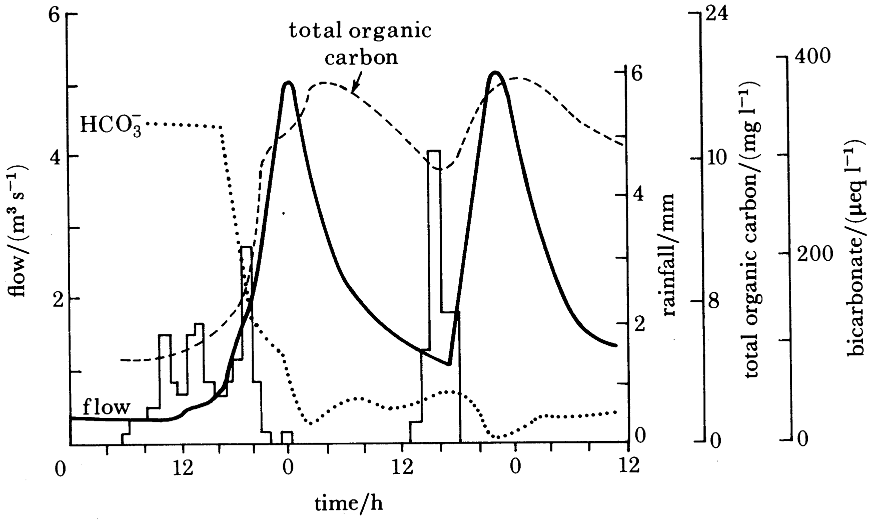

FIGURE 5. Concentrations of bicarbonate and total organic carbon in stream water during storm events in Glendye, Grampian. Water pH dropped from 7 to 5, following the drop in bicarbonate concentration. From Reid *et al.* (1981).

The pattern that seems to be emerging is that a high proportion of even storm or snowmelt water passes through rock or soil at some stage on its journey to a stream or lake. The only obvious exception is direct precipitation onto saturated areas of land, or onto lakes. When very large volumes of water from heavy storms or snowmelt are encountered, a small proportion of stream runoff may come from direct overland flow.

Modification of chemistry by water flow patterns

The picture given earlier of the chemical interaction of percolating water with acid podzolic soils can be profoundly modified, not only by changes in hydrological pathways, as in figure 2*b*, but also by the rate of water movement. Some interaction with rain occurs even with bare rock surfaces (Abrahamsen *et al.* 1979), but very little would occur during pipe flow, or when rain enters surface water channels by direct precipitation. Whether these processes occur in a particular case can only be decided by observation. Braekke (1981) found that about one third of the water draining a shallow soil catchment in south Norway had 'short circuited' any soil interaction.

Although cation exchange reactions in soils are rapid in the laboratory, there seems to be no experimental information on the flow rate or flow pattern of water through soil that is required to produce a quasi-equilibrium between water and soil. However, it is clearly possible that during high flow rates some water has insufficient time to react with soil. But many of the occurrences of surface waters that are more acid than would be expected from base flow waters, are more than likely to be caused by soil-induced acidity, rather than by precipitation acidity. Two situations in particular have been observed.

(i) Water from superficial organic horizons may move directly into water courses during heavy rain, either as straightforward subsurface flow, or as return flow or overload flow (figure 2*b*). Such water is typically coloured pale brown by soluble organic compounds (fulvic acids), and has low pH and low calcium and aluminium concentrations. These conditions have been reported during storms in a large granitic catchment in Scotland, see figure 5, taken from Reid *et al.* (1981), and from waters flowing from bog areas into Swedish lakes (Hultberg & Johanssen 1981). Bog areas frequently occur around the stream outlet to upland catchments, and in Braekke's (1981*a*, *b*) study, 62% of the catchment water drained from such peatlands, but only 2.5% directly from bedrock and shallow soils, although the latter occupied 73% of the area of the catchment. This gives ample opportunity for the peat to control water composition. A recent study of lake water in the Adirondack mountains (Everett *et al.* 1983), where the most-acid lakes frequently had areas of *Sphagnum*-rich wetlands draining into them, suggested that return flow through acid humic horizons may well have been a major source of the acidity. Acid deposition could, however, still contribute to this acidity, if strong-acid anions from the deposition have moved through the catchment without adsorption by soil processes. Even neutralized high pH waters can become acidified again provided they contain some strong-acid anions, because bicarbonate will be decomposed by reaction with acid peat.

(ii) Water from podzol B horizons may enter lakes or streams directly if the profile is exposed at the bank of a stream or lake. This could have occurred for water draining from shallow moraines into two Swedish lakes that had pH 4.2–4.8 and Al concentrations from 0.28 to 0.08 meq l^{-1} (Hultberg & Johansson *et al.* 1981). Drainage channels in forests that inadvertently cut into B horizons could also tap acid aluminous waters and lead them into streams. Some of the throughflow down slopes during storm events must occur in B horizons, so increasing its Al concentration, but return flow through humic horizons may well make the water more acid but remove Al by organic complexation.

SOME UNRESOLVED ISSUES

Additional sources of strong acid anions

The importance of strong acid anions in mediating acidity during the interaction of waters with soils is well accepted. It is often assumed that excess sulphate in deposition, after subtracting the sea salt contribution, has been derived from pollution sources (Henrikson 1980).

Other workers, however, claim that there is a greater background contribution of neutral sulphates than is normally recognized (Sørensen 1979). The principles described above show that neutral sulphates will generate acidity in streams and lakes because of the exchange interaction with acid soils, and thus contribute to lake acidity.

The formation of strong acid anions *in situ* is probably a more important source of natural acidity, and is caused by oxidation of previously reduced soils by changes in water levels. Microbial action combined with aeration causes oxidation of organic matter, and can release carbon as CO_2, nitrogen as NO_3 and sulphur as SO_4. Much of the sulphur in bogs probably occurs as sulphide, and this is oxidized to sulphuric acid when previously waterlogged soils dry sufficiently for air entry to occur. Drainage operations frequently precede tree planting, and the increasing evapotranspiration of a growing forest must alter soil hydrology towards a more oxidized condition. Some weathering rocks may also contain mineral sulphides, but these are of only local occurrence.

A related phenomenon that has frequently been observed, is the release of sulphate and nitrate from soils on rewetting after a hot dry spell, such as reported by Braekke (1981*a*, *b*), and Christopherson & Wright (1981), for organic soils in Norway. Because waterlogged peats absorb sulphate by reduction, it is possible that sulphate re-mobilized on drying has in any case been deposited in recent times from the atmosphere. This, however, seems unlikely in the example quoted, because the total sulphur contents of the surface horizons were less than in the deeper layers of peat (Braekke 1981*a*, *b*).

Contrasting behaviour of similar catchments

Catchments on the same geology and receiving similar deposition are reported to give waters with different chemical compositions. A broad regional survey of Adirondack lake waters found that those with pH $\leqslant 5$ occurred in areas with bedrock containing less than 5% CaO (Everett *et al.* 1983), but in any survey there seem to be exceptions to the principle of geological control of water composition. A detailed examination of the soils that supply water to streams and lakes is necessary to resolve these anomalies. The detailed water flow pattern is clearly also important but is difficult to measure; however, it may be possible to gain much information on this from simple observation during contrasting flow patterns. Very few studies have attempted detailed soil examination. Most work relies instead on input–output data, and fits them to conceptual models of what may, or may not be, happening in between (Henriksen 1980; Christopherson & Wright 1981). It seems essential to perform some detailed soil–water investigations on landscape segments in areas where there is still controversy over the causes of surface water acidification.

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Discussion

J. G. OGDEN, III (*Department of Biology, Dalhousie University, Halifax, N.S. B3H 4J1, Canada.*). Sulphate reduction to H_2S in acidic bogs now appears to be generally observed. In a seasonal ionic mass balance study of a small bog in central Nova Scotia, I observed that a 33% and 45% decrease in sulphate-sulphur over two summers was exactly balanced as H_2S by H^+ resulting from pH differences between volume-weighted precipitation and outflow (Ogden 1982). Have specific low pH sulphate-reducing bacteria been identified and characterized?

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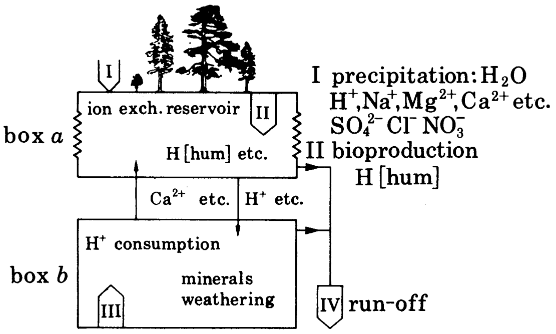
Ogden, J. G., III 1982 *Wat. Air Soil Pollut.* **17**, 119–130.

K. A. Brown (*Central Electricity Research Laboratories, Kelvin Avenue, Leatherhead, Surrey KT22 7SE, U.K.*). Sulphate reduction certainly occurs in the anaerobic zone of peat bogs, with much of the hydrogen sulphide being incorporated into humic materials, and less than 0.5% being released into the atmosphere. We have not, however, identified the species performing the reduction.

I. Th. Rosenqvist (*Oslo University, Box* 1047, *Blindern, Oslo, Norway*). In his presentation Dr Bache ignored the Na^+ and Cl^- in the precipitation. Skartveit *et al.* (1980) showed that the content of seasalts in otherwise unpolluted rain caused a high increase in acidity in rivers: they became more than seven times more acid than the main stream that caused the flood. When Seip *et al.* (1980) sprayed the snow of a catchment area with NaOH so that it melted to water with pH 8.5, the runoff in the spring was just as acid as the year before, that is pH 4.3. There is also an upwards movement from the groundwater in frozen ground and in dry periods to be taken into account. In a severe winter we have measured a capillary rise of more than 100 kg m^{-2} of water.

Professor Rosenqvist illustrated some of these points by referring to the following diagram.



type reactions

box a $Na^+ + An^- + H[hum] \longrightarrow Na[hum] + H^+ + An^-$

box b $2H^+ + Ca\ silicate \longrightarrow Ca^{2+} + H_4SiO_4 + Al(OH)_3$

box a $Ca^{2+} + 2Na[hum] \longrightarrow Ca[hum] + 2Na^+$

$An = SO_4^{2-}, Cl^-, NO_3$

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B. W. Bache. Professor Rosenqvist is quite correct to point out that NaCl in precipitation derived from seasalts can interact with soils. However, Na^+ exchanges for H^+ in humus much less strongly than does Ca^{2+}, but Cl^- is at least as effective as SO_4^{2-} and NO_3^- as a mobile anion in allowing leaching of H^+ and Al^{3+} from soils. Upward movement of water in soils certainly occurs when climatic conditions are favourable for it, but acidification processes are the result of downward leaching.

P. Goldsmith (*Meteorological Office, Bracknell, Berkshire, U.K.*). In describing Dr Bache's conceptual model no mention is made of the role of evaporation. There can be no doubt that the concentration of pollutants in the soil because of evaporation can in itself subsequently lead to pulses of high acidity in soil water.

B. W. Bache. This is perfectly correct.

D. Fowler (*Institute of Terrestrial Ecology, Bush Estate, Penicuik, Midlothian EH*26 0*QB, U.K.*). Dr Bache indicated that for rainfall with a pH the same as that of a soil we should expect no reaction with the soil, but rainfall events show very variable acidity. Would you expect any net change in the soil as a consequence of rainfall whose volume-weighted mean acidity is the same as that of a given soil, but whose individual events are log-normally distributed in the pH range 3.0–6.0?

B. W. Bache. I think this depends very much on the cation composition of the rain. If the only electrolyte in the rain was an acid (that is, hydrogen ion and an anion), I would expect the situation you describe to result in net soil acidification. But if (as often happens) the rain contains some Ca^{2+}, Mg^{2+}, NH_4^+ and Na^+, an acid soil will adsorb these cations and release hydrogen, if the pH of the rain is above that of the soil, thus compensating for the acidification that occurs when the pH of the rain is lower than that of the soil. What actually happens must depend very much on the precise composition of soil and rain.