# Chemical processes governing soil and water acidification

**J. O. Reuss*, B. J. Cosby† & R. F. Wright‡**

* Department of Agronomy, Colorado State University, Fort Collins, Colorado 80523, USA
† Department of Environmental Sciences, University of Virginia, Charlottesville, Virginia 20903, USA
‡ Norwegian Institute for Water Research, Box 333, 0314 Oslo 3, Norway

*Strong empirical evidence links deposition of strong acids from the atmosphere to acidification of freshwaters and loss of fish populations. Chemical processes in soils explain the composition of soil solution and surface waters and when coupled with input–output fluxes these processes, in concert with acid deposition, account for observed trends in soil and water acidification. The widespread recent acidification of surface water in eastern North America and Europe is due to the superposition of acid deposition upon natural acidifying processes in soils.*

DURING the past several decades, lakes and streams in large regions of northern Europe and eastern North America have undergone acidification and suffered loss of fisheries[1-3]. These same regions currently receive atmospheric inputs of strong acids at levels several times greater than pre-industrial background levels[4]. There is thus strong empirical evidence linking acid deposition to acidification of surface waters in both time and space[1,2,5].

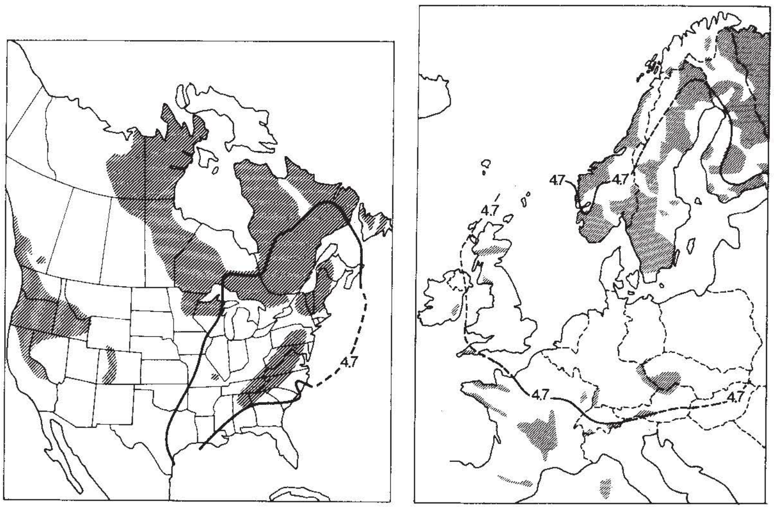
Two factors appear necessary and sufficient to explain the distribution of acidified waters: the inherent sensitivity of the landscape to acidification and acidic atmospheric deposition[1,2,6] (Fig. 1). Acidification is most pronounced in poorly buffered, low-ionic-strength surface waters. Many thousands of lakes of this type dot the glaciated regions of the Precambrian shields of North America and northern Europe. Such 'sensitive' waters typically drain areas underlain by granitic or other highly siliceous bedrock covered by thin and patchy soils.

Freshwaters in sensitive regions not receiving acidic deposition are generally calcium-magnesium bicarbonate waters with $p$H levels above 5.5 (ref. 7). Such waters are abundant, for example, in northern Scandinavia[1,8], Labrador[9], northwestern Ontario[9], and the western United States[10]. Sensitive regions receiving acidic deposition, on the other hand, commonly have sulphate-dominated waters that are often acidic and aluminium-rich, with $p$H levels below 5.5 (ref. 7). Such acid waters are found, for example, in southern Scandinavia[11], southern Quebec[12], and the Adirondack Mountains of New York[13].

In spite of the strong correlation in time and space between the deposition of strong acids and the acidification of freshwaters and resultant loss of fisheries in sensitive regions, the soil-mediated processes by which acidification occurs have only recently been quantitatively described[14]. The fact that acidified waters are generally found in areas with acidic soils has led some to question the role of acid deposition and instead argue that changes in the terrestrial ecosystem alone can account for the observed acidification of freshwaters[15,16]. These sceptics point out that acidic podzolic soils contain acid in amounts equivalent to thousands of years of acid deposition, and thus draw the conclusion that atmospheric acidic deposition is inconsequential compared to naturally produced acid stored in the soils. As we show here, neither the empirical evidence nor basic soil science theory supports this conclusion.

Soil chemical processes lie at the heart of the acidification process; the typical recently acidified lake is a drainage lake which receives only a minor fraction of water directly from the atmosphere. (Seepage and perched lakes, of course, receive significant acid inputs directly from the atmosphere.) Resolution of the apparent paradox by which alkaline waters can be derived from acidic soils in regions not receiving acid deposition, and by which a relatively small amount of strong acid added to an acidic soil can cause a dramatic decrease in the $p$H of runoff, requires consideration of several key soil-chemical processes. We examine here the influence of several such processes: the adsorption and desorption of anions and cations on soil surfaces,

**Fig. 1** Maps of Europe and North America showing areas sensitive to freshwater acidification (from bedrock geology). Sensitive areas are characterized by carbonate-free, highly siliceous bedrock, overburden and soils. Soils in such areas are typically podzolic, acidic and have low base saturation. Freshwaters in these are poorly buffered and of low ionic strength[1]. Areas within the $p$H 4.7 isoline receive precipitation of acidity exceeding the threshold for ecological effects in the most sensitive waters. Acidified freshwaters are largely confined to areas within the $p$H 4.7 isoline (modified from refs 2, 6).



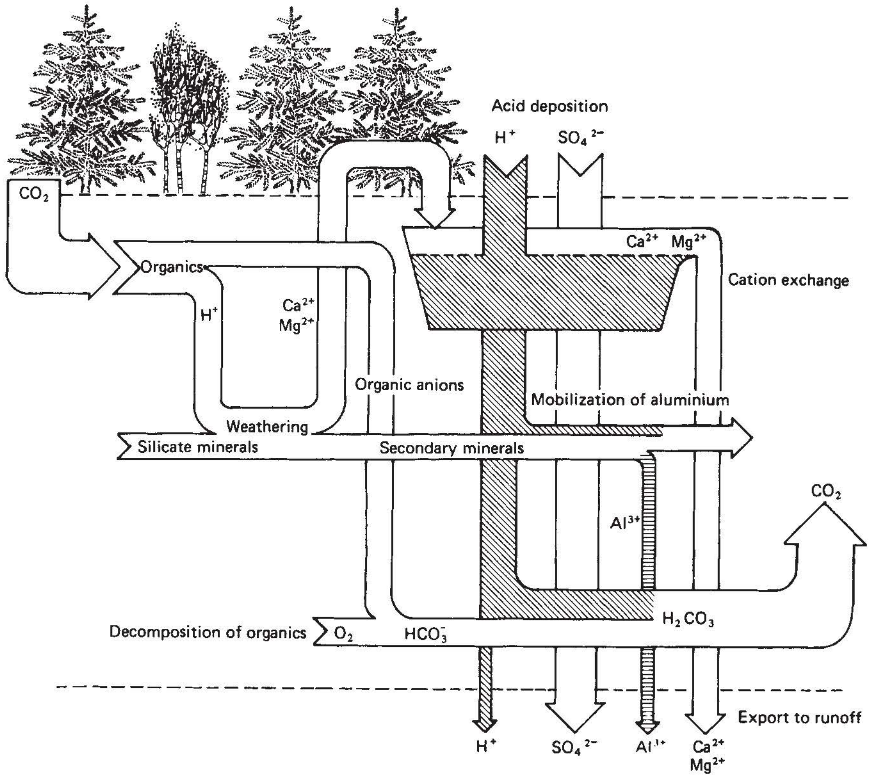


**Fig. 2** Schematic view of key processes governing acidification of soil and water. Nitrogen processes are not included; nitrate and ammonium are minor ions in most surface waters. (Modified after ref. 8.)

the dissolution of minerals, and the natural formation of alkalinity in soils (Fig. 2). Although these processes by no means exhaust the possible processes influencing soil and water acidification, they can account for much of the empirical evidence linking acid deposition to water acidification.

## Equilibrium relationships

Acid deposition increases the external input of strong acid anions ($SO_4^{2-}$ and $NO_3^-$), while the accompanying cations are largely $H^+$ and $NH_4^+$. The acid-base relationships of nitrogen processes are complex, but the acidifying effect in soils of the oxidation of $NH_4^+$ to $NO_3^-$ is well known[14,17]. The potential of sulphur and nitrogen compounds to acidify surface waters is determined by the flux of strong acid anions $SO_4^{2-}$ and $NO_3^-$ from the soil; the nitrate comes either directly from the atmosphere or from oxidation of atmospheric ammonium. In most areas acid deposition generally contains more sulphate than nitrate. Furthermore most of incoming nitrogen is retained by the terrestrial catchment. Sulphate levels in acidified surface waters are commonly 5–10 times higher than nitrate[7-9,11,13], and $NH_4^+$ concentrations in surface waters are usually minor[9-11,13]. We thus confine our discussion here to the effect of the $SO_4^{2-}$ ion.

Sulphate concentrations of sensitive surface waters can be accounted for by atmospheric deposition[9,11,13,18,19]. Increased $SO_4^{2-}$ deposition is usually reflected in elevated concentrations of $SO_4^{2-}$ in soil solution and surface waters. Atmospheric inputs generally far exceed the biological sulphur requirement. Sulphate adsorption may delay the response in sulphate concentrations in runoff to changes in sulphur deposition[20]. Sulphate adsorption is a concentration-dependent process, commonly described by a Langmuir isotherm[21]. The process may not be simple, nonspecific and completely reversible, however, in which case sulphate concentrations in runoff may exhibit a different response to decreasing deposition than to increasing deposition[20].

The capacity to adsorb $SO_4^{2-}$ is apparently related to the processes of soil formation; relatively young forest soils found in northern North America and northern Europe adsorb very little $SO_4^{2-}$ as compared to the more highly weathered soils rich in amorphous sesquioxides common in the southeastern United States[22]. Sulphate flux in runoff in these northern areas is generally at steady-state with respect to atmospheric inputs, while $SO_4^{2-}$ flux in runoff in the southeastern United States lies generally well below atmospheric inputs[14,18,23-25].

Hydrogen-ion inputs to acid soils will participate in two important processes—cation exchange and release of inorganic Al species through the dissolution of soil minerals. $Al^{3+}$ will tend to displace base cations $Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$ from negatively charged exchange sites, because ions of higher valence are preferentially adsorbed[26]. The net effect of these processes is to provide a buffer for $H^+$ in soil solution[27]. As $H^+$ concentration increases in solution, both processes cause a net removal of $H^+$ and a net release of base cations and aluminium. The increase in anion concentration in soil solution brought about by acid deposition results in a relatively larger increase in aluminium than base cation concentrations. In acid soils with low base saturation significant amounts of $Al^{3+}$ may remain in solution. The effectiveness of these buffer processes and the

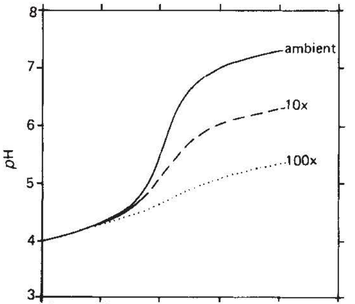


**Fig. 3** $p$H as a function of water alkalinity at ambient ($10^{-3.5}$ atm), 10, and 100 times ambient $P_{CO_2}$. Elevated $P_{CO_2}$ and $p$H buffering in soil solutions are ultimately responsible for the $p$H and alkalinity of surface waters. A $p$H 5.2 soil solution at ambient, ×10 and ×100 $CO_2$ levels will have alkalinities of −6, 0, 61 μequiv. $l^{-1}$, respectively. When these waters equilibrate with ambient $CO_2$, the $p$H from the respective soil $P_{CO_2}$ levels will be 5.2, 5.7 and 7.1. Thus, for soil solution at $p$H 5.2 the resultant surface water $p$H may vary by 1.7 units, depending on the $P_{CO_2}$ in the soil (from ref. 14).

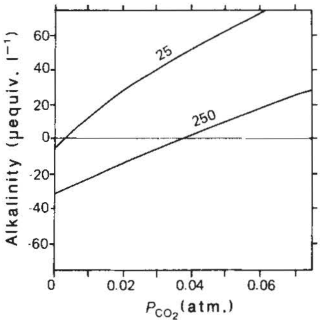


**Fig. 4** The effect of strong acid anion concentration (25 and 250 μequiv. l$^{-1}$) and $P_{CO_2}$ on the alkalinity of water in contact with the soil ion exchange complex (from ref. 14). Degassing of soil solution affects the concentrations of bicarbonate and hydrogen ions but not the alkalinity or strong acid anions.

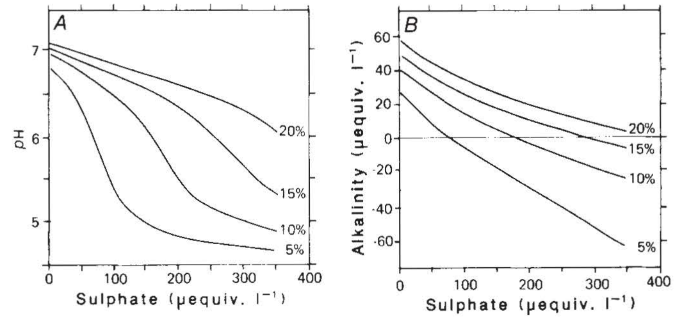


**Fig. 5** $p$H of surface water ($A$) and soil solution alkalinity ($B$) for soils in which 5%, 10%, 15%, and 20% of exchange sites are occupied by $Ca^{2+}$. Calculations were made using the model of Reuss and Johnson[14] assuming $P_{CO_2}$ in soil of $10^{-1.5}$ atm and $10^{-3.5}$ atm for the surface water. Al solubility ($3\,p\mathrm{H}+\log(\mathrm{Al}^{3+})$) was set at 8.75, and the log of the Al-Ca selectivity coefficient set at 2.25.

relative amounts of $Al^{3+}$ and base cations brought into solution depends on the aluminium solubility, the ion-exchange selectivity coefficients, and the base saturation of the soil.

The overall importance of the $CO_2$-$HCO_3^-$ equilibrium to both soil and water chemistry is well known, although its role in determining the alkalinity of water draining acid soils has often been overlooked. In acid soils the $CO_3^{2-}$ and $OH^-$ ions can be neglected, and the alkalinity (acid neutralizing capacity) can be defined as

$$\mathrm{alk} = (\mathrm{HCO_3^-}) - (\mathrm{H^+}) - \sum \mathrm{Al}^* \qquad (1)$$

where the aluminium term includes $Al^{3+}$ as well as other positively charged inorganic aluminium species. Organic anions of high $pK$ may also contribute to alkalinity; the $(H^+)$ term in our definition includes the acidic effect of organic acids not protonated at $p$H values above about 5.0-5.5. For surface waters alkalinity is commonly defined as the excess of positive charges over the anions of strong acids[28], but by this definition alkalinity is not conserved for water draining acid soils. In soils most $H^+$ reacts with minerals so that acidity is stored as Al species. In drainage water the reverse reaction acts to buffer increases in $p$H.

For solutions in contact with soils alkalinity as defined by (1) changes with $P_{CO_2}$. The product $(H^+)(HCO_3^-)$ increases directly with $P_{CO_2}$, but $(H^+)$ is held relatively constant by the dissolution of soil minerals and the exchange of $H^+$ and Al species for base cations. Thus when $P_{CO_2}$ increases, $(HCO_3^-)$ increases. This gives rise to increased alkalinity to the extent that this increase in anion concentration is compensated by increases in concentrations of base cations from the exchange sites. In surface waters, ion exchange is insignificant, and alkalinity is independent of $P_{CO_2}$; here most of the response to change in $P_{CO_2}$ is in $p$H (Fig. 3).

Natural organic acids play a major role in podzolic soils. Organic anions can comprise a significant fraction of the anion sum in soil solution in surface horizons[29,30]. These organic compounds, however, are typically precipitated as organo-aluminium complexes in deeper soil horizons such as the Bh or Bhs horizons in spodozols[30]. This process plays a major role in the formation of the spodic layer in the podzolic soils that are widespread in glaciated regions of North America and Europe. Thus although surface soil solutions might contain high concentrations of organic anions and be highly acidic, organic anion concentrations and acidity are lower in subsoil solutions and runoff. At the Adirondack sites in New York, USA, studied by Cronan and Aiken[30], for example, dissolved organic carbon concentrations were 21-32 mg C l$^{-1}$ in surface soil leachate, but only 5-7 mg C l$^{-1}$ in B horizon leachates, and 2-8 mg C l$^{-1}$ in surface waters.

Increased sulphate concentration in soil solution resulting from increased acid deposition can produce large decreases in soil solution alkalinity (Fig. 4). This decrease in alkalinity results from increased concentrations of acid cations necessary to balance the higher sulphate concentration. The magnitude of decrease in alkalinity depends on the soil exchange and aluminium solubility reactions. Decreases will be larger in acid soils. Surface waters draining such soils are thus highly sensitive to the concentration of strong acid anions ($SO_4^{-2}$). At low levels of base saturation the alkalinity can decrease from positive to negative and thus result in a major change in the $p$H of the surface water (Fig. 5).

Together the process of sulphate adsorption, cation exchange, dissolution of soil minerals and dissolution of $CO_2$ can account for the general equilibrium relationships between acid deposition, soil, soil solution, and surface waters.

## Flux relationships

The equilibrium reactions between soil and soil solution address surface water quality at a particular time. Over the long-term, however, the flux of acids and bases into and out of the soil may change the chemical state of the soil thus affecting the soil/soil solution equilibria.

Sulphate adsorption and the base cation status are two key capacity factors. Acid deposition progressively fills sulphate adsorption sites which in turn leads to increased concentrations of sulphate in soil solution and a flux of sulphate through the soil. The increased concentration of anions in soil solution necessitates increased concentrations of cations including base cations. Increasing the flux of sulphate in runoff will thus increase the flux of base cations out of the soil. If not replenished by base cation inputs from the atmosphere or weathering of soil minerals, the long-term response will be a decrease in the pool of base cations on the cation exchange complex.

The rate of change in base saturation is the net sum of fluxes of base cations into and out of the soil:

$$\mathrm{dBCX}/\mathrm{d}t = \mathrm{AD} + W - B - Q(\mathrm{BC}) \qquad (2)$$

where dBCX/d$t$ is the rate of change of exchangeable base cations on the soil, AD is the atmospheric deposition of base cations, $W$ is the release of base cations from mineral weathering, $B$ is net incorporation into biomass, and $Q$(BC) is the export of dissolved base cations in drainage waters (given by the product of runoff volume and base cation concentration).

For a typical shallow acidic podzol the annual flux of base cations is a few per cent of the total stored in the cation exchange pool[31] (Fig. 6). Even moderate levels of sulphate deposition with the subsequent increased anion flux through the soil will cause a significant increase in flux of base cations from the exchange sites.

Long-term changes in soils also lead to changes in surface

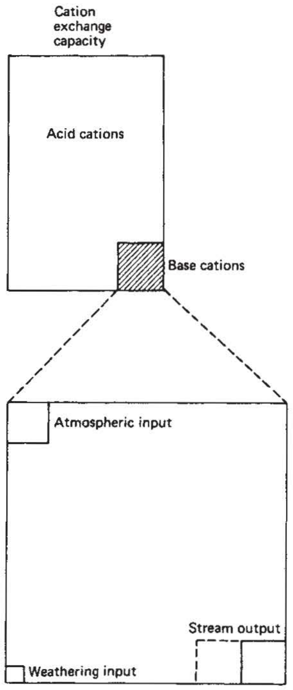


**Fig. 6** The relative sizes of cation pools and yearly cation fluxes for a typical soil in a sensitive area receiving acidic deposition. We use here data for an acidified forest lake on the Swedish west coast[31]. The upper box depicts the total exchangeable cation pool in the soil; 95% are acid cations ($H^+$, $Al^{3+}$) and only 5% are base cations ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$). In the lower box the pool of base cations is enlarged to illustrate pool size in relationship to the annual fluxes of base cations into and out of the soil. Under steady-state conditions the annual flux of base cations leaving the soil in streamwater equals the annual inputs of base cations from the atmosphere and weathering. Acid deposition at Gårdsjön has increased the stream output of base cations (dashed box), and the pool of exchangeable base cations in system is presently decreasing.

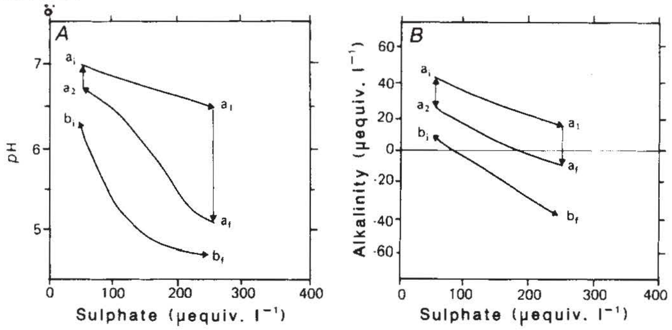


**Fig. 7** An illustration of the pathways followed by $p$H and alkalinity of surface waters in response to changes in sulphate concentrations for two of the soils (20% and 5% base saturation, *A* and *B*, respectively) shown in Fig. 5. Pathway $a_i$ to $a_f$ is typical of systems with moderately buffered soils (base saturation 20%). Surface water alkalinity and $p$H decline slightly in response to increased $SO_4^{2-}$ flux through the soils, but the largest changes in alkalinity and $p$H occur over the longterm as the soils are leached of base cations. Pathway $b_i$ to $b_f$ is typical of acid soils (base saturation 5%). Here loss of alkalinity and sharp declines in $p$H occur immediately as the $SO_4^{2-}$ flux increases, with further reductions coming as the base saturation of the soil is reduced. Recovery of surface water $p$H and alkalinity following decreases in sulphate deposition can also be inferred. As sulphur deposition declines (and sulphate flux through the soil decreases) the system will move along lines of constant base saturation ($a_f$ to $a_2$) until the leaching of base cations accompanying the sulphate flux has been reduced sufficiently such that mineral weathering replenishes base cations on the exchange complex. As base saturation increases ($a_2$ to $a_i$), the system returns to original state.

water pH and alkalinity (Fig. 7). Here the type and rate of response depends on capacity factors, primarily sulphate adsorption and size of pool of exchangeable base cations, that is, the base saturation.

Mathematical models provide a means by which these equilibrium and flux relationships can be quantitatively coupled to examine the effects of acid deposition on soil and water acidification[23,32-35]. These models consist essentially of a combination of a set of chemical equilibria equations with a set of book-keeping procedures by which the fluxes of cations and anions into and out of the soil are tallied. Because the chemical reactions are nonlinear, their interactions produce nonlinear and hysteretic behaviour. Mathematical models of these interactions can expose the full range of implications inherent in assuming these chemical processes control soil and surface water response to acidic deposition. Successful application of such numerical models to catchments in many parts of the world illustrates the general utility of this approach. Such process-oriented models offer a promising tool for the prediction of the future acidification status of soil and water[36-38].

## Discussion

Acidification of soils and surface waters due to the deposition of strong acids from the atmosphere is superimposed upon natural acidification processes. Natural acidification is dominated by carbonic and organic acids both of which are products of biological activity in the terrestrial environment. These acids are responsible for the acid podzolic soils characteristic of sensitive regions of North America and Europe.

Carbonic acid or the associated bicarbonate processes cannot give rise to acidic surface waters. Large overpressures of $P_{CO_2}$ are necessary to yield $p$H levels below 5.0 (Fig. 3). Surface waters with $P_{CO_2}$ levels at or near atmospheric will have significant bicarbonate concentrations only if $p$H is above 5.5. Bicarbonate thus is not the mobile anion responsible for widespread surface water acidification.

Natural organic acids can cause acidic ($pH < 5.0$) surface waters in regions not receiving significant acidic deposition, for example, in bog waters in central Canada[39], several lakes in Florida[40], and rivers in the Amazon region[41]. Such waters are usually highly coloured. Two chemical conditions must be met for these waters to be acidic ($pH < 5$); the sum of concentrations of strong acid and organic anions must exceed that of base cations, and the organic acids must be significantly dissociated at $pH < 5.0$ ($pK < 5.0$). High colour or high concentration of dissolved organic carbon (DOC) alone thus does not ensure high acidity.

The effect of acid deposition on soil solution and surface water depends on both intensity and capacity factors. Intensity effects include the changes in soil solution and surface water chemistry that occur in direct response to increases in strong acid anion concentrations brought about by acid deposition. Soil solutions are buffered by a combination of exchange and dissolution processes (Fig. 2). In soil with low base saturation, the $H^+$ and Al species brought into solution as a result of acid deposition may be sufficient to cause a shift from positive to negative alkalinity, resulting in acidic surface water (Figs 5 and 7). Acidification of surface waters can occur on the short term without first requiring a change in base saturation.

The principal capacity effects are sulphate adsorption and the increased leaching of base cations accompanying the mobile strong acid anions. Such long-term changes in soils have been reported from acid-impacted areas such as Germany and southern Sweden[42-45].

Acid addition experiments in Norway exemplify the decisive role of atmospheric inputs of strong acids in the acidification of runoff. Beginning in 1984 70-100 kequiv. km$^{-2}$ yr$^{-1}$ of $H_2SO_4$ has been added to a 0.7 ha pristine headwater catchment. Prior to treatment, runoff draining the thin and patchy acidic soils (*p*H 4.2-5.8) was of Ca-Mg bicarbonate composition with *p*H 5.4-6.5, typical of waters in sensitive areas. Acid addition at levels comparable to those in acidified areas of southernmost Norway caused large and rapid changes in runoff chemistry; *p*H decreased to below 5, sulphate became the dominant anion, and aluminium reached levels toxic to fish[46,47].

Changes in land use affect the base status of soils, and uptake of bases by aggrading forests can result in soil acidification through depletion of the exchangeable base cation pool[14,44,45,48].The rate of depletion may be very similar to that caused by moderate level of acidic deposition[49,50]. The transfer of acidity from soils to surface water, however, can only be accomplished by "carrier" anions that are not protonated in acid soil solution. Mobile anions are thus required to produce negative alkalinity in surface waters[51,52]. That the transfer of acidity may be accomplished by organic anions is attested to by the acidity of some highly coloured waters both in regions receiving acid deposition and in pristine regions[39,40,53]. In the case of the recently acidified lakes and streams in eastern North America and Europe, however, sulphate is generally the dominant mobile anion[2,8,9,11,13].

Krug and Frink[16] have proposed that acidification of lakes and streams entails a switch from organic-acid dominated waters to sulphate dominated waters without a large change in *p*H. If this is the case, however, then the typical sulphate-rich acidified lake today would have been extremely coloured in the past. Several studies indicate that dissolved organic matter (DOC) contains about 4-11 μequiv. l$^{-1}$ of organic anions per mg DOC l$^{-1}$ (refs 30, 54, 55), and thus the typical Adiriondack Park lake with present-day sulphate concentration of about 120 μequiv. l$^{-1}$ would have had an additional 10-30 mg DOC l$^{-1}$ in the past. There is no evidence for such major change. Furthermore the vast majority of lakes in areas not receiving acid deposition have *p*H levels above 5.5. Of 720 lakes in the western United States only 1 had *p*H below 5.0 and it was associated with a mineral hot spring[10]. Repeated surveys of lakes in northern Norway encountered no lake with *p*H below 5.5 (ref. 56), and of 198 lakes in Labrador only 1 had *p*H below 5.0 (ref. 9). The empirical data simply do not suggest a major role for organic acids in the widespread recent acidification of lakes in eastern North America and northern Europe.

## Conclusions

Key soil processes in concert with inputs of strong acids from the atmosphere explain the observed trends in soil and water acidification in North America and Europe. The apparent paradox of waters with $pH > 5.5$ draining acidic soils in pristine areas not receiving significant acid deposition is readily understood as the result of the simultaneous effect of inorganic carbon equilibria, cation exchange, inorganic aluminium equilibria and chemical weathering. These are well-known and important components in soil solution chemistry; it is their simultaneous interaction that results in the apparent paradox. The elevated $P_{CO_2}$ in soils results in acidic soil solution with positive alkalinity; upon emerging as streamwater degassing occurs and *p*H increases. The result is $pH > 5.5$ waters draining acidic soils found in such areas as Alaska, northern Canada, northern Norway and northern Sweden.

These equilibria and flux relationships also explain a second apparent paradox. Acidic soils contain exchangeable $H^+$ and $Al^{3+}$ in amounts equivalent to thousands of years of acid deposition; yet acid deposition to such soils causes acidification of runoff with subsequent loss of fish and other biological effects. In the absence of mobile strong acid anions the enormous store of acid in such soils seldom results in the acidification of freshwaters to the stage at which alkalinity becomes negative; $H^+$ and inorganic $Al^{3+}$ are not mobilized to levels toxic to fish. Addition of relatively small amounts of strong acids to such acid soils, however, can have a major effect on the acidity and concentration of inorganic Al in runoff. Mobile strong acid anions such as $SO_4^{2-}$ and $NO_3^-$ readily transport $H^+$ and $Al^{3+}$ out of the soil. Whereas degassing will reduce bicarbonate anion concentrations, these strong acid anions are unaffected. The result is the acidic, aluminium-rich sulphate waters found in sensitive regions receiving acid deposition such as southern Quebec, Adirondack Mountains of New York, southwestern Scotland, southern Norway and southern Sweden.

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## ARTICLES

# Viscous fingering on percolation clusters

**Unni Oxaal*, Michael Murat†, Finn Boger*, Amnon Aharony†, Jens Feder* & Torstein Jøssang***

* Institute of Physics, University of Oslo, Box 1048, Blindern, 0316 Oslo 3, Norway
† School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Israel

*The displacement of a high-viscosity fluid by a low-viscosity fluid leads to fractal viscous fingering in homogeneous porous media. A study of the viscous fingering at high and low displacement rates in percolating models that are inhomogeneous on all length scales makes it possible to construct different theoretical models for these two rates. Applying these two models to computer simulations on exactly the same geometry as in the experiments suggests that the underlying geometry determines the viscous fingering structure almost entirely.*

THE physical phenomena that occur when a low-viscosity fluid is forced into a high-viscosity one, inside a porous medium—such as water pushing oil in a rock—are clearly of much practical interest. These phenomena became the centre of much recent scientific interest when it was realized[1] that under some conditions flow instabilities yield viscous fingers (VF)[1-11] that are fractal[7-11]. Fractals are self-similar objects, which look the same at different magnifications[12]. Their number of sites, or mass $M(L)$ within a region of linear scale $L$ behaves as

$$M(L) \sim L^D \tag{1}$$

with a usually non-integer fractal dimensionality, $D$.

The interest in viscous fingers grew when it was observed that for two immiscible fluids, with a high capillary number for the displaced one, the fractal shapes of the VF (generated experimentally in two-dimensional Hele-Shaw cells)[7,8,11] and in two-dimensional porous media[9,10] have strong qualitative and some quantitative similarities to those observed in a diverse range of apparently different problems, including dielectric breakdown[13], diffusion-limited electrodeposition or growth in aqueous solution[14-17] and computer simulations of diffusion-limited aggregation (DLA)[18]. All of these structures have fractal dimensionalities $D = 1.70 \pm 0.05$ in two dimensions. These striking similarities suggested the existence of universality among growth patterns. This suggestion was put forward by Paterson[1] who showed that two-fluid displacement in porous media can be described by Laplace's equation, with boundary conditions similar to those used in the DLA problem. As DLA is a process that is simple to simulate numerically (particles are released at the boundary, and perform random walks until they hit (and stick to) the growing aggregate[18]), it was suggested that such simulations may be used to imitate two-fluid flow under various conditions[1,19]. Recent modifications of the DLA model also allow a quantitative simulation of the time dependence of finger growth in porous media[20].

The expectation that flow in Hele-Shaw cells (two parallel glass plates, with a small separation) exhibits the same properties as in real porous media is based on Darcy's law, relating the fluid velocity $\mathbf{v}$ to the pressure gradient in the viscous fluid being displaced,

$$\mathbf{v} = -\frac{k}{\mu}\nabla P \tag{2}$$

where $k$ is the average permeability of the porous medium and $\mu$ is the fluid viscosity. For incompressible fluids, $\nabla \cdot \mathbf{v} = 0$ and therefore,

$$\nabla \cdot (k \nabla P) = 0 \tag{3}$$

If the permeability $k$ is constant over the whole system (as it is in conventional Hele-Shaw cells[2-4,7]), equation (3) reduces to the Laplace equation, $\nabla^2 P = 0$. If the viscosity of the 'pushing' fluid is negligible, then the pressure in it is uniform, $P = P_0$. Neglecting the surface tension, this is also the pressure in the displaced fluid, at the interface. The pressure on the free boundaries of this fluid is equal to another constant, $P = P_{\mathrm{ext}}$. As the same Laplace equation, with similar boundary conditions, applies to the electrostatic potential in the dielectric breakdown problem[13], and to the equilibrium probability density of random walkers in the DLA problem[18], the analogy between all the problems follows[1].

In real porous media, the local permeability $k$ fluctuates randomly in space. Therefore, the arguments connecting DLA and VF must be critically reconsidered. Chen and Wilkinson[9] solved the flow equation (2) inside a square-lattice network of tubes with a statistical distribution of radii using a deterministic growth algorithm. Their resulting viscous fingers were similar to DLA clusters, with $D \approx 1.72$.

Although Chen and Wilkinson[9] introduced a distribution of channel radii, they had no tubes which were completely blocked. In real porous media, there is usually a finite concentration, $(1-p)$, of blocked paths (which may either be completely blocked or be so narrow that no fluid flows in them in practice). As the concentration $p$ decreases, approaching the percolation threshold $p_c$, there appears a correlation length $\xi \sim |p - p_c|^{-\nu}$, with $\nu = \frac{4}{3}$, such that the percolating network of open pores has a fractal geometry on length scales[21] $L < \xi$. In many cases, physical phenomena exhibit a sharp crossover from a fractal behaviour $L < \xi$ to that of a homogeneous random system $L > \xi$ (refs 22–24). Although the work of Chen and Wilkinson[9] demon-