2 The Chemistry and Physics of Nitrate

Chemistry

The chemistry of nitrate is not complicated, and it detains most students of chemistry only briefly.

General chemistry

Nitrate is the most fully oxidized compound of nitrogen and is therefore stable to oxidation but potentially a strong oxidizing agent. Saltpetre (potassium nitrate) has long been the oxidizing constituent of gunpowder and solid ammonium nitrate can explode, with the nitrate moiety oxidizing the ammonium moiety. But this does not mean that nitrate dissolved in water is dangerous. Because of the stability conferred by its structure (see below), nitrate in a very dilute near-neutral solution of its dissociated salts (as found in natural waters) is unreactive chemically and certainly cannot explode. However, it retains the capacity of all oxidizing agents to accept electrons. A brief account of oxidation and its opposite, reduction, is given in Box 2.1.

Box 2.1. Oxidation and reduction.

Oxidation and reduction were originally perceived in terms of the gain or loss of oxygen atoms or conversely the loss or gain of hydrogen atoms. The conversion of ammonia (NH_4^+) to nitrate (NO_3^-) is clearly an oxidation in such terms because hydrogen atoms are lost and oxygen atoms gained. The more fundamental understanding introduced later is that a substance that is oxidized accepts electrons in the process, while the substance that is reduced gives them up. In its conversion to nitrate, ammonia not only loses its hydrogen atoms and gains oxygen atoms; it also gains two electrons, which change it from a positively charged cation to a negatively charged anion.

Nitrate and nitrates

Almost all press comment on nitrate concentrations in natural waters refers to nitrates – in the plural. This is simply wrong. There are admittedly several nitrates – sodium nitrate, potassium nitrate and calcium nitrate for example – but we are concerned with nitrate in water. When potassium nitrate, for example, dissolves in water, it does not remain as potassium nitrate. It undergoes a process known as 'dissociation', in which potassium and nitrate become independent entities in the solution. If potassium nitrate and calcium nitrate are dissolved in the same solution, both dissociate and there is no way of knowing whether a particular nitrate was previously associated with potassium or calcium. A laboratory shelf containing bottles of potassium, sodium, calcium and magnesium nitrates can be said correctly to hold nitrates. If, however, you tip the contents into a large bucket of water and they all dissolve, the water has nitrate in it, not nitrates. There are also a few organic chemicals that are nitrates, but these have totally different properties from nitrate and some are toxic. They are not relevant to this book. (But see Box 2.2.)

Ionic nature

When potassium nitrate (KNO_3) dissociates, the K and the NO_3 both acquire an electric charge. The K becomes K^+ with a positive charge and the NO_3 acquires a negative charge to become NO_3^-. Positive- and negative-charged entities in solution such as these are known as *ions*, positively charged ions being *cations* and negatively charged ions *anions*. The soil solution has to contain the same number of positive and negative charges, but this does not necessarily mean the same number of cations and anions, because some ions carry two or more charges. The calcium ion, for example, is Ca_4^{2+}, while

Box 2.2. Organic and inorganic chemicals.

'Organic' originally referred to substances produced by living organisms, under the influence of some kind of 'vital force'. The 'vital force' idea was shown to be redundant when in 1845 Kolbe synthesized acetic acid from its elements, and again in 1856 when Berthelot did the same for methane. Organic chemistry is now the chemistry of carbon compounds, particularly those in which the carbon forms four covalent bonds. The distinction between organic and inorganic chemistry arguably became redundant with the work of Kolbe and Berthelot but has been retained because the compounds of carbon vastly exceed the known compounds of all the other elements put together, making a separate classification necessary.

The word 'organic' has been now been appropriated by the organic farming movement, but the original use of the word precedes its use by organic farmers by about 200 years. It is difficult to avoid both uses of the word in this book but, where necessary, the text will make it clear which use is intended.

Table 2.1. Solubilities in cold water[a] of the salts of the nitrate ion. (From Weast, 1964.)

Cation	Salt	Solubility (g/m^3)	
		Salt	Nitrate[b]
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	2.66×10^6	1.40×10^6
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	1.25×10^6	0.61×10^6
K^+	KNO_3	0.32×10^6	0.18×10^6
Na^+	$NaNO_3$	0.92×10^6	0.67×10^6
NH_4^+	NH_4NO_3	1.18×10^6	0.91×10^6
Fe^{2+}	$Fe(NO_3)_2 \cdot 6H_2O$	0.84×10^6	0.36×10^6
Fe^{3+}	$Fe(NO_3)_3 \cdot 6H_2O$	1.50×10^6	0.80×10^6
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	0.64×10^6	0.32×10^6

[a] The temperatures at which the solubilities in the table (Weast, 1964) had been determined were not all the same and ranged from 0 to 25 K.
[b] The 'nitrate' concentration is that corresponding to the solubility of the salt.

sulphate is SO_4^{2-}. Phosphate can have one, two or three negative charges according to the acidity or alkalinity of the soil. Nitrate, however, always has a single negative charge.

Solubility

The salts formed by nitrate are generally soluble, and calcium nitrate has such a high affinity for water that it is deliquescent, which means that it will pick up moisture from the air and dissolve in it. The main cations in groundwater are likely to be calcium, magnesium, potassium, sodium, iron and aluminium, and the salts they form with nitrate are all highly soluble (Table 2.1). Ammonium nitrate is also highly soluble. Calcium is usually the dominant cation in groundwater, and the nitrate concentration at the limit of solubility for calcium nitrate is 32,000 times greater than the US limit for nitrate concentration in potable water and 28,000 times greater than the European Community limit.

This extreme solubility has two consequences. One is that virtually all the nitrate we encounter in the environment is dissolved in water and the other is that solubility does not limit nitrate concentrations in natural waters.

Structure

The nitrate ion always has the same chemical structure, in which the nitrogen atom and the three oxygen atoms lie in the same plane in a symmetrical trigonal arrangement. For those with an interest in such matters, the nitrogen atom has a formal positive charge, while two negative charges are shared between the three oxygen atoms in a resonance structure comprising three electronic conformations in which each of the oxygen atoms in turn is without charge. The uncharged oxygen atom has two electron pairs and is attached to the nitrogen atom by a π bond, and the charged oxygen atoms have three electron pairs.

This is the only structure that nitrate can have, and it is the same regardless of its origin. Nitrate from a bag of fertilizer and nitrate from a soil on an organic farm both have exactly the same structure and properties, and there is no way in which a chemist, or anyone else, can tell by examining it from which source a particular nitrate ion came.

Sorption by soils

We saw above that nitrate is too soluble for its concentration in water to be limited by solubility. Can it be held by sorption on the soil? By finely divided material, for example? Charcoal is useful for removing impurities from water. The finest particles in soils are the clays. We refer to them in the plural because the clays are a family of materials that have broadly the same general nature but differ in the way in which their constituent elements, aluminium, silicon and oxygen, are put together in the clay structure. Clays can adsorb some substances strongly, but what they adsorb depends on the acidity or alkalinity of the soil as well as the properties of the clay. Clays may bear either a permanent charge (usually negative) or a pH-dependent charge, which arises from the reversible dissociation of hydrogen ions from sites at the edges of the clays, from metal oxide surfaces, or from the phenolic or carboxylic groups of organic matter. Most agricultural soils in the developed world are maintained at pH values of 5.5 to 8.0 by applying lime. This means slightly acid to slightly alkaline, pH 7.0 being neutral. (See Box 2.3.) At these pH values, clays carry an overall negative charge. With electric charges, like repels like; so cations such as potassium and calcium are attracted to the surface of the clay, while anions like nitrate and chloride are not only not adsorbed by the clay but actually repelled by it. This gives rise

Box 2.3. pH.

pH is the measure of acidity and alkalinity and is the negative logarithm (to the base of 10) of the activity of hydrogen ions in a solution. Those unfamiliar with the concept of 'activity' can often replace it by 'concentration' without great error. The pH scale has a range from 0 to 14 in which a pH of 7.0 is neutral. The system becomes more acid as the pH goes below 7.0 and the activity of hydrogen ions increases. It becomes more alkaline as the pH goes above 7.0 and the activity of hydroxyl (OH^-) ions increases. The pH of a soil is measured in a paste made by stirring the soil with distilled water or a dilute electrolyte solution, usually 0.01 M $CaCl_2$. It is important to know in which the pH was measured because the results can differ by up to one pH unit. The pH measured in electrolyte solution will be the greater.

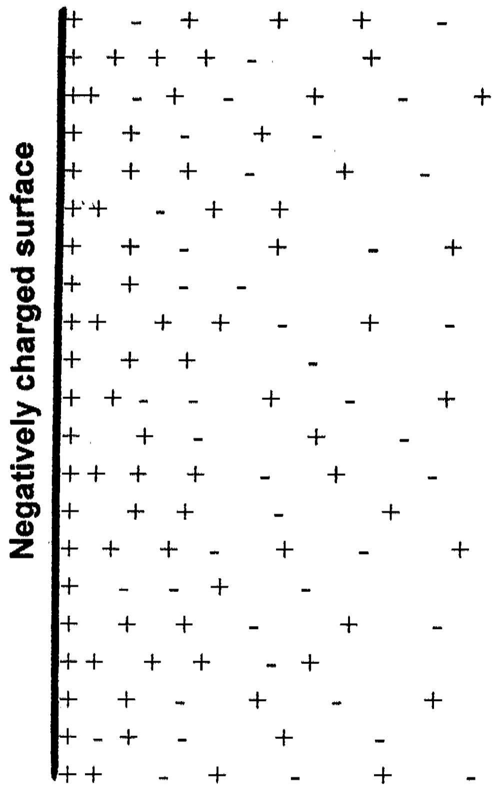

Fig. 2.1. The electrical double layer at a clay surface.

to an electrical double layer (Fig. 2.1) comprising a layer of cations held tightly at the surface (the Stern layer) and a diffuse layer in which cations outnumber anions but to a decreasing extent as we move away from the surface.

Not all soils have an overall negative charge. The humid tropics are hotter and have greater water flows than the temperate regions, so weathering processes proceed faster. Some of the soils, notably those growing tea, are very acid, with pH values around 4.0, and contain oxides of iron and aluminium, which have pH-dependent charge. Soils such as these can carry an overall positive charge. In such soils nitrate is attracted to the clay or oxide surfaces, and Wong *et al.* (1987) and Duwig *et al.* (2003) have shown that this sorption holds it back from being washed out of the soil. The results of Duwig *et al.* suggested two categories of sorption site in a strongly weathered soil, one with strong affinity for nitrate at small concentrations and another with a weak affinity for larger concentrations. In the absence of clear evidence that the soil is positively charged, it will be advisable to assume that sorption, like solubility, does nothing to limit nitrate concentrations in groundwater.

Ammonium

Among soil scientists, ammonium is often lumped together with nitrate as 'mineral nitrogen' because it is so readily converted by soil microbes to nitrate, a process known as nitrification and described in Chapter 3. We therefore need to consider its chemistry in conjunction with that of nitrate, although it is very different from that of nitrate. As its name implies, this ion is a close relative of ammonia, whose pungent smell may be familiar. Like nitrate, ammonium exists as a single entity only in water, and the relation between ammonia, water and ammonium can be summarized as follows, with ammonium hydroxide in the middle:

$$NH_3 + H_2O \leftrightarrow NH_4OH \leftrightarrow NH_4^+ + OH^- \qquad (2.1)$$

The formation of the hydroxyl ion OH^- means a solution of ammonia is alkaline (Box 2.3), but the double arrows imply that the change can go in either direction.

Ammonium in the soil

Ammonium is a cation. Its behaviour is therefore in many respects the opposite of that of nitrate. Like potassium and calcium, for example, it is strongly attracted by clays, rather than excluded from them, and is rarely lost in any quantity from non-acid soil unless the soil is very sandy and contains less than 10% clay. We therefore have an incentive to keep it as ammonium by discouraging the process of nitrification. This is discussed further when ammonia is considered as a fertilizer in Chapter 4.

The Root of the Nitrate Issue – Untimely Nitrate

A simple 'equation' summarizes the problem at the root of the nitrate issue:

Availability = Vulnerability

Any nitrogen in the soil that is *available* to crops is usually in one of two forms: ammonium, which is readily converted to nitrate, or nitrate itself. Nitrate is freely soluble and is not adsorbed on to non-acid soils and is therefore *vulnerable* to being washed out of the soil by rain or irrigation water. Ammonium and nitrate together comprise what is commonly known as mineral nitrogen. We need to limit the vulnerability of nitrate.

The surest way to avoid losing money is to carry no more than you need. Much the same is true of nitrate. The less you have in the soil, the less you lose. When crops are growing fast they need a generous supply of nitrate in the soil, but once they have ceased to grow and absorb nitrate we need to ensure that there is as little nitrate there as possible. Any nitrate there is there at the wrong time. So what we have is not so much a nitrate problem as a problem of *untimely nitrate.*

Whether or not untimely nitrate becomes nitrate pollution depends on the fate of rainfall or irrigation water falling on the soil. This is determined largely by the physical behaviour of water in the soil. The remainder of the chapter is therefore devoted to an account of how the physics of the soil influences the downward movement of water and nitrate. But before we turn to soil physics we need to turn briefly to a topic that straddles the realms of chemistry and physics and is important in soil science – diffusion.

Diffusion

Pour some water into a glass and it arranges itself such that the surface is level. The water has distributed itself such that its potential energy, its potential to flow downhill, is the same at all points. Introduce a gas into a closed vessel and something similar happens. The gas distributes itself such that the pressure is the same at all points. Pressure is another form of potential energy. If there is a mixture of gases, each exerts its own 'partial pressure' and distributes itself such that the partial pressure is the same throughout the vessel. If you change the partial pressure in any part of the vessel, there will be a gradient of partial pressure and the gas will flow in such a way as to equalize it. This process is *diffusion* and the flow is *diffusive flow.*

Gaseous diffusion occurs in the soil when bacteria or other organisms in the soil consume oxygen and release carbon dioxide (Currie, 1961; Greenwood and Goodman, 1965). Oxygen diffuses into the soil in response to a gradient in its partial pressure, while carbon dioxide diffuses out of the soil in the same way but in the opposite direction.

A solute in a solution behaves in several ways like a gas in a closed vessel. It has potential energy, its chemical potential, which is related to the partial pressure of a gas. It distributes itself so that its concentration is the same throughout the system, as a gas does with its partial pressure in a closed vessel. And changing the concentration in any part of the solution leads to a gradient in concentration down which solute moves to equalize the concentration. This process is another form of diffusion, and it occurs in the water in the soil where it is important in plant nutrition. A plant root that removes a nutrient from the soil solution creates a concentration gradient down which further supplies of the same nutrient move to replace the nutrient taken by the root. This diffusive supply is usually most important for soil phosphate, because its concentration in the soil is very small. Nitrate is usually present at larger concentrations in the soil solution and is supplied by convective flow.

Diffusion is of particular interest in the context of nitrate losses from the soil as the only process in most soils that can hold nitrate back, albeit temporarily, from being carried away in water passing through the soil. This is discussed later in the chapter.

Physics

In soil science, there is no such thing as the 'physics of nitrate', only the physics of the water in which the nitrate is dissolved – soil water physics.

Dig out a block of soil without disturbing its structure, dry it and weigh it. Then measure the size of the hole by refilling it with a measured amount of water. The bulk density, the ratio of the mass to the volume, will probably be 1.0–1.3 g/cm^3 depending on the type of soil. If you can crush it so effectively that you drive out all the air, which you probably cannot do, the density will be about 2.6 g/m^3. Solid matter therefore only occupies about half the volume of the soil, and the rest is air and water. There seems little to stop water moving through the soil and carrying nitrate with it. In some types of soil this is broadly true, but in others the water moves downward with difficulty or not at all. Much depends on the texture and structure of the soil.

Soil texture

The texture of the soil is the relative proportions of sand, silt and clay in the soil. The structure is related to the texture but is more concerned with how these particles are brought together in aggregates (soil crumbs) or larger soil units.

Soil texture is regarded as sufficiently important for the sizes of the particles have an international classification (Table 2.2). The two sand fractions feel gritty to the touch, as you would expect, but at the other end of the scale the clay particles are so fine that if you wet them thoroughly and rub them between your fingers they feel almost soapy. Most soils contain a mixture of all three constituents, but there are some very sandy soils that contain less than 10% clay, some soils from around the Wash with a large proportion of silt, and some heavy clay soils about which more will be said. It is very common for the texture of the soil to change as you dig deeper, and it may change as you move from one part of the field to another. This 'spatial variability' is so widespread and affects so many soil properties that it has attracted its own discipline of 'geostatistics'.

Soil structure

We met the clays earlier in the chapter in the context of their electrical charge characteristics. They are also remarkable for the way in which their particles adhere to each other. Were it not for this characteristic, there would be no such craft as pottery – or any discernible structure in the soil. Both depend crucially on the adhesion of clays.

Topsoil

In the topsoil, the part that is cultivated, ploughing and harrowing fragment the soil, as do wetting and drying, which make many soils shrink and then swell and crack. The soil may also freeze, which causes the water in it to

Table 2.2. The International Union of Soil Sciences' classification of particle sizes.

Fraction	Particle diameter (μm)
Coarse sand	0.2–2.0
Fine sand	0.02–0.2
Silt	0.002–0.02
Clay	< 0.002

Larger particles are classified, in order of increasing size, as gravel, cobbles, stones and boulders. These are not usually considered to be soil material.

expand and shatter it. There would not be much structure to it were it not for the ability of the clay to cement the particles together. In this, the clay is aided by the organic matter in the soil, the residues of generations of plant remains decomposed by soil microbes as described in Chapter 3 and converted to a form in which it is able to coat and stabilize the clay particles.

The result of all this activity is what we call the soil structure. The main features of the structure in the topsoil are the 'aggregates', or 'soil crumbs', which are the cemented and stabilized fragments whose genesis was described in the previous paragraph. All agricultural soils are aggregated to some extent, but the degree of aggregation depends on the texture of the soil. In general the more clay a soil contains the more aggregated it will be. This is due partly to the cementing effect of the clay and partly to the mutually stabilizing effect of the clay and the organic matter, which means that more clay implies more stabilization by organic matter. Aggregation has less impact on the soil in sandy soils, partly because more sand usually implies less clay, and partly because large sand particles are not easily bound into aggregates and tend to break them apart if incorporated. A farmer wanting a good 'seedbed' that will give the best environment for germination and early growth will aim to produce aggregates of 0.5–2.0 mm.

Subsoil

The main difference between the topsoil and the subsoil in arable land is obviously that the subsoil is not ploughed, unless the farmer has opted for a no-till strategy for the topsoil. And of the natural influences on topsoils, only wetting and drying affect the subsoil and then only in clay subsoils. Topsoil and subsoil usually differ least in sandy soils – the difference may just be the larger amount of organic matter in the topsoil. Silt soils also show little difference where the subsoil is silt, but there are quite large areas where wind-blown silt (loess) is deposited on another material. Where topsoil and subsoil differ most is in a clay soil. The topsoil will comprise aggregates from 0.5 mm upwards, together with larger clods in which aggregates are bound together. But clay subsoil is a much more massive structure whose structural units are measured in centimetres or tens of centimetres rather than millimetres. This is a consequence of the cementing characteristics of clays discussed above.

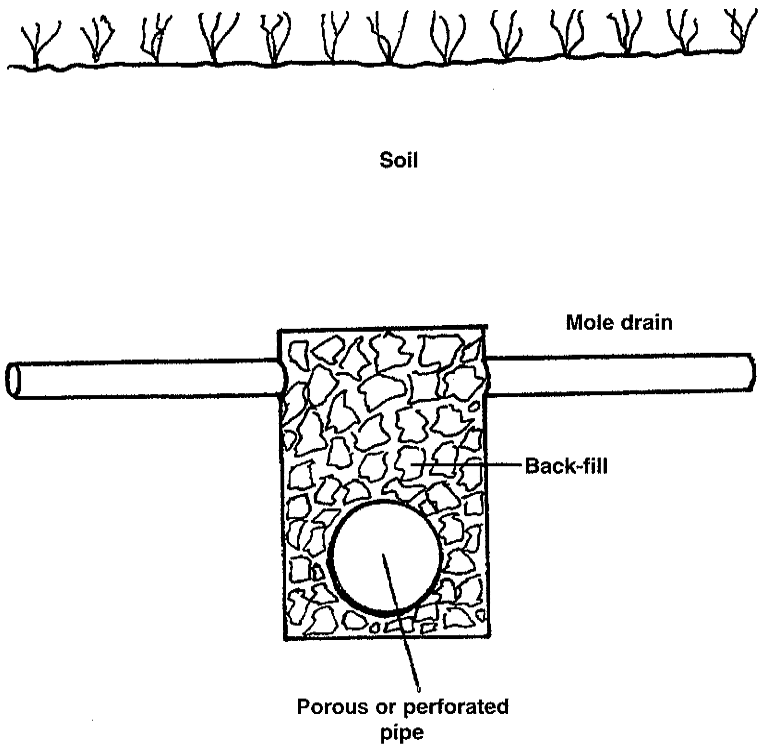

Fig. 2.2. The connection of mole and pipe drains at a trench.

This massive structure can often mean that clay subsoils are virtually impenetrable to water and roots below a certain depth or in a particular layer. In many soils some kind of man-made drainage is needed for the soils to be farmed effectively. This is often of the mole and pipe variety, in which a steel 'mole', shaped like a mole, is drawn through the soil at a depth of approximately 0.6 m. This is attached to a frame on the tractor by a 'leg', a metal connecting bar which leaves behind it a 'leg-slot' and a series of herring-bone cracks, all of which facilitate the entry of the water into the soil. The resulting 'mole drain' interconnects at right angles with a trench filled with gravel (Fig. 2.2) at the base of which is a porous or perforated pipe which carries the water away to a ditch or stream. (See also Fig. 5.6.) This type of drainage has come under question after the flooding in some recent years because it arguably removes the water from the land too rapidly for other parts of the system to dispose of it, but without it some fields simply could not be cultivated. Some subsoils develop a particular layer that is impenetrable to roots and water. This may be tackled by a process known as 'subsoiling' or soil 'busting' in which an implement is torn through the impenetrable layer to make pathways for roots and water. This operation uses a lot of energy and is not undertaken lightly.

Cracking clays

Some clay subsoils have the ability to imbibe water so that they swell when wetted and shrink when dried. If crop roots can gradually draw water out, cracks develop that enable roots and water to penetrate. Such subsoils tend to shrink and crack during summer and then swell and close up again during winter, but in others the cracks become permanent. The Dutch Polders comprise areas of land reclaimed from the sea. During reclamation reeds are grown initially to remove water and salt from the soil, so that cracks form and allow water to drain, a process the Dutch call 'ripening'. I saw one of the polders at an early stage when the reeds were still growing and again 12 years later when the ripening was complete. On the first occasion the soil profile was largely featureless but after the 12 years the cracks were enormous.

Soil water

Water can exist as a solid, a liquid or a gas, and all three phases may be found in soil. The solid (ice) is obviously to be found wherever the soil freezes more than transiently but, as we saw earlier in the chapter, freezing is usually helpful by holding ammonium as ammonium, and ice cannot move or carry nitrate with it. The gas phase (water vapour or steam) is important when soils dry out, but it cannot carry nitrate. We are almost entirely concerned with water in the liquid phase.

We saw earlier in the chapter that solid matter occupies roughly half the volume of the soil, with water and air filling the rest in a network of pores. Having water but no air in the pores means that the soil is *saturated*, but this is unusual. The pores normally contain a substantial amount of air, and the soil is then *unsaturated*. The soil does not need to be saturated for water to flow in it. Indeed, saturation is bad for the soil because air cannot flow in a saturated soil and this restricts plant roots from growing and alters the behaviour of soil microbes.

Water flows in the soil

Water flows in response to a gradient in potential, which may be in any direction but is usually downwards. The rate of flow depends on the transmission of water through the soil pores, but the flow in an individual pore is proportional to the fourth power of its radius. Thus the flow in a pore of 0.1 mm is 10,000 times smaller than the flow in a 1.0 mm pore, other things being equal. We virtually never have measurements of the range of pore sizes in a soil, so the transfer of water in a soil is defined by a parameter, the *hydraulic conductivity*, which lumps all the pore sizes together for a particular soil. It is a highly variable parameter because of the characteristics of the individual pores and can vary by an order of magnitude over a distance of 100 mm. (A difference of an order of magnitude might be, for example, between 10^{-1} and 10^{-2}; that is, 0.1 and 0.01.)

The Richards equation and the convection–dispersion equation

The hydraulic conductivity has been incorporated into solutions of the first of two equations widely used in conjunction with each other – the Richards equation and the convection–dispersion equation. The former describes how water flows through the soil in response to a gradient in the potential of water and the latter how the water carries the solute (convection) and how the solute spreads out within the flow of water (dispersion). The phenomenon of dispersion within a flow is fairly closely related to diffusion. These equations (Box 2.4) have been described by several authors (e.g. Wagenet, 1983). They are fairly easy to use for conditions of steady-state flow, a condition that is attained when an already wet soil experiences an

Box 2.4. The flow equations.

Steady-state flow implies that neither the flow nor the amount of water in the soil changes with time. The theory considers the fluxes of water and solute; that is, the quantities of solute and solute crossing unit area in unit time (Wagenet, 1983). If the fluxes of water and solute are J_s and J_w, J_s is related to J_w as follows:

$$J_s = [\theta D_m(J_w) = D_p(\theta)]\ \mathrm{d}c/\mathrm{d}z + J_w c \qquad (2.4.1)$$

in which θ is the volumetric water content, c is the concentration of solute and z is the depth from the surface of the soil. D_m is the mechanical dispersion coefficient, and reflects the effects of the differing pore sizes. It depends on the flow and is therefore presented as $D_m(J_w)$. D_p is the diffusion coefficient, and since diffusion depends on the water content of the soil, it is presented as $D_p(\theta)$.

If the amount of solute changes at any depth, z, in the soil, the flux of solute, J_s, is no longer a steady-state flux, and we need to define the rate of change of the amount, s, of solute with time, t:

$$(\delta s/\delta t)_z = -\delta/\delta z\ \{-[\theta D_m(J_w) + D_p(\theta)]\ \mathrm{d}c/\mathrm{d}z + J_w c\} \qquad (2.4.2)$$

The water flow remains a steady-state flow, so this equation, like the previous one, is amenable to an analytical solution, but it is limited to steady-state water flows, which are rare.

Non-steady-state flows in which both J_w and θ change with time are far more common in nature. They need to be computed at each time interval using equation (2.4.3), in which K is the hydraulic conductivity and H the hydraulic potential (Wagenet, 1983):

$$\delta\theta/\delta t = \delta/\delta z\ [K(\theta)\delta H/\delta z] \qquad (2.4.3)$$

For flows of water in soils K and H are not independent of each other. K depends on θ [hence $K(\theta)$] and θ depends on H. We can only describe non-steady-state flows if the K–θ–H relationship is defined. No analytical solution is possible and a finite element approach is necessary. This has become feasible with modern computers, but the problem does not end there. The parameters that link K, θ and H vary greatly from point to point in a field (e.g. Wagenet and Addiscott, 1987), making the whole enterprise very difficult.

unvarying flow of water, usually downwards. These conditions may exist during irrigation but otherwise they exist rarely, other than in experiments designed to test equations for steady-state water flow (or during camping holidays). In conditions of intermittent flow, such as usually occur in the real world, they become very complicated to use particularly if, as is virtually always the case, the parameters connecting the hydraulic conductivity to the volumetric water content and the hydraulic potential vary in space (e.g. Wagenet and Addiscott, 1987).

The stochastic approach

Some researchers concluded that the soil varies so much that that its variability dominates the leaching of solutes. If that is so, all that is needed is an ultra-simple description of the process such as the travel time, the time taken by the solute to move from the surface to a specified depth, backed up by good statistics. This approach, developed by Jury (1982), considers the probability density function $f_z(w)$ that summarizes the probability P_z that solute applied to the soil surface will arrive at depth z as the water applied increases from w to $(w+dw)$:

$$P_z(w) = \int f_z(w)\,dw \qquad (2.2)$$

The underlying concept is of a bundle of twisted capillaries of differing lengths through which solute moves by piston flow (see below). Calibrating the equation for one depth and one quantity of water enables it to estimate the time of arrival of solute at a greater depth when further water is applied. This is subject to the provision that the soil does not change with depth, a condition that may restrict its use to sandy or silty soils.

Piston flow

The simplest concept of solute movement in soil is that water or a solution applied to the surface of the soil simply pushes out the solution already there without mixing with it. This is analogous to a piston pushing out fluid from a cylinder, so it is called 'piston flow'. The depth, z_p, to which the front of the displacing solution penetrates depends on the quantity, Q, of the displacing solution and the volumetric moisture content, θ, the fraction of the soil's volume that can hold water:

$$z_p = Q/\theta \qquad (2.3)$$

Obviously z_p and Q have to be in the same units. Rainfall or applications of water are usually expressed in mm (the number of mm that would accumulate on an impermeable surface) and z_p can have the same units. Piston flow never occurs without some spreading of the solute front by dispersion, but the idea can provide a useful rule of thumb for estimating the depth reached by the solute.

Another useful aid to estimating the depth reached by a solute is a leaching equation developed by Burns (1975). This gives the fraction, f, of nitrate or a similar solute that is leached below a depth h (in cm) by the percolation of P cm of rain:

$$f = [P/(P + \theta)]^h \qquad (2.4)$$

The author of this equation also developed a leaching model (Burns, 1974) based on the concept of 'temporary over-saturation' of the soil.

Soils with mobile and immobile water

All the approaches to water and solute movement discussed so far presume that the water and the solute move uniformly through the whole soil. This is simply not so. Water does not flow through soil aggregates; it goes round them, while the water inside the aggregate remains largely immobile. The solute moves between the interior of the aggregate and the water on the outside by diffusion (Fig. 2.3). It is the slowness of this diffusion – the time it takes nitrate and other solutes to diffuse out of the aggregate – that helps to protect them from leaching, particularly from larger aggregates and clods when the concentration inside the aggregate is greater than that outside (Addiscott *et al.*, 1983). The slowness of the diffusion is a disadvantage when the concentration is the greater outside the aggregate. This phenomenon is sometimes described as 'hold-back'. Models for soil with mobile and immobile water were developed by Van Genuchten and Wierenga (1976) and

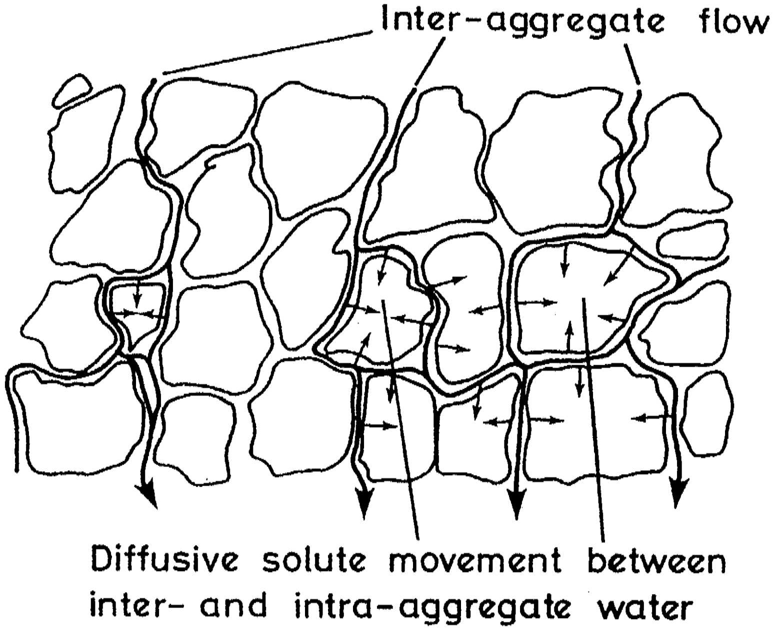

Fig. 2.3. Diffusion of a solute from inside an aggregate, where it is safe from leaching, to water flowing through the soil. (Diagram drawn by Joyce Munden.)

Addiscott (1977), but the principle was established nearly 100 years earlier by Lawes, Gilbert and Warington (1882).

Mobile and immobile water would not be expected in sandy soils with little aggregation, but solute flows studied by Hesketh *et al.* (1998) in such a soil suggested they were there. And when De Smedt *et al.* (1986) did all they could to measure uniform flow by passing tritiated water through a carefully packed sand column, they still found evidence of mobile and immobile water. But these results can be interpreted in terms of the range of pore sizes – and thence velocities of flow in the soil – rather than mobile and immobile water.

By-pass flow

In soils with mobile and immobile water the two categories of water can interact by diffusion. In by-pass flow water moves rapidly through large cracks or channels in the soil, often when more rain falls than can be absorbed by the soil matrix, but without any appreciable interaction with the rest of the soil. This is known as 'channelling' or 'by-pass' flow (Beven, 1981). Such flow may not remove much of the nitrate from within the soil. However, if the nitrate is on the surface rather than in the soil, after fertilizer application for example, it can be carried rapidly through the soil and lost.

This account of the chemistry and physics of nitrate is only the beginning of the story. The effects described interact with many biological processes in the soil, making the behaviour of nitrate remarkably complex for such an essentially simple ion.