### Storyline: answers to assignments

1 The average temperature is much higher. Reaction rates often increase dramatically with temperature, so all the reactions involved in chemical weathering of rocks will be much faster, giving higher concentrations of the breakdown products in the soils.



- **a** The NH<sub>4</sub><sup>+</sup> ions will be held to the negatively charged clay surfaces, displacing other ions such as Ca<sup>2+</sup>. The NO<sub>3</sub><sup>-</sup> ions will remain in solution and will seep through the soil.
  - **b** Nitrate(V) ions are not bound to the clay and can be lost by leaching in heavy rain if not quickly taken up by the plants.  $NH_4^+$  ions are leached more slowly because they are bound to the clay. (However, rainwater is slightly acidic as a result of dissolved  $CO_2$ . Some ion exchange will take place in which  $H^+$  ions displace  $NH_4^+$  ions from the clay surfaces.)
- 4 a Kaolinite
  - **b** Kaolinite has a smaller surface area (ions cannot penetrate between the layers), and lower cation-exchange capacity than the other two minerals. This means it will have less bound H<sup>+</sup> ions to buffer the addition of OH<sup>-</sup> ions.
- **5 a** > 1.6%
  - **b** 4.7%
- 6 a The quantities mineralised in the top 20 cm of soil are: A  $0.01 \times 1000 = 10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ 
  - B  $0.03 \times 2000 = 60 \text{ kg ha}^{-1} \text{ yr}^{-1}$
  - C  $0.06 \times 2000 = 120 \text{ kg ha}^{-1} \text{ yr}^{-1}$
  - **b** The important factors are the organic nitrogen content and the temperature. Humid tropical soils have the lowest organic nitrogen content of the three soils shown in Figure 28, but they have the highest temperature and hence the highest value of *k*. The temperature effect is more important and humid tropical soils have the fastest rate of mineralisation. (The concentration of organic nitrogen is lower because it is being mineralised so quickly.)
- 7 a 1008 kg

**b** N in cow manure =  $4.7 \, \text{kg} \, \text{t}^{-1}$ 

Mass of manure needed = 
$$\frac{1008 \text{ kg}}{4.7 \text{ kg t}^{-1}} = 214 \text{ t}$$

8 Percentages by mass of N in fertilisers (listed in order of increasing transport costs).

urea	46.7%
ammonium nitrate(V)	35.0%
ammonium sulphate	21.2%

A2 LEVEL

- **9 a** The forward reaction is exothermic. Therefore the forward reaction leads to heating of the mixture. The back reaction leads to cooling of the reaction mixture. By Le Chatelier's Principle, raising the temperature favours the back reaction. The equilibrium yield of ammonia goes down.
  - i High pressure, low temperature; 1000 atm, 100 °C
     ii High pressure, high temperature; 1000 atm, 700 °C
  - **c** High pressure apparatus is expensive to build and operate. Need thick-walled reaction vessels and pipework, which can withstand high pressure, and compressors to compress the gases. High pressures can be dangerous; risks of leaks go up as pressure is increased.
  - **d** If the mixture is cooled, ammonia will liquefy, while nitrogen and hydrogen remain as gases. At higher pressures ammonia will liquefy at a higher temperature, and so not as much cooling is needed.
- 10 a It increases it.

It introduces oxygen into the soil and so increases the activity of microbes and the rates of mineralisation and nitrification. Nitrate(V) concentrations in the soil rise.

 b In autumn the soil is still warm, so rates of mineralisation and nitrification are high. It rains more frequently so that nitrate(V) ions in the soil are vulnerable to leaching.

Nitrate(V) concentrations in ground water rise.

- **c** The soil gets waterlogged, so the oxygen concentration is low. Anaerobic bacteria convert nitrate(V) to N<sub>2</sub>O and N<sub>2</sub>.
- **d** Farmyard manure contains a lot of microorganisms. Their activity increases rates of mineralisation in the still warm soil, and so increases the nitrate(V) concentration and loss by leaching.
- **e** They are catching nitrate(V) which would otherwise be leached.

Catch crops should be ploughed in just before the new crop is sown.



- **b** alkene groups (4) ketone group ester group (cyclopropane ring; cyclopentene ring)
- 12 a Cl replaces methyl groups on alkene on bottom left; benzene rings replace cyclopentene and alkene groups on the right-hand side; ether group instead of ketone.

**b** Students should use balls of different colours to represent the ester and halogenoalkene side chains attached to the cyclopropane ring in permethrin, and so make models of the *cis* and *trans* forms.



The hydrolysis products are more soluble in water because they contain groups (–COOH and –OH) which can hydrogen bond to water molecules.

## Activities: notes and answers to questions \_

# AA2.1 How does temperature affect the rate of a reaction?

*Safety note* Information about hazardous chemicals is given on the activity sheet.

Students can control the temperature by putting the tubes in a beaker of water. The peroxodisulphate can be placed in a small test-tube, and the other three reagents in a boiling tube. When the required temperature is reached, the peroxodisulphate can be added to the boiling tube and the time taken for a permanent blue colour to appear is noted. The times should vary between 1400 s and 40 s for the concentrations and temperature range suggested.

Students should be aware that the 'rule' that a rise of  $10 \,^{\circ}\text{C}$  causes the rate of many reactions to double is not valid in many cases. It is true for reactions with an activation enthalpy of about  $+50 \,\text{kJ} \,\text{mol}^{-1}$  for a temperature rise between  $20 \,^{\circ}\text{C}$  and  $30 \,^{\circ}\text{C}$ . The activation enthalpy for this reaction is  $+54 \,\text{kJ} \,\text{mol}^{-1}$ .

(You may wish to take the analysis of results further to give a straight line plot, and bring out the logarithmic relationship.)

## AA2.2 Making models of silicates and clays

The models are intended to help students interpret the diagrams of silicates in the Storyline (and in many textbooks) and to help them visualise the structures.

Students should work in groups so that the activity does not become too time consuming. (It takes one person about an hour to cut and glue all the polyhedra in the templates.)

They should be encouraged to cut out and glue the polyhedra at home. They can then assemble them into sheets in class. If groups of students work together they should be able to assemble reasonable models of 1:1 and 2:1 clays.

- **b** Make up a solution of permethrin, and add a small quantity of enzyme. Mix and start a stopwatch. Withdraw small samples at known times and run a chromatogram. Spray with the appropriate detecting agent and inspect the chromatograms for spots at the  $R_{\rm f}$  values for permethrin and its alcohol derivative. The sketches should show two spots when the reaction is incomplete, and only one spot, for the alcohol derivative, when the reaction is complete.
- **c** A decrease from 100% to 2% represents about 6 half-lives. The time taken is 2 months, so the half-life must be about 10 days.
- **14 a** Soils high in clay have high values of strong adsorption capacity.
  - **b** Clay has a high cation exchange capacity. Sand does not. Clay can adsorb paraquat, which is a flat molecule with two positive charges, and so is held to the clay by the surface negative charges on clays.
  - **c** Measurement of ion exchange capacity of different soils. (Ion exchange to displace paraquat into solution. Estimation of the concentration of paraquat can be done spectroscopically.)
  - **d** Use paraquat sparingly. Bagshot soil is low in clay and has a very low adsorption capacity. This means that paraquat added to the soil may not be completely inactivated. It could then be displaced into soil water and damage growing plants.

### AA2.3 Structure and properties

This is intended to be a fairly quick activity in which students should be encouraged to examine carefully the properties of substances with which they are familiar. They have all played with sand and mud, used talcum powder and handled clay. Here they are made to apply what they know about structure and bonding to explain the observed properties.

- **a** Quartz crystals are hard with sharp edges. In sand, the weathered quartz crystals are hard and abrasive. Talc is soft and has a slippery feel. In talc, the very small crystals have a flat layer-like structure. The layers can slip over each other easily because the forces between them are weak. (Compare with graphite.) In sand, the crystals have quite a different shape; they are not flat and plate-like.
- **b** In mica, the forces between the layers are stronger than in talc. (They are ionic in nature, between K<sup>+</sup> ions and the negative charges on the silicate sheets.) Therefore, the layers do not slip over one another so easily.

You can prise apart flakes of mica which are plate-like and shiny.

Mica does not absorb water because the water molecules cannot force their way in-between the layers which are strongly bound together.

**c** Clays absorb water and become sticky because water is held to the surfaces of clay crystals. The water can also enter the interlayer spaces in many clay minerals, causing the mineral to expand.

Evidence for the small size of clay crystals is that a suspension of clay in water is colloidal. The clay does not



settle out rapidly, but must first coagulate, and then slowly settle out.

 $Al^{3+}$  or other small highly charged ions attract the negatively charged surfaces of clay crystals, and help them to coagulate. ( $Al^{3+}$  or Fe<sup>3+</sup> ions are added by some water authorities to reservoirs to coagulate suspended solids.)

- **d** Clay soils crack in dry weather because of the shrinkage as water is lost from between the layers. The layers are then closer together and the size of each clay crystal is reduced. This shrinkage of the soil can have serious effects on buildings.
- **e** Vermiculite is a 2:1 clay mineral. The layers are negatively charged, and many hydrated cations are held in the interlayer spaces to balance the charge.

Vermiculite slowly swells in water as water molecules penetrate between the layers.

When unexpanded vermiculite is heated, water held by the hydrated cations is driven off as steam. This forces the layers apart and the mineral expands. (The layers can be clearly seen in the heated material.)

### AA2.4 Investigating ion exchange

*Safety note* Ion exchange resins from a bottle are dry. They swell when soaked in water. If contained in a confined space, like a test-tube or a burette, they can cause the glass to shatter explosively. Soak the resin in water in a beaker before putting it into the test-tubes in Part 1. Information about other hazardous chemicals is given on the activity sheet.

You may prefer to do Part 1 as a teacher demonstration to save time. Dry cation exchange resin in the hydrogen form is required for Part 2 of the activity. (If purchased in the hydrogen form, no pre-treatment is necessary.) The collected resin can be stored in 6 mol dm<sup>-3</sup> HCl until enough has been collected to make regeneration worthwhile. The recovery of the resin after use involves regeneration in a column using an appropriate solution.

Using a Dowex 50X8-100 resin, a value of  $2.9 \text{ mol}_{\rm c} \text{ kg}^{-1}$  was obtained for its cation exchange capacity.

- **a** When the resin is shaken with NaCl, H<sup>+</sup> ions are displaced from the resin by Na<sup>+</sup> ions. As the H<sup>+</sup> ions move into solution, the pH of the solution goes down and the indicator changes colour.
- **b** They should be able from the colour changes to identify whether the solution contains a coloured anion or cation. For example, copper sulphate solution goes paler when shaken with a cation exchange resin, but not when shaken with an anion exchange resin. The blue Cu<sup>2+</sup>(aq) ions replace H<sup>+</sup> ions on the cation exchange resin.
- $c \quad \mbox{In this case, you would need to titrate the solution with } 0.100\,\mbox{mol}\,\mbox{dm}^{-3}\,\mbox{HCl rather than with NaOH.}$

### AA2.5 and AA3.1 Activities involving soils

These two activities involve investigations of soil samples. If the activities are shared round the class, each group can present its results to the rest of the class. Activity AA3.1 can be shared between two groups.

# AA2.5 The pH, buffering capacity and lime requirement of soil (optional extension)

*Safety note* Information about hazardous chemicals is given on the activity sheet.

#### Advance preparation

You will need to have samples of dry soil available for student use. It is a good idea to share different types of soils around the class, and for one group of students to measure the buffering capacities of sand and clay.

#### Comments

You may need to adjust the concentration of the calcium hydroxide solution to give good results with the soil samples your students are using in Part 2. The plots for the soil samples should lie approximately on a straight line over the range studied.

- **a** Without soil present, the pH changes rapidly as soon as any alkali is added. With soil present, the pH change is much slower. More alkali must be added in order to cause a measurable change in pH. The soil is said to have a *buffering* action because alkali can be added without causing a sudden change in pH.
- **b** The answers will vary with soil type. A typical value for a clay soil is 0.06 mol kg<sup>-1</sup>. If they study sand and clay they should find that it is the clay which has the high buffering capacity.
- **c** CaCO<sub>3</sub>(s) + 2H<sup>+</sup>(aq) → Ca<sup>2+</sup>(aq) + H<sub>2</sub>O(l) + CO<sub>2</sub>(g)
- **d** Again the answer depends on the soil used. If X mol of OH<sup>-</sup> were needed per kg of soil, then  $\frac{X \text{ mol}}{2}$  CaCO<sub>3</sub> are needed.

Molar mass  $CaCO_3 = 100 \text{ g mol}^{-1}$ . Therefore the mass of  $CaCO_3$  per kg of soil is  $\frac{X \text{ mol}}{2} \times 100 \text{ g mol}^{-1} = \text{Yg}$ 

- e If the answer to d is Yg, then the answer to e is Y × 2500 ×  $10^{-3}$  tonnes limestone per hectare for a rise of 1 pH unit.
- **f** If the calcium ion concentration in the soil solution is raised, calcium ions will displace magnesium ions from soil solids. Plant roots can absorb this magnesium, but any not absorbed will be lost by leaching. If all the exchangeable magnesium is replaced by calcium, then after a time there will be little or no magnesium in the soil solution.
- **g** It is the clay and organic matter in soil which have a cation exchange capacity, and can hold H<sup>+</sup> ions.

# AA3.1 What is the nitrogen content of soil? (optional extension)

*Safety note* Information about hazardous chemicals is given on the activity sheet.

#### Advance preparation

You will need to have samples of dry soil available for student use. Part 1 can be done in advance and the filtrate stored in a stoppered flask in a fridge until required.

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#### Comments

This activity can be divided between two groups. One group can determine nitrogen present as ammonium ions, and the other can determine the nitrogen present as nitrate(V) and ammonium ions. They can then combine their results to get the nitrogen present as nitrate(V) ions.

The steam distillation will take some time so work needs to be carefully planned.

- **a** clay-NH<sub>4</sub><sup>+</sup>(s) + K<sup>+</sup>(aq)  $\rightarrow$  clay-K<sup>+</sup>(s) + NH<sub>4</sub><sup>+</sup>(aq)
- **b** The high concentration of potassium ions ensures that *all* the ammonium ions are displaced from the surfaces of soil solids.
- **c** MgO(s) + 2NH<sub>4</sub><sup>+</sup>(aq) → Mg<sup>2+</sup>(aq) + 2NH<sub>3</sub>(aq) + H<sub>2</sub>O(l)

The nitrogen content of soils varies. It is best to do a rough titration first using a 10 cm<sup>3</sup> aliquot of the soil extract solution, and then decide on the most appropriate aliquot to use in the accurate titration.

**d**  $H_2BO_3^- + H^+ \rightarrow H_3BO_3$ 

# AA3.2 The nitrogen balance in UK agriculture

The data are from a Royal Society document, published in 1983 and are based on estimates originating in the 1970s. It is a very time-consuming exercise to collect such data and it has not been repeated. It is considered that the figures have not altered significantly in the intervening years. It may be worth explaining this background to students when discussing the activity.

**a** Total input = 2668 thousand tonnes per year. Total output = 2668 thousand tonnes per year. There is a balance between the input and output fluxes, so that there is no net loss of nitrogen from the soil. The annual fluxes are *very* small in comparison with the total nitrogen reserves in the soil and the atmosphere.

b	NH <sub>3</sub>	-3	N <sub>2</sub> O	+1
	$NH_4^+$	-3	NŌ	+2
	N <sub>2</sub>	0	$NO_2^{-}$	+3
	-		$NO_2$	+4
			$NO_3^{-}$	+5

### AA4.1 Dilemma over malaria

This activity provides opportunities for students to develop their communication and IT skills by first reading and extracting information from an article dealing with a complex subject, then searching for additional evidence from other sources including the Internet (see the **Salters Advanced Chemistry Web Site**) followed by the preparation of a presentation.

It is likely that a number of general issues could arise from this work and any subsequent discussions, such as:

- where health is concerned, there may be conflict between environmental concerns and the use of pesticides
- societies in different parts of the world will have different priorities and yet there is a great need to think about the problems globally
- the quality of scientific evidence is important but it is not always easy to judge the quality
- decisions about the use of pesticides and about the direction of future research are based on other factors as well as scientific evidence.

The problem discussed here is one of many such issues which can be debated in the same way.

### AA4.2 Partition equilibrium

*Safety note* Information about hazardous chemicals is given on the activity sheet.

# Part 1: The partition of iodine between two solvents

You may prefer to do this as a teacher demonstration so that students are not handling iodine.

Students should see that the same equilibrium mixture is reached from two different directions. Adding different volumes of the second solvent to each of the separated layers demonstrates the way the system readjusts when the equilibrium is disturbed.

A **colorimeter** can be used to determine the equilibrium concentrations of iodine in the aqueous and cyclohexane layers. (Only the concentration of the 'total dissolved iodine' in aqueous potassium iodide and not the concentration of  $I_2(aq)$  can be measured.) You could ask students to draw up a plan to show how they would measure the partition coefficient of iodine between aqueous potassium iodide and cyclohexane, and check that it is constant at a particular temperature and independent of the initial concentration of iodine in the first solvent.

#### Part 2: Partition coefficients and pesticides

- **a** Students should produce straight line graphs. There is a linear relationship between lg (bioconcentration factor) and lg  $K_{ow}$ ; higher values of lg  $K_{ow}$  lead to high bioconcentration factors.
- **b** DDT and its degradation products all have high values of  $K_{ow}$ . This means that they are very soluble in non-polar organic matter, and have high bioconcentration factors. They therefore persist in the organic matter in soil, and are soluble in the fatty tissues of living organisms.

Permethrin itself has a smaller value of  $K_{ow}$  (smaller than DDT by a factor of 10) and it is rapidly hydrolysed to much more polar products, with low values of  $K_{ow}$ .

### AA4.3 What makes an active pyretbroid?

You may want to copy the structures on to card for students to inspect first, stage by stage, so that they don't see them all at once, and only issue the information on pages 258 and 259 of the activity sheets after they have puzzled over the structures by themselves for a short time.

When running this activity with groups of students, do not let them spend a *long* time looking for similarities between F, G and H and the earlier structures.

- 1 Two halogen atoms bonded to an alkene group on lefthand side of molecule; cyclopropane ring; two methyl groups on same carbon atom; ester group; two benzene rings joined by an ether group on the right-hand side of the molecule. There is *cis*-*trans* isomerism about the cyclopropane ring, and all the molecules have chiral centres (but the stereochemistry is not the same in the three compounds).
- 2 The two methyl groups, ester linkage, benzene rings joined by ether group. D differs from biocypermethrin by having a –CF<sub>3</sub> in place of a –Cl group. In E, a

chlorobenzene group replaces the cyclopropane ring and alkene group.

- 3 Two methyl groups on the same carbon atom and two benzene rings joined by an ether group.
  E, F and G all have a benzene ring on the left-hand side of the molecule with a polar group attached, a halogen group in E and F and an ether in G. Also, the two benzene rings joined by an ether group on the right-hand side.
- 4 There is no unsaturated group on the left-hand side of the molecule. The two benzene rings joined by an ether group have been replaced by another unsaturated group. The fact that it does not kill insects is in agreement with the suggestion made in 3.