

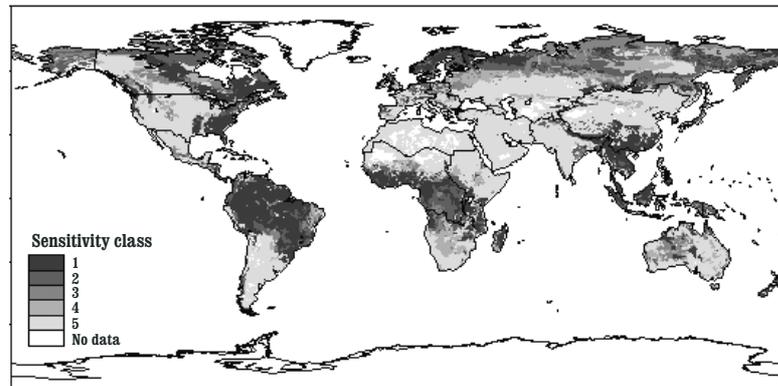
# Acidification

**A**cidification as an environmental problem was first given serious attention in the late 1960s. However, its effects began to appear long before that, and we now know that emissions of acidifying substances cause serious damage to nature, to ourselves and to our built environment.

This chapter explains the chemical changes that take place in soil and water when they are acidified, the various causes, why some areas are affected while others are not, how much emissions must be reduced, and whether the affected areas can recover.

The effects of acidification on nature and people are described in chapters 2 and 3 respectively.

## AIR AND THE ENVIRONMENT



**FIGURE 5.1.** Sensitivity to acid deposition around the world. The darker the shade on the map, the greater the sensitivity to acid deposition. (Global assessment of acidification and eutrophication of natural ecosystems. Report UNEP/DEIA&EW/TR.99-6 and RIVM 402001012. AF Bouwman and DP van Vuuren, 1999.)

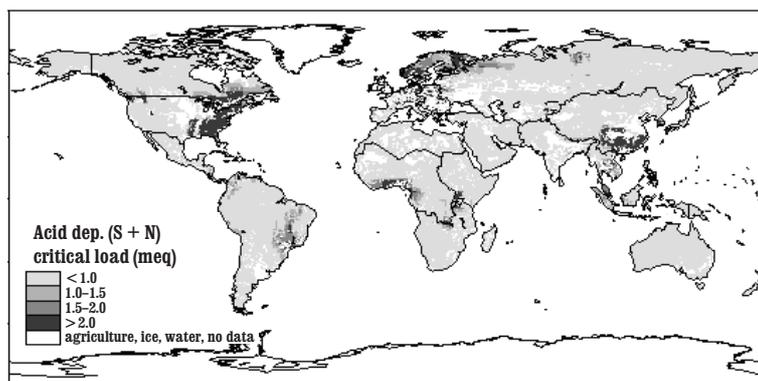
### WHICH AREAS ARE AFFECTED?

There are two main factors that determine which areas are affected by acidification:

1. The amount of acid deposition.
2. The resistance of the soil.

When soil has a high content of easily weathered minerals it can absorb a relatively large amount of acid deposition without becoming acidic. But if the minerals in the soil do not weather easily, as is the case in large parts of the Scandinavia peninsular for example, there is little natural resistance. If the resistance of the soil is low then lakes are also sensitive to acid deposition.

Figure 5.1 is a preliminary survey of the sensitivity of ecosystems on a worldwide scale. In those cases where high sensitivity is combined with a high level of acid deposition – as in parts of Europe, North America, east Asia, West Africa and



**FIGURE 5.2.** Areas where the critical loads for acid deposition on land-based ecosystems is exceeded. Where the ratio is higher than 1, the deposition of acid pollutants is greater than the soil can tolerate in the long term, i.e. the critical limit is exceeded. Deposition data from 1992. (Global assessment of acidification and eutrophication of natural ecosystems. Report UNEP/DEIA&EW/TR.99-6 and RIVM 402001012. AF Bouwman and DP van Vuuren, 1999.)

northern parts of South America – acidification problems occur sooner or later.

Figure 5.2 shows the places in the world where the critical loads for acid deposition are exceeded. We will come back to the situation in Europe later in this chapter.

## SOIL ACIDIFICATION

Soil is acidified slowly as a result of natural processes. This has been going on since the end of the last ice age, but has been greatly accelerated by forestry and acid deposition. The most serious consequences can be summarized in three points:

1. **Plant nutrients are leached out.** Nutrients that are important to plants, particularly base cations (mainly magnesium, potassium and calcium), are leached out by the added acid. This, combined with lower pH levels, can lead to the displacement of sensitive species of plants. Growth in the forest can be affected by the reduction in the availability of nutri-

## AIR AND THE ENVIRONMENT

ents, although it does seem that coniferous trees in symbiosis with mycorrhizal fungi and bacteria can speed up weathering to some extent themselves if needed. Several studies have shown that, over the last 50 years, forest land in southern Sweden has lost around half its reserves of base cations that are available to plants.

**2. Toxic metals are freed.** When soil is acidified it increases the concentration of free aluminium ions in the water that is in the soil, and these are potentially toxic to the root systems of plants. The mobility of many heavy metals also increases when soil becomes more acidic (see figure 5.3). Perhaps the most serious consequence of the higher metal concentrations is their negative effect on many of the decomposers that live in the soil.

**3. Phosphates become bound.** Increasing levels of dissolved aluminium also affect plants indirectly. The “released” aluminium ions are able to bind the vital nutrient phosphorus (in the form of aluminium phosphate) and make it less accessible to plants. The shortage of phosphate is aggravated by the fact that decomposition in the soil slows down under acid

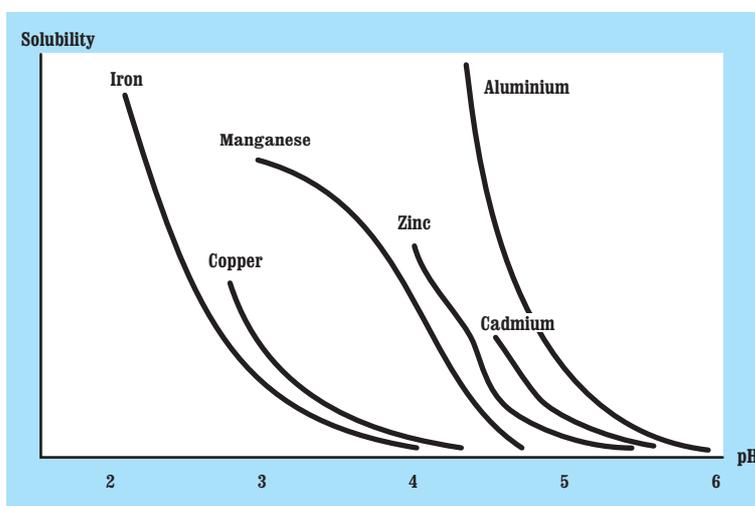


FIGURE 5.3. Release of metals from mineral soil at different pH levels.

conditions. In addition to phosphate, certain important micro nutrients – such as molybdenum, boron and selenium – also become less accessible to plants when soil is acidified.

Until the 1980s most soil researchers believed that the soil could hardly be affected by acid deposition. Later studies show a different picture however. When earlier soil sampling trials were repeated in southern Sweden it was found that the pH level had fallen by between 0.3 and 1.0 pH units in just a few decades. Similar results have been obtained in Austria and Germany, as well as other places. This reduction has not just taken place in the upper layers of the soil, but deep down in the mineral soil, which indicates that the main cause is acid deposition.

#### **Liming as a countermeasure**

The acidification process can be countered by liming. This raises the pH level and tops up reserves of exchangeable cations (increases the base saturation), while also reducing the concentration of free aluminium ions. Lime acts like a filter in the upper layer of the forest soil, where it can capture and neutralize future acid deposition before it has time to leach out base cations and/or dissolve toxic aluminium.

The effect of the added lime penetrates slowly into the soil, at roughly one centimetre per year, but on the other hand persists for a long time in the future. The liming of soil can therefore help counter the acidification of surface water in the long term. A dosage of 3–5 tonnes of lime per hectare is estimated to protect soil from acidification for 20–30 years with current levels of acid deposition in southern Sweden.

## **ACIDIFICATION OF SURFACE WATER**

A small proportion, perhaps one tenth, of the water in lakes reaches them in the form of precipitation directly on the water surface. The rest comes via the land. The quality of surface water therefore depends to a large extent on the characteristics of the surrounding land.

The natural buffering system in lakes and waterways is provided by bicarbonate ( $\text{HCO}_3^-$ ), that reaches the water from

## AIR AND THE ENVIRONMENT

---

the surrounding land. Bicarbonate is released by the weathering of minerals on land and during the decomposition of organic matter. Lakes and waterways that are surrounded by easily weathered types of soil or cultivated land are constantly fed with significant amounts of bicarbonate and therefore generally have good resistance to acidification. However, water that is surrounded by soil that does not weather easily usually has limited buffering capacity, and acidification can occur if acid is added.

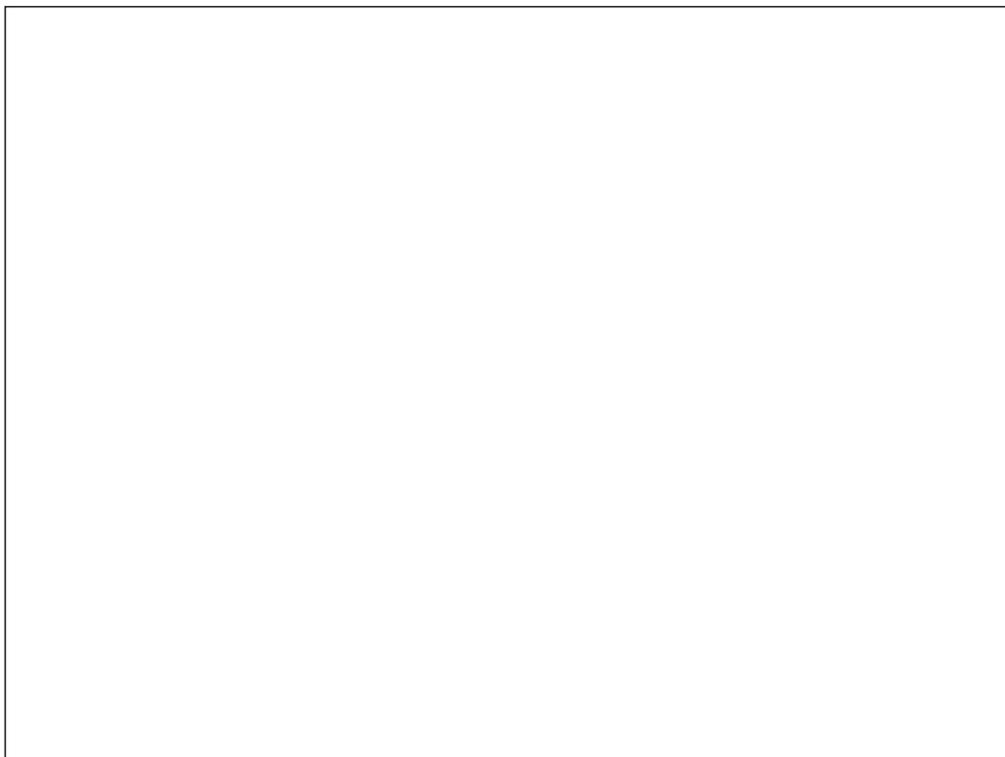
The chemical limits that are commonly used to classify water as acidic are a pH value below 6.2 and an alkalinity (buffering capacity) of less than 0.05–0.10 milli-equivalents of  $\text{HCO}_3^-$  per litre. Acidified surface water is water in which the pH and/or alkalinity have fallen significantly below pre-industrial levels. Lakes that have pH levels lower than 5.6, and zero or insignificant alkalinity (less than 0.02 meq/l) are classified as very acidic.

One change that occurs in acidified lakes that is important for biological life is that the concentration of inorganic aluminium rises. In non-acidified water the levels of inorganic aluminium are generally very low, but when the pH drops below 5.5 the level increases sharply. The aluminium ions come mainly from the surrounding soil, where they are released when the soil is acidified. The damage to fish stocks that occurs in acidic water is largely due to elevated levels of toxic aluminium compounds.

It is not just chemical measurements that demonstrate the presence of acidification. One visible sign is that the water becomes clearer. This is mainly because the humic substances that normally colour the water precipitate out and fall to the bottom when the water becomes acidic. Decomposition slows down, which means that leaves and other organic matter often collect on the lake beds. As already mentioned, a number of biological changes also take place, see chapter 2.

### Many acidic lakes

At present, acidification damage to flora and fauna in lakes and waterways has mainly been reported in Norway, Sweden, Finland and Scotland, and in parts of eastern North America.



**The Scandinavian peninsula is dominated by hard types of rock that are slow to erode, which means that the environment is sensitive to acidification. In the worst affected parts of Sweden more than half the lakes have suffered damage.**

A survey in 1990 estimated that around 14,000 Swedish lakes out of the 85,000 that are larger than one hectare were acidified. Without liming, this number would have been 17,000. In the worst affected regions in southern and south-west Sweden over half the lakes had suffered damage through acidification. At the same time it was estimated that around one third of the country's 300,000 kilometres of waterways were markedly acidified.

A co-ordinated study of the lakes in several north European countries was carried out in 1995, but since new methods were used it is not possible to compare this data with the figures for 1990. The 1995 study does however indicate that the average resistance of the lakes to acid deposition (alkalinity) is slowly improving – which means that a slow process of recov-

#### pH AND BUFFERING

A defining property of acids is their ability to release hydrogen ions ( $H^+$ ). Acidification is the effect of increasing the concentration of hydrogen ions. The concentration of these ions in a solution is used as a measure of acidity, and is normally expressed in the form of a pH value. A low pH means a high concentration of hydrogen ions and hence an acid solution. Water that is neither acid or basic is called neutral and has a pH of 7. The pH scale is logarithmic, which means that the pH drops by one unit when the concentration of hydrogen ions increases by a factor of ten. A solution with a pH of 6 is ten

times more acidic than one with a pH of 7. At a pH of 5 the solution is a hundred times more acid than at pH 7.

There are natural processes that counteract the addition of acid. These processes, known as buffer reactions, are able to neutralize the acid that is added. In a lake it is the availability of bicarbonate ( $HCO_3^-$ ) that determines the buffering capacity. This availability depends largely on the characteristics of the surrounding soil. Soil has several buffering systems, but the most important in the long term is the weathering of various minerals.

ery has begun. This is presumably a result of the halving of sulphur deposition since the early 1980s.

### Acid shock

If the flow of water is rapid it minimises the contact between water and soil. This means that the minerals in the soil do not have time to neutralize the acidic substances in the water, with the result that the pH can drop rapidly over a short period. This can even happen in areas with limestone bedrock, which would normally be considered to give protection against acidification problems.

These so-called acid shocks happen when snow thaws in spring and occasionally when there is heavy autumn rain, and they mostly affect small waterways but also lakes. They last for perhaps just a couple of days or a week, but can still have considerable effects on ecosystems – perhaps just as serious as if the water was acidified all year round. They also occur at a time when many fish are spawning or when the young have

recently hatched, which makes them especially vulnerable. They can even lead to the death of large numbers of fish.

## **Liming of lakes and waterways**

If finely ground limestone ( $\text{CaCO}_3$ ) is added to water it raises the pH and increases resistance to acidification. The liming of lakes and waterways is carried out on a large scale in Sweden and Norway. In Sweden around 7500 lakes and 11,000 kilometres of waterways are now limed each year. Annual Swedish grants for liming during the 1990s have been around 150–200 million kronor (approx. 20 million euros), while the figure for Norway is around 100 million kronor.

The goal of liming is partly to restore acidified lakes and waterways, and partly to increase the resistance of the lakes and waterways that are at risk but not yet affected. Because the water in a lake is constantly being replaced, liming must be repeated every few years. In running water, lime dosing equipment is used to continuously add lime to the water. In order to raise the pH in small waterways, and to increase the duration of the effect when lakes are limed, part of the lime is often spread on wetlands in the catchment area. This causes damage to plants, including killing off bog moss, but the area is limited and the benefits are generally considered to outweigh the harm.

## **WHAT CAN NATURE TOLERATE?**

For a period of about ten years from middle of the 1980s a great deal of research was put into estimating the amounts of pollutants that nature can tolerate without harming it. These limits to what “nature can tolerate” are called critical loads.

The international definition of critical load for acidification is “*the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function*”. Although the definition leaves some room for interpretation, its foundation is that the limits must be set for the most sensitive organisms and ecosystems. For practical reasons the limits are however based on key

organisms in different types of ecosystems. In contrast to medical limit values, for example, these critical loads do not include any safety margins.

## **Forest soil**

In forest ecosystems, trees are used as the key organism, and the measurement used to decide how much acidification a tree can “tolerate” is the ratio between base cations and aluminium ions in soil water. Base cations are released during the weathering of soil, as well being supplied by airborne deposition. Aluminium ions are brought into solution by acid deposition. As long as weathering is able to keep this ratio higher than 1, i.e. when there are more base cations available to plants than aluminium ions, the critical limit is not exceeded.

The reason for setting the threshold at 1 is based on a large number of studies that have shown that trees can suffer root damage when the ratio falls below this value. This choice of limit value has been criticized, partly because most of the studies were carried out on young trees in a laboratory environment, so there is some uncertainty about the way that trees react in the considerably more complex conditions that exist in different types of forest soil.

### **Weathering is key factor**

The most important factor in determining the critical load for acid deposition is the weathering ability of the minerals in the soil. The faster they weather, the more base cations are released and the more acid deposition can be neutralized. The most vulnerable soils are in areas where the bedrock is dominated by gneiss, granite and other slow-weathering types of rock. Here, the limit for forest soils is often less than 200 hydrogen ion equivalents per hectare per year. This corresponds to 3 kilograms of sulphur, assuming that sulphur is the only acidifying agent. In areas with rock types that weather more readily, such as greenstone and, even better, limestone, the soil can tolerate considerably higher levels. See table 5.1.

However, it is not just the chemical properties of the soil that decide how much acid deposition can be neutralized. Vegetation, soil depth, the size of soil particles, temperature

**TABLE 5.1. Critical loads for acidification of forest soils.** (Critical loads for sulphur and nitrogen. P. Grennfelt & J. Nilsson [Eds.] Nordic Council of Ministers, Report 1988:15. Copenhagen, 1988.)

Class	Minerals controlling weathering	Total acidity, H <sup>+</sup> eq/ha · yr	Equivalent amount of S, kg/ha · yr
1	quartz, k-feldspar	<200	<3
2	muscovite, plagioclase, biotite (<5 %)	200–500	3–8
3	biotite, amfibole (<5 %)	500–1,000	8–16
4	pyroxene, epidote, olivine (<5 %)	1,000–2,000	16–32
5	carbonates	>2,000	>32

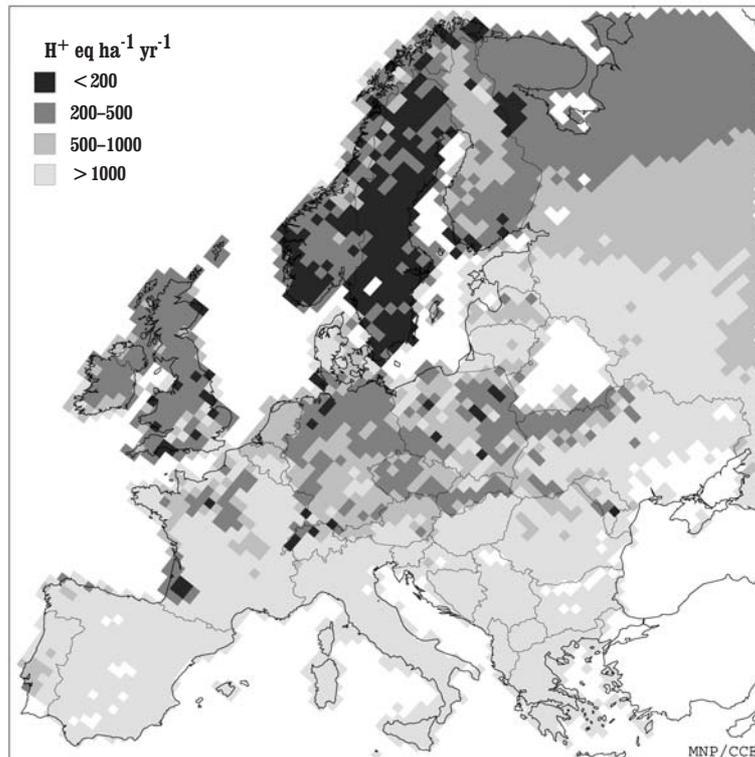
and the deposition of base cations also affect the buffering capacity. Long contact time and a large contact area between soil particles and the water that is supplied are favourable for neutralization. Shallow, coarse-grained soils can therefore tolerate considerably less deposition than deep, fine-grained soils.

Low temperatures lead to increased sensitivity, since they slow down weathering in the soil and plant growth – the latter reduces nitrogen uptake and increases the risk that nitrogen will have an acidifying effect. A warmer climate could possibly increase resistance to acid deposition, since it would speed up the weathering processes. A number of other factors also come into play however, so the net effect is difficult to predict.

The map of Europe (figure 5.4) is an attempt to weigh together all the factors that influence the tolerance of soils to acid deposition.

## Lakes and waterways

The critical loads for surface waters and groundwater generally follows that of the soil, since sensitivity is closely linked to soil properties. The critical limits for lakes are generally given as a pH of 6.0 and a buffering capacity – or acid neutralizing capacity, ANC – of 0.02 milli-equivalents per litre. If conditions become more acidic than this we know that fish and other sensitive aquatic organisms are likely to suffer harm.

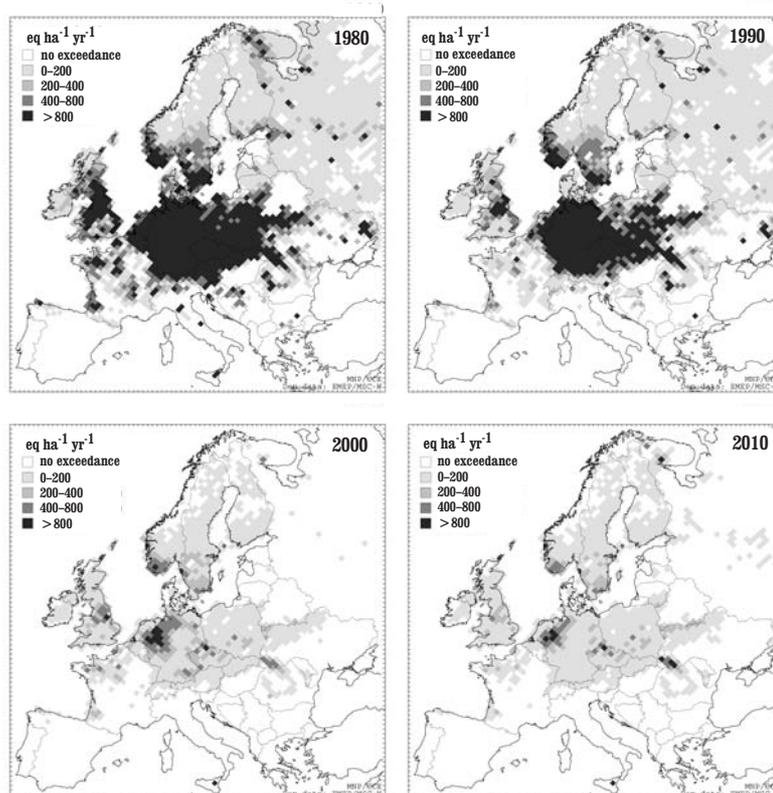


**FIGURE 5.4.** Critical loads for acidity in Europe. The map shows the deposition of hydrogen ions that forest soils and surface water can tolerate without being acidified. At each load level 95 per cent of the ecosystems in the relevant square are protected. (Max Posch, Coordination Centre for Effects, RIVM, Netherlands, 2003.)

## Europe yesterday, today and tomorrow

If acid deposition exceeds the critical limit value, acidification damage will occur sooner or later. Calculations show that the critical limit value for acid deposition was exceeded over approximately 207 million hectares of European ecosystems in 1980.

## ACIDIFICATION



**FIGURE 5.5.** Areas where the critical loads for acidity were exceeded in 1980, 1990 and 2000, and the forecast for 2010. The latter is based on all countries meeting their undertakings in the Gothenburg Protocol. (Max Posch, CCE/RIVM, the Netherlands, 2003.)

Emissions have fallen since then however. New, still preliminary calculations at a higher resolution indicate that the exceeded area had shrunk to about 38 million hectares by 2000. If all countries that have signed the Gothenburg Protocol do as promised (see table 9.2) and if emissions in non-signatory countries develop as officially projected this area will stabilize at 38 million hectares in 2010 – less than one fifth of its size in 1980. The four maps in figure 5.5 illustrate the progress.

It is important to note that acidification damage in an area can last for a long time, even when the critical limit is no longer exceeded.

## CAUSES OF ACIDIFICATION

In some areas the acidification of soil and water is a natural process that has been going on ever since the last ice age. But natural acidification is a slow process, and by far the most dominant cause of today's problems is the airborne deposition of acidifying substances – sulphur, nitrogen oxides and ammonia – as well as the harvesting of biomass. The contributions made by the various components vary, depending on local circumstances.

**Sulphur deposition**, in the form of sulphuric acid, is generally the most important. Because sulphate ions, which are negatively charged, are only taken up by vegetation or retained in the soil in small amounts, the majority remain in the percolating water and carry with them the positively charged base cations. On their way through the soil the hydrogen ions that accompany sulphate deposition are replaced with base cations or react with minerals in the soil. Some of the hydrogen ions remain in the soil and acidify it. Others pass with the sulphate and base cations into the groundwater and surface water, and acidify these too.

In the case of **nitrogen pollutants**, which originate from emissions of nitrogen oxides and ammonia, the situation is more complex, since they only cause acidification under certain circumstances, see factfile on next page. The collective contribution of nitrogen deposition to acidification varies a great deal with the area and time. In Sweden, the contribution of nitrogen deposition to acidification has been estimated at 5–30 per cent, with the highest value in the south. In parts of southern Norway, where the soil is very shallow, a large proportion of nitrogen deposition passes straight through without being taken up by vegetation, and there the contribution of nitrogen deposition to acidification is estimated as 40 per cent.

**The harvesting of biomass**, i.e. normal forestry operations, also leads to soil acidification, see page 101.

#### NITROGEN CAUSES ACIDIFICATION – SOMETIMES...

Because nitrogen in a form that is available to plants is a scarce resource in almost all ecosystems, plants quickly take up most nitrogen that is deposited.

If the nitrogen is deposited as nitric acid ( $\text{HNO}_3$ ) the plants take up the nitrate ion ( $\text{NO}_3^-$ ) and in exchange release another negatively charged ion, usually  $\text{OH}^-$  or  $\text{HCO}_3^-$ , which neutralizes the hydrogen ion from the nitric acid. When this happens the nitric acid does not therefore contribute to acidification (although it does contribute to eutrophication).

If the nitrate ion is not taken up by plants it can be leached out, and neutralization does not take place. In this case the deposition is acidifying. This can happen when the activity of the ecosystem is low, e.g. in winter, or when large amounts are deposited in a short time, e.g. when snow thaws, but also if the plants are unable to take up all the nitrogen that is supplied.

The surplus can then be leached out. This phenomenon has been observed in areas with a high nitrogen load and soil that is relatively poor in nutrients, for example in parts of the Netherlands and northern Germany, and locally in south-western Sweden and southern Norway.

Ammonium ions ( $\text{NH}_4^+$ ) that are taken up by vegetation cause acidification, since hydrogen ions are generally released in exchange. The situation is worse if the ammonium ion is first converted into nitrate and then leached out. Nitrification, the microbiological conversion to nitrate, is an acidifying process that releases hydrogen ions. Nitrification also increases the risk of nitrogen leaching, since nitrate is more mobile than ammonium in the soil. Nitrification is favoured by relatively high pH levels and if more ammonium is supplied than the vegetation is able to cope with immediately.

## Sulphur emissions

Coal and oil consist of the remains of organisms that were deposited on the beds of lakes and seas several hundred million years ago. These were then slowly transformed into fossil fuels. Because all living matter contains sulphur this element is later released when coal and oil are burned. The amount of sulphur that a given fuel contains depends on when and where it was formed. Low-sulphur oil from the North Sea, for instance, contains only a few tenths of a per cent of sulphur, while some types of coal from Spain may have a sulphur content of between five and ten per cent. Fossil gas is practically sulphur-free.

In addition to the burning of coal and oil, some industrial processes, such as roasting of sulphur-containing ores, also make a considerable contribution to sulphur emissions.

During combustion the sulphur in the fuel reacts with the oxygen in the air to form sulphur dioxide gas (SO<sub>2</sub>), the fate of which is described later in this chapter.

The gas itself is toxic to both people and plants. The critical level for forest trees has been determined as 10–20 micrograms per cubic metre (µg/m<sup>3</sup>) as an annual mean value. The most sensitive organisms are believed to be certain lichens, which can be damaged by annual mean levels as low as 10 µg/m<sup>3</sup>. In the 1970s and 1980s the critical levels were exceeded by a wide margin, especially in central and eastern Europe. In Europe today these levels are only exceeded in certain hot-spot regions.

Sulphur dioxide can also contribute to the formation of particles, see chapter 3.

### **Sulphur emissions worldwide**

Annual worldwide emissions of sulphur produced by man were estimated at just over 70 million tonnes (expressed as S) in 1990. The global trend is upwards, mainly due to increased use of fossil fuels in many Asiatic countries. In East Asia, where there is rapid industrial expansion, it is expected that current emissions will double within a few decades if no countermeasures are taken.

Globally, it is calculated that the sulphur emissions produced by mankind are around three times higher than the natural emissions from volcanoes, bacterial production of dimethyl sulphide in the sea, anaerobic decay, etc. Over northern Europe, the eastern US and parts of China, emissions from human activities are around ten times higher than natural emissions.

### **Sulphur emissions in Europe**

Anthropogenic emissions of sulphur rose sharply from the end of the Second World War until the end of the 1970s. Between 1980 and 2000 emissions from land-based sources in Europe fell by 70 per cent – from 53 to 15 million tonnes of sulphur dioxide a year (see table 5.2).

**ACIDIFICATION**

**TABLE 5.2. European emissions of sulphur dioxide (SO<sub>2</sub>), nitrogen oxides (as NO<sub>x</sub>), and ammonia, 1990 and 2000. Unit: 1000 tonnes a year. (EMEP, 2003.)**

	SO <sub>2</sub>		NO <sub>x</sub> (as NO <sub>2</sub> )		Ammonia	
	1990	2000	1990	2000	1990	2000
Austria	79	38	204	196	52	54
Belgium	362	165	334	329	99	81
Denmark	180	28	277	209	133	104
Finland	260	74	300	236	38	33
France	1323	654	1897	1441	779	784
Germany	5322	638	2728	1584	736	596
Greece	493	483	290	321	79	73
Ireland	186	131	118	125	112	122
Italy	1651	758	1938	1372	466	437
Luxembourg	15	3	23	17	7	7
Netherlands	202	92	570	413	232	152
Portugal	273	274	272	385	106	102
Spain	2102	1484	1207	1335	327	386
Sweden	106	57	334	252	54	57
United Kingdom	3719	1188	2759	1737	341	297
<b>Sum EU-15</b>	<b>16273</b>	<b>6067</b>	<b>13255</b>	<b>9952</b>	<b>3561</b>	<b>3285</b>
Albania	72	58	24	29	32	32
Bosnia & Herzeg.	482	419	79	55	31	23
Belarus	637	143	285	135	142	142
Bulgaria	2008	982	361	185	144	56
Croatia	180	58	88	77	37	23
Cyprus	46	50	18	23	4	4
Czech Republic	1881	264	544	321	156	74
Estonia	252	95	68	41	24	9
Hungary	1010	486	238	185	124	71
Iceland	24	27	26	28	3	3
Latvia	95	17	80	35	44	12
Lithuania	222	43	158	48	109	50
Norway	52	27	224	224	23	25
Poland	3210	1511	1280	838	508	322
FYR Macedonia	107	105	39	30	17	16
Moldova	265	12	100	17	49	25
Romania	1311	912	546	319	300	221
Russia	4671	1997	3600	2357	1191	650
Serbia & Monten.	508	387	211	158	90	79
Slovakia	542	124	215	106	63	30
Slovenia	196	96	63	58	24	19
Switzerland	42	19	154	96	72	68
Ukraine	2783	1029	1097	561	729	358
<b>Sum non-EU</b>	<b>20596</b>	<b>8861</b>	<b>9534</b>	<b>5926</b>	<b>3916</b>	<b>2312</b>
<b>Sum Europe</b>	<b>36869</b>	<b>14928</b>	<b>22789</b>	<b>15878</b>	<b>7477</b>	<b>5597</b>
Sum Int. shipping	2829	2829	3991	3991	–	–
<b>Sum Eur.+ ships</b>	<b>39698</b>	<b>17757</b>	<b>26780</b>	<b>19869</b>		
Turkey	1590	2112	644	951	321	321

There are several reasons for this fall. Some countries, such as Germany and Sweden, have focused deliberately on emission control. In other countries the reduction has come about because it was economically advantageous to switch from coal to gas (UK), or because of a sharp fall or change in the nature of industrial production (several countries in central and eastern Europe). There are also countries where emissions have continued to rise in recent years – in Turkey for instance they have doubled between 1980 and 2000.

A major proportion of emissions comes from large combustion plants. At the end of the 1990s it was calculated that the hundred largest individual point sources were responsible for over 40 per cent of the total emissions of sulphur dioxide from land-based sources in Europe. 80 of these 100 sources were power plants – almost all coal-fired.

At the same time as emissions from land-based sources have fallen significantly in recent decades, emissions from international shipping have increased. In 2000 the annual emissions from international shipping in the seas surrounding Europe – the Baltic Sea, the North Sea, the north-eastern Atlantic, the Mediterranean and the Black Sea – amounted to 2.8 million tonnes of sulphur dioxide.

## Nitrogen emissions

Air consists of four-fifths nitrogen gas ( $N_2$ ). However, nitrogen gas can only be exploited as a nutrient by nitrogen-fixing bacteria, and indirectly by plants that live in symbiosis with such bacteria (e.g. legumes). Most plants take up nitrogen in the form of nitrate ( $NO_3^-$ ) or ammonium ( $NH_4^+$ ), or in some cases in organic form (amino acids).

When air is heated to high temperatures, as in combustion, the nitrogen and oxygen in the air react to form **nitrogen oxides**. Nitrogen oxides,  $NO_x$ , is the collective name for nitrogen monoxide, NO, and nitrogen dioxide,  $NO_2$ . Nitrous oxide,  $N_2O$  (laughing gas), is also a nitrogen oxide, but it is usually described separately and is not included in the emission figures for nitrogen oxides given in this book.

The amount of nitrogen oxides that is formed depends mainly on the combustion temperature – the higher, the more

nitrogen oxides are formed. The nitrogen content of the fuel, where present, also contributes to formation.

The main source of **ammonia** emissions is manure. The amount that evaporates depends primarily on how the manure is handled during storage and spreading.

In addition to acidification, emissions of nitrogen oxides and ammonia also contribute to eutrophication, see chapter 6. Nitrogen oxides can also cause health problems and damage to plants, as well as contributing to the formation of particles and ground-level ozone, see chapters 2 and 3.

The critical level for plant damage caused by **nitrogen oxides** has been set at  $30 \mu\text{g}/\text{m}^3$  as an annual mean value. This level is usually exceeded in urban environments and near roads with heavy traffic. The corresponding critical level for **ammonia** is  $8 \mu\text{g}/\text{m}^3$  as an annual mean. This level is only exceeded locally in areas with extensive livestock farming and agriculture.

### **Nitrogen emissions worldwide**

In most countries the main sources of emissions of **nitrogen oxides** are the combustion of coal and oil in power stations and emissions from vehicles. Manmade emissions worldwide are estimated at around 35 million tonnes a year, calculated as nitrogen (N). These emissions are largely due to the combustion of fossil fuels and are concentrated in the industrialized parts of the world, where they are many times higher than naturally occurring emissions. The actual magnitude of the latter is however difficult to give with any precision.

By far the largest source of **ammonia** emissions is livestock farming. Ammonia evaporates from manure during storage and when it is spread on fields. Worldwide emissions originating from human activity were estimated to be 43 million tonnes a year in 1990, calculated as nitrogen (N).

### **Nitrogen emissions in Europe**

Emissions of **nitrogen oxides** from land-based sources in Europe rose slightly between 1980 and 1990. Since then they have fallen from 23 million tonnes a year in 1990 to barely 16 million tonnes a year in 2000, a reduction of just over 30 per cent, see table 5.2. A significant source that is not included in

the figures above is international shipping in the waters around Europe. These emissions are rising and in 2000 amounted to 3.9 million tonnes a year.

For Europe as a whole, roughly 50 per cent of nitrogen oxides come from road traffic, 20 per cent from combustion plants and 15 per cent from other mobile sources (contracting machinery, etc.).

90 per cent of **ammonia** emissions in Europe come from agriculture and they are highest where livestock farming is most intensive, e.g. in the Netherlands, Denmark and northern Germany. There is a shortage of information about ammonia emissions in many countries, but according to statistics emissions have fallen by 25 per cent between 1990 and 2000 – from 7.5 to 5.6 million tonnes per year, see table 5.2.

## Conversion, transport and fallout

Most **sulphur** is emitted in the form of sulphur dioxide ( $\text{SO}_2$ ). As a result of chemical reactions in the air this sulphur dioxide is then converted into sulphuric acid ( $\text{H}_2\text{SO}_4$ ). The sulphuric acid takes the form of droplets or small particles. The sulphuric acid molecule dissolves in water to form two hydrogen ions ( $\text{H}^+$ ) and one sulphate ion ( $\text{SO}_4^{2-}$ ).

More than 90 per cent of emissions of **nitrogen oxides** consist of nitrogen monoxide (NO). This is converted relatively quickly in the air into nitrogen dioxide ( $\text{NO}_2$ ). Nitrogen dioxide can then be converted into nitric acid ( $\text{HNO}_3$ ), which mostly ends up on particles and in droplets of water. Some is deposited in vapour form. Nitric acid dissolves in water to form hydrogen ions ( $\text{H}^+$ ) and nitrate ions ( $\text{NO}_3^-$ ).

The **ammonia** that is released can form ammonium ions ( $\text{NH}_4^+$ ) on contact with water vapour in the atmosphere, which raises the pH level of rainwater (the ammonia bonds with a hydrogen ion and therefore acts as a base). However, this pH raising effect disappears if and when the ammonium ion is taken up by vegetation, since the plants give off acidifying hydrogen ions in exchange for ammonium ions. The am-

monium ion can also be converted into nitrate by bacteria in the soil, a process that is also acidifying.

### **Long-range transport**

Sulphur compounds and oxidized nitrogen compounds are among the substances that can be transported long distances, up to thousands of kilometres in the air. In many countries the majority of acid deposition actually comes from other countries.

Compared with sulphate and nitrate, ammonium tends to be deposited closer to the source of emissions – it is estimated that half of it falls within a radius of one hundred kilometres. Some ammonia can however react with sulphuric acid in the air to form small particles (ammonium sulphate), which can be transported very long distances. The average transport distance is still shorter for ammonium than for sulphates and nitrates, but all three are important in the long-range transport of air pollutants across Europe.

### **Imports and exports**

The information on the import and export of pollutants that is given here comes from the European Monitoring and Evaluation Programme (EMEP), and is based on a model in which the whole of Europe is divided into a grid system. The size of each square was originally 150 × 150 kilometres, but it is now 50 × 50 kilometres. Each country contributes information about the level of emissions, square by square. With the aid of air chemistry models and meteorological data it is then possible to calculate how the emissions spread and where fall-out occurs.

All European countries import and export air pollution. Depending on the level of the emissions and the predominant wind direction some are net exporters, i.e. more pollution leaves the country than falls on it, while others, such as Sweden and Norway, are net importers. Sweden's own contribution to sulphur deposition across the country amounted to just 7 per cent in 1998 – more than nine-tenths came from abroad.

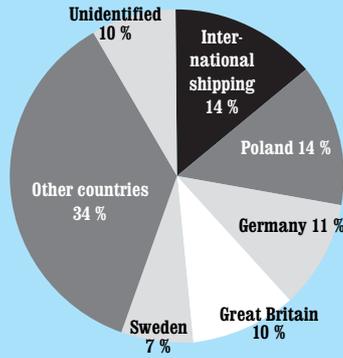
Around 60 per cent of the nitrogen deposition over Sweden comes from emissions of nitrogen oxides, and 40 per cent

**AIR AND THE ENVIRONMENT**

**FIGURE 5.6. The origins of acid deposition over Sweden.**  
(EMEP Report 1/2000.)

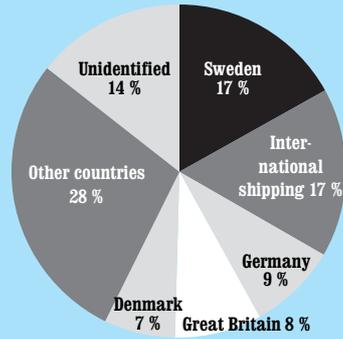
**SULPHUR DIOXIDE**  
(1998, thousands of tonnes)

Total deposition over Sweden: 144,000 tonnes S.  
Imported from other countries: 133,000 tonnes S.  
(Exported Swedish emissions: 14,000 tonnes S.)



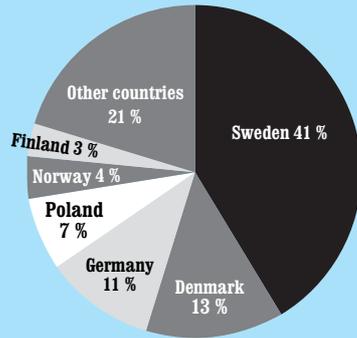
**NITROGEN OXIDES**  
(1998, thousands of tonnes)

Total deposition over Sweden: 107,000 tonnes N.  
Imported from other countries: 89,000 tonnes N.  
(Exported Swedish emissions: 60,000 tonnes N.)



**AMMONIA**  
(1998, thousands of tonnes)

Total deposition over Sweden: 63,000 tonnes N.  
Imported from other countries: 37,000 tonnes N.  
(Exported Swedish emissions: 23,000 tonnes N.)



from ammonia. The proportion of nitrogen oxides that were imported was 83 per cent. Ammonia does not travel such long distances, and a larger proportion of the ammonia that was deposited therefore came from domestic sources – 41 per cent in 1998. The countries that contribute the most of each pollutant are shown in figure 5.6.

### **Pollutant fallout**

Because European emissions of sulphur dioxide have fallen since the start of the 1980s the deposition of sulphur has also decreased. Reductions of 50 per cent have been reported from western Sweden and southern Norway since 1989. The greatest reduction has been in dry deposition. Emissions of nitrogen compounds have also fallen in Europe during the 1990s, but no major change has been seen in deposition levels so far.

### **Harvesting of biomass**

While they are growing the trees in the forest take up more positive than negative ions. The positive ions include several important nutrients, e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ . To avoid becoming electrically charged the trees exchange these for hydrogen ions, which are also positively charged, but acidifying. The soil therefore becomes more acidic when the forest is growing. But when the trees eventually die and decompose the process is reversed. In a system that is left to its own devices the end result is no significant acidification.

The harvesting of biomass, however, means that the soil remains acidified. The removal of nutrients – and hence the residual acidity – is roughly doubled if branches and twigs are harvested rather than just the trunks of trees. But even normal forestry operations often remove more from the soil's reserves of base cations than weathering is able to release. And the more that is harvested, the greater the acidification it causes.

This impoverishment of the soil has increasingly been brought to attention in countries such as Sweden in recent years. It has been proposed that the removal of nutrients along with biomass must be compensated for, for example by spreading wood ash, possibly in combination with liming. There are critics of this approach, however. Swedish nature-conservation organizations believe

## AIR AND THE ENVIRONMENT

---

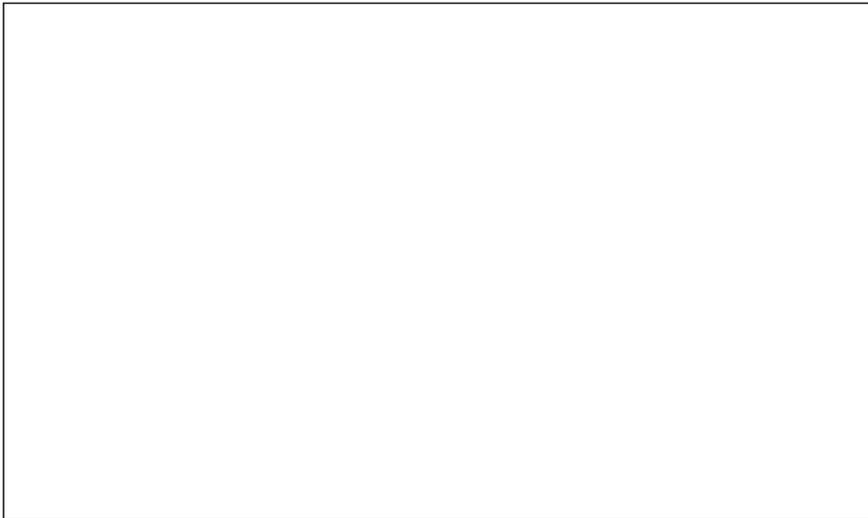
that forestry should be carried out on nature's terms – they do not want to see an “agricultural” system in which nutrients must be added on a regular basis.

### CAN NATURE RECOVER?

Thanks to reductions in the deposition of acidifying substances, a slow improvement can now be seen in the water chemistry of many acidified lakes and waterways in Sweden. The recovery process that can be expected in the future is being studied closely. In the early 1990s Swedish researchers took a practical approach to this question by building a roof over an entire catchment area on the Swedish west coast.

The 6300-square-metre roof trapped all the precipitation and water from the tree canopy, while an equal amount of unacidified water was spread by a sprinkler system under the roof. This led to a 95 per cent reduction in acid deposition. As a result, the amount of acid substances that was added was no

**A 6300-square-metre roof has halted acidification in a small catchment area at Lake Gårdsjön on the west coast of Sweden. Measured changes in soil chemistry and run-off water have helped researchers to model the future.**



## ACIDIFICATION

---

greater than the soil was able to neutralize – i.e. the critical load was not exceeded. This is an essential requirement for sustainable recovery.

Once the roof was in place a number of major changes were observed within a short time. The outflow of sulphur and toxic aluminium compounds from the area into surface water dropped markedly after a few years. But the pH of the run-off water remained unchanged and the concentration of base cations remained low. This is seen as a sign that the soil is in the process of recovery – the buffer of exchangeable ions that was drained by acid deposition is now slowly being replenished.

But this also means that the situation remains critical for the organisms that live in the surface water. The soil reacts slowly, and the effects of reducing deposition will only benefit the aquatic organisms once the soil has made a decent recovery.

Along with information about measured deposition from some twenty locations in southern Sweden and existing knowledge about how the soil works, the results of the roof project have been used to build up a mathematical model. This has been used to make forecasts of likely developments over coming decades.

The conclusion of researchers is that if sulphur deposition is reduced by 70 per cent – in other words a slightly smaller improvement than has been agreed internationally for the year 2010 – the level of acidification will fall in most places. However, this reduction is not generally large enough to allow the soil to recover, i.e. to regain its own resistance to acid deposition.

In the poorest soils, where acidification has already reached an advanced stage, reductions in emissions are needed that are considerably greater than those already agreed. And even with such a scenario it may take a long time to repair the damage that decades of acid deposition have already caused. Because of the depth and composition of the soil this could take centuries. In other parts of the country, where there has been less overall acid deposition, recovery ought to be faster.

In summary it may be worth pointing out that even if the soil and surface water are gradually able to recover their original chemical identity it is not certain that the ecosystems will

#### **AIR AND THE ENVIRONMENT**

---

be restored. The extent to which this happens depends, among other factors, on the ability of various species to spread. And some things will never be the same. For example the impoverishment of genetic diversity within species that has been caused by acidification is irreversible.