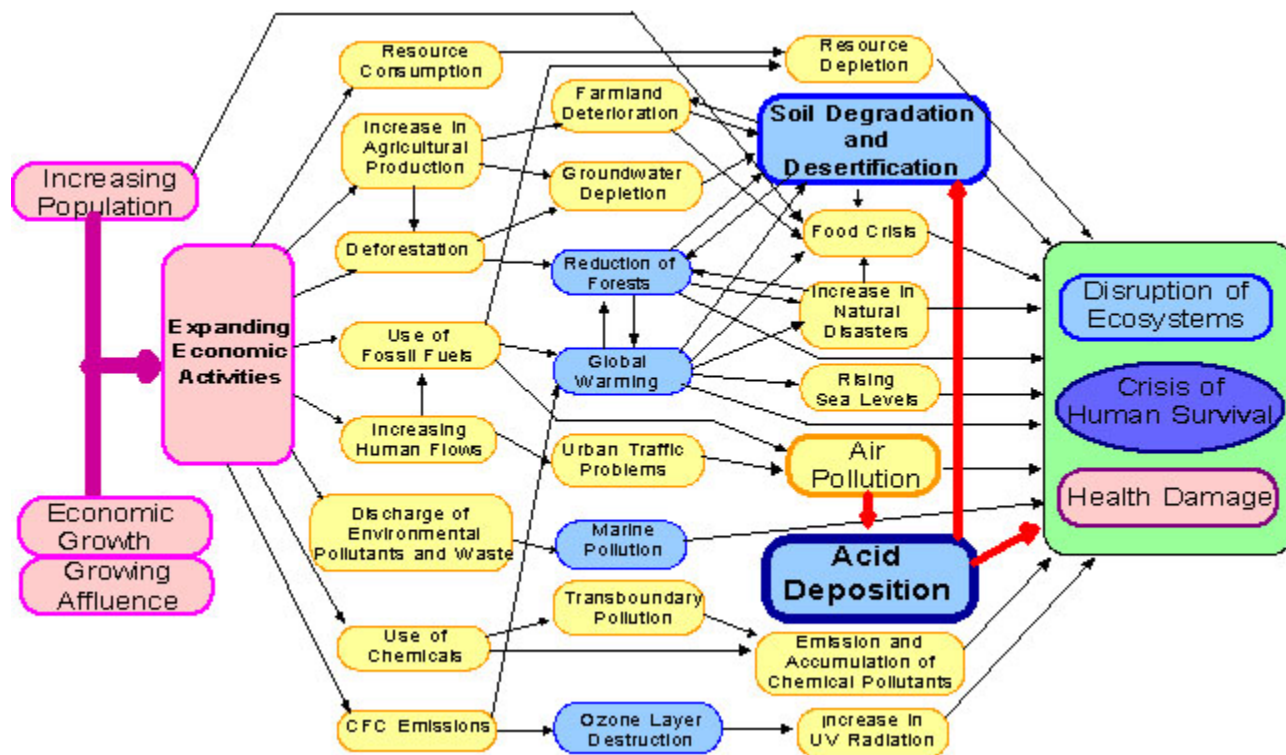


## Acid Deposition and the Environment

This material was developed by the Acid Deposition and Oxidant Research Center (ADORC), and the Network Center for the Acid Deposition Monitoring Network in East Asia (EANET) in collaboration with Institute for Global Environmental Strategies (IGES).

### CAUSES AND EFFECTS OF ACID DEPOSITION

#### 1: Global Environmental Issues as an Interconnected System



The effects and damage caused by the impacts of global environmental issues are characterised as occurring not only in the country of origin, but also across national borders and with global proportions. As a result, international measures are needed to solve them.

The world's so-called developed countries produce and consume goods in large quantities, and then release emissions and dispose of waste in large quantities. These activities require huge amounts of material resources and energy, not only in developed but in developing countries as well. At the same time, they intensify global environmental problems such as acid deposition, global warming, and many others.

#### 2: Air Pollution

**Air pollution occurs when pollutants, such as sulphur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) formed during the combustion of fossil fuels (oil, coal, etc.) are released into the atmosphere and cause adverse effects on ecosystems and the human body, plants and animals.**

Examples include SO<sub>2</sub> emitted from factories, which has been implicated in diseases such as asthma in surrounding neighbourhoods, which became a major public concern in Japan since the 1960s; NO<sub>x</sub> exhaust from cars, which continues to have harmful effects on human health; and the smoke haze from forest fires in Indonesia that drifted into surrounding countries and becoming an international air pollution issue starting in the late 1990s.

### **3: What is Acid Deposition?**

The general consensus is that precipitation with a pH level of less than 5.6 is considered to be acidic, and when it falls on the Earth it is considered to be "acid deposition." Acid deposition from atmospheric precipitation makes soils, lakes and ponds become acidic. Sulphur dioxide and nitrogen oxides, typical air pollutants, are transformed into sulfuric and nitric acid compounds in the atmosphere, with resultant changes of their properties. These acid compounds are carried by the wind as fine particles (aerosols) on sunny days. They dissolve in rain drops on rainy days or within clouds, then fall to the Earth's surface, making the environment acidic. Research has detected this transport on a continental scale, with effects extending beyond national borders.

### **Acid Deposition and pH**

When acid is dissolved in rain, the rain may become strongly acidic, which is why it is called "acid rain." pH is a measurement of acidity and alkalinity: A pH level of 7 is neutral, less than 7 is acidic, and greater than 7 is alkaline.

Carbon dioxide in the atmosphere is converted to carbonic acid when dissolved in water. When dissolved in distilled water it produces a pH of around 5.6. Some people use this value as the criterion by which to judge acid rain. Alkaline substances from the soil or forests and acids from volcanic gases in the atmosphere, when dissolved in the rain, can raise or lower its pH level. Thus, unpolluted rain sometimes has a pH value of less than or greater than 5.6. Furthermore, there are also alkalis in the atmosphere, such as ammonia produced by human activities, which increase the rain's pH level.

The deposition of hydrogen ions is another important point to consider. Gaseous and particulate acids are deposited onto the Earth's surface after being carried by wind. Acid deposition on non-rainy days, or "dry deposition," is also significant. The amount of the dry deposition is on the same order of magnitude as wet deposition by rain and snow.

Regardless of whether the acid deposition process is wet or dry, hydrogen ions affect the soil and other environmental elements in the same manner. Too much of a focus on the pH levels of precipitation could cause people to ignore the significance of dry deposition.

With reference to the above, using pH to judge acid deposition is not the

most important criterion. It might be better to regard pH as only one of several criteria by which to judge precipitation acidity.

#### 4: Sources and Emissions of Agents Causing Acid Deposition

Pollutant gases such as  $\text{SO}_2$  and  $\text{NO}_x$  are released into the atmosphere when fuels such as oil and coal are burnt. Sulphur oxides and other sulphur compounds are also released by natural sources, in particular during volcanic activity.  $\text{SO}_2$  and  $\text{NO}_x$  are the major causative agents (precursors) of acid deposition.

When released into the atmosphere,  $\text{SO}_2$  and  $\text{NO}_x$  change into sulphuric and nitric acid compounds by chemical transformation, making the air acidic. Let us examine this process.

### Overall Description of Acid Deposition

#### 1. Introduction

This part explains acid deposition in general. A reliable dictionary might define the term as “acidic rain” or “rain that has a pH of lower than 5.6”. “pH” is a measurement on an inverse scale of the concentration of hydrogen ions in water: the lower the pH, the greater the concentration of hydrogen ions and the more concentrated the acid. If the pH of rain is lower than 5.6, people often suspect that the rain water could contain nitric or sulphuric acid ( $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ ). It is therefore a serious matter if the pH of rain is low. Nevertheless, one should not be concerned with pH alone. Here we cover issues that should be considered along with pH.

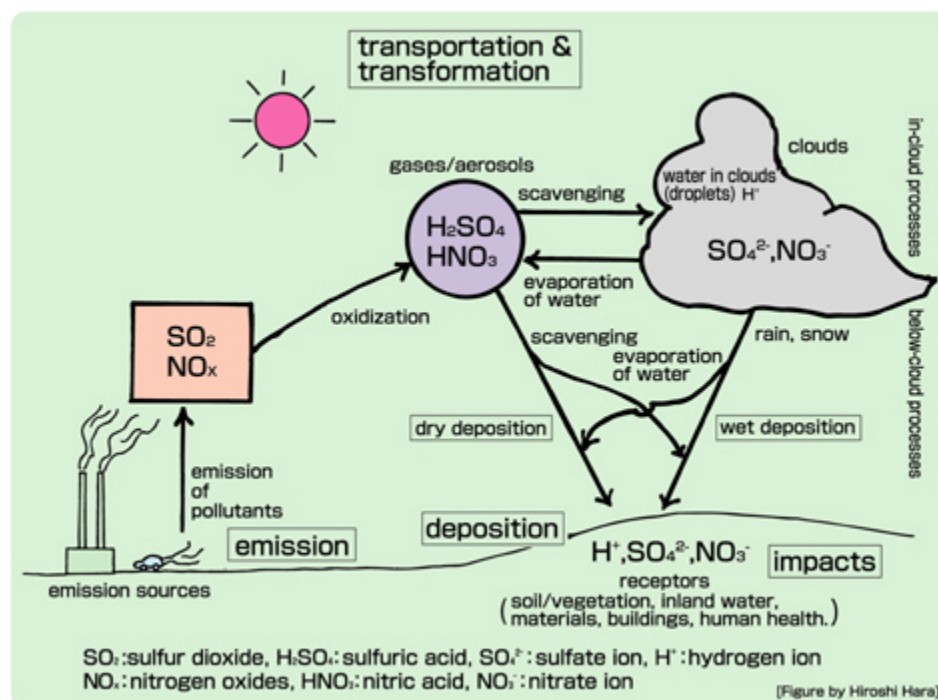


Figure 1. Transportation and transformation involved in acid

#### 2. Basic Processes of Acid Deposition

The phenomenon of acid deposition begins when oil or coal is burnt (Figure 1) and sulfur dioxide ( $\text{SO}_2$ ) and nitrogen oxides ( $\text{NO}_x$ ), normally considered as manmade pollutants, are

emitted into the air. These substances are not acidic in themselves, but can be the source of acids. SO<sub>2</sub> and NO<sub>x</sub> are changed into H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> in the air as a result of photochemical reactions. These reactions normally happen outside clouds, although the production of H<sub>2</sub>SO<sub>4</sub> can also happen inside cloud droplets. The concentration of acid increases in the air and airborne admixtures become acidic. These acids can remain in the air and be carried for days by winds before finally being deposited on the ground. As Schwartz (1989) illustrated, "What goes up must come down"\*1. They can be deposited after being carried up to 2,000 km or more from their starting point. This distance demonstrates why we call this "continental" air pollution. The acids that are deposited on the ground affect ecosystems, including our own living environment, making them acidic. They affect forests, soil, water and buildings, including cultural assets. This is the overall picture of acid deposition as a phenomenon.

#### The process of deposition

HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> exist in the air in the form of microscopic particles or as gas. These acids are deposited on the ground through two different deposition processes (Figure 1). "Wet deposition" occurs during the precipitation of rain or snow containing acids. This deposition sometimes shows strong acidity (i.e., pH 4–5 or lower) and gives rise to the term "acid rain." In "dry deposition," the acid remains in the form of aerosol particles or gas and is carried away by the wind before finally settling on the surfaces of water, leaves, soil or buildings. Dry deposition happens in both dry and wet weather, so it could be called "invisible acid rain." No adequate way has yet been developed to directly measure the amount of dry deposition, making it difficult to estimate accurately. When calculated theoretically with help of simplified modeling, the amount of dry deposition is usually the same as wet deposition. This means that about half of the deposited acid is not contained in rain. Care is needed in the use of terminology, because using the term "acid rain" alone could conceal the significance of dry deposition.

#### Problems not revealed by using pH alone as an indicator

Here we consider problems that could be overlooked if using pH only as an indicator of acidity. When we evaluate the impact of acid deposition, we should consider both the concentration of substances and the amount of their deposition. The concentration is the strength of the acid and the deposited amount is the quantity of acids inputted. In the case of wet deposition, the amount of deposition is calculated by multiplying the concentration by the volume of precipitation. So, even if the pH level is higher (and therefore the strength of the acid is lower), the amount of acid deposition can be large if the volume of rainfall is large. In places with high levels of total precipitation, not only the concentration but also the amount of wet deposition is important for evaluation in different regions. Also, even if rain water initially has a lower pH (i.e., higher acid concentration), the amount of deposited acid can be lowered by neutralization with alkalis if, for example, an alkali like ammonia gas is dissolved in the rain. When this happens, the pH will increase to the level of a weak acid. That means that even if the rain is not detected as being acidic, its pH could have been very low before neutralization. We can recognise the chemical features of the rain more clearly if we study the pH of the rain without any neutralization, or under the assumption that no neutralization took place throughout its fate.

#### Ammonia after deposition

It is important to pay attention to the chemical transformation of ammonia after deposition. Although it neutralizes and weakens acidity in the air, once it has been deposited, it is transformed into acid by microbial activity in soil and water through the following chemical reaction:  $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+$ . This complex phenomenon is not implied by the term "acid deposition," and cannot be inferred if we consider only pH levels. The latter are often overemphasized as the most important problem, but it is also necessary to acknowledge

other problems associated with acid deposition.

#### Impact on the environment

Acids are deposited on the ground by both wet and dry deposition. Ecological systems are affected by them in different ways. The effects on forests, soils, water, buildings and human bodies have been discussed extensively. The impact of acid deposition on water is clearly revealed by its degradation effect on European and Canadian lakes, and the subsequent extermination of some fish species. The impact of acid deposition on other ecosystems, such as forests, is not yet clear. The role of acid deposition on forests can be classified into five issues that harm the ecosystem: (1) increase in aluminium poisoning, (2) increase or decrease of salts in the soil, (3) tropospheric ozone, (4) excess of nitrogen, and (5) multiple stresses. In many cases, it is difficult to prove that acid deposition is the single cause of environmental changes, but it is likely one of the causes.

#### Comprehensive point of view

This explanation described acid deposition as a phenomenon in itself, from the perspective of environmental problems. Broader consideration is needed, however, that takes into account social factors, as well as scientific, technical, and policy factors. The problem of acid deposition arises from the use of fossil fuels. In this sense, it is similar to the issue of climate change in terms of scientific, technical and policy aspects. The use of fossil fuels causes many problems, including acid deposition and global warming, which fall under the umbrella of environmental preservation and impact prevention. Thus, acid deposition is not the sole problem. Any attempts to address this issue should also consider what each part brings to the whole and what actions need to be taken.

#### 3. Deposition

The deposition of gases or aerosols is the final link in a complex chain of processes in the air, but it is also the first link in a chain of ecosystem processes on the Earth's surface (Figure 2). Therefore, deposition connects the atmospheric reservoir of acid compounds with terrestrial ecosystems. Airborne gases and aerosols settle on the ground after being carried by the wind or dissolved in rain water. It is important to note, however, that we cannot avoid dry deposition by using an umbrella, for example; deposition can occur even on the undersides of leaves, as acidic substances can be taken up into stomata located there.

\*1 : Schwartz, S. E., 1989. Acid Deposition: Unraveling a Regional Phenomenon. Science 243, 753-763.

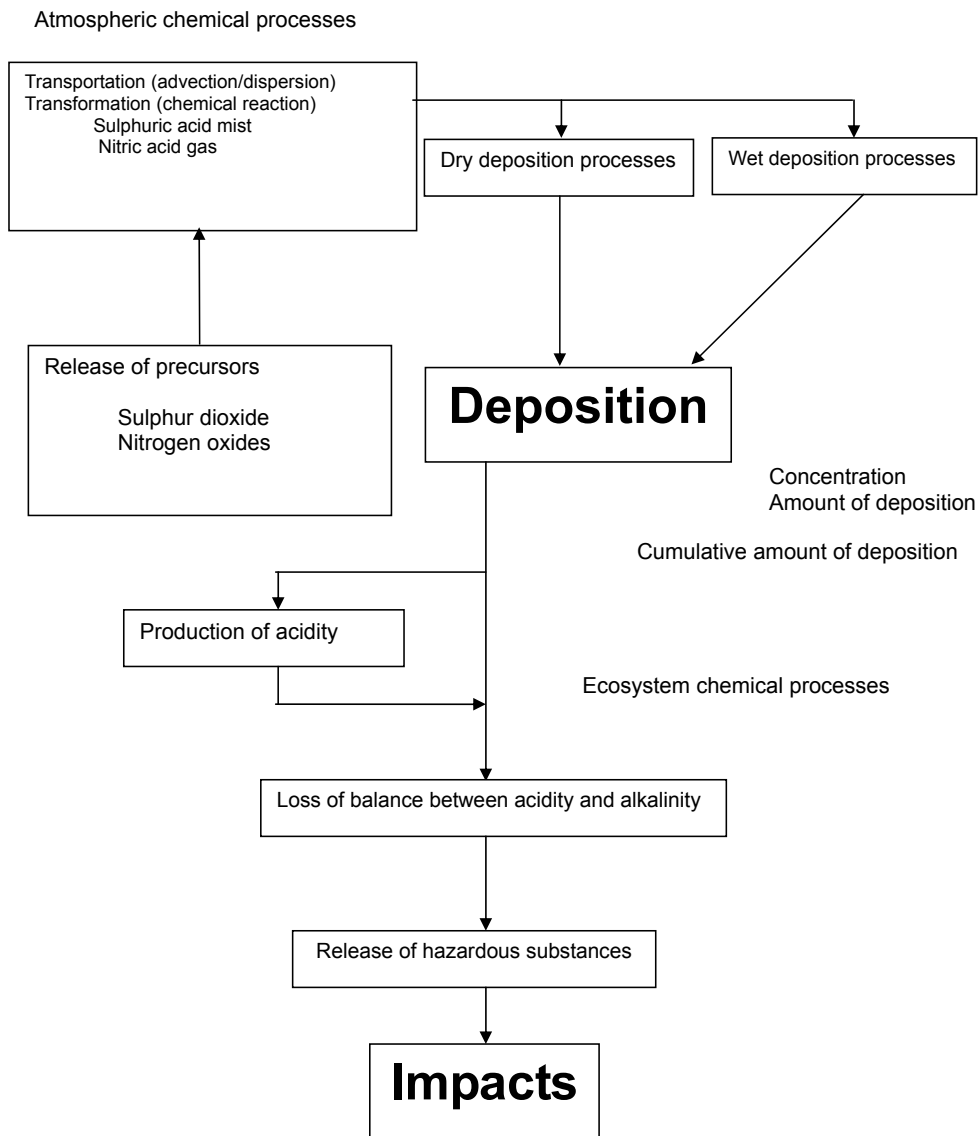


Figure 2. Acid deposition: The connection between atmospheric chemical processes and surface ecosystems.

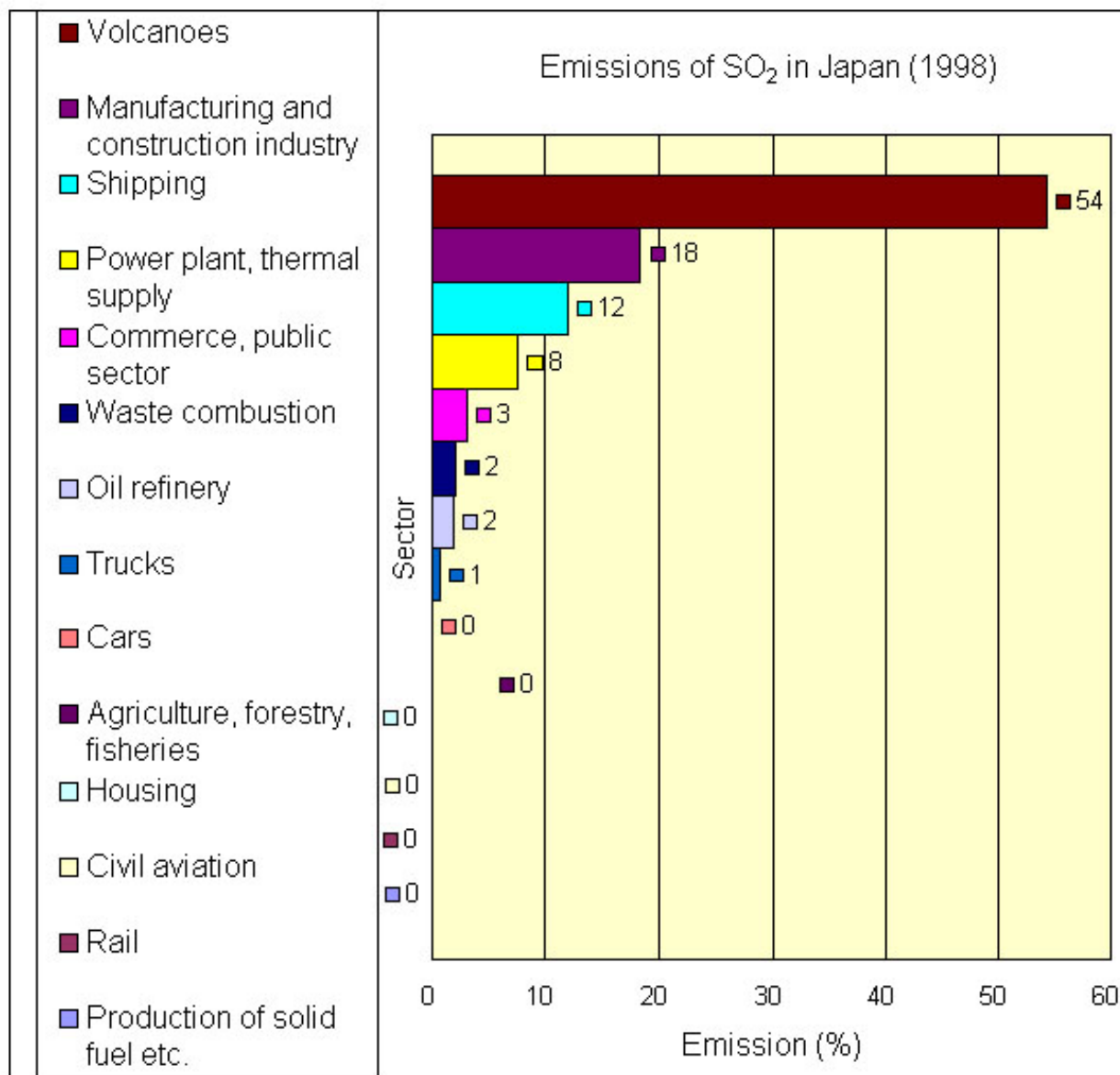
**Compartmental Domestic Emissions Summary (1998)**

Emissions Inventory in Japan (1998)

		NO <sub>x</sub> (t)	SO <sub>2</sub> (t)
	Total	2,212,597	2,176,473
1	Energy	2,150,380	950,061
1A	Combustion	2,150,380	950,061
1A1	Energy industry	246,510	206,366
1A1a	Power plants, thermal supply	206,789	164,273
1A1b	Oil refineries	39,016	42,040
1A1c	Production of solid fuel etc.	705	53
1A2	Manufacturing/construction industry	531,995	396,465
1A2a	Steel	113,831	78,481
1A2b	Non-ferrous metal	18,459	15,740
1A2c	Chemical products	108,954	86,715
1A2d	Pulp, paper, printing	60,400	84,718
1A2e	Food, drinks, cigarettes	16,632	38,131
1A2f	Others	213,719	92,680
1A3	Transport	1,279,651	279,471
1A3a	Civil aviation	88,138	477
1	International aviation	16,218	83
2	Domestic aviation	71,920	394
1A3b	Road transport	668,983	20,378
1	Cars	131,629	4,612
2	Trucks	537,354	15,765
1A3c	Railway transport		
1A3d	Shipping	522,530	258,616
1	International shipping	237,283	141,835
2	Domestic shipping	285,247	116,781
1A3e	Other transport		
1A4	Other sectors	92,224	67,759
1A4a	Commerce, public sector	50,383	66,139
1	Commerce, public sector (large facilities)	16,301	26,859
2	Commerce, public sector (other)	34,082	39,280
1A4b	Housing	41,015	788
1A4c	Agriculture, forestry, fisheries	826	832
6	Waste		
6C	Waste combustion	62,217	45,412
7	Natural source		1,181,000
7A	Volcanoes		1,181,000
Estimation for reference			
1A2f 2	Industry, construction machinery	54,003	370
1A3c	Railway transport	9,795	83
1A4c 2	Agricultural machinery	37,079	246
1A4c 3	Fisheries	19,742	155
2B	Chemical industry	137	101
4F	Combustion of agricultural waste	7,742	

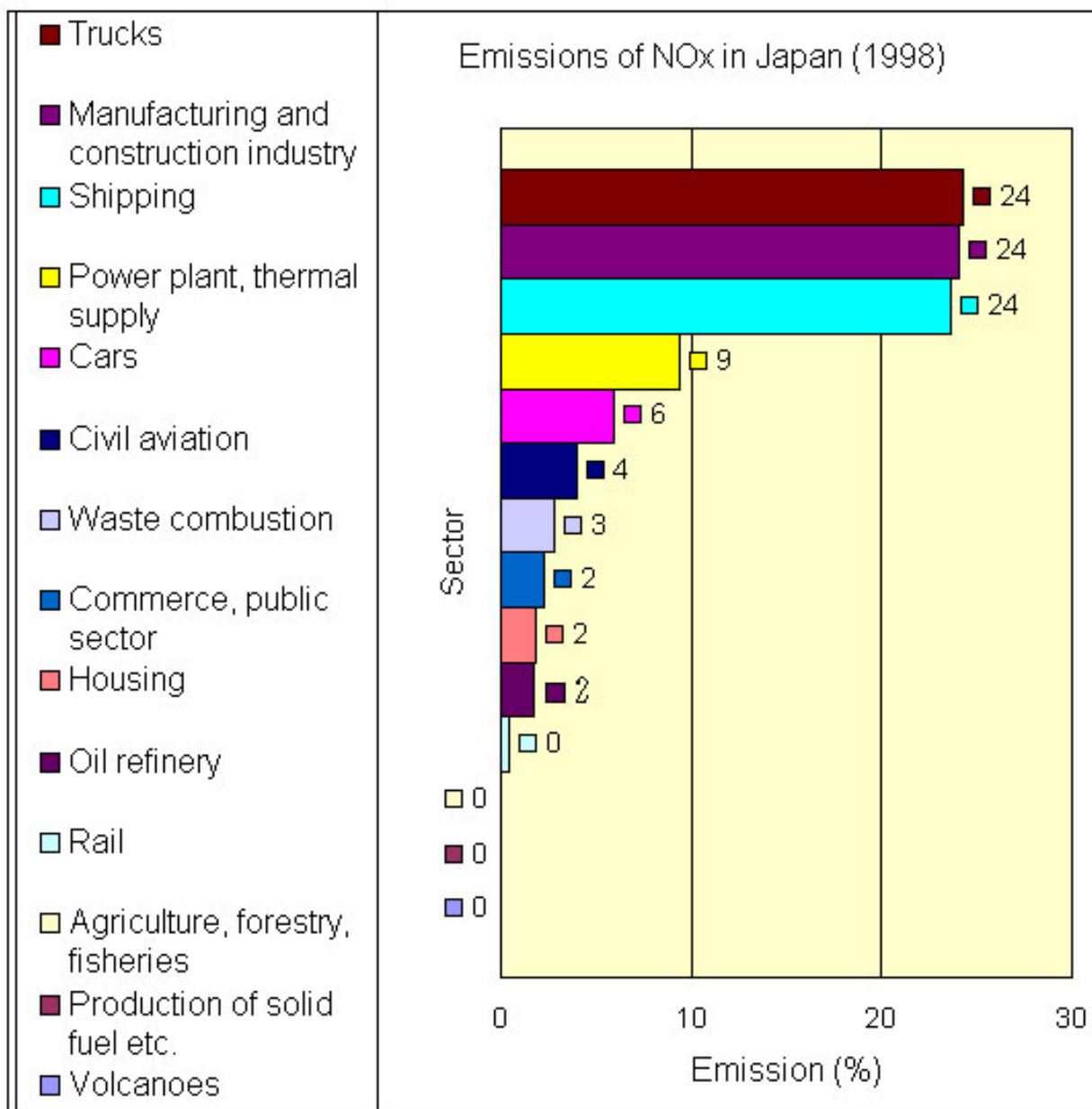
Source: Institute of Behavioral Sciences, March 2000. "Report on grid data of air pollutant emission project," Environment Agency of Japan, 1999.

### Compartmental SO<sub>2</sub> Emissions Ratio of Japan (1998)



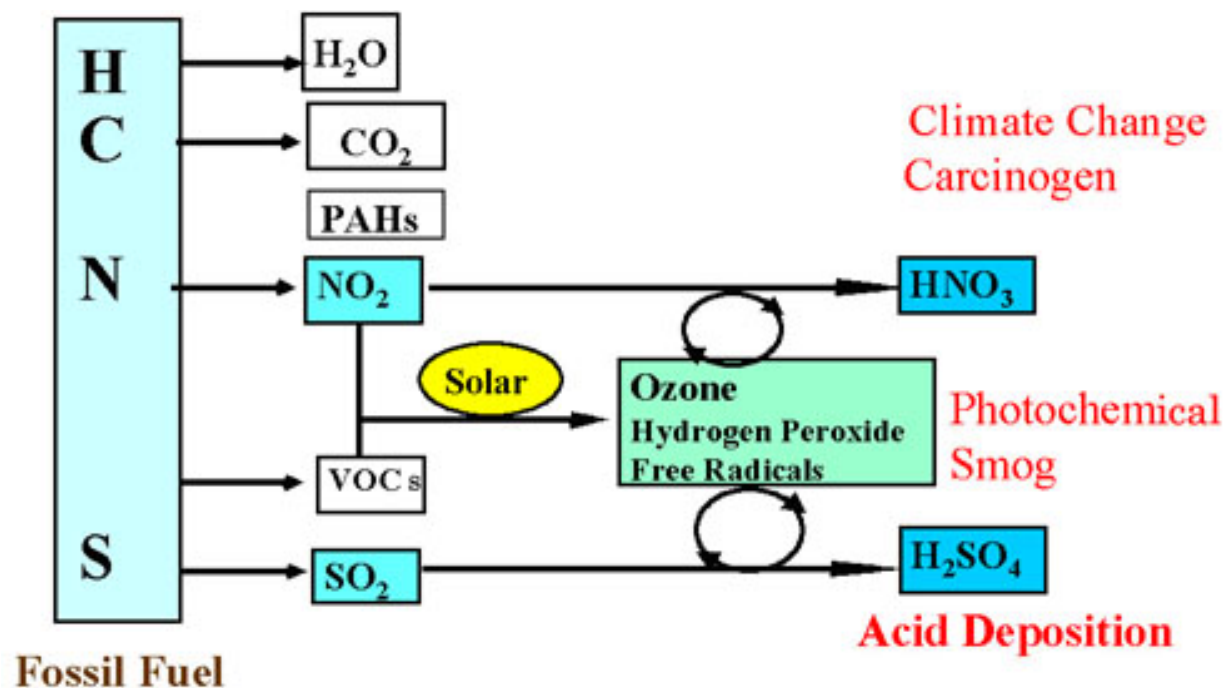


**Compartmental NO<sub>x</sub> Emissions Ratio of Japan (1998)**



## 5: Air Pollution and Acid Deposition Caused by the Combustion of Fossil Fuels

$\text{SO}_2$  and  $\text{NO}_x$ , are released into the atmosphere during the combustion of fossil fuels. They are later transformed into sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and nitric acid ( $\text{HNO}_3$ ). The process of chemical transformation is presented in simplified form below.



### Air Pollution due to Fossil Fuel Combustion

$\text{SO}_2$  and  $\text{NO}_2$  → (by reacting with an oxidant) →  
 $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  → (in the presence of water) →  
sulphate ions ( $\text{SO}_4^{2-}$ ) and nitrate ions ( $\text{NO}_3^-$ )

These substances are carried in the atmosphere over long distances through diffusion and dispersion, and can be deposited thousands of kilometers away from their points of origin.

## 6: Deposition

**Pollutants that have been transformed into  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  fall to the Earth's surface after being suspended in the atmosphere for a number of days. This process of "deposition" occurs in two forms: (1) wet and (2) dry.**

(1) Wet deposition occurs when  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , dissolved in the water droplets of clouds, is transported to surface with rain, snow or fog. Rainwater demonstrates strong acidity when a large amount of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  has been dissolved in it. This is the origin of the name "acid rain."

(2) Dry deposition occurs when  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , carried as in gaseous

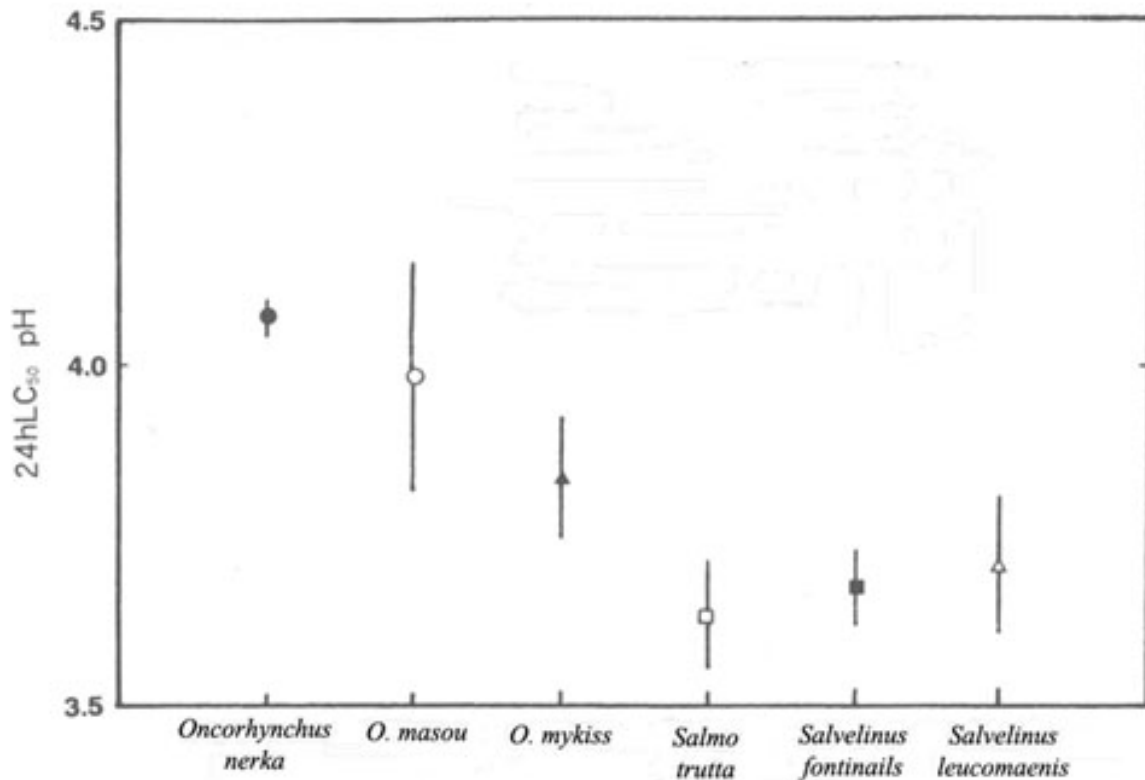
state or as fine particles by the wind, settle on trees, buildings, etc. As extra-fine aerosols, these acidic particles can also enter the lungs.  $H_2SO_4$  and  $HNO_3$  carried by the wind can be deposited even on sunny days and in the absence of clouds.

## IMPACTS OF ACID DEPOSITION

### 1: Effects on Rivers and Lakes - Effects on Fish

**High levels of acidity in many rivers and lakes in northern Europe have led to the disappearance of fish species (e.g., Atlantic salmon, Brown trout, etc.).**

One factor is the cold winters in northern countries, when snow laden with acidic pollutants settles on the ground. In the spring as air temperatures rise, the snow melts, releasing acidic water into rivers and lakes.



LC<sub>50</sub>: 50% lethal concentration

24 h LC<sub>50</sub> pH indicates lethal pH causing 50% mortality in 24 hours.

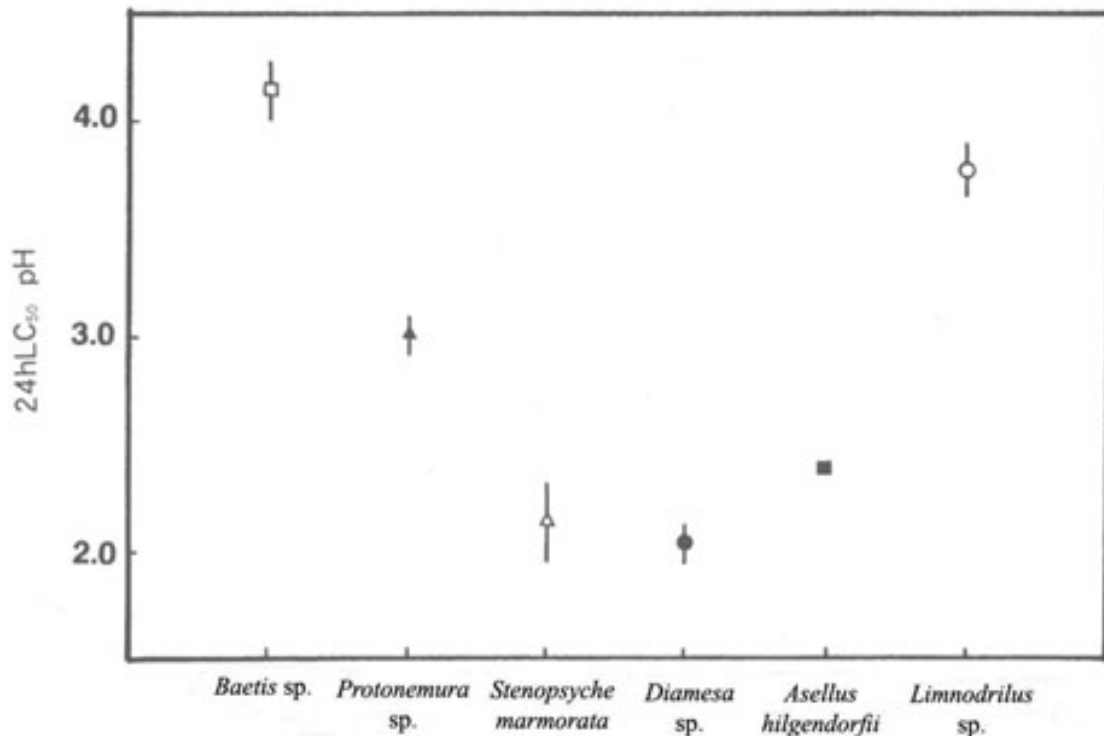
Vertical lines indicate 95 % confidence limits.

Source: Kenichi Satake, ed. (1999), Ecology of acid environment, Aichi Shuppan Co., Ltd. p.18 (Chapter 2: Kazumasa Ikuta et al.) (in Japanese).

## 2: Effects on Rivers and Lakes - Effects on Aquatic Organisms Besides Fish

In acidic rivers and lakes, the aquatic insects, shrimp and shellfish that serve as food for fish also decrease in population. Acidification also affects aquatic plants, changes the species composition of phytoplankton, and affects bacteria and fungi (molds).

Acidification of the aquatic environment seriously affects ecosystems, including all organisms living in the water.



LC<sub>50</sub>: 50% lethal concentration

24 h LC<sub>50</sub> pH indicates lethal pH causing 50% mortality in 24 hours.

Vertical lines indicate 95 % confidence limits.

Source: Kenichi Satake, ed. (1999), Ecology of acid environment, Aichi Shuppan Co., Ltd. p.18 (Chapter 2: Kazumasa Ikuta et al.) (in Japanese).

## 3: Effects on Forests - Effects on Trees

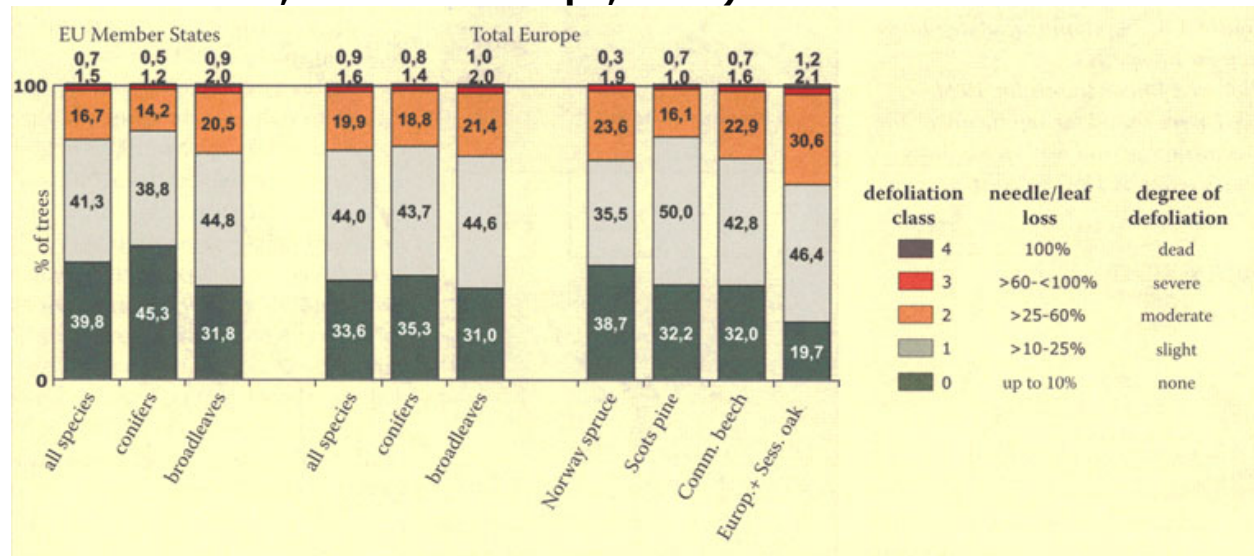
**Acid deposition affects many components of ecosystems, and impacts on trees are often significant. Along the borders of Germany, the Czech Republic, Slovakia and Poland is an area called the Black Triangle.**

The coal produced here is high in sulfur, and it emits sulfur dioxide when burned. The combustion of this coal for thermal power generation and other uses has killed many trees in forests in that region. The same type of forest

damage is evident in many places around the world, including many in Asia.

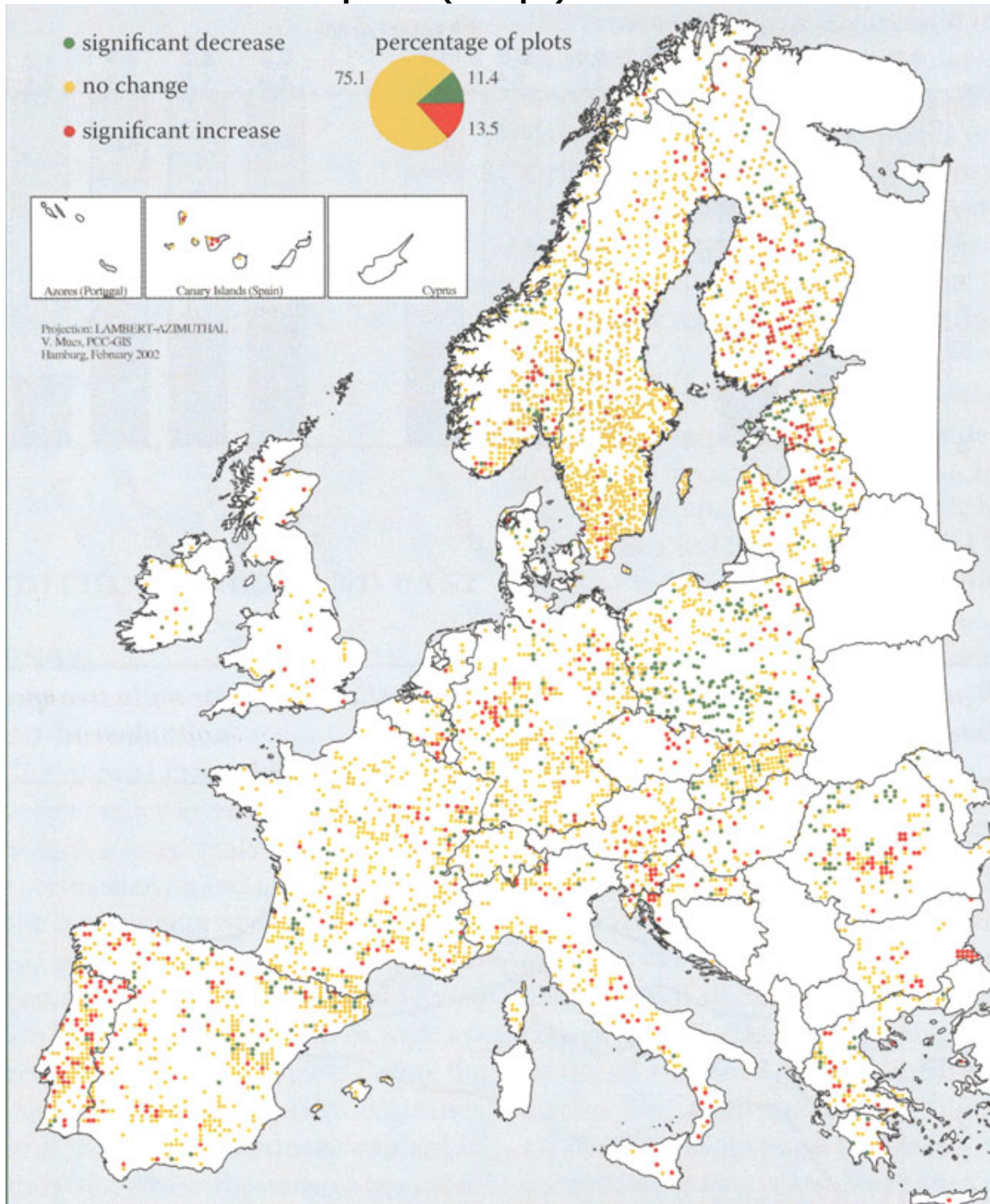
Sulfur dioxide is emitted during the refining of copper, nickel and other metal ores that contain sulfur. In Ashio, Japan, when copper was refined years ago, much sulfur dioxide was released, killing many trees in the area. The environmental consequences of this type of pollution are now well known, but this same type of damage is still occurring around the world today. For example, trees have died dozens of kilometers around a nickel refinery in the Kola Peninsula of western Russia.

### Extent of Defoliation for Principal Tree Species (European Union Member States, and Total Europe, 2001)



Source: CLRTAP (Convention on Long-range Transboundary Air Pollution): ICP-Forest (International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests) (2002), The Condition of Forests in Europe, 2002 Executive Report, UNECE and EC, Geneva and Brussels, pp.13-14.

## Defoliation of All Tree Species (Europe)



Plot wise linear trends for 1994-2001 were tested for significance. The evaluation period for France, Italy and Sweden is 1997 to 2001.

Source: CLRTAP (Convention on Long-range Transboundary Air Pollution): ICP-Forest (International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests) (2002), The Condition of Forests in Europe, 2002 Executive Report, UNECE and EC, Geneva and Brussels, pp.13-14.

#### **4: Effects of Bootlace Fungus (Honey Fungus) on Forests**

**Besides direct damage from acid deposition, damage can also be indirect, for example, from the bootlace fungus (honey fungus) that can kill trees. Bootlace fungus grows in acidified soil. It then invades injured and weak trees and can kill them.**

Many Japanese cedars have been planted throughout Japan. Although the Japanese cedar itself is an acid-resistant species, acid deposition can cause an excess or deficiency of nutrients in the soil. This has influenced the growth of Japanese cedars in some parts of Japan.

Weakened trees can also be damaged by wind from typhoons, snow, lightning, diseases, and by insects, such as the pine weevil. The impacts of each of these threats can compound the impacts of the others.

#### **Primary Causes of Damage to Forest Vegetation**

The causes of damage to forests and trees can be classified into three types: predisposing causes, inciting causes, and contributing causes (UNEP-ECE 1991). Air pollution (including acidic precipitation) is an example of a predisposing cause; droughts are an example of an inciting cause; and damage caused by disease and harmful insects is an example of a contributing cause. These environmental stresses are closely related to one another and together cause tree decline. It is often difficult to define the effect of one cause alone, because the effect of each cause on its own is usually not very pronounced.

Schlaepfer (1992)\*<sup>1</sup> summarized the results of European research and concluded that although the proportion of forests experiencing defoliation is increasing, there is no evidence that the overall condition of trees in European forests is deteriorating. Additionally, there are various types of deforestation, as judged by the proportion of forest area experiencing defoliation, the causes of which are different in each area. Therefore, it is likely that deforestation is due to multiple impacts arising from various causes. Although the impact of air pollution on forests appears to be less important than had once been hypothesized, long-term acid deposition on forest soil may be a potential threat to forest ecosystems.

\*<sup>1</sup>: Schlaepfer, R. 1992. In Acidification Research: Evaluation and Policy Applications (Schneider, T. ed.), 27-44, Elsevier, 583pp.

#### **5: Effects on Buildings and Cultural Assets**

**Have you ever seen something like a concrete icicle hanging from the wall of an old building, under a highway, or under the eaves of a structure?**

It occurs when acidic rainwater enters through cracks in concrete, dissolves the calcium hydroxide in the concrete, and releases calcium ions. Calcium

ions react with carbon dioxide and form calcium carbonate on the surface of concrete. Acid rain then dissolves calcium carbonate again, and educes calcium carbonate as stalactites with the escape of carbon dioxide. When you pick up the stalactite and examine it, you will notice that it is round at the tip, and it gets longer as it gathers water droplets containing impurities.

Besides concrete, acid deposition also corrodes marble floors, sculptures, and copper roofs, and it causes verdigris to form on bronze and copper statues. If acid deposition continues, the above effects will increase, and our environment will change.

### **Effects on Buildings and Cultural Assets (Photos)**



Photo 1: Concrete statue (Ueno Park in Tokyo)





Photo 2: Copper statue (Ueno Park in Tokyo)



Photo 3: Copper statue (Ueno Park in Tokyo)



Photo 4: Bronze statue (Yokohama Park in Yokohama City)



Photo 5: Bronze statue (Yokohama Park in Yokohama City)



Photo 6: Bronze statue (Silk Centre in Yokohama City)



Photo 7: Marble statue in Foreigners' Cemetery (Yokohama City)



Photo 8: Marble statue in Foreigners' Cemetery (Yokohama City)



Photo 9: Concrete "icicles" under a highway bridge (Yokohama City)



Photo 10: Concrete "icicles" under a bridge on the Tsurumi River (Yokohama City)

## **6: Effects on the Human Body**

**Precipitation in Japan has an average pH level of approximately 4.8. This level of acidity is considered to have no effect on the human body.**

However, direct contact with rain with a pH level of 2 has affected skin. One well-known historical incident is the London Smog of 1952. On the week beginning December 5, the city of London, England was enshrouded in a thick blanket of fog and rain fell with a pH level of 1.4-1.9. Within a few months, about 4,000 more people than usual had died. Most deaths resulted from bronchial infections or heart attacks; some claim these were triggered by sulfur dioxide in the smog.

### **Previous Examples of Effects on the Human Body (Japan)**

In June 1973, 441 people living in the area around Suruga Bay in Shizuoka Prefecture and the town of Uenohara in Yamanashi Prefecture reported that they had sore eyes and throats and bad coughs, symptoms that had developed during light rain. On July 3, 1974, 32,000 people reported the same symptoms across almost the whole of the Kanto area. On the following day, 730 people in the Tokyo area reported irritation to their eyes as the seasonal front moved southwards. During this time, the rain was reported to be strongly acidic, with the lowest pH reading being 2.85. In June 1975, 144 people around Kanuma City in Tochigi and Kumagaya City in Saitama reported eye and skin irritation. It is highly probable that the acid rain or mist in these cases contained pollutants such as formaldehyde and formic acid. There have been no similar reports in recent years.

### **7: Complex Environmental Problems**

#### **The effects of acid deposition are not just regional.**

It is well known that the burning of oil and coal not only emits carbon dioxide, which contributes to global warming, but it also emits sulfur dioxide and nitrogen oxides. This causes acid deposition. As these pollutants travel long distances, not only across local areas, but also across national boundaries, they are called "long-range transboundary air pollutants".

"Long-range transboundary air pollutants" contribute to widespread deforestation and a decrease in wildlife. Thus, the problem of acid deposition is a tangled web of complex environmental issues.

Humans are inextricably involved in the Earth's ecosystems. If rivers, lakes, forests, and soils become acidic, and animals and plants are adversely affected, humans, who are at the top of the ecosystem, cannot avoid being adversely affected. Furthermore, not only are buildings and cultural assets valuable in and of themselves, but the warning we get from damage inflicted upon them is also important.