

A wide-angle photograph of an Arctic landscape. The foreground is filled with numerous icebergs of various sizes floating in dark blue water. In the background, there are snow-capped mountains and a large glacier. The sky is clear and blue.

# Acidification in the Arctic

# General Question about Acidification

- **Acid deposition** occurs when sulfuric acid, nitric acid, or hydrochloric acid, emitted into or produced in the air as a gas or liquid, deposits to soils, lakes, farmland, forests, or buildings. Deposition of acid gases is **dry acid deposition**, and deposition of acid liquids is **wet acid deposition**. Wet acid deposition can be through rain (**acid rain**), fog (**acid fog**), or aerosol particles (**acid haze**).

# General Question about Acidification

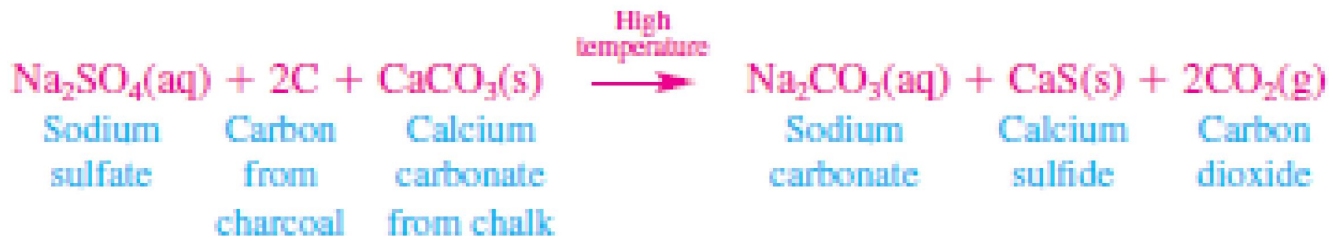
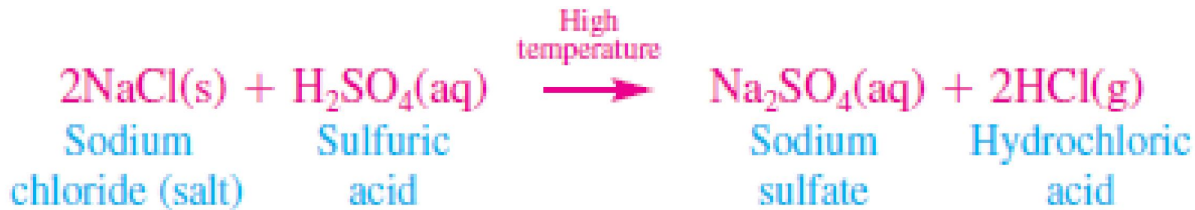
- Acid deposition is caused by the emission or atmospheric formation of gas- or aqueous-phase **sulfuric acid** ( $\text{H}_2\text{SO}_4$ ), **nitric acid** ( $\text{HNO}_3$ ), or **hydrochloric acid** ( $\text{HCl}$ ).

# History of the problem

- Historically, coal was the first and largest source of anthropogenically produced atmospheric acids.
- During the **Industrial Revolution**, which started in the eighteenth century, coal was used to provide energy for the steam engine.
- In the late eighteenth century, a second major source of atmospheric acids emerged. Around 1780,
- the demand for **sodium carbonate** [ $\text{Na}_2\text{CO}_3(\text{s})$ ] (also known as **soda ash**, **washing soda**, and **salt cake**), used in the production of soaps, detergents, cleansers, glass, paper, bleaches, and dyes, increased

# History of the problem

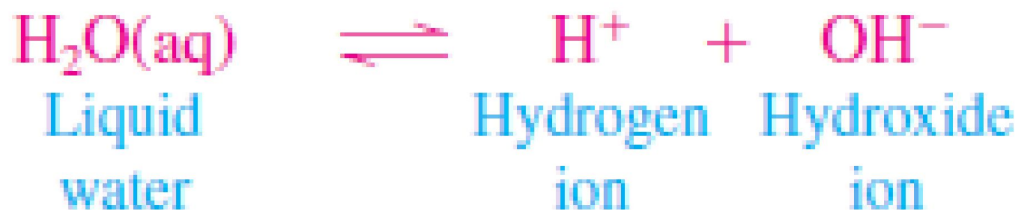
- Method of producing soda ash:

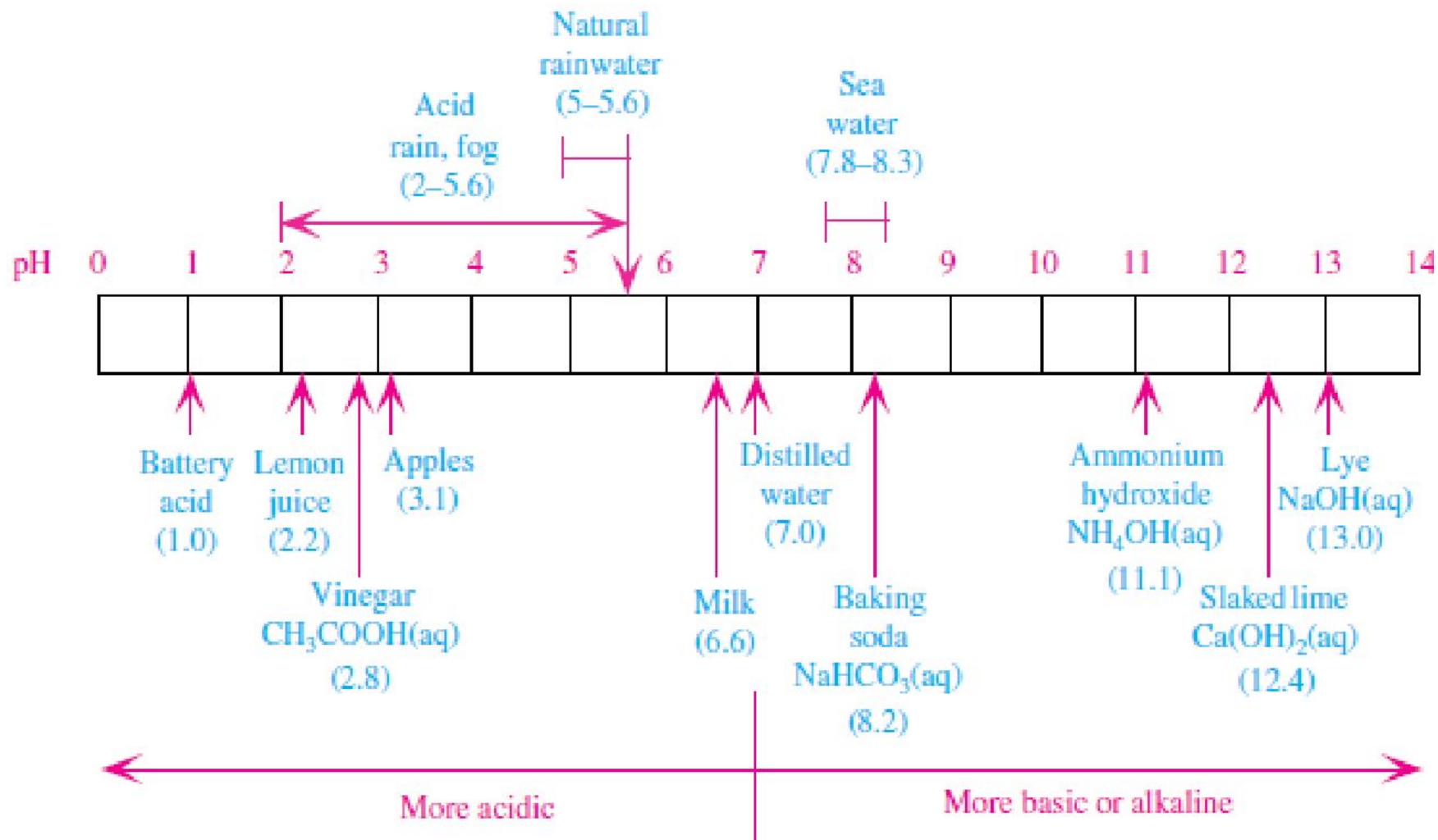


In 1863, an estimated 1.76 million tons of raw material were burned to form soda ash, producing only 0.28 million tons of useful products. Most of the remaining 1.48 million tons was emitted as HCl(g) or other gases and produced as solid waste

# pH

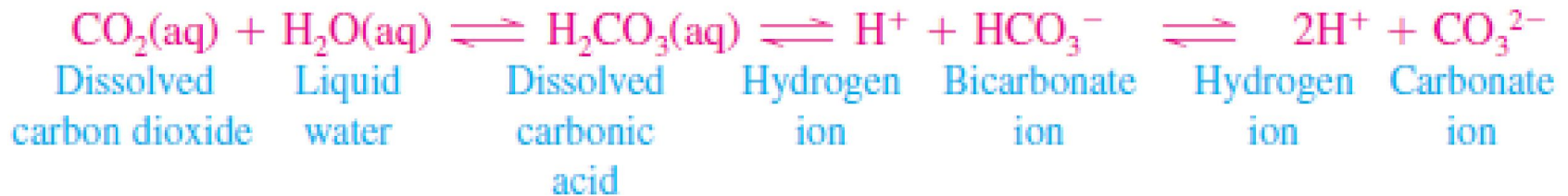
- pH was defined as  $\text{pH} = -\log_{10}[\text{H}^+]$ ,
- where  $[\text{H}^+]$  is the molarity (moles per liter) of  $\text{H}^+$  in a solution containing a solvent and one or more solutes.
- The pH scale varies from less than 0 (lots of  $\text{H}^+$  and very acidic) to greater than 14 (very little  $\text{H}^+$  and very basic or alkaline). Neutral pH, the pH of distilled water, is 7.0. At this pH, the molarity of  $\text{H}^+$  is  $10^{-7} \text{ mol L}^{-1}$ .





# Carbonic Acid

- Water can be acidified in one of several ways. When gas-phase carbon dioxide dissolves in water, it reacts rapidly with a water molecule to form aqueous **carbonic acid** [H<sub>2</sub>CO<sub>3</sub>(aq)], a weak acid, which dissociates by the reversible reactions

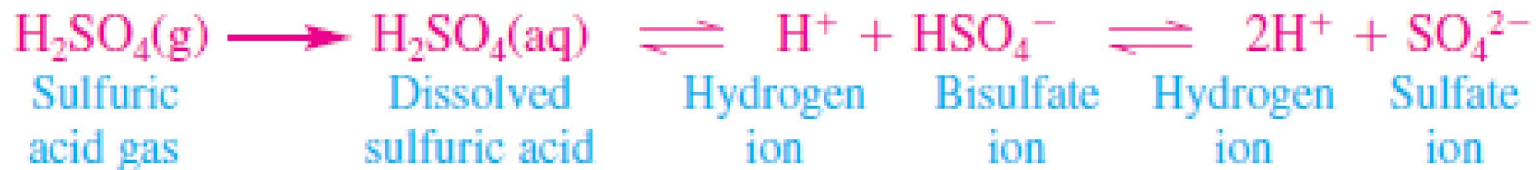




- A fraction of  $\text{CO}_2(\text{g})$  always dissolves in rainwater. Thus, rainwater, even in the cleanest environment on Earth, is naturally acidic due to the presence of background carbonic acid in it. The **pH of rainwater affected by only carbonic acid is about 5.6**, indicating that its hydrogen ion molarity is 25 times that of distilled water.

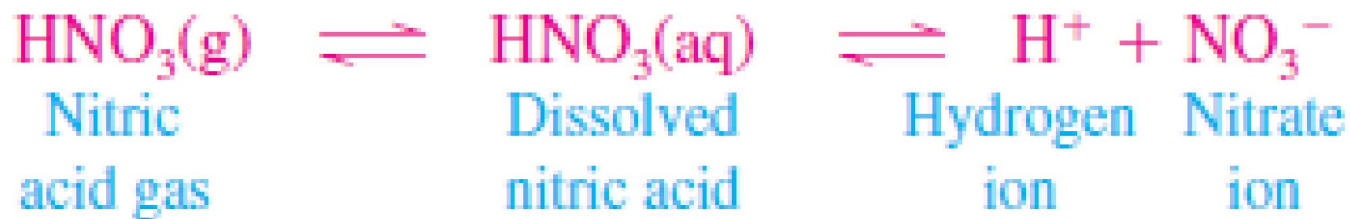
# Sulfuric Acid

- When gas-phase sulfuric acid condenses onto rain drops, the resulting aqueous-phase **sulfuric acid** [H<sub>2</sub>SO<sub>4</sub>(aq)], a strong acid, dissociates by



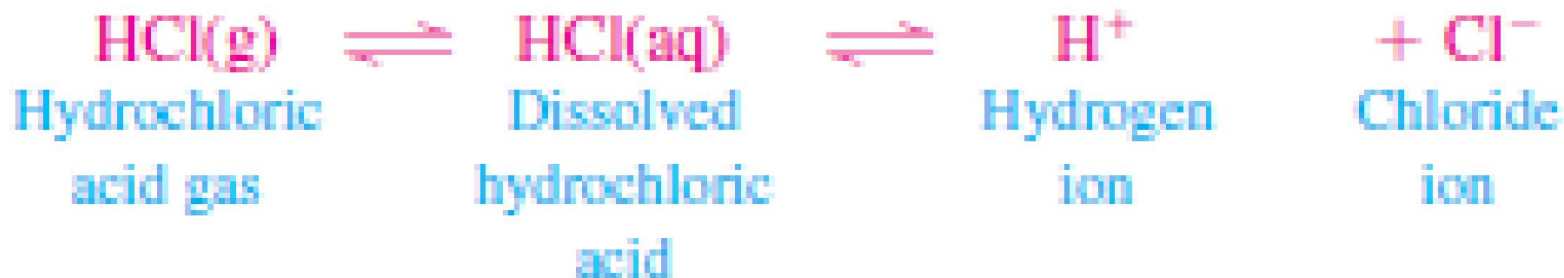
# Nitric acid

- When gas-phase nitric acid dissolves in raindrops, it forms aqueous **nitric acid** [HNO<sub>3</sub>(aq)], a strong acid that dissociates almost completely by



# Hydrochloric Acid

- When gas-phase hydrochloric acid dissolves in raindrops, it forms aqueous **hydrochloric acid** [HCl(aq)], a strong acid that dissociates almost completely by



# Sources of Acids

- Some of the enhanced acidity of rainwater from sulfuric acid, nitric acid, and hydrochloric acid is natural.
- Volcanos, for example, emit  $\text{SO}_2(\text{g})$ , a source of sulfuric acid, and  $\text{HCl}(\text{g})$ .
- Phytoplankton over the oceans emit dimethylsulfide [ $\text{DMS}(\text{g})$ ], which oxidizes to  $\text{SO}_2(\text{g})$ .
- The main natural source of  $\text{HNO}_3(\text{g})$  is gas-phase oxidation of natural nitrogen dioxide [ $\text{NO}_2(\text{g})$ ].
- The addition of natural acids to rainwater containing carbonic acid results in typical natural rainwater pHs of between 5.0 and 5.6

# Sources of Acids

- Acid deposition occurs when anthropogenically produced acids are deposited to the ground, plants, or lakes in dry or wet form.
- The two most important anthropogenically produced acids today are sulfuric and nitric acid, although hydrochloric acid can be important in some areas. In the eastern United States, about 60 to 70 percent of excess acidity of rainwater is due to sulfuric acid, whereas 30 to 40 percent is due to nitric acid.
- Thus, sulfuric acid is the predominant acid of concern. In polluted cities where fog is present, such as in Los Angeles, California, nitric acid fog is a problem.
- In locations where  $\text{HCl(g)}$  is emitted anthropogenically, such as near wood burning or industrial processing,  $\text{HCl(aq)}$  affects the acidity of rainwater. Today, however,  $\text{HCl(aq)}$  contributes to less than 5 percent of total rainwater acidity by mass. Other acids that are occasionally important in rainwater include formic acid [ $\text{HCOOH(aq)}$ ], produced from formaldehyde and acetic acid [ $\text{CH}_3\text{COOH(aq)}$ ], produced from acetaldehyde and the main ingredient in vinegar].

# Sulfuric Acid Deposition

- The most abundant acid in the air is usually sulfuric acid [ $\text{H}_2\text{SO}_4(\text{aq})$ ], whose source is sulfur dioxide gas [ $\text{SO}_2(\text{g})$ ], emitted anthropogenically from coal-fire power plants, metalsmelter operations, and other sources.

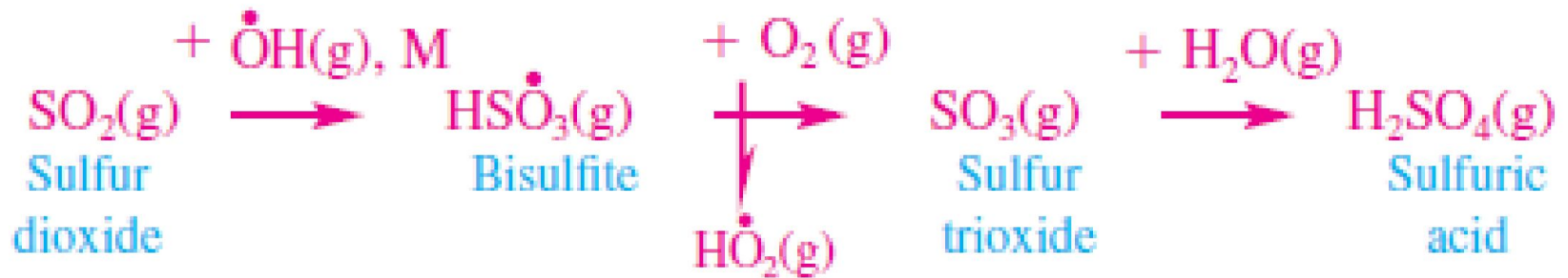
- Power plants usually emit  $\text{SO}_2(\text{g})$  from high stacks so that the pollutant is not easily downwashed to the surface nearby. The higher the stack, the further the wind carries the gas before it is removed from the air. The wind transports  $\text{SO}_2(\text{g})$  over long distances, sometimes hundreds to thousands of kilometers.
- Thus, acid deposition is often a regional and **long-range transport** problem. When acids or acid precursors are transported across political boundaries, they create **transboundary air pollution**.



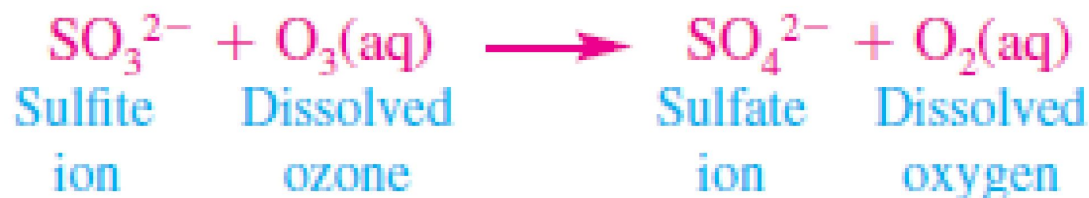
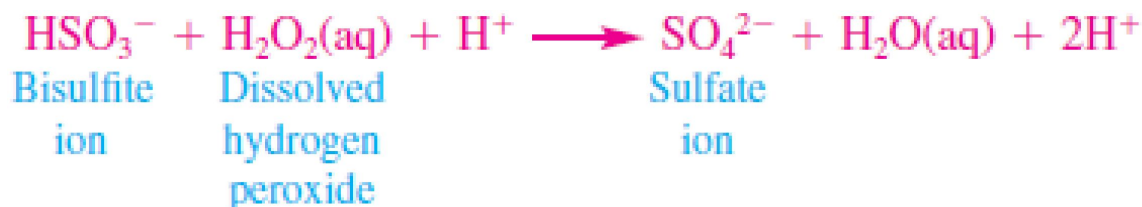
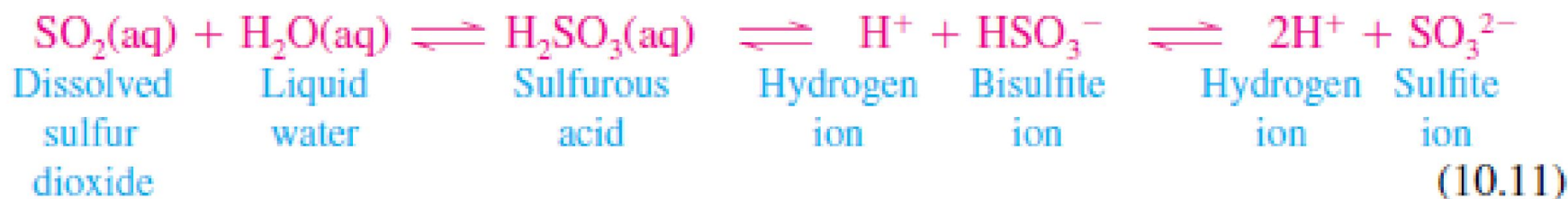
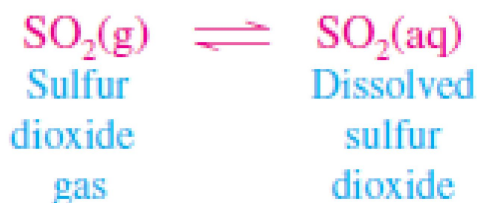
# the S(IV) and S(VI) families

S(IV) Family		S(VI) Family	
Chemical Name	Chemical Formula	Chemical Name	Chemical Formula
Sulfur dioxide	$\text{SO}_2(\text{g}, \text{aq})$	Sulfuric acid	$\text{H}_2\text{SO}_4(\text{g}, \text{aq})$
Sulfurous acid	$\text{H}_2\text{SO}_3(\text{aq})$	Bisulfate ion	$\text{HSO}_4^-$
Bisulfite ion	$\text{HSO}_3^-$	Sulfate ion	$\text{SO}_4^{2-}$
Sulfite ion	$\text{SO}_3^{2-}$		

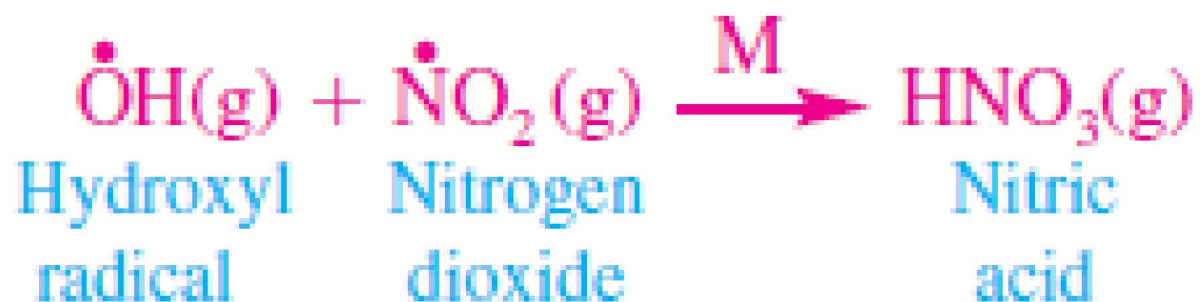
# Gas-Phase Oxidation of S(IV)



# Aqueous-Phase Oxidation of S(IV)



# Nitric acid deposition



# Effect of acid deposition.

## London-type smog

- were recorded in London in the IX and XX centuries.

*December 1873 (270–700 deaths more than the average rate),*

*January 1880 (700–1,100 excess deaths),*

*December 1892 (1,000 excess deaths),*

*November 1948 (300 excess deaths),*

*December 1952 (4,000 excess deaths),*

*January 1956 (480 excess deaths),*

*December 1957 (300–800 excess deaths),*

*December 1962 (340–700 excess deaths).*

- Excess deaths occurred in every age group, but the number was greater for people older than 45. People with a history of heart or respiratory problems made up 80 % of those who died. During the episodes, temperature inversions coupled with fog and heavy emissions of pollutants, particularly from combustion of coal and other raw materials, were blamed for the disasters. During the 1952 episode, peak concentrations of  $\text{SO}_2(\text{g})$  and particulate smoke were estimated to be 1.4 ppmv and  $4,460 \text{ g m}^{-3}$ , respectively. The particle and fog cover was so heavy during that event that the streets of London were dark at noontime, and it was necessary for buses to be guided by lantern light.

# Effect of acid deposition.

- Effects on Lakes and Streams
- Effects on Biomass



- a) Acidified forest, Oberwiesenthal, Germany, near the border with the Czechoslovakia, taken in 1991. The trees are of the *Picea* family. Photo by Stefan Rosengren, available from Naturbild.
- (b) Acidified forest in the Erzgebirge Mountains, north of the town of Most, Czechoslovakia, taken in 1987. Photo by Owen Bricker, USGS.

# Effect of acid deposition

- Effects on Buildings and Sculptures



Sandstone figure over the portal of a castle, built in 1702, in Westphalia, Germany, photographed in 1908 (left) and in 1968 (right). The erosion of the figure is due to a combination of acid deposition and air pollution produced from the industrialized Ruhr region of Germany. Courtesy Herr Schmidt-Thomsen.

# Acidification in the Arctic





# Sources

## *Industrial areas farther south contribute to Arctic air pollution*

- Most sulfur in Arctic air comes **from industrial areas** further south. Eurasia (**40 percent**) and eastern North America (**20 percent**) are the major global sources. A large part of the remaining global emissions occur in the Far East, particularly China.
- Emissions of sulfur dioxide have decreased considerably in North America and Europe after a peak in the late 1970s and early 1980s. This results from an interplay of political decisions to cut emissions, the replacement of 'dirty' fuels, and new technologies for removing sulfur from fossil fuel and for cleaning flue gases in power plants. Nonetheless, power generation and smelting remain major sources.

# Sources outside the Arctic

Source	Tg S	%	Tg N	%
Power generation	14.9	54	3.8	21
Commercial and residential combustion	3.0	11	0.8	4
Industrial combustion	7.0	25	2.4	13
Production processes	0.9	3	0.4	2
Fossil fuel extraction	0.05	0	0.08	0
Road transport	0.7	3	7.8	44
Other mobile sources	0.6	2	2.3	13
Waste treatment/disposal	0.09	0	0.2	1
Agriculture	0.001	0	0.05	0
Natural	0.6	2	0.05	0
<hr/>				
Total	27.8		17.9	

# Natural sources

- The algae in ocean surface waters are a source of sulfur to the atmosphere in the form of dimethylsulfide (DMS:  $\text{CH}_3 - \text{S} - \text{CH}_3$ ), which is oxidized in the atmosphere to sulfur dioxide, sulfate and methyl sulfonic acid (MSA:  $\text{CH}_3\text{SO}_3\text{H}$ ).
- Emissions of reduced sulfur compounds from terrestrial environments and vegetation are about one order of magnitude smaller than the marine emissions.
- Volcanic emissions of sulfur include both hydrogen sulfide ( $\text{H}_2\text{S}$ ), elemental sulfur and sulfur dioxide. The emissions are located in areas of volcanic activity and are extremely variable from one year to another. Annual emissions of sulfur from volcanoes between 1964 and 1972 have been estimated at 7.8 Tg S/y.

- Ammonia ( $\text{NH}_3$ ) is also involved in acidification processes; it is a neutralizing compound in the atmosphere, but acts as a net acidifying agent in soils. Ammonia combines with sulfuric acid in the atmosphere to form  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$  and other semi neutralized sulfates.
- Acidification is not solely a function of sulfate (or nitrate) deposition but is also controlled by the base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) contained in aerosols or precipitation. There is considerable evidence that recent declines in sulfate levels have occurred together with an accompanying decrease in base cations. While some of these base cations can be argued to have a natural source (e.g., soil dust), European decreases in base cations have been attributed to an anthropogenic decrease. For the latter reason, decreases in emissions of sulfur species may not result in an equivalent decrease in acidity.

# Sources within the Arctic

## *Metal smelters have the largest emissions within the Arctic*

- Production of copper, nickel and other nonferrous metals from sulfur-bearing ores create the largest emissions of acidifying substances within the Arctic. The traditional smelting method roasts the ore to remove the sulfur as sulfur dioxide and to oxidize the iron in the ore before further smelting and refining. The sulfur dioxide can be recovered in modern smelters and used as a raw material for producing sulfuric acid, gypsum, and some other inorganic chemicals.
- Most smelter emissions come from the Nikel, Zapolyarnyy, and Monchegorsk complexes on the Kola Peninsula and from Norilsk in northwestern Siberia. Compared with similar industries in other areas, emissions from these smelters are extremely high. Norilsk is the largest source, spewing out more than a million tonnes of sulfur every year.

# Sources within the Arctic

## Exploitation and usage of fossil fuels

- Within the Arctic, there is coal mining on Spitsbergen (Norway), in Vorkuta (Russia) and in the Tiksi region (northeastern Siberia). Moreover, there is a large coal mining area in the Pechora Basin, which lies just south of the Arctic Circle in northern Russia.
- Because of the small number of inhabitants in much of the Arctic, fuel and energy consumption is low and the emissions from the usage of fossil fuels are mainly located in towns. For example, there are coal-fired power plants in Vorkuta and Inta (Russia), which serve the local settlements, and coal mining and oil and gas exploration in these areas.
- Other examples include the mining settlements on Spitsbergen which are also served by small, coal-fired electric power plants in Longyearbyen and Pyramiden.

# Sources within the Arctic

- Shipping and fishing activities are also sources of air pollutants in the Arctic. For example, extensive deep-sea fishing for cod, capelin and prawns takes place in the Barents Sea. Marine transport, particularly of timber and timber products, is also important along the Siberian coast and on the Siberian rivers.

# Natural emissions

- There are areas of volcanic activity in the North Atlantic and Bering Sea regions, and in southern Alaska, however, the associated sulfur emissions are relatively low and sporadic.
- A notable area with respect to natural emissions of sulfur is the Smoking Hills area in Canada, where the 'natural' combustion of pyrite-bearing bituminous shale, releasing sulfur dioxide and sulfuric acid mist and aerosol, has caused phytological damage within 500 m of the source. However, these emissions are relatively low compared to anthropogenic inputs.
- The Arctic Ocean and adjacent seas are generally quite productive and hence the biogenic production of dimethylsulfide (DMS) and transport of DMS through the sea-air interface must be considered a potential source of atmospheric sulfur.



# Natural emissions

- In winter, anthropogenic sources account for almost all of the sulfur in the Arctic atmosphere, whereas in summer about 30% of the sulfur is from natural sources.

# ***Local energy production is a small source***

- Emissions from energy production in the Arctic are generally low because the population is sparse. There are coal-fired power plants in Vorkuta and Inta in Russia, serving local settlements around coal mines and gas fields in the area. The mining settlements on Spitsbergen also have coal-fired power plants.
- Shipping and fishing fleets are also sources of sulfur. The extensive fishing fleet in the Barents Sea uses large amounts of diesel fuel.
- Marine transport, particularly of timber and timber products, is important along the Siberian coast and on Siberian rivers.

# ***Nitrogen emissions are less important***

- Burning of fossil fuels also creates nitrogen oxides. In more densely populated areas, traffic and power production are the most important sources. Emissions increased rapidly from the 1950s to 1975. In North America and
- Europe, they have remained fairly constant since 1980. Nitrogen oxides contribute to acidification in non-Arctic parts of Europe and North America, but are less important in the Arctic context.

# Atmospheric processes

- The fate of sulfur and nitrogen emissions depends on what happens in the atmosphere. Light, moisture, and reactive chemical compounds in the air act together to transform sulfur dioxide and nitrogen oxides into acid precipitation and into particles that can settle on surfaces they encounter. The box to the left describes the air chemistry of sulfur.
- When air from mid-latitudes moves northward with its load of contaminants, it rises, forming layers of dirty air at higher altitudes.
- However, pollution released into the Arctic airmass tends to remain within a couple of kilometers of the ground because of temperature inversions that create a lid of cold air.
- In the spring and winter, lack of precipitation in the High Arctic keeps acidifying contaminants suspended in the air. Sparse vegetation also provides for low deposition rates of particulate matter. During summer, two mechanisms keep the air cleaner: first, the northward shift of the Arctic front, away from major source regions, reduces contaminant inputs, and second, increased precipitation washes acid contaminants out of the air.

### *Sulfur dioxide turns into haze and acid precipitation*

Fossil fuels with high sulfur content produce sulfur dioxide when they burn. In the atmosphere, the gas reacts with hydroxyl radicals (OH), ozone, and peroxide ( $\text{H}_2\text{O}_2$ ), creating sulfuric acid ( $\text{H}_2\text{SO}_4$ ).

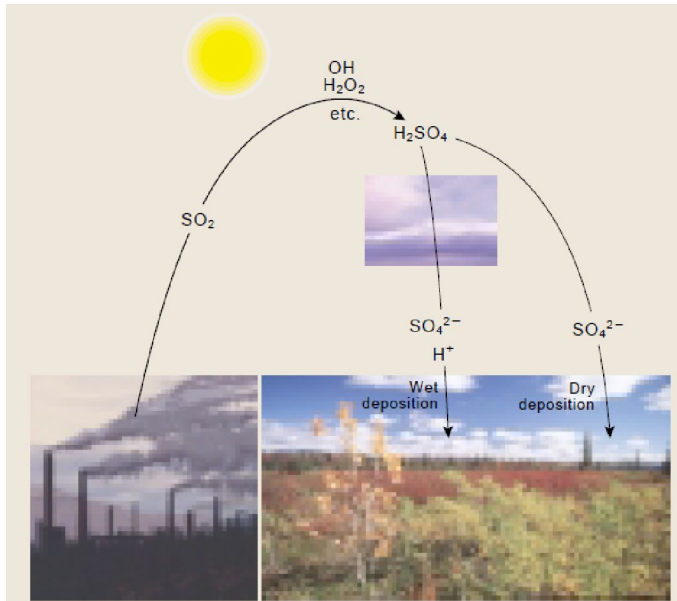
In the cold air of the High Arctic, sulfuric acid takes the form of sub-micrometer particles, which are the main components of Arctic haze. Sulfate particles can adhere directly to surfaces as dry deposition.

Sulfuric acid can also react with water in rain, snow, and fog, dissociating into hydrogen and sulfate ions, which get washed out as wet deposition.

Biogenic sulfur compounds, such as dimethyl sulfide (DMS) from plankton and hydrogen sulfide ( $\text{H}_2\text{S}$ ) from volcanoes, enter the same chemical cycle in the atmosphere via a reaction with hydroxyl radicals (OH).

The rates of different chemical reactions in the sulfur cycle depend on energy from the sun. In the Arctic, lack of sunlight during the polar winter limits production of the hydroxyl radical, which in turn slows production of sulfuric acid from sulfur dioxide.

When the sun returns in the early spring, there is a load of sulfur dioxide in the air, ready to be converted into sulfate aerosols. This photochemical mechanism explains why Arctic haze is most pronounced in March and April, after the Arctic sunrise.



# The atmospheric chemistry of the sulfur cycle

- The atmospheric chemistry of the sulfur cycle is dominated by OH radical reactions in the gas phase with  $\text{H}_2\text{S}$ , DMS, and  $\text{SO}_2$ , all of which lead to the production of gaseous sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and by gaseous and aqueous phase reactions between  $\text{SO}_2$  and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ozone ( $\text{O}_3$ ).
- Once sulfate is produced, its removal is relatively rapid with an atmospheric half-life in the order of 3 to 7 days at mid-latitudes and about two weeks or more in the High Arctic during winter.
- The atmospheric emission, production, transport and deposition cycle of sulfate aerosol (whether sulfuric acid or ammoniated sulfate compounds such as  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$ ) has been the subject of intense research activity during the last 20 years
- There are transport and chemical processes in the sulfur cycle that are strongly latitude-dependent. The lack of sunlight in the Arctic for large parts of the year limits the production of the OH radical and  $\text{H}_2\text{O}_2$ . The former is produced from the photodissociation of ozone in clean air and, incrementally, from hydrocarbon radicals in more polluted areas. Lower OH and  $\text{H}_2\text{O}_2$  concentrations in winter slow the sulfate production cycle and increase the  $\text{SO}_2/\text{SO}_4^{2-}$  ratio observed in the Arctic. This photochemical mechanism is critical to the timing of the Arctic haze maximum. The seasonality of  $\text{SO}_2$  oxidation to sulfate is important in prolonging the presence of sulfate aerosols in the Arctic into April and May.

# Nitrogen chemistry

- Nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) are the two most important nitrogen oxide air pollutants. They are frequently lumped together under the designation NO<sub>x</sub>, although analytical techniques can distinguish clearly between them. Of the two, NO<sub>2</sub> is the more toxic and irritating compound.
- Nitric oxide is a principal by-product of combustion processes, arising from the high-temperature reaction between N<sub>2</sub> and O<sub>2</sub> in the combustion air and from the oxidation of organically bound nitrogen in certain fuels such as coal and oil. The oxidation of N<sub>2</sub> by the O<sub>2</sub> in combustion air occurs primarily through the two reactions

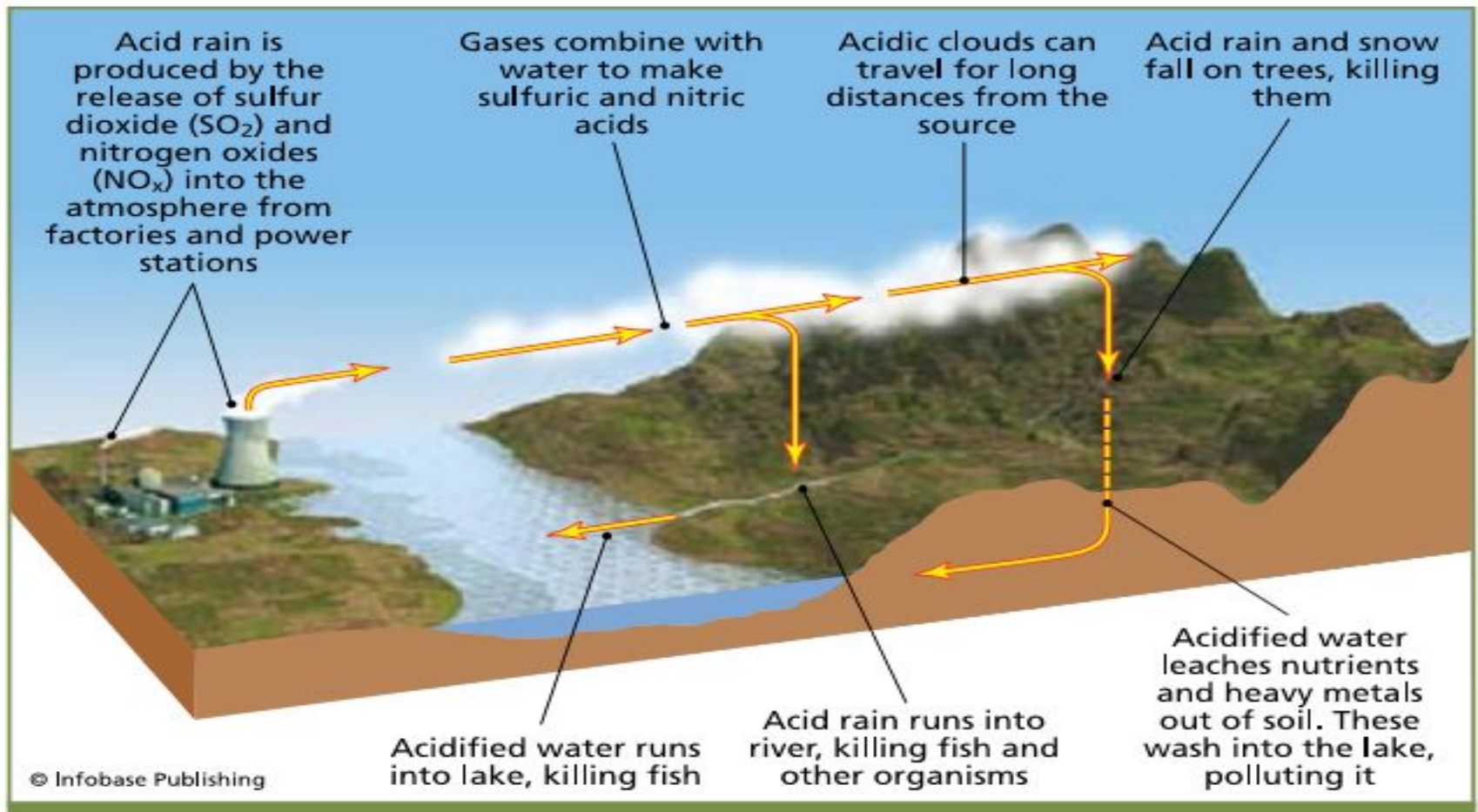
## the Zeldovich mechanism.

The first reaction above has a relatively high activation energy, due to the need to break the strong N<sub>2</sub> bond. Because of the high activation energy, the first reaction is the rate-limiting step for NO production, proceeds at a somewhat slower rate than the combustion of the fuel, and is highly temperature sensitive.



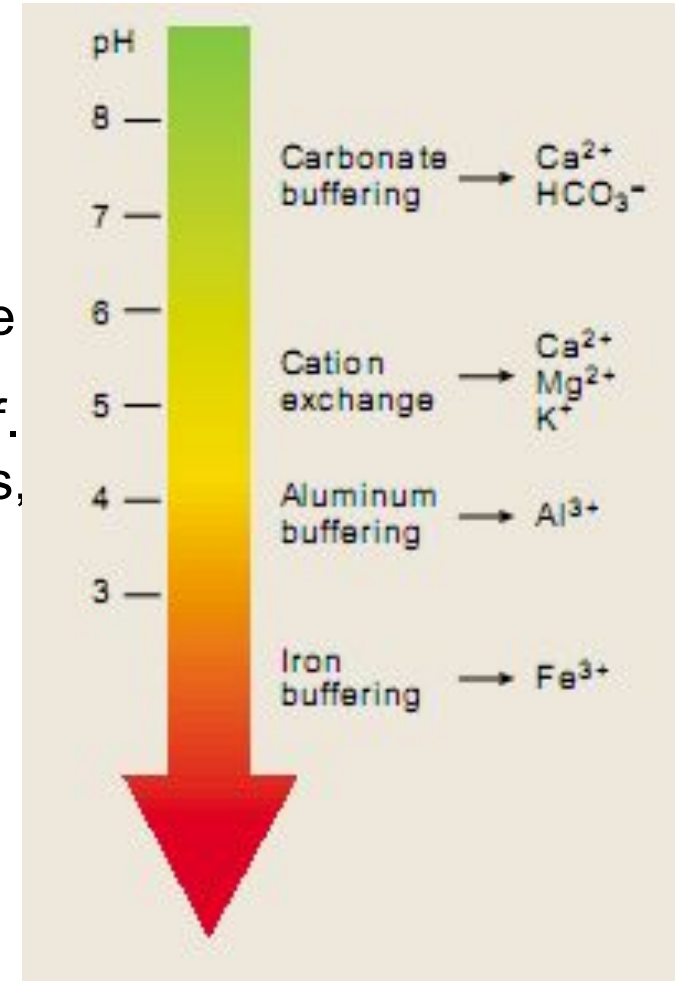
Nitric oxide formed via this route is referred to as *thermal-NOx*. The second major mechanism for NO formation in combustion is by the oxidation of organically bound nitrogen in the fuel. For example, number 6 residual fuel oil contains 0.2 to 0.8% by weight bound nitrogen, and coal typically contains 1 to 2 %, a portion of which is converted to NO<sub>x</sub> during combustion. (The remainder is generally converted to N<sub>2</sub> .) Nitric oxide formed in this manner is referred to as *fuel-NOx*.

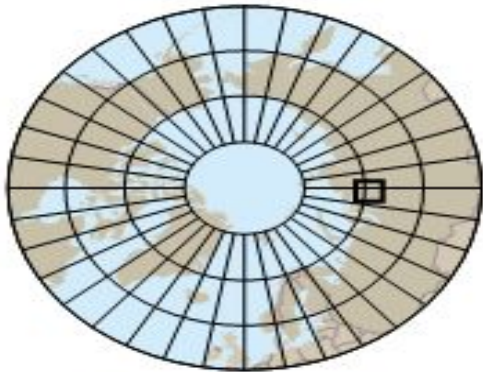




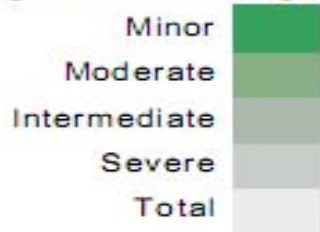
# Effect in the Arctic

- Loss of soil fertility contributes to tree death
- Most Arctic mineral soils are naturally acidic, because slow weathering limits the rate at which they can replace the base ions that trees use for nutrients. Acid deposition amplifies this natural acidification process when hydrogen ions replace base ions, causing the base ions to leach further down into the soil or to be washed away in runoff.
- Tree damage from acidification has many causes, but the lack of nutrients and the excess of aluminum ions are two important culprits. The figure shows the pH at which different base ions become mobile.

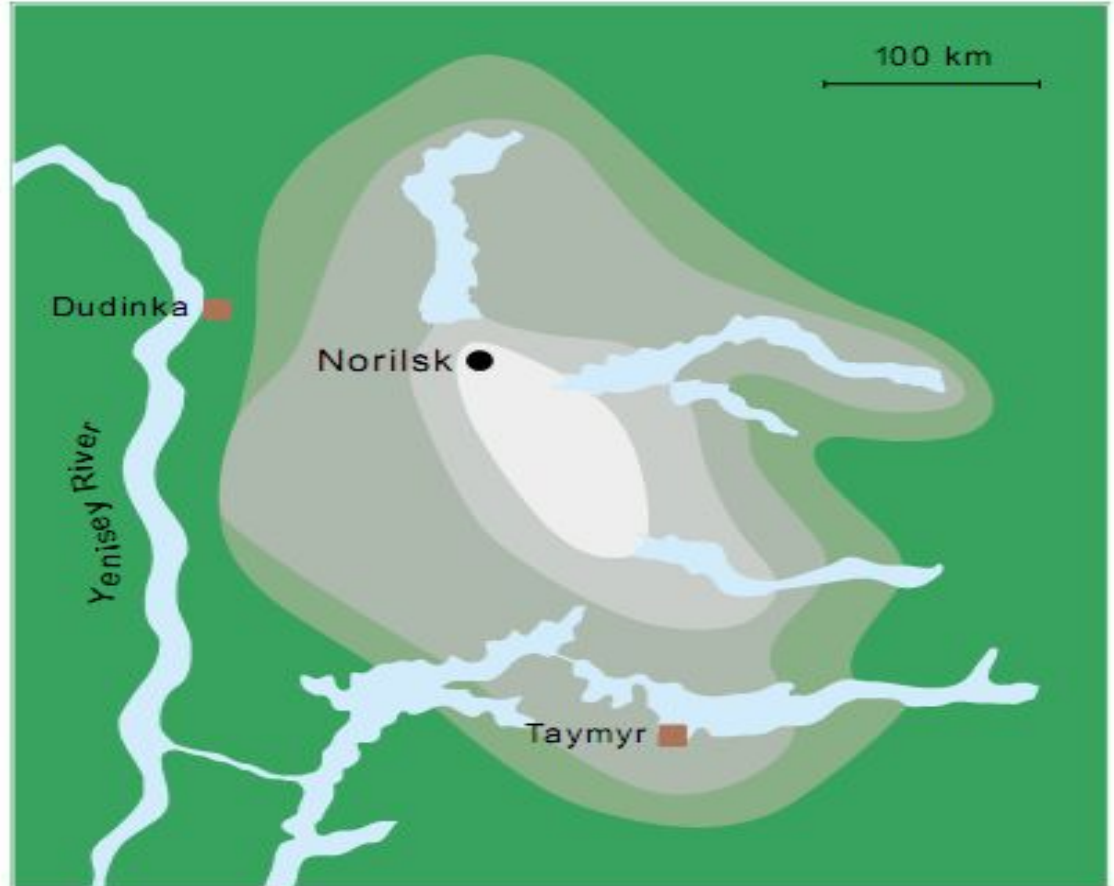




Vegetation damage



Extent of vegetation damage around Norilsk, Russia.



# Effect in the Arctic

- Sulfur dioxide has damaged the forest, killed lichens and some shrubs
- Sensitive invertebrates have disappeared

