Se Cd

Ni

Zn

V

Pb

Al Hg

As Cu

MAGNUS ELANDER

# Heavy metals

Snowman, Norilsk

Anthropogenic sources of metals can have severe and obvious impacts on the local environment, but signs of environmental change across a larger region and on a broader scale are subtle and difficult to interpret. Connecting dead trees and bare ground to a nearby smelter complex is not hard. But what does it mean when mercury levels are higher in the upper part of ocean and lake sediments. Could it be evidence of an increased circulation of this toxic element, a sign that human activities may be adding to an existing burden of mercury in Arctic animals and the people who eat those animals? With cadmium, what role does natural geology play in relation to anthropogenic inputs in explaining levels in animals that are high enough to raise health concerns? In spite of such uncertainties, one message is clear: these metals matter because they accumulate in the bodies of Arctic animals and hence become available to humans who depend on wildlife for their survival.

This chapter discusses the sources of heavy metals in the Arctic environment and describes their levels in air, sediment, water, and biota. Based on current understanding of the behavior of metals in the environment and their toxicology, the chapter attempts to assess the impact of some metals on plants and animals. The focus is both on large-scale contamination and on the severe local ecological effects found near some industrial sites in the Arctic. The potential impacts of metals on human health are covered in the chapter *Pollution and Human Health*.

# Heavy metals – an introduction

Metals occur naturally in the environment and are present in rocks, soil, plants, and animals. Metals occur in different forms: as ions dissolved in water, as vapors, or as salts or minerals in rock, sand, and soil. They can also be bound in organic or inorganic molecules, or attached to particles in the air. Both natural and anthropogenic processes and sources emit metals into air and water.

Plants and animals depend on some metals as micronutrients. However, certain forms of some metals can also be toxic, even in relatively small amounts, and therefore pose a risk to the health of animals and people. While the effects of chronic exposure to trace amounts of some metals is not well understood, a legacy of incidents tells us about the seriousness of high levels of exposure to some metals, especially cadmium and methyl mercury. In the 1950s, chronic cadmium poisoning from rice, coupled with dietary deficiencies, caused an epidemic of kidney damage and a painful skeletal disease among middle-aged women in Japan, the Itai-itai disease. Also in Japan, mercury poisoning from fish in a polluted bay became known as Minimata disease. For mercury, severe effects on wildlife have been well documented. In the 1950s and 1960s, many farmers laced their seeds with methyl mercury to prevent mold growth. The result was extensive bird kills.

In the Arctic, sources of heavy metals include weathering of rock. As elsewhere, there is also concern that human activities, such as mining, metal processing, and burning of fossil fuels, will increase the flux of metals that can be transported by wind and water and thus become available to plants and animals. Moreover, heavy metals in consumer goods and industrial processes enter the environment when we burn or dump waste. Metals are elements and therefore cannot degrade, but can only change form. Unless precautions are taken, the legacy of exploiting metal-containing natural resources is thus likely to stay with us for a long time.

The major heavy metals of concern to AMAP are mercury, cadmium, and lead. All three can be toxic at levels that are only moderately above background levels. They are believed to be present in some regions of the Arctic at levels that may pose risks to the environment and to human health. Moreover, the Arctic region is a recipient of heavy metals generated in other regions of the northern hemisphere because they are carried on particles that stay suspended in the cold polar air. This input adds to naturally high levels of cadmium and mercury in some parts of the AMAP region. The chapter also discusses selenium, which is not a true metal, but is important because it reduces the toxicity of mercury.

AMAP also considers the metals arsenic, copper, chromium, nickel, vanadium, and zinc, especially in its assessment of sources.

Organotins are covered in the chapter *Persistent Organic Pollutants*.

# Metals in the environment

We start with a short profile of the major metals in the assessment followed by a general discussion of environmental factors and chemical transformations that affect the uptake and impact of metals on animals.

### *Mercury (Hg)*

Mercury occurs naturally as elemental mercury and as organic and inorganic compounds. Much of the mercury in the environment is strongly bound to sediments and organic matter, and thus unavailable to organisms. Microorganisms can convert inorganic mercury into methyl mercury, which is a fat-soluble molecule that easily passes through cell membranes, accumulates in animals, and biomagnifies in the food web.

Mercury is a nerve toxin and the main health concern is its effect on the brain, particularly in the growing fetus and the young. The phrase ‘mad as a hatter’ and the term ‘hatter’s shake’ stem from mercury poisoning of hat makers using the metal for curing felt. Mercury can damage reproduction in mammals by interfering with the formation of sperm. Neurological and reproductive effects have also been seen in birds. In fish, its effects also include a decreased sense of smell, damage to the gills, blindness, and changes in the ability to absorb nutrients in the intestines. Plants can be sensitive to mercury, where high concentrations lead to reduced growth.

The most important anthropogenic sources of mercury to the Arctic atmosphere are combustion of fossil fuels, particularly coal, and waste incineration. Other sources are the chlorine-alkali industry and non-ferrous metal production. Mercury is used in thermometers, barometers, dental fillings, batteries, and fluorescent lamps.

### *Cadmium (Cd)*

Cadmium is toxic to most forms of life. It can be taken up directly from water, and to some extent from air and via food, and it has a tendency to accumulate in both plants and animals. Mushrooms in particular can be very rich in cadmium.

Cadmium is moderately toxic to aquatic invertebrates, reducing their growth and decreasing the survival of larvae. In fish, cadmium poisoning can lead to an ion imbalance and interfere with calcium metabolism.

In higher animals, cadmium accumulates in


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Norilsk, Russia.

the kidneys and liver, where most of it binds to a special protein that makes the metal harmless to the animal. If the uptake is greater than this natural defense, cadmium can damage the kidneys and upset metabolism of vitamin D and calcium. Kidney damage and a decalcification of the skeleton are the serious chronic effects of high cadmium exposure. Kidney damage in seabirds has been seen at cadmium levels in the tissue of 60 to 480 micrograms per gram. Based on human toxicology, cadmium concentrations of 100 to 200 micrograms per gram (wet weight) in the kidneys probably represent a risk for mammals. With a half-life of decades, cadmium leaves the body extremely slowly.

Cadmium is a byproduct in the production of zinc and lead, and the pyrometallurgical production of zinc is the most important anthropogenic source to the environment. Other major sources are fossil fuel combustion and waste incineration. Cadmium is used in a wide spectrum of applications, including alloys, pigments, metal coatings, batteries, and in the electronics industry. It is also a contaminant in chemical fertilizer, manure, compost, and sewage sludge.

### *Lead (Pb)*

Lead in the environment is strongly absorbed by sediments and soil particles, and is therefore largely unavailable to plants and animals. Many of the inorganic salts of lead (lead oxides and sulfides) are not readily soluble in water and are sequestered in sediments. In aquatic systems, uptake is influenced by various environmental factors such as temperature, salinity, pH, and the presence of organic matter.

It is not clear whether animals absorb lead through the skin or take it up via lungs or contaminated food. Lead accumulates in the liver, kidney, spleen, and skeleton. Once it has been integrated into the skeleton, it takes several years to leave the body. Lead can also accumulate in eggs and embryos.

Damage to the nervous system and gastrointestinal symptoms are the main signs of lead poisoning. Lead also interferes with the formation of red blood cells, leading to anemia. Lead is especially toxic to the growing brain and can affect the behavioral development of young, even at low concentrations. For example, in polluted cities, fumes from cars burning leaded gasoline have probably caused air concentrations high enough to affect children’s development. Lead can pass through the placenta and thus affect a growing fetus. Organic lead compounds are fat-soluble and are more toxic than other forms.

In fish, lead accumulates primarily in the gill, liver, kidney, and bone. In juvenile fish, lead causes a blackening of the tail followed by damage to the spine. It also reduces larvae survival. Birds are only sensitive to lead at very high concentrations but can get lead poisoning symptoms and eventually die from ingesting pellets of lead shot.

Leaded gasoline is the major source of increased environmental levels on a global scale. Other anthropogenic sources include mining and metallurgic industries, ammunition, and trash incineration.

### *Selenium (Se)*

Selenium is not a true metal, but interacts with many metals in the environment. It is an essential nutrient in small amounts but toxic in higher concentrations, damaging hair and nails. In the environment as well as in the body, it forms an insoluble salt with mercury, which reduces the toxicity of both mercury and selenium.

## *Surrounding environment influences metal uptake*

The effects of metals in the environment depend to a large extent on whether they occur in forms that can be taken up by plants or animals. For example, lead may be strongly adsorbed onto sediment particles and therefore largely unavailable, while cadmium ions can be directly absorbed from water. Mercury is strongly bound to sediment and organic material, but microorganisms have an ability to transform inorganic mercury into methyl mercury, which is readily taken up by both aquatic and terrestrial organisms.

Environmental variables, such as the presence of ions that may bind the metals, often play an important role in uptake. For example, in saltwater, chloride ions bind some metal ions, making them less available to living cells. Cadmium and lead thus appear to be less toxic in saltwater than in freshwater. Other factors that influence bioavailability are acidity, the amount of suspended matter, and the amount of organic carbon in the water.

Uptake of metals in an animal involves metal ions crossing a cell membrane. Often a ligand, or carrier, executes this transport. Sometimes there are additional specific carriers within the cell. The biological effects of metals in air, water, or sediment therefore depend as much on the transport capacity of the cell membrane as on their concentration in the surrounding medium. Several different ions might compete for the same sites on the carrier molecule and the levels of one metal may influence the uptake of another.

## *Metals can transform and accumulate in the body*

Once absorbed, metals are distributed in the body by the circulatory system. A fraction of this will be taken up in specific organs in processes that are not very well understood.

Many metals undergo a chemical transformation in the body, which sometimes can make them less toxic but in other cases may increase their harmful potential. The most important processes for such biotransformation are the formation of inert complexes and the cleaving or building of bonds with carbon (methylation/demethylation).

The formation of inert metal-protein complexes plays an important role in detoxifying cadmium, zinc, copper, and mercury. Selenium can reduce the toxicity of arsenic, cadmium, and mercury in a similar manner. High selenium levels in the environment can thus protect against the toxicity of these metals.

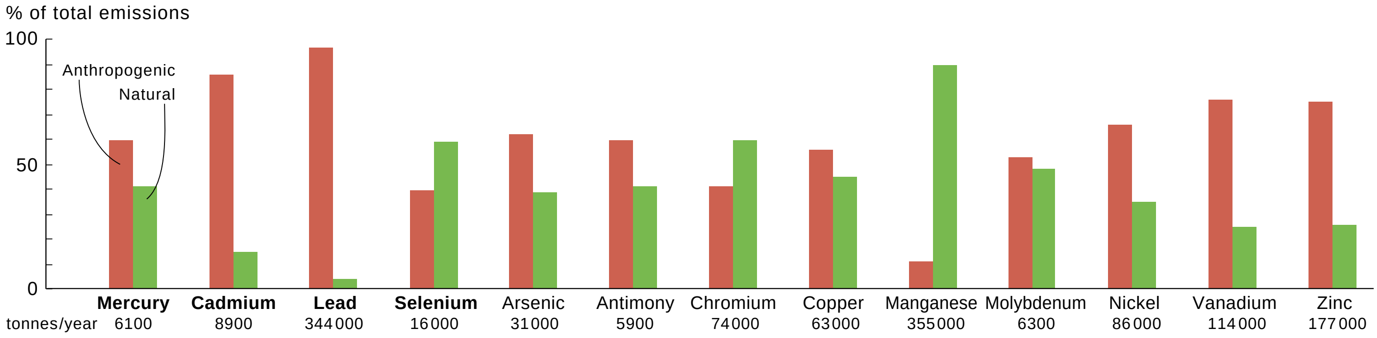
Methylation, i.e. the creation of carbon bonds, reduces the toxicity of arsenic and selenium, because it allows an animal to excrete the metal. For mercury, methylation increases toxicity, since methyl mercury is more toxic than inorganic forms of mercury.

If an organism's uptake of a metal is greater than its ability to get rid of it, the metal will accumulate. Heavy metals tend to accumulate in storage compartments. For example, cadmium accumulates preferentially in the kidneys, mercury in the liver, and lead in the skeleton. The accumulation can continue throughout the organism's life and is the major cause of chronic toxicity. In contrast to organic pollutants, metals accumulate in protein tissues and bone rather than fat.

Most measurements from animals have been made on key storage organs, because of concern for human health and diet intake. However, these levels may say very little about toxic effects on the animal, since the target tissue may be different than the storage tissue. For example, very little is known about mercury levels in brain tissue, which is the most sensitive target for mercury damage.

The table below shows some selected values for how efficiently organisms are able to absorb mercury, cadmium, and lead, and how fast they can get rid of these substances.

| Metal | Organism | Uptake efficiency (how much of available metal is taken up in the indicated tissue) | Half-life (time it takes for the tissue concentration to be reduced by half) |
|---|---|---|---|
| Lead | Mammals | 5-10% via intestines<br>30-50% via the lungs | 40 days in soft tissues<br>20 years in bone |
| Cadmium | Fish | 1% via intestines<br>0.1% via gills | 24-63 days |
| - | Mammals | 1-7% via intestines<br>7-50% via lungs | 10-50% of life span in liver<br>10-30 years in kidney |
| Mercury | Fish | depends on chemical form, water temperature, and water hardness | 323 days for organic mercury from diet<br>45-61 days for inorganic mercury from water or diet |
| | Mammals | >95% for organic mercury via intestines<br>>15% for inorganic mercury | 500-1000 days in seals and dolphins for methyl mercury, 52-93 days for methyl mercury and 40 days for inorganic mercury in whole body of humans |



Global emissions of metals to the atmosphere in 1983, natural versus anthropogenic. The percentages shown in the bars are based on range values and therefore do not sum to 100 percent.

# Sources

Both natural and industrial sources contribute metals to the Arctic environment. It is difficult to accurately determine the magnitude of these sources, but the figure above gives a reasonable estimate of their relative size and yearly emissions. Most anthropogenic emissions have decreased in recent years, but there is still room for improvement.

## *Natural sources account for a significant part of emissions*

Atmospheric particles from natural sources can account for varying proportions of the atmospheric metal load. In remote areas, the proportion due to natural processes may dominate, while the opposite may be the case close to anthropogenic sources. Erosion allows the wind to pick up soil particles and such particles might, on a global scale, account for more than half of all chromium emissions to the atmosphere, and 20 to 30 percent of emissions of copper, nickel, and zinc. Eroded soils also end up in rivers that transport metal-containing particles to lakes and to the ocean. Volcanoes spew out material from the Earth's mantle and this source alone can account for a significant portion of the cadmium and mercury in the air. Metals that have been part of vegetation can be released and spread by forest fires.

An accurate inventory of heavy metal sources and emissions to the atmosphere from natural sources is needed to make a complete assessment of the regional and global pollution of heavy metals in the Arctic.

## *The metal industry is a major source to the atmosphere*

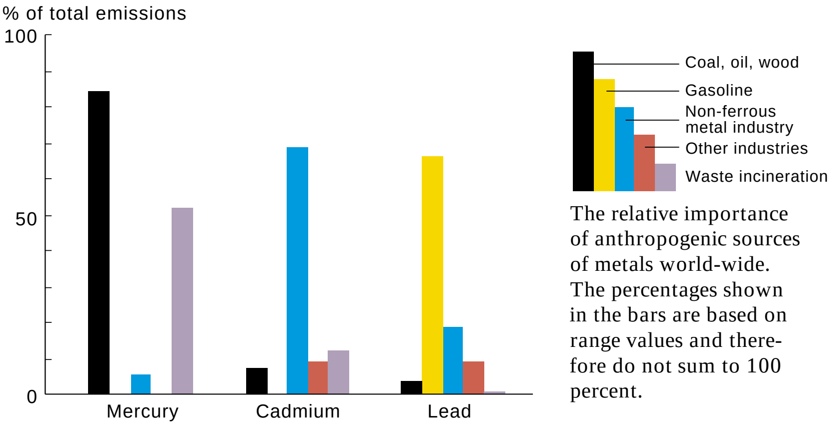
Practically every industry discharges one heavy metal or another into the environment. A major source of air contamination is the non-ferrous metals industry, which emits cadmium, lead, nickel, arsenic, copper, selenium, and zinc.

The use of fossil fuels is also a major contributor to the increased flux of metals. Coal burning is the major source of mercury, arsenic, chromium, and selenium, while combustion of oil is the most important source of nickel and vanadium.

Many industrial products containing heavy metals eventually end up as trash. Emissions from waste incineration are difficult to estimate but are an important source of mercury, cadmium, arsenic, and zinc.

The figure below summarizes the relative importance of the sources of world-wide anthropogenic emission of mercury, cadmium, and lead.

Within the Arctic, combustion of fossil fuels to produce electricity and heat is a major anthropogenic source of heavy metals, followed by industrial processes, particularly in the Russian Arctic.



The relative importance of anthropogenic sources of metals world-wide. The percentages shown in the bars are based on range values and therefore do not sum to 100 percent.

## *Eurasia is the major source region to Arctic air*

Which emissions of heavy metals are important for the Arctic environment? The answer depends on the magnitude of emission, the location of the source, and transport pathways. The prevailing air movement over the Arctic is

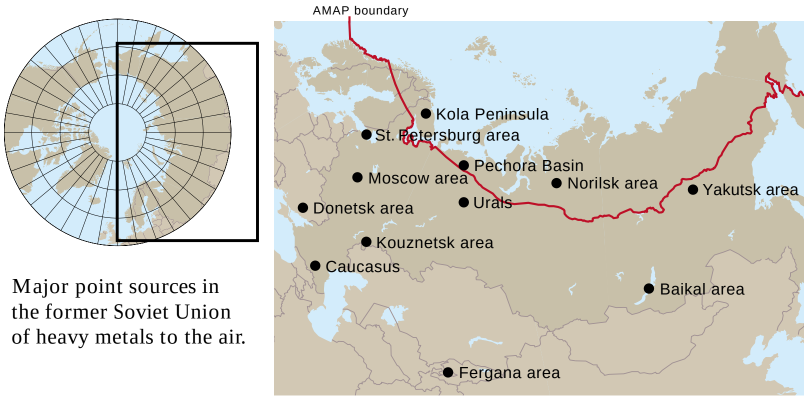
### *Chemical form determines environmental fate*

The fate of a metal in the environment depends to a large extent on its form. Mercury is a case in point. When fossil fuels or trash are burned, mercury contained in these materials will evaporate as a gas, some of which will oxidize in the flue gases. Without emission-control systems, this mercury will reach the atmosphere and be carried by the winds. The residence time of mercury vapor in the atmosphere is between 0.4 and 3 years, and, as a consequence, mercury vapor is globally distributed. Mercury in soluble form has a residence time on the order of weeks and is therefore only transported over shorter distances. Modern flue-gas cleaning systems can retain the oxidized mercury. Another potential route to the environment is fly ash, as well as bottom ash, which are often disposed of on land. Some of this disposed ash may leach mercury to nearby waterways and lakes.

Other volatile compounds that follow flue gases are elemental cadmium, cadmium chloride, elemental arsenic, arsenic trioxide, and arsenic chloride. Lead chloride is only somewhat volatile. Elemental lead, lead oxide, and cadmium oxide are non-volatile and will largely be emitted as fly ash, even at high temperatures.

from Eurasia to North America, and models show that Eurasia contributes more than half of the air pollution measured in the Arctic.

The Russian sources are most important, partly because they are situated far north, within the Arctic airmass, and partly because the strong Siberian high-pressure system drives air northward during the winte; see map below. Emissions from sources in the Urals and the Norilsk area contaminate the air over Alaska and Arctic Canada, whereas emissions from the Kola Peninsula contribute more to northern Fennoscandia. Emissions from Europe contaminate the subarctic in northern Fennoscandia, while emissions from North America reach the subarctic areas of northern Canada.



Major point sources in the former Soviet Union of heavy metals to the air.

Much of the heavy metal contamination in the Arctic comes from hot spots of emissions. These are the Pechenganikel industrial complex and the Severonickel smelter complex on the Kola Peninsula and the industries in Norilsk. In the 1980s, Severonickel became the largest nickel-copper smelter in the world. Preliminary estimates of emissions to the atmosphere from Severonickel are approximately 3000 tonnes of copper and 2700 tonnes of nickel annually, but this information needs verification.

### *Most emissions are decreasing*

Most emission and modeling studies have been performed on data from the early 1980s. Since then, the input of most metals seems to be decreasing; see the figure below. Further improvement is also likely. If the best-available technology is applied, emissions of arsenic could be reduced by a factor of three and cadmium emissions by a factor of two by the end of the century. For lead, the decrease depends on how fast leaded gasoline disappears from use. The predicted decrease until the year 2000 ranges from a factor of four to ten.

The amount of mercury transported from central and eastern Europe to Scandinavia has declined during the past few years. However, this decline may only be temporary. What happens in the future depends to a large extent on how fast industrial production recovers from the economic slump of the early 1990s. The potential for long-term lower emissions from western Europe and North America is better, because the technology to clean sulfur and nitrogen from industrial emissions also removes mercury and other heavy metals that are emitted as gases. Efforts to decrease metal emission are on the agenda in current political negotiations about long-range transboundary pollution.

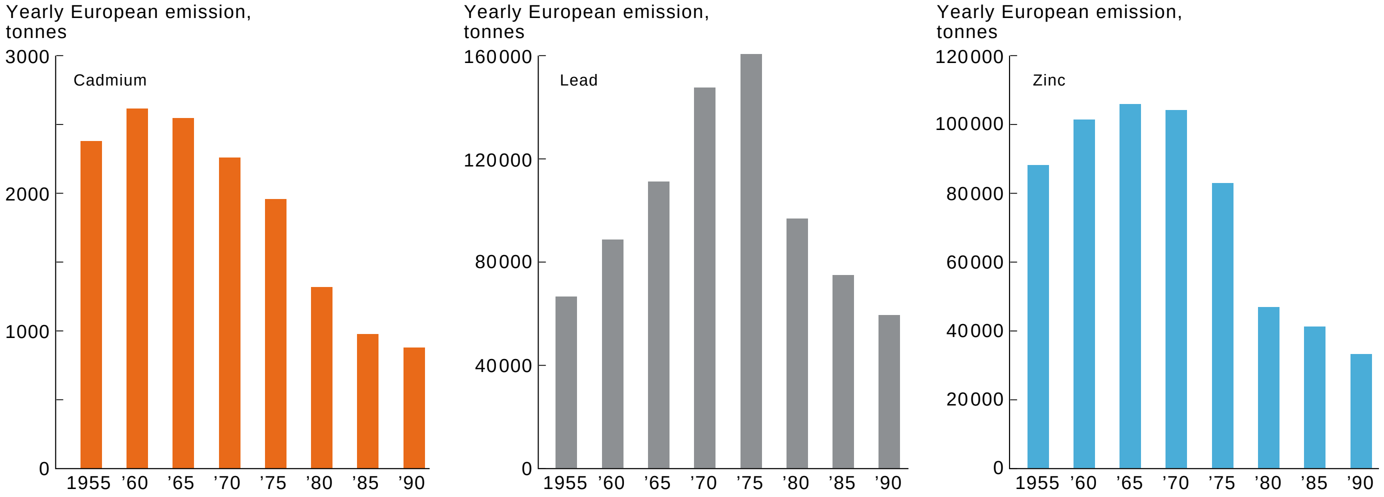
Emissions from Russian smelters have decreased or remained the same for the past ten years, mostly because the industry has not run on full capacity. Future emissions will depend greatly on the success of efforts to improve the technology used in the smelters.

### *Metal industry contaminates rivers, lakes, and the ocean*

Global budgets of metal discharge to the aquatic environment show that domestic waste water is a major source of heavy metals into rivers, lakes, and oceans. So is sewage sludge. Other sources include coal-burning power plants and the metals industry. Regionally, human inputs into the aquatic environment are sufficient to elevate levels of heavy metals above natural background levels. Known global emissions to water exceed those to the atmosphere.

The importance of riverine transport of heavy metals to the Arctic Ocean varies by the metal, the distance to the river mouth, and the season. Though heavy metal concentrations in

Time trend in European atmospheric emissions of cadmium, lead, and zinc.

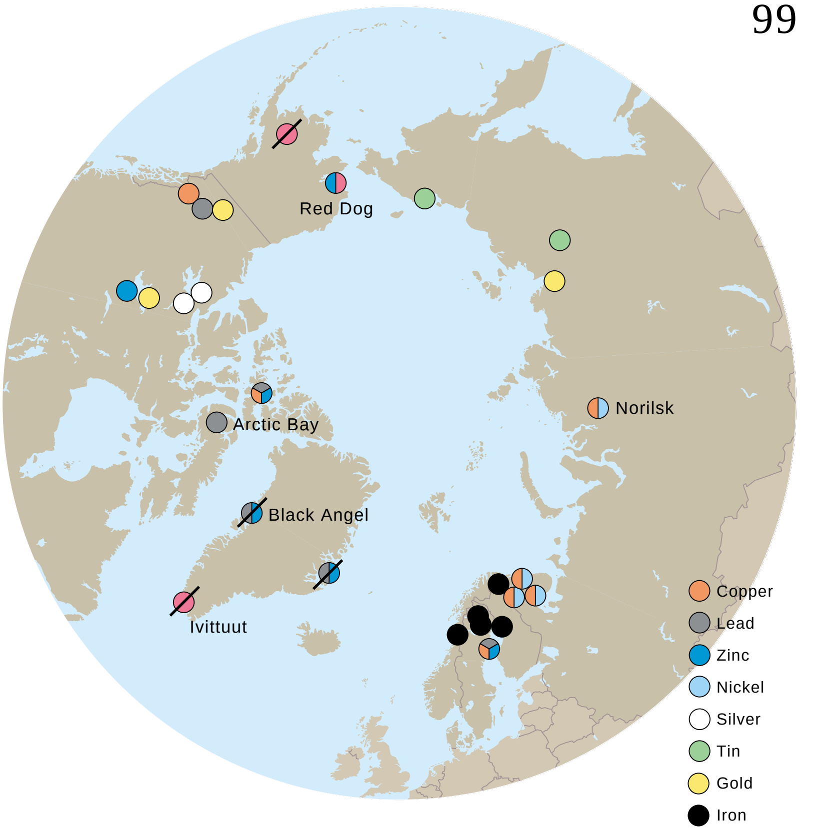


the lower reaches of the largest Russian rivers (Ob, Yenisey, and Lena) are at global background levels, preliminary mass balance calculations suggest that for cadmium and lead, rivers contribute about half of what the atmosphere contributes. For zinc, rivers are the most important source, with inputs up to five times higher than from the atmosphere.

In the Arctic, mining and metallurgical industries on the Kola Peninsula and in the Norilsk region are major contributors of metals to the aquatic environment.

Local contamination around mines is a recognized problem in the Arctic. One documented example is the Black Angel lead and zinc mine at Maarmorilik, Greenland. The mine, which operated from 1973 to 1990, discharged its tailings to the bottom of a nearby fjord. During production, about 10 tonnes of zinc, 1 tonne of lead, and 50 kilograms of cadmium were released annually in soluble form into the sea.

The map to the right shows past and present mining activities in the AMAP region having a local effect on the environment.



Past and present metal mines in the Arctic that still have a significant effect on the local environment.

### *Soils serve as dump sites and as sources*

Soils play an important role for the global flux of metals in the environment. Most trash is stored in dump sites, where metal-containing products often contaminate the soil. Ash from coal combustion is another important source to the soil. Wastes from animal husbandry, agriculture, and logging may not have high concentrations of heavy metals, but the volumes of waste are huge, and can affect the heavy-metal budget of many soils. Locally, sewage sludge can also be an important source of contamination. Global metal budgets for soil are mostly relevant for mercury due to its potential to evaporate and be transported farther by air. Other metals disposed on land cause primarily local problems.

#### *Acidification and metals*

Acidification of soil and water has a major affect on many, but not all, metals. Cadmium, lead, and zinc become more mobile when acidity increases. They may then move further down in the soil profile or leach more easily into waterways

The mobility of metals into living cells and thus their biological uptake also depend on the acidity. The form of metals most easily taken up by plants and animals is the divalent ion of cadmium, lead, and zinc. Acidification favors the formation of these ions.

Mercury behaves differently. It adheres strongly to organic material in the soil and does not become more mobile when the soil is acidified. The opposite can actually be true as the acid environment makes mercury adhere even more strongly to humus in soil and water.

Soils have a natural ability to hold on to metals. One concern is that the current input of contaminants might overload this capacity. Moreover, acidification makes some metals less tightly bound to soil particles, one exception being mercury. Metals freed in this way become available to plants, to which they might be toxic, and also leach into waterways.

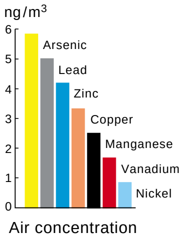
For some metals, particularly mercury, soil is also an important source to the air. In fact, emissions of mercury from soil and water can in certain regions be of the same magnitude as mercury emissions from anthropogenic sources. The mercury cycle is so influenced by these processes that it is more relevant to talk about preindustrial and postindustrial emission levels than to distinguish between natural and anthropogenic sources.

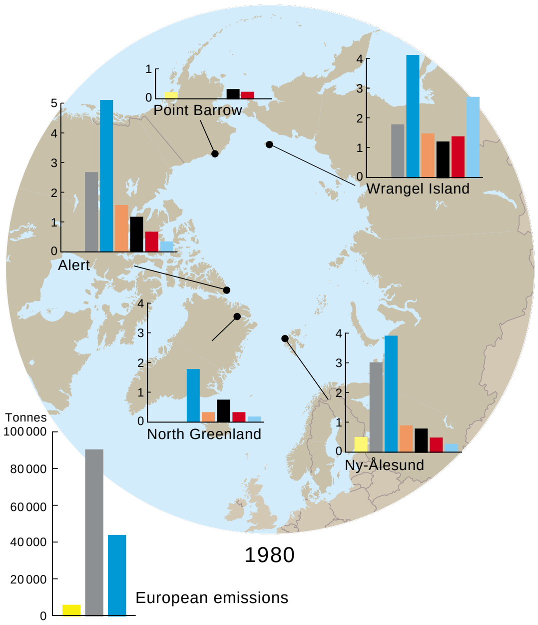
# Atmospheric transport, levels in the air, and deposition

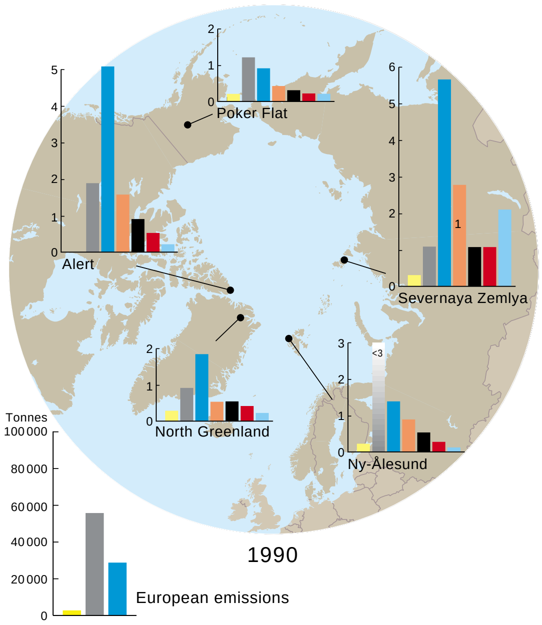
Air measurements show that long-range transport of metals contributes to the load in the Arctic. However, the highest load in the environment is in the vicinity of the Russian smelters.

### *The metals follow the prevailing winds*

Metals in their gas form often condense on fine particles in flue emissions before they are released to the atmosphere. Unless they are trapped by emission control systems, these particles are carried by the prevailing winds. This is especially true in winter when the particles remain suspended in the air and only a small proportion are washed out close to the sources. In the Arctic, air measurements show that concentrations of heavy metals are higher in winter than in summer by more than one order of magnitude.



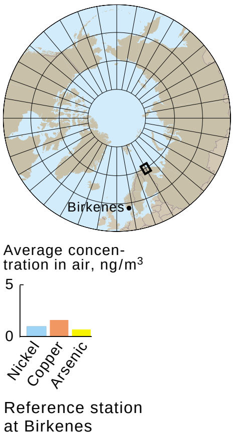


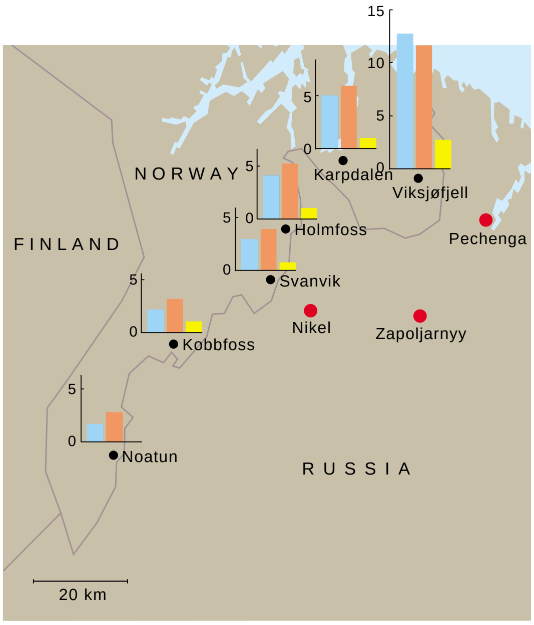


Winter air concentrations of heavy metals at remote Arctic sites and European emissions of arsenic, lead, and zinc in 1980 and 1990.

These metal-carrying particles get trapped in the cold air mass during the winter and can circulate throughout the Arctic. Therefore, metals that originate in northern Eurasia may go first to Alaska and then travel back over the pole to the Norwegian Arctic. The map above shows the winter concentrations at different sites. Aside from hot spots of pollution, levels around the Arctic are similarly low. Concentrations of heavy metals in Arctic winter air are about ten times as high as in the Antarctic, whereas summer levels are similar.

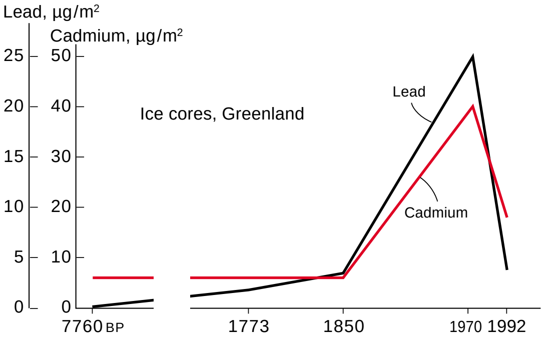
The air around large point sources is much more contaminated than air in the High Arctic or reference sites in southern Norway; see maps on this page. For example, the concentrations of nickel, copper, and arsenic in parts of northern Norway and the Kola Peninsula are at least one order of magnitude higher than the concentrations at Ny-Ålesund. Closest to the smelter stacks of Severonickel on the Kola Peninsula, the contamination is a thousand times higher than the maximum levels at Ny-Ålesund.





Average air concentrations of nickel, copper and arsenic on the Kola Peninsula.

The processes that wash particles out of Arctic air are not well understood, but they are clearly different over ice sheets than along the coasts. In trying to understand the impact of industrial emissions on the High Arctic environment, one central question is whether the deposition process within the Arctic region is efficient enough to retain small particles that carry heavy metals, or if they are carried out as fast as they come in. Current models of winter air transport suggest that five to ten percent of the cadmium, lead, arsenic, vanadium, and zinc emitted in the Eurasian region deposits in the High Arctic. In summer, these emissions are less important.

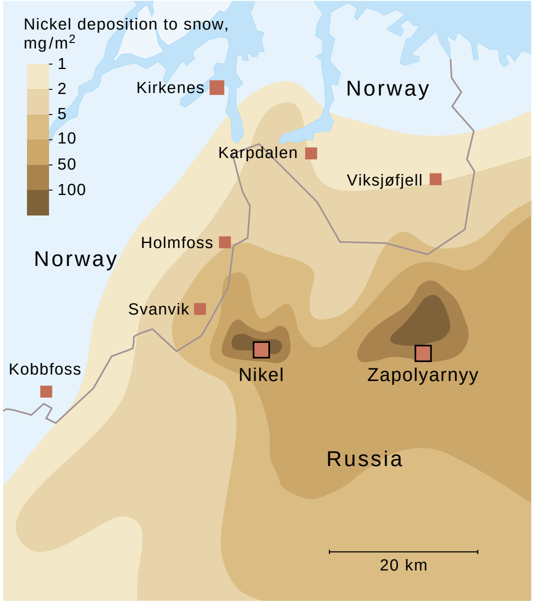


Time trends for estimated deposition of lead and cadmium as determined in Greenland ice cores.

Past and present atmospheric deposition of heavy metals in the Arctic can be estimated by looking at metals in snow and ice cores. A hundred to a thousand times more lead has been deposited in the period after the industrial revolution (i.e., since 1773) than was deposited in the millennium before industrialization. The graph above illustrates lead and cadmium deposition to the Greenland icecap since prehistoric times.

### *Deposition is highest close to smelter stacks*

Most of the deposition studies for metals have been made in the subarctic region, especially around the nickel-copper smelters known to emit large amounts of metals. Measurements



Yearly nickel deposition to snow on the Kola Peninsula.

from the Kola Peninsula show that the yearly deposition of copper and nickel can reach a few hundred milligrams per square meter close to the smelter stacks. However, the levels decrease to a few milligrams per square meter within a few tens of kilometers. This lower value is also representative for northern Finland. The figure above shows the deposition in snow around the Kola smelters.

Latitudinal gradient of deposition of lead in Norway, as measured in moss, 1990.

In some parts of northern Scandinavia, deposition from smelters results in levels similar to those caused in southern Scandinavia by long-range transport from Europe. Lead is an exception, with higher deposition in the south; see map immediately above.

Deposition of heavy metals on the Kola Peninsula has increased, and was at least one order of magnitude higher in the 1980s than in the 1960s. Trends over the past 30 years mirror emissions, and deposition has decreased in the 1990s, reflecting reduced production.

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Snow and –40°C at the Norilsk smelter.

## Terrestrial ecosystems

The levels of heavy metals in the biota of terrestrial ecosystems represent weathering of local bedrock combined with input from distant and local pollution sources. The AMAP assessment points to two major concerns: the severe pollution of nickel and copper around the Russian metallurgical complexes and the bioaccumulation of cadmium in grazing birds and mammals.

### *Some soil concentrations are high enough to damage vegetation*

Metal concentrations in soil vary greatly, depending on vicinity to pollution sources and on local geology. Close to the nickel-copper smelters on the Kola Peninsula and in Norilsk, metal concentrations sometimes reach exceedingly high levels. For example, some soils close to the Severonickel copper smelter have copper concentrations 50 to 80 times higher than the background level. The overall effect of the metal pollution in combination with acidifying emissions has been devastating. The smelters, constructed approximately 50 years ago, have created industrial deserts, where all or almost all the vegetation is gone. Originally, parts of

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Zapolyarnyy, Russia.

the Kola Peninsula were covered by bogs, but the mosses disappeared some decades ago from the most heavily polluted areas. Today, an area of 10 to 15 kilometers around the smelters is dry sandy and stony ground, with only remnants of peat. The Kola Peninsula is one of the eight most seriously polluted 'eco-catastrophe' areas of the former Soviet Union.

Away from local pollution sources, metal levels in soils depend on the type of bedrock, movement of water, weathering, and biological processes. An extreme example of high natural levels is Karasjok in Norway, where the copper content of the soil is so high that the ground is barren in patches. The copper is probably weathered from sulfide minerals, carried with the groundwater and re-precipitated when the water emerges from the ground.

### *Pollution from smelters and oil exploitation shows up in moss*

Studying moss is a useful way to estimate how much airborne metal ends up on the ground. Such studies around the nickel-copper smelters on the Kola Peninsula show that the concentration of copper can be 200 times higher close to the smelters than in northern Finland, 200 kilometers west of the emission sources. The nickel content was more than a thousand times higher close to the smelters. Around Norilsk, lead and copper from the smelter complex show up in a zone up to about 200 kilometers from the source. Copper concentrations in the mosses are one to two orders of magnitude higher than in an area further north of Norilsk.

Moss samples taken near the Prudhoe Bay oil fields in Alaska also show high levels of lead and copper, comparable to the industrialized regions of Siberia and western Russia. Similar levels are found along the Dalton Highway, which connects the oilfields to the southern road system.

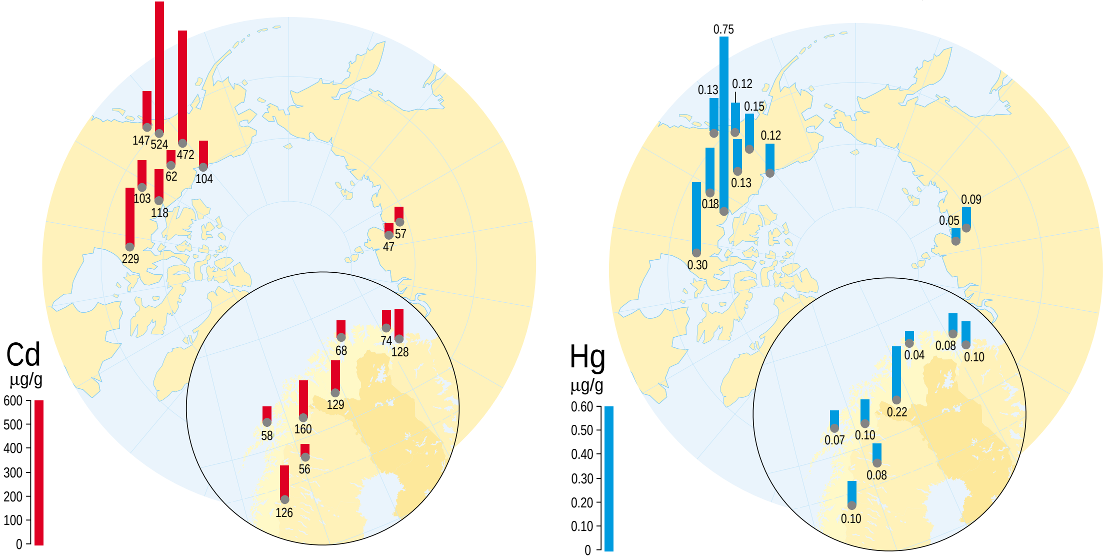
### *Birds and caribou/reindeer accumulate cadmium*

The main source of heavy metals for land animals is the food they eat. The figure below shows the levels of cadmium and mercury in ptarmigan across the Arctic.

The willow and rock ptarmigan provide examples of how heavy metals can accumulate in specific organs. The birds can get rid of some of the metals when they molt, but adult birds from Norway and from the Yukon Territory in Canada still have exceptionally high concentrations of cadmium in their kidneys, up to 1020 micrograms per gram dry weight, among the highest values ever recorded in birds. This may be linked to the particular geology of these areas. So far, no one has studied the effects on the birds, but in some individuals, the concentrations exceed threshold values that are believed to cause kidney damage.

Measurements in Russian birds show that lead, cadmium, and mercury are all higher in predatory birds than in birds that feed only on vegetation or have a mixed diet.

Reindeer/caribou are also known to accumulate high levels of cadmium, especially in the kidneys. Some of these levels exceed threshold values believed to cause kidney dysfunction, but no such effects have been investigated. There are clear differences in cadmium concentrations among herds in the Arctic, linked to differences in diet and the natural soil composition of their range areas. The values range from 0.3 micrograms cadmium per gram kidney (dry weight) in Norway to 880 micrograms cadmium per gram kidney (dry weight) in the Finlayson herd in the Yukon Territory. Some Russian values are extremely low (0.05 microgram per gram). The reason for these low values is unknown. In Norway, cadmium burdens in the kidneys of reindeer from the Arctic are strikingly lower than those from farther south. This is consistent with the decreasing gradient in acid and cadmium deposition as one moves from south to north, and also with the concentration of cadmium in the soils.



Circumpolar distribution of cadmium and mercury in ptarmigan kidney.

In Sweden, livers and kidneys of reindeer from Saami villages in the easternmost part of the mountain chain have been monitored for cadmium, lead, and mercury since the early 1980s. So far, no time trends in the levels are evident.

Other metals in caribou/reindeer are generally not of environmental concern. Mercury may be an exception in Canadian animals, probably as a consequence of natural geological sources within the Canadian Shield.

In most other land animals, metal concentrations are low. The exceptions are moose from the Yukon Territory, which have extremely high values of cadmium, moose in Norway, and several small mammals in the Yukon Territory.

# Freshwater ecosystems

Point sources, runoff from surrounding areas, and deposition from the atmosphere add metals to lakes and rivers. However, their movement and uptake is also governed by acidification. A major concern for aquatic ecosystems is local pollution from metal industries and old mines. The AMAP assessment also points to a circumpolar increase in the load of mercury in freshwater sediments, probably due to global processes.

Lead, cadmium, and mercury generally occur at levels below one microgram per liter in all Arctic freshwater, similar to unpolluted areas outside the Arctic. However, in certain regions of Arctic Canada, Russia, Finland, and Alaska, there are rivers with lead concentrations that exceed the most stringent indicators of water quality for southern latitudes.

## *Russian rivers are severely polluted with metals*

There are numerous examples of local metal contamination of rivers and lakes, often in connection with mining and metal processing. One example is Garrow Lake in the Northwest Territories in Canada, which has been used to dump waste from a lead–zinc mine. Typical concentrations are 360 micrograms of zinc per liter, in contrast to 0.5-2.5 micrograms per liter in the Mackenzie River delta.

In Arctic Russia and on the Kola Peninsula, the freshwater ecosystem is polluted on a much larger scale. Ten micrograms of copper and nickel per liter of water is not uncommon within a 30-kilometer radius of the major metal smelters in the Murmansk region. Between 1991 and 1994, the copper concentration reached up to 2524 times the permissible limit and the nickel concentration was occasionally up to 135 times the permissible limit. The ecosystems of at least five water bodies are completely destroyed. Similar problems have been reported from the Norilsk region. The table above shows the extent of the pollution.

Metal contamination of freshwater in the Murmansk region, Russia, µg/liter. Maximum allowable concentrations are: copper, 1 µg/liter; nickel, 10 µg/liter.

| | | Highest recorded level | | | |
|---|---|---|---|---|---|
| Water body | Metal | 1991 | 1992 | 1993 | 1994 |
| Kolos-Yoki River, mouth | Cu | 47 | 14 | 29 | 27 |
| | Ni | 102 | 60 | 195 | 53 |
| Luotn-Yoki River | Ni | 56 | 38.5 | 32 | 17 |
| Hayki-Lampi-Yoki River | Ni | 32 | 43 | 24 | 24 |
| Nyuduay River | Cu | 2524 | 300 | 168 | 518 |
| | Ni | 1347 | 409 | 465 | 400 |
| Monche Lake | Cu | 225 | 260 | 176 | 113 |
| Imandra Lake (Monche-Guba) | Cu | 105 | 35 | 20 | 11 |
| | Ni | 195 | 6 | 37 | 5 |

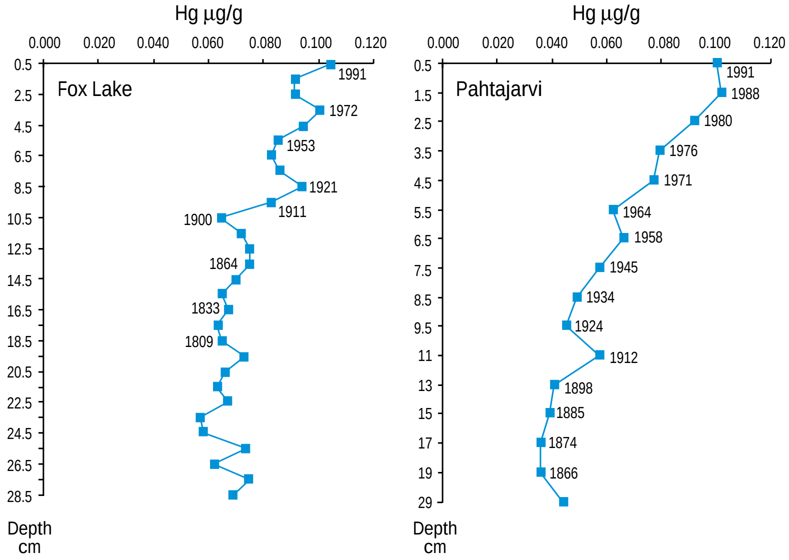
Russian ecologists have noted severe ecological damage along portions of major Siberian rivers and watercourses. However, it is difficult to say what role metals play. In the most affected areas, sewage, petroleum hydrocarbons, acidification, and chemicals are also prominent pollutants.

Wetland ecosystems, which serve as transitional compartments between the terrestrial and aquatic environment, can accumulate large loads of heavy metals and serve as sources to rivers. A survey of more than 250 wetlands in the Russian Arctic points to three areas of local pollution. These are in the Kola Peninsula in the vicinity of the non-ferrous smelters, the Vorkuta area of the north Komi Republic, and the Norilsk area in central Siberia. These are the same areas that have elevated levels of heavy metals in river waters. Metal concentrations in remote parts of the same regions are close to other unpolluted regions, with the exception of north-east Asia. Here, a mercury ore belt is a natural source that contributes to elevated environmental levels.

## *Sediments tell about increasing metal loads*

Lake sediment profile data (see figure below) indicate that metal levels are highly variable. They have been influenced by local conditions and by inputs from anthropogenic sources

Elevated levels of mercury in the upper layers of lake sediments reflect increasing inputs over time.



over time. The situation can vary considerably from lake to lake, but samples from Arctic and subarctic lakes indicate that the levels of mercury, cadmium, lead, and zinc are elevated in the upper parts of the sedimen. There is discussion as to whether this phenomenon is due to natural physico-chemical processes, the so-called diagenic processes, or is a result of anthropogenic metal input over the past century. Decreasing concentrations from south to north in Norwegian, Swedish, and Finnish lakes point to long-range transport from sources in Central Europe. The pattern of higher concentrations in the top layer of the sediment is also more prominent further south. For example, lead is enriched up to 50 times in the top layer in southern Norwegian lakes, compared with only a doubling in northern lakes.

In Canada, lead levels have decreased over the past decade and a half, mirroring the decline in North American emissions. This decline is largely a result of eliminating leaded gasoline.

In Scandinavia, copper and zinc have a different geographic pattern than other metals, with higher levels in the north, which indicates that local sources are more important than long-range transport. Sediment studies show clearly that Russian smelters contribute to nickel and copper concentrations in two Norwegian lakes close to the Russian border and downwind from the smelters.

In Russia, the greatest metal pollution is near the metallurgical complexes of the Kola Peninsula and Norilsk. In an area up to 40 kilometers from the smelters, concentrations of nickel, copper, cobalt, cadmium, and mercury in the surface sediments of the lakes are 10-380 times background values. Because lake sediments are excellent storage reservoirs for metals, these levels will probably remain high for many decades.

### *Is mercury on the rise?*

The most significant trend in the sediment data is the increasing input of mercury. For example, two lakes that have been studied in Finnish Lapland show striking increases of mercury in sediment from recent years. Two other lakes in the study show a moderate increase. The high input of mercury seems to be circumpolar. In Canada, levels in recent sediments are two to three times higher than preindustrial levels. The levels further north are also high. The excess mercury measured in the Canadian lakes was usually connected to a high content of organic carbon in the sediments, which points to the surrounding soils as an important source. The increase in mercury concentration in lake sediments might be caused by an increase in fallout of atmospheric mercury in the catchment area.

The high level of mercury contamination is probably connected to the unique properties of mercury as a metal. As a gas, it is highly mobile and, similar to many organic contaminants, it can be re-emitted into the atmosphere and thus travel to the Arctic in several hops. The cold Arctic climate may favor a final deposition here rather than in warmer climates.

### *Mercury follows the organic matter*

The adverse effects of mercury in fish and fish-eating birds outside the Arctic have provided an incentive to understand how this metal behaves and why some freshwater ecosystems seem to be harder hit than others. Many studies support a connection between mercury levels and the concentration of humic matter. For example, mercury concentrations in the soil, the transport of humic matter from the soil, and the humic content of the water seem to be the main factors that govern mercury transport in runoff water in forested areas of Sweden. High levels of organic matter in the soil also correlate with high levels of methyl mercury in fish.

The Swedish studies also emphasize that the type of landscape can influence the rate of leaching. Moraine landscapes with thin soils and few wetlands leak more mercury than landscapes where water passes through bogs and marshes before it reaches a lake.

Most of the cadmium and zinc in lakes with acid runoff is leached from the surrounding soils, while fallout from the atmosphere directly on the lake surface plays only a minor role. As only a small fraction of the metals is leached every year, any change in acidity would increase the input. The fact that lakes in northern Sweden have less zinc and cadmium than southern lakes may partly be a result of widespread acidification in southern Sweden.

### *Predatory fish have the highest mercury levels*

Most of the studies on metals in fish have focused on mercury, and it is clear that high levels of mercury and organic matter in surrounding soils can lead to high levels of methyl mercury in fish. The table left shows mercury levels in Arctic char, whitefish, and burbot. The highest levels occur in Greenland and Arctic Canada, which probably reflects the

Mercury concentrations in Arctic freshwater fish.

| | Mercury concentration, μg/g wet weight | | |
|---|---|---|---|
| Region | Arctic char | Whitefish | Burbot |
| Northern Canada | 0.01-0.57 | 0.01-2.49 | 0.11-0.30 |
| Greenland | 0.17-0.99 | – | – |
| Finnish Lapland | 0.09-0.32 | 0.23 | 0.23 |
| Iceland | 0.02-0.03 | – | – |
| Norway | 0.03-0.25 | – | – |
| Russia | 0.01 | 0.01 | 0.01 |
| Sweden | 0.10 | – | – |

naturally elevated background of mercury from the Canadian Shield.

Because fish get most of their metals from food, their place in the food web becomes very important. Predatory fish such as pike and perch tend to have larger loads than the grazers. Moreover, concentrations are usually higher in older fish.

Many other factors than mercury concentration in water and sediment determine the concentrations of mercury in the fish. If selenium is present, the uptake is lower, because mercury and selenium bind together in an inert salt. However, selenium will probably not influence the uptake of methyl mercury. An acid environment will bind mercury tighter in soil, and large amounts of humic matter can make the mercury less available because it binds strongly to humus particles. However, in spite of this decreased mobility, acidified lakes often have fish with high mercury concentrations. There are many possible explanations. One of the most important may be that the acid environment favors a different plankton and bottom fauna, which can accumulate the metal over longer lifetimes than in non-acidified lakes. Other changes in species composition might also play a role.

Data from freshwater birds and mammals are scarce but provide one of the few documented effects of heavy metals on Arctic wildlife. In the 1960s and 1970s, ringed seals in Lake Saimaa in Finland experienced many stillbirths and a sharp population decline. One reason may have been insufficient selenium in the lake, making the seals more susceptible to the toxic effects of mercury. The mercury levels in their hair were 50 micrograms per gram in 1965. In 1984, mercury levels ranged from 3.2 to 20.7 micrograms per gram.

Aquatic birds do not appear to accumulate heavy metals as efficiently as terrestrial birds and none of the measured levels is within the range of suspected effect thresholds.

## Marine ecosystems

The Arctic marine environment receives heavy metals from atmospheric deposition, river runoff, and local pollution. The relative importance of these sources will differ between regions. For example, rivers carrying metal-laden sediments, deposit almost all of their load in the shelf seas and only a minor portion reaches the deep ocean. Natural sources of metals are important and in many cases are found to be the main source to the marine environment. The discussion of metals in the Arctic marine environment is divided into two parts: local contamination by mines, and the level of contamination in the Arctic Ocean away from local anthropogenic sources.

### *Mining has added lead and cadmium to local fjords*

Mining has contaminated local Arctic areas with several heavy metals. One documented example is in the fjord outside the Black Angel zinc mine in Greenland, where the levels of lead in the bottom water are up to 200 micrograms of lead per kilogram of water. These high lead levels are also reflected in seaweed, blue mussels, prawns, and in some fish; see the map below. In capelin, lead levels are up to 5 micrograms per gram in the bone. However, no one has been able to document any biological effects in the fish. Cadmium levels in the water are also high, up to 2.5 micrograms per kilogram of water, but in contrast to lead, the animals in the fjord have cadmium levels close to background.

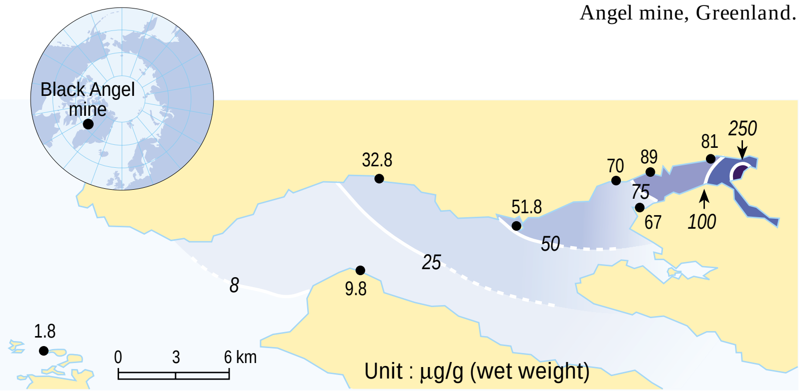
The cryolite mine in Ivittuut in southern Greenland has also contaminated the nearby water. Lead levels of 18 micrograms per kilogram of water have been measured. At Strathcona Sound in northern Baffin Bay, a lead-zinc mine has released lead, making concentrations in the fjord water one to two orders of magnitude higher than background concentrations in the open ocean. Some of the lead has also been taken up by seaweed and crustaceans. Outside a lead–zinc mine in east Greenland, shorthorn sculpins also have elevated levels of lead, whereas the fish outside the cryolite mine on southern Greenland have not been affected.

The mines at Ivittuut and Strathcona Sound have also contaminated their respective fjords with cadmium, but the levels are much lower than those outside the Black Angel mine. At these sites, the cadmium is not affecting the local sediment, nor are elevated levels found in nearby plants and animals.

Local contamination can be expected around several other mine sites in the Arctic, but there is a lack of information on which to base an assessment.

### *Lead levels tell about anthropogenic input*

Metal levels in Arctic Ocean water away from local sources are generally similar to global background levels. Today's global lead concentrations in oceans are generally more than ten



Lead levels in mussels in the fjord outside Black Angel mine, Greenland.

times higher than in prehistoric times. The levels are consistently higher in surface waters than in deeper layers. One might expect the lead levels in the upper Arctic sediments to mirror this increased long-distance transport, but this does not seem to be the case.

Recent seawater analyses from the Pechora Bay and the Kara and Laptev Seas show very high lead levels, ranging from 0.16 to 0.5 micrograms per kilogram water. However, these data require confirmation before any conclusions are drawn.

Filter feeders such as mussels take up lead from sediment particles. The concentration increases slightly with increasing shell length, indicating a moderate accumulation with the age of the mussel. However, lead levels are low in crustaceans as well as in fish. The highest levels, 0.05 micrograms per gram liver, have been recorded in Orkdalsfjorden in Norway.

Lead does not seem to accumulate in fish-eating birds or in marine mammals. In general, levels in marine mammals are low.

An overall assessment is that lead levels in the Arctic marine environment are low, and there is no indication that they increase at higher trophic levels. The only places where effects on biota are likely to occur are hot spots such as mining areas and possibly in some Russian estuaries.

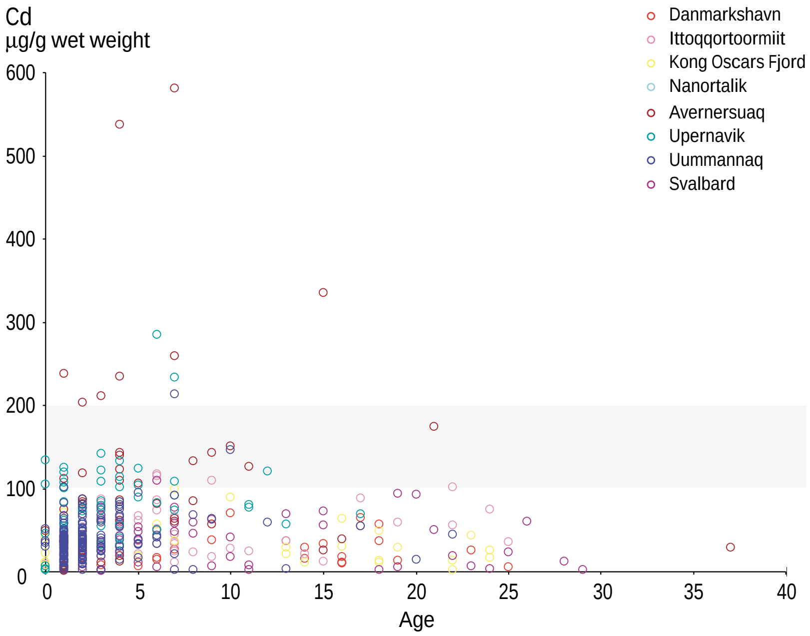
## *Cadmium levels are high in marine biota*

Cadmium levels in Arctic seawater fall within what could be considered natural background levels. Moreover, there is no indication from sediments that the levels have increased from preindustrial times, nor have temporal trends been detected.

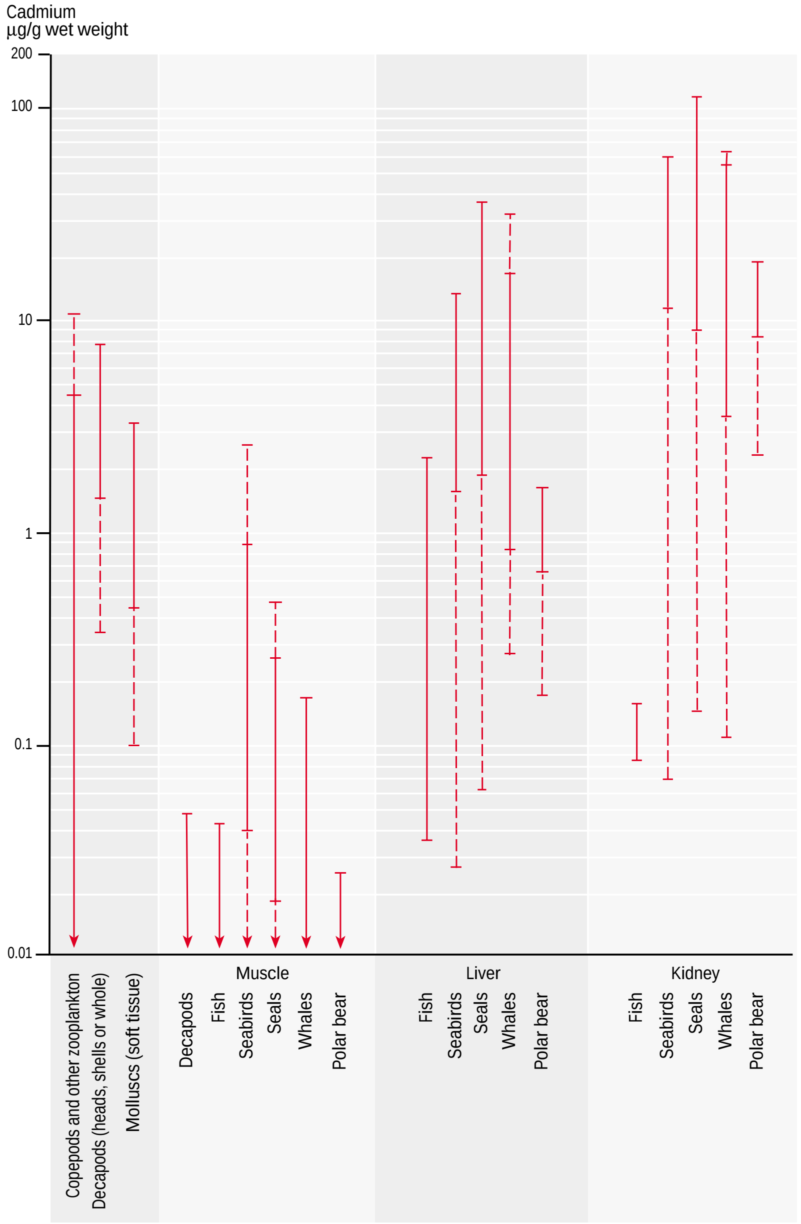
An interesting phenomenon relating to cadmium is that its concentration increases farther away from the coast. This is probably connected with the change in salinity of the water. The result is that cadmium levels in both plants and animals are higher in the open ocean than in the inner region of large fjords, even when there are local sources contaminating the water. The same pattern is evident in the estuaries of the large Russian rivers.

Cadmium accumulates with age in mussels and crustaceans. In general, the levels in crustaceans are higher than global background levels but show large variations.

Cadmium levels in fish muscle are generally low compared to other species, whereas liver values can be high, up to 12 micrograms per



Upper figure.
Cadmium in kidney of ringed seals from Greenland and Svalbard. Levels associated with potential for kidney damage are above 100 to 200 micrograms per gram wet weight.



Lower figure.
Summary of ranges of cadmium levels in marine organisms. Solid lines indicate range for Greenlandic data.

gram liver in long-lived species, such as wolffish, Greenland halibut, and redfish. Livers of Pacific herring and broad whitefish from Tuktoyaktuk Harbor, Canada, have extremely cadmium high levels (30.6 and 40.3 micrograms per gram).

In marine mammals and birds, cadmium seems to accumulate with age. Despite relatively low levels in water, this bioaccumulation leads to cadmium levels in birds and mammals that may be high enough to cause kidney damage in certain age groups. See graph at the top of opposite page. However, a pilot study in which pathologists examined kidney tissue from some of the most highly exposed seals did not reveal any damage. The seals may have developed effective mechanisms for detoxifying the cadmium.

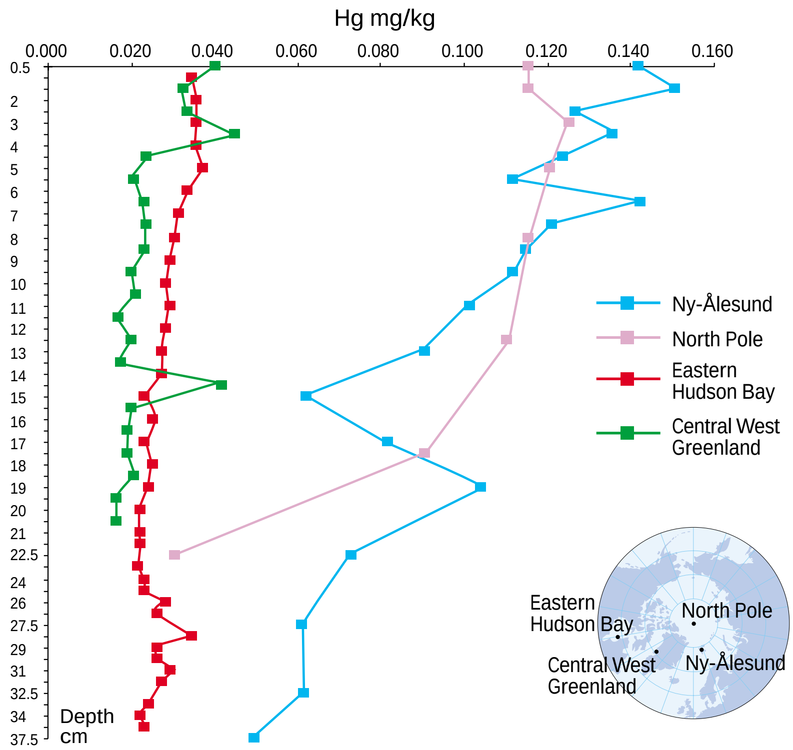
The diagram at the bottom of opposite page summarizes cadmium levels in marine animals. The highest cadmium levels in the marine environment are in northeastern Canada and northwestern Greenland, higher than in polluted seas such as the Baltic. One explanation may be that species composition and other characteristics of Arctic ecosystems favor cadmium uptake because animals grow slowly and live longer. Food habits may also play a role.

## *Mercury levels are high and may be increasing*

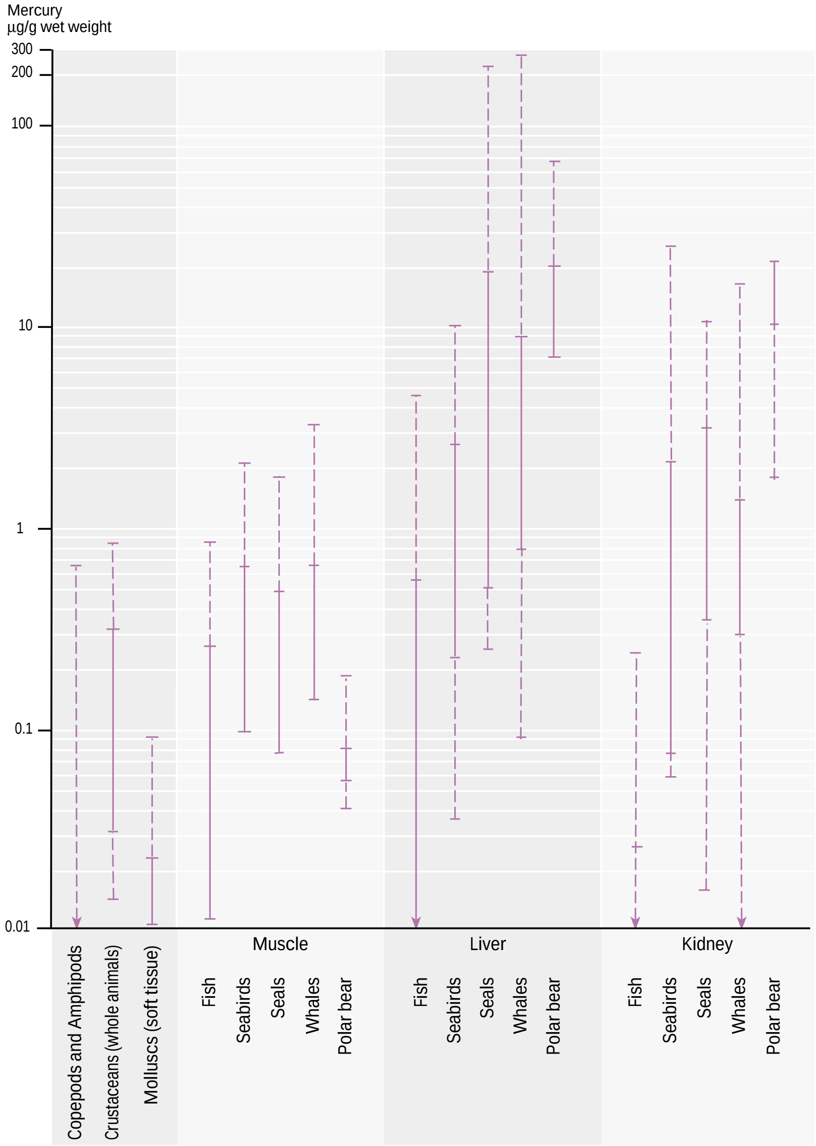
Several sets of data indicate that mercury levels are higher in the upper layers of Arctic marine sediments than in the layers representing preindustrial inputs; see the diagram at top right. Mercury is enriched even in the marine sediments taken at the North Pole. Natural processes may have caused these profiles, as previously noted for freshwater sediments, but they could indicate that human activities have increased the environmental mobility of existing stores of mercury.

The diagram at the bottom of this page summarizes mercury levels in marine animals. In bivalves and crustaceans, levels are generally low, whereas mercury seems to accumulate in fish. The highest values in fish are from northern Canada.

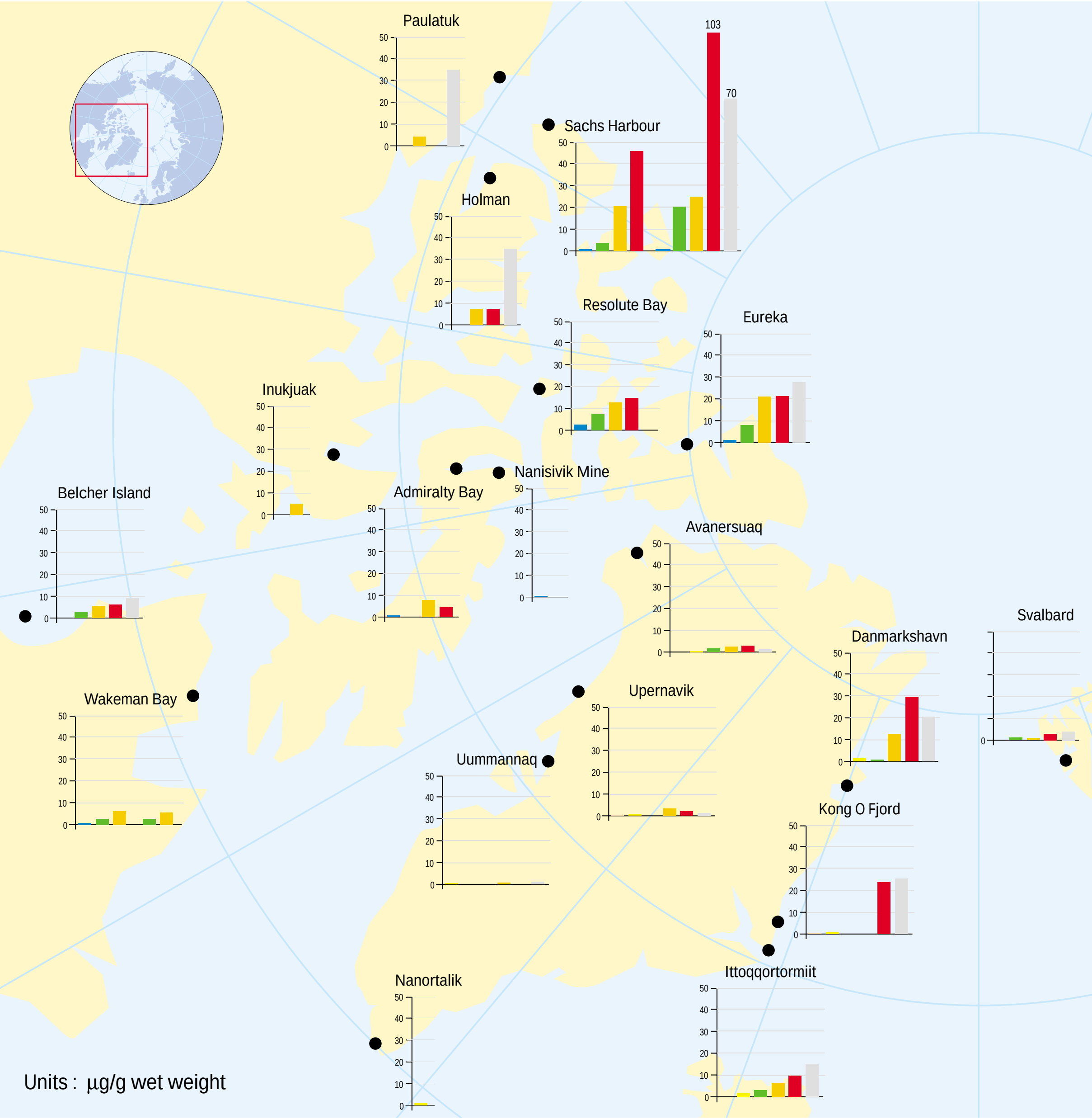
For seals and whales, concentrations often exceed 0.5 micrograms per gram of muscle, especially in older individuals. Livers from ringed seals in the western Canadian Arctic have very high levels of mercury; up to 205 micrograms per gram of liver have been measured; see the map at the top of next page. Levels in livers of bearded seals from the Amundsen Gulf are also higher than both



Upper figure.
Mercury concentration at different depths in marine sediment cores.

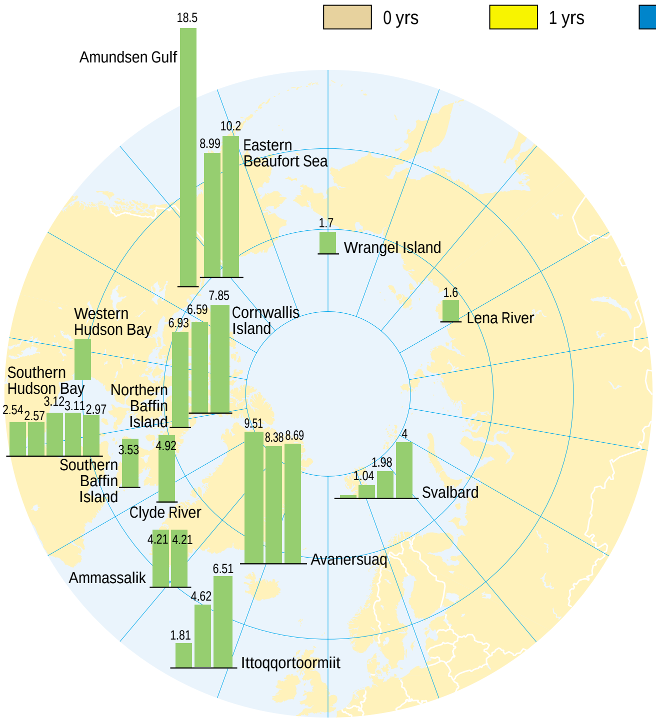


Lower figure.
Summary of ranges for mercury in marine organisms. Solid lines indicate range for Greenlandic data.



Mercury levels in liver from ringed seals of different ages.

Mercury levels in polar bear hair; micrograms per gram.



global background and other Arctic areas, as are mercury levels in toothed whales and polar bears; see the map at the bottom of this page. Some of the highest levels, 280 microgram per gram liver (wet weight) have been recorded in pilot whales from the Faroe Islands.

The effects of these mercury levels on the animals are difficult to assess, because some of the mercury may be inactivated by high selenium levels. Moreover, the scientific focus so far has been on tissues relevant for human consumption and very little information is available on the target organs for mercury, such as the brain. There are no effects studies from the Arctic. However, even for the most exposed animal populations in the western Canadian Arctic and in Greenland, selenium should be abundant enough to protect against mercury poisoning.

A major concern with mercury is that the levels in some animals high in the food chain indicate that the environmental load may have increased in recent years. For example, mercury levels in ringed seals from western Canada show that they accumulated mercury about three times faster during the late 1980s and early 1990s than in the early 1970s. Similar increases have been seen in ringed seals from northwest Greenland taken in 1984 and 1994 and in beluga livers from the western Canadian Arctic. Interpreting these findings is difficult because natural variations that may affect the trends are unknown. Moreover, other data, such as those from Atlantic walrus and ringed seal from central-east Greenland, have not indicated any temporal trends. Very little information is available on temporal trends in Arctic marine fish, but measurements from the Baltic Sea from 1980 to 1993 seem to confirm observations that mercury levels are increasing.

Looking at differences over longer time spans, hair has been analyzed in seal fur from the 15th century and compared with similar analysis of recent fur samples. The mercury concentration has increased approximately four times. Similar analysis of human mummies showed an approximately three-fold increase.

## Summary

The most severe effects of metals on Arctic ecosystems are from local pollution. The nickel-copper smelters on the Kola Peninsula and in the Norilsk region of Russia have severely polluted nearby terrestrial and freshwater environments. In the areas closest to the smelters, the deposition of nickel and copper has, in combination with acidifying emissions, severely damaged the soil and ground vegetation, resulting in an industrial desert. Moreover, the freshwater ecosystem is completely destroyed in at least five water bodies.

Most of the smelter emissions are deposited very close to their source. However, they are still the major source of circumpolar contamination. Emissions from the Kola Peninsula are the major source of metals in northern Fennoscandian air, and emissions from the Urals and Norilsk are the most important for air concentrations of metals over Alaska and northern Canada.

Mines are sources of local contamination, but only a few mines have been assessed.

Metals are taken up by Arctic biota and levels often reflect local geology or local anthropogenic activities. In the circumpolar assessment, the most troubling findings concern mercury and cadmium, as they occur in concentrations that may have health implications for individual animals as well as human consumers.

Mercury seems to be increasing in both lake and ocean sediments. An increase over the past two to three decades is also evident in livers and kidneys from some marine mammals. This may indicate an increased global flux of mercury, which is deposited in the Arctic because of the cold climate. In some parts of the Arctic, notably Greenland and western Canada, any increase in the mercury load is in addition to high natural levels from the local geology. Several uncertainties about the observed time trends must be resolved before firm conclusions are drawn. For example, the gradients in sediments might be caused by natural processes. For biota, lack of information about the natural variation of mercury levels complicates the interpretation of results.

Mercury levels in several species of marine mammals seem to be highest in the northwestern part of Canada.

Mercury biomagnifies in freshwater and in marine ecosystems. However, in all marine animal populations, even the most exposed ones, selenium is abundant enough to detoxify the mercury.

From a research point of view, further studies of the increase in mercury are a high priority. It is important to verify time trends and also to investigate the sources or processes behind the increase, as well as any biological effects.

In some areas, cadmium levels are very high both in terrestrial and marine birds and mammals, possibly due to local geology. For example, in reindeer/caribou, the highest cadmium levels have been recorded in the Yukon Territory in Canada, which is known to have cadmium-rich geology. Cadmium levels seem to be highest in marine animals from northeastern Canada and Northwest Greenland. For certain age groups and populations of marine birds and mammals, the levels might be high enough to cause kidney damage.

Lead generally does not pose a threat to Arctic ecosystems because it does not bioaccumulate. Moreover, lead levels have been decreasing for the past two decades.