Photo: ALIMDI.NET

Tracing **the Noxious Five**

In many regions of the world, air pollution is set to worsen in the decades to come. **Jos Lelieveld** and his colleagues at the **Max Planck Institute for Chemistry** in Mainz forecast where this will happen. Their studies of atmospheric chemistry also uncover the unexpected effects of some substances.

TEXT **DIETER LOHMANN**

The "noxious five" are already making life difficult for people in many parts of the world. High pollutant concentrations can be found in the megacities of Southeast Asia and Africa, for example. They include the Indian city of Mumbai, Pakistan's Karachi, Lagos in Nigeria and the Chinese capital, Beijing. Some days, city dwellers don't dare to go out onto the street without their face masks on.

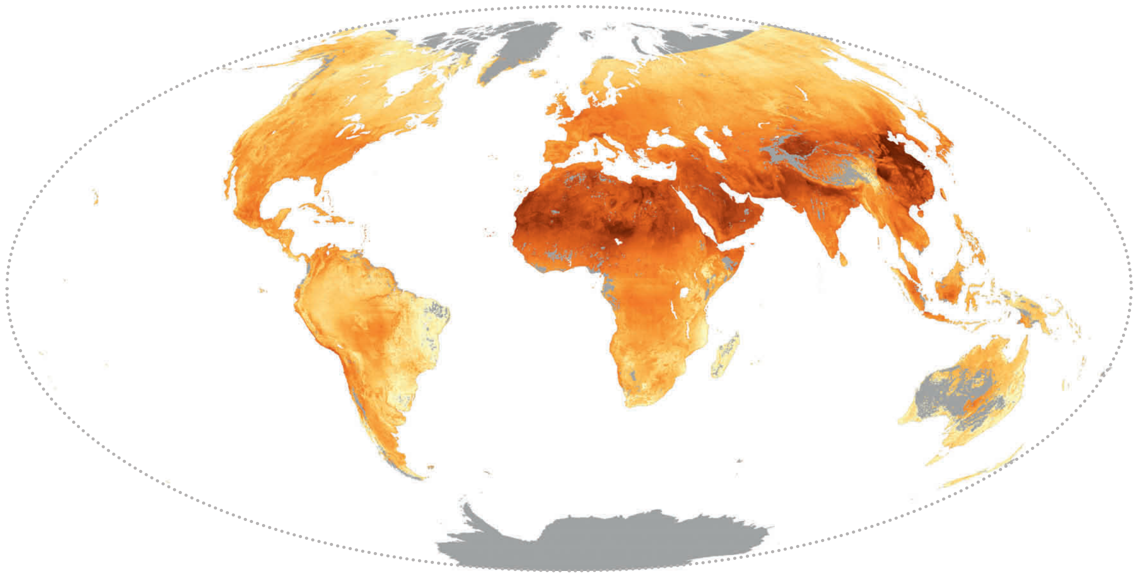
Five nasty air pollutants are released into Earth's atmosphere primarily via car exhausts and industrial emissions. A large proportion of the sulfur dioxide and particulate matter originates from power plants fired by fossil fuels; nitrogen dioxide, on the other hand, comes largely from the ever-increasing volumes of traffic worldwide. The effects of this "bad air" are considerable. Epidemiological studies have shown that, even when only small amounts are inhaled, the pollutants can cause cardiovascular diseases and lung cancer, not to mention asthma and chronic obstructive pulmonary disease (COPD).

One man who has been studying the noxious five for many years is Jos Lelieveld, Director at the Max Planck Institute for Chemistry in Mainz. However, the researcher isn't directly involved with combating air pollution – he sees that as the job of governments. "Our work helps clarify the large-scale atmospheric processes associated with the bad air – especially in our globalized world," says Lelieveld.

On the one hand, his team looks back in time into the history of the Earth's atmosphere in order to determine how pollutant concentrations have developed over the past decades and centuries. The scientists are also interested in how the air quality will change in the future. Their main tool is EMAC (ECHAM-MESSy Atmospheric Chemistry) – the chemical atmospheric model they use to carry out computationally intensive global and regional simulations.

EMAC was developed during the past decade at the institute in Mainz. The ECHAM climate model of the Max Planck Institute for Meteorology in Hamburg, which had already been around for some time, was linked up

A particularly bad atmosphere: Industrial growth and ever-increasing volumes of traffic mean that, in the decades to come, atmospheric pollution will increase considerably in South and East Asia in particular.



A global map of air pollution: Satellites have measured large amounts of particulate matter above dark-colored regions. Natural pollution is high in North Africa and Arabia. The light yellow regions are the only regions where the concentrations are below the WHO limit.

with new, modular software for Earth system modeling (MESSy, Modular Earth Submodel System).

Today, EMAC is one of the very best models available to atmospheric researchers around the world, because it allows flexible computer simulation of the close spatial and temporal coupling of atmospheric chemistry and meteorological processes worldwide. The researchers can thus uncover, for example, what interactions exist between solar insolation, the water vapor content of the atmosphere, clouds, rainfall and atmospheric pollution. EMAC now provides them with a comprehensive Earth system model that can be used to investigate the chemical interactions between processes in the atmosphere, on land and in the oceans.

EMAC is the first to incorporate all five of the most noxious atmospheric pollutants into the calculations. While it sounds simple at first, it's actually much more complicated than you would think. "In order to be able to simulate these pollutants, dozens of chemical components have to be incorporated into the model," explains Lelieveld. These include the precursor substances of ozone and aerosol particles. For example, a host of hydrocarbons are released into the atmosphere, where chemical interactions produce additional harmful substances.

Moreover, all of these members of the cast have different sources and sinks. Clouds, rain and exchange processes with vegetation play a particularly important role here. A key metric in EMAC is what's known as the Multi-Pollutant Index, which combines the degree of atmospheric pollution caused by nitrogen dioxide, sulfur dioxide, ozone, carbon monoxide and particulate matter in a single value.

PRECISE FORECASTS OF ATMOSPHERIC POLLUTION

The latest simulations at the institute in Mainz were based on actual emissions of the noxious five in 2005 and their trends in the ensuing years. They were used to calculate a business-as-usual scenario where it was assumed

Graphics: MPI for Chemistry; photo: Thomas Hartmann

» We need a better understanding of the effects the rapidly changing composition of the atmosphere has on global air quality and climate change.

that the current environmental laws and their implementation wouldn't change significantly. The results were unique "global maps of atmospheric pollution," which provide unusually precise forecasts for 2025 and 2050.

These worlds of the future show something of real concern: Air quality could worsen drastically over the coming decades in many parts of the world. Especially in the conurbations of the newly industrialized countries and developing nations, breathing would then ultimately become torture, and dense smog would be a part of daily life. It is thought that particularly China, Northern India and the Middle East could become real pollution hotspots by 2050. Then atmospheric pollution there could, in some cases, reach three times today's levels.

According to the business-as-usual scenario, which assumes that no new air quality legislation will be introduced beyond what is currently implemented, the main protagonists of atmospheric pollution differ from region to region. In East Asia, it will probably be nitrogen oxides, sulfur dioxide and particulate matter that will really plague people. In Northern India and the Arabian Gulf region, the ozone levels could reach new record highs, as well.

CONCENTRATIONS OF POLLUTANTS ARE TOO HIGH

The cause of the increasing atmospheric pollution is the forecast economic growth in these regions. This will drastically increase the amount of traffic and industrial production – and thus emissions, too. In addition to the emissions from the petroleum industry, it is the high insolation by the Sun and other meteorological factors that are primarily responsible for the very specific pollutant profile in the Middle East, for example.

Europe and North America get off lightly compared to the potential regions of crisis. Here, the researchers expect only moderately rising levels. This is related to the greater environmental awareness on these continents, which already manifests itself in what are sometimes restrictive, though effective, environmental regulations. These include emission filters for coal-fired power plants, as well as efficient catalytic converters in motor vehicles. Nevertheless, the concentrations of atmospheric pollutants are still much too high even in Europe and North America, causing illness and premature mortality.

But the latest simulations are only the beginning. In the next step, the Max Planck researchers in Mainz want to take a closer look at many more factors that have an impact on atmospheric pollution. One thing they are planning is a study to investigate the effects of the South Asian monsoon on the redistribution of pollutants in the northern hemisphere and even in the stratosphere. "We need a better understanding of the effects of the rapidly changing composition of the atmosphere on global air quality and climate change," says Jos Lelieveld.

He and his team also intend to train their sights more closely on the atmosphere over Africa in the future. A unique mixture of pollutants can already be found in the air there. Apart from large amounts of airborne desert dust, the mixture includes huge quantities caused by emissions from the burning of biomass.

Nowhere else on Earth are so many savannahs and forests being set on fire in order to create more space for agri-

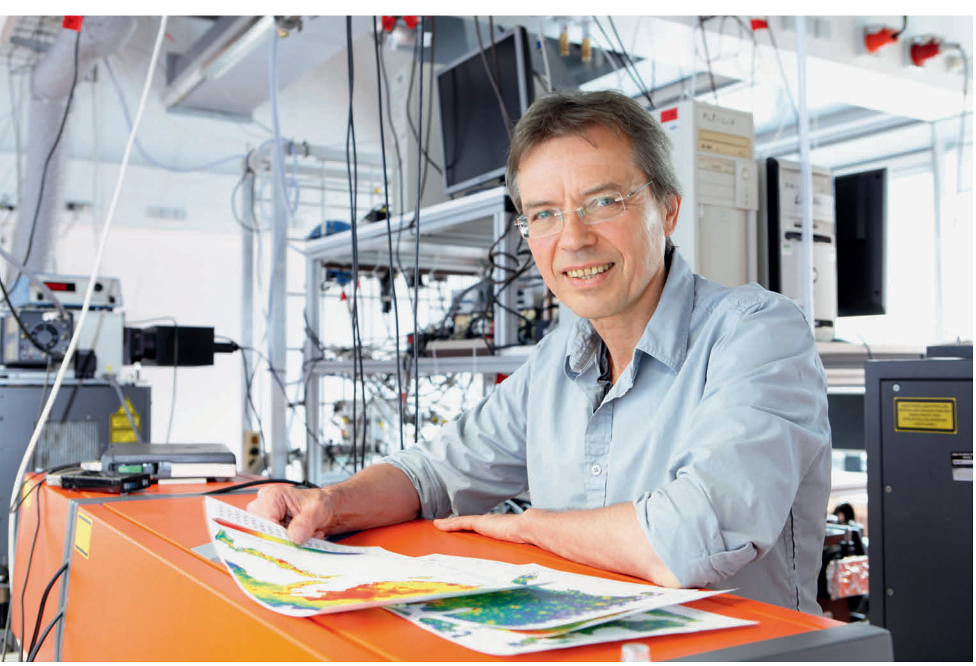


Photo: Thomas Hartmann

Atmospheric research in the lab: Jos Lelieveld and his team also conduct experiments at their institute in Mainz to investigate the complex interplay of the constituents of air.

left: Face masks protect against the harmful air: Japan is one of the countries where the air will become dirtier in the years to come. Residents of Tokyo already try to protect themselves against pollutants on some days.

right: In early January 2012, the Chinese cities of Beijing and Tianjin (bottom right, near the bay) were clearly visible on satellite images (photo on the left). In mid-January, they were hidden by an extraordinarily dense blanket of smog (photo on the right).

culture. The Mainz-based researchers want to know how this bad air will evolve over the coming decades under the influence of global warming and the expected increase in industrial emissions.

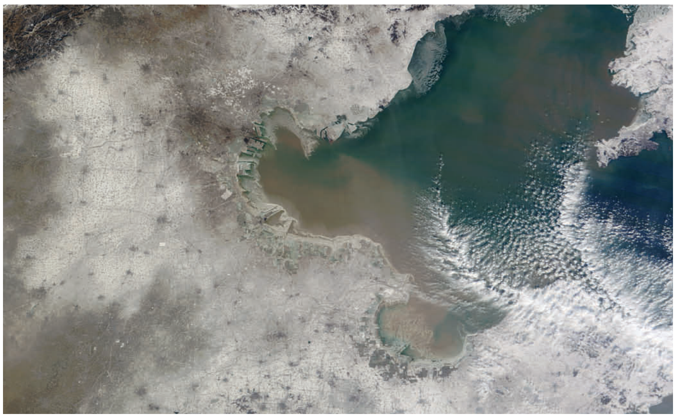
As pessimistic as the vision of the future may be in large parts of the ailing atmosphere, there is still every reason for hope, because the cast of this environmental drama includes not only many villains, but also some heroes. The latter include the so-called hydroxyl radicals (OH radicals), as has been known for some time. They are a kind of fast-response force in the atmosphere, an effective "detergent" to cleanse the Earth's atmosphere of pollutants.

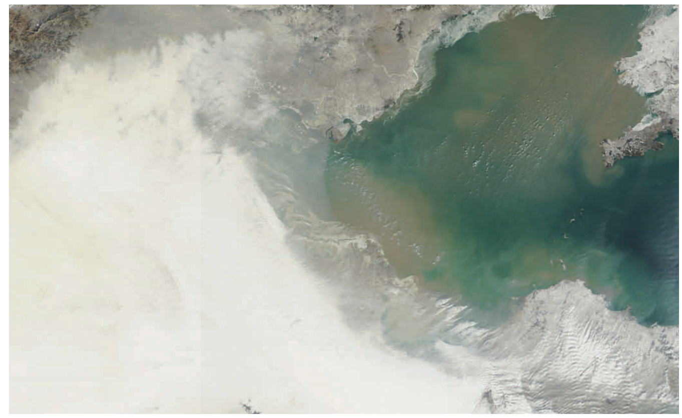
THE POWER TO SELF-CLEAN IS ASTONISHINGLY RESILIENT

Each individual one of these "scrubbing molecules" consists of one hydrogen and one oxygen atom and has an average lifetime of less than one second. In the atmosphere, hydroxyl radicals form primarily from ozone and water molecules, usually in the presence of sunlight, or in the photolytic decomposition of hydrogen peroxide (H_2O_2).

As part of their chemical cleaning duties, the OH radicals oxidize pollutants such as carbon monoxide and other gases – methane, for example, which is particularly harmful to the climate. This process turns the original materials into water-soluble substances and

Photo: Corbis





particles, which are packaged in water droplets by serving as condensation nuclei and are subsequently washed out of the atmosphere with the rain. Without the hydroxyl radicals, climate change would already have progressed much further and the air quality would be even worse than it is already. The one sticking point of this effective disposal process: hydroxyl radicals are also used up in the course of oxidation.

The researchers in Mainz discovered that their atmospheric concentration has nevertheless remained surprisingly stable over the years. This was confirmed by a 2011 study involving not only the Max Planck Institute for Chemistry, but also the National Oceanic and Atmospheric Administration (NOAA) in the USA.

The atmospheric scientists thus disproved earlier ideas that said that hydroxyl radical values would fluctuate annually by up to 25 percent. The results indicate that the self-cleaning power of the Earth's atmosphere is less affected by the environmental changes to date than was thought.

"Although we predicted that the self-cleaning was well buffered, we were able to prove this only by taking systematic measurements over many years and employing state-of-the-art modeling methods," explains Lelieveld. The results also make forecasting the climate and the global air quality more reliable, because computer models can now provide a better description of the composition of the atmosphere.

But why are the production and consumption of the atmospheric cleaning agents still almost in equilibrium despite increasing atmospheric pollution? The answer lies in recycling. This process is evidently widespread in Earth's atmosphere. The Mainz-based researchers managed to get on the trail of the precise recycling sequence just over 18 months ago. Their starting point was a glaring discrepancy between the model calculations on the hydroxyl radicals at that time and the results of measurement programs in the field.

Above the Earth's rainforest regions, in particular, the atmosphere had much more cleaning potential than really ought to be there, according to the simulations. How was that possible? The scientists proposed several hypotheses, only to discard most of them very quickly. Finally, their search for a solution to the problem led them to isoprene.

Like the much more familiar methane, this unsaturated hydrocarbon is produced in huge quantities by plants and released into the environment. At least 500 million tons of isoprene thus end up in the atmosphere around the globe every year. Most of it originates from the trees of the tropical rainforests, where it is used in the volatile oils of the scents, among other things.

Was there a connection between the high concentrations of hydroxyl radicals and isoprene? In order to test this, the atmospheric researchers used a virtual trick: they expanded one of the previous models of atmospheric chemistry by adding a further reaction cascade and assigned a Janus-faced effect to the isoprene. So when isoprene decomposes, the initial breakdown product is hydroperoxyaldehyde (HPAL). This uses up hydroxyl radicals.

PLANT SCENT RECYCLES HYDROXYL RADICALS

To help with the next step in the process, the scientists inserted a chemical switch: if a large number of "detergent" molecules are whizzing through the air at the time the HPAL is being formed, they help decompose the HPAL further. But if only a few hydroxyl radicals are present, the switch shifts: under the influence of sunlight, the hydroperoxyaldehyde then reacts with the atmospheric oxygen in a complex sequence of chemical reactions.

The end result is that more hydroxyl radicals are produced than are required to convert the plant- and tree-produced isoprene to HPAL. That was the theory. But there was still no practical test for the improved model. New simulations then brought further proof: their thinking was correct; actual measurements and model calculations were again in agreement.

This recycling of the cleaning agents is an important element in keeping the air clean, especially in the tropics. "But our results also mean that rising isoprene emissions, as we expect from global warming, don't actually make

Photos: NASA (2)

» Is it possible that pollutants that happen to have an antagonistic effect and effective buffering mechanisms can solve the problem of the predicted dramatic rise in pollutant concentrations? No, says Jos Lelieveld.

the climate effect worse," concludes Lelieveld. This is because a higher concentration of isoprene in the air can support the production of hydroxyl radicals – and help combat climate-damaging gases.

The mechanism uncovered in 2012 may, however, not be a special case. The researchers in Mainz now suspect that several natural and manmade pollutants emitted into the air also have an antagonistic effect and could buffer the self-cleaning power of the atmosphere in a manner similar to isoprene.

That there could be some truth in this is shown indirectly by another example from the Earth system with its diverse interactions between the atmosphere, lithosphere, hydrosphere and biosphere. Nitrogen over-fertilization has long been considered a massive problem because it can result in dangerous nitrates getting into the groundwater. Acidic soils also have a bad image, they are one of the reasons why forests are dying. But apparently two villains together can do some good.

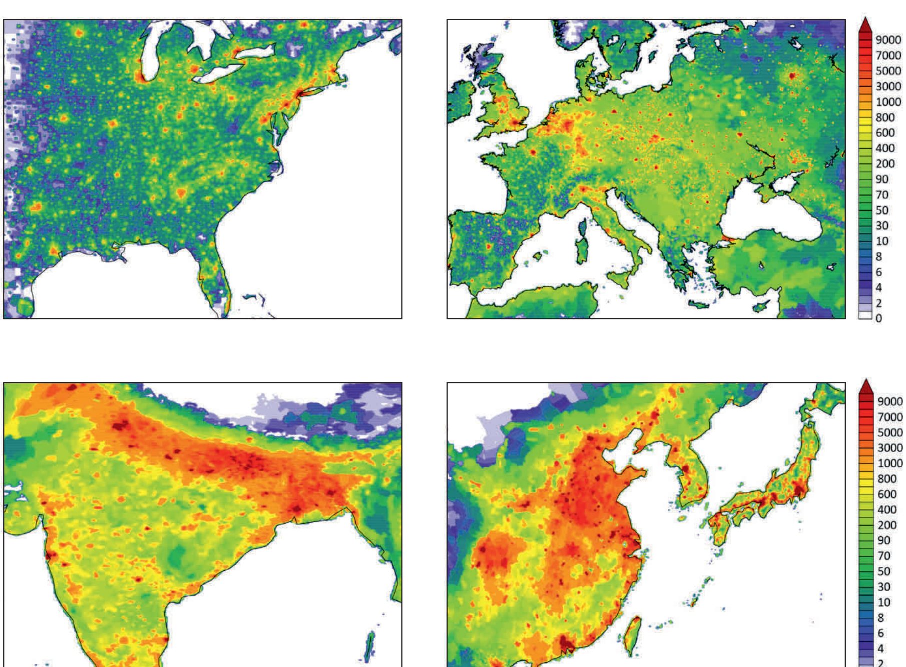
DOES CLIMATE CHANGE CREATE MORE HYDROXYL?

This fact was uncovered by a new nitrogen cycle path that was discovered in lab experiments a short while ago. According to the discovery, nitrous acid (HNO_2) is formed out of nitrite ions and water in soils that are well supplied with nitrogen. The higher the nitrite concentration and the more acidic the soil, the more HNO_2 is produced. This then gets into the atmosphere as gaseous nitrous acid (HONO), where it serves as the starting product for the formation of hydroxyl radicals.

As climate change advances, the driving force behind the production of this detergent could become more and more important. In a predicted triad of increased fertilizer use, rising soil acidification and global warming, scientists think significantly more nitrous acid will likely be released from the soil, especially in developing countries. The end effect is that more fodder is available for the formation of hydroxyl radicals and the self-cleaning power of the atmosphere increases, at least locally.

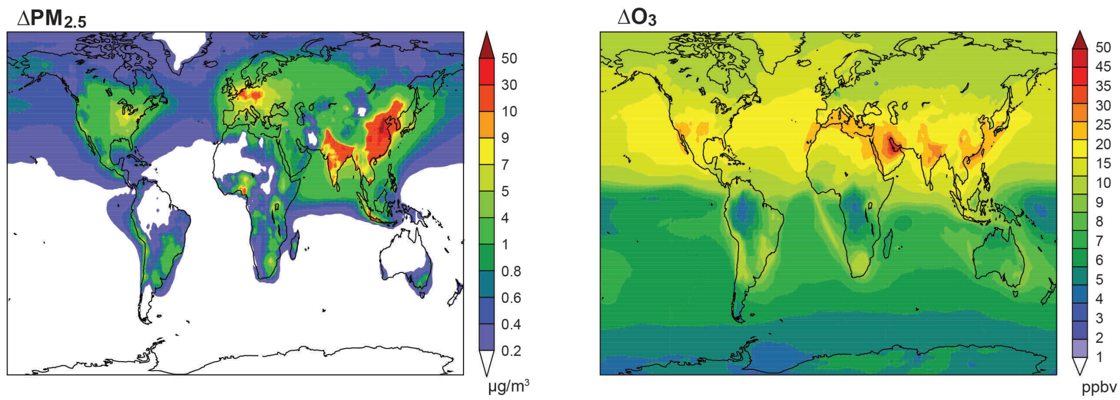
The stock of cleaning agents in the atmosphere has thus produced some good news. But can pollutants that happen to have an antagonistic effect and effective buffering mechanisms really solve the problem of the predicted dramatic rise in pollutant concentrations? No, says Jos Lelieveld decisively: "Even if these phenomena mean we have less cause to worry about our atmosphere, we should still do all we can to reduce the emission of climate-active gases and toxic air pollutants as much as possible."

The Mainz-based researchers believe that new legislation and technologies to reduce industrial, traffic and household emissions are an essential element in the battle against atmospheric pollution. We need to ensure that the business-as-usual scenario doesn't become reality. Particularly for the regions considered to be future pollutant hotspots, this could possibly be their only salvation. But can such measures even be implemented at all in countries with enormous economic growth?



The air is a health risk: The maps of the eastern USA, Europe, and South and East Asia show how high the mortality rate there was in 2005 due to cardiovascular diseases, lung cancer and respiratory diseases that can be traced back to particulate matter and ozone pollution (given in deaths per 10,000 square kilometers).

Graphics: MPI for Chemistry



The atmospheric trails left by industrialization: From pre-industrial times until 2005, particulate matter pollution (left, values in micrograms per cubic meter) and ozone pollution (right, values in parts per billion in the gas volume) increased in many regions of the world. Blue shows a slight increase, red a strong one.

Lelieveld is optimistic: “I see no reason why better environmental laws and technologies shouldn’t be possible in China, India and other countries.” He is utterly convinced that they don’t harm economic growth – especially long term. But he also says: “Environmental regulations are like many highly effective operations: it’s a case of no pain, no gain.”

BETTER AIR QUALITY BRINGS HEALTH COSTS DOWN

First, there has to be substantial investment in the development of green technologies, such as energy-efficient cars and low-emission power plants, but ultimately, the optimized technologies also benefit industry and the national economy in question. Better air quality, for example, brings down costs for the health system, and workers take less time off due to illness.

What is possible in terms of clean air in a very short time was demonstrated by China in 2008 when it hosted the Olympic Games. Back then, it applied numerous environmental regulations and succeeded in reducing the dramatic atmospheric pollution to such a degree that the athletes had at least reasonably acceptable conditions in which to compete. Yet the other side of the coin is that China has since returned to its old ways. Air pollution has long been back at the same levels as before the Olympics.

Not only newly industrialized and developing countries have a duty to fight for better air. Europe and North America have no reason to be complacent, either. “Atmospheric pollution moves around the world as fast as money does,” is the interesting comparison Jos Lelieveld draws. The emissions billowing out of power plant smokestacks and car exhaust fumes in East Asia can reach us within one or two weeks on global winds such as the jet streams.

The existing environmental regulations and technologies must therefore be advanced here at home, as well, and adapted to possible future conditions. “Our research serves as the basis for applied projects, which, in turn, will lead to low-cost measures for keeping the air clean and help optimize the networks that monitor atmospheric pollution,” explains the Max Planck Director.

Recent calculations undertaken by the Mainz-based scientists show how vital the fight is against the noxious five and other atmospheric pollutants. At present, some three million people around the globe die every year because of the anthropogenic bad air – 50,000 of them in Germany alone. If no measures are taken against the pollution of the Earth’s atmosphere in the next few decades, the “deadly quintet” will be responsible for many more illnesses and deaths in the future. ◀

TO THE POINT

- **Five atmospheric pollutants (nitrogen dioxide, sulfur dioxide, ozone, carbon monoxide and particulate matter) from car exhausts, industrial emissions and the burning of biomass harm both humans and the environment. Moreover, a host of natural and man-made hydrocarbons chemically interact with these pollutants in the atmosphere, forming additional noxious gases and particulates.**
- **Researchers use the EMAC model to simulate the close spatial and temporal coupling of atmospheric chemistry and meteorological processes on the computer. The outcomes are used to assess the effects on human health worldwide.**
- **A drastic worsening of the air quality could take place during the coming decades, especially in the conurbations of the emerging industrialized countries, causing premature mortality.**
- **Although the quantities of cleaning agents in the atmosphere have remained astonishingly constant over the years, new legislation and technologies are needed in order to counteract further increases in atmospheric pollution.**

Graphics: MPI for Chemistry