Nature Mimics Industry

By ACSH Staff — March 22, 2005

Who's to blame for carbon dioxide emissions to the atmosphere, persistent dioxins, PCBs, vinyl chloride, perchlorates, elevated concentrations of nitrates in stream water throughout the world, and unusual fish kills? The initial knee-jerk reaction is to lay the blame on present-day humans (read: ourselves), endlessly accused of fouling our own nest, and there's some truth to this. No doubt we humans are responsible for many egregious environmental actions, but here's something new. Recent research has shown that some of the pollutants heretofore blamed on industrial activities can now also be laid at the doorstep of Mother Nature.

Dioxins from Burning Wood and Biomass

Dioxins, for example, are ubiquitous, toxic, and environmentally persistent organochlorine compounds, which have been assumed to be by-products of the organochlorine-based industries that underwent rapid expansion during the 1950s. Yet R. R. Bumb and colleagues found dioxins in soot from wood burning ovens.(1) This shows that dioxins were present on Earth from the first fire of forests or grasslands. Can't blame man for dioxins in 40 million year-old clay deposits, since he wasn't around at the time.(2)

Przemyslaw Mastalerz notes, "Comparisons of industrial emissions of dioxins with emissions from wood and biomass burning are not possible at present because emissions from wood burning are not yet sufficiently quantified, and there is no consensus on emissions from industrial sources. Published estimates of global industrial emissions vary from less than 100kg to 3,000kg annually. In view of these numbers, it is probable that wood-burning is the most important source of dioxins in the environment. There is no doubt that learning the exact balance of dioxins is very important for our understanding of the contamination of environment. It seems peculiar, therefore, that the environmentalists who spare no effort to measure dioxin emissions from incinerators of hospital waste or human corpses show so little interest in wood and biomass burning."(3) An EPA study concluded a single trash-burning barrel in a homeowner's backyard can release as much dioxin into the air as a well-controlled municipal waste incinerator.(4)

In 2002, Pirjo Isosaari and his colleagues found dioxins in sediments that were over 8,000 years old in a lake in Finland. An added interesting result of this work was that besides dioxins, these researchers also found PCBs.(5) This is unusual because supposedly PCBs have no natural sources and their formation in the pre-industrial era appears not to be possible. No explanation has been offered. However, natural sources of PCBs may not be as far-fetched as it seems at first blush. Researchers with Canada's Wildlife Service discovered in marine aquatics an unusual brominated and chlorinated chemical, $C_{10}H_6N_2Br_4Cl_2$ (1,1-dimethyltetrabromodichloro-2,2-bipyrrole), that behaves like PCBs.(6) They christened the chemical HDBPs for Halogenated Dimethyl BiPyrroles (7). Characterization and speculation on how it originates cast doubt on the

premise that substances combining chlorine and organic molecules do not result from biosynthesis (production of a chemical compound by a living organism). These chemicals were found in Pacific Ocean and Atlantic Ocean samples but not in samples from the Great Lakes, so industry couldn't be blamed for their existence. Furthermore, the apparent absence of HDBPs from the five freshwater Great Lakes also suggests that they are not airborne.(8)

Recently, Andrew Meharg and Kenneth Killham reported in *Nature* that the burning of coastal peat was a significant source of dioxins long before the industrial revolution.(9) The burning of peat, which is decaying tropical plant matter, was how people in much of the British Isles kept themselves warm during the eighteenth and nineteenth centuries, and the researchers report that Scotland, with well under half a million people, probably produced as much as a tenth of the amount produced by municipal waste incinerators in the entire United Kingdom today. The Scotland Isle of Hirta, which was evacuated in 1930, still has dioxin in the soil from peat burning, clear evidence that modern humans were not the first to generate large amounts of dioxins.(9)

Peat burning can also spew massive amounts of carbon into the atmosphere. Emissions from the 1997-1998 wildfires in Indonesia consumed vast amounts of peat and released a total of 0.81 to 2.57 billion tons of carbon into the air. This amounts to 13 to 40 percent of the average annual amount produced globally from combustion of fossil fuels. Susan Page and her colleagues report that the Indonesia fires contributed greatly to the largest annual increase in atmospheric carbon dioxide concentration detected since records began in 1957.(10) The emissions from the Indonesia fires were comparable to the global carbon uptake by the terrestrial biosphere in a typical year, yet they came from a relatively tiny area of the globe.(11) These data support the case that some events can significantly affect atmospheric carbon worldwide and throw a monkey wrench into most global temperature modeling strategies.

Nature Maketh and Taketh Away Ozone

Jay Lehr asks the question, what do you get when you go into the North Woods, a great, beautiful unspoiled area where there is no industry for miles? The answer is you inhale the pine odor. Guess what? Pine odor is made up of polycyclic aromatics, carcinogens, in the cleanest air we supposedly have in this country.(12) Further, in regards to forests, when discussing neglected sources of ozone, Janet Pelley says, "Scientists are beginning to blame local forests and pollutants blown in from overseas for the fact that concentrations of ground level ozone and its accompanying smog have not declined during the past ten years in the United States, despite cuts in ozone precursors. Thus, national smog fighting regulations may actually be doing a better job than they have been given credit for, but measurably reducing ozone levels may require international efforts and rethinking forestry management."(13) Research by Allen H. Goldstein, an atmospheric chemist at the University of California, Berkeley, suggests that the amounts of ozone absorbed by trees in a California pine forest also suggest the presence of unidentified volatile organic compounds (VOCs). He proposes that they're related to terpenes."(14)

Peretti Hari and his colleagues report that global NOx emissions from boreal coniferous forests may be comparable to those produced by worldwide industrial and traffic sources. Hari suspects that other evergreens and perhaps even all plants might also release the compounds under many natural conditions.(15) Jessica German adds that tree emissions can react with humanmade

compounds to make chemicals that further pollute the air or contribute to climate change. She quotes Alex Guenther of the National Center for Atmospheric Research in Boulder, Colorado, regarding large poplar plantations in Oregon that "actually are changing the chemistry of that region because they have much higher emissions rates of organic gases than many other trees do."(16)

Volatile halogenated organic compounds (VHOC) contribute to stratospheric ozone depletion. It's becoming more evident that halogenated compounds of natural origin can contribute significantly to the levels of VHOC in the atmosphere. The oceans are a major source, and some terrestrial sources include wood rotting fungi, biomass burning, and volcanic emissions -- in addition to human activity. A recently identified terrestrial source of naturally occurring VHOC is in soils and sediments, where halide ions can be alkylated during the oxidation of organic matter by an electron acceptor source, as Dr. Frank Keppler and his colleagues report: "Sunlight or microbial mediation are not required for these reactions and such abiotic processes could make a significant contribution to important atmospheric compounds CH_3Cl, CH_3Br, and CH_3I."(17)

Vinyl Chloride from the Earth, Nitrates from the Sea

Vinyl chloride, a highly reactive and toxic substance that is widely used in industry, was thought to be exclusively manmade, or the degradation product of other anthropogenic substances, such as trichloroethylene and tetrachloroethylene. Not any longer. Frank Keppler and his colleagues have demonstrated that vinyl chloride also comes from natural sources such as soil. They conclude, "The presumption that vinyl chloride is solely manmade must now be considered as incorrect. There is no doubt that industrial and anthropogenic activity has contributed significantly to the burden of vinyl chloride in the environment, but our results show that vinyl chloride in the environment also has natural sources. One possible source comes from the reaction of organic matter, Fe(III), and chloride. As humic substances, catechols, Fe(III), and chloride ions are widespread in nature, the magnitude of this soil source of VC and other volatile chlorinated substances is potentially enormous and could make a contribution to the budget of vinyl chloride in the environment."(18)

Elevated concentrations of nitrates in stream water throughout the world have been blamed on human activities. Again, recent research lays some of the blame on Mother Nature, which until now had been considered innocent. Seawater has been shown to be a possible significant source of some nitrates in one study,(19) and another revealed that bedrock contains fixed nitrogen that contributes appreciable concentrations of nitrate to surface waters in certain California watersheds.(20) Adele Chuck and her colleagues report, "Measurements of methyl and ethyl nitrate in seawater and air samples along two Atlantic Ocean transects provide the first direct evidence for an oceanic source of these compounds. Equatorial surface waters were highly supersaturated (up to 800%) in both species, with the waters in the temperate regions generally being closer to equilibrium." The mechanism behind all this is unclear at present, but the findings raise questions about the formation of nitrogen compounds in remote marine environments and could have important implications for the formation and destruction of tropospheric ozone.

There's more to the story. Another study has revealed that bedrock containing high concentrations of fixed nitrogen contribute appreciable concentrations of nitrate to surface waters in certain

California watersheds, to the extent that even small areas of these rocks have a profound influence on water quality. "As 75% of the rocks now exposed at the Earth's surface are sedimentary in origin, and as these rocks contain about 20% of the global nitrogen inventory, 'geological' nitrogen may be a large and hitherto unappreciated source of nitrate to surface waters."(20) The same geological formations where the nitrogen was found "extend for 300 km along the western flank of the Sierra Nevada, indicating the potential for nitrate contamination of much of California's surface water supply." As with nitrates in the ocean, here's another case where nitrogen as a non-point source of contamination needs to be reevaluated.

It's Raining Rocket Fuel; Thar She Flame-Retards

Controversy has swirled around estimates of the health risks posed by perchlorate in drinking water [1]. The source of most contamination has been facilities that manufacture or use perchlorate-containing rocket fuel. However, recent work shows that traces of perchlorate can be found in rain and snow and can be created in lab experiments simulating tropospheric processes. This suggests that there is a natural flux of atmospheric perchlorate to the earth and a natural perchlorate level. Once again, nature mimics industry.(21)

Brominated organic chemicals are used as flame-retardants for electronics, furniture, and textiles. They have been found throughout the environment, accumulating in fish and marine animals and sometimes detected in human breast milk. Some researchers suspect that these compounds may affect animal and human health, and several compounds have been banned.(22) Recent work at Woods Hole Oceanographic Institution (WHOI) debunks some of this. Researchers at WHOI have found that two chemicals accumulating in the tissues of marine animals and suspected to be manmade pollutants actually came from natural sources.(23)

The chemicals, methoxylated polybrominated diphenyl ethers or MeO-BDEs, found in whale blubber, raise questions about the accumulation of both natural and industrial compounds in marine life and is causing researchers to rethink the sources and fates of many chemical compounds in the environment. Michal Raucher reports [2], "This discovery is significant because environmental activists have been sending scary messages about the dangers of all the chemicals in our clothing, furniture, and pesticides from human-produced sources. Their intimidating statements urge us to stop using certain chemicals because they accumulate in humans, animals, and the food we eat and air we breathe -- but scientists are discovering that the chemicals found in wildlife are of natural origin."(24)

How were the chemicals found? The researchers used a mass spectrometry facility at Woods Hole that does precision carbon dating. They took advantage of the fact that natural sources have a detectable radiocarbon signal while human produced sources from petrochemicals do not.(23) This is another example of advances in analytical techniques that are helping find chemicals previously impossible to analyze. Says Gordon Gribble of Dartmouth College, "This radiation technique is very exciting. There's been no other way to distinguish the origin of the same compounds that are produced by both nature and man."(22)

Summary

Note the dates on the references discussed in this article. These are all very recent findings.

Remember this next time you hear about how we humans are adding pollutants to the atmosphere. Mother Nature is providing a lot of help, and as time goes on we're finding she's not an innocent bystander watching us create havoc with our environment.

For decades, environmental groups have said that nature would never make brominated compounds or other halogenated chemicals. But in recent years these compounds have been found in forest fires, volcanic ash, soil, peat bogs, and myriad marine organisms. This is one examples of nature mimicking industry, and there are many more. Vinyl chloride, dioxins, volatile halogenated organic compounds, and perchlorates are formed in nature, and nitrates from sea water and bedrock have now been shown to be significant sources adding to the increasing amounts of nitrates observed. These recent results influence regulatory work, making it impossible to assign elevated concentrations purely to industrial sources. Instead of setting demands on manmade contributions to the environment with the goal of eliminating or minimizing various chemicals, it would be necessary to distinguish natural background from anthropogenic pollution. And with the passage of time and with improved analytical techniques this is a moving target.

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