Fact or Fiction?

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Mother Nature's Surprising Pollutants

"Whales Contain Natural 'Flame Retardant' After All"[1]

Researchers at the Woods Hole Oceanographic Institution (WHOI) have found that two chemicals accumulating in the tissues of marine animals and suspected to be manmade pollutants actually came from natural sources.[2]

Brominated organic chemicals are used as flame retardants for electronics, furniture, and textiles. In recent years, 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.[3]

The recent work at WHOI debunks some of this. 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, "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."[1]

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.[2] 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."[3]

More Examples

Here are some other examples of natural sources mimicking industry. Human made chemical compounds called organohalogens get loads of attention since they are best known for their often harmful effects on the environment. This includes substances like the CFCs (the ozone damaging chemicals), dioxin (found in the herbicide Agent Orange), PCBs (industrial fluids) and several pesticides. Their naturally occurring cousins, however, don't get the recognition they deserve, says Gordon Gribble . Yet, with the passing of time we are finding more and more of these chemicals and others in nature.[4]

Vinyl chloride, a highly reactive and toxic substance widely used in industry, was thought to be exclusively man-made, or the degradation of other anthropogenic substances, such as trichloroethylene and tetrachloroethylene. Not so 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 man-made 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."[5]

Environmentalists have also claimed that dioxins are man-made chemicals. And, again, this is not so. R.R. Bumb and his colleagues found dioxins in soot from wood burning ovens.[6] Przemyslaw Mastalerz says this about the Bumb *et al*. research: "This report is of fundamental importance because from the presence of dioxins among the products of wood combustion there immediately follows that the dioxins were present on Earth from the first fire of forests or grasslands."[7] Can't blame man for dioxins in 40 million year old clay deposits since he wasn't around at the time.[8]

Mastalerz adds, "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 100 kg to 3,000 kg 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."[9]

Medical and municipal waste incineration, plus pulp and paper processing had been thought to be the source of most manmade dioxide emissions. However, an EPA study issued in January 2000 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.[10]

In 2002, Pirjo Isosaari and his colleagues found dioxins in sediments that were over 8000 years old in a lake in Finland. An added interesting result of this work was that besides dioxins, these researchers also found PCBs. 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.[11] However, natural sources of PCBs may not be as far-fetched as it seems at first blush. In a column titled "Nature's New Chemical," published in September 2001, I reported that researchers in Canada had discovered an unusual brominated and chlorinated chemical that behaved like PCBs. 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.[12] Now here's another possible Mother Nature source of PCBs.

It's doubtful that these facts published in reputable scientific journals will stop activists from claiming that dioxins are exclusively man-made. Even some folks in the scientific community continue the charade. A paper by Signorini and colleagues, published in 2000, is a good example. They referred to dioxins as man-made chemicals.[13]

Another claim by activists is that dioxin is more toxic than other man-made poisons. Its a false claim. Nobody ever died of dioxin poisoning, not even Viktor Yushchenko, the Ukranian politician who was given a high dose of dioxin in a failed attempt to remove him from the political scene. The would-be assassins must have been reading claims from activists and took them at face value.[14]

Peat bogs are a vast natural reservoir of organic carbon. Fred Pearce notes that by one estimate, the bogs of Europe, Siberia and North America hold the equivalent of 70 years of global industrial emissions. Dissolved organic carbon emissions from these bogs and rivers could be as big a source of CO_2 to the atmosphere as burning fossils fuels.[15]

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.[16] 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 10 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."[17] 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.[18]

Volatile halogenated organic compounds (VHOC) contribute to stratospheric ozone depletion. Besides man-made contributions, its becoming more evident that halogenated compounds of natural origin can also 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. 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 Fe. 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 the budget of the important atmospheric compounds CH_3Cl, CH_3Br, and CH_3I."[19]

Isoprene is a volatile organic compound that is emitted in large quantities by forest vegetation. Its annual emission is estimated to be 500 million tons worldwide. But, although isoprene readily oxidizes to form volatile products, popular wisdom held that it didn't form products that could contribute to aerosol particle formation. (Aerosols are small particles such as soot, dust, and smoke that can influence the structure of marine stratus clouds, thus influencing rainfall and temperature.) Intensive measurements over the Amazon Basin, however, revealed the presence of two novel methyltetrol compounds. These compounds are formed in the atmosphere through reaction of isoprene with hydroxyl radicals. It's estimated that the photooxidation of isoprene results in an annual production of about two million tons of the new compounds. This represents between 5 and 25% of the organic aerosol formed by atmospheric photochemistry from biogenic precursors.[20]

One last item relates to perchlorates. In recent years controversy has swirled around estimates of the health risks posed by perchlorate in drinking water. 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]

Summary

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. These are some examples of earth mimicking industry. Numerous other examples are presented in this article as well as one published in July 2004.[22]

The fact that vinyl chloride, dioxins, volatile halogenated organic compounds, and perchlorates are formed in nature could influence regulatory work, making it impossible to assign elevated concentrations purely to industrial sources. Instead of setting demands on man-made contributions to the environment with the goal of eliminating or minimizing various chemicals, it would be essential to distinguish natural background from anthropogenic pollution. And with the passage of time and with improved analytical techniques this is a moving target. ***P&SF***

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In *Memoriam*

Marshal "Marsh" Whitehurst (by Jill Robbins)
Marshal Whitehurst, 85, a former chemical engineer at RCA Records, passed away on January 19, 2006. He was a chemical engineer in the RCA electroplating department in Indianapolis, IN, from 1946 to 1981.

His work at RCA improved the quality of the plating process to produce audio records and, later, video discs. Ralph Fox, a co-worker, recalls: "Marsh spent endless hours on a binocular microscope looking at the miles of grooves on a master to find out where a problem had occurred." Whitehurst's methodical attention to detail and problem-solving ability was a very important contribution to the quality of records that RCA was able to produce. The company produced records more rapidly and of a higher quality than any of its competitors. In fact, some competitors had their records pressed by RCA before putting their own labels on them.

Whitehurst's efforts were key to developing the nickel electroforming process used to produce stampers for pressing the video discs that RCA began developing in the early 70s. Fox says, "Marsh found a way to eliminate the tiny pockets (of occluded hydrogen) in the deposited copper that would form at the bottom of a groove." (U.S. Patent #4,316,778)

Robert Huck, another colleague, said: "Marsh was instrumental in moving the technology from the audio recording industry to the manufacture of the video disc. The grooves were a hundred times smaller so it required a higher level of cleanliness and better solutions. He helped develop the amorphous copper substrate used in producing RCA's CED video disc masters in the mid 1970s. The first electro-mechanical recording in a metal substrate (copper), a significant process enhancement, was made in March 1974. The electroplating process for producing the amorphous copper substrate used in the mechanical recording was developed by Marshal Whitehurst."

RCA co-worker Joann Fox remembers Whitehurst's willingness to tackle any problem. "Every time one of the managers was given a farewell party, Marsh would gold-plate something for him," she said. "Once he was asked to gold-plate a toilet seat—and he did it."

After retiring, Whitehurst helped others in a number of ways, such as helping to maintain a drop-in center for inner-city youth operated by an area youth ministry. He also helped to build and maintain food pantries for The Sharing Place, an outreach of Lutheran Child and Family Services. He also tutored local students who were struggling with math and science, and taught plating courses at Ivy Tech Community College.

Among numerous awards presented to Whitehurst, he received the "Living Saint" award from Lutheran Child and Family Services and a "Thousand Points of Light" award presented by former President George H.W. Bush.

Edwin James Smith
Edwin James Smith, 88, died December 23, 2005, at the Carolina Meadows Health Center following a long illness.

Before he retired to North Carolina, he lived in Weirton, WV, where he was vice president for National Steel Corporation Research and Development, Pittsburgh, PA. He was a former National President of the AESF (1974–75), and a member of the American Institute of Chemical Engineers and American Iron and Steel Institute. He held a professional degree in Metallurgical Engineering from the University of Cincinnati.

Lewis Midgley Walker
Lewis Midgley Walker, 88, of James Island, SC, died January 8, 2006, at Roper Hospital in Charleston following a long illness. A retired U.S. Navy Commander, he was founder, president and CEO of Roll Technology Corporation, Greenville, SC, from 1972 to 1986. He served as chairman of the board from 1986 to 1992. A veteran of World War II, he began a career in metal finishing with Chromium Corporation of American in Waterbury CT. He was president of U.S. Metal Coatings Company in Middlesex, NJ, from 1952 to 1968. He served on the boards of the Greenville Chamber of Commerce, the National Association of Metal Finishers (NAMF), the Alliance for Quality Education, the Palmetto Branch of AESF, and he Southeastern Association of Metal Finishers. He was the recipient of several professional awards, including the Award of Merit from NAMF.

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