Anthropogenic Geochemistry

(1) Local – Regional – Global scale emissions

(2) Types of emissions:

- solid waste
- liquid waste
- acid mine drainage
- volatile emissions
- fine particle emissions to the atmosphere
- “natural pollution”,

e.g. arsenic in Bangladesh well waters.

3) Regional and global scale anthropogenic emissions. some elements of particular interest:

- Lead (Pb): globally, the most anthropogenically enhanced element; emitted to the atmosphere by high temperature industrial processes (smelting, coal combustion, etc.) and by automobiles using leaded gasoline.

- Mercury (Hg): one of the most volatile toxic elements; emitted from high temperature industrial activities (similar to lead); exists in toxic organic mercury compounds. Also used in industrial processing and gold mining, released into natural waters. Mercury is high in fish in lakes located downwind of coal combustion regions. It bioaccumulates in predatory fish such as salmon and swordfish.

Hg, continued: “Minamata Bay Disease” from industrial mercury release into a fished harbor is one of the most infamous pollution episodes. Minamata is a small town in Japan facing an ocean embayment. From 1932 to 1968, a company dumped approximately 27 tons of mercury compounds into the bay. Thousands of people who ate fish from the bay developed symptoms of methyl mercury poisoning.

• Cadmium (Cd): also volatile and used in industrial activities (Ni-Cd batteries; Cd-plated metals, etc.). “Itai-Itai” disease is perhaps the second most infamous pollution episodes. In the early years of the 20th century, villagers along the Jinzu River basin in Japan developed a painful disease that was dubbed “Itai-Itai” (“it hurts, it hurts”). Research didn’t begin until the 1950s when and in May 1968 it was determined that it was due to chronic cadmium poisoning caused by commercial mining operations. It impairs kidney function and leads to calcium deficiency and brittle bones.

Toxic metal found in kids' jewelry very dangerous

By JUSTIN PRITCHARD

The Associated Press

Sunday, January 10, 2010; 2:26 PM

-- Cadmium is a soft, whitish metal that occurs naturally in soil. It's perhaps best known as one half of rechargeable nickel-cadmium batteries, but also is used in pigments, electroplating and plastic.

Lab testing organized by The Associated Press shows that it also is present in children's jewelry - sometimes at eye-popping levels exceeding 90 percent of the item's total weight.

Most people get a microscopic dose of the heavy metal just by breathing and eating. Plants, including tobacco, take up cadmium through their roots and people absorb it during digestion or inhalation. Without direct exposure, however, people usually don't experience its nasty side: cancer, kidneys that leak vital protein, bones that spontaneously snap.

Cadmium is particularly dangerous for children because growing bodies readily absorb substances, and cadmium accumulates in the kidneys for decades.

"Just small amounts of chemicals may radically alter development," said Dr. Robert O. Wright, a professor at Harvard University's medical school and school of public health. "I can't even fathom why anyone would allow for even a small amount to be accessible."

Recent research by Wright found that as cadmium exposure increased, kids were more likely to report learning disabilities.

Dr. Aimin Chen of the University of Cincinnati's medical school also has studied how cadmium affects young brains. While lead is the heavy metal most associated with harming cognitive development, Chen has concluded that cadmium lowers IQ even more than lead - though cadmium isn't harming the average American child because the typical exposure is not as large as lead.

Scientists don't know how much cadmium it takes to kill a child. The only child's death attributed to cadmium that AP found was a nearly 3-year-old boy from Toronto. According to a case study published in 1994, an autopsy showed his brain had swollen; the researchers concluded his exposure came from items around his home such as paint pigments, batteries or cadmium-electroplated utensils.

• Nitrogen – as NO_3^-, usually from fertilizers. Too much nitrate in waters damages infant's brain development. It also can lead to "eutrophication" of coastal seawaters (e.g. Gulf of Mexico "dead zone").

• Phosphorus – as PO_4^{3-} usually from fertilizers now (although also from detergents in the past). Can lead to "eutrophication" of lakes and rivers.

• Selenium - Human selenosis at the population level is rare and is generally related to excesses from food rather than from drinking water. It has been reported from China and Venezuela where selenium-rich food is grown and consumed locally (Tan, 1989; WHO, 1996). Cancers of the skin and pancreas have been attributed to high selenium intake (Vinceti et al., 1998). Selenium sulfide is used in antidandruff shampoos and is potentially carcinogenic but is not absorbed through the skin unless there are lesions (WHO, 1987). Selenium toxicity can lead to hair and nail loss and disruption of the nervous and digestive systems in humans and to alkali disease in animals. Chronic selenosis in animals is not common but has been reported from parts of Australia, China, Ireland, Israel, Russia, South Africa, USA, and Venezuela (Oldfield, 1999). Liver damage is a feature of chronic selenosis in animals (WHO, 1987). Source: Plant, J. A., Kinniburgh, D. G., Smedley, P. L., Fordyce, F. M. & Klinck, B. A. in Treatise on Geochemistry Vol. 9 (eds. Holland, H. D. & Turekian, K. K.) (Elsevier, Amsterdam, 2004).

Kesterson Reservoir, Central California

One of the best-documented cases of selenium toxicity in animals occurred at Kesterson Reservoir, California, USA (Jacobs, 1989; Wu et al., 2000). Soil irrigation in the western San Joaquin Valley of California began in the late 1800s and accelerated, particularly in the 1930s – 1940s. Irrigation water was taken from both surface water and groundwater (Deverel and Fujii, 1988). During the 1970s, flow into the reservoir was mainly surface water, but over the period 1981 – 1986 almost all the inflow was from shallow agricultural drainage for which the reservoir acted as a set of evaporation ponds. This inflow contained 250 – 350 mg L selenium, mostly present as bioavailable selenate (Se(VI)). The primary source of the selenium is believed to have been pyrite in shales, particularly the Upper Cretaceous – Paleocene Moreno Shale and the Eocene – Oligocene Kreyenhagen Shale. Concentrations of selenium in these formations range up to 45 mg kg, median concentrations being 6.5 mg kg and 8.7 mg kg, respectively (Presser, 1994). The concentration of selenium in the surface sediments (0 – 0.3 m depth) of the old playas is in the range 1 – 20 mg kg reflecting the historical accumulation of selenium from the selenium-rich drain water. Deeper sediments typically contain much lower selenium concentrations of 0.1 – 1 mg kg (Tokunaga et al., 1994). Between 1983 and 1985, the USA Wildlife Service compared the biological impact of the high selenium in the Kesterson Reservoir region to that of the adjacent Volta Wildlife area, which was supplied with water containing normal selenium concentrations. The research showed that the high concentrations of selenium in the irrigation waters were having a detrimental effect on the health of fish and wildlife (Tokunaga et al., 1994). Health effects on birds in the Kesterson Reservoir area were very marked. Twenty-two percent of the eggs contained dead or deformed embryos. The developmental deformities included missing or abnormal eyes, beaks, wings, legs, and feet as well as hydrocephaly. It has been estimated that at least 1,000 adult and young birds died between 1983 and 1985 as a result of consuming plants and fish containing 12 – 120 times the normal amount of selenium. No overt adverse health effects were noted in reptile or mammalian species, but the concentrations of selenium present were of concern in terms of bioaccumulation through the food chain.

- Source: Plant, J. A., Kinniburgh, D. G., Smedley, P. L., Fordyce, F. M. & Klinck, B. A. in Treatise on Geochemistry Vol. 9 (eds. Holland, H. D. & Turekian, K. K.) (Elsevier, Amsterdam, 2004).

Acid Mine Drainage

- Pyrite oxidation:

$$2\ FeS_2 + {}^{15}/_{2}\ O_2 + 4\ H_2O \dashrightarrow Fe_2O_3 + 4\ SO_4^{=} + 8\ H^+$$

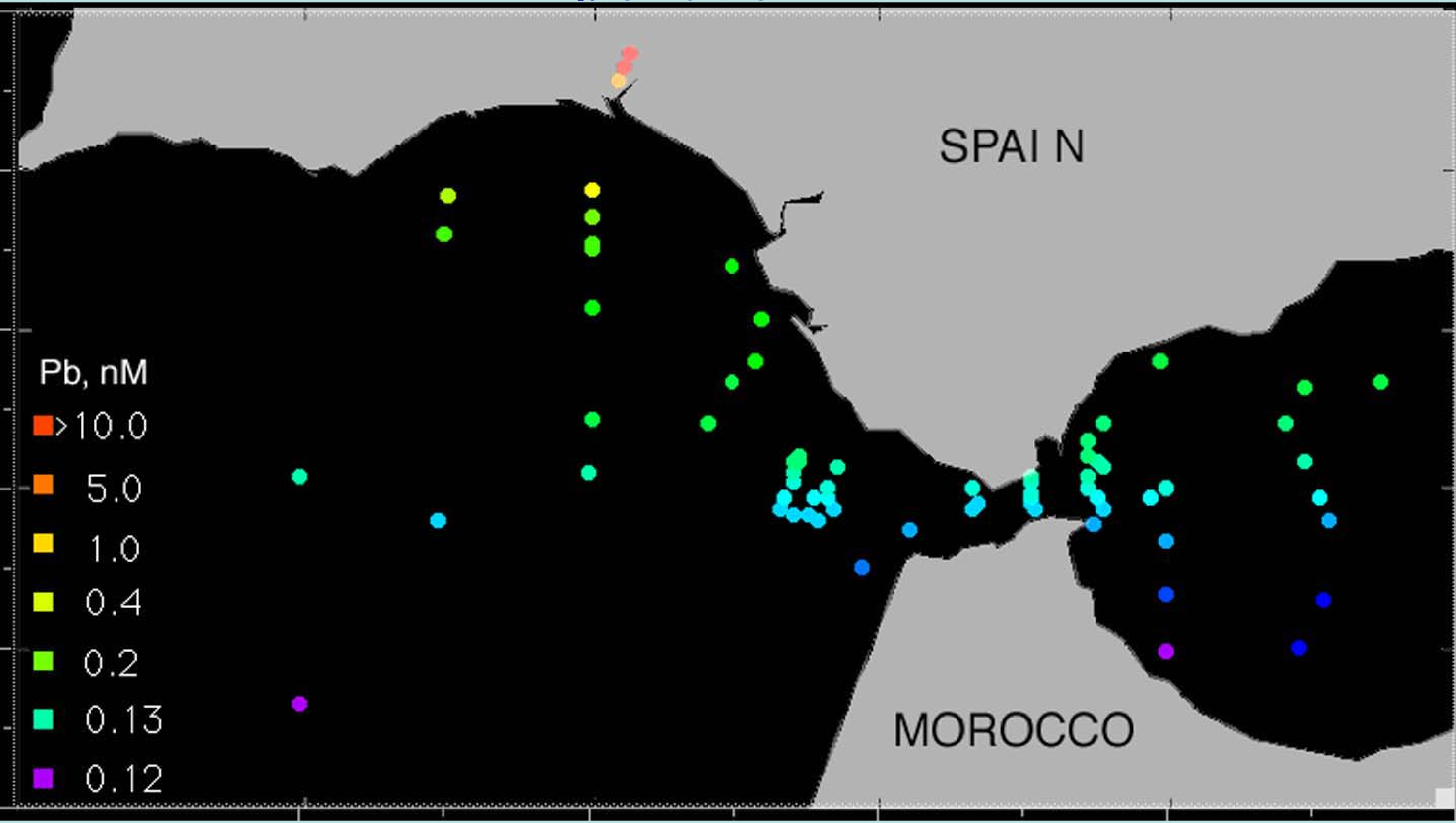
- Sulfide ores are common sources of Fe, Zn, Cd, and H2SO4. Coal deposits often contain sulfide minerals, so acid mine drainage commonly affects both sulfide ore and coal tailings (the waste leftover after mining).

- Acidic waters are in themselves damaging to organisms (e.g. fish do not live in low-pH waters, perhaps because of enhanced aluminum solubility at low pH). The low pH can also mobilize toxic trace metals such as Cd, As, and Pb.

- Example: Rio Tinto mining complex (Spain): drains into pH ~ 2 rivers that enter the Atlantic coastal waters of southern Spain having more than a millionfold more Zn than normal ocean surface waters, along with other metals such as Pb, Cd, and As. This effluent can be traced into the Mediterranean Sea.

Rio Tinto picture

Rio Tinto Pb pollution



The Global Anthropogenic Lead Experiment

- Lead is a volatile element and it is emitted by high temperature industrial activities (smelting, coal combustion, incineration, cement manufacture).
- Leaded gasoline utilization creates fine particles that the atmosphere transports to remote regions of the world.
- Most of the lead in the present ocean derives from human activities.
- Changes in the patterns of industrial and gasoline Pb emissions have led to time-dependent changes for oceanic lead during the past 180 years.

Anthropogenic Pb – how we use Pb and release it into the environment

- Automobile batteries
- Solder – electronics and pipe sealing
- Cathode ray tubes
- PVC stabilizer
- Wine bottle seals
- High temperature industrial activities (smelting, coal burning, etc.)
- Incineration

- "Tin" can solder seams
- Gasoline anti-knock compound
- House paint
- Water pipes

Health effects of lead

- Pb^{++} interferes with Ca^{++} biochemistry.
- Ca^{++} is used extensively in intra- and inter-cellular electrical messaging.
- At high levels, Pb causes extreme and permanent mental and physical damage.
- Damage to workers at tetraethyl Pb plant gave it the moniker “looney gas” (1924, Bayway New Jersey: 80% of staff die or suffer severe Pb poisoning).
- A study of the achievement, behavior, and baby tooth Pb content of children in Somerville MA (Needleman et al. 1979) showed a strong (negative) correlation between Pb and behavioral indices with no evidence of a threshold.
- Subsequent detailed medical and biochemical studies have elucidated the pathways of Pb’s effects on humans.

Clair Patterson and Lead

Geochimica et Cosmochimica Acta, 1956, Vol. 10, pp. 230 to 237. Pergamon Press Ltd., London

Age of meteorites and the earth

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(*Received* 23 *January* 1956)

Abstract—Within experimental error, meteorites have one age as determined by three independent radiometric methods. The most accurate method (Pb^{207}/Pb^{206}) gives an age of $4{\cdot}55 \pm 0{\cdot}07 \times 10^9$ yr. Using certain assumptions which are apparently justified, one can define the isotopic evolution of lead for any meteoritic body. It is found that earth lead meets the requirements of this definition. It is therefore believed that the age for the earth is the same as for meteorites. This is the time since the earth attained its present mass.

IT seems we now should admit that the age of the earth is known as accurately and with about as much confidence as the concentration of aluminium is known in the Westerly, Rhode Island granite.

Pb in Camp Century Greenland Ice Core

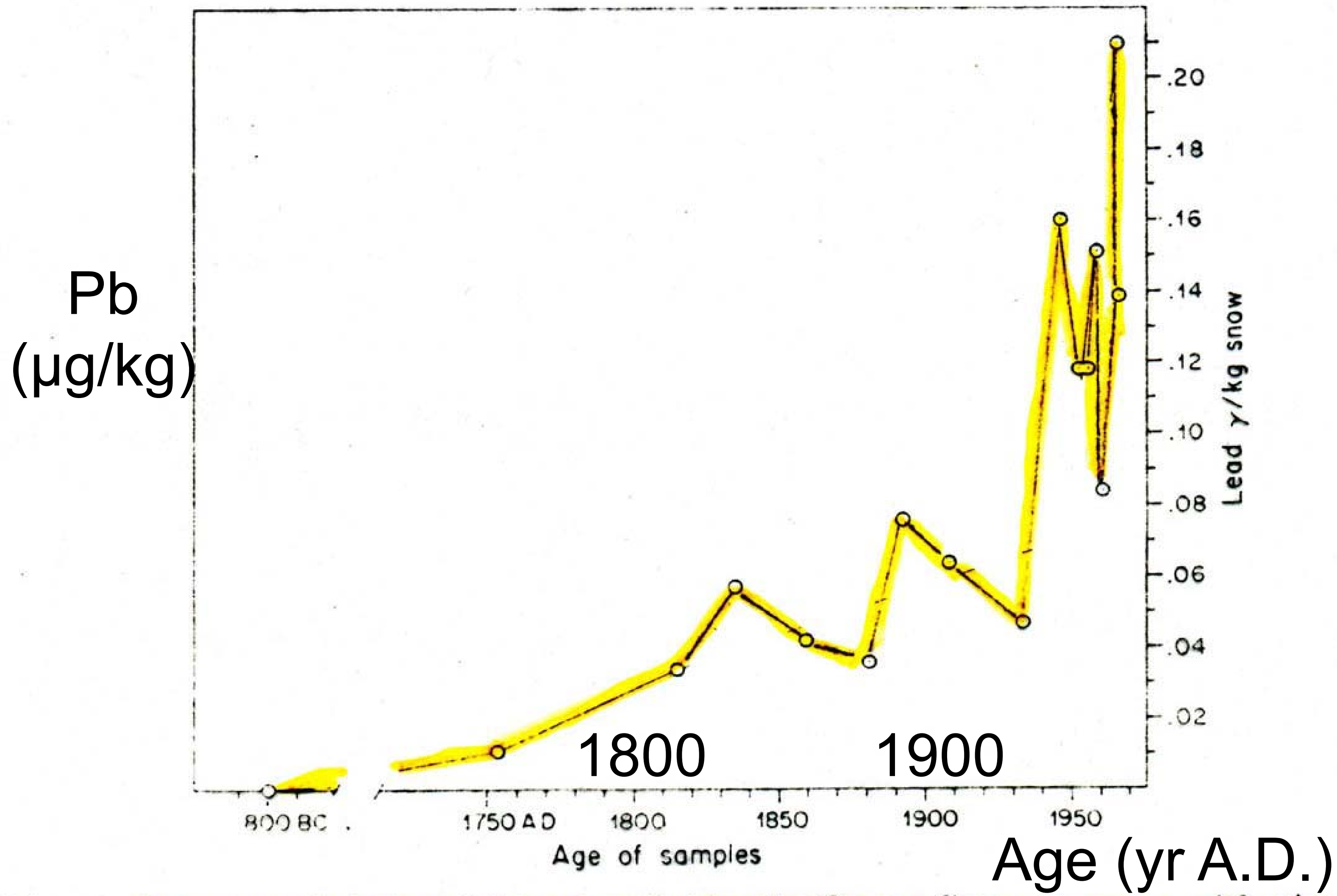

Fig. 6. Increase of industrial lead pollution in Camp Century snow with time since 800 BC. Scale adjusted so that height of lead value at 1753 AD is same as height of salt and dust values at 1753 AD in Fig. 4.

Murozumi, Chow, and Patterson, 1969

Pb in the human environment according to Patterson:

- Some of the uses of lead have increased Pb in air, food and water by orders of magnitude above prehistoric levels.
- Pb in ancient Peruvian bones is orders of magnitude lower than those of modern humans.
- Pb in (lead soldered) canned tuna fish is 10,000 times higher than tuna when they are caught.
- Modern nearshore marine sediments show much higher Pb concentrations than those deposited 100’s of years ago.
- Leaded gasoline and high temperature industrial activities have spread lead to remote regions. Human activities have increased the flux of lead into the earth surface environment by more than a factor of ten.
- The typical individual in the U.S. in the middle of the 20^{th} century was within an order of magnitude of demonstrated toxic levels.

Pb in the human environment according to the lead industry:

- Lead isn't a problem (except maybe at very extreme exposures).
- Patterson's data are wrong: Pb in food and water isn't any different than it was in pre-industrial times.
- Volcanoes and other natural sources emit plenty of lead. How could humans emit more than they do?
- Even if it is a problem, it isn't our fault.
- Can you prove it was my lead that caused your problem?

Other Pb industry responses to Patterson:

- Representatives of the Ethyl corporation, in Patterson's words, tried to "buy me out through research support that would yield results favorable to their cause."
- Instead of joining forces with Ethyl, Patterson delivered a lecture assailing the company's activities and predicting the demise of their TEL operation.
- Following these events, his longstanding contract with the Public Health Service was not renewed, nor was a substantial contract with the American Petroleum Institute.
- Members of the board of trustees at Cal Tech leaned on the chairman of his department to fire him. Others have alleged that Ethyl offered to endow a chair at Cal Tech if Patterson was sent packing.

(J. Kitman, The Nation, March 20, 2000)

August 31, 2005

A Back to School Warning: Children's Vinyl Lunch Boxes Can Contain Dangerous Levels of Lead

Oakland, CA – The Center for Environmental Health (CEH) announced it is filing lawsuits today against makers and retailers of soft vinyl lunch boxes that can expose children to harmful levels of lead. The Center has also notified several other companies of violations under California's toxics law Proposition 65 (Prop 65) for lunch boxes with high lead levels. The lawsuits and violation notices against companies including Toys "R" Us, Warner Brothers, DC Comics, Time Warner, Walgreens, and others involve many lunch boxes featuring beloved children's characters including Superman, Tweety Bird, Powerpuff Girls, and Hamtaro. The level of lead in one lunch box, an Angela Anaconda box made by Targus International, tested at 56,400 parts per million (ppm) of lead, more than 90 times the 600 ppm legal limit for lead in paint in children's products.

In most cases, the highest lead levels were found in the lining of lunch boxes, where lead could come into direct contact with food. Lead is known to be harmful to children even in minute amounts, as it can impair brain development and cause other behavioral and developmental problems. Children may be exposed to lead from lunch boxes when they eat food that has been stored in them. Handling the lunchboxes just before eating could also be an exposure risk.

It is not possible to tell by appearance whether a vinyl lunch box may contain lead, so CEH is advising parents to avoid vinyl lunch boxes altogether.

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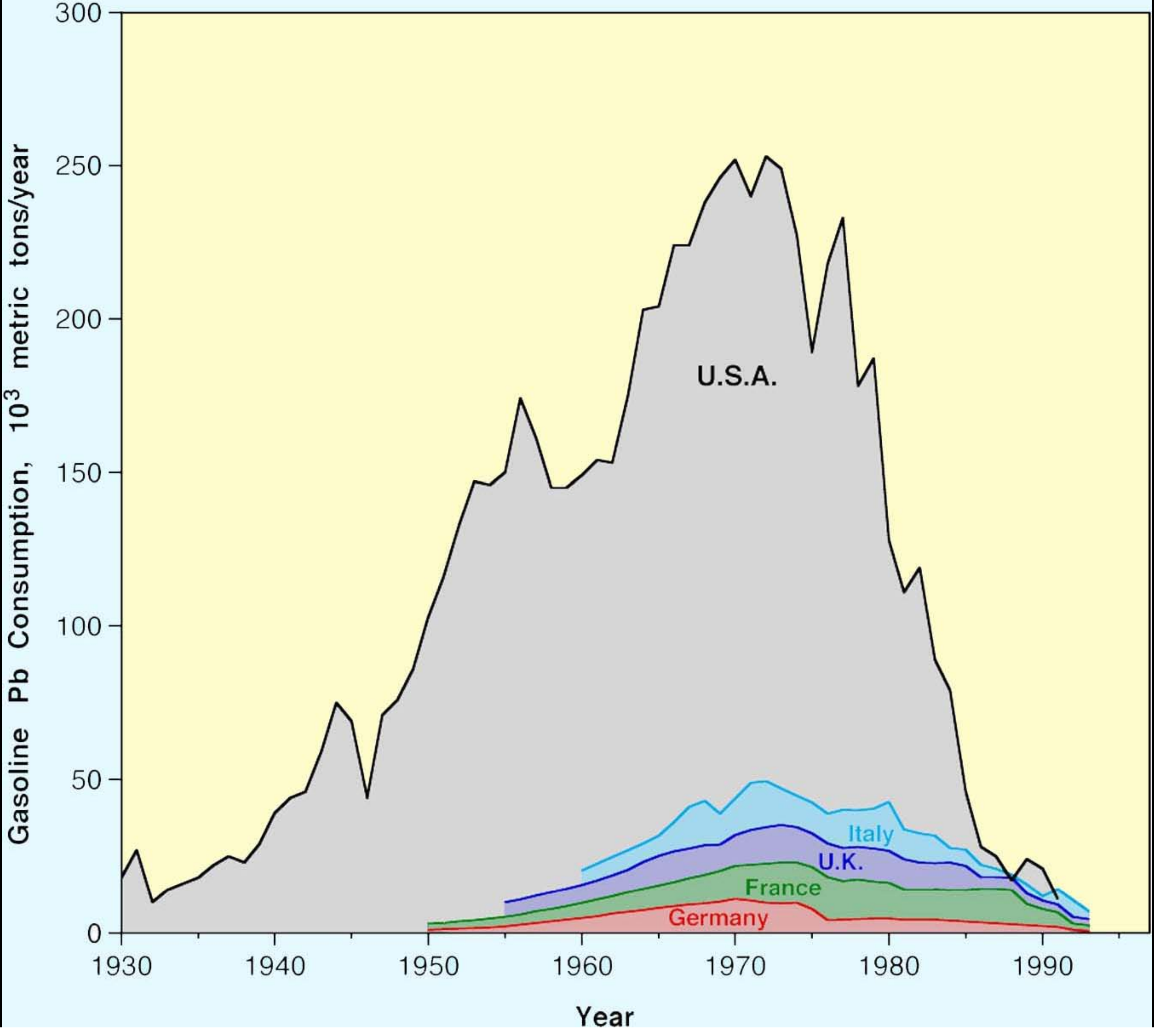
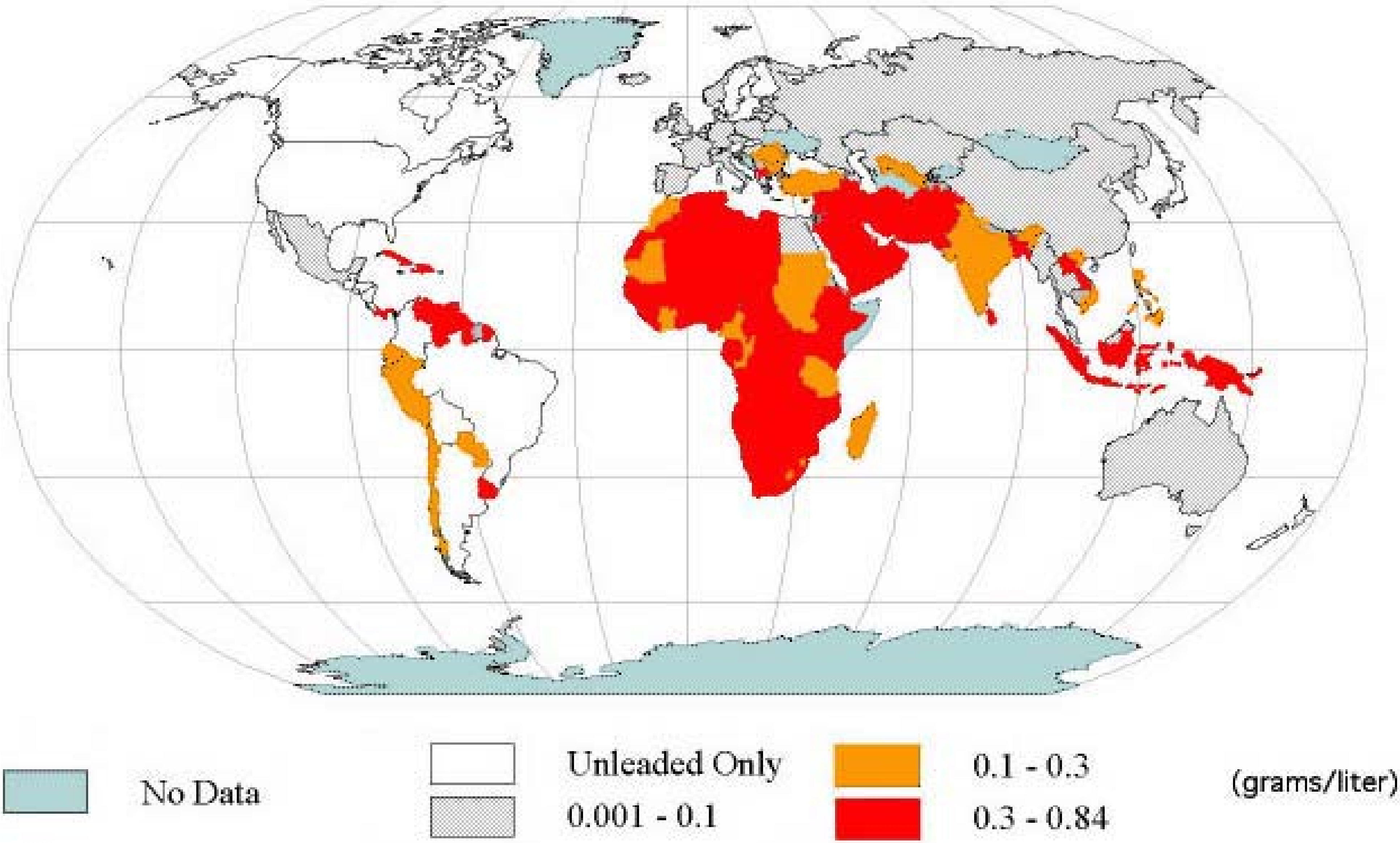
Figure 2. Flegal et al., 1983

US and European gasoline Pb consumption,1930-1993



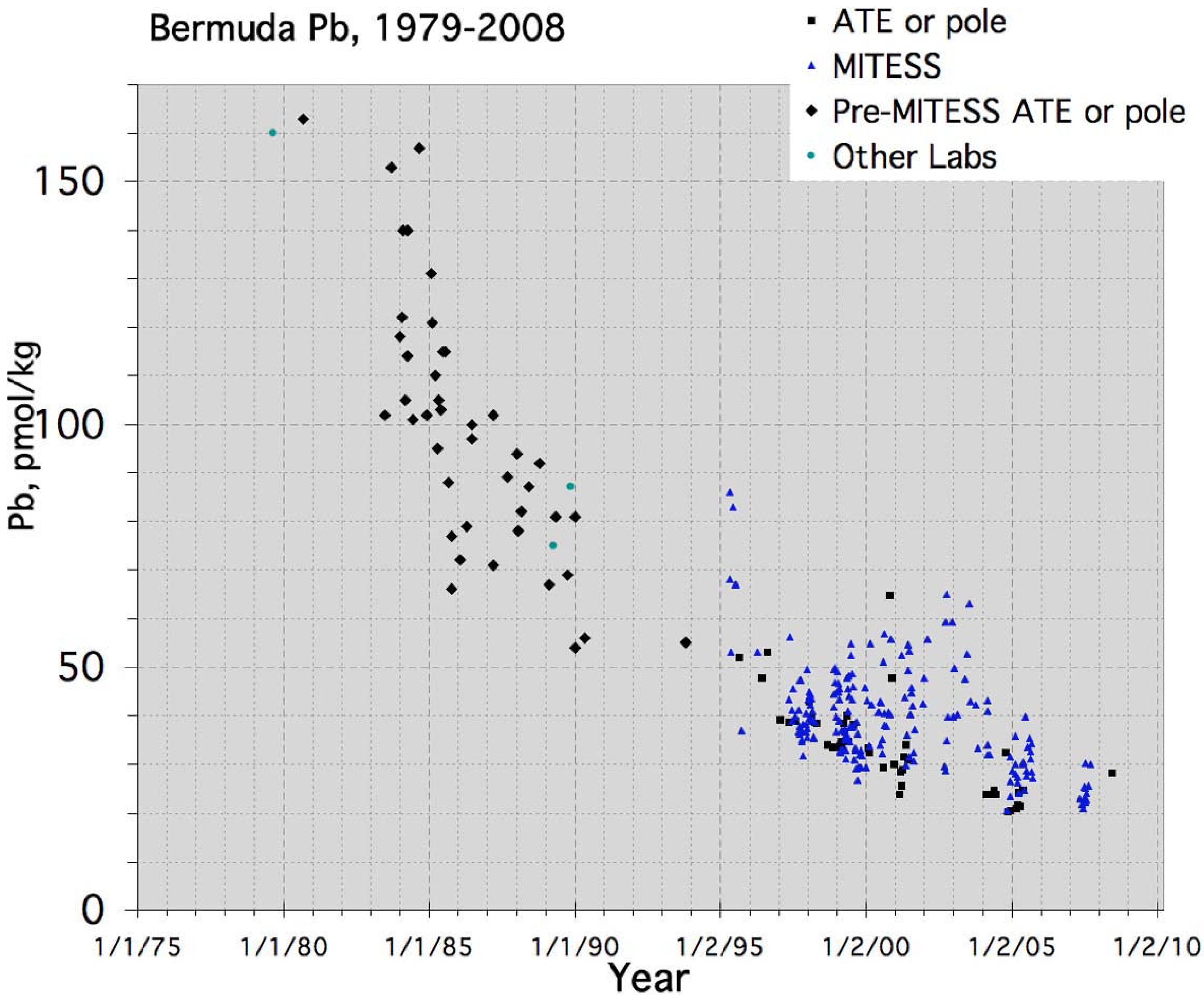


Concentration of lead in gasoline, 1995. Thomas and Kwong, Energy Policy

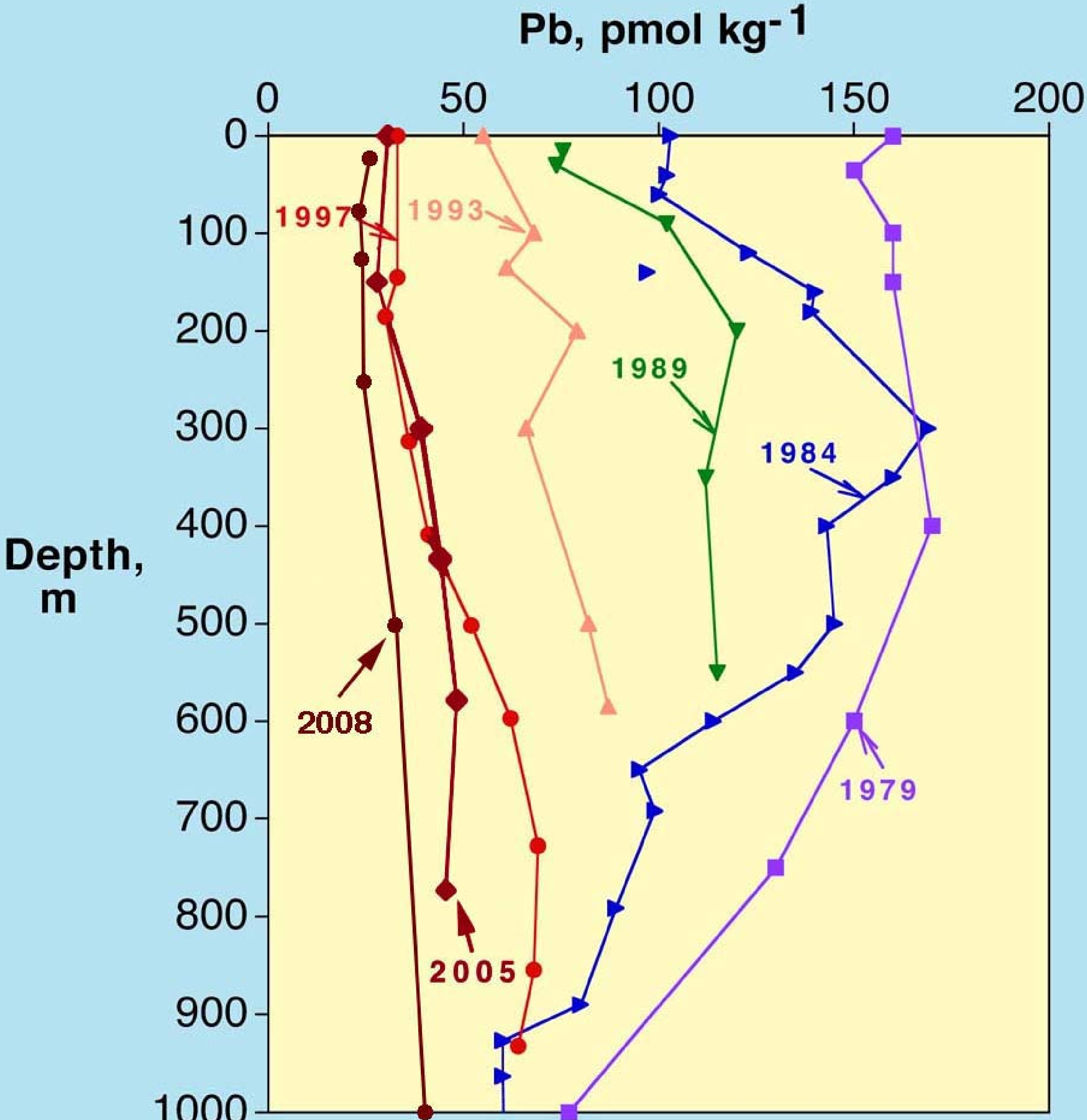
Global gas and Pb gas consumption, 1992

This image has been removed due to copyright restrictions.
Please see the pie charts showing global gas and Pb gas consumption in 1992.
Thomas, V. M. "The Elimination of Lead in Gasoline." *Ann Rev Energy Environ* 20 (1995): 301-24.

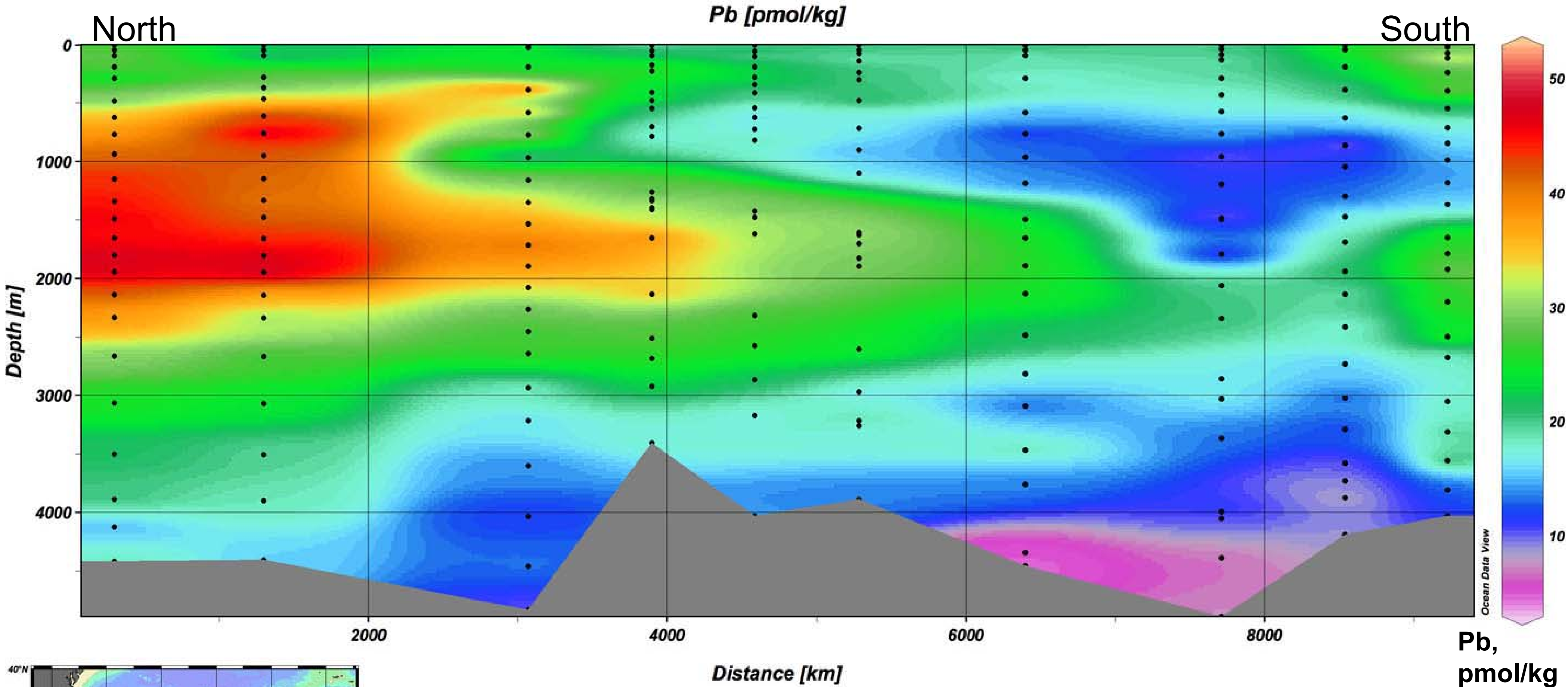
Surface Water Pb in the Western North Atlantic is still decreasing!

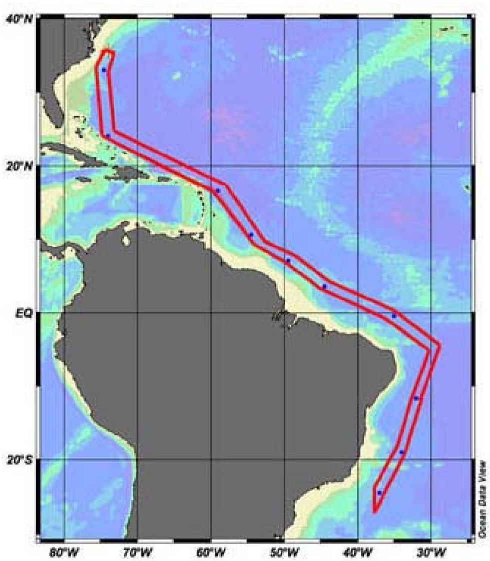


Lead Profiles near Bermuda, 1979-2008

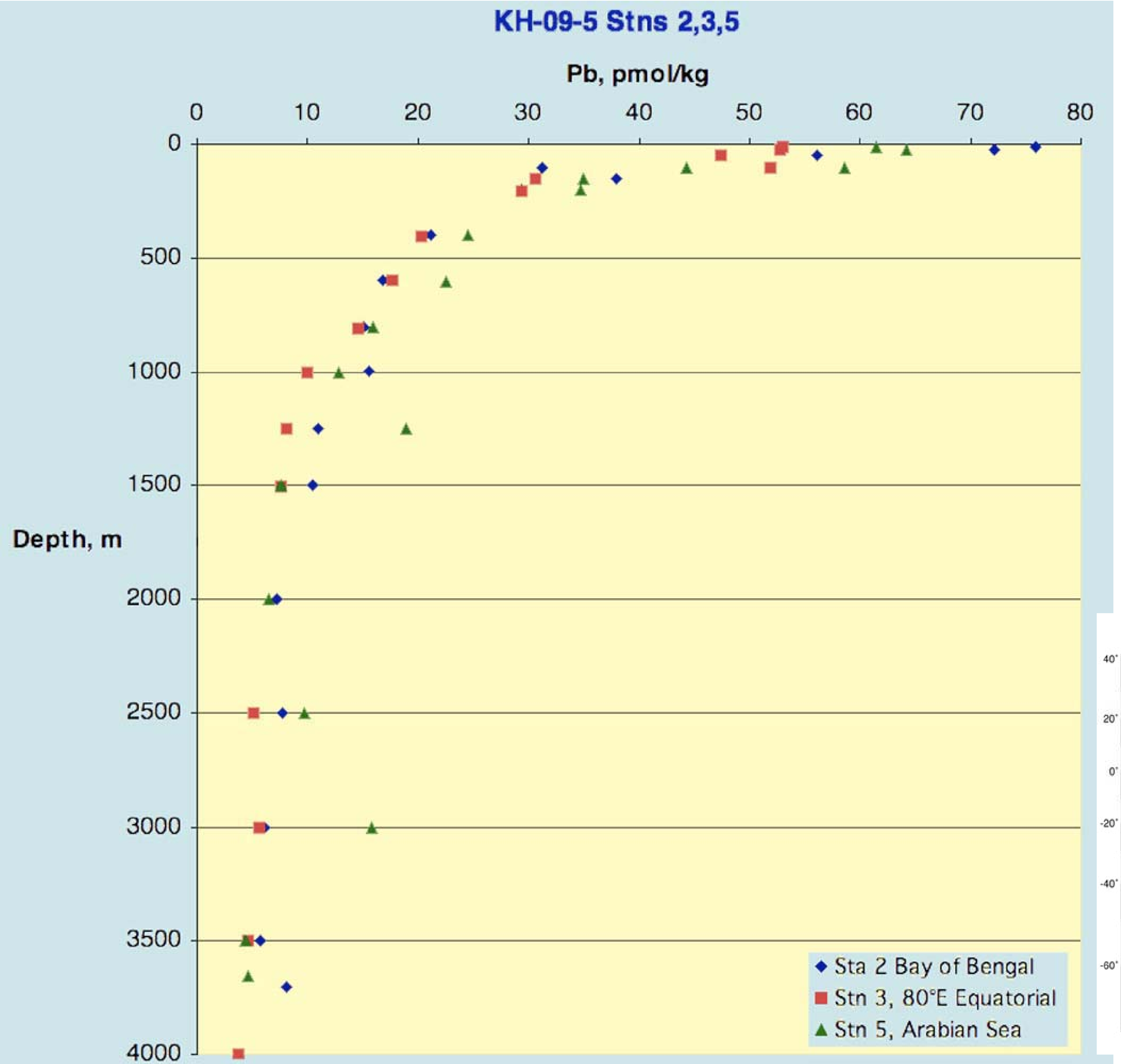


Meridional Pb section in the Western North Atlantic (2002, 2005)

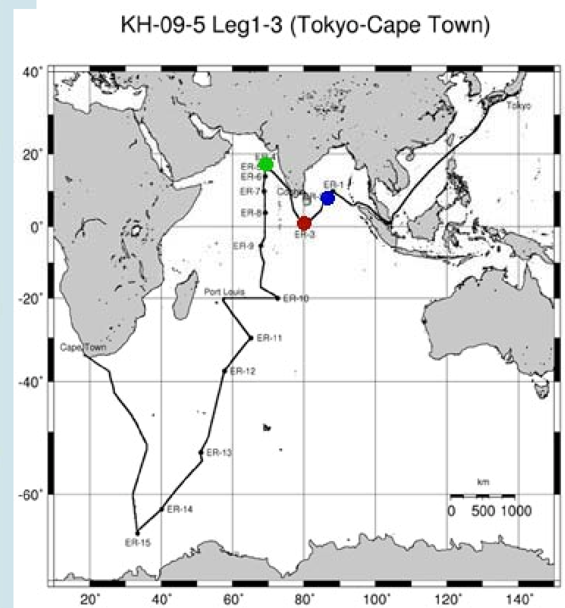




ODV graphics



Pb in the Indian Ocean, 2010



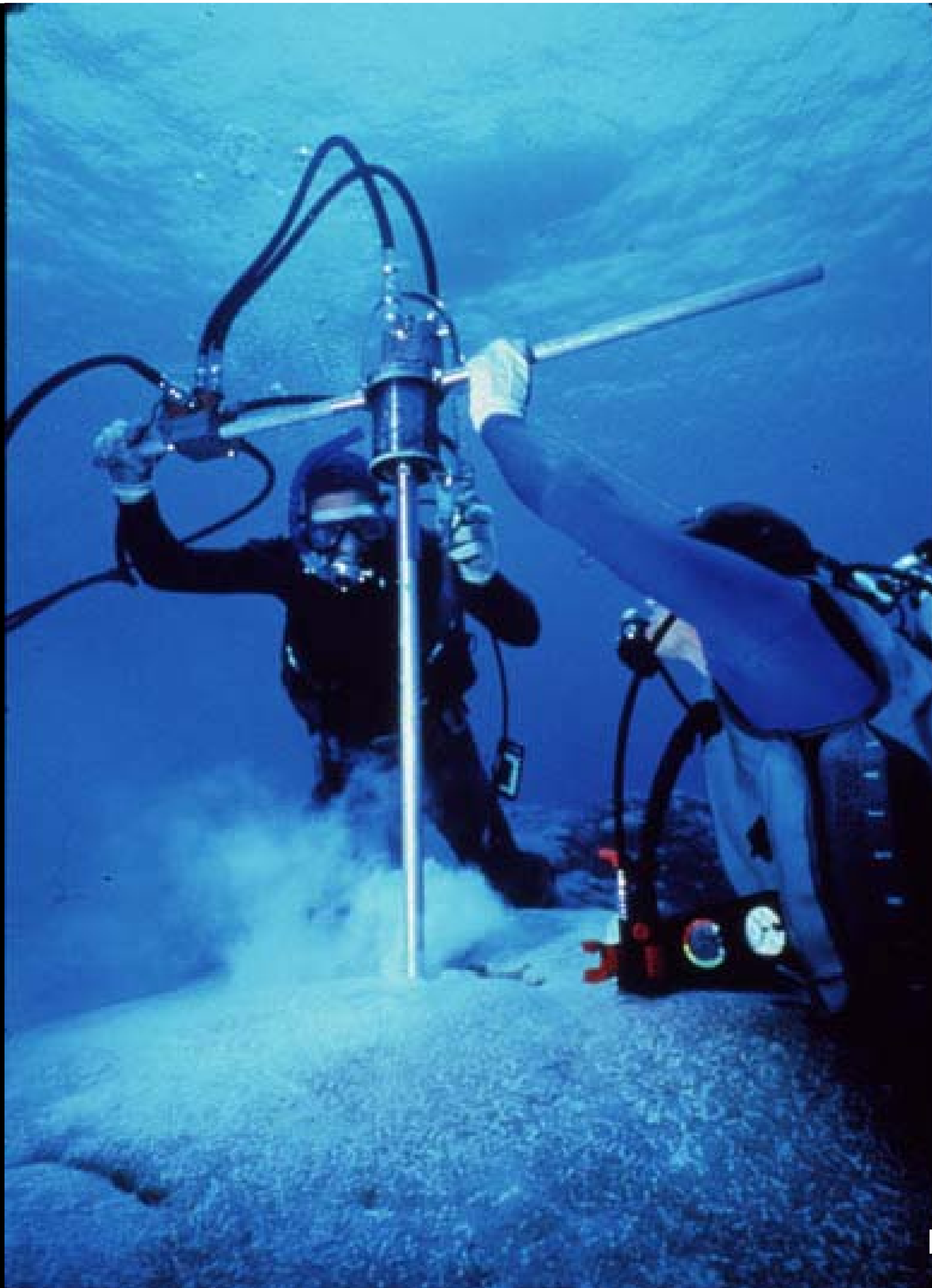
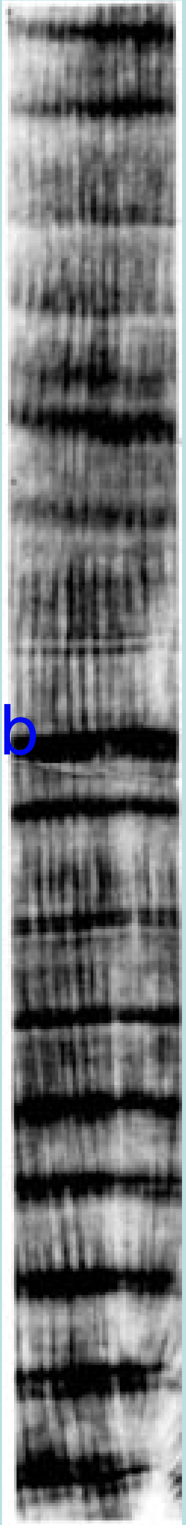
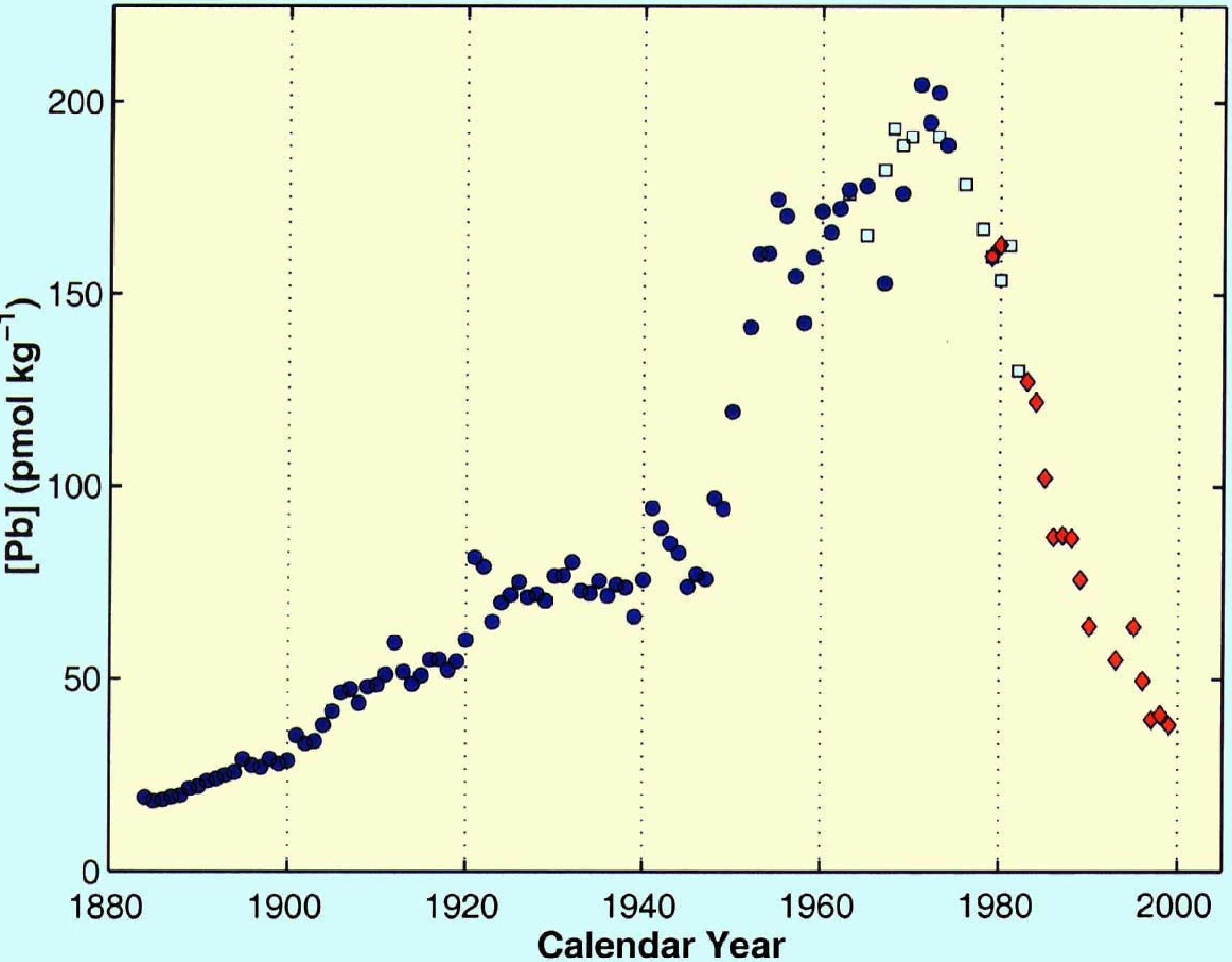


Image courtesy of NOAA.

x-ray image of a coral core slab



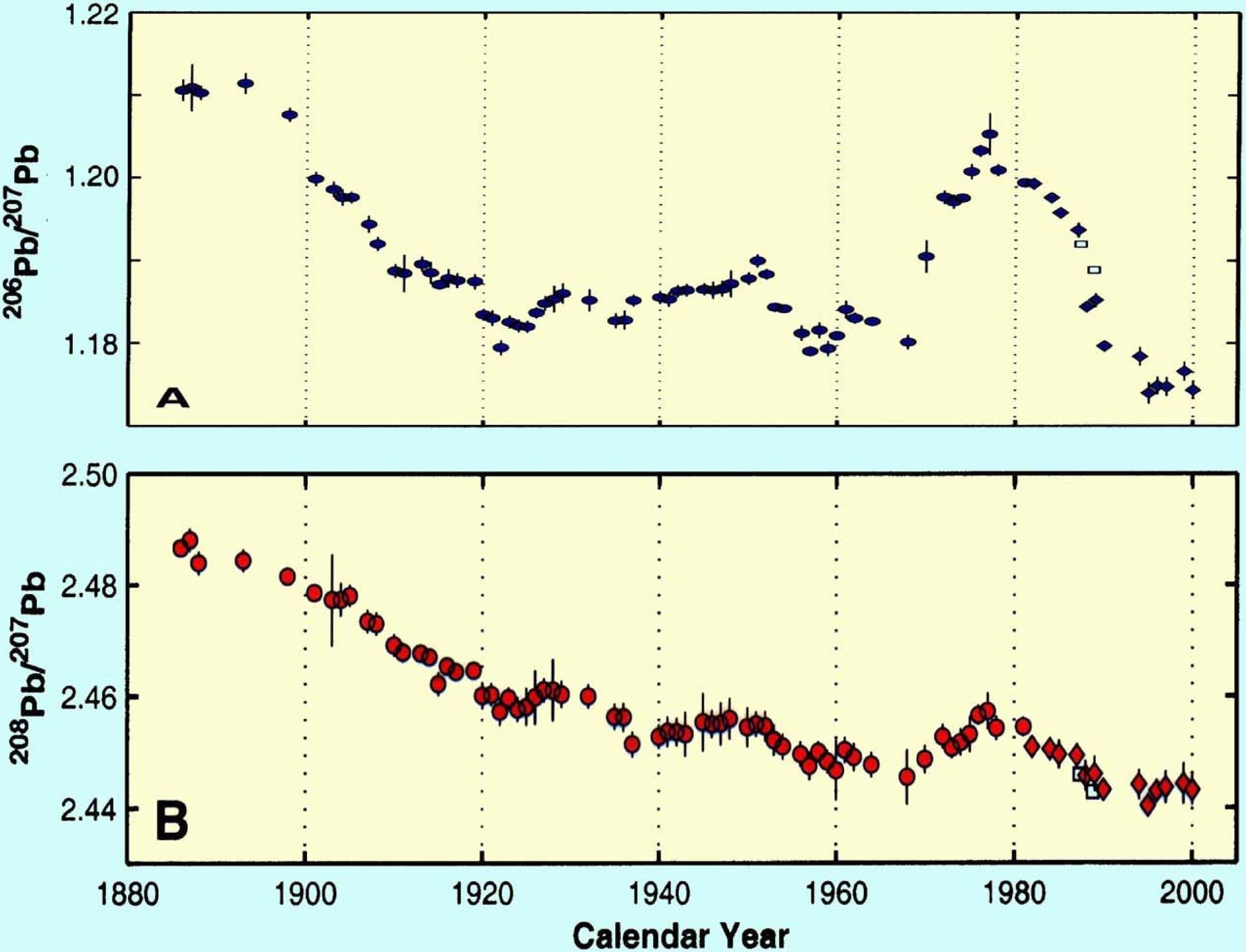
Western North Atlantic
Seawater Lead Reconstruction

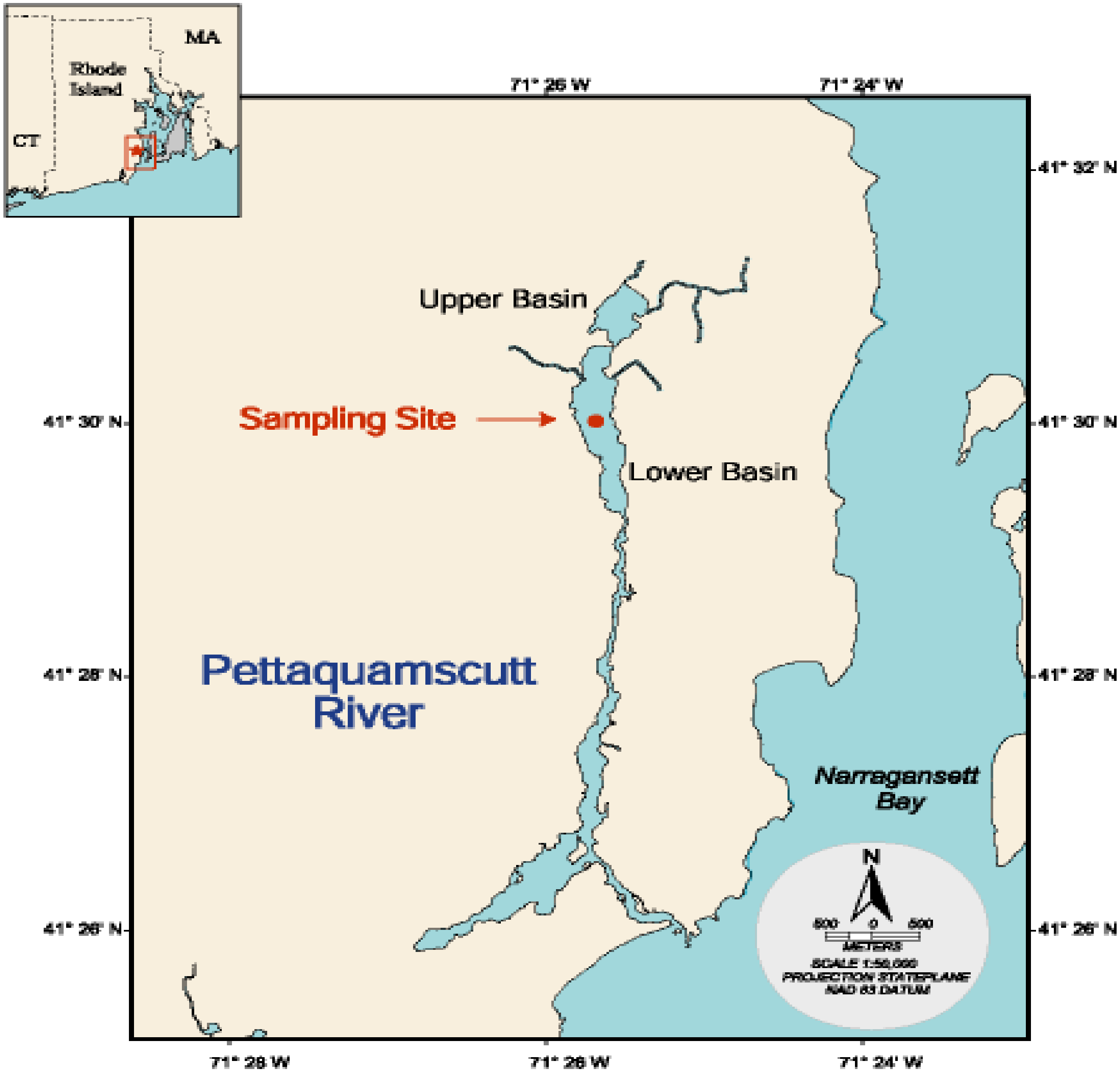


Pb isotopes

- ^{238}U => ^{206}Pb (24.1%)
- ^{235}U => ^{207}Pb (22.1%)
- ^{232}Th => ^{208}Pb (52.4%)
- Solar nebula => ^{204}Pb (1.4%)

Evolution of Pb isotopes in North Atlantic Surface waters 1880-2000

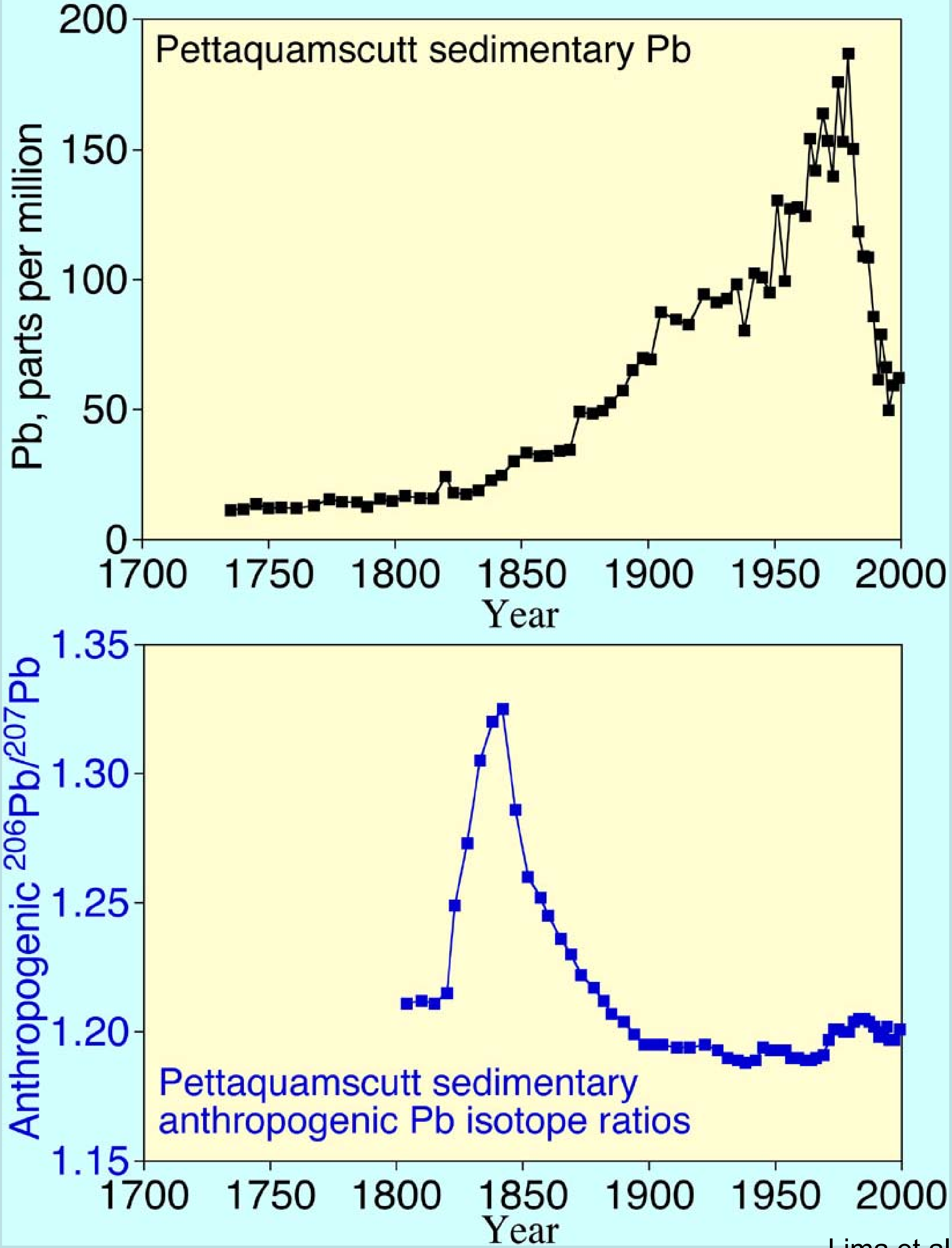




Lima et al. (2005)

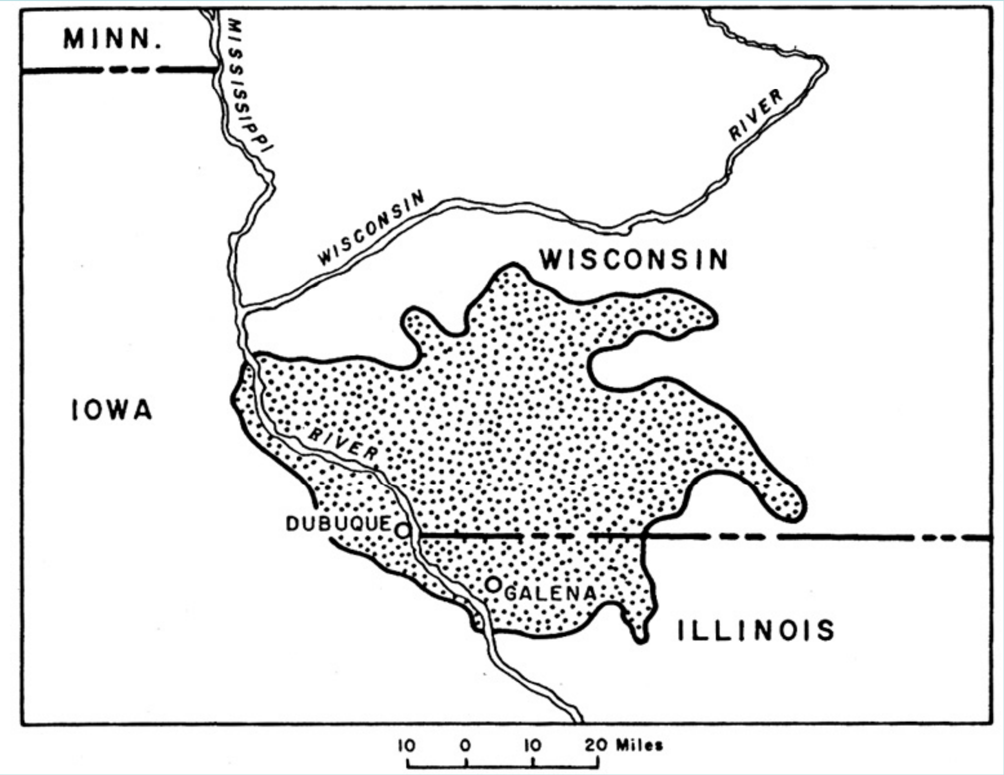
Anthropogenic Lead deposition in the Northeast U.S. (past 250 years)

Pettaquamscutt Estuary, Rhode Island, USA (near URI Graduate School of Oceanography): a permanently anoxic estuary with varved sediments (established by ^{137}Cs, ^{14}C, and ^{210}Pb: Lima, King, et al., Geochim. Cosmochim. Acta .)



Lima et al. (2005)

The Upper Mississippi Valley District dominated lead mining in the middle of the 19th century, because the ores were near the surface, were easily processed by 1-2 person operations (charcoal kilns), and were near appropriate transportation (Mississippi River system).



Prevailing winds

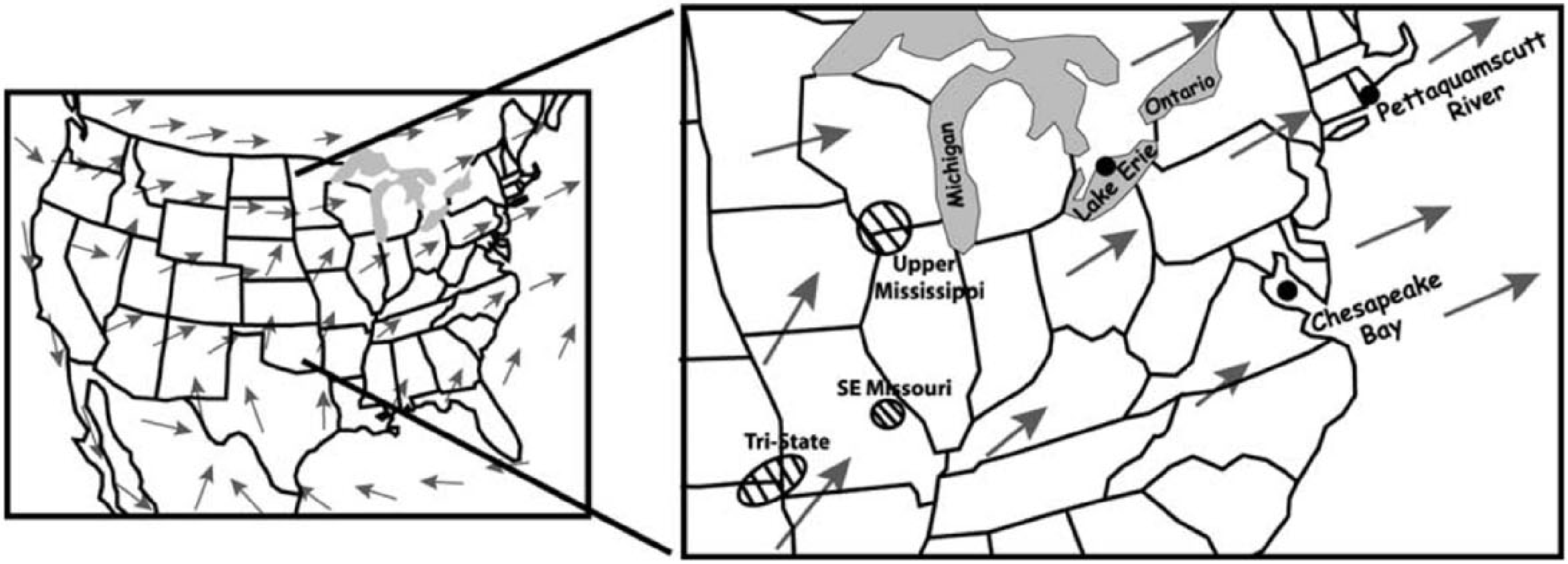
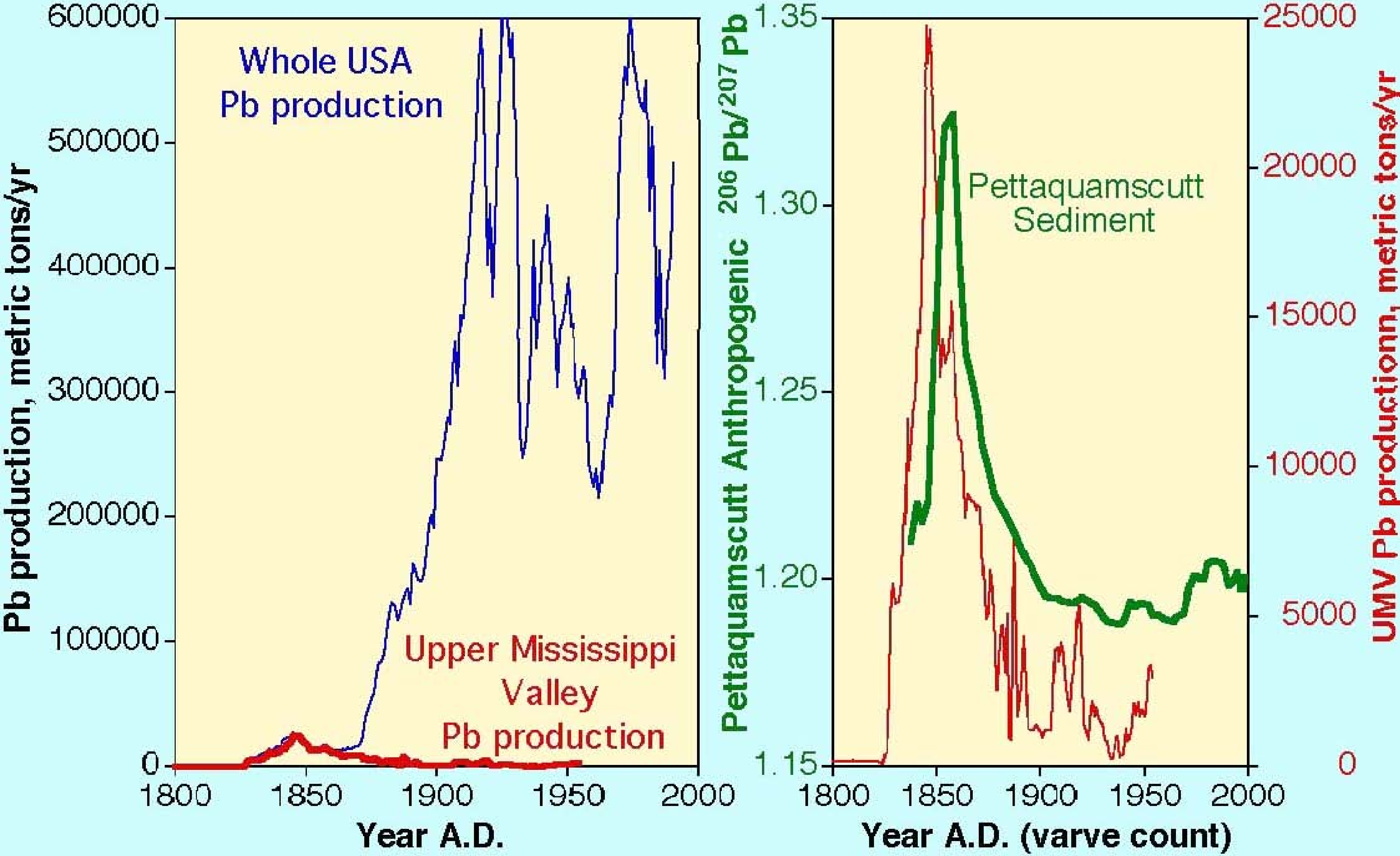
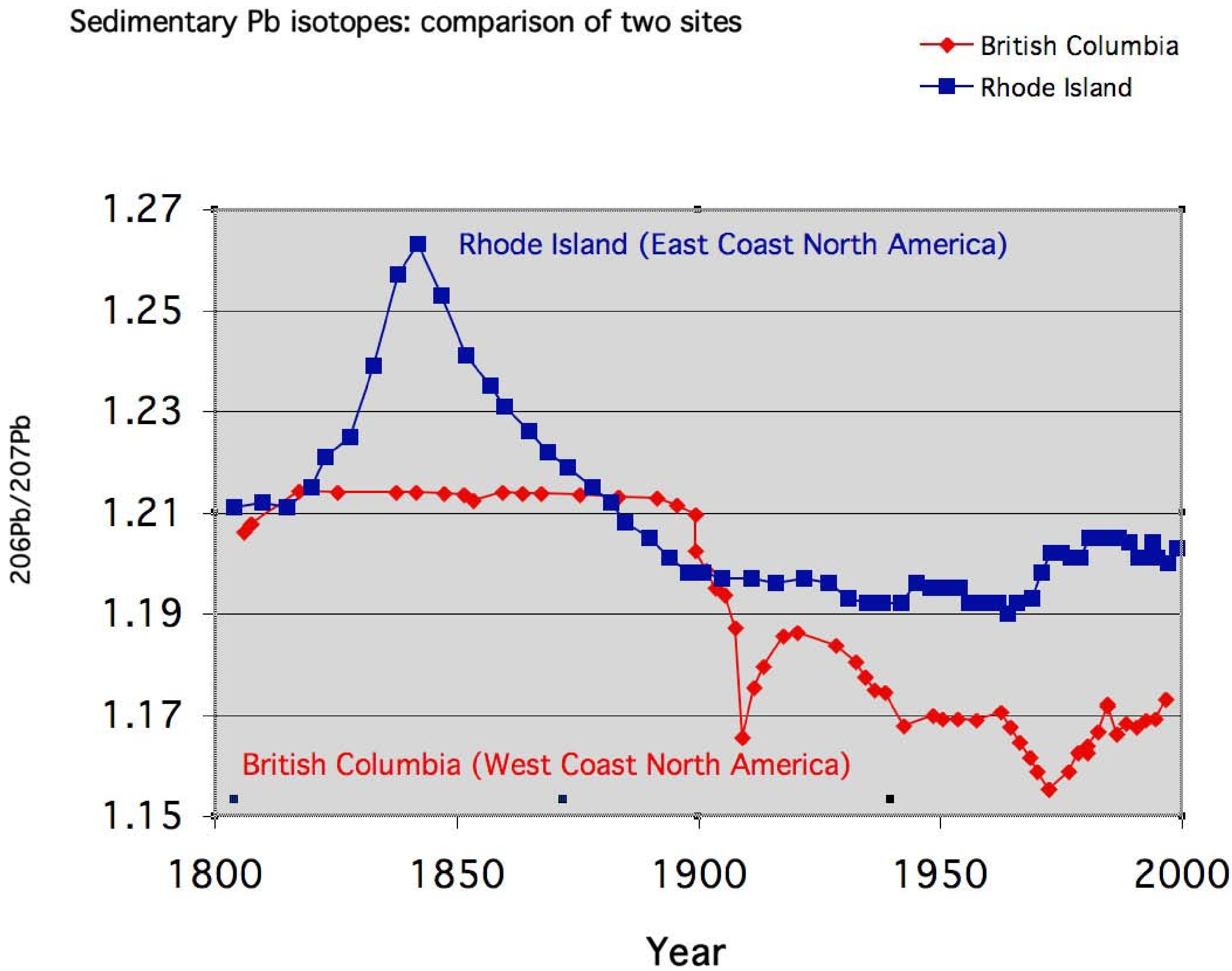


Fig. 6. Vector wind composite mean from January to December (1948 to 1998) calculated using the NCEP/NCAR Reanalysis program (http://www.cdc.noaa.gov/cgi-bin/Composites/printpage.pl) shows that the Pettaquamscutt River is located downwind from Lake Erie, while the Chesapeake Bay receives a higher contribution of winds from the southwest. Location of Tri-State, SE Missouri and Upper Mississippi mining districts were based on Brockie et al. (1970), Snyder and Gerdemann (1970), and Heyl (1970), respectively.

Lima et al. (2005) GCA 69:1813

A Large Anthropogenic Pb Isotope Spike in the Mid-18th Century U.S





- Note the very rapid decrease in $^{206}Pb/^{207}Pb$ at 1909. What caused this event?

12.119 Analytical Techniques for Studying Environmental and Geologic Samples
Spring 2011