A Statue of a Different Color

For almost a century, wind and rain sweeping across New York harbor have buffeted the Statue of Liberty. Faced with this constant assault, the statue's gleaming copper skin first dulled to a brownish color, then blackened before finally developing a sturdy green coat that has lasted for decades. But the statue's green patina, washed by acid rain, may be changing color again. A close look reveals a patchwork of darker areas that now poke through her weathered green coat.

Attention focused on these blackened areas about a year ago, after an aluminum scaffold was erected around the statue in preparation for an extensive renovation. This allowed corrosion specialist Robert Baboian, head of the electrochemical and corrosion laboratory at Texas Instruments, Inc., in Attleboro, Mass., to collect and analyze scrapings from small areas of the statue's surface.

Baboian's results suggest that acid rain may be converting a stable form of basic copper sulfate called brochantite, $CuSO_4 \cdot 3Cu(OH)_2$, which formed naturally on the statue's copper surface, into a less stable form of copper sulfate called antlerite, $CuSO_4 \cdot 2Cu(OH)_2$. With a slightly different composition and crystal structure, antlerite dissolves more readily in water and is more susceptible to wind erosion.

Thus, the antlerite-loaded green patina may be washing away, especially in areas exposed to the prevailing winds. This uncovers the underlying black layer, which consists mainly of copper sulfide and copper oxide. "We feel that acid rain is affecting at least the aesthetic properties of the statue," says Baboian.

E. Blaine Cliver, chief of the National Park Service's preservation center responsible for the Statue of Liberty restoration, is a little more cautious about implicating acid rain. "A lot of these dark areas may always have been dark," he says. "We're in the process now of having the patina mapped over time so we know what changes have occurred." This involves careful computer analysis of black and white photographs of the statue as she appeared during her first century.

Last month, Cliver and Baboian also completed measurements of the thickness of the statue's skin to see if the copper's rate of corrosion was changing. Using an ultrasonic caliper, they took enough readings to conclude that no one side of the statue was weathering more than any other, and that the copper in green and dark areas had about the same thickness. Overall, the statue's skin, originally 96 mils (or 0.096 inch) thick, is only about 4 mils thinner than it was 100 years ago.

Baboian, with these preliminary results, guesses that acid deposition has not yet affected the copper's corrosion rate. Although the green patina may be washing away in some places, the copper is actually protected by its thin but tenacious and very compact black layer.

On the other hand, if the black layer starts to wear away faster than it forms at the underlying copper surface, Baboian says, "then we would see a drastic reduction in the thickness of the black, color changes and an increased corrosion rate." The National Park Service plans to monitor the skin's thickness at selected points to track these corrosion rates.

Nothing can be done about the present color of the statue, says Cliver, because any skin treatment would have to be reapplied periodically. The statue will not even be washed using a detergent, as originally planned, because of fears of disturbing or damaging the patina.

Work on the Statue of Liberty is also generating some intriguing mysteries. On the arm holding up the torch, for example, is a single green copper plate surrounded by dark panels. Says Baboian, "The actual composition of the copper varies from one panel to another on the statue." Analyzing and comparing these adjacent panels, he says, may suggest possible acid-rain-resistant formulations for copper roofing materials. — *I. Peterson*

Chinese salted fish linked to cancer

In the United States and most developed countries, the incidence of nasopharyngeal carcinoma (NPC) has dwindled over the past 50 years. Not so in southern China. There, this cancer, affecting a silver-dollar-sized region at the back of the nose, is the leading cancer among men and ranks third or fourth among women. A new epidemiologic study now strongly suggests that its prevalence in China results from a single dietary factor — consumption from early childhood of salted, partially rotted fish common to the Chinese diet.

Brian Henderson, director of the University of Southern California (USC) Comprehensive Cancer Center and a collaborator on the study, says, "To my knowledge, this is the first human food to be proved epidemiologically as a cause of a human cancer." Henderson suspects that a chemical formed during the fish's decomposition leads to this cancer.

Southern China's high NPC rate had historically been attributed to inhalation of indoor air pollutants emitted by unvented wood stoves during cooking. But Hong Kong radiotherapist John Ho had his doubts. For one thing, although southern Chinese women tend to do all the cooking, their nasopharyngeal cancer rate is only half that of men's. Moreover, a disproportionate share of Ho's NPC patients were boat dwellers who cooked only in the open air.

Ho decided that what most differentiated the boat dwellers from their land-based kin was the proportion of their diet made up of salted, partially rotted fish. Having seen signs of a similar link between that disease and dietary consumption of the salted fish in Los Angeles's Chinese population, Henderson and USC cancer epidemiologist Mimi Yu teamed up with Ho to study it further.

Their just-completed epidemiologic study, which they plan to publish soon, involved 250 Hong Kong NPC patients and an equal number of matched controls. It shows "that consumption of this food during early childhood can explain over 90 percent of all cases," Yu told SCIENCE NEWS. Most critical, she says, is the role of the fish as "the most popular weaning food in that population." Exposures begin early and remain high. In fact, the Hong Kong data show that if the fish is eaten during infancy and childhood, there is no apparent decrease in risk by omitting it from the adult diet. Reinforcing the apparent significance of this early exposure, the researchers say, is the young age — usually 15 to 30 — at which the cancer appears in the Chinese.

"We've also demonstrated a dose response," Yu says. Their data show that by age 10, those who had eaten the fish daily had roughly a 40-fold greater risk of developing the cancer than did those who had eaten it rarely. It's "a magnitude of risk approaching that between lung cancer and smoking," she says.

Lacking refrigeration, most Chinese families rely on salt-cured fish, Yu notes. Ironically, because the fish is intentionally allowed to rot for a few days before salting, its softness makes it a favorite for flavoring the rice of weaning children. Interviews also suggest that when Chinese families have little fish, they preferentially feed sons — perhaps explaining NPC's higher incidence in males.

Yu expects their follow-up study in Guangzhou (formerly Canton) to be completed within a year. Back at USC she's feeding the fish — collected from Hong Kong street stalls — to rats to see if they might serve as animal models in which to study the fish's cancer causation. — *J. Raloff*