Dead *Daphnia* flag mystery water contaminants

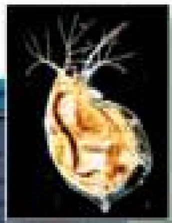
On March 19, 2004, alarms went off at the Evides water company's monitoring station on the Meuse River in the south of The Netherlands. Half of the *Daphnia* water fleas in the station's aquarium had died. The search for what caused the deaths—a true detective story—is described in research published in this issue of *ES&T* (pp 2678–2685). The research shows that combining continuous biomonitoring with chemical analysis can help utilities to detect toxic mixtures of contaminants that conventional technologies would miss.

The water fleas in Evides's aquarium are akin to canaries in a coal mine—their deaths are a quick indicator that something could be seriously wrong with the water quality. Evides immediately stopped pumping water from their reservoir 9 km downstream from the monitoring station on the Meuse. Evides provides drinking water to 1.3 million people and uses the reservoirs for storage.

Although the biomonitoring systems managed by Evides and other utilities generally trigger alarms three or four times a year, causing temporary pump shutdowns and mostly uneventful inspections, this was the third alarm that dying *Daphnia* had set off in just over a month. Evides's technicians were befuddled as to the cause and handed over the case to experts at Kiwa Water Research an institute in Nieuwegein (The Netherlands).

When standard analytical methods failed to detect anything unusual in the water samples, Kiwa researchers turned to quadrupole time-of-flight mass spectrometry. They determined that the culprit in the *Daphnia* deaths was 3-cyclohexyl-1,1-dimethylurea, a compound they had never seen before in the Meuse.

"This is one of the few success stories," says Ariadne Hogenboom, an analytical chemist at Kiwa and the paper's coauthor. Researchers at Kiwa handle water contamination cases for many countries in the EU, but they are not always successful in identifying new and previously unknown contaminants.



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A biomonitor continuously monitors the swimming speed and behavior of *Daphnia* water fleas (inset photo). Significantly abnormal behavior indicates water contamination and triggers an alarm.

However, the mystery wasn't solved yet. The researchers found ≤5 μg/L of the urea in the water samples in which the *Daphnia* died. But when exposed to the same levels of the compound in follow-up tests, the tiny crustaceans did not seem to be affected by it. So the researchers looked at the samples more closely. "We found that the compound was never alone in water; it was found either in combination with HMMM [hexa(methoxymethyl)melamine] or isoproturon," says Corina de Hoogh, the paper's lead author. This suggested that the *Daphnia* responded to the toxic effects of these compounds together, she says, even though "these compounds may be in very [low concentrations], so they are not even detectable."

The researchers did not get a chance to test their suspicion that the compounds' mixture was toxic, but no other explanation for the *Daphnia*'s deaths seems to exist, de Hoogh says. And without the combination of continuous biomonitoring and chemical analysis, they would never have known about the deadly mix present in the water. This is why it is crucial for water companies to use the techniques together, she says. "What we can detect [with chemical analysis] is a fraction of what we find in surface water," she says, but biotests clearly indicate when something more needs to be done. "Both techniques are not really new; it's the combination that's unique."

Joel Allen, an environmental scientist at the U.S. EPA, agrees. "The uniqueness is that they were able to take an alarm from an online toxicity monitor and translate that into a specific compound that was causing the toxicity," he says. This process occurs rarely, he says. The use of on-line biomonitors is limited—the method is barely used in the U.S., although Allen is trying to change that—and not every alarm is worth pursuing. The Kiwa research demonstrates how the combination of on-line monitoring and analytical tools can be effectively used, he says. "It starts to help build the case that these systems, when they are deployed, are doing what we expect them to do." Biomonitoring is currently used in Germany, France, and Italy, de Hoogh says.

For all its benefits, the combination system hasn't helped investigators find the source of the contaminant. Because of the urea's patented uses and the HMMM levels that accompanied it, the Kiwa researchers speculate that it came from a hydraulic fluid drainage. At this point, not much else can be done, Allen says, because a one-time contamination event is not enough to trigger remedial action.

Kiwa researchers are now investigating another series of alarms at Evides's monitoring station, and de Hoogh thinks that they could be caused by a similar culprit. "If we see it again this year between March and May, and again next year, then it's more urgent to look for the source," she says.
—PRACHI PATEL-PREDD

A tiny but powerful microbial fuel cell

Imagine a submarine fleet of small machines at work in the ocean or a wastewater plant that can collect data while drawing their power from the "food" around them. Researchers from the U.S. Naval Research Laboratory (NRL) describe in this issue of *ES&T* (pp 2629–2634) the first step toward reaching that goal in the form of a miniature microbial fuel cell (mini-MFC) with a cross-section area of just 2 cm^2.

MFCs harness the metabolic energy of bacteria to generate electrical power. Any organic material can be a rich source of food for these bacteria and hence power for the fuel cell. However, generating enough power to do something useful has been a major hurdle.

In a notable advance, the NRL scientists upped power output by using a spaghetti-like 3D graphite felt electrode to capture electrons. "Three-dimensional electrodes . . . are a good approach," says MFC researcher Uwe Schröder of the University of Greifswald (Germany). This electrode sits in the 1.2-mL anode chamber within a flow-through reactor, which is connected to a flask that holds bacteria and food. The mini-MFC produces 0.6 mW of power, says corresponding author Bradley Ringeisen.

Moreover, the cell generates this power by using a pure bacterial culture of *Shewanella oneidensis*. Another MFC pioneer, Korneel Rabaey of Ghent University (Belgium), says that obtaining these power levels from a pure culture is noteworthy because MFCs that use a mix of bacteria usually produce more power than pure cultures. By implication, switching to a mixed

BRADLEY RINGEISEN

In a big step for little devices, this miniature microbial fuel cell produces remarkably high power levels. The spaghetti-like 3D graphite felt electrode visible inside the chamber is the key to its power.

News Briefs

Water, a shared responsibility

In its second World Water Development Report, the UN calls for improved governance of safe drinking water and basic sanitation services. The report, *Water, a Shared Responsibility*, is a joint effort by 24 UN agencies. Released in March, the document includes the most comprehensive assessment of freshwater resources and detailed regional analyses backed up by the latest available data, maps, and graphs. Total official development assistance to the water sector in recent years has averaged $3 billion annually with an additional $1.5 billion in loans, the UN estimates. However, only 12% of these funds reaches the neediest people. Private-sector investment is also declining. The report is at www.unesco.org/water/wwap/wwdr2/index.shtml.

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Chemical connections

The European Commission has launched a research project to investigate whether chemicals found in food and the environment may be linked to childhood cancer and immune disorders. *NewGeneris* brings together 25 institutions from 16 European countries and has a 5-year budget of €15 million. The program will fund studies that seek to find effects in young children brought about by maternal exposure to carcinogenic and immunotoxic chemicals during pregnancy. The selected chemicals include dioxins, PCBs, alcohol, and various substances found in contaminated food, tobacco smoke, and air pollution. To assess chemical exposure, the researchers will analyze blood and urine samples stored in biobanks in Norway, Denmark, the U.K., Spain, and Greece from 300,000 mother-and-baby pairs. *NewGeneris* is expected to release its results in 2011.