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TAINTED KILLER Cousteau with "Rakey," a small female orca found stranded on the beach in Little Huia, New Zealand.

GREEN CHEMISTRY IN THE MAINSTREAM

CLEANER, CHEAPER, SMARTER chemistry is no longer a pie-in-the-sky idea

STEPHEN K. RITTER, C&EN WASHINGTON

KILLER WHALES, clean white socks, and race cars aren't exactly what people associate with green chemistry. Yet they were among many compelling topics on the agenda at the 13th Annual Green Chemistry & Engineering Conference (GC&E), held on June 23–25, in College Park, Md.

That green chemistry has permeated such a miscellaneous mix of topics suggests that it is no longer just the bold new idea that it was when a few scientists at the Environmental Protection Agency first formalized the concept nearly 20 years ago. Rather, it indicates that green chemistry has matured as a design framework and is now helping chemists and chemical engineers of all stripes to develop better chemical processes and products across-the-board.

"The tag line green chemists and engineers are now using is cleaner, cheaper, smarter chemistry," pointed out GC&E Chair Liz U. Gron, an analytical chemist at Hendrix College, in Conway, Ark. "That is exactly what we need in these tough economic times, when everyone is looking to gain a professional or business advantage. Plus, if we go greener, ethically you feel better—everyone feels better."

At GC&E, academics and industrial researchers, business professionals, and policymakers come together to advance green chemistry concepts—"it's a coalescence point," Gron observed. "The scheduled talks are a reason to come. But the ensuing discussions provide inspiration, and the personal interactions encourage the exchange of ideas and flow of creativity, leading to unexpected collaborations and new policy and business platforms. It's the power of people getting together that really drives green chemistry."

The week started with a daylong student workshop on green chemistry funded by the National Science Foundation. That first evening, EPA and the American Chemical Society hosted the Presidential Green Chemistry Challenge Awards ceremony (C&EN, June 29, page 5).

"Those two extremes dovetail together nicely," Gron said. "It's important to recognize that you have to pay in—seed the future—to help develop new minds to get to the end results that are honored by the awards. Those students represent the future of the chemistry enterprise, and the award winners represent the best of green chemistry."

At the end of the week, a "train the trainers" workshop instructed green chemistry practitioners how to advocate for greener chemistry and how to incorporate the principles of green chemistry and engineering into their curricula and business plans once they returned home.

In between, the award winners gave plenary talks on their chemical research and technologies, and the conference's 400 attendees—about 10% more than last year—gave some 190 presentations as part of the technical program. And attendees had plenty of time for discussion during the sessions and around the coffee urns.

Enter the killer whales, courtesy of keynote speaker Jean-Michel Cousteau, son of famed ocean explorer Jacques Cousteau and a noted explorer, film producer, and environmental activist in his own right. Some attendees wondered at first what celebrity oceanography and green chemistry have in common, but Cousteau soon made the connection.

"TODAY WE barely know as much about the ocean floor as we do about the hidden side of the moon," Cousteau said. "But we do know that the health of the oceans is declining due to human impacts." Cousteau created the Ocean Futures Society, a nonprofit marine conservation and environmental education organization, in response to his observation that "people were using the sea as a garbage can," he explained. "That realization empowered me with the desire to make people aware of the problem by providing them with information to make better decisions."

Drawing on the work that he and his team are doing to document the plight of killer whales, also known as orcas, Cousteau pointed to the parallels between humans at the top of the terrestrial food chain and orcas at the top of the marine food chain: People and orcas have similar social structures, dietary habits, and life spans, he said. And he is concerned about the future of both species.

GOING GREEN To view a slideshow of the Presidential Green Chemistry Challenge Award winners, click on this article at *C&EN Online*. To read more articles on green chemistry, go to www.cen-online.org/greenchemistry.html.

"Orcas are to the oceans what we are to the land—our human counterparts in the sea," Cousteau noted. "We need to protect orcas and the oceans as though we are protecting ourselves."

The livelihood of killer whales is being diminished by polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and other persistent man-made chemicals that end up in the environment, Cousteau explained. PCBs were once widely used as industrial coolants and insulating fluids; stabilizers in consumer electronic plastics; and flame retardants in furniture fabrics, mattresses, and children's clothing. The chemicals were banned more than 30 years ago once they were discovered to be persistent and toxic, but they are still circulating in the environment.

The chemical industry switched to PBDEs as replacements, but those also accumulate in the environment. Early indications from animal tests are that PBDEs impair liver and thyroid function and affect reproductive and neurobehavioral development, including learning and memory.

These compounds are hydrophobic and tend to build up in lipid-rich tissues,

Sauers

ELIZABETH WOODWELL

especially in animals at the top of the food chain. Research published during the past two decades on blubber biopsies of killer whales have shown the presence of PCBs and PBDEs at high levels in the marine mammals, with the highest levels found in young orcas. Biomonitoring in people likewise has shown that these chemicals accumulate in human blood and breast milk and that the levels tend to be highest in children. Cousteau himself has been tested for PCBs and PBDEs; because he is a longtime resident of California, which mandates the use of flame retardants, his blood levels for the compounds are above average.

People often react emotionally when they realize that potentially toxic chemicals are coursing through their veins or are impacting a beloved animal like the orca, Cousteau said. The chemicals may not be at biologically active concentrations and result in toxic effects—scientists conducting the studies caution that there still isn't enough information to correlate levels of these chemicals to the risk of adverse health effects, he noted. But high levels of nonnatural chemicals in the bodies of people and orcas are not good, he added.

Cousteau pointed out that people didn't know these consequences when the good intentions for flame retardants were first put forward. "But now that we know, we need to change," Cousteau said. "We need to be smarter."

The reality is that flame retardants, which typically delay flames for only about 12 seconds, probably aren't worth the environmental cost for the amount of protection they afford, Cousteau suggested. If they are necessary, then safer alternatives that don't have a long lifetime in the environment are needed. Some products that are inherently flameproof are already available, but their cost remains too high for general use.

"I am not a chemist," Cousteau told the audience. "So I cannot give you the answer. I am here to help identify these problems. You are the chemists. It is your job to find solutions. I think we can, and I know ultimately we will. My father always told me, people protect what they love. I hope that we all do."

DEVELOPING SAFER materials with the properties people need, such as flame retardance, is where one of the primary tools of green chemistry can help: life-cycle analysis. LCA lays out all assumptions related to making a chemical or a manufactured good and provides real numbers on energy and raw materials use; greenhouse gas emissions; waste generation; recyclability; and, most critically, cost.

Toxicologist Len Sauers, vice president of global sustainability at Procter & Gamble, explained how LCA can reap green benefits—including keeping white socks white with a green twist—during his keynote lecture. A company like P&G that sells commodity consumer products looks for every business advantage it can get, Sauers said. The company is willing to do its share for sustainability, he noted, but customers won't accept a higher price or a decrease in performance just to gain an edge in sustainability.

To get at sustainable but high-performance products, P&G is using LCA to find opportunities for improvements in energy use, packaging volume, water consumption, solid-waste reduction, transportation costs, and more. "We are using these data to help guide our decisions on where to target our R&D efforts to make the most meaningful improvements," Sauers pointed out.

FAST AND GREEN Corsa Motorsports' Ginetta-Zytek E10 gasoline-electric hybrid car debuted at the Utah Grand Prix in May.

Energy use is one key parameter for all of P&G's product lines, which include Tide laundry detergent, Downy fabric softener, Dawn dishwashing liquid, Charmin bathroom tissue, and Pampers diapers. P&G has quantified the energy use for every step in the life cycle of every product it makes.

Use of its laundry products is the top contributor to P&G's overall energy footprint, Sauers noted. "Most people assume it is the energy to operate the appliance," he said. "But that is wrong. The majority of the energy for laundry, about 85%, comes from heating water. As a company, that is one major target for improving our energy footprint."

Reducing energy use was the impetus for P&G to develop Tide Coldwater detergent (C&EN, Jan. 26, page 13). The product is similar in performance and sells for the same price as regular Tide. The green connection is that P&G's chemistry for cold-water washing is based on new enzyme technology and reformulated surfactants that are more soluble in cold water, Sauers explained.

The potential energy savings from cold-water washing should raise some eyebrows. According to P&G estimates, 3% of household energy use in the U.S. goes to heating water for laundry. But saving some of that energy requires changing consumer habits.

"Consumer education suddenly becomes very important with a product like Tide Coldwater," Sauers noted. P&G has made

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progress on this front in Europe, but not so much in the U.S. thus far, Sauers said. The company is working with utility companies and nongovernmental organizations to get the word out about the benefits of cold-water washing. "This is just one example of an opportunity to use green chemistry to create a product that enables people to be more sustainable," Sauers concluded.

One consumer who's already onboard is Gron. She has a pair of teenage sons, and like many parents, she cringes when her kids wear their white socks without shoes everywhere—inside and outside the house. "We usually wash our whites in warm water out of habit to make sure they will come clean," said Gron, who is conscientious about the amount of energy her family uses. "Cold-water detergent is definitely a move we should make."

WHAT IS GREEN and goes 200 mph? A hybrid-electric race car, of course. New for auto racing, going green allows the fast and furious sport to stay true to its fans but ratchets up the interest to a new level with the quest to use cleaner-burning fuels in more energy efficient engines. The sport has partnered with no less than EPA in this quest.

EPA's Green Racing Initiative is a "race within a race" experiment that rewards the fastest car that produces the smallest environmental footprint in a race, explained EPA environmental specialist John C. Glenn at GC&E. Motor sports might seem frivolous at a time when natural resource conservation is becoming more critical, Glenn acknowledged. But the green racing strategy aims to improve sustainability by stimulating faster development of energy-efficient and less-polluting passenger cars and fuel technologies.

Historically, auto racing has spurred innovations in automobile safety, durability, performance, tire technology, and more, Glenn said. And racing fans represent a ready market to help carry the new technologies forward to passenger cars.

Leveling the playing field in the sport traditionally has depended on regulating the engine size and type, Glenn explained. Because the sport has controlled the volume displaced by the cylinders, engine designers have been forced to maximize the power generated in the volume allowed. For example, Formula 1 cars in the 1960s produced about 400 hp at 7,000 rpm and got 8–10 mpg, he said. Formula 1 cars today produce 950 hp at 22,000 rpm and get 3.1 mpg.

The rules for engine design created a metric that rewards power density over energy efficiency, Glenn said. And engine designers went down the path of small, powerful, spark-ignition gasoline engines, which are the least energy-efficient type of engine. "Millions of dollars of R&D money and the careers of some of the best engineers in the world were used to increase power density," he said. Emulating race cars, passenger cars also emphasized power density. If energy efficiency had been the metric, a different kind of race car, and passenger car, engine would now be the norm—

"You are the chemists. It is your job to find solutions."

probably a diesel-electric hybrid, he said.

Knowing the influence of race car technology on passenger cars, in 2006 Glenn enlisted a team—which included members from EPA, the Department of Energy, Argonne National Laboratory, and SAE International—to set up the Green Racing Working Group to establish criteria for the new genre of racing. "These are still 200-mph cars," Glenn emphasized. "We clearly did not want to change racing."

Last October, the American Le Mans Series became the first racing series to test what is now called the Michelin Green X Challenge during the Petit Le Mans race at the Road Atlanta track—with some 110,000 spectators watching, which is why car companies invest so heavily in auto racing, Glenn noted.

During such green races, officials track the fuel used, greenhouse gases emitted, and amount of petroleum displaced by an alternative fuel. Then they apply life-cycle energy and environmental analyses to the data to determine the Green X Challenge winners for different classes of cars. For the Petit Le Mans event, which is a 1,000-mile, high-speed endurance race on a 2.5-mile road course, the green winner in the prototype car category was a Porsche equipped with an E10 gasoline engine. The green winner in the GT class was a General Motors Corvette fueled by cellulosic E85 ethanol. Cars running on other fuels and other engine types—including a hybrid-electric car—are currently participating in the racing series.

One reason the racing world has agreed to work with EPA is that the organizers realize they are on the wrong side of energy security and global warming, Glenn said. With EPA as a partner, racing series like American Le Mans suddenly become "entertainment with a purpose—the sport that solves energy problems, solves global warming, and accelerates the development of energy-efficient technologies," he added.

Down the road, racing could turn to energy allotments rather than engine size as a rule, Glenn predicted. "One day you'll see electric cars racing, and pit stops will involve changing tires and batteries," he said. New generations of cars would have a computerized management system that aids recapture of energy from the radiator, exhaust, engine friction, braking, and aerodynamics. All these functions will require new chemical technologies for their development, Glenn added. "The nice thing about that is it will accelerate development in passenger vehicles—racing really accelerates technology."

Be it healthier killer whales, cleaner white socks, or greener race cars, "you can feel that there is a big shift taking place in green chemistry," ACS GCI Director Robert Peoples told C&EN. "Green chemistry is moving from the lab, to scale-up, and to the commercial implementation phase for many products. We have now reached a critical mass of green practitioners. It is no longer just an academic topic. The chemistry community at large has really embraced it." ■