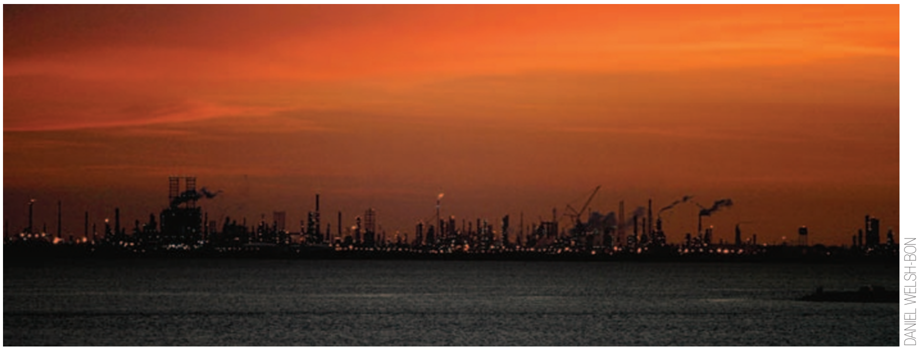
Hunting for halogen chemistry

Jim Roberts and colleagues inhaled petrochemical fumes and navigated between ships and oil platforms in order to understand halogen chemistry in the Houston area and along the Texas coast.

What was the location of your field project?
We cruised on a research vessel from Charleston, South Carolina, around Florida and across the Gulf to the Houston–Galveston area. Many of the interesting observations were made in Barbour's Cut, a small inlet off Galveston Bay.

Why did you choose this particular location for the fieldwork?
We had the dual goals of examining the air quality in the Houston–Galveston area and studying the clean-air chemistry and aerosol properties in the more remote Gulf of Mexico. The greater Houston region contains about 25% of the US petrochemical capacity, which contributes greatly to the photochemical air pollution problems endemic to that area.


DANIEL WELSH-BON

Sunset over the Texas City refinery complex. This is one of the largest single petrochemical installations in the US.

What was the objective of the work at the beginning of the project? Did it change as work progressed?
We set out to look at night-time nitrogen oxide chemistry with the goal of finding a new compound, nitryl chloride ($ClNO_2$). After the first few plume encounters, mostly from ships, it became clear that this chemistry was going to be dominated by plumes rather than background NO_x-aerosol chemistry, so we tried to focus on those.

Did you encounter any difficulties, for example, of a technical, human or administrative nature?
Trying to encounter plumes emanating from ships and oil platforms at night is tricky because the operations area is so packed with these ships and oil platforms (see the dots in Fig. 1 of the main paper) that we had a difficult time maneuvering our ship safely. This limited our ability to track plumes and there were really only one or two cases where we intercepted the same plume more than once at different times after emission, which was the kind of data that yielded valuable kinetic information.

What sorts of data or samples were you after?
We made continuous measurements of the atmosphere by sampling air into specialized instruments. In order to obtain levels of $ClNO_2$, we analysed the sample stream with a chemical ionization mass spectrometer (CIMS).

What have you found to be the most satisfying aspect of this work?
About a year and a half before this project I challenged myself to get into CIMS technology for the measurement of PAN compounds — organic nitrates peculiar to the atmosphere — and my bosses were foolish enough to support me in this. I built the instrument with the benefit of some very knowledgeable and generous colleagues (see acknowledgements, main paper). In the process of fielding this instrument, we have found four or five very promising research spin-offs, including the work published here.

Any low points?
I think we all agreed that the low point was a night spent moored alongside a pier in Jacintoport, part of the Houston Ship Channel. It was the industrial version of Conrad's *Heart of Darkness* as we were surrounded by industrial and petrochemical facilities that seemed to close in on the ship. We were awakened in the early morning by the stench of a petrochemical plume, acrylate esters and other monomers, and a bunch of other things one should not be breathing. These kinds of 'releases' are common and contribute substantially to the volatile organic compound reactivity in this area, and, as 'Air Toxics', are an issue in their own right.

Did you learn anything new about yourself or your team members?
Hans Osthoff is a reckless Bridge player. I, myself, am quite seat-of-the pants, but even I knew there was no way that hand should have ended up at four spades.

Did the trip give you any ideas for future research projects?
Yes, as the paper goes to press we are at the start of two extensive Arctic campaigns. We hope to find out how widespread the $ClNO_2$ phenomenon is, if there is some involvement of this N_2O_5–$ClNO_2$ chemistry in Arctic halogen activation, and whether we can observe measurable concentrations of the dihalogens Cl_2, BrCl, and Br_2, and associated radical BrO. Arctic halogen chemistry is involved in surface ozone depletion events and is an important mechanism for the removal of gaseous elemental mercury from the troposphere.

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This is the Backstory to the work by Jim Roberts and colleagues, published on page 324 of this issue.