

***PERFLUOROCARBON TRACER STUDIES FOR VISUALIZATION/VERIFICATION
OF VERTICAL TRANSPORT AND MIXING (VTMX) PROCESSES***

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ABSTRACT

Vertical transport and mixing (VTMX) processes play a very significant but not yet well-defined role in the transport, dilution, and subsequent fate of pollutants in urban basins located within intermountain basin regions. In the VTMX program, the important role of tracers in visualizing the effects of these processes has been recognized and the perfluorocarbon tracer (PFT) technology will be used to fulfill that role in this four-year program. Details of the PFT technology, under development at Brookhaven since the late 1970s, are available at <http://www.ecd.bnl.gov/TTC.html>.

Many of the types of tools developed at that time that are relevant to VTMX have not changed; ground-based programmable multi-adsorption tube samplers (BATS), passive sampling tubes (CATS), and balloon-borne vertical atmospheric sampling cables (VASCs) are still relevant to tracer visualization and verification of complex meteorological phenomenon. What is new in the last few years and critically important to the VTMX project is: 1) capillary graphitized carbon-layer, open-tubular (CLOT) column chromatography for higher-resolution separation of more PFTs in shorter analysis times with enhanced detectability; 2) enhanced detectability allowing simpler release of PFTs not only from compressed gas standard cylinders for short-scale (<50 km), short-duration (<24 hours) point-source tracer-release periods, but also from distributed diffusion-source devices which can serve as surrogates for area pollutant sources; and 3) new generation real-time analyzers which can be used in urban mobile traverses, on new balloon-borne VASCs, and on aircraft platforms.

The number of PFTs that will be available for release at the same time in the proposed October 2000 field campaign is estimated now to be six or seven distinct types - up to four with very low backgrounds near or less than $0.1 \text{ pp } 10^{15}$ and three with moderate backgrounds near 2 to $5 \text{ pp } 10^{15}$. Each distinct PFT type can be separately released but simultaneously sampled and subsequently analyzed within a single gas chromatogram, thereby providing a very cost-effective multi-tracer technology. With implementation of preparative chromatography, in the third year five new low background and one new moderate background PFT would be added bringing the total available to about 12 or 13 types. For these short scales of transport and with such low backgrounds, releases of dilute PFT-in- N_2 mixtures from compressed gas cylinders makes vertical releases feasible from tethered balloons as well as area source releases from miniature diffusion devices.

A vertical atmospheric sampling cable (VASC-II)--see reference--with time-integrated vertical PFT measurements at up to 17 levels (maximum at 200 m above the ground) will be deployed on a $3 \frac{1}{4} \text{ m}^3$ tethered balloon. Vertical sampling could also be accommodated on others' existing meteorological tethered balloons, kites, or towers using existing passive sampling tubes, but mounted on a clip-on weather-vane type attachment for wind-driven active collection on the adsorbent tube; such a system might weigh less than 10 g per vertical station. In the third year, a new design of VASC-I consisting of six tubings running in 50-m increments to 300 m at the maximum would provide 15-min resolution at 6 altitudes with continuous sampling and/or analyses on the ground and requiring lift with only a $5 \frac{1}{4} \text{ m}^3$ balloon.

A new real-time PFT analyzer, based on a Varian 3800 GC and an extension of the original dual-trap analyzer (DTA), will be capable of analyzing for five PFTs in a 30- to 45-second cycle time and for the full number of PFTs in about a 2 1/2-min cycle time. One system will be deployed in a vehicle for urban traverses, providing multi-location, multi-tracer impacts during the first field program. A second system could be deployed at a selected fixed location or in an aircraft. During the third year field program, a unit would be deployed on the VASC I' vertical sampling system.

The VTMX program's modelers will use the PFT technological measurements in conjunction with the assemblage of meteorological measurements to provide for visualization of boundary-layer and cold-pool vertical transport and mixing processes and for verification of hypotheses regarding physical processes through the use of coupled mesoscale meteorological and Lagrangian particle dispersion models.

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