4. Tracer

Purpose

During the intensive study periods, an artificial tracer will be released from the stack of the MPP and monitored at the same 31 locations as the air quality monitoring. There are several reasons for releasing tracer. Tracer monitoring data will identify the general transport patterns for the MPP plume. Knowing where the plume goes is critical to begin to understand the larger question of the MPP's visibility effects. To fully resolve the plume position and extent, a very extensive monitoring network, including aircraft measurements would be required. This is beyond the resources of the study. The 31 monitoring locations should provide the approximate location of the plume, although its horizontal and vertical extent will be uncertain.

Different artificial tracers will be released from the Los Angeles Basin and San Joaquin Valley during one-half or more of the summer intensive. These additional tracers will be released to gain insight into the transport of emissions from these large source areas into the Project MOHAVE study area. They will help identify the interaction between MPP and southern California emissions and provide dilution ratios for southern California emittants.

The tracer will be used to provide a check of deterministic modeling results. A transport model, using wind fields generated by a dynamic meteorological model, will predict plume locations. The tracer data will be compared to the transport model predictions to evaluate the model performance. The concentrations of the tracer will be used to evaluate dispersion of the plume predicted by the models as well as location. The dynamic meteorological and transport models are discussed in section 10.

The tracer will also be used for receptor and hybrid modeling purposes. The tracer will serve as a unique "tag" for the MPP. The receptor and hybrid modeling is described in section 13.

Choice of Tracer

Ideally, a tracer should closely mimic the species of interest for receptor modeling and chemical transformations; in this instance SO_2 and its conversion to SO_4, and deposition of the sulfate particles. This would suggest using isotopes of sulfur or oxygen. However, the large amounts of these materials that would be required are not available; to produce them would require resources greater than those available for this study.

Among the potential tracer materials are deuterated methane (CD_4), various perfluorocarbons (PFT's), Sulfur hexafluoride (SF_6), and particulate rare earth oxides. CD_4 and PFT's and SF_6 are conservative tracers; thus conversion of SO_2 to SO_4 and deposition of SO_2 and SO_4 can not be directly simulated. It has been suggested that nonconservative rare earth particle tracers be used because of their potential to mimic sulfate particles. However, sulfate particles are not directly emitted in significant quantities; rather they are typically formed during transport at rates which vary with meteorologic and other atmospheric conditions. Thus some variable proportion of the rare earth particles will have deposited before the sulfates are formed. Additionally the deposition of SO_2 occurs more rapidly than either sulfate or rare earth particles. A combination of conservative and particulate tracers could yield additional insights into the fate of MPP emissions than that obtained using a single tracer. However, the additional expenses associated with using an additional class of tracer is beyond the resources of Project MOHAVE.

SF_6 has been used in many short range experiments. Although the cost per kilogram is low compared to other conservative gaseous tracers, the background concentration is much higher, which more than offsets the decreased unit cost. SF_6 is not practical for the spatial scale of the study region.

CD_4, used in WHITEX has low background values and is detectable at very low concentrations, so small amounts of this tracer are sufficient. Though the cost per unit mass is high, the total cost of tracer material is less than the cost of PFT's. However, the sample analysis cost is very high ($800-$1000/sample), compared to about $20/sample for PFT's. The lower cost of PFT analysis encourages the analysis of many more samples for the available budget. For CD_4 the strategy is to analyze a subset of all possible samples. Analysis of all samples allows a more thorough evaluation of the deterministic modeling. Different PFTs can be released from other sources of interest and analyzed from the same sample for virtually the same low analytical cost.

The SRP tracer study, which used PFT's, apparently had some major problems with the tracer portion of the study. Collocated samplers showed near zero correlation. Apparently this was at least partially due to the fact that many samples were near the limit of detection. Other tracer studies have also had apparent quality control problems, for example, contaminated samples. It is imperative to have a rigorous quality control program for the tracer components of the study. The quality control methods to be used for the Project MOHAVE tracer study is described later in this section. There is no fundamental reason that would prohibit PFT's or other tracers from giving reliable, quantitative results.

Project MOHAVE will use perfluorocarbon tracers. The tracer to be used to track the MPP plume is ortho-cis perflorodimethylcyclohexane (ocPDCH). The tracer material to be released is ortho (o) PDCH, 45% of which is ocPDCH. Perfluoromethylcyclopentane (PMCP) will be used to tag the Los Angeles Basin. Perfluorotrimethylcyclohexane (PTCH) will be used to track emissions from the San Joaquin Valley. The ambient background of ortho-cis PDCH is very low, 0.3 parts per quadrillion (ppq) (Dietz, 1987). The SRP study used PDCH and other PFT's but analyzed for total PDCH, not individual isomers. The background of total PDCH is 22 ppq. PMCP background concentrations are 3.3 ppq; PTCH background is 0.3 ppq. Brookhaven National Laboratory (BNL) will do the tracer analysis for Project MOHAVE. In addition to analyzing isomers, BNL pre-concentrates the sample; thus much greater sensitivity is achieved compared to the SRP analysis methodology (Dietz, 1991).

Tracer Release

Tracer can be released at a constant emission rate or at a constant ratio of tracer to SO_2. Variation of tracer to SO_2 ratios was a complicating factor in the WHITEX receptor modeling analysis. If released at a constant rate, SO_2 emission rate variations would complicate the receptor modeling, requiring adjustment of the ratio of tracer to sulfur dioxide concentration. This requires knowledge of plume age. However, for use in deterministic modeling, it is more desirable to have a constant tracer emission rate, to simplify the dispersion calculations. If a constant release rate were used, the deterministic model would be used to give the plume age necessary to adjust the tracer to sulfur dioxide emission rates in the receptor modeling. The MPP is a base loaded unit. It typically operates at either full capacity, 1/2 capacity (one unit down) or is down. Tracer will be released at a rate proportional to the SO_2 emissions if a practical approach to do it can be devised. If not, then the tracer release rate will track the status of the power generation units with full, one-half or zero tracer emissions, corresponding to two, one, or zero units operating. This will more closely preserve the ratio of tracer to SO_2 emissions than a constant tracer release rate. Good coordination between MPP operators and the tracer release personnel will be expected. Tracer release from the San Joaquin Valley and Los Angeles Basin will be at a constant rate.

Release Equipment

The perfluorocarbon tracer liquids are very similar in viscosity to silicone fluids, but are quite dense (densities from 1.7 to 1.8 g/mL liq.). Large release rates, tens of kilograms per hour, have been accomplished with (1) atomizers spraying directly into the air, or (2) by vaporizing a PFT liquid stream, diluting with air below the PFT dewpoint at the exit, and emitting the diluted stream into the air or other fluid (such as the flue gases going up a power plant stack).

For low release rates, tenths of kilograms per hour, such as will be needed for Project MOHAVE and as was used in METREX in 1984 (Draxler, 1985), the tracer can be released by evaporation using the METREX-designed equipment. The release unit has only two moving parts: a squirrel cage fan motor and a metering pump. The tracer flows in a closed circuit from the reservoir through the peristaltic pump rollers (the tubing is compressed to move the liquid) directly into the airstream on the surface of a heated disk. The disk and heater are located in a cylindrical mixing chamber. The heater, adjustable up to 600 W, maintains the temperature of the disk above the tracer's boiling point. The system's electronics control the duration of release and the duration that the system is off. Times for each on-off cycle can be set by tens/whole/tenths of an hour for each cycle. A small strip chart recorder notes when the pump and heater are on. The pump rate is preset on a calibrated dial. The airflow should be sufficient to ensure all the vapor is diluted below the saturation mixing ratio for the expected ambient temperature without blowing the tracer drops off the heater before they vaporize.

Three release units were built by the NOAA Air Resources Laboratory in Silver Spring, MD, and now reside at their laboratory in Idaho Falls. The system was designed to handle release rates of the magnitude needed for Project MOHAVE. However, substantial design changes may be made by NOAA in consultation with Brookhaven in order to insure reliable operation (including accurate release rates and constancy of release).

PFT Programmable Samplers

Each site will be equipped with a programmable Brookhaven atmospheric tracer sampler (BATS). The sampler was initially developed by BNL and was commercially manufactured by the Gilian Instrument Corporation (West Caldwell, New Jersey). The unit consists of two sections: the lid, containing the sample tubes, and the base, containing the power control. The entire unit is housed in a weather-resistant 36 cm x 25 cm x 20 cm container and weighs approximately 7 kg. Power is supplied by an internal rechargeable nominal 8-VDC battery for operation at remote locations, or by a charger where 155-VAC is available. For Project MOHAVE, each unit must be run on a charger in order to collect the full twenty-three (23) 36-or 72-L air samples.

The BATS removable lid holds 23 stainless steel sampling tubes, each packed with approximately 150 mg. of Ambersorb adsorbent. The Ambersorb adsorbs the tracers from the sample air flowing through the tube. Breakthrough of the perfluorocarbon tracer gases is less than 0.1%. The tracer gases remain adsorbed until extreme heat is applied to the tube to desorb the tracer at analysis time. The sample air flow is directed consecutively through the adsorbent tubes by means of a multiple port switching valve which is controlled by the base. Since the lid is removable and interchangeable, multiple lids can be used on a single base.

The BATS base contains a DOE-Environmental Measurement Laboratory constant mass flow pumping system (Latner, 1986) which draws sampler air through each tube. The flow rate is selected by setting an internal switch to draw either 10, 20, 30, 40, or 50 mL/min of air; the switch controls the on-off cycling rate of the pump over a 1-min period. A constant flow rate through each sample tube in the lid is regulated by a pressure sensing circuit located at the outlet side of the pump. The circuit is an integrator that supplies a voltage ramp to the pump motor, rising or falling as indicated by the outlet pressure. A flashing light-emitting-diode (LED), mounted on the BATS base control panel, gives a visual indication that the pumping system is operating properly. This pumping system has proved to be more reliable than the originally installed pump, but consumes more power. Programmable controls are also placed on the base control panel which are used to control the number of samples, the sample duration, and to control either single or multiple sample start and stop times of a 7-day period. Two liquid crystal displays (LCDs), also mounted on the control panel, show the clock time, day of the week, and current tube number. A digital printer and integrated circuit memory module (Lagomarsino, 1989) record the start time, the day of the week, and the tube number for each sample. The BATS base controls are also used to assist in automated analyses when the lid is coupled to a gas chromatograph (GC).

For analysis, the perfluorocarbon tracers, retained on the Ambersorb adsorbent in the BATS tubes from the sampled air, are desorbed by resistance heating of the stainless steel tubes to 460°C. Current from the BNL gas chromatograph system (16.3 Amps AC) is supplied from a low voltage transformer (~1.55 VAC at the lid jacks) through the Canivalve solenoid assembly. The assembly consists of a 24-position rotary solenoid having two power decks capable of handling 20 amps. Twenty-three leads are wired to the power deck, each connected to the adsorbent tube floating clamp at one end of the respective tubes. The clamp at one end must float to allow for thermal expansion of the tube on heating (~0.8mm). A set screw secures the collar on the tube within the clamp; a similar set screw on a common aluminum rail secures the other end. Polyurethane rubber tubing (1/8-inch OD by 1/16-inch ID) is expanded over the 1/8-inch OD stainless steel adsorbent tubes and wire clamped to secure; the other end is attached to the Scanivalve 1/16-inch protrusions.

Tracer sample analysis

Tracer sample analysis will be done with a gas chromatography system. The gas chromatograph system is composed of a gas chromatograph, of data handling devices, gas standards, and a BATS. The Varian 6000 gas chromatograph consists of a series of specially designed traps, catalysts, columns, and an ECD-electron capture detector. The data handling system consists of an analogue electronic filter on the ECD electrometer output connected to a Nelson Analytical 300 Chromatograph system comprised of a Model 7653 Intelligent Interface and an IBM PC/AT with an ink jet printer and Nelson 2600 Chromatography Software. Brookhaven has also written extended software for further data processing and GC calibrations.

Analysis of a sample occurs when the sample is automatically thermally desorbed from the BATS sample tube. The sample is passed through a precut column and a Pd catalyst bed before being reconcentrated in an *in-situ* Florisil trap. Once the trap is thermally desorbed, the sample again passes through the same catalyst bed, another Pd catalyst bed, and then through a permeation dryer.

The sample is then passed into the main column where it is separated into the various perfluorocarbon constituents and then ultimately into the ECD for detection. Further details on the analytical system is given in Dietz (1987).

Release rates and expected crosswind average peak centerline concentrations at the Long Mesa and Hopi Point receptor locations are shown in the table below.

Summary of Expected Tracer Concentration					
Tracer Release			Receptor Site	Expected PFT levels	
Site	PFT	Rate, kg/h		PFT	Conc.[d], fL[*]/
MPP	oPDCH	0.14[a]	Long Mesa	ocPDCH	4 ± 2
San Joaquin Valley	PTCH	0.14[b]	Hopi Point	PTCH	2 ± 1
Los Angeles Basin	PMCP	0.50[c]	Hopi Point	PMCP	14 ± 5

[*] fL = femto Liter = 10^{-15}L

[a] 100 kg for 30 days in January 1992 and 170 kg for 50 days in July-August 1992

[b] 70 kg for 21 days in July 1992

[c] 250 kg for 21 days in July 1992

[d] Crosswind average peak centerline concentration

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At receptor sites, 12-hour tracer samples will be collected, and will sample 36 liters (L) of air. All other sites will sample 72 L over a 24-hour period. The table on the next page shows relevant information regarding the amounts of tracer expected, backgrounds, levels of detection, and signal to background ratios for the GC analysis. It can be seen that the limit of detection (LOD) and uncertainty are very small compared to background, except for PTCH, which has a limit of detection of about 16% of background and uncertainty of 50% of background. Thus, for the MPP and Los Angeles Basin tracers (ocPDCH and PMCP), even an additional tracer concentration of a fraction of background can be reliably quantified. For all 3 tracers, the uncertainty of the amount of tracer above background (signal-background) is small for expected crosswind plume centerline concentrations.

A sample chromatogram for a 20 L of ambient (background) air is shown in Figure 8. Background levels of the tracers used (ocPDCH, PMCP, and PTCH) can be clearly distinguished and quantified. PMCH, which is not being released, can be used as a reference.

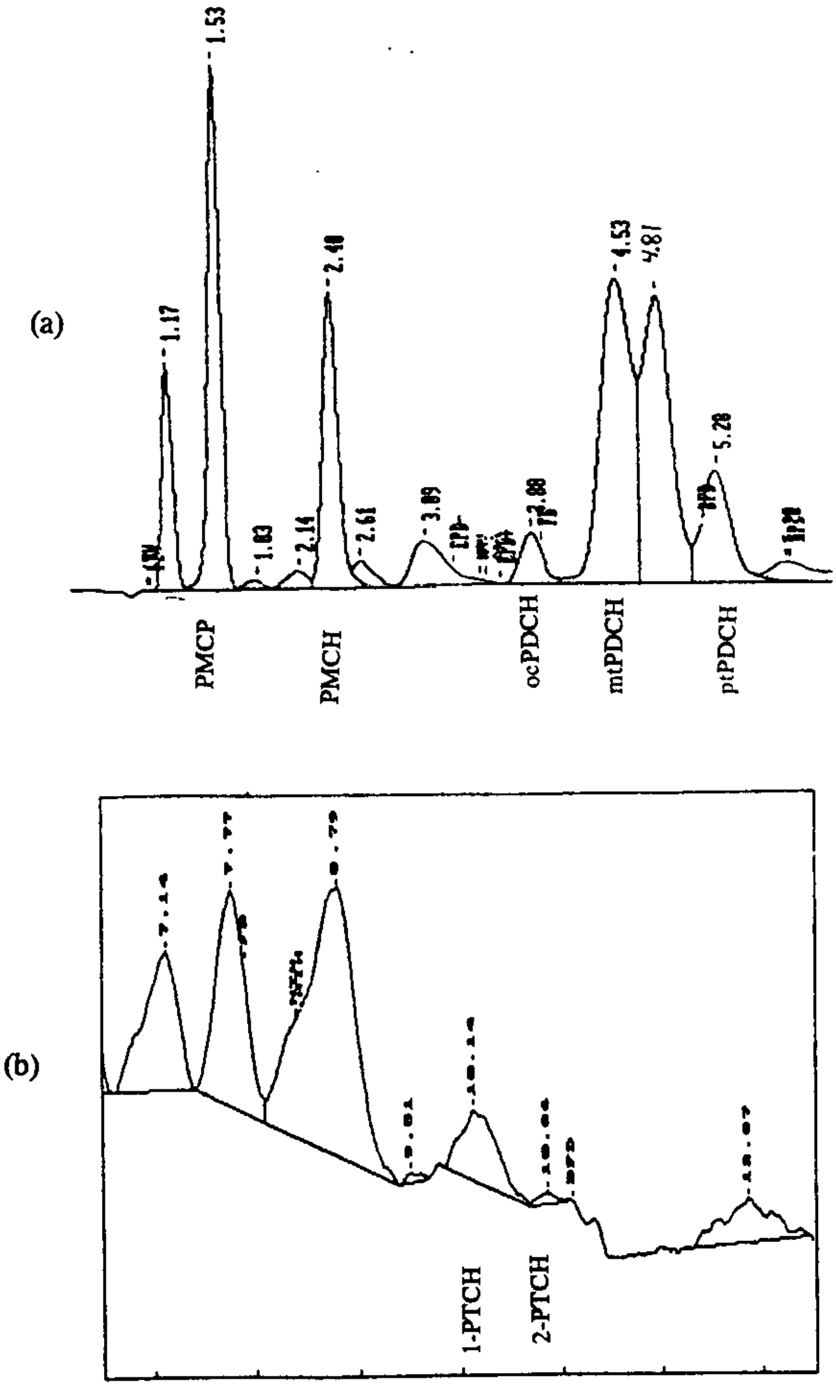

Figure 8. Chromatogram of 20 L sample of ambient air. (a) Elution time up to 6.5 minutes. (b) Elution time 6.5 to 13 minutes.

For 12 hour (36L) samples			
Background	**ocPDCH = 0.3 fL[*]/L**	**PMCP = 3.3 fL/L**	**PTCH ≈ 0.1 fL/**
Area of Response (counts/fL)	**360**	**160**	**300**
Receptor concentration (fL/L)	**4**	**14**	**2**
Quantity in 36L (sample and background) fL	**155**	**623**	**72**
Quantity in 36 L background, fL	**10.8**	**119**	**3.6**
Limit of Detection, fL	**0.05**	**0.12**	**0.6**
Limit of Detection, counts	**20**	**20**	**180**
Uncertainty = 3 Limits of Detection, counts	**60**	**60**	**500**
Counts in 36L (sample and background)	**55,800 ± 60**	**99,680 ± 60**	**21,600 ± 5**
Counts in 36L background	**3,888 ± 60**	**19,040 ± 60**	**1080 ± 500**
Signal to background	**14.35 ± 0.22 (± 1.5%)**	**5.24 ±0.017 (± 0.3%)**	**20.00 ± 9.2 (± 46.4%**
Signal - background, counts	**51,912 ± 85 (± 0.16%)**	**80,640 ± 85 (± 0.11%)**	**20,520 ± 7 (± 3.4%)**

[*] **fL = femto Liter = 10^{-15}L**

Tracer Quality Control

Rates of air flow through the sampler are checked before and after the sampler is sent to the field monitoring site. This is to determine the total quantity of air sampled each sampling period. Adjustments are made to compensate for altitude and temperature differences. Three additional PFTs that are not released are used as a cross-check of the sampling volume. The concentration of these PFTs is essentially constant, so the quantity of air sampled can also be calculated from the amount of these tracers collected.

The sample analysis is done at 460°C. This is 50°C above the temperature needed to desorb all PFTs. After analysis, the sample tubes are "baked out" at 510°C to remove any remaining traces of PFTs. Before sending the tubes out to the monitoring sites, every fourth tube is analyzed. At this time, the tubes should have zero tracer. They are analyzed down to 30-50 counts, which is about 1% of background. If a tube has zero signal, then it has not been sampled, because the ambient background has not been detected. The samplers will be programmed to collect 20 or 21 samples; tubes 22 and 23 should be zero.