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INFORMAL REPORT

Feasibility of Perfluorocarbon Tracers (PFTs) in Atmospheric Source-Receptor Experiments

A
Position Paper
Prepared by

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MASTER

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<u>Section</u>	<u>Page</u>
7. SAMPLING LOCATIONS AND FREQUENCY.....	7-1
A. Ground Sampling Density.....	7-1
A.1. Number of Ground Samples to be Analyzed.....	7-2
A.2. Number of Ground Sampler Bases and Lids Required.....	7-3
A.3. Cost Optimization of GC Systems and BATS Lids.....	7-4
B. Required Aircraft Density.....	7-4
B.1. Crosswind Tracer Plume Extent.....	7-4
B.2. Vertical Tracer Plume Extent.....	7-5
B.3. Alongwind Tracer Plume Extent.....	7-5
B.4. Estimated Aircraft Requirements.....	7-6
8. NEEDED PERFLUOROCARBON TRACER SYSTEM RESEARCH.....	8-1
A. Availability of PFTs.....	8-1
B. Tracer Release Needs.....	8-2
C. PFT Sampler Needs.....	8-2
D. PFT Analytical Advances.....	8-3

ABSTRACT

A brief description of the perfluorocarbon tracer (PFT) system, which includes the tracers and the release equipment, the air samplers and the analyzers, is presented along with details on the research needs to provide a viable system for MATEX-scenario experiments. The present family of 2 viable PFTs needs to be increased to 5 to 6. Given the present precision of the analysis system, a one year long tracer experiment consisting of 4 hour releases every 60 hours from 5 different sites would require nearly 150 metric tons of PFTs at a cost of \$15,000,000. Shortcomings in the programmable sampler include the pump, the sampling sequence control flexibility, data storage and retrieval, and the lack of remote communication capability; sampler adsorbent studies are also needed. The analytical system, including the catalyst processing bed, the chromatography column resolution, and the linearity of the detector, is in need of significant improvement. A higher resolution analysis system could significantly reduce analysis time but, more importantly, reduce tracer requirements more than 10-fold, for a cost savings potential of more than \$13,000,000. A model is presented to demonstrate the feasibility of tracer material balances. Assessment of earlier long-range tracer experiments indicates the need for possibly 400 ground sampling sites requiring \$8 to \$14 million worth of samplers for a one-year tracer experiment. As many as six aircraft would be needed to conduct airborne model validation and material balance studies for each tracer plume.

SUMMARY

The perfluorocarbon tracer (PFT) system includes the tracers and their release equipment, air samplers for PFTs, the analytical system for recovering and quantifying the PFTs, and associated data processing and handling equipment. The present capabilities and shortcomings of the system are described and the research needed to make the system feasibly and economically viable for MATEX-type studies is presented.

Only PFTs appear to meet all the critical requirements of a MATEX-scenario experiment including high electron capture detector (ECD) sensitivity, low atmospheric background, limited industrial use, simplified sampling and analysis, innocuous to health and environment, publicly acceptable, low cost, available in quantity, and non-reactive in the atmosphere in any way. Although 9 such compounds exist, only 4 have been used to date as tracers and of those, only 2 currently meet the cost and availability requirements, namely, perfluoromethylcyclohexane (PMCH) and perfluoromethylcyclopentane (PMCP). Research must be initiated now such that in about 2 years the family of PFTs for MATEX can be as large as 5 or 6.

Based on a study of two long range tracer experiments involving PFTs, it would appear that with the present analytical system precision, about 50 kg/h of a PFT must be released in order to meet a requisite $\pm 10\%$ precision at a receptor 1000 km from a source. For a particular one-year long MATEX-type experiment, it was estimated that almost 30 metric tons of one tracer would be needed. With 5 tracers released simultaneously at 5 different locations for 4 hours every 60 hours, the total tracer cost would approach \$15,000,000 based on the present analytical system precision. Some studies should also be conducted to improve the reliability and durability of tracer release equipment.

A critical component in the PFT system, the programmable sampler has been successfully deployed in a number of experiments. The overall performance record, about 75 to 80% data return, must be improved. Components of the sampler that need additional research and development include the pump, system controls, data storage and retrieval, and the adsorbent material. The pump reliability must be improved and its pumping rate should be electronically controllable. A microcomputer system should be installed for system controls, data collection, remote programming, and remote communication including performance status and data retrieval. For new samplers, the presently used adsorbent, which is no longer commercially available, must be replaced by a substitute material or another manufacturer of the original material must be found.

The laboratory and real-time analyzers both employ sample recovery, processing, chromatographic separation, detection, and signal processing. Sample recovery from the programmable sampler has been shown to be adequate. Additional research is needed to improve the reliability of the catalyst processing bed and to reduce its effect on the resolution of the tracer components. Although a high resolution packed column is currently in use, only about 3 to 4 PFTs can be adequately resolved. The real-time analyzer, which uses essentially the same system components as the laboratory gas chromatograph (GC), performed adequately for CAPTEX 1983, but will benefit from any column resolution improvements made to the laboratory GC system. Such improvements include finding improved packed columns, incorporating temperature programming (both of which are not expected to be viable), performing round-the-clock analyses, employing high resolution capillary chromatography and/or microparticulate packed column

chromatography, and improving column switching and sample transfer techniques. Details are given on the use of the reference tracer approach with a high resolution GC system, which can significantly reduce tracer costs while improving receptor-source allocation precision. With the reference tracer approach, using PDCH as the reference tracer, it is shown that for linear detection response the tracer concentration at a receptor site due to the source is solely dependent on the precision of the peak area ratio (tracer-to-reference) of the sample and that of the ambient air. With a high resolution GC system, the potential is for a 10- to 50-fold reduction in tracer release quantity for a savings of more than \$13,000,000.

A model is presented for the determination of the crosswind (σ_y) and alongwind (σ_x) dispersion coefficients or standard deviations and is applied to the CAPTEX 1983 real-time aircraft data. The σ_y values ranged from about 15 to 60 km at about 600 to 800 km downwind. Application of the alongwind model will have to await the availability of the ground sampler data. It is estimated that given a large number of crosswind traverses during the entire transit of the plume, a mass balance precision of $\pm 20\%$ should be attainable.

Based on the Oklahoma and CAPTEX 1983 tracer experiments, the density of ground sampler sites required for an East Coast experiment is estimated to be 400. For the proposed MATEX-type year long scenario, 4 samples would be collected per day at each site or 584,000 samples in a year, requiring a total of 432 sampler bases (\$1,300,000) and a maximum of 6240 lids (\$12,500,000). The CAPTEX 1983 experience dictated that a team of three aircraft at one downwind location (~250 km) and another team at a second location (~750 km downwind) would be needed to fully characterize a single tracer plume and provide information in σ_y , σ_x , and the material balance at both downwind locations.

A summary of the PFT tracer system research needs is presented including the search for new PFTs, validation of tracer release equipment, improvements in the programmable samplers, and analytical system advances.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
Abstract.....	iii
Summary.	iv
1. INTRODUCTION.....	1-1
2. PERFLUOROCARBON TRACERS (PFTs).....	2-1
A. Tracer Selection Criteria.....	2-1
B. Available MATEX-Compatible Tracers.....	2-5
C. New PFT Studies.....	2-7
3. TRACER RELEASE CONSIDERATIONS.....	3-1
A. Estimated Release Rate.....	3-1
B. Estimated MATEX-Type Tracer Needs and Cost.....	3-2
C. Release Equipment.....	3-3
4. SAMPLING FOR PFTs.....	4-1
A. Types of Sampling Equipment.....	4-1
A.1. Whole Air Sampling.....	4-1
A.2. Adsorbent Sampling.....	4-1
Programmable PFT Sampler.....	4-2
Passive PFT Sampler.....	4-3
B. Needed Programmable Sampler Improvements.....	4-4
B.1. The Pump.....	4-4
B.2. The Controls, Data Storage and Retrieval.....	4-6
B.3. Sampler Performance Studies.....	4-7
5. ANALYSIS OF PFTs.....	5-1
A. Laboratory Gas Chromatograph.....	5-1
B. Real-Time Analyzer.....	5-6
C. Needed Improvements to the Analyzers.....	5-7
C.1. Present Laboratory Gas Chromatograph System.....	5-8
C.2. Improved Laboratory GC for MATEX.....	5-9
Analysis Time and Costs for the Present System.....	5-9
Effect of Improved GC Techniques on Time and Cost....	5-10
D. The Reference Tracer Approach.....	5-13
D.1. Formulation of the Tracer Ratio Technique.....	5-13
D.2. Precision of the Source Concentration Determination..	5-16
Present G.C. System.....	5-17
High Resolution GC System.....	5-17
Tracer Reduction Benefits.....	5-18
6. FEASIBILITY OF TRACER MATERIAL BALANCES.....	6-1
A. Crosswind Dispersion.....	6-2
B. Vertical Dispersion.....	6-6
C. Alongwind Dispersion.....	6-6
D. Precision of a Tracer Material Balance.....	6-9

Section 2

PERFLUOROCARBON TRACERS (PFTs)

Critical to the design of any atmospheric transport tracing experiment is the tracer selection. The number of tracers used in an experiment will significantly influence the nature and scope of any proposed experiment. This section provides a brief description of the tracer selection criteria and the number of presently available MATEX-compatible tracers as well as work needed to provide additional tracers such as the ones listed in Table 2-1.

A. Tracer Selection Criteria

The number of available tracers is limited by the following selection criteria:

1. High Electron Capture Detectability.

Tracers should be chosen so as to allow the highest degree of electron capture detectability (ECD), which is one of the most sensitive analytical detection methods available in an inexpensive and portable technology. As a class of compounds, the perfluorocalkylcycloalkanes (PACAs), have proved to be the most viable tracer compounds to be used in atmospheric transport tracing. Other compounds such as SF₆, various freons, and other halogenated organic compounds also have high ECD sensitivities and have been used in other small scale tracing experiments, but their high atmospheric background concentrations preclude use in long-range tracing.

2. Low Atmospheric Background.

With the present use of preconcentration techniques for tracer collections, tracers with the lowest atmospheric background should be used, thus minimizing the amount of tracer used per release and consequently the

Table 2-1
CURRENT AND POTENTIAL PFTs

No. ^a	Symbol ^e	Name(perfluoro-)	Ambient Concentration, ^f fL/L	
			Measured	Expected ^b
1	PDCH(mixture) ^c	-dimethylcyclohexane	25.6	25.6
	" (meta)	"	11.8	
	" (para)	"	9.9	
	" (ortho) ^d	"	4.0	
2	PMCH ^c	-methylcyclohexane	3.6	3.4
3	PDCH	-dimethylcyclobutane	0.35	--
4	PMCP ^d	-methylcyclopentane	--	0.06
5	PCB	-cyclobutane	--	--
6	PCH	-cyclohexane	--	--
7	PDCH	-dimethylcyclopentane	--	--
8	PECH	-ethylcyclopentane	--	--
9	PECH ^d	-ethylcyclohexane	--	--

^aOnly 1, 2, and 5 are currently commercially available in economically large quantities.

^bBased on composition of commercial grade PDCH (contained 11.7 vol. % PMCH and 0.2 vol. % PMCP) and present ambient PDCH concentration.

^cCurrently available in large quantity from I.S.C. Chemical Limited, England.

^dHas been prepared in the past by I.S.C.C.

^eAll are liquids at room temperature with the exceptions of PCB (supplied as a liquefied gas) and PCH (a subliming solid).

^fConcentration units, fL/L (femtoliters/liter), are equivalent to parts in 10¹⁵ parts of air.

cost per release. The effect that the tracer background concentration has on the cost of a tracer experiment is shown in Table 2-2. PMCH and PDCH, two viable perfluorocarbon tracers have relatively the same cost but approximately ten times more PDCH than PMCH is required per experiment in order to achieve the same experimental results. This is solely due to the ten fold higher background concentration of PDCH compared to PMCH, which had its genesis in the early 1940s when a mixture of the two was used as a special coolant. Currently a number of PACAs are used as electronic cooling liquids and in a number of other minor applications totalling only a few metric tons per year.

3. Limited Industrial Use.

If the source of the tracer being measured in an experiment is not unique to the release, then measured concentrations may not unambiguously identify the source-receptor relationship.

4. Easy Analytical Workup.

The tracer should be sampled easily and inexpensively and, to make full use of its capability, be detectable down to the current ambient levels at low cost.

5. Harmless.

Neither the users nor the general public must be affected in any adverse way. The tracers should have a low toxicity and not exhibit mutagenicity or carcinogenicity. In addition, the tracer should not cause any adverse environmental impact.

6. Available at the Lowest Cost.

This is perhaps the most difficult criteria to satisfy. There are only a certain number of tracer compounds which satisfy this criteria.

Table 2-2

GASEOUS CONSERVATIVE TRACERS: PROPERTIES AND COSTS

Distance: 100 km
Desired Concentration: 100 times background at centerline
Release Time 3 hours

Tracer	Symbol	Formula	Molecular weight	Phase at 20°C	Boiling point, °C	Supplied form	Ambient conc., fL/L ^a	Cost \$/kg	Released qty., kg	Relative tracer cost, 1000 \$
Sulfur hexafluoride	SF ₆	SF ₆	146	gas	-64	liq. gas	2000 ^b	10	2320	23.2
Bromotrifluoromethane	F13B1	CBrF ₃	149	gas	-58	liq. gas	750	15	887	13.3
Perfluorodimethylcyclohexane	PDCH	C ₈ F ₁₆	400	liquid	102	liquid	26	120	82	9.8
Dibromodifluoromethane	F12B2	CBr ₂ F ₂	210	liquid	25	liquid	<20	30	<33	<1.0
Perfluorocyclobutane	FC-318	C ₄ F ₈	200	gas	-6	liq. gas	?	250	-	-
Perfluoromethylcyclohexane	PMCH	C ₇ F ₁₄	350	liquid	76	liquid	3.6	100	10	1.0
Perfluorodimethylcyclobutane	PDCB	C ₆ F ₁₂	300	liquid	45	liquid	0.35	500	0.83	0.42
Perfluoromethylcyclopentane	PMCP	C ₆ F ₁₂	300	liquid	48	liquid	2.8	100	9 ^c	0.9

^a1000 fL/L equals pL/L or 1 part-per-trillion.

^bNear-urban SF₆ is 2000 fL/L or more in many locations because of significant use; tropospheric background is 850 fL/L.

^cBased on ~85% purity readily available.

An additional selection criteria is necessary for conservative PFT namely

7. Non reactive.

Neither photochemical, aqueous phase, heterogeneous, nor other homogeneous reactions must involve the tracer. The half-life of the tracer in the troposphere should be greater than several months and several years for global experiments.

B. Available MATEX-Compatible Tracers

As mentioned in the first selection criteria, the only compounds which satisfy all of the necessary criteria are the family of perfluoroalkylcycloalkanes, also sometimes referred to as perfluorocarbon tracers (PFTs) or perfluorocarbon compounds (PFCs), which will be discussed individually as follows:

1. Perfluorodimethylcyclobutane (PDCB).

PDCB was a product developed by DuPont as Freon C-51-12. DuPont was not able to develop a market for this product and subsequently sold their PDCB stock.

DuPont is no longer interested in producing this product and other chemical companies such as 3M, and ISC, Ltd. are not able to manufacture this nor similar cyclobutane compounds. Consequently, this was once a viable tracer, but is no longer due to its present unavailability.

2. Perfluoromethylcyclohexane (PMCH).

PMCH is a product marketed by ISC, Ltd. as an electronic cooling liquid. It is made by the fluorination of toluene and is presently available.

3. Perfluorodimethylcyclohexane (PDCH)

PDCH is a product also marketed by ISC, Ltd. as an electronic cooling liquid. It is sold commercially as PP3, containing approximately 10-15% of PMCH. It is manufactured by the electrochemical fluorination of xylenes, producing a mix which is distilled to yield PP3. Pure PDCH is also available from ISC, however, the atmospheric background concentration of PDCH is approximately an order of magnitude greater than PMCH, which makes it essentially non-viable as a MATEX tracer. However, as mentioned later in the analyses of PFTs, Section 5, this tracer may serve a valuable role as a reference for determining sample volume.

4. Perfluoromethylcyclopentane (PMCP).

PMCP is obtained as a side product during the electrochemical fluorination of hexane. ICS, Ltd. obtains PMCP from their preparation of PP1, perfluoro-n-hexane. PMCP has not been field tested as a perfluorocarbon tracer, but it is fully expected that it will behave as the other validated tracers, PMCH and PDCH. As noted in Table 2-1, the cost and background concentration of PMCP make it comparable to PMCH in viability as a MATEX tracer.

5. Perfluorocyclohexane (PCH).

PCH is obtained as a side product in the electrochemical fluorination of n-hexane or toluene. Unfortunately, PCH is a volatile solid at room temperature which requires it to be dissolved in a solvent for use as an atmospheric tracer. Furthermore, PCH elutes very close to PMCP on the analyzer system and appears to have only one-fourth the detector response of the other PFTs. Thus, a second aspect to be considered in the choice of

perfluorocarbon tracers, their analytical separation and response to electron capture detection, is considered in detail in Section 5.

In conclusion, the only PFTs that currently are available and viable for MATEX are two, PMCH and PMCP.

C. New PFT Studies

Table 2-1 lists a number of potentially new PFTs and most certainly the list can be extended significantly. For the success of MATEX, a major effort must be initiated now in order to develop the needed three or four new tracers. The steps necessary include:

- o A literature review
- o Discussion with PFC manufacturers
- o Procurement of samples of existing PFCs
- o Contracted synthesis of new or previously available PFCs
- o Fabrication and calibration of new PFC standards
- o Compatibility with release equipment, samplers, and analyzers
- o Field tests
- o Cost and purity of PFCs

It is estimated that to develop the extra three or four new tracers to a point of their commercial availability will require a minimum of two years of research, testing, and validating. The motive for developing the greatest number of allowable tracers is that it increases the diversity and flexibility of any proposed experiment. With a large number of tracers it is possible to have a simultaneous release of tracers from spatially separated sites, thus, for example, determining the relative impact of various source regions (tracer release sites) on receptor regions (the tracer collection sites) with respect to air mass dispersion and transport.

Section 1

INTRODUCTION

In order to determine uniquely and unambiguously an air parcel's trajectory as well as the magnitude of the extent to which that parcel of air, carrying pollutants from a specific source, impacts on a specific receptor, experiments must be conducted with conservative and non-conservative tracers. Such experiments will establish 1) a database of source-receptor consequences determined on a frequent basis and 2) a database of both tracer and meteorological information which can be applied to test source-receptor models.

One important ingredient in MATEX and other atmospheric transport and diffusion studies is the role of perfluorocarbon tracers (PFTs) and related sampling and analysis equipment. At the present time there is no other viable alternative to PFTs for the conservative tracing of air parcels on the scale of greater than 200 km, that is, viable in terms of cost, availability, and reasonable time constraints (e.g., time for analyses, real-time sampling, etc.). But are PFTs ready for the potential large-scale applications envisioned in MATEX?

This paper addresses the PFT system capabilities for use in MATEX-scale studies and needed additions for the use of PFTs to be entirely feasible.

Section 3

TRACER RELEASE CONSIDERATIONS

This section briefly discusses the quantity and, hence, cost of a PFT that might be considered for one version of a proposed year-long MATEX field study and considers the release equipment needed.

A. Estimated Release Rate

For plume model validation studies, it is generally accepted practice to release a quantity of tracer such that the measured concentration is ten times either the ambient background concentration or the sampling and analysis equipment's minimum detectable concentration, whichever is larger, when that concentration is measured a distance of two standard deviations away from the plume centerline. In the case of PFTs, generally the background concentration is the limiting (larger) quantity, since a large enough air sample can generally be collected to exceed the limit of detection. For example, the limit of detection for PMCH, which has a background concentration of 3.6 fL/L, is about 1 fL (femtoliter is equivalent to 10^{-15} liter) at a signal-to-noise ratio of 3. Thus a 5-L air sample, sampled on an adsorbent trap at 500 mL/min for 10 min, would contain 18 fL of PMCH, that is, 18 times the limit of detection.

Since, for a Gaussian plume profile, the peak concentration is approximately 10 times the 2-sigma concentration, the desired centerline peak concentration is 100 times background. Based on a number of 100 km tracer experiments, it has been demonstrated that about 5 kg/h of PMCH would meet this criterion. From the limited number of long-range tracer experiments, the 600-km Oklahoma experiment in 1980 and the CAPTEX 1983 tests, it was

shown that about 50 kg/h was necessary to meet this criterion at a distance of 1000 km between the source and the receptor.

B. Estimated MATEX-Type Tracer Needs and Cost

Several types of long duration (several hours per day), long term (up to 1 year) conservative PFT experiments are being considered. In general, such experiments would comprise a statistically sound database of the impact of multiple source locations on a regional scale receptor area.

In order to place at least a "ball-park" estimate on the maximum quantity and cost of PFTs, it is assumed that the following experiment would be conducted.

1. Tracer release sources	: 5
2. No. of PFTs (1 type per source)	: 5
3. Each release duration	: 4 hours
4. Release frequency	: Every 60 hours (2-1/2 days)
5. Release rate per source	: 50 kg/h
6. Term of experiment	: 1 year

Based on this scenario, the number of releases per source for the term of 1 year would be 146. At 200 kg for each 4-hour release, the total quantity of each tracer needed would be 29200 kg or 29 metric tons.

It is interesting to note two points. First, a background concentration of 3.6 fL/L for PMCH is equivalent to a total global atmospheric quantity of 175 metric tons, just 6 times what might be released in one year. Thus, this single one-year long experiment would increase the ambient background of PMCH by about 17%.

The second, more significant, point is that the current annual world production of PMCH is probably less than 5 metric tons per year. Thus,

Section 4

SAMPLING FOR PFTs

The various methods for determining the PFT concentration in air are either in situ real-time analysis or collection of air samples for subsequent analysis in the laboratory. Real-time as well as laboratory analyses are discussed in the next section. In this section, the various methods for collecting and recovering PFTs in air will be briefly mentioned. The present methods of adsorbent sampling for PFTs will be described and shortcomings in the hardware will be addressed.

A. Types of Sampling Equipment

The various approaches that have been used for PFTs consist of whole air sampling and adsorbent sampling.

A.1. Whole Air Sampling

By this technique, quantities of air are collected within a container and then transported to a laboratory for analysis. Containers that have been used are plastic bags filled via small pumps, syringes (manual or automated), and evacuated bottles.

Plastic bags, used both with individual pumps and automated pumping devices, are the most common approach for sampling. The major disadvantage to plastic bags is their ultimate failure due to cracks and pinholes with subsequent loss of sample. For certain scenarios, automated bag samplers followed by rapid (within 24 hours) laboratory analysis can be quite satisfactory. For MATEX, however, the desired sample quantity per analysis is quite large, typically 5 L of air, and may increase another factor of 4. Since the shipment of such volumes would be difficult and the time between collection and analysis might approach several weeks of months, whole air sampling in general is not practical for PFTs.

Evacuated bottles would have the appropriate container integrity, but there is a concern for absorption losses in such container. And again the volume of the containers would be an impediment to shipping, storing, and handling.

A.2. Adsorbent Sampling

Two types of adsorbent samplers have been developed for PFTs, a programmable sampler and a passive sampler.

Programmable PFT Sampler. This was developed by Dietz at Brookhaven and commercially manufactured for the National Oceanic and Atmospheric Administration (NOAA) by Gilian Instrument Corporation as the Brookhaven Atmospheric Tracer Sampler (BATS). The entire unit measures just 14 x 10 x 8 inches and weighs 7 kg. The lid contains 23 sampling tubes, each containing 150 mg of 20-50 mesh type 347 Amborsorb (Rohm and Haas Co.), which can retain all the PFTs in more than 30 L of air. Internal batteries provide power for up to one month of unattended operation of all the automatic sampling and recording features.

Sample recovery was accomplished by direct ohmic heating of the adsorption tube to 400°C, with the PFTs being purged from the BATS tube through an automated ECD-GC system as described in Section 5. All 23 tubes were automatically analyzed in about 3 h.

The PFT programmable sampler/laboratory GC system was tested both in the Oklahoma 600 km experiment and in the 100 km CAPTEX 1983 tests. Despite a significant amount of success with this system, a number of shortcomings with the BATS must be resolved for their viable application in experiments on the scale of MATEX. These shortcomings and potential solutions are discussed in Section 4-B.

By far, the BATS unit concept is the only effective technique for sampling atmospheric perfluorocarbon tracers on a MATEX-type scale. But the type of unit that is needed for MATEX is still not available.

Passive PFT Sampler. Originally developed as a means to measure the indoor PFT concentration during the determination of air infiltration and air exchange rates in homes and buildings using miniature PFT permeation sources, the passive sampler has also been used in atmospheric tracer studies.

In its first configuration, one end of the sampler contained a 1-mm capillary tube and so was coined the Capillary Adsorption Tube Sampler (CATS). The present configuration of the passive sampler, which is made from 6 mm OD by 4 mm ID glass tubing exactly 2.5 inches (6.4 cm) long, contains 64 mg of Ambersorb 347. Sampling occurs by the process of Fickian diffusion when one cap is removed. From the depth to the bed (2.76 cm), the cross-sectional area (0.126 cm^2), and the empirically derived diffusion coefficients of the PFTs in air, it was determined that the CATS sampled at a rate equivalent to about 200 mL of air per day for PMCH. In some recent comparisons between BATS and CATS, the actual sampling rate was found to be equivalent to 232 mL air/day for PMCH and 217 mL air/day for PDCH. With two caps removed, increasing wind speed causes increasing errors. The present detection limit is about 0.1 part-per-trillion-hour (i.e., 100 fL-h/L), adequate to detect ambient PMCH (3.6 fL/L) in a one-month integrated sample.

Ambient concentration measurements of PMCH and PDCH were recently determined with 10 CATS deployed in the Washington, D.C. area for a period

of 30 days. As shown in Table 4-1, the background of both tracers was comparable to that shown in Table 2-1.

Where short term temporal (less than 2 h) resolution is not a concern, the passive sampler could be quite useful for ground level sampling and vertical tracer distribution. The latter could be obtained by attaching the CATS to a tethered balloon cable at various altitudes, as it weighs just 4 g. Essentially no further work is necessary for the application of CATS in atmospheric tracer studies.

If, in any MATEX scenario, long term average tracer concentrations are desired (e.g., weekly or monthly), then the very simple and inexpensive (~ \$4 each) CATS could play a role.

B. Needed Programmable Sampler Improvements

Three aspects of the present BATS unit need to be improved: 1) the pump, its performance features and its reliability, 2) the control features and an ability to determine if the unit is working correctly, and 3) data storage and automatic retrieval.

B.1. The Pump

Here are listed the features of the ideal BATS unit pump compared with the present (modified Accuhaler) pump.

1. Electronically controlled flowrates.

The new BATS should have flowrates that are electronically selected and controlled from 0 to 60 mL/min. The present pump flowrates are manually selected by changing an orifice. Once deployed in the field, there is no way to change the pumping rate remotely nor in any pre-programmed way.

2. Optional capacity to 300 mL/min.

The present pump is limited to a maximum rate of 25 to 38 mL/min, depending on the specific pump.

Table 4-1

AMBIENT PFT DETERMINATIONS WITH PASSIVE SAMPLERS (CATS)^a
 Washington D.C. Area, 30-day period, June 1983

<u>No.</u>	CATS	PFT Concentration, fL/L	
	<u>No.</u>	<u>PMCH</u>	<u>PDCH</u>
1	925	3.52	26.3
2	936 ^b	22.33	40.1
3	953	3.85	26.9
4	913	4.00	28.5
5	969	3.91	27.9
6	932	3.39	26.3
7	926	3.07	24.3
8	300 ^b	25.40	45.8
9	954	3.14	27.3
10	959	2.90	20.5
Average:		3.5±0.4	26.0±2.6

^aEquivalent sampled air volumes were 7.0 and 6.5L, respectively, for PMCH and PDCH.

^bExcluded from averages; CATS no. 936 had a cracked cap.

3. Positive and uninterrupted sampling.

The pumping rate of the present pump is quite non-uniform over the range of each stroke, starting near the rated capacity but decreasing abruptly near the end of its stroke. Many times the pump fails to activate the end-of-stroke microswitch and simply stops operating. The new pumps should have a constant cyclical rate.

B.2. The Controls, Data Storage and Retrieval

The control features of the BATS should be improved beyond the capabilities of the present unit.

1. Microcomputer controlled operation.

The present BATS must be manually programmed for the sampling duration (which is necessarily the same for each tube), the number of sampling tubes, and the start time of the first tube. In conjunction with the improved pumps, the new BATS microcomputer would allow for setting individual pumping rates for each tube and individual start and stop times.

2. Remote programming and performance check.

At the present time, field personnel must set the BATS controls just prior to an experiment. And an observer must read the printer tape to determine if the unit is functioning properly. The new BATS would be capable of remote programming via a telephone jack or field programmed from a hand-held digital pre-programmed terminal.

3. Recorded operational data.

Presently the tube number, start time and day, and number of pump strokes are printed on a paper tape. There have been many failures of the printing system. The new BATS should have a solid-state memory which can either be read in the field on an LCD, transmitted via phone, or physically removed when the lid assembly is replaced.

Other features of a new BATS might include temperature and barometric pressure transducer readings for sampled volume correction and storage of multiple pre-programmed sampling protocols.

In some preliminary discussions with Demaray Scientific Instrument, Ltd., Pullman, WA, a type of pumping concept was described which should be pursued as an alternative to the present BATS pump. According to persons involved in computer communication fields, the microcomputer concepts should also be attainable with current technology. Both these aspects of an improved performance BATS should be explored now such that the second generation BATS would be available within the next 2 to 2.5 years.

B.3. Sampler Adsorption Performance

The programmable sampler is a key component in the implementation of the FFT system. Aspects of the sampler adsorption performance that need to be addressed are:

- Laboratory evaluation of compatibility with new PFTs
 - Breakthrough sample volume with current adsorbent
 - Evaluate sample recovery
- Study sampler adsorbents
 - Evaluate new sampler adsorbents
 - Find new source of current adsorbent

With the current adsorbent material, type 347 Ambersorb by Rohm and Haas, breakthrough volumes greater than 30 L of air have been demonstrated for the volatile tracer, PDCE. And recovery of the least volatile tracer, PDCH, has also been shown to be greater than 99.9%. For each new tracer with a boiling point between that of PDCB (45°C) and PDCH (102°C), there is not expected to be any breakthrough or sample recovery problems. However,

for lower boiling point compounds, the breakthrough volumes must be experimentally determined and/or predicted from chromatographic considerations. For higher boiling compounds, if any, sample recovery would have to be considered.

Ambersorb has been ideal for the BATS samplers because it is hydrophobic (its sampling capacity is not affected by ambient humidity), has high integrity (non-dusting qualities preclude desorption and memory problems), low bed pressure drop, and excellent thermal stability. Discussion will be initiated with Rohm and Haas to have limited quantities manufactured (it is currently no longer commercially available). In addition, tests will be conducted with a variety of charcoals to determine a suitable substitute. Early tests were conducted with coconut charcoal which appeared to be suitable, but the shift was subsequently made to Ambersorb, primarily because of its non-dusting qualities.

Section 5

ANALYSIS OF PFTs

The determination of PFT concentrations in air can be performed in two ways--the collection of air samples with subsequent analysis in the laboratory and the real-time determination with a field portable analyzer. In this section, a brief description is given of both the laboratory and real-time analyzers and the improvements that will be needed to make MATEX-scale experiments a viable system.

A. Laboratory Gas Chromatograph

Whether from programmable or passive samplers, the sample is automatically thermally desorbed and passed through a Pd catalyst bed, permeation dryer, and a pre-cut column before being re-concentrated on an in situ trap. The trap prevents the collection of unwanted low molecular weight constituents, the pre-cut column prevents the passage of unwanted high molecular weight constituents, and the dryer removes moisture from the ambient samples. After thermally desorbing the trap, it is injected into the main column after passing through another Pd catalyst bed and finally the ECD. Limits of detection range from 0.5 to 5 fL up to a maximum of about 5000 pL or, roughly, 6 orders of magnitude.

Initially the chromatographic column packing was 20 feet of Porosil F, and an example chromatograph of the three earliest used tracers, PDCB, PMCH, and PDCH separated on Porosil F is shown in Fig. 5-1. As is apparent in this figure, three is nearly the maximum number of tracers that can be simultaneously analyzed with the resolution available with this column packing. Recently, a new column packing has been introduced, i.e., Carbowack C with 0.1% SP-1000, which is the presently used packing. Figures 5-2 and 5-3

Figure S-1. Chromatogram of 41.7-L Long Island air sample on a 20-foot column of porosil F at 85°C and a 5% CH₄ in N₂ carrier flow rate of 10 mL/min.

Figure 5-2. Chromatograms of 25-L Long Island air samples on a 4-foot column of carbopack C with 0.1% SP-1000 at 140°C and a 5% H₂ in N₂ carrier flow rate of 22 mL/min.

Figure 5-3. Same as Figure 5-2 but with column at 100°C.

increase in resolution for these three tracers, and even PDCH is partially resolved into its respective isomers. This increase in resolution has allowed the number of tracers, analyzed in each sample, to be increased, by developing new tracers which would elute in the empty areas present in the chromatograms. It can, however, not be expected that a large number of new tracers can be fitted into these empty areas, and perhaps we are nearing the limit of a packed chromatographic column for simultaneously separating a large number of tracers.

The peak areas from the integration are currently stored in three ways--printed on paper tape, stored on magnetic tape, and punched on paper tape. This redundancy has proved useful when one or another system has failed or is out for repair. The magnetic tape is read to a small desk top computer where other pertinent sample data such as sample volume and duration are entered and the sampled concentrations computed. A new system in preparation will make use of dual floppy disks with nearly a megabyte of storage capacity.

Since ambient air samples currently contain uniform tropospheric background concentrations of many PFCs, once resolved and quantified, any one of them can become an internal reference standard to determine the volume of air sampled, assuming, of course, that the reference material is not one of the released tracers or an impurity therein. This provides redundancy in the recording of the sample volume size and a means of quality assurance for sampler liability.

Many long range tracer studies (such as CAPTEX and MATEX) as well as complex terrain experiments (e.g., ASCOT) will benefit from multi-conservative tracer releases to determine the impact of many source regions

on a given receptor. It is envisioned that the current laboratory gas chromatograph system developed at Brookhaven will ultimately be able to adequately resolve and quantify up to 3 or 4 PFTs on a single chromatogram. However, new advancements are needed to

- improve resolution PFTs
- provide lower limits-of-detection
- increase speed of analysis
- resolve less-stable tracers

The additional research and developments needed in this area will be discussed later.

B. Real-Time Analyzer

The peak PFT concentration typically encountered in long range tracer experiments range from 1 to 5 pL/L at 100 km downwind to about 100 to 400 fL/L at 800 km downwind. These concentrations can easily be measured with BATS located both on the ground and in aircraft. The expense of an aircraft platform, however, mandates that the sampling occur where the plume is actually located. Thus, the need exists for a real-time PFT analyzer.

Originally conceived and developed by Lovelock, an instrument was modified by Brookhaven to concentrate the PFTs in a 5-L air sample and analyze the desorbed sample on an in situ chromatograph column and detector. This version had two Ambersorb traps. While one was sampling at 1 L/min for 5 min, the other was desorbed and analyzed. Since the traps reversed position every 5 min, no tracer was lost. The limit of detection was about 10 fL/L making it quite useful for potential aircraft traverses in long range (1000 km) PFT experiments. At the very least the dual-trap analyzer would direct

the aircraft for on-board programmable sampler collection of the otherwise invisible plume.

A new version of the dual-trap analyzer was recently completed for use in the 1983 CAPTEX tests in September and October. This unit resolves 2 or 3 tracers in a 4-min chromatogram of a 4-min air sample collected at the rate of 1 L/min. For CAPTEX, the conditions were set to monitor the concentrations of ambient PMCH and PMCP, which are about 3.6 and 2.8 pL/L, respectively. Ultimately, one tracer will be a reference tracer, since it will not be released during the experiment. An internal microprocessor will automatically compute the response of each released tracer relative to the referenced ambient tracer in order to display the concentration of each directly on an analog output. Eventually, a commercial manufacturer for this analyzer should be sought.

C. Needed Improvements to the Analyzers

The analysis of PFTs is by a system approach rather than just by gas chromatography. The system is comprised of sample recovery, processing, transfer, injection, and analysis, and data handling. Improvements in any portion of the system will be aimed at one of three important goals:

- High resolution
- High speed
- Automation

In addition, studies must be conducted with the present gas chromatograph (GC) system to:

- Improve resolution
- Characterize new PFTs
- Determine ambient concentrations of new PFTs

C.1. Present Laboratory Gas Chromatograph System

The resolution of the present gas chromatograph system may be improved by investigating alternative packed columns. The original packed column, Porosil F, did not have the resolving power that the current SP 1000 on Carbopack C column has. Only by reviewing the literature and then trying various columns can these improvements be realized.

Another option is to attempt to incorporate temperature programming. The earlier eluting PFTs, those before PDCB in Figure 5-3, can only best be resolved (separated sharply one from another) at column temperatures of 60° to 80°C. But at 80°C, PDCH has an elution time of 20 to 25 min, much too long when analyzing thousands of samples. At 140°C, the PDCH isomers are eluted in 6 to 7 min (Figure 5-2), but the earlier PFTs are not resolved. Therefore temperature programming of the column from 80°C to 160°C may provide an answer. The problems associated with this technique (e.g., column bleed, etc.) need to be examined.

The new PFTs must be characterized for their performance on the present GC system including:

- Retention times at several column temperatures
- Trapping and recovery efficiency of the on-line concentrator
- Stability in the Pd-catalyst bed which destroys interfering compounds
- Response in the electron capture detector versus sample size

Recently, it has become clear that the present 3% Pd on molecular sieve 4A catalyst beds do not remain active and also play a role in broadening the tracer peaks, that is, reduce resolution and precision. Research needs to be applied to find a long-lived, non-interfering catalyst.

Finally the present GC system can be operated at either low isothermal temperatures, precutting the ambient PDCH, or in a temperature programmed mode to determine the current ambient concentrations of the new potential PFTs. The limiting factors in detection of a new tracer are its ambient background, the ability to separate it from other interfering background constituents, and its limit of detection relative to signal noise at its elution window. All need to be investigated.

C.2. Improved Laboratory GC for MATEX

As indicated earlier, the present GC system can be expected at best to resolve only 4 to 5 PFTs in a single chromatogram. Further improvements are needed to resolve a greater number of PFTs and simultaneously to reduce analysis time.

Analysis Time and Costs for the Present System. This can be a critical component, especially if results are desired early in the one-year MATEX study in order to modify the manner in which the tests are being conducted. For example, with the present system, one sample tube is analyzed every 10 min. With 23 tubes per lid, it presently takes almost 4 hours per lid with the high resolution 0.1% SP 1000 on Carboxpack C column packing. Thus in a single 8-hour day, only 46 samples are analyzed. Allowing one day per week for calibration, system maintenance and repair, etc., the total number of samples analyzed in one week is typically 184 per system per week.

As noted in Section 7-A, about 584,000 samples per year may be anticipated for MATEX from the 400 possible ground sampling stations or 11,230 samples per week. At 184 samples per GC system per week, a total of 61 GC systems would be needed or 15 GC stations. Each station consists of 4 GCs connected to one data system at a total cost of \$125,000 per station. Thus, the 15 stations would cost about \$2,000,000 in capital outlay.

Operating costs for the analyses at each station would be for one full time data operator and one full time GC operator; for 15 stations the total operating cost is estimated to be \$3,000,000. Thus, the total capital and operating cost of the 15 stations is \$5,000,000, not counting personnel for the shipping, handling, baking out, repairs, etc. to the BATS units.

Effect of Improved GC Techniques on Time and Costs. To reduce capital and operating costs, to improve the precision and accuracy of analyses, and to provide for the simultaneous determination of 5 or more tracers, high resolution chromatography is needed.

One approach to saving time is to initiate an automatic round-the-clock analysis system. This could reduce total system requirements by about 2.5-fold including capital and operating costs while providing only slight improvement in the ability to resolve the required number of tracers. Such a system should be available in a year.

The literature is replete with techniques employing the application of glass capillary gas chromatography, (GC)², to detection of multiple trace components, certainly a second approach to reducing analysis time and capital equipment costs. In principal, (GC)² is ideal for the analyses of PFTs since the quantities being detected are in the sub-nanogram range. The literature will be reviewed to determine those columns which might be the best to test for high speed, high resolution of the PFTs and limited studies will be conducted using some existing instrumentation. The goal will be to obtain a complete chromatogram of up to 6 or more PFTs in a period of 2 to 3 min compared with the present 3 or 4 PFTs in 7 to 10 min. With the large number of MATEX samples to be analyzed, a 2- to 3-fold reduction for the high resolution GC system and the 2.5-fold gain for round-the-clock

capability would combine to save \$3 to \$4 million in capital and operating costs. As mentioned in Section 5-D, the savings in tracer costs would also be substantial, greater than \$10,000,000.

An alternative to the high speed and resolution of the capillary open tubular column is the microparticulate packed column. In many tracer applications, for example, the ASCOT studies, there is a need for a wide dynamic range in concentrations. Only with a miniaturized GC system based on the microparticulate packed column, can this wide dynamic range be achieved. Together with a reasonable signal-to-noise ratio and a high separation speed, the microparticulate packed column is superior to the open tubular (capillary) column.

The present laboratory and real-time dual-trap gas chromatographs make use of low-volume Valco rotary multi-port switching valves. However excellent these valves are, problems associated with them for the trace PFT analyses include

- Temperature restrictions
- Sealing materials compatible with PFTs
- Leakage
- Operating speed

The presently used valves are limited to 175°C. Since they are mounted in the GC column oven to reduce both contamination and path length (i.e., internal volume), columns requiring temperatures in excess of 150°C cannot be used (allowing 25° over operating temperature for bakeout). The high temperature valve has a lower limit of 150°C; thus the valve technology is limiting the column temperature flexibility. In addition, the shaft seal assembly material, ceramic filled Teflon, has a substantial solubility for

fluorinated organic compounds. Inadvertent exposure to a high concentration of such compounds can result in some memory effects; the laboratory GC is currently experiencing this problem. Such seals can develop leaks and the operating speed of the valves is in the range of about 1 second, which introduces flow perturbations.

To circumvent these limitations and to provide the following improvements:

- High speed flow direction switching
- Minimum delay volume
- Automated "heart cutting"
- Automated cold trapping

a GC system based on the Deans pressure balance principle, in which all the valves are located outside the heated zone, will be explored. Such a system has been incorporated into automated dual-column capillary chromatography, providing a heart cutting technique to divert desired fractions of the first column elute into the second column.

Attempts to incorporate the pressure switching technique will be compared with automated approaches to transfer the PFT sample from the field adsorbent collector to an on-line capillary cold trap. Packed cold traps can be made essentially 100% efficient, but techniques such as the pressure switching method will be needed to automate the process. A combination of a microparticulate packed precut column with backflushing together with pressure switch heart cutting and/or capillary cold trapping with separation on a capillary column would provide increased speed, resolution and selectivity. Such a system will not only be useful for conservative gaseous tracers, but may also prove essential for studies with non-conservative

tracers (for which severe catalytic clean-up may not be possible) and for determination of atmospheric trace hydrocarbons.

D. The Reference Tracer Approach

As pointed out in Section 3-B, based on the criterion of a measured tracer concentration 10 times background at 2 standard deviations from the plume centerline, the annual cost of 5 tracers for the 1 year pseudo-continuous experiment would be \$15,000,000. In this part, the technique is presented for calculating the minimum receptor tracer concentration due to the source in terms of the error associated with the GC reference tracer approach as well as the allowable error in the measured receptor concentration. The technique is then used to demonstrate the tracer cost savings due to the higher resolution potential of the capillary column GC system or any other high resolution approach.

D.1. Formulation of the Tracer Ratio Technique

The error associated with the measurement of a tracer concentration at a receptor site due to a distant tracer source is partly the error in the sampled volume and partly the error in the analysis. If, however, the released tracer is measured relative to another tracer which is not released and whose ambient concentration is known, then the sampled volume is not needed.

As pointed out in Section 2-B, because of its high ambient background concentration of 25.6 fL/L, PDCH cannot be cost effectively used as a tracer. But it may serve as a reference tracer to improve the precision of the determination of the concentration of the released tracer. Letting C_t be the concentration of the released tracer, then the tracer concentration at a receptor site due to the source is the sample concentration minus the ambient concentration, namely,

$$(C_t)_{\text{source}} = (C_t)_{\text{sam}} - (C_t)_{\text{amb}} \quad (1)$$

But letting PDCH (subscript code r) be the reference tracer. the sample tracer concentration can be equated to

$$(C_t)_{\text{sam}} = \left(\frac{v_t}{v_r} \right)_{\text{sam}} \times (C_r)_{\text{amb}} \quad (2)$$

where v_t , v_r = the volume of tracer and reference tracer (PDCH), respectively, contained within the measured sample (pL)

C_t , C_r = the concentration of tracer and reference tracer, respectively (pL/L).

Furthermore, the tracer volume ratio can be equated to the calibration factor ratio times the sample chromatogram peak area ratio, namely

$$(C_t)_{\text{sam}} = \left(\frac{a_t}{a_r} \right)_{\text{calib}} \left(\frac{A_t}{A_r} \right)_{\text{sam}} (C_r)_{\text{amb}} \quad (3)$$

Substituting Eq. (3) into Eq. (1) and dividing by $(C_t)_{\text{amb}}$ gives

$$\frac{(C_t)_{\text{source}}}{(C_t)_{\text{amb}}} = \frac{\left(\frac{a_t}{a_r} \right)_{\text{calib}} \left(\frac{A_t}{A_r} \right)_{\text{sam}}}{\left(\frac{C_t}{C_r} \right)_{\text{amb}}} - 1 \quad (4)$$

which is also equivalent to

$$\frac{(C_t)_{\text{source}}}{(C_t)_{\text{amb}}} = \frac{\left(\frac{a_t}{a_r} \right)_{\text{calib}} \left(\frac{A_t}{A_r} \right)_{\text{sam}}}{\left(\frac{a_t}{a_r} \right)_{\text{calib}} \left(\frac{A_t}{A_r} \right)_{\text{amb}}} - 1 \quad (5)$$

or

$$\frac{(C_T)_{\text{source}}}{(C_T)_{\text{amb}}} = \frac{\left(\frac{A_T}{A_R}\right)_{\text{sam}}}{\left(\frac{A_T}{A_R}\right)_{\text{amb}}} - 1 \quad (6)$$

Eq. (6) shows that the concentration of the released tracer (C_T) attributable to the source relative to its ambient concentration is equal to the ratio of the peak area of the released tracer to the reference tracer in the measured sample divided by that in an ambient background sample minus 1.

Quite clearly Eqs. (5) or (6) show that as long as the ambient concentration of the released tracer, $(C_T)_{\text{amb}}$, is known, the concentration at the receptor site of the source tracer, $(C_T)_{\text{source}}$, is independent of the sampled volume.

In arriving at Eq. (6), it was assumed that the calibration factor ratio, $(a_T/a_R)_{\text{calib}}$, was constant, independent of peak area or sample size. For a constant frequency, variable current electron capture detector (ECD), this calibration ratio is constant up to about 5 to 20 pL of tracer, more than sufficient for MATEX-type experiments. But today's modern GCs use the "linear" constant current, variable frequency ECD because of its greater dynamic range--about 6 orders of magnitude compared to 3.5 orders for the former. Unfortunately, for strongly electronegative compounds, such as the PFTs, the "linear" detector is not linear; significant (greater than 0.5%) deviation from linearity commences between 0.1 and 0.5 pL. Thus, MATEX-dedicated GCs should be operated with the ECD in a constant frequency mode.

With the ECD operating in the constant frequency mode, Eq. (6) is applicable up to 5 to 20 pL of tracer, which means that calibration is unnecessary. It is only necessary to precisely determine, once, the ambient concentration of each of the tracers and then to precisely determine the area ratios for the sample and ambient air. If it can be determined that

the area ratios for ambient air are essentially constant and known, independent of slight unintentional changes in the operating conditions of the GC, then Eq. (6) indicates that no periodic calibration is necessary. These conditions must be investigated.

D.2. Precision of the Source Concentration Determination

Equation (6) can be redefined as

$$R_C = \frac{R_{As}}{R_{Aa}} - 1 \quad (7)$$

where R_C = the source-to-ambient tracer concentration ratio and R_{As} , R_{Aa} = the tracer-to-reference tracer area ratios in the sample and ambient air, respectively.

Defining E as the maximum fractional error allowable in the concentration ratio, R_C (e.g., 0.1 means a 10% error in the ratio), and d as the fractional error normally encountered in the determination of the GC area ratios, then Eq. (7) can be used to derive the minimum allowable tracer ratio at the receptor site. By definition

$$E = \frac{\max R_C - R_C}{R_C} \quad (8)$$

where the $\max R_C$ is given by

$$\max R_C = \frac{R_{As}(1 + d)}{R_{Aa}(1 - d)} \quad (9)$$

that is, the maximum value for R_C is obtained by maximizing R_{As} and minimizing R_{Aa} .

Substituting Eqs. (7) and (9) into Eq. (8), it can be shown that the minimum tracer concentration ratio allowable at the receptor site for a given precision is

$$\min R_c = \frac{\frac{1+d}{1-d} - 1}{E - (\frac{1+d}{1-d} - 1)} = \min \frac{(C_t)_{\text{source}}}{(C_t)_{\text{amb}}} \quad (10)$$

Eq. (10) can now be used to compute this minimum source-to-ambient concentration ratio at the 2σ receptor site for the present GC precision and the expected improved precision for a high resolution GC system.

Present GC System. With the present GC system, the fractional error normally associated with the GC area ratios when high PFT volumes (greater than 5 pL) are encountered corresponds to $d = 0.01$ (i.e., $\pm 1\%$ precision). But for typical ambient quantities of tracer, $d = 0.04$.

For the following allowable errors in the precision of the determination of the receptor site concentration ratio, the following minimum concentration ratio is computed for near ambient levels ($d = 0.04$):

Error in R_c : <u>$\pm 10\%$</u>	<u>$\pm 15\%$</u>	<u>$\pm 20\%$</u>	<u>$\pm 25\%$</u>
E : 0.10	0.15	0.20	0.25
min R_c : 5.0	1.25	0.714	0.50

For an allowable error of $\pm 10\%$, the min R_c is 5.0, that is, 5 times ambient at 2σ . Note that this is close to the typical design release consideration of 10 times ambient at 2σ as discussed in Section 3-A. If a 25% uncertainty could be tolerated, then the min R_c , and, hence, the quantity of tracer released, would decrease by 10-fold. But for these source-receptor relationship studies, a 25% uncertainty cannot be tolerated.

High Resolution GC System. There is significant evidence to indicate that for high resolution GC systems the precision of area ratios will be markedly better than for packed columns. As indicated above, even for the packed columns, the precision is $\pm 1\%$ when the sampled volume is large

enough. Thus, it is anticipated that for the high resolution GC system, the precision of the area ratio will be $\pm 0.5\%$ or less, that is, $d \leq 0.005$.

Using a d of 0.005, the following minimum concentration ratio is computed:

Error in R_c :	<u>$\pm 10\%$</u>	<u>$\pm 15\%$</u>	<u>$\pm 20\%$</u>	<u>$\pm 25\%$</u>
E :	0.10	0.15	0.20	0.25
min R_c :	0.112	0.0718	0.0529	0.0419

With the high resolution GC system and for an allowable error of $\pm 10\%$, the min R_c is 0.11, that is, only 11% of ambient at 2σ . This represents almost a 50-fold reduction in the quantity of tracer that must be released to obtain the source contribution within $\pm 10\%$.

Tracer Reduction Benefits. Since, as shown in Section 3-B, the annual tracer cost requirement with the present GC precision is about \$15,000,000, a 50-fold reduction in the tracer quantity would reduce the cost to \$300,000 for a savings of \$14,700,000. In addition, instead of requiring almost 30 metric tons per year of each tracer, the consumption would drop to less than 1 ton, well within the reach of current manufacturing capacity.

Even if the high performance GC system only gave a 10-fold reduction in tracer requirements, the cost savings in tracer would still be more than \$13,000,000, quite significant. Thus it is essential that research proceed on the development and testing of a viable, high resolution GC system.

Section 6

FEASIBILITY OF TRACER MATERIAL BALANCES

The question of whether a material balance for a conservative perfluorocarbon tracer release can be achieved is dependent on

1. The degree of atmospheric dispersion
2. The length of time of tracer release, and transport.

These ultimately depend on the meteorological conditions and terrain over which the tracer plume has traversed.

A tracer release over a period of time, typically a few hours is essentially a line source which broadens in width, lengthens in time (or equivalently distance) as the tracer release plume is transported in time. The tracer plume will expand in height (assuming a ground release) until the top of the mixed layer is reached, when the dispersion will be reflected back downwards. Consequently, the answer is dependent on how well can we sample an "expanded" tracer plume so as to define its extent, in order to integrate the observed tracer concentrations over this expanded tracer plume volume, which reduces to the question, how big is it?

In order to provide an estimate as to the extent of a tracer plume, I shall define the direction and degree of the tracer plume dispersion by characterizing the dispersion as being Gaussian, this being more based on empirical observation, as will be evident in examples of previous field experiments. By Gaussian, I mean the tracer concentration, $C(t)$, in a transported plume, can be expressed in terms of three orthogonal dispersion coefficients σ_x , σ_y , and σ_v ; the alongwind, the crosswind and the vertical dispersion coefficients. One can then assume that the three atmospheric dispersions are more or less independent of one another.

A. Crosswind Dispersion

A lateral traverse of a transported tracer plume can be analyzed using the Gaussian dispersion equation,

$$C(y) = C \exp[-(y-y_0)^2/2 \sigma_y^2]$$

in order to give the crosswind dispersion coefficient, σ_y . The parameter C includes the effects of the alongwind and vertical dispersion of the transported tracer plume and can be regarded as a constant for a lateral sampling traverse at a constant downwind distance and vertical height. Figure 6-1 gives an example of a lateral aircraft traverse at 750 km downwind of a tracer release as derived from a CAPTEX II experiment of 9/26/83. The tracer concentration was determined in real-time and the best Gaussian fit is represented by the line yielding a σ_y of 61.5 km. As can be seen, the degree of fit is only average and the value of C can be fitted as 114 ± 19 fL/L PMCH, or to within 15 to 20%. Another CAPTEX mission, is shown in Figure 6-2, which again yields a σ_y of 16.1 ± 0.4 km. In this instance the degree of fit is much greater than the first example and is within 5%. Consequently, it can be reasonably assumed, that based on the experience in the CAPTEX missions, we can determine the lateral constant, C, in less than average instances to at least within 20%.

The crosswind dispersion coefficients as determined from several CAPTEX missions are plotted on an extrapolated Pasquill-Gifford crosswind standard deviation versus downwind distance plot, and is shown in Figure 6-3. The experimentally derived crosswind dispersion coefficients, assuming a simple Gaussian dispersion function, agree well within the range of predicted values. This leads to a confidence in predicting the crosswind width of a tracer plume based on assuming a simple Gaussian dispersion model.

Figure 6-1. Captex Mission II, Sortie 2, 9/26/83, 750km downwind, Altitude 4000ft(AMSL)

Figure 6-2. CAPTEX Mission IV, Scouring Sortie, 10/15/83, 750 km downwind,
altitude 4000 ft (ANSL).

Figure 6-3. Crosswind dispersion coefficients as determined from several CAPTEX missions plotted on an extrapolated Pasquill-Gifford plot.

B. Vertical Dispersion

Some model calculations and limited field data can be used to estimate the vertical dispersion parameter. For the examples given above with a plume transport distance of 750 km, it would be expected that $\sigma_y = 50$ km. With the height of the mixed layer being less than several kilometers, we can expect the tracer plume concentration to be uniform from the ground level to the top of the mixed layer. In other words, the tracer plume has grown in height reaching the top of the mixed layer, consequently, lateral traverses across the tracer plume at differing heights within the mixed layer should yield the same tracer concentration profiles. As a result, in order to perform a tracer material balance it is only necessary to know the height of the mixed layer, when integrating the vertical distribution of the tracer concentration, assumed to be constant within the mixing layer.

This will be complicated by the fact that a tracer plume transported, for example, 750 km, will have had to travel at least 10-20 hr after release, through various terrains and meteorological conditions with differing heights for the mixed layer. The height of the mixed layer needed for the material balance calculation will be the maximum mixed layer height encountered by the tracer plume, not the height measured at the sampling location. This will introduce an additional uncertainty in the material balance.

C. Alongwind Dispersion

Calculation of the degree of dispersion of a tracer plume in the alongwind direction is complicated by the fact that the tracer release is not a point source in the alongwind direction, but rather an extended line source. However, again assuming Gaussian dispersion, it can be shown that

the $C(t)$ in the alongwind direction should be

$$C(t) = (A/2) \left\{ \operatorname{erfc} ((tr-t)/2^{1/2}\sigma) - \operatorname{erfc} ((tr-t+T)/2^{1/2}\sigma) \right\} \\ + (A/2) \left\{ \operatorname{erfc} ((tr+t)/2^{1/2}\sigma) - \operatorname{erfc} ((tr+t+T)/2^{1/2}\sigma) \right\}$$

in which the dependent variable is time, t , which is simply related to the alongwind travel distance, knowing an average wind velocity. In this equation, tr is the equivalent transit time, where the tracer concentration is measured, i.e., $tr = x/u$, x being the distance from the release site to the sampling site and u , the average wind velocity. σ is the alongwind dispersion coefficient and T is the time-length of the tracer release. A is again proportional to the amount of tracer released and the degree of tracer dispersion in crosswind and vertical directions, again, assumed to be constant in the alongwind direction at long distances from the release site.

Now, the above equation is not simple but can be simplified by noting that the last two terms, taken together, are approximately zero for long sampling times, by long times is meant $tr > \sigma$, i.e., if $\sigma = 100$ km then tr should be several hundred km.

Some examples of the tracer concentration profiles are given as follows. I have chosen $tr = 670$ km, $T = 3$ hr = 118.8 km when $u = 11$ m/sec. Two curves are given in Figure 6-4, one for $\sigma = 160$ km and the other for $\sigma = 100$ km. The resulting full widths at half maxima are 384 and 242 km respectively. The obvious conclusion is that the smaller the dispersion, the narrower the distribution. Also note that the tracer concentrations will be higher with lower dispersion coefficient, due to the conservation of

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mass requirement. Thus we see from this model that the tracer plume is lengthened after being transported 670 km. Now, in order to experimentally determine the alongwind dispersion of a tracer plume, we need to measure the tracer concentration down the centerline of the plume, which is experimentally unfeasible. The only other method is to make a series of lateral traverses across the plume, from which, the alongwind profile can be constructed. The minimum number of crosswind traverses needed is three, one somewhat after the arrival of the plume, one near the plume maximum, and one somewhat near the end of the plume. From these three crosswind traverses, it is possible to determine the three unknowns in the alongwind dispersion equation, i.e., the alongwind dispersion coefficient, the normalizing constant and the location of the plume maximum. Once these are determined, then the alongwind extent of the tracer plume can be calculated.

D. Precision of a Tracer Material Balance.

It can be seen as a result of the above discussion, that in order to calculate the total tracer concentration in a transported and dispersed tracer plume, so as to calculate a tracer material balance, the lateral tracer concentration profile has to be measured at a minimum of three alongwind distances. Also needed is the maximum height of the mixed layer through which the plume has been transported. Now, it was determined that in the less than average instance, the precision of a lateral plume traverse was 15 to 20%, and with at least three traverses needed, the precision would decrease to 45 to 60%. The precision of determining the maximum height of mixed layer could range from a low of 2 to 3% for the best and most frequent determination along the plume transit path to a high of 12 to 15% for the typical situation of extrapolating heights from twice daily radiosondes.

Consequently, we can now bound the precision to which we can calculate a material balance:

(i) A "best of all worlds" case.

In this case we assume we can determine the plume crosswind and alongwind concentration tracer profiles to at best 15%, and the height of mixed layer to 2 to 3%, summing to a total precision of approximately 20%. This would require frequent aircraft determinations of height of mixed layer along the transit path of plume and many lateral traverses across the plume itself before and after its arrival.

(ii) A dedicated determination.

More realistically we can expect the plume crosswind and alongwind concentration profiles to be determined with a precision of about 45 to 60%, assuming a minimum of three lateral traverses. The maximum height of mixed layer can be determined to a precision of about 12 to 15% assuming a conventional frequency of radiosonde determinations. This gives an estimate of the precision of approximately 55 to 75% in the calculation of the conservative tracer material balance.

(iii) A typical experiment.

Clearly, even the dedicated determination requires the alongwind tracer concentration profile to be measured (indirectly, though). This requires the beginning of the plume to be located sufficiently early so as to obtain the required early arrival tracer concentration profiles. This is no easy task, and in some situations the plume may only be located after the alongwind plume maximum has passed; in this case it would be impossible to do a tracer material balance. A more probable situation would be if the early arrival profile is missed, but profiles are obtained near and after

there would have to be a significant increase in production capacity to meet the potential MATEX needs.

At \$100/kg, the 29 metric tons of PMCH would cost \$3 million. With 5 release sources, the total tracer bill would be \$15 million. Quite obviously, ways to reduce the quantity of tracer needed per release could have significant cost savings benefits. This is discussed in more detail in Section 5-D.

C. Release Equipment

As shown in Table 2-2, the PFTs are predominantly liquids at room temperature and therefore must either be atomized directly into the air or vaporized in a heated chamber and diluted with compressed air below the dew point concentration before being released to the atmosphere. Equipment for performing automated releases on a preprogrammed schedule has been built and successfully field tested. Only a modest amount of engineering would be required to provide the necessary MATEX release equipment.

the maximum including the near end plume profile; then a material balance could be calculated but with a decrease in precision beyond the 55 to 75% estimate of the above situation, probably greater than the 100% level.

Section 7

SAMPLING LOCATIONS AND FREQUENCY

Specific details on the requirements for ground and aircraft sampling including such things as the number of ground samplers and the frequency of their sampling or the number of aircraft needed to adequately define the vertical extent of a given tracer plume must necessarily await the description and goal of the actual MATEX experiment.

However, in this section some general bounds will be placed on the requirements for the number of ground samplers and the number of aircraft needed to meet the needs of the experiment and/or provide information for an adequate plume material balance.

A. Ground Sampling Density

The 600 km Oklahoma experiment was performed with about 20 BATS on a 100 km arc and 30 on a 600 km arc, the latter covering about 65° of the arc. Thus, the samplers were spaced about every 2° or about 20 km apart at 600 km downwind. The standard deviation of the plume width (σ_y) from the ground samplers was between 20 to 25 km. With that spacing, only four samplers on average had concentrations exceeding one-fifth the peak concentration. For modeling purposes, that is, for calculating σ_y , three samples exceeding 1/5 the peak concentration is the minimum number necessary. Thus we can assume that in the form of north-to-south sampling lines, the minimum spacing between samplers should be 25 km.

The real-time analyses from the CAPTEX 1983 tests also showed σ_y 's of 15 to 60 km (cf. Fig. 6-3). This would further corroborate the need for 25 km spacing.

Now we will make a further assumption that the U.S. and southeastern Canada is to be covered from east of the Mississippi River to the East Coast in 5 parallel sampling lines each about 200 km apart. This would provide crosswind resolution for the essentially westerly prevailing winds and adequate resolution in the alongwind direction. Obviously the array could be modified slightly from this pattern, but the quantity would not change significantly. Since each line would be about 2000 km long, 80 stations would be needed per line. With 5 lines, the total would be about 400 ground sampling stations. About 80 such stations were used in the Ohio, Pennsylvania, New York and surrounding area (including nearby Canada) during the CAPTEX 83 missions, so 400 would appear to be appropriate for the MATEX tests.

A.1. Number of Ground Samples to be Analyzed

An estimate can also be made for the number of samples collected in one year. The following assumptions are made:

No. of Ground Stations: 400 stations

Duration of Sample : 6 hours

Sampling Period : 365 days

On a 600 km scale, CAPTEX 1983 showed that the plume duration in the alongwind direction could be as much as 12 to 15 hours for just a puff release. Then on a 1000 km scale this might increase to 15 to 18 hours. Since it is desirable to sample frequently enough to resolve to some extent the arrival and departure of the plume as well as the peak concentrations, it is estimated that the sampling duration per tube should be no more than 6 hours, that is, no less frequently than 4 samples per day per station. Thus, a total of 584,000 samples would be collected in one year.

Based on the success of the real-time dual-trap analyzer, it is expected that all vertical sampling conducted from aircraft platforms will be performed with real-time analyzers and no additional sampling tubes will result from such aircraft sampling.

A.2. Number of Ground Sampler Bases and Lids Required

For the above scenario, it is assumed that during the course of the experiment there will be an 8% failure for BATS bases and 4% for lids. Since each lid contains 23 sampling tubes and four 6-hour samples are to be collected each day, one lid will last 5.75 days. If we make the assumption that all the lids used in the first month are collected, returned to a central laboratory, analyzed, checked out and repaired, baked out, and returned to the field for use commencing about 2 months later, then 15 lids per station would be adequate. Five lids would be used in the first 29 days; the 10 remaining lids would last for another 58 days until the first 5 were returned to the site.

With these assumptions, the total number of lids and bases needed for the 400 ground stations and their costs are:

	<u>Qty.</u>	<u>Cost</u>
No. of Ground Stations :	400	
No. of BATS Bases (\$3000 each):	432	\$ 1,300,000
No. of BATS Lids (\$2000 each) :	6240	\$12,500,000

This further assumes that the 584,000 samples are analyzed in 52 weeks or 11,230 samples per week. The equipment needed to meet this rate was discussed in Section 5-C.2.

A.3. Cost Optimization of GC Systems and BATS Lids

As shown in Section 5-C.2., the operating and capital cost of these GC stations when optimized with high resolution GCs equipped for round-the-clock analyses is only about \$2,000,000 including the cost for handling the 2000 BATS lids per month. By doubling the number of GC stations at a cost of \$2,000,000, perhaps 2000 fewer BATS lids need be purchased (\$4,000,000), at a net savings of \$2,000,000.

B. Required Aircraft Density

Section 6 has provided an extended discussion regarding the size of a transported tracer plume which has been subjected to atmospheric dispersion. It is this extent of the tracer plume that will determine the required aircraft density needed in an experiment. Each aircraft will be equipped with a real-time dual-trap tracer analyzer to facilitate the location of the sampling paths.

B.1. Crosswind Tracer Plume Extent

It can be expected that after a tracer release has been transported over, for example, 750 km, that the plume crosswind full width at half maximum will range from 30 to 150 km. In order to obtain a crosswind tracer concentration profile with a precision of at least 15 to 20%, at least twice the plume crosswind fullwidth must be sampled, that is, 100 to 300 km of lateral plume sampling. For the purposes of this discussion, it is assumed that the aircraft will only be sampling the details of one tracer plume, even though other plumes may be emanating from different regions of the country. At a speed of 220 km/h, the plane can make a total of 3 or 4 complete passes between refueling and rest periods.

B.2. Vertical Tracer Plume Extent

Under the same atmospheric conditions as in the above example, it can be expected that the tracer concentration will be completely uniform in the vertical direction throughout the mixed layer. Consequently, only one aircraft tracer sampling run need be done, as long as it is within the mixed layer. To verify the tracer uniformity in the vertical, two aircraft should traverse the tracer plume at two different altitudes and return at a second set of altitudes. This will also provide information on the possible shear of the tracer plume with altitude as well as the extent of vertical uniformity.

B.3. Alongwind Tracer Plume Extent

Again, for the purpose of example, we assume the same conditions for the transported tracer plume as in the above examples. Under these conditions we can expect the alongwind plume fullwidths at half maximum to range from 200 to 400 km, assuming a three hour tracer release. Consequently, we would need to sample alongwind for 400 to 800 km along the centerline of the plume. These distances can, of course, be expressed equivalently as time, at a fixed sampling arc. The 400 to 800 km alongwind extent of the tracer plume is equivalent to the plume taking 10 to 20 hours to pass through a fixed sampling arc location. Now, it is not feasible to sample down the centerline in the alongwind direction of the plume, simply because we do not know where that is. Consequently, a series of lateral (or crosswind) traverses must be made, from which the alongwind tracer concentration profile can be constructed. The absolute minimum is three lateral traverses, one slightly after the plume arrival, one near the alongwind plume tracer maximum, and one near the end of the plume. More preferred would be twice that,

or six lateral aircraft traverses over a 10 to 20 hour plume transiting time. However, this assumes one knows when and where the beginning of the plume will be, clearly a major assumption, if the first sampling runs are at several hundred km past the release site. More realistic would be to allow at least three more aircraft sampling runs just to allow for locating the beginning of plume. This brings the number of aircraft runs to at least ten for a 10-20 hr alongwind wide plume, with a sampling frequency more heavily biased at the beginning of the plume. The individual sampling runs would have to span 100 to 300 km in the crosswind direction of the plume.

This type of aircraft plume sampling will allow a full three dimensional characterization of the tracer plume to be calculated, with a possibility of a tracer material balance being made.

B.4. Estimated Aircraft Requirements

As a minimum, then, it is proposed that a team of three aircraft be used to determine the above ground extent of the plume at 750 km downwind. Each plane should be a twin-engine-type equipped with pilot, co-pilot, and a real-time tracer analyzer operator plus automatic recording navigational equipment. In addition, one plane, the scouting plane, should be equipped with automatic recording meteorological equipment for temperature and winds aloft obtained during normal crosswind traverses as well as during several vertical soundings.

A complete change of crew would be necessary for each plane such that following 3 or 4 passes (about 4.5 h), the planes could refuel, change crews, and repeat another 3 or 4 passes. This process would be repeated 4 times to cover the necessary 20 h period. To aid in the starting of the process, one plane would serve as a scouting plane, perhaps flying about 100

to 150 km upwind of the main sampling arc, in order to pinpoint the arrival time of the plume. That plane would then rejoin the other two. The scouting plane would also perform the vertical soundings.

For some experiments, a second team of three aircraft might also be deployed at a closer arc, perhaps 250 km, in order to determine the changing character of the plume with distance. This is especially interesting to document the change in the alongwind spread of the plume with distance as there are little quality data available.

Section 8

NEEDED PERFLUOROCARBON TRACER SYSTEM RESEARCH

The perfluorocarbon tracer (PFT) system is comprised of the PFTs themselves, tracer release equipment, sampling devices, analytical instruments, and data handling approaches.

Although considered in detail in the earlier sections, the purpose of this section is to summarize in one place, the research that should be conducted now such that a feasibly and economically viable tracer system is available for MATEX in about 2 years from now.

A. Availability of PFTs

As discussed in Section 2, only 2 tracers currently meet the long-range (>500 km) tracer specifications. The two tracers are:

<u>Name</u>	<u>Background Conc., fL/L</u>	<u>Cost</u>
1. Perfluoromethylcyclohexane (PMCH)	3.6	\$100/kg
2. Perfluoromethylcyclopentane (PMCP)	2.8	\$100/kg

The first, FMCH, has been thoroughly tested, both in the laboratory and in the field, and is established as a reliable tracer. The second, PMCP, is currently being evaluated, but it appears to be suitable in all respects.

Another tracer, perfluorodimethylcyclohexane, because of its almost 10-fold higher background concentration (26 fL/L), is not economically viable. However, it will serve an important role in the data interpretation since it can serve as an internal atmospheric reference standard (see Section 5-D).

A potential of 3 more tracers (nos. 7-9 in Table 2-1) that would be made by the current tracer suppliers need to be investigated. Similarly

PDCB (no. 3 in the table) as well as a small family of other perfluoro-alkylcyclobutanes, could be potentially manufactured by the once-used duPont process.

Unless a number of the new potential tracers are investigated soon, the family of tracers available to MATEX may be limited to 2, which would be a significant disadvantage.

B. Tracer Release Needs

For the past 6 years or so, a number of different types of release techniques have been used for the PFTs, most notably, atomization and vaporization followed by dilution. A minor amount of engineering should be applied to be certain that one such apparatus will have the requisite release rate accuracy and equipment durability.

C. PFT Sampler Needs

The present PFT programmable sampler has allowed a number of significantly useful long range and complex terrain experiments to be conducted which otherwise would not have been possible. However, their field use and to a lesser extent their subsequent laboratory analysis has pointed to a number of deficiencies including the internal pump reliability, flexibility and ease of setting operating parameters, and reliability and recovery of stored data. In addition, the adsorbent currently used in the sampling tubes is no longer commercially available.

Research should be initiated now to develop and commercialize a second generation sampler that includes all the features described in Section 4 such as electronically controlled pumping rates; microcomputer controlled operation; and remote (e.g., telephone jack) programming and system performance interrogation. It is anticipated that 2 to 2.5 years of research and prototype fabrication would be required before the first units are commercially produced.

D. PFT Analytical Advances

As discussed in detail in Section 5, the present analytical system has only enough resolving capability to handle 3 or 4 PFTs effectively. In addition, the area ratio precision is currently only about $\pm 4\%$ for 5L air samples at or near ambient concentrations. This restriction limits the quantity of tracers that must be released in order to precisely determine the tracer concentration at a receptor that is attributable to a particular source. In terms of tracer cost, this was shown to amount to about \$15,000,000 for 5 tracers released for 4 hours every 2.5 days for one year (cf. Section 2-B).

Advancement required to increase the tracer handling capability, to reduce analysis time, and to reduce the tracer release quantities include round-the-clock automation, high resolution chromatography research with capillary and micro particulate packed columns, and advanced flow switching concepts (cf. Section 5-C). The benefit of advanced chromatography techniques would be the ability to analyze up to 6 to 8 PFTs in a single chromatogram and as much as a 10- to 50-fold reduction in tracer release requirements for a savings of about \$14,000,000 (cf. Section 5-D).

Again these types of advancements will require about 2 years of research, testing, and validation.