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FIELD TESTING OF A FLUORESCEIN-ZINC SULFIDE DUAL ATMOSPHERIC TRACER TECHNIQUE

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ABSTRACT

Four field experiments were conducted in investigation of the compatibility of fluorescein and fluorescent zinc sulfide as dual atmospheric tracers. The two tracers were emitted simultaneously from a common source and collected on common filters. Qualitative and quantitative comparisons of the sampled tracer distributions are presented. The agreement is good.

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INTRODUCTION

The atmosphere is one of the great "disposal grounds" for man-made and natural wastes. With man contributing an ever-growing proportion of the pollutants (intentionally and accidentally), it is increasingly important that the diffusive properties of the atmosphere be predictable under a variety of meteorological conditions.

Theoretical treatments and predictions based on scaled (wind tunnel) studies can aid in the understanding. However, the free atmosphere itself is the laboratory in which pollution prediction techniques must eventually be proven. The release of a tracer into the atmosphere and subsequent sampling for this tracer offers the possibility of directly measuring the parameters of concern. If one can measure the appropriate meteorological variables during a series of tracer releases, a prediction equation or scheme can possibly be derived.

Unfortunately, the free atmosphere proves to be a very uncooperative laboratory. One is never able to completely duplicate the weather conditions existing during a given tracer release. The effects, then, of such a variable as pollutant source height are always somewhat obscured by the change in meteorological factors in a repeat experiment under similar (but not identical) conditions.

This problem could be partially overcome if it were possible to simultaneously release and sample more than one atmospheric tracer with identical aerodynamic properties. For instance, different tracers could be dispersed from two different elevations at the same time which would assure the meteorological factors existing during their transport being identical.

This paper reports the results of several field experiments designed to test a dual tracer technique.

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PROCEDURES

The primary atmospheric tracer used by Atmospheric Physics at Hanford is U. S. Radium Corporation's pigment 2210, a fluorescing zinc sulfide with a log normal size distribution. The geometric mean diameter of the particle is about 2.3μ. Computed terminal fall velocities are low (centimeters to a few meters) during the time interval the tracer traverses the few miles on the primary Hanford diffusion grids. Simple dispersal, sampling and assaying techniques have been developed for this tracer.[1]

The ideal atmospheric tracer is an inert gas, a tagged "air molecule," instead of a particulate tracer. Pigment 2210 does not fit into the perfect tracer category. However, suspended 2210 does reasonably approximate ambient atmospheric motions, the technology for its dissemination, sampling and assay is available, and much concerning its relationship to meteorological parameters has already been demonstrated. It was appropriate to search for a second tracer compatible with the existing fluorescent pigment 2210 technique.

One candidate for a second tracer was the water-soluble dye fluorescein. This dye has been used as an atmospheric tracer by other investigators.[2] J. D. Ludwick[3] demonstrated the feasibility of laboratory separation and quantitative analysis of pigment 2210 and fluorescein which had been simultaneously collected on a membrane filter. A modification[4] of the original technique was used in fluorescein determinations which are reported in this paper.

In December, 1962, a field experiment, designated MT-1, was performed in which fluorescein and pigment 2210 were simultaneously dispersed from adjacent generators* placed at ground level. Both tracers were collected on the same filter. Results of this test, described in the Hanford Radiological Sciences Research and Development Annual Report for 1962[4], were not encouraging. Although analysis of field samples showed qualitative agreement, the generation of approximately equal masses of fluorescein and 2210 resulted

* Todd Insecticidal Fog Applicator, manufactured by Products Division, Todd Shipyards Corp., Houston, Texas.

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in an average of about 1.7 times as much fluorescein as 2210 on field filters. The variance in the fluorescein to 2210 masses from filter to filter was large. Unfortunately, a change in wind direction near the beginning of the field experiment resulted in significant samples being collected on only 30 filters.

Microscopic examination of several field filters from MT-1 showed the 2210 particles to be larger than the fluorescein. Whereas, in the generation of insoluble particulate tracer 2210, the particle size is predetermined, the dissolving of the soluble fluorescein, and subsequent spraying of a mist permit a variation in the size of particulates left in the atmosphere. The fluorescein particle size distribution is a function of the concentration of dissolved fluorescein fed to the generator and of the size distribution of the droplets being generated. An effort was made to increase the size of fluorescein particles in the atmosphere in multitracer tests conducted after MT-1. This was done by increasing the concentration of the fluorescein formulation solution.

Table I lists information pertinent to generation during multitracer tests to date. The "Particle Size Setting" is a nomenclature marked on the generator which qualitatively controls size of the emitted spray droplets. Large settings indicate larger spray droplets. Under "Formulation" is listed the concentration of the source tracer solution (fluorescein) or suspension (2210). Also noted is the liquid used in preparation of the solution or suspension for generation. Trichloroethane (CH_3CCl_3) was used as the carrier for 2210 in tests MT-2, MT-3 and MT-4. The generation technique involves atomizing the formulation, heating it, and spraying it into the atmosphere where the liquid carrier evaporates. The dry tracer particulates remain. Since trichloroethane is more volatile than water, greater quantities of formulation could be emitted without having droplets fall to the surface before evaporation.

Run MT-2 was a failure for several reasons. During the generation, the pigment 2210 generator faltered and finally failed. Despite the fact that the fluorescein generator was turned off a few seconds after the 2210 generator stopped, there is considerable doubt about the constancy

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of the generation rate of 2210 during this run. The expectation, then, that the ratio of masses of tracer on each filter should be the same as the ratio of masses emitted, would no longer be true. Additionally, the generator operator felt uncertain as to whether he had set the fluorescein "particle size setting" at 7 and the 2210 at 16, or vice versa. Dispersal of the fluorescein water solution at the 16 setting would have resulted in considerable droplet deposition near the generator. Regardless, run MT-2 is listed in the table primarily to retain continuity in experiment nomenclature.

TABLE I

GENERATOR DATA FOR MULTITRACER FIELD EXPERIMENTS

		Fluorescein				Pigment 2210				
Experiment	Date	Formulation, g/liter	Generator Number	Particle Size Setting	Mass Generated, g	Formulation, g/liter	Generator Number	Particle Size Setting	Mass Generated, g	Generated Ratio, 2210/ Fluorescein
MT-1	3 Dec. 62	9.09 (water)	Unknown	7	527	9.09 (water)	Unknown	7	509*	1.04
MT-2	19 May 64	50.0 (water)	POO 1029	7**	1050	20.0 (CH_3CCl_3)	78-19096	16¶	340	0.32
MT-3	12 June 64	31.2 (water)	78-19095	7	750	16.7 (CH_3CCl_3)	78-19096	16	2000	2.67
MT-4	26 June 64	31.2 (water)	78-19096	7	906	16.7 (CH_3CCl_3)	78-19095	16	2000	2.21

* Approximate. Estimated 3 liters of formulation leaked through bad packing in generator.

** May have been 16.

¶ May have been 7.

Experiments MT-3 and MT-4 provided hundreds of field filters upon which significant amounts of both tracers were collected. There was no apparent malfunction of any of the generation equipment and a minimum of missing or questionable field samples.

The diffusion sampling grid on which the dual tracers were released consists of four arcs of about 90°, which were concentric about the generation site. "Ground" samples were collected at an elevation of 1.5 m at 268 sampling positions on these arcs. Distances of the arcs from the source were 0.2, 0.8, 1.6 and 3.2 km. Additionally, five towers on each arc permitted vertical sampling to heights of 27, 42, 62 and 62 m on arcs at 0.2 0.8, 1.6 and 3.2 km, respectively. Towers were located at azimuths of 98, 106, 114, 122 and 130° with respect to the source.

Horizontal and vertical distributions of tracers are given in Figures 1 through 8. Examination of these figures reveals that experiment MT-4 was more

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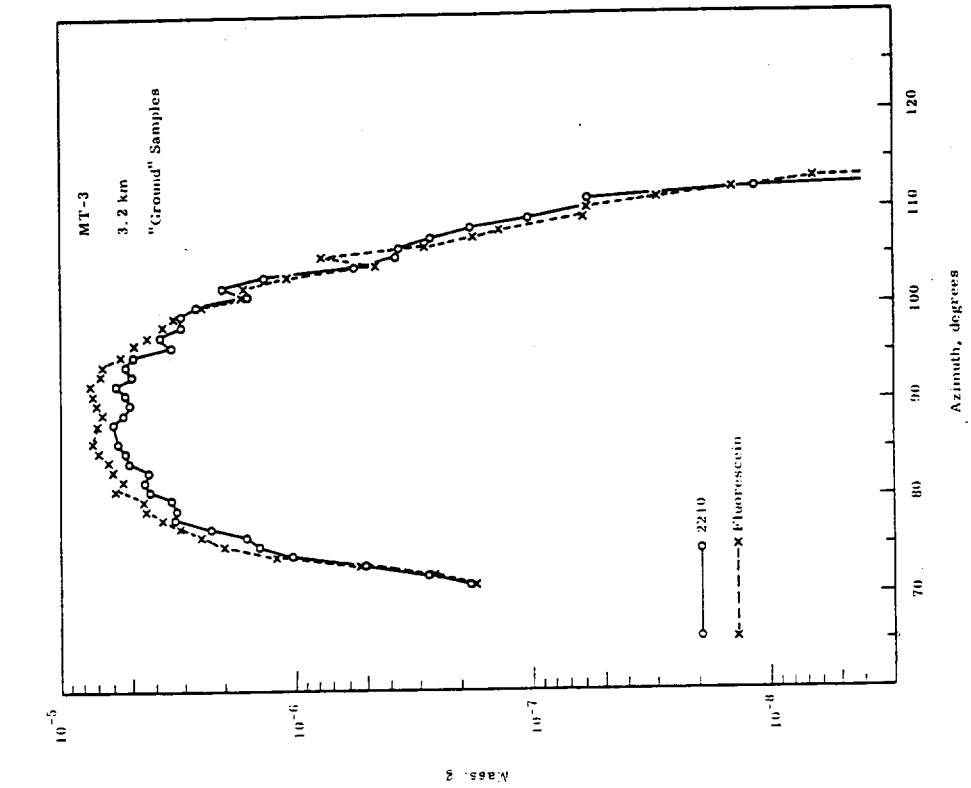

Figure 2

Horizontal Mass Distribution, 3.2 km, MT-3

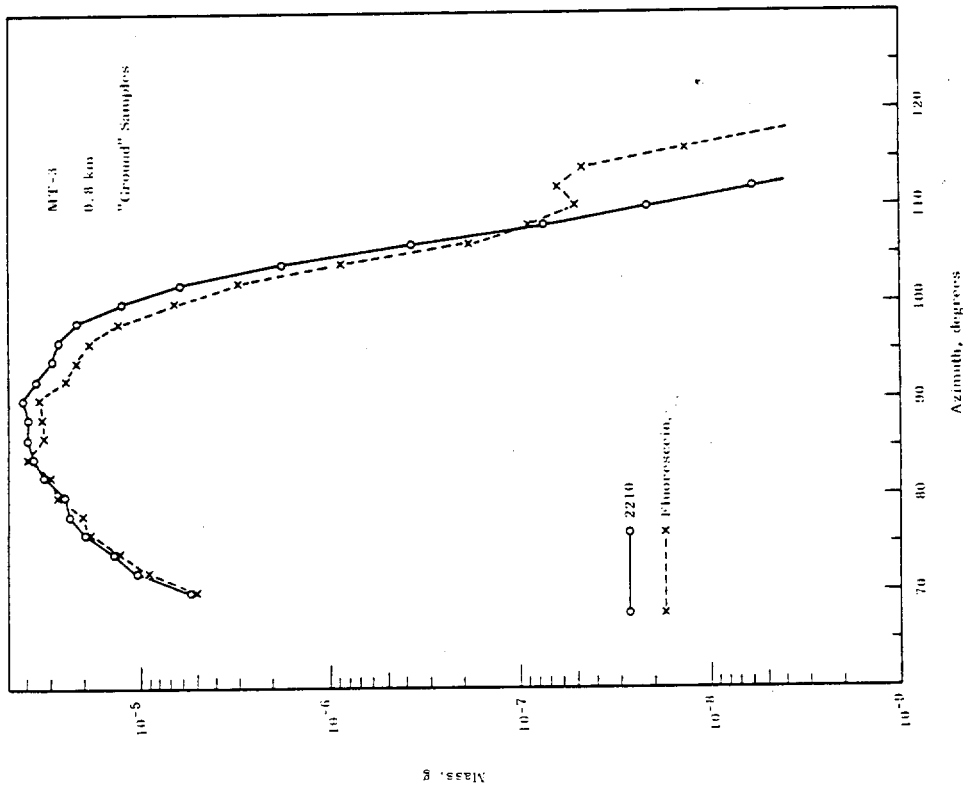

Figure 1

Horizontal Mass Distribution, 0.8 km, MT-3

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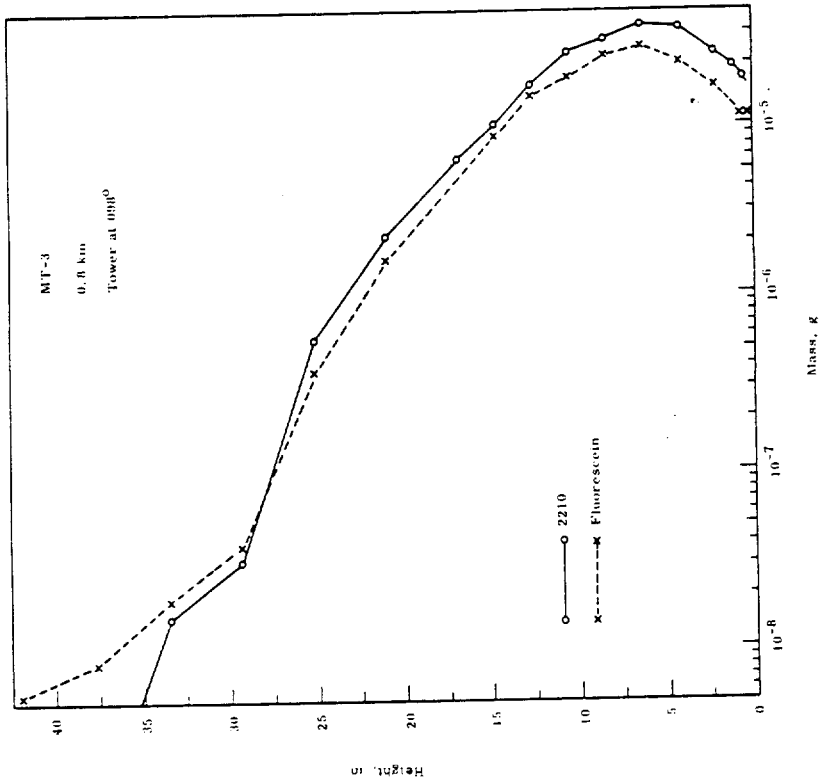

Figure 3
Vertical Mass Distribution, 0.8 km, MT-3

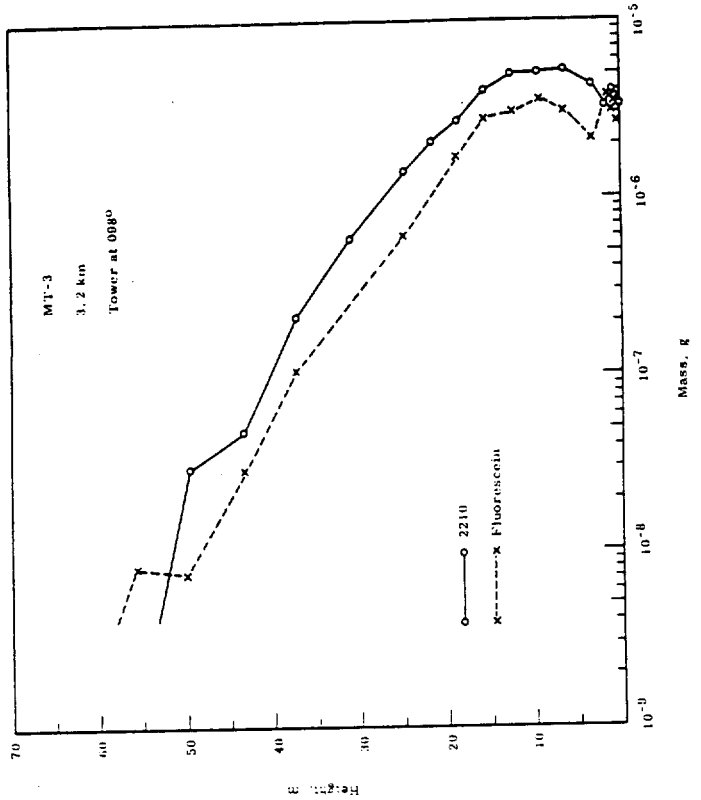

Figure 4
Vertical Mass Distribution, 3.2 km, MT-3

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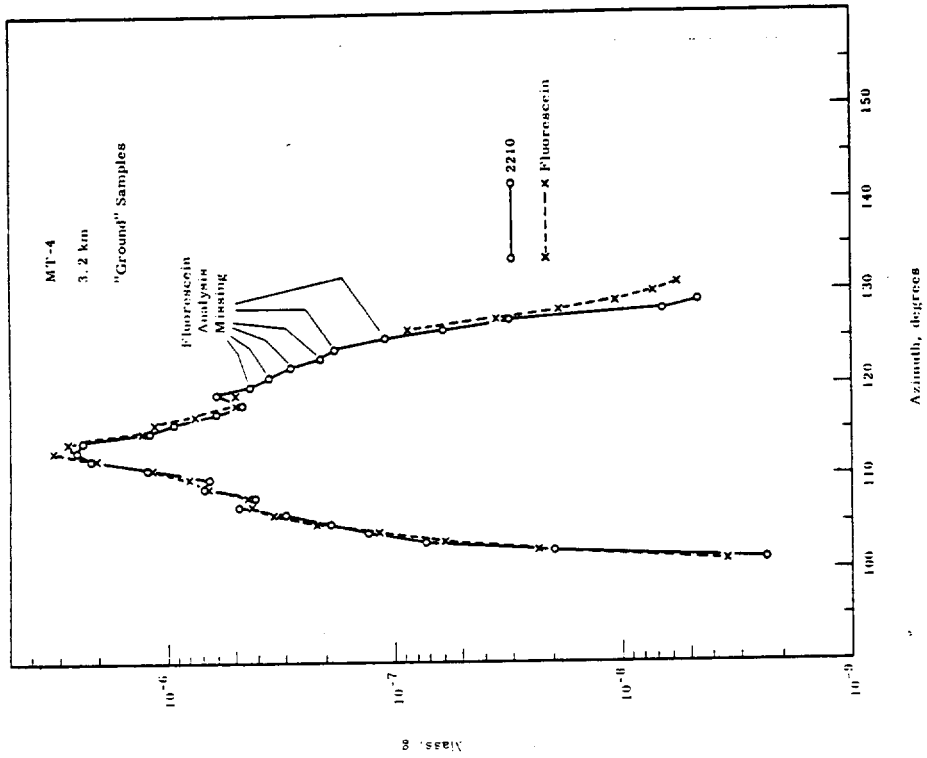

Figure 6
Horizontal Mass Distribution, 3.2 km, MT-4

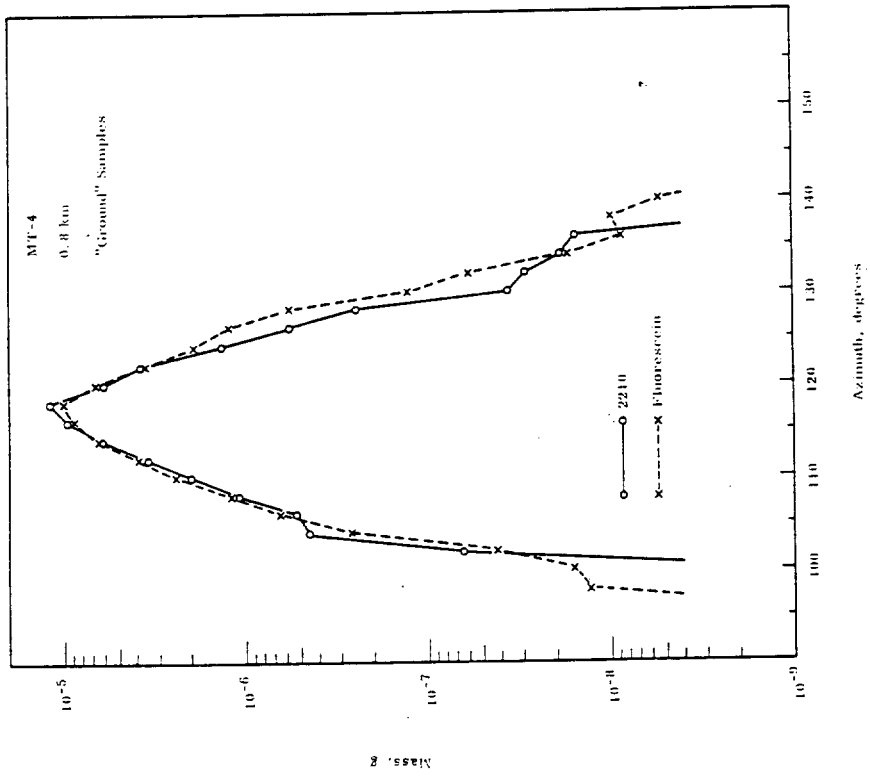

Figure 5
Horizontal Mass Distribution, 0.8 km, MT-4

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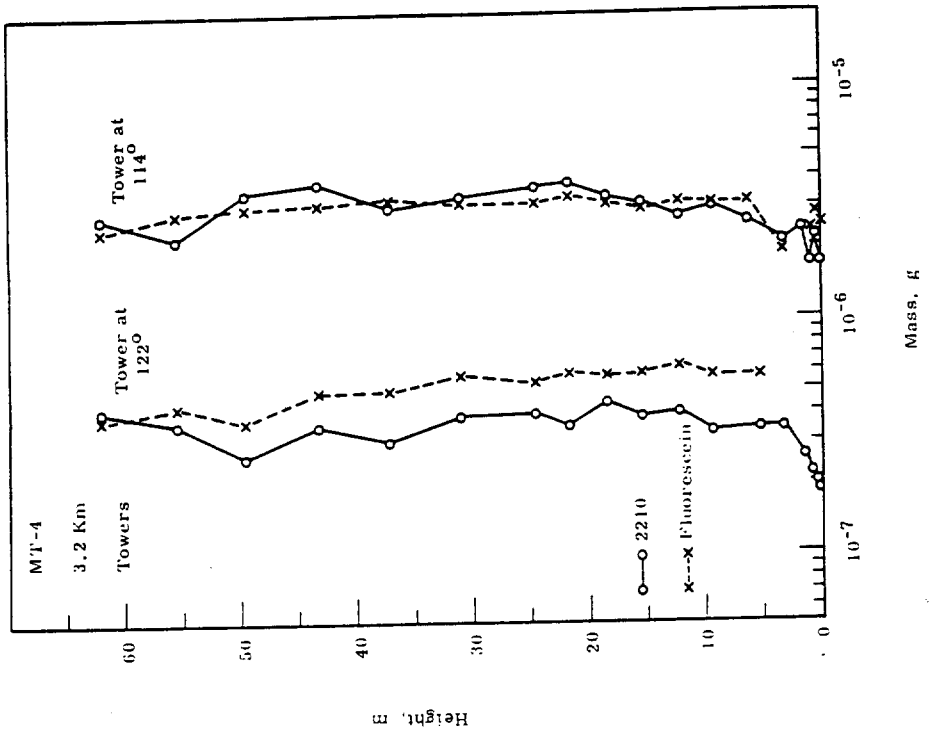

Figure 8
Vertical Mass Distribution, 3.2 km, MT-4

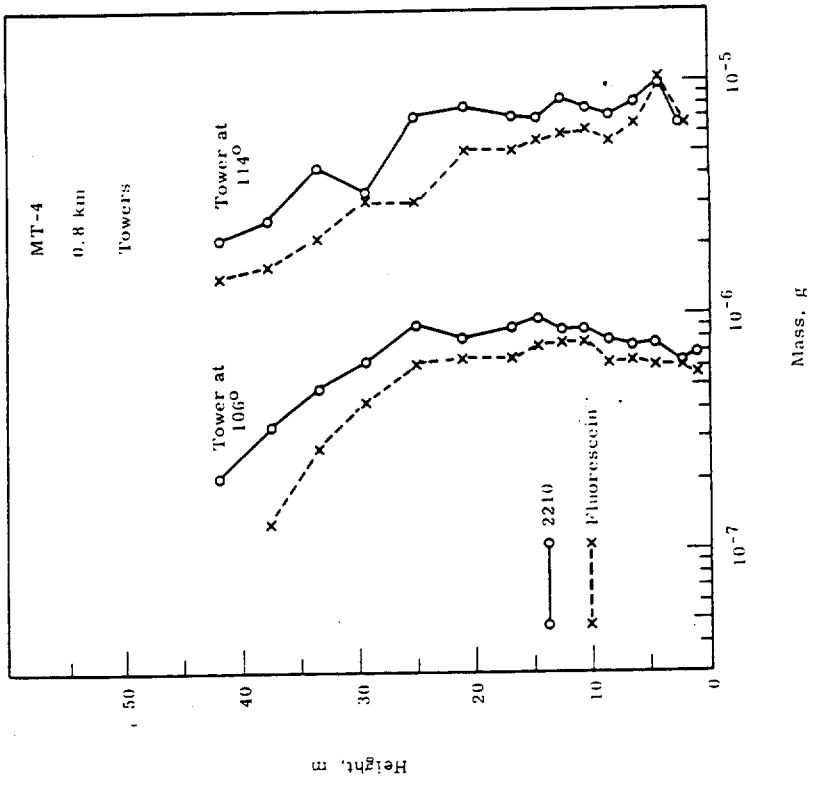

Figure 7
Vertical Mass Distribution, 0.8 km, MT-4

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successful than MT-3. During test MT-3, the mean wind direction was such that the northernmost tail of the tracer distribution was off course. This is illustrated in Figures 1 and 2. The entire crosswind distribution of the tracer was sampled during MT-4 (Figures 5 and 6). Also, distribution of tracer on the tower samplers was ideal during run MT-4 since the maximum masses were collected on the middle radial row of towers, with decreasing masses on the towers at both sides. During experiment MT-3, the peak tower masses were collected on towers at 98°, an end radial row of towers. Thus the crosswind distribution of tracer above the ground level was not well defined for run MT-3.

For ease in comparison of the masses of tracer collected on each filter, the determined mass of fluorescein was multiplied by the ratio of tracer masses emitted. This ratio is listed at the extreme right in Table I. Henceforth in this paper, then, perfect agreement of samples will be indicated by identical masses of fluorescein and 2210.

ANALYSIS

There is no single obvious way to make an investigation of the compatibility of these two tracers. One may qualitatively look at the horizontal or vertical crosswind mass distributions and compare them. Figures 1 through 8 give examples of such comparisons. There is certainly agreement in the general character of the distributions.

The ratio of masses of tracers on each filter could be examined. For instance, on Figure 2, the ratio of mass of fluorescein to 2210 varies from the extreme highs of 2.10 at 105° and 1.44 at 96° to the extreme lows of 0.50 at 111° and 0.59 at 109°. The modal ratio for the illustrated arc is 1.16.

Some errors in assay or sampling might be smoothed by summing crosswind the mass of tracer collected on all "ground" samples. This procedure discloses that at ground level, the worst agreement on all arcs for runs MT-3 and MT-4 is observed at the 3.2-km arc during test MT-3, the arc just discussed in the preceding paragraph and shown on Figure 2. The appropriate mass sums are 1.40×10^{-4} g and 1.13×10^{-4} g with a

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resulting fluorescein to 2210 mass ratio of 1.24. Conversely, the best agreement by this technique is found on the 0.8-km arc during experiment MT-4 (Figure 5). Fluorescein and 2210 masses here were 4.81×10^{-5} g and 4.77×10^{-5} g, for a ratio of 1.01. Table II summarizes for both field tests, the ratio of sums of fluorescein mass to 2210 mass for ground samples.

TABLE II

RATIO OF CROSSWIND SUMS OF FLUORESCEIN MASS TO PIGMENT 2210 MASS FOR "GROUND" SAMPLES

	Arc			
Experiment	0.2 km	0.8 km	1.6 km	3.2 km
MT-3	0.94	0.83	1.04	1.24
MT-4	0.83	1.01	1.05	1.10

A technique similar to that described in the preceding paragraph can be applied at levels above the 1.5-m "ground" level if sufficient tower samples are available (as in test MT-4). But, whereas the ratios in Table II result from the summing of 15 to 46 individual samples, a maximum of 5 samples are available for summing at each aloft level, i. e., only one mass at each tower azimuth. For example, summing across the 0.8-km arc at the 20-m level (see Figure 7), masses of 7.5×10^{-6} and 5.0×10^{-6} for 2210 and fluorescein, respectively, would be employed at the 114° tower. These figures would be added to similarly determined masses at other towers on the 0.8-km arc. The ratios resulting from these sums are presented in Table III.

Table III also presents the sum of the crosswind samples for both tracers. The figures reported for arcs at 0.2 km and 0.8 km are those actually collected at the flow rate employed on these arcs, 0.15 liter/sec. For the purpose of comparing masses collected at different arcs, masses reported for the 1.6- and 3.2-km arcs have been normalized to the flow rate observed at the inner two arcs. Thus, we are actually comparing exposures or dosages, a mass divided by a flow rate. It is somewhat unfortunate that the flow rate to which the masses were normalized to obtain

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exposure was 0.15 liter/sec. The resulting units of gram-sec/0.15 liter is a bit unconventional, but does not alter the validity of the data. Presently, it is questionable in the mind of the author whether the hundred or so calculations avoided by normalizing to the 0.15 flow rate (instead of 1.00) is not more than offset by the extra words of explanation required.

TABLE III

CROSSWIND SUMS OF EXPOSURES AND THE RATIO OF THESE SUMS (FLUORESCEIN TO 2210) FOR ALOFT LEVELS DURING EXPERIMENT MT-4 (MULTIPLY EACH MASS SUM BY 10^{-6} FOR TRUE MASS SUM IN GRAMS.)

	0.2-km Arc			0.8-km Arc			1.6-km Arc			3.2-km Arc		
Level	2210	Fluorescein	Ratio	2210	Fluorescein	Ratio	2210*	Fluorescein*	Ratio	2210*	Fluorescein*	Ratio
1.5 m	136	122	0.90	10.8	10.8	1.00	2.24	2.45	1.11	0.745	0.852	1.14
5	115	104	0.90	12.5	12.1	0.97	2.84	2.72	0.96	0.830	M	M
10	87.4	68.7	0.79	13.0	11.2	0.86	2.93	2.81	0.96	0.983	1.08	1.10
15	72.8	M	M	12.2	10.4	0.85	3.18	3.13	0.98	1.00	1.07	1.07
20	30.7	M	M	13.3	9.8	0.74	2.65	2.43	0.92	1.17	1.11	0.95
25	12.3	M	M	14.1	7.35	0.52	2.38	2.11	0.88	1.13	1.07	0.94
30				9.45	7.59	0.80	2.33	2.18	0.94	1.04	1.06	1.02
35				7.66	5.90	0.77	2.04	1.85	0.91	0.966	1.05	1.08
40				5.15	4.40	0.85	1.94	1.64	0.84	1.04	1.03	0.99
45							1.86	1.49	0.80	1.14	1.01	0.89
50							1.46	1.36	0.93	0.994	0.975	0.98
55							1.58	M	M	0.753	M	M
62							1.24	M	M	0.925	0.876	0.95

* Collected mass normalized to flow rate of arcs at 0.2 and 0.8 km.

The exposure values in Table III can be used to construct the profile of crosswind exposure sums in Figure 9. A line separates the level above which there is an excess of 2210 and below which there is an excess of fluorescein. One finds the greatest disagreement in isopleths in the vicinity of 1 km from the source.

Cross sections and overlays of the mass of tracers sampled for each arc during test MT-4 are given on Figures 10 to 13. Isopleths of mass are drawn. The labeled azimuths are those at which tower samples were taken. Demonstrated again is the good but not perfect agreement of the sampled masses. Probably the most serious disagreement here is in the location of the 5×10^{-5} and the 10^{-4} g isopleths at the 0.2-km arc (Figure 10).

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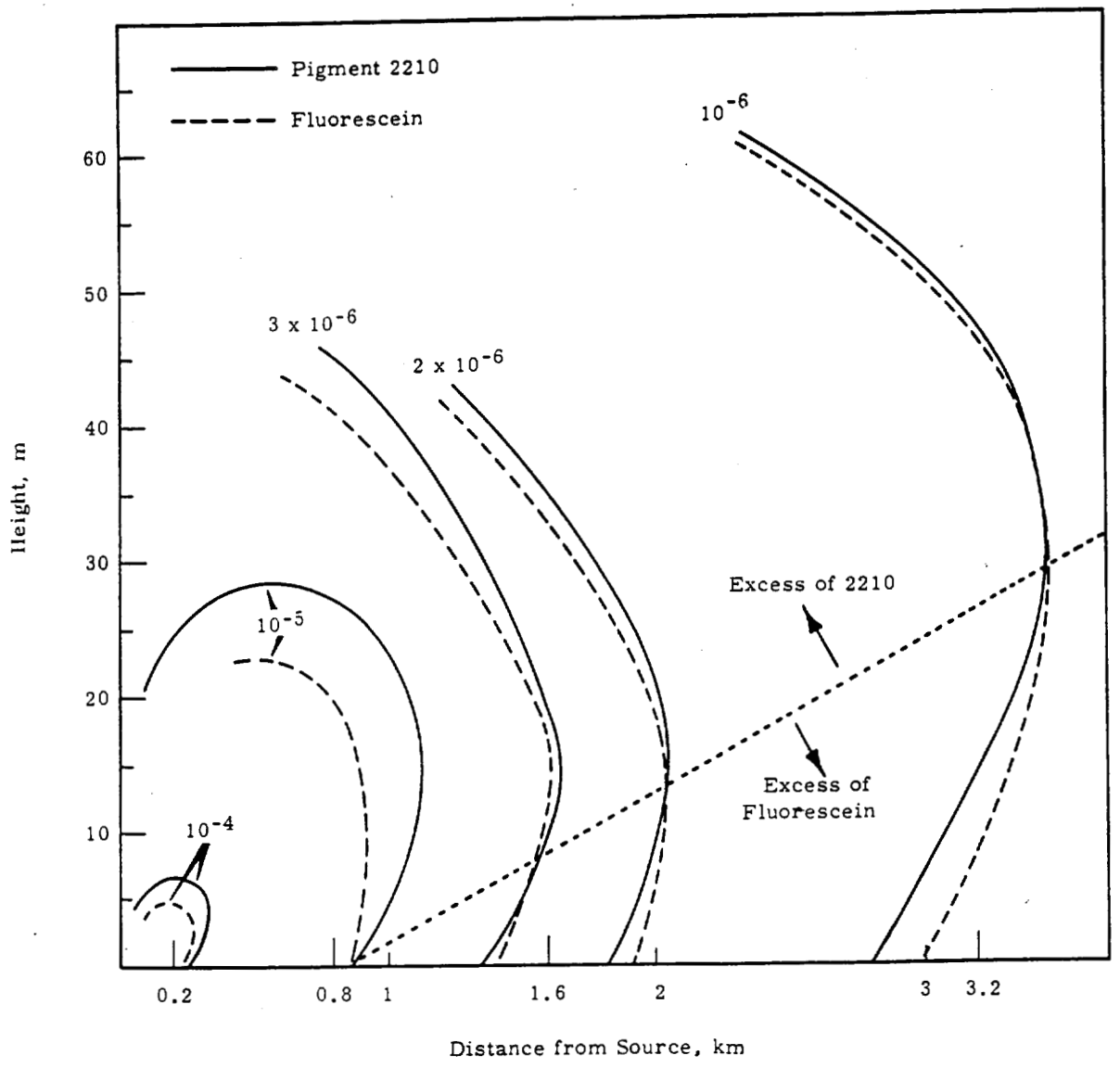

Figure 9

Sum of Crosswind Exposures (3 m-sec/0.15 liters) at Tower Locations for Test MT-4.

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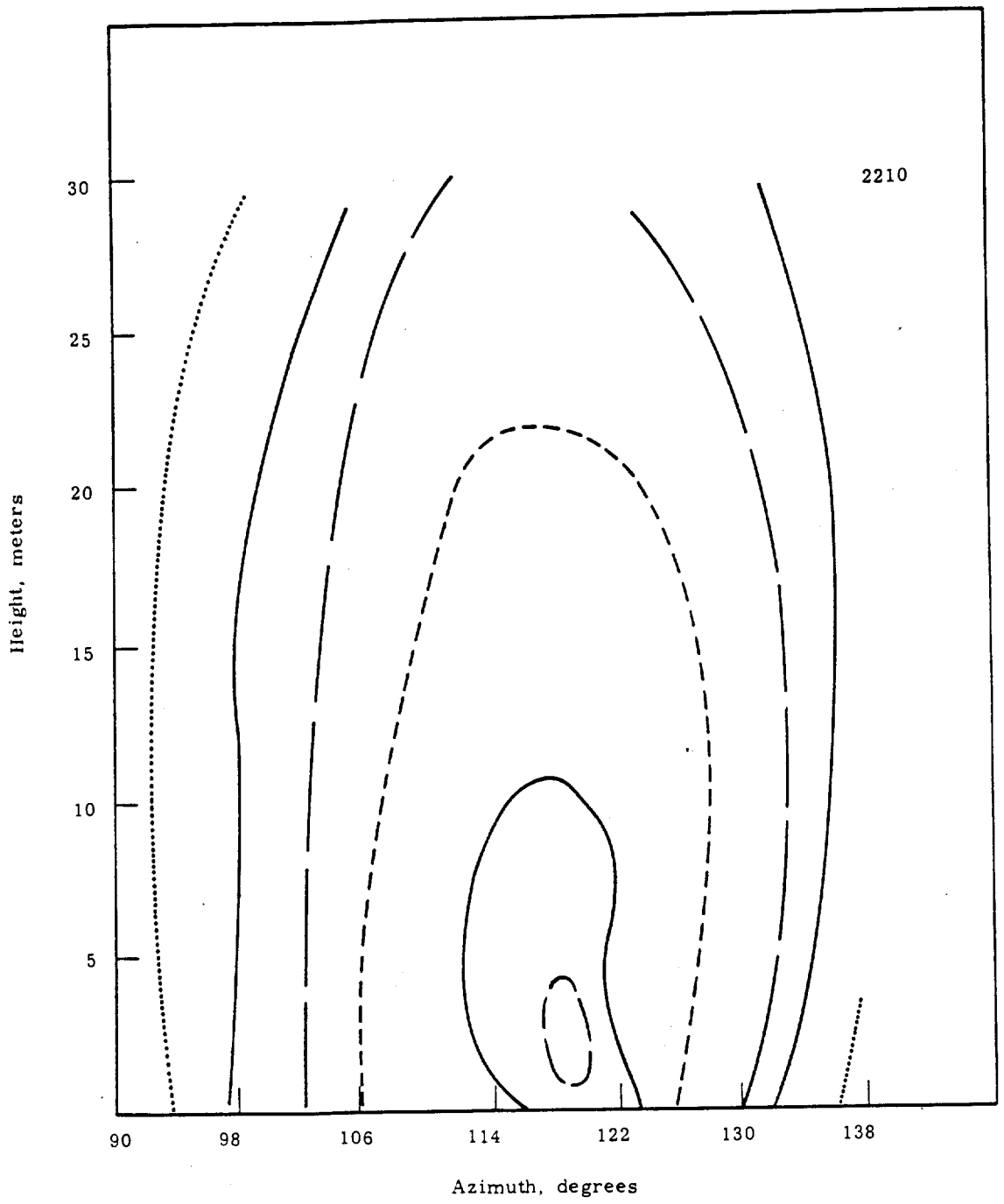
2210
30
25
20
15
10
5
Height, meters
90
98
106
114
122
130
138
Azimuth, degrees

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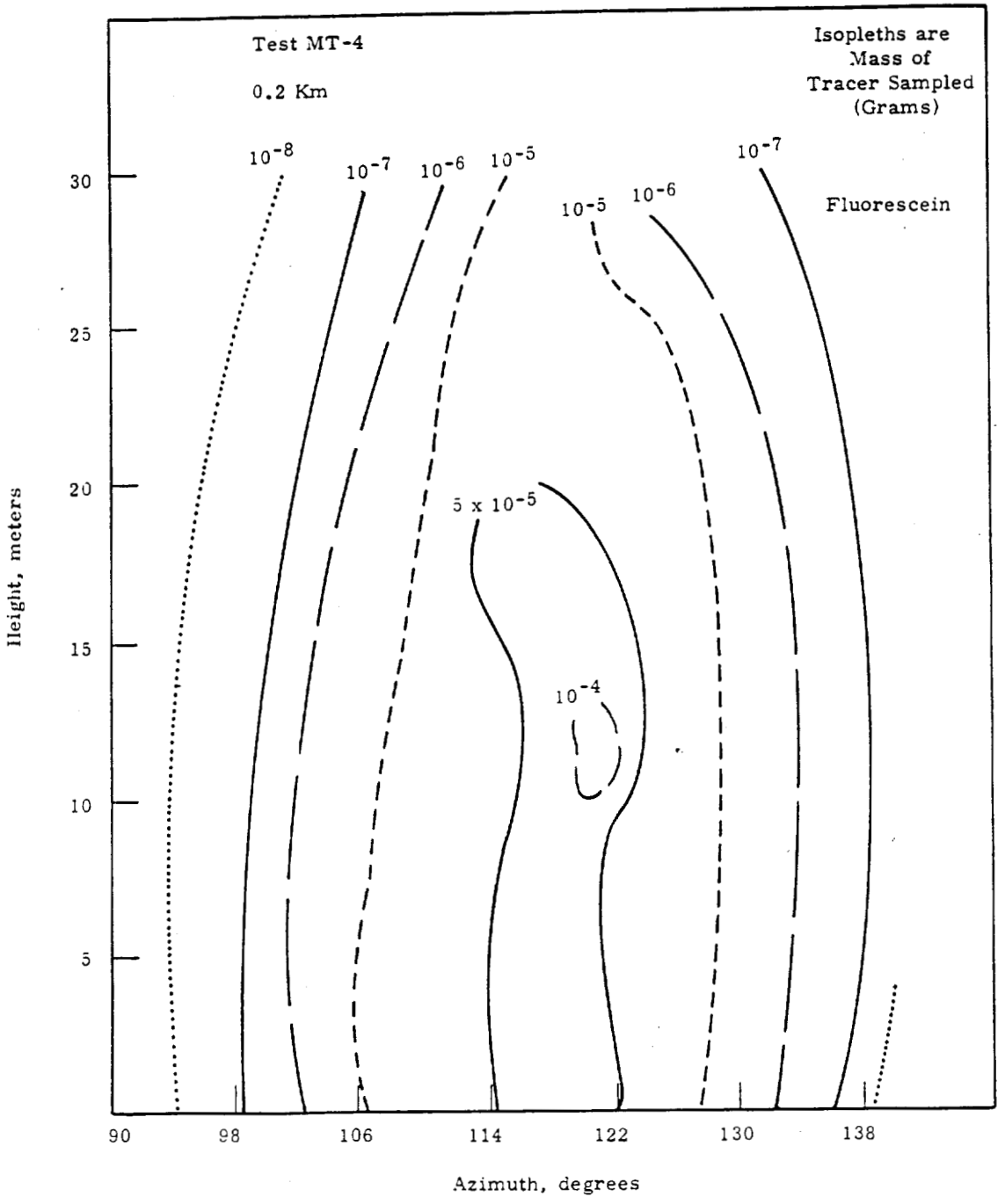

FIGURE 10

Cross Section at 0.2 km, MT-4

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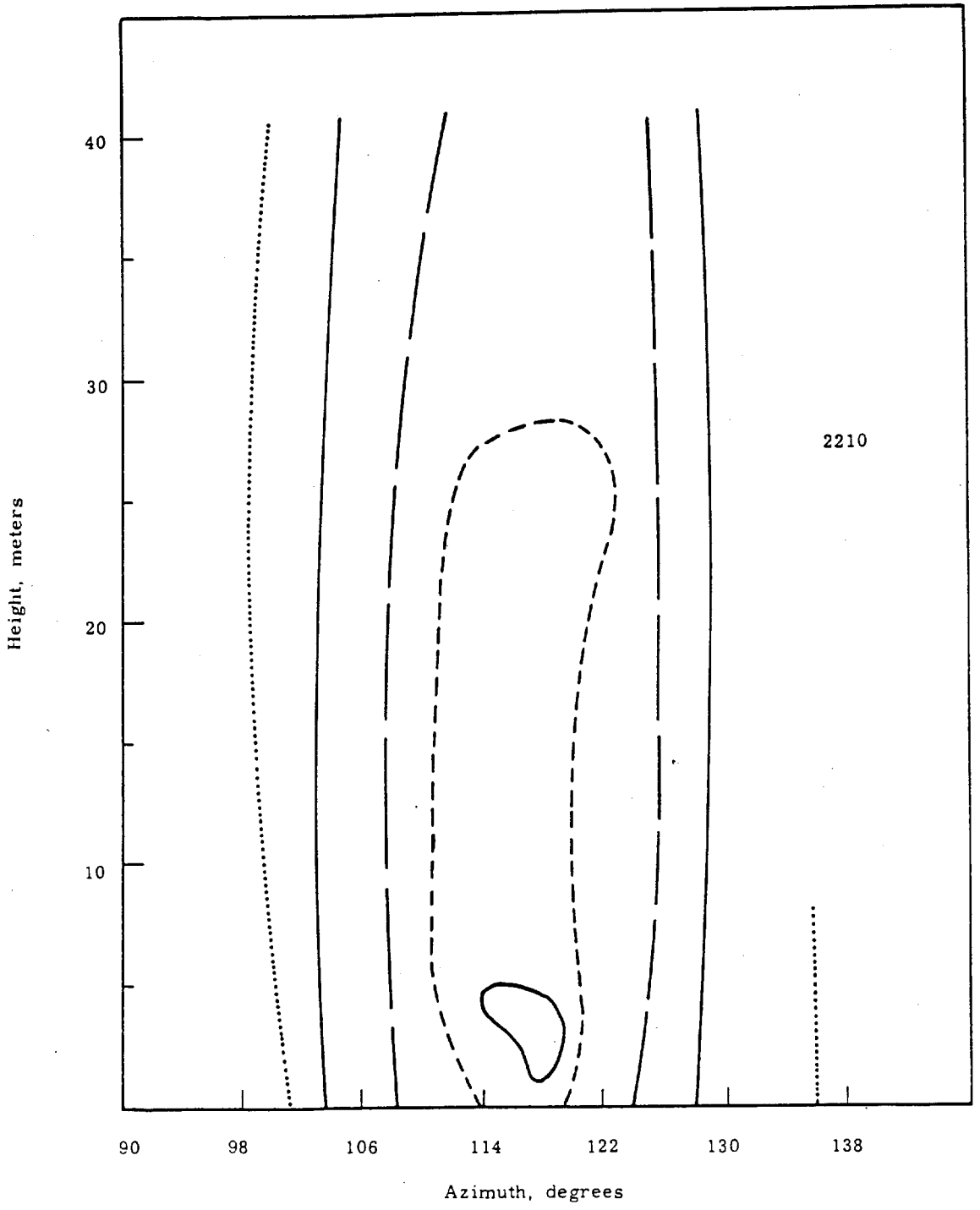
40
30
20
10
Height, meters
2210
90
98
106
114
122
130
138
Azimuth, degrees

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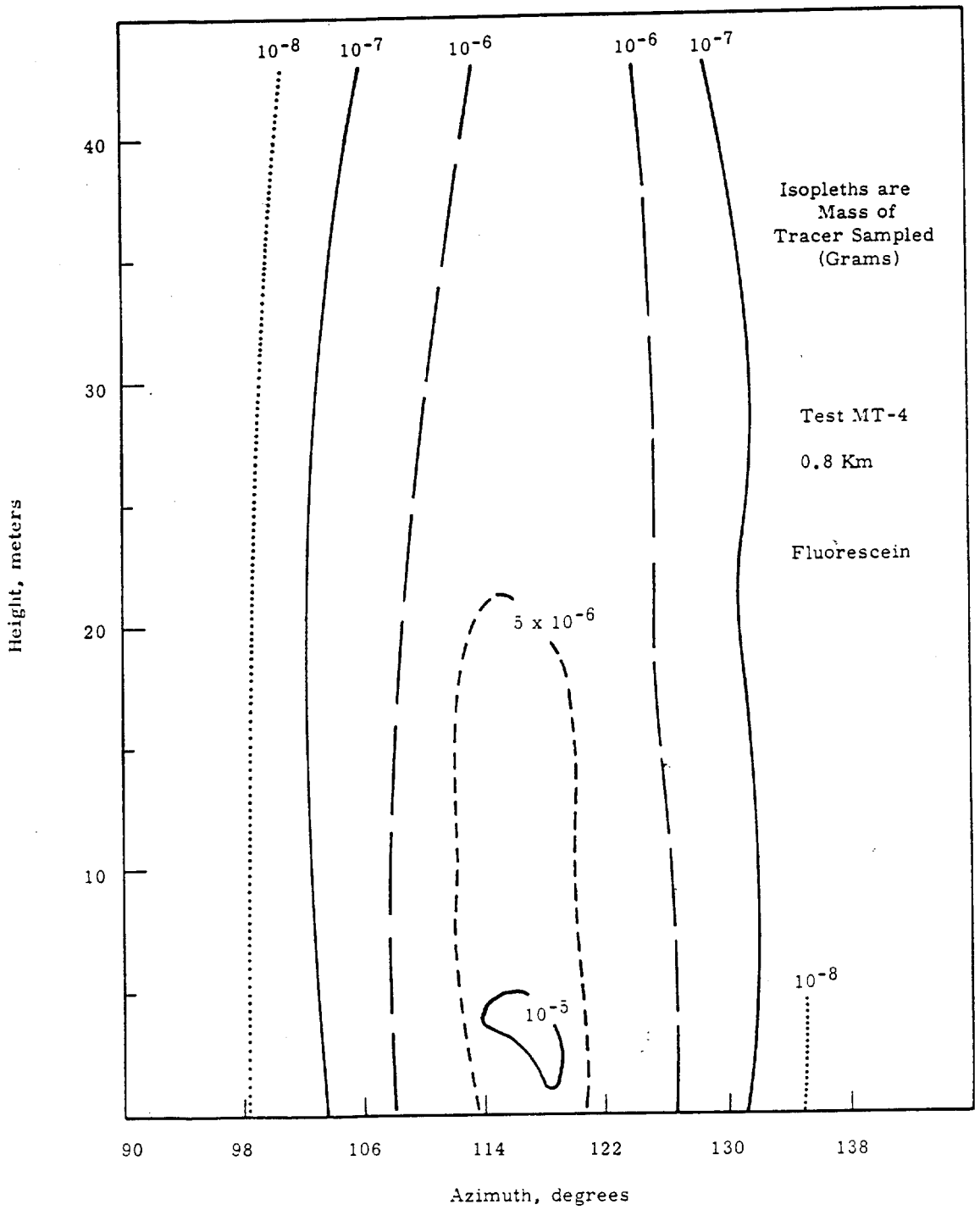

FIGURE 11

Cross Section at 0.8 km, MT-4

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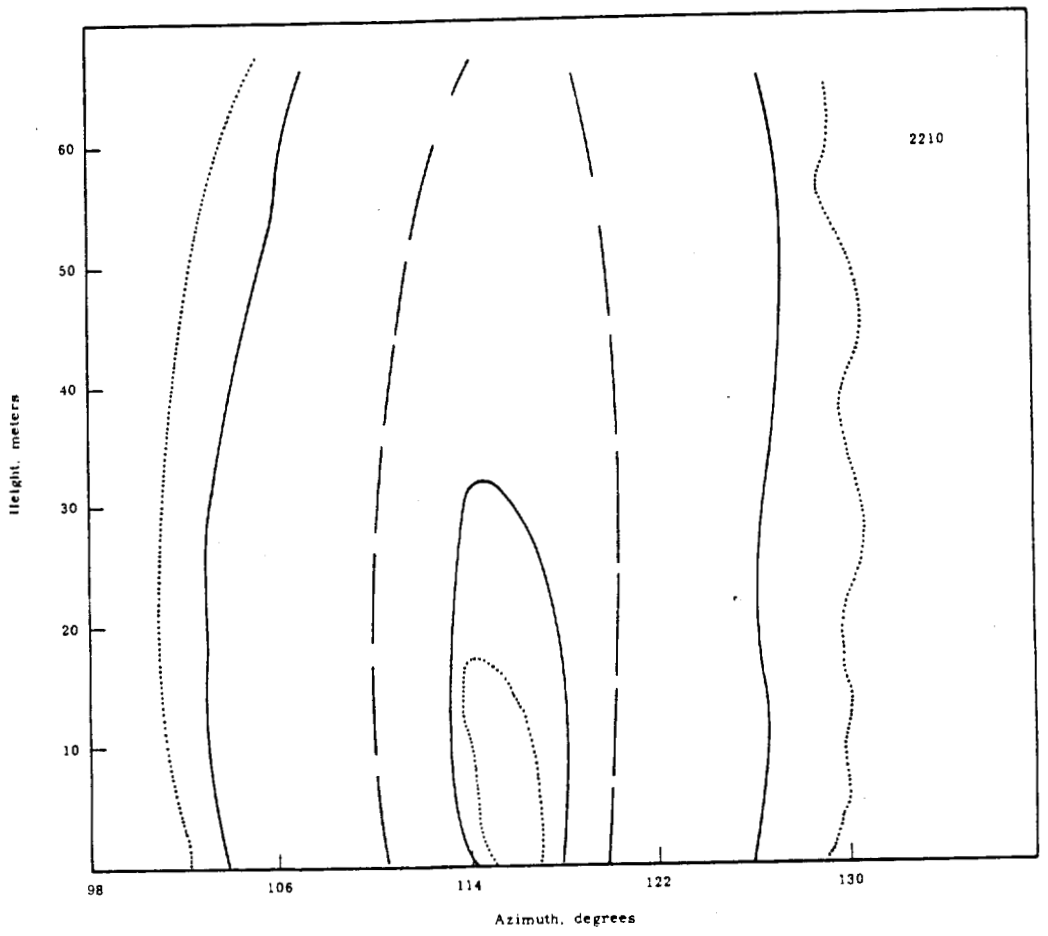
2210
60
50
40
30
20
10
Height, meters
98
106
114
122
130
Azimuth, degrees

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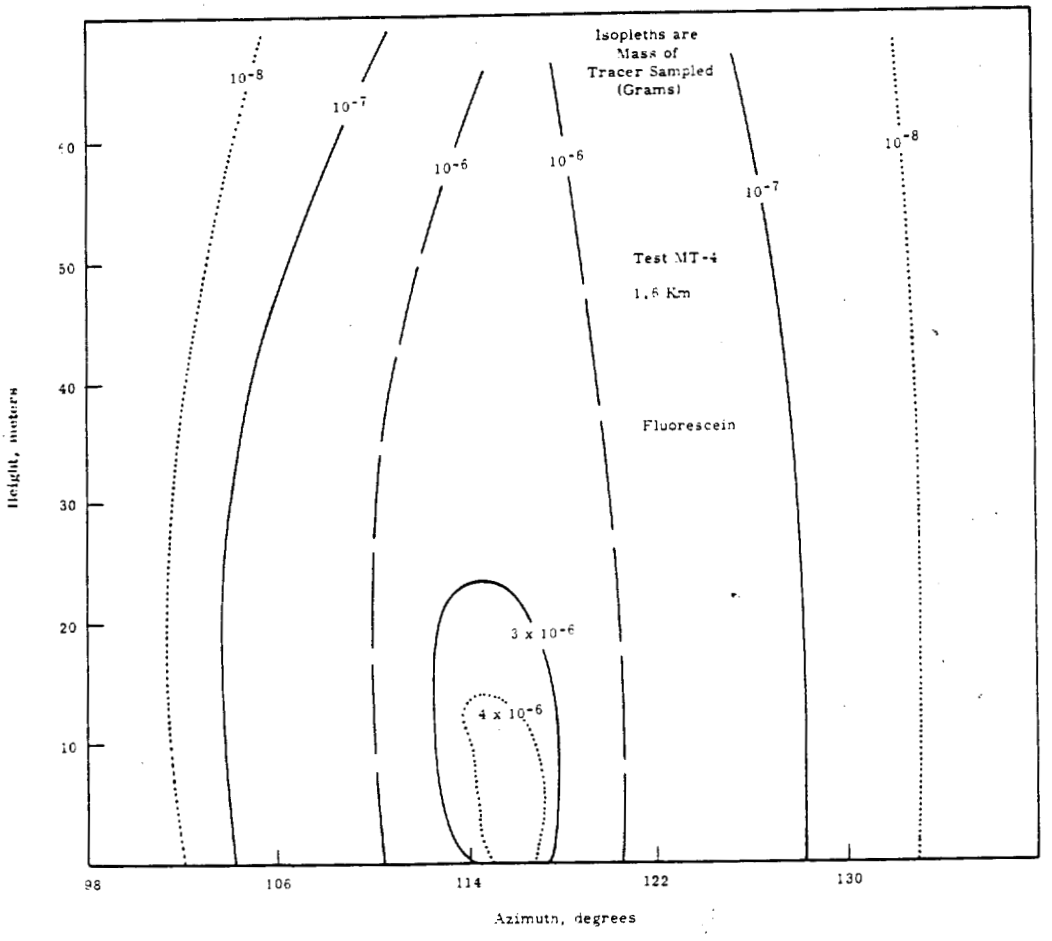
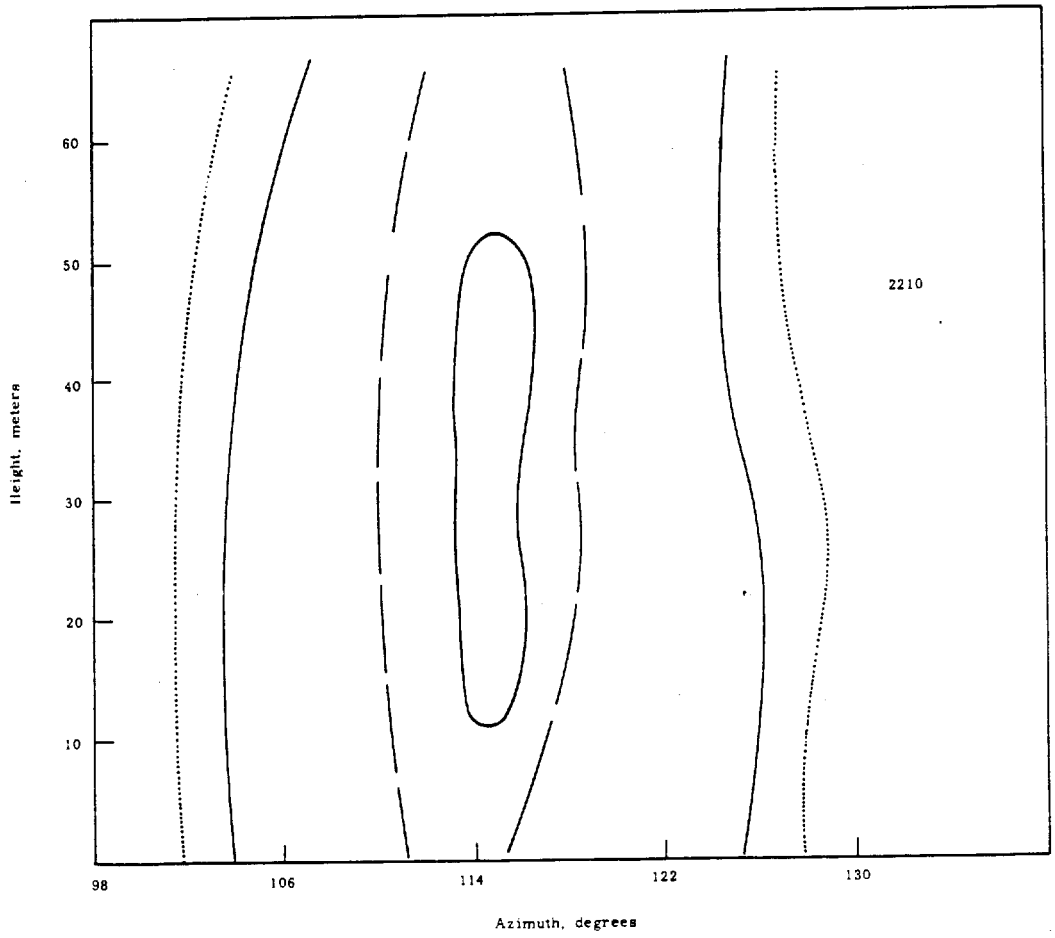


FIGURE 12

Cross Section at 1.6 km, MT-4


60
50
40
30
20
10
Height, meters
2210
98
106
114
122
130
Azimuth, degrees

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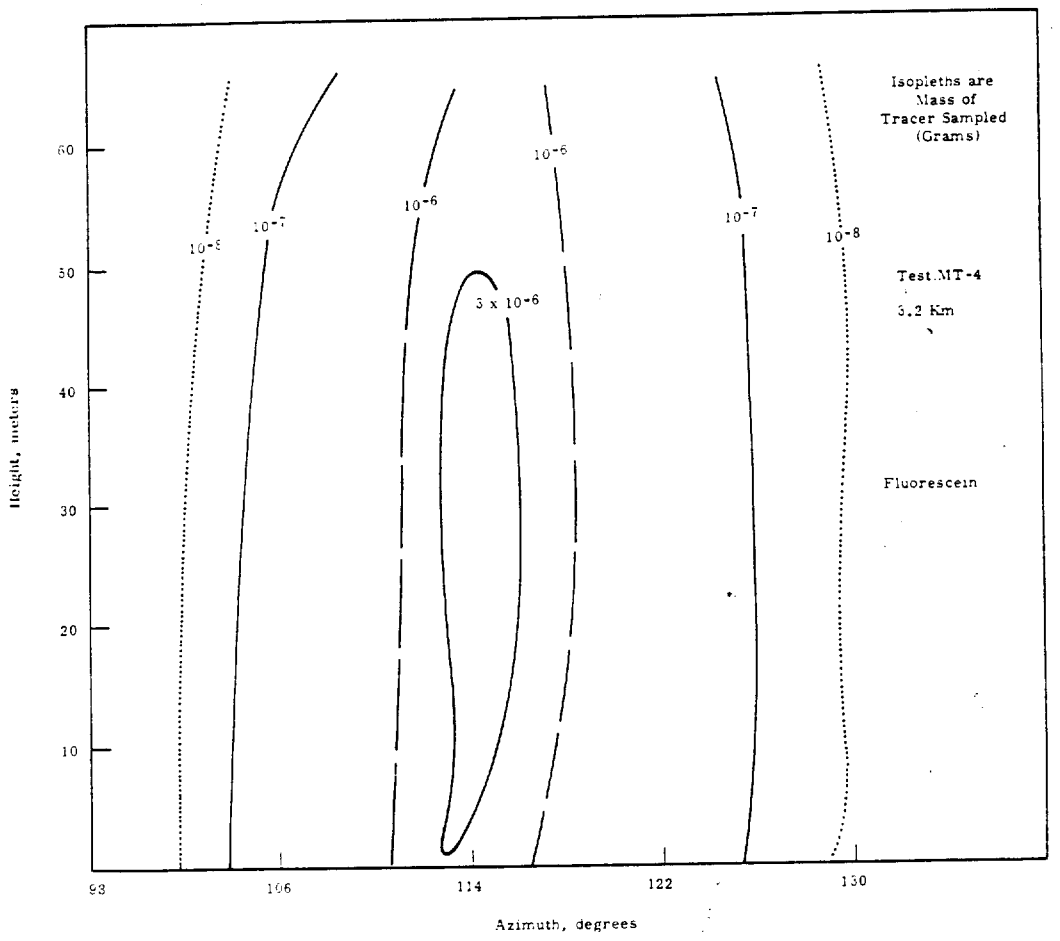

FIGURE 13

Cross Section at 3.2 km, MT-4

OBSERVATIONS, CONJECTURES AND CONCLUSIONS

On run MT-3 (Figure 1), fluorescein masses tend to be relatively high on the more northerly end of the arc while the 2210 is relatively high on the southern end. Although no such tendency is obvious for the ground samples on run MT-4, just the opposite effect is suggested by examination of tower data (Figure 8). Here the fluorescein is relatively high on the south end i.e., on the more southerly tower (122°). The isopleths on Figures 10 and 13 also generally suggest a "skewing" of the fluorescein to the south of the 2210. The generation of tracers took place within 5 ft of each other, and the emission nozzles were aimed at a common point about 15 ft downwind. Thus, source location was probably not a factor. No explanation is apparent.

From Tables II and III, it might be concluded that the fluorescein to 2210 ratio increases with distance from the source. However, the ratios for the 0.2- and 0.8-km arcs during MT-3 show the opposite.

There is another difference between the inner two arcs and the outer two which could affect these ratios. Flow rate through the filters at 0.2 and 0.8 km is 0.15 liter/sec; at 1.6 km, it is 0.23 liter/sec; and at 3.2 km, it is 0.51 liter/sec. Diameter of the filter face (47 mm) used, results in all these flow rates being less than isokinetic. However, the deviation from isokinetic is less at the higher two flow rates. If we hypothesize that the 2210 particles were larger than the fluorescein, the error due to impaction would have been greater on the inner two arcs, and the fluorescein to 2210 ratios would have been less. The hypothesis for small fluorescein particles is supported where vacuum pump failure resulted in pure impaction samples. Nearly all the fluorescein to 2210 ratios were less than 1.00, and in one instance, it was 1/30.

Further speculation on particle size effects can be done on Figure 9. For example, is the deficiency of fluorescein near the source due to an excess of "very large" fluorescein particles that immediately fall out of the plume? The improving agreement with distance could be attributed to the slower depletion of the "not quite so large" particles of pigment, 2210, which finally leaves only the particles of both tracers having negligible

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fall velocities. But how, then, does one explain the excess of fluorescein which develops near the ground? Pigment 2210 has a continuous size spectrum. If, in contrast, the fluorescein particles were either extremely large or extremely small, (a bimodal size distribution) they could be removed from the diffusing plume essentially immediately or not at all. This process could result in a distribution of tracers as shown on Figure 9.

The microscopic sizing of particulates is a tedious, time-consuming, and eye-straining job. Primarily for this reason, only a few filters from the multitracer tests were microscopically examined, and these only qualitatively. Unfortunately, the fluorescein analysis is a destructive assaying technique, so the filters cannot be retrieved. Of the filters examined, it was not obvious that the pigment 2210 particles were larger.

Perhaps such speculation is useless. Perhaps, any reasonably small particulates of fluorescein would be compatible with pigment 2210. The best estimates of fall velocities of 2210 particulates indicate that the bulk of this pigment would fall less than 5 m during a one-half hour transit to the 3.2-km arc. Other factors, such as nonlinear errors in mass calibration, differing interactions between tracers and vegetation, or errors in determining masses emitted, could significantly affect the conclusion drawn about particle fall characteristics.

Let us recall that the purpose of the experiments was to demonstrate, if possible, that fluorescein and 2210 are compatible atmospheric tracers, even if they are not the ultimate. Some estimates of atmospheric diffusion parameters have been considered acceptable if they were within an order of magnitude of the observed. The discrepancies in the present technique certainly fall within these generous limits. The applicability of this dual tracer system would be determined by examination (for each intended application) of the possible discrepancies as evidenced in the tables and graphs already presented. For example, Figure 10 discloses that the technique would be inappropriate in investigation of source height difference of 10 m. However, the technique is applicable in the more reasonable investigation of a difference in source height of 50 m.

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Speaking generally, claims of accuracy may be earnestly given for a measuring technique. If an independent check of the measurement is impossible, it is difficult to prove or disprove the claims. Thus, one could carry out a field diffusion experiment under a certain set of meteorological conditions and catalog the results with accompanying best estimates of accuracy. Even if we could control the weather and duplicate the meteorological conditions of the first experiment, is it not possible that the results of a second experiment could fall outside the confidence limits specified by the first experiment? Could not differing results be due to unavoidable or unknown changes in equipment used in generation, sampling, or assay? The point is that nonreproducible weather precludes control experiments. Discrepancies observed in our dual tracer results could well be of the same magnitude as those which would be observed if control experiments were possible. If the differences even approach this same magnitude, then the dual tracer technique has the distinct advantage of eliminating meteorological parameters from the experimental variables.

One drawback of the technique could be the fluorescein dispersal dependency upon the specific generator used. The generators used at Hanford are commercially available insecticidal sprayers. Their control settings are not scientifically precise. Thus, settings which would result in a satisfactory size distribution of fluorescein in one generator might not apply to another. A minimal effort to investigate this possibility was made in the switching of generators for tests MT-3 and MT-4. (See Table I.) In this instance, it appears that no extreme differences resulted.

It is quite possible that continuance of field experiments in the MT-series would result in better combinations of fluorescein formulation concentration and/or generator control settings. It might also be demonstrated that generator-to-generator difference and moderately different control settings are of minor significance. In any event, field experiments MT-3 and MT-4 do demonstrate that generator settings exist which result in a reasonably compatible fluorescein-2210 technique.

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SUMMARY

Field experiments MT-3 and MT-4 demonstrated that the commercial TIFA generator used at Hanford could be used to disperse fluorescein particulates in the atmosphere. Resultant distribution of atmospheric concentrations of fluorescein were similar to those for fluorescent zinc sulfide 2210 generated during the same time interval.

Several methods were employed in analyzing the compatibility of the two tracer techniques. No one method of analysis completely described the relationship.

Since the tracers do not behave identically but do behave similarly, close examination of these experimental results is needed before applying the technique to a given situation.

The technique is sufficiently discriminatory to aid in the study of such practical problems as the effects of source height differences of 20 m or more.

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