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Oxidation of Sulfur Dioxide in Power Plant Plumes*

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ABSTRACT

The extent of oxidation of sulfur dioxide to sulfate was measured at two coal-fired and four oil-fired power plant plumes. Samples were collected at various distances downwind of the source by employing a high-volume filter pack in a fixed-wing aircraft. Particulate sulfur to total sulfur concentration ratios and ^{34}S to ^{32}S isotope ratios were measured and interpreted. In almost all instances essentially all of the oxidation was found to occur during the first few kilometers of plume transit and even when plumes were followed for more than 70 kilometers. In the coal-fired plumes the extent of oxidation seldom exceeded 4%, one-third of which could be attributed to primary sulfate production during the combustion of the coal. In the oil-fired plumes the extent of oxidation was approximately twice that observed for coal. However, the primary production of sulfate is much more variable and probably higher during oil-fired operations and could account for some of the apparent difference observed for the atmospheric oxidation. In addition, there is some indication that sulfate could be dropping out of the power plant plumes which might cause observations of sulfate formation to appear to be less than their true values.

INTRODUCTION

Sulfur dioxide has long been recognized as a major pollutant of our atmosphere. However, recent studies have indicated that oxidation product sulfate is significantly more deleterious and presents a greater health hazard. Consequently there is particular concern that regulatory efforts directed at reduced emissions of sulfur dioxide have only led to reduced urban concentrations of sulfur dioxide without a concomitant decrease in the sulfate levels.(1) Furthermore, construction of new power plants in rural areas has spread the dispersion of pollutants over wider geographical areas and enhanced long distance transport. To cope with these problems, increasing attention is being directed toward the fate of sulfur dioxide and its conversion mechanisms.

As a convenient vehicle for studying oxidation of atmospheric sulfur dioxide, power plant plumes have been utilized by many investigators.(2,3,4,5) Relatively high concentrations of SO_2 and particulate sulfate facilitate their measurement during minimal sampling times. Under favorable atmospheric conditions, cohesive plumes may be tracked over large distances. Notwithstanding the numerous measurements made by various techniques such as helicopter and fixed-wing sampling, correlation spectrometry and plume touchdown data, considerable disagreement still exists regarding the rate and mechanism of atmospheric sulfate formation from sulfur dioxide and the relative importance of meteorological parameters.

Previous papers(2) have described work performed by Brookhaven on sulfur dioxide oxidation to sulfate in both oil- and coal-fired power plant plumes. Both particulate S/total S concentration ratios and $^{34}S/^{32}S$ isotope ratio measurements were made. A rate limiting process involving particulates was suggested by the observations. The postulated mechanism required that some SO_2

dissolve in the water associated with the emitted particulates, followed by a rapid catalytic conversion to sulfate, permitting additional SO_2 to dissolve. The difference in conversion rates, higher in oil-fired plumes than in coal-fired plumes, was attributed to the respective nature and concentration of the particulates.

Experiments have since been performed at two additional coal-fired plants in Labadie, Missouri, and Charleston, West Virginia, and also at four oil-fired plants: Port Jefferson, N.Y.; Northport, N.Y.; Albany, N.Y.; and Devon, Connecticut. Results of these experiments are reported herein.

EXPERIMENTAL

A. Plant Description

A series of runs was performed at the Labadie, Missouri, plant of Union Electric Company during the summer of 1974. The plant, situated on the Missouri River about 45 miles west of St. Louis, contains four tangentially fired units and burns 3% sulfur coal. Rated capacity is 2400 MW. Two runs were made at the coal-fired Kyger Creek plant of Ohio Valley Electric Company, located near Charleston, West Virginia, and rated at 1,000 MW.

The oil-fired plants in this study were the Northport plant of Long Island Lighting Company at Northport, New York, rated at 1,160 MW; the Port Jefferson plant of Long Island Lighting Company generating 467 MW; the Albany plant of Niagara Mohawk Power Corp. at Bethlehem, New York, rated at 400 MW; and the Devon plant of Connecticut Light and Power Company at Milford, Connecticut, with a capacity of 454 MW.

B. Sampling

A single-engine Cessna 182 was used to sample the power plant plumes. Outside air was sampled via a scoop in the window and drawn past a filter pack by means of a 24 V dc high-volume sampler. The 8 x 10" filter pack consisted of a glass-fiber prefilter (Whatmen No. 81) for trepping particulate sulfate followed by two cellulose papers (Schleicher and Schuell Fast Flow No. 2W) impregnated with KOH-triethanolamine to absorb SO_2. Samples were returned to the laboratory for suitable processing. A Sign-X Laboratories' (Essex, Conn.) electroconductivity SO_2 analyzer was used to locate the plume.

Background samples of SO_2 and SO_4^{2-} were taken upwind of the plant at plume elevation. The plume itself was sampled by repeated cross-wind traverses, with the sampler turned on only within the plume. Sufficient passes were made until adequate sample had been accumulated. This process was repeated at multiple locations downwind of the stack.

C. Analysis

Sampled filter packs were analyzed for SO_2 and SO_4^{2-} by a previously described procedure, converting both to Ag_2S containing tracer ^{110}Ag.(6) The Ag_2S was further processed for $^{34}S/^{32}S$ isotope ratios by combustion in O_2 to SO_2 and measurement of the isotope ratios in a high-precision double-beam isotope ratio mass spectrometer.

Calculations of percent SO_2 converted to SO_4^{2-} were made in all runs on the basis of concentration measurements by the relationship

$$\% \text{ Converted} = \frac{\text{Particulate S}}{\text{Total S}} \times 100 \qquad (1)$$

The Isotope Ratio Technique depends upon changes in the $^{34}S/^{32}S$ ratio caused by slight isotopic fractionation during the conversion of SO_2 to SO_4^{2-}. Small differences in this ratio are more easily compared when they are expressed in "del values", or deviations from a standard:

$$\delta^{34}S = \left[\frac{^{34}S/^{32}S\ (\text{Sample})}{^{34}S/^{32}S\ (\text{Standard})} - 1\right] X\ 1000 \qquad (2)$$

where the standard is meteoritic sulfur. As SO_2 is slowly oxidized, the oxidation product becomes enriched in ^{34}S while the SO_2 is depleted in this isotope, resulting in a lower del value for the remaining SO_2. Considering the complete combustion of sulfur in the fuel and an isotope material balance, one can calculate the fraction converted (1-f) by application of the formula

$$\delta\ SO_2 = \delta\ SO_2\ (\text{fuel}) - \propto (1-f)\ 1000 \qquad (3)$$

where $\propto$ is the previously measured constant, 0.02.(2) The difference in conversion between two points may be determined by

$$1\text{-}f = \frac{\Delta\delta SO_2}{1000 \propto} \qquad (4)$$

representing the changes in the isotope ratios between those two points. Previous experiments in oil-fired plumes have indeed shown a decreasing del value of plume SO_2 with increasing distance from the source.(2)

Reproducibility

On the basis of numerous controlled experiments both within the laboratory and in the field, we feel confident that the precision and reproducibility of our measurement techniques do not exceed 20%.(6,7) We would nonetheless be unjustified to apply these figures as representative of plume data reproducibility. Continuous variability in plant operating conditions as well as meteorological parameters such as temperature, wind speed and direction, humidity, and solar radiation will all affect plume behavior, even under stable conditions. One would expect these variations to be reflected in plume data reproducibility even within the time frame of an experimental run.

Table 1 summarizes the results of an experiment which was conducted to more precisely define plume variability. Samples were taken at 1.6, 4.8 and 16 km. from the stack, and after a 30-minute interval for background sampling a second series of samples was taken at similar distances. Differences by a factor of two in percent converted can apparently be encountered. It would be difficult to attribute any specific reason for these variations. One should recognize that attempts at interpreting differences in oxidation of less than a factor of two can only be accomplished with an adequate number of measurements to obtain statistical significance.

RESULTS

A. Oil-Fired Plumes

The data for the five oil-fired plumes are tabulated in Tables 2 to 6. Subtractive background corrections have been applied to the listed SO_2 and SO_4^{2-} concentrations, excluding the September 13 run at Northport (Table 5) where no background samples were taken. Consequently the numbers represent only the dispersed SO_2 emitted from the stack. Similar corrections were made for the SO_2 del values. Percent SO_2 converted based on concentration was calculated from equation (1). It includes sulfate found during combustion and emitted from the stack. No corrections were made for this source of sulfate.

During extensive earlier experiments$^{(2)}$ flue gas samples were taken at the breechings and analyzed for SO_2 $^{34}S/^{32}S$ isotope ratios. Utilizing equation (4), changes in % SO_2 converted were then calculated from the differences in the SO_2 del values between the emitted SO_2 and that collected at varying distances downwind. For logistical reasons, no flue gas samples were taken during the current series of oil-fired experiments. Nevertheless, at Albany and Devon (Tables 2 and 3), representative samples of fuel oil were obtained and analyzed for isotopic sulfur ratios. Relying upon our previous experiences, the assumption was made that SO_2 del values of the resulting flue gas should be about 0.1 per mil less than the del value of the fuel oil sulfur. Utilizing this information, conversions from the stack downwind were calculated for these two runs. They are listed in the final columns. Lacking similar information at Northport and Port Jefferson (Tables 4 to 6), isotope ratio measurements could only describe oxidation changes between discrete sampling locations.

In Tables 2 and 3 weather conditions limited the extent to which the plumes were tracked. Both runs show a decrease in del values from stack to 3.2 km. representing initial oxidation. There is reasonable correspondence between the values obtained for SO_4^{2-} formation based on either isotope ratio or concentration measurements. Del values for the experiments at Port Jefferson and Northport (Tables 4 to 6) appear to be invariant with distance, indicating slight or no conversion after the first sampling location. Again, these results generally agree with concentration measurements. Without a flue gas or oil sample for comparison, the del value at 1.6 km in Table 4 seems excessively high. One possible reason for this aberration, as well as the increase in percent converted at 24 km, may be the fact that two distinct operations at the plants, each burning a different type of oil, contribute to the plume in a variable manner. Conceivably the results may have arisen from the sampling of different plume sections. However, isotope ratios at the remaining locations were constant.

Conversion of SO_2 (based upon concentration ratios) as a function of distance for the oil-fired plumes is displayed in Fig. 1. The overall oxidation rate is comparatively low, falling within a 1-6% bracket within the time frame and distances of the experiments. In Fig. 2, conversion of SO_2 was plotted against elapsed time from emission source. Most of the oxidation occurred by the time the first sample was taken. Interestingly, the curves display a generally negative slope, the significance of which is open to speculation.

B. Coal-Fired Plumes

Charleston, West Virginia, was the location for two runs, the results of which are reported in Table 7. As listed in the final column, sulfate to total sulfur ratios were confined within a very narrow range of ~ 1 - 2%. The $^{34}S/^{32}S$ isotope ratios were remarkably constant with distance supplying further evidence of almost no additional oxidation beyond the 1.6 km. location.

Tables 8 to 13 present the data from Labadie, Missouri. In contrast to the experiments and numerous runs made previously at the coal-fired Keystone plant of Pennsylvania Electric Co. at Shelocta, Pennsylvania(2), information obtained from isotope ratios at Labadie was not very useful. Nonetheless, reliable conversion rates were obtained from concentration measurements and are listed in the final columns of Tables 8 to 13. Figures 3 and 4 graphically display percent SO_2 conversion at Labadie as a function of distance and time respectively. Straight lines were drawn between individual points at succeeding distances in each run. No particular trend seems to emerge from these plots. The data falls within a range of ~ 1 - 4%. The observed variations are within the expected variability of plume data (Table 1).

DISCUSSION

In reviewing the composite results for both types of plumes, we observe that the overall extent of oxidation is rather low. Coal-fired plumes for Labadie and Charleston fall within a range of ~ 1-4%, in accordance with previous observations made at Keystone where reaction reached ~ 3-4%.(2) No trend seems to exist and most of the oxidation would appear to occur within the envelope of Fig. 3, before 1-2 km. Certainly no evidence is present of a sharp increase in rate at some downwind distances, even up to 50 km.

We had previously found(2) that the extent of reaction in oil-fired plumes was indeed greater than coal-fired plumes. Our present data qualitatively reinforces this observation. The amount converted during the first few kilometers in the oil-fired plumes appears to be somewhat greater than coal-fired, ranging from 3-6% vs. 1-3%. Nevertheless, in both cases no further oxidation seems to take place downwind; in fact, one may even be tempted to state that a reverse trend exists.

This characteristic behavior of plumes, i.e., initial oxidation during early stages followed by no further increases has been attributed to a heterogeneous particulate-catalyzed reaction whereby the catalyst is poisoned with sulfate formation.(2) The available catalyst surface area was calculated to be barely sufficient to support this theory. It was suggested that the factor of 3 higher ratio of particulates to SO_2 at Northport than at Keystone could explain the limited reaction rate in the coal-fired plume.

Some of the differences between oil- and coal-fired plumes observed in this study may also arise from the fact that oil-fired plants require more stringent operational control of excess air. Slight operational variations could produce greater quantities of primary sulfate giving rise to variable and somewhat higher values than the 1-2% observed for coal. In addition, the differences in the chemical composition of the particulates and the corresponding differences in catalytic activity could be invoked as a further explanation for greater reaction in oil-fired plumes.

Modern utility plants are equipped with highly efficient electrostatic precipitators. If the rate-limiting process depended upon particulate loading, then the presently observed similar results at Labadie and Charleston with those previously measured at Keystone were to be expected. However, since our previous experiments at Northport, they have modernized their operation with the installation of some electrostatic precipitator capability. It could indeed be concluded that the apparently lower oxidation rate now measured is attributable to the plant modernization program.

The observed decrease in particulate sulfate with distance and time for the oil-fired plumes (Figs. 1 and 2) is strongly suggestive of plume drop-out. However, considering the variability of plume data, the reality of these negative slopes could be questioned but strong evidence of this phenomenon was found at Keystone. If plume dropout reaches significant proportions, measured oxidation rates could be erroneously low. Additional future experiments should be devoted to investigate plume dropout.

A model for the SO_2 oxidation to sulfuric acid in dispersing plumes, based upon catalysis by iron particulates, has been described by Freiberg.(8) He predicts a dependency of oxidation upon temperature and relative humidity. With the limited data available and the narrow confines of the parameters within which our runs were made, we are unable to comment on this model at the present time. Additional work has since been performed at Labadie and will be reported in the future, at which time more definitive information may be forthcoming.

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Table 1. Plume sampling reproducibility

Distance (km)	Particulate S/Total S (%)	
	1st Series	2nd Series
1.6	4.2	1.9
4.8	2.0	3.1
16	1.9	2.8

Table 2. Results of plume run made at Albany 8 December

Distance from stack (km)	Time from stack (min.)	Concentrations		Del Value of SO_2	% SO_2 Converted based on	
		SO_2 (ppm)	SO_4^{2-} ($\mu g/m^3$)		Conc.	Del*
Background		0.005	9.1	4.5		
Oil				5.6		
3.2	8.2	0.116	19.4	4.8	3.8	3.5
8	22	0.056	8.7	5.4	3.6	0.5

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*Assumed flue gas del = 5.5

Temp, 1°C; wind, 6.2 m/sec., 40°; WX, ⊕

Table 3. Results of plume run made at Devon 6 February

Distance from stack (km)	Time from stack (min)	Concentrations SO_2 (ppm)	Concentrations SO_4^{2-} ($\mu g/m^3$)	Del Value of SO_2	% SO_2 Converted based on Conc.	% SO_2 Converted based on Del*
Background		0.005	4.4	4.8		
Oil				5.3		
3.2	9	0.064	17.2	4.6	5.9	3.8

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*Assumed flue gas del = 5.2

Wind, 6 m/sec.; WX, 0; unstable

Table 4. Results of plume run at Port Jefferson 19 November 0740 - 0940

Distance from stack (km)	Time from stack (min.)	Concentrations SO_2 (ppm)	Concentrations SO_4^{2-} ($\mu g/m^3$)	Del Value of SO_2	% SO_2 Converted based on Conc.
Background		0.031	10.7	2.9	
1.6	9	1.04	129	2.6	2.8
4.8	27	0.50	32	0.7	1.4
11.2	62	0.46	26	0.8	1.3
16	89	0.51	29	0.6	1.3
24	133	0.20	46	0.4	4.6

Temp., 7° C; r.h., 65%; wind, 3 m/sec., 330°; plume elevation, 300 m; WX, ⦶-⦷ Ci; neutral to stable

Table 5. Results of plume run made at Northport 13 September

Distance from stack (km)	Time from stack (min.)	Concentrations SO_2 (ppm)	SO_4^{2-} ($\mu g/m^3$)	Del Value of SO_2	% SO_2 Converted based on Conc.
1.6	6.7	1.01	195	4.6	4.7
3.2	13	1.02	160	4.7	3.8
8	33	0.58	67	4.5	2.9
16	67	0.39	35	5.1	2.2

Temp., 22° C; r.h., 31%; wind, 4 m/sec., 287°; WX, ⦶ - ⦷ ; stable.

Table 6. Results of plume run made at Northport 23 October

Distance from stack (km)	Time from stack (min.)	Concentrations SO_2 (ppm)	Concentrations SO_4^{2-} ($\mu g/m^3$)	Del Value of SO_2	% SO_2 Converted based on Conc.
Background		0.019	12.2	3.0	
1.6	3.8	1.89	510	5.0	6.2
4.8	11.4	2.09	184	4.1	2.1
16	38	1.61	91	4.5	1.4
24	57	0.79	46	4.4	1.4
32	76	0.50	42	4.1	2.0

Temp., 14° C; r.h., 26%; wind, 7 m/sec., 280-330° ; plume elevation, 245 m; WX, ⦶-⦷ ; stable

Table 7. Results of plume runs made at Charleston 27-28 April

Distance from stack (km)	Concentrations SO_2 (ppm)	Concentrations SO_4^{2-} ($\mu g/m^3$)	Del Value of SO_2	% SO_2 Converted based on Conc.
Background	0.004	8.6	- 2.5	
1.6	2.79	166	5.3	1.5
3.2	1.56	100	5.4	1.7
4.8	0.89	33	5.5	0.9
8	0.66	23	5.3	0.9
16	0.31	7.7	5.1	0.6
Background	0.012	8.1	1.6	
1.6	4.35	259	4.8	1.5
3.2	4.41	182	5.0	1.0
4.8	2.90	120	5.2	1.0
8	1.62	77	4.9	1.2
16	1.31	45	5.0	0.9

Table 8. Results of plume run made at Labadie 12 June

Distance from stack (km)	Time from stack (min.)	Concentrations SO_2 (ppm)	 SO_4^{2-} ($\mu g/m^3$)	%SO_2 Converted
Background		0.051	4.3	
1.6	7.5	1.21	110	2.1
4.8	22	2.49	123	1.2
16	75	2.42	121	1.2
32	149	1.27	71	1.3
48	224	0.66	87	3.0

Temp., 17°C; r.h., 40%; wind, 3.1 m/sec., 0°; plume elevation; 540 m; WX,○,① Cu; neutral to stable.

Table 9. Results of plume run made at Labadie 13 June

Distance from stack (km)	Time from stack (min.)	Concentrations		% SO_2 Converted
		SO_2 (ppm)	SO_4^{2-} ($\mu g/m^3$)	
Background		0.04		
1.6	2.4	1.61	155	2.3
4.8	7.1	2.06	105	1.2
16	24	2.10	83	0.9
32	47	0.56	22	0.8

Temp., 18° C; r.h., 46%; wind, 11 m/sec., 200°; plume elevation, 330 m; WX, ⊕ Ac; stable.

Table 10. Results of plume run made at Labadie 16 June

Distance from stack (km)	Time from stack (min.)	Concentrations SO_2 (ppm)	SO_4^{2-} ($\mu g/m^3$)	% SO_2 Converted
Background		0.070	1.4	
1.6	3.1	1.33	80	1.5
4.8	9.2	0.98	121	3.0
16	31	1.18	218	4.3
32	61	1.43	62	1.1
72	138	0.40	25	1.5

Temp., 13° C; r.h., 40%; wind, 8.7 m/sec., 330°; plume elevation, 510 m; WX, ⦶ Ac; neutral to stable

Table 11. Results of plume run made at Labadie 30 July

Distance from stack (km)	Time from stack (min.)	Concentrations		% SO_2 Converted
		SO_2 (ppm)	SO_4^{2-} ($\mu g/m^3$)	
Background		0.028	5.2	
1.6	5.4	2.14	210	2.4
4.8	16	1.58	248	3.9
16	54	0.93	97	2.6
32	107	0.83	91	2.8
56	187	0.43	29	1.8

Temp., 16° C; r.h., 52%; wind, 4.9 m/sec., 350° ; plume elevation; 970 m; WX, 0; neutral to stable.

Table 12. Results of plume run made at Labadie 31 July

Distance from stack (km)	Time from stack (min.)	Concentrations		% SO_2 Converted
		SO_2 (ppm)	SO_4^{2-} ($\mu g/m^3$)	
Background		0.026	7.8	
1.6	8.4	3.60	159	1.1
4.8	25	2.04	250	3.0
16	84	3.21	90	0.7
32	168	1.49	158	2.6
36	189	1.85	68	1.0
40	210	0.75	31	0.9

Temp., 21°C; r.h., 39%; wind, 3.2 m/sec., 170°; plume elevation, 480 m; WX, ○-⦶ Ci; neutral to stable.

Table 13. Results of plume run made at Labadie 1 August

Distance from stack (km)	Time from stack (min.)	Concentrations SO_2 (ppm)	 SO_4^{2-} ($\mu g/m^3$)	% SO_2 Converted
Background		0.011	6.0	
1.6	3.9	2.90	154	1.3
4.8	12	2.78	161	1.4
8.1	19	1.48	105	1.8
16	39	1.82	234	3.1

Temp., 24° C; r.h., 44%; wind, 7 m/sec., 255°; plume elevation, 340 m; WX, ○-⦶ Ac; very stable.

Table 14. Key to weather symbols (WX)

○	Clear	Cir	Cumulus
⦶	Scattered	Ci	Cirrus
⦷	Broken	Sc	Stratocumulus
⊕	Overcast	Ac	Altocumulus

FIGURES

Fig. 1	Conversion of SO_2 as a function of distance in oil-fired plumes.
Fig. 2	Conversion of SO_2 as a function of time in oil-fired plumes.
Fig. 3	Conversion of SO_2 as a function of distance in coal-fired plumes.
Fig. 4	Conversion of SO_2 as a function of time in coal-fired plumes.

Neg. #7-1079-76
Neg. #7-1078-76
Neg. #7-1080-76
Neg. #7-1077-76

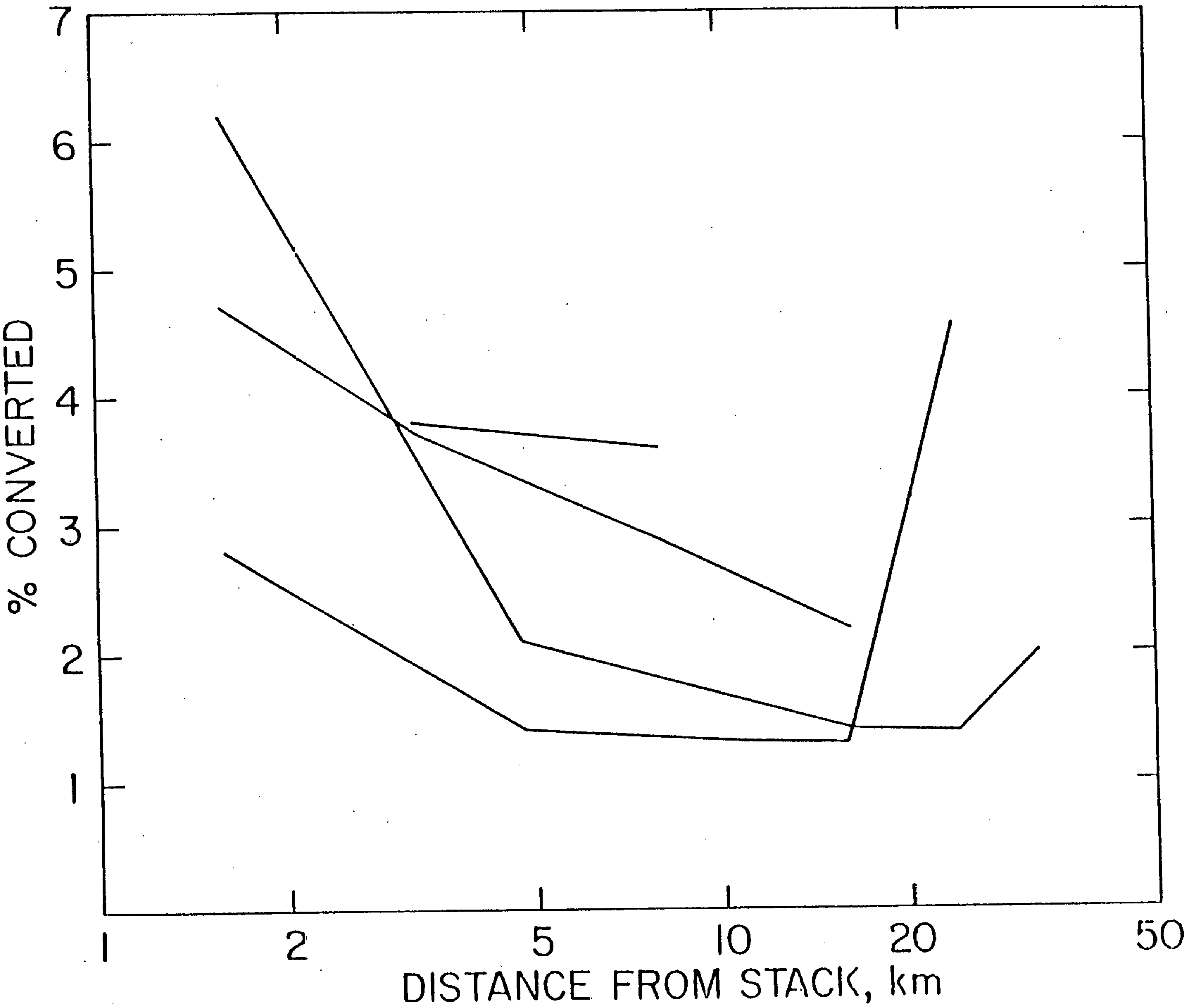

Fig. 1

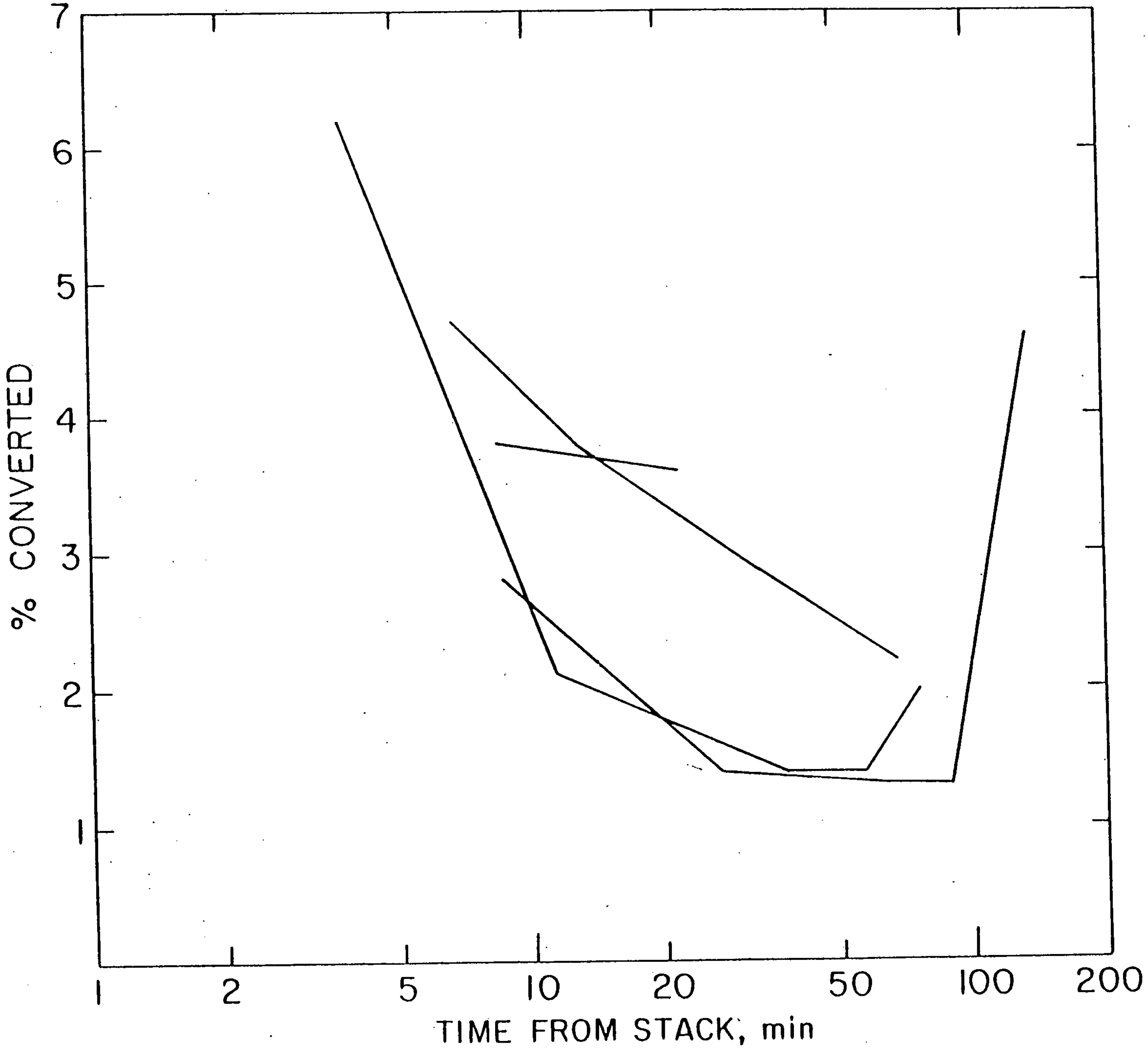

Fig. 2

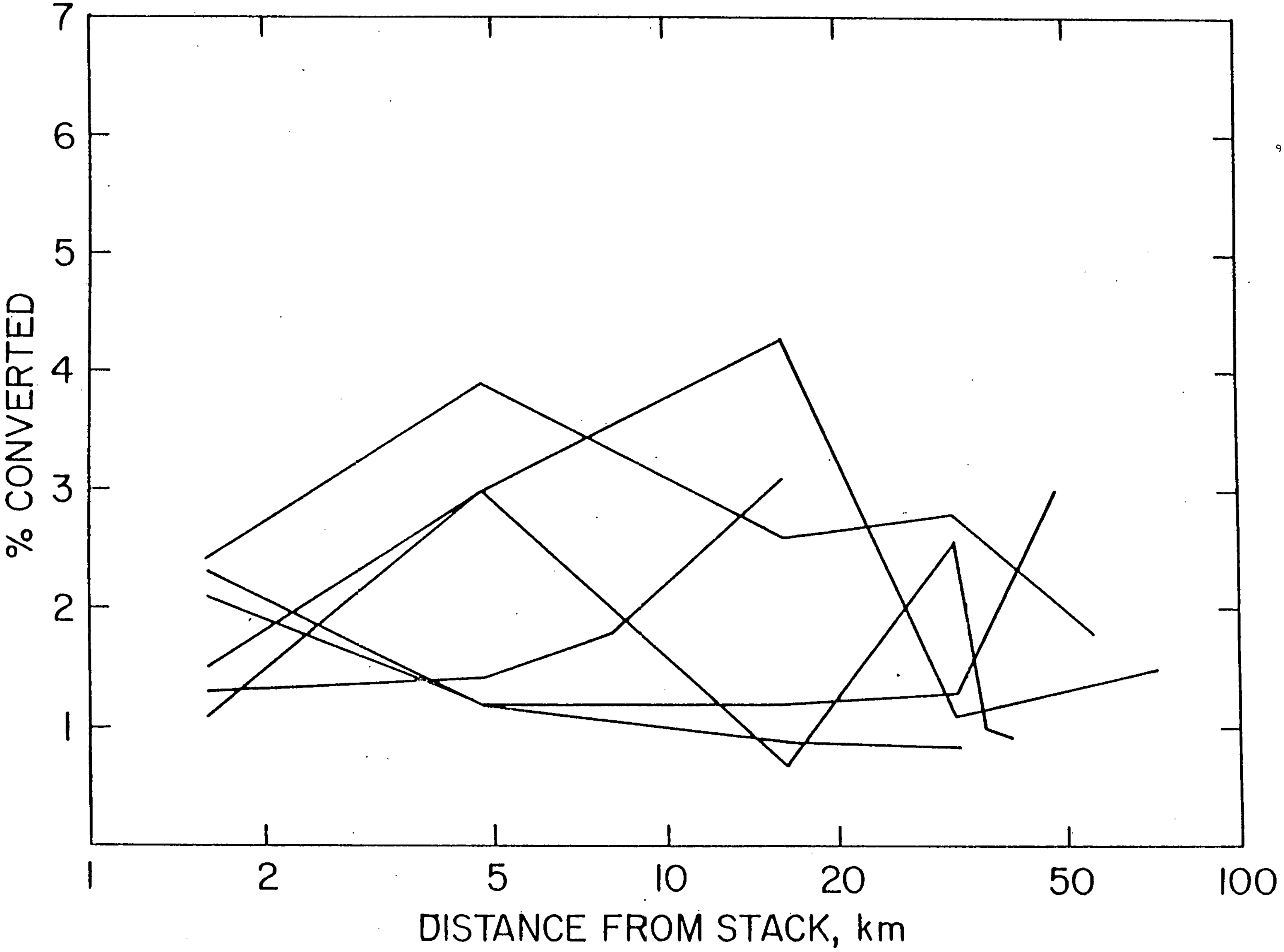

Fig. 3

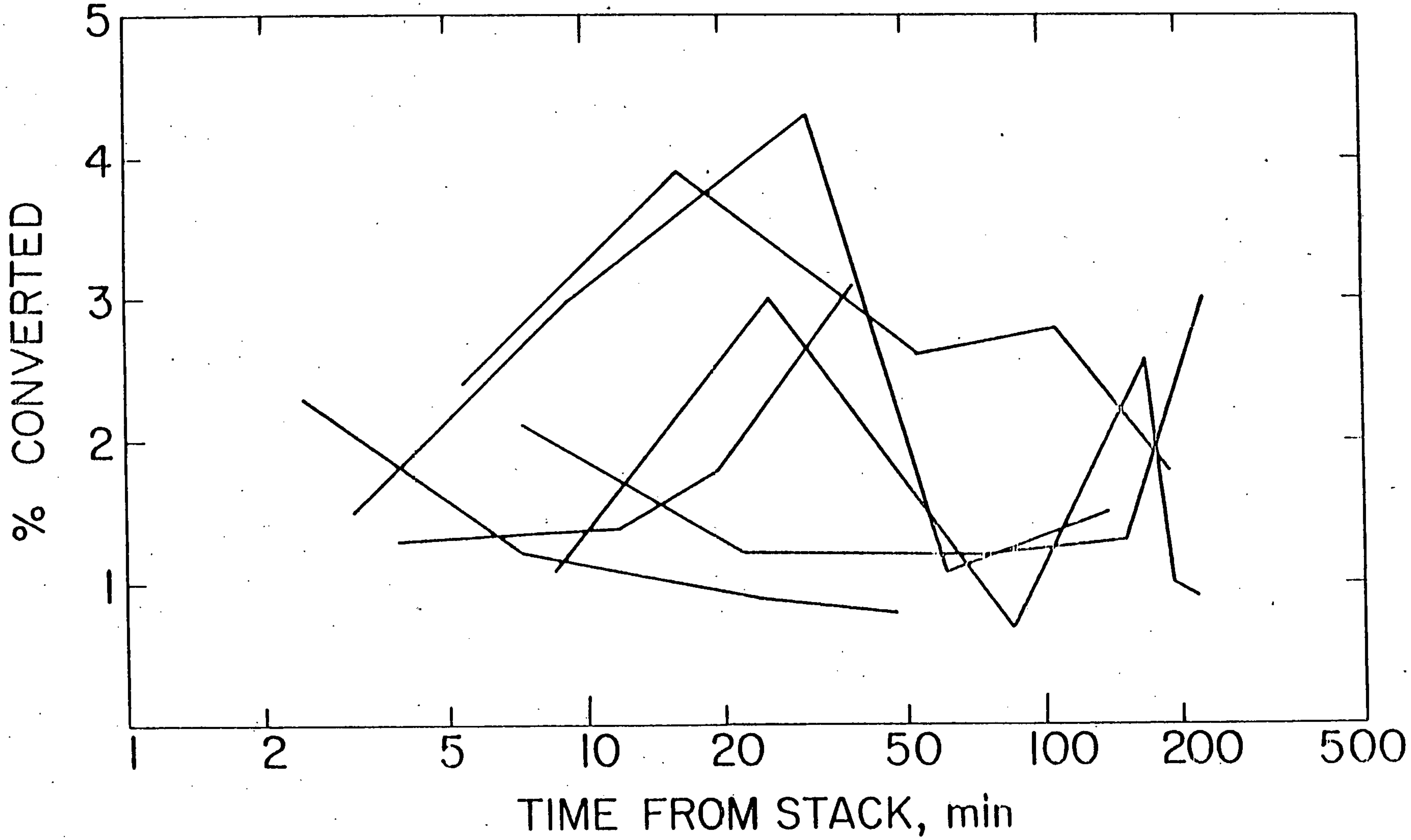

Fig. 4