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ESTIMATES OF SPRINGTIME SOOT AND SULFUR FLUXES INTO THE ARCTIC TROPOSPHERE: IMPLICATIONS TO SOURCE REGIONS

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Abstract

A box model calculation is used to make preliminary estimates of the springtime fluxes of carbon and sulfur particles into the Arctic troposphere. These fluxes are large and can only be accounted for by major sulfur and soot sources. Comparison of these fluxes with the amount of fuel burned in various latitude bands indicates that the Arctic haze cannot be due to Arctic sources and strongly suggests that the dominant source regions are below 60°N latitude. Comparisons of Arctic sulfur fluxes with sulfur emissions on a regional and global basis indicate that significant fractions enter the Arctic.

Introduction

During winter and spring, the Arctic atmosphere contains significant concentrations of sulfur- (Rahn and McCaffrey, 1980; Barrie et al., 1981; Ottar, 1981) and carbon- (Rosen et al., 1981; Rosen and Novakov, 1983) containing particles that scatter (Bodhaine et al., 1981) and absorb (Rosen et al., 1981; Heintzenberg, 1982; Patterson et al., 1982; Valero et al., 1983) solar radiation, leading to rather substantial optical depths (Shaw, 1975). On the basis of trace element analyses, it has been suggested that these particles are transported long distances from combustion sources at midlatitudes in Eurasia (Rahn and McCaffrey, 1980). These analyses are largely based on ground-level aerosol samples collected on the periphery of the Arctic. In March-April, 1983, a series of aircraft flights coordinated by N.O.A.A. (AGASP) explored the horizontal and vertical distributions of the haze throughout the western Arctic. (See Special Issue of Geophysical Research Letters, v. 11, 1984, for details.) One of the instruments on these flights was an aethalometer (Hansen et al., 1982), which has the capability of measuring graphitic carbon concentrations on a real-time basis. This instrument has been used to determine vertical profiles of graphitic particles in the Arctic troposphere (Rosen and Hansen, 1984; Hansen and Rosen, 1984). In this paper, we use these vertical profiles in conjunction with a box model calculation to make a first estimate of the fluxes of graphitic carbon, total carbon, and sulfur particles into the Arctic troposphere. These fluxes are compared with the fluxes of carbon and sulfur produced from fossil fuel combustion on a regional and global basis.

Experimental Details

The aethalometer is an instrument recently developed at LBL that responds in real time to the concentration of graphitic carbon (Hansen et al., 1982). It collects the aerosol on a filter (Pallflex quartz fiber, type 2500 QAO) and

uses an optical technique (Rosen and Novakov, 1983) to measure the concentration of graphitic or black carbon. The filter is changed from time to time to yield a sample available for chemical analysis. Methods for the determination of black carbon in aerosol samples have been developed at LBL (Gundel et al., 1984), giving a calibration curve for the aethalometer. Vertical distributions of graphitic carbon concentration are determined by grouping the data from the various flights into ranges of altitude and calculating the average. The measurement accuracy is proportional to the total data acquisition time in the range, so the range boundaries are chosen for each flight profile to optimize the balance between accuracy and vertical resolution. Examples of vertical profiles for two flights in the Alaskan Arctic and one flight in the Norwegian Arctic are shown respectively in Figs. 1-3.

During AGASP we also used two filter sampling lines to collect approximately 25 pairs of aerosol samples on cellulose filters (Millipore, Type RATF) and prefired quartz filters (Pallflex type QAO-2500). The Millipore filters were analyzed by XRF for sulfur and other elements with $Z > 11$, while the quartz fiber filters were analyzed for total carbon. Sulfur concentrations could be determined with an uncertainty of ±10% from these airborne filters, but the total carbon determinations have large uncertainties due to detection limits and blank variability. For this reason, the total carbon measurements used in this paper are obtained from ground-level sampling on QFF filters at the N.O.A.A.-G.M.C.C. station near Barrow, Alaska. The total carbon determinations were made by measuring the total evolved CO_2 from samples collected on quartz fiber filters heated to 800°C in an oxygen atmosphere (Mueller et al., 1971).

Box Model Calculation

For this calculation, we view the Arctic troposphere as a cylindrical

volume with a radius extending from the North Pole to 70°N latitude and a height of 7 km, corresponding to the approximate level of the tropopause. Consider a conserved species like graphitic carbon that is not produced or destroyed in the atmosphere. For such a component, the rate of change of the mass of particles within this box is equal to the flux of particles entering the box minus the flux leaving the box. This equation can be put in a simple mathematical form:

$$\frac{dM(t)}{dt} = F_M - \frac{M(t)}{\tau} \quad , \tag{1}$$

where M(t) is the mass of the component with the box at time t; $\frac{dM(t)}{dt}$ is the rate of change of this mass within the box; F_M is the input flux through all surfaces of the box; and $\frac{M(t)}{\tau}$ is the flux leaving the box, which we assume can be represented by an exponential decay with an effective residence time, τ. This residence time includes both losses by deposition and by transport of air masses out of the Arctic basin. For equilibrium, $\frac{dM}{dt} = 0$, and the input flux equals the decay rate:

$$F_M = \frac{M(t)}{\tau} \quad . \tag{2}$$

For nonequilibrium situations, the input flux can be greater or less than the decay rate. If the input flux at time t is less than $\frac{M(t)}{\tau}$, it is easy to show that at some previous time the input flux had to be at least as large as this decay rate. In other words, even for a nonequilbrium situation, Eq. (2) can be used to get a lower limit on the maximum input flux.

Results and Conclusions

If one can estimate the mass of graphitic particles in the Arctic troposphere, then using Eq. (2), the input flux as a function of residence time can be determined. The mass of graphitic particles G(t) is given by:

$$G(t) = \int_{\text{Arctic troposphere}} G(\theta,\phi,h,t)dV \quad ,$$

where $G(\theta,\phi,h,t)$ is the concentration of graphitic particles at latitude θ, longitude ϕ, height h, and time t. The profiles of graphitic particles obtained during AGASP can be used to make an estimate of the average value of G(t) from March to April, 1983. In this analysis we neglect the dependence of the graphitic concentrations on latitude and longitude and use an average vertical distribution obtained from the nine tropospheric AGASP flights to characterize the whole Arctic region. These flights include four flights in the Alaskan Arctic; three flights in the Norwegian Arctic; one transit flight from Anchorage, Alaska, to Thule, Geeenland, via the Canadian Arctic; and one transit flight from Thule to Bodo, Norway, via the North Pole. We assume the eastern Arctic is equally as dirty as the western Arctic, which probably underestimates the soot concentrations since the primary source regions appear to be in the eastern sector (Rahn and McCaffrey, 1980). With these assumptions,

$$G = \langle G(t) \rangle = \int_{\theta = 70°}^{\theta = 90°} 2\pi R^2 \cos\theta d\theta \int_{h = 0}^{h = 7\text{ km}} \langle G(h) \rangle \, dh \quad ,$$

where R is the radius of the earth and $\langle G(h) \rangle$ is the average vertical distribution of graphitic particles, Substituting into this equation, we determine the average mass of graphitic particles in the Arctic troposphere during AGASP to be $G = 2.45 \times 10^{10}$ g $= 2.45 \times 10^4$ metric tons. Soot is composed of both graphitic particles and organics. As shown by Novakov (1980), one can make a good estimate of soot concentrations from the graphitic component by assuming

it represents approximately 25% of the soot mass. Reliable total carbon determinations could not be obtained from the airborne filters on these flights. However, ground-level determinations at the NOAA-GMCC station at Barrow, Alaska, have been made and indicate that during March-April approximately 20% of the total carbon is graphitic (Rosen et al., 1981). This would suggest that most of the particulate carbon at this time of year in the Arctic is soot, but this should be viewed only as a working hypothesis that it is important to validate in airborne and ground-level samples in other parts of the Arctic. However, for the purposes of this paper, we assume that we can make as estimate of the total carbon in the Arctic from the ground-level measurements at Barrow by multiplying the graphitic component by 5; i.e., the estimated total particulate carbon mass is 1.2×10^5 tons. It is also possible to make an estimate of the total sulfur in the Arctic because we collected approximately 20 airborne filters in AGASP, from which we have determined the sulfur and graphitic carbon contents. The sulfur-to-graphitic-carbon ratio for these filters is 3.26 ± 0.75. If we assume that the vertical profiles of sulfur and graphitic carbon are similar, then the total amount of particulate sulfur in the Arctic can be estimated by multiplying the graphitic mass by 3.26; i.e., the estimated particulate sulfur mass = 8×10^4 tons, which would represent a lower limit on the total amount of sulfur in the Arctic because it does not include the gas-phase contribution.

These estimates of the mass of graphitic carbon, total carbon, and sulfur can be used in conjunction with Eq. (2) to estimate the input fluxes of each of these components into the Arctic troposphere. These estimates as a function of residence time are shown respectively in Figs. 4-6. The shaded region in the figures represents what appears to be a reasonable range of values for the residence time of particles in the Arctic atmosphere, which we estimate to

be from 1 week to 1 month. This effective residence time includes the effects of deposition as well as transport of air parcels out of the Arctic basin. These estimates may have to be revised as a better understanding of air parcel trajectories and deposition rates becomes available. The range of values is consistent with the estimates of 2-3 weeks by Rahn and McCaffrey (1980) and the very rapid transport ($\sim$ 1 week) of aerosols from Eurasia to Barrow estimated by Raatz and Shaw (1983) and Harris (1984).

For comparing the fluxes shown in Figs. 4-6 with fluxes from source regions, we chose a residence time of 2 weeks, which will give fluxes within a factor of 2 of the extreme values of residence time. This uncertainty should be kept in mind when comparisons are being made. Recently, Marland et al. (1984) have made estimates of fossil fuel burned as a function of latitude in 5° latitude bands. In Table 1 we compare the fluxes of graphitic carbon (F_G), total carbon (F_C), and sulfur (F_S) entering the Arctic to the carbon burned in various latitude ranges. It becomes immediately obvious from this table that sources between 70-90°N cannot account for these fluxes since the amount of carbon burned in this region is less than the fluxes (i.e., sources in the Arctic cannot account for the Arctic haze). In the latitude range 65-70°N, the fluxes are less than the carbon burned but are too large a fraction of it to be reasonable. The fuel would have to contain $\sim$ 20% sulfur, and one-third of it would have to be burned incompletely. For comparison, the emission factor for soot as a fraction of the mass of carbonaceous fuel burned ranges from zero for complete combustion to $\sim$ 4% for very dirty burning of soft coal. Significant source contributions in the 60-65°N latitude range are more reasonable; however, even there it would require extremely dirty combustion of very high sulfur fuels. Furthermore, it would require almost all the emissions from this region to be transported only in a northerly direction toward the Arctic

with minimal deposition along the transport path. Given the uncertainties of the flux calculations, one cannot eliminate this latitude band as a significant source region; but it does appear to be a prime source region. Major contributors to the Arctic haze in the 55-60° latitude band become more reasonable, but even here it would require very effective transport of source emissions to the Arctic. As one goes below 55°N latitude, the fluxes become a very reasonable fraction of the fuel burned, which is consistent with the midlatitude sources proposed on the basis of trace element analyses by Rahn and McCaffrey (1980).

The flux of sulfur, F_S, entering the Arctic can be compared with estimated sulfur emissions in various source regions (Möller, 1984). These estimates are based on the sulfur content of the fuels and obviously represent a maximum possible aerosol sulfur input into the atmosphere because SO_2 may be scavenged before being converted to particulate sulfur. Table 2 shows this comparison, with the Arctic sulfur flux shown as a percentage of the sulfur emissions from potential source regions. It is clear from the table that F_S is a substantial fraction of the sulfur emissions from each region individually (e.g., capitalist Europe, 14.5%; socialist Europe, 11.4%; U.S.S.R., 14.5%; Canada, 64%). These fractions are large, given the fact that the Arctic is only one of many possible receptor areas and the likelihood of significant deposition of SO_2 and particulate sulfur along pathways to the Arctic. The results could indicate that the Arctic haze is due to the combined input of several major source regions. On a global scale, these calculations estimate that 2.5% of the global sulfur emissions enter the Arctic. This is a rather substantial fraction, given the distance of the Arctic from major source regions and the fact that the Arctic accounts for only $\sim$ 6% of the northern hemisphere's surface area. (The Arctic is defined in this paper as latitudes above 70°N.) It should be kept in mind

that these conclusions can only be viewed as preliminary because of uncertainties in the vertical and horizontal distribution of the Arctic haze and its residence time. However, they do indicate that the fluxes entering the Arctic are large, must be due to major combustion source regions, and have to be taken into account in the global sulfur and carbon budget.

Acknowledgments

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Table 1. Comparison of graphitic carbon, total carbon, and sulfur fluxes to the amount of fuel burned at various latitudes.

Latitude	Carbon burned (tons month^{-1})	F_G as % of carbon burned	F_C as % of carbon burned	F_S as % of carbon burned
75-90°N	1.5×10^3	3,200	16,300	10,600
70-75°N	5×10^4	98	490	320
65-70°N	7.6×10^5	6.4	32	21
60-65°N	3.3×10^6	1.5	7.4	4.8
55-60°N	2.5×10^7	0.2	1	0.6
50-55°N	7.1×10^7	0.07	0.35	0.2
45-50°N	5.3×10^7	0.09	0.45	0.3
0-45°N	2.3×10^8	0.02	0.1	0.07
Global	4.4×10^8	0.01	0.05	0.04

Table 2. Comparison of Arctic sulfur fluxes to sulfur emissions in various regions.[a]

Region	Sulfur emissions (tons $month^{-1}$)	Arctic sulfur flux as % of emissions
Europe	2.5×10^6	6.4
Capitalist Europe	1.1×10^6	14.5
Socialist Europe	1.4×10^6	11.4
U.S.S.R.	1.1×10^6	14.5
U.S.A.	1.3×10^6	12.3
Canada	2.5×10^5	64
Global	6.6×10^6	2.4

[a]Sulfur emission data obtained from Møller (1984).

Figure Captions

Figure 1. Vertical profile of graphitic carbon in ng m^{-1} obtained on March 11, 1983, in the Alaskan Arctic (AGASP flight 1).

Figure 2. Vertical profile of graphitic carbon in ng m^{-1} obtained on March 15, 1983, in the Alaskan Arctic (AGASP flight 3).

Figure 3. Vertical profile of graphitic carbon in ng m^{-1} obtained on April 5, 1983, in the Norwegian Arctic (AGASP flight 10).

Figure 4. Estimated flux of graphitic carbon entering the Arctic troposphere as a function of residence time. The shaded area represents a range of residence times of 1 week to 4 weeks.

Figure 5. Estimated flux of total particulate carbon entering the Arctic troposphere as a function of residence time. The shaded area represents a range of residence times of 1 week to 4 weeks.

Figure 6. Estimated flux of sulfur entering the Arctic troposphere as a function of residence time. The shaded area represents a range of residence times of 1 week to 4 weeks.

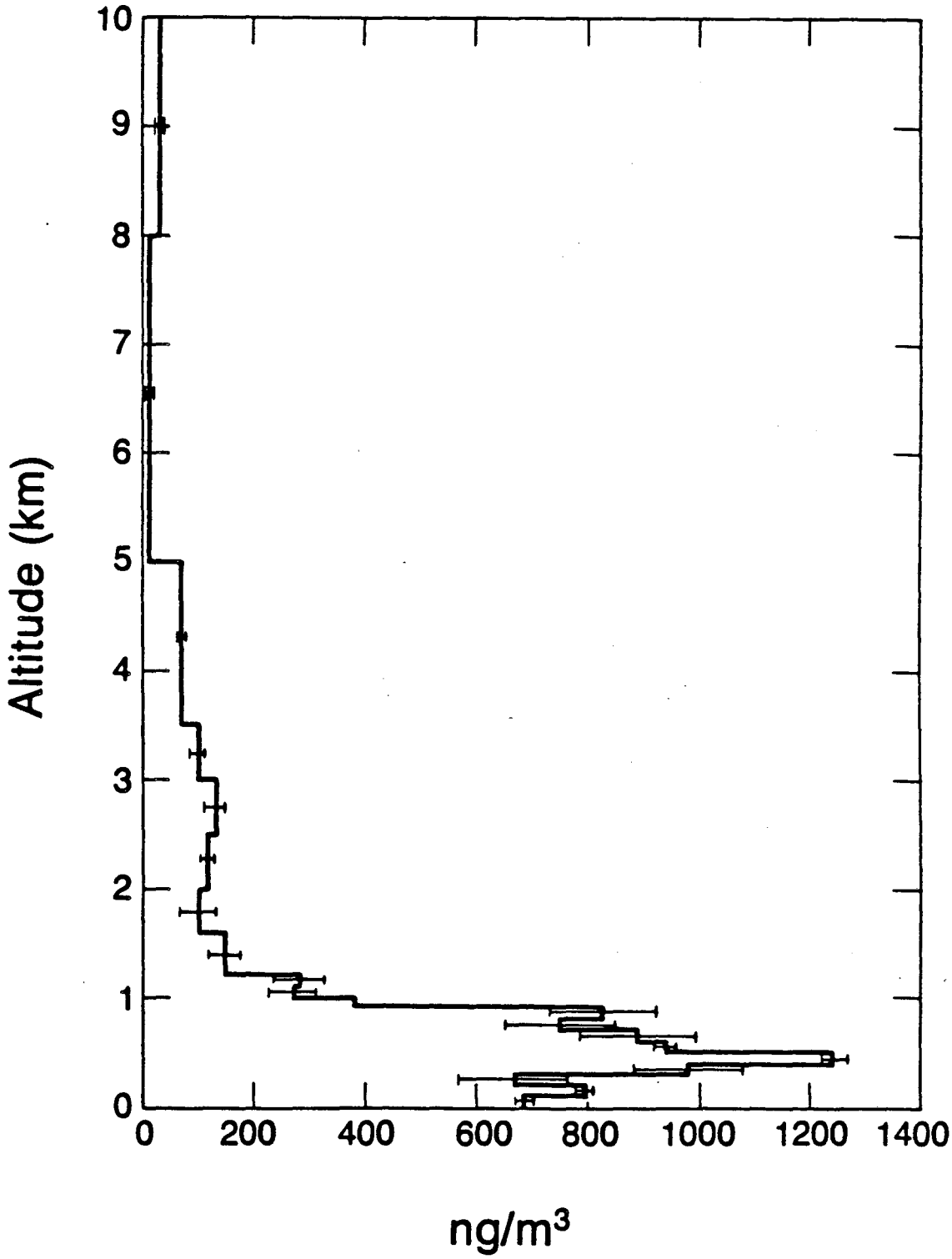

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Figure 1

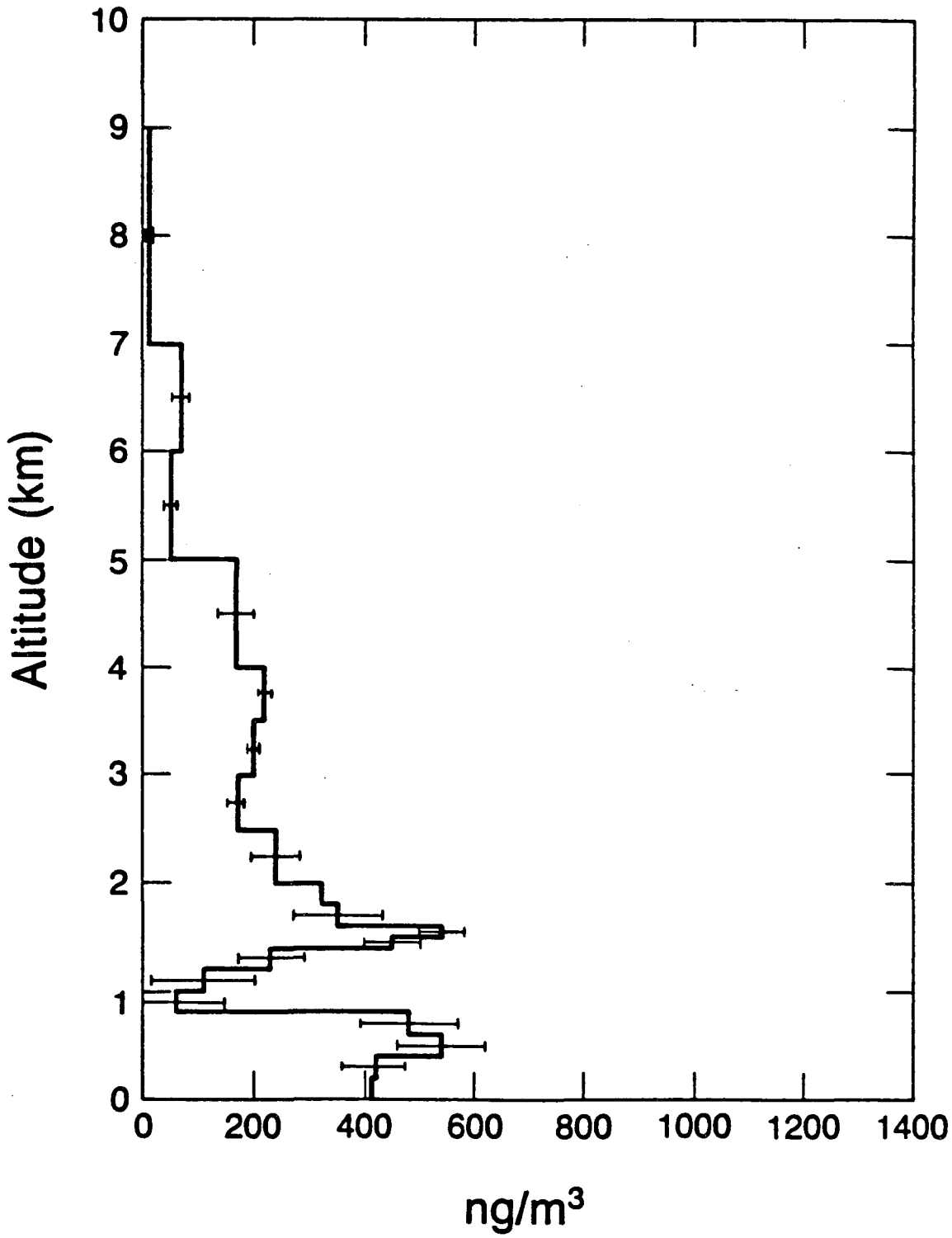

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Figure 2

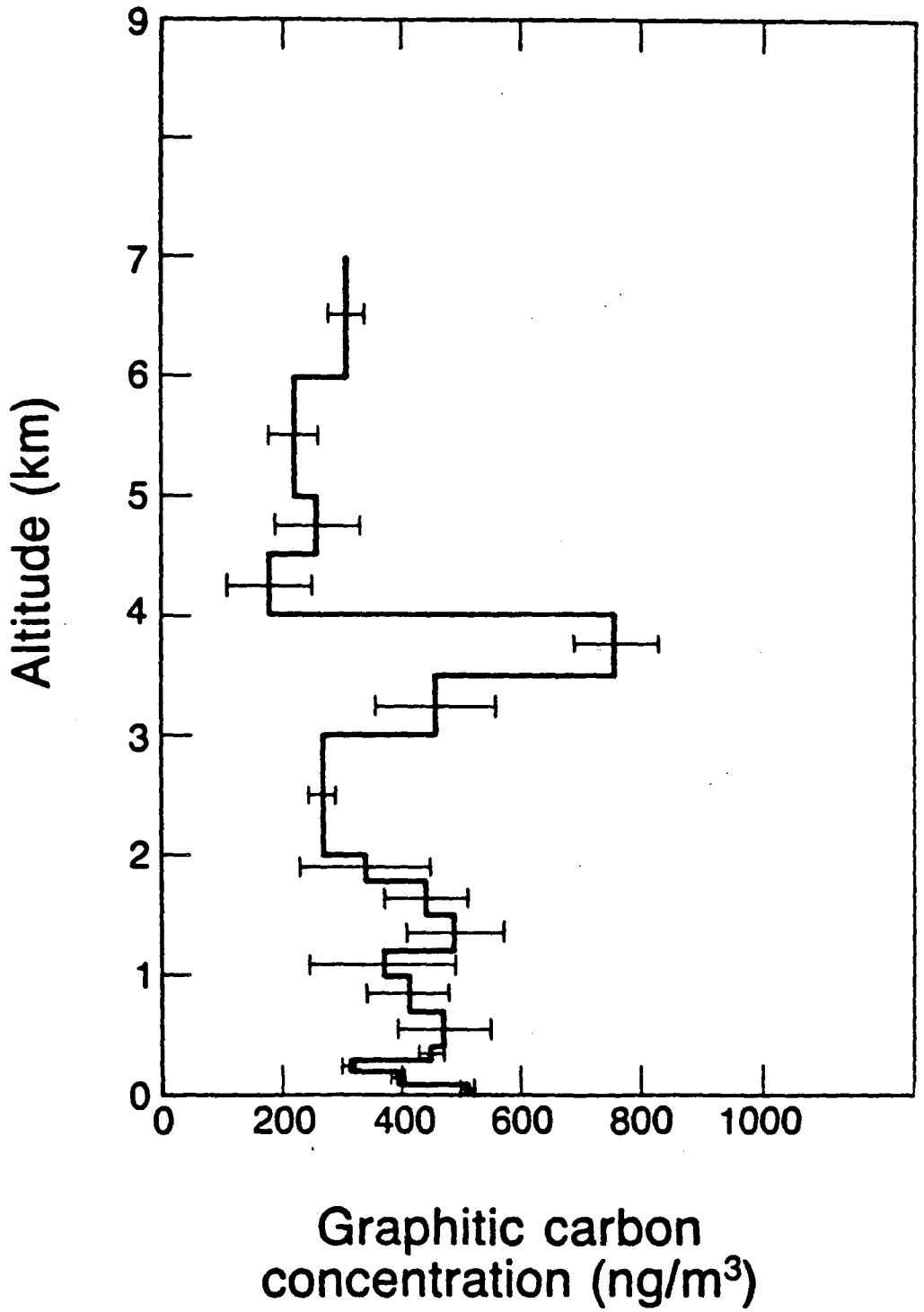

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Figure 3

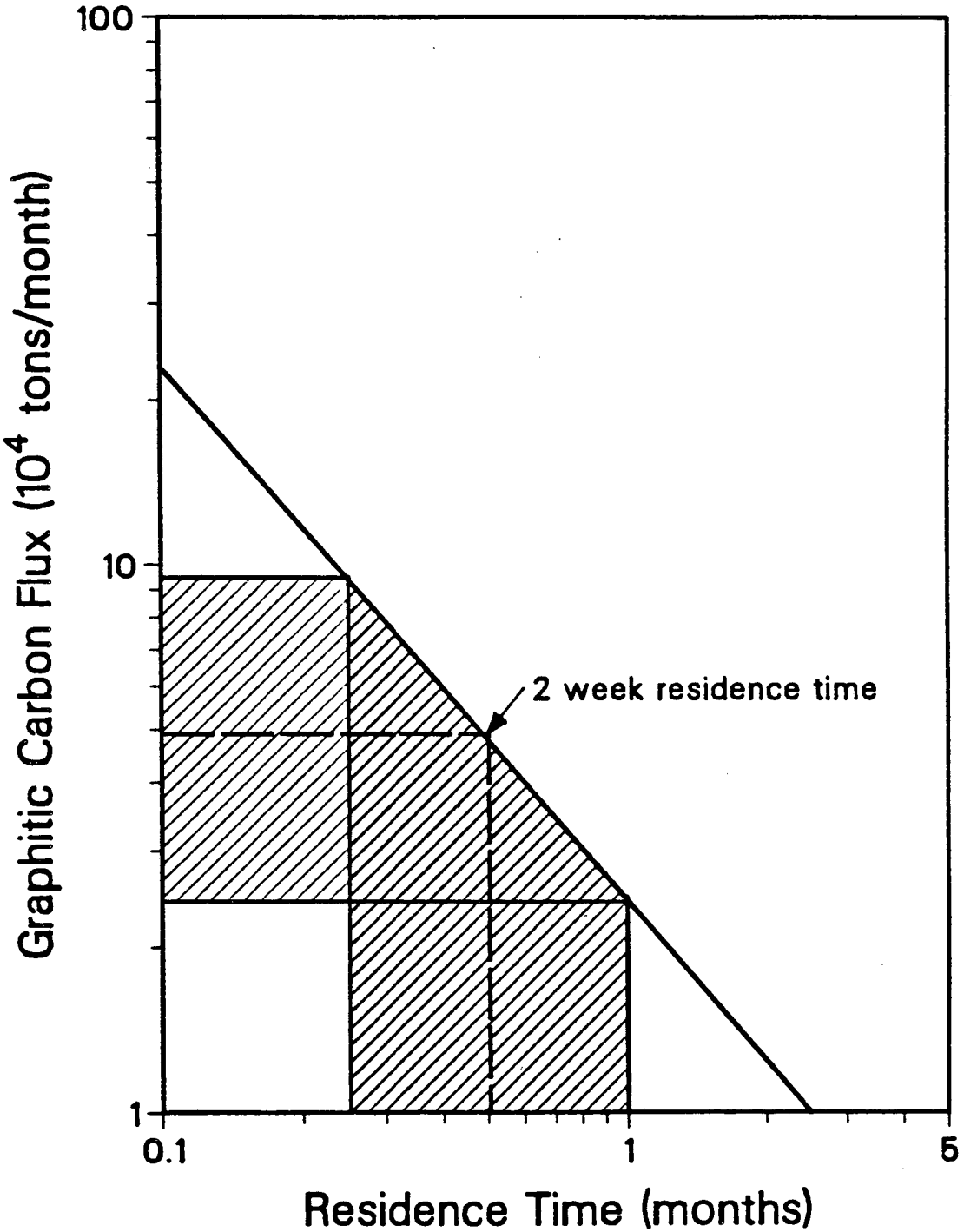

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Figure 4

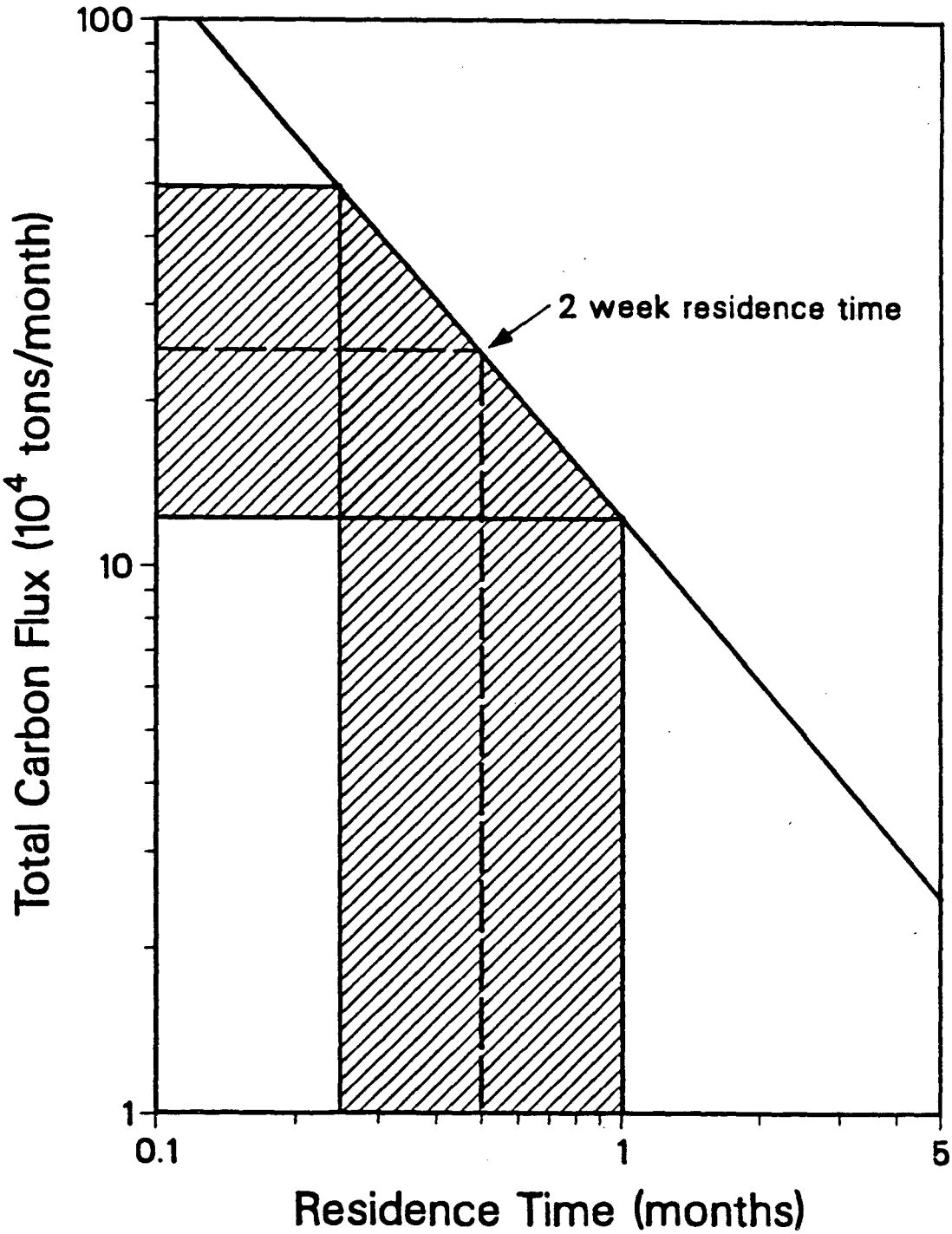

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Figure 5

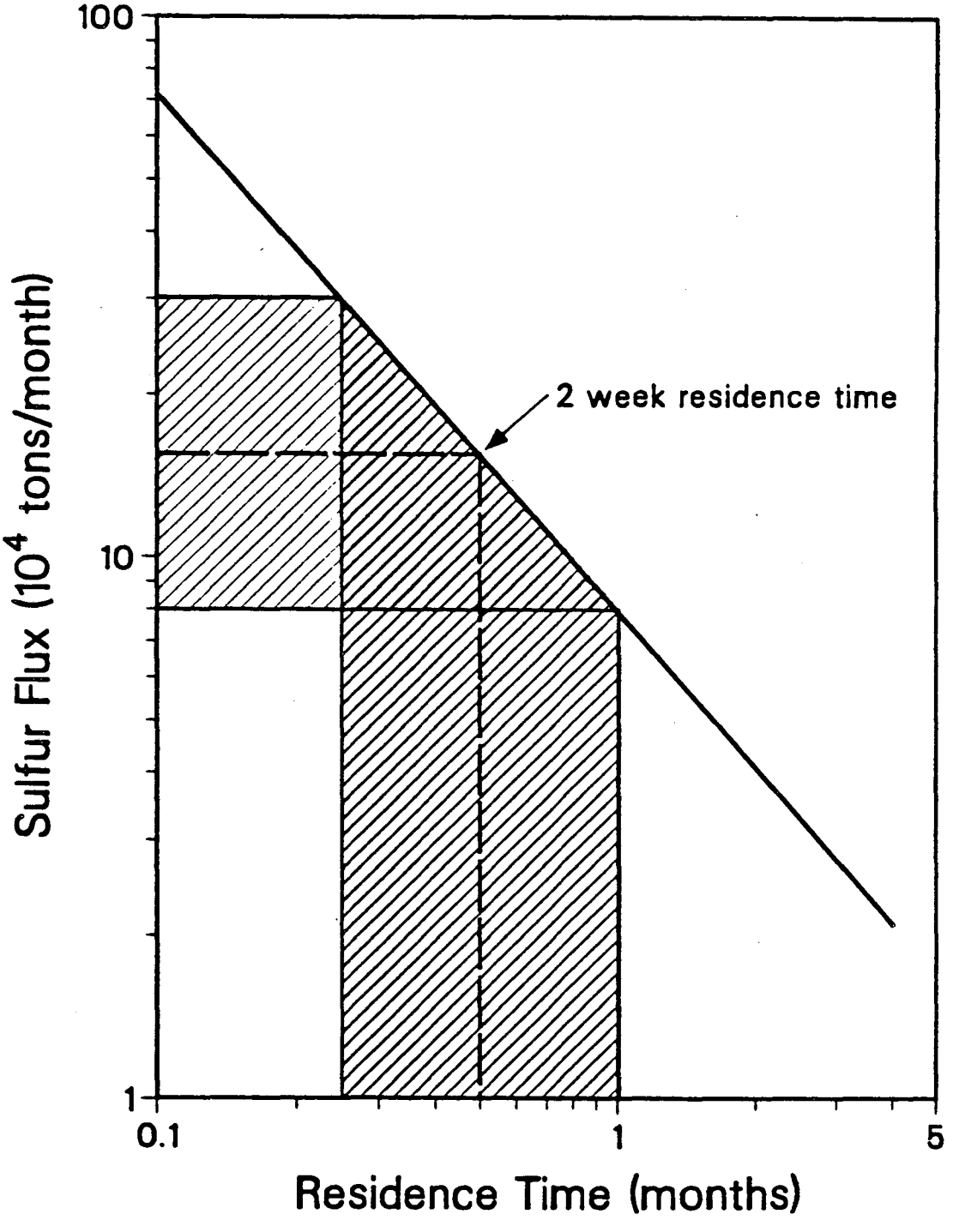

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Figure 6

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