glaciated surface, indicates that Jones Mountains were glaciated more than 22 ± 12 million years ago (*4*). Paleomagnetic stratigraphy and the occurrence of ice-rafted debris in Antarctic deep-sea cores indicate that calving glaciers were present in Antarctica at least 3 million years ago, and that the greatest amount of ice-rafted debris was produced between 2 and 3 million years ago (*5*). From the ranges of sub-Antarctic and Antarctic planktonic Foraminifera in deep-sea cores, Bandy (*6*) concluded that Antarctica was largely covered by ice during the late Miocene and middle Pliocene; thus the potassium-argon dates from Taylor Valley are consistent with these other data in pointing to the great antiquity of major Antarctic glaciation.

Note added in proof: Fieldwork now in progress has confirmed that till deposited by Taylor Glacier underlies the dated volcanics, and that subsequent advances of the glacier have overrun the volcanics at least up to an altitude of approximately 1250 m.

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References and Notes

1. T. L. Péwé, *J. Geol.* **68**, 498 (1960).
2. E. E. Angino, M. D. Turner, E. J. Zeller, *Bull. Geol. Soc. Amer.* **73**, 1553 (1962).
3. J. D. McCraw, *New Zealand J. Geol. Geophys.* **5**, 740 (1962).
4. C. Craddock, T. W. Bastien, R. H. Rutford, in *Antarctic Geology*, R. J. Adie, Ed. (North-Holland, Amterdam, 1964), p. 171.
5. N. D. Opdyke, B. Glass, J. D. Hays, J. Foster, *Science* **154**, 349 (1966); N. D. Watkins, H. G. Goodell, T. T. Mather, S. Koster, in *Program Southeastern Sec. Geol. Soc. Amer. 1967 Ann. Meeting* (1967), p. 58.
6. O. L. Bandy, *Amer. Assoc. Petrol. Geol. Bull.* **50**, 643 (1966); in *Program Southeastern Sec. Geol. Soc. Amer. 1967 Ann. Meeting* (1967), p. 17.
7. The potassium-argon dating was done by one of us (R.L.A.) at Yale University; the laboratory was constructed with funds from the Research Corporation and the Sheffield Scientific School of Yale University; operating expenses are provided by NSF grant GP-5383. The samples were collected in Taylor Valley in 1958 by W. Hamilton and P. T. Hayes; field expenses were provided by NSF grant G-6689. The chemical analyses of basalt samples were made by P. L. D. Elmore, I. H. Barlow, S. D. Botts, and G. Chloe of the U.S. Geological Survey. We thank R. F. Flint, T. L. Péwé, R. F. Black, and M. D. Turner for their comments on early drafts of this manuscript. Publication authorized by the director, U.S. Geological Survey.

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Cosmic Ray–Produced Radionuclides as Tracers of Atmospheric Precipitation Processes

Abstract. *Through recent developments in instrumental analysis it is now possible to measure with good precision the rainwater concentrations of five short-lived radionuclides which are produced by cosmic ray spallation of atmospheric argon. These measurements provide a method for studying the in-cloud nucleation times and aerosol scavenging efficiencies, and promise to provide information on short-term processes which occur in rain and snow formation.*

Radionuclides are produced continuously in the atmosphere by cosmic rays. Their absolute production rates vary considerably with both altitude and latitude but remain relatively constant with time. Following formation, most of these radionuclides quickly become attached to the normal atmospheric aerosols and thus can serve as tracers of the subsequent behavior of these aerosols. Some of the radionuclides with half-lives of months to years have been used in studying atmospheric mixing processes, while the longer-lived radionuclides have served as tracers of geophysical processes and in dating biological and geological phenomena. It has been recognized that radionuclides with half-lives of minutes to hours would be useful in studying atmospheric precipitation scavenging mechanisms since their half-lives are of the same order of magnitude as the time scale on which precipitation processes occur (*1, 2*).

The main deterrent in the use of these radionuclides as tracers of atmospheric processes has been the fact that they are present in extremely small concentrations and are therefore very difficult to detect and measure. With the development of ultrasensitive counting techniques, it has become possible to measure several of these short-lived radionuclides with high precision (*3, 4*). The five radionuclides, ^{34m}Cl ($T_{1/2}$ = 32 minutes), ^{38}Cl ($T_{1/2}$ = 37.3 minutes), ^{39}Cl ($T_{1/2}$ = 55 minutes), ^{38}S ($T_{1/2}$ = 2.9 hours), and ^{24}Na ($T_{1/2}$ = 15 hours), which are spallation products of atmospheric argon, have been measured in several rains and their relative and absolute concentrations determined. Their absolute concentrations in precipitation are related to the scavenging efficiency and the altitude from which the precipitation occurred, while their relative concentrations provide information on the time spent by the host particles subsequent to collection in the cloud but prior to their deposition at the earth's surface.

In spallation reactions with the atmosphere, high-energy primary cosmic rays produce large numbers of secondary neutrons and protons which in turn are responsible for most of the spallation reactions resulting in radionuclide production in the atmosphere. The production rate of radionuclides in the atmosphere depends on both altitude and latitude, and are discussed in detail by Lal and Peters (*5*). The overall relative production rate per gram of air increases by 2 to 3 orders of magnitude between sea level and the top of the atmosphere. Although the total atmospheric production rate increases by almost an order of magnitude in moving from the geomagnetic equator to the poles, the tropospheric production rate only varies by about twofold. About 30 percent of the radionuclide production takes place in the troposphere and the remainder in the stratosphere.

The radionuclides resulting from cosmic ray spallation reactions in the atmosphere which have been observed to date, with their half-lives, include ^{10}Be (2.7×10^6 years), ^{36}Cl (3×10^5 years), ^{14}C (5730 years), ^{32}Si (~ 700 years), ^{3}H (12.26 years), ^{22}Na (2.60 years), ^{35}S (86.7 days), ^{7}Be (53 days), ^{33}P (25 days), ^{32}P (14.3 days), ^{28}Mg (21.3 hours), ^{24}Na (15.0 hours), ^{38}S (2.9 hours), ^{31}Si (2.62 hours), ^{39}Cl (55 minutes), ^{38}Cl (37.3 minutes), and ^{34m}Cl (32.0 minutes) (*2, 6*). The latter of this group, with half-lives of minutes to hours, can be used as tracers of precipitation-scavenging processes.

Measurements of the absolute production rates of these radionuclides have not been reported; however, estimates which are good to within a factor of 3 or 4 can be made which are based on spallation-yield curves extrapolated to argon (*5*). The absolute atmospheric production rates of these short-lived radionuclides are now being more precisely estimated from measurements of the equilibrium concentration of the radionuclides in the air (*7*).

Atmospheric precipitation samples (rain or snow) are collected on plastic sheets with surface areas of about 100 m^2. These water samples, which may amount to about 2 to 100 liters, are transferred to the laboratory, where the chlorine radionuclides, ^{34m}Cl, ^{38}Cl, and ^{39}Cl, are separated by a rapid silver chloride precipitation using lead and bismuth holdback carriers (*1*). The water, or filtrate, which still contains ^{38}S, ^{24}Na, and other airborne radionuclides, is then evaporated to dryness. The radionuclides are measured by direct counting of the two fractions on a multidimensional gamma-ray spectrometer. The spectrometer used for the 1966–1967 measurements had two sodium iodide crystals 11 inches in diameter by 6 inches thick (28 by 15 cm) between which the sample was precisely positioned for counting. This ultra-low-level counting instrument, which is described in detail elsewhere (*4*), measures both the single and coincidence gamma rays emitted from the sample and stores the events in a computer memory at locations which uniquely define the energies of the gamma rays. Where coincidence gamma rays from a radionuclide are used for its measurement, the natural background and the interference from other radionuclides are extremely low. This instrument is particularly suitable for this group of cosmic ray–produced radionuclides since their decay involves the emission of two or more gamma rays per disintegration. The coincidence counting efficiencies (defined as counts per disintegration) for the radionuclides

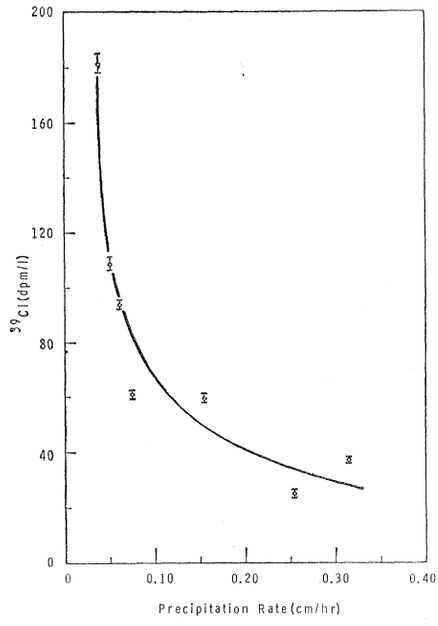

Fig. 1. Concentration of ^{39}Cl as a function of precipitation rate.

^{24}Na, ^{34m}Cl, ^{38}Cl, and ^{39}Cl were 6, 7, 2.5, and 5.5 percent respectively, while the background was 0.5, 1.5, 0.6, and 3.5 counts per hour respectively. The corrections necessary for cross interference between these radionuclides and from other radionuclides present were very low, being less than 1 percent for ^{24}Na, ^{38}Cl, ^{39}Cl, and ^{34m}Cl.

The concentrations of the five short-lived radionuclides in water from several rain and snow storms are tabulated in Table 1. The plus-or-minus values listed next to the concentrations are the percent standard deviations associated with the measurements. For the measurements made during 1966–1967 the standard deviations for ^{38}Cl, ^{39}Cl, and ^{24}Na were between 2 and 11 percent, while for ^{34m}Cl and ^{38}S some of the standard deviations were as high as ± 33 percent. The data show that absolute concentrations of each of the various radionuclides vary by more than an order of magnitude in different rains. Unfortunately, neither the relative nor absolute production rates of these radionuclides are as yet known, and one is therefore presently limited to comparing the concentration in different rains to infer cloud processes. It was observed that the concentration of a given radionuclide varied inversely with the precipitation rate. In Fig. 1 the observed concentrations of ^{39}Cl are plotted as a function of precipitation rate. The concentration of ^{39}Cl decreases by almost an order of magnitude while the precipitation rate increases from a few hundredths to about three-tenths of a centimeter per hour. This decrease in radionuclide concentration with increase in precipitation rate may simply result from nearly complete removal of aerosol particles, along with their attached radionuclides, even in a modest rain. If this were the case, the total radioactivity which could be carried down per unit area of earth surface by a rainstorm would be related to cloud height and wind speed rather than the precipitation rate.

It appears, however, that this oversimplified picture is at best only partially responsible for the observations.

Table 1. Cosmic ray–produced radionuclides observed in rainwater (first 13 rows) and snow water (last 2 rows), Richland, Washington. The ± values are the percent standard deviations for the measurements.

Date of precipitation	Precipitation rate (cm/hr)	Collection time (min)	Volume (liters)	Concentration (dpm/liter)				
				^{39}Cl	^{38}Cl	^{34m}Cl	^{38}S	^{24}Na
6-15-64			60					0.70 ± 29
6-17-64			6.64					2.22 ± 11
6-18-64			14.32					0.59 ± 15
7-29-64		50	5.10	200 ± 8.5	147 ± 10		13 ± 38	2.0 ± 10
8-01-64		50	3.50	15 ± 20	9 ± 55			
8-12-64		5	2.20	62 ± 19	42 ± 31			2.3 ± 17
11-14-66	0.255	30	30.16	24.4 ± 5	20.4 ± 10	0.3 ± 33	1.22 ± 13	0.227 ± 7
11-28-66	.0767	44	13.32	60.5 ± 3	45.3 ± 7	.7 ± 29	2.07 ± 15	2.06 ± 4
12-01-66	.316	25	97.87	37.2 ± 2	22.9 ± 7	.5 ± 20	1.85 ± 8	0.608 ± 3
12-12-66	.0515	40	25.50	108.7 ± 2	82.7 ± 4	1.1 ± 11	8.24 ± 18	6.14 ± 2
12-13-66	.0638	37	29.20	93.5 ± 2	60.5 ± 4	1.4 ± 14	3.29 ± 20	1.77 ± 6
1-26-67	.155	40	76.80	59.2 ± 2	43.9 ± 5	0.9 ± 33	1.11 ± 14	1.06 ± 3
1-26-67*	.0384	40	19.00	181.6 ± 2	113.9 ± 4	1.5 ± 27		1.07 ± 11
12-7-66†		660	21.00					0.53 ± 4
12-9-66†		240	50.00					2.53 ± 2

* End of rain 1-26-67. † The same storm, at places 150 miles apart.

Regardless of the size of a cloud droplet, at least one condensation nucleus would be required for its formation; thus, for smaller cloud drops one would expect to find higher radionuclide concentrations. Growth of drops through coalescence will tend to keep this concentration constant, while growth through condensation of moisture will decrease this concentration. The growth of cloud drops to a large size prior to any coalescence in the heavier rain, and growth mainly through coalescence in the lighter rain, would help account for the observations. Also, since lesser rainfall rates are associated with greater evaporation of drops, either during their cloud cycling or during their fall to earth, these should be associated with increased particulate or radionuclide concentrations.

The observation that cosmic ray–produced radionuclide concentrations in rainwater vary inversely with precipitation rate helps to explain the large difference between our observed concentrations and those recently reported by Bhandari *et al.*, 1966 (*2*), in Bombay, India. Their reported concentrations of these short-lived radionuclides were several fold lower than ours, and this is evidently due to the much higher rainfall rates in the storms they studied. The annual rainfall rate in Bombay, India, is about 70 inches per year, compared to about 7 inches per year at Richland, Washington.

Only two measurements of radionuclides in snow have been made, and the observed concentrations of ^{24}Na are included in Table 1. It appears that the concentrations of cosmic ray–produced radionuclides in snow are comparable with those in rain. The ratios of the concentrations of the various cosmic ray–produced radionuclides in precipitation provide an insight into the condensation processes and air movements within a storm system.

In an air mass where no precipitation scavenging or significant vertical mixing has recently occurred the ratio of the various short-lived radionuclides would be constant, since their production rates would be in equilibrium with their decay rates. This equilibrium could be disturbed by the upward or downward movement of air masses, and by partial removal of these radionuclides by nucleation and subsequent precipitation.

Following the upward movement of an air mass to an altitude of higher production rate, the short-lived radionuclides, ^{38}Cl and ^{39}Cl, would build up at a much faster rate than would ^{24}Na, and the air mass would thus be characterized by a high radiochlorine to ^{24}Na ratio and a relatively low ^{24}Na concentration. Conversely, following the movement of an air mass from a higher to a lower elevation where the overall production rate is lower, the more rapid decay of the short-lived chlorine radioisotopes would result in a low radiochlorine to ^{24}Na ratio accompanied by a high ^{24}Na concentration. This condition of high radiochlorine to ^{24}Na ratios accompanied by low ^{24}Na concentrations, and low radiochlorine to ^{24}Na ratios accompanied by high ^{24}Na concentrations, is evident in the measurements made in this study as is illustrated in Fig. 2. This type of relationship, which was also observed by Bhandari *et al.* (*2*) on comparing ^{39}Cl to ^{38}S ratios with ^{38}S concentrations in rainwater, was used by Bhandari in estimating possible intervals for vertical transport of air masses.

Table 2. Comparison of short- to long-lived radionuclide ratios with classification of rain.

Date	$^{39}Cl/^{24}Na$ ratio	$^{38}Cl/^{24}Na$ ratio	Meteorological qualifier
12-12-66	18	14	Early in long rain
11-28-66	29	22	Light, intermittent precipitation
12-13-66	53	34	Near end of long rain
12-01-66	61	38	End of long rain
1-26-67	56	41	Near end of rain
11-14-66	107	90	End of considerable rain
1-26-67	170	106	End of rain

There are, however, two other conditions which could also produce these observed relationships. For example, following removal by precipitation of a major fraction of the atmospheric aerosol and its associated cosmic ray–produced radionuclides, the rapid buildup of the short-lived chlorine radioisotopes would also result in a high chlorine radioisotopes to ^{24}Na ratio associated with a low ^{24}Na concentration. By comparison, unwashed air would have a low radiochlorine to ^{24}Na ratio and a high ^{24}Na concentration. A third condition which could produce the observed radionuclide concentrations and one which appears more probable is the retention of aerosol particles, which have served as condensation nuclei, by cloud droplets for long periods of time. The ratio of a short-lived to a long-lived radionuclide in the droplets would then be much lower than that of the equilibrium condition in the atmosphere. In the storms

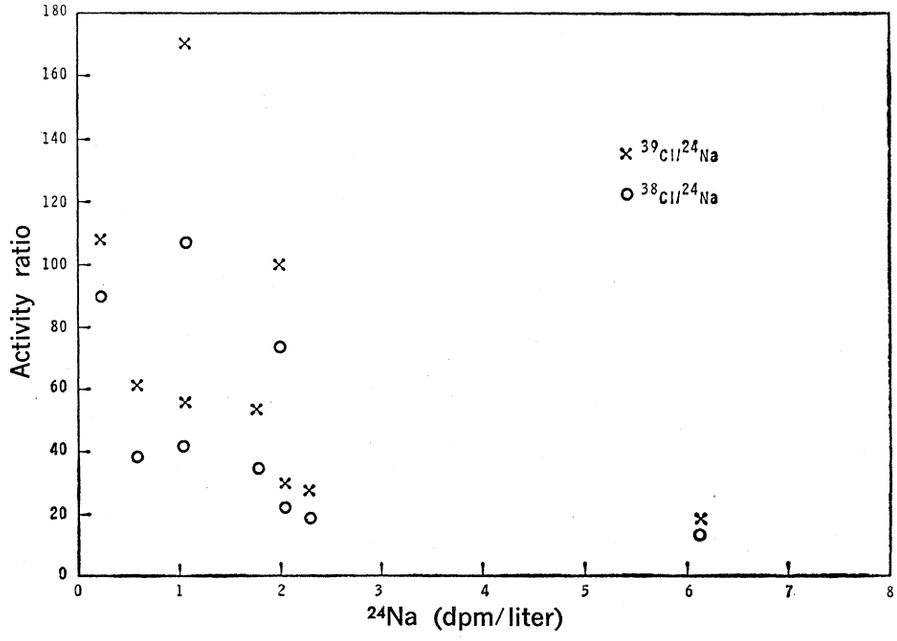

Fig. 2. Relationship of the radiochlorine/^{24}Na ratio to the ^{24}Na concentration in rainwater.

which we have studied, the lowest ^{39}Cl and ^{38}Cl to ^{24}Na ratios were observed near the beginning of the storm. The ^{39}Cl and ^{38}Cl to ^{24}Na ratios observed in the various storms are compared in Table 2 with "meteorological qualifiers" which were used in subjectively classifying the sampling period within the rainstorm.

An apparent relationship between the ratios of ^{39}Cl and ^{38}Cl to ^{24}Na, and the period in the storm when the sample was collected is clearly evident. The two entries of 26 January in Table 2 are especially interesting because these were successive samples 1 hour apart near the end of a rain. The concentration of the longer-lived ^{24}Na was the same, but the short-lived ^{39}Cl and ^{38}Cl increased by about a factor of three.

An explanation for this change in ratio and for the range of ratios shown in Table 2 is evident if one views the storm cloud system as a filter, with unwashed, saturated air entering at the upwind end and moving through the storm cloud with a wind speed V relative to the earth. This unwashed air could contain condensation nuclei which have the cosmic ray–produced radionuclides attached to them in a ratio approaching their steady-state production rates. At the same time, the storm cloud moves with a slower speed v relative to the earth. Then precipitation sampled at the earth at times Δt apart is actually from times in-cloud which are ΔT apart, where $\Delta T = [v/(V - v)]\,\Delta t$.

For the storm of 26 January 1967 approximate values of $V = 35$ and $v = 25$ could be used along with the known Δt of 1 hour, to give $\Delta T = 2.5$ hours. If this were the actual in-cloud period, changes in the ^{39}Cl to ^{24}Na and ^{38}Cl to ^{24}Na ratios of about 8- and 16-fold respectively could occur. The observed ^{38}Cl and ^{39}Cl to ^{24}Na ratio changes of about threefold suggest a shortened in-cloud period or perhaps that other processes are important. This possibility, that aerosols do spend a substantial period of time in the cloud after their incorporation in cloud droplets, was offered as an explanation for the nonequilibrium ratios of ^{214}Bi to ^{214}Pb in rains in India (*8*).

This group of short-lived cosmic ray–produced radionuclides has a great potential in studying short-range vertical atmospheric transport rates and in-cloud precipitation-scavenging mechanisms. Their value for many applications will of course increase when their absolute production rates as a function of altitude and latitude have been determined. It is likely that on a careful observation of the absolute and relative concentrations of these radionuclides at several periods during storms, it will be possible to define the processes responsible for changes in radionuclide ratios and to learn a great deal about in-cloud residence time of aerosols, and the efficiency of in-cloud and below-cloud scavenging of aerosol particles by precipitation.

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References and Notes

1. R. W Perkins, C. W. Thomas, M. W. Hill, J. M. Nielsen, *Nature* **205**, 790 (1965).
2. N. Bhandari, S. G. Bhat, D P. Kharkar, S. Krishna Swamy, D. Lal, A. S. Tamhane, *Tellus* **18**, 504 (1966).
3. R W. Perkins, *Nucl. Instr. Methods* **33**, 71 (1965).
4. N. A. Wogman, D. E. Robertson, R. W. Perkins, *ibid.* **50**, 1 (1967).
5. D. Lal and B. Peters, in *Progress in Elementary Particle and Cosmic Ray Physics,* vol. 6 [Interscience (Wiley), New York, 1962].
6. R. W. Perkins and J. M. Nielsen, *Health Phys.* **11**, 1297 (1965); L. Husain and P. K. Kuroda, *Science* **154**, 1180 (1966).
7. N. A. Wogman, J. A. Young, C. W. Thomas, work in progress.
8. N. Bhandari and Rama, *J. Geochem. Res.* **68**, 3823 (1963).
9. Based on work performed under AEC contract AT(45-1)-1830.
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Urban Haze: The Extent of Automotive Contribution

Abstract. *Observation of the correlation between nitrogen oxides and the extinction coefficient of atmospheric air suggests that the automobile exhaust aerosol (nonphotochemical) may be important to visibility in cities.*

It is frequently difficult to ascribe in a logical fashion the chemical composition of urban air to specific emissions. Besides the difficult-to-describe mesoscale meteorological mixing process, the heterogeneity of sources and pollutants and a sometimes nearly random pattern of human activities pose serious difficulties for the scientist. Our purpose is to describe one case in which some simplification seems justified: the case of automobile-related urban haze.

With an instrument described (*1*, *2*), the extinction coefficient (due to scatter) of a sample flow of atmospheric air was monitored continuously for about 9 months (*3*). Because the scattering coefficient is determined on a sample of a few liters, the resultant data are appropriate for studies of correlation of aerosol and gas pollutants, where the gas (such as SO_2 or NO_x) is measured in the same sample of air. These correlations are particularly pertinent since the light-scattering coefficient can be used to infer the mass of particulates per volume of air ($\mu g/m^3$) (*2*). Although the correlation coefficient of SO_2 with the scattering coefficient (and hence with particulate mass) was only 0.27 for about 3 months (between September and December 1966) of hourly averages, a higher and perhaps significant correlation of NO_x (0.53) resulted from a similar number of hourly averages during the same period. Sulfur dioxide was measured with a Scientific Industries conductimetric instrument; NO_x, with Saltzman reagent in a Beckman Acralyzer. Air was sampled 13 m above a little-used street, and tests ascertained that local traffic was unimportant to this study (*4*).

This relation between NO_x and scattering coefficient is also suggested by similar time dependencies of the average of hourly values for each, especially on weekdays (Fig. 1). A wind-rose pattern of scattering coefficient (Fig. 2a), corresponding closely to the asymmetric shape of Seattle, suggests a uniform production of particulate matter rather than by a few point sources. The NO_x wind-rose pattern (Fig. 2b) has some similar features: a concentric pattern, with high values toward the northwest and low values to the southwest, corresponding to the shortest trajectory over populated areas for clean maritime air masses. Meteorological data were obtained from Sand Point Naval Air Base, Seattle, which is about 5 km northeast of the sampling site. Once again, study of systematic influences of this distance found them unimportant to the results of this report (*4*).

Although not conclusive, our data suggest a source of part of the urban haze in some cities: the automobile. Although no estimates were made of sources of NO_x other than traffic, Fig. 1 and previous work (*5*) indicate that such were probably unimportant. The data in Fig. 1 resemble results obtained in California towns (*5*) in which automobiles clearly dominate the diur-