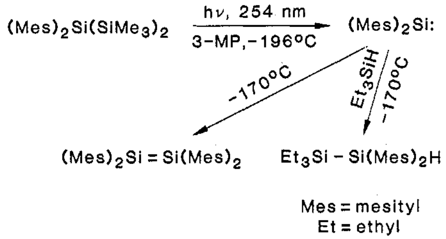
results were obtained when the photolysis was carried out in hexane or 3-methylpentane (3-MP) at −100°C (photochemical conversion about 80 percent). Under these conditions, the yield of tetramesityldisilene based on the amount of starting material photolyzed is ~ 95 percent. The product was purified by recrystallization from hexane. The physical and spectroscopic properties of tetramesityldisilene support the assigned structure (*7*).

Tetramesityldisilene is stable at room temperature in the absence of air, and in solution in hydrocarbons it is unchanged by brief heating to 160°C. The reactions of tetramesityldisilene are analogous to those of olefins in that this compound undergoes addition reactions across the double bond. For instance, it reacts rapidly with HCl to give the monochlorodisilane and with $O_2$ to yield 1,1,2,2-tetramesityl-1,2-disila-3,4-dioxetane. Ethanol adds slowly to the double bond to yield the ethoxydisilane (Fig. 1) (*8*).

The ultraviolet-visible absorption and fluorescence spectra of tetramesityldisilene are shown in Fig. 2. The strong absorption band at a wavelength (λ) of 420 nm, which we assign to the first $\pi \rightarrow \pi^*$ transition, is responsible for the yellow color of the compound. The large Stokes shift between the maxima of absorption and fluorescence (4000 $cm^{-1}$) indicates that the optical electron contributes significantly to Si=Si bonding, but the transition energy is much less than that found for analogous olefins; these results suggest that the Si=Si π bond is distinctly weaker than the C=C π bond.

The probable route of formation of tetramesityldisilene is by dimerization of the divalent silicon intermediate, dimesitylsilylene. Photolysis of the starting material in 3-MP at −196°C produces the blue silylene, isolated in the hydrocarbon matrix. The silylene may be trapped with a suitable reagent, for example, triethylsilane. If no trapping agent is present, dimerization to tetramesityldisilene takes place as the matrix is melted.



We have isolated a number of silylenes in 3-MP or argon matrices, including dimethyl- (*9*), diethyl-, and phenylmethylsilylenes. When the matrix is slowly and carefully warmed, all of these species undergo transformation into yellow intermediates with $\lambda_{max}$ of 345, 345, and 420 nm, respectively. These also disappear with the formation of colorless polymeric products when the matrix is finally melted. We believe that the yellow intermediates are also disilenes and that in solution in the absence of trapping agents dimerization of silylenes to disilenes is general (*10*). Further polymerization takes place when the Si=Si bond is not protected by sterically bulky groups such as mesityl.

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## Airborne Lead and Other Elements Derived from Local Fires in the Himalayas

Abstract. *The combustion of wood and yak dung for heating and cooking in a populated Nepal Himalayan valley contributes significantly to the ambient airborne concentrations of lead, copper, aluminum, magnesium, and elemental and organic carbon. A comparison of the concentrations of these elements in fresh snow with corresponding values in air suggests that the pollution aerosol is confined to the valley, with pristine air aloft.*

Evidence of global transport of Pb and other elements in recent years has raised concerns about possible widespread human exposure to toxic species. Defining the natural concentrations is particularly important. Although typical concentrations of Pb in the blood of modern Americans are in the range of 15 to 25 μg per deciliter of blood, it has been estimated that concentrations were as low as 0.2 μg/dl before use of the element had become widespread (*1*). Studies of human tissue as a more accurate indicator of long-term exposure than blood have also shown present-day elevations in Pb concentrations (*2*). It is thus possible that current American Pb body burdens often regarded as "normal" may actually be much greater than preindustrial concentrations and could be causing deleterious health effects (*3*).

The Pb concentrations in the bodies of people living in industrialized settings are probably linked to high overall concentrations in air, dust, water, and food. For example, typical airborne Pb concentrations in the United States are 30 to 450 ng/$m^3$ for rural areas and 500 to 2000 ng/$m^3$ for urban areas (*4*). Concentrations in the range from 0.05 to 0.2 ng/$m^3$ have been measured in the polar regions (*5, 6*), whereas preindustrial concentrations are thought to have been as low as 0.01 ng/$m^3$ (*3*). Our understanding of the relationships between environmental concentrations and exposure to Pb and other elements is far from complete, partly because of a lack of data on sources, transport pathways, and sinks, particularly in nonindustrialized areas.

The purpose of our study was to investigate sources of airborne Pb, Cu, Al,

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Table 1. Air and snow data in the vicinity of Kumjung, Nepal. The outdoor airborne concentrations represent the average of three sequential measurements, with standard deviations shown in parentheses; STP, standard temperature and pressure. Each indoor concentration represents a single filter measurement; the standard deviations here are based on analytical and blank uncertainties. Each of the concentrations for fresh snow and old snow is based on the average of two 1000-g samples.

| Element | Outdoor airborne concentration ($ng/m^3$ STP) | Indoor airborne concentration ($ng/m^3$.STP) | | Concentration in fresh snow (ng/g) | Concentration in old snow (ng/g) | EF, outdoor air | EF, fresh snow | Dry deposition velocity (cm/sec) |
|---|---|---|---|---|---|---|---|---|
| | | Measurement 1 (undried wood and pine needles) | Measurement 2 (dry wood and yak dung) | | | | | |
| Pb | 0.86 (0.17) | 160 (16) | 110 (8) | 0.16 (0.01) | 0.18 (0.06) | 60 | 8.6 | * |
| Cu | 2.7 (0.64) | 850 (150) | 1,200 (97) | 0.19 (0.02) | 0.43 (0.14) | 43 | 2.3 | 0.12 |
| Al | 94 (80) | 40,000 (2,100) | 6,800 (960) | 120 (5) | 200 (7) | 1 | 1 | 3.4 |
| Mg | 15 (9.1) | 15,000 (200) | 2,600 (87) | 74 (1.1) | 110 (5) | 0.6 | 2.1 | 6.1 |

*The difference in the Pb concentration in fresh and old snow is smaller than the experimental error. Based on uncertainties in the data. the dry deposition velocity for Pb must be less than 0.16 cm/sec.

Mg, and C in a populated region distant from industrial emissions such as those associated with fossil-fuel combustion. The atmospheric transport of these elements was also examined. We chose the Dudh Kosi River valley in the Khumbu district of Nepal for study, because it is more than 75 km from the nearest road or industry. A lack of industrialization also characterizes the Manang district of Nepal; Piomelli *et al.* (*7*) reported an average blood Pb concentration for the local population of 3.4 μg/dl.

Our experiments were conducted during December 1979 in and near the village of Kumjung (population 1400) at an elevation of 3900 m, surrounded by peaks more than 6000 m high. The location is 26 km southwest of Mount Everest and about 130 km east of Katmandu (population 150,000). There are no other cities of appreciable size in this part of the country. The 50,000 inhabitants of this region (Sherpas), spread out in numerous small villages, represent a possible target population for future detailed work on exposure and environmental characterization.

Sampling consisted of outdoor and indoor aerosol measurements and collection of fresh and older surface snow. We collected the snow to obtain estimates of dry deposition so as to acquire information on the relative particle sizes and corresponding atmospheric transport for each element.

The outdoor air sampling was conducted at Hotel Everest View, 1 km east of Kumjung, and included three sequential trace element measurements with cellulose filters (Millipore HAWP-047); each sampling period was approximately 60 hours, and the flow rates averaged 3 liter/min. Limited size-distribution data were provided by a single measurement with a cascade impactor (Andersen 20-800) for 52 hours at a flow rate of 7 liter/min. Millipore filters and FEP Teflon impactor substrates had been acid-washed prior to sampling (*8*). For the C measurements, we used two quartz filters for an average of 25 hours each at a flow rate of 4 liter/min (*9*). A 3-kW generator using kerosene (< 0.01 part per million Pb), positioned 100 m northwest of the samplers in a small shed, provided power for the vacuum pumps. Experiments were conducted only during the predominant southeasterly winds.

Indoor sampling included measurements made with two Millipore filters at a typical Sherpa residence in Kumjung. A single room (5 by 7 by 2.5 m) represented the family living quarters, with an open fire toward one side kept burning constantly for warmth. The smoke was poorly ventilated through a hole in the roof; much of the smoke drifted out into the room. For each measurement, the filter was placed on a bench near the fire at breathing level and operated for 30 minutes at 1.6 liter/min. Pine wood, including undried twigs and needles, was used on the first day. Yak dung and dry wood were used on the second day. Both filters were discolored yellow-brown in spite of the small air volumes sampled.

We collected snow samples several hundred meters southeast of the hotel during a snowstorm and 3 days after the end of the storm. Acid-washed conventional polyethylene bottles were used to scoop the snow to a depth of 1 cm, each sample corresponding to approximately 3000 $cm^2$ of surface area per liter of meltwater. Light southeasterly winds and below-freezing temperatures characterized the 3-day interval.

Millipore filters, impactor substrates, and snow samples were brought back to the laboratory and digested in vessels of quartz or Teflon. Analyses were conducted by flameless atomic absorption spectrophotometry with background correction; standard additions and multiple wavelength testing were used to check for interference (*10*). A minimum of three replicate analyses for each sample and for each element yielded standard deviations of less than ± 20 percent.

Four filter blanks handled in the field in the same manner as the samples gave averages and standard deviations (in nanograms) as follows: Pb, 2.0 ± 0.6; Cu, 31 ± 5.3; Al, 120 ± 75; and Mg, 14 ± 3.7. Average values for three snow blanks (1 liter of laboratory distilled water) were as follows: Pb, 3.0 ± 2.6; Cu, 56 ± 74; Al, 230 ± 160; and Mg, 110 ± 15. The average sample/blank ratios were greater than 5/1 for the air and snow analyses, except for airborne Cu which had an average ratio of 2.5/1. The small uncertainty associated with the Cu filter blanks (17 percent) suggests that the airborne data for Cu are reliable.

Results of the analyses are shown in Table 1. The small outdoor and large indoor airborne concentrations suggest the importance of local fires in affecting air quality in the region. A significant mass of combustion-generated particles is continuously ventilated from numerous houses into a pristine environment. High ambient C concentrations averaging 10 $\mu g/m^3$ at standard temperature and pressure (8.7 $\mu g/m^3$ organic, 1.5 $\mu g/m^3$ inorganic) also suggest the importance of the fires (*11*). The large organic fraction probably arises from the condensation of volatiles emitted from the combustion of the wood and dung. Excessive Al and Mg concentrations were observed when undried vegetation was burned.

The airborne and snow concentrations can be used to determine crustal enrichment factors ($EF_{air}$ and $EF_{snow}$) based on Al (*12*). Values close to unity imply the earth's crust as a source of that particular element, whereas large values suggest that the element is associated with other sources such as anthropogenic activities, volcanism, or emissions from vegetation.

Enrichments for Mg are near unity for both air and snow, with greater values for Pb and Cu. However, the $EF_{air}$ for Pb and Cu are not as large as the values observed in more industrialized areas. For example, Rahn (13) reported mean values for $EF_{air}$ of 3800 for Pb and 149 for Cu for 29 urban areas throughout the world. The unusually small aerosol enrichments for these two elements in our measurements reflect the nature of aerosols generated by combustion of wood and dung, with some influence of soil dust (14).

The very small enrichments for fresh snow at Kumjung imply a more crustal character for snow than for air. This is possibly due to a gradient in trace element concentrations in the valley: snow formed aloft would be more influenced by natural soil dust from the 6000-m peaks surrounding Kumjung, whereas air near the ground should be more influenced by the fires. Aerosol measurements in other parts of Nepal have shown evidence of combustion-generated material at ground level, with sulfates and soil dust found at higher elevations (15). The high atmospheric turbidity occasionally observed near the ground during these experiments also suggests the existence of a concentration gradient. Another possible explanation for the difference in enrichments is that crustal material, found in larger particle sizes than enriched aerosol, may be more efficiently scavenged as condensation nuclei during snowflake formation (16).

Dry deposition velocities were calculated as the ratio of the flux (in nanograms per square centimeter per second) to the airborne concentration (in nanograms per cubic centimeter), with the fluxes determined by taking the difference between old and fresh snow concentrations. Earlier work has shown the utility of this method, provided that sublimation is minimal and below-freezing temperatures are maintained (6, 17). Such conditions prevailed during this study.

The greater values of deposition velocity for Al and Mg reflect larger particle sizes. This conclusion is supported by the impactor data, which indicate a mass mean aerodynamic diameter of 9 μm for Mg and 0.9 μm for Pb (18). Smaller deposition velocities and particle sizes for enriched relative to crustal elements have been reported for other remote and populated areas (19).

Overall, these data for Pb, Cu, Al, Mg, and C suggest that local fires fueled with wood and dung significantly influence air quality in a populated Himalayan valley. Differences in the chemical composition of freshly fallen snow as compared with that of air in the valley indicate the pristine nature of air aloft.

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## Gonadotropin-Releasing Hormone: Regulation of Adenosine 3′,5′-Monophosphate in Ovarian Granulosa Cells

Abstract. *The antigonadal effects of gonadotropin-releasing hormone in ovarian granulosa cells are due to attenuation of the adenosine 3′,5′-monophosphate (cyclic AMP) response to follicle-stimulating hormone. Agonists of gonadotropin-releasing hormone progressively inhibit adenylate cyclase and stimulate phosphodiesterase activities in cultured granulosa cells, indicating that blockade of gonadotropin action is attributable to the combined effects of decreased production and increased degradation of cyclic AMP.*

The induction of ovarian follicular differentiation by follicle-stimulating hormone (FSH) is mediated by adenosine 3′,5′-monphosphate (cyclic AMP), which elicits the expression of peptide hormone receptors, steroidogenic enzymes, and morphological maturation of granulosa cells (1). These responses are prevented by gonadotropin-releasing hormone (GnRH) and its potent agonist analogs, which inhibit developmental processes in the rat ovary by a direct action on granulosa cells in intact animals and in vitro (1, 2). The detection of specific binding sites for GnRH in ovarian tissue indicates that this peptide expresses its inhibitory actions by way of receptor-dependent mechanisms (3). We recently demonstrated that GnRH suppresses FSH-induced accumulation of both intracellular and extracellular cyclic AMP and guanosine 3′,5′-monophosphate (cyclic GMP) in granulosa cells isolated from hypophysectomized rats

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