are linear below 943 and 990 m, respectively, indicating an unstratified water mass (*12*). Corresponding plots of Al versus salinity (Figs. 4 and 5) display curvature, an indication that scavenging of Al from solution (*13*) dominates any solution of Al from aluminosilicate particles that is taking place. I suggest that, when the organic coatings of diatoms and radiolaria are degraded after the death of the organisms, the silica shells become the most likely active site for Al scavenging. Lewin (*14*) found that leached diatom shells adsorb Al (up to 1.9 percent as Al_2O_3), and Hurd (*15*) observed mineral overgrowths on siliceous shells containing 0.8 percent Al_2O_3. In addition, Al concentrations up to 1.8 percent Al_2O_3 in diatoms have been reported; however, the origin of this Al is uncertain, and much of it may be due to contamination of samples caused by clay minerals (*16*).

Mackenzie *et al.* (*3*) observed in a partial profile from the Mediterranean that the Al and Si concentrations covaried. They proposed that Al is removed from seawater during the growth of siliceous microorganisms and is regenerated below the productive zone. In comparison, the distributions of Al and Si in Fig. 6 show none of these correspondences. Similarly, if the distributions of Al and Si covary in the Pacific as claimed for the Mediterranean by Mackenzie *et al.*, then at station 219 the concentration of Al should increase sixfold in parallel to the Si increase from 32.2 μm of Si per kilogram of water to 190.1 μm at a depth of 1676 m (*3, 4*). The data in Fig. 1 show no indication of such a change.

The above evidence suggests that the situation observed by Mackenzie *et al.* in the Mediterranean is anomalous. Certainly, the Al concentration they report is five times higher than those reported here and in earlier studies (*7, 17*). Further, in spite of contamination, the mean Al concentration measured at both Pacific GEOSECS stations is 0.6 μg/liter, which is significantly below the mean of 0.85 μg/liter for the unacidified samples at station K69/10. The mean Al concentration at GEOSECS station 37 is 1.61 μg/liter. Atlantic stations show higher Al concentrations than Pacific ones whereas the reverse is true for Si, and so an inverse rather than a direct relation may apply to Al and Si concentrations on an oceanic scale. This inverse relationship between Al and Si may reflect the greater flux of Si through Pacific water, producing greater scavenging and probably a lower input of Al.

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References and Notes

1. E. A. Boyle, F. Sclater, J. M. Edmond, *Nature (London)* **263**, 42 (1976); F. Sclater, E. A. Boyle, J. M. Edmond, *Earth Planet. Sci. Lett.* **31**, 119 (1976); K. W. Bruland, G. A. Knauer, J. H. Martin, *Nature (London)* **271**, 741 (1978).
2. E. A. Boyle, F. Sclater, J. M. Edmond, *Earth Planet. Sci. Lett.* **37**, 38 (1977).
3. F. T. Mackenzie, M. Stoffyn, R. Wollast, *Science* **199**, 680 (1978).
4. S. Caschetto and R. Wollast, *Mar. Chem.* **7**, 141 (1979).
5. D. W. Spencer made the GEOSECS samples available and S. Kadar, C. L. Smith, and D. W. Spencer provided the Si analyses for station K69/10.
6. D. J. Hydes and P. S. Liss, *Analyst (London)* **101**, 922 (1976). This is the same method as that used by Mackenzie *et al.* (*3*).
7. ——, *Estuarine Coastal Mar. Sci.* **5**, 755 (1977).
8. Woods Hole *Knorr* cruise 69, station K69/10, September 1977; position, 40°51'N, 64°10'W; water depth, 4195 m.
9. J. B. Moody and R. M. Lindstrom, *Anal. Chem.* **49**, 2264 (1977).
10. V. Hodge, S. R. Johnson, E. D. Goldberg, *Geochem. J.* **12**, 7 (1978).
11. D. J. Hydes, *Nature (London)* **268**, 136 (1977).
12. North Atlantic deep water is a complex mixture of five different water masses. [L. V. Worthington and W. R. Wright, *North Atlantic Ocean Atlas* (Woods Hole Oceanographic Institution Atlas Series, Woods Hole, Mass., 1970), vol. 2]. It is possible that this apparent linearity is the fortuitous result of insufficient hydrographic data.
13. H. Craig, *Earth Planet. Sci. Lett.* **23**, 149 (1973).
14. J. C. Lewin, *Geochim. Cosmochim. Acta* **21**, 182 (1961).
15. D. C. Hurd, *ibid.* **37**, 2257 (1973).
16. A. J. van Bennekom and S. J. van der Gaast, *ibid.* **40**, 1149 (1976).
17. J. J. Alberts, D. F. Leyden, T. A. Paterson, *Mar. Chem.* **4**, 51 (1976); W. M. Sackett and G. O. S. Arrhenius, *Geochim. Cosmochim. Acta* **26**, 955 (1962).
18. I thank D. W. Spencer for providing GEOSECS samples. I am grateful to S. Kadar, C. L. Smith, and D. W. Spencer for supplying the Si analyses. This work was supported by National Science Foundation grant OCE 76-10277 and the Woods Hole Oceanographic Institution. Woods Hole Oceanographic Institution Contribution 4289.

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N-Nitrosamines in the Rubber and Tire Industry

Abstract. *Airborne* N-*nitrosomorpholine (0 to 27 micrograms per cubic meter) was found in two of four rubber industry factories.* N-*Nitrosodimethylamine was also found in two factories, but at lower levels. These findings may be relevant to the reported increased risk of certain types of cancer in rubber workers in some of the same areas where the* N-*nitrosomorpholine levels were highest.*

A number of studies have shown that workers in the American rubber industry have a significantly increased incidence of several types of cancer (*1*). It has been suggested that various chemicals used in the rubber industry are associated with this excess cancer risk. We now report the presence of an additional agent, *N*-nitrosomorpholine (NMOR), a well-known animal carcinogen (*2*), in rubber factory air and in bulk samples. Smaller amounts of a related carcinogen, *N*-nitrosodimethylamine (NDMA), were also found in two of the four factories sampled.

The laboratory apparatus, including gas and high-pressure liquid chromatographs, fume hood, and detectors, was located inside a fully equipped mobile laboratory, which was parked near each site (*3*). A TEA analyzer (Thermo Electron model 502LC) was used as a nitrosyl-specific detector for an isothermal gas chromatograph (GC) (*4*). The high-pressure liquid chromatograph (HPLC) was constructed (*5*) by combining a high-pressure pump (Altex model 110) with an injector (Rheodyne model 7120), a stainless steel column (4 by 39 mm) packed with 10-μm Lichrosorb Si60 (Merck), and a second TEA detector. Authentic samples of NMOR, NDMA, *N*-nitrosodipropylamine (NDPA), and *N*-nitrosodiphenylamine (NDPhA) were obtained from Thermo Electron. Solvents (distilled-in-glass grade) were supplied by Burdick & Jackson Laboratories.

Table 1 summarizes the findings at four rubber industry factories in Ohio visited in the spring of 1978. *N*-Nitrosodiphenylamine, which is used as a vulcanization retarder, was found at a tire chemical factory where it was being produced. Thus it was not unexpected to find it there in the air, in wastewater from the NDPhA reaction (730 μg/g), or in scrapings from the floor (up to 15,000 μg/g) (*6*). It was even found in the soil outside the building (47 μg/g). It was not found at the other three factories, although it is sometimes used in the manufacture of tires. *N*-Nitrosodiphenylamine is not generally considered to be carcinogenic (*7*), although a recent report casts some doubt on this conclusion (*8*).

N-Nitrosodimethylamine was found as an air pollutant at both the chemical factory and the industrial rubber products factory. In the chemical factory, the concentration ranged from 0.05 to 0.5 $\mu g/m^3$ close to a tank where dimethylamine (DMA) was being stored (Table 1). The DMA was found to be contaminated with NDMA (1.3 μg/g), and this may have contributed to the airborne NDMA. In the industrial rubber products factory, all four samples contained NDMA at levels between 0.07 and 0.14 $\mu g/m^3$. The source of the NDMA at this factory was not determined.

N-Nitrosomorpholine was found as an air pollutant inside both the chemical factory and the aircraft tire factory. In the chemical factory, it was found as an

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impurity in morpholine (MOR) (0.8 μg/g) and in the rubber cross-linking accelerator bismorpholinecarbamylsulfenamide (BMCS) (0.4 to 0.7 μg/g). A wastewater sample from this factory contained NMOR at 0.003 μg/g. Utility steam condensate contained 0.002 μg/g, possibly due to the use of MOR as a corrosion inhibitor in the steam process equipment. Surprisingly, an NMOR level of 730 μg/g was found in a dirt scraping from a staircase in this factory; this extraordinarily high value was confirmed by mass spectrometry. A soil sample taken outside the chemical plant contained NMOR at 4.4 μg/g. In the air at the chemical factory, NMOR was found in the lunchroom (0.07 $\mu g/m^3$) and at levels that varied from 0.7 $\mu g/m^3$ near the BMCS drier to 5.1 $\mu g/m^3$ near the NDPhA reactor (Table 1). In the tire factory, NMOR was found at every site sampled. The lowest level was 0.6 $\mu g/m^3$ in the finishing and inspection area; the highest level, 27 $\mu g/m^3$, was found immediately adjacent to an extruder for tire treads.

As with other *N*-nitroso compounds, the possibility of artifactual formation of NMOR during the collection and analytic procedures had to be considered. Nitrogen oxides are known to nitrosate amines under a variety of conditions (*9*). In addition, NDPhA has been shown to readily transfer its nitrosyl moiety to secondary amines (*10*). For these reasons, the following series of experiments were carried out to establish that NMOR was not formed during the collection or analysis steps.

1) The MOR levels at the tire factory and tire chemical factory were 230 ± 110 and 42 ± 5 $\mu g/m^3$, respectively (*11*). *N*-Nitrosodiphenylamine was not found in the air of the tire factory at the time the samples were collected. Thus the NMOR found at this site could not have been formed by transnitrosation during analysis because the MOR level was too low (*12*) and NDPhA was absent. In the chemical factory, similar levels of NMOR were observed regardless of whether NDPhA was present.

2) The possibility that oxides of nitrogen had converted trapped MOR to NMOR in the impinger was excluded by the following experiments. Morpholine and four other secondary amines (50 μg each) were added to the traps. After bubbling 100 liters of air containing nitrogen oxides (2 parts per million; equal parts of NO and NO_2) through the traps, there was still no detectable formation of any nitrosamine (detection limit, 0.01 μg per trap). In addition, 2000 μg of dipropylamine (DPA) was added to one set of traps at each factory and, after sample collection, the traps were analyzed for NDPA. At the tire factory, NDPA was not found in the trap. At the chemical factory, the air already contained NDPA at approximately 0.1 $\mu g/m^3$ in addition to the *N*-nitrosamines shown in Table 1. At both sites an additional 2000 μg of DPA was added to one set of traps after the sample had been collected. No enhancement of the NDPA level was found in any trap to which DPA had been added.

3) At the tire plant, 10 μl of the 1*N* KOH trapping solution was injected directly into the GC-TEA, without any sample cleanup, extraction, or concentration. Not only was NMOR shown to be present, but the amount measured (2.5 $\mu g/m^3$) agreed within experimental error with the amount determined by extraction and concentration (2.3 $\mu g/m^3$). At the chemical site, a 1*N* KOH trapping solution was extracted with four volumes of dichloromethane (DCM). The amount of NMOR was the same both before and after a 90-fold concentration of this extract.

We believe that this is the first report of the measurement of airborne NMOR in the environment. Although the effects of inhaled NMOR have not been tested (*13*) and its effects in humans are uncertain, it has been shown to be carcinogenic in a variety of animal species after both oral and parenteral administration (*2*). A human doing moderately heavy work near the DMA tank in the tire chemical plant (Table 1) would be exposed to NMOR at approximately 44 μg/day (*14*) and to NDMA at 4.8 μg/day. In the most highly contaminated areas of the tire factory, a similar worker would breathe approximately 260 μg of NMOR a day. An average worker is probably ex-

Table 1. Nitrosamines in air samples collected at four rubber industry plants. Samples were collected by passing air at a flow rate of 1 to 2 liter/min for approximately 3 hours through a glass impinger containing 45 ml of 1*N* KOH. Sampling pumps were battery-operated (Bendix model C115) and were calibrated with a mass flowmeter (Hastings model ALL10K). The KOH solution was extracted with DCM, and the DCM was concentrated in a Kuderna-Danish evaporator at 52°C to less than 1.0 ml, using 0.5 ml of isooctane as a keeper. All concentrates were analyzed by both GC-TEA and HPLC-TEA (*4*, *5*). Representative samples were also analyzed by GC with a flame ionization detector and by HPLC plus ultraviolet absorbance.

Location	NMOR ($\mu g/m^3$)	NDMA ($\mu g/m^3$)	NDPhA ($\mu g/m^3$)
Tire chemical factory			
DMA tank	0.9, 4.6*	0.2, 0.5	0.8, 0.6
Chemical storage	1.5	0.08	17
BMCS centrifuge	3.4	0.3	0.2
BMCS reactor	3.0	0.3	0.9
BMCS drier	0.7	0	0.3
BMCS discharge	1.6	0.1	0
NDPhA reactor	4.1, 5.1†	0.2, 0.1	47, 0
NDPhA decanter	4.6, 3.9	0.05, 0.07	12, 25
Lunchroom	0.07	0	0.7
Outdoors	0	0	0
Industrial rubber products factory			
Solution area	0	0.14	0
Banbury machining	0	0.14	0
Batch off mill area	0	0.09	0
Office	0	0.07	0
Aircraft tire factory			
Curing press	2.2, 4.9	0	0
Extruder	1.7, 2.4	0	0
Extruder	27, 12	0	0
Warm-up and mixing	2.2, 1.3	0	0
Cooling pool	3.3	0	0
Cutting area	2.2	0	0
Large tire curing	7.1, 2.6†	0	0
Small tire curing	4.6	0	0
Batch stock storage	2.5	0	0
Finishing and inspection	0.6	0	0
Office	1.0	0	0
Outdoors	0	0	0
Synthetic rubber and latex factory			
Four areas	0	0	0

*Both results are shown for repeat samples obtained at the same site on a second visit; the detection limit is 0.05 $\mu g/m^3$. †Confirmed by GC-mass spectrometry (GC-MS). The contents of several traps at the same location and time were combined and concentrated to 0.1 ml under a gentle stream of nitrogen; 15 μl at a time was injected onto a μBondapak NH_2 column (Waters) and eluted with 50:50 pentane and dichloromethane (2.0 ml/min). An ultraviolet detector (Spectraphysics model 230) was used to observe the NMOR response at 256 nm. Fractions containing NMOR were combined and carefully blown down with nitrogen to a final volume of less than 0.05 ml. Structural confirmation of the NMOR was obtained by GC-MS under the chromatographic conditions already described (*4*), using a modified mass spectrometer (Hitachi RMU-6L) and computer (IBM-1800) (*17*); this was also done with combined samples collected at several other sites in the chemical and tire factories.

posed to one-half to one-fifth of these levels (*15*).

Our very limited survey has shown that NMOR (and in some cases NDMA) was present in the highest amounts at the chemical plant in the compounding and mixing areas and at the tire factory in the curing, extrusion, mixing, and cooling areas. A much more comprehensive survey is needed to firmly establish that these are indeed the most contaminated areas (*16*). However, several recent studies show increased rates of lung and gastrointestinal (including colorectal) cancers among workers in several of these areas (*1*). In addition, an increased risk of several other types of cancer has been reported for rubber workers (*1*). However, it would be premature to speculate further on the possible involvement of *N*-nitroso compounds in the etiology of the cancer of rubber workers until more extensive workplace monitoring has been carried out.

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References and Notes

1. R. R. Monson and K. K. Nakano, *Am. J. Epidemiol.* **103**, 284 (1976); J. M. Peters, R. R. Monson, W. A. Burgess, L. J. Fine, *Environ. Health Perspect.* **17**, 31 (1976); T. F. Mancuso, *ibid.*, p. 21; A. M. McMichael, R. Spirtas, J. F. Gamble, P. M. Tousey, *J. Occup. Health* **18**, 178 (1976); R. R. Monson and L. J. Fine, *J. Natl. Cancer Inst.* **61**, 1047 (1978).
2. *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Some* N-*Nitroso Compounds* (International Agency for Research on Cancer, Lyon, 1978), No. 17, p. 263.
3. I. S. Krull, T. Y. Fan, D. H. Fine, R. Young, E. Egan, *Ind. Res. Dev.* (May 1978), p. 119.
4. D. H. Fine and D. P. Rounbehler, *J. Chromatogr.* **109**, 271 (1975). The GC column was a stainless steel column (14 feet by 1/8 inch) packed with 10 percent Carbowax 20*M* plus 0.5 percent KOH on Chromosorb W HP (80 to 100 mesh), operated isothermally at 160°C for NDMA and 210°C for NMOR with argon gas (15 ml/min) as the carrier. The TEA cold trap temperature was −78°C.
5. D. H. Fine, D. P. Rounbehler, A. P. Silvergleid, in *Proceedings of the 2nd Symposium on Nitrite in Meat Products*, B. J. Tinbergen, and B. Krol, Eds. (Pudoc, Wageningen, Netherlands, 1977), p. 191. The HPLC-TEA was operated isocratically with the following solvent mixtures (2 ml/min); acetone and hexane (15:85) for NDMA and NMOR, and acetone and hexane (5:95) for NDPhA. Exhaustive HPLC-TEA screening for *N*-nitroso compounds was also carried out with acetone (2 ml/min) as the elution solvent. An acetone-isooctane solvent system was also used in the screen in the following proportions: 50:50, 25:75, and 5:95. The detection limit for both GC-TEA and HPLC-TEA was 0.05 μg/m^3.
6. Bulk aqueous samples were prepared for analysis by exhaustively extracting with DCM and then concentrating the DCM in a Kuderna-Danish evaporator, using 0.1 ml of isooctane as a "keeper." Solids, chemicals, and soil samples were extracted with DCM in the presence of excess sulfamic acid, dried over sodium sulfate, and then concentrated. Samples were analyzed by both GC-TEA and HPLC-TEA.
7. H. Druckrey, R. Preussmann, S. Ivankovic, D. Schmahl, *Z. Krebsforsch.* **69**, 103 (1967).
8. R. H. Cardy, W. Lijinsky, P. K. Hildebrandt, *Ecotoxins Environ. Saf.*, in press.
9. B. C. Challis, A. Edwards, R. R. Hunma, S. A. Kyrtopoulos, J. R. Outram, in *Environmental Aspects of* N-*Nitroso Compounds*, E. A. Walker, M. Castegnaro, L. Griciute, R. E. Lyle, W. Davis, Eds. (International Agency for Research on Cancer, Lyon, 1978), p. 127.
10. P. Welzel, *Chem. Ber.* **104**, 808 (1971); A. J. Buglass, B. C. Challis, M. R. Osborne, in N-*Nitroso Compounds in the Environment*, P. Bogovski and E. Walker, Eds. (International Agency for Research on Cancer, Lyon, 1974), p. 94; S. S. Singer, W. Lijinksy, G. M. Singer, in *Environmental Aspects of* N-*Nitroso Compounds*, E. A. Walker, M. Castegnaro, L. Griciute, R. E. Lyle, W. Davis, Eds. (International Agency for Research on Cancer, Lyon, 1978), p. 175.
11. A 1-ml portion of the $1N$ KOH air-trapping solution was acidified to *p*H 3 with H_2SO_4 and then nitrosated at 53°C with sodium nitrite. The reaction mix was extracted with 6 ml of DCM and analyzed for NMOR by GC-TEA and HPLC-TEA. The increase in NMOR compared to that in an unnitrosated sample was assumed to be due to MOR (or a MOR-generating substance) in the trap. Calibration curves for standard MOR solutions were used for quantitation.
12. In separate experiments, not reported here, we demonstrated that airborne MOR and NDPhA levels had to be above 600 and 6000 μg/m^3, respectively, for detectable transnitrosation to occur.
13. Long-term inhalation of NDMA has been shown to cause liver and kidney tumors in rats [G. E. Moiseev and V. V. Benemansky, *Vopr. Onkol.* **21** (No. 6), 107 (1975)].
14. We assume a 70-kg man breathing 20 liter/min for 8 hours per day. Because NMOR is relatively nonvolatile (boiling point, 225°C) and soluble in both water and lipids, we assume most of it is removed from inspired air.
15. To put this in perspective, eating 100 g (approximately five strips) of cooked bacon containing nitrosamines at the U.S. Department of Agriculture limit of 10 parts per billion would mean exposure to 1.0 μg.
16. Since submitting this report, we visited six other tire factories. All had NMOR present in the factory air at similar levels.
17. J. E. Biller, thesis, Massachusetts Institute of Technology (1972). The computer-compiled total-ion plot indicated several peaks, the major one eluting with the same retention time as control samples and showing a fragmentation pattern identical to that of NMOR. The spectrum is characterized by three major ions, the M^+ as mass-to-charge ratio *m/e* 116, the M^+-NO at *m/e* 86, and an ion with about 40 percent of the intensity of the base ion at *m/e* 56. Samples of lower concentration could be detected with greater sensitivity by selected ion monitoring of one of these three ions at the time of elution of NMOR.
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Submarine Seep of Carbon Dioxide in Norton Sound, Alaska

Abstract. *Earlier workers have described a submarine gas seep in Norton Sound having an unusual mixture of petroleum-like, low-molecular-weight hydrocarbons. Actually, only about 0.04 percent of the seeping gas is hydrocarbons and 98 percent is carbon dioxide. The isotopic compositions of carbon dioxide ($\delta^{13}C_{PDB} = -2.7$ per mil) and methane ($\delta^{13}C_{PDB} = -36$ per mil, where PDB is the Peedee belemnite standard) indicate that geothermal processes are active here.*

During the summer of 1976 Cline and Holmes (*1*) discovered anomalous concentrations of hydrocarbon gases, particularly ethane (C_2), propane (C_3), *n*-butane (*n*-C_4), and isobutane (i-C_4), in the waters of Norton Sound, south of the Seward Peninsula of Alaska. The hydrocarbon plume appeared to be emanating from a point source on the sea floor south of Nome (Fig. 1) and moving to the north and northwest, following current movements in the sound. The relative molecular composition of these hydrocarbons indicated that they could have a deep-seated thermal origin and could possibly be related to a liquid petroleum deposit (*1, 2*). In the summer of 1977 a geochemical investigation of bottom sediment beneath the hydrocarbon-rich plume showed that near-surface sediment at a site approximately 50 km south of Nome and at a water depth of 19 m also contains unusually high concentrations of hydrocarbons heavier than methane (C_1), including gasoline-range (C_{5+}) hydrocarbons (*3, 4*). Although geophysical surveys over this area showed near-surface acoustic anomalies apparently caused by gas-saturated sediment, the measured concentrations of hydrocarbon gases in the sediment were unusually high but well below saturation (*4*). The contradiction between the geophysical and geochemical evidence led to a further investigation of the seep site during the summer of 1978 when we discovered that hydrocarbons are only a minor component of the seep gas and that, in fact, CO_2 is the principal gas bubbling from the sea floor. This report is the first to describe both the molecular and carbon isotopic composition of a submarine seep off the shore of Alaska.

Detailed geophysical, geological, and geochemical measurements made during 1978 clearly indicate the presence of an active gas seep (*5*). Acoustic anomalies from geophysical records at the seep site have characteristics similar to those observed elsewhere by Schubel (*6*), who attributed the anomalous acoustic responses to the presence of gas bubbles in the sediment. Further geophysical evidence for an active gas seep comes from high-resolution geophysical records that show trains of gas bubbles rising from

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