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NEW DIRECTIONS

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New Directions: An unusual odor phenomenon in an urban atmosphere ☆

The occurrence of a particularly strong and unusual odor has been reported in an Indian city with a population of more than 1.5 million. Over 200 complaints were lodged with the authorities while it persisted. The odor was unusual in that it did not resemble the normal odor experienced from typical sources that lead to "rotten egg" smells, LPG cylinder leaks, or refuse dumps. As the origin of the odorous problem was not clear, a scientific investigation was undertaken to assess the cause of the odor.

The smell was pungent and occurred particularly during the nighttime. Questions considered included whether the drifting odor occurred in combination with low temperatures, low clouds, or low wind levels. A surprising outcome was that it appears the odorous substance may actually have been produced by chemical reactions in the atmosphere and not as a direct emission from nearby industrial source (e.g. not as H_2S or methyl mercaptan).

The meteorological data recorded during the investigations indicated a low speed of 2–3 $m\,s^{-1}$ during the daytime, which reduced to less than 1 $m\,s^{-1}$ (calm conditions) during the nighttime. The prominent wind direction was from the SW–W–WNW sector. Several large industries were located 25–30 km west of the city (coastal belt) i.e. in the predominant upwind direction. During nighttime, the emissions were likely being contained close to ground by a nocturnal boundary layer (stable conditions), instead of being mixing, diluted, and dispersed. The odor appeared to have the distinctive smell of sulfur compounds, hence, sampling and analysis started with measurement of H_2S and mercaptans in the ambient air. In order to identify some other possible odor-causing organic chemicals in the air, samples were collected on absorbing media containing hexane, preserved at low temperature, and subsequently transported to the laboratory for analysis by gas chromatography–mass spectrometry (GC–MS).

The result of this ambient air monitoring of sulfur compounds for 24 h over a 15-day period, in locations reported to have experienced the odor problem, indicated the presence of H_2S with a maximum concentration of 18.5 $\mu g\,m^{-3}$ in urban areas, and up to 13.6 $\mu g\,m^{-3}$ in rural areas. These concentrations are far below the limit of 500 $\mu g\,m^{-3}$ set by the Gujarat Pollution Control Board (GPCB), and 150 $\mu g\,m^{-3}$ set by the World Health Organization (WHO: Urban Air Quality Management Strategy in Asia—Guide Book, The World Bank, Washington, DC, 1997, p. 37). The mercaptan concentrations were up to 8.5 $\mu g\,m^{-3}$ in the city and up to 5.7 $\mu g\,m^{-3}$ in the rural areas. These low concentrations indicate that the odor problem did not originate directly from emissions of these particular chemicals from nearby industries.

A literature search was carried out to find other odorous compounds that might have formed in the atmosphere. The use of various chemical processes in the nearby industries could also generate soluble organic molecules derived from atmospheric gas phase processing. Grosjean and Wright (1983, Atmospheric Environment 17, 2093–2096) and Facchini et al. (1992, Tellus 44B, 533–544) both reported that formic, acetic and other lightweight carboxylic acids, together with other gas phase carbonyls, contribute to the main mass of dissolved organic compounds. A speciation approach was

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thus adopted to find the likely organic chemicals involved in generating the obnoxious smell. A GC–MS technique was used to separate the mixture of compounds. Various organosulfur, organonitrogen, and organooxygen compounds were identified. The identification of mass peaks at $m/z = 47, 45, 92$ indicated the likely presence of mercaptoacetic acid, also known as thioglycolic acid. It still remained, however, to identify the likely source of precursors, and the reaction mechanism, that might have led to the presence of thioglycolic acid in the atmosphere. The potential health effects of thioglycolic acid include irritation to the nasal passages, mucous membranes, and upper respiratory tract. It is colorless with a very strong and unpleasant odor.

Consider the presence of carboxylic acids in the atmosphere, two molecules of which can eliminate a molecule of water to form anhydrides. These anhydrides are regarded as highly reactive compounds. When mixed with alcohols they give rise to esters. Similarly, if one considers mercaptans (R–SH) as sulfur analogs of alcohols (R–OH), then it is likely that compounds such as thioesters might be produced:

$$R'-SH + R-CO-O-CO-R \rightarrow R'-S-CO-R + R-COOH.$$

Upon hydrolysis, these thioesters would generate thioglycolic acid ($HSCH_2COOH$).

Another hypothesis for the formation of thioglycolic acid relates to the presence of hydrogen sulfide in the atmosphere. It is known that if H_2S is in the alkaline form of hydrogen sulfide, it will react with carboxylic acids emitted from various industrial sources, again to form thioglycolic acid.

We conclude that the most probable cause of the reported odor problem was due to formation of compounds of the type SCH_2COOH, arising from the presence of carboxylic acids generated from nearby industries. Such industries include those producing purified terephthalic acid (PTA) and industries using chloroacetic acid in the manufacture of polyvinyl chloride (PVC) resins. The odor was exacerbated during the nighttime due to the presence of moisture, which initiated the carboxylic acid reactions leading to formation of this, and other, noxious secondary organic pollutants.

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