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SHORT CONTRIBUTION

Atmospheric formic acid from formicine ants: a preliminary assessment

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ABSTRACT

Formic acid is a ubiquitous constituent of the atmospheric gas and of precipitation, but its sources and their fluxes are poorly understood. One source not previously examined, emissions from formicine ants, is assessed in this work, and it is shown that, except in urban areas and particularly in tropical areas, these ants may be a significant source of the formic acid found in some parts of the continental troposphere. This process could thus provide a new example of a potentially strong interaction linking the biosphere and the atmosphere.

Formic acid (HCOOH) has, within the past few years, been realized to be ubiquitous or nearly so in atmospheric gases, aerosols, and droplets. It is found in remote areas of the world in precipitation (Keene et al., 1983), aerosols (Andreae et al., 1986), and the gas phase (Andreae et al., 1986), in urban areas (Kawamura et al., 1985), and in continental regimes not contiguous to urban centers (Chapman et al., 1986). Formic acid (and, to a lesser extent, its higher analogues) is a major chemical constituent of precipitation in remote areas, where carboxylic acids contribute between 25 and 98% of the volume-weighted free acidity (Keene and Galloway, 1986).

Aqueous-phase atmospheric chemistry is thought to be a significant source of HCOOH. As shown by Chameides and Davis (1983), Graedel et al. (1986) and Jacob (1986), the reaction of dissolved formaldehyde with OH radicals in droplets will produce HCOOH, some of which may then be volatilized. The calculations of Chameides and Davis (1983) predict gas phase concentrations of HCOOH of 35-65 ppt, significantly smaller than the concentrations measured (Andreae et al., 1986) in nonurban continental areas typical of those which Chameides and Davis simulated.

A number of urban sources of formic acid are known. The most prolific is probably exhaust gases from motor vehicles (Kawamura et al., 1985), but biomass combustion (Hartstein and Forshey, 1974), plastics combustion (Hartstein and Forshey, 1974), and refuse combustion (Busso, 1971) also produce formic acid.

A potential source of formic acid not previously investigated is formicine ants. The formicine ants are among the most numerous of the world's ants, and are characterized by possessing large sacs containing high concentrations of formic acid (Fig. 1). The formic acid functions both as a defense when sprayed and as an alarm pheromone when secreted (Blum, 1978). For alarm communication purposes, at least, the required gas phase concentrations are of order 300 ppm (Löfqvist, 1976), indicating that truly substantial formic acid emission relative to the size of the ant must take place.

One can approximate the global flux Φ of formic acid from ants as follows:

$$\Phi = N_a m_a \psi / \delta, \tag{1}$$

in which N_a is the worldwide population of formicine ants, m_a is the average mass of an ant, ψ is the percentage of body mass present as volatilizable formic acid, and δ is the time scale

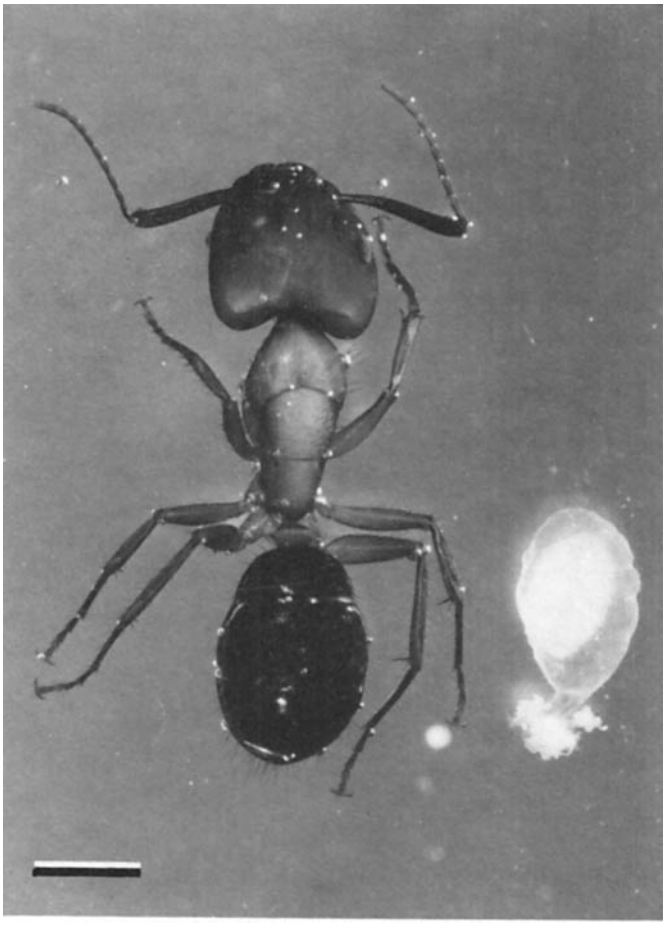

Fig. 1. Worker of the formicine ant, *Camponotus floridanus*, beside a replete formic acid sac excised from another worker of the same size. The acid sac in this species may weigh up to 20% of body mass but is typically 10%. The white oval zone of the sac denotes the disc of glandular tissue on the sac wall [reference bar = 2 mm].

for formic acid release. The number of ants contained in the earth's biomass has been estimated by Wilson (1975) to be "at least 1×10^{15}". This figure is based on an estimate of the total number of insects on the earth and of the fraction of insects that are ants. An alternative estimate is provided by P. R. Zimmerman (private communication, 1986). He begins with the estimate that the biomass of ants and termites is similar (Brian, 1978) and is of order 5×10^{14} g (Zimmerman et al., 1982). Taking a typical ant body mass of $m_a = 5$ mg (Nielsen et al., 1982) then gives $N_a = 1 \times 10^{17}$. The mid-range N_a value, which may be uncertain by up to an order of magnitude, is 1×10^{16} ants.

Other necessary values have been estimated by us in consultation with world experts in ant biology. One result is the estimate that about $30\% \pm 10\%$ of the world's ants are formicine ants, with somewhat higher percentages typical of the temperate zones and somewhat lower percentages typical of the tropics. The percentage of body weight present as formic acid is $\psi = 0.02 \pm 0.005$, given sac mass as 10% of the ant mass, with formic acid accounting for about 20% of the contents. For the typical "duty cycle" for formic acid release, it is necessary to consider two components: "active" emission and "passive" emission. The former constitutes formic acid emitted for communications or

defense purposes; we and our consultants estimate 0.1 sac emissions per ant lifetime (about 2 months) for this purposeful emission. The second component, passive emissions, refers to the fate of the formic acid within the ant upon the ant's death. A rigorous estimate of this parameter involves knowledge of ant burial procedures, sac dissolution at death, and reactivity of released formic acid with ant body parts and soil. We assume that about 20% of the formic acid present in an ant at death enters the atmosphere. (This number is probably uncertain up to a factor of two.)

Inserting values into eq. (1) gives a resulting global formic acid flux from ants of

$$\Phi = [(1 \times 10^{16} \text{ ants})(0.3)(0.005 \text{ g/ant}) \times (0.02 \text{ g HCOOH/g})]/(0.5 \text{ yr}) = 6 \times 10^{11} \text{ g HCOOH/yr},$$

or 0.6 Tg/yr. The source area for the emissions is restricted to tropical forest and midlatitude temperate environments, which together constitute about 13% of the surface of the earth.

The significance of the formic acid flux from ants can be assessed by comparison with the fluxes of formic acid from other sources. For the formic acid flux resulting from atmospheric chemistry, one must recognize that one of the principal formic acid precursors is formaldehyde. Formaldehyde measurements are extensive, and the rates of formation and removal of formaldehyde in the atmosphere have been calculated. An especially useful series of measurements was made over the north Atlantic in October of 1980 (Lowe et al., 1981). When fit to a model of sources and sinks for atmospheric formaldehyde, the data indicated a loss of formaldehyde to atmospheric water droplets at a rate of order 2×10^4 molec HCHO/cm^{3}s. If such a rate is in effect across the earth's sea surface and through a 1 km boundary layer, and all the formaldehyde lost to atmospheric water droplets is converted to formic acid (Chameides and Davis, 1983), the maximum formic acid flux from aqueous chemical processes can be no more than about 15 Tg/yr. To this amount must be added the formic acid flux from HCHO produced from reactions of the vegetative emittant isoprene with ozone. Jacob and Wofsy (1988) have used the isoprene emission data of Crutzen et al. (1985) and Zimmerman et al. (1988) to show that the formic acid chemical fluxes can be significant in forested areas, but are insufficient to explain measured formic acid concentrations. The global formic acid flux from isoprene is less quantifiable, but seems likely to be of the same order of magnitude as that from HCHO in the marine atmosphere. The result of these considerations is an estimated global formic acid flux from atmospheric chemical processes of order 30 Tg/yr, with wide error bars on the number being appropriate.

In the case of motor vehicles, it is possible to use the typical exhaust concentration of formic acid of 9 ppb (Kawamura et al., 1985), together with the information that total volatile organic carbon (VOC) concentrations in exhaust are of order 100 ppm (J. Elston, private communication, 1987). US VOC emissions from vehicles are about 7 Tg/yr (Environmental Protection Agency, 1985), and the world vehicle population is about three times the US vehicle population (Motor Vehicle Manufacturers Association, 1986). This gives a global formic acid flux from motor vehicles of about 0.002 Tg/yr; clearly approximate, but apparently much too small to be significant.

There is insufficient data to permit a quantitative estimate of the flux of formic acid from biomass and waste combustion. Kawamura et al. (1985) note that in urban areas, motor vehicles appear to be the most potent direct source of formic acid. It therefore seems reasonable to suspect that the fluxes of formic acid from urban biomass and waste combustion are small compared with that from motor vehicles. In remote areas, data suggest that biomass burning may produce significant amounts of formate and acetate (Andreae et al., 1988), but fluxes remain to be determined.

In Table 1, the formic acid fluxes discussed above are assembled for comparison. Given these estimates, formic acid from ants is unlikely to be

Table 1. *Estimated fluxes of formic acid to the atmosphere*

Source	Flux (Tg/yr)
formicine ants	0.6
atmospheric chemistry	30
motor vehicles	0.002
biomass and refuse combustion	<0.002

important to the global atmospheric formic acid budget. However, the atmospheric chemistry source is spread over the entire earth, although probably enhanced near isoprene-emitting trees, while the formicine ant source is concentrated near ant habitats. In such regions, the formic acid fluxes from ants would be much closer to those from atmospheric chemical processes than the global data of Table 1 suggest. The direct fluxes of formic acid from anthropogenic sources appear in all cases to be several orders of magnitude smaller than the natural or indirect sources, in agreement with the data of Keene and Galloway (1986).

Keene and Galloway (1986) and Andreae et al. (1986) have proposed that atmospheric formic acid in remote land areas must have two significant sources: a strong ground-level source and a weaker source dispersed throughout the boundary layer. The former is tentatively attributed to vegetation, the latter to atmospheric chemistry. There seems no reason why the former source might not be wholly or partially formicine ants, however. In the Amazonian region where the observations of Andreae et al. (1986) were made, the living animal biomass is about 200 kg/hectare, of which about 30 kg/hectare is formicine ants (Fittgau and Klinge, 1973). A calculation similar to that outlined above gives an average formic acid flux from ants of about 5×10^4 molec cm^{-3} s^{-1}, uncertain to perhaps an order of magnitude. Jacob and Wofsy (1988) have used a computer model to estimate the HCOOH flux in Amazonia from atmospheric chemical reactions of vegetative precursors; their noontime result is about 7×10^4 molec cm^{-3} s^{-1}. Hence, it appears that in Amazonia at least, formic acid emission from ants may be approximately as important as formic acid produced by atmospheric chemistry.

Ants which emit formic acid (formicine ants) are very numerous throughout the world, particularly in the tropics and the mid latitudes. We estimated the global flux of formic acid from ants, as well as the flux in Amazonia. Globally, ants appear not to be important sources of formic acid. Where abundant, however (such as in Amazonia), ants may be an important source of atmospheric formic acid, perhaps adequate to explain the formic acid concentrations in the gas phase of a few ppb as measured by Andreae et al. (1986). The result may thus provide a new example of the potentially significant interactions linking the biosphere and the atmosphere.

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REFERENCES

Andreae, M. O., Talbot, R. W., Andreae, T. W. and Harriss, R. C. 1986. Formic and acetic acids over the central Amazon region, Brazil. *EOS-Trans. AGU 67*, 249.

Andreae, M. O., Browell, E. V., Garstang, M., Gregory, G. L., Harriss, R. C., Hill, G. F., Jacob, D. J., Pereira, M. C., Sachse, G. W., Setzer, A. W., Silva Dias, P. L., Talbot, R. W., Torres, A. L. and Wofsy, S. C. 1988. Biomass-burning emissions and associated haze layers over Amazonia. *J. Geophys. Res. 93*, 1509–1527.

Blum, M. S. 1978. Biochemical defenses of insects. In *Biochemistry of insects* (ed. M. Rockstein). New York: Academic Press, 465–513.

Brian, M. V. (Ed.). 1978. *Production ecology of ants and termites*. IBP 13. Cambridge: Univ. Press, 405 pp.

Busso, R. H. 1971. *Identification and determination of pollutants emitted by the principal types of urban waste incinerator plants (Final Report)*. Centre d'Etudes et Recherches Charbonnages de France, Laboratoire du CERCHAR, Creil, France, Contract 69-01-758, A.R. 144.

Chameides, W. L. and Davis, D. D. 1983. Aqueous phase source of formic acid in clouds. *Nature 304*, 427–429.

Chapman, E. G., Sklarew, D. S. and Flickinger, J. S. 1986. Organic acids in springtime Wisconsin precipitation samples. *Atmos. Environ. 20*, 1717–1725.

Crutzen, P. J., Delany, A. C., Greenberg, J. P., Haagenson, P., Heidt, L., Leub, R., Pollock, W., Seiler, W., Wartburg, A. and Zimmerman, P. R. 1985. Tropospheric chemical composition measurements in Brazil during the dry season. *J. Atmos. Chem. 2*, 233–256.

Environmental Protection Agency. 1985. *National air quality and emission trends report, 1983*, Report EPA-450/4-84-029, Research Triangle Park, NC, U.S.A.

Fittgau, E. J. and Klinge, H. 1973. On biomass and

trophic structure of the central Amazonian rain forest ecosystem. *Biotropica 5*, 2–14.

Graedel, T. E., Mandich, M. L. and Weschler, C. J. 1986. Kinetic model studies of atmospheric droplet chemistry. 2. Homogeneous transition metal chemistry in raindrops. *J. Geophys. Res. 91*, 5205–5221.

Hartstein, A. M. and Forshey, D. R. 1974. *Coal mine combustion products: neoprenes, polyvinyl chloride compositions, urethane foam, and wood.* Bureau of Mines Report of Investigations 7977, US Dept. of the Interior, Washington, D.C.

Jacob, D. J. 1986. Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate. *J. Geophys. Res. 91*, 9807–9826.

Jacob, D. J. and Wofsy, S. C. 1988. Photochemical production of carboxylic acids in a remote continental atmosphere. In: *Acid deposition processes at high elevation sites* (ed. M. H. Unsworth) Hingham, Mass: D. Reidel, in press.

Kawamura, K., Ng, L. L. and Kaplan, I. R. 1985. Determination of organic acids ($C_1 - C_{10}$) in the atmosphere, motor-exhausts and engine oils. *Environ. Sci. Technol. 19*, 1082–1086.

Keene, W. C. and Galloway, J. N. 1986. Considerations regarding sources for formic and acetic acids in the troposphere. *J. Geophys. Res. 91*, 14466–14474.

Keene, W. C., Galloway, J. N. and Holden, J. D., Jr. 1983. Measurements of weak organic acidity in precipitation from remote areas of the world. *J. Geophys. Res. 88*, 5122–5130.

Löfqvist, J. 1976. Formic acid and saturated hydrocarbons as alarm pheromones for the ant *Formica rufa*. *J. Insect Physiol. 22*, 1331–1346.

Lowe, D. C., Schmidt, U. and Ehhalt, D. H. 1981. *The tropospheric distribution of formaldehyde.* Report 1756, Kernforschungsanlage Jülich, FRG.

Motor Vehicle Manufacturers Association. 1986. *World motor vehicle data.* Detroit, MI, U.S.A.

Nielsen, M. G., Jensen, T. F. and Holm-Jensen, I. 1982. Effect of load carriage on respiratory metabolism of running worker ants of Camponotus herculeanus (Formicidae). *Oikos 39*, 137–142.

Wilson E. O. 1975. *Sociobiology. The new synthesis.* Cambridge, MA: Belknap Press, 421 pp.

Zimmerman, P. R., Greenberg, J. P., Wandiga, S. O. and Crutzen, P. C. 1982. Termites: a potentially large source of atmospheric methane, carbon dioxide and molecular hydrogen. *Science 218*, 563–565.

Zimmerman, P. R., Greenberg, J. P. and Westberg, C. E. 1988. Measurements of atmospheric hydrocarbons and biogenic emission fluxes in the Amazon boundary layer. *J. Geophys. Res. 93*, 1407–1416.