Formation of Cloud and Ice Nuclei by the Combustion of Crude Oil

C. C. VAN VALIN, R. F. PUESCHEL AND F. P. PARUNGO

Environmental Research Laboratories, NOAA, Boulder, Colo. 80302

2 October 1974 and 10 March 1975

ABSTRACT

Aitken nuclei and ice nuclei concentrations in the smoke plume from an oil well fire near Glenrock, Wyo., on 14 December 1973, were found to be elevated by at least an order of magnitude as compared with the surrounding atmosphere. The composition of most particles in the plume was suggestive of the clay minerals; these could account for the increased ice nuclei concentrations.

1. Introduction

On 5 December 1973 the newly drilled Patterson No. 1 oil well near Glenrock, Wyo., caught fire. For several weeks it burned about 200 barrels of crude oil per hour. The smoke plume was visible for at least 50 km downwind and presented an opportunity for measurement of some of the characteristics of crude oil combustion products in an otherwise clean atmosphere.

2. Sample collection

On 14 December 1973, one of us (RFP), along with a pilot and an assistant, flew from Boulder, Colo., to the well site to measure Aitken nuclei concentrations (N_A) and obtain membrane filter samples for subsequent measurement of deposition ice nuclei concentrations (N_I) and analysis of collected particles for their elemental composition and surface characteristics. Values of N_A were measured *in-situ* with a Gardner Small Particle Counter. A Cessna Model 205, single engine, six place airplane was used. Samples were collected while the plane crossed the plume, turned, and crossed again, as shown in Fig. 1. Sampling was done from 5 to 50 km downwind from the well; position keeping was within ±1 km of the distance shown. The time consumed in turning and repositioning for another crossing was estimated at from 45 s to 1 min; at the greater plume distances a Gardner Counter reading (N_A)

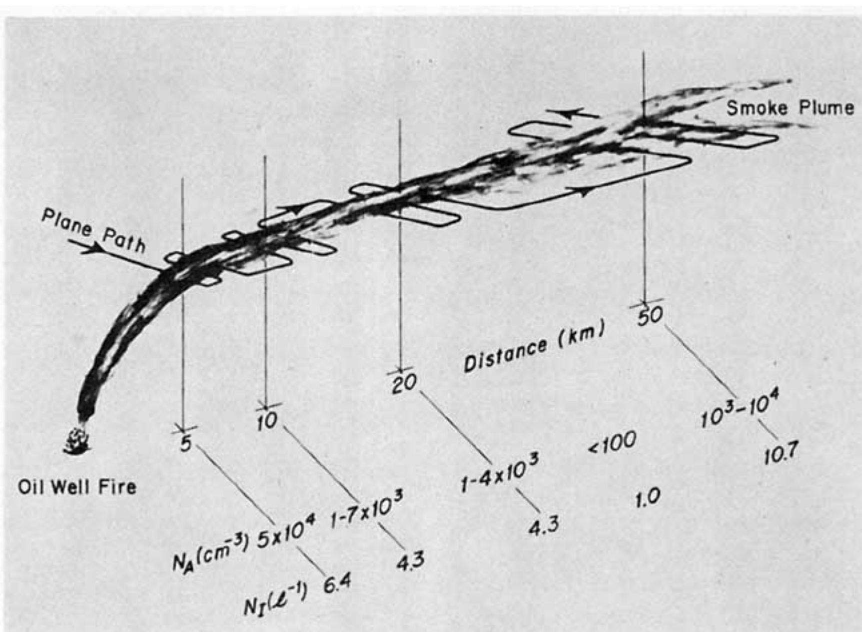

FIG. 1. Aitken nuclei (N_A) and ice nuclei (N_I) concentrations downwind from the Patterson No. 1 oil-well fire 14 December 1974. An N_A of <100 cm^{-3} was measured in the adjacent undisturbed atmosphere. The N_I of 1.0 ℓ$^{-1}$ was measured by Allee (1974) at Lander, Wyo., on this date.

indicative of background was obtained before the turn was accomplished. Since the time required to cross the plume varied from 15 s to 1 min, from half to three-quarters of the sampling time was spent outside the plume, with the consequence that N_I (Fig. 1) is proportionately understated.

Aerosols were collected by drawing outside air through a 0.45 μm pore size, mixed cellulose ester membrane filter. Flow rate was 10 ℓ min^{-1}, sampling time was 5 min per filter. Ice nuclei collected on half of the filter were measured in the laboratory by the method of Bigg *et al.* (1963), at -20°C, in an atmosphere saturated with respect to water. Another part of the filter was used for elemental and surface characterization of individual particles on the filter by scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDX).

The smoke from the burning oil formed a well-defined plume at an elevation of 3000 m MSL (surface elevation, 1550 m). The pilot estimated the vertical thickness to be 300–400 m, with a horizontal width of 1 km at 10 km downwind, and 4 km at a downwind distance of 50 km. As viewed from ~70 km away and perpendicular to its axis, at least 50 km of the plume length was visible as it extended from west to east. In the surrounding atmosphere N_A varied from 200 cm^{-3} to fewer than 100 cm^{-3}; within the smoke plume N_A was from one to several times an order of magnitude higher, even at the maximum sampling distance of 50 km downwind from the fire.

3. Discussion and conclusions

According to Allee[1], the 14 December 1973 24 h average N_I, and the December 1973 monthly average N_I at Lander, Wyo., were 1.0 and 1.2 ℓ^{-1} respectively, as measured by the same procedure as used here (Allee, 1974).

We consider the Lander sample of 14 December 1973 to be representative of the same air mass present at the site of the oil well fire on the same day. Hence, the background concentration of 1.0 ℓ^{-1} is shown in Fig. 1. As mentioned earlier, the ice nuclei measurements in the plume and vicinity probably understate the N_I in the plume by factors of 2–4, with the smaller factor occurring at the greatest distance. On this basis, N_I in the plume is seen to be elevated by more than an order of magnitude.

The energy dispersive x-ray analyses of two particles, collected 5 and 10 km downwind from the fire, are shown in Fig. 2. These are representative of the majority of particles found on the collection filters in the sense that they contain a variety of elements suggestive of mixed mineral origin. Silicon, oxygen and aluminum are the most abundant elements in the earth's crust, and the lower x-ray spectrograph is typical of our analyses of clay mineral particles (elements lighter

[1] Private communication.

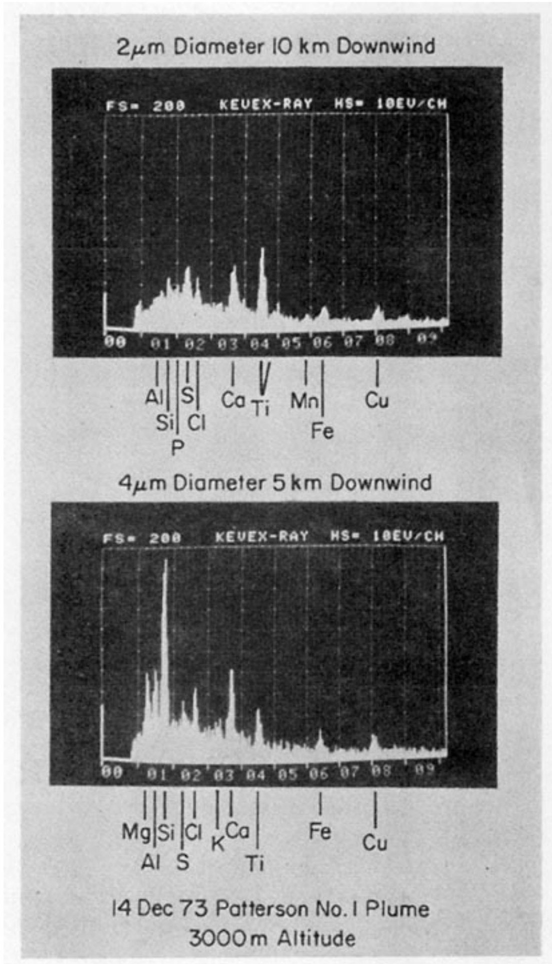

FIG. 2. Energy dispersive x-ray analyses of particles collected on 0.45 μm membrane filters.

than sodium do not respond in our x-ray energy spectrometer). These are hydrous aluminum silicates, with magnesium, iron, sodium, potassium and calcium often present as essential constituents (Hurlbut, 1971).

Several investigators have attempted to assay the ice nucleating effectiveness of various natural mineral dusts (e.g., Fukuta, 1958; Mason and Maybank, 1958; Mason, 1960). In general, the silicate minerals of the clay and mica groups were most active. Laboratory studies have also shown that many metallic oxides are capable of ice nucleation at rather high temperatures, i.e., above -10°C (Mason, 1971). Ice nucleation appears to depend upon a suitable crystalline substrate for initiating ice crystal growth either by contact or by deposition (Fletcher, 1970).

In the upper x-ray spectrograph of Fig. 2, the prominent signal for titanium is suggestive of rutile (TiO_2), or along with the calcium, of perovskite ($CaTiO_3$). Both of these, according to their crystal lattice dimensions, might be effective as ice nuclei at -10 to -8°C.

TABLE 1. Elemental composition of particles.

Approximate distance downwind (km)	5	10	20	50	Total	Percent occurrence in plume	Percent occurrence in Lander, Wyo.
Number of particles within 1 mm^2	27	19	22	21	89		
Element detected							
Na	1	3	4	1	9	10	20
Mg	5	2	3	1	11	12	20
Al	24	11	9	9	53	60	70
Si	16	14	19	18	67	75	90
P	7	10	8	10	35	39	15
S	18	15	11	14	58	65	35
Cl	9	13	8	11	41	46	30
K	4	8	5	6	23	26	50
Ca	6	6	6	6	24	27	50
Ti	4	9	3	6	22	25	5
V	6	7	3	8	24	27	
Fe	7	7	5	4	23	26	40
Cr	1				1	1	
Ni		2			2	2	
Co		1	1	1	3	3	
Ag		1	3	2	6	7	
Cu*				1	1	1	

* When the Cu mounting stud is used, the estimation of sample Cu is very uncertain.

For the elemental analyses, we evaluated all particles on 1 mm^2 of each filter. The findings are summarized in Table 1.

By far the most abundant organometallic compounds in crude petroleum are the vanadium-containing porphyrins (Baker, 1969), and the vanadium in these samples is probably from this source. (Vanadium was not detected in the samples collected at Lander.) Although the higher oxides of vanadium, that would be produced during the combustion of petroleum, are slightly soluble in water, their crystal spacings appear to be suitable for ice deposition. Therefore they may be active as ice nuclei. The higher incidence of sulfur, chlorine and phosphorus in these samples, as compared with their occurrence in the Lander samples, indicates that the petroleum was an important source of these elements. Combustion of the petroleum carrier would result in soluble products. Such water-soluble products would not be active as ice nuclei, and in fact, would probably deactivate otherwise active mineral particles by forming a water-soluble surface coating (Pueschel *et al.*, 1974).

In eleven oil wells in the state of Wyoming, nickel was the metal next in abundance to vanadium, occurring at an average of one-fifth the concentration of vanadium (Ball *et al.*, 1960). However, nickel was found in only two of the examined particles from our samples, and therefore cannot be considered as significant here in terms of possible ice nucleating sites.

The other elements found in the particles sampled are abundant and widespread in the earth's crust, and probably represent minerals resident in the petroleum deposit or eroded from the bore hole. Of the minerals that may be represented here, some have fairly high-temperature thresholds of ice nucleating ability, e.g., kaolinite [$Al_4(Si_4O_{10})(OH)_8$], tridymite (SiO_2), magnetite (Fe_3O_4, which often contains significant quantities of Ti), hypersthene [$(Mg,Fe)_2(Si_2O_6)$, often containing Al], and calcite ($CaCO_3$) (Mason, 1971).

It is also appropriate to comment on the probable contribution of these particles to the cloud condensation nuclei (CCN) budget, even though our lack of a suitable instrument made it impossible to measure CCN within the smoke plume. CCN activity appears to depend upon surface capillarity or surface solubility (Pueschel *et al.*, 1974); the high incidence of sulfur, chlorine and phosphorus in particles from the oil-well fire suggests the presence of soluble sulfates, chlorides and phosphates on the particle surface, and consequently, a high CCN activity.

4. Summary

We have shown that the smoke plume from an oil-well fire contains at least an order of magnitude more Aitken and ice nuclei per unit volume than the surrounding atmosphere, and the particles remain airborne for considerable distances downwind. An elemental analysis of individual particles by SEM-EDX has identified elements in abundances and combinations suggestive of minerals that are known to be active ice nucleators. On the other hand, the relatively high concentrations of sulfur, chlorine and phosphorus suggest the presence of other substances that are inactive as ice nuclei, but which may be effective as CCN.

Acknowledgments. We thank Helmut K. Weickmann for suggesting and assisting in the preparation for this research flight. We also take this opportunity to thank Robert S. Lawrence of the Wave Propagation Laboratory, NOAA, and Richard A. Proulx for their participation as pilot and technician, respectively.

REFERENCES

Allee, P. A., 1974: Ice nuclei concentration measured by a benchmark network. *Preprints Fourth Conf. Weather Modification*, Ft. Lauderdale, Amer. Meteor. Soc., 242–245.

Baker, E. W., 1969: Porphyrins. *Organic Geochemistry*, G. Eglinton and M. T. J. Murphy, Eds., Springer-Verlag, 464–497.

Ball, J. S., W. J. Wenger, H. J. Hyden, C. A. Horr and A. T. Myers, 1960: Metal content of twenty-four petroleums. *J. Chem. Eng. Data*, 5, 553–557.

Bigg, E. K., S. C. Mossop, R. T. Mead and N. S. C. Thorndike, 1963: The measurement of ice nucleus concentrations by means of Millipore filters. *J. Appl. Meteor.*, 2, 266–269.

Fletcher, N. H., 1970: *The Chemical Physics of Ice.* Cambridge University Press, 271 pp.

Fukuta, N., 1958: Experimental investigations on the ice-forming ability of various chemical substances. *J. Meteor.*, 15, 17–26.

Hurlbut, C. S., Jr., 1971: *Dana's Manual of Minerology*, 18th ed. Wiley, 579 pp.

Mason, B. J., 1960: Ice-nucleating properties of clay minerals and stony meteorites. *Quart. J. Roy. Meteor. Soc.*, 86, 552–556.

——, 1971: *The Physics of Clouds*. Oxford, Clarendon Press, 671 pp.

——, and J. Maybank, 1958: Ice-nucleating properties of some natural mineral dusts. *Quart. J. Roy. Meteor. Soc.*, 84, 235–241.

Pueschel, R. F., C. C. Van Valin and F. P. Parungo, 1974: Effects of air pollutants on cloud nucleation. *Geophys. Res. Lett.*, 1, 51–54.