

ATMOSPHERIC CHEMISTRY EFFECTS OF THE 1998 MEXICAN/CENTRAL
AMERICAN FIRES MEASURED IN CENTRAL NEW MEXICO USA

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Work supported by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research, under contract W-31-109-Eng-38.

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"PREPRINT EXTENDED ABSTRACT"

Presented Before the Division of Environmental Chemistry
American Chemical Society
Anaheim, California March 21-25, 1999

ATMOSPHERIC CHEMISTRY EFFECTS OF THE 1998 MEXICAN/CENTRAL AMERICAN FIRES MEASURED IN CENTRAL NEW MEXICO USA.

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Introduction

Atmospheric effects from large fires have received a great deal of interest recently, especially when the fires have the potential to effect human health when the plumes are transported long distances over areas of high population density. Examples are the recent large fires in Southeast Asia in 1997 (1) and the wildfires occurring in southern Mexico and Central America that were manifested in decreased visibility and high aerosol concentrations in the United States at distances of 2500-4000 km from the fires. In addition to fine aerosols, these biomass fires have the potential to produce and transport large quantities of oxygenated organic species such as aldehydes, ketones and carboxylic acids, hydrocarbons, and sulfate and nitrate species. Most of the literature reports dealing with products of biomass burning have been related to fireplace and wood burning stove emissions (2,3) and with local effects from forest fires(4). The recent super-large fires occurring in Indonesia and Mexico/Central America also bring about the issue of atmospheric reactivity because long-range transport affords long reaction times for photochemical reactions, wet and dry deposition and surface reactions on the aerosol particles. The smoke/haze conditions prompted considerable concern among the general population in New Mexico regarding health hazards and a large number of calls to the Albuquerque, NM Air Quality Division which reported the PM₁₀ samples collected showed no significant increase in mass(5). The conclusion was that the particles were very fine and therefore had considerable influence on the visibility but did not violate health standards. In this study, organic and inorganic chemical species in the gaseous and aerosol phases have been identified and quantified under non-smoky and smoky conditions in Central New Mexico approximately 3000 km from the source of the fires.

Experimental

Field Site and Sampling Protocol

The field sample site is located in an agricultural area in the Rio Grande flood plain near Socorro, NM (Lat. 34°, Long. 106° - pop.~9,500) in south central New Mexico about 120 km south of Albuquerque. The sample site has been used for several years for studies of biogenic emissions from cottonwood trees. About a week before there was visible evidence of haze attributed to the Mexican/Central American fires, ambient concentrations of carbonyl compounds, low molecular weight carboxylic acids and hydrocarbons were determined on a diurnal basis for two days. A week later the haze was extremely bad and we again undertook a two-day sampling for the same species. Samples of carbonyl compounds and carboxylic acids were collected over 2-hour sampling periods with mid-sample times at 0800, 1200, 1600, 1800 and 2400 hr. Hydrocarbons were collected over a 10-minute period at mid-sample times. NO_x and O₃ data were provided as one-hour averages by the city of Albuquerque, NM Air Quality Control Division Laboratory. No NO_x or O₃ instrumentation was available in Socorro and Albuquerque was experiencing a smoke episode at the same time. Particulates were collected over 22-98 hour sampling periods on 47 mm Teflon filters at flow rates of 42 L/min.

Analyses

Aldehydes and ketones were sampled with Sep-Pac C₁₈ cartridges (Waters/Millipore Corp.) coated in the laboratory with acidified 2,4-dinitrophenylhydrazine (DNPH) after procedures previously described (6,7,8). The analyses followed the specific descriptions regarding blanks, duplicates, detection limits, instrumentation, and calibration described in Gaffney, et al. (9)

Organic acid samples were collected at 2-hour intervals, corresponding to the collection schedule for the carbonyl compounds. Water mist nebulizers (40mL capacity) specially constructed for trapping acids were used with the procedures described by Popp et al. (10). Specific descriptions of all protocols for blanks, duplicates, detection limits, instrumentation and calibration used are given in Gaffney, et al. (9).

Gas analysis for NO_x and O₃ was performed by the city of Albuquerque Air Quality Control Division according to EPA approved standard methods. The NO_x was analyzed using standard ozone chemiluminescence analyzers, O₃ was measured by using standard UV absorption methods.

Hydrocarbons were collected in Tedlar bags and were analyzed by GC-FID.

Particulates were analyzed for SO₄²⁻ and NO₃¹⁻ by ion chromatography after extraction by deionized water.

Results and Discussion

Average concentrations of Carbonyl Compounds are summarized in Table 1 and shown graphically in Figure 1. The smoke episode showed two stages during the three sampling days. During the early stage (six samples) the smoke was lying close to the ground and in the later

stage (nine samples), the smoke had lifted to a height of about one km. The data in Figure 1 clearly show the periods with total measured carbonyl compounds a factor of 4.4 higher than found in clean air. The bulk of the increase was due to increases in acetone, propionaldehyde and methyl ethyl ketone (factors of 6.2 – 8.4 greater than clean air). These compounds have longer atmospheric lifetimes than found for acetaldehyde and formaldehyde.

The concentrations of formic and acetic acids did not show increases similar to the carbonyl compounds. Only slight increases of factors of 1.1 (acetic acid) and 1.4 (formic acid) were found. It is likely that dry deposition and scavenging by aerosols may have attenuated long-range transport of these species.

NO_x concentrations increased by a factor of 2.1 and O₃ concentrations decreased by a factor of 1.6 during the smoke episode when compared to ambient air measurements a week earlier. Decreased UV and increases in reactive species due to the smoke may account for the O₃ decrease. Both NO (1.5x) and NO₂ (1.8x) increased about the same amount and these increases may be due to the atmospheric conditions trapping NO_x as well as smoke.

While PM₁₀ concentrations showed little differences, the very fine particles caused significant visibility decreases with mountain ranges 5-6 km distant being obscured when normally mountains are visible 80-130 km distant. The nitrate and sulfate associated with the particulates increased 13x and 1.8x respectively.

Conclusions

Some chemical species such as carbonyl compounds, nitrate and sulfate, may be transported long distances as a consequence of large fires. Other species such as O₃ and NO_x may also be affected. Carboxylic acids did not show up as increases in the study.

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Table I

Average Concentrations of Carbonyl Compounds, Short Chain Carboxylic Acids, NO_x, O₃, PM₁₀, Particulate Nitrate and Sulfate. All concentrations in ppbv except PM₁₀ and Nitrate/Sulfate (μg/m³)

| Species | 5/11-13/98 Before Smoke | 5/19-21/98 During Smoke | Ratio Before/After |
|------------------------------|----------------------------|----------------------------|--------------------|
| Acetaldehyde | 1.13 | 3.61 | 3.2 |
| Formaldehyde | 2.24 | 3.73 | 1.7 |
| Acetone | 1.02 | 2.94 | 2.9 |
| Propionaldehyde | 0.31 | 1.19 | 8.1 |
| Other 4-Carbon Compounds | 0.16 | 0.75 | 6.9 |
| Methyl Ethyl Ketone | 0.79 | 3.26 | 8.4 |
| Σ Carbonyls | 5.65 | 15.48 | 4.4 |
| Acetic Acid | 4.29 | 4.66 | 1.1 |
| Formic Acid | 2.92 | 3.99 | 1.4 |
| Σ Acids | 7.21 | 8.65 | 1.2 |
| PM ₁₀ | 15-20 ² | 18.9 | ~1.0 |
| Particulate NO ₃ | 0.1 | 1.3 | 13 |
| Particulate SO ₄ | 1.24 | 3.39 | 2.7 |
| NO _x ¹ | 18 | 38 | 2.1 |
| O ₃ ¹ | 41 | 25 | 0.6 |

¹All measurements in Socorro, NM except O₃ and NO_x from Albuquerque, NM, Air Quality Control Division

²Measured in March, 1998

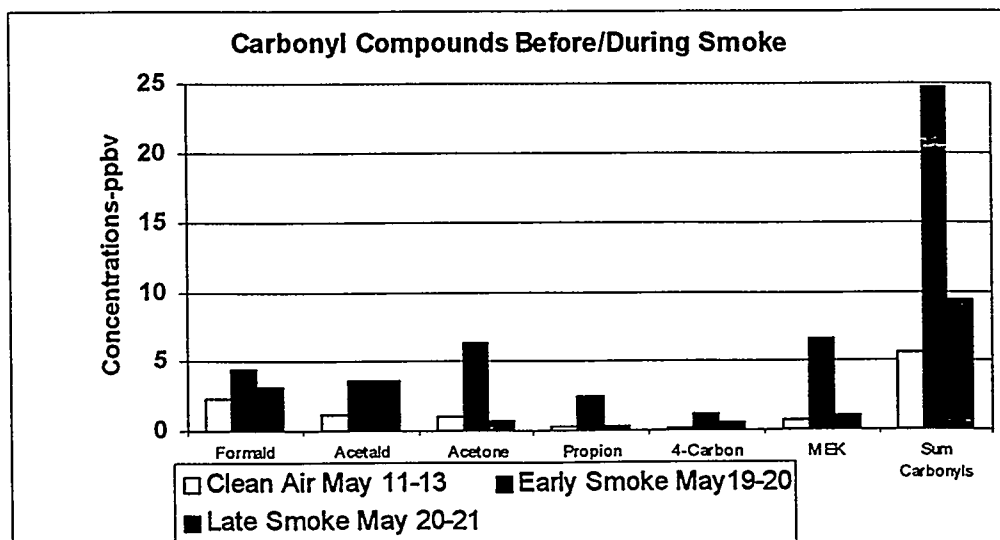


Figure I. Concentration of aldehydes and ketones in clean air before the smoke episode and in the two stages of the smoke episode.