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CHEMICAL AND MUTAGENIC ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN RALEIGH AIR SAMPLES AT THREE DIFFERENT ELEVATIONS BEFORE, DURING, AND AFTER HURRICANE GORDON

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ABSTRACT

Volatile organic compounds (VOCs) were collected and measured at a television tower 10 km southeast of downtown Raleigh, North Carolina at three different levels (Surface, <1m; Mid, 240 m; and Top, 433 m) during the summer and fall of 1994. The combined presence of ozone, arenes, and nitrogen oxides (NO_x) suggested possible nitration of arenes during atmospheric mixing. Air samples, therefore, were collected using XAD-filled canisters at each level on the tower prior to, during, and after Hurricane Gordon. Collected air samples were Soxhlet extracted and analyzed with the *Salmonella typhimurium* microsuspension mutagenicity assay using strains YG1021 and YG1026 which are sensitive to nitrarenes. Significant mutagenicity was observed only in the Top and Mid level samples for the post-hurricane, normal weather air samples. Surface samples were not mutagenic, which suggests the long-range transport of these mutagenic nitrarenes. Published by Elsevier Science Ltd

Key Words: Salmonella, mutagenicity, volatile organic compounds, ambient air monitoring, meteorology, Hurricane

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INTRODUCTION

Photochemical pollution results from the interaction of ozone, VOCs, and NO_x. Previous research demonstrated that the sun's energy promotes the atmospheric nitration of hydrocarbons and that the presence of nitrated aromatics can be substantiated through the use of bioassays [1, 2]. Airborne organic compounds can arise from either natural emissions [3, 4] or anthropogenic sources [3, 5]. Airborne aromatic hydrocarbons originate primarily from combustion (automotive emissions and biomass, coal, and refuse combustion) [2]. The reactive nitrogen emissions in the atmosphere are generally half oxidized (NO_x) and half reduced (ammonia). Combustion, microbial activity in soils, and biomass burning cause most of the NO_x emissions [6]. Recent NO_x emission estimations reveal that in the US combustion and biogenic sources produce most of the NO_x [3]. Ammonia is generated predominantly from animal waste and its chemistry is less well understood than NO_x.

It has been very difficult for researchers to precisely measure the concentrations, sources, and reaction rates associated with airborne nitrated species, because variables such as location, dynamic conditions combined with complex chemical reactions, varying precursor compounds, and airborne-generated nitrated species must be addressed. Several investigators, however, have measured both photochemical precursors (e.g., VOCs, arenes, ozone, and NO_x) and transformation products (e.g., NO_y, nitrated alkanes and alkenes, other nitrated and oxygenated organic compounds) during ambient air studies [7, 8] and smog chamber studies [9]. NO_y is a combination of the following: NO_x, organic nitrates ($RONO_2$), nitric acid (HNO_3), peroxyacetic nitric anhydride (PAN), aerosol nitrate (NO_3), dinitrogen pentoxide (N_2O_5) and chlorine nitrate ($ClONO_2$) [10].

Previous measurements of diurnal ozone and VOC concentrations also taken at the location of this study support the presence of a highly reactive upper atmosphere [11]. Prior to this study, air samples collected at three levels (surface, <1 m; 240 m; and 433 m) on a TV tower near Clayton, North Carolina revealed measurable concentrations of aromatic hydrocarbons aloft that are available for nitration reactions [7]. Although arene concentrations were increased at the elevated heights, alkene and alkane concentrations decreased with increased height. Also, of the VOCs measured, only the arene concentrations statistically correlated in a positive manner with wind direction from Raleigh [7]. Carbonyl concentrations did not correlate with the wind direction coming from Raleigh; however, this was probably due to chemical reaction times. At this location, the highest concentrations of carbonyls were seen above 240 m when winds originated from relatively distant large cities [11, 12].

More surface friction occurs when substances are transported over land than when they are tranported over water. This surface friction over land produces diffusion, shear turbulence, and deposition of VOCs (especially the heavier nitrated VOCs like nitrated PAHs) and particles on surfaces (e.g., plant leaf surfaces) [13, 14]. Because the lower molecular weight VOCs are more buoyant, they remain aloft for relatively long periods. Concurrently in the upper air boundaries, the jet stream and upper air pressure fluctuations transport pollutants horizontally thus leading to long range transport [15]. As turbulent buoyancy lifts anthropogenic emissions like arenes, atmospheric nitration and long range horizontal transport of the pollutant and its atmospheric transformation products occurs.

Bacterial assays have proven useful in demonstrating the presence of mutagenic nitrated arenes in complex mixtures [2]. Analytical methods such as GC and the GC-MS can speciate but cannot differentiate alkyl nitrates from nitrogenated VOCs; and neither method, on its own, can discern which species are hazardous. The most frequently used genotoxicity test for complex environmental mixtures is the Salmonella/microsome test [16] which has been used for a variety of ambient air studies [17, 18, 19]. The presence of nitroarenes in atmospherically transformed air was first shown by Claxton and Huisingh [20] who found that nitroreductase-deficient strains of *S. typhimurium* produced less mutagenicity when testing the combustion emissions. Most ambient air samples from the US that have been bioassayed have been mutagenic [2].

Nitrogenated arenes, many of which are mutagenic, can be collected with XAD [21] and removed from the XAD (for analysis and bioassay) by solid-liquid-vapor extraction. *Salmonella typhimurium* strains YG1021 and YG0126 provide increased sensitivity for these types of mutagenic nitroaromatic compounds. Watanabe et al. [22] found the *S. typhimurium* YG1021 strain to have 275 fold increase in response over TA98 for 2,6-dinitrotoluene (2,6-DNT) on a revertant per microgram basis. The strains YG1021 and YG1026 have increased nitrofurazone-reductase enzyme activity which enables increased sensitivity for nitroaromatic compounds.

In ambient air monitoring studies, therefore, detection of samples with direct-acting mutagenicity using YG1021 and YG1026 and elevated concentrations of arenes (as detected by the GC analysis) supports the concept that nitrated arenes are present. If the samples are mutagenic only with S9 activation, this would argue against the presence of nitroarenes. A finding that the air samples from the higher elevations are more mutagenic than lower levels would support the idea of nitrification of arenes during long range transport.

The hypothesis of this work was that photochemical processes drive the atmospheric nitration of VOCs, which generates biologically active species in the atmosphere. It was speculated that some of the nitrated VOCs would be mutagenic and would have half-lives that would allow long-range transport in the atmosphere. Because the Salmonella mutagenicity assay can measure mutagenic arenes in ambient air samples, samples collected at three levels were bioassayed using the strains of Watanabe, et al. [22]. The ozone concentrations [23], and VOCs [7, 24], and NO_x levels [25] are reported elsewhere, and much of this information is contained in detail in the thesis by Stratton de Pollok [26].

EXPERIMENTAL METHODS

Sampling: Ambient air samples were collected on a 610 m TV tower located about 15 km southeast of Raleigh. Volatile and semi-volatile organic matter sampling with XAD began November 15, 1994 prior to Tropical Storm Gordon (Table 1). XAD canisters then were exchanged as Hurricane Gordon approached the North Carolina coast. The second sampling period was from November 18-23, 1994, during Hurricane Gordon. The sample was again exchanged for the third and final sampling period (November 23-30, 1994). Samples were collected at three levels: Surface (<1 m); Mid , 240 m; and Top, 433 m. Samples for bioassay were collected with high volume Gillian pumps through 1/4 inch stainless steel tubing positioned six feet away from the tower. Ambient air flowed at 15 L/minute through XAD-2 (Supelco, Bellefonte, PA) filled canisters to collect volatile and semi-volatile organic matter. The procedure of Williams et al. [27] was used to clean the XAD canisters and XAD resin. PM10 sampling heads and pre-filters were installed upstream from the XAD canisters to remove particulate matter. A blank reference control XAD-2 filled canister accompanied the three exposed canisters during each sampling period. Following sample collection, canister samples were kept in a cooler on ice and then stored briefly at -40°C until analysis.

Gravimetric and TCO Analysis: Following sample collection, the XAD resin of each canister was Soxhlet extracted individually for 24 hours with 1 liter of dichloromethane per XAD resin sample volume by the method of Williams, et al., [27]. XAD resin samples were Kuderna-Danish concentrated for 40 hours to isolate the semi-volatile and non-volatile VOCs. Non-volatile VOCs (boiling point (BP) >300°C) were gravimetrically analyzed. Semi-volatile VOCs (BP = 100-300°C) were also analyzed for total chromatographable organics (TCO). The remaining samples were each diluted in DMSO, and the dichloromethane was evaporated under nitrogen before the bioassays were conducted.

Table 1: Summary of Weather Conditions During Sampling Periods[a].

Date	Local Conditions[b]		Tropical Storm(TS) /Hurricane (H) Gordon Information		Comments
	WD(A/S)	WS(A/S)	Stage	Location	
11/15	Variable	<10 (S)	Low	Atlantic	Sampling started at 1620
11/16	NE/E (S) NE/E (A)	<10 (S) ~30 (A)	TS	Near Florida east coast	
11/17	E/NE	15-30 (S)	TS/H	Atlantic Gulf Stream	TS becomes H
11/18	E (S) N/NE (A)	~25 (S) 30-35 (A)	H	400 km E of Myrtle Beach	Second sampling period starts
11/19-20	E	10-20 (S)	H/TS	Atlantic E of NC	Stays on east coast then heads S and E toward Florida east coast
11/21-23	NE/W/N	<15 (S)	[Normal weather]		Third Sampling Period starts on 11/23; On 11/22 NC winds from W part of day; Late on 11/23 NC winds start from N
11/23-30	N/NW	0-10	[Normal weather]		Normal weather with variable winds

[a]For a more in depth summary see the thesis of Stratton de Pollok [1996].

[b]Wind Direction (WD) at the Surface (S) or Aloft (A) with approximate Wind Speeds (WS) given in knots.

Mutagenicity Bioassays: Mutagenic response was measured using a *Salmonella typhimurium* microsuspension assay. The procedures of Kado et al. [28, 29] were used; except that, instead of continuous shaking, shaking was done only before and after the 90 minute preincubation. Samples were bioassayed both with and without 8% S9 (Aroclor 1254-induced rat liver homogenate [Organon Teknika Corp., Durham, NC]). The tester strains used were YG1021 and YG1026 [30] kindly supplied by Dr. Watanabe. Initial microsuspension assays used five doses of extracted ambient air at 5, 10, 15, 20, and 25 μg (in a 5 μl volume) to obtain a dose-response curve. This was changed to a logarithmic dose-response curve after several assays due to limited sample size. Spontaneous and positive controls were used as follows: 0.5 μg/plate of sodium azide (SA), 0.3 μg/plate of 2-nitrofluorene (2NF), 0.25 μg/plate of 2-anthramine (2AN), 1.0 μg/plate of benzo(a)pyrene (BaP), and 0.25 μg/plate of 4-methyl-3-nitrophenol (4M3NP). After 72 hours of incubation at 37°C, the revertant colonies were counted and slope values (mutagenic activity in revertants/μg of organics) were generated by the model of Bernstein et al. [31] with the Gene Tox manager [32].

RESULTS

Meterology and Chemistry: Table 1 summarizes key aspects of the weather patterns during the three sampling periods. A detailed analysis of the meterological conditions is contained in the thesis by Stratton de Pollok [26]. During the first two sampling periods, the winds originated primarily from the northeast and east. Prior to the arrival of Hurricane Gordon, the winds were relatively calm (<10 knots); however, as the hurricane approached North Carolina the wind speeds increased. During the third sampling period, normal weather conditions existed and air flow came primarily from the north and northwest. A previous study [7] found that when the wind direction was from Raleigh, there was a correlatable increase in arenes. The correlation between wind direction and arene concentration was better than the correlations between wind direction and either alkanes or alkenes, [7].

Following the extraction of air samples, the gravimetric and TCO analysis (Table 2) was surprising because the amount of mass collected was not proportional to the length of the collection period. The first sampling period was the shortest, yet it yielded the most mass. During the approach of Hurricane Gordon, 12.76 mg of higher molecular weight compounds (BP>300) and 37.00 mg of more volatile components were collected. This amount was nearly four times the amount collected for the final week long period.

Bioassays: Preliminary screening by the standard Salmonella plate incorporation assay (results not presented) indicated that some of the samples were mutagenic but that the amount of sample available was too limited for complete testing using this protocol. A microsuspension bioassay, therefore, was used.

Table 2: Gravametric (GRAV) and Total Chromatographical Organics (TCO) Analysis of XAD Collected Ambient Air Samples

Analysis	Boiling Point	Sampling Level	Sampling Dates (November 1994)		
			15-18[a]	18-23[b]	23-30[c]
GRAV	>300°C	Top	12.76	3.48	3.66
		Mid	5.44	8.88	3.66
		Surface	5.54	3.46	5.36
		Blank	3.78	3.32	4.94
TCO	<300°C	Top	37.0	2.0	0.3
		Mid	6.5	0.6	1.4
		Surface	1.1	1.1	1.8
		Blank	1.6	0.7	<0.1

[a]As Hurricane Gordon approached the North Carolina coast.

[b]As Hurricane Gordon moved away from the North Carolina coast.

[c]During normal seasonal weather conditions.

When the air samples were collected, the meteorological effects of Hurricane Gordon on the air samples were not anticipated. Table 3 summarizes the results of mutagenicity testing, and Figure 1 illustrates the mutagenic response for the most responsive tester strain (YG1026). The mutagenicity values presented in Table 3 and Figure 1 are based on the Bernstein et al. [31] statistical analysis method using the GeneTox Management Software [32].

The sample for 11/15-18/1994 was collected as Hurricane Gordon approached North Carolina. For YG1026 with and without S9, all 11/15-18/1994 samples were not mutagenic. For YG1021 without S9, all samples appear to be non-mutagenic; although for one sample (Surface), a single plate gave a response outside the normal spontaneous range. For YG1021 with S9, all samples were not mutagenic.

Table 3: *Salmonella typhimurium* mutagenicity (revertants/ug) of ambient air samples.

Tower Sample	YG1021 Without S9	YG1021 With S9	YG1026 Without S9	YG1026 With S9
November 15-18 Sampling Period[a]:				
Top	Negative	Negative	Negative[c]	Negative[c]
Mid	Negative	Negative	Negative	Negative
Surface	(2.0)[d]	Negative	Negative	Negative
Blank	Negative	Negative	Negative	Negative
November 18-23 Sampling Period[b]:				
Top	Negative	Negative	Negative	0.7 ?[e]
Mid	Negative	Negative	Negative	Negative
Surface	Negative	Negative	1.2 ?	0.9 ?
Blank	Negative	Negative	Negative	1.0 ?
November 23-30 Sampling Period[c]:				
Top	1.2	Negative	1.7	5.3
Mid	Negative	Negative	3.9	3.0
Surface	Negative	Negative	Negative	Negative
Blank	Negative	Negative	Negative	Negative

[a]As Hurricane Gordon approached the North Carolina coast.

[b]As Hurricane Gordon moved away from the North Carolina coast.

[c]During normal seasonal weather conditions.

[d]Only one dose gave a significant response; therefore, biological significance is uncertain.

[e]? = borderline response, see text for discussion.

The surface-level samples collected 11/18-23/1994 (during and immediately after Hurricane Gordon's approach toward North Carolina) showed some indication of mutagenicity with

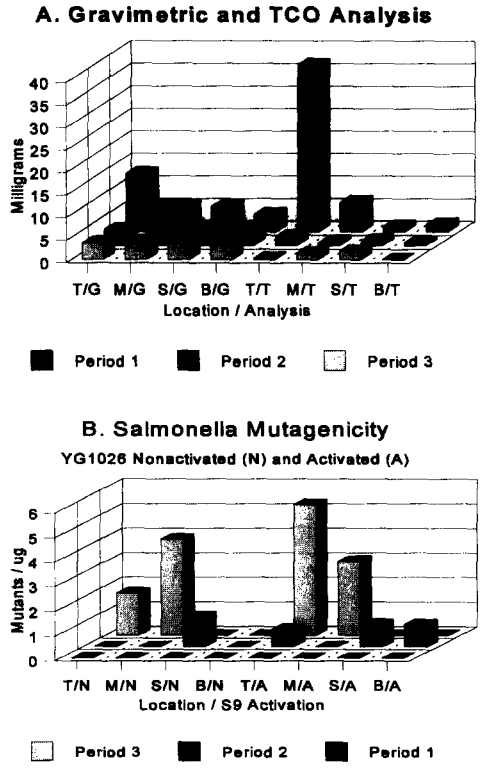

Figure 1. Comparison of gravimetric and TCO analysis with *Salmonella typhimurium* YG1026 mutagenicity for three sampling periods at three elevations.

Period 1 = November 15-18; Period 2 = November 18-23; Period 3 = November 23-30

For display purposes, the order of periods is reversed in the two graphs.

Locations (Elevations): T = Top (433 m); M = Mid (240 m); S = Surface; B = Blank

Analysis: G = Gravimetric; T = TCO; S9 Action: N = Without S9; A = With S9 .

YG1026 with and without S9; however, the results were borderline and for the S9 condition gave results similar to the blank. The top level sample also gave a borderline response when using strain YG1026 with S9. The results were consisdered borderline when a dose-responsive result

that approached a two-fold increase over the spontaneous values occurred but the results were not statistically significant. The borderline results are noted with a question mark in Table 3. The mid-level and top-level samples were slightly toxic to the bacteria at the highest doses. For strain YG1021 both with and without S9, none of the 11/18-23/1994 samples were mutagenic.

Some of the tower samples collected 11/23-30/1994 (during more normal weather conditions) were clearly mutagenic. Samples were considered clearly mutagenic if a definable dose response was seen, more than a two-fold increase over spontaneous values was seen at one or more doses, statistical evaluation indicated significance (95% level of confidence), and the response was repeatable in an independent trial. Using strain YG1021 without S9, the top level showed some mutagenicity. All other samples were non-mutagenic for YG1021 both with and without activation. The YG1021 results were similar to those for 11/18-23/1994. The most significant mutagenicity was observed using YG1026 for air samples collected during this period not affected by a hurricane or tropical storm. The top and mid level samples were mutagenic both with and without S9 activation. The blank and surface samples were not mutagenic.

DISCUSSION

The hurricane conditions provided surprisingly unique conditions for the XAD sampling of non-particulate organic material in this ambient air study. Both the gravimetric analysis and bioassay results were comprehended after realizing the meteorological importance of this hurricane. After Tropical Storm Gordon moved over Florida, the warmth of the Gulf Stream increased its strength to hurricane force. During the first sampling period (11/15-18/1994), as is typical with pre-hurricane conditions, there was a huge pull of dry polluted air away from the continent and an analogous pull of clean moist marine air from the sea surface into the continent as seen historically [33]. A dry cusp seen on the south side clouds of the hurricane near the east coast confirmed that the dry air was pulled out from the continent [26]. The high pressure region in the North increased the clean inland sea breeze in North Carolina. Mass analysis of the collected tower air samples showed that the high winds transported VOCs, but the VOCs initially transported by Hurricane Gordon were not particularly mutagenic. These upper air samples for the first period (November 15-18, 1994) would not be expected to be mutagenic because the arenes had little opportunity for nitration because the air mass spent little time over land. Atmospheric nitrogen fixation occurs primarily over land because ammonia and NO_x emissions

are primarily anthropogenic or agricultural [2]. Only the surface level sample during this time period produced any indication of a mutagenic response for YG1021 (Table 3). Because YG1021 detects primarily compounds that cause frameshift mutations (e.g., PAHs, nitroaromatics, etc.), local anthropogenic sources may account for this activity. Although the rural location around the tower provided few anthropogenic emission sources, motor vehicles around the tower would have produced some PAH emissions.

The clean sea air aloft resulting from Hurricane Gordon continued into the second sampling period and limited the production of mutagens in the upper level samples (Table 3). Clean sea air most likely would not be nitrated but still could be oxidized by the upper oxidative atmosphere. For the sample collected during the second sampling period (November 18-23) as Hurricane Gordon traveled south, the mid level had twice as much mass as the other levels (Table 2). This increase in mid level mass probably was caused by the settling of arenes as the storm's disturbance left the North Carolina area. Many of the GC measurements [26] found the mid level having higher arene concentrations than either the top or surface levels. The mutagenicity of the top level with YG1021 when tested with S9 was questionably positive. All results with strain YG1026 were either non-mutagenic (negative) or gave borderline mutagenic (positive) results. When S9 was added to the bioassay, the blank for November 18-23, 1994 also gave a questionable mutagenic response with strain YG1026 (Table 3). Because all the blank canisters were never exposed to air outside the laboratory, preparation of the XAD, break-down by-products, or the chemical extraction procedure could be the source of this blank's contamination. All of the other blanks were clearly non-mutagenic.

The most mutagenic samples were obtained during the third period (November 23-30) that began several days after Hurricane Gordon had made land fall and turned into a tropical depression. Even though the final sampling period was the longest period, relatively small amounts of mass were recovered; however, these samples were the most mutagenic at the top and mid levels (Figure 1). Because this sampling period occurred during relatively normal weather patterns, expected atmospheric chemistry most likely occurred. Buoyant turbulence lifts the anthropogenic arenes and other emitted VOCs aloft where they could be oxidized by the photolytic decomposition of ozone in the production of free radicals. Turbulent eddies then would carry these oxidized arenes and other VOCs near the surface where they would combine with NO_x emissions to undergo nitrogen fixation. According to Pitts et al. [17], the collection of VOCs on the surface of water droplets combined with collection of HNO_3 along with the low pH of water droplets activates nitrogen fixation of VOCs. This nitrogen fixation reaction is generally so violent that no VOCs remain intact except for arenes that retain their aromatic

structure. In general, PAHs are so large that they attach to particles and are deposited more quickly than arenes [2,4]. Therefore, we postulate that arenes which are not degraded during atmospheric chemical nitration and do not undergo surface deposition are found aloft where they undergo long-range transport and nitration. As a result of their stability and dispersion, arenes would have higher concentrations at 240 m aloft when wind directions are from locations with significant anthropogenic sources. Nitrogenated arenes not only would retain their aromatic structure but many would be mutagenic. This explanation would be consistent with the GC measurement of high arene concentrations at mid and top levels (measured the previous two summers at this location [7, 26]) and the presence of direct-acting mutagens.

CONCLUSIONS

The mutagenicity results of this study support atmospheric nitrogen fixation of VOCs. In combination with previous studies done at this site using GC measurements and the observation of the frequent dispersion of anthropogenic pollutants from major cities, this study also supports the long-range transport of nitrogenated, mutagenic pollutants. Once buoyant turbulence lifts VOCs aloft to enable atmospheric oxidation, turbulence then brings these oxidized VOCs near the surface to mix with NO_x emissions. The resulting nitrogen fixation of atmospherically stable arenes would account for the mutagenic response seen at both the top and mid levels under normal meteorological conditions.

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