FINAL SUMMARY of RESEARCH -- NAG-1-02004

Calibration of EcoBadge Test-Strips for Ozone Measurement for GLOBE

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Background:

GLOBE protocols for ozone measurements involve the use of a colorimetric passive ozone monitoring system consisting of chemically-treated test papers marketed by the Vistanomics company[1] as EcoBadge® papers. While the performance of these papers has been adequate for periodic over-exposure detection in industrial settings and other environmental studies, the GLOBE program desires to use the indicator strips as a basis for data collection on a routine and global scale. As laboratory and field work with the strips progressed, it was found that their reliability was not as good as expected. We therefore undertook to improve the efficacy of the test papers in collaboration with their manufacturer, under the oversight of, and for the benefit of, the GLOBE project.

In early work[2] on the project we advised Vistanomics in formulation changes which improved the reproducibility and linearity of test strip response. There were, however, lingering concerns over the reliability of the monitoring papers when used under a great variety of conditions (heat, humidity, presence of other pollutants), and we believed that study of another system might be valuable. Thus we investigated an alternative indicator system[3,4,5] which we hoped would out-perform the current formulation. Our results[6] in this regard were disappointing, but we did verify to our satisfaction that the chemical indicator in current use is indeed the most effective reagent system available for this purpose (something the manufacturer had never verified). This simple, but effective, system[7] consists of absorbent paper treated with tin(II) diphenylcarbazide which reacts with ozone to change from white to purple. The intensity of the purple coloration is dependent on the concentration of ozone.

Of continuing concern to us, as well, was the erratic performance of the test papers at low ozone concentrations. Since it is anticipated that many of the field readings would be in the range of 0-100 ppb ozone, we felt it was important to determine whether a longer exposure period at such concentrations could improve the reliability and decrease the percent error of the readings. Some preliminary experiments had led us to believe this could be a fruitful undertaking. The work proposed under the grant (NAG-1-02004) then set out mainly to investigate the possibility of an alternative calibration curve for use at low ozone concentrations. At the time, the method of field measurement determination was a visual comparison to a calibrated color chart. Detection of small variations in very slightly colored samples was extremely difficult for many fieldtesters.

We also proposed to test the strips at both low and high ozone concentrations in a smog chamber where other parameters (temperature, humidity, competing oxidants) might be easily varied. Difficulties arose in scheduling the chamber originally planned, but an alternative site was found. Although all team members were unable to attend during the window of opportunity, a few tests were run by NASA-Langley colleagues Jack Fishman and Margaret Pippin. Their

results confirmed the earlier assertion that humidity and/or temperature could cause inconsistent and inaccurate color development in the monitoring strips. The smog chamber was not available for subsequent experiments during the period of this grant, but we have since then obtained funding[8] and resources for further laboratory experiments in this vein as it still remains a significant concern.

Plan and Progress:

The majority of our work, therefore, centered on experiments at an extended exposure period at low ozone concentrations, creating and programming the necessary calibration curve into a Zikua reader, and verifying that the Zikua would use the curve reliably. Zikua is a device supplied by Vistanomics to "read" the exposed EcoBadge cards and provide a read-out of measured ozone concentration in ppb. This device replaces the visual comparison to a calibrated color chart

For our initial studies, test papers were prepared by the usual method[9] in small batches. Although testing would also eventually include Vistanomics' EcoBadge papers, we began with papers prepared in our lab so that we could be assured of the freshness of each batch. We felt this would allow us better comparison among our runs as we varied exposure time. At the outset, our target acceptable error was about ±10 %. For example, if the actual ozone concen-tration was 20 ppb, then we hoped to be in the range 18-22 ppb. If the actual ozone concentration was 100 ppb, then we hoped to fall within 90-110 ppb in our measurements. Clearly a systematic error in the range of 3-4 ppb or more would significantly affect the lower exposure data.

Figure 1 shows an example of data collected at one-hour exposures to ozone concentrations below 100 ppb. The lines show the region of acceptable error. The inner (lighter) line indicates the ±10 % range, and the outer (darker) line demarcates the region for ±20 % error. The lines are derived from the average least-squares fit line for the data shown. While data are typical for this type of experiment, some variation may occur with a larger sample size.

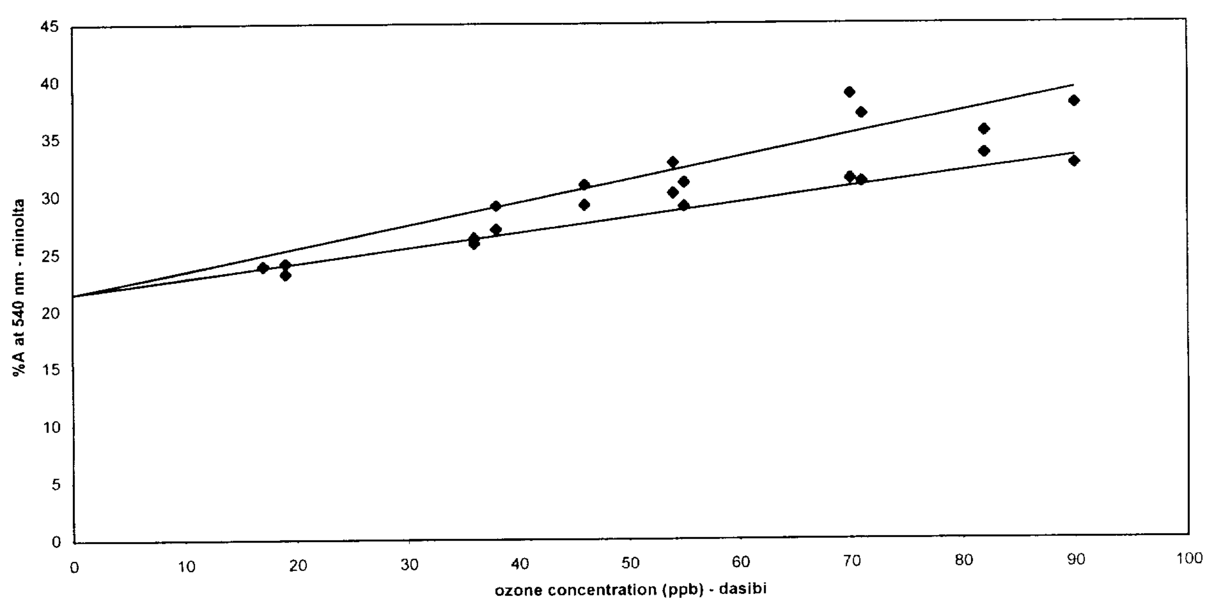

Figure 1. Results of one hour exposure to ozone. Absorbance was measured using a Minolta portable reflectance spectrophotometer. Ozone concentration was determined by a Dasibi down stream from the chamber.

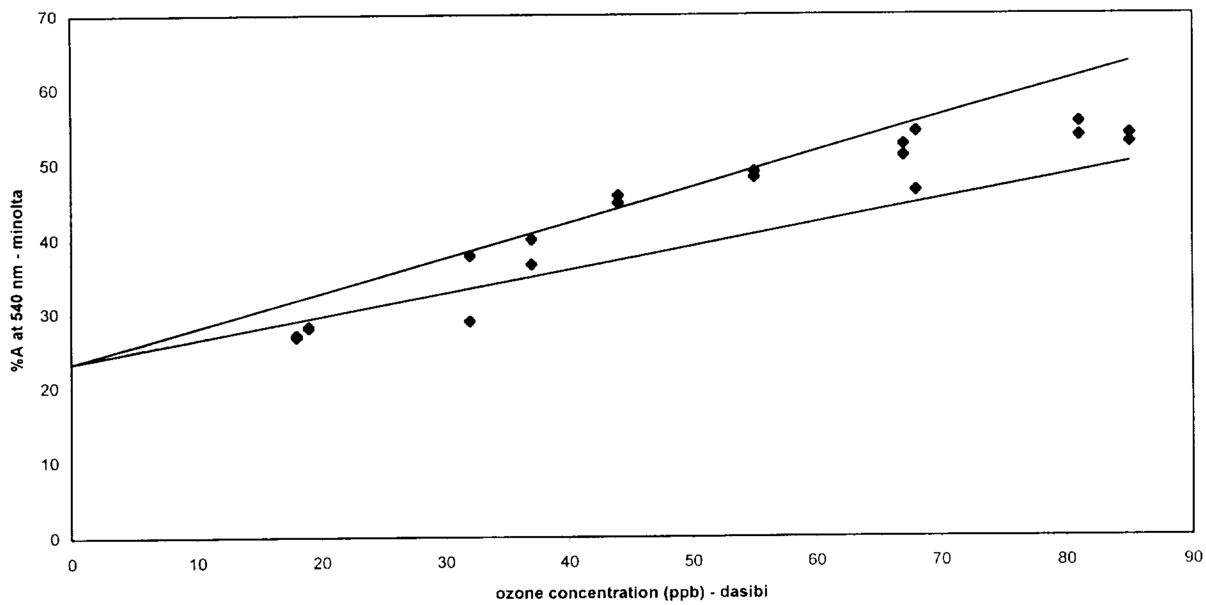

Figure 2. Results of two hour exposure to ozone. Absorbance was measured using a Minolta portable reflectance spectrophotometer. Ozone concentration was determined by a Dasibi down stream from the chamber.

Figure 2 shows example data points and error ranges for two-hour exposure times at ozone concentrations up to 100 ppb. Lines were derived in the same way as for Figure 1. Interestingly, it would seem that neither one- nor two-hour exposure times reliably give the ±10 % accuracy we were hoping to see. It is important to remember, however, that these tests were not run with actual EcoBadge papers. At this point we merely hoped to see if our hypothesis about extending exposure time was reasonable - and it did appear to be at least worth trying.

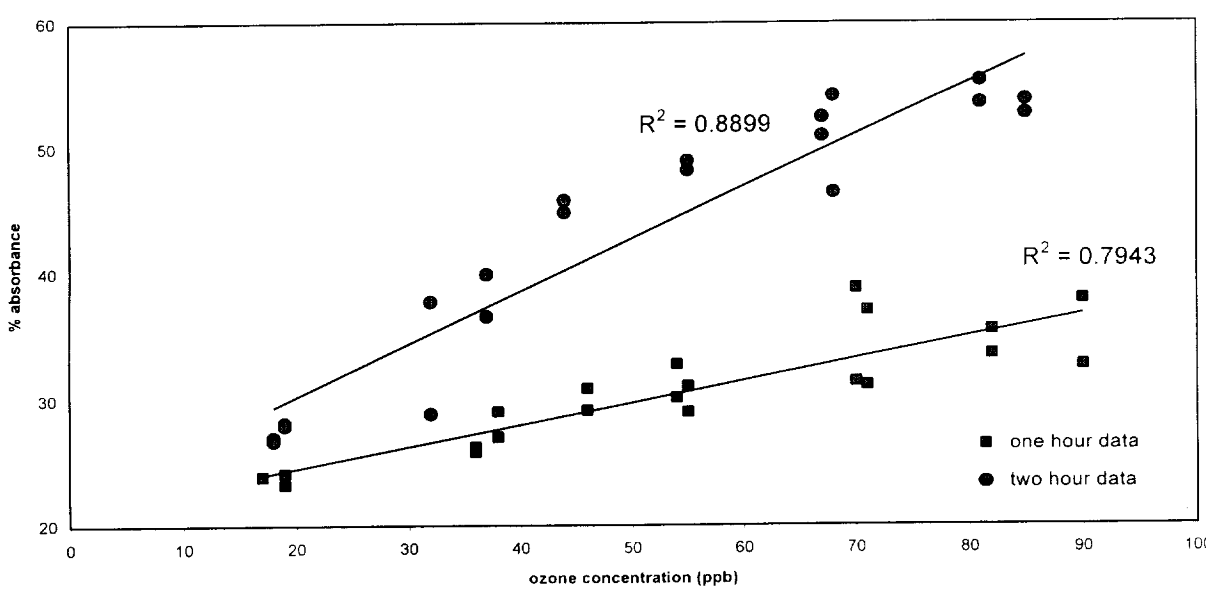

Figure 3. Comparison of one- and two-hour exposure data with least-squares analysis.

Figure 3 illustrates that the slope of the data line for the two-hour exposure is significantly greater than that for one-hour exposure. Qualitatively this manifests as a more pronounced coloration on the test strip. Even though the visual color comparison is no longer required one comment repeatedly made by fieldtesters has been that the test strips sometimes don't appear to show much color change, and therefore it is not clear to the experimenters whether that indicates very low ozone levels or a dysfunctional test strip! For our data we also found a better R^2 value for this least-squares analysis for the two-hour exposure. It is unclear whether this seemingly better linearity is coincidental or real. A larger sample size would be required for better statistical analysis.

At this point we began to experiment with EcoBadge papers and the Zikua reader supplied by Vistanomics. The Zikua is a compact device which measures the reflectance at a wavelength near 540 nm. The device then essentially compares the reading to a pre-programmed calibration curve and displays the concentration of ozone in ppb. The device comes with a default curve programmed for one-hour and 8-hour exposures. Because these are the readers being recommended in the GLOBE protocol, we wanted to learn how to program in a two-hour exposure calibration curve and test the results.

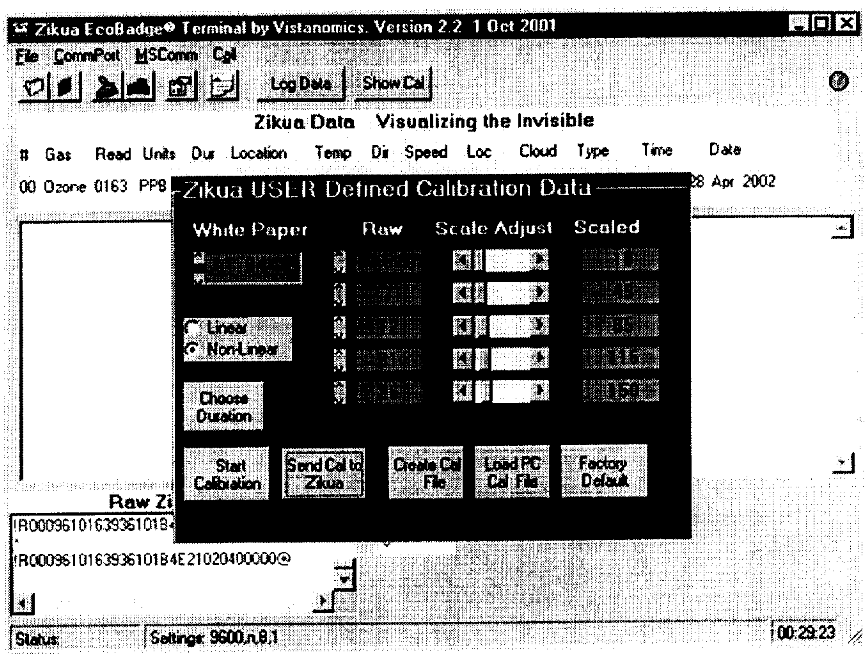

Figure 4. Screen shot showing Zikua calibration window for PC-user interface. All number values can be adjusted by the user to provide points on the calibration curve.

Several experimental runs at two-hour exposures (10-150 ppb ozone) were made to acquire points for our "user defined" two-hour exposure calibration curve. Raw data points from Zikua fell largely outside a linear least-squares relationship over this range when compared to reflectance spectrophotometer readings (R^2=0.8). However, we did use our data to attempt programming the Zikua. When further tests were run we measured the concentration of ozone in ppb on the Zikua (as well as measuring reflectance with the spectrophotometer). Predictably, the calibrated Zikua values corresponded disappointingly with a calibration curve based on spectrophotometric data. Figure 5 shows this comparison. For this analysis we see a slope of 0.75 (ideal = 1.0) and an R^2 of 0.786 (ideal 1.0).

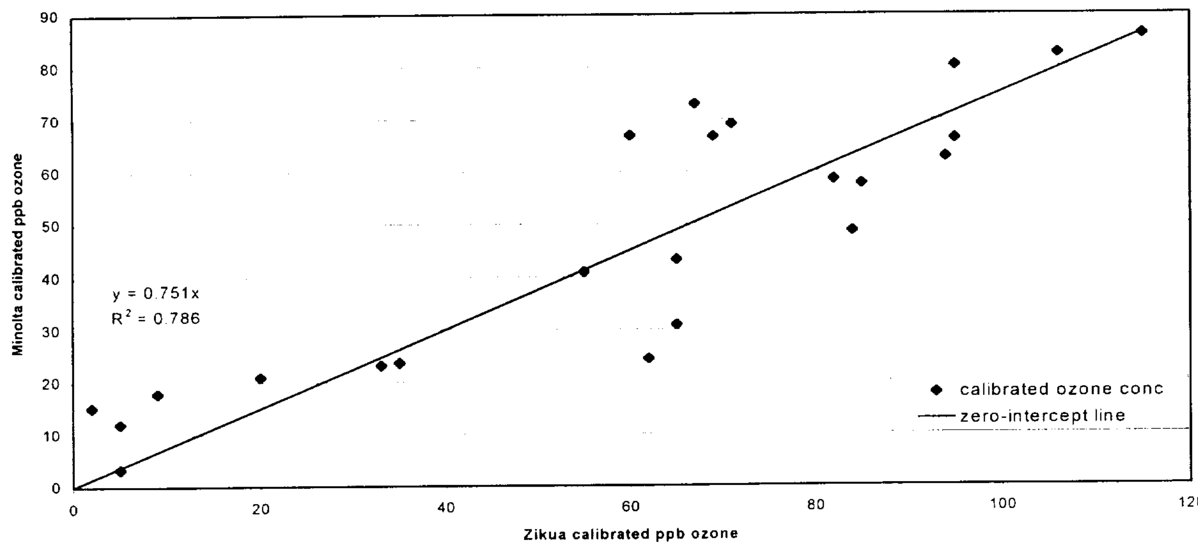

Figure 5. Comparison of ozone concentrations measured by calibrated Zikua and from a calibration curve based on reflectance spectrophotometer data. Readings were made on the same papers after two hour exposure.

However, Figure 6 shows the relationship of values from these calibration curves to actual ozone concentration (measured by a Dasibi) during the runs. The Zikua performed very well in this regard. We later learned[10] that EcoBadge papers are thin enough to allow the reflectance readings to vary depending on what is underneath them. This was something which did not apply to our runs with test papers prepared in our lab. For this data we cannot be sure the background was uniform for all spectrophotometer measurements, thus we can not make any conclusions with regard to the correspondence of spectrophotometer readings and Zikua values. More importantly, the potential for this same error exists in the Zikua readings when a second layer is used to assist in holding the sample paper against the detector. Later experiments[10] (after the period of this grant) led Vistanomics to work toward an opaque backing for the test papers.

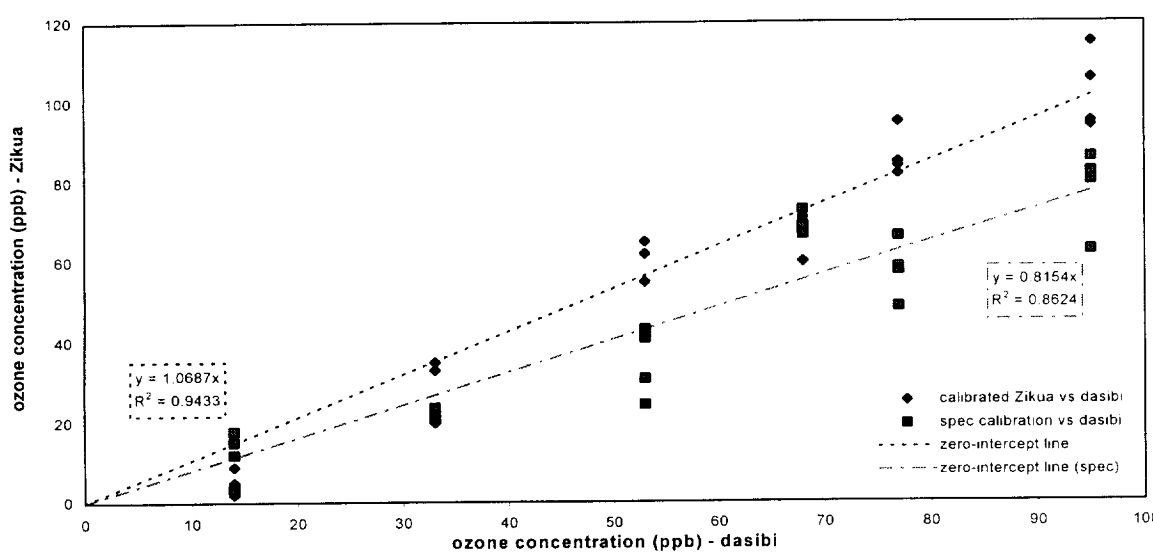

Figure 6. Comparison of two-hour exposure ozone measurements made by calibrated Zikua and by using a calibration curve based on spectrophotometric data. Both lines are constrained for zero-intercept.

Conclusions:

Our work under this grant has helped us to evaluate the feasibility of extending the exposure times for EcoBadge papers at low ozone concentrations. It would appear that a two-hour reading could at least be used to verify a low ozone measurement at the one-hour mark. This may help fieldtesters build confidence in the EcoBadge system and Zikua reader.

Unfortunately our specific data will be of little help in setting new calibration curves for the Zikua readers since the manufacturer has changed the programming in the intervening period. And, while the change corrected an inherent error in the device and its output, it renders our results somewhat suspect for future use. We hope to repeat our tests soon with improved Zikua readers (current available version) and verify our findings so that others can employ the extended exposure technique.

Acknowledgements:

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10. M. R. Pippin and L. C. Bush, experiments in November 2002.