Airborne observations of vegetation and implications for biogenic emission characterization

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Measuring hydrocarbons from aircraft represents one way to infer biogenic emissions at the surface. The focus of this paper is to show that complementary remote sensing information can be provided by optical measurements of a vegetation index, which is readily measured with high temporal coverage using reflectance data. We examine the similarities between the vegetation index and in situ measurements of the chemicals isoprene, methacrolein, and alpha-pinene to estimate whether the temporal behavior of the in situ measurements of these chemicals could be better understood by the addition of the vegetation index. Data were compared for flights conducted around Houston in August and September 2000. The three independent sets of chemical measurements examined correspond reasonably well with the vegetation index curves for the majority of flight days. While low values of the vegetation index always correspond to low values of the in situ chemical measurements, high values of the index correspond to both high and low values of the chemical measurements. In this sense it represents an upper limit when compared with in situ data (assuming the calibration constant is adequately chosen). This result suggests that while the vegetation index cannot represent a purely predictive relationship between vegetation indices and local concentrations of these chemicals, it represents a complementary measurement that can be useful in understanding comparisons of various in situ observations, particularly when these observations occur with relatively low temporal frequency. In situ isoprene measurements and the vegetation index were also compared to an isoprene emission inventory to provide additional insight on broad issues relating to the use of vegetation indices in emission database development.

1. Introduction

Understanding the contributions of biogenic sources to total hydrocarbon emissions has taken on greater importance in recent years. This is due in part to research showing that biogenic gases, such as isoprene and monoterpenes emitted largely by plants, have an important impact on atmospheric chemistry, particularly on the formation of tropospheric ozone.1–3 The spatial distribution of the concentrations of these biogenic chemicals can be measured, for example, from an aircraft using in situ measurements or collecting samples in canisters. However, many of these measurement techniques tend to be too infrequent to give complete information over the duration of a flight. Such measurements may be aided if information could be inferred from fast-response remote sensing observations of the underlying 'greenness' of the surface, quantified as a vegetation index. Further, studies of the relationship between vegetation indices and local concentrations of biogenic gases could assist efforts to use satellite observations to infer information about emissions on broader scales. In this paper, we present an aircraft-based case study carried out over Houston, Texas and surrounding areas comparing a spectrally-derived vegetation index and in situ measurements of three chemicals associated with plant emissions: isoprene (direct emission), methacrolein (a product of isoprene photo-oxidation), and alpha-pinene (direct emission).

In the next section, we briefly discuss the sources and properties of these biogenic gases, summarize the spectral properties of chlorophyll, and describe our spectral measurements. In section 3, we compare the vegetation index to the measured abundances of these chemical species as well as to a surface emission map of isoprene. We then discuss the implications for the improvement of biogenic emissions inventories.

2. Background

2.1 Isoprene, methacrolein, alpha-pinene

Isoprene is a principal reactive biogenic non-methane hydrocarbon in the atmosphere and is emitted by some deciduous tree species, primarily oak trees.4 Isoprene fluxes have been found to depend on light intensity, leaf temperature, seasonal temperature variations, and carbon dioxide concentrations.5–8 Emissions generally increase with light intensity, but become saturated at higher light intensities; similarly, emissions increase with leaf temperature up to about 35 °C, and then start to decrease with temperatures above 40 °C.5 In general, water stress has been found to cause little, if any, reduction in the isoprene emission rate during both short and prolonged periods of drought.9–11 Isoprene has a lifetime of only a few hours in the sunlit atmosphere because it reacts readily with the hydroxyl radical.12–13 In the presence of high concentrations of NOx, the oxidation of isoprene can lead to the formation of tropospheric ozone, Trainer et al.2 and Chameides et al.3 estimated that up to 40% of the elevated ozone concentration in some cities comes from biogenic isoprene emissions. Isoprene reactions also can affect the amount of carbon monoxide and methane in the atmosphere. In one study by Jacob et al.,14 it

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was found that as much as 27% of carbon monoxide in North America comes from reactions of isoprene. For these reasons, the need to know how much isoprene is emitted in any given region is becoming more and more apparent. While isoprene is the primary focus of this study, we have also examined methacrolein and alpha-pinene. Methacrolein is an oxidation product of isoprene, and alpha-pinene is a monoterpene emitted by coniferous species. Monoterpene emissions may also be affected by diurnal variations in relative humidity, foliar moisture, light intensity, and leaf temperature.\textsuperscript{5, 15–17}

Concentrations of these species and other hydrocarbons were measured with \textit{in situ} techniques in Texas aboard the Electra aircraft in August and September 2000 as part of the Texas Air Quality Study (TexAQS). Eight flights have been analyzed and two representative flights are discussed here. Three different research teams measured these three gases: one from the National Center for Atmospheric Research (NCAR), one from the National Oceanic and Atmospheric Administration (NOAA), and one from the Institut für Ionenphysik at the Universität Innsbruck in Innsbruck, Austria. NCAR’s measurement technique was to use stainless steel canisters to collect air samples on the plane and then analyze the samples post-flight using gas chromatography with flame ionization and mass spectrometric detection. The canisters, which are originally kept at vacuum, take about 10–18 s to fill 2.5 atmospheres, and the operator can fill them at his discretion. The details of this process are described by Greenberg\textsuperscript{18}.

Approximately 40 canisters were filled during each flight.

NOAA’s samples were collected and analyzed in near real-time using an automated gas chromatograph-flame ionization detector system, as described by Goldan \textit{et al.}\textsuperscript{19} NOAA’s automated gas chromatography (GC) system took measurements at equal intervals throughout the flights, about every 15 min. In general, it took around 18 s to collect these samples.

A third set of measurements were made and analyzed using the Proton-Transfer-Reaction Mass Spectrometer system described by Hansel and Wisthaler\textsuperscript{20} and references therein. These measurements were taken at a faster sampling rate, about every 25 s.

### 2.2 The chlorophyll spectrum and definition of a vegetation index

Chlorophyll \textit{a}, one of the pigments within plant leaves, has a unique spectral fingerprint at visible wavelengths, so that observations of reflected radiation are affected by the amount of chlorophyll present in a certain region.\textsuperscript{21} Chlorophyll \textit{a} absorbs strongly in the red part of the visible spectrum and reflects strongly in the green and infrared. The absorption peak (or reflectance dip) between 660–680 nm is characteristic of chlorophyll \textit{a} and is termed the \textit{red edge}. While other forms of chlorophyll are more stable in plants under some conditions, such as during the autumn color change, here we focus on green plants in mid-summer, and hence, on chlorophyll \textit{a} (Raven \textit{et al.}\textsuperscript{22} notes that chlorophyll \textit{b} generally constitutes 25% of the total chlorophyll content in green plants).

A vegetation index is a ratio between the amount of reflected radiation measured by a spectrometer at two different wavelengths. There are many different vegetation indices that have been developed in the last few decades, but most use some choice of near infrared reflectance divided by visible reflectance. The vegetation index used in this study is the PSSRa index, which was chosen because of its high correlation to the actual extracted chlorophyll \textit{a} concentration from deciduous plant leaves.\textsuperscript{23} The PSSRa index is defined by

\[ PSSRa = \frac{R_{800 \text{ nm}}}{R_{680 \text{ nm}}} \]  

where \( R \) is the percentage reflectance at the specified wavelength for the observation.

It should be noted that our observations are of radiance and not reflectance, but that in clear skies, the ratio of reflectance is proportional to the ratio of radiance at these wavelengths, since the atmospheric scattering due to Rayleigh and aerosol scattering is relatively small. In other words, there is the implicit assumption that the ratio of the incident energies at 800 nm to 680 nm on the vegetation index remains unchanged. In order to distinguish that the index we use in this study is based on radiance, we will refer to our index as PSSRa*. The index R750/R705 developed by Gitelson and Merzlyak\textsuperscript{23} and discussed in Sims and Gamon\textsuperscript{24} was also examined, but the differences between the two indices in this case were negligible.

The reflectance data used for calculating the vegetation index was taken from the absorption spectrograph MIDAS (Miniature Differential Absorption Spectroscopy), which was deployed by NOAA, Melamed \textit{et al.}\textsuperscript{25} The primary application of this instrument has been to measure trace gases such as NO\textsubscript{2}. However, here we demonstrate its utility in providing information about vegetation “greenness”. MIDAS is composed of two commercially purchased crossed Czerny-Turner spectographs that collected spectra of light reflected from the ground or scattered from the sky during the TexAQS campaign. The spectrographs were cooled to \(-20 \degree C\) to reduce noise and to improve the stability of the dark current from the 2048 element charge-coupled device (CCD) array. A grating with 1200 lines per mm and a slit width of 50 \( \mu \text{m}\) produces a full-width-half-maximum (FWHM) resolution of approximately 1.0 nm over the 425–725 nm wavelength range. Fiber optics directed the incoming light, which was collected by zenith and nadir viewing lenses, into each spectrograph; however, only nadir viewing spectrograph data was used.

![Fig. 1](image)

\( \text{Fig. 1.} \) (a) The spectrum for a low value of the vegetation index PSSRa* and (b) the spectrum for a high value PSSRa*. Several major molecular absorption bands are shown, and the vertical gray lines indicate 680 and 800 nm.
here. This spectrometer used a 0.2 neutral density filter. The field of view was approximately 1°.

To illustrate the principle behind the vegetation index, we present a spectrum for a measurement with little green vegetation and one for a region with abundant green vegetation, as gauged by an onboard observer (Fig. 1). The spectrum for a vegetation “low” in Fig. 1(a) appears markedly different than the spectrum for a vegetation “peak” in Fig. 1(b). The “low” spectrum is comparable in spectral character and shape to a normal sky spectrum, since chlorophyll, as expected, is of minor importance. Fig. 1 identifies spectral features of oxygen and water vapor, illustrating where these atmospheric absorbers influence the measurements and thus delineating what wavelengths may best provide information on chlorophyll. No other significant molecular absorption features occur near the wavelengths used to calculate PSSRa* (680 and 800 nm, marked in Fig. 1 with vertical gray lines). Dividing the intensity at 800 nm by 680 nm for the “low” spectrum gives a small ratio, indicating little vegetation. However, the “high” spectrum shows strong absorption around 660–680 nm, the red edge for chlorophyll a. The calculated vegetation index for this spectrum is large, indicating the predominant role of vegetation in determining the spectral behavior of light reflected from the surface.

Spectra similar to those in Fig. 1 were taken every 5 s during the TexAQS campaign, providing continuous high temporal resolution.

3. Results and discussion

In this section, we compare in situ observations of isoprene, methacrolein, and alpha-pinene with the vegetation index. We also examine the similarities between the vegetation index and an isoprene emission inventory.

3.1 Data processing

In calculating the vegetation index for each spectrum, ±1.5 nm (around 680 and 800 nm) were averaged in order to reduce random measurement noise. Moreover, the wavelength response of the spectrometer was taken into account using a factor of 2.8 ± 0.15, which was estimated from observations of a laboratory light source of known spectral shape.

Data taken when the plane was above 1 km in altitude (approximately the top of the boundary layer) were not considered in this study, because above this height, the in situ chemical measurements are often decoupled from surface emissions. Errors may still result because the chosen cut-off altitude (1 km) may be higher than the boundary layer on some occasions. Finally, data taken over the ocean were not included in the analysis because, in the absence of advection, low vegetation index values and low in situ hydrocarbon abundances are expected, which would contribute little information to our comparisons.

The vegetation index PSSRa* was examined for 8 days of NOAA’s MIDAS intensity data in order to determine areas of vegetation for each day. The 8 days were chosen based on whether the three in situ techniques acquired an adequate number of measurements and whether there was too much cloud cover, as cloud cover could degrade the correspondence between PSSRa and PSSRa*. The 2 days discussed here represent results consistent during all 8 days. In making comparisons to the in situ data, 2 min smoothing is performed on the vegetation index data and the surface emission data in

![Map of isoprene emissions](https://example.com/map.png)

**Fig. 2** Map of isoprene emissions (µg C m⁻² h⁻¹) over the Houston area (outlined in gold) for a typical summer day at 12 pm local time. The thick black line represents the flight track for September 1, 2000, and the markers (yellow = NOAA, red = NCAR) indicate where a chemical measurement was made. Labeled markers are discussed below. Light blue lines indicate rivers, brown lines indicate major roads, and the Texas coast is outlined in black. Areas of zero isoprene emission are purple, while areas of high isoprene emission are yellow and orange (Wiedinmyer et al.²⁷).
order to spatially average the data, since the in situ measurements capture air that is emitted over an extended region due to atmospheric mixing. The same smoothing is also applied to the proton-transfer data for consistency.

### 3.2 Example: September 1st, 2000

September 1st is one of the days chosen to illustrate the similarities and differences between the vegetation index PSSRa* and the chemical measurements. A map of isoprene emission estimates (Fig. 2) was created by applying the GLOBal Biogenic Emissions and Interactions System version 2 (GLOBEIS2) model to Texas land cover data, using algorithms and land cover data discussed by Wiedinmyer et al.\textsuperscript{26,27} The mapped isoprene emissions represent flux estimates for a typical summer day at 12 pm local time; this inventory has a 4 km resolution, and the emissions are in units of µg C m\textsuperscript{-2} h\textsuperscript{-1}. The flight path and measurement locations for September 1, 2000 are plotted over the mapped isoprene flux estimates on Fig. 2 to show the spatial locations of NCAR and NOAA measurements (the points where measurements were taken are illustrated with yellow circles for NOAA GC measurements and red triangles for NCAR canister measurements, and the marked points are discussed below). The vegetation index measurements were taken along the flight path approximately every 5 s with MIDAS.

Fig. 3 compares the vegetation index and the mapped isoprene emissions along the flight path for September 1st from Fig. 2. A correlation between the mapped isoprene emissions and the MIDAS data could be expected because they are both related to land cover and remote measurements. However, the mapped isoprene data also includes data other than remote sensing data (including ground-based land inventories), and their land type map is input into a model (which differentiates between species) to compute the isoprene emissions. Thus, we are encouraged by the high degree of correlation (the linear correlation coefficient, $r$, is 0.822)

![Fig. 3 PSSRa* versus mapped isoprene emissions.](image)

![Fig. 4 PSSRa* and NCAR/NOAA (a) isoprene, (b) methacrolein, and (c) alpha-pinene versus time for September 1st. Black line in (a) shows isoprene emissions estimates (refer to Fig. 2) along September 1st flight path.](image)
between the data sets, even though there is much scatter. There are many factors that could cause scatter between these data. First, the vegetation is not static and could have changed after the emissions inventory was produced. Second, the vegetation index is based on data sampled with higher spatial frequency than is resolved by the isoprene emissions map. Third, the PSSRa* index is based on "greenness" alone, and not the type of vegetation (which can greatly influence the isoprene emission). Given these, the relatively strong correlation seen in Fig. 3 is encouraging and shows that this index can possibly aid the interpretation of isoprene measurements.

Fig. 4(a), (b), and (c) show the PSSRa* index along with the NCAR (red) and NOAA (yellow) isoprene, methacrolein, and alpha-pinene data, respectively, for September 1st, 2000. Alpha-pinene was measured only by NCAR, while both NOAA and NCAR measured the other gases. Additionally, Fig. 4(a) shows the mapped isoprene emissions along the flight path. The spaces in the vegetation curve indicate regions where the aircraft was above 1 km in altitude, thus times excluded from the analysis. NOAA measurements have ±3% precision with a detection limit of 5 pptv. NCAR isoprene measurements have a precision of ±5% and NCAR alpha-pinene and methacrolein measurements have a precision of ±15%, with a detection limit of about 5 pptv. The error bars are not shown on the graphs for clarity, but the errors are too small to account for any differences between the curves.

It is clear that while the vegetation index captures some of the variation of the chemical measurements, there are important differences as well. In addition, the large temporal spacing between the chemical measurements causes challenges in the comparisons. An example of this occurs between NCAR (red) points A and B (Fig. 4(a)), where NOAA happens to measure a peak in isoprene (yellow point 1) at the same time that a peak in vegetation is measured, while the NCAR measurement misses this particular peak. The vegetation index data convincingly show, however, that there were substantial surface vegetation variations during this time period and that the NOAA/NCAR measured differences were likely consistent with these variations. The emissions map (Fig. 2) illustrates why NCAR missed the peak in isoprene between these two points; during that time, the aircraft passed over a large forest, and NCAR happened to not take a measurement. Looking at both NOAA and NCAR measurements reveals more information about how much isoprene was actually present. In addition, Fig. 4(a) suggests that the vegetation index presents useful qualitative information regarding the relative amount of isoprene for those locations where both in situ measurements are too sparse. A similar conclusion can be drawn from the comparison of alpha-pinene and methacrolein to the vegetation index.

At some locations when both NCAR and NOAA took measurements at nearly the same time, different isoprene concentrations were measured (red point C and yellow point 2). This discrepancy probably indicates that hydrocarbon concentrations can change rapidly in both space and time depending on ambient atmospheric conditions. This raises a concern that the in situ chemical measurements do not adequately characterize the compounds on the timescale of the vegetation index measurements (which have been sampled more frequently). In addition, there are many locations where very low chemical concentrations are measured at locations where the vegetation index is moderate or high (yellow points 3 and 4). While there could be many causes for this, one possibility is that the compounds are not well mixed due to their short lifetimes.

Fig. 4(a) includes a curve of the estimated isoprene emissions, also averaged over a 2 min interval, from the GLOBEIS2 model along the flight path on September 1st (refer to Fig. 2). The relatively close relationship between the vegetation index and the mapped isoprene estimates is evident (refer to Fig. 3).

In general, the peak isoprene measurements for both NOAA and NCAR agree broadly with the PSSRa* index and modeled isoprene emissions curve (i.e., they fall in areas of expected high isoprene emissions or greenness). Inconsistencies that do occur between the mapped emissions and the in situ measurements probably reflect factors such as inaccuracies in the emission estimates or the role of winds in transporting isoprene away from its sources (although wind speeds were generally low throughout the TexAQS experiment, which occurred largely during a summer high pressure event), or incomplete mixing in the boundary layer. There are also locations where the vegetation index measures a high level of greenness even though the isoprene emission inventory and the in situ measurements have...
low values (e.g., red point A), which may indicate that we were passing over a type of green vegetation that emits little isoprene.

Isoprene was also measured using the proton-transfer technique at much faster sampling rate than the NOAA and NCAR measurements. Two-minute averages of the proton-transfer isoprene measurements are compared in Fig. 5(a) with the vegetation index averaged in the same way. The proton-transfer isoprene data show much of the same behavior as the NOAA and NCAR isoprene data discussed above. This is demonstrated in a scatter plot of the proton-transfer isoprene and PSSRa* index in Fig. 5(b). We see that the PSSRa* index is loosely correlated with the proton-transfer isoprene data but with large scatter, especially at larger values of isoprene. High values of isoprene are generally only measured concurrently with high PSSRa* (i.e., green vegetation) but small values of isoprene are measured over all levels of the vegetation index. In other words, the vegetation index tends to overestimate the spatial extent of elevated concentrations. The vegetation index could be used as an upper limit estimate of the in situ data (assuming a calibration constant is adequately chosen).

The lack of high isoprene being measured over vegetation with low PSSRa* suggests that isoprene rarely gets transported far from the regions where it is emitted during the measurement period, which is consistent with its short lifetime of about 2 h and the relatively windless conditions prevalent. In addition, it shows that non-green vegetation does not emit isoprene. The large scatter over areas with high PSSRa* could have many causes, including the lack of mixing in the boundary layer, the fact that different vegetation with the same greenness emit isoprene differently, and the effects of changes in temperature and humidity when the measurements were taken. The first of these is likely to be the dominant source of inconsistency, since the vegetation index was shown to be well correlated with the mapped isoprene emission inventory above (see Fig. 3). This is demonstrated in Fig. 5(c), which shows a scatter plot between the proton-transfer isoprene and the mapped isoprene emissions. This has the same characteristics as the scatter plot between the proton-transfer isoprene and the PSSRa* index (Fig. 5(b)), which implies that the vegetation index does as well as the isoprene emission map in predicting the measured isoprene. Thus, effects of the varying emission rates of different green vegetation must not be playing a large role.

### 3.3 Example: September 6th, 2000

September 6th provides another example of comparing the vegetation index with chemical measurements. Fig. 6(a), (b), and (c) show the September 6th time series for the vegetation index and the chemicals isoprene, methacrolein, and alpha-pinene, respectively. Fig. 6(a) also includes the mapped isoprene emissions curve. These figures show results similar to those of September 1st, including the relatively good correlation of the PSSRa* index with the mapped isoprene emissions and the fact that the chemical measurements capture some of the peaks in the vegetation index while missing others.

![Figure 6](image_url)

**Fig. 6** PSSRa* and NCAR/NOAA (a) isoprene, (b) methacrolein, and (c) alpha-pinene versus time for September 6th. Black line in (a) shows isoprene emissions estimates along September 6th flight path.
Again, low values of chemical concentrations and the vegetation index correspond, but both low and high values of the chemicals are measured for high values of the vegetation index.

4. Conclusions

The relationships between the vegetation index, PSSRa*, and the concentrations of isoprene, methacrolein, and alpha-pinene have been examined in this study. In particular, low values of the vegetation index always coincide with low values of the in situ measurements, and high values of the chemical species coincide with high values of the vegetation index. However, low values for the chemical abundances do occur even when the vegetation index is high. There are many natural phenomena that could cause this disparity to occur, such as uneven mixing in the atmosphere, the high reactivity of hydrocarbons, differences in isoprene emission from different types of vegetation, localized winds, or effects on hydrocarbon emission rates due to changes in temperature and humidity. Due to these factors, the relationship of the vegetation index to actual in situ measurements is not unique. In general, the vegetation index has a tendency to overestimate the spatial extent of elevated concentration and when the calibration constant is adequately chosen provides an upper limit to the in situ measurements.

Nevertheless, the relationship between the vegetative index and the mapped isoprene emissions database is reasonably linear, indicating the promise of using the index for inferring concentrations of biogenic chemicals over vegetated areas. In areas where the scarcity of measurements or a disagreement between two measurement methods exists, looking at the vegetation index may prove useful as a guideline. This technique for estimating the abundances of biogenic chemicals could serve to indicate approximate levels of certain hydrocarbons when other data are too infrequent to provide the complete picture.

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