## Conference or Workshop Item

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# PTR-MS measurements of concentrations and fluxes of biogenic VOCs in the humid tropics - rain forest vs. oil palm plantation

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## Abstract

For the first time, concentrations and eddy covariance fluxes of several of the most abundant biogenic volatile organic compounds (VOCs) have been measured by PTR-MS in SE Asia (Malaysian Borneo) at two locations: at 75 m on a GAW tower over secondary rain forest and above an oil palm canopy. The operation of the instrument at both sites and the results are discussed in respect of the extremely high ambient humidity levels, which are not generally encountered outside of the humid tropics. Despite the challenging conditions, smooth operation could be achieved through instrument optimisation and anticondensation protection of the instrument set-up generally. The most abundant VOC was isoprene, with peak emissions of 4.7 mg m$^{-2}$ h$^{-1}$ above the rainforest and 30 mg m$^{-2}$ h$^{-1}$ above the oil palms. For most VOCs good sensitivities were obtained, but some of the strongly cluster-dependent OVOC species suffered a reduction in their detection limits. The results from both sites are presented, focussing on the effect of the different ambient humidity, which affected the normalised signal. At standard drift conditions the proton transfer reaction is known to dominate over the reaction with water clusters. However, at high humidities, water clusters appear to play a more significant role in the ultimate detection efficiencies. Nevertheless, PTR-MS has been proven to be capable of measuring various VOCs even in extreme tropical environments. In addition, some ideas for future instrument adjustments to facilitate tropical measurements are proposed.

## Introduction

For more than a decade Proton Transfer Reaction Mass Spectrometry (PTR-MS) has been serving as an enormously useful analytical tool among others in atmospheric sciences. Facing environmental issues such as Global Warming or Global Climate Change, it becomes necessary to better understand atmospheric processes. However, since many important atmospheric constituents are present in low concentrations PTR-MS requires appropriate optimisation to come up with the desired detection limit. Both ambient humidity and the level of relative $H_2O$ clusters in the reaction chamber impact the optimal detection limit that can be achieved. Thus, adaptation of PTR-MS technique to measurements in very humid environment can be essential for the precise quantification of volatile organic compounds (VOCs) emitted to the atmosphere. This, in turn, is needed for elaboration of dynamic models predicting regional and global climate changes.

PTR-MS was indeed a breakthrough invention allowing for its combination with most direct and accurate micrometeorological methods such as eddy covariance for obtaining VOC fluxes at ecosystem and regional scales. It is also possible to measure water vapour fluxes by PTR-MS, but in order to obtain absolute values calibration against a sensor of absolute humidity is necessary.

Not a long time ago it was observed that plants emit vast amounts of volatile substances to the atmosphere. These include for example compounds like isoprene, monoterpenes, methanol, acetaldehyde or acetone as well as a variety of other metabolic, stress, or signalling compounds. According to recent estimates [1] , biogenic sources globally far exceed those of an anthropogenic origin, which on the other hand can dominate locally around large cities. There have been numerous studies already involving PTR-MS of the polluted urban environment, as well as focussing on emissions from forests and other vegetation types. There is still a limited number of VOC flux measurements over tropical regions apart from some data from the Amazon. In the collaborative projects of OP3 and ACES ground and aircraft measurements were carried out for the first time in Borneo in 2008. Some of these results are presented here. Although the PTR-MS technique is now quite well known, at some conditions running the instrument can be quite difficult, for example at extremely high specific humidity levels and high temperature. When sampling the air along a sampling inlet line (e.g. PTFE), one needs to prevent water condensation, which could potentially result in a loss of the flux data and flood the instrument. One of the widely used methods is heating the line, although some groups limit the heated segment to inside the building only and some heat the whole length of the tubing. Another way is to decrease the pressure in the line by using a high flow vacuum pump for the inlet line. A combination of those methods was used at the rainforest and the oil palm sites and specific optimisation of the PTR-MS led to its steady operation.

## Experimental Methods

### Rainforest

The VOC analyzer was the PTR-MS from CEH Edinburgh, corresponding to the high sensitivity (HS) type, and described elsewhere in detail (e.g.). The fluxes were measured by the virtual Disjunct Eddy Covariance (vDEC) technique, which was introduced by Thomas Karl in 2002 [2]. The schematic of the setup is presented in Fig. 1a. The air was drawn from 76 m above the ground level through ½'' PTFE tubing, of which the inlet was connected in the vicinity of the Windmaster Pro sonic anemometer. The flow rate in the sample line was kept constant at 56 l/min (measured at the inlet), so as to sustain the turbulence and to prevent water condensation. For the latter reason, the segments of the tube at the ground and inside the building were additionally heated to approx. 40 °C by a heating tape wrapped around the tube and were further protected by enclosure in an insulation sleeve. Following previous studies of dew point influence on sensitivity according to the E/N ratio, the PTR-MS system was optimized for operation at relatively high E/N ratio of 130 Td for the purpose of preventing excessive clustering. In order to keep the drift pressure at a constant value (fluctuation free) when connected to the low pressure line it was lowered from 200 Pa (normally used) to 178 Pa, and the drift voltage was adjusted to 500 V and the temperature to 45 °C.

**Oil palm plantation**

The same PTR-MS was used at the oil plantation and the same flux technique was used. The pictures of the site set up are presented in Fig. 2. The E/N ratio was kept constant at 140 Td by adjusting drift tube parameters of pressure to 160 Pa, temperature to 45 °C and the drift voltage to 485 V. The sampling inlet and the 20Hz R3 sonic anemometer were placed at about 15 m (5 m above the canopy level). The instrument and tubing were protected against water condensation by heating above the ambient temperature (approx. 50 ºC). The inlet pressure was reduced by maintaining the constant flow in the sampling line of 35 l/min.



a)                                                                                          b)
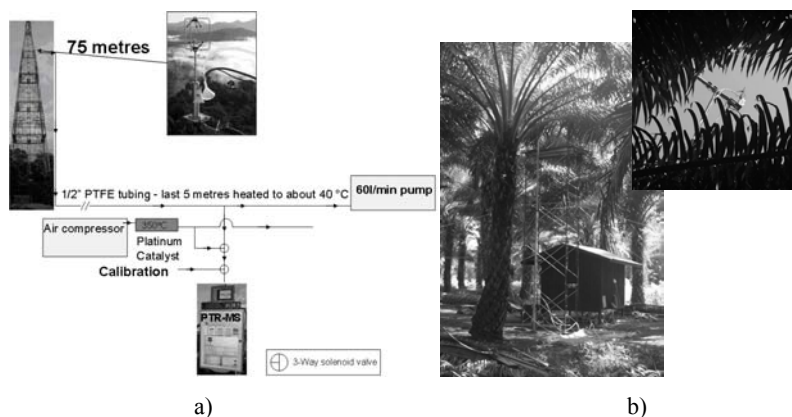
*Figure 1: Setup a) rainforest b) oil palm plantation*

## Results and discussion

The PTR-MS technique was coupled to virtual disjunct eddy covariance at both the rainforest and the oil palm sites. The concentrations and fluxes of several key compounds were obtained as well as the scans of the whole spectrum of m/z of the ambient air. For several VOCs (i.e. methanol, acetone, acetaldehyde, isoprene, monoterpenes and acetonitrile) external calibration was used in deriving their sensitivities, while remaining compounds had their sensitivity approximated from the relationship between calibration and transmission curves. The calibrated sensitivities for the compounds contained in the standard were dependent on the level of water clusters at m/z 37, which was different at the two sites. The air sampled from 15 meters at the plantation was usually completely saturated with water and its specific humidity exceeded the one sampled at the rainforest site. Thus generally higher normalised sensitivities were obtained at the rainforest for m/z susceptible to clustering. Sensitivities for isoprene were similar. The clear water vapour flux could be derived from m/z 37. Figure 2 shows the diurnal patterns of water vapour fluxes measured at the oil palm plantation by PTR-MS and Li-COR (infra-red gas analyser).
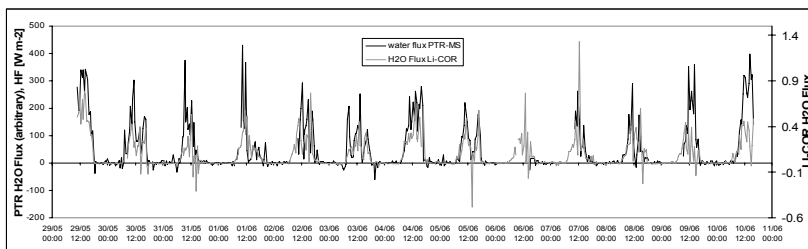
*Figure 2: The  timeseries of water fluxes at oil palm plantation derived from PTR-MS (black) and contrasted with the same data from Li-COR (grey).*

At both sites the most abundant VOC was isoprene, with peak emissions of 4.7 mg m$^{-2}$ h$^{-1}$ above the rainforest and 30 mg m$^{-2}$ h$^{-1}$ above the oil palms. The averaged diurnal fluxes throughout the campaigns are shown in Figure 3.
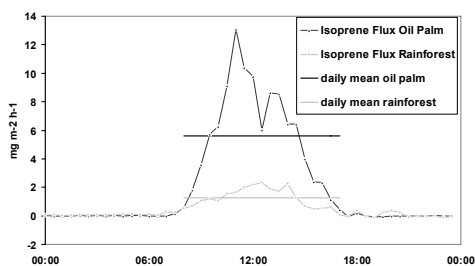


*Figure 3: Isoprene flux comparison between the sites based on diurnal averages. Horizontal lines denote means of the whole periods.*

Six times higher isoprene emissions from oil palm can have implications for regional zone, for example in terms of ozone and secondary organic aerosol formation as well as radical chemistry in troposphere.In addition, a range of other VOCs were measured and examples are presented as diurnal averages in Figure 4.
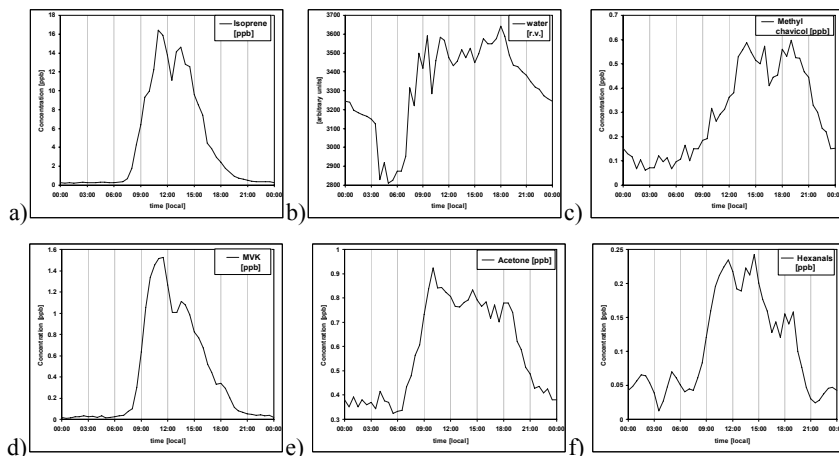


*Figure 4: Diurnal averages of concentrations of selected VOCs at the oil palm site.a) isoprene; b) water vapour c) methyl chavicol d) methyl vinyl ketone / methacroleine   e) acetone f) hexanals*

A similar trend of isoprene and its oxidation products (MVK/MACR) as well as acetone and hexanals was observed. Processing and analysis of the results from both campaigns are ongoing.

## References

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