



THE EFFECT OF ELEVATED ATMOSPHERIC CARBON DIOXIDE  
MIXING RATIOS ON THE EMISSION OF VOLATILE ORGANIC  
COMPOUNDS FROM *CORYMBIA CITRIODORA* AND *TRISTANIOPSIS*  
*LAURINA*.

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Bachelor of Science in Analytical Chemistry

This thesis is presented for the degree of Master of Philosophy in Environmental Chemistry



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## ABBREVIATIONS, ACRONYMS AND SYMBOLS

$\alpha = 0.0027$  (empirical parameter – Guenther model)

$A$  = efficiency factor (Bartelt and Zilkowski model)

$\alpha$  = parameter which describes how fast the partition equilibrium can be achieved

$A_p$  = GC-FID peak area / mV.s

$A_{SPME}$  = total BVOC peak area for n extractions (background subtracted)

$B$  = fibre radius / nm

$b$  = intercept of a linear function

$BVOC$  = Biogenic Volatile Organic Compound

$C$  = isoprene emission rate /  $\mu\text{g g}^{-1}(\text{dry leaf weight}) \text{ hr}^{-1}$  (Guenther model)

$\Phi_{\text{CO}_2}$  = atmospheric carbon dioxide mixing ratio / ppm

$C_I = 0.00195$  for  $\Phi_{\text{CO}_2} < 100$  ppm, 0 for  $100 < \Phi_{\text{CO}_2} < 600$  ppm, and  $-0.0041$  for

$\Phi_{\text{CO}_2} > 600$  ppm (empirical parameter – Guenther model)

$C_2 = 0.805$  for  $\Phi_{\text{CO}_2} < 100$  ppm, 1 for  $100 < \Phi_{\text{CO}_2} < 600$  ppm, and 1.28 for  $\Phi_{\text{CO}_2} > 600$  ppm (empirical parameter – Guenther model)

$C_{\text{air}}$  = concentration of analyte in the air stream /  $\text{ng ml}^{-1}$

$C_{\text{fibre}}$  = concentration of analyte on the SPME fibre

$C_L$  = light dependent term of the Guenther model

$c_{L1} = 1.066$  (empirical parameter – Guenther model)

$C_T$  = temperature dependent term of the Guenther model

$C_{T1} = 95000 \text{ J mol}^{-1}$  (empirical parameter – Guenther model)

$C_{T2} = 230000 \text{ J mol}^{-1}$  (empirical parameter – Guenther model)

$C_{T3} = 0.961$  (empirical parameter – Guenther model)

$\delta$  = thickness of the effective static boundary layer surrounding the fibre / nm

$\Delta H_{\text{vap}}$  = heat of vaporization for the pure analyte /  $\text{kJ mol}^{-1}$

$D_g$  = diffusion coefficient of the analyte in air

$DMAPP$  = dimethylallyl pyrophosphate

$DOXP$  = 1-deoxy-D-xylulose-5-phosphate

$F$  = SPME efficiency factor (as ratio)

$FACE$  = Free-Air Carbon dioxide Enrichment

$FTIR$  = Fourier Transform InfraRed

$G$  = functional group correction term (Bartelt and Zilkowski model)

$GC-FID$  = Gas Chromatography-Flame Ionisation Detector

$GC-MS$  = Gas Chromatography-Mass Spectrometry

$\gamma_i$  = analyte activity coefficient defined by  $C_{air} RT = \gamma_i C_{fibre} p^\circ$

$IR$  = InfraRed

$K$  = fibre partition coefficient

$L$  = fibre length / cm

$L.O.D_x$  = limit of detection/ ng

$L.O.Q_x$  = limit of quantification/ ng

$LTPRI$  = linear temperature - programmed retention index of the analyte on a non-polar column

$m$  = mass of analyte on fibre /ng

$M_{air}$  = average of the molecular weights of the components in air / g mol<sup>-1</sup>

$M_{VOC}$  = molecular weight of the analyte /g mol<sup>-1</sup>

$\nu$  = air kinematic viscosity /cm<sup>2</sup> s<sup>-1</sup>

$\nu_{air}$  = volumetric flow rate past the fibre

$ng_{(BVOC)}$  = mass of BVOC either injected or extracted /ng

$n_{f,i}^i$  = amount of analyte extracted by the fibre during the  $i^{th}$  extraction /ng

$n_s^\circ$  = amount of analyte in sample before the extraction /ng

$n_{total}$  = total amount of analyte extracted from all SPME extractions /ng

$p$  = ambient pressure during analysis/ Pa

$p^\circ$  = pure analyte vapor pressure at a known temperature/Pa

$p^*$  = analyte vapor pressure at a known temperature /Pa

$PAN$  = peroxyacyl nitrate

$PAR$  = Photosynthetically Active Radiation

$PDMS/DVB$  = polydimethylsiloxane / divinylbenzene

$Q$  = flux of PAR /  $\mu\text{mol m}^{-2} \text{s}^{-1}$

$R$  = universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )

$R^2$  = Correlation coefficient of a function fitted to experimental data

$Re$  = the Reynolds number ( $Re = 2ub/v$ )

$RH$  = Relative Humidity

$RF$  = Radiative Forcing

$s$  = gradient of a linear function

$\sigma_b$  = standard deviation of the intercept

$Sc$  = the Schmidt number ( $Sc = \nu/D_g$ )

$SEF$  = standard emission factor (Guenther model)

$SOA$  = Secondary Organic Aerosol

$SPME$  = Solid-Phase Microextraction

$T$  = temperature of analysis / K

$T_{abs}$  = absolute temperature / K

$T_{leaf}$  = leaf temperature / K

$t$  = SPME sampling or extraction time / mins

$T^*$  = temperature at which  $p^*$  is known

$T_M$  = 314 K (Guenther model)

$TPA\text{-}SPME$  = Total Peak Area-Solid-Phase Microextraction

$T_S$  = 303 K (Guenther model)

$u$  = linear velocity of the air /  $\text{cm s}^{-1}$

$V_{air}$  = molar volume of air / l

$V_f$  = fibre coating volume /  $\text{m}^3$

$VOC$  = Volatile Organic Compound

$V_s$  = sample volume / ml

$V_{VOC}$  = molar volume of analyte/ ml

## ABSTRACT

Biogenic Volatile Organic Compounds (BVOCs) emitted by plants can affect the climate and play important roles in the chemistry of the troposphere. As ambient atmospheric carbon dioxide (CO<sub>2</sub>) levels are rapidly increasing knowledge of the effect of elevated atmospheric CO<sub>2</sub> on plant BVOC emissions is necessary for the development of global climate models.

During this study, the effect of elevated atmospheric CO<sub>2</sub> mixing ratios on BVOC emissions from *Corymbia citriodora* (Lemon Scented Gum) and *Tristaniopsis laurina* (Water Gum) was determined for the first time through the combination of Solid-Phase Microextraction (SPME), Gas Chromatography-Flame Ionisation Detection (GC-FID), Gas Chromatography-Mass Spectrometry (GC-MS) and an environment chamber. For *C. citriodora* elevated atmospheric CO<sub>2</sub> led to a decrease in the emission rate of  $\alpha$ -pinene,  $\beta$ -pinene, eucalyptol, citronellal and  $\beta$ -caryophyllene, however, elevated CO<sub>2</sub> had no effect on the emission rate of citronellol. The emission profile of *T. laurina* has been determined for the first time. For *T. laurina* elevated CO<sub>2</sub> led to a decrease in the emission rate of  $\alpha$ -pinene but the emission rates of  $\beta$ -pinene, limonene, eucalyptol and citronellol were unaffected. The results obtained in this work confirm that the effect of elevated atmospheric CO<sub>2</sub> on plant BVOC emissions is species-specific.

**STATEMENT BY THE CANDIDATE**

I, Michelle Camenzuli, state that the work presented within this thesis was not submitted as part of a higher degree at any University or institution other than Macquarie University. I have indicated the source of any information that is not my own, that has been used throughout this thesis. The work of others utilised during this work has been acknowledged within this text. No ethics approval was required for this work.

  
.....  
Michelle Camenzuli

24 Jun 08  
Date

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*“We are continually faced with a series of great opportunities brilliantly disguised as insolvable problems”*

*- J.W. Gardner -*