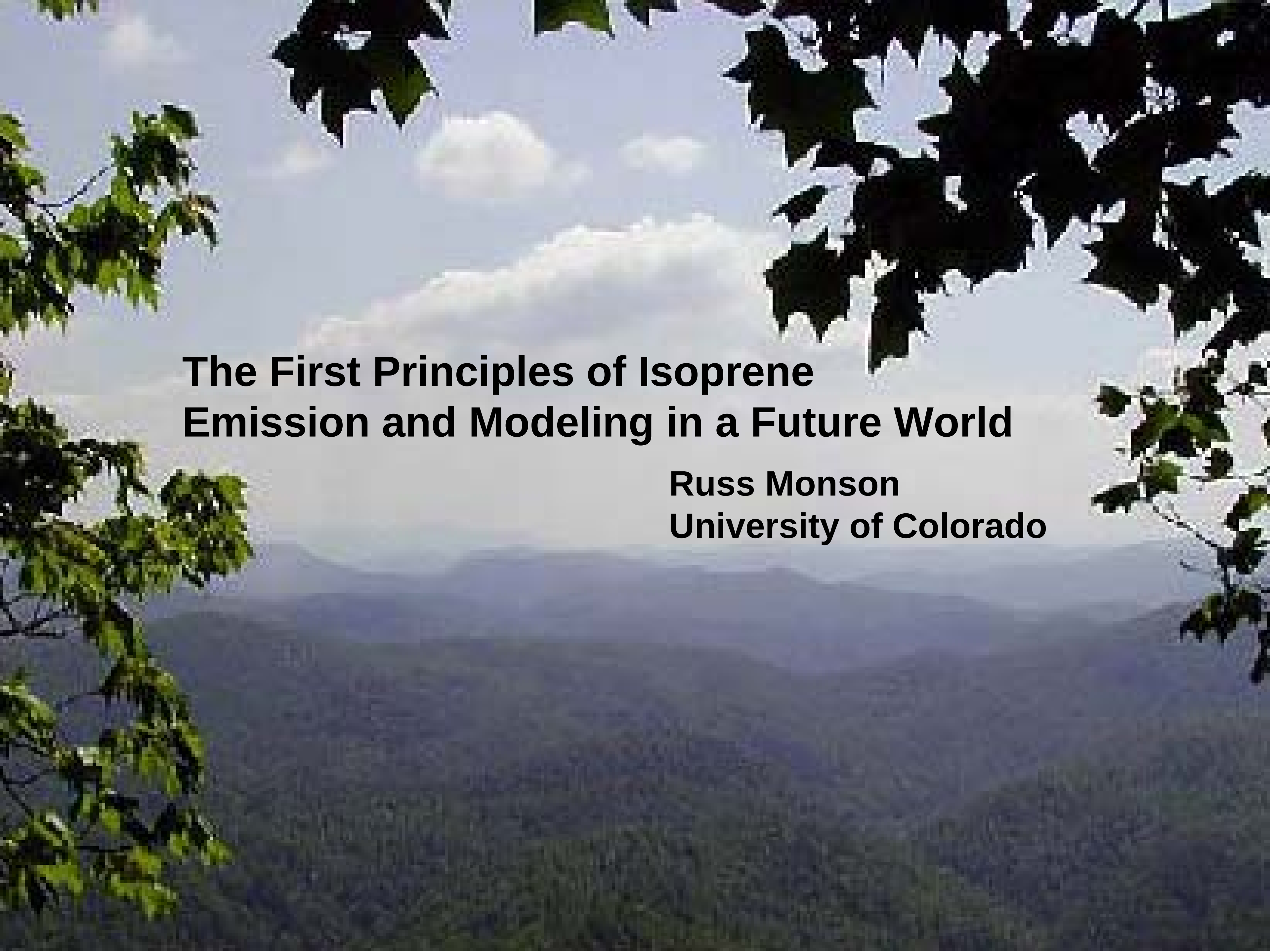
US EPA ARCHIVE DOCUMENT



The First Principles of Isoprene Emission and Modeling in a Future World

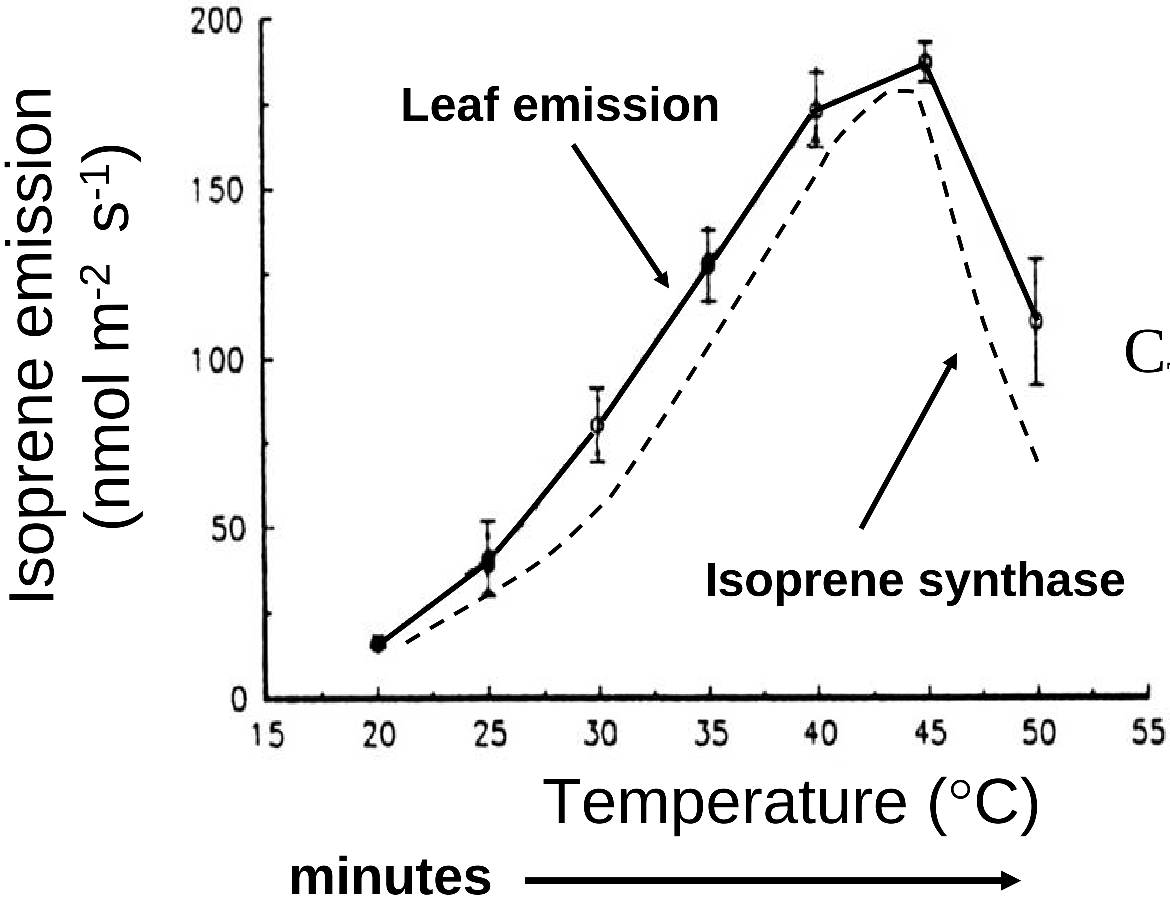
Russ Monson
University of Colorado

I begin with a premise…

For the purpose of prognosis, it's best to construct biogenic VOC emissions models with as direct a connection to the first-principles of biochemistry and physiology as is possible.

‘Guenther algorithm’

(Guenther, Monson and Fall, 1991, JGR)



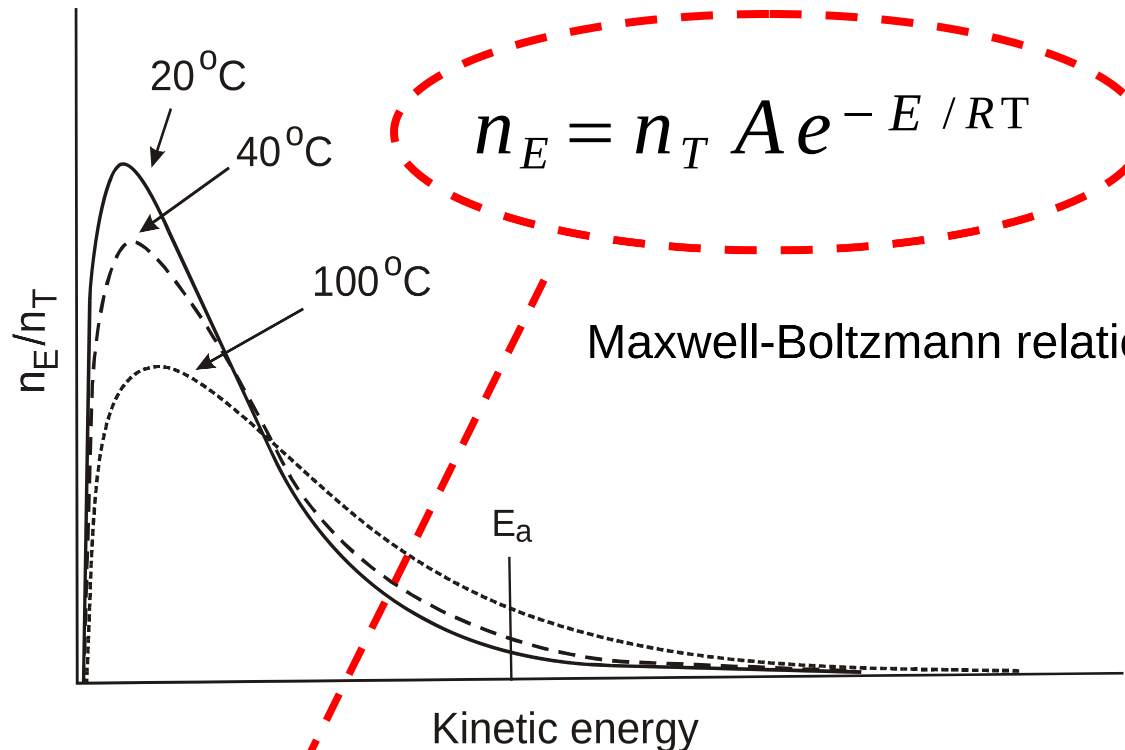
based on enzyme bioenergetics

$$C_{T\,iso} = \exp \frac{c_{T1}(T - T_s)}{R\, T_s\, T}$$

Temperature algorithm has foundations in transition-state bioenergetics

$$n_E = n_T\, A\, e^{-E/RT}$$

Maxwell-Boltzmann relationship



Guenther algorithm

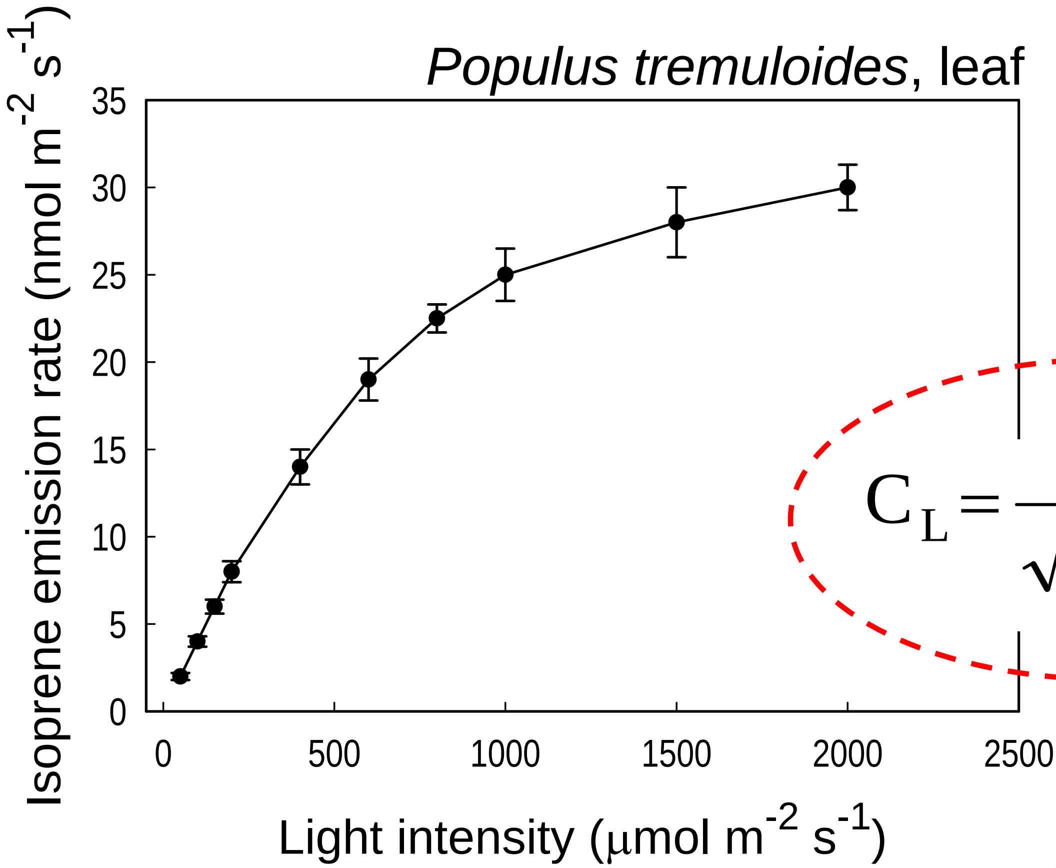
$$k = C\, exp^{Ea/RT}$$

(Arrhenius model)

$$C_{T\,iso} = \exp \frac{c_{T1}(T - T_s)}{R\, T_s\, T}$$

Isoprene emission rate increases with light intensity

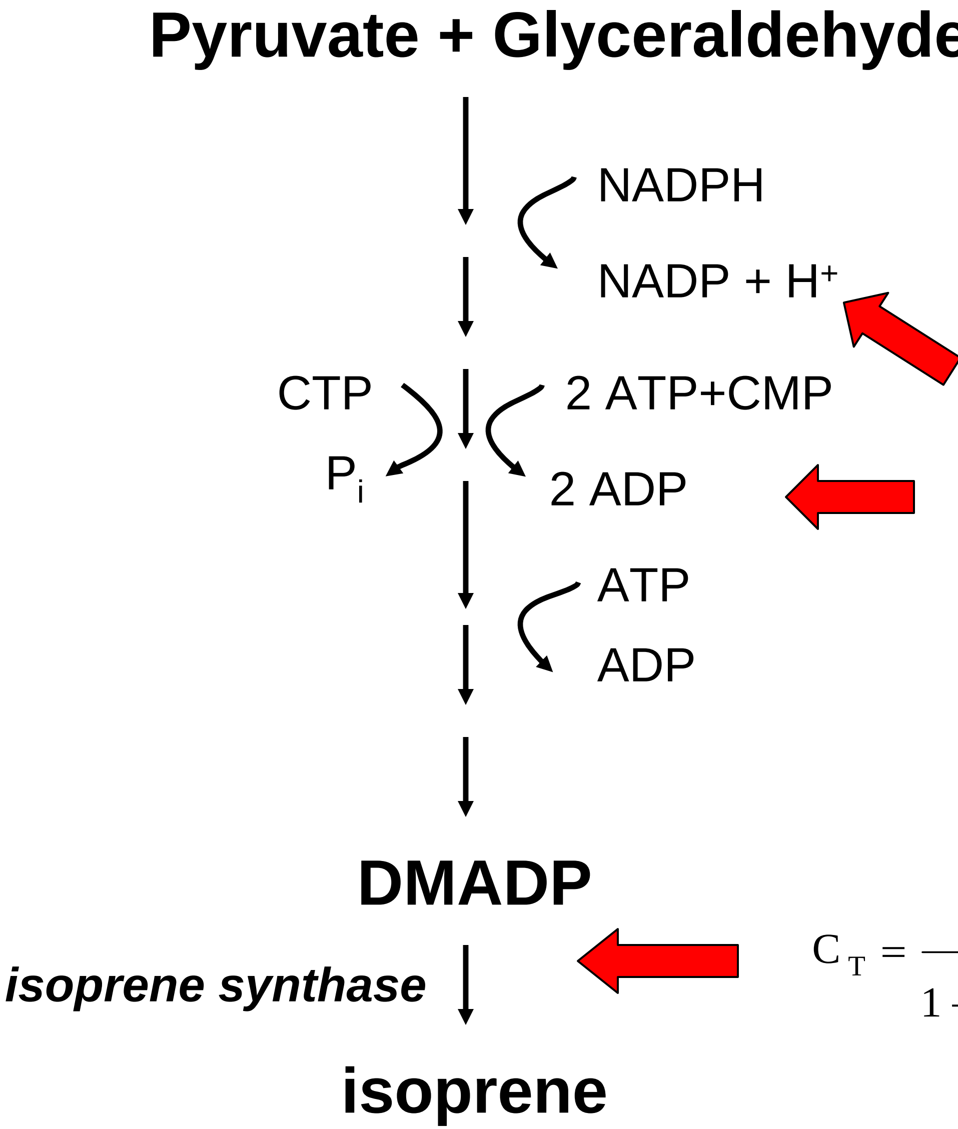
(Monson and Fall, 1989, *Plant Physiology*)



$$C_L = \frac{\alpha \, c_{L1} \, L}{\sqrt{1 + \alpha^2 L^2}}$$

The ‘Guenther’ algorithm is based on the light dependence of photosynthetic electron transport

The temperature and light algorithms have good biochemical justification



$$C_L = \frac{\alpha\, c_{L1}\, L}{\sqrt{1 + \alpha^2 L^2}}$$

(light)

$$C_T = \frac{\exp \frac{c_{T1}(T - T_s)}{R\, T_s\, T}}{1 + \exp \frac{c_{T2}(T - T_m)}{R\, T_s\, T}}$$

(temperature)

The Current Modeling Framework for Predicting Isoprene Emissions

$$I_s = BER * C_L * C_T$$

"Base" Emission Rate
(emission factor)

$$C_L = \frac{\alpha \, c_{L1} \, L}{\sqrt{1 + \alpha^2 L^2}}$$

$$C_T = \frac{\exp \frac{c_{T1} (T - T_s)}{R \, T_s \, T}}{1 + \exp \frac{c_{T2} (T - T_m)}{R \, T_s \, T}}$$

Modeling the Response of VOC Emissions to Global Change

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 109, D06301, doi:10.1029/2003JD004236, 2004

Sensitivity of global biogenic isoprenoid emissions to climate variability and atmospheric CO_2

Vaishali Naik[1]
Department of Atmospheric Sciences, Universityof Illinois, Urbana, Illinois, USA

Christine Delire
Center for Sustainability and the Global Environment, Gaylord Nelson Institute for Environmental Studies, University of Wisconsin-Madison, Madison, Wisconsin, USA

Atmos. Chem. Phys., 6, 2129–2146, 2006
www.atmos-chem-phys.net/6/2129/2006/
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Atmospheric Chemistry and Physics

Impact of climate variability and land use changes on global biogenic volatile organic compound emissions

J. Lathière[1], D. A. Hauglustaine[1], A. D. Friend[1], N. De Noblet-Ducoudré[1], N. Viovy[1], and G. A. Folberth[2]
[1]Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif-sur-Yvette, France
[2]School of Earth and Ocean Sciences (SEOS), University of Victoria, Victoria, Canada

Received: 19 July 2005 – Published in Atmos. Chem. Phys. Discuss.: 25 October 2005
Revised: 28 February 2006 – Accepted: 22 April 2006 – Published: 20 June 2006

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 111, D12304, doi:10.1029/2005JD006852, 2006

Role of climate change in global predictions of future tropospheric ozone and aerosols

Hong Liao,[1] Wei-Ting Chen,[1] and John H. Seinfeld[1,2]

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 110, D21309, doi:10.1029/2005JD005874, 2005

Modeling of global biogenic emissions for key indirect greenhouse gases and their response to atmospheric CO_2 increases and changes in land cover and climate

Zhining Tao and Atul K. Jain
Department of Atmospheric Science, University of Illinois, Urbana, Illinois, USA

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 113, D14307, doi:10.1029/2007JD008497, 2008

Linking global to regional models to assess future climate impacts on surface ozone levels in the United States

Christopher G. Nolte,[1,2] Alice B. Gilliland,[1,2] Christian Hogrefe,[3] and Loretta J. Mickley[4]

Received 2 February 2007; revised 11 February 2008; accepted 27 February 2008; published 22 July 2008.

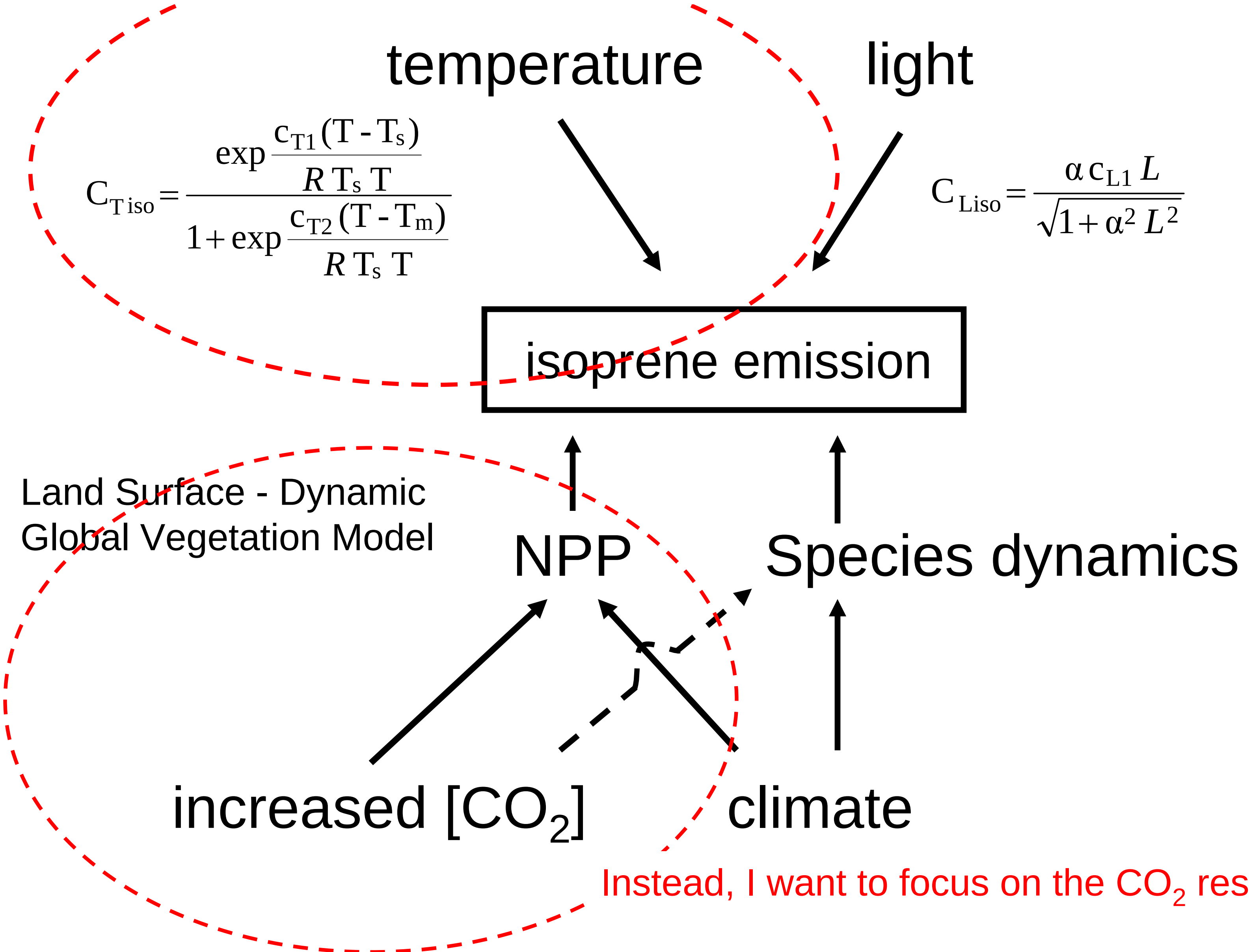
GEOPHYSICAL RESEARCH LETTERS, VOL. 30, NO. 7, 1392, doi:10.1029/2002GL016708, 2003

Changes in tropospheric ozone between 2000 and 2100 modeled in a chemistry-climate model

Guang Zeng and John A. Pyle
Centre for Atmospheric Science, University of Cambridge, Cambridge, UK

Model Logic

This is not entirely justified on biochemical grounds, but no time to go into it now…

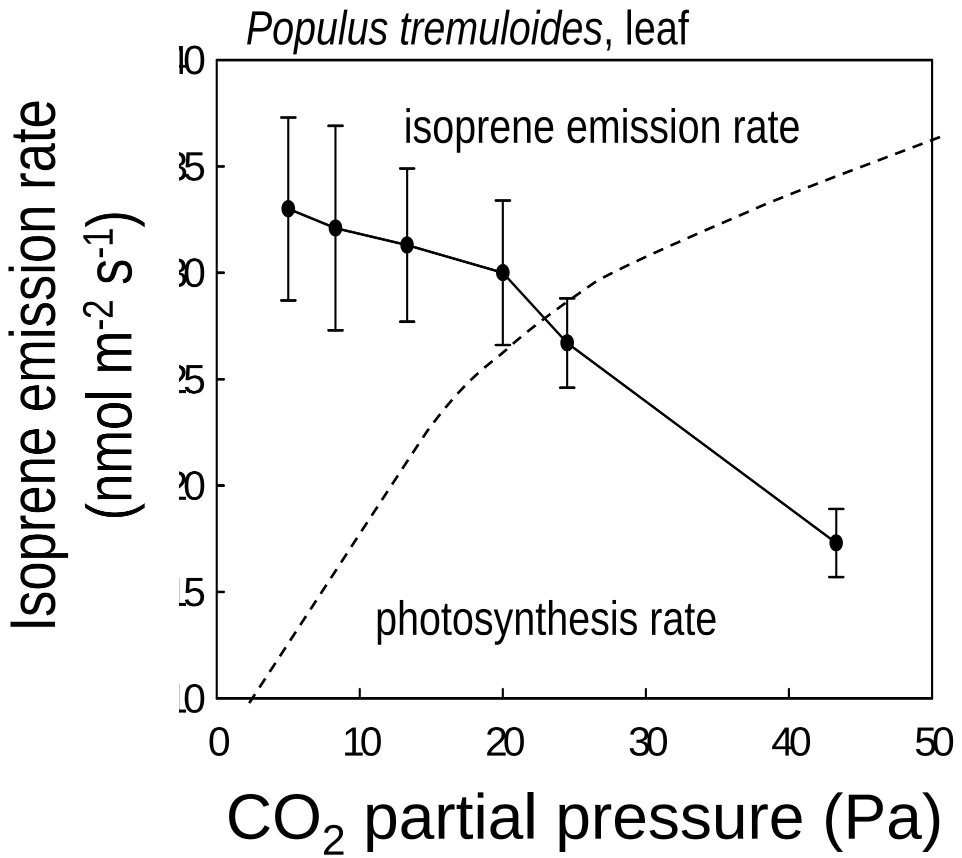


$$C_{T\,iso} = \frac{\exp \frac{c_{T1}(T - T_s)}{R\,T_s\,T}}{1 + \exp \frac{c_{T2}(T - T_m)}{R\,T_s\,T}}$$

$$C_{L\,iso} = \frac{\alpha\, c_{L1}\, L}{\sqrt{1 + \alpha^2 L^2}}$$

Instead, I want to focus on the CO_2 response…

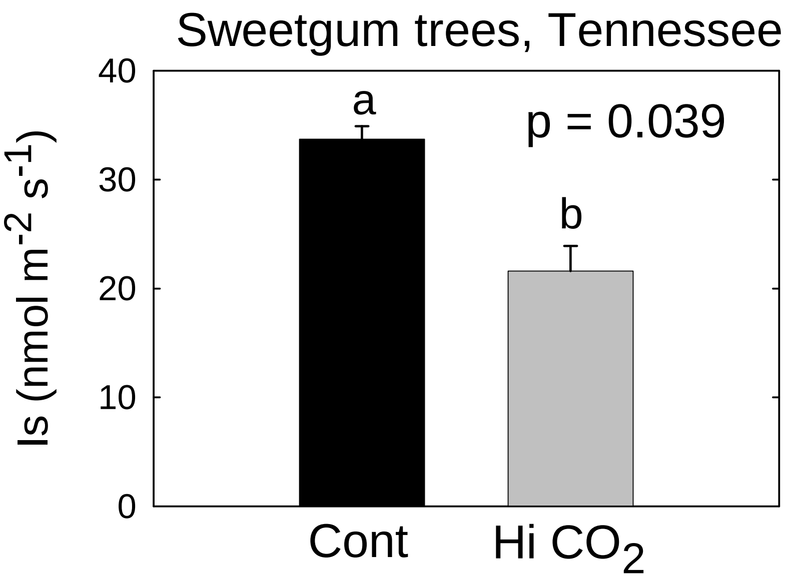
Elevated atmospheric [CO_2] suppresses isoprene emissions



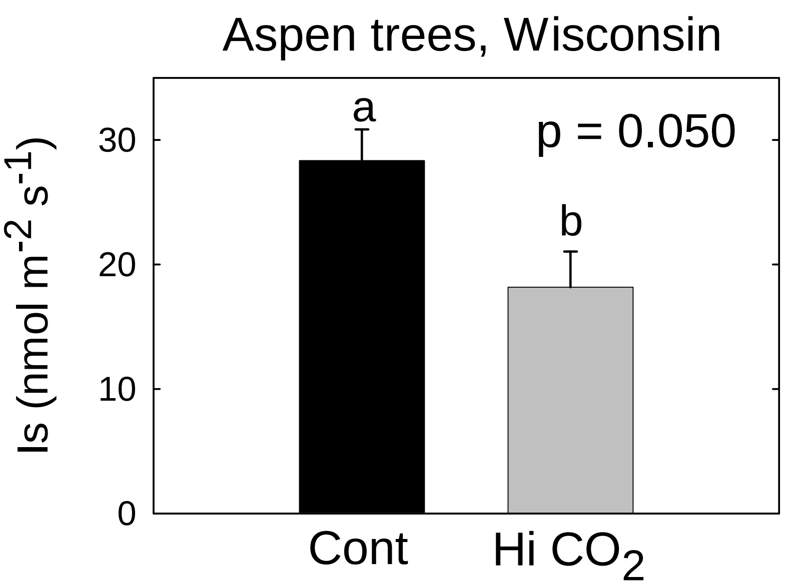
(Monson and Fall, 1989, *Plant Physiology*)

Rhinelander FACE, Wisconsin

Oak Ridge FACE site



Rhinelander FACE site

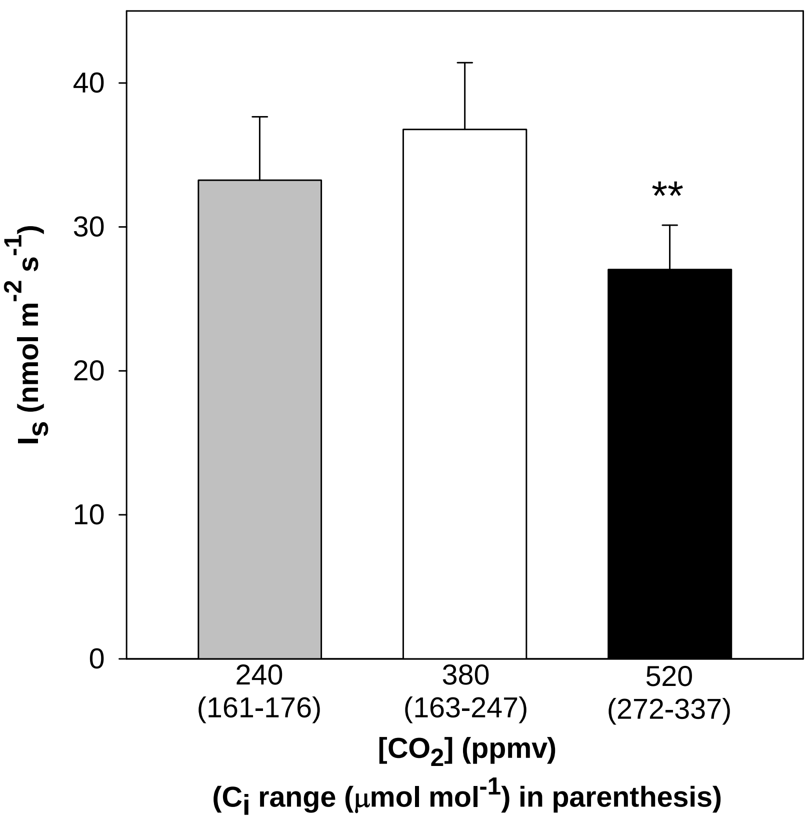


Monson, R.K. et al. (2007) Isoprene emission from terrestrial ecosystems in response to global change: *Philosophical Transactions of the Royal Society, London* A365: 1677-1695.

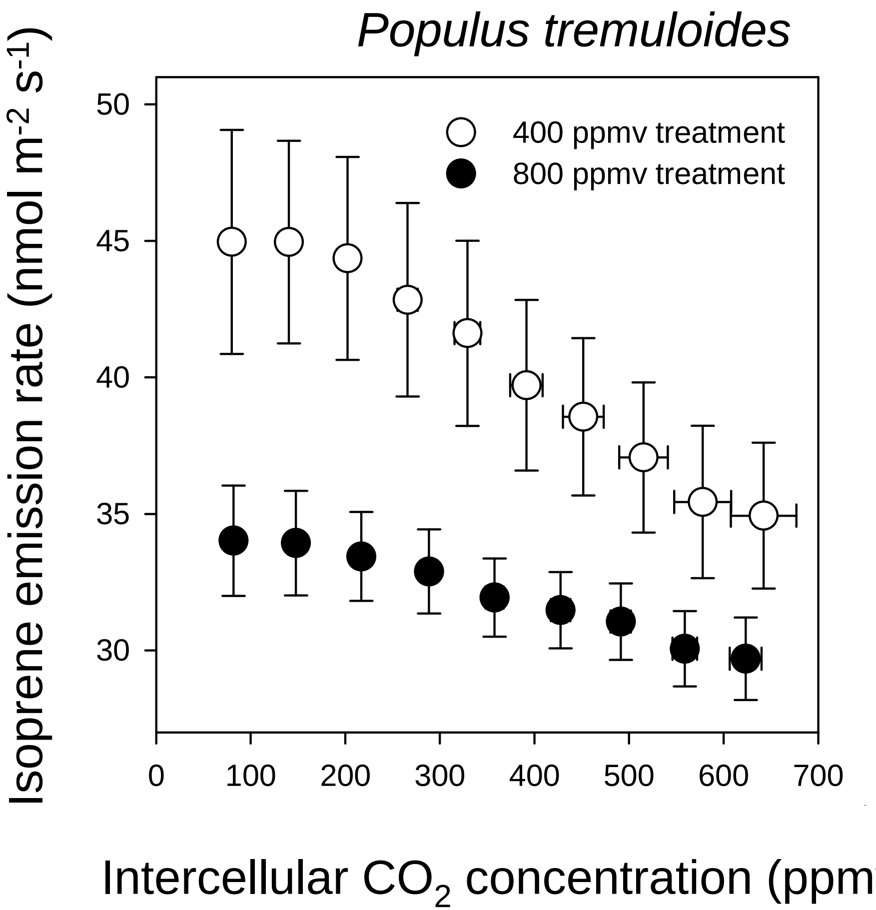
Temple, Texas

The Texas ‘CO_2 Tube’

Liquidambar styraciflua

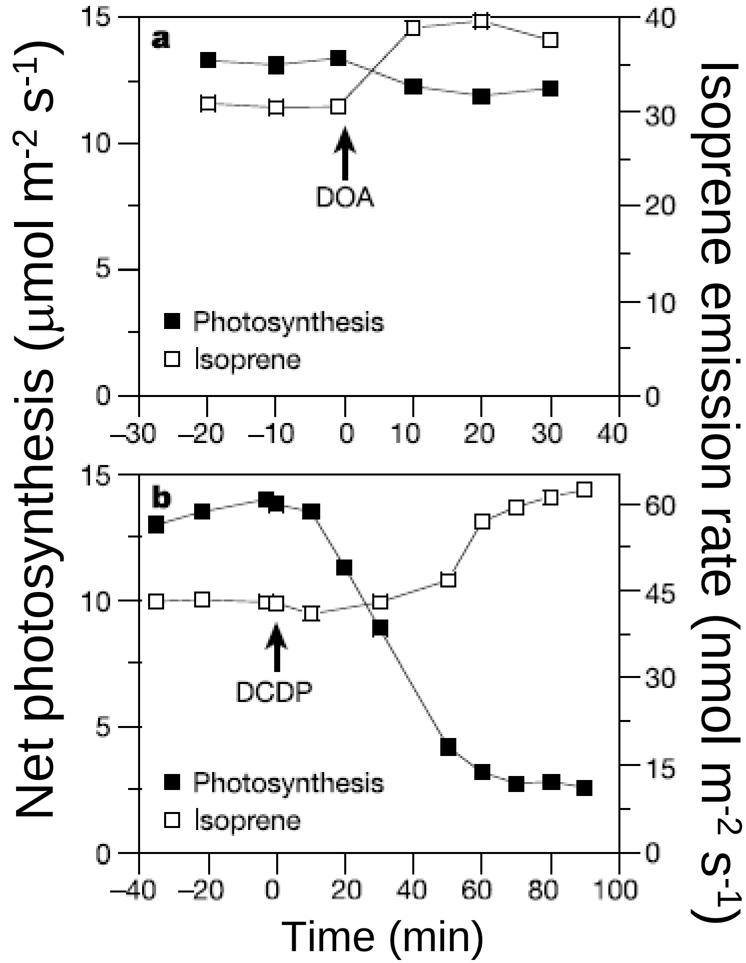


Growth Chamber Studies of the CO_2 Effect



Wilkinson, M.J., Monson, R.K., Trahan, N., Lee., S., Brown, E., Jackson, R.B., Polley, H.W., Fay, P. and Fall, R. (2008) Leaf isoprene emission rate as a function of atmospheric CO_2 concentration. *Global Change Biology* (in press).

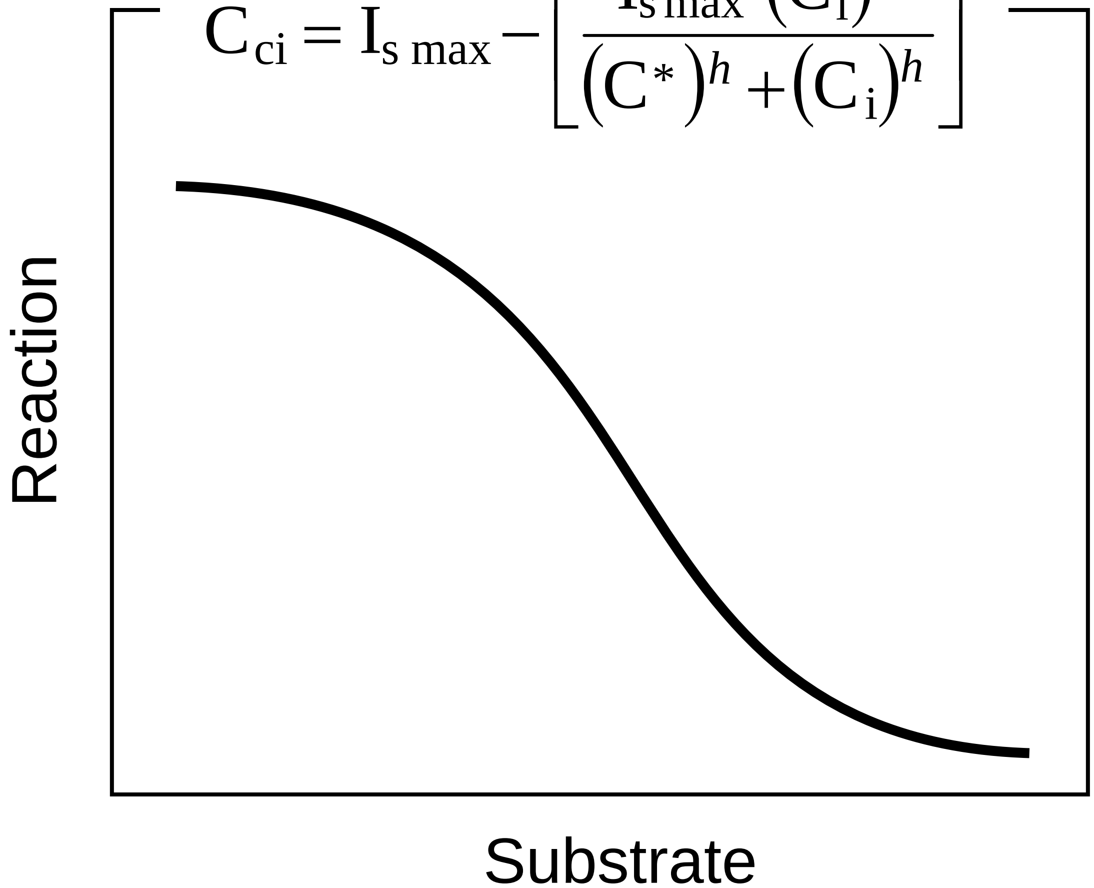
We understand the biochemical reasons for these responses – PEP carboxylase

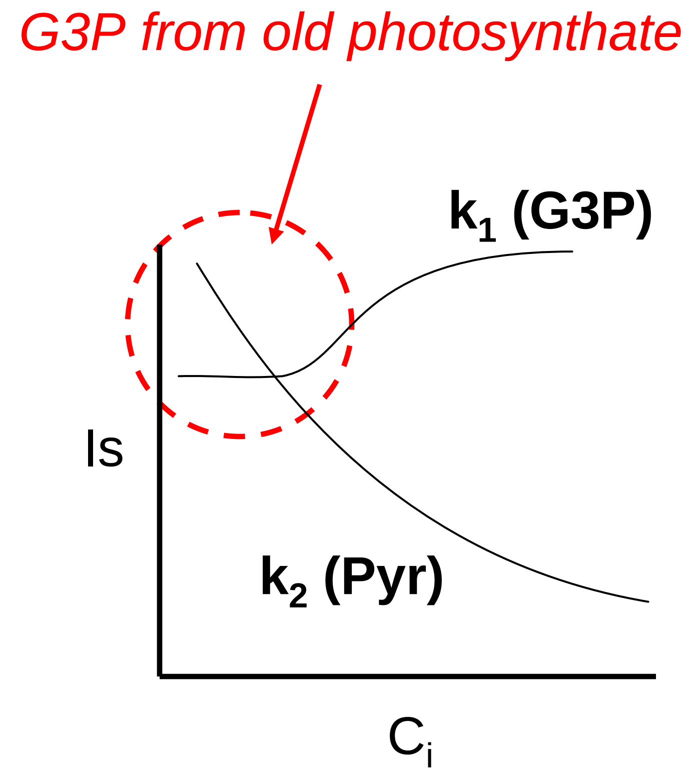


Rosenstiel, T., Potosnak, M., Griffen, K., Fall, R. and Monson, R.K. (2003) Elevated CO_2 uncouples growth and isoprene emission in a model agriforest ecosystem. *Nature* 421: 256-259.

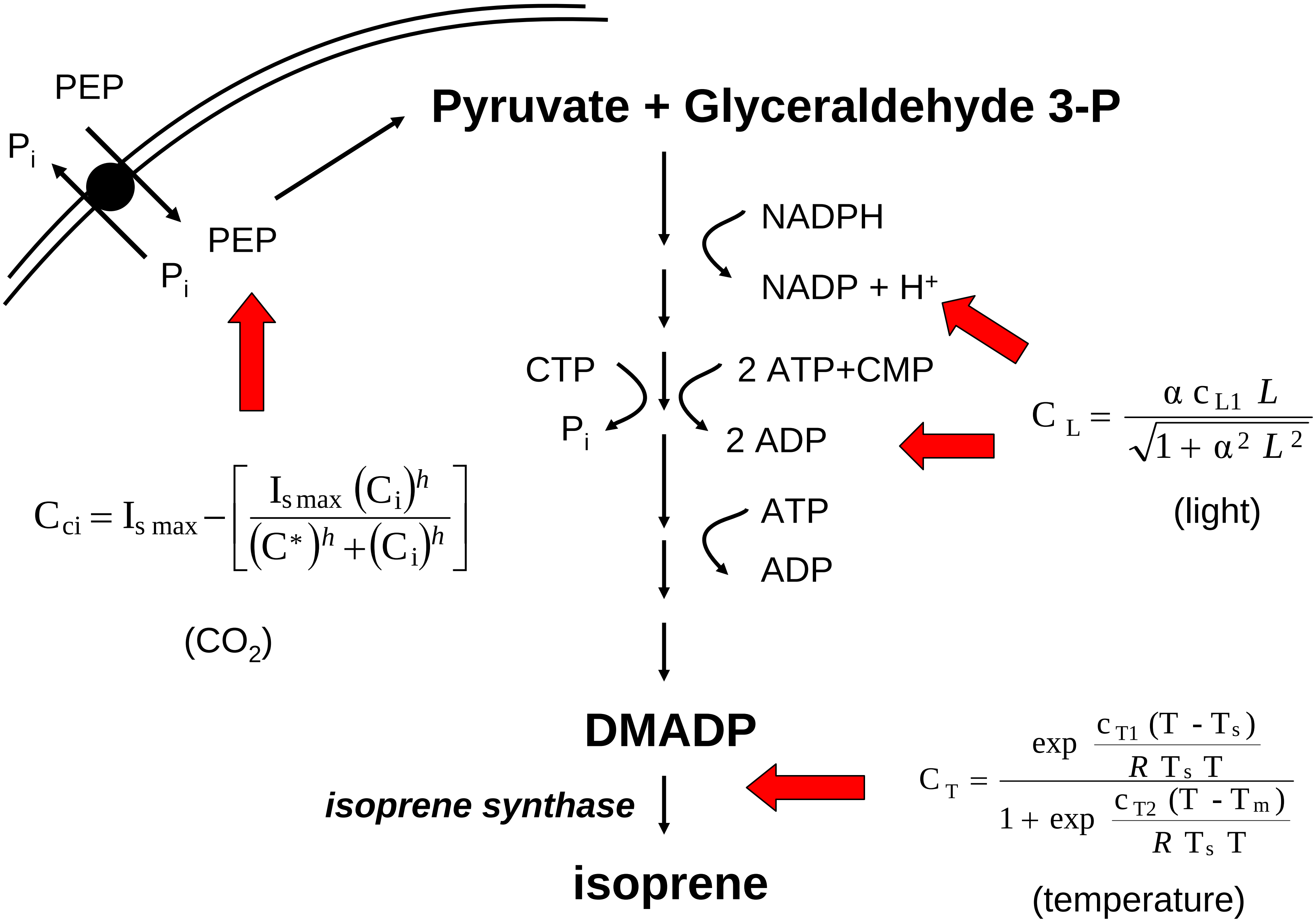
A possible mechanism for the CO_2 response

$$C_{ci} = I_{s\,max} - \left[\frac{I_{s\,max}\,(C_i)^h}{(C^*)^h + (C_i)^h}\right]$$





Progressive amplification of positive influence of one substrate and negative influence of a second substrate



PEP
P_i
P_i
PEP
Pyruvate + Glyceraldehyde 3-P
NADPH
NADP + H^+
CTP
P_i
2 ATP+CMP
2 ADP
ATP
ADP
DMADP
isoprene synthase
isoprene
$C_{ci} = I_{s\,max} - \left[\frac{I_{s\,max} (C_i)^h}{(C^*)^h + (C_i)^h} \right]$
(CO_2)
$C_L = \frac{\alpha \, c_{L1} \, L}{\sqrt{1 + \alpha^2 L^2}}$
(light)
$C_T = \frac{\exp \frac{c_{T1} (T - T_s)}{R \, T_s \, T}}{1 + \exp \frac{c_{T2} (T - T_m)}{R \, T_s \, T}}$
(temperature)

Revised Modeling Framework for Predicting Isoprene Emissions

$$I_s = BER * C_L * C_T * C_{ci}$$

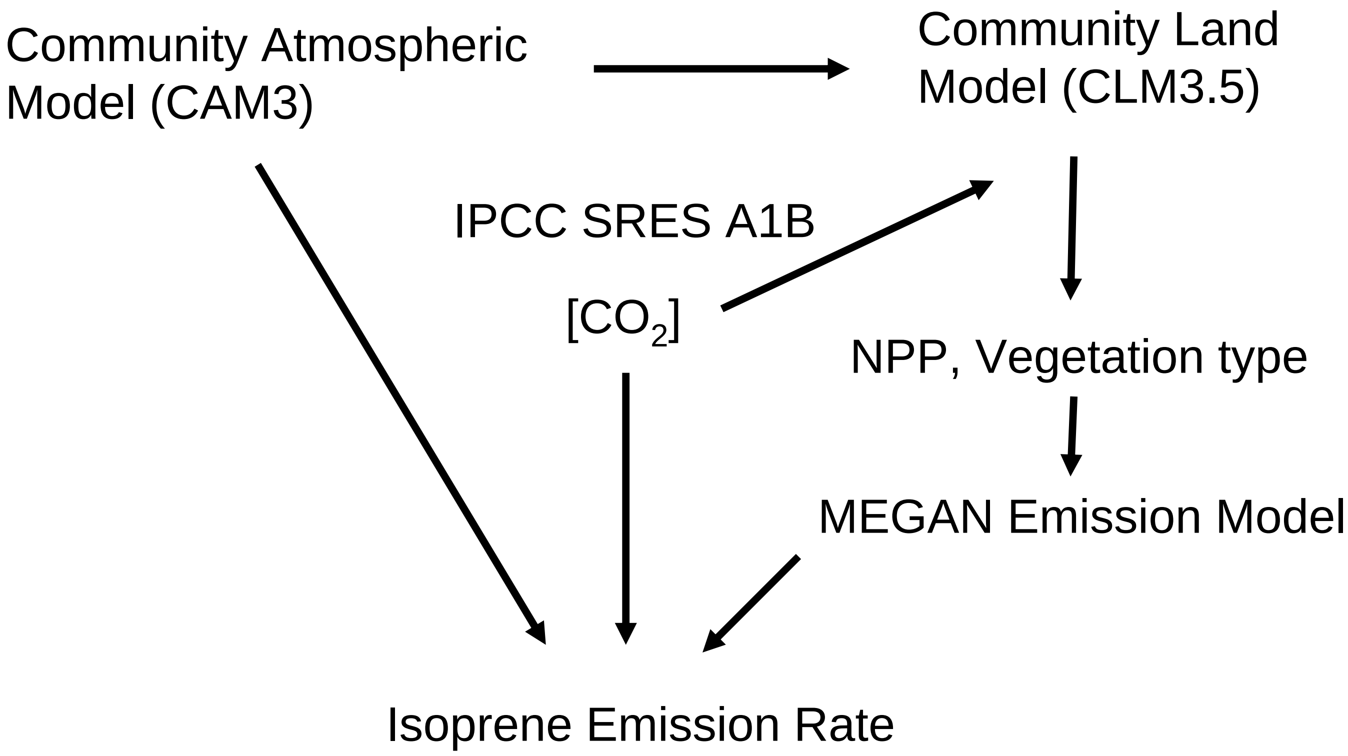
"Base" Emission Rate (emission factor)

$$C_L = \frac{\alpha \, c_{L1} \, L}{\sqrt{1 + \alpha^2 L^2}}$$

$$C_{ci} = I_{s\,max} - \left[\frac{I_{s\,max} \, (C_i)^h}{(C^*)^h + (C_i)^h} \right]$$

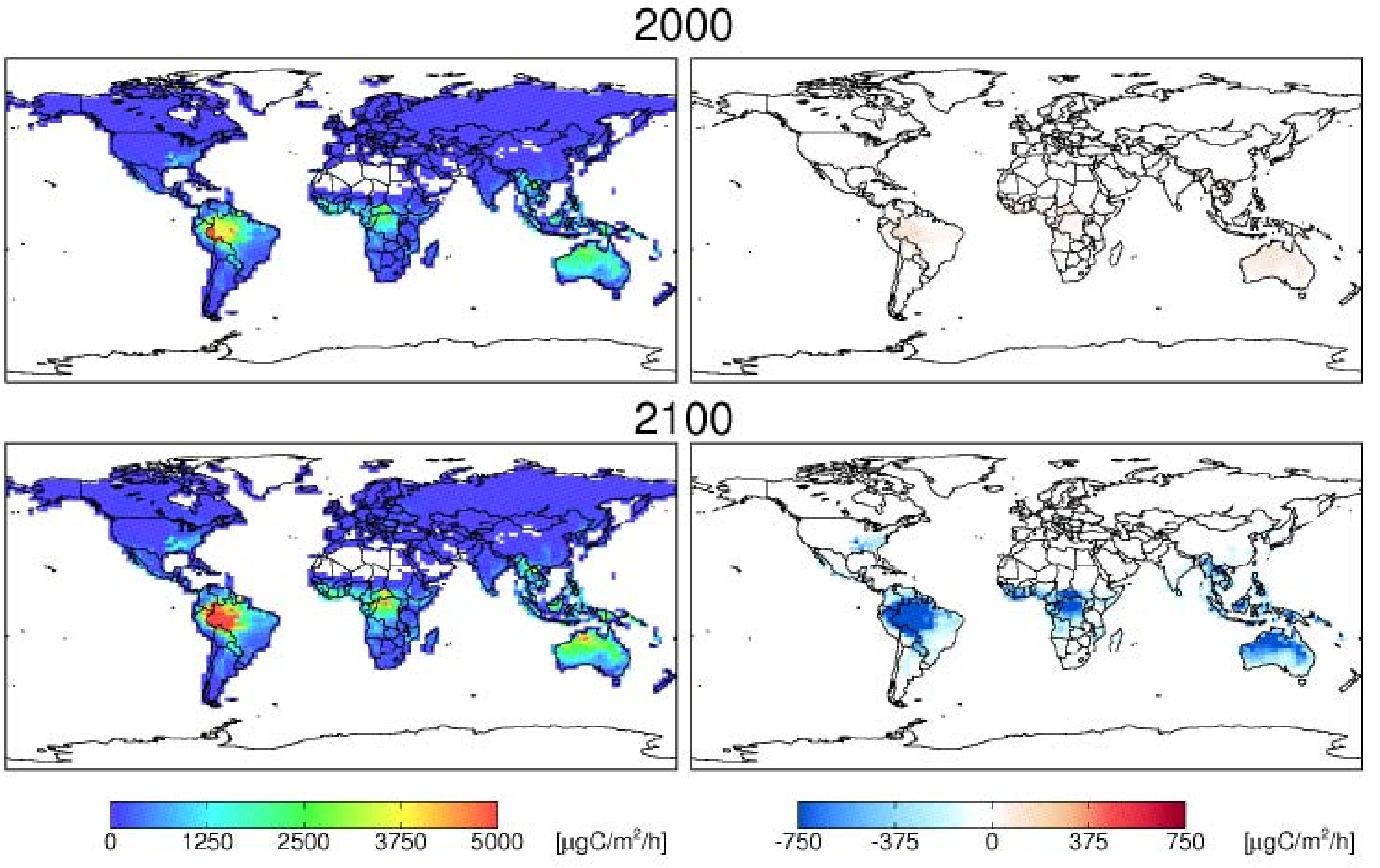
$$C_T = \frac{\exp \dfrac{c_{T1}(T - T_s)}{R \, T_s \, T}}{1 + \exp \dfrac{c_{T2}(T - T_m)}{R \, T_s \, T}}$$

NCAR Community Climate System Model 3



Heald, C.L., Wilkinson, M.J., Monson, R.K., Alo, C.A., Wang, G. and Guenther, A. (2008) Response of the global isoprene emission rate to future changes in climate and atmospheric CO_2 concentration. *Global Change Biology* (in press).

Isoprene emission in present day and future without CO_2 effect (left) or with CO_2 effect (right). The effect of CO_2 on NPP is not included.



isoprene emission rate

We find that the direct effect of [CO_2] can completely compensate for the effect of climate warming on isoprene emissions

Year	Standard MEGAN2	MEGAN2 with CO2 Activity Factor
2000	508	523
2100 (A1B) with fixed vegetation	696	479
2100 (A1B) with dynamic vegetation	1852	1242

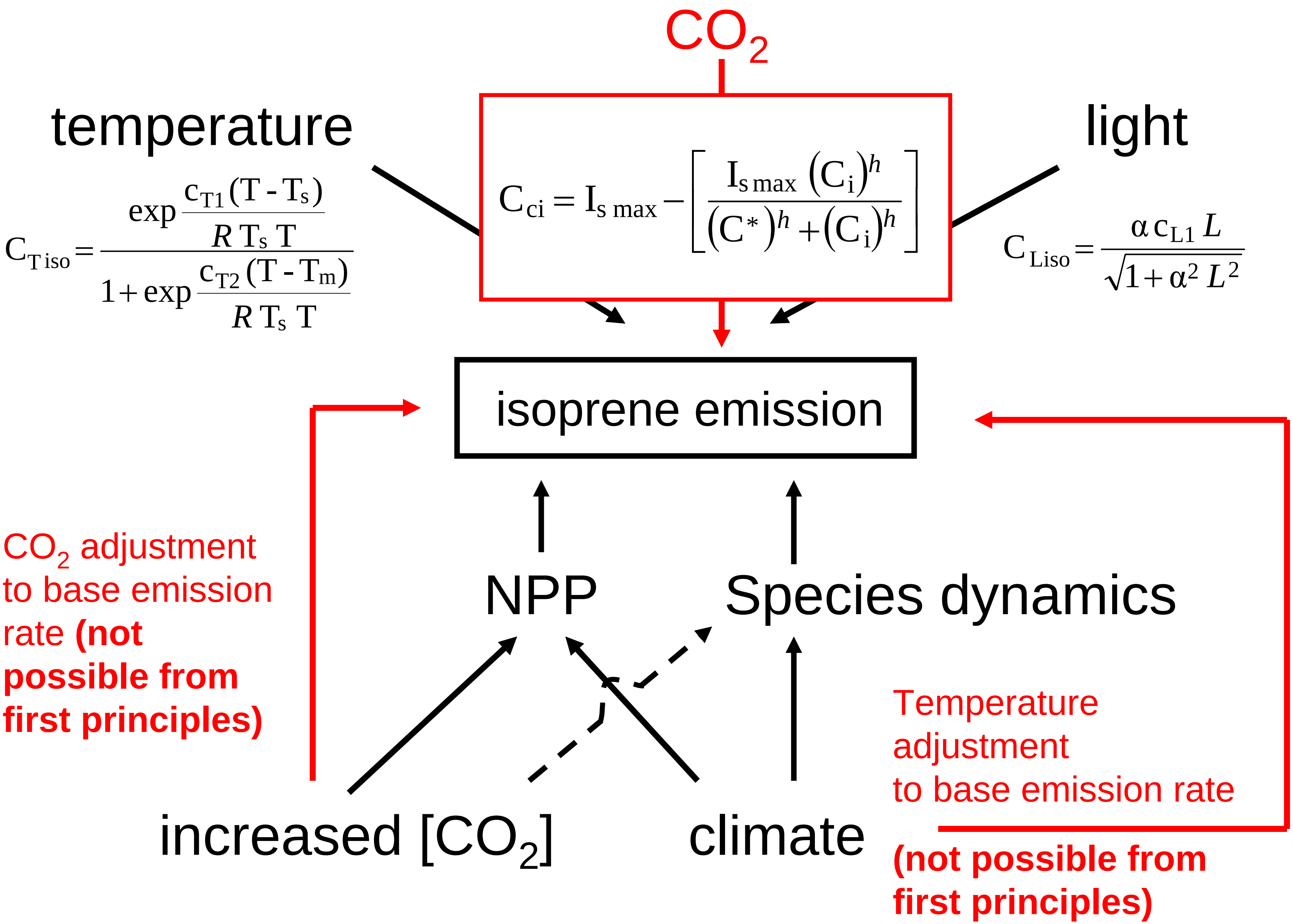
Without CO_2 effect climate warming causes a 37% increase
With CO_2 effect climate warming results in an 8% decrease

We find that the direct effect of [CO_2] can significantly reduce the effect of increasing NPP on isoprene emissions

Year	Standard MEGAN2	MEGAN2 with CO2 Activity Factor
2000	508	523
2100 (A1B) with fixed vegetation	696	479
2100 (A1B) with dynamic vegetation	1852	1242

Without CO_2 effect climate + CO_2 causes a 166% increase
With CO_2 effect climate + CO_2 results in a 78% increase

Model Logic



CO_2
temperature
light
$C_{T\,iso} = \frac{\exp \frac{c_{T1}(T - T_s)}{R\,T_s\,T}}{1 + \exp \frac{c_{T2}(T - T_m)}{R\,T_s\,T}}$
$C_{ci} = I_{s\,max} - \left[\frac{I_{s\,max}\,(C_i)^h}{(C^*)^h + (C_i)^h} \right]$
$C_{L\,iso} = \frac{\alpha\, c_{L1}\, L}{\sqrt{1 + \alpha^2 L^2}}$
isoprene emission
CO_2 adjustment to base emission rate **(not possible from first principles)**
NPP
Species dynamics
increased $[CO_2]$
climate
Temperature adjustment to base emission rate
(not possible from first principles)

Two points from today's talk:

1. We currently have access to relatively accurate equations for describing the ***short-term*** responses of isoprene emission to light, temperature and [CO_2] at the leaf scale.

2. There is much work to be done in defining the ***longer-term*** effects and ***interactions*** among forcing variables.

Acknowledgements

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Colorado State University

Colette Heald