Compostos orgânicos voláteis na atmosfera

Prof. Pérola

Leitura

Journal of Hazardous Materials 166 (2009) 17–26

DEFINIÇÃO DE COV:
Environmental Protection Agency (EPA)

- Qualquer composto que participe de reações fotoquímicas na atmosfera,
- compostos que têm pressão de vapor maior de 10 Pa à 25◦C,
- temperatura de ebulição abaixo de 260◦C à pressão atmosférica,
- Composto com 15 átomos de C ou menos.

In: Volatile Organic Compounds in the atmosphere, Ed. Ralph Koppmann, 2007.

COMPOSTOS ORGÂNICOS VOLÁTEIS

Ocorrência: Líquidos
Vapores
Sólidos

Usos: Combustíveis
Solventes
Fragrâncias
Flavorizantes

Efeitos na saúde:
Câncer
Efeitos irritantes
Mutagênese
Teratogênese

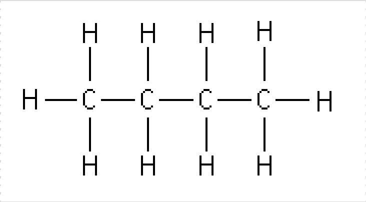
Compostos orgânicos voláteis: hidrocarbonetos

antrópicas

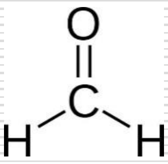
- fontes: combustão, solventes, vazamentos, petroquímica,...
- alcanos, alcenos, alcinos, aromáticos, compostos oxigenados

Biogênicas

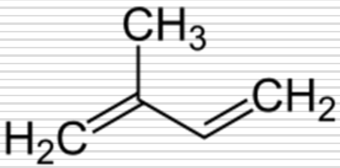
- Solo, plantas
- > 1000 substâncias conhecidas
- isopreno
- terpenos
- Compostos oxigenados



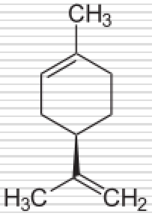
n-butano



formaldeído



isopreno



limoneno

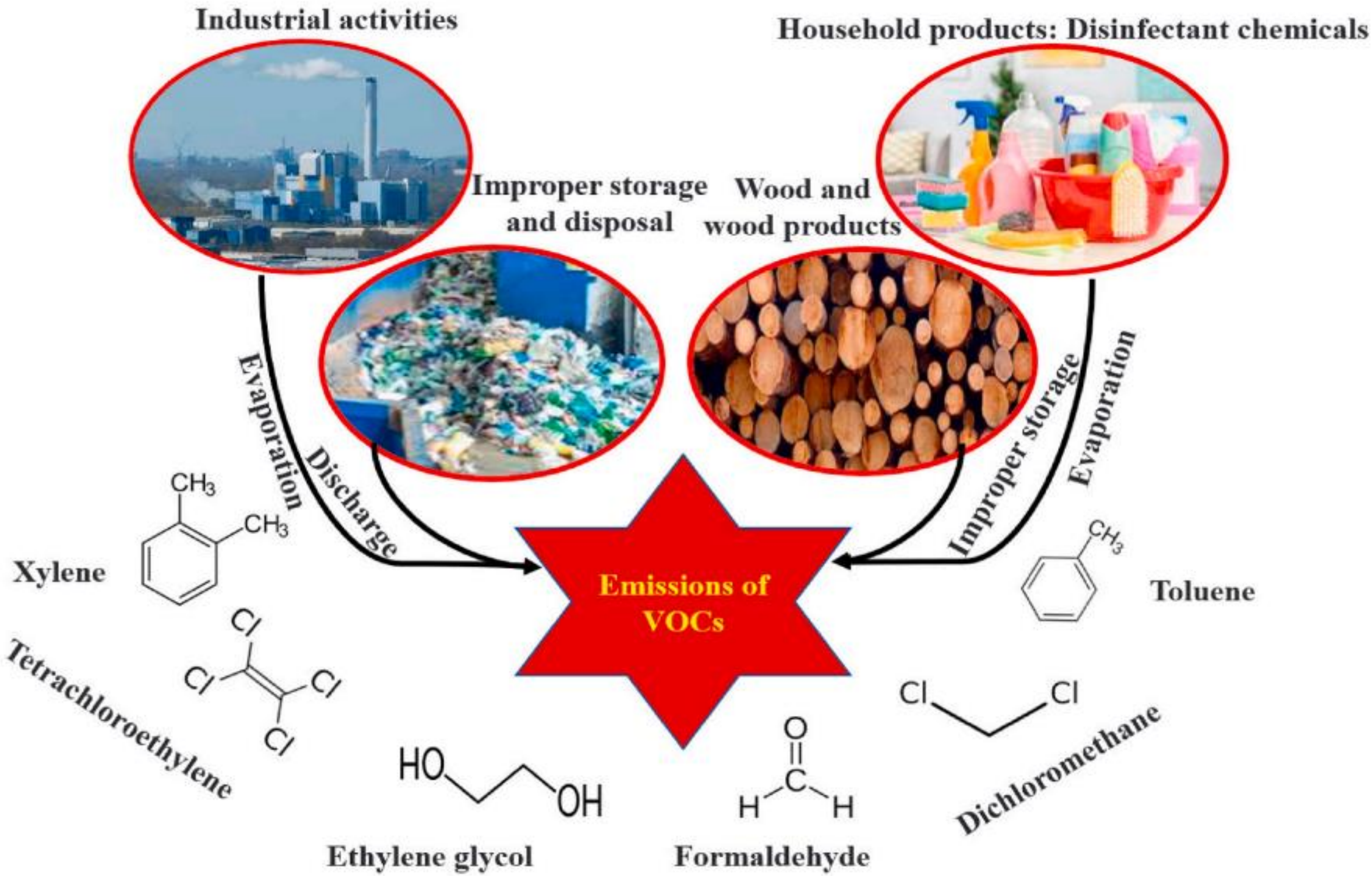


Fig. 1. Emission of most common problematic VOCs from various sources.

Table 1
Health impact assessment of some of well studied volatile organic compounds.

VOCs	Class	Assessed health impacts	Location	Reference
Dichloroethane, bromodichlomethane, trichloroethane and toluene	Chlorinated VOCs and aromatic VOC	Carcinogenic Non-carcinogenic	China China	Huang et al. (2014) (Li et al., 2020b)
Benzene, butadiene, chloroform, acrolein, and acetaldehyde	Aromatic VOC	Carcinogenic	China	Li et al. (2020a)
Polychloroethylene, polychloromethan, and polychloethane	Ethane-based VOCs	Cancer in bladder, rectum, esophagal, cervical, and colon	China	Jin et al. (2022)
Dichloroethane, bromodichlomethane, and trichloroethane	Chlorinated VOCs	Reproductive defects and frequent abortions		(Lynge et al., 1997; Scott and Jinot, 2011)
21 VOCs	Aromatic, chlorinated, ethane and non-methane VOCs	Carcinogenic	India	(Huang et al., 2014; Puttaswamy et al., 2021)
Toluene Formaldehyde Acetaldehyde	Aromatic VOC	Non-carcinogenic	China	Lin et al. (2019)
Acrolein Crotanaldehyde and butadiene	Aromatic VOC	Altered systolic blood pressure, and endothelial dysfunction	USA	McGraw et al. (2021)
Dichloro-propane and dichloroethane	Aromatic VOC	Carcinogenic	UK	Chen et al. (2021)
Toluene and benzene derivatives	Aromatic VOC	Obesity and diabetes	Korea	Lee et al. (2022)

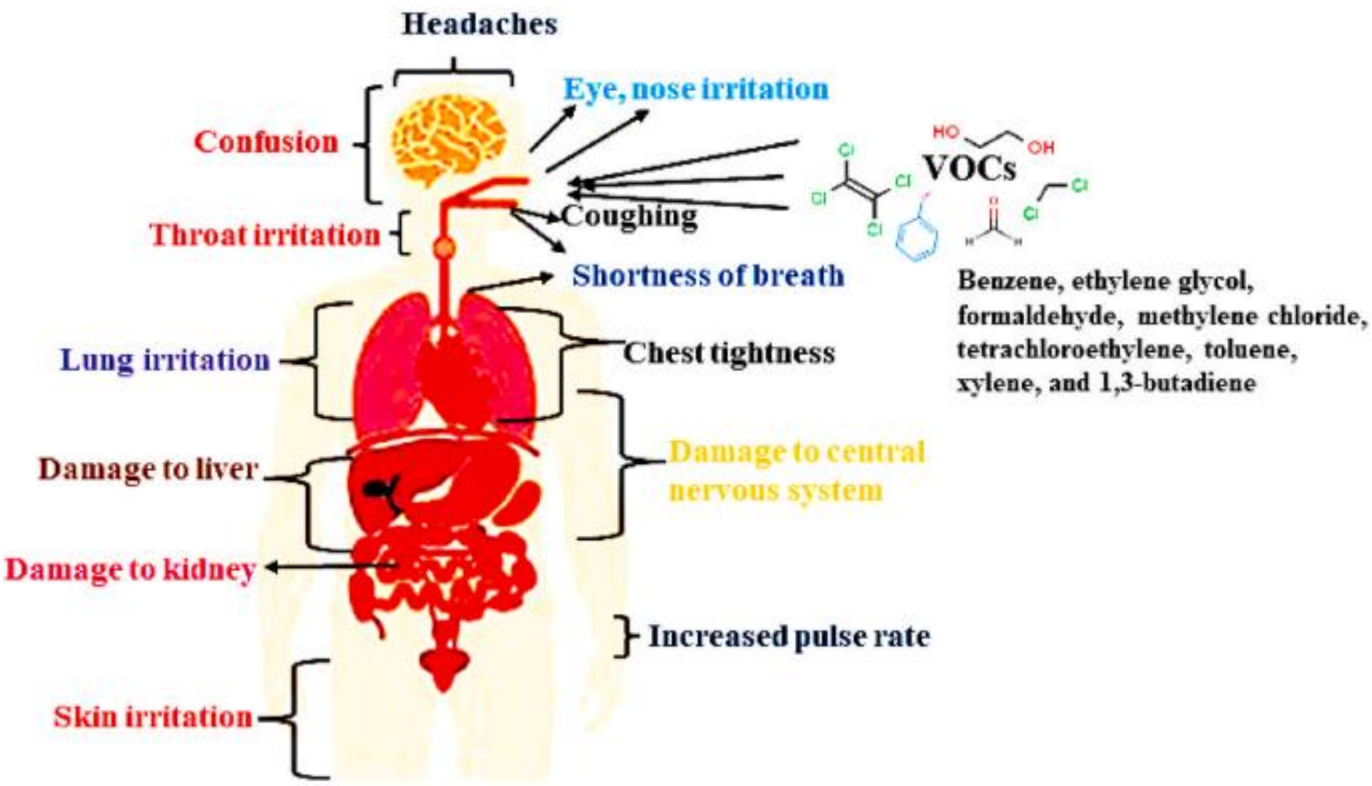


Fig. 4. Possible health impacts of VOCs on human when exposed.

Table 1.1 Overview of important sources and global annual emission rates of selected groups of VOC per year

TgC/year	Emission rate	Uncertainty range
Fossil fuel use		
Alkanes	28	15–60
Alkenes	12	5–25
Aromatic compounds	20	10–30
Biomass burning		
Alkanes	15	7–30
Alkenes	20	10–30
Aromatic compounds	5	2–10
Terrestrial plants		
Isoprene	460	200–1 800
Sum of monoterpenes	140	50–400
Sum of other VOC	580	150–2 400
Oceans		
Alkanes	1	0–2
Alkenes	6	3–12
Sum of anthropogenic and oceanic emissions		
Alkanes	44	
Alkenes	38	
Aromatic compounds	25	
Terrestrial plants	1 180	
Total	1 287	

In: Volatile Organic Compounds in the atmosphere, Ed. Ralph Koppmann, 2007.

1. FONTES MÓVEIS

2. INDUSTRIAL

3. COMBUSTÃO INDUSTRIAL

4. EVAPORAÇÃO DE SOLVENTES

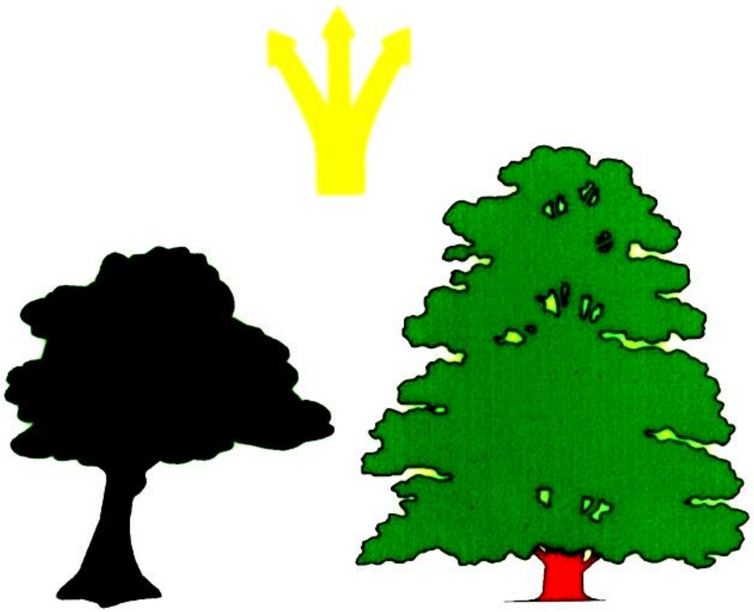
5. TRATAMENTO DE ESGOTO

6. AGRICULTURA E INDÚSTRIA DE ALIMENTOS

7. FONTES NATURAIS - FLORESTAS

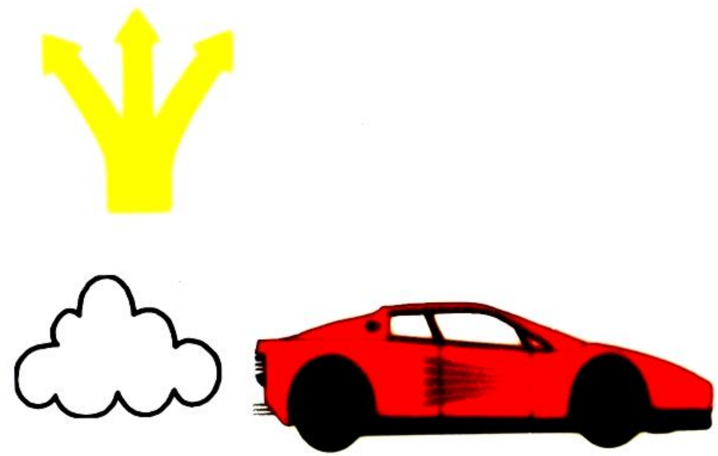
COVs de fontes naturais

1150 Tg C/ano



COVs de fontes antropogênicas

100-140 Tg C/ano



Área urbana

Formaldeído Acetaldeído
Ácido fórmico Propanal
Fenol

Área florestal

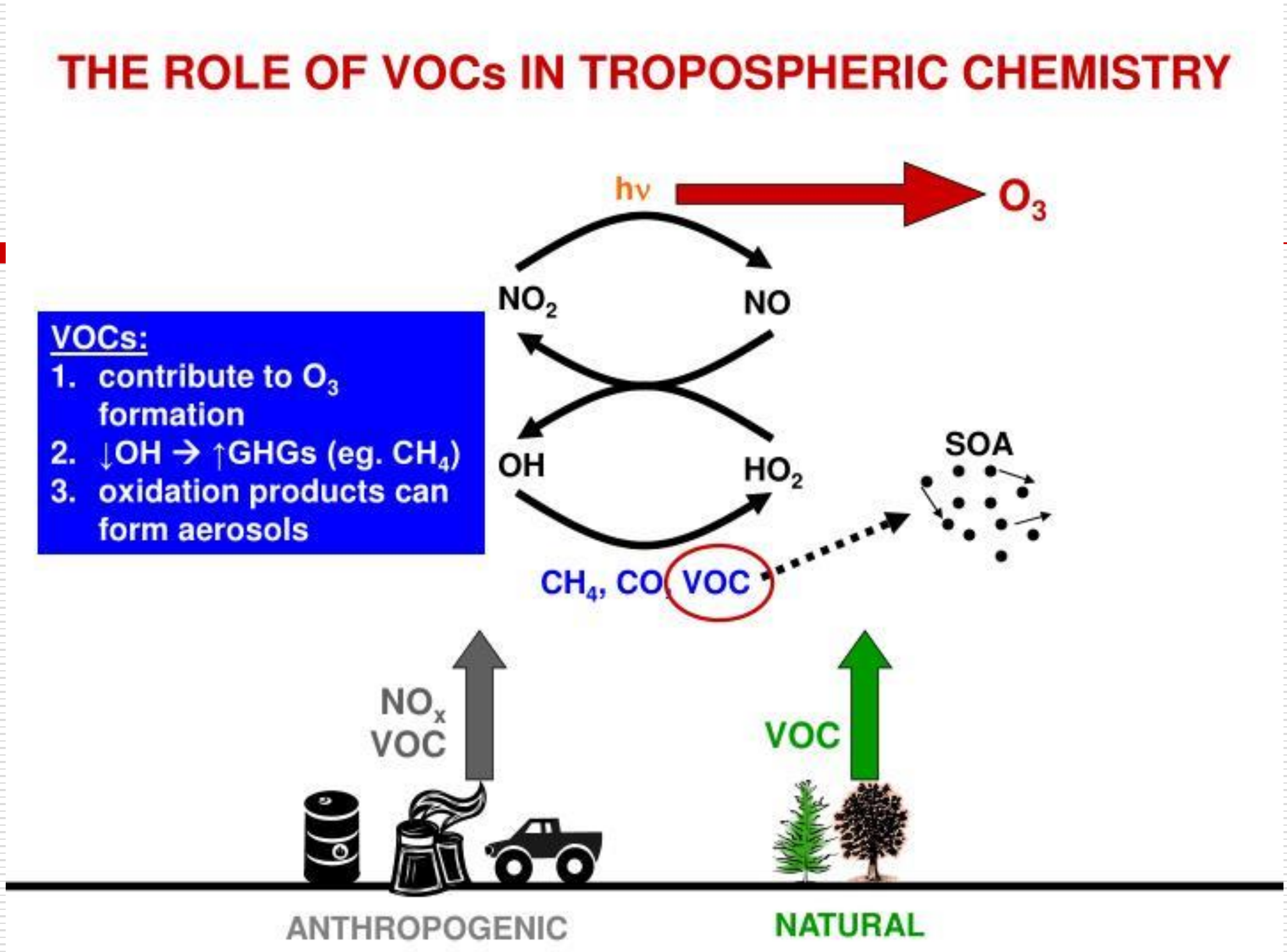
isopreno, terpenos, álcoois

Processos que ocorrem depois de serem emitidos

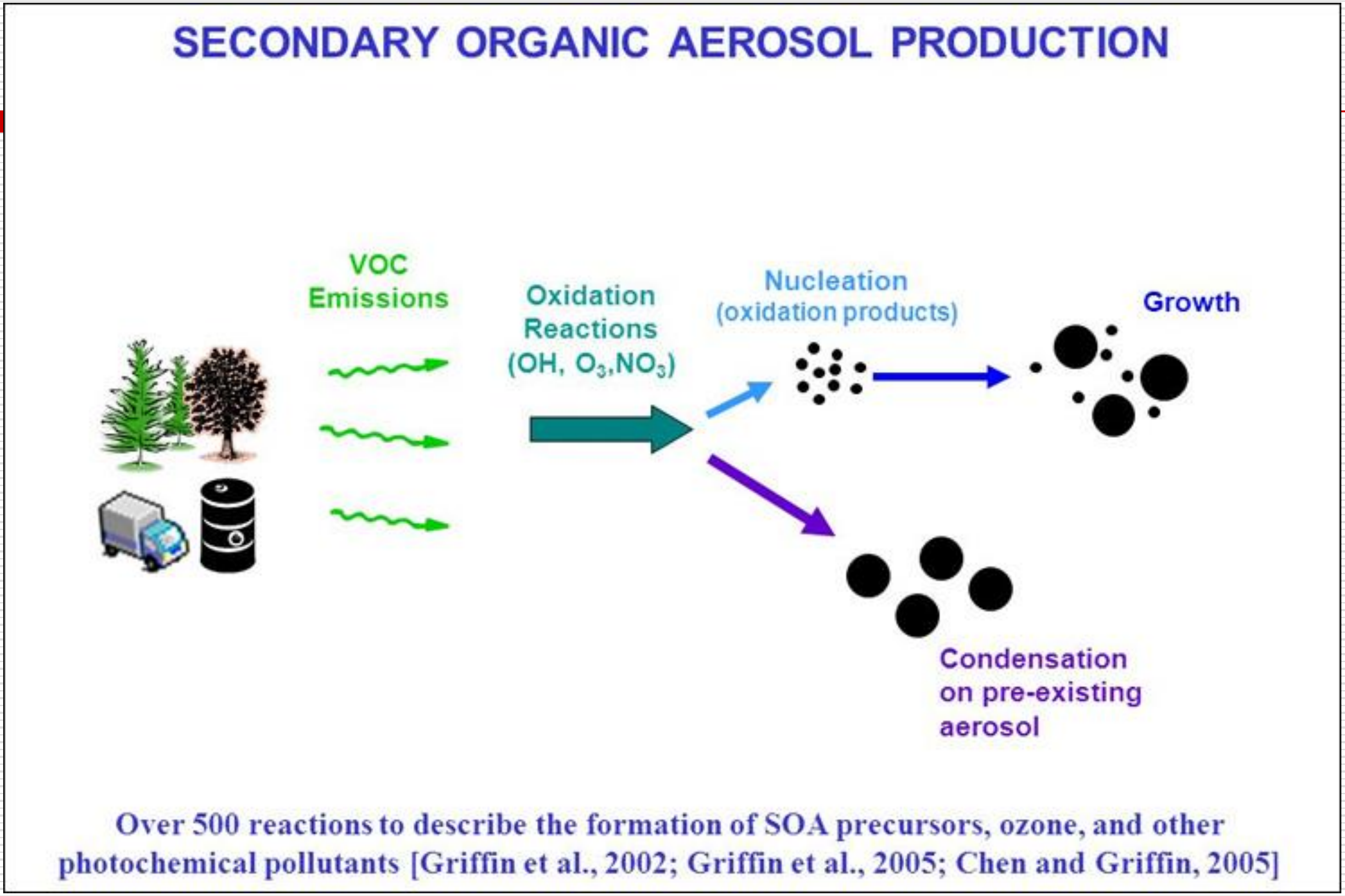
Dispersão
Reações químicas
Deposição

Degradação fotoquímica dos COV reativos

Formaldeído
Acetaldeído
Ácido fórmico

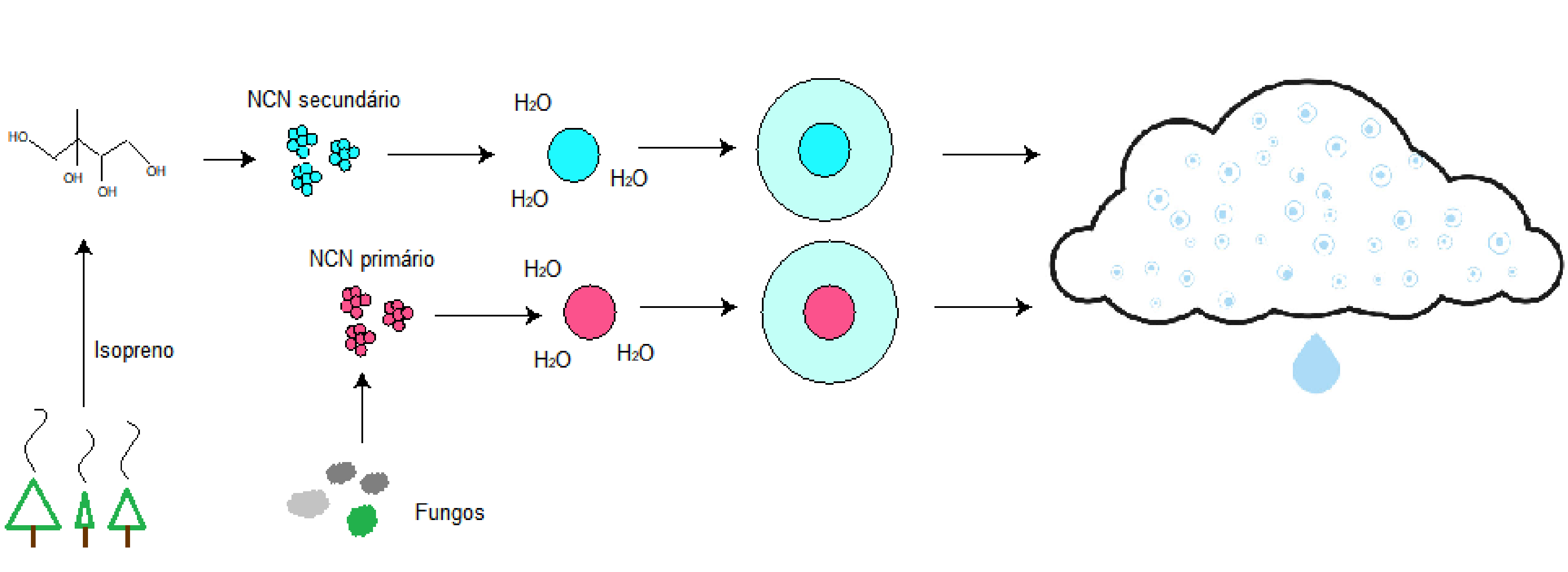


Fonte: Update on CAM/CLM Biogenic VOC Emissions and Secondary Organic Aerosols. Colette L. Heald. Chemistry-Climate Working Group Meeting, CCSM February, 2007

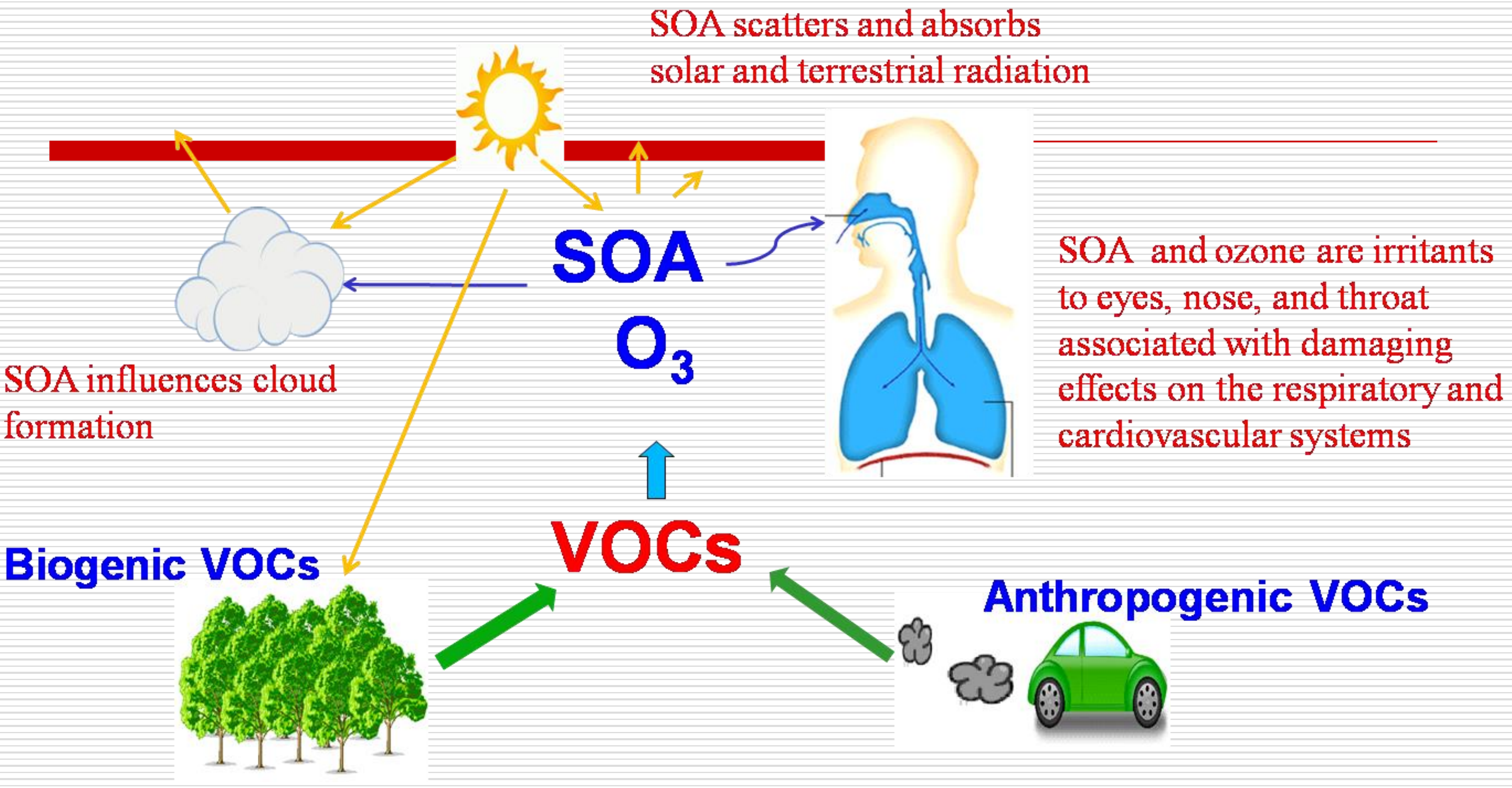


Fonte: **Molecular Characterisation of Anthropogenic Secondary Organic Aerosols (MOCHA)**
https://www.ucc.ie/en/crac/research/mocha/

NCN



Fröhlich-Nowoisky, et al., *Atm. Research*, **2016,** *182*, 346 (desenhado por Caumo, S.).



Fonte: **http://www.rcec.sinica.edu.tw/index.php?action=research_detail&id=6**

1ª. Importância

$$CH_4(g) + \dot{O}H(g) \longrightarrow \dot{C}H_3(g) + H_2O(g) \quad (4.16)$$

Methane + Hydroxyl radical → Methyl radical + Water vapor

$$\dot{C}H_3(g) + O_2(g) \xrightarrow{M} CH_3\dot{O}_2(g) \quad (4.17)$$

Methyl radical + Molecular oxygen → Methylperoxy radical

$$\dot{N}O(g) + CH_3\dot{O}_2(g) \longrightarrow \dot{N}O_2(g) + CH_3\dot{O}(g) \quad (4.18)$$

Nitric oxide + Methylperoxy radical → Nitrogen dioxide + Methoxy radical

$$\dot{N}O_2(g) + h\nu \longrightarrow \dot{N}O(g) + \cdot\dot{O}(g) \qquad \lambda < 420\ nm \quad (4.19)$$

Nitrogen dioxide → Nitric oxide + Atomic oxygen

$$\cdot\dot{O}(g) + O_2(g) \xrightarrow{M} O_3(g) \quad (4.20)$$

Ground-state atomic oxygen + Molecular oxygen → Ozone

In: Mark Jacobson, Atmospheric Pollution. Capítulo 4: Urban air pollution, pag. 96

Table 3.1 Photochemical ozone creating potentials (POCPs) of some VOCs calculated for the British Isles using a Lagrangian model. Selected values from Derwent and Jenkin (1991); compounds marked with an asterisk from Derwent (1991).

VOC	POCP	VOC	POCP
Alkanes		**Aromatic hydrocarbons**	
Methane	1	Benzene	20
Ethane	10	Toluene	55
Propane	40	Ethylbenzene	60
n-Pentane	40	*o*-Xylene	65
Isopentane	30	*m*-Xylene	105
n-Hexane	50	*p*-Xylene	90
2,3-Dimethylbutane	40	1,2,3-Trimethylbenzene	115
Branched C12 alkanes	40	1,2,4-Trimethylbenzene	120
		C10-Trisubstituted benzene	115
Cycloalkanes			
Cyclopentane*	50	**Oxygenated hydrocarbons**	
Methylcyclopentane*	50	Formaldehyde	40
Cyclohexane*	25	Acetaldehyde	55
		Propionaldehyde*	60
Olefins		Acrolein	120
Ethylene	100	Benzaldehyde	−35
Propylene	105	Acetone	20
1-Butene	95	Methanol	10
2-Butene	100	Ethanol*	25
1-Pentene	70	*n*-Propanol	45
2-Methylbut-2-ene	80		
1,3-Butadiene*	105	**Chlorinated hydrocarbons**	
Isoprene*	100	Methylene chloride	1
α-Pinene*	50	Chloroform	1
β-Pinene*	50	Methyl chloroform	0
Acetylenes			
Acetylene	15		

In: Chemistry and Analysis of VOC in the environment, 1993

Table 1.2 Overview of average tropospheric lifetimes of VOC compound groups and some selected VOCs as examples. Lifetimes are given for an average OH concentration of 6×10^5 per cm^3 and an average ozone concentration of 7×10^{11} per cm^3 (about 30 ppb)

Compound	Average lifetime
Alkanes	Months–days
Ethane	2.5 months
Propane	2.5 weeks
n-Pentane	4 days
Alkenes	Days–hours
Ethene	1.5 days
Propene	11 h
1-Butene	10 h
Cyclic compounds	Days–hours
Cyclopentane	4 days
Methylcyclohexane	2 days
Cyclohexane	3 h
Aromatic compounds	Weeks–hours
Benzene	2 weeks
Toluene	2 days
1,3,5-Trimethylbenzene	7.5 h
Biogenic compounds	Hours–minutes
Isoprene	3 h
α-Pinene	4 h
Limonene	30 min

In: Volatile Organic Compounds in the atmosphere, Ed. Ralph Koppmann, 2007.

Comportamento químico dos COV

- Oxidação por processos fotoquímicos
- Maioria dos COV reage com: ·OH, NO_3, O_3 e Cl·.
- Alguns COVO (acetona e formaldeído) sofrem fotólise direta (acima de 290 nm)
- Tempo de residência:

  -estrutura química

  -concentração do radical

  -intensidade da radiação solar

Processos físico-químicos dos COV

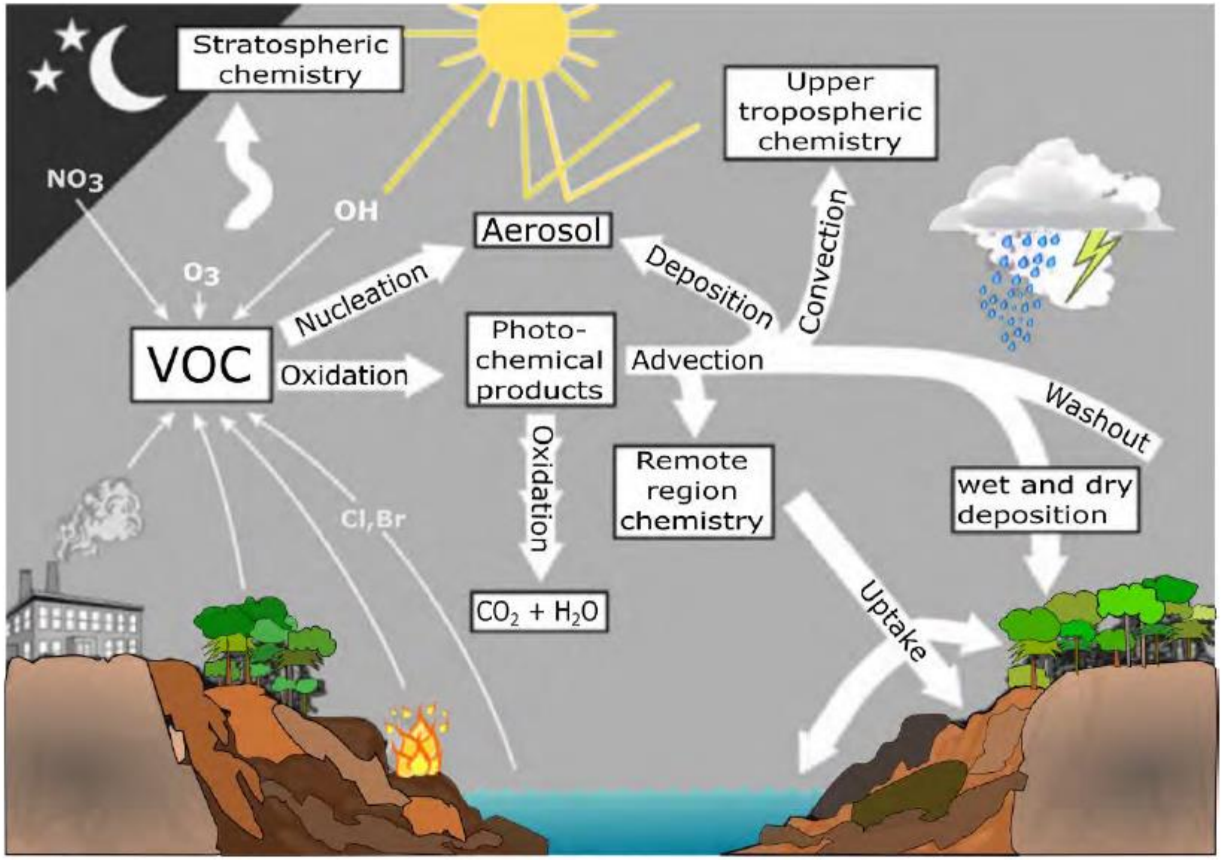
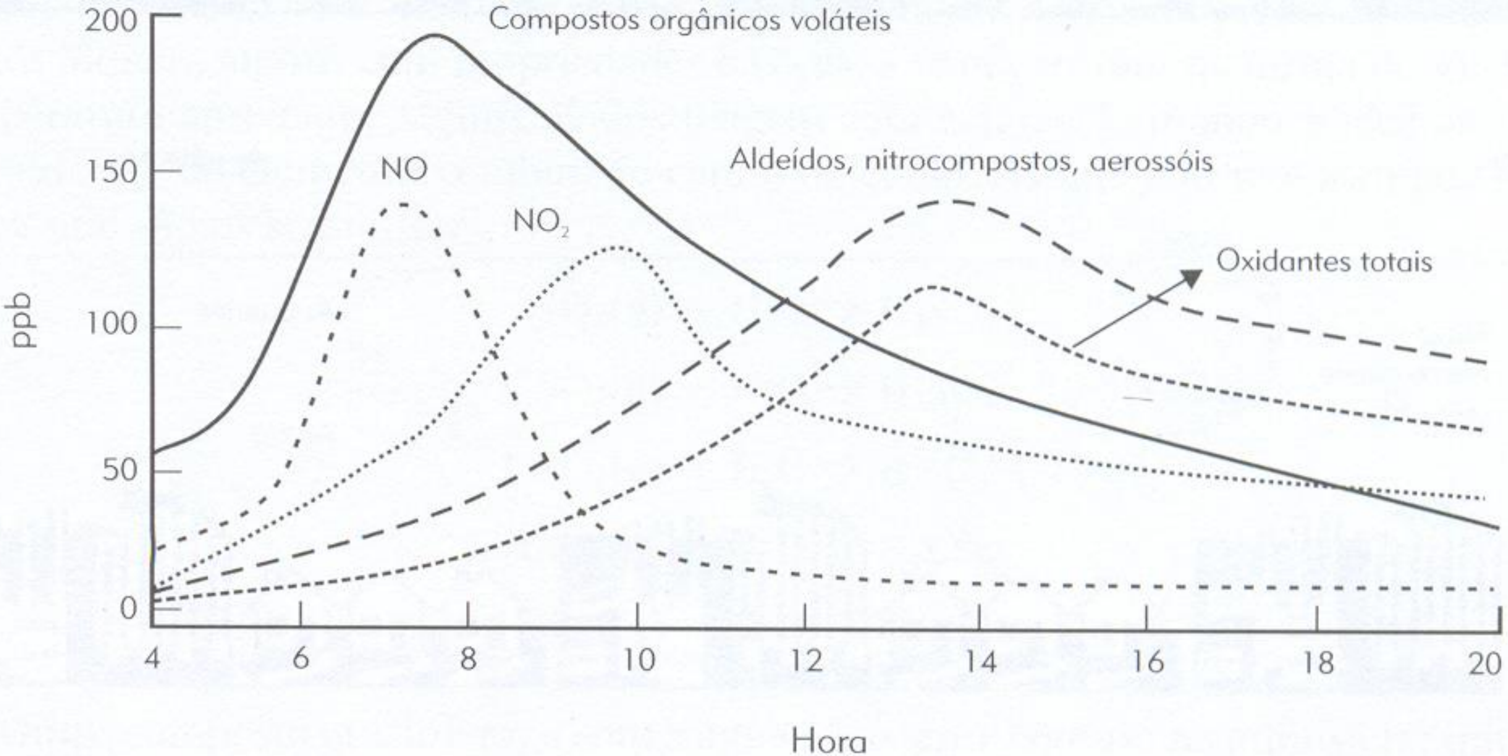


Figure I. 9: Physical and chemical processes of VOCs in the atmosphere.
Adapted from Williams and Koppmann, 2007.

Figure 4.4. Panoramic view of Los Angeles, California, taken from Third and Olive Streets, December 3, 1909. Photo by Chas. Z. Bailey, available from Library of Congress Prints and Photographs Division, Washington, DC.

Figure 4.3. Noontime photograph of Donora, Pennsylvania, on October 29, 1948, during a deadly smog event. Courtesy of the Pittsburgh Post-Gazette.



▲ **FIGURA 3.6** Variação da composição dos gases atmosféricos envolvidos no *smog* fotoquímico, ao longo do dia.

In: Introdução à Química Ambiental, 2004.

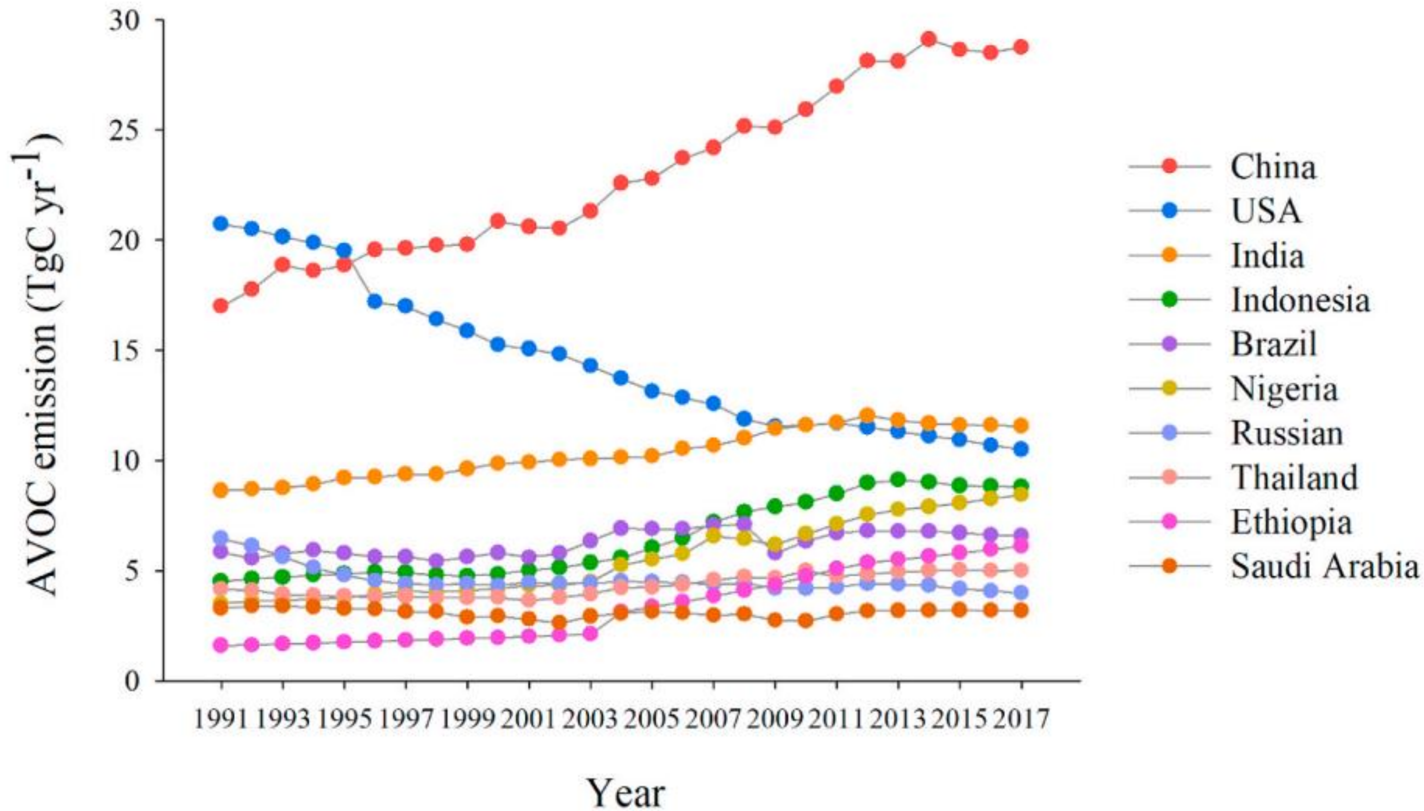


Fig. 4. Time series of AVOC emissions from the top 10 countries from 1991 to 2017.

Table I. 4: Photolysis channels for formaldehyde, acetaldehyde, and acetone.
Respective yield of HOx radicals in the troposphere, wavelenght thresholds and quantum yields. Adapted from (Koppmann and Wildt, 2007).

Reaction			HOx yield	λ (nm)[a]	φ[b]
$HCHO + h\nu$	→	$H^{\bullet} + HCO^{\bullet}$	$2\ HO_2$	≤ 324	0.75 at 304 nm
	→	$H_2 + CO$		all	0.58 at 339 nm
$CH_3CHO + h\nu$	→	$CH_3^{\bullet} + HCO^{\bullet}$	$2\ HO_2$	≤ 337	0.48 at 300 nm
	→	$CH_4 + CO$		all	0.18 at 275 nm
	→	$CH_3CO^{\bullet} + H$	$1\ HO_2$	< 320	0.052 at 280
$CH_3COCH_3 + h\nu$	→	$CH_3^{\bullet} + CH_3CO^{\bullet}$	$1\ HO_2$	< 338	0.77 – 0.50 at
	→	$2CH_3^{\bullet} + CO$	$2\ HO_2$	< 299	280 nm

a - from IUPAC vol II (Atkinson et al., 2006).

b – from Calvert, 2011.

ISOPLETAS DE OZÔNIO

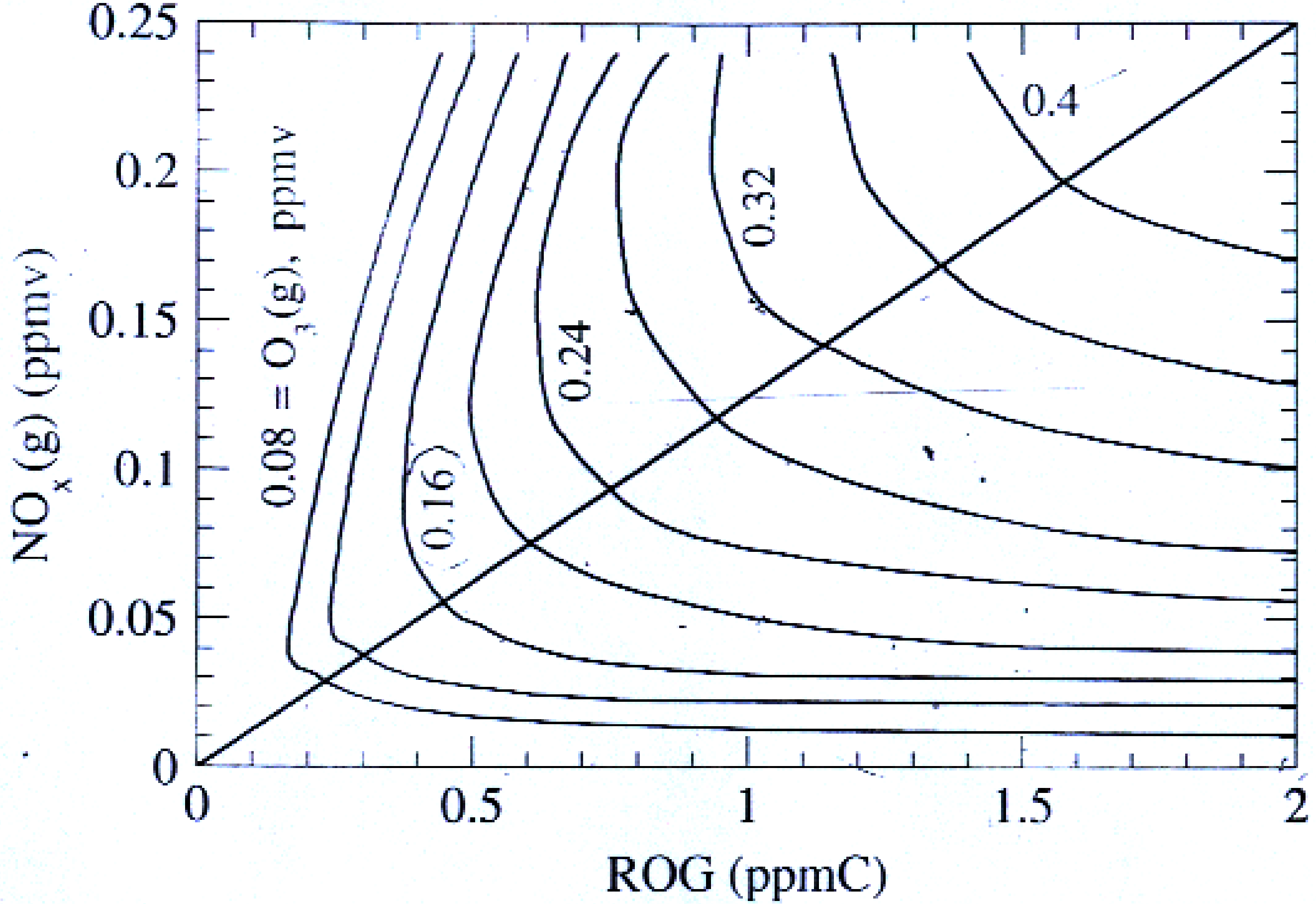
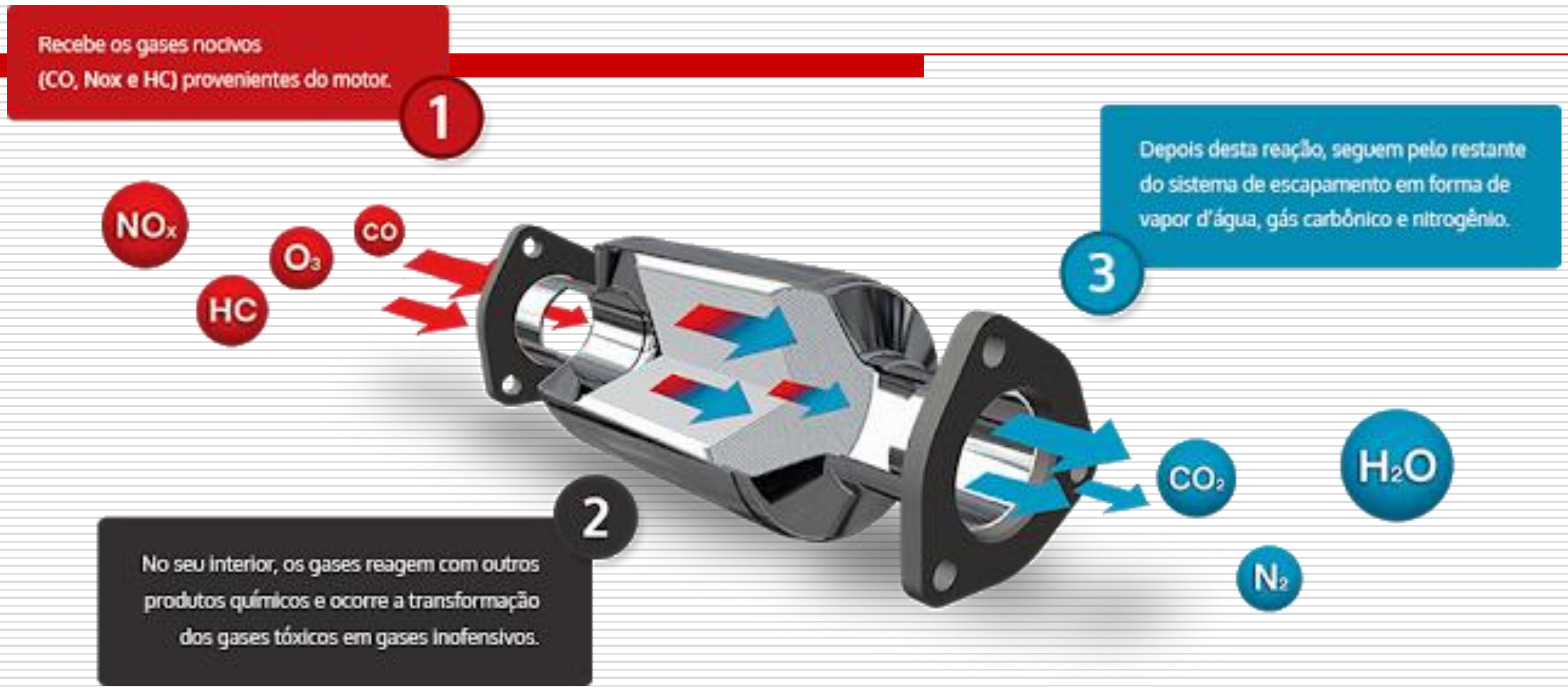


Figure 4.9. Peak ozone mixing ratios resulting from different initial mixing ratios of NO_x(g) and ROGs. The ROG:NO_x(g) ratio along the line through zero is 8:1. Adapted from Finlayson-Pitts and Pitts (1999).

M. Jacobson, 2002.

Uso de catalisadores em veículos automotores



http://cienciatecnologiafoco.blogspot.com/2017/12/catalisador-industria-automobilistica.html

$2CO + O_2 \rightarrow 2CO_2$

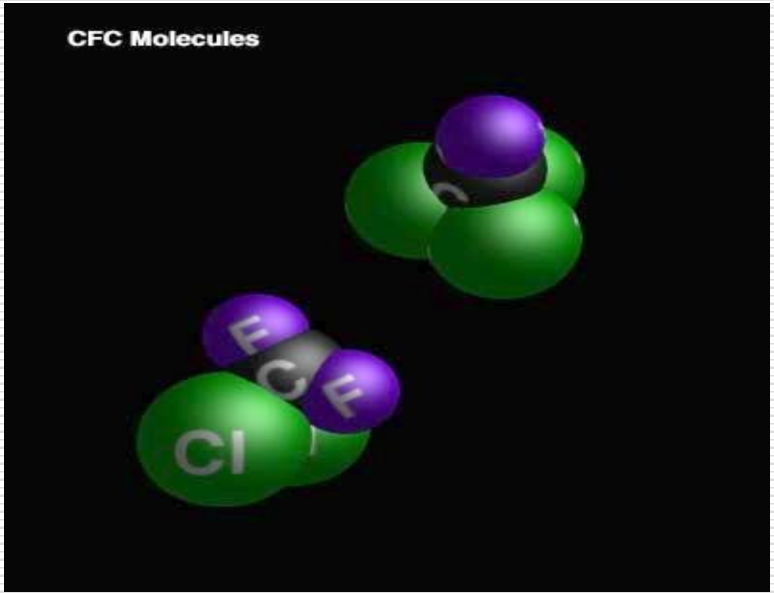
$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

$2NO + 4CO \rightarrow N_2 + 4CO_2$ ou

$2NO + 2CO \rightarrow N_2 + 2CO_2$

Importância

2. COV e a destruição da camada de O_3



$CF_2Cl_2 + h\nu \rightarrow Cl\bullet + CCLF_2\bullet$

$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$

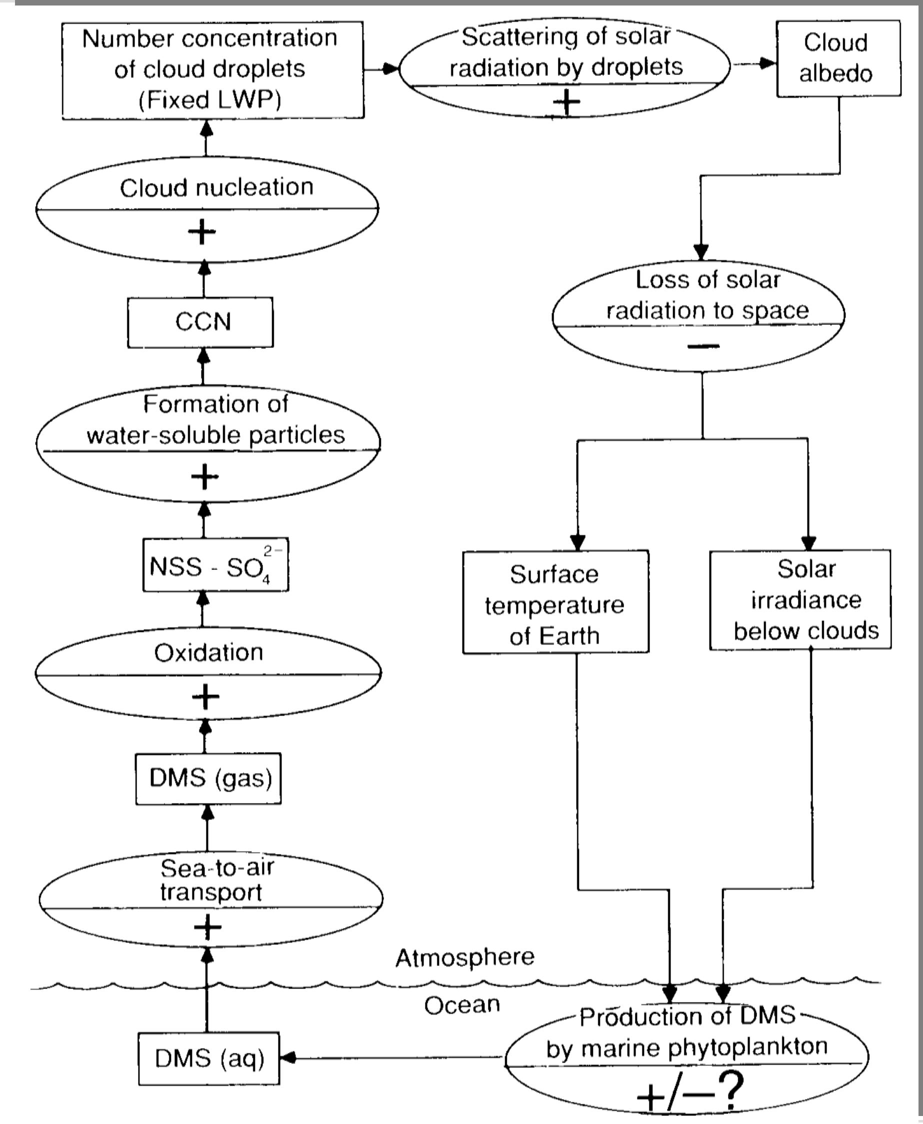
$ClO\bullet + O\bullet \rightarrow Cl\bullet + O_2$

Table 5.2 Lifetimes, Radiative Forcings, GWPs and ODPs for the ozone-depleting substances (ODSs) and their replacements

		Lifetime[a] (years)	Radiative Forcing[a] (Wm^{-2}/ppb)	GWP		ODP[e]
				TH-20[b]	TH-100[b]	
PFCs						
	SF_6	3200	0.52	15290	22450	
PFC-14	CF_4	50000	0.08	3920	5820	
PFC-116	C_2F_6	10000	0.26	8110	12010	
PFC-218	C_3F_8	2600	0.26	5940	8690	
PFC-31-10	C_4F_{10}	2600	0.33	5950	8710	
PFC-51-14	C_6F_{14}	3200	0.49	6230	9140	
PFC-318	c-C_4F_8	3200	0.32	6870	10090	
CFCs						
CFC-11	CCl_3F	45	0.25	6300	4600	1
CFC-12	CCl_2F_2	100	0.32	10200	10600	1.0
CFC-113	CCl_2FCClF_2	85	0.3	6150	6030	1.0
CFC-114	$CClF_2CClF_2$	300	0.31	7560	9880	0.9[f]
CFC-115	$CClF_2CF_3$	1700	0.18	4990	7250	0.4[f]
Halons						
Halon-1301	$CBrF_3$	65	0.32	7970	7030	12.0
Halon-1211	$CBrClF_2$	16[b]	0.3	4460	1860	6.0
Halon-2402	$CBrF_2CBrF_2$	20[b]	0.33[b]	3460	1620	<8.6
Chlorocarbons						
Carbon tetrachloride	CCl_4	26[b]	0.13	2540	1380	0.73
Methyl bromide	CH_3Br	0.7	0.01	16	5	0.38
Bromochloromethane	CH_2BrCl					
Methylchloroform	CH_3CCl_3	5[b]	0.06	476	144	0.12
Methylene chloride	CH_2Cl_2	0.46	0.03	35[a]	10[a]	<0.001[f]
Methyl chloride	CH_3Cl	1.3	0.01	55[a]	16[a]	0.02[f]

- 3. COV e as interações entre organismos
- As plantas retiram 120 Pg C ano^{-1}
- 36% do C assimilado é emitido para a atmosfera como COV
- Alguns mediam polinização e processos de defesa entre plantas e outros organismos.
- "*Talking Trees*"- plantas se beneficiam com o aviso de defesa das plantas adjacentes. Ataque microbiano
- →moléculas sinalizantes: ácidos salicíclico e jasmônico e, etileno.

“Hipótese CLAW”



Charlson et al., 1992

COV Biogênicos

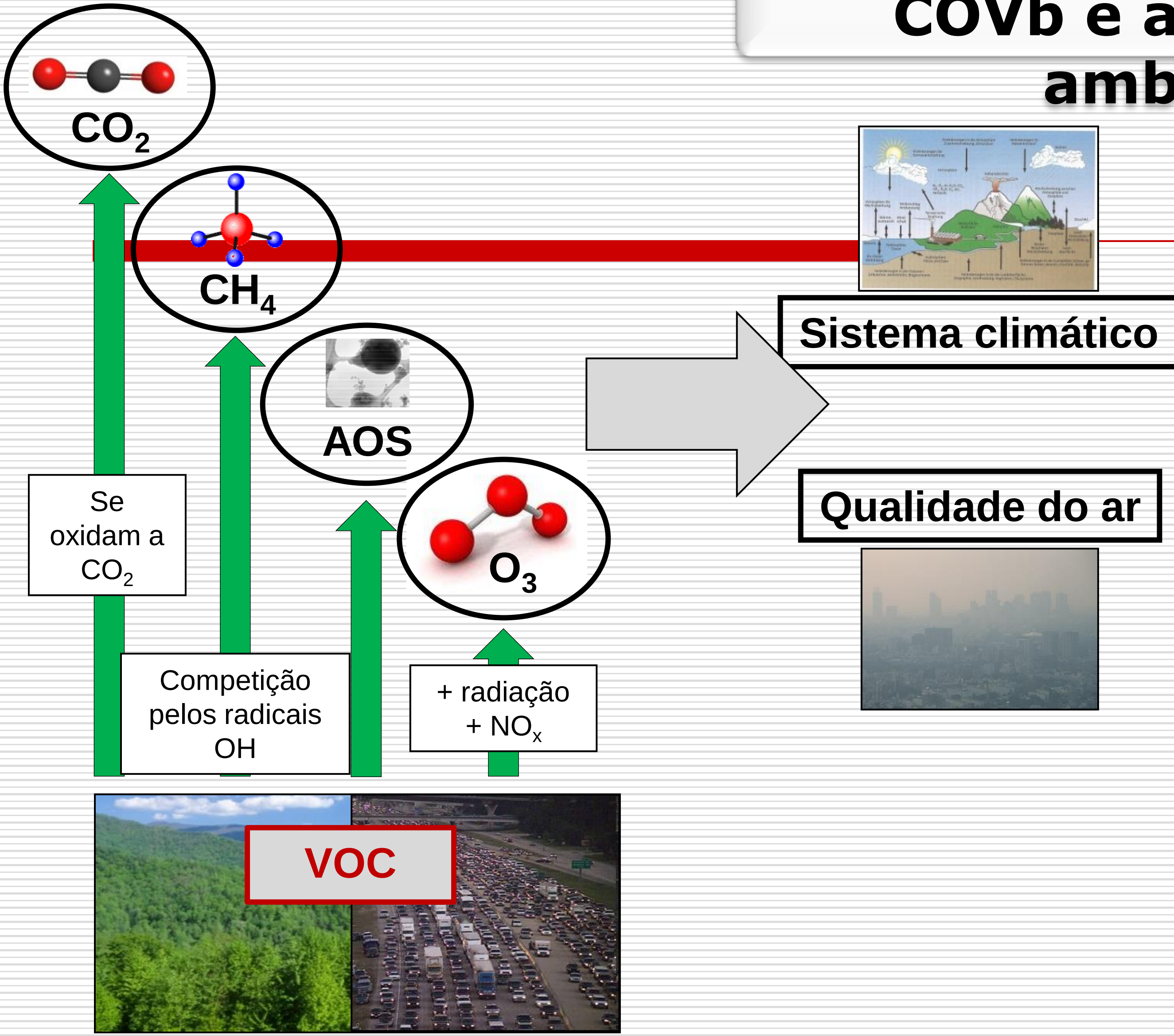
COVB

sinalização
(sob estresse, grau de maturidade,
germinação, florescimento,
herbívoros,...)

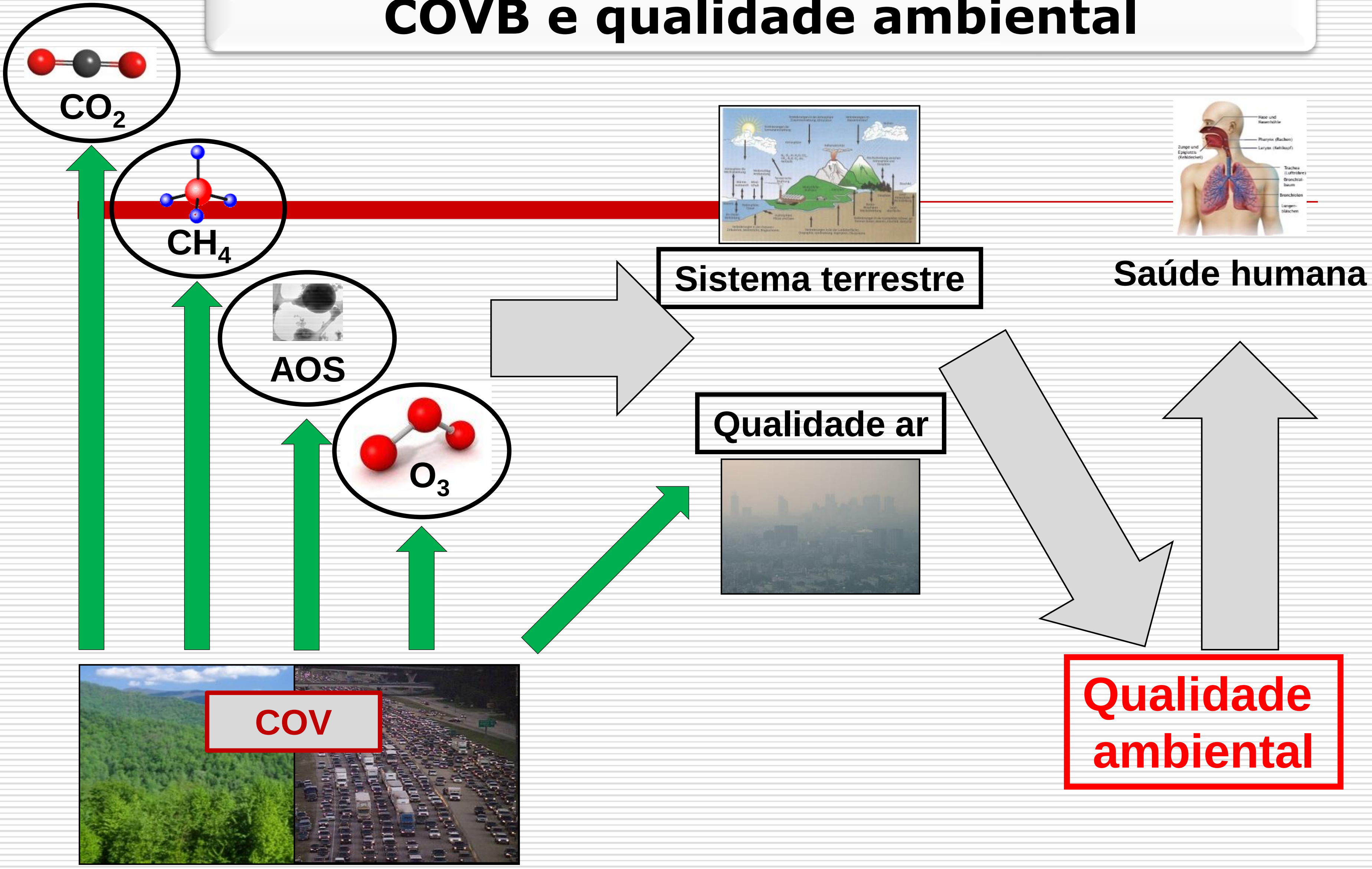
defesa,
proteção de estresses abióticos,
esp. calor, seca e estresse oxidativo

→ Pouco é conhecido sobre o impacto das mudanças climáticas nas emissões de COVB (efeitos extremos, interações.

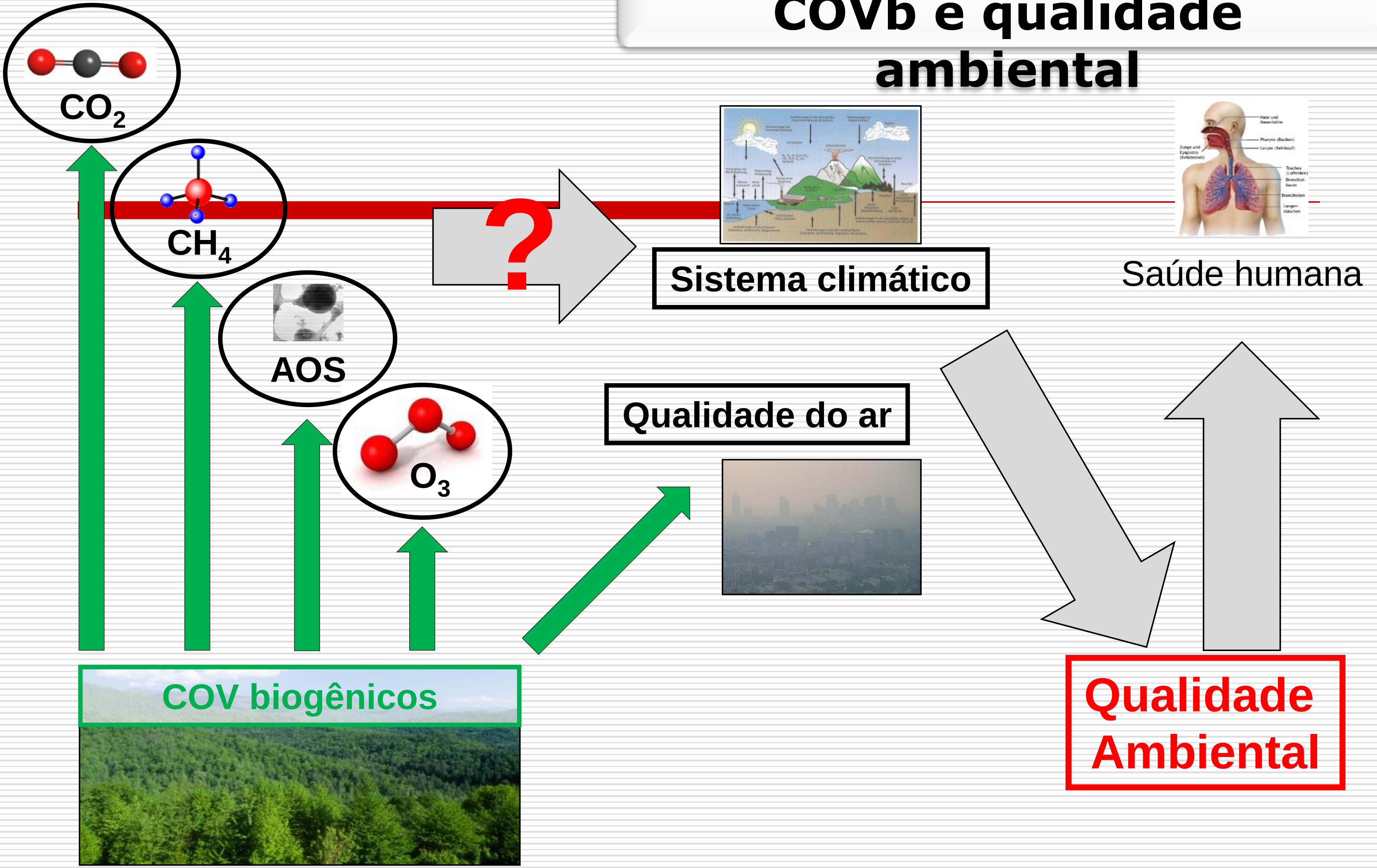
COVb e a qualidade ambiental



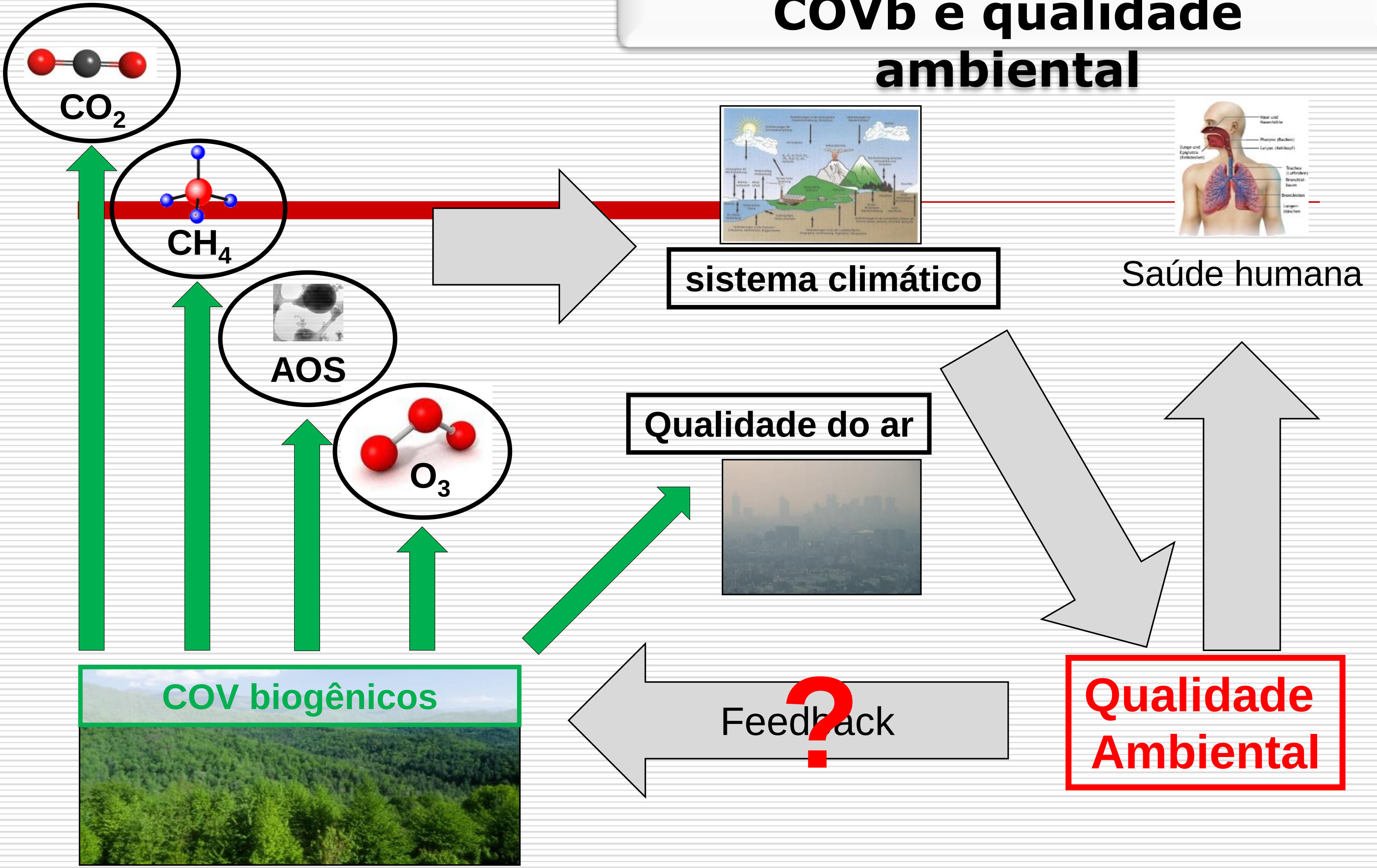
COVB e qualidade ambiental



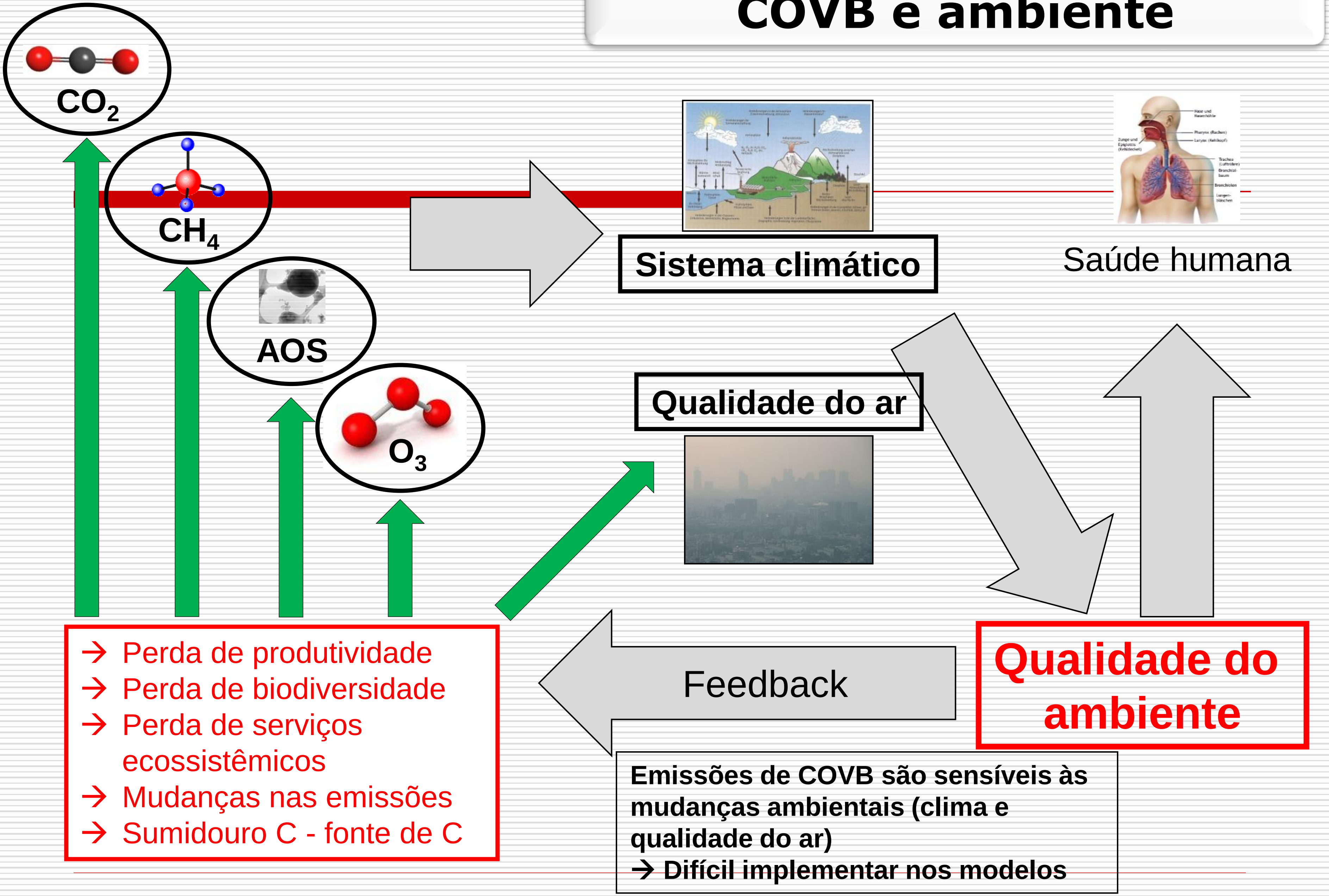
COVb e qualidade ambiental

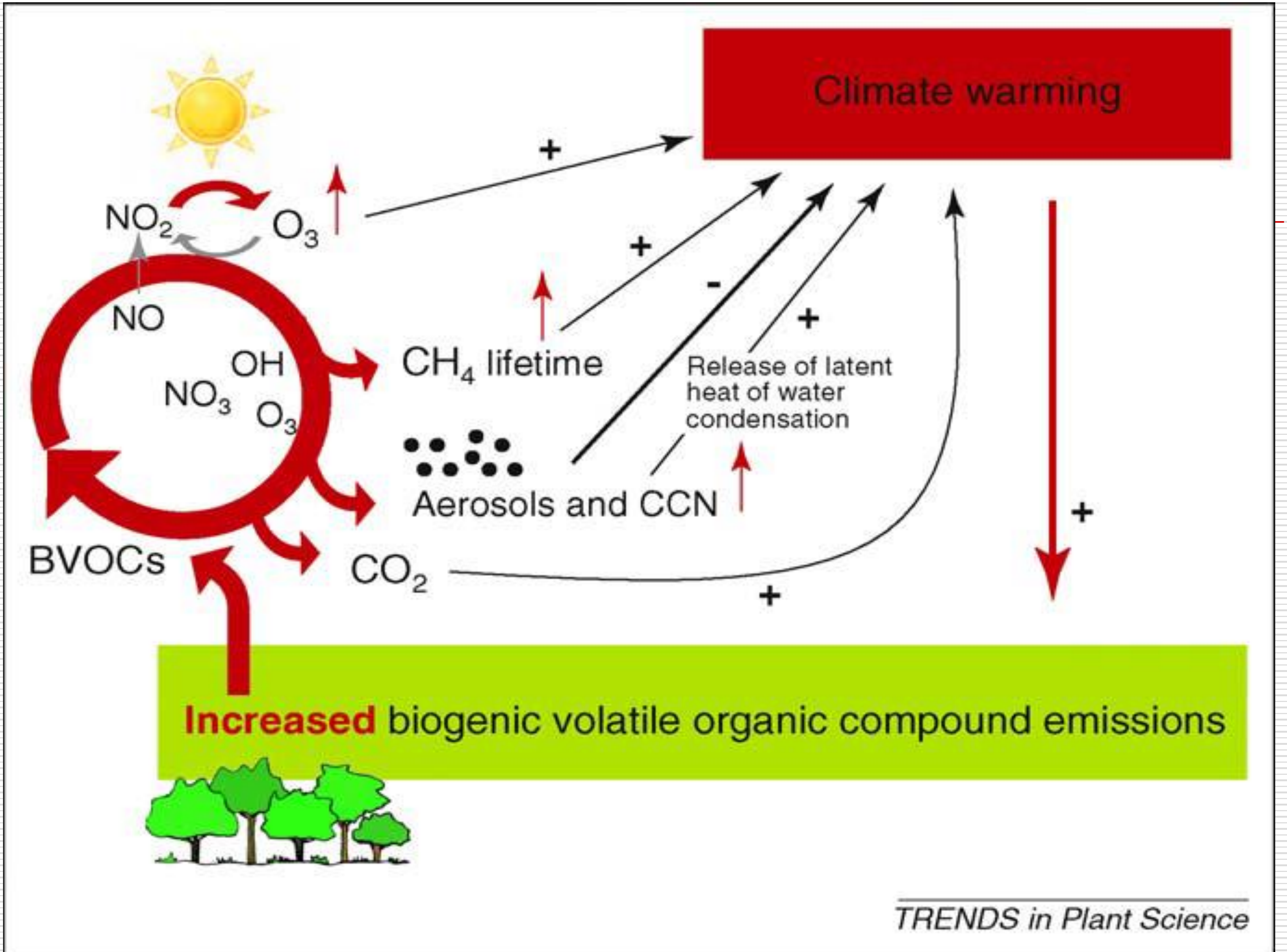


COVb e qualidade ambiental



COVB e ambiente

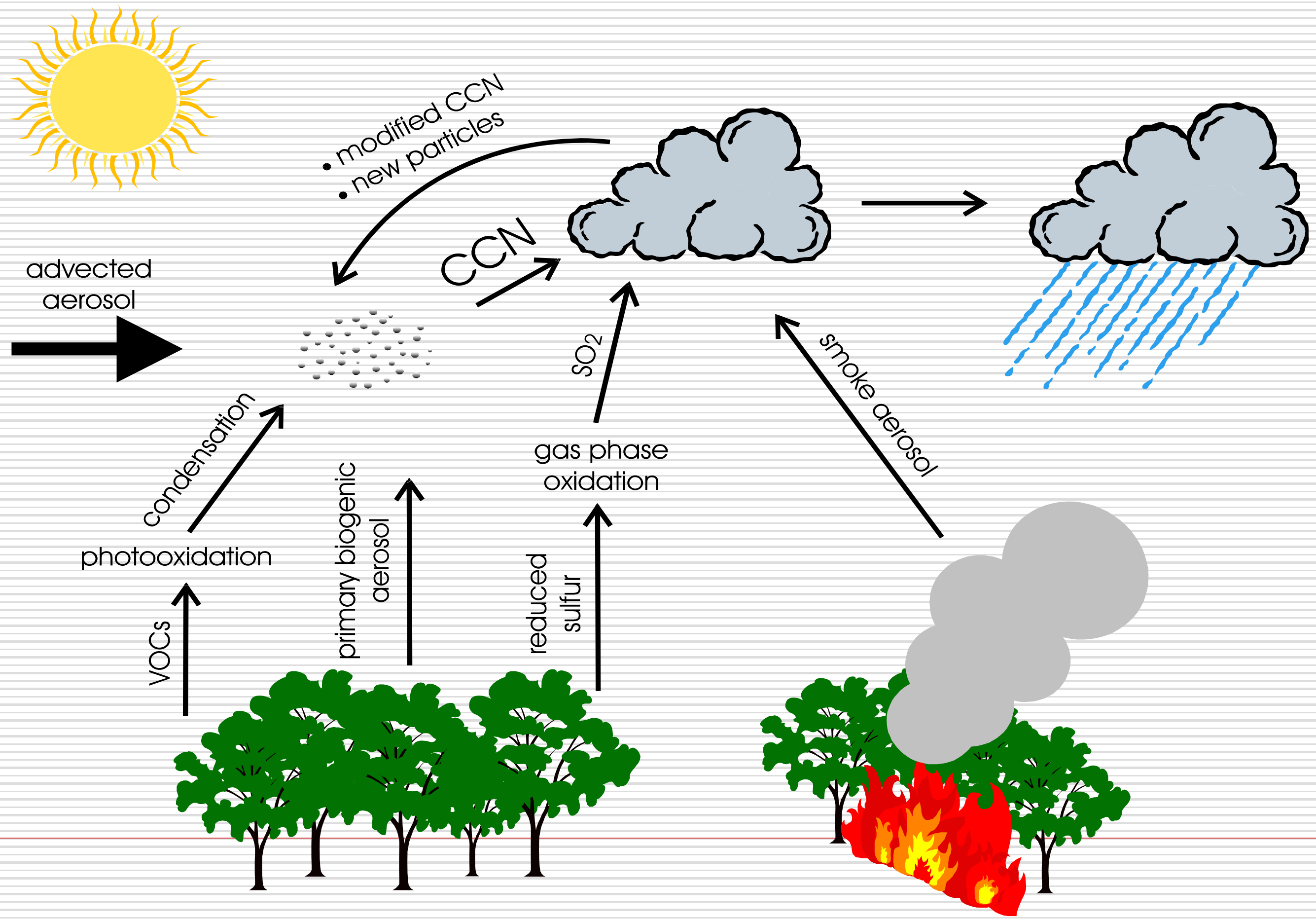




Trends in Plant Science Vol.15 No.3

4. Importância

COV e formação de nuvens



Class	Compound
Hemiterpene	Isoprene
Monoterpenes	Camphene
	Δ3-Carene
	d-Limonene
	Myrcene
	cis-Ocimene
	Trans-Ocimene
	α-Phellandrene
	β-Phellandrene
	α-Pinene
	β-Pinene
	Sabinene
	α-Terpinene
	γ-Terpinene
	Terpinolene
	Tricyclene or α-Thujene*
Sesquiterpenes	β-Caryophyllene
	Cyperene
	α-Humulene
Alcohols	p-Cymen-8-ol*
	cis-3-Hexen-1-ol
	Linalool

*tentative

Class	Compound
Acetates	Bornylacetate
	Butylacetate*
	cis-3-Hexenylacetate
Aldehydes	n-Hexenal
	trans-2-Hexenal
Ketones	2-Heptanone
	2-Methyl-6-Methylene-1,7-octadien-3-one*
	Pinocarvone*
	Verbenone*
Ethers	1,8-Cineole
	p-Dimethoxybenzene*
	Estragole*
	p-Methylanisole*
Esters	Methylsalicylate*
n-Alkanes	n-Hexane
	C10 – C17
Alkenes	1-Decene
	1-Dodecene
	1-Hexadecene*
	p-Mentha-1,3,8-triene*
	1-Pentadecene*
	1-Tetradecene
Aromatics	p-Cymene

Winer et al., 1989

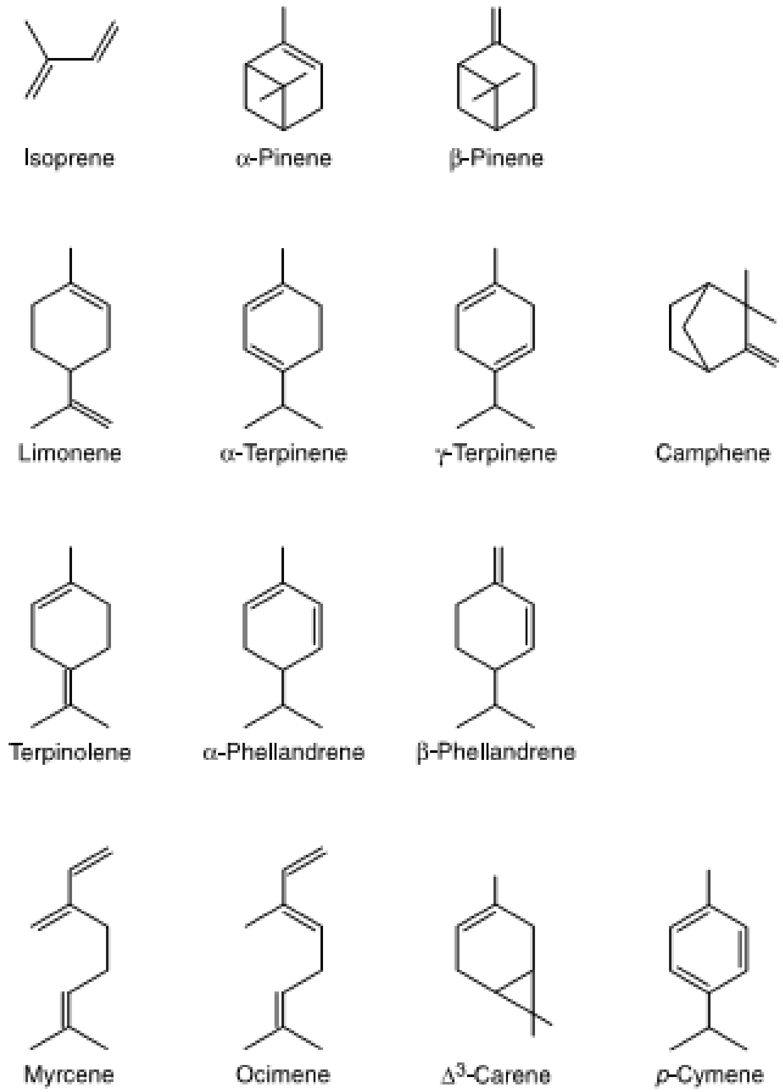


FIGURE 6.22 Chemical structures of some biogenically emitted hydrocarbons.

Seinfeld and Pandis, 2008.

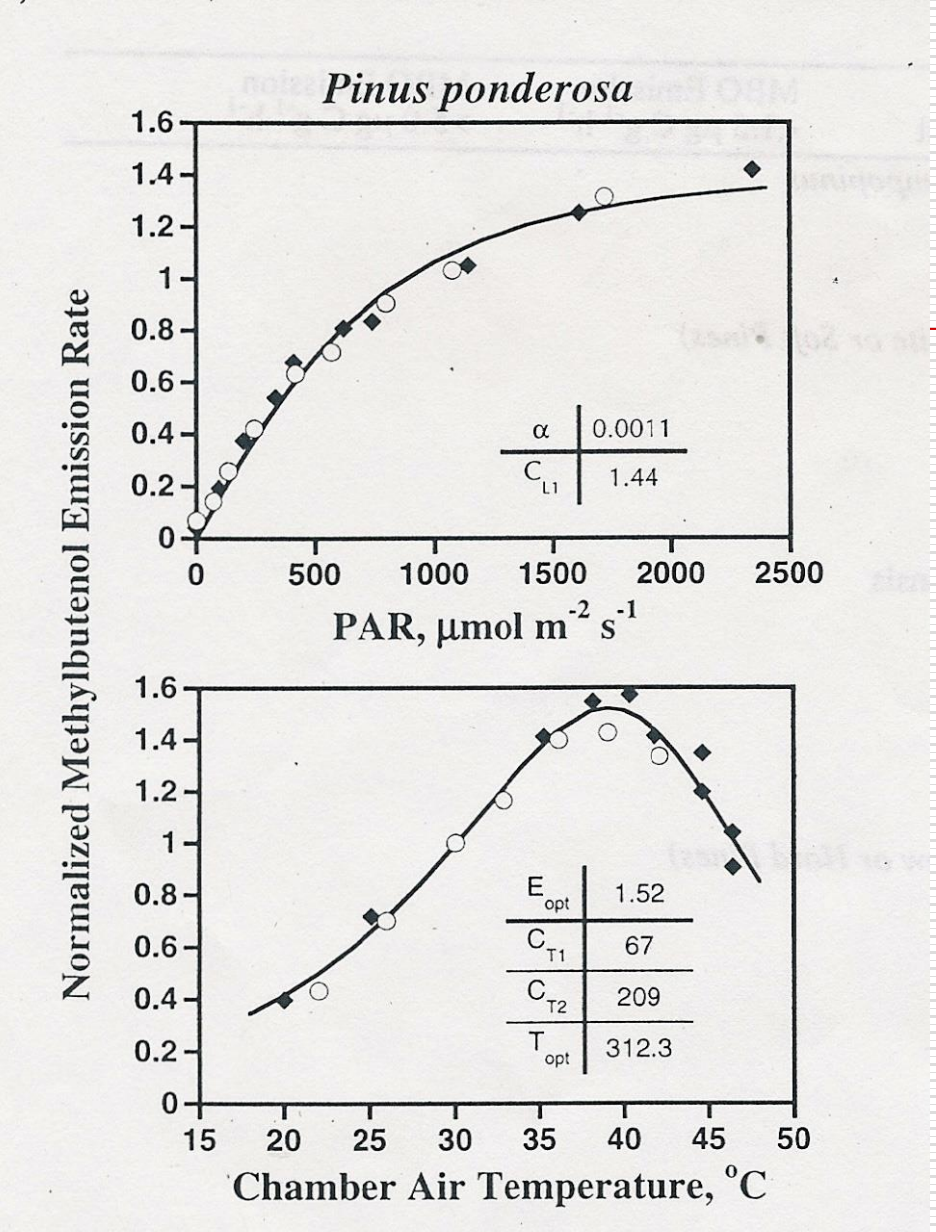
COV biogênicos

Espécie	Fontes primárias	Estimativa anual de emissão global, Tg C. (Tg= 10^{12}g)	Tempo de permanência em dias.
Metano	Pântanos	319-412	400
Isopreno	Plantas	175-503	0,2
Monoterpenos	Plantas	127-480	0,1-0,2
Dimetilsulfeto	Fitoplâncton marinho	15-30	< 0,9
Etileno	Plantas e solo	8-25	1,9
Acetaldeído	Plantas	~260	>1
2-metil-3-buteno-2-ol (MBO)	Plantas	~260	>1
Hexanol	Plantas	~260	>1
Ac. carboxílicos	Plantas e solo	~260	>1
Etanol	Plantas e solo	~260	>1
Metanol	Plantas e solo	~260	>1

Principais compostos emitidos por fontes biogênicas e suas fontes, tempo de permanência e estimativa de emissão global.

Fatores abióticos e bióticos que influenciam as emissões dos COV

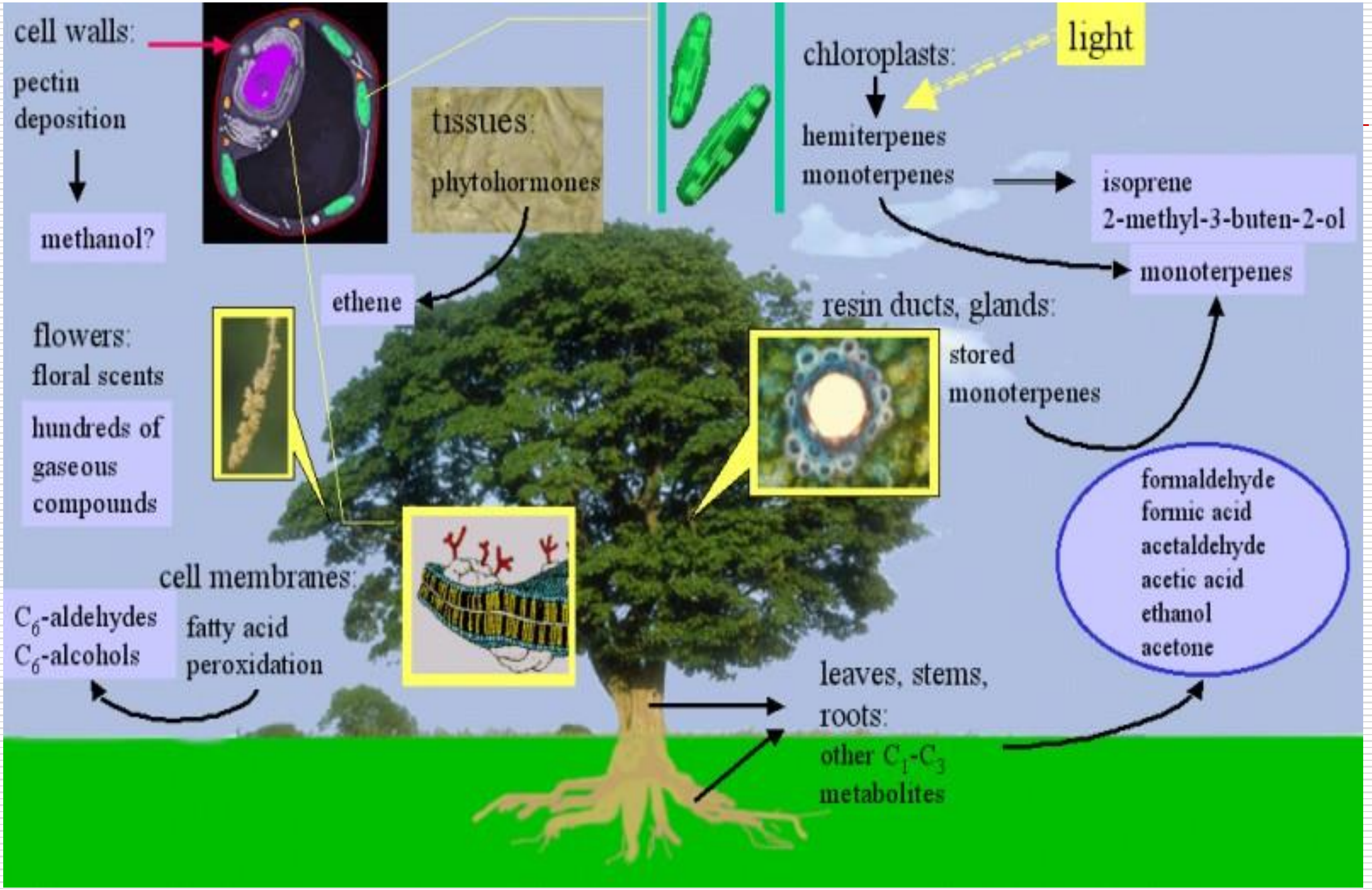
Factor	Influence	
	long term	Short term
Temperature		+ + +
Light intensity	+	+ + +
Humidity	?	
Plant development	+	
Seasonality	+	
Nutrition	+	
Herbivory		+ + +
Injury		+ + +
Heat stress		+ +
Water stress	+ +	
Oxidative stress (ozone)	?	+ +
SO_2	?	?



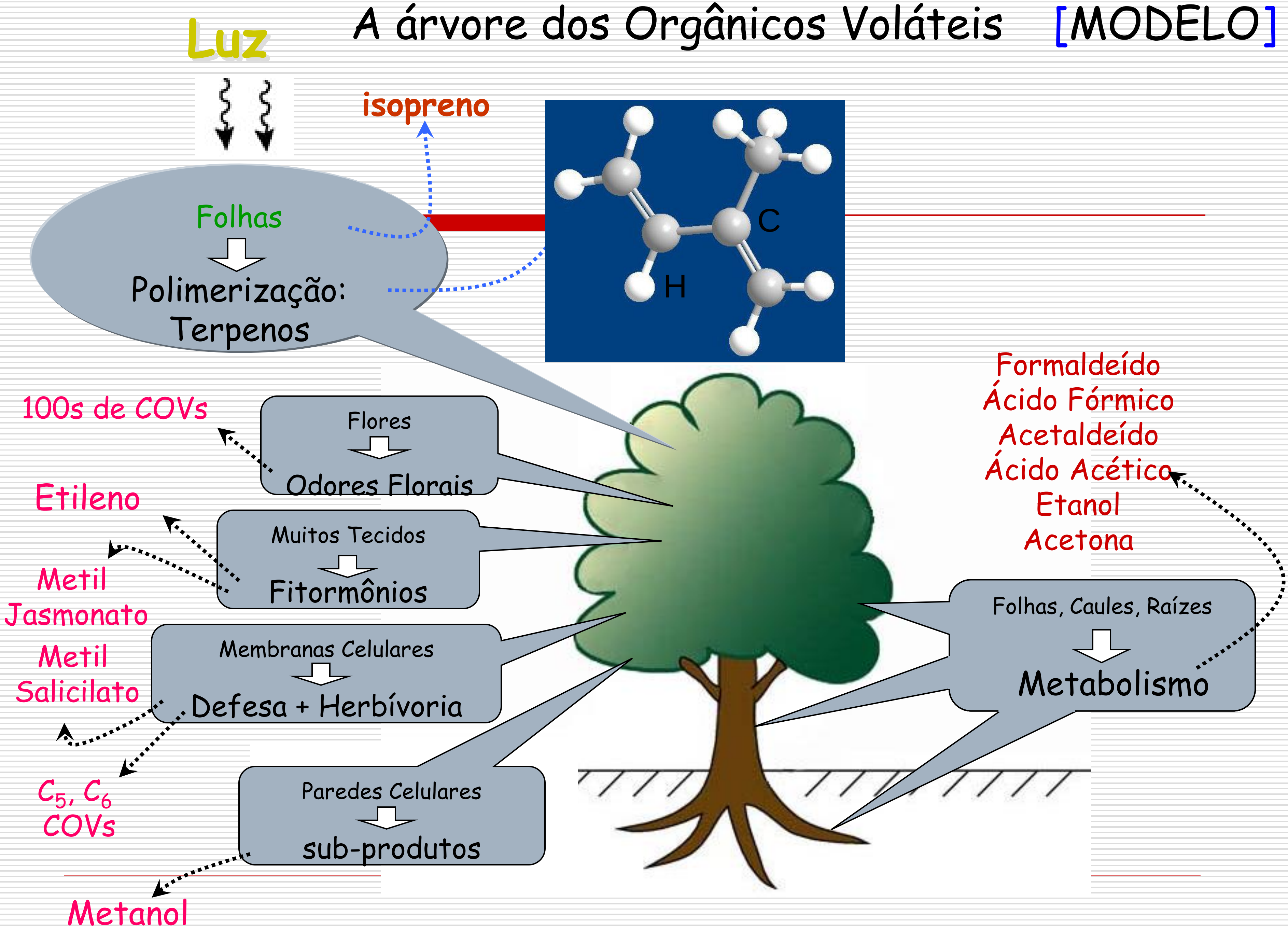
Harley, Vasconcellos, Greenberg, Gunther **1998** ***J. Geoph. Res.***


As Emissões
de Compostos Orgânicos Voláteis
estão Associadas com a Biodiversidade
Photo Credit Antonio D Nobre

Emissões biogênicas



A árvore dos Orgânicos Voláteis [MODELO]



Modificado de *Fall, R.*, University of Colorado, Boulder at http://www.rfall.net/

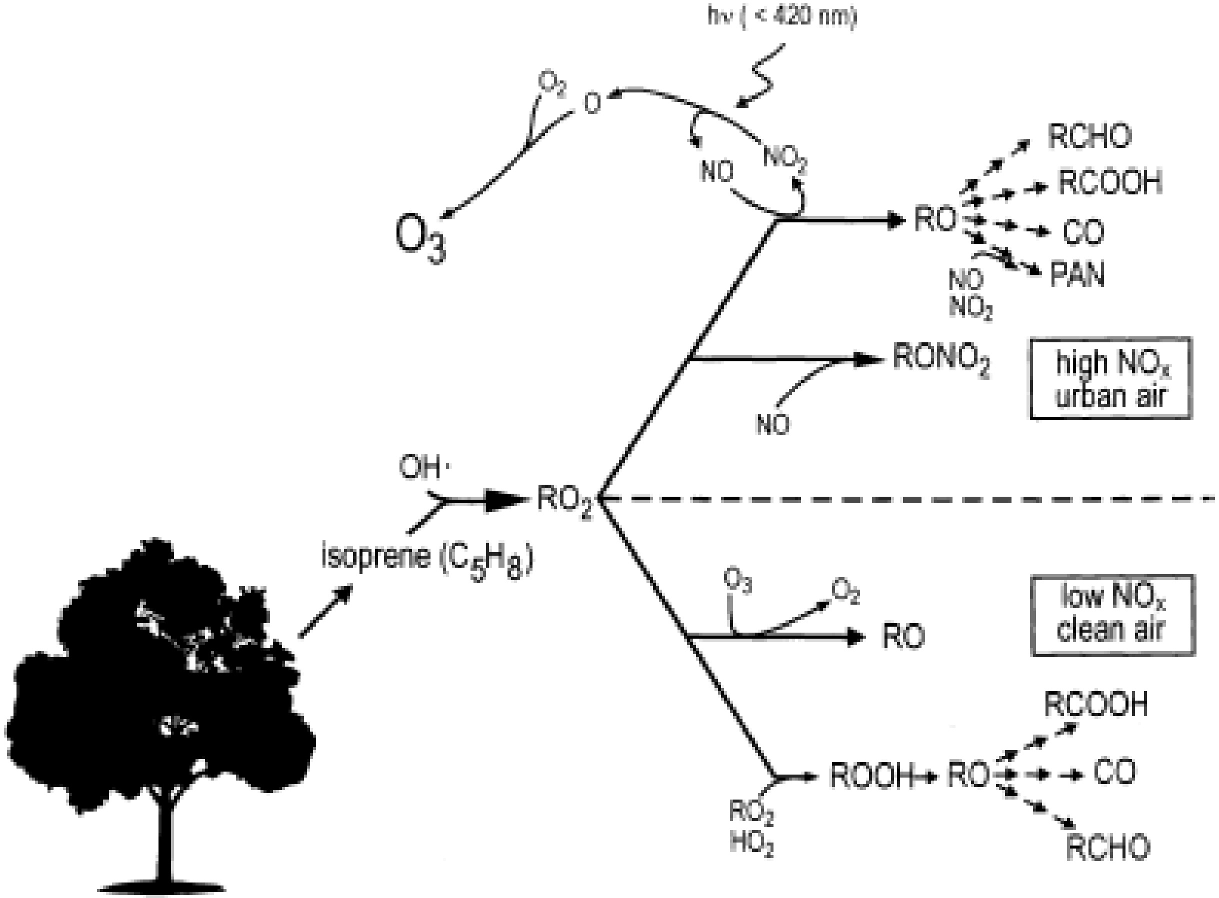


Fig. 1 Extremely simplified reaction scheme illustrating potential products arising from the oxidation of isoprene by the OH radical. The top half of the diagram illustrates the situation in polluted air containing high concentrations of nitrogen oxides; the bottom half illustrates the situation in clean air

Oecologia (1999) 118:109–123

isopreno

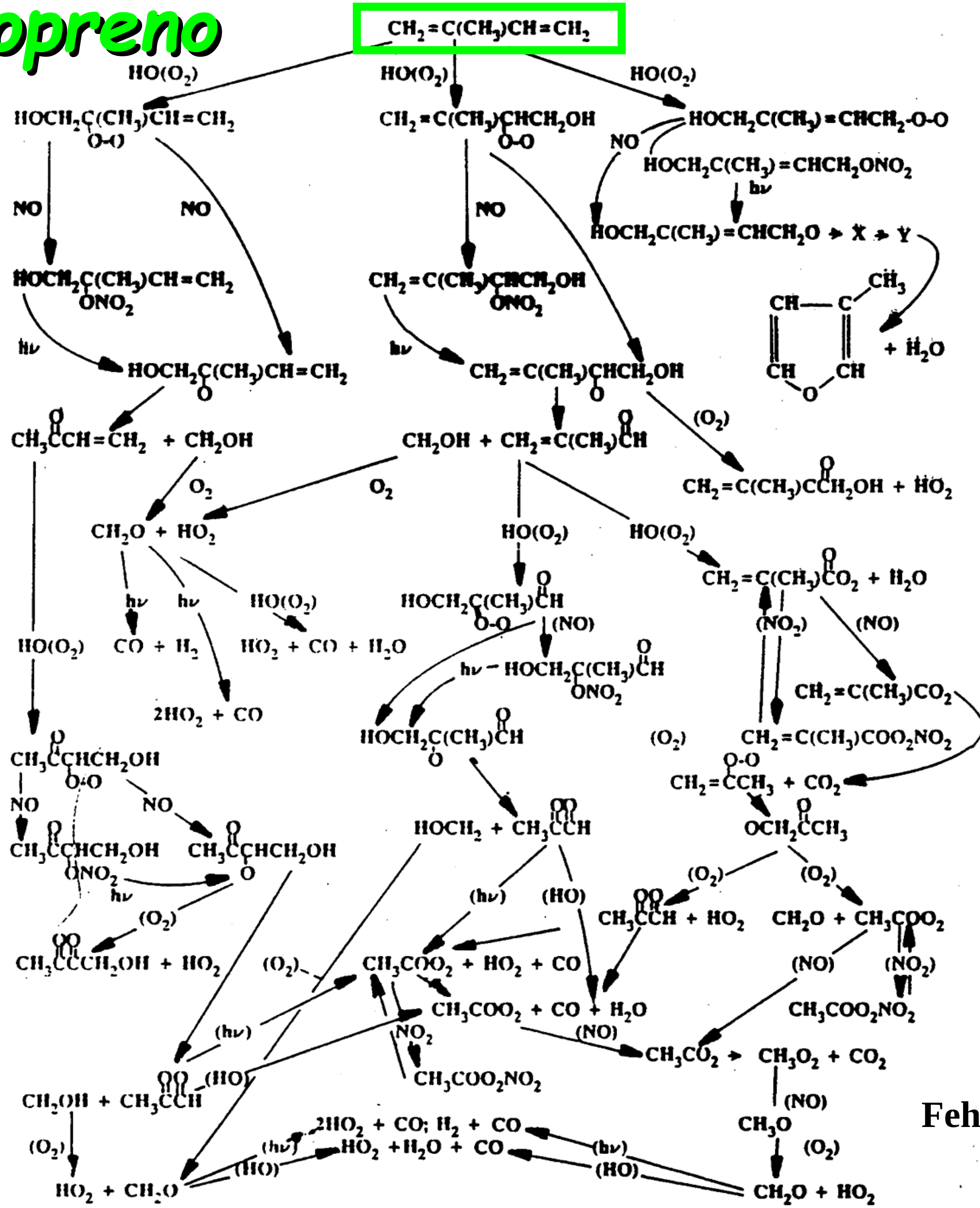
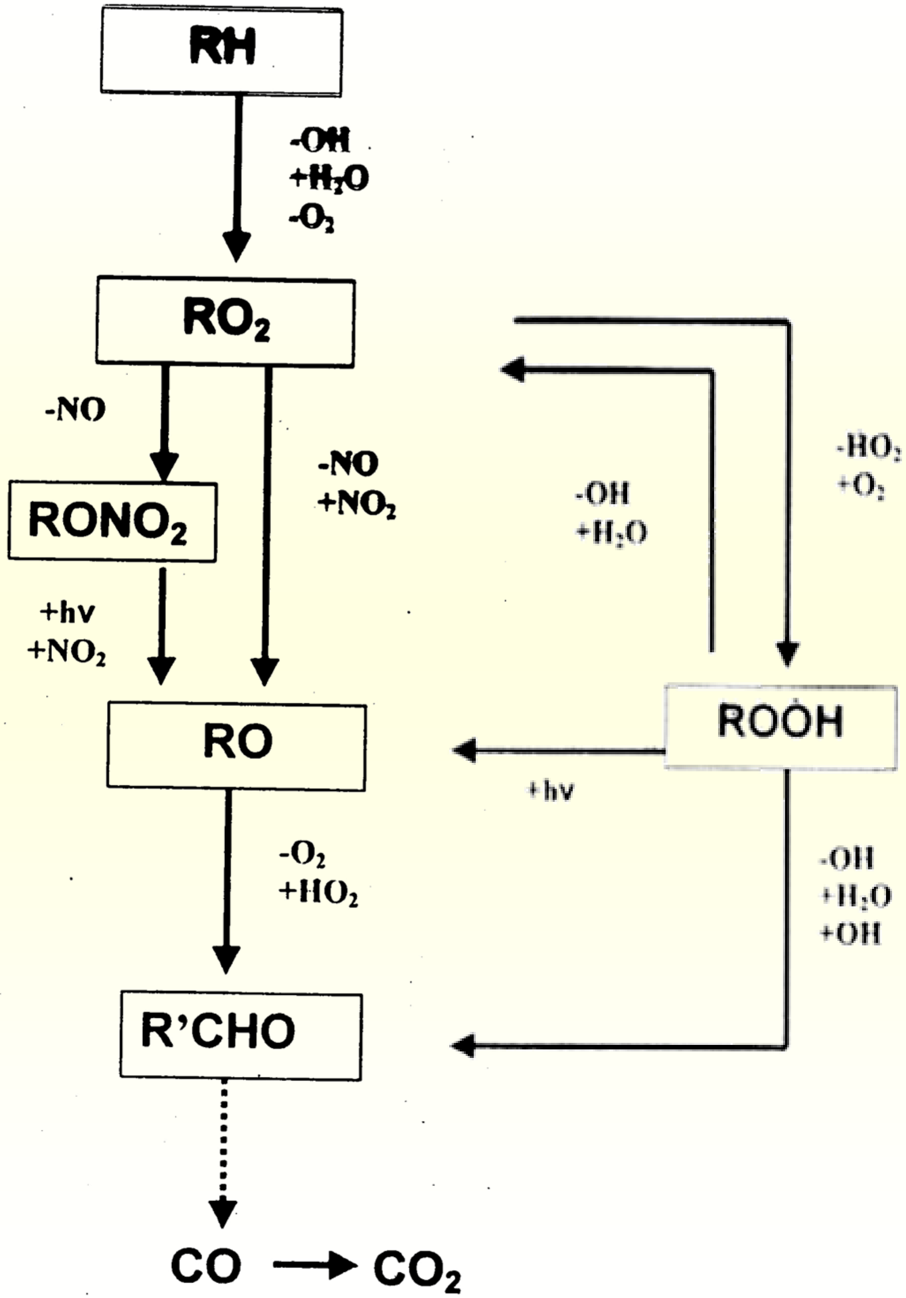


Fig. 20. Major reaction pathways for isoprene oxidation in atmospheres high in $[NO_x]$.

Fehsenfeld,1992

Oxidação dos hidrocarbonetos



Guenther, 1998

NO_2 + hv (<430 nm)$\rightarrow$NO + O(3P) (1)

Em seguida o átomo de oxigênio gerado na reação (1) se combina com uma molécula de gás oxigênio, formando assim o ozônio:

O(3P) + $O_2 \rightarrow O_3$ (2)

Em atmosferas consideradas limpas, o O_3 reage rapidamente com o NO, sendo consumido:

NO + $O_3 \rightarrow NO_2 + O_2$ (3)

Biogenic VOC	Lifetime[a] for reaction with		
	OH[b]	O_3[c]	NO_3[d]
Isoprene	1.4 h	1.3 days	1.6 h
Monoterpenes			
Camphene	2.6 h	18 days	1.7 h
2-Carene	1.7 h	1.7 h	4 min
3-Carene	1.6 h	11 h	7 min
Limonene	49 min	2.0 h	5 min
Myrcene	39 min	50 min	6 min
cis-/trans-Ocimene	33 min	44 min	3 min
α-Phellandrene	27 min	8 min	0.9 min
β-Phellandrene	50 min	8.4 h	8 min
α-Pinene	2.6 h	4.6 h	11 min
β-Pinene	1.8 h	1.1 days	27 min
Sabinene	1.2 h	4.8 h	7 min
α-Terpinene	23 min	1 min	0.5 min
γ-Terpinene	47 min	2.8 h	2 min
Terpinolene	37 min	13 min	0.7 min
Sesquiterpenes			
β-Caryophyllene	42 min	2 min	3 min
α-Cedrene	2.1 h	14 h	8 min
α-Copaene	1.5 h	2.5 h	4 min
α-Humulene	28 min	2 min	2 min
Longifolene	2.9 h	>33 days	1.6 h
Oxygenated VOCs			
Acetone[e]	61 days (Atkinson et al. 1999)	>4.5 year[f]	>8 year (Atkinson et al. 1999)
Camphor	2.5 days (Reissell et al. 2001)	>235 days (Reissell et al. 2001)	>300 days (Reissell et al. 2001)
1,8-Cineole	1.0 days (Corchnoy and Atkinson 1990)	>110 days (Atkinson et al. 1990)	1.5 year (Corchnoy and Atkinson 1990)
cis-3-hexen-1-ol	1.3 h (Atkinson et al. 1995)	6.2 h (Atkinson et al. 1995)	4.1 h (Atkinson et al. 1995)
cis-3-hexenyl acetate	1.8 h (Atkinson et al. 1995)	7.3 h (Atkinson et al. 1995)	4.5 h (Atkinson et al. 1995)
Linalool	52 min (Atkinson et al. 1995)	55 min (Atkinson et al. 1995)	6 min (Atkinson et al. 1995)
Methanol	12 days (Atkinson et al. 1999)	>4.5 year[f]	2.0 year (Atkinson et al. 1999)
MBO	2.4 h (Papagni et al. 2001)	1.7 days (Grosjean and Grosjean 1994)	7.7 days (Rudich et al. 1996)
6-methyl-5-hepten-2-ol	53 min (Smith et al. 1996)	1.0 h (Smith et al. 1996)	9 min (Smith et al. 1996)

Compostos mais estudados:

Isopreno e monoterpenos

Aldeídos e ácidos carboxílicos

Isopreno

emissão dependente da temperatura e radiação

Reage com:

a. O_3 $\Rightarrow$ ac. carboxílicos, formaldeído

b. OH $\Rightarrow$ formaldeído, MAC, MVC

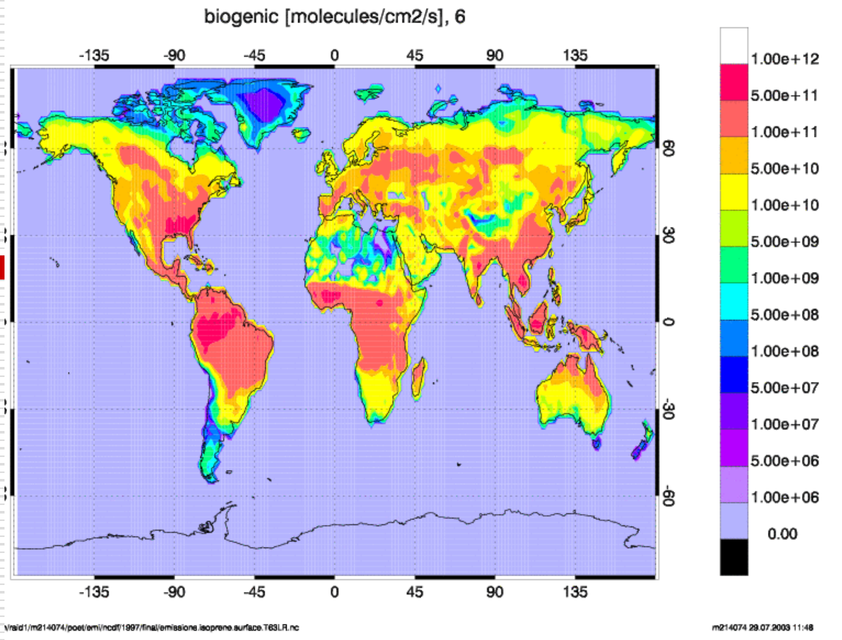
c. NO_3 $\Rightarrow$ carbonilas nitradas

Não é estocado nas plantas

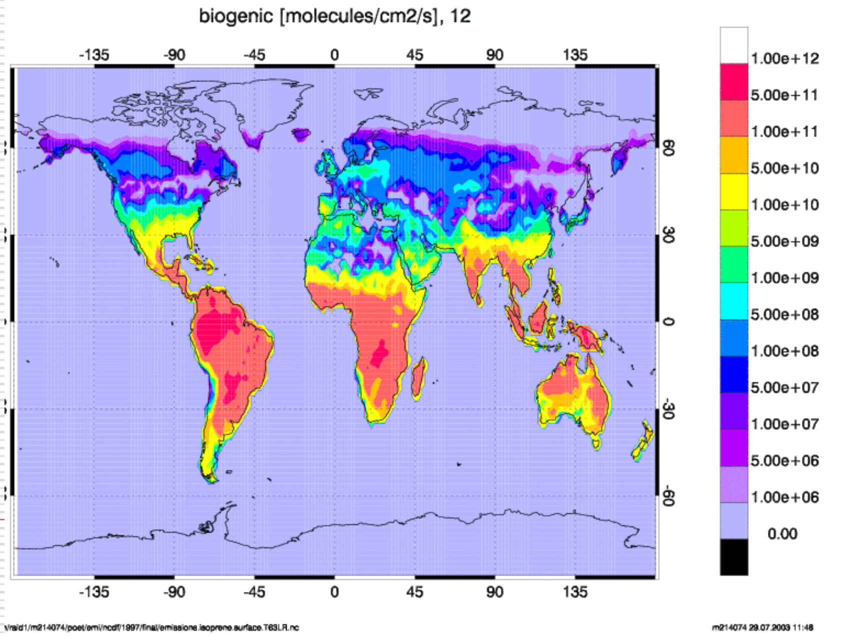
(estresse térmico)

Isoprene Emissions

June



December



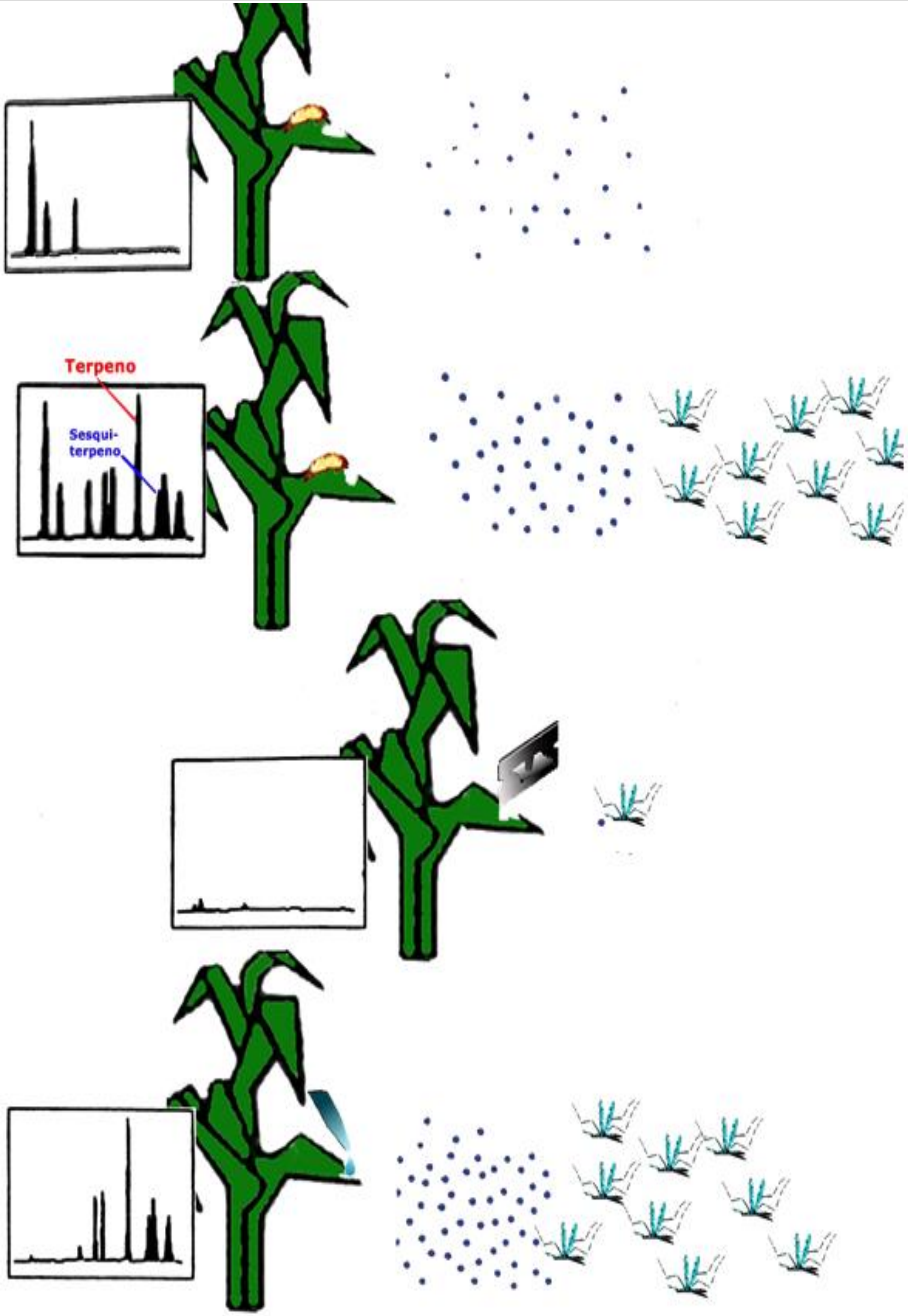
Terpenos

- Produtos do metabolismo das plantas
- Tóxicos para insetos
- Feromônios de insetos
- Executam relações alelopáticas

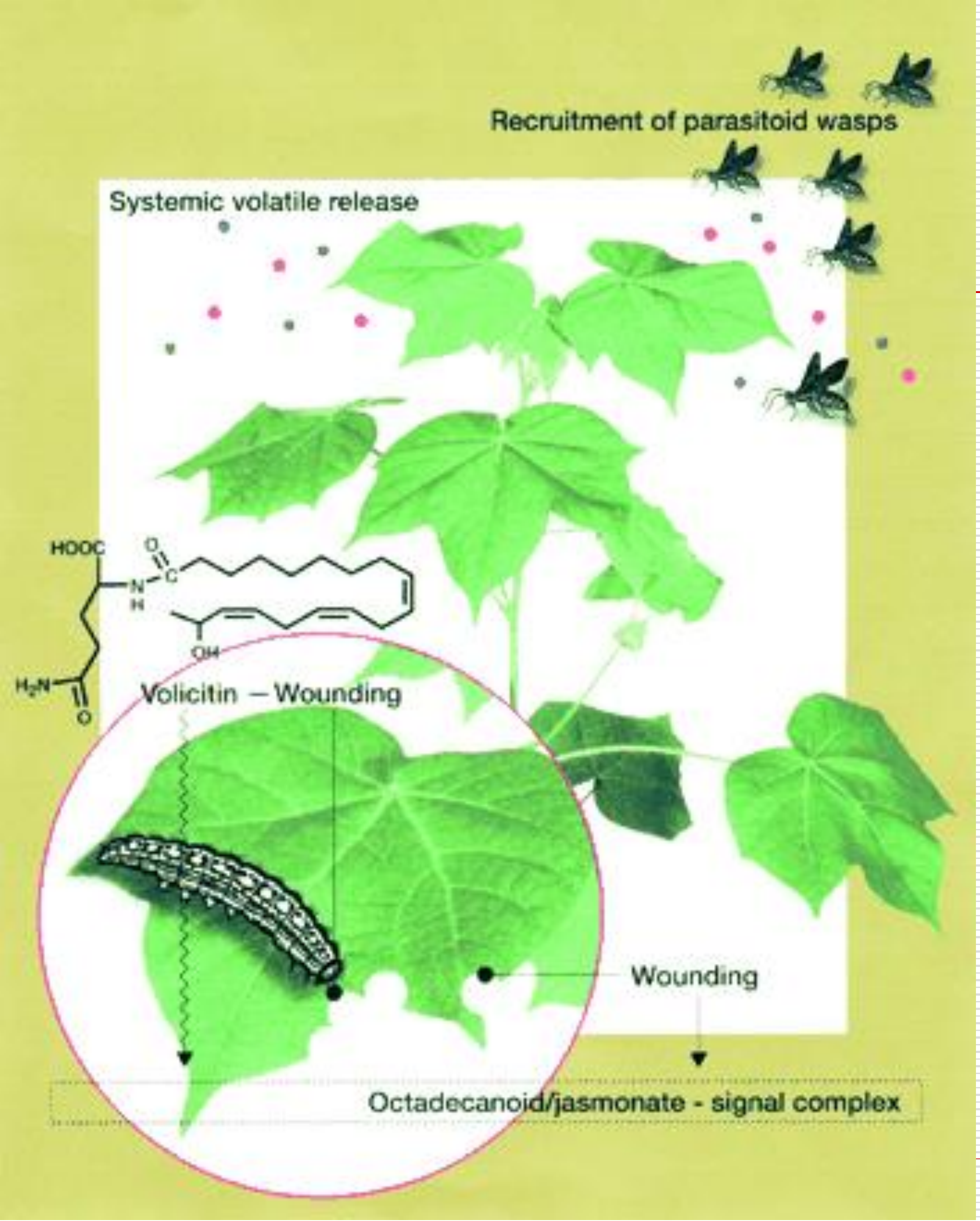
Reagem com:

O_3 $\Rightarrow$ formaldeído, cetonas, dicarbonilas
OH $\Rightarrow$ carbonilas
NO_3 $\Rightarrow$ carbonilas nitradas

α e β-pineno, careno, limoneno $\Rightarrow$ aerossol

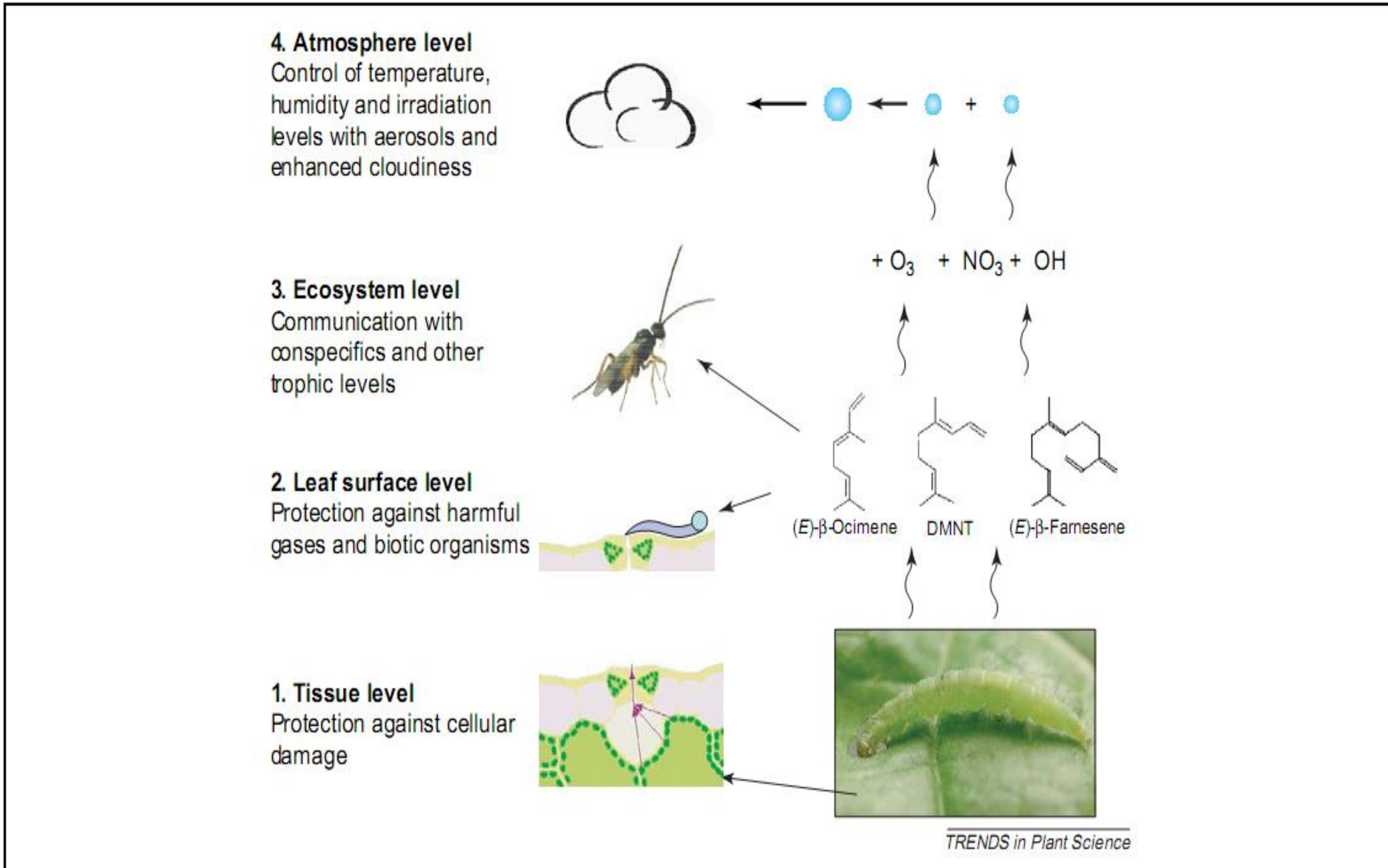


Engelberth et al. 2004
PNAS 101(6)1781.

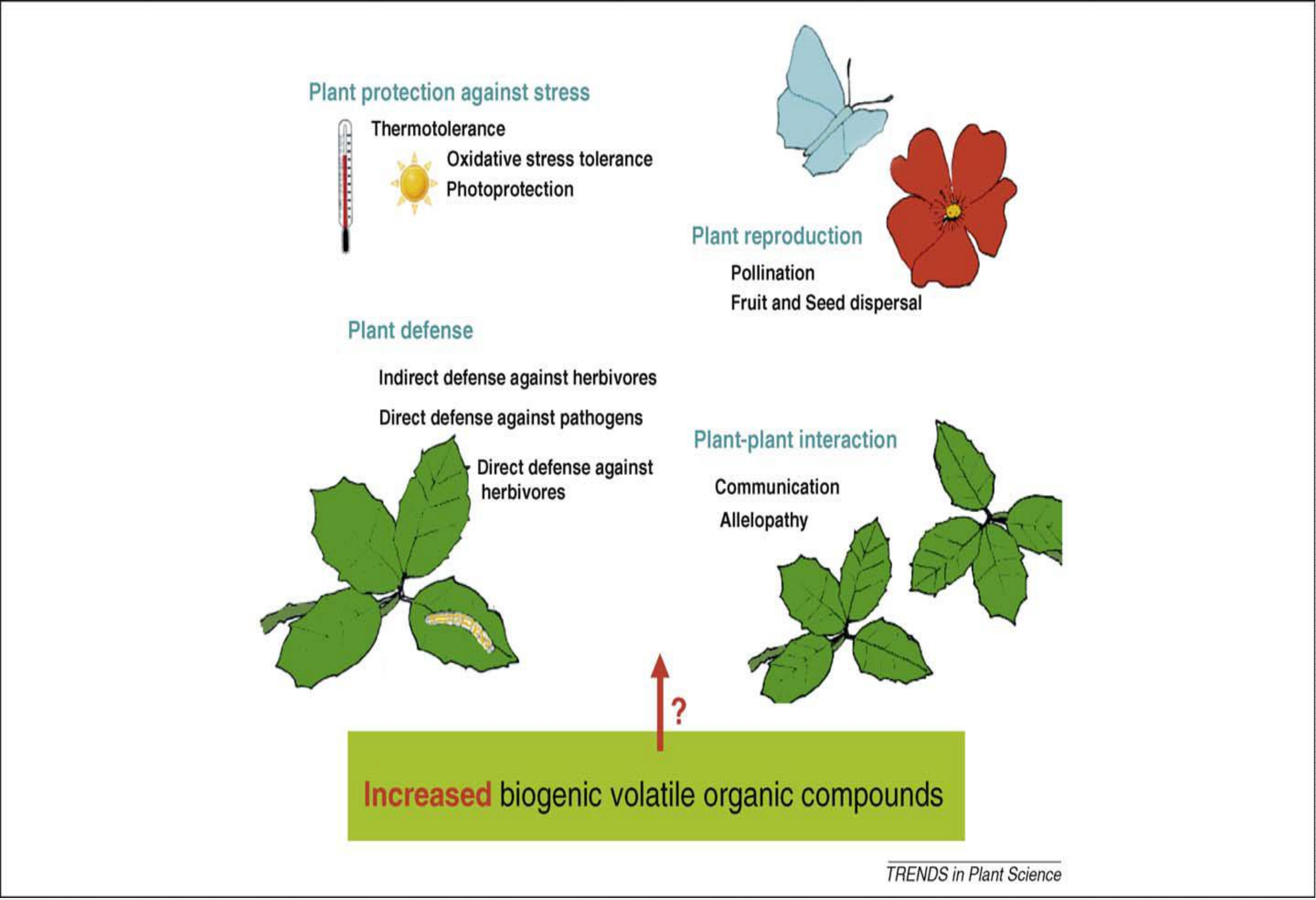


Recruitment of parasitoid wasps
Systemic volatile release
HOOC
N
H
O
C
OH
H_2N
O
Volicitin – Wounding
Wounding
Octadecanoid/jasmonate - signal complex

Níveis de atuação dos COV biogênicos.



Trends in Plants Science 9(11)529-533,2004.



Trends in Plant Science Vol.15 No.3

COV BIOGÊNICOS

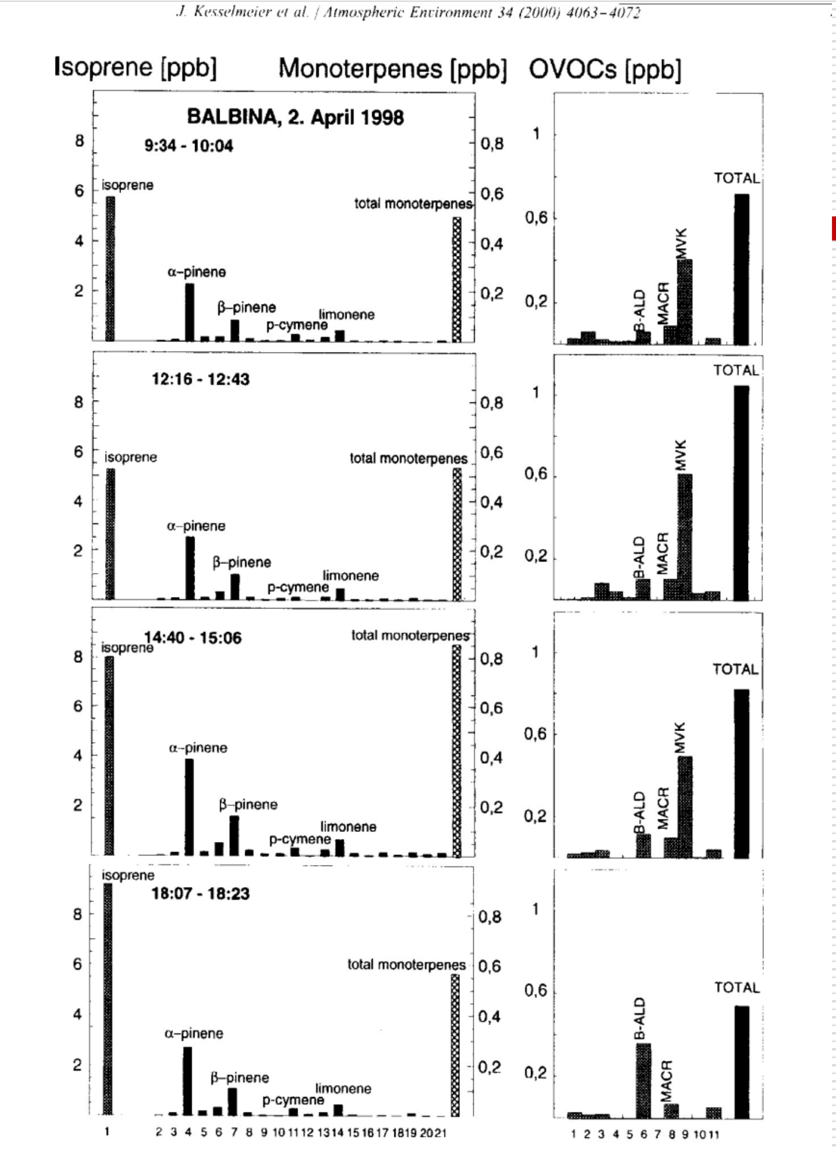
1.Os insetos detectam os COV das plantas e estocam substâncias (feromônios). A fêmea do besouro do pinheiro atrai os machos através de 3 feromônios: dois sintetizados pelo besouro e, o mirceno, extraído da planta, controlando o número de machos. Quando a população de insetos alcança um tamanho ideal, a fêmea cessa a produção do feromônio, e emite Verbenona →um repelente de machos.

2. Quando a larva da vespa do pinheiro é atacada por um predador (formiga), levanta-se e libera de sua boca uma gota viscosa repelente contendo terpenos.

In: Ecologia das interações entre insetos e plantas. EDUSP.

Cartucho

CUVETTE



MAC,MVK→isopreno

MAC+MVK/isopreno →capacidade oxidativa da atmosfera

formal>acetal →fotoquímica e oxidação de terpenos, isopreno e alcenos

Tolueno → **biogênico**

terpenos →aerossóis

Kesselmeier, Gunther, Greenberg, Vasconcellos, Atmospheric Chemistry 2000.

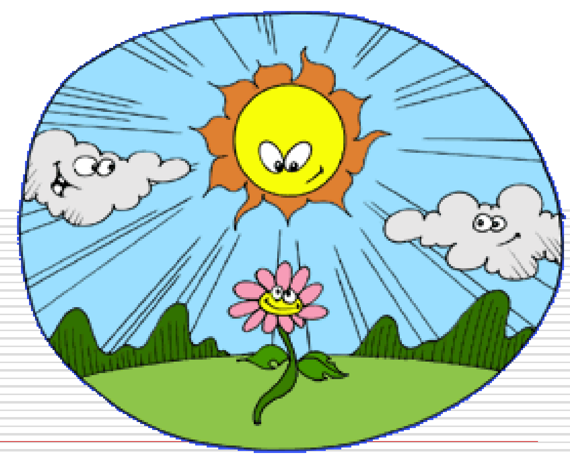
→os trópicos dominam a fotoquímica global

- Temperaturas altas
- Radiação
- Umidade
- Abundância de espécies

TABLE 2. Typical Mean Concentrations of Isoprene and Terpenes From Selected Terrestrial Sites

Species	Niwot Ridge[a,b] 3 km elevation, Rocky Mountains			Georgia FSU[c] Forest	Rome Italy[d] Forest	Brazil Amazon Basin[e] Forest		Kenya[e] Agricultural Land		Nigeria[e] Coastal Tropical	Appalachian Mountains[f] Forested hill sites				Southwest France[g] Rural
	S	S	F	S	S	F	S	DS	WS	S	W	SP	S	F	S
Isoprene		0.63	0.11	1.4	--	5.45	2.04	0.04	<0.01	1.21	0.02	0.1	1.1	<.01	0.19
α-pinene	0.05	0.14	0.07	0.8	1.5	0.2	0.10	<0.01	<0.01	0.06	0.03	0.04	0.04	0.05	--
β-pinene	0.97	0.08	0.07	0.43	0.18	0.01	0.03	<0.01	<0.01	<0.01	--	--	--	--	--
Δ-3-carene	0.05			0.90	0.06	<0.01	0.01	<0.01	<0.01	<0.01	--	--	--	--	--
Camphene	0.04	0.04	0.05	0.09	--	0.04	0.03	<0.01	<0.01	0.01	--	--	--	--	--
Limonene	0.03	0.05	0.03	0.08	0.04	--	--	--	--	--	--	--	--	--	--
Mycrene		--	--	0.68	--	--	--	--	--	--	--	--	--	--	--

[a] Data are from Roberts et al. [1983].
[b] Data are from Greenberg and Zimmerman [1984].
[c] Data are from Shaw et al. [1983].
[d] Data are from Ciccioli et al. [1984].
[e] Data are from Zimmerman et al. [1988].
[f] Data are from Seila [1984].
[g] Data are from Kanakidou et al. [1989].
Mean concentrations are in ppbv. S: summer; F: fall; W: winter; SP: spring; DS: dry season; WS: wet season.



Transformation of (urban) landscape – how should cities and forests of the future look like?

short rotation forestry / energy wood

Ecocities,
Urban Greening,
Urban Gardening

Biello 2008,
nationalgeographic.com,
constructiondigital.com,
agroforst.de

QUÍMICA DA ATMOSFERA

Poluição em ambientes internos

Prof. Pérola

Poluição em ambientes fechados

⇒ **Ambientes indoor x oudoor**

indoor **x** ***outdoor***

- **indoor**
  - **escolas**
  - **casas**
  - **escritórios**
- **outdoor**
  - **Ambientes abertos**

IAEA: **50% das doenças são agravadas/causadas**

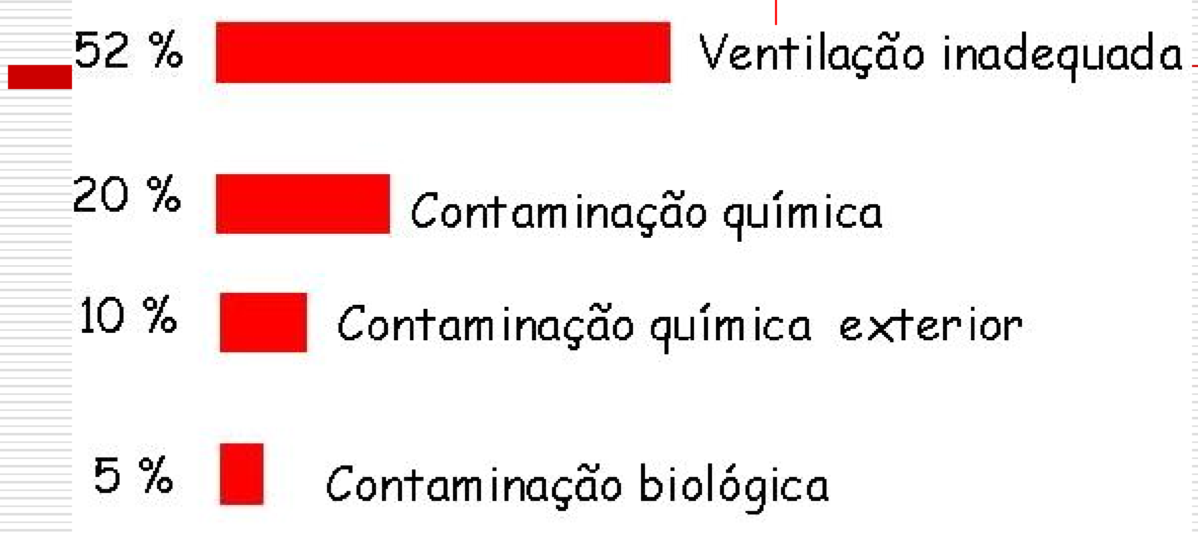
(Instituto Americano Estudos Alérgicos)

EPA: **2 a 10 vezes mais perigoso**

(Agência de Proteção Ambiental)

Poluição em ambientes fechados

⇒ **Razões**



Pesquisa NY
Edifícios
36 % → sujas
58 % → imundas

1982 OMS: "Síndrome do Edifício Doente" (SED)

20% ocupantes revelam sintomatologias

- **Garganta: irritação, rouquidão**
- **Dor cabeça, náuseas, tontura**
- **Irritação na pele**
- **Olhos: irritação, secura**
- **Nariz: irritação, congestionamento**

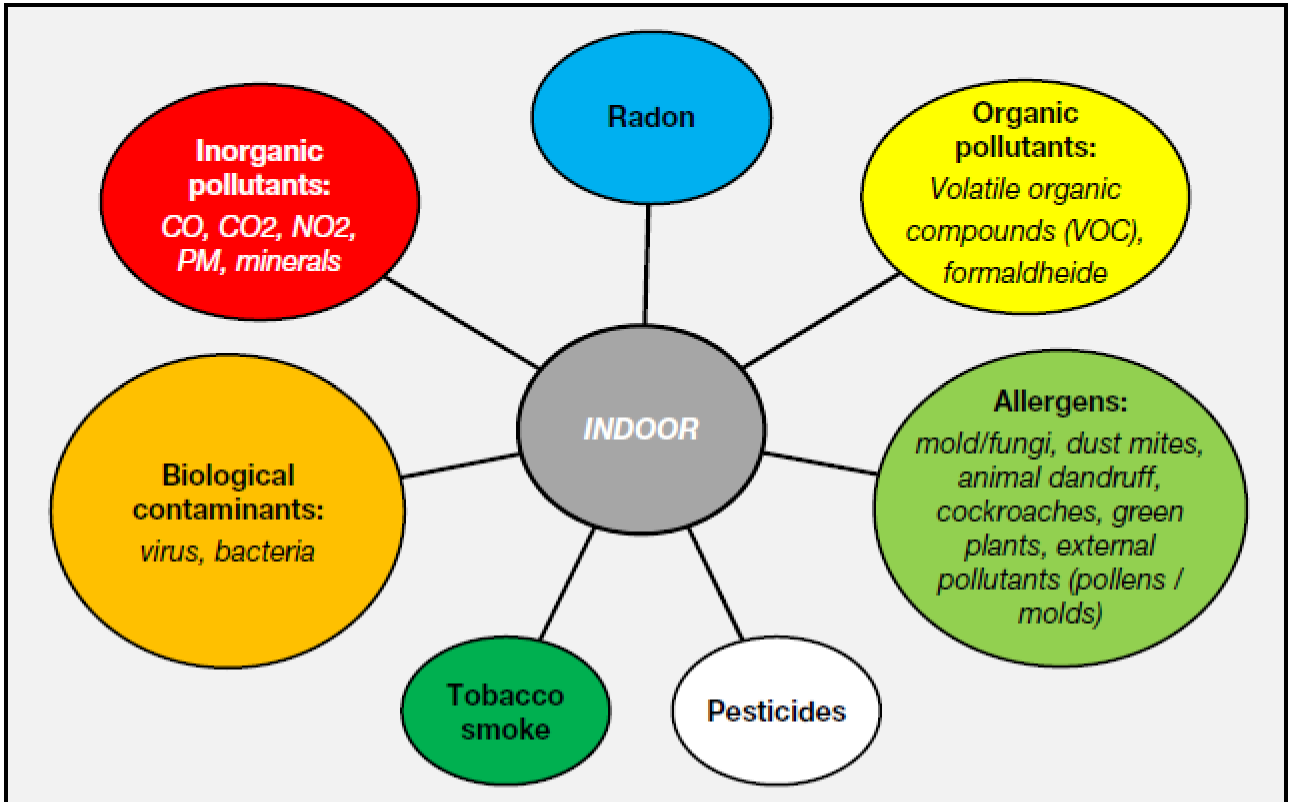
Síndrome do edifício doente

⇒ **OMS: Classificação**

SED

- **Temporariamente doentes**
- **Permanentemente doentes**

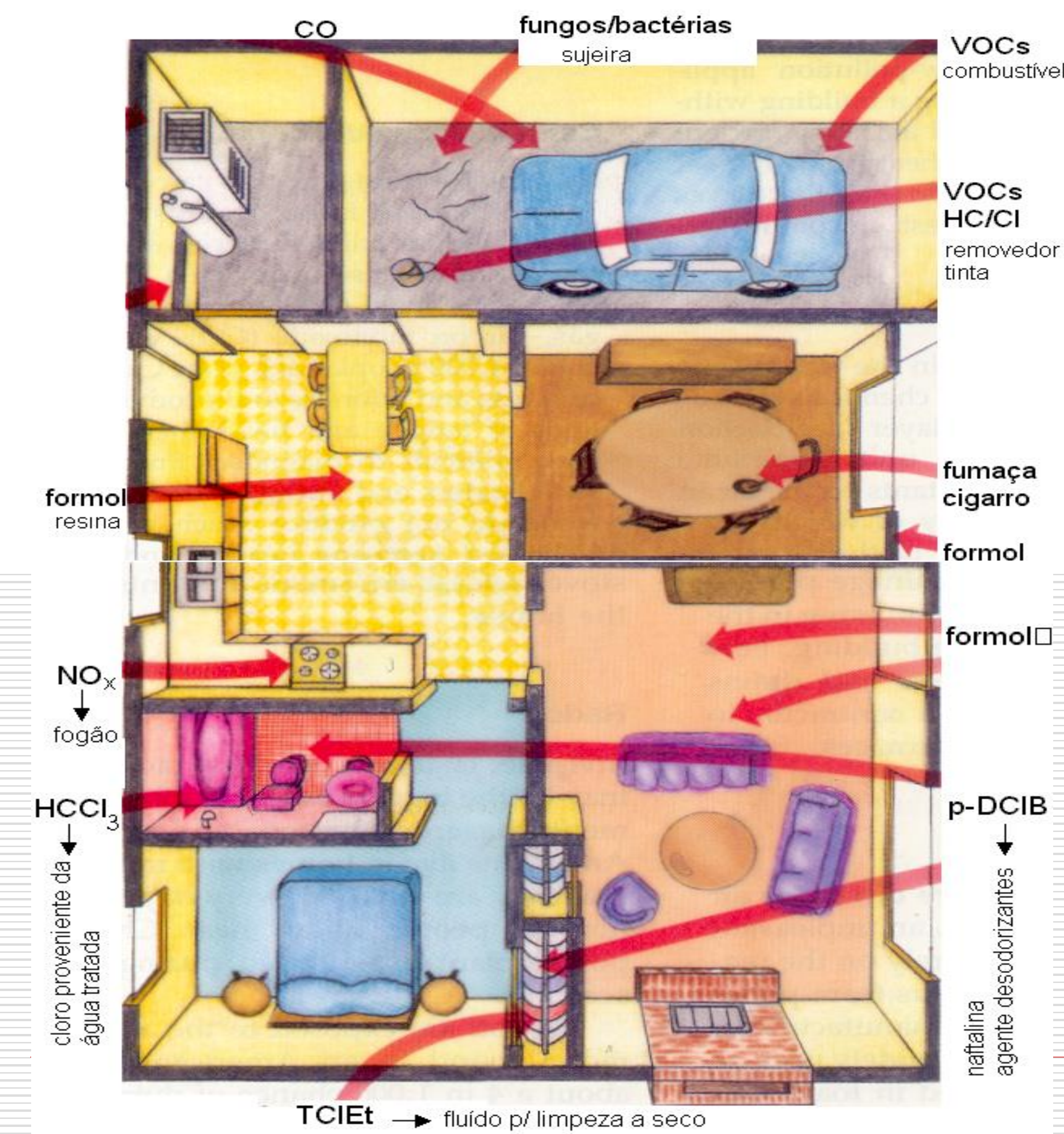
sintomas → **COV** (identificação de mais 900 diferentes COV)



CO=carbon oxide, CO_2=carbon dioxide, NO_2=nitrogen dioxide, PM=Particulate matter

Fig. 1 Main indoor pollutants.

Poluentes *indoor*



Garagem

Sala de jantar

sala

cozinha

COV

quarto

tetracloroetileno

quarto/banheiro

p-diclorobenzeno

desodorante

bolinhas anti-traças

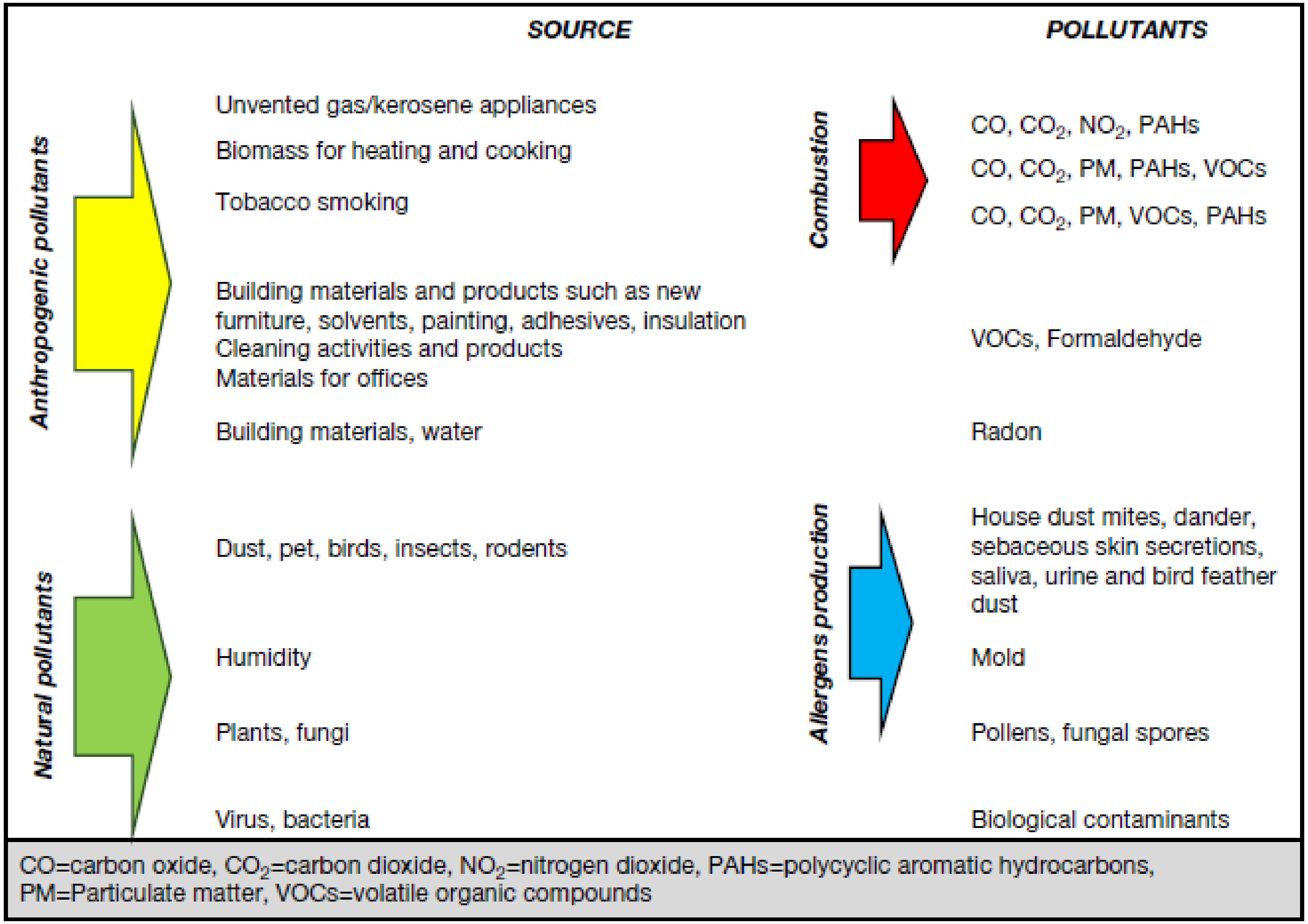


Fig. 2 Sources of common pollutants.

Poluentes *indoor*

GARAGEM

⇒Contaminantes biológicos

Exemplos:fungos, bactérias, ácaros

doenças infecciosas, alergias

Ar condicionado (manutenção deficiente)

⇒ COV

vapores de combustíveis (benzeno e derivados)

tintas, vernizes, colas

agentes de limpeza, aromatizantes

suspeitas: carcinogênicos

Poluentes *indoor*

SALA DE JANTAR

⇒ Fumaça de cigarro

Composição complexa: 5000 compostos

Nicotina

CO, NO_2

COV (formaldeído, benzeno), HC

Cádmio, polônio

MP_{10} (alcatrão)

HPA (hidrocarbonetos policíclicos aromáticos)

50 compostos carcinogênicos e mutagênicos

5 milhões de morte/ano, sendo 600 mil mortes dos passivos

Poluentes *indoor*

SALA

⇒ Formaldeído

outdoor: 0,01 ppm

indoor: 0,1 - 1 ppm

fumaça de cigarro

produtos de limpeza

móveis, carpetes, pisos (resina formaldeído uréia)

produtos de higiene

carcinogênicos e mutagênicos em animais

(provável cancerígeno humano)

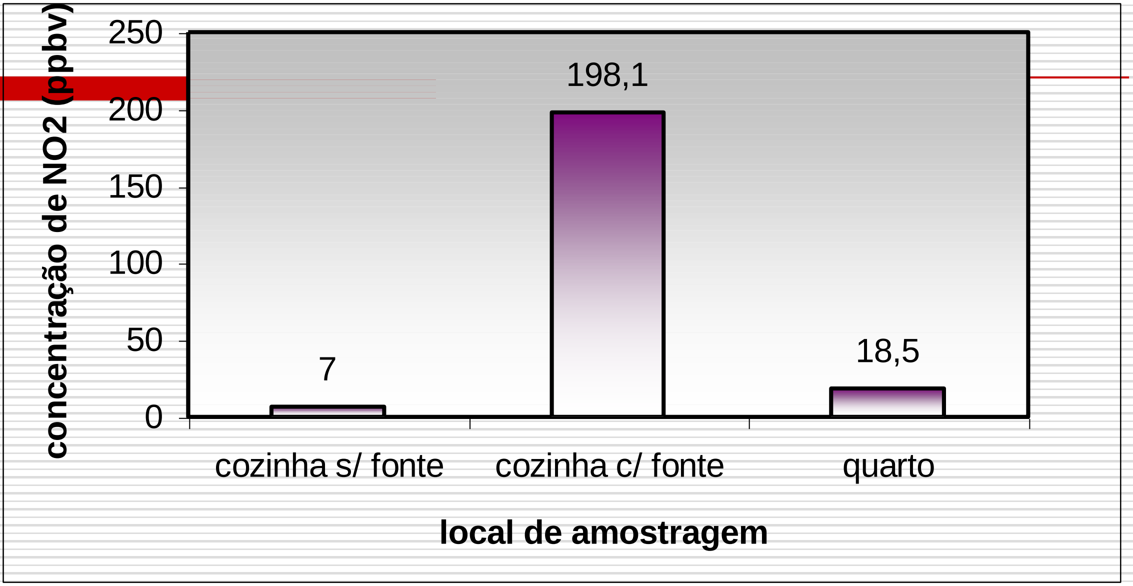
Poluentes *indoor*

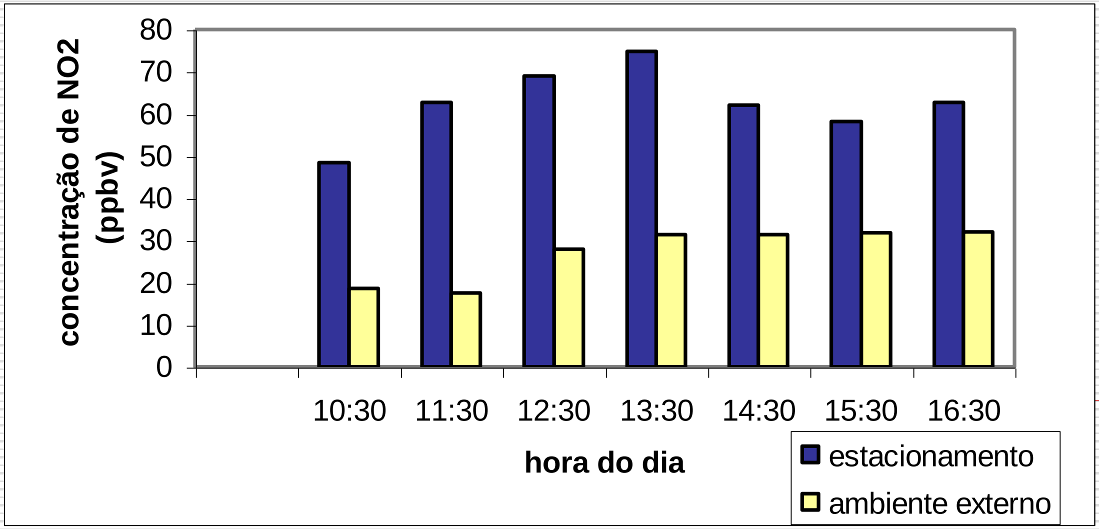
Cozinha

⇒ NO_x

***outdoor*: 5-20 ppb**

***indoor*: 300 ppb**





Estacionamento de supermercado

Tabela 1. Fontes típicas de poluição do ar em ambientes internos[2,3]

Poluente	Maior fonte de emissão
Dióxido de carbono	atividade metabólica, atividades de combustão, veículos motores em garagem
Monóxido de carbono	queima de combustível fóssil, aquecedores a gás ou querosene, fogão, fumaça de cigarro
Formaldeído	materiais de construção e mobiliário
COVs	adesivos, solventes, materiais de construção, volatilização, combustão, pintura, fumaça de cigarro; atividades de limpeza; fotocopiadoras, impressoras a laser
Partículas	re-suspensão, fumaça de cigarro, produtos de combustão, atividades de limpeza

Quim. Nova, Vol. 26, No. 3, 359-365, 2003

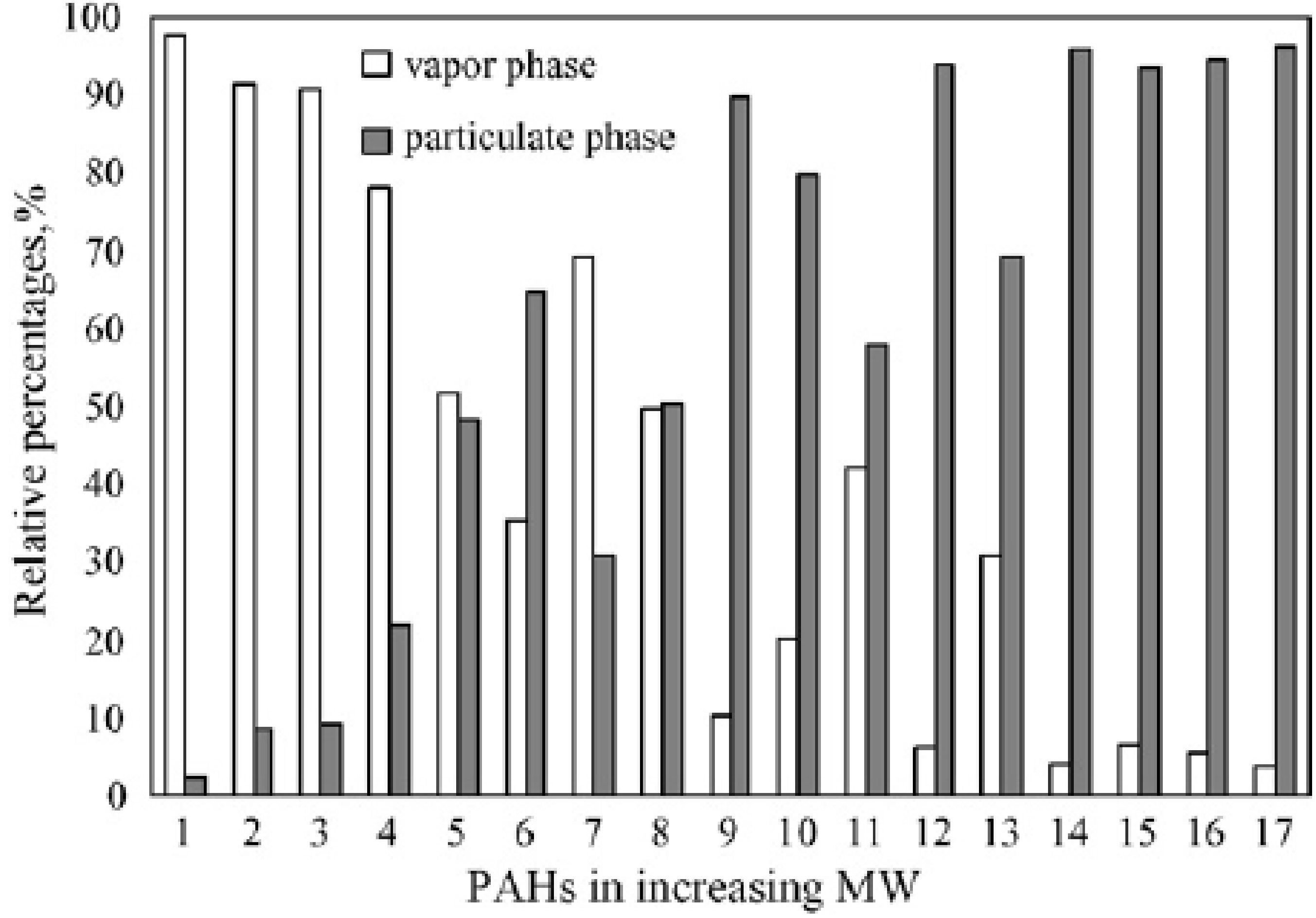


Fig. 1. Distribution of PAHs in vapor phase and particulate phase in tobacco smoke (1–17 on abscissa stand for NAPH, AC, ACY, FLUOR, PHEN, AN, FLUR, PY, BaA, CHRY, BeP, BbF, BkF, BaP, DA, BP, IN, respectively. Figure was acquired by averaging the data for 12 brand cigarettes).

J. Hazardous Materials A139,193-198,2007.

TABLE 8

Formaldehyde and Acetaldehyde Concentrations ($\mu g/m^3$) and I/O Ratios

	formaldehyde			acetaldehyde		
site	indoors	outdoors	I/O ratio	indoors	outdoors	I/O ratio
RJ-1	14.3	4.71	3.0	37.3	9.32	4.0
RJ-2	38.0	27.7	1.4	59.1	53.2	1.1
RJ-3	13.6	5.14	2.6	24.2	11.8	2.0
RJ-4	4.71	4.00	1.2	6.08	11.2	0.5
RJ-5	10.6	23.9	0.4	56.4	178	0.3
RJ-6	6.14	6.00	1.1	69.1	25.9	2.7
SP-7	10.9	9.71	1.1	13.2	17.5	0.8
SP-8	18.9	10.1	1.9	67.8	24.0	2.8
SP-9	23.6	12.9	1.8	67.2	34.4	2.0
SP-10	28.4	10.6	2.7	28.1	14.3	2.0
SP-11	60.7	6.28	9.6	14.9	12.6	1.2
SP-12	15.3	7.85	2.0	16.9	13.9	1.2
av	20.4	10.7	2.4	38.4	33.8	1.72

RJ-1, RJ-2, RJ-3, SP-9, SP-11, SP-12 = escritórios
RJ-4, SP-8 = churrascarias
RJ-5, RJ-6, = restaurante
SP-7 = hotel/restaurante
SP-10 = pizzaria

Environmental Science & Technology 29(2)338-345

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Atmospheric Environment 40 (2006) 6956–6965

ATMOSPHERIC ENVIRONMENT

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Polycyclic aromatic hydrocarbons in dust from computers: one possible indoor source of human exposure

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Volume 9, No. 1, March 2009, Pages 120-138 _PDF(367 KB)

Measurement of Particulate *n*-alkanes and PAHs Inside and Outside a Temple in Xiamen, China

Shui-Ping Wu[1,2], Xin-Hong Wang[1,2], Hua-Sheng Hong[1,2], Jing-Ming Yan[1,2]

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[2] *College of Oceanography and Environmental Science, Xiamen University, Xiamen 361005, P. R. China*

Abstract

Total suspended particles samples inside and outside the South Pu-Tuo Temple (SPT), a traditional Buddhist temple in Xiamen, China were collected and further analyzed for *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) during the periods of worship. It was observed that the concentrations of particulate *n*-alkanes at SPT were abnormally higher compared to the surrounding bus terminus and campus. In addition, benzo[a]pyrene (BaP) equivalent concentrations at SPT (7.1-26.3 ng/m^3) were significantly higher than those at the bus terminus (5.1-6.9 ng/m^3) although the PAH concentrations were comparable. The hazard potential of PAHs in terms of the carcinogenicity of BaP inside SPT is not acceptable because the indoor air quality standard of BaP recommended by the State Environmental Protection Administration of China is 1 ng/m^3 (daily mean). Ratios of fluoranthene to fluoranthene plus pyrene, indeno[1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene plus benzo[g,h,i]perylene and 1,7-DMP (dimethylphenanthrene) to 2,6-DMP plus 1,7-DMP were further calculated; the values of these three together with the ratio of retene to phenanthrene separated the SPT samples from the bus terminus samples, in that SPT samples showed a strong influence of wood burning (such as bamboo sticks, stick coatings, and joss paper).

Keywords: Incense burning; Particulate matter; *n*-alkanes; Polycyclic aromatic hydrocarbons; Health risk.


Newest desgin
Cigarette
8.5(D)*89(L)mm
KR-808A
8.5(D)*98(L)mm
KR-808
9.2(D)*110(L)mm
KR-308
9.2(D)*110(L)mm
KR-308
9.2(D)*110(L)mm
KR-308
9.2(D)*119(L)mm
KR-208
9.2(D)*153(L)mm
KR-108

Smoke without fire

Suck on an e-cigarette and it produces a cloud of nicotine-carrying vapour with none of the toxic by-products of burning tobacco