

A satellite view of Earth showing the continent of South America and the surrounding Atlantic Ocean. The image is a curved slice of the planet, showing the curvature of the horizon. The colors are vibrant, with deep blues for the ocean, greens and yellows for the land, and white for the clouds. The text is overlaid on the right side of the image.

# Aerossóis, aula 1

Física Atmosférica, 2019

Henrique M. J. Barbosa  
Instituto de Física – USP

Com slides de Veronika Brand, Adalgiza  
Fornaro, Luciana Rizzo, Peter Tunved, etc.

# O que é poluição?

Estado indesejável do ambiente natural contaminado por substâncias nocivas como consequência de atividades humanas.

# O que é poluição do ar?

Estado indesejável **da atmosfera natural contaminada** por substâncias nocivas como consequência de atividades humanas.

OK, mas...

na atmosfera que substâncias ou  
tipo de substâncias nocivas  
estamos falando?

gases

aerossóis

OK, mas...

Todo gás é poluente atmosférico?

Claro que não!!  $O_2$ ,  $N_2$ ,...

OK, mas...

Então o  $CO_2$  é um poluente?

Depende...

Vem de atividade humana?

Ok, mas...

Todo aerossol é poluente atmosférico?

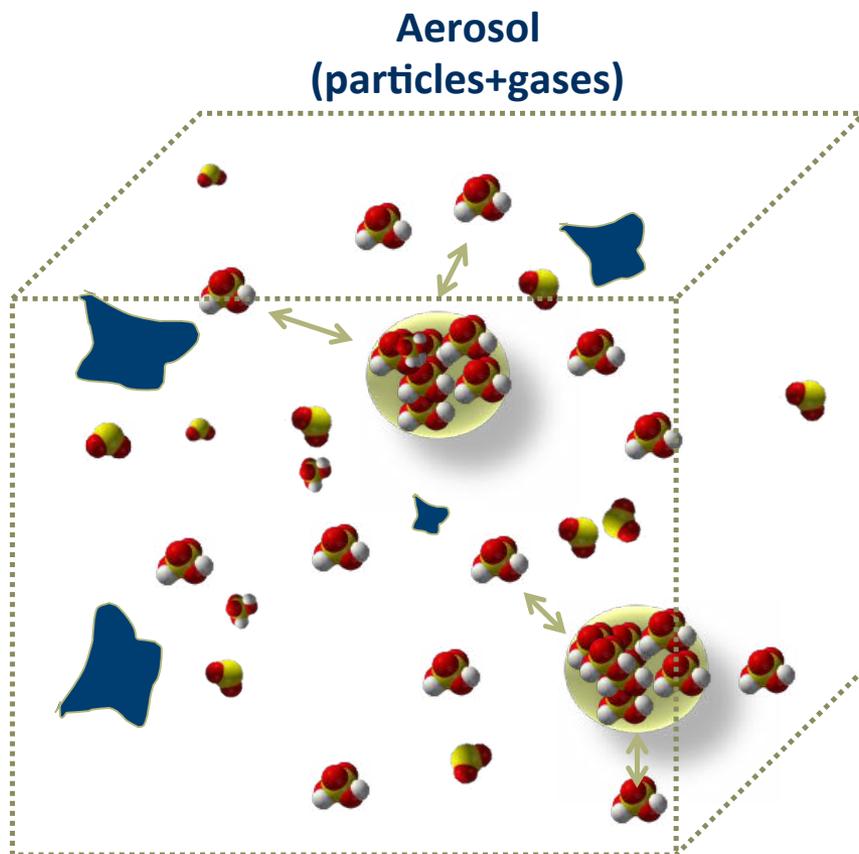
Claro que não!! Sal marinho, poeira,...

Ok, mas...

O que é mesmo aerossol??

O termo aerossol se refere às partículas líquidas e/ou sólidas, em suspensão em um gás (*Seinfeld e Pandis, 1998*).

# Definição de aerossol

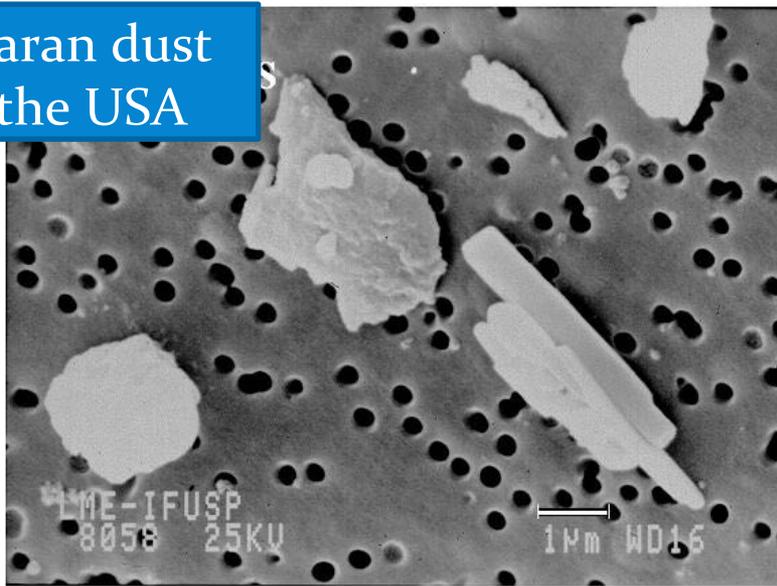


Partículas sólidas  
ou líquidas em  
suspensão em  
fase gasosa

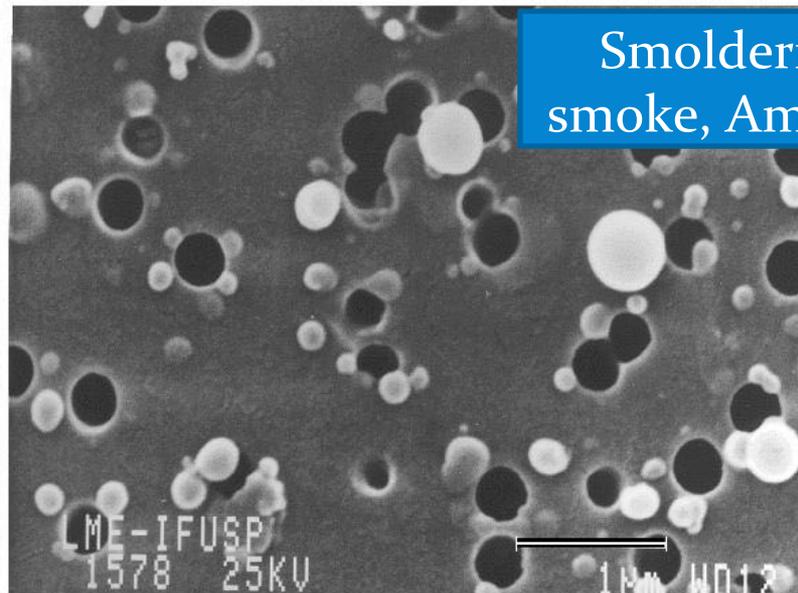


# Exemplos

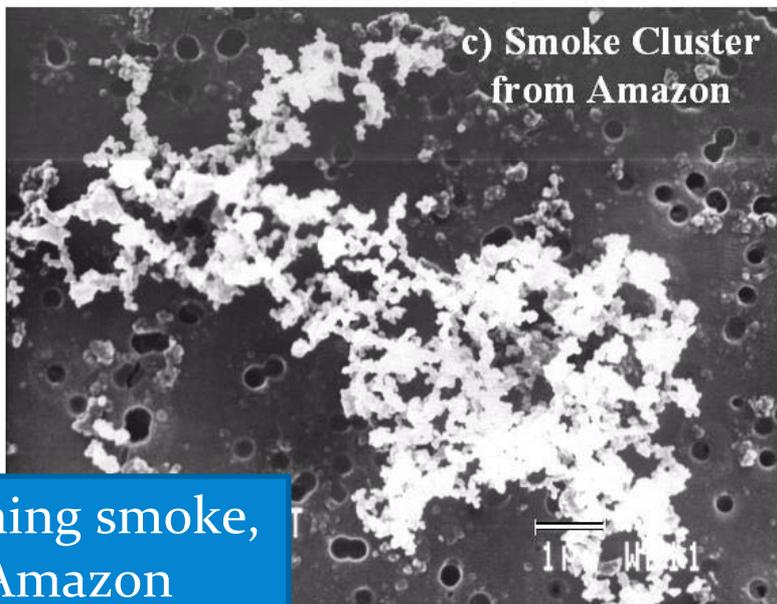
Saharan dust  
in the USA



Smoldering  
smoke, Amazon

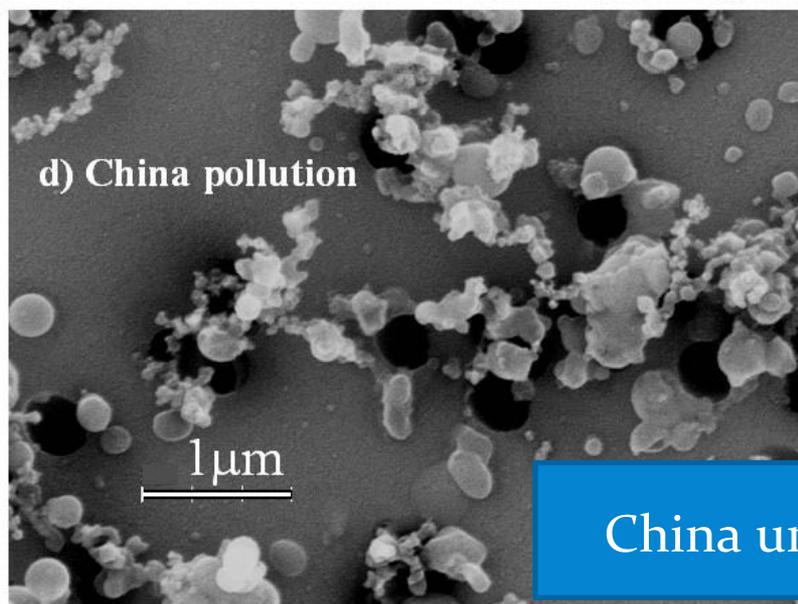


c) Smoke Cluster  
from Amazon



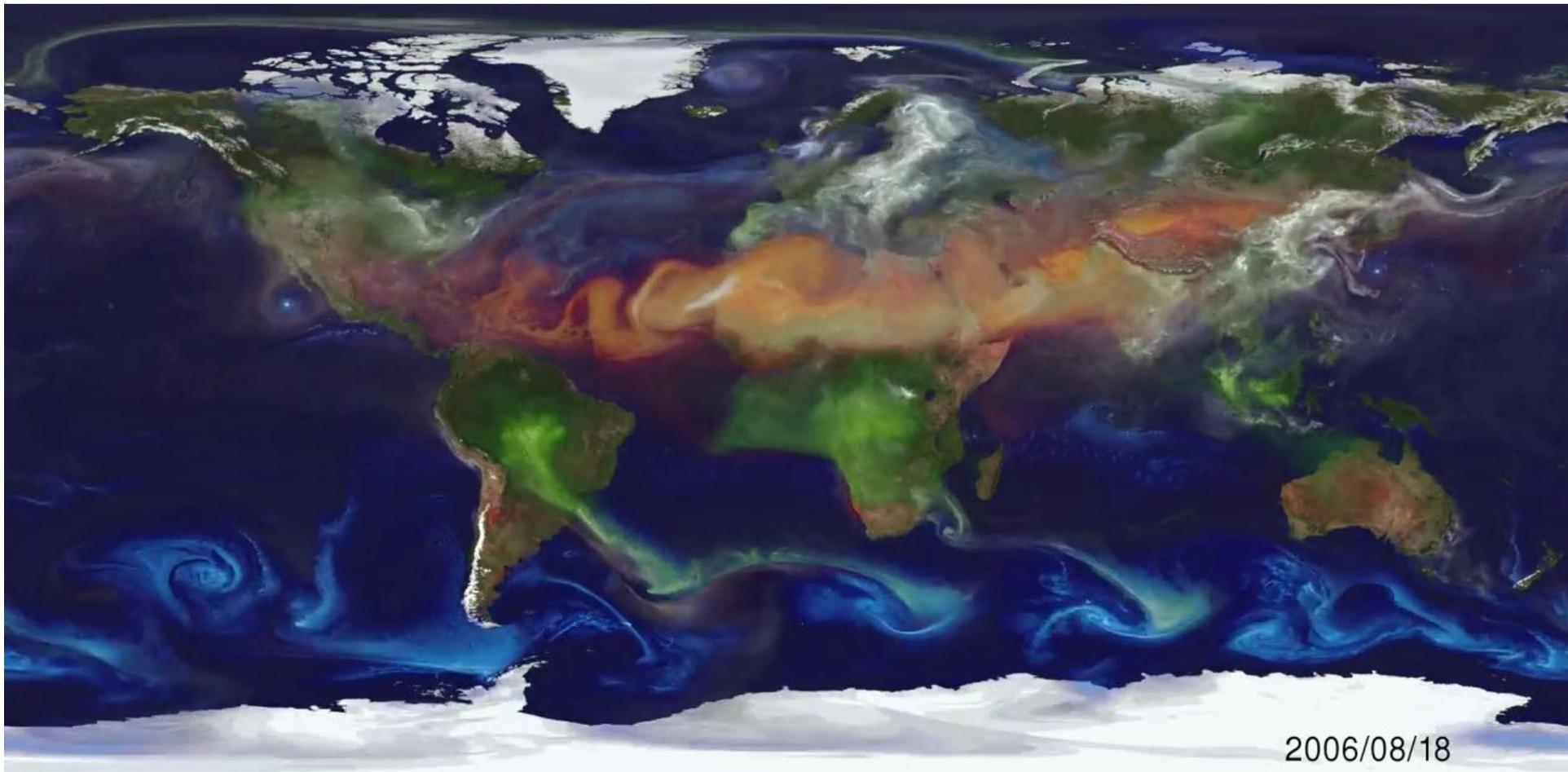
Flaming smoke,  
Amazon

d) China pollution



China urban

# Variam no tempo e no espaço



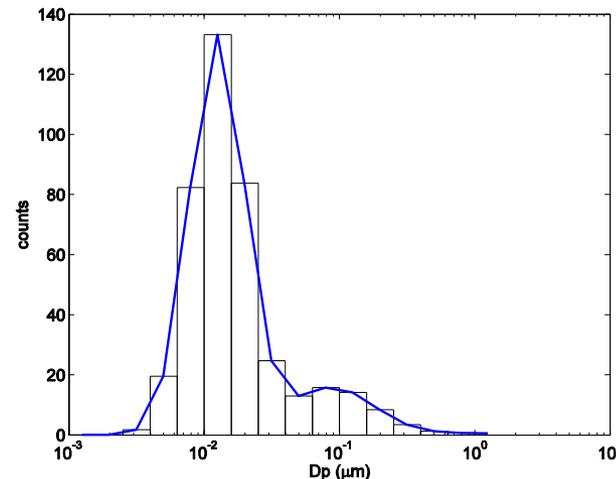
# Classificação

- **Aerossóis primários** – emitidos diretamente na atmosfera, como partículas sólidas ou líquidas
  - Exemplo: Poeira, Sal Marinho, Fuligem, Pólen, etc.
- **Aerossóis secundários** – formados na atmosfera através de nucleação e/ou condensação em partículas existentes
  - Exemplo: Sulfato, Orgânicos secundários, etc.

# Observando Aerossóis

- Estamos interessados em saber:
  - Concentração
  - Propriedades ópticas
  - Composição química
- Valor total ou Valor distribuído por tamanho

540  $\text{cm}^{-3}$  or...



# Concentração

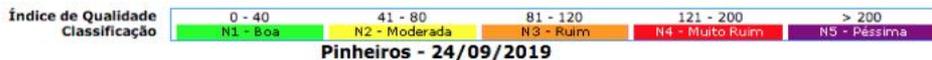
- A concentração numérica é representada por  $N$
- É definida como o número de partículas por unidade de volume, tipicamente em  $\#/cm^3$
- Outras concentrações:
  - Concentração de área,  $S$  [ $\mu m^2/cm^3$ ]
  - Concentração volumétrica,  $V$  [ $\mu m^3/cm^3$ ]
  - Concentração mássica,  $M$  [ $\mu g/cm^3$ ]
- $M$  pode ser calculada a partir de  $V$  e da densidade da partícula,  $\rho$ ,  $g/cm^3$

# Aerossóis

- Sempre presentes na atmosfera, de  $\sim 10 \text{ cm}^{-3}$  em um ambiente limpo, até  $10^6 \text{ cm}^{-3}$  em ambientes poluídos
- A massa na atmosfera também varia, de  $\sim 0.1 \mu\text{g m}^{-3}$  até  $1 \text{ mg m}^{-3}$  em condições extremas
- Tempo de vida na troposfera: dias a semanas
- É polidisperso, ou seja, se apresenta com tamanhos diversos, de  $\sim 1 \text{ nm}$  até  $100 \mu\text{m}$

## Dados Horários

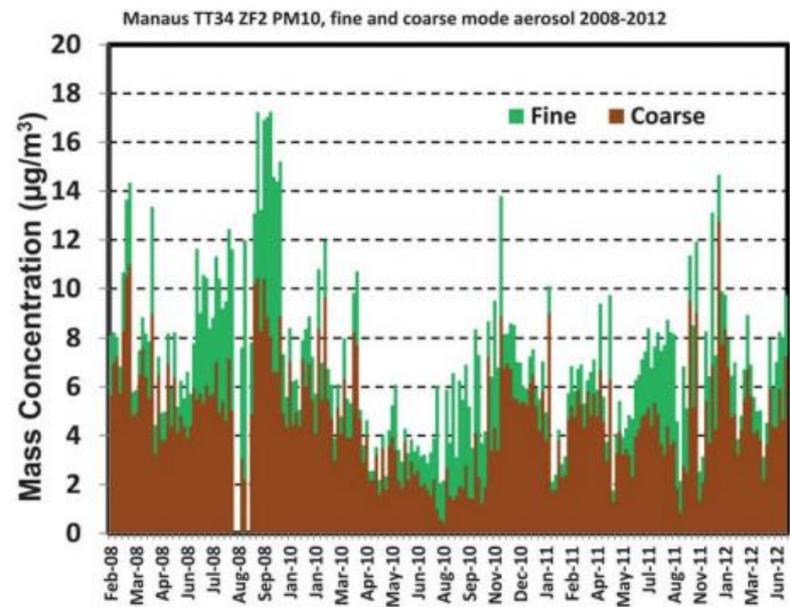
# Sao Paulo



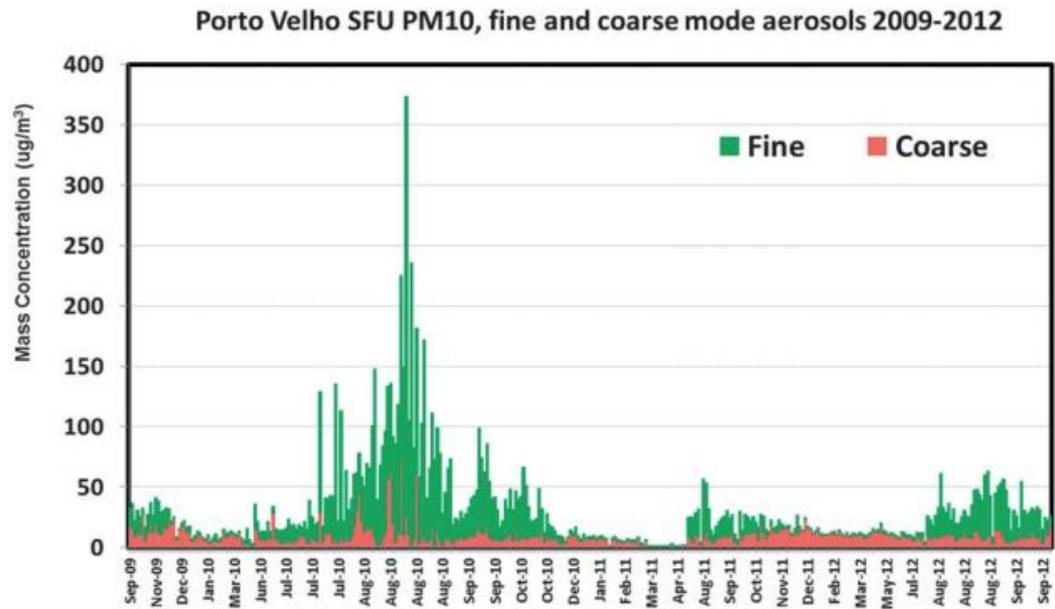
Hora	NO2 µg/m³		MP10 µg/m³		CO ppm		O3 µg/m³			MP2.5 µg/m³			BENZENO ug/m3	TOLUENO ug/m3		
	Média Horária	Índice / Qualidade	Média horária	Média 24 h	Índice / Qualidade	Média horária	Média 8 h	Índice / Qualidade	Média horária	Média 8 h	Índice / Qualidade	Média horária	Média 24 h	Índice / Qualidade	Média Horária	
01:00	6	1	7	--	--	0,1	0,2	1	30	33	13	3	5	8	0,0	0,1
02:00	4	1	4	--	--	0,1	0,2	1	38	34	14	--	6	9	0,1	0,1
03:00	3	0	8	17	13	0,1	0,2	1	40	35	14	3	5	8	0,0	0,2
04:00	2	0	9	16	13	0,1	0,1	1	43	37	15	2	5	8	0,0	0,1
05:00	3	0	15	16	13	0,1	0,1	1	40	37	15	--	5	8	0,0	0,1
06:00	6	1	18	16	13	0,2	0,1	1	31	36	14	5	5	8	0,0	0,0
07:00	9	2	22	17	13	0,3	0,2	1	25	35	14	9	6	9	0,0	0,0
08:00	11	2	29	17	13	0,4	0,2	1	20	33	13	12	6	9	0,0	0,1
09:00	12	2	21	17	13	0,5	0,2	1	20	32	13	13	6	9	0,0	0,1
10:00	10	2	39	18	14	0,4	0,3	1	25	30	12	16	7	11	0,0	0,1
11:00	10	2	28	19	15	0,4	0,3	1	31	29	12	19	7	11	0,0	0,3
12:00	13	3	27	19	15	0,5	0,3	2	42	29	12	17	8	13	0,2	1,9
13:00	15	3	45	20	16	0,5	0,4	2	76	34	14	20	9	14	0,1	0,9
14:00	14	3	33	21	17	0,4	0,4	2	81	40	16	19	9	14	0,1	1,0
15:00	14	3	36	22	17	0,3	0,4	2	64	45	18	19	10	16	0,2	1,3
16:00	16	3	46	22	17	0,4	0,4	2	56	49	20	21	11	17	0,1	1,6
17:00	15	3	39	23	18	0,4	0,4	2	41	52	21	21	11	17	0,1	5,6
18:00	16	3	29	23	18	0,4	0,4	2	27	52	21	16	12	19	0,1	2,3
19:00	18	4	33	24	19	0,5	0,4	2	9	50	20	15	12	19	0,1	0,9
20:00	11	2	26	24	19	0,3	0,4	2	22	47	19	17	12	19	0,1	0,4
21:00	13	3	21	24	19	0,4	0,4	2	18	40	16	15	13	20	0,0	0,1
22:00	10	2	31	25	20	0,3	0,4	2	24	33	13	13	13	20	0,0	0,3
23:00	9	2	23	25	20	0,3	0,4	2	25	28	11	17	14	22	0,0	0,2
24:00	7	2	27	26	21	0,3	0,4	2	32	25	10	15	14	22	0,1	0,2

# Amazonia

## Manaus x Porto Velho

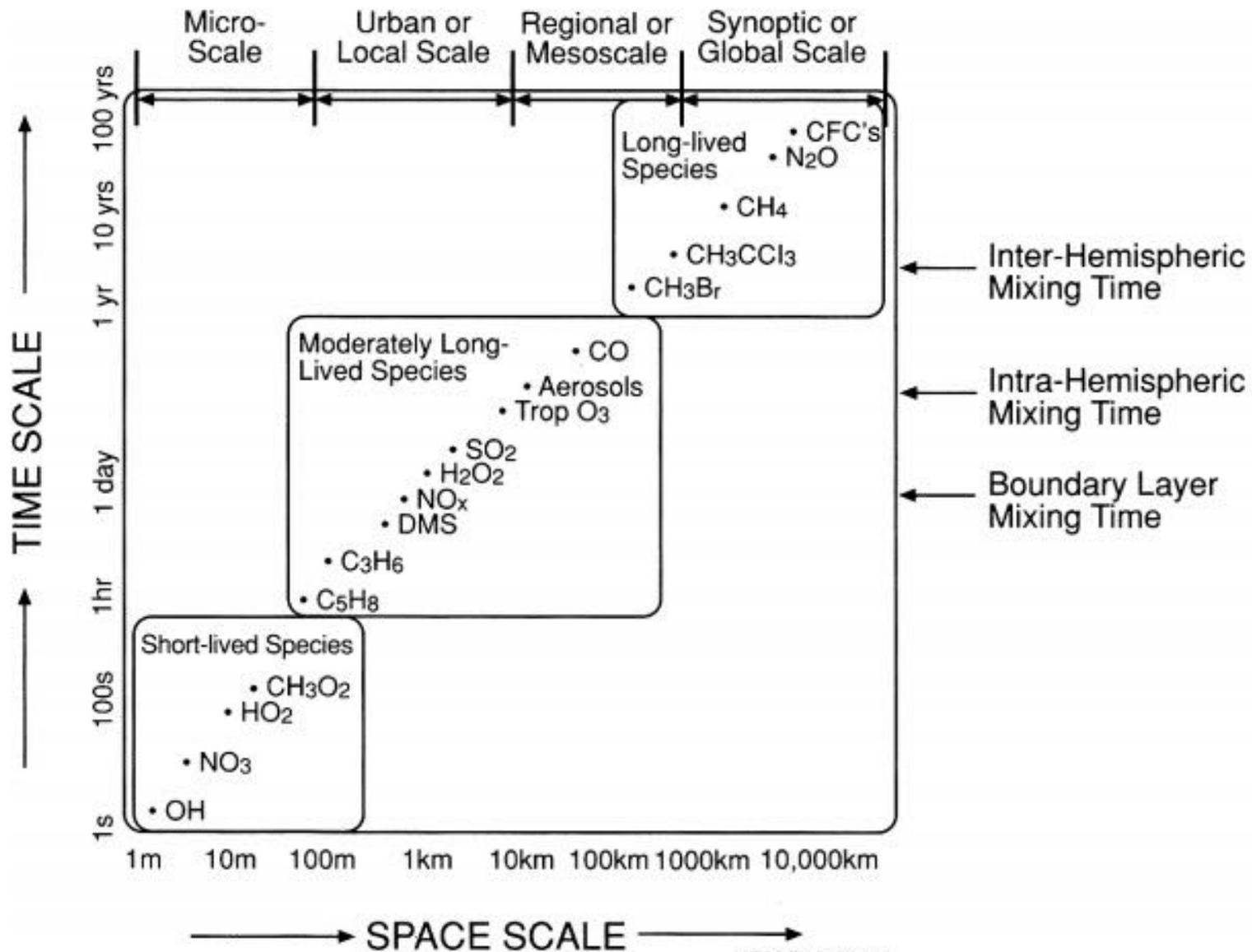


**Fig. 3** Time series of fine (PM<sub>2.5</sub>) and coarse mode aerosol mass concentrations at the central Amazonia TT34 forest site from 2008 to 2012.



**Fig. 5** Time series of fine and coarse mode aerosol mass concentrations at the PVH anthropogenic impacted site, from 2009 to 2012.

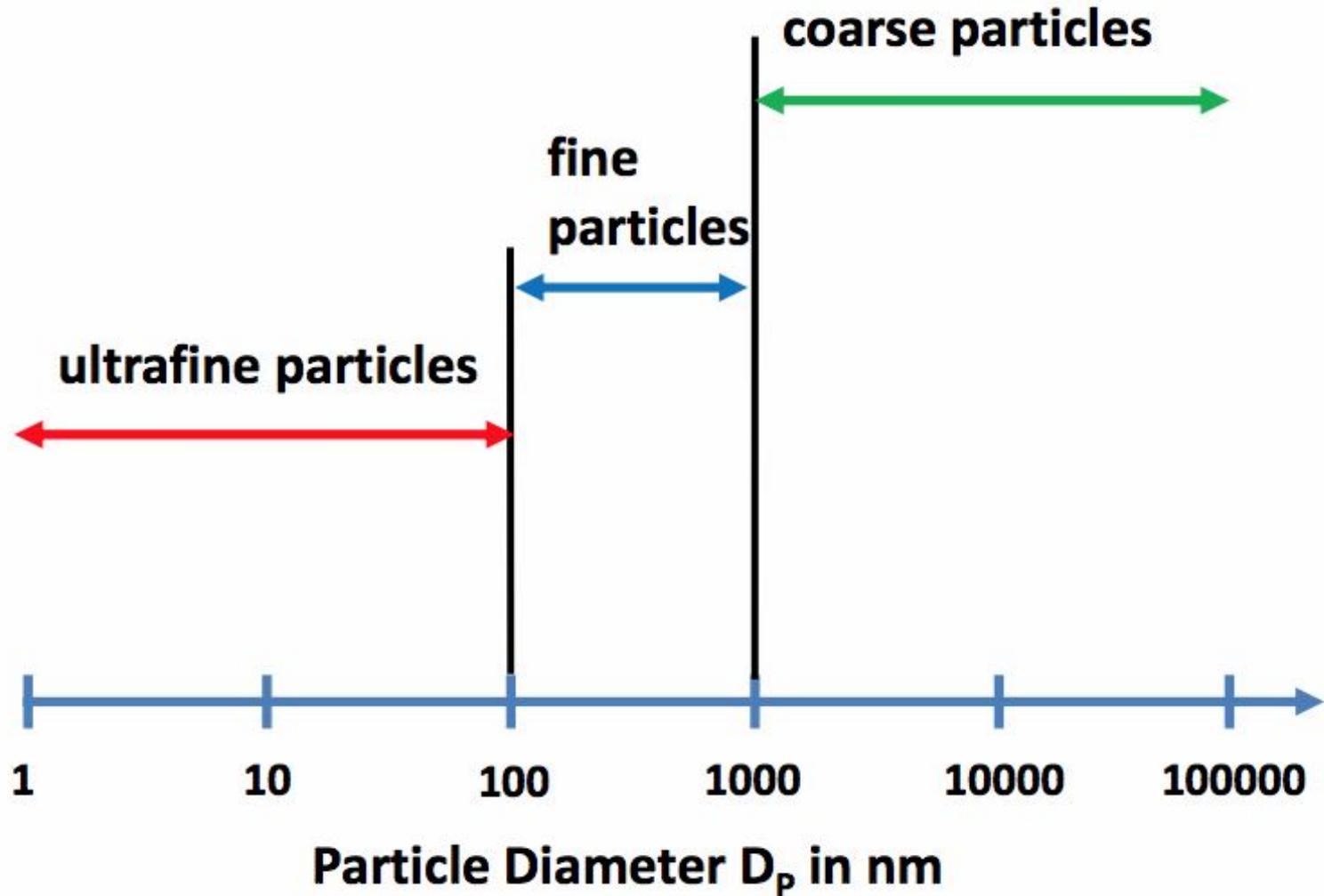
# Aerossóis



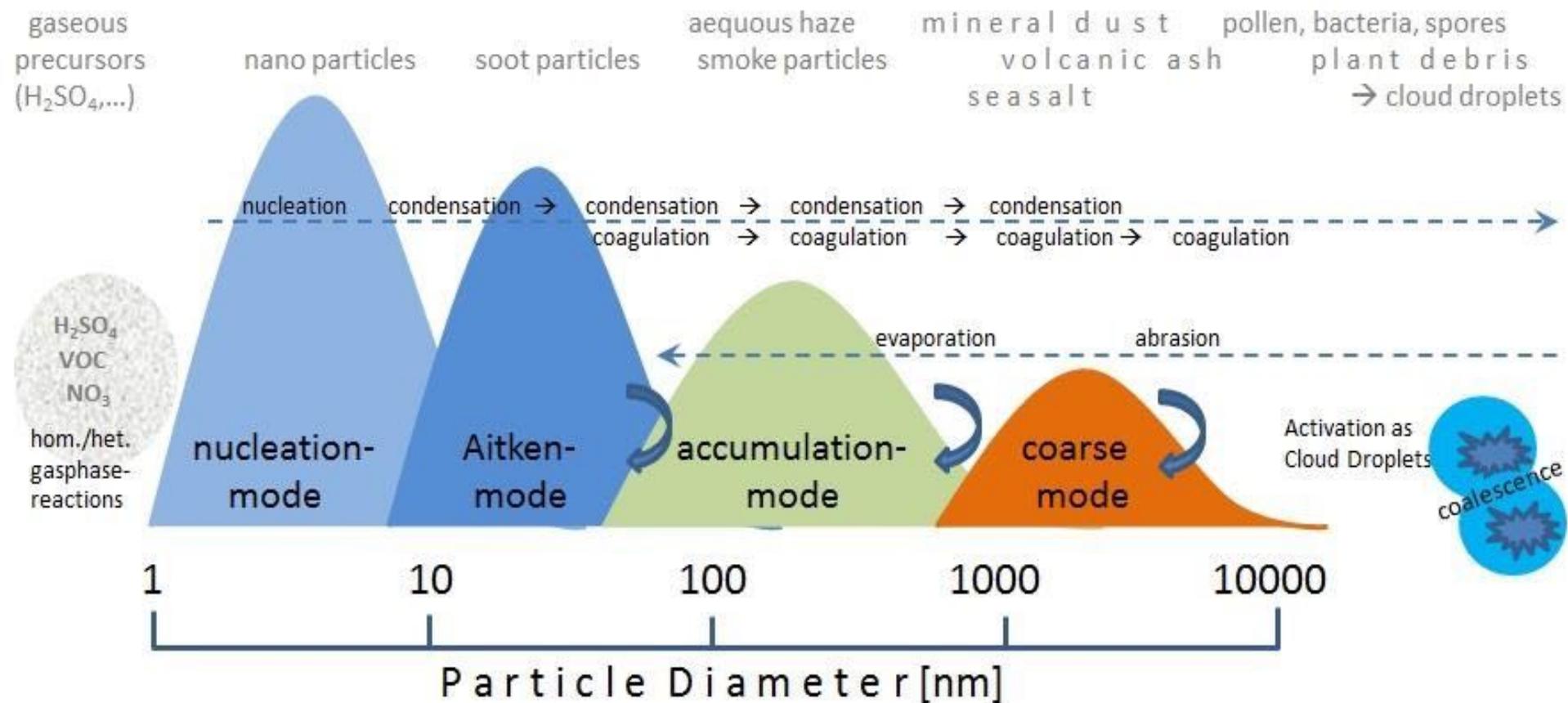
# Classificação por tamanho

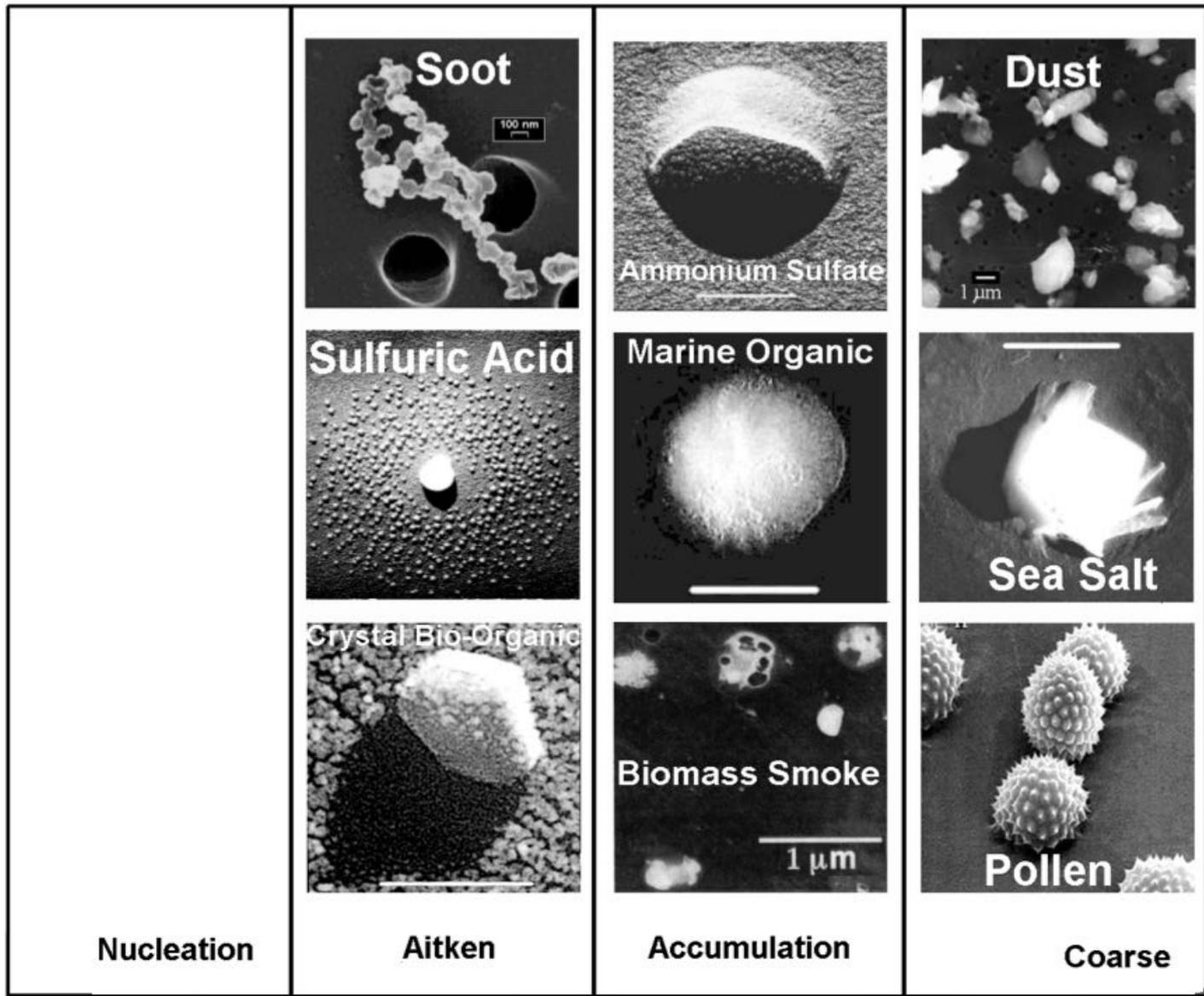
- Partículas grossas
  - $> 1\mu\text{m}$
- Partículas finas
  - $< 1\mu\text{m}$
  - Moda de acumulação (100-1000 nm)
- Partículas ultrafinas
  - $< 100\text{ nm}$
  - Moda de Aitken (10-100 nm)
  - Moda de nucleação (1-10 nm)

# Classificação por tamanho



# Distribuição de tamanho





1

10

100

1000

1000

Particle Diameter, nm

# Tamanhos relativos

Partícula com 1nm

Ponta de uma agulha (0.1 mm)

Partícula com 350 nm

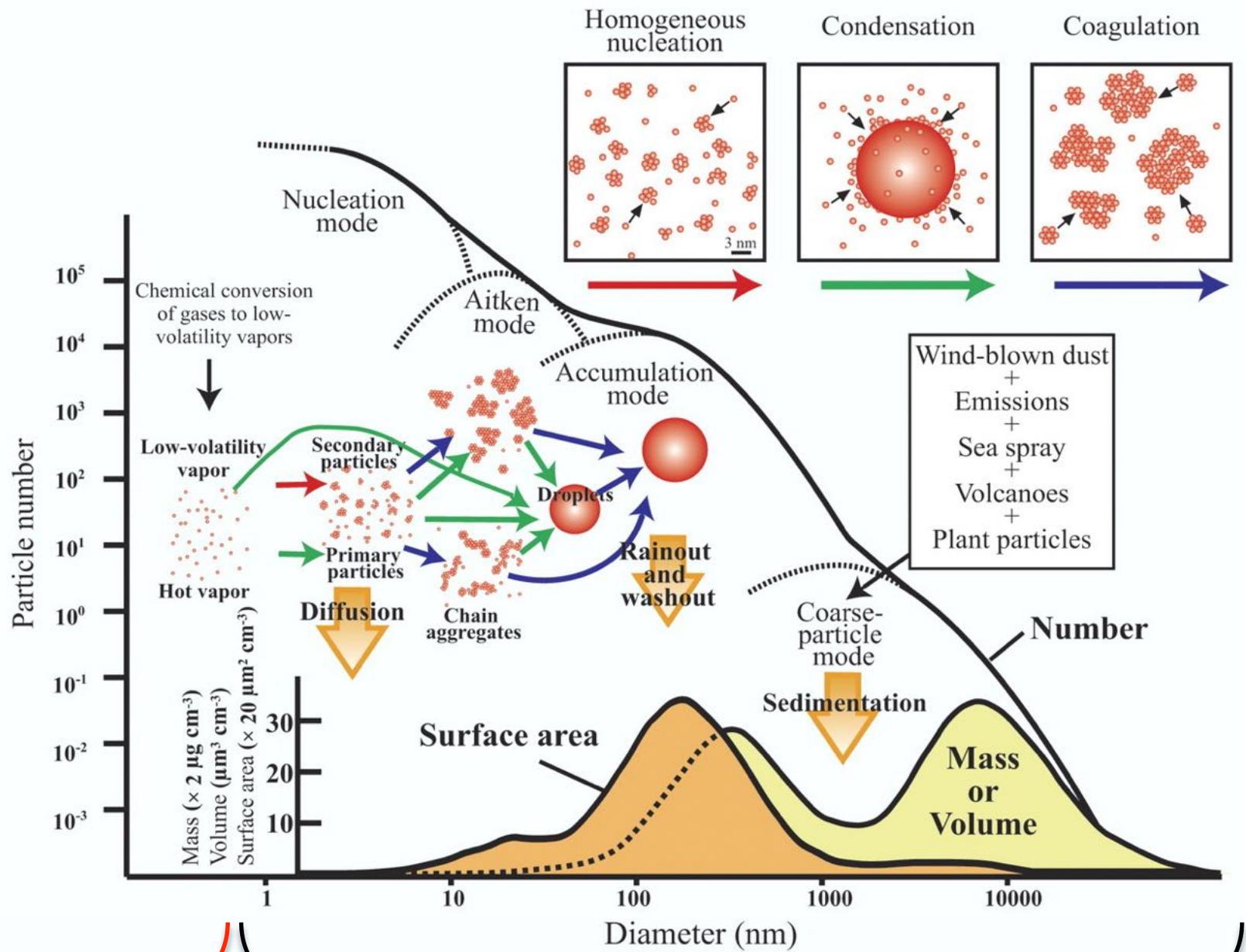
Bola de ping-pong (3.5 cm)

Partícula com 2.5  $\mu\text{m}$

Bola de futebol (25 cm)

Partícula com 100  $\mu\text{m}$

Balão de ar quente (10 m)



## Quais são as fontes dos aerossóis?

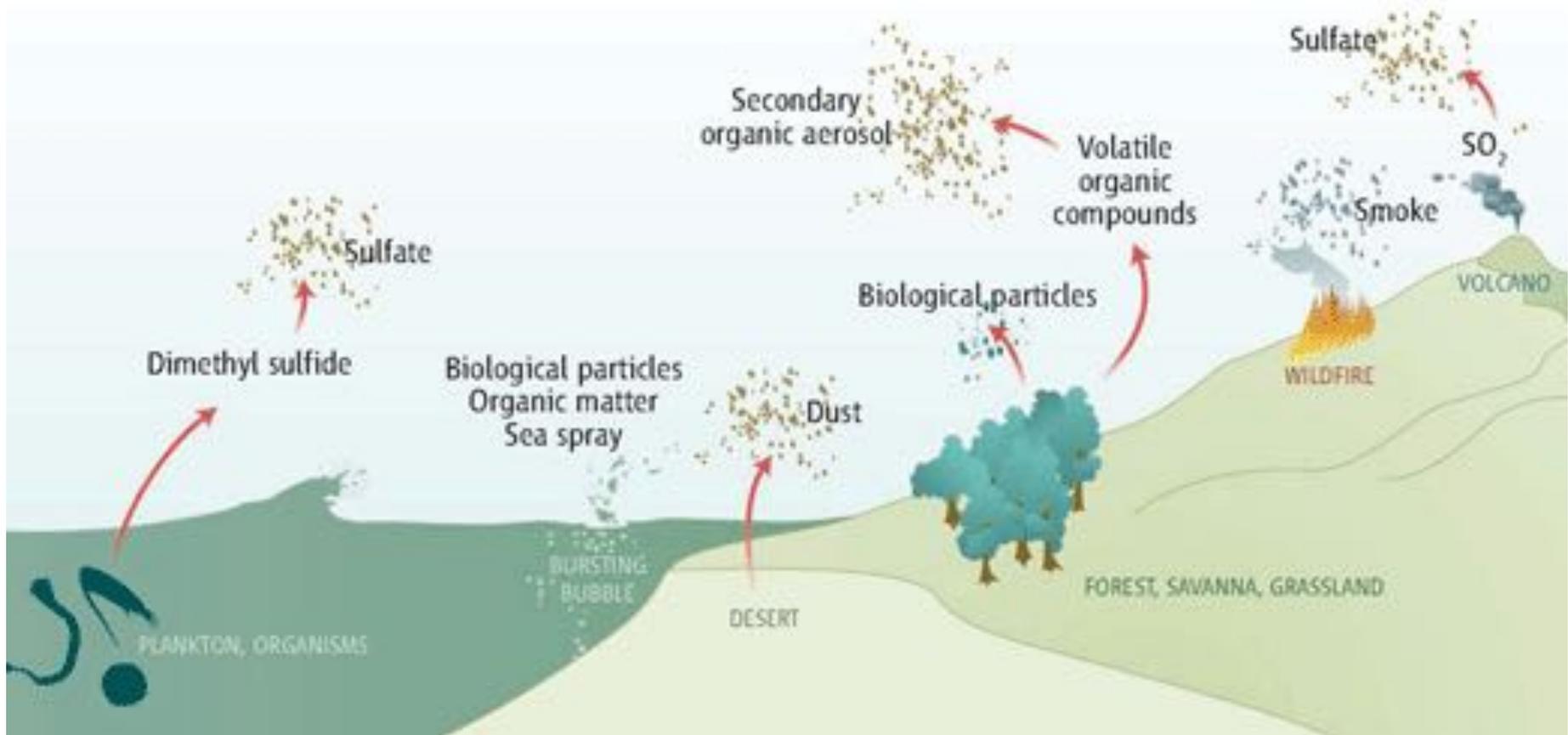
Os oceanos, são 66 % da superfície da Terra

Áreas semiáridas e desertos, são 37% da área continental

Os ecossistemas, e.g. as florestas que cobrem 30% da área continental, e a vida marinha



# Quais são as fontes dos aerossóis?



**Table 5.3** Estimates (in Tg per year) for the year 2000 of (a) direct particle emissions into the atmosphere and (b) *in situ* production

<b>(a) Direct emissions</b>		
	<b>Northern hemisphere</b>	<b>Southern hemisphere</b>
Carbonaceous aerosols		
Organic matter (0-2 $\mu\text{m}$ ) <sup>a</sup>		
Biomass burning	28	26
Fossil fuel	28	0.4
Biogenic (>1 $\mu\text{m}$ )	—	—
Black carbon (0-2 $\mu\text{m}$ )		
Biomass burning	2.9	2.7
Fossil fuel	6.5	0.1
Aircraft	0.005	0.0004
Industrial dust, etc. (>1 $\mu\text{m}$ )		
Sea salt		
<1 $\mu\text{m}$	23	31
1-16 $\mu\text{m}$	1,420	1,870
Total	1,440	1,900
Mineral (soil) dust		
<1 $\mu\text{m}$	90	17
1-2 $\mu\text{m}$	240	50
2-20 $\mu\text{m}$	1,470	282
Total	1,800	349

<b>(b) In situ</b>		
	<b>Northern hemisphere</b>	<b>Southern hemisphere</b>
Sulfates (as $\text{NH}_4\text{HSO}_4$ )		
Anthropogenic	145	55
Biogenic	106	15
Volcanic	25	32
Nitrate (as $\text{NO}_3^-$ )		
Anthropogenic	14	7
Natural	12.4	1.8
Organic compounds		
Anthropogenic	2.2	1.7
Biogenic	0.15	0.45
	8.2	7.4

<sup>a</sup> Sizes refer to diameters. [Adapted from Intergovernmental Panel on Climate Change, *Climate Change 2001*, Cambridge University Press, pp. 297 and 301, 2001.]

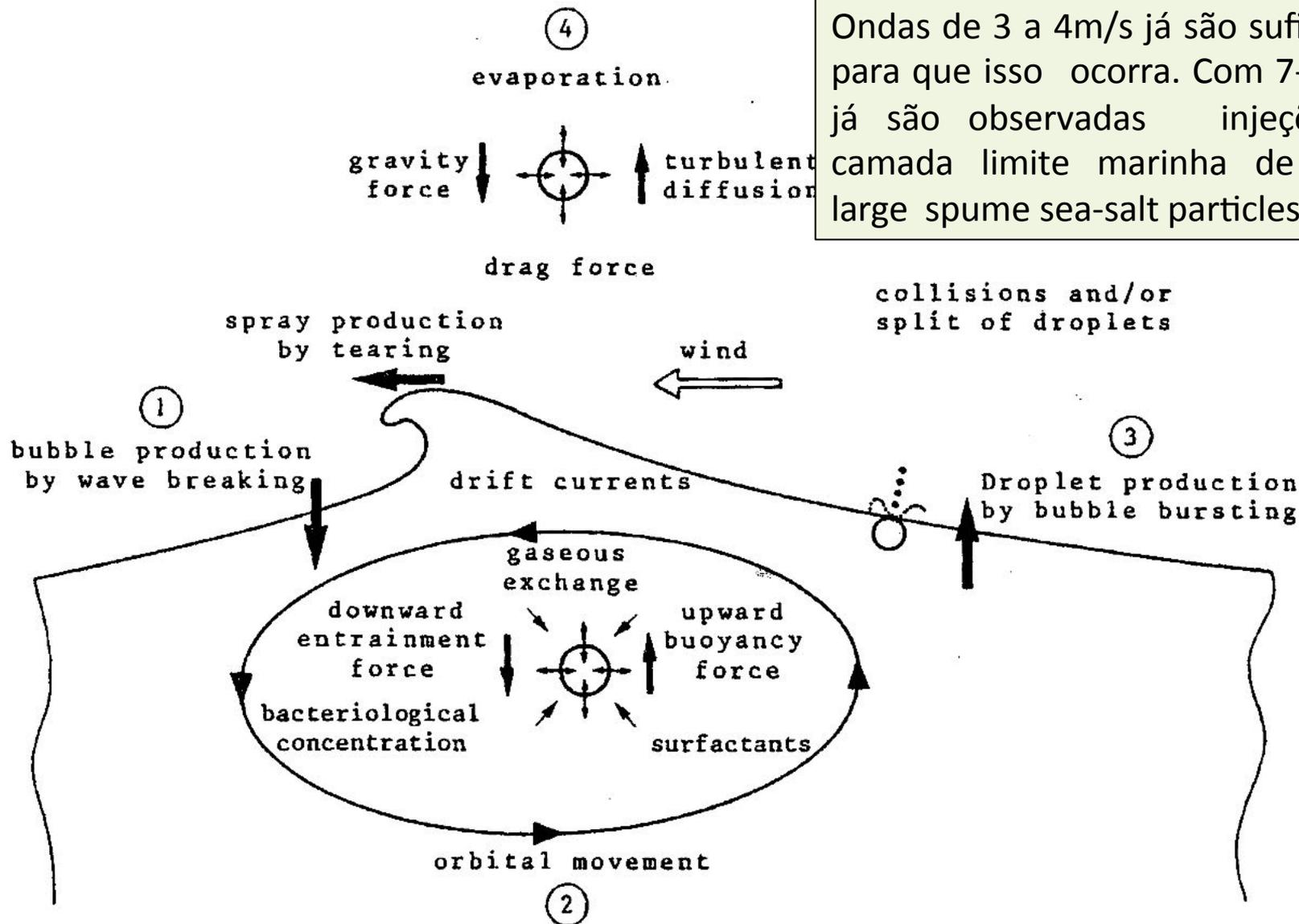
# Aerossóis Marinhos



# Oceano

- Ocupa 66% da superfície terrestre;
- Participa intensamente dos ciclos biogeoquímicos, sendo fonte e sumidouro de partículas e gases presentes na atmosfera;
- Maresia (Sea Spray Aerosol) é a maior fonte global de aerossol;





Ondas de 3 a 4m/s já são suficientes para que isso ocorra. Com 7-11m/s, já são observadas injeções na camada limite marinha de 'ultra-large spume sea-salt particles'.

Fig. 2. Physical processes leading to the production of marine liquid aerosols responsible for air-sea particulate exchanges. Circled numbers refer to chronological steps indicated in Figure 1. We are mainly interested in this study by step 3. The ultimate goal is to propose a model for the transfer function between air bubbles in seawater and liquid aerosols in the atmosphere.

Uma onda quebrando, vista com uma câmera.

A onda entranha air na água, que forma bolhas ar, que irão subir até a superfície.

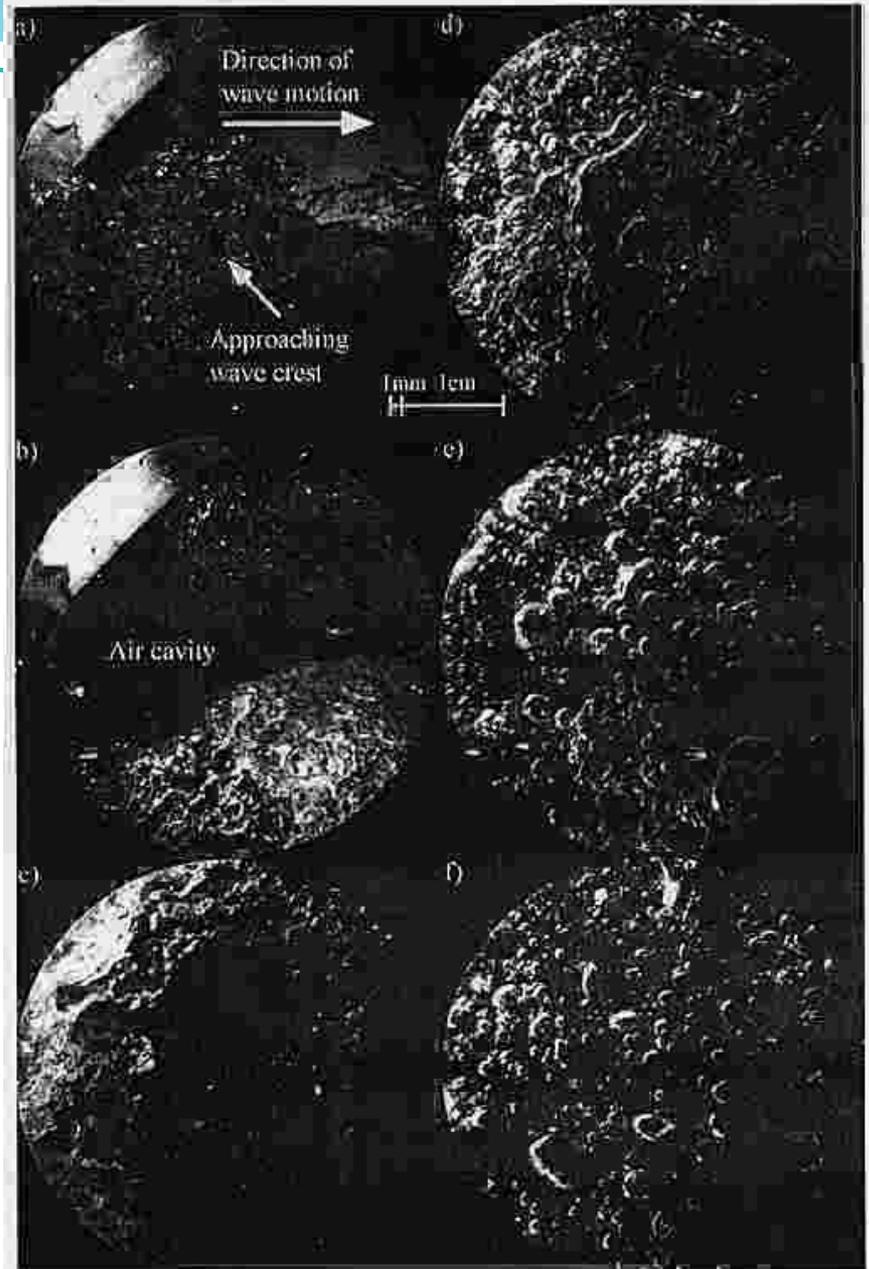


FIG. 7. Images taken in a breaking wave crest showing the crushing of an air cavity. Successive images were taken every 90 milliseconds. (a) The approaching wave crest. (b) The air cavity trapped by the overrunning wave crest. (c)-(f) The evolving air-water mixture behind the wave crest.

# Modelo conceitual

- Gotas de filmes e de jatos que formam partículas pequenas e grandes, respectivamente

RESCH ET AL.: MARINE LIQUID AEROSOL PRODUCTION FROM BURSTING OF AIR BUBBLES

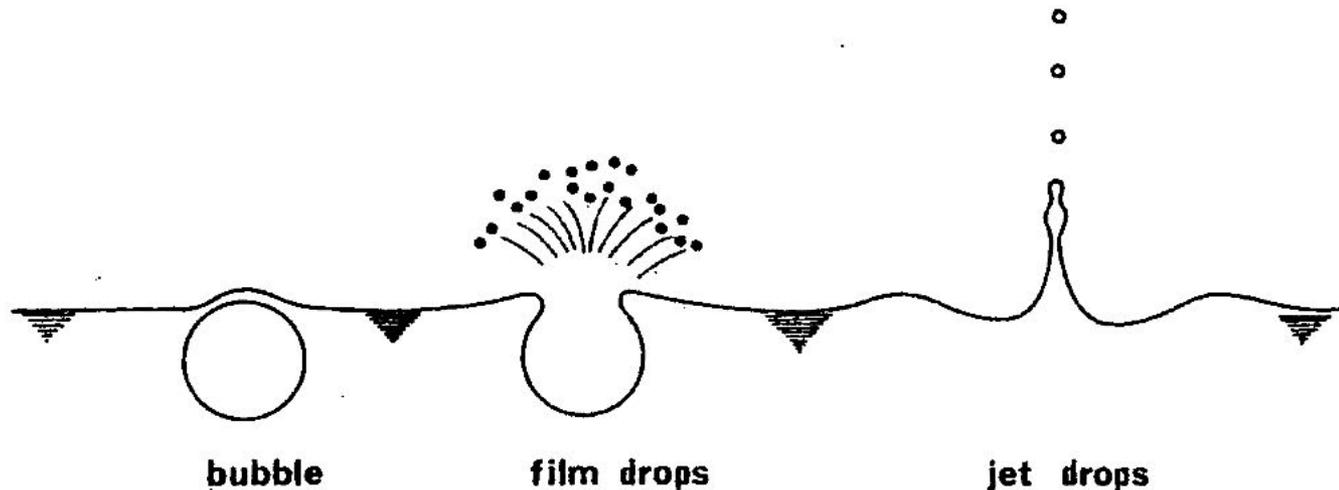


Fig. 3. Schematic representation of the production of film drops and jet drops by bubble bursting. In a time sequence the onset of film cap breaking is detected after  $150 \mu\text{s}$ , film drops are detected after  $300 \mu\text{s}$ , and jet drops appear between 1 and 30 ms after the rupture of the bubble cap.

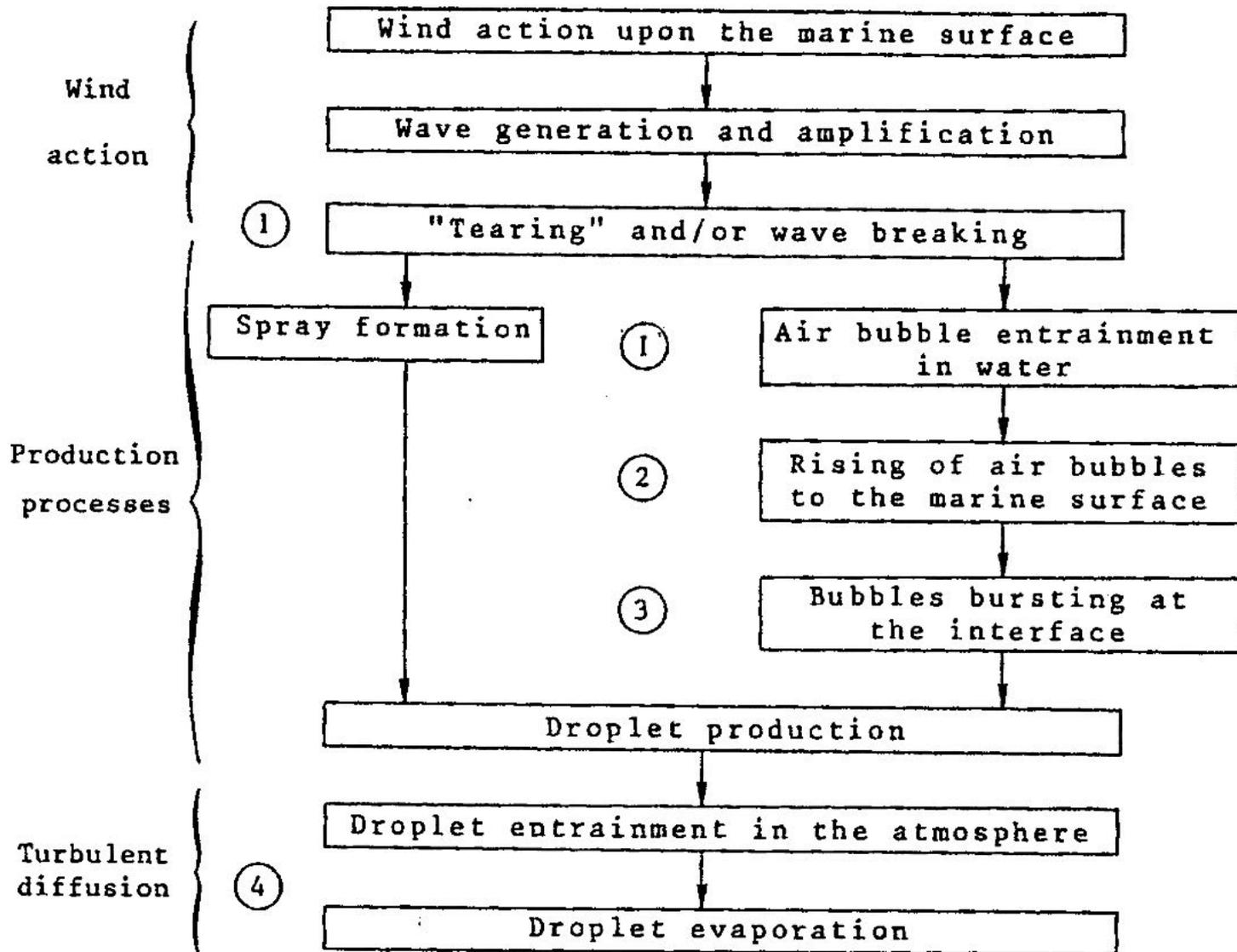


Fig. 1. Various steps involved in the process of air-sea particulate exchange.

Área coberta  
com espuma  
branca  
aumenta com  
a velocidade  
do vento

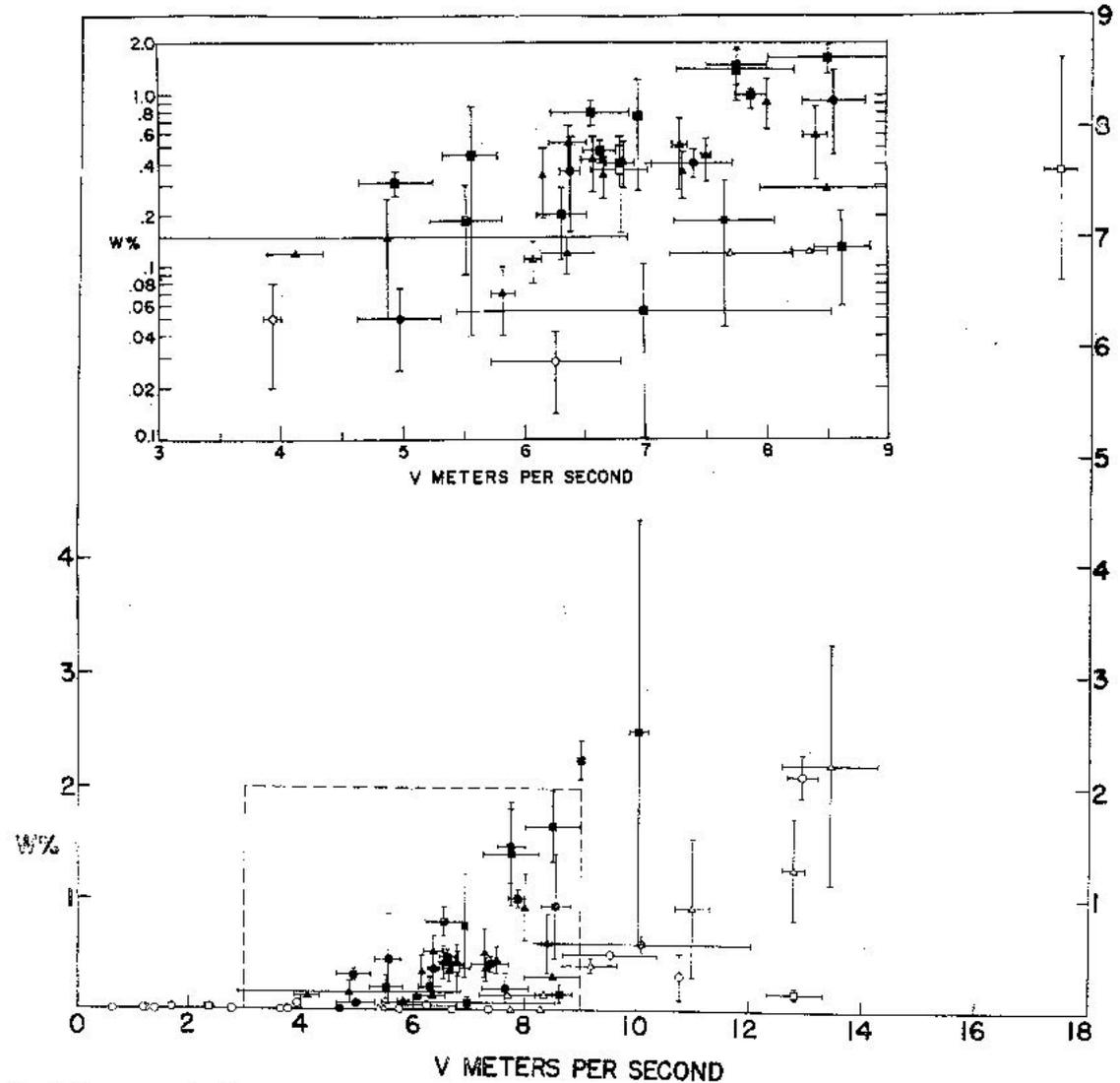


FIG. 1. Percent oceanic whitecap coverage ( $W$ ) vs 10 m elevation wind speed ( $V$ ): squares, observations when atmosphere was thermally stable; triangles, stability near neutral ( $-0.4\text{C} < \Delta T < 0.6\text{C}$ ); circles, thermally unstable. Filled symbols represent BOMEX results, open symbols all other results (see Table 1). Vertical bars indicate standard deviations from mean values. Horizontal bars span range of wind speeds measured during observation periods. Insert shows semi-log representation of data from within box formed by dashed line.

# O Oceano – Aerossóis

- A geração de aerossol por processos mecânicos resulta em partículas de aerossóis variando entre 0,1 e 100 $\mu\text{m}$  enquanto que a conversão gás-partícula produz partículas nanométricas;
- O espectro de aerossol marinho, normalmente ultrapassa 5 ordens de grandeza

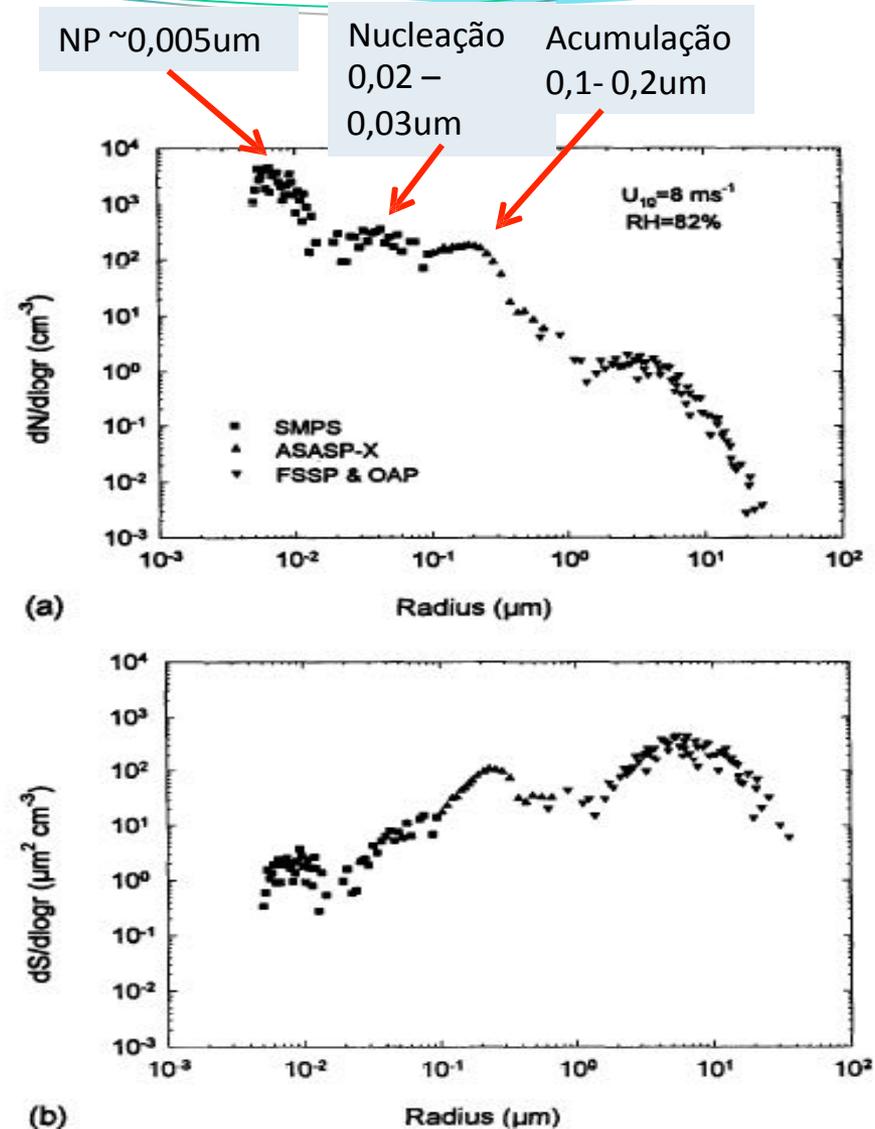


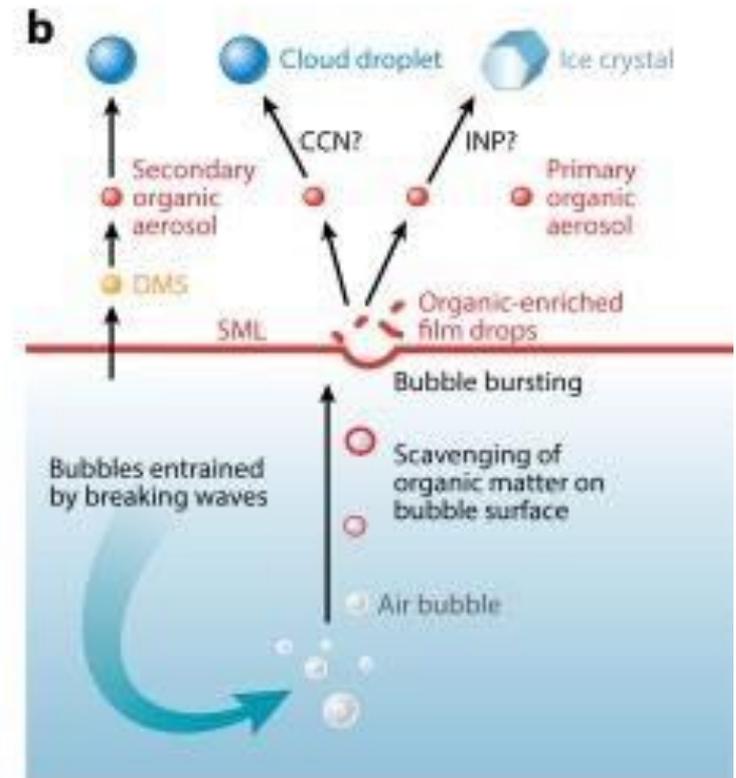
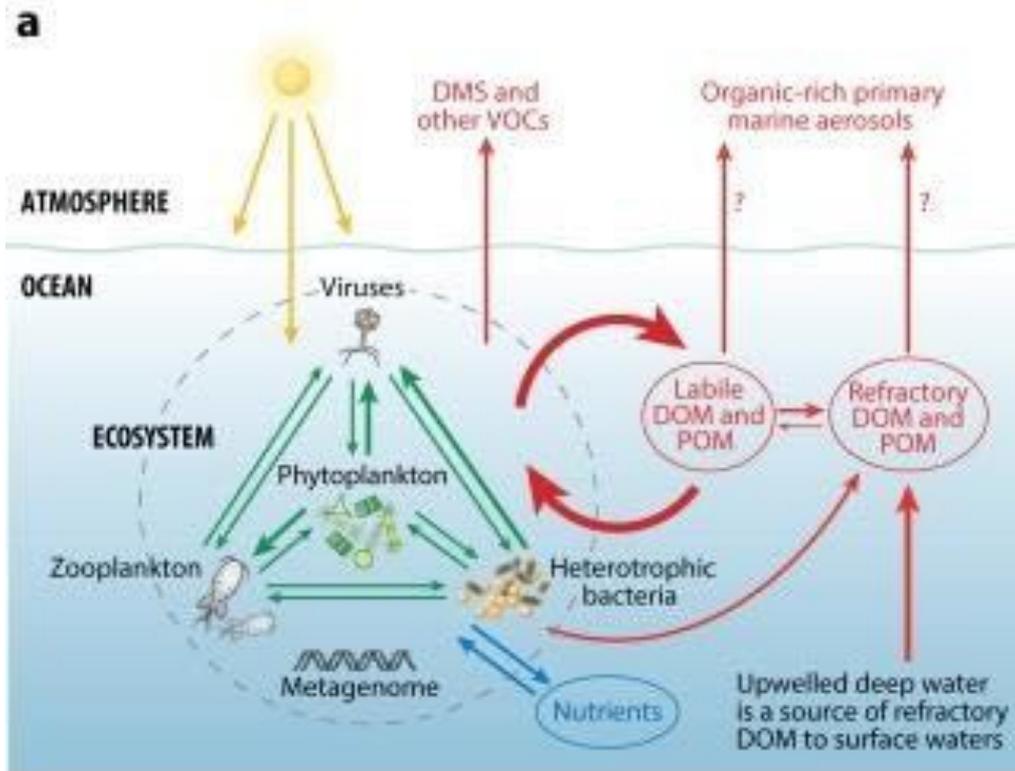
Fig. 1. (a) Typical North East Atlantic maritime number distribution. (b) Typical North East Atlantic maritime surface area distribution.

O'Dowd, C.D. et al., 1995, Marine aerosol, sea-salt, and the marine sulphur cycle: a short review

# O Oceano – Aerossóis

- Os principais aerossóis são:
  - NaCl ( $PM_{2,5-10}$ )
  - DMS, que oxidado na atmosfera se torna Sulfato
- Muitos outros sais inorgânicos (com Br, Cl, etc.) e espécies orgânicas produzidas por seres vivos:
  - Ecossistemas planctônicos na superfície do oceano formam partículas de aerossóis primários e precursores gasosos;

# Aerossóis Marinhos



Brooks SD, Thornton DC. 2018.  
*Annu. Rev. Mar. Sci.* 10:289–313

**DOM: Dissolved Organic Matter**  
**INP: Ice Nuclei Particle**

# O Oceano – Distribuição Geográfica

Primary Marine Organic Aerosols

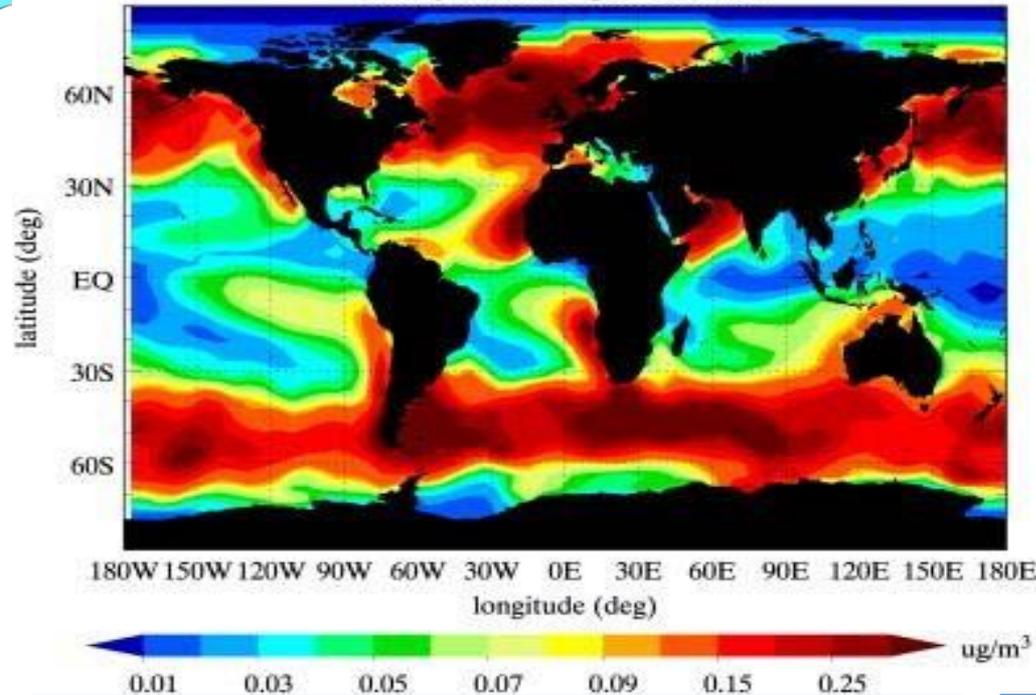


Fig. 1. Annual mean surface concentrations of modelled primary marine POM ( $\mu\text{g m}^{-3}$ ).

Sea salt mass accumulation mode

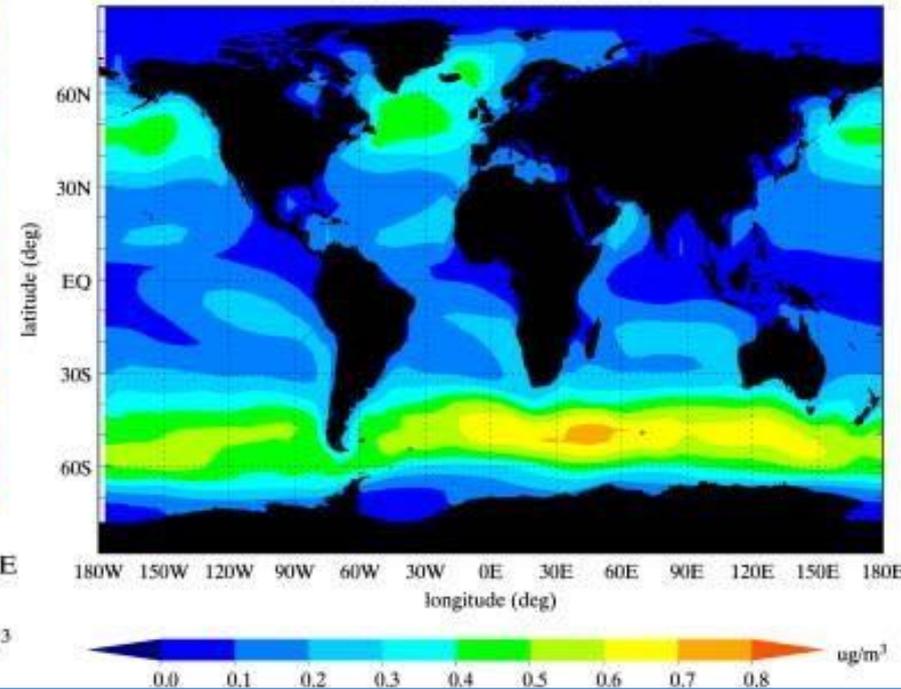
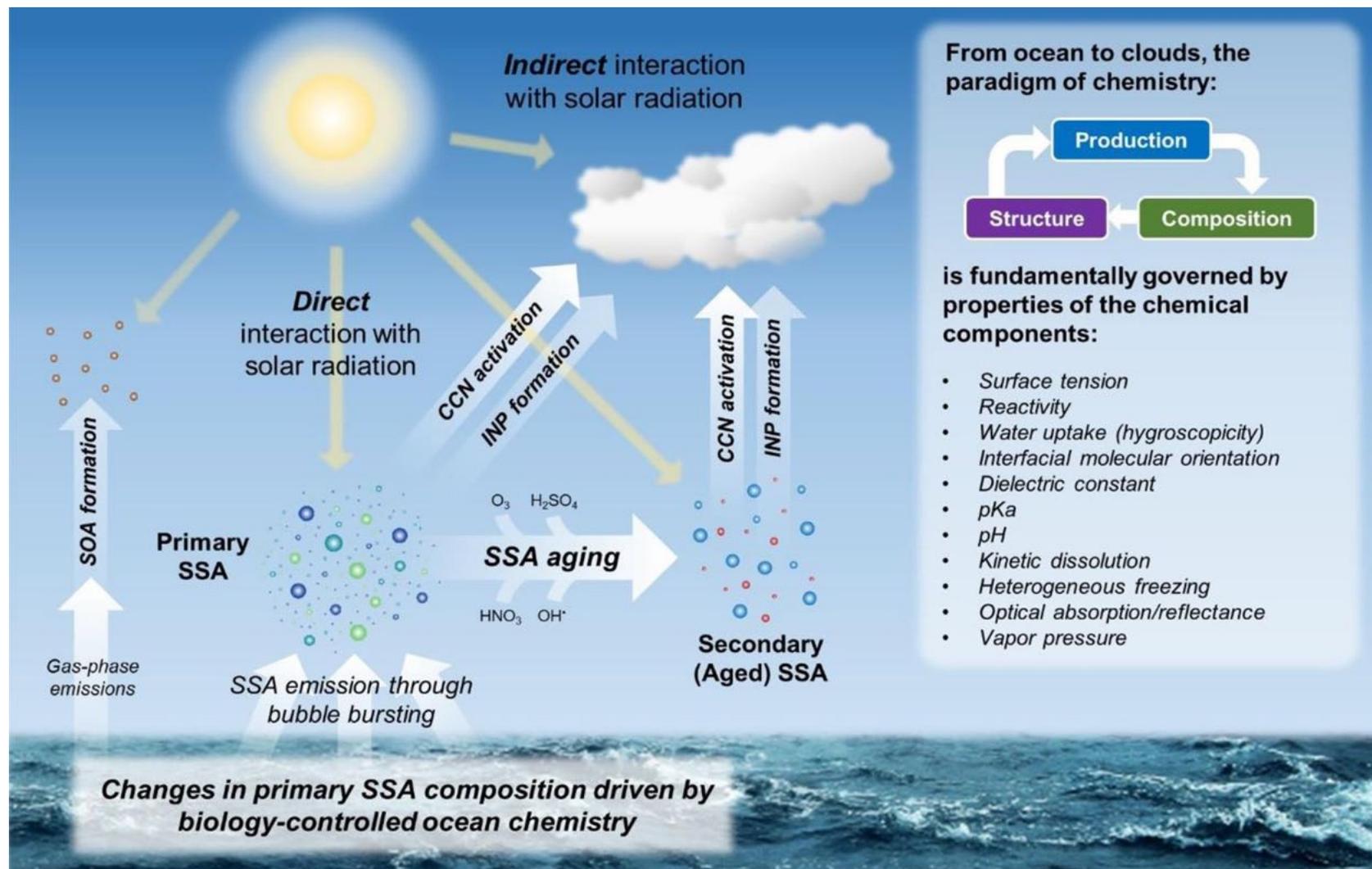


Fig. 2. Annual average surface concentrations of sea salt mass in accumulation mode ( $\mu\text{g m}^{-3}$ ).

- POM: Influência da velocidade do vento e da atividade biológica;
- Sea Salt: influência do impacto do vento no oceano;

# Aerossóis Marinhos – Interação com a atmosfera



Acc. Chem. Res., 2017, 50 (3), pp 599–604 DOI: 10.1021/acs.accounts.6b00603

Cochran et al., Sea Spray Aerosol: The Chemical Link between the Oceans, Atmosphere, and Climate

More cloud  
condensation  
nuclei



Elevated  
SO<sub>2</sub>  
concentration



Elevated  
DMS  
concentration



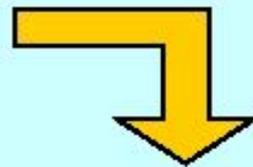
Enhanced  
DMS  
production



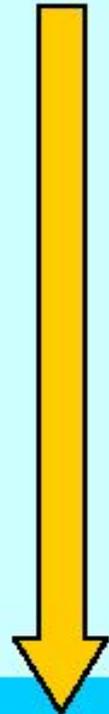
Enhanced  
phytoplankton  
growth



Ocean  
warms



Increased Earth albedo  
more sunlight reflected



Charlson, Lovelock, Andreae, Warren

# CLAW hypothesis

## Negative feedback loop

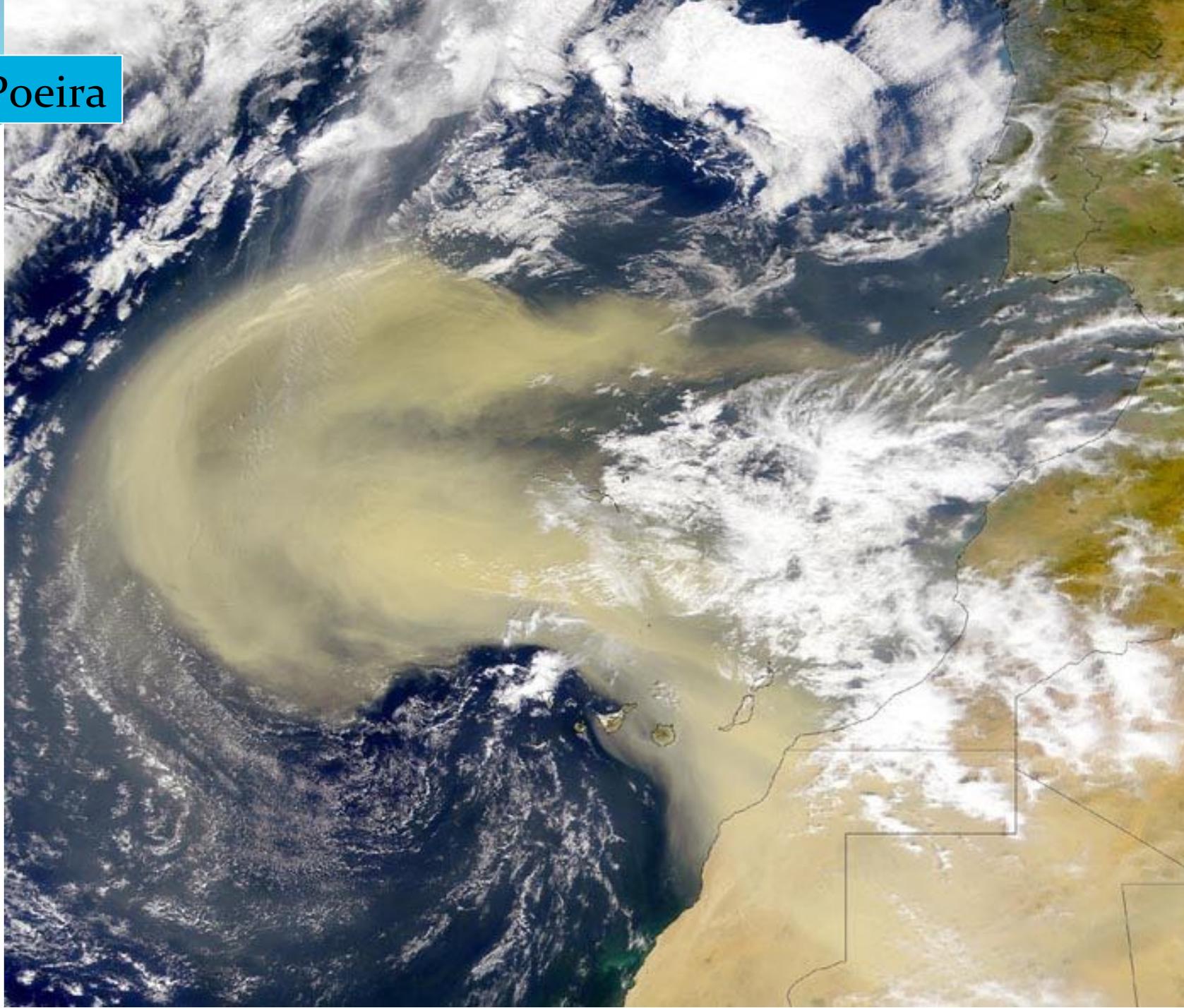
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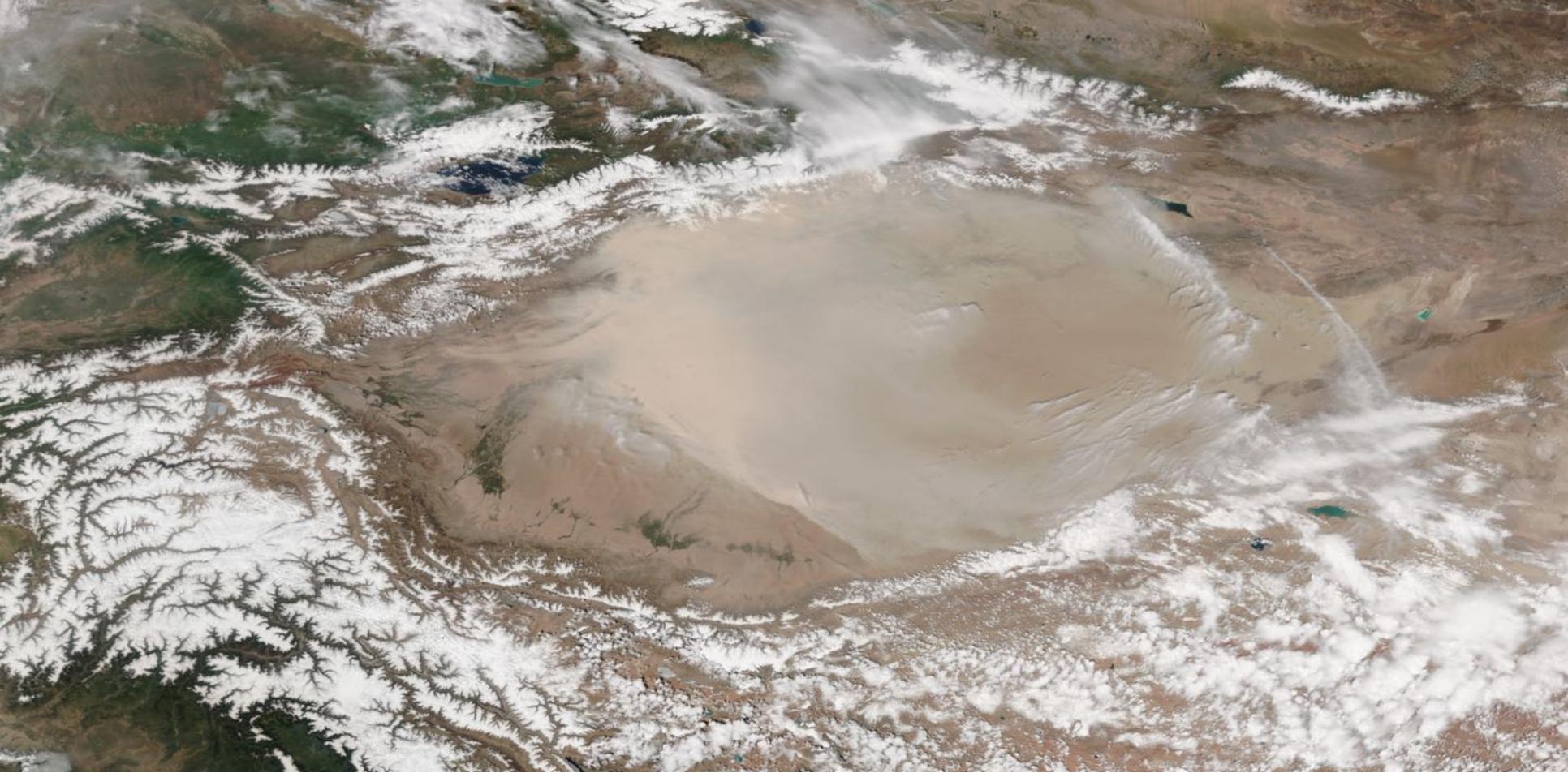
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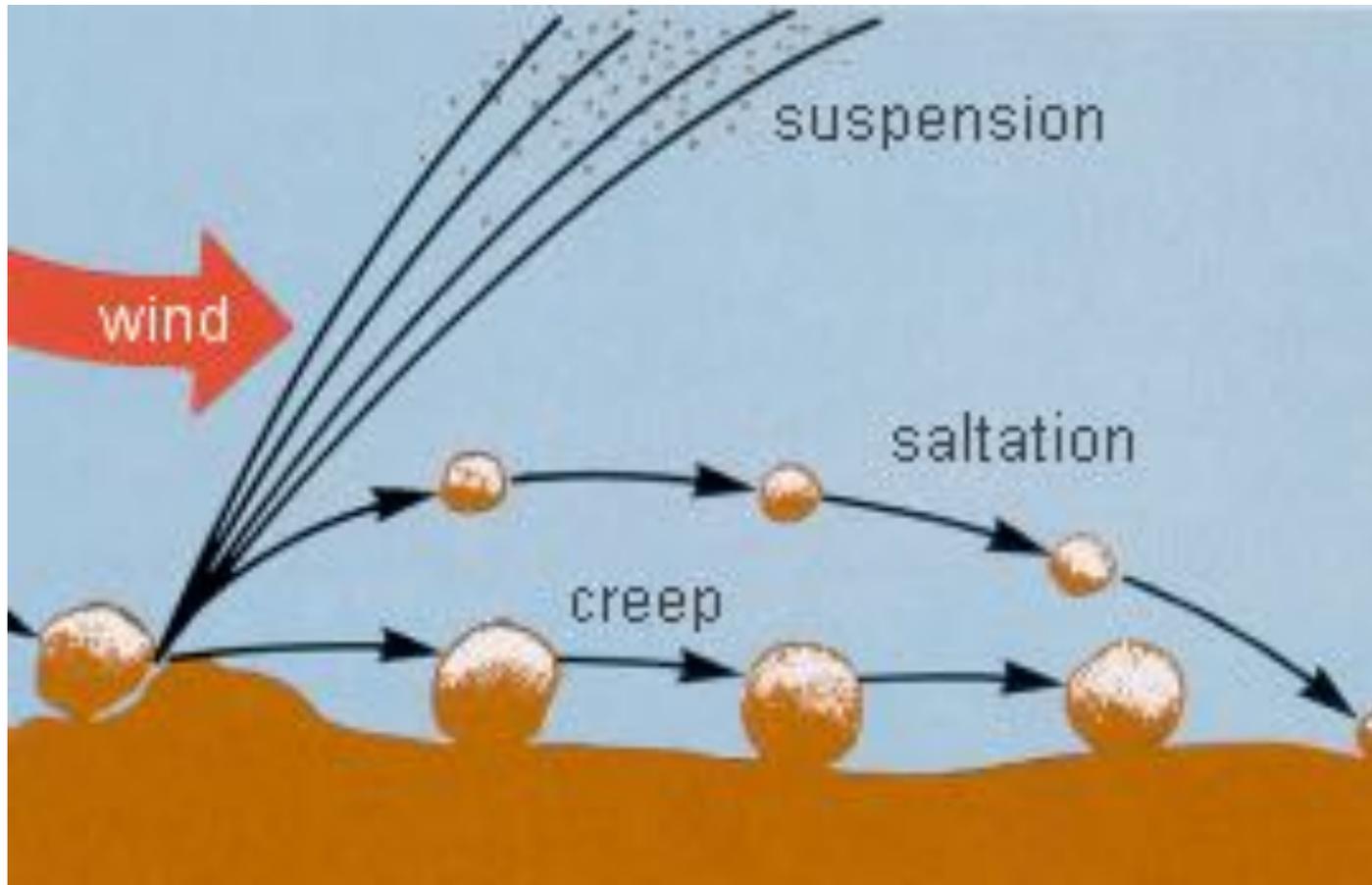
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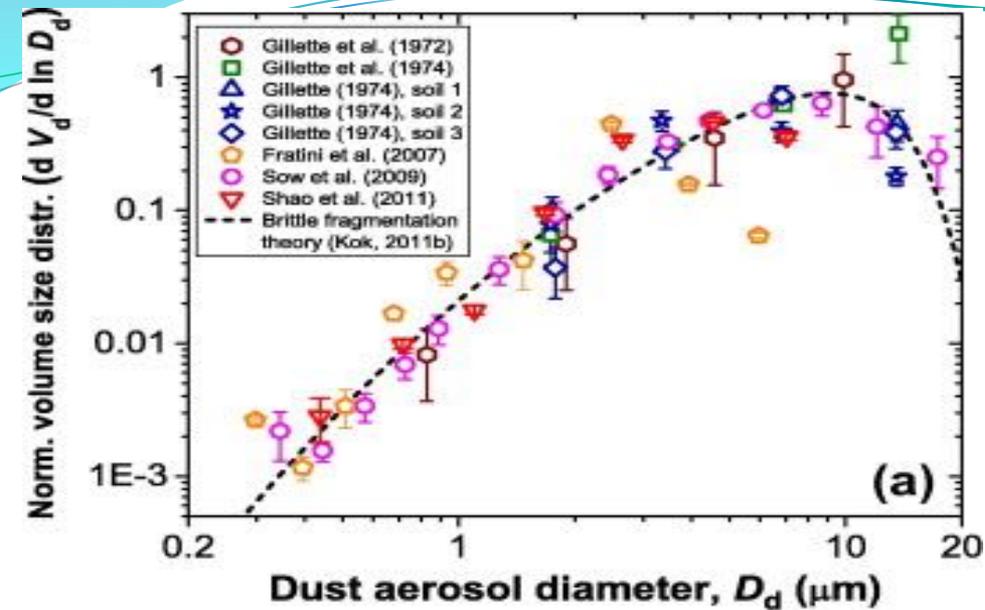
Poeira



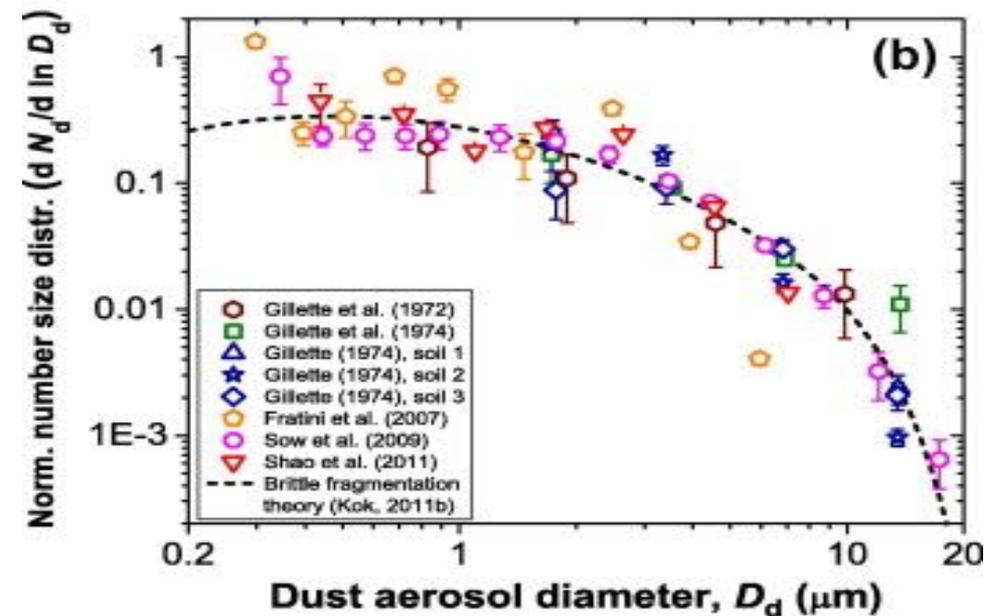


This true-color image of northwestern China's Taklimakan Desert from Suomi NPP shows a dust cloud over a light background. The Taklimakan is among the handful of well-known dust-producing regions around the globe.





Compilação de medidas da distribuição de tamanhos em volume (A) e número (B) para emissões de poeira.



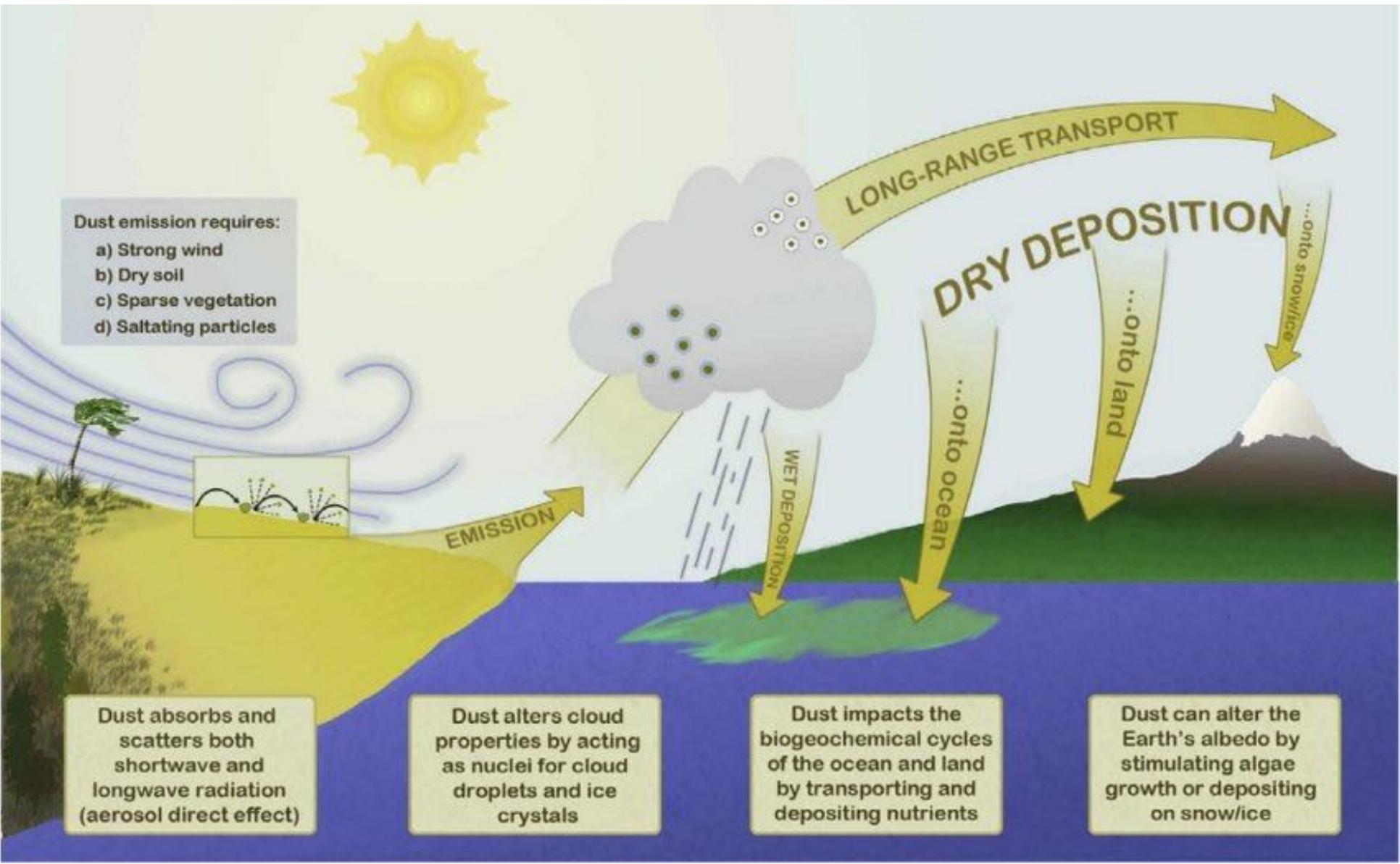
Measurements by Gillette and colleagues used optical microscopy, and were taken in Nebraska and Texas. Conversely, measurements by Fratini et al., 2007, Sow et al., 2009, and Shao et al. (2011) used optical particle counters. These measurements were made in China, Niger, and Australia, respectively. All measurements were normalized following the procedure described in Kok (2011b).

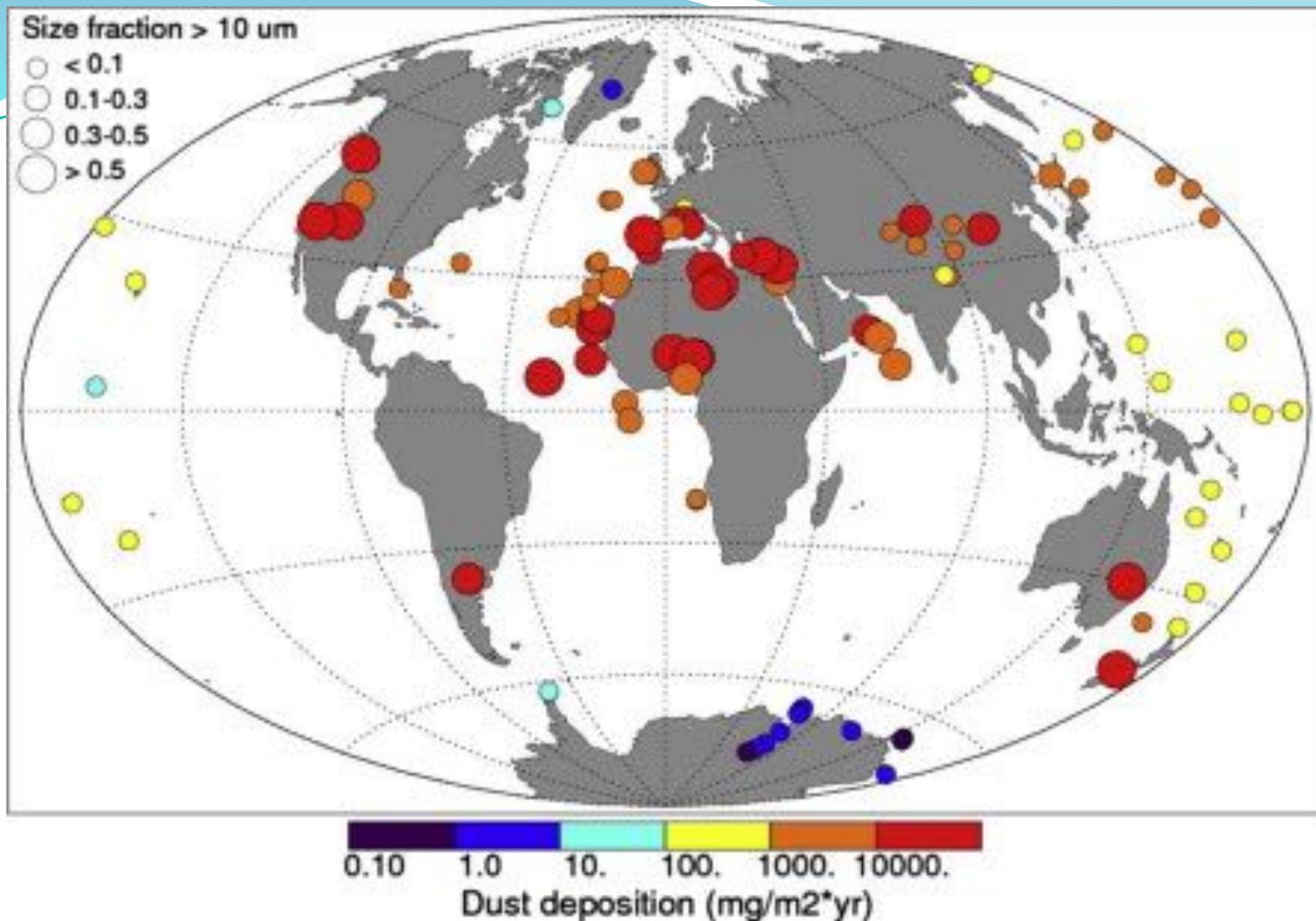
# Poeira do solo

- Áreas semiáridas e desertos, são 37% da área continental.
- Grande parte da emissão ocorre em locais com solos secos, pouca vegetação e ventos fortes.
- É a principal fonte de ferro e fósforo na atmosfera que afetam, por exemplo, o ecossistema marinho.
- Partículas não coagulam e não pouco recebem condensação de vapores orgânicos (i.e. a distribuição de tamanho na emissão é importante).
- A distribuição de tamanho evolui por deposição seca e úmida.

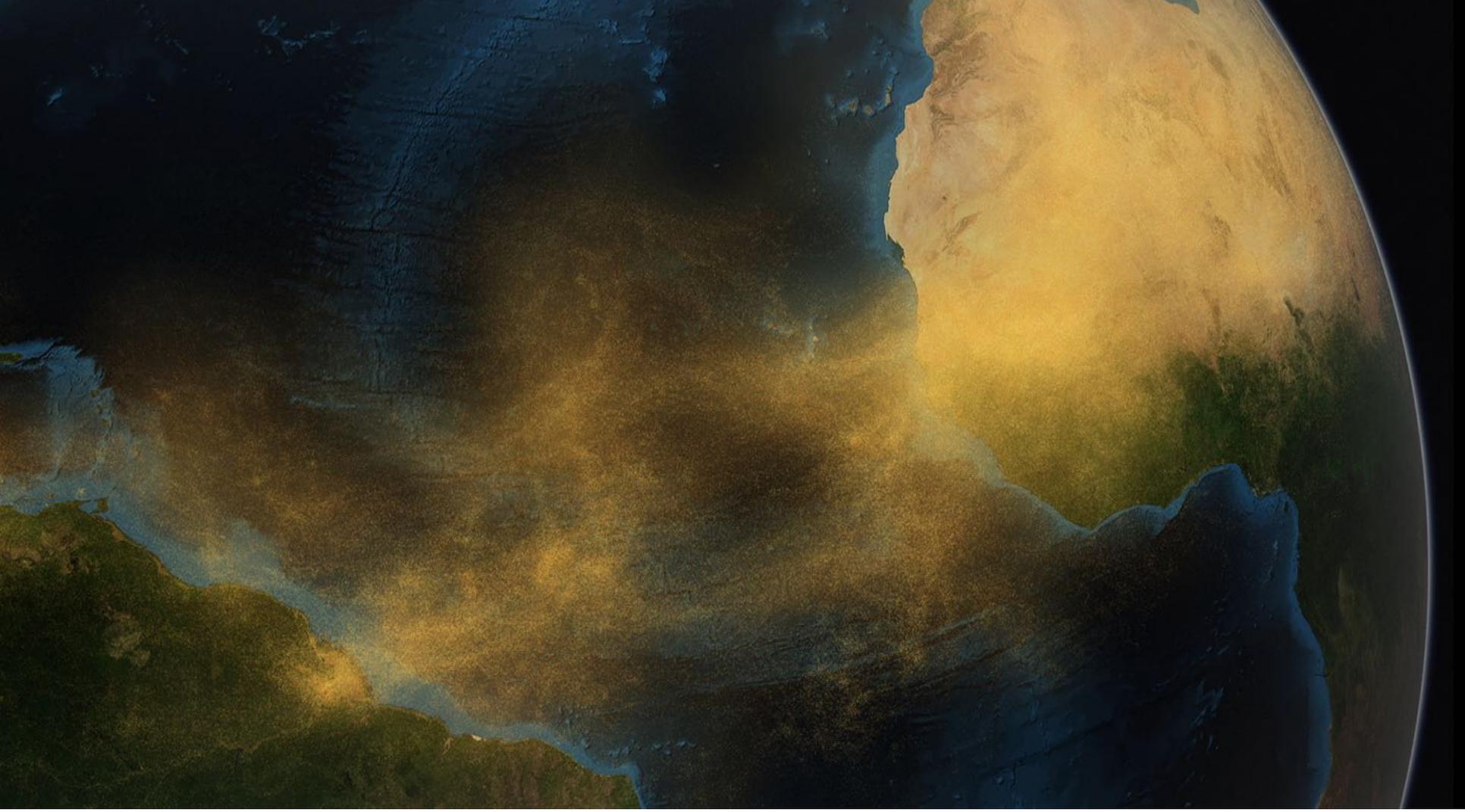
# Poeira do solo

Mahowald et al., Aeolian Research, 15, 2014





Deposition flux and size class of present-day dust observational estimates from Albani et al. (submitted). The color scale represent the varying order of magnitude of dust deposition, while the circles radius is proportional to the relative content of coarse (i.e.  $>10 \mu\text{m}$  diameter) particles.



**Table 5.3** Estimates (in Tg per year) for the year 2000 of (a) direct particle emissions into the atmosphere and (b) *in situ* production

<b>(a) Direct emissions</b>		
	<b>Northern hemisphere</b>	<b>Southern hemisphere</b>
Carbonaceous aerosols		
Organic matter (0-2 $\mu\text{m}$ ) <sup>a</sup>		
Biomass burning	28	26
Fossil fuel	28	0.4
Biogenic (>1 $\mu\text{m}$ )	—	—
Black carbon (0-2 $\mu\text{m}$ )		
Biomass burning	2.9	2.7
Fossil fuel	6.5	0.1
Aircraft	0.005	0.0004
Industrial dust, etc. (>1 $\mu\text{m}$ )		
Sea salt		
<1 $\mu\text{m}$	23	31
1-16 $\mu\text{m}$	1,420	1,870
Total	1,440	1,900
Mineral (soil) dust		
<1 $\mu\text{m}$	90	17
1-2 $\mu\text{m}$	240	50
2-20 $\mu\text{m}$	1,470	282
Total	1,800	349

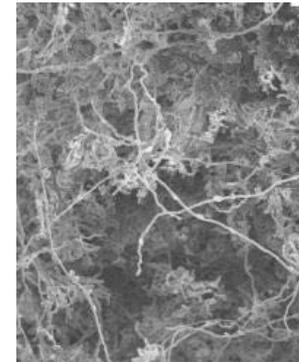
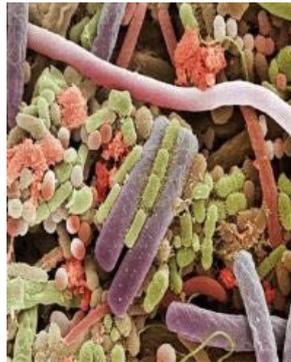
<b>(b) In situ</b>		
	<b>Northern hemisphere</b>	<b>Southern hemisphere</b>
Sulfates (as $\text{NH}_4\text{HSO}_4$ )		
Anthropogenic	145	55
Biogenic	106	15
Volcanic	25	32
Nitrate (as $\text{NO}_3^-$ )		
Anthropogenic	14	7
Natural	12.4	1.8
Organic compounds		
Anthropogenic	2.2	1.7
Biogenic	0.15	0.45
	8.2	7.4

<sup>a</sup> Sizes refer to diameters. [Adapted from Intergovernmental Panel on Climate Change, *Climate Change 2001*, Cambridge University Press, pp. 297 and 301, 2001.]

# Biogenicos

## 1. Emissão Biogênica

- *primary biological aerosol particles*: partículas biológicas como fungos, pólen, detritos da vegetação, etc. dominante na fração grossa (MARTIN *et al.*, 2010);

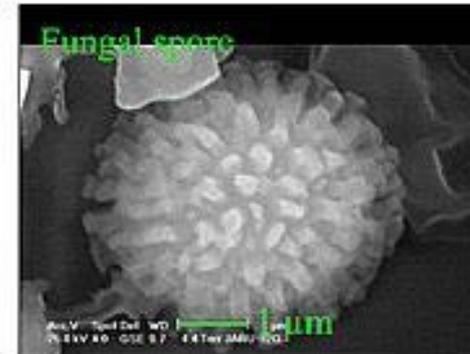
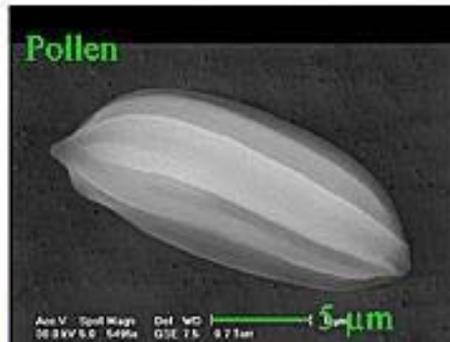
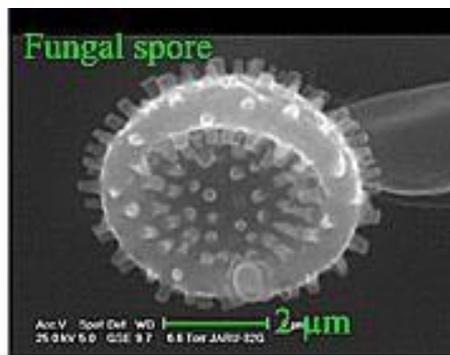
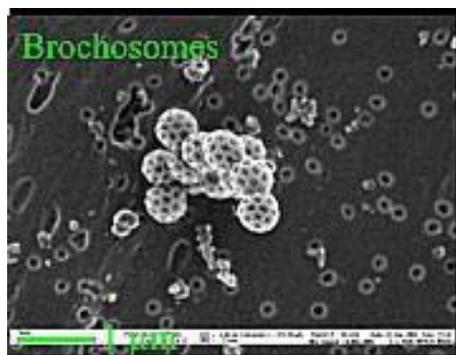


- *Aerossóis secundários*:

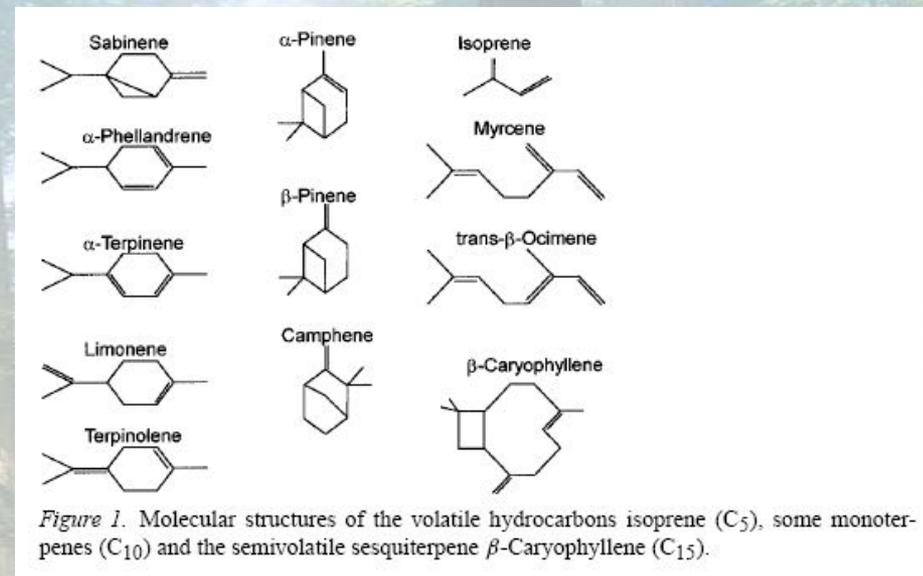
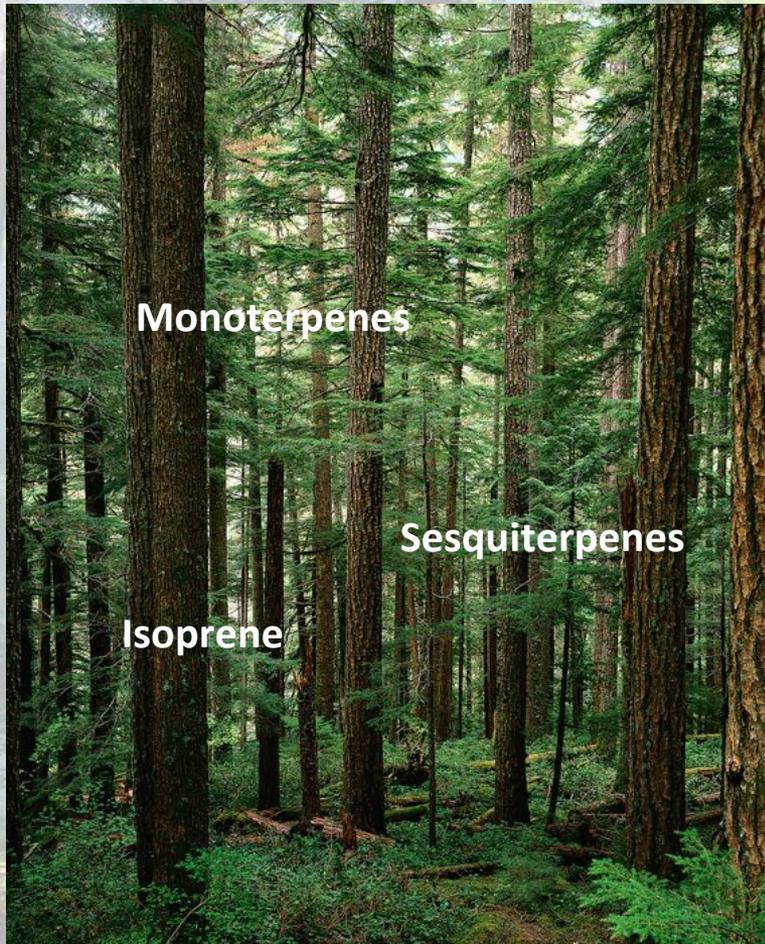
*Provenientes de bVOC (POSCHL et al., 2010).*

# Aerossóis naturais da Amazônia na moda grossa

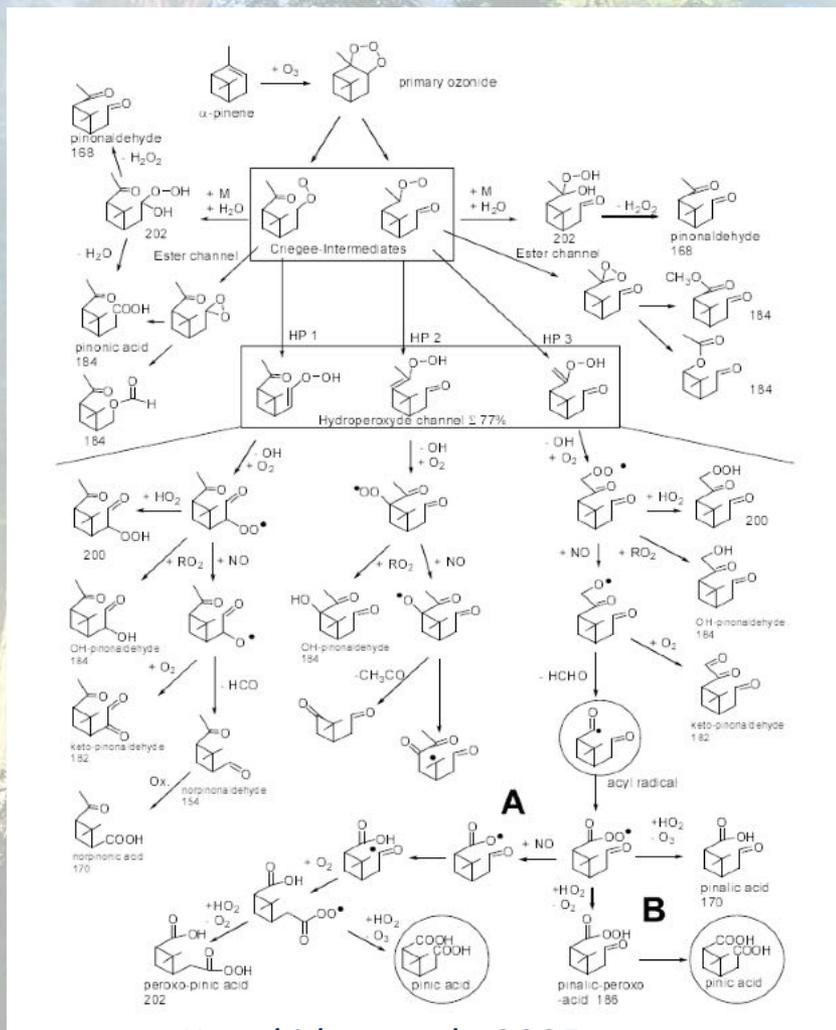
- Partículas primárias produzidas a partir do metabolismo da vegetação (pólen, esporos de fungo);



# Terpenoids: globally a very important source of secondary aerosols



# Terpene chemistry: $\alpha$ -pinene



*Kanakidou et al., 2005*

**Very complex chemistry!**

**Most well studied for  $\alpha$ -pinene and  $\beta$ -pinene**

**For most compounds, secondary oxidation steps are largely unknown**

**$\alpha$ -pinene most commonly abundant monoterpene**

**The ozone reaction believed to dominate SOA production**