

# Talking About Dust Ground Observations

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Training School of Dust Products





Aerosol Measuring problems Dust: Overview Source Apportionment of dust

Example: Project CVDUST

Conditions Sampling Quality Control PMF/Back Trajectories Ionic and Mass Balance

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#### Aerosol Measuring problems

Dust: Overview Source Apportionment of dust

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### Framing:

- Aerosol particles are ubiquitous in the Atmosphere.
- Behavior and Effects result from Physical and Chemical Characteristics

#### Particle Size is a fundamental property of the aerosol



Schematic Size Distribution of Atmospheric Aerosol with Sources, Processes and Removal Mechanisms (ref: Whitby, 1978)

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#### Size Distribution of Aerosol Mass in Aveiro suburban area





Ref: Rijo et al., (2009)

\_\_\_\_\_ Tab

The problem of measuring **Giant Particles**:

Isokinetic Sampling



Tabela 4.17: Eficiência do "High Vol. Sampler", com vento de 15 pés/seg.

		diâmet	ro das p	particul	as (um)			-
5		15		30		50		
		orie	ntação d	lo amost	rador			
00	450	00	450	00	450	00	450	
97%	100%	35%	55%	18%	41%	7%	34%	

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# Why to study atmospheric dust?

Estimated Global Emission rates of particles into the Atmosphere (Tg yr-1)

	Fine Particles	Coarse Particles			
Sea Salt	82.1	2460			
Dust	250	1000-4875			
Carbon	81				
Sulfate	150				
Nitrate	11.3				
Ammonium	33.6				

ref: Raes et al., (2000)

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### **Global Atmospheric dust**

Seasonal AOD averaged for 2001-2011 from MISR satellite

- Sahara emissions predominate
- Higher AI values during summer



Fig. 1. Seasonally averaged AOD at 0.55 µm from 2001 to 2011 retrieved from the Multiangle Imaging Spectroradiometer (MISR) in (a) DJF, (b) MAM, (c) JJA and (d) SON.

Ref: Shoobari and Sturman, AR (2014)

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### **Global dust budget – Modeled annually averaged values**



ref: Tanaka and Chiba, (2006)

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### Main causes for Sahara dust emissions: dryness



Mean annual rainfall in mm (1961-90). (ref: Engelstaedter, 2006)

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# **Dust Sources:**

- Natural Soil emissions;
- Agriculture (example "Dust Bowl" in USA);
- Transports;
- Building
- Industry (cement; mining)

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# Natural Dust versus Agricultural Emissions



from MODIS deep blue aerosol products



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# **Sources of Soil Dust:**

- North Africa the major source of dust. Estimates of Sahara emissions: 130-760 Tg yr-1 (Goudie and Middleton, 2001);
- Some estimates annual Saharan dust emission of 1600 Tg yr-1 (Ozer, 2001).
- Sahel cultivation contributes with up to 15% dust North Africa emissions;
- Other dust sources: Arabian Peninsula, Iran, Turkmenistan, Afghanistan, Pakistan, Northern India, the Namib and Kalahari desert and the Tarim Basin in China.





## Sinks of out of Sahara emitted dust:

Kaufman et al. (2005) estimated North Africa annual dust transport to west 240±80 Tg:

- 140 Tg are deposited in the Atlantic Ocean,
- 50 Tg fertilize the Amazon Basin
- 50 Tg are transported to the Caribbean.
- 20 Tg are transported towards Europe.





## **Impacts of desert dust emissions:**

- Atmospheric Heat Balance and Climate Control
  - Weakening of Atlantic Tropical Cyclones
- Biogeochemical Cycles
  - Biogeochemical Cycles in Atlantic and Amazon Basin
  - Toxic Algae Blooms
- Human Health
  - Spreading of meningitis in Sahel (Sultan et al., 2005)
  - Kawasaki disease in Japan and Western USA (Fraser, 2012)

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#### Source Apportionment for Roadside and Urban background sites in Porto

#### Parallel Sampling





750

500

Roadside

1000

#### PCA/MLRA for fine and coarse fractions

R-Road-side; UB-Urban Background

PC1-Traffic; PC2- Industrial; PC3- Soil dust; PC4- Sea Salt; PC5- Secondary



ref: Oliveira et al., (2010)

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### Calculation of traffic re-suspended dust in Porto by Inter-site Mass Balance (IMB)

#### Table 5

Emission Rates (ER) by cars, for Cu and Zr, calculated from equation (1) and fraction traffic contribution (road resuspension) to suspended soil dust (TF) calculated from equations (2) and (3), at R and UB sites, discriminated for PM<sub>2.5</sub> and PM<sub>2.5-10</sub>. Four estimates are present for each TF case, based in different combinations of tracer elements.

Inter-site mass balance	Emission factors (µg veh <sup>-1</sup> km <sup>-1</sup> )		Fraction fro	Fraction from traffic (TF <sub>R</sub> )				Fraction from traffic (TF <sub>UB</sub> )			
	Cu	Zr	(Cu, Al)	(Zr, Si)	(Cu, Si)	(Zr, Al)	(Cu, Al)	(Zr, Si)	(Cu, Si)	(Zr, Al)	
Winter coarse day	357	47	0.53	0.57	0.58	0.53	0.25	0.28	0.29	0.24	
Winter coarse night	406	36	0.51	0.66	0.58	0.51	0.25	0.44	0.31	0.29	
Winter fine day	264	24	0.34	0.49	0.56	0.34	0.19	0.26	0.36	0.16	
Winter fine night	297	22	0.55	0.40	0.45	0.55	0.38	0.23	0.29	0.35	
Summer coarse day	312	36	0.81	0.89	0.91	0.81	0.63	0.75	0.81	0.62	
Summer coarse night	371	36	0.72	0.74	0.72	0.72	0.53	0.55	0.53	0.53	
Summer fine day	263	15	0.66	0.94	0.81	0.66	0.46	0.89	0.65	0.50	
Summer fine night	293	17	0.63	0.31	0.33	0.63	0.47	0.19	0.20	0.46	

ref: Oliveira et al., (2010)

#### **ER-Emission Rate**

#### **IMB-** Inter-site Mass Balance

 $ER_{CII} = ER_{NO_{x}}(Cu_{R} - Cu_{IIB})/(NO_{x_{P}} - NO_{x_{IIB}})$ 

ref: Johanson et al., (2009)

 $TF_R = RIs/RIc$  =Soil Traffic Fraction at Roadside

 $TF_{UB} = (RIs/RIc)(1 - RIc)/(1 - RIs) = Soil Traffic Fraction at UB$ 

RI=(R-UB)/R= Road Impact Factor

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#### Weekend/weekday ratios applied in anthropogenic dust evaluation



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### The problem of differentiating natural from anthropogenic dust in urban areas

PMF Source Apportionment of urban aerosol from Jan13 to Feb14

**AIRUSE Project** 

BCN-UB - Barcelona ATH-SUB - Athens POR-TR - Porto

Ref: Amato et al., subm APC (2015)



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# Back-Trajectory Statistical Methods. Redistributed Concentration Field method (RCF)

Compounds footprint applied to CARBOSOL measured compounds at mountain sites

ref: Salvador et al., (2010)



RCF - PDD-SIL - SO<sup>2-</sup> (ng m<sup>-3</sup>) - Warm season







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### **Monitoring and Sampling:**

Performed at Cape Verde, Praia during one year (Jan2011-Jan2012)









#### **Equipment:**

2 PM10 LowVol filter samplers; 1 PM10 HighVol filter sampler

#### Chemical characterization of collected samples:

PM10 mass concentration; Water Soluble ions; Carbonate and Carbonaceous forms; Elemental Composition (PIXE; INAA)

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# Monthly averaged meteorological conditions at Praia, during 2011

Harmattan
 Trade Winds
 from North East, with
 exception of
 rainy season



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# Dust emission Regions in Sahara, from TOMS Abs. Index (1980-92)



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#### Why "Bruma Seca" Season during October-April periods?



Surface wind Speed in North Africa (1980-92). ITCZ in orange (ref: Engelstaedter, 2006)

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- Initial station mounting and training at Aveiro
- Prevention for electric supply instabilities and failure
- Spare equipment and spare parts
- Tough program of frequent testing, calibration and maintenance
- Close contacts and rapid answer to new situations
- Rapid evaluation of collected samples and data
- Continuous inter-comparison of results during analysis
- Inter-calibration with external equipment

87% measuring efficiency

140 PM10 filtering periods11 HV Impactor sampling periods5 Berner Impactor sampling periods

24 HV flow calibrations 25 LV flow calibrations

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#### Mass balance evaluation and comparison



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### **Ionic Balance without and with Carbonates**



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# Evaluation of Calcium carbonate presence



XRD mineral composition of aerosol dust during the whole sampling period



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#### PM10 (dry-haze)=117 μg.m<sup>-3</sup> PM10 (dust-free)=39 μg.m<sup>-3</sup>



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### Particulate Pollution Levels and daily exceedances, at Praia

Particulate
 pollution levels
 clearly exceed
 WHO Guides and
 probably affect
 local Human
 Health, principally
 during "BRUMA
 SECA" Season

Parameter	Annual Average* (µg/m <sup>3</sup> )	WHO Guide Values (µg/m <sup>3</sup> )			
PM <sub>2.5</sub>	17.5	10			
<b>PM</b> <sub>10</sub>	37.5	20			
TSP	66.0	-			
No of daily exceedances		PM 2.5 PM 10			

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# **PMF Analysis**

**PMF** Source Contributions and Profiles for the seven identified factors (Graphs A-G). Graph H presents the fraction contribution of each main compound to each source.



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### **PMF Analysis: Continuation**



70% Soil



Figure 6. PMF source apportionment results for the total campaign and during the two pollution seasons. Values are in  $\mu g m^{-3}$  and percentage of measured total mass.

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#### **Backward Trajectory Analysis and concentrations**



ref: Gama et al., (2015)

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#### **Back-Trajectory Statistical Analysis. Redistributed Concentration Field method (RCF)**



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RCF PMF: ARCILLAS





#### **Redistributed Concentration Field method (RCF)**



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# Summary

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Ratios of soil dust elements in CV aerosol and comparison with Sahara Soils and crustal averages



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Concentrations of major elemental species (as oxides) at nine sites in Sahara region, according to Moreno et al., (2006), and average crustal levels taken from Manson and Moore, (1982). The table presents also the estimation of factor F

Soil dust mass =SiO2 + Al2O3 + Fe2O3 + MnO + TiO2 + etc.

Soil dust mass =F(2.14Si + 1.89Al + 1.43Fe+ 1.39Mn + 1.67Ti + etc.)

Soil dust =1.15(2.14Si + 1.89Al + 1.43Fe + 1.39Mn + 1.67Ti +1.66MgSoil + 1.40Casoil + 1.20Ksoil),

	CrustalAvor	Hoggar Massif		Chad Basin		Niger		Western Sahara		Sahara	
	CiustaiAvei	HM1	HM2	CB1	CB2	MON	HAR	WS1	WS2	WS3	Average
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
SiO <sub>2</sub>	59.3	62.1	62.5	63.2	70.2	69.5	66.7	49.4	46.2	56.8	60.7
TiO <sub>2</sub>	0.7	1.4	1.2	1.0	1.2	1.4	1.2	0.6	0.4	0.9	1.0
Al <sub>2</sub> O <sub>3</sub>	15.4	14.7	13.6	14.0	11.7	11.6	12.2	8.8	7.0	5.1	11.0
Fe <sub>2</sub> O <sub>3</sub>	7.2	6.1	5.2	6.7	4.7	4.4	5.7	4.4	2.8	4.2	4.9
MnO	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.1
MgO	3.5	1.8	1.6	1.2	0.8	0.5	0.9	2.9	2.6	1.9	1.6
CaO	5.1	2.4	2.0	1.4	1.4	0.4	1.6	12.9	17.7	12.2	5.8
K <sub>2</sub> O	3.1	2.5	2.5	1.5	1.5	1.2	1.8	1.9	1.7	1.4	1.8
SUM	94.4	91.0	88.6	89.0	91.5	88.9	90.1	80.9	78.5	82.6	86.8
Na <sub>2</sub> O	3.8	1.6	1.9	1.1	0.5	0.4	0.6	0.9	0.7	0.8	0.9
$P_2O_5$	3.1	2.5	2.5	1.5	1.5	1.2	1.8	1.9	1.7	1.4	1.8
SO3	0.1	0.2	0.2	0.3	0.2	0.0	0.1	0.1	0.1	0.1	0.1
TOTAL	98.5	93.1	91.0	90.6	92.3	89.4	91.0	82.2	79.7	83.9	88.1

F=100/86.8= 1.15

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#### Sea Salt concentrations calculated from the values of Na<sup>+</sup> :Sea Salt increases during dust intrusions



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#### Mass and Ionic Balance for Sea Salt:

- 1. Start calculating SoilNa<sup>+</sup> and SoilMg<sup>2+</sup> from Fe/Na<sup>+</sup> and Fe/Mg<sup>2+</sup> edge lines.
- 2. Recalculate Sea Salt Na<sup>+</sup> and Mg<sup>2+</sup> using Na/Mg ratio in sea water.
- 3. Calculate Sea Salt Mass concentration and Composition from sea water ratios.



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SeaSaltstand (dry-haze)= 14.2 µg.m<sup>-3</sup> SeaSaltstand (dust-free)= 14.1 µg.m<sup>-3</sup> **SeaSalt**<sub>Rec</sub> (dry-haze)= 7.8 µg.m<sup>-3</sup> (7%) **SeaSalt**<sub>Rec</sub> (dust-free)= 9.7 µg.m<sup>-3</sup> (25%)



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#### **Ionic Balance (continuation):**

4. From difference between total and sea salt calculate soil Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>.

- 5. Calculate Non Sea Salt  $SO_4^{2-}$ ,  $NO_3^{-}$  and  $CI^{-}$ .
- 6. Associate sequentially free  $SO_4^{2-}$  and  $NO_3^{-}$  with NH<sup>4+</sup> until all NH<sup>4+</sup> is neutralized.
- 7. Associate free  $NO_3^-$  sequentially with free sea salt cations and dust cations.
- 8. Associate totally CO32-, sequentially with free soil Ca2+, Mg2+, Na+ and K+
- 9. Associate free Sulphate sequentially wit Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>
- 10. Associate free CI<sup>-</sup> with free Na<sup>+</sup> and Mg<sup>2+</sup>. Any excess CI<sup>-</sup> is associated with K<sup>+</sup>
- 11. Calculate total masses of water soluble soil sulphate, nitrate and chloride.

12. Edge line ratios between Fe and sulphates, nitrates and chlorides permit a rough calculation of the fraction of these compounds that are present in the soil or that result from secondary reaction with atmospheric produced acids.



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**Calculation of Water Soluble dust and Secondary Inorganic Compounds** 

SoilDust WaterSoluble (dry-haze)= 6.6 µg.m<sup>-3</sup> SoilDust WaterSoluble (dust-free)= 0.8 µg.m<sup>-3</sup>

SIC ammonium (dry-haze)= 0.4  $\mu$ g.m<sup>-3</sup> SIC ammonium (dust-free)= 1.1  $\mu$ g.m<sup>-3</sup>

SIC SSalt+Dust (dry-haze)= 1.8 μg.m<sup>-3</sup> SIC SSalt+Dust (dust-free)= 2.4 μg.m<sup>-3</sup>

Carbonaceous (dry-haze)= 2.5 µg.m<sup>-3</sup> Carbonaceous (dust-free)= 2.1 µg.m<sup>-3</sup>



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#### Calculation of Soil Dust from elemental aerosol composition



MM82 - ref Manson and Moore (1982)

 $\textbf{Soil Dust} = (SiO_2 + TiO_2 + AI_2O_3 + Fe_2O_3 + MnO + MgO_{ins} + CaO_{ins} + K_2O_{ins} + SO_{3ins} + \textbf{Dust}_{sol} - \textbf{Dust}_{SIC})/\textbf{0.91}$ 

Soil Dust (dry-haze)=83.3 µg.m<sup>-3</sup> (71%) Soil Dust (dust-free)=12.7 µg.m<sup>-3</sup> (33%)

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#### Mass Balance accounts only for 76% of PM10 measured mass



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### **Aerosol Water**

(Filters weighted at 50% RH)

Water in Sea Salt =0.9\*SS Water in SIC AmSul=0.4\*AmSul Water in Organic Matter=0.2\*OC Water in Soluble Dust=0.4\*SoilDu ws

#### **References:**

(Harrison et al., 2003) (Speer et al. (2003) (Speer et al. (2003) (Xu et al.) (Tang et al., Water=0.29\*AmSulphate Water=0.45\*AmSulphate Water=0.20\*OC Water=0.4\*AmSulphate Water=1.4\*SeaSalt (eflorescence) Water=0.4\*SeaSalt (deliquescence)









# Final Results of Material / Ionic Balance for dust-free and dry-fog periods



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Comparison of Mass Balance and PMF Results



WetSoilDust ins WetSoilDust sol WetSeaSalt WetSIC am WetSIC ss+du WetCarbon Unaccounted

	Year A	verage	Dry-l	Haze	Dust-Free		
	PMF	MassBal	PMF	MassBal	PMF	MassBal	
	(µg/m3)	(µg/m3)	(µg/m3)	(µg/m3)	(µg/m3)	(µg/m3)	
Soil	34.7	33.5	92.6	91.2	10.8	10.2	
SeaSalt	15.1	16.3	15.9	14.2	12.9	16.0	
SIC	4.8	4.6	3.5	4.2	5.4	4.4	
Carbon	3.7	2.4	2.1	3.1	5.0	2.2	
SUM	58.3	56.8	114.1	112.7	34.1	32.8	
PM10	57	.7	11	7.3	33.9		

Ref: Salvador et al., (2016)

mDust

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# Thanks for your attention!

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#### CVDUST Measurements with the GRIMM Spectrometer

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#### **Evaluation of GRIMM measurements and size distributions**

Grimm is Optical Aerosol Spectrometer based on light scattering by particles



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#### Light Scattering is described by Maxwell's Equations.

#### For aerosol:

- The intensity scattering function can be calculated for spherical particles by Mie theory
- For non-spherical particles by DDA (Discrete Dipole Approximation)

$$I(d,m) = k \cdot \int_{\theta_{start}}^{\theta_{stop}} d^2 \cdot f(\theta,d,m) \cdot \sin(\theta) d\theta$$

- I scattering intensityΘ angled- diameter (form)
- m refractive index





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#### Calibration

All GRIMM Aerosol Spectrometers are calibrated with polystyrene latex (PSL). The calibration curve of the spectrometer illustrates correlation between the particle size and the scattered light system - the basis for a precise particle detection and calculation of masses.



**Response function for PSL** 

PSL refractive Index - 1.59

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## **Characteristics of aerosol dust and particles**

aerosol type	density in g/cm <sup>3</sup>	dynamic shape factor (>1µm)	refractive index at $\lambda$ =780 nm	intensity scattering function
PSL	1.06 to 1.12	1.0	1.586	exact solution from Mie theory
sea salt	2.2	1.06	1.51	good solution from Mie theory
dust	2.0 to 2.7	1.2 to 1.3	1.53-i 0.001 to 1.53-i 0.005	'highly uncertainty' using DDA
marine (no sea salt)	1.49	1 to 1.06	1.5-i 0.001	good solution from Mie theory

#### For our studies we used:

- Density- 2.5
- Dyn. Shape factor 1.25

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### Intercomparison with PM10 weighted filter data

# Stokes Law approximation:

$$d_{vol} = d_{aer} \sqrt{\frac{\chi}{\rho / \rho_0}}$$

 $\chi$  – dynamic shape factor

Inlet efficiency of PM10 sampling head



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# Results of Grimm/PM10 filters intercomparison with GRIMM original calibration



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## Re-calculation of GRIMM optical diameters based on different refractive index



Figure: intensity curves for particles of refractive index m=1.58-0i (PSL) and m=1.53-i0

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# Recalibration curve using Mie equation applied to the instrument geometry, for particles with a RI=1.53-0.005i



ref: Pio et al., (2014)

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# Results of Grimm/PM10 filters intercomparison with GRIMM new re-calculated diameters



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ref: Pio et al., (2014)



#### **GRIMM 5 Minutes PM averages during the month of January**



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#### **Daily and Monthly Averaged PM concentrations from GRIMM**



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### **Dust Size Distribution from GRIMM measurements**



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# Dust Size Distribution from GRIMM

#### Dust mass mainly in size range 1-10 μm, but much less is known for Giant Particles

Yearly Average dust size profile





FIGURE 12 | Four hours average mass concentration size distributions during 2 days without direct Saharan dust intrusions. (A) 2nd May, 2011; (B) 12th June, 2011.

 Local suspension processes probably responsible for dust particles outside "Bruma Seca"

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## Hourly averaged dust size distribution variability along a dust episode day (18/01/2011)

Local re-suspension processes probably responsible for dust particles above 10 μm, even during "Bruma Seca"



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CVDUST Measurements with the Aethalometer

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### **BC** measurements with the Aethalometer

Daily Cycles show an important local influence on BC levels, principally in periods outside the "Bruma Seca" season



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## **BC** seasonal data with the Aethalometer

ref: Fialho et al., (2014)



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## Using the aethalometer to measure Fe and BC

$$\begin{split} \sigma_{\text{ATN}-\text{aerosol}}(\lambda,t) &= \sigma_{\text{BC}}(\lambda,t) + \sigma_{\text{dust}}(\lambda,t) \\ \sigma_{\text{ATN}-\text{aerosol}}(\lambda,t) &= 14.625 \times \lambda^{-1} \times C_{\text{BC}}(t) + 0.234 \times \lambda^{-4} \times C_{\text{Fe}}(t) \end{split}$$



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## Aethalometer deconvolution process to differentiate between BC (Black Carbon) and Iron Oxide dust. Results for February 2011

 Iron oxide dust and BC concentrations, recalculated with the deconvolution algorithm



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