

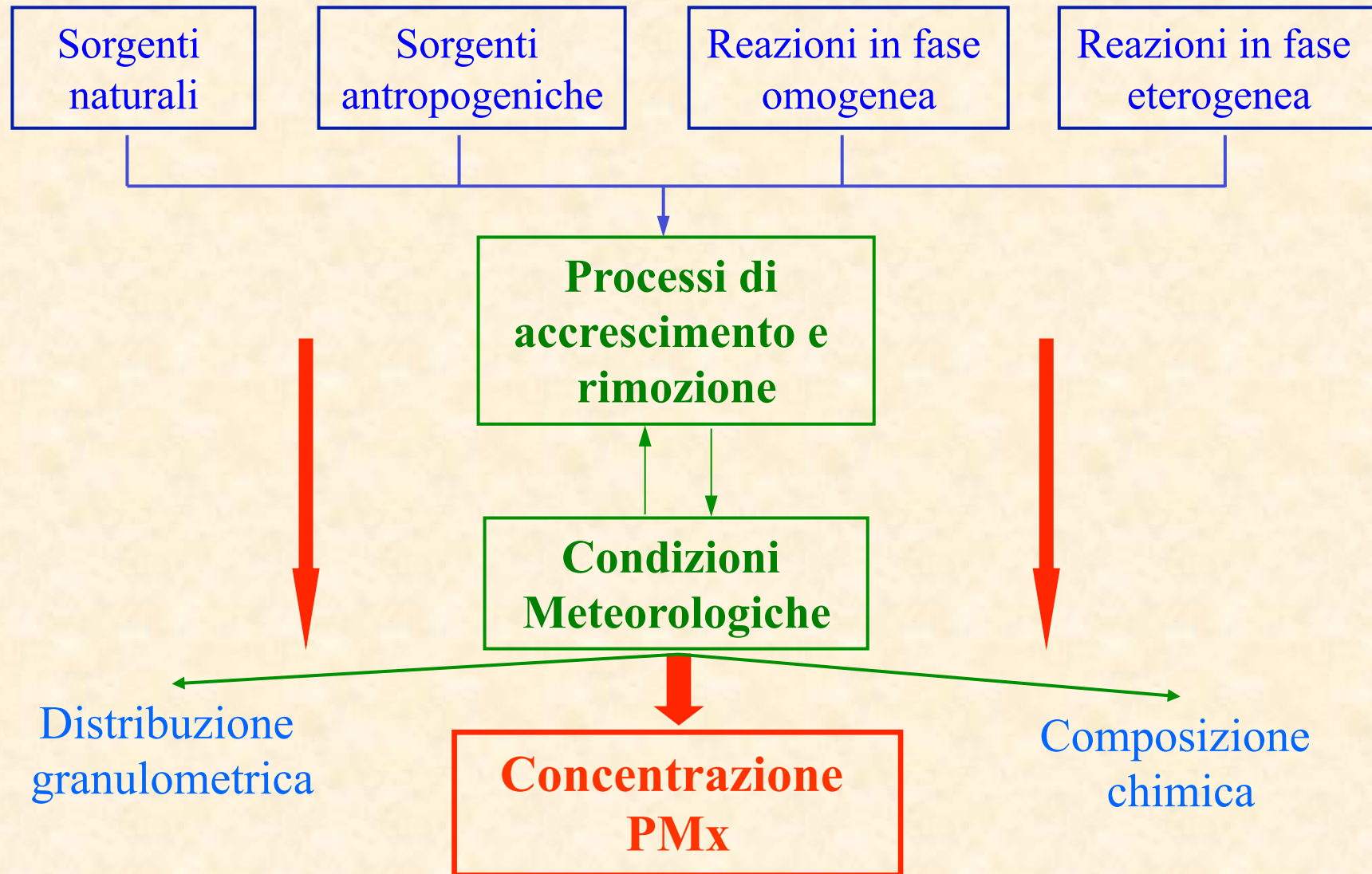
CARATTERIZZAZIONE DEL PM_x IN ATMOSFERA

Antonio Febo

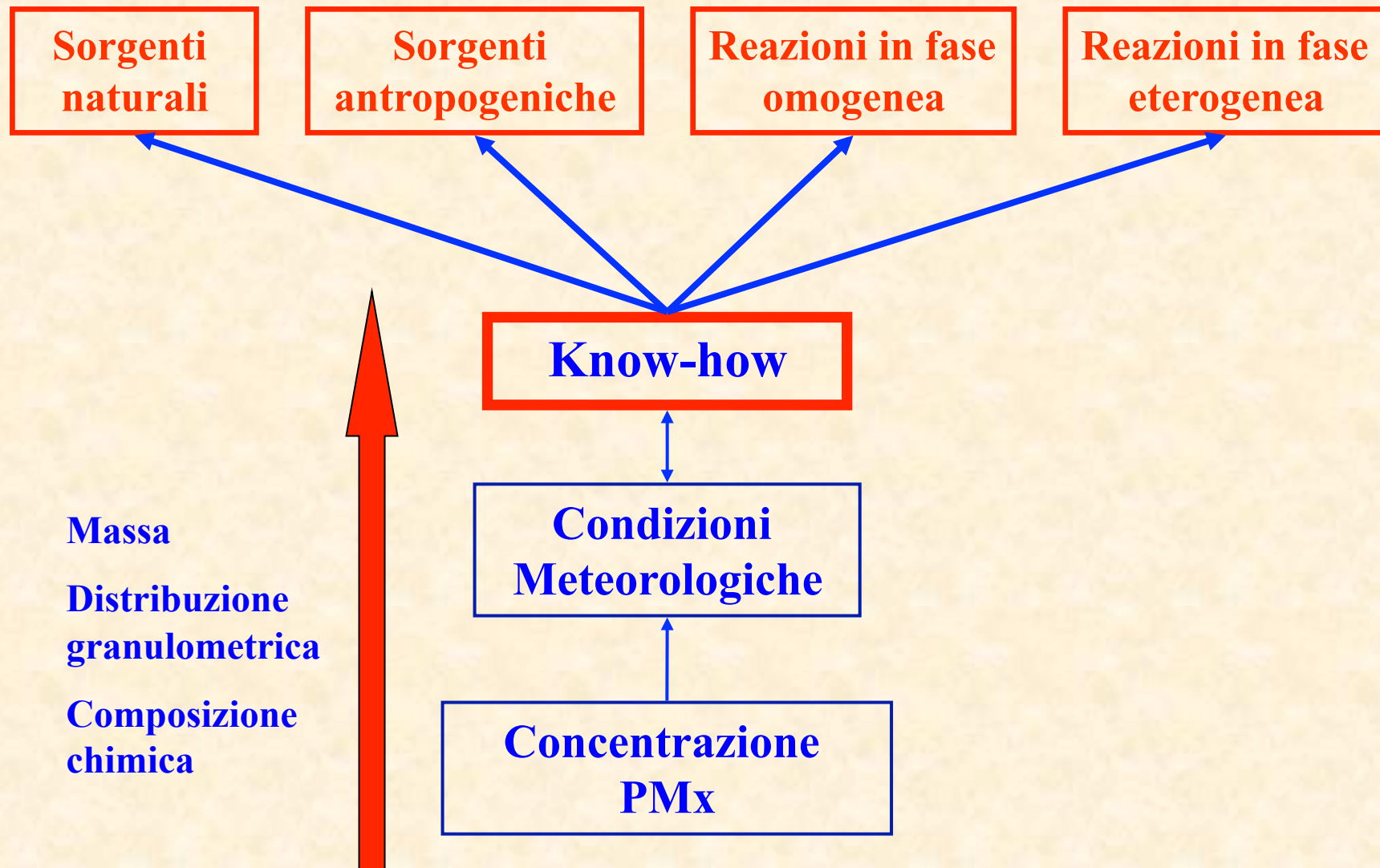
CNR IIA

Roma 15/12/2011

PM_x IN AMBIENTE



ATTRIBUZIONE DELLE SORGENTI (piani di risanamento della qualità dell'aria)



- **MISURA DI MASSA**

PM_{10} ; $PM_{2,5}$; PM_1

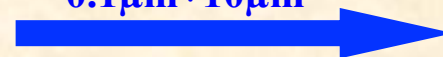
- **CARATTERIZZAZIONE CHIMICA**

Composizione ionica, metalli, carbonio,
idrocarburi policiclici aromatici, etc.

- **CARATTERIZZAZIONE GRANULOMETRICA**

*“MASS MODE
ACCUMULATION”*
(concentrazione in massa)

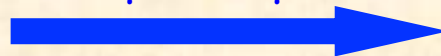
$0.1\mu\text{m}\div 10\mu\text{m}$



Impattori inerziali,
APS, OPC

NANO-PARTICELLE
(concentrazione in numero)

$0.005\mu\text{m}\div 0.2\mu\text{m}$



DMA, CNC, DMSS

COMPLESSITÀ DEL SISTEMA PM_x

METROLOGIA

Massa del PM_x



- Armonizzazione dei metodi
- Valutazione dei dispositivi di taglio granulometrico
- Perdite di materiale volatile
- Valutazione dell'incertezza

Granulometria del PM_x



- Metodi ottici
- Metodi aerodinamici
- Metodi a mobilità elettrica

Composizione chimica del PM_x



- Armonizzazione dei metodi
- Valutazione dell'incertezza

Dimensioni lineari delle particelle quale diametro?

- **Diametro geometrico (particelle sferiche)**
- **Diametro di Stokes**
- **Diametro aerodinamico**
- **Diametro ottico**

**Aerosol naturali monodispersi,
polidispersi (quale significato?)**

Comportamento dinamico delle particelle in aria ($Re < 1$)

- Resistenza al trascinamento (forza di Stokes)

$$F_S = \frac{3\pi\eta v d}{C_c}$$

η : viscosità dell'aria

v : velocità relativa delle particelle

d : diametro della particella (sferica)

C_c : fattore di correzione di Cunningham

$$C_c = 1 + \frac{\lambda}{d} \left[2.34 + 1.05 \exp\left(-0.39 \frac{d}{\lambda}\right) \right]$$

λ : cammino libero molecolare medio

Comportamento dinamico delle particelle in aria ($Re < 1$)

$$F_e = F_s = \frac{3\pi\eta vd}{C_c}$$

La Mobilità B delle particelle

$$B = \frac{C_c}{3\pi\eta d} \quad \text{mobilità meccanica}$$

definisce il legame tra la forza esterna F_e applicata alla particella e la sua velocità finale V_T

$$F_e B = V_T$$

Forze esterne volumiche

$$F_e = F_D \quad V_T = BF_e$$

(velocità terminale V_T costante) (B = mobilità meccanica)

$$B = \frac{C_c}{3\pi\eta d}$$

Campo di gravità

$$V_{TS} = gmB$$

$$V_{TS} \cong \frac{\rho d_p^2 g C_c}{18\eta} = \frac{d_a^2 g C_c}{18\eta}$$

Forze centrifughe

$$V_{TC} = a_c mB$$

$$V_{TC} \cong \frac{\rho d_p^2 a_c C_c}{18\eta} = \frac{d_a^2 a_c C_c}{18\eta}$$

$$V_T \longrightarrow C_c d_a^2$$

$$d_a = \sqrt{\rho d_p^2} \quad (\text{diametro aerodinamico equiv.})$$

Forze esterne (campo elettrico)

Campo elettrico uniforme E , particelle con carica $q=ne$

$$V_{TE} = BF_e \quad V_{TE} = neEB$$

$$V_{TE} = neEB = \frac{neC_c}{3\pi\eta d} E = Z_i E$$

$$Z_i = neB = \frac{neC_c}{3\pi\eta d} \quad (\text{mobilit  elettrica})$$

$$V_T \longrightarrow Z_i \quad \text{Se } n = 1 \quad V_T \longrightarrow \frac{C_c}{d}$$

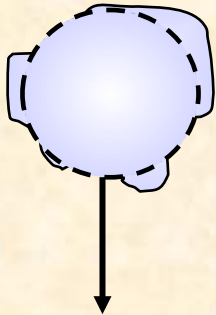
(diametro di Stokes)

Dimensioni lineari delle particelle

Diametri equivalenti

Irregolare

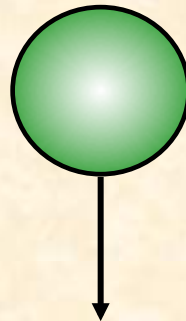
$$d_e = 5.0 \mu\text{m}$$
$$\rho_p = 4 \text{ g/cm}^3$$
$$\chi = 1.36$$



$$V_{TS} = 0.22 \text{ cm/s}$$

Stokes

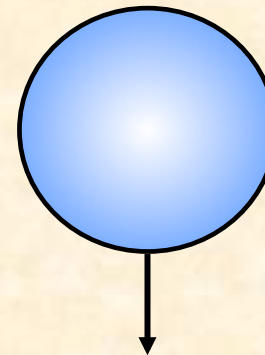
$$d_s = 4.3 \mu\text{m}$$
$$\rho_p = 4 \text{ g/cm}^3$$



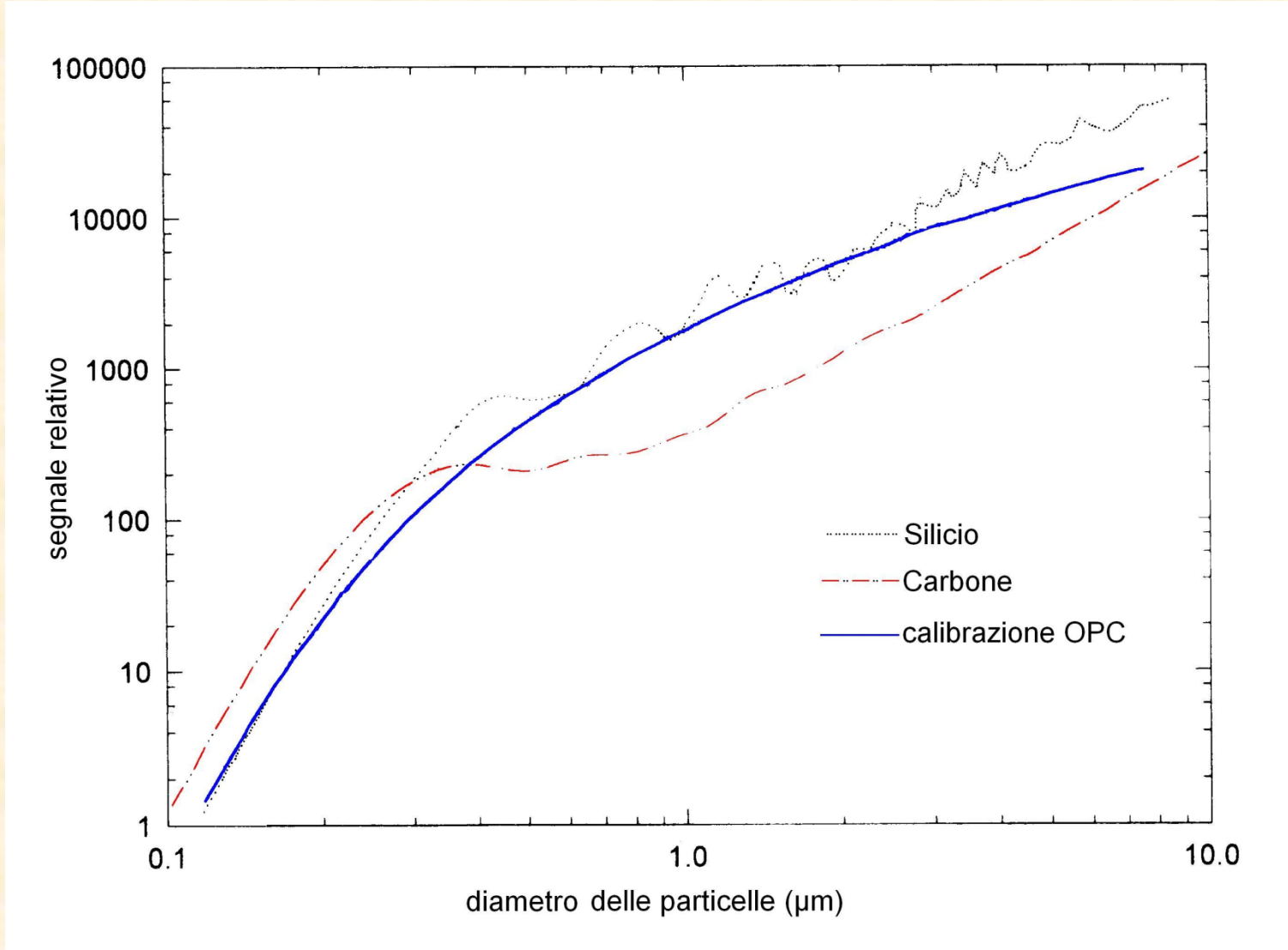
$$V_{TS} = 0.22 \text{ cm/s}$$

Aerodinamico

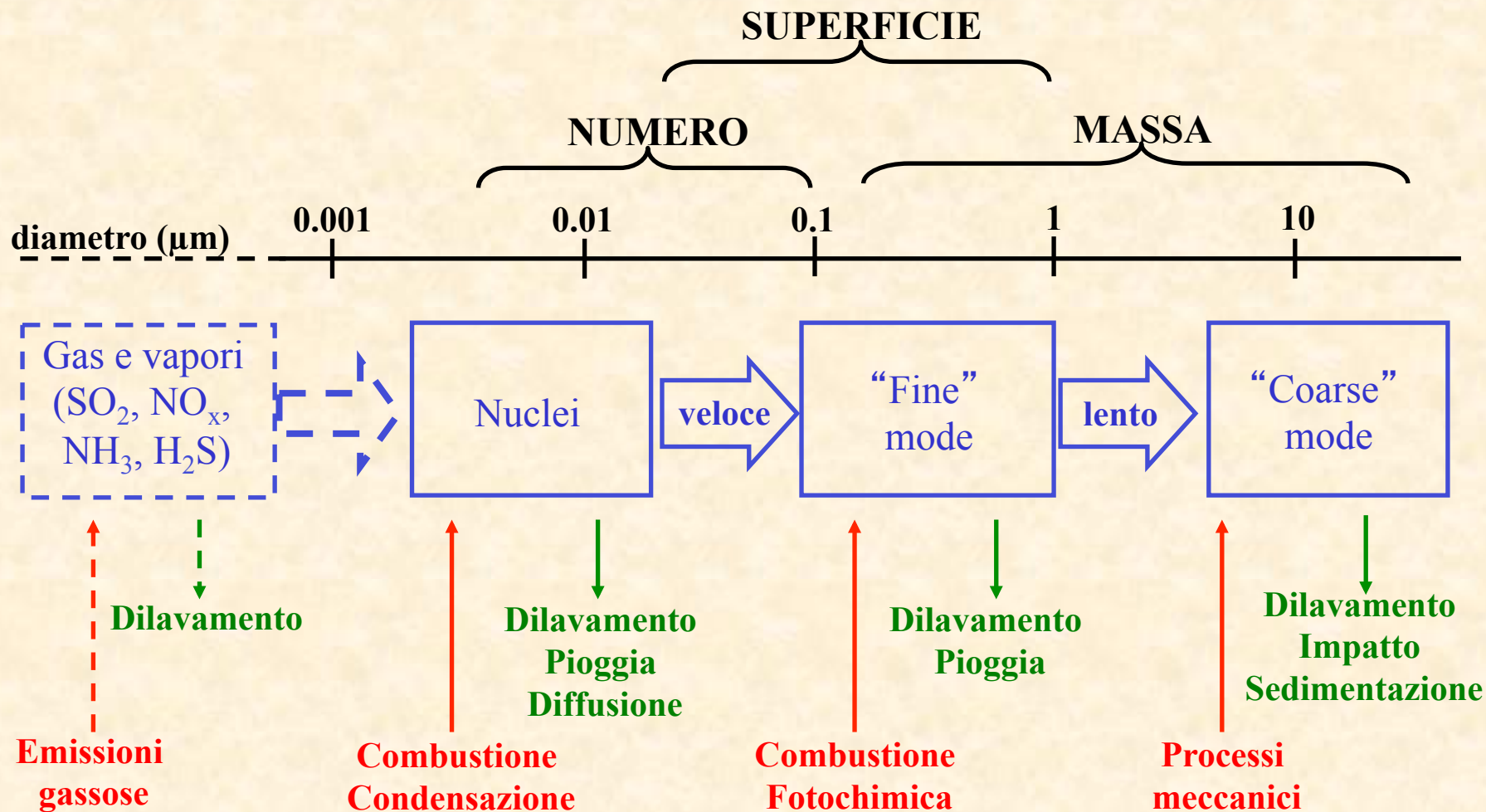
$$d_a = 8.6 \mu\text{m}$$
$$\rho_p = 1 \text{ g/cm}^3$$



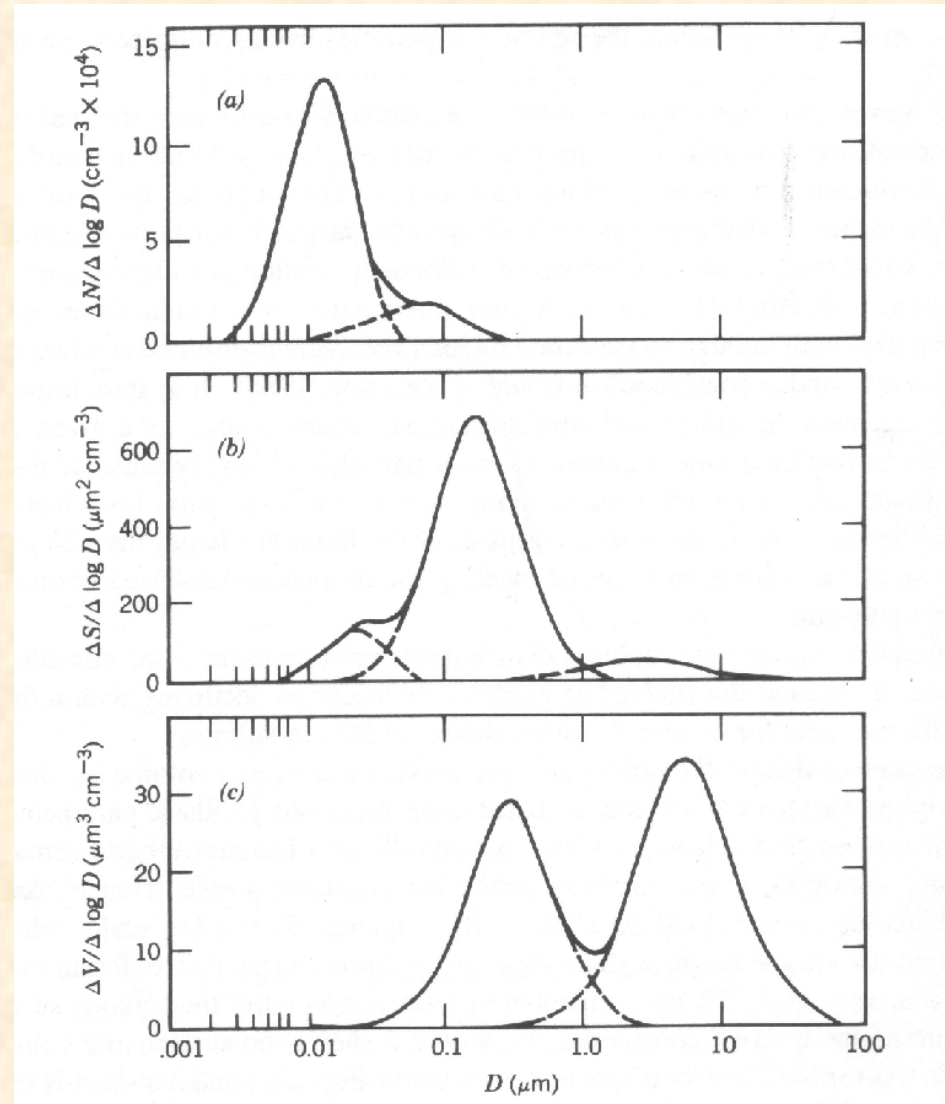
$$V_{TS} = 0.22 \text{ cm/s}$$



DISTRIBUZIONE GRANULOMETRICA DI AEROSOL IN ATMOSFERA



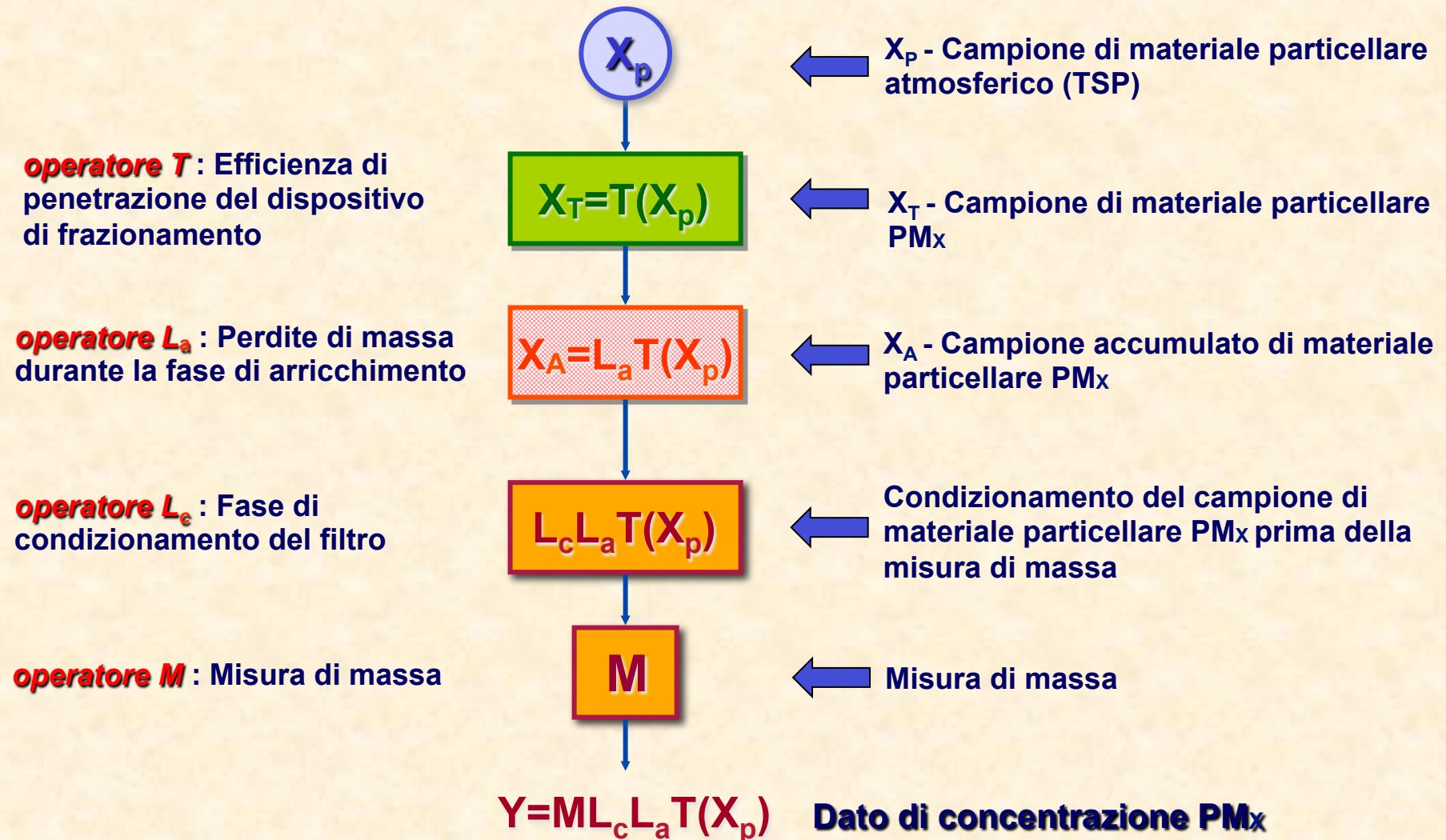
TIPICA DISTRIBUZIONE DEL MATERIALE PARTICELLARE IN UN' AREA URBANA



**METODO DI
CAMPIONAMENTO PM_x
PER ACCUMULAZIONE**

MISURA DELLA CONCENTRAZIONE DI MASSA DEL PM_x

FLOW CHART



Valutazione dei “bias” negli step di campionamento

- Bias nella distribuzione granulometrica (cambiamenti nell'efficienza di taglio)
- Bias nella composizione chimica (perdita di composti volatili)

Valutazione dell'incertezza nella misura della concentrazione di massa

- Step del campionamento
- Step della misura di massa

METODO D' ACCUMULAZIONE

Concentrazione media su T

$$\bar{C} = \frac{1}{T} \int_0^T C(t) dt$$

Valore determinato

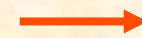
$$C^* = \frac{M}{V}$$

Massa del materiale
particellare campionato

$$M = \int_0^T C(t) \cdot Q(t) dt$$

Volume campionato

$$V = \int_0^T Q(t) dt$$



$$C^* = \frac{\int_0^T C(t) \cdot Q(t) dt}{\int_0^T Q(t) dt}$$

C* coincide con \bar{C} solo se la portata volumetrica è costante durante il campionamento

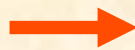
$$C^* = \frac{Q \cdot \int_0^T C(t) dt}{Q \cdot T} = \frac{1}{T} \cdot \int_0^T C(t) dt$$

Rappresentatività granulometrica di un campione PMx

$$(d_{50} \sqrt{C_c})^2 = \frac{9 \cdot \pi \cdot \eta \cdot d_{ugello}^3 \cdot Stk_{50}}{4 \cdot Q_{ugello} \cdot \rho_{particella}}$$

- C_c = fattore di correzione di Cunningham
- Q_{ugello} = portata volumetrica per il singolo ugello
- η = viscosità dell'aria
- Stk_{50} = numero di Stokes pari a 0.24
- d_{ugello} = diametro dell'ugello

$$\frac{Q}{\eta} = \text{costante}$$



**Diametro di taglio indipendente
dai valori di temperatura e
pressione**

SOLUZIONE RIGOROSA

SCHEMA DI UN SISTEMA DI CAMPIONAMENTO DI RIFERIMENTO



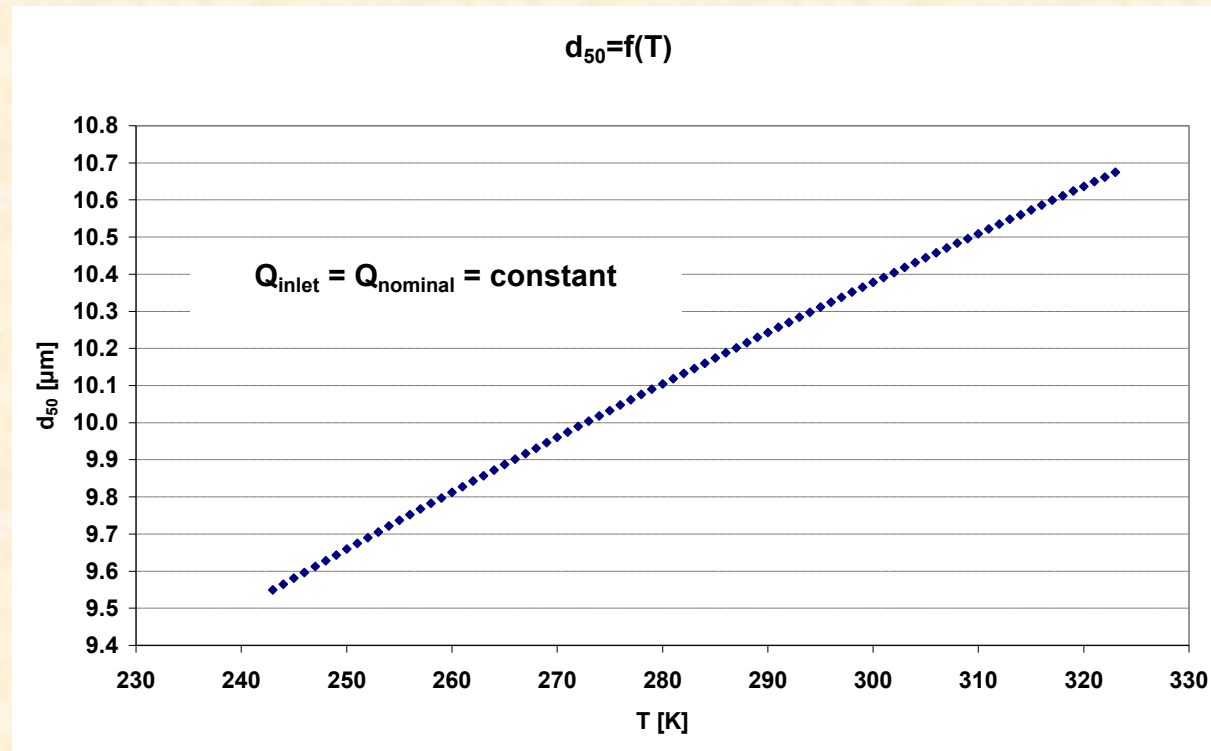
Campionamento a portata nominale costante

Il taglio cambia con la temperatura (effetto della viscosità)

Q= valore di portata costante

$$d_{50} = g[\eta(T)] = f(T)$$

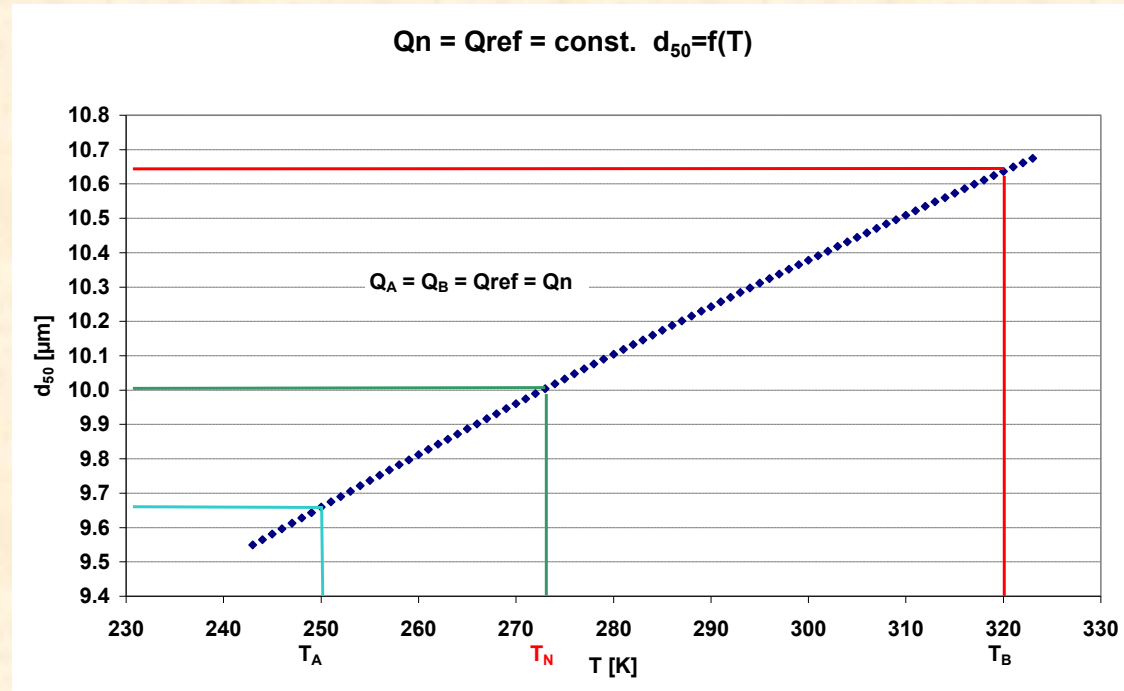
$$d_{50} \sqrt{C_c} = \sqrt{\frac{9\pi d_u^3 Stk_{50} \cdot \eta}{4\rho_p Q}}$$



$$\eta_T = \frac{1.458 \cdot 10^{-6} \cdot T^{1,5}}{T + 110.4} \quad (100 \div 1800 \text{ K})$$

BIAS NELLA CONCENTRAZIONE DI MASSA (bias nella frazione coarse)

Variazioni nel taglio



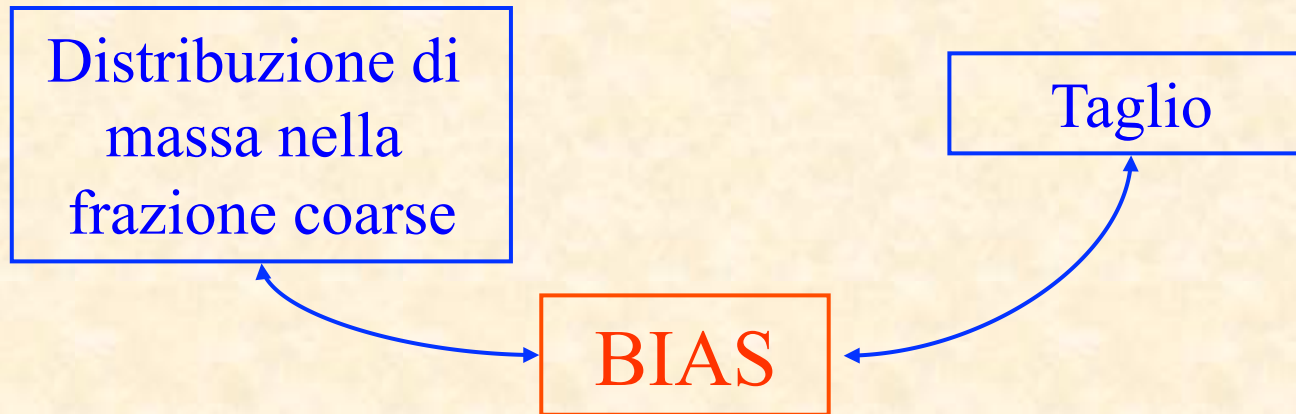
$T \rightarrow f[\text{geometria}, Q/\eta(T), \dots]$ $Y_n = T_n(x_p)$ $T_n = \text{valore nominale di riferimento (2.5, 10 \dots \mu\text{m})}$

$Y_a = T_a(x_p)$ $T_a = \text{taglio nelle condizioni operative}$

$$M(Y_a) = M(Y_n) + \delta$$

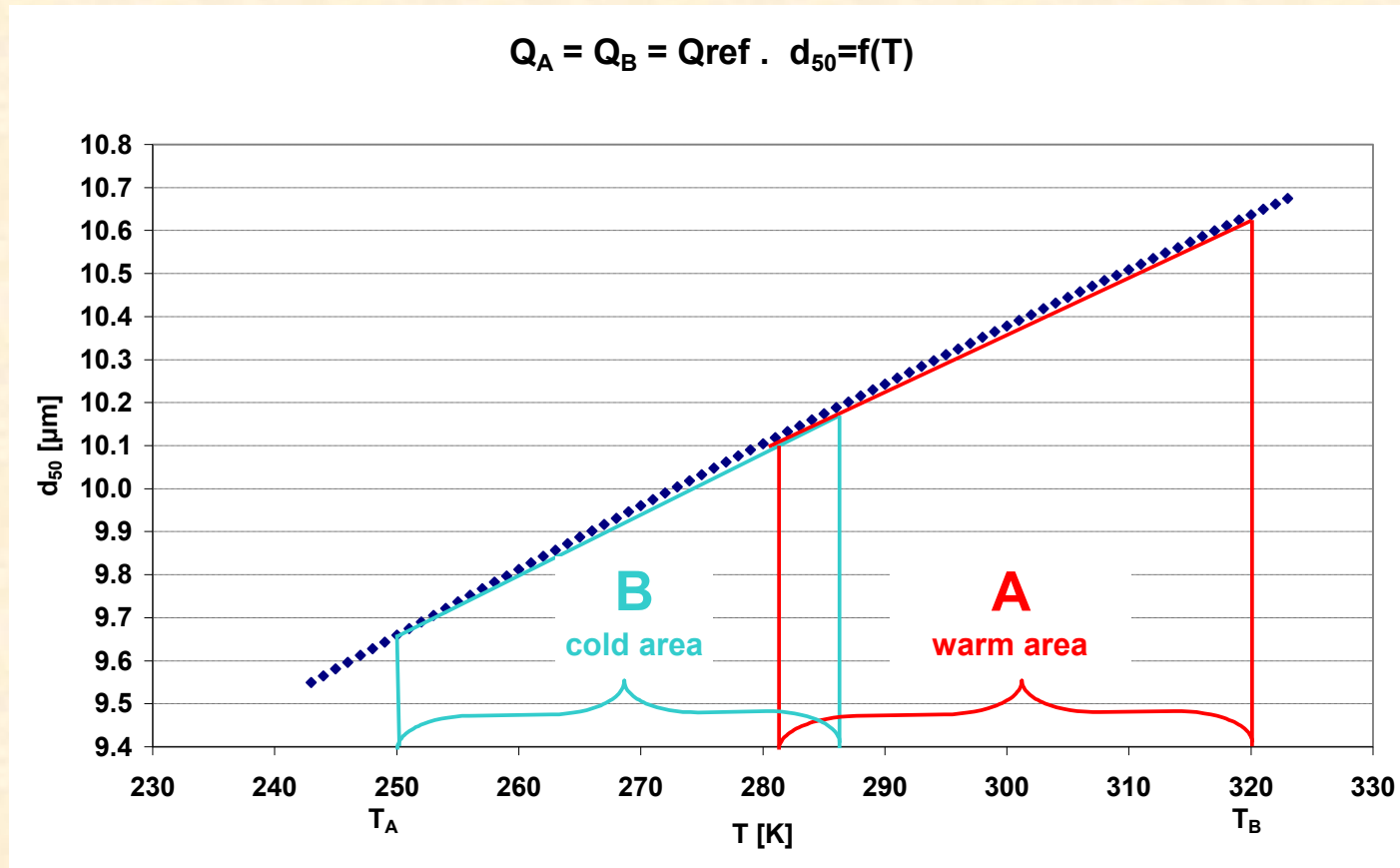
$$\delta = M[(T_a - T_n)(x_p)]$$

Bias nella frazione coarse



- δ_+ \Rightarrow Condizioni ambientali calde
Risospensione turbolenta delle polveri
- δ_- \Rightarrow Condizioni ambientali fredde
Risospensione meccanica delle polveri

Disarmonizzazione geografica



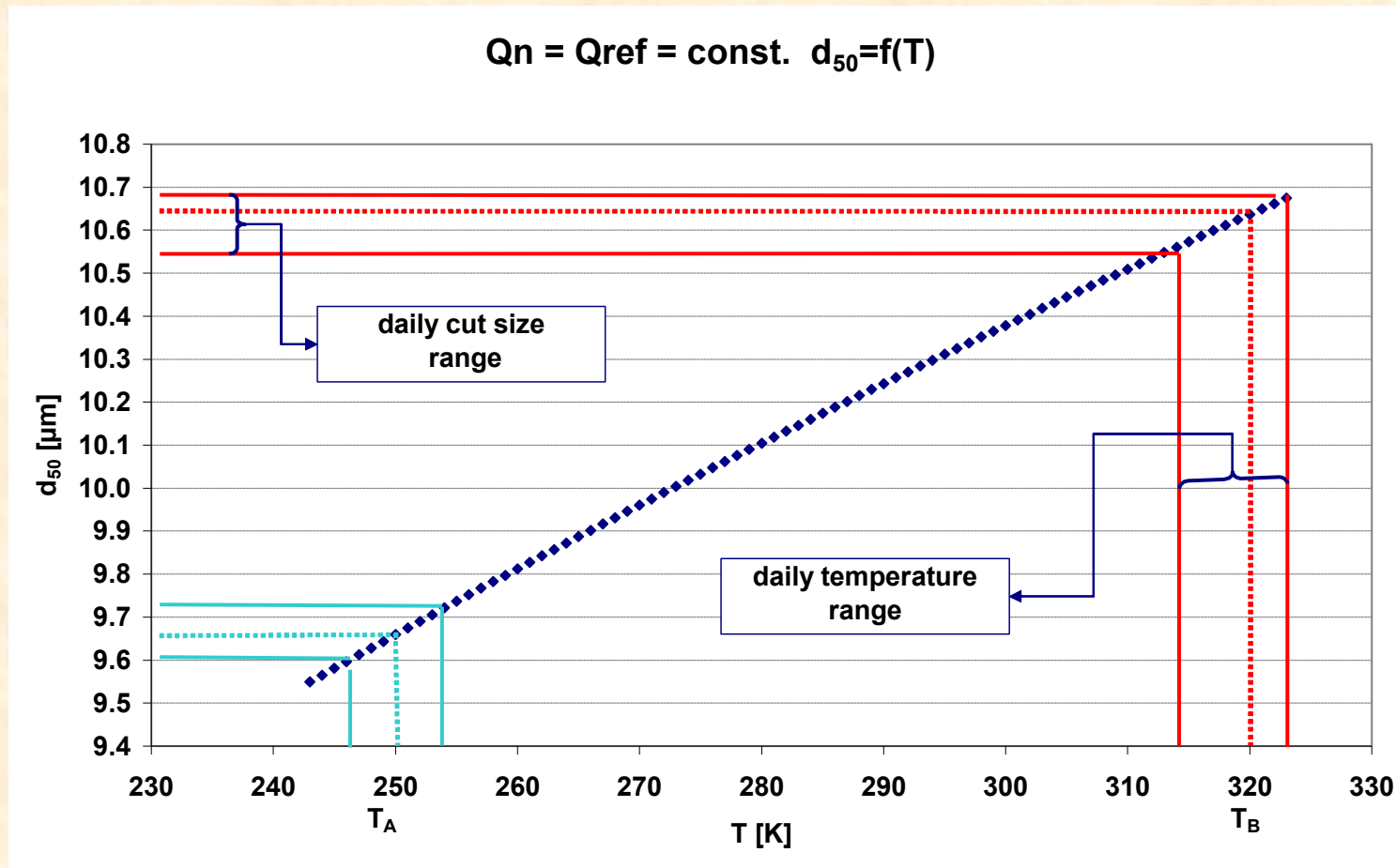
$$Y_A = Y_{nA} + \delta_A$$

$$Y_B = Y_{nB} + \delta_B$$

$$Y_A - Y_B = Y_{nA} - Y_{nB} + (\delta_A - \delta_B)$$

$$(\delta_A - \delta_B) > 0$$

Variazione giornaliera del diametro di taglio



Le variazioni giornaliere del diametro di taglio sono correlate a:

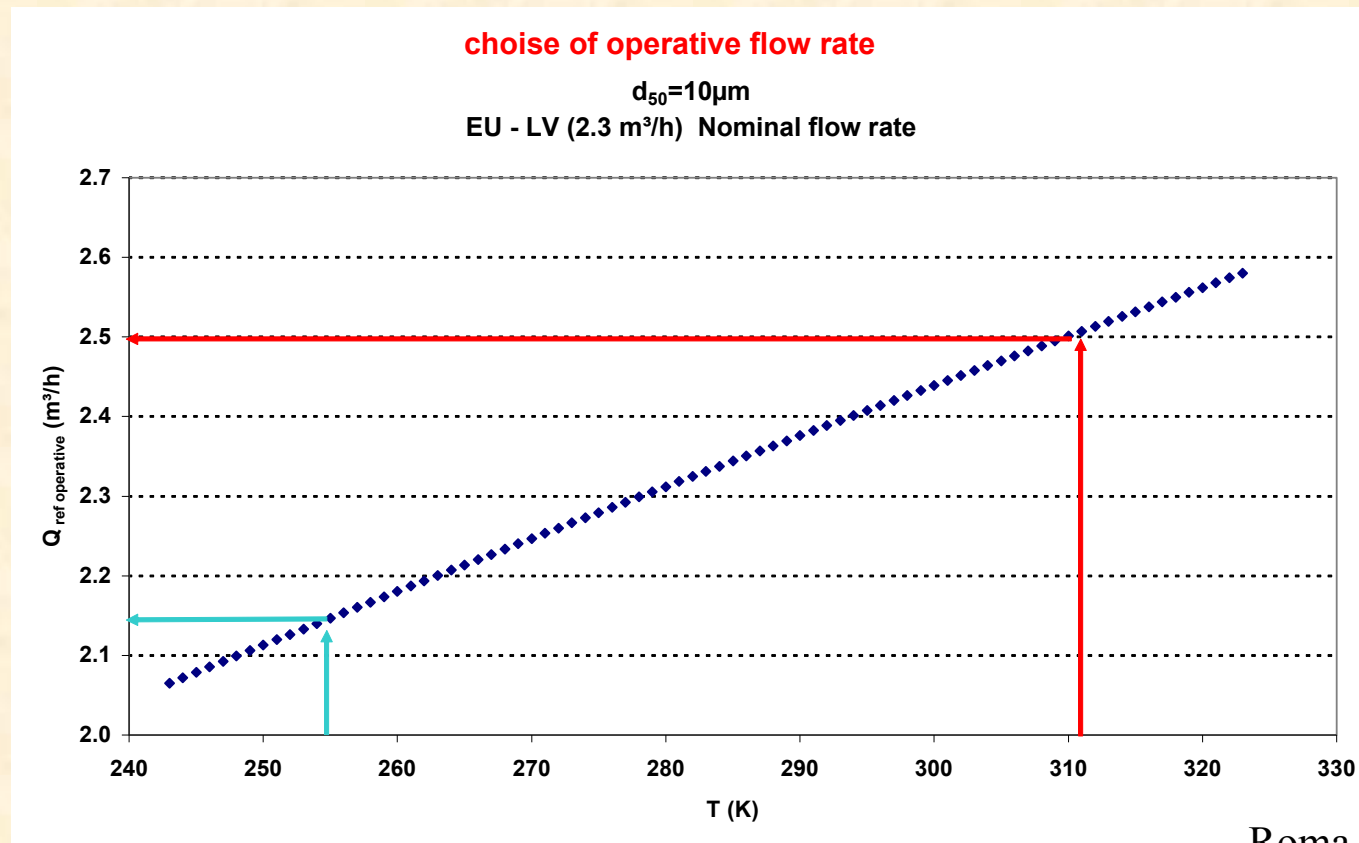
$$\left[\frac{T_{\max} - T_{\min}}{T} \right]$$

MINIMIZZAZIONE DEI BIAS

Per avere $\delta = 0$

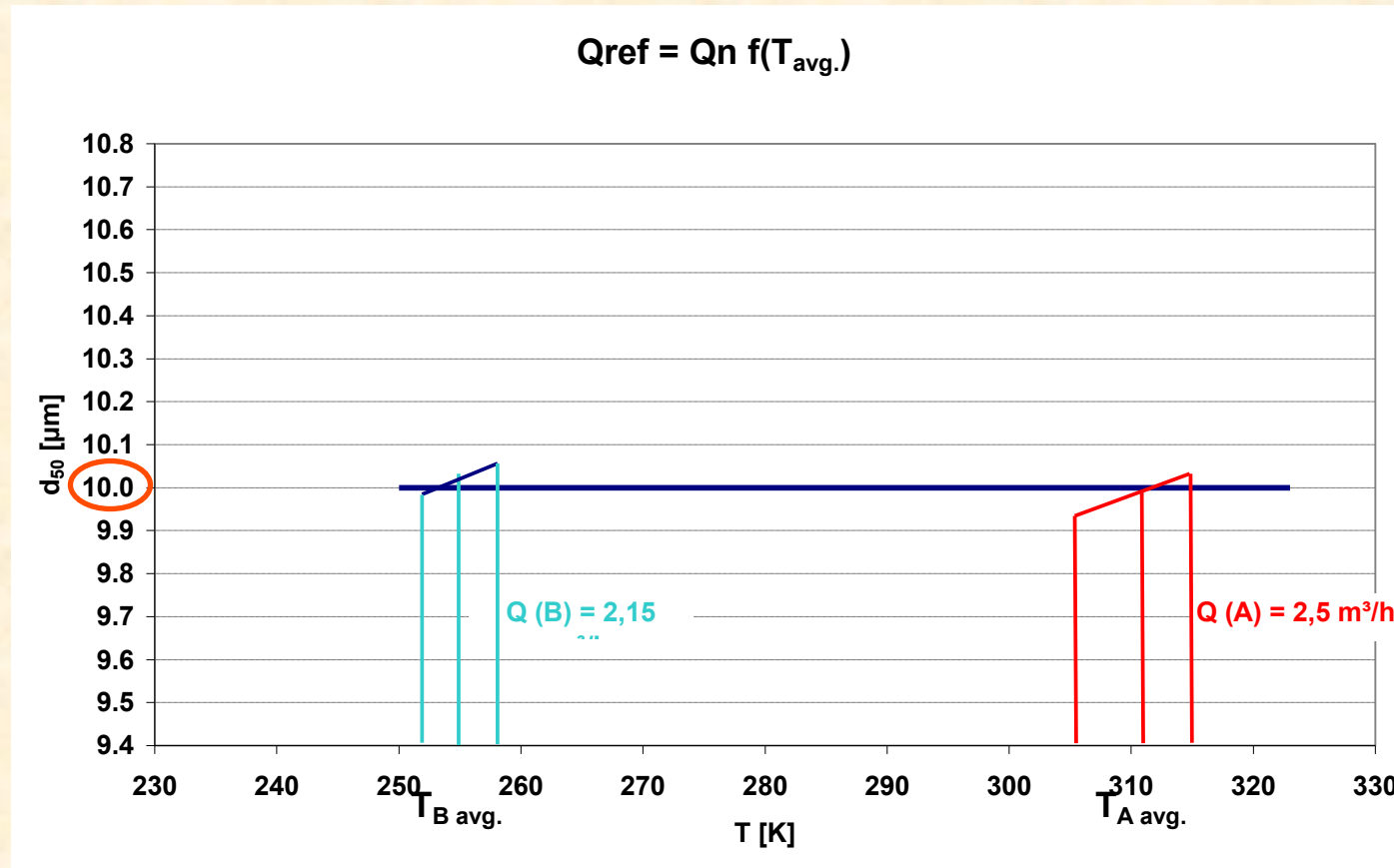
$$\frac{Q_n}{\eta(T_n)} = \frac{Q_A}{\eta(T_A)}$$

$$Q_A = Q_n \quad \frac{\eta(T_A)}{\eta(T_n)} \cong Q_n f\left(\frac{T_A}{Q}\right)$$



•Stima della temperatura media giornaliera (dati del giorno precedente)

•Scelta della portata operativa utilizzando: $Q_{ref\ operative} = Q_n f(T)$



IN TALI CONDIZIONI OPERATIVE LA VARIAZIONE RELATIVA DEL DIAMETRO DI TAGLIO DAL VALORE NOMINALE E' ESTREMAMENTE RIDOTTA

BIAS NELLA COMPOSIZIONE CHIMICA

PERDITE PER VOLATILIZZAZIONE

NEL METODO D' ACCUMULAZIONE PER IL PM_x:

- **Evaporazione del Nitrato d' ammonio**
- **Evaporazione di composti organici**

ARTEFATTI PER INTERAZIONI GAS-PARTICELLE E GAS-MATRICE

Perdite nel metodo d' accumulazione

Composti volatili (es. Nitrato d' ammonio)

$M T(X_p) \longrightarrow$ **Massa di PM_x prelevato**

$M = M^s + M^v$ M^s massa dei composti stabili prelevati

M^v massa dei composti volatili prelevati

Frazione accumulata sul filtro $M^F = M^{Fs} + M^{Fv}$

STABILE $\dot{M}^{Fs} = C^s(t) Q$
 $M^{Fs} = Q \int_0^t C^s(t) dt = C^s V = M^s$

VOLATILE $\dot{M}^{Fv} = C^v(t) Q - \Omega$ $\Omega(\text{perdite}) = \eta(t) M^{Fv}$
 $\dot{M}^{Fv} = C^v(t) Q - \eta(t) M^{Fv}$ $\eta(t) = g(\text{temperatura, U.R., pressione parziale...})$

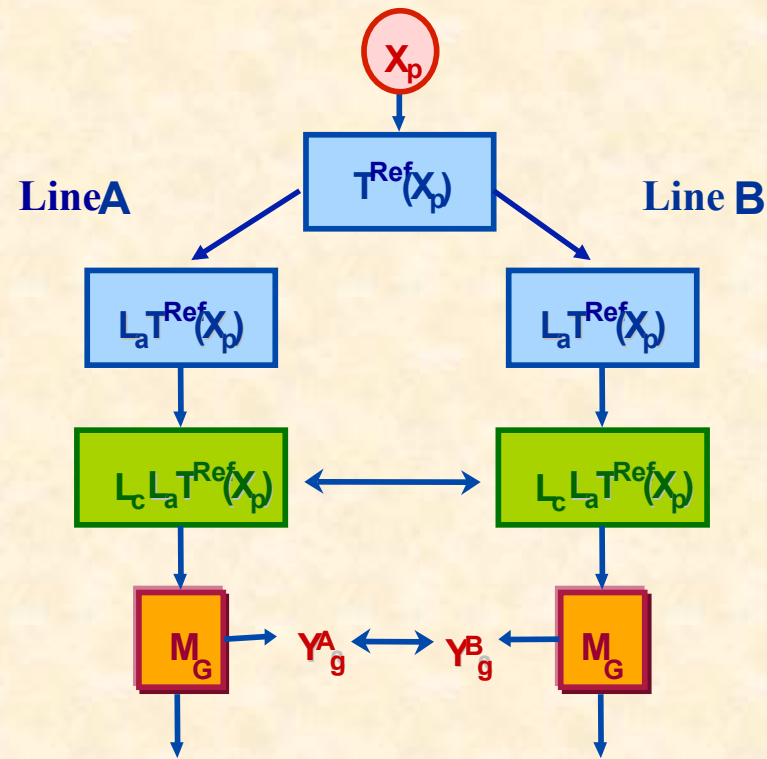
$$M^{Fv} = M_0^{Fv} \exp \left[- \int \eta(t) dt \right] + \left[\int C^v Q \exp \left\{ \int \eta(t) dt \right\} \exp \left[- \int \eta(t) dt \right] < M^v$$

$$M^{Fv} < M^v$$

PERDITE COMPLESSIVE NEGLI STEP D' ACCUMULAZIONE

- Durata del campionamento (12h, 24h.....)
- Ora d' inizio del campionamento (00:00 am, 12:00 am.....)
- Andamento temporale di T e RH durante il campionamento
- Andamento temporale della pressione parziale dei composti volatili in fase gassosa
- Andamento temporale della concentrazione dei composti volatili in fase particellare
-

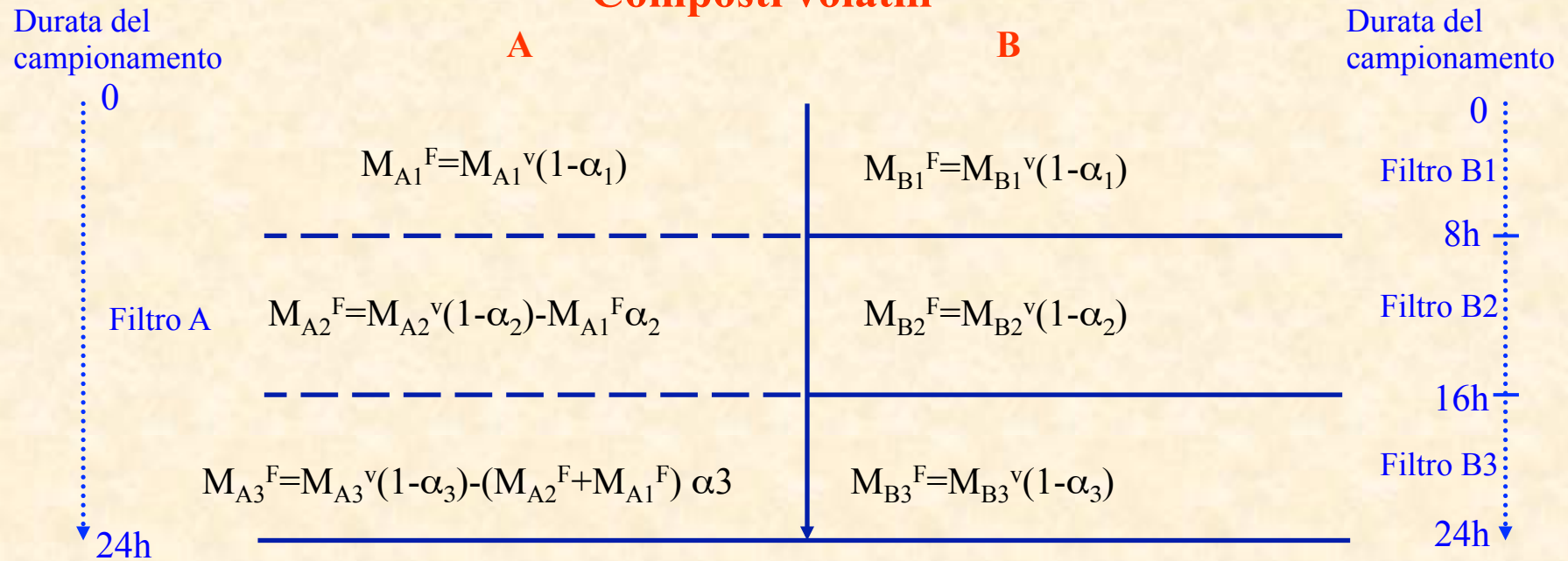
STIMA DELLE PERDITE NEI METODI D' ACCUMULAZIONE DEL PM_x



multi-component ion analysis

ANALISI DI AUTOCONSISTENZA TEMPORALE

Composti volatili



$$M_{A_{tot}}^F = M_{B_{tot}}^F - [M_{A1}^F \alpha_2 + (M_{A2}^F + M_{A1}^F) \alpha_3] \quad M_{B_{tot}}^F = M_{B1}^F + M_{B2}^F + M_{B3}^F$$

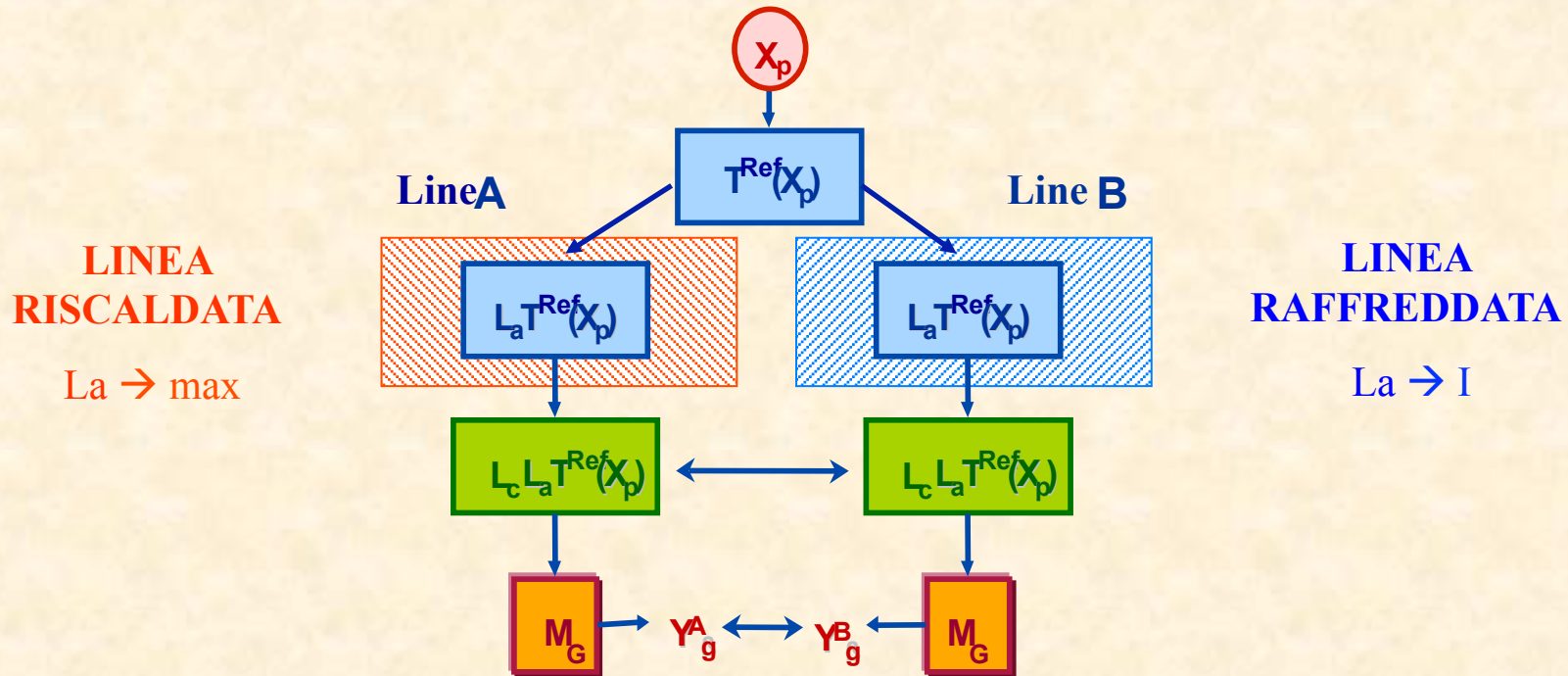
$$M_{A_{tot}}^F < M_{B_{tot}}^F$$

If $\alpha_i = 0$ (nessuna perdita)

$$M_{A_{tot}}^F = M_{B_{tot}}^F = M^v$$

Valutazione delle perdite:
$$\beta = \frac{M_{B_{tot}}^F - M_{A_{tot}}^F}{M_{B_{tot}}^F}$$

Valutazione quantitativa delle perdite di composti volatili presenti nel PMx utilizzando il metodo d' accumulazione



$$\beta_{max} = \frac{M_B^F - M_A^F}{M_B^F} \quad \beta_i = \frac{Mi_B^F - Mi_A^F}{Mi_B^F} \quad \text{con } Mi \text{ massa dell' } i\text{-esimo composto}$$

Composti stabili: $\beta_i \rightarrow 0$ Alta volatilità: $\beta_i \rightarrow 1$

Caratterizzazione chimica dei campioni Y^A e Y^B

Multi-Component Ion Analysis

Ioni nella frazione fine: SO_4^{2-} , NH_4^+ , NO_3^-

Stabili: SO_4^{2-} (rappresentativo delle particelle fine)

Volatili: NH_4^+ , NO_3^-

Ioni nella frazione coarse: Ca^{++} , Na^+ , Mg^{++}

Stabili: Ca^{++} , Na^+ , Mg^{++}

Ca^{++} (rappresentativo del range 5-20 μm)

Volatili: ##

ARTEFATTI POSITIVI

interazioni gas-particelle e gas-matrice

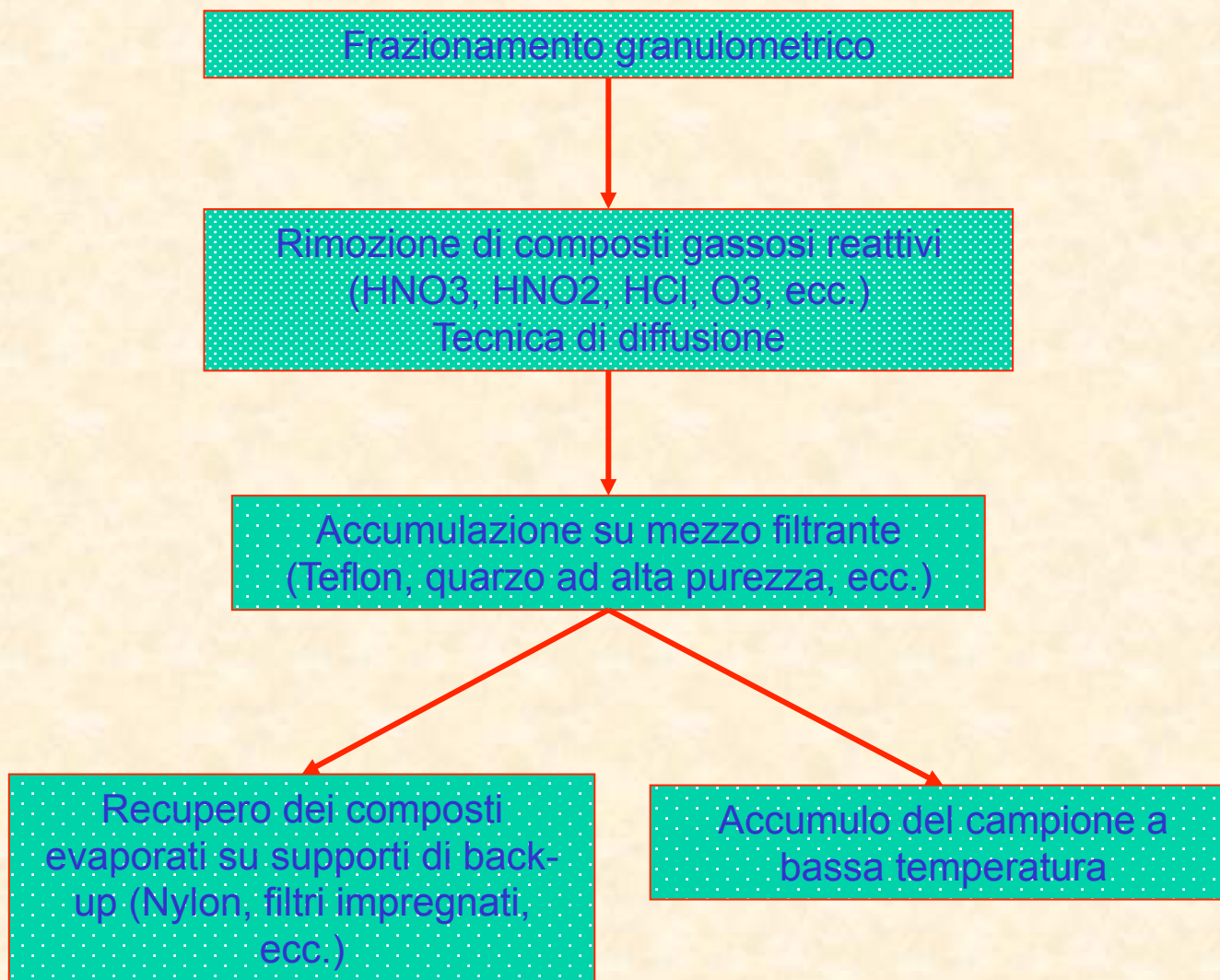
- HNO_3 gassoso → particelle e o matrice → Nitrato
- Nitrito → mezzo filtrante + ossidanti → Nitrato
- Organici → mezzo filtrante + ossidanti → *Organici*
-

BIAS NELLA COMPOSIZIONE CHIMICA

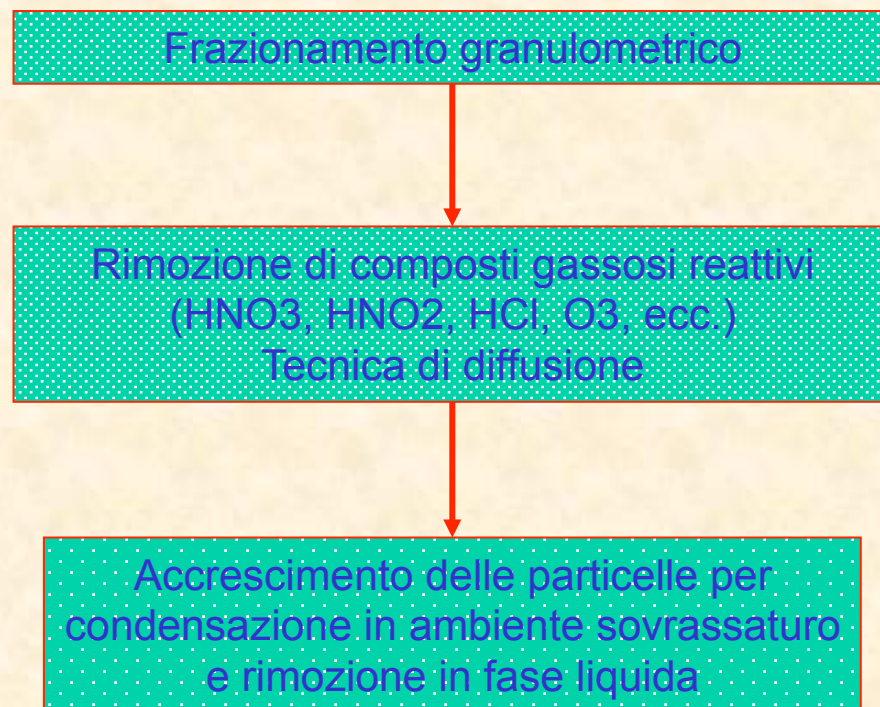
SOLUZIONE IDEALE:

Sistema di campionamento integrato basato su tecniche di accumulazione su mezzi filtranti con rimozione selettiva di gas reattivi attraverso tecniche a diffusione (annular denuder)

RAPPRESENTATIVITÀ CHIMICA DEL CAMPIONE (SOLUZIONE OPERATIVA 1)



RAPPRESENTATIVITÀ CHIMICA DEL CAMPIONE (SOLUZIONE OPERATIVA 2)



**RILEVANZA DEGLI ARTEFATTI NELLA
COMPARAZIONE DEI DATI DI
CONCENTRAZIONE DI MASSA DEL PM_x
OTTENUTI CON TECNICHE DIFFERENTI O
CON TECNICHE DI ACCUMULAZIONE CHE
UTILIZZANO DIFFERENTI MATRICI FILTRANTI**

TEOM_(standard) ≠ REFERENCE

Bias

- **Perdita di composti volatili**
- **Differenza nel diametro di taglio teste LV-EU e LV-EPA**

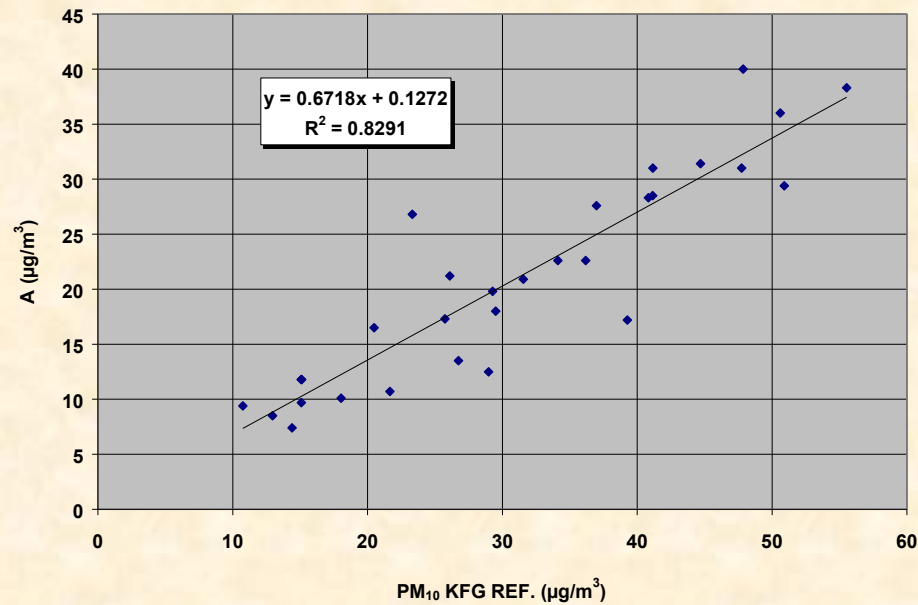
ANALISI D' EQUIVALENZA

REGRESSIONE LINEARE

O ANALISI FUNZIONALE ?

**UN ESEMPIO DI APPROCCIO
UTILIZZANDO LA METODOLOGIA
DELLA REGRESSIONE LINEARE
SECONDO LINEE GUIDA UE**

30 consecutive runs



A e B sono equivalenti al REF?

Approccio triviale

A → funz di correzione → $A^* = A/0.672 - 0.127/0.672$

R² = 0.83

B → funz di correzione → $B^* = B/0.724 - 2.449/0.724$

R² = 0.83

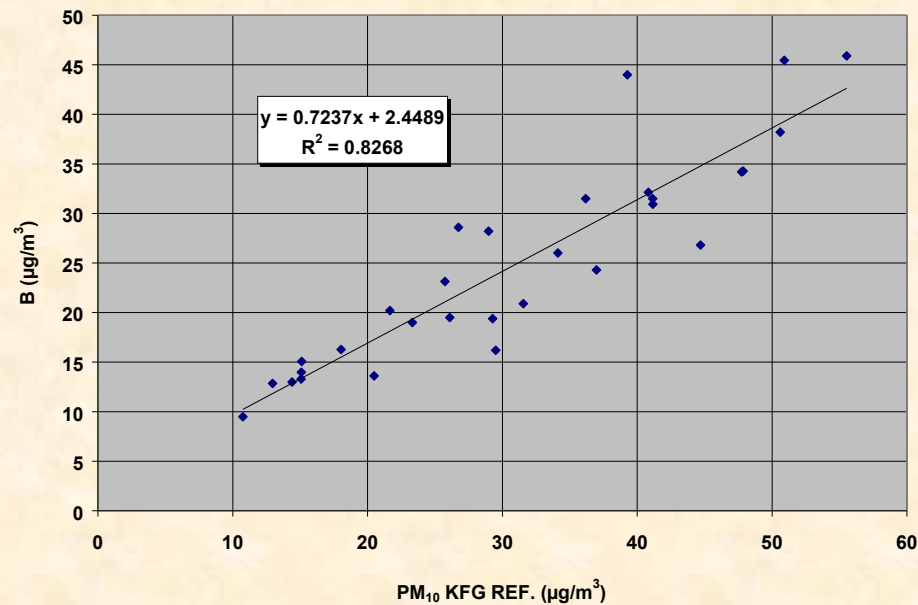
quindi ci aspettiamo

A* equivalente REF equivalente B*

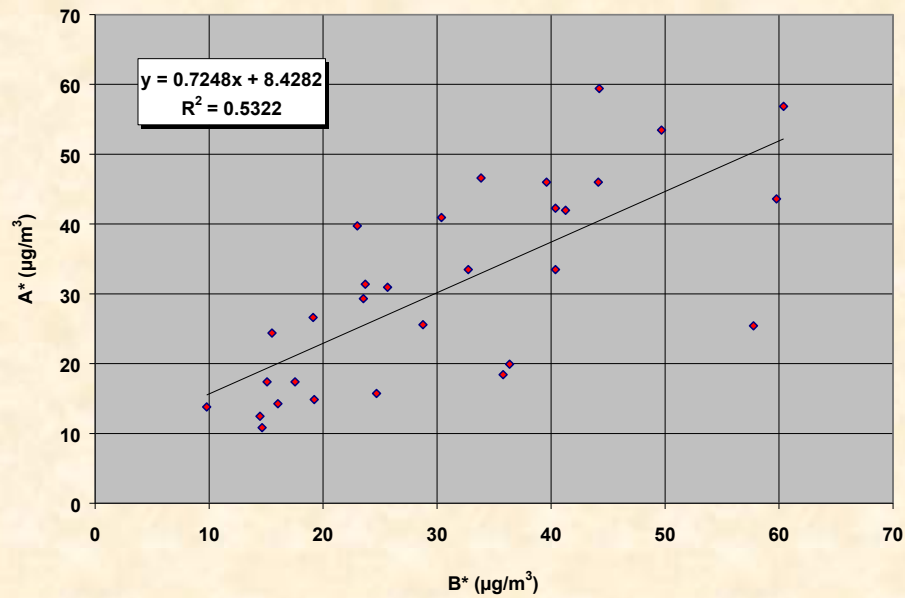
conseguentemente

A* equivalente B*

30 consecutive runs



30 consecutive runs



E' vero che A* e B* sono equivalenti?

Attraverso lo scatter plots di A* vs B* e B* vs A* osserviamo che

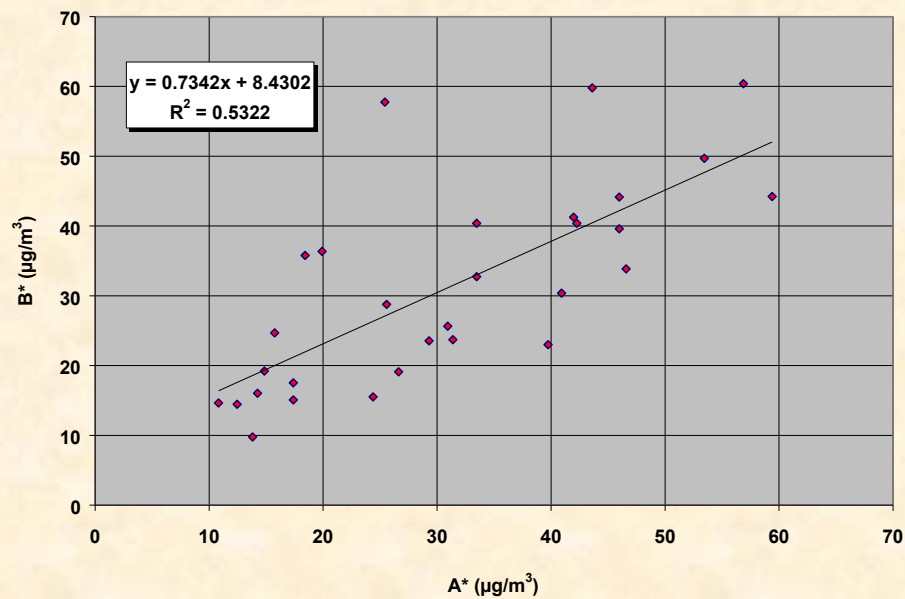
$R^2 = 0.53$

$|q|_1 \cong |q|_2 \cong 8.4$ (stessa intercetta!)

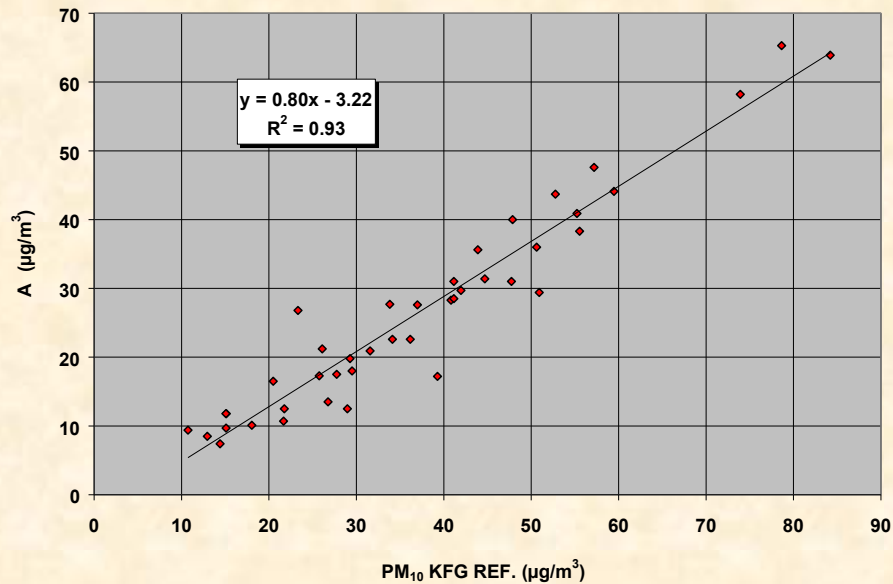
$m_1 \cong m_2 \cong 0.73$ (stessa pendenza!)

A* and B* NON SONO equivalenti!

30 consecutive runs



42 consecutive runs



Confronto di due set di dati di campo di concentrazione di materiale particellare con dati PM₁₀ di riferimento

Approccio triviale

A → funz di correzione → $A^* = A/0.800 + 0.322/0.800$

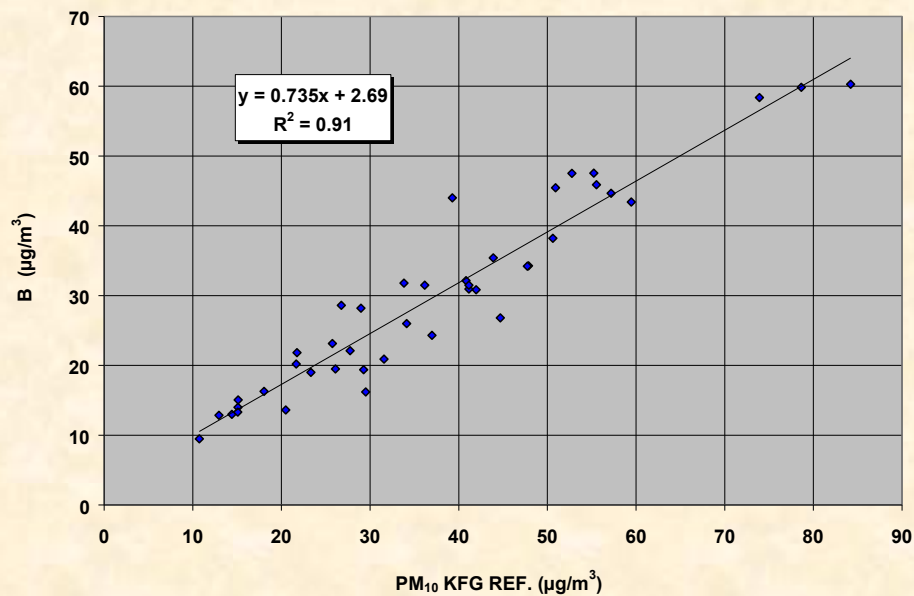
$R^2 = 0.93$

B → funz di correzione → $B^* = B/0.735 - 2.690/0.735$

$R^2 = 0.91$

quindi

42 consecutive runs

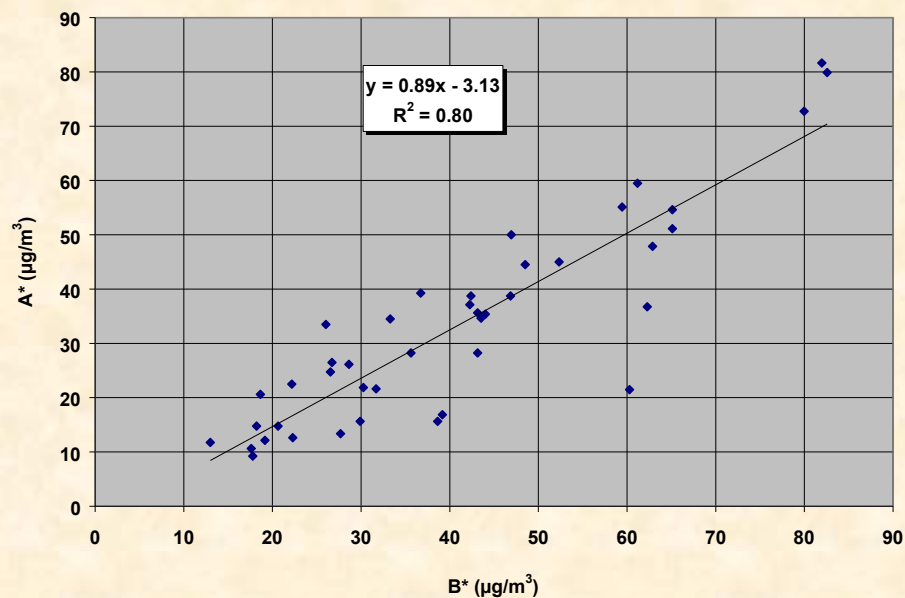


A* equivalente REF equivalente B*

e

A* equivalente B*

42 consecutive runs



A* e B* verifica di equivalenza

Approccio triviale

Dallo scatter plots di A* vs B* e B* vs A* osserviamo che

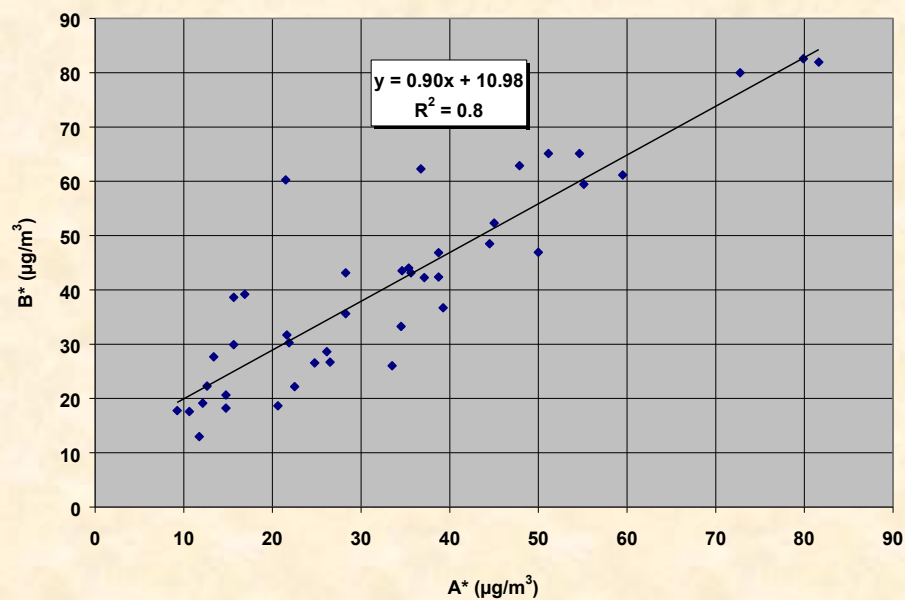
$$R^2 = 0.80$$

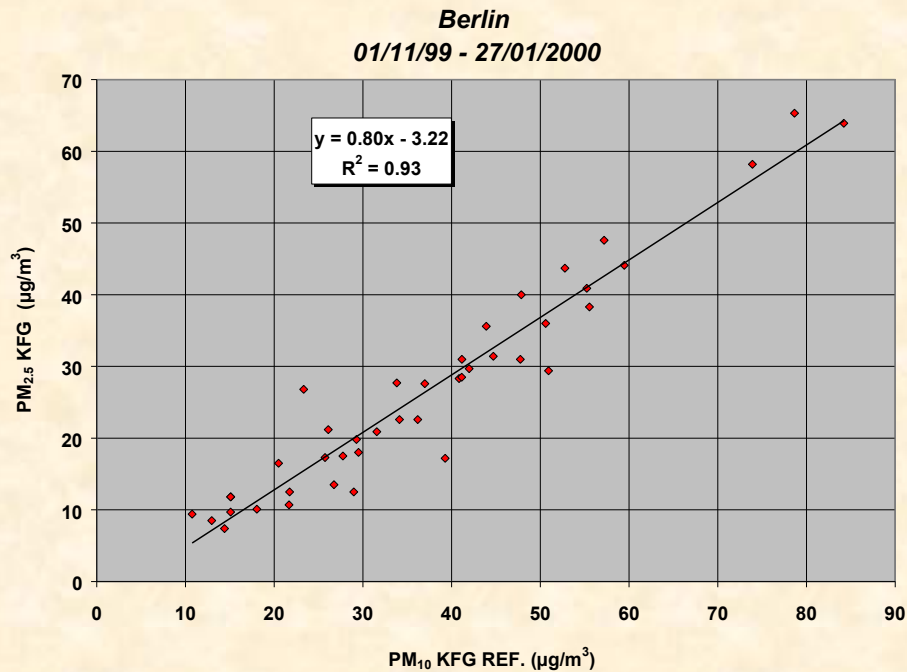
$$|q|_1 \approx |q|_2$$

$$m_1 \approx m_2 \approx 0.90$$

A* e B* soddisfano le condizioni di equivalenza espresse dalle linee guida

42 consecutive runs





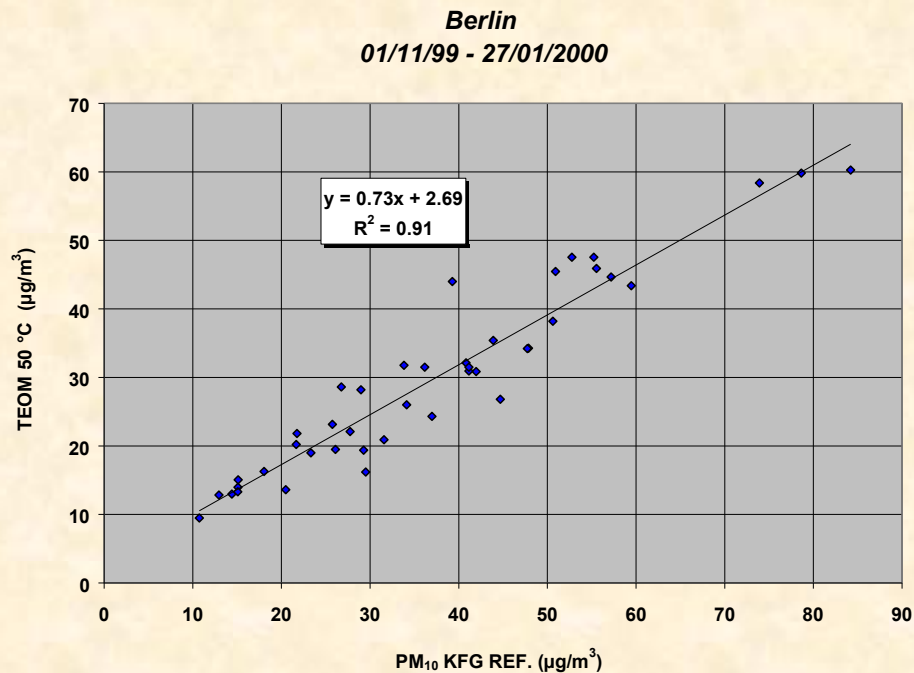
Ora consideriamo le popolazioni reali

- il set A è un PM_{2.5} (frazione fine di materiale particellare)
- il set B è un TEOM PM₁₀ con linea di ingresso riscaldata a 50°C (prevalente contenuto di materiale coarse. La frazione volatile del fine è praticamente assente)

PARADOSSO

Usando tale metodo triviale abbiamo **dimostrato** l'equivalenza tra un campione di PM_{2.5} e PM₁₀ con un contenuto molto basso di frazione fine volatile!!!

In altre parole, abbiamo dimostrato l'**equivalenza** tra due parametri assolutamente **non-equivalenti**.



**ESEMPIO DI ANALISI DI
EQUIVALENZA FRA UN METODO
AUTOMATICO PM₁₀ E IL METODO DI
RIFERIMENTO**

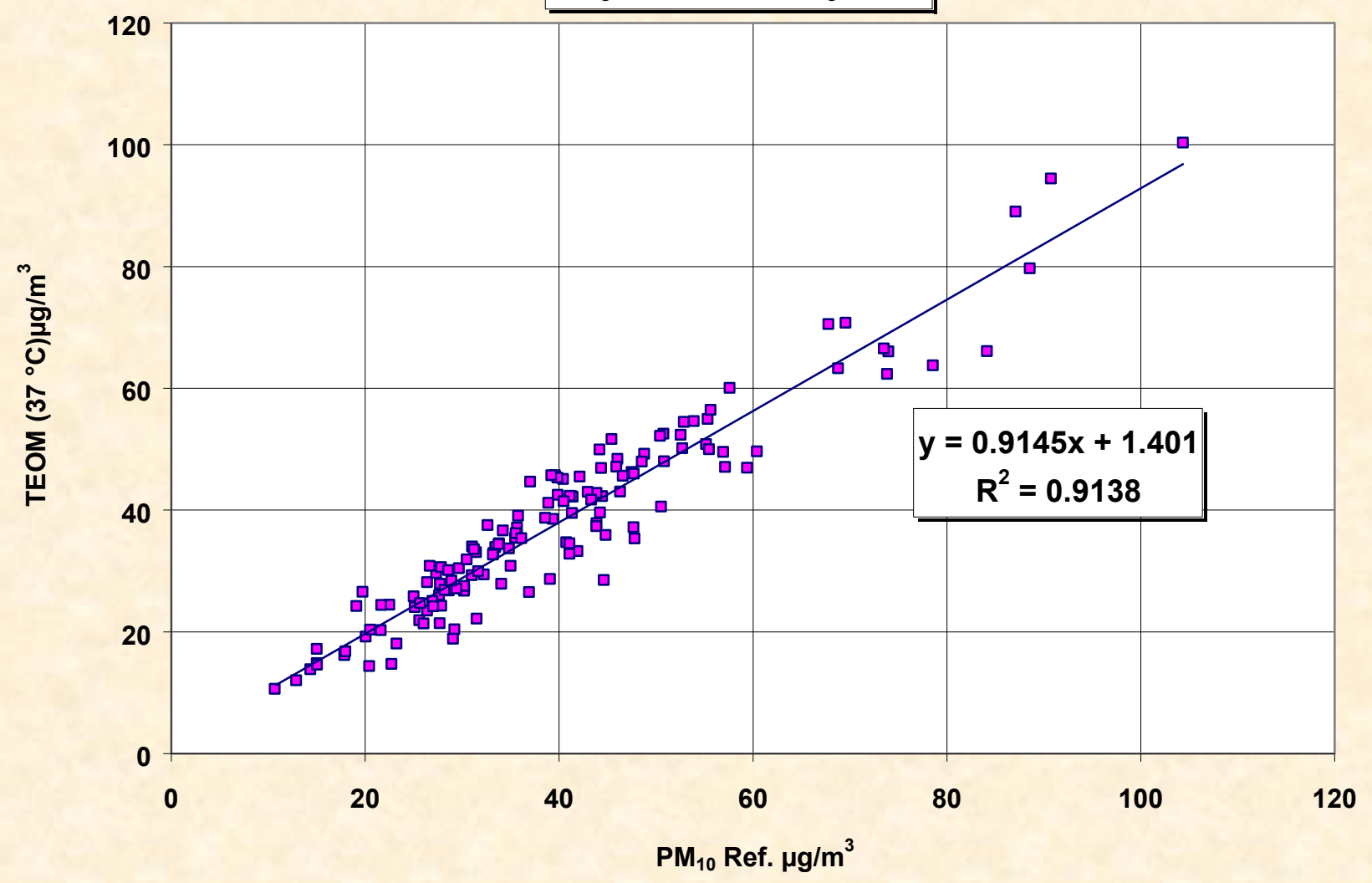
ANALISI FUNZIONALE

$$\text{TEOM} = \eta \text{ REF}$$

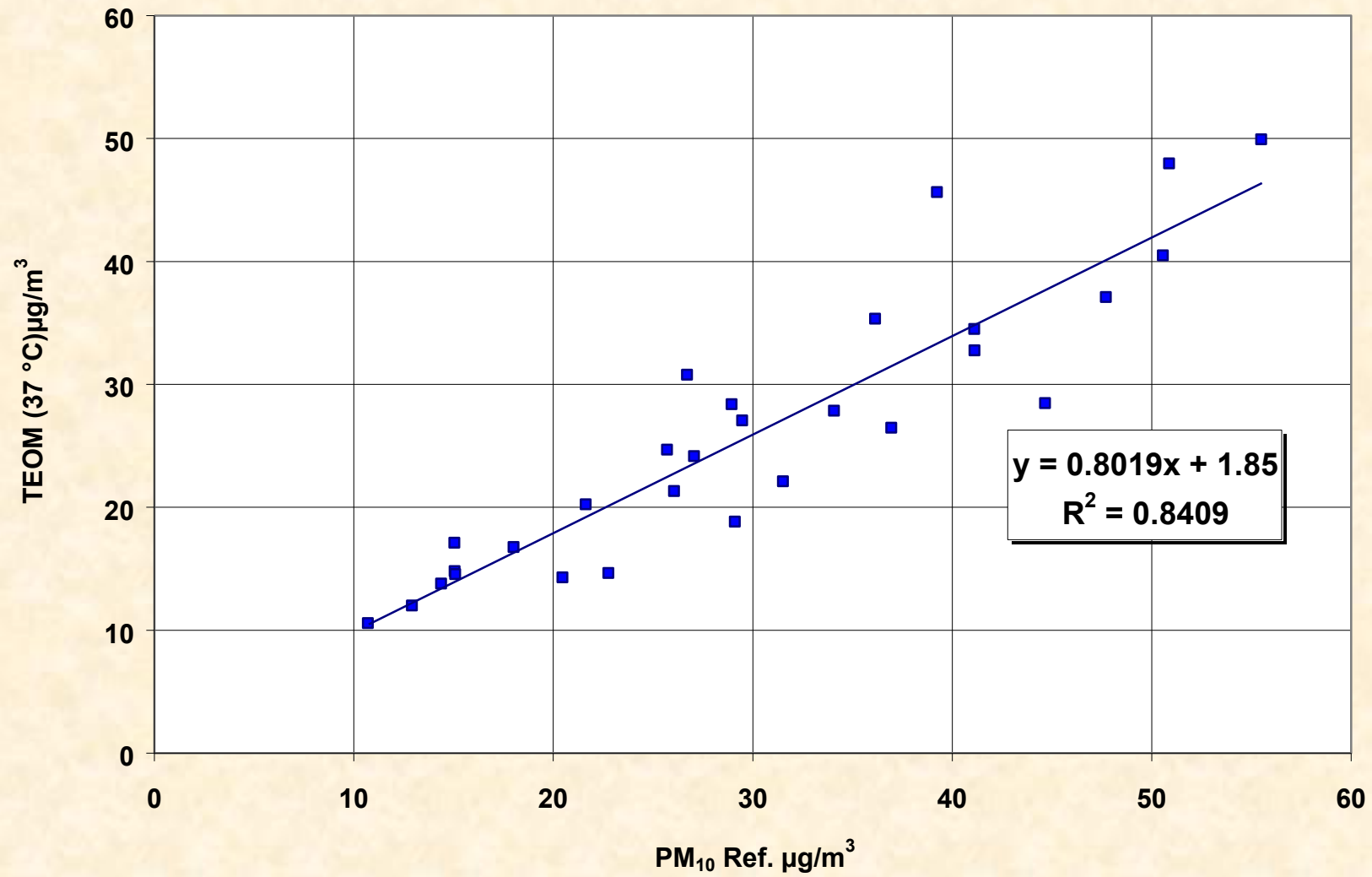
$$M(\text{TEOM}) = M(\eta \text{ REF})$$

η ?

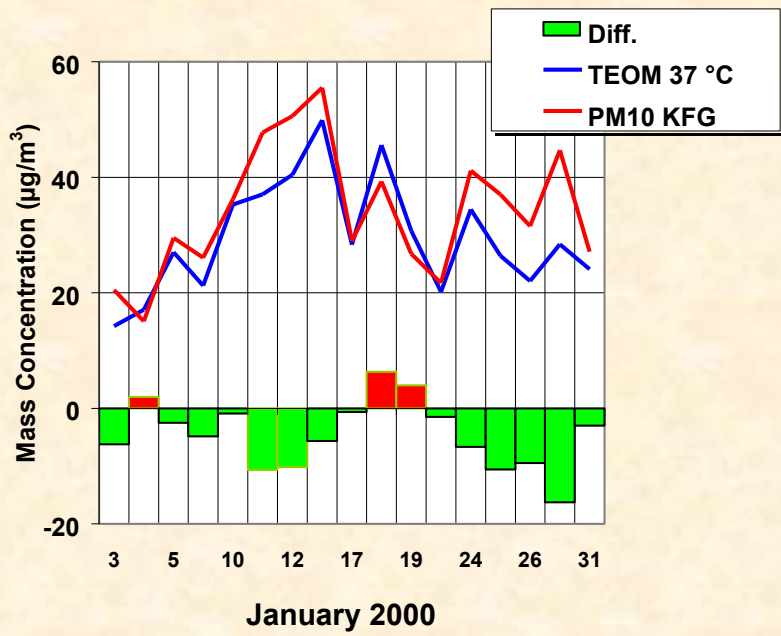
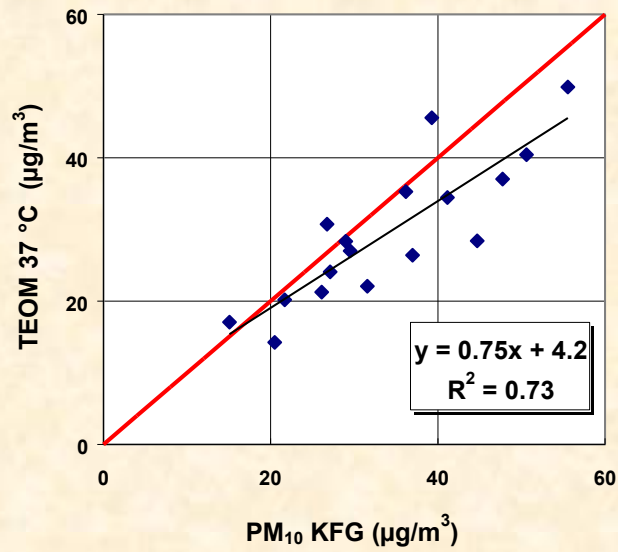
Berlin
May 1999 - January 2000



Berlin
December 1999 - January 2000



Berlin, January 2000



$$(Y_{\text{TEOM}} - Y_{\text{REF}}) = ?$$

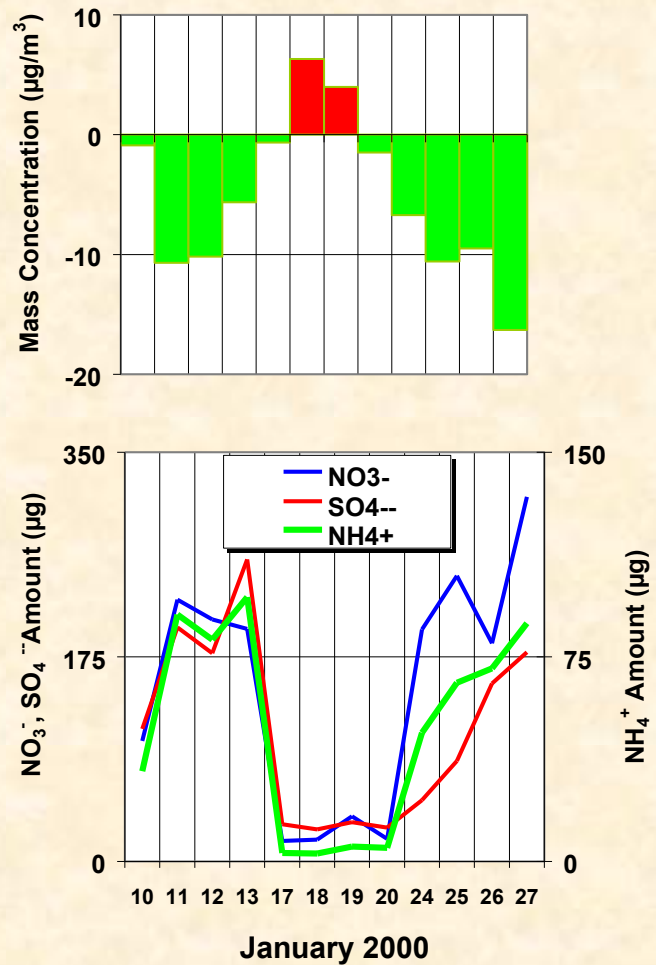
$$Y_{\text{REF}} = M_g L_{\text{REF}} T_{\text{REF}} \mathbf{X}_P = a_{\text{REF}} X_L + X_S + \varepsilon$$

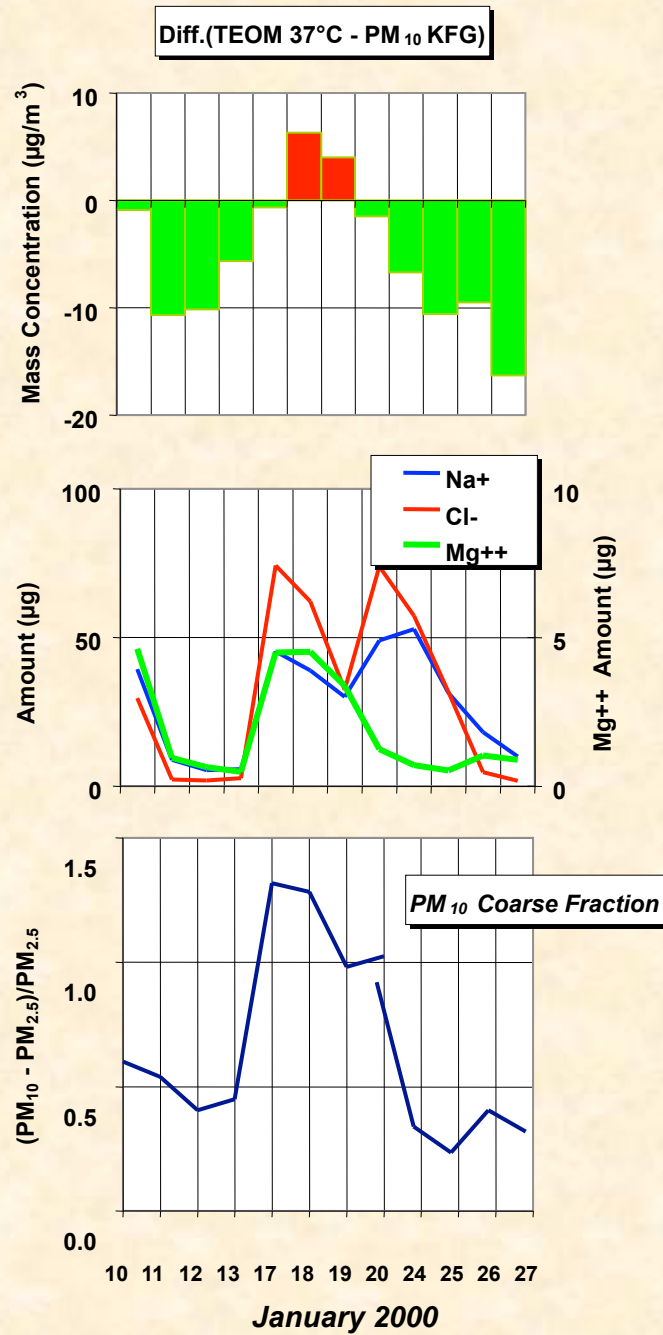
$$\begin{aligned} Y_{\text{TEOM}} &= M_{\text{TEOM}} L_{\text{TEOM}} T_{\text{EPA}} \mathbf{X}_P = \\ &= a_{\text{EPA}} X_L + b_{\text{TEOM}} X_S + \varepsilon \end{aligned}$$

where $b_{\text{TEOM}} < 1$ (losses)

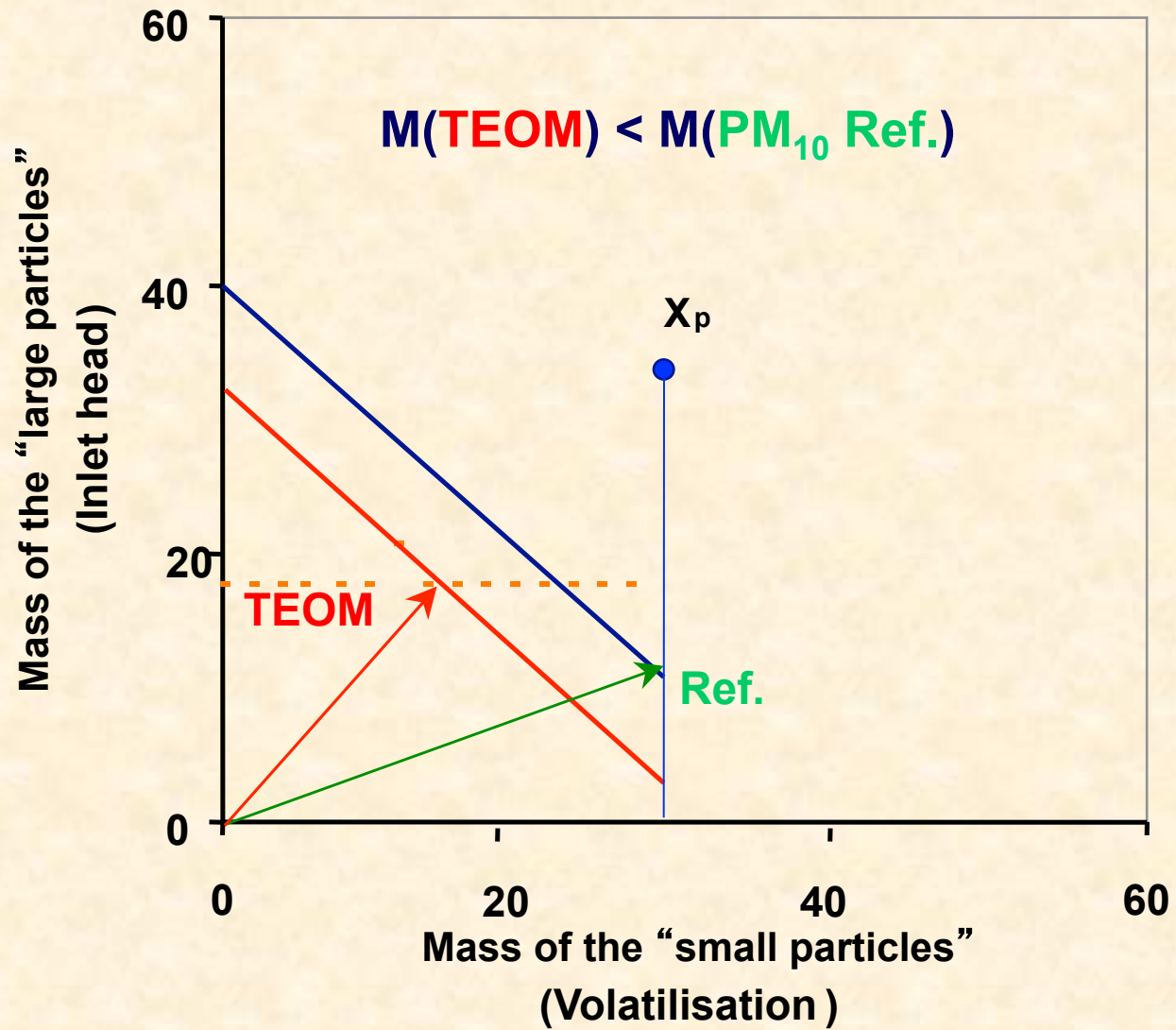
$$(Y_{\text{TEOM}} - Y_{\text{REF}}) = (a_{\text{EPA}} - a_{\text{REF}}) X_L - (1 - b) X_S + \varepsilon$$

Diff. (TEOM 37° C - PM₁₀ KFG)

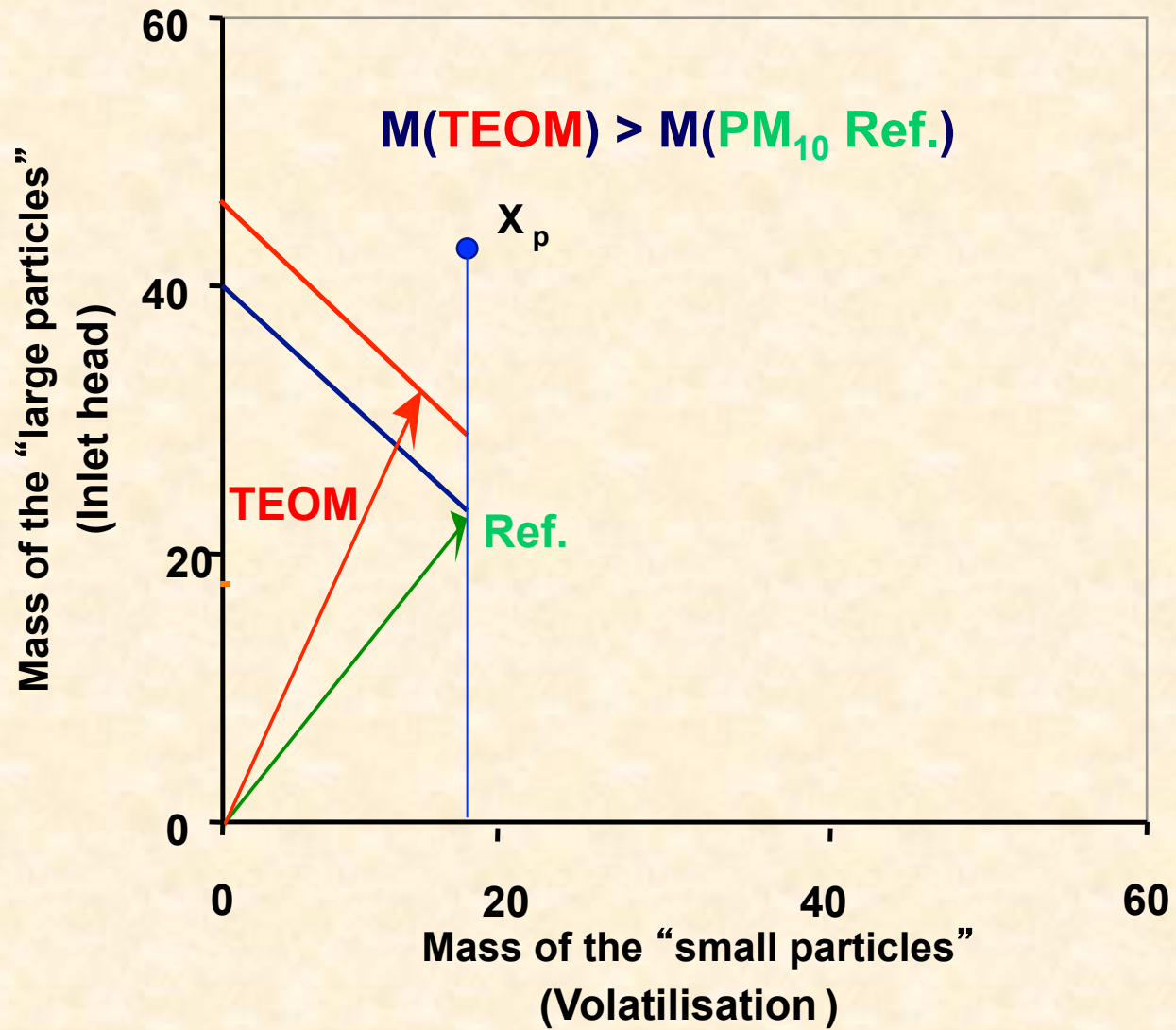




high amount of fine particles

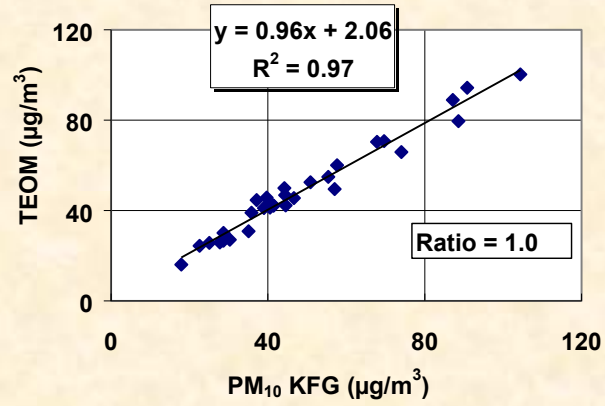


low amount of fine particles
high amount of coarse particles

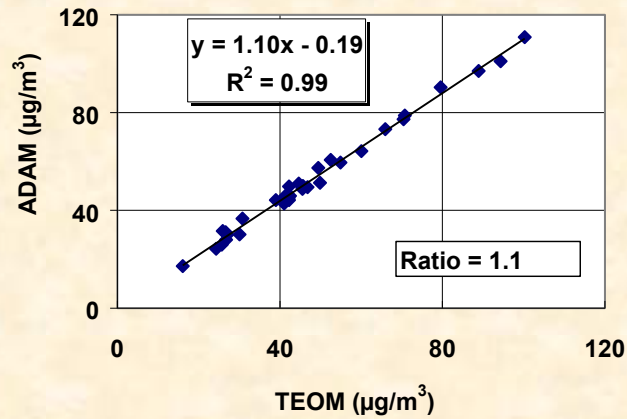
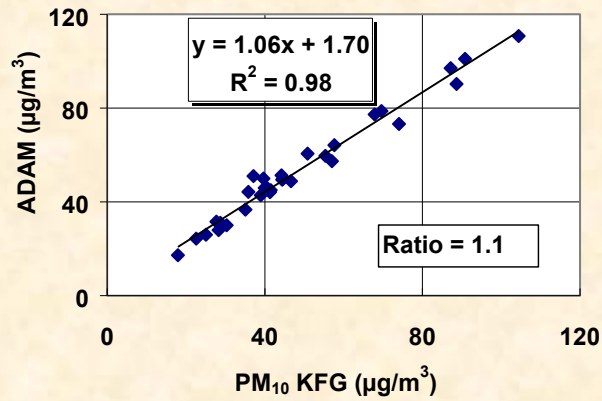


TEOM and ADAM
EPA LV Sampling head

May and September 1999



TEOM equiv. REF ?



TEOM and REF data are not **equivalent**

DEMONSTRATION

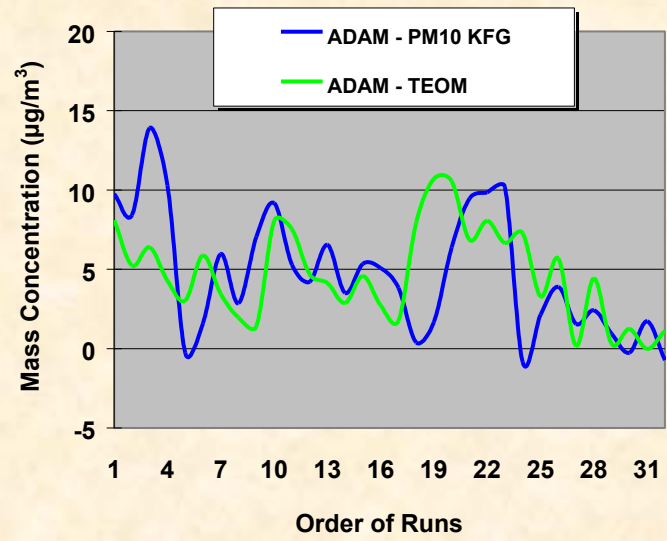
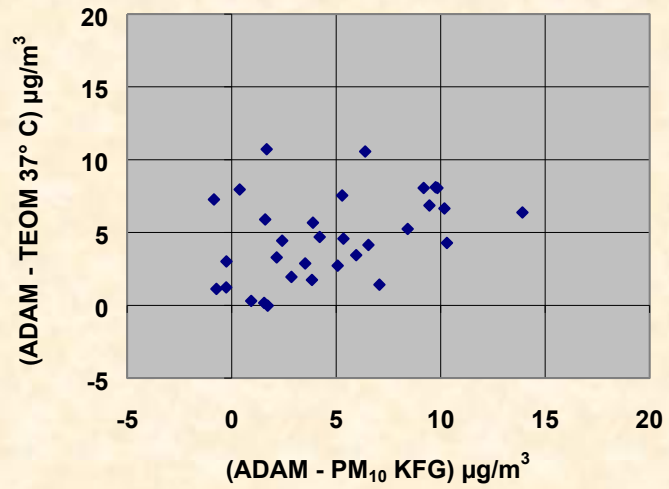
● IF Y_{TEOM} equivalent Y_{REF}

then

$(Y_{\text{ADAM}} - Y_{\text{REF}})$ equivalent $(Y_{\text{ADAM}} - Y_{\text{TEOM}})$

BUT

Berlin, May and September 1999



BUT

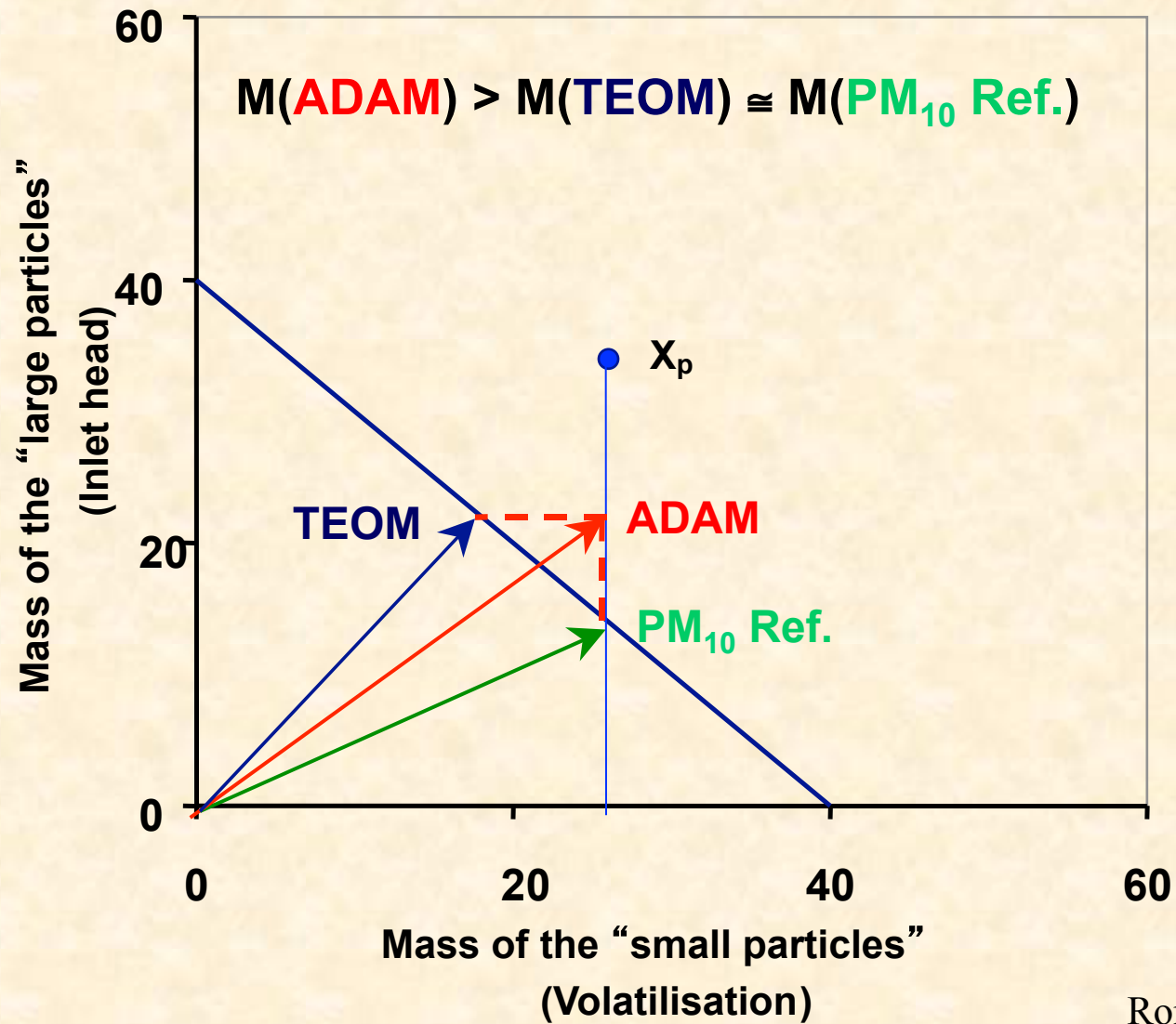
$(Y_{ADAM} - Y_{REF})$ and $(Y_{ADAM} - Y_{TEOM})$

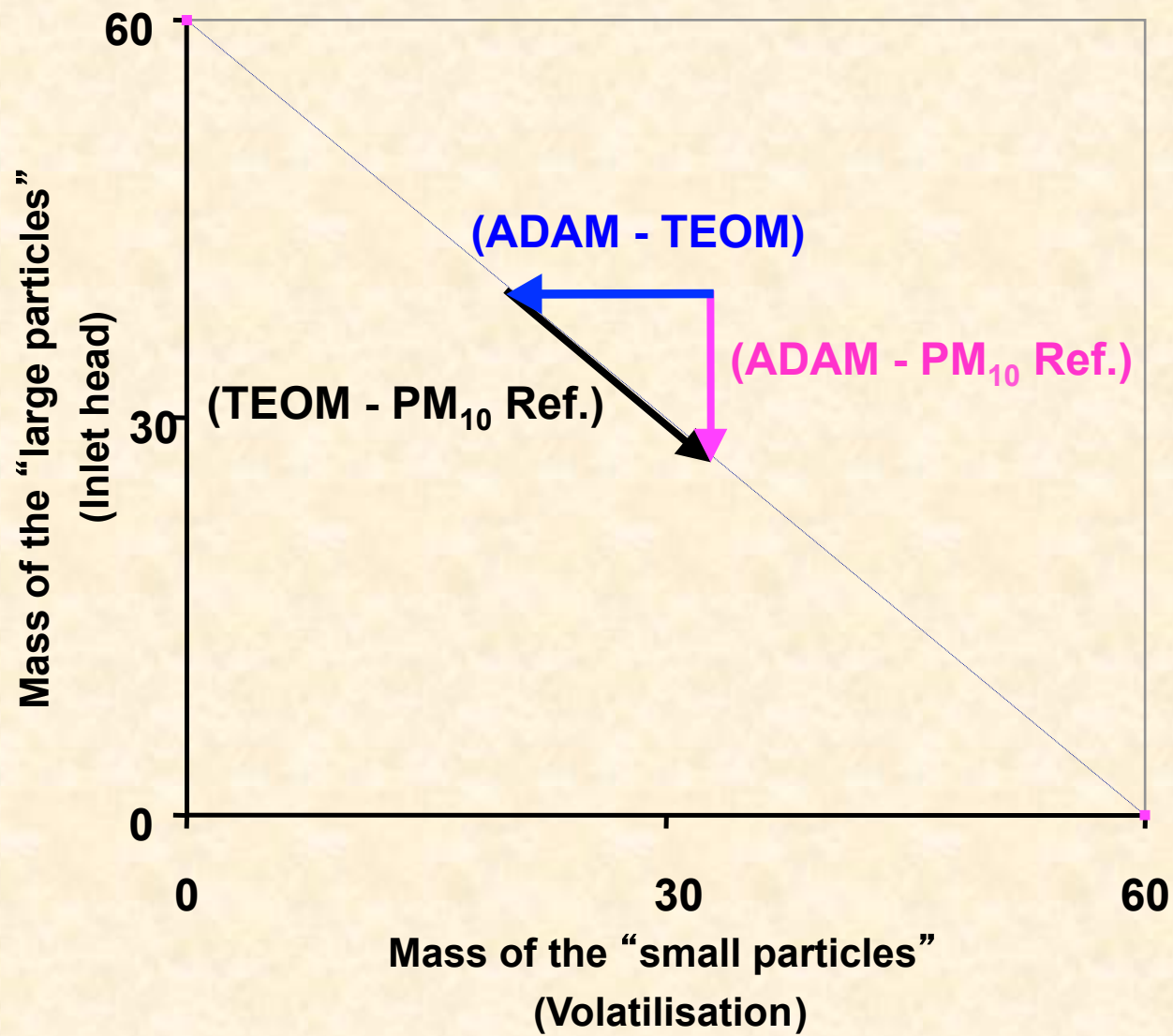
UNCORRELATED

then

TEOM and REF data are not **equivalent**

VECTORIAL SOLUTION





$$(Y_{ADAM} - Y_{REF}) \perp (Y_{ADAM} - Y_{TEOM})$$

Then

UNCORRELATED

SCALAR SOLUTION

$$(Y_{ADAM} - Y_{REF}) = (a_{EPA} - a_{REF}) X_L + \varepsilon$$

$$(Y_{ADAM} - Y_{TEOM}) = (1 - b_{TEOM}) X_S + \varepsilon$$

Then

UNCORRELATED

While

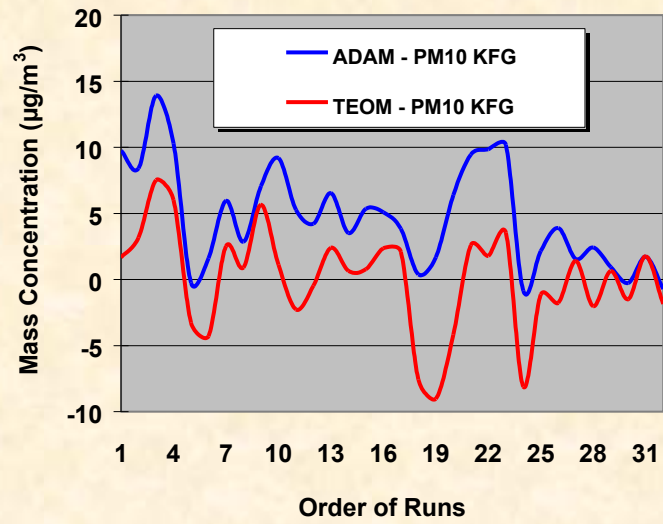
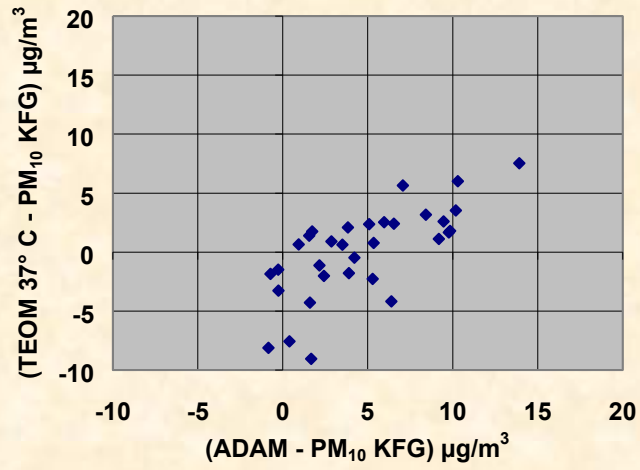
$(Y_{ADAM} - Y_{REF})$ and $(Y_{TEOM} - Y_{REF})$

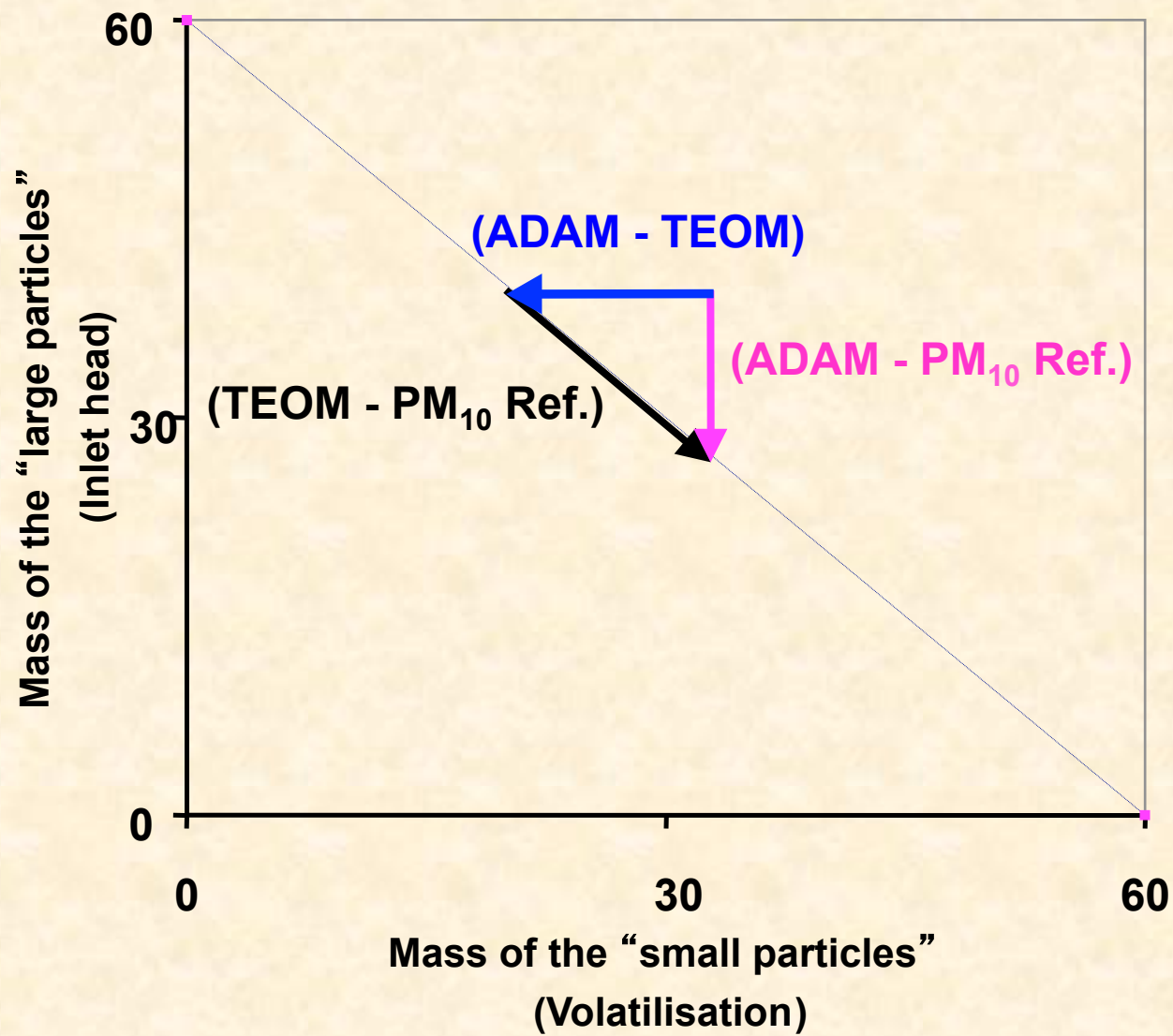
Must be expected partially correlated

$$(Y_{ADAM} - Y_{REF}) = (a_{EPA} - a_{REF}) X_L + \varepsilon$$

$$(Y_{TEOM} - Y_{REF}) = (b_{TEOM} - 1) X_S + (a_{EPA} - a_{REF}) X_L + \varepsilon$$

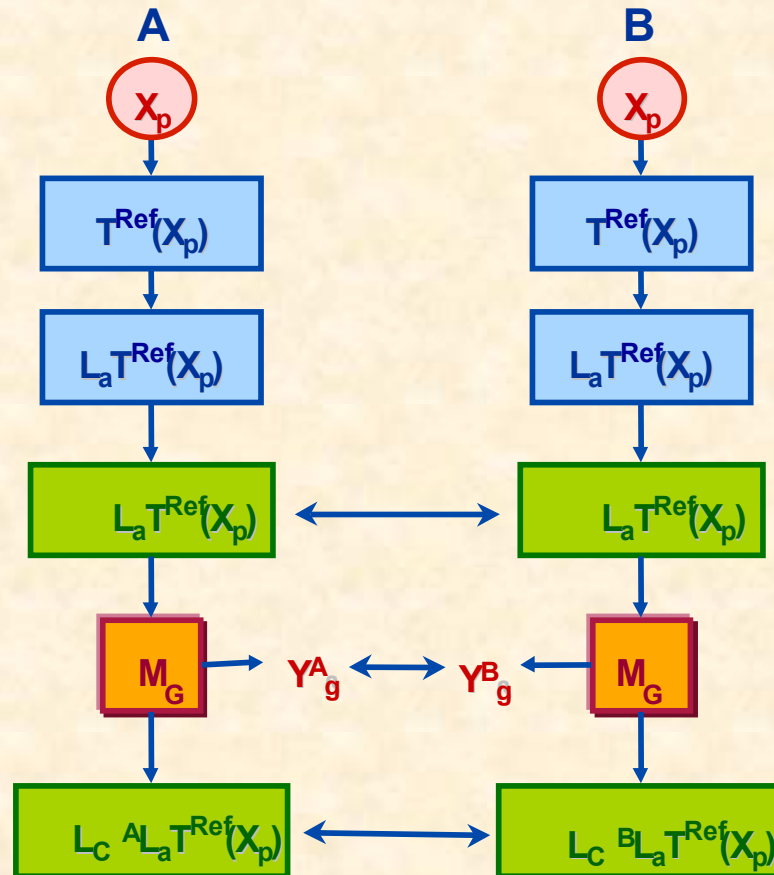
Berlin, May and September 1999



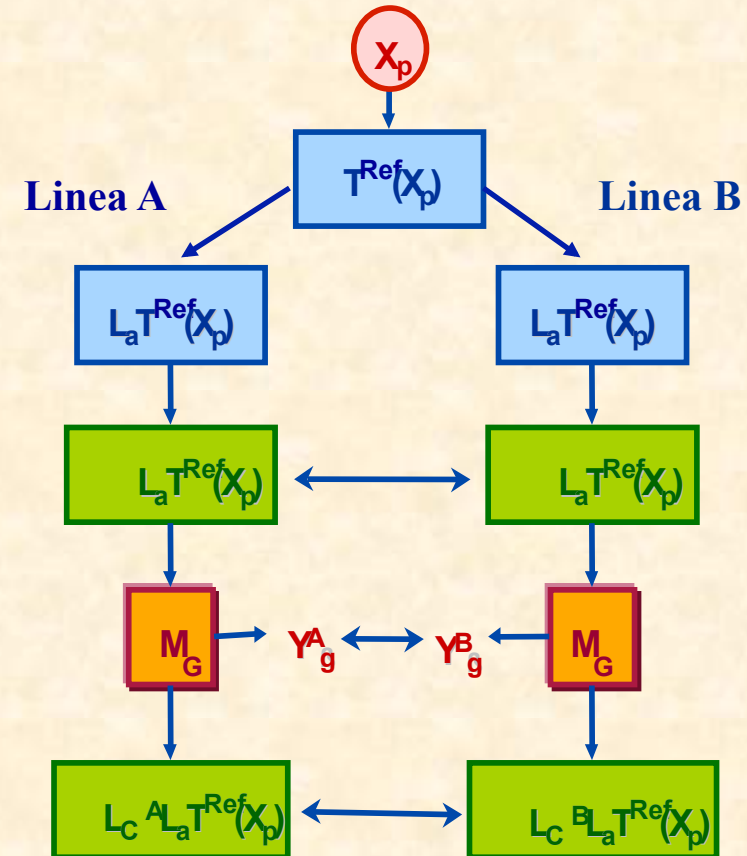


TECNICHE DI ACCUMULAZIONE CHE UTILIZZANO DIFFERENTI MATRICI FILTRANTI

DUE CAMPIONATORI



CAMPIONATORE A DUE CANALI



Confronto concentrazione di massa e composizione chimica

VALUTAZIONE DELLE TECNICHE DI MISURA DI CONCENTRAZIONE DI MASSA

Metodologia

Implementazione della metodologia

Gravimetrica

*Accuratezza intrinseca
elevatissima*

- *Fase di condizionamento*
- *Riproducibilità della misura nel tempo (tecnica differenziale)*
- *Cariche elettrostatiche*
- *Procedure operative*

Inerziale a oscillazione

*Accuratezza intrinseca
elevata*

- *Condizionamento della matrice di accumulazione*
- *Qualità progettuale*
- *Qualità strumentale*

Attenuazione beta

*Accuratezza intrinseca
buona*

- *Qualità progettuale*
- *Qualità strumentale*

Metodologie ottiche

*Accuratezza intrinseca
non definibile*

- *Calibrazione in situ*
- *Qualità progettuale*
- *Qualità strumentale*

**CONSIDERAZIONI SULL' UTILIZZO DI TECNICHE
OTTICHE PER LA DETERMINAZIONE DELLA
CONCENTRAZIONE DI MASSA DEL PM_x**

Nefelometri

Risposta fortemente dipendente da:

- superficie equivalente totale
- distribuzione granulometrica
- composizione chimica e contenuto di vapor d' acqua (indice di rifrazione)



Optical Particle Counter (OPC)

Risposta fortemente dipendente da:

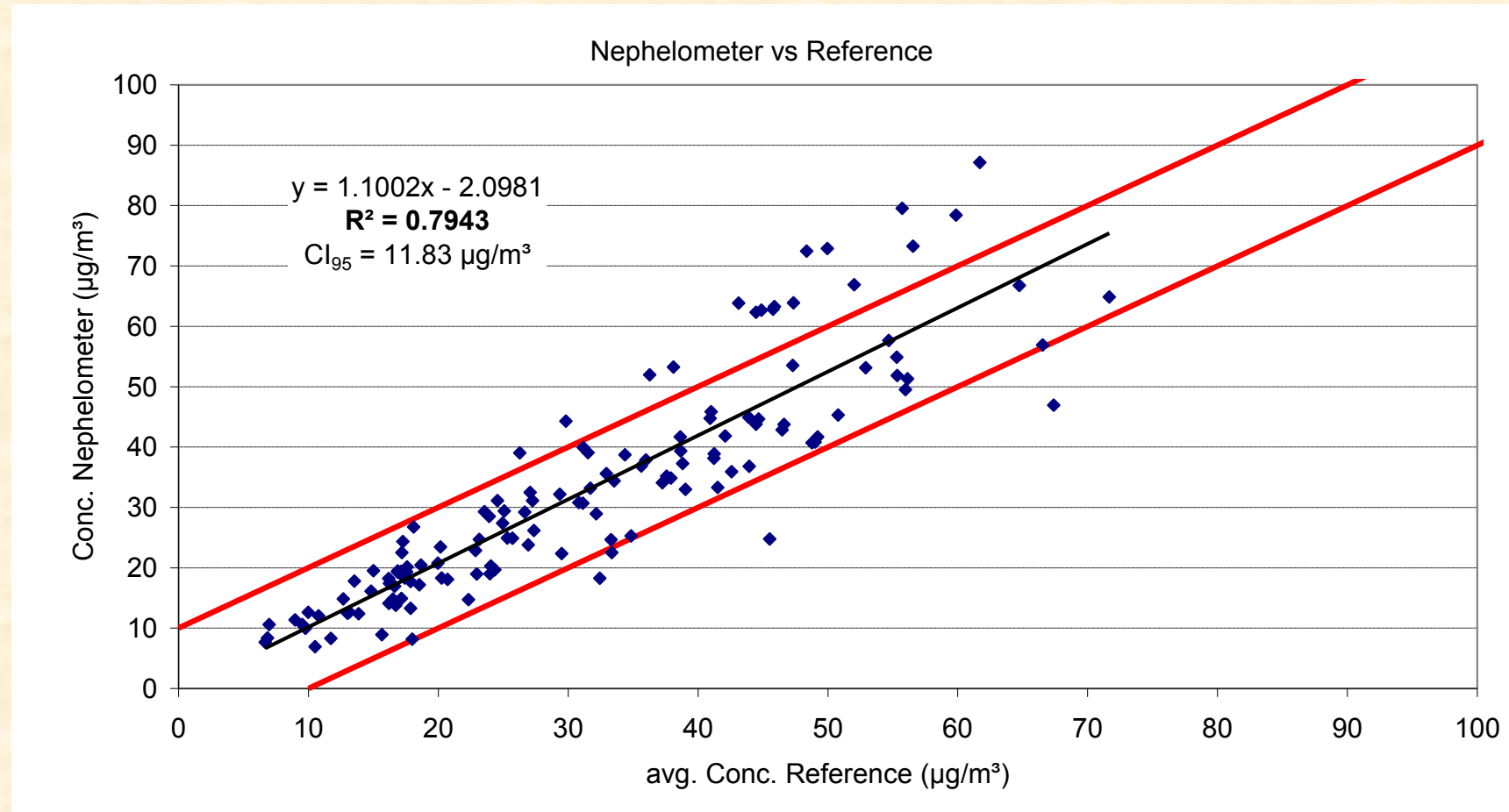
- composizione chimica e contenuto di vapor d' acqua (indice di rifrazione)
- fattore di forma delle particelle



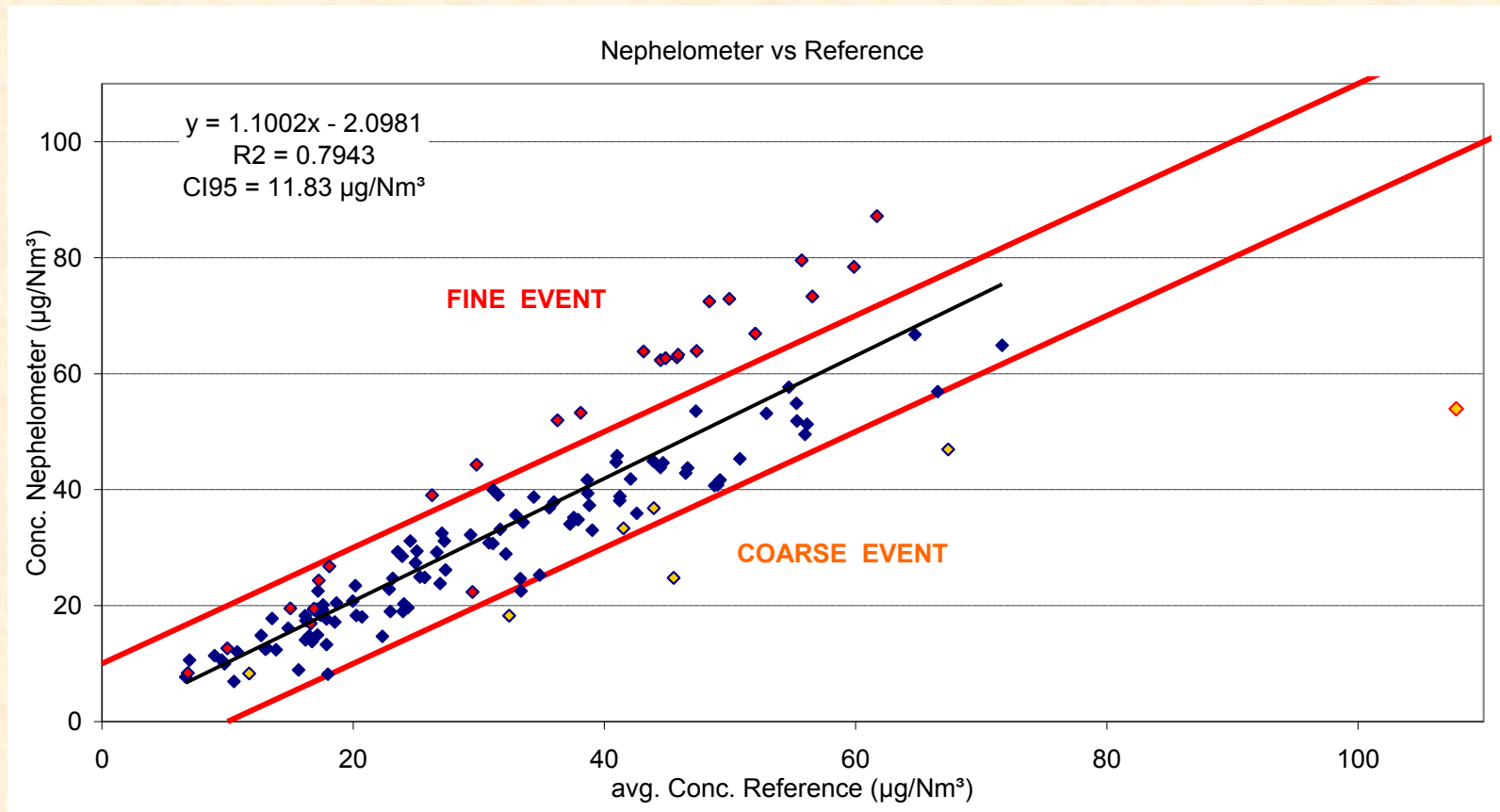
Impossibilità di eseguire corrette calibrazioni

Nessuna tracciabilità

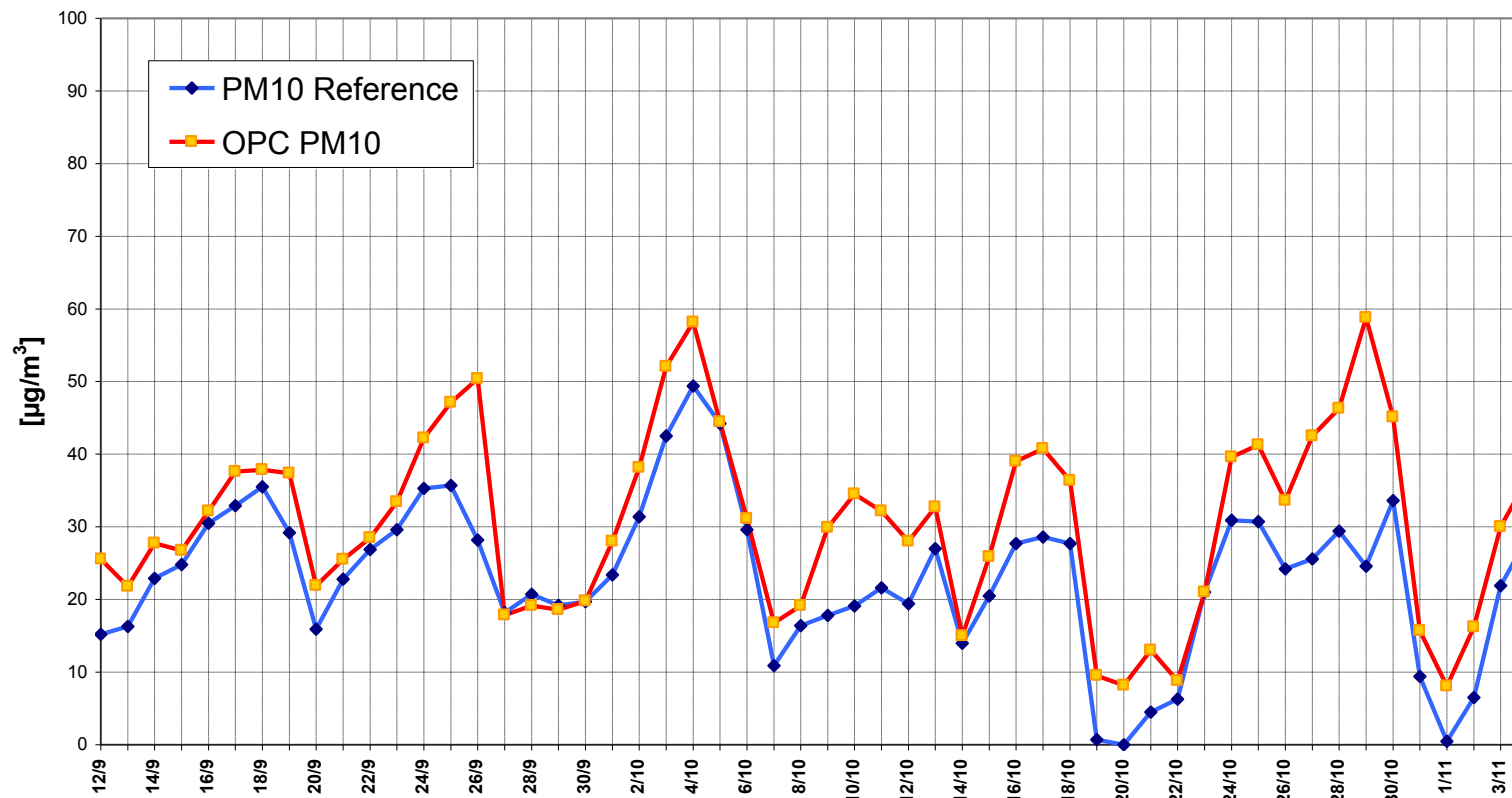
Nefelometro



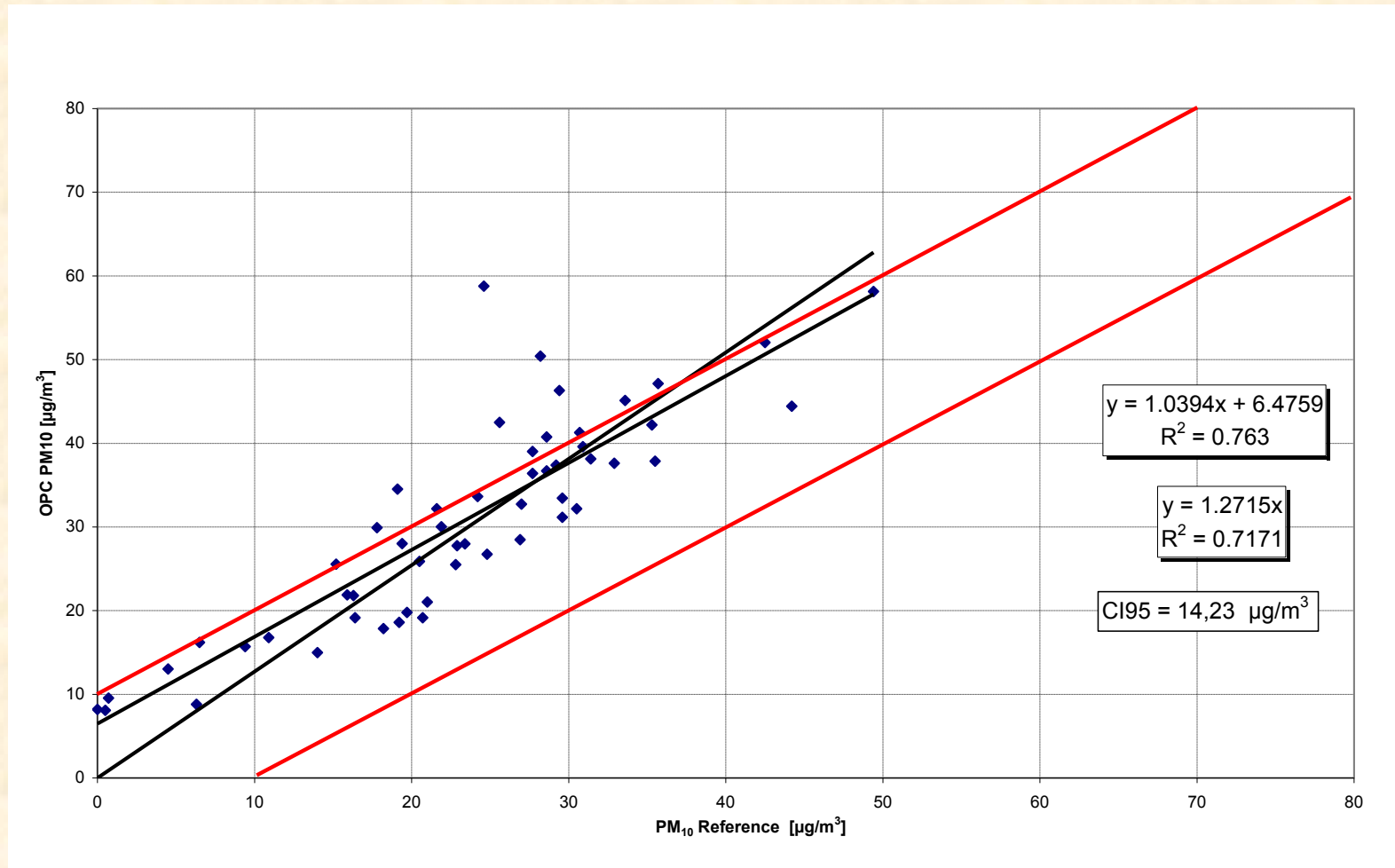
Nefelometro



Optical Particle Counter



Optical Particle Counter



**INFORMAZIONI IN TEMPO REALE SULLA
DISTRIBUZIONE DEL MATERIALE PARTICELLARE
FRA LE FRAZIONI “FINE” E “COARSE” COME
SUPPORTO ALLA VALUTAZIONE DEGLI EVENTI DI
INQUINAMENTO DI PM_x E ALL' ATTRIBUZIONE
DEL PESO RELATIVO DELLE POTENZIALI
SORGENTI.**

PM10 source apportionment studies

some considerations

PM10 can not be considered as a “monocomponent” pollutant

- PM10 is a “multicomponent” pollutant: two main modes

“fine” and “coarse” mode

- Fine and coarse mode are generally independent

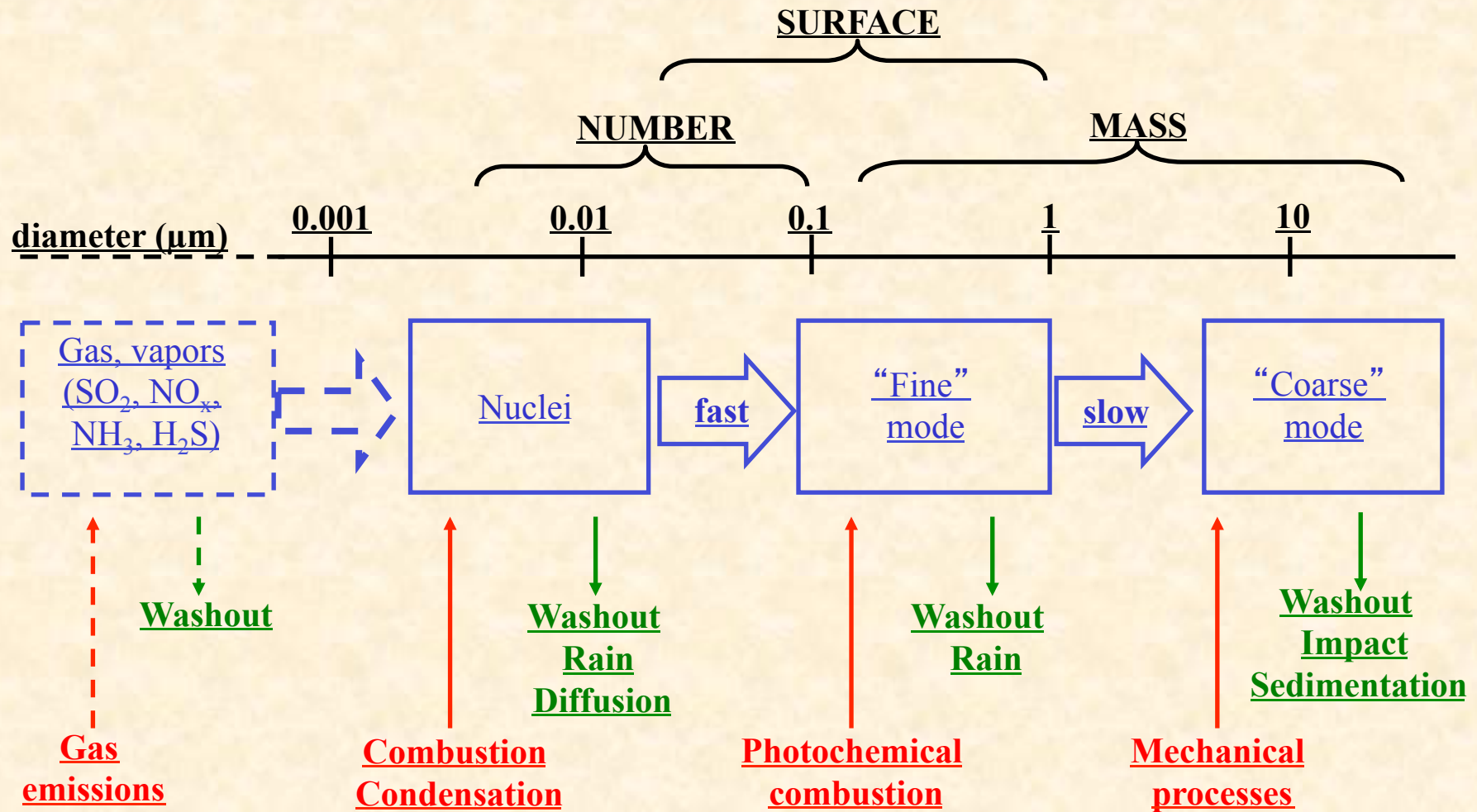
- different sources,

- different chemical composition,

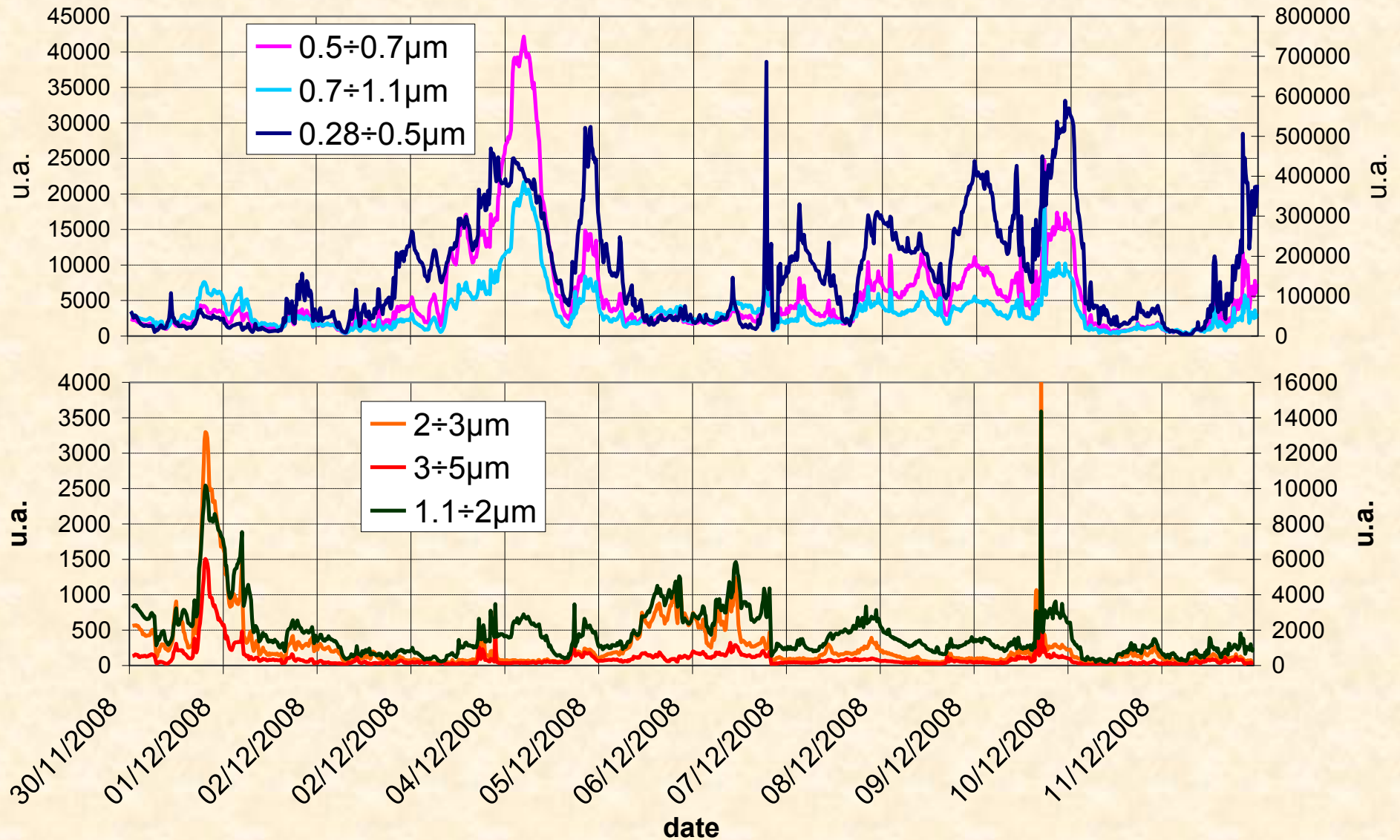
- different spatiotemporal trend

(dynamic of Planetary Boundary Layer)

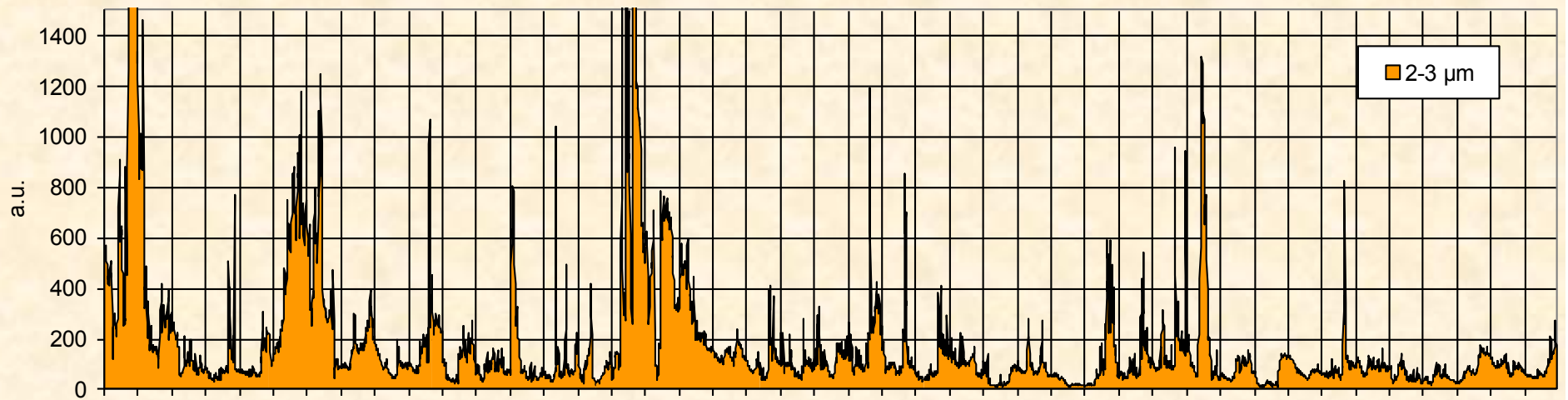
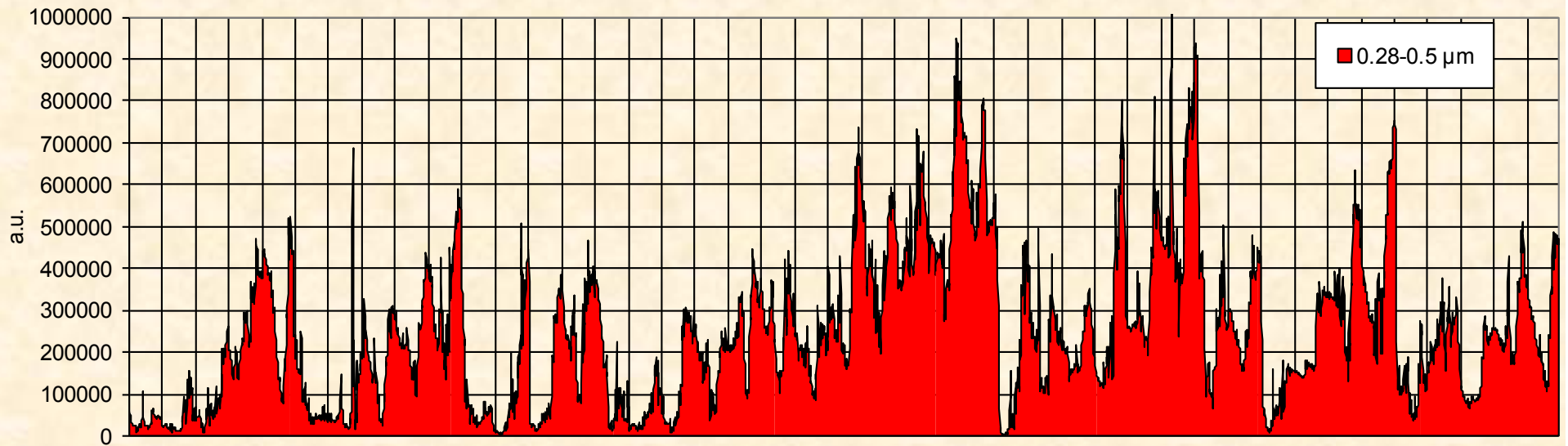
GRANULOMETRIC DISTRIBUTION OF AEROSOL IN THE ATMOSPHERE



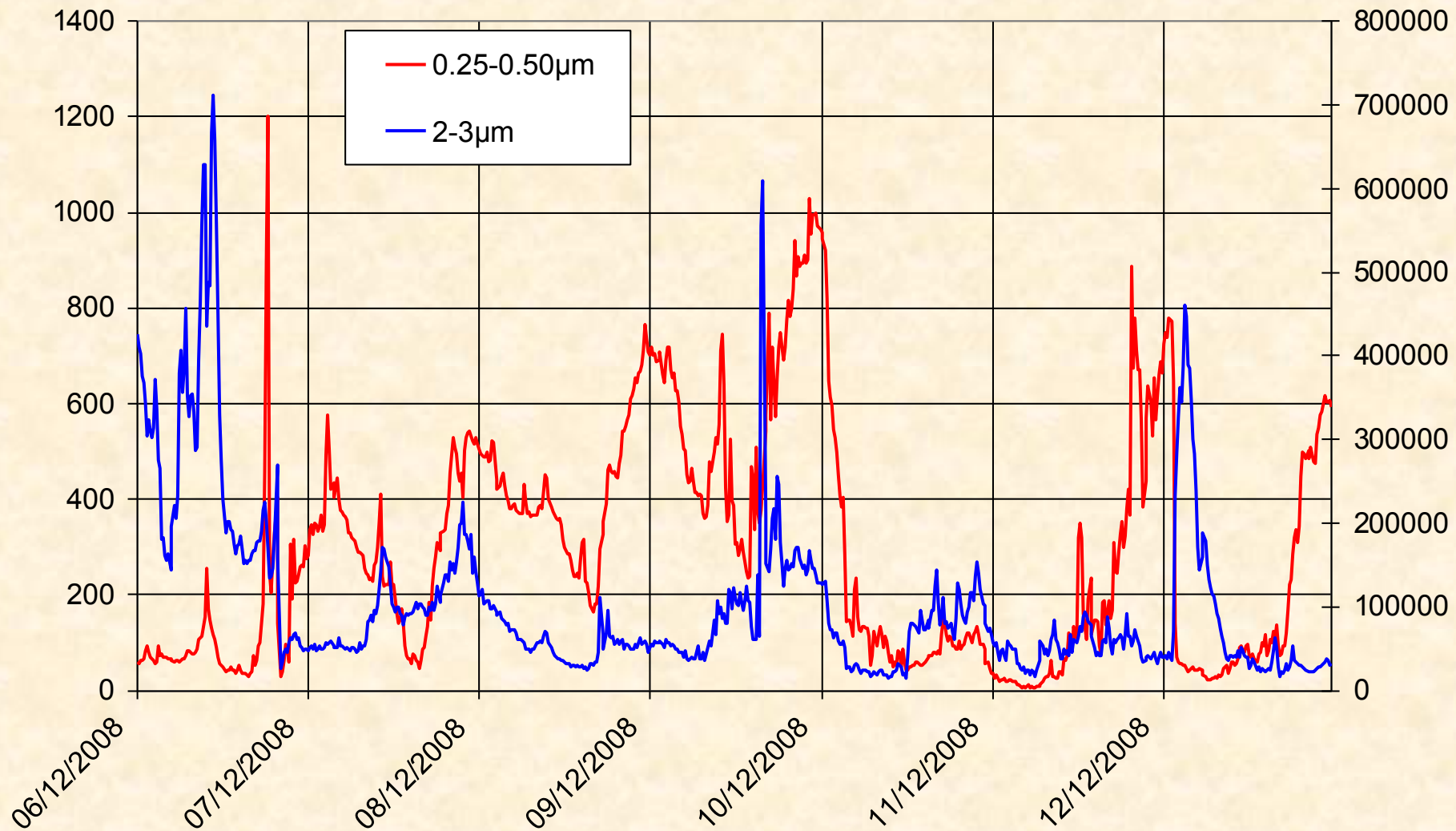
30-11-2008 / 11-01-2009 FINE AND COARSE MODE TREND



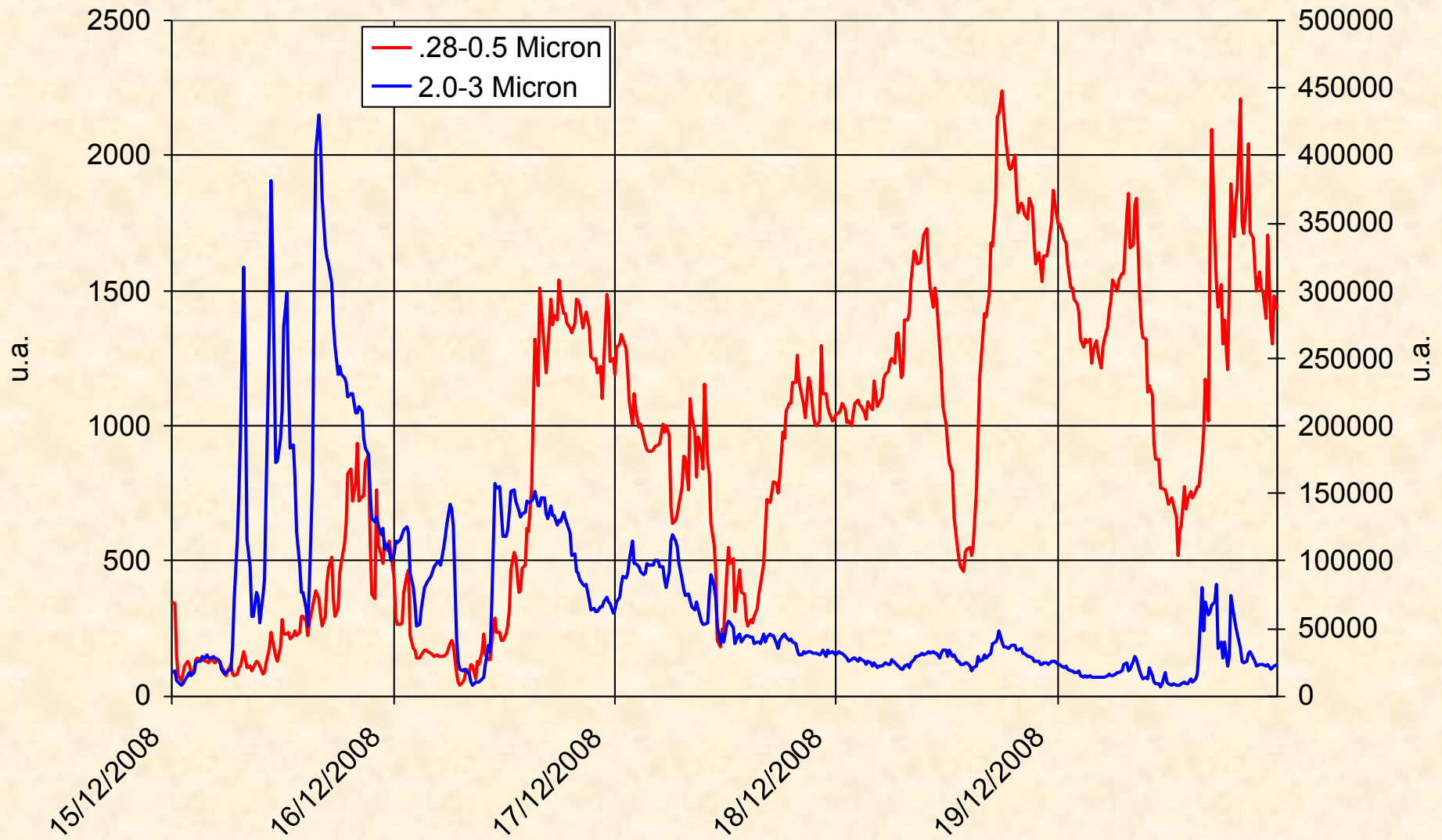
30-11-2008 / 11-01-2009 FINE AND COARSE MODE TREND
(0.28÷0.50 μ m & 2÷3 μ m)



06-12-2008 / 12-12-2008 FINE AND COARSE MODE TREND
(0.28÷0.50 μ m & 2÷3 μ m)



15-12-2008 / 19-12-2008 FINE AND COARSE MODE TREND (0.28÷0.50 μ m & 2÷3 μ m)



INTERPRETATION OF THE ATMOSPHERIC POLLUTION DATA

1. **Emission fluxes**
2. **Chemico-physical transformations in
atmosphere**
3. **Vertical transport and advective processes**

Pollutant concentration temporal trend on ground level: general differential equation

$$\frac{\partial C}{\partial t} = \alpha[\Phi_p + \Phi_s] - \beta(C) + \sum P_i - \sum L_j - L_s[\alpha; \beta(C)] + Adv$$

- C = pollutant concentration
- α = stability term
- Φ_p = primary emission flux; Φ_s = emission flux from surfaces
- $\beta(C)$ = vertical mass exchange due to diffusion
- P_i = i -th production process
- L_j = j -th removal process
- L_s = dry deposition removal
- Adv = advective term

How we can describe α and β ?

$$\frac{\partial C}{\partial t} = \alpha [\Phi_p + \Phi_s] - \beta(C) + \sum P_i - \sum L_j - L_s[\alpha; \beta(C)] + Adv$$

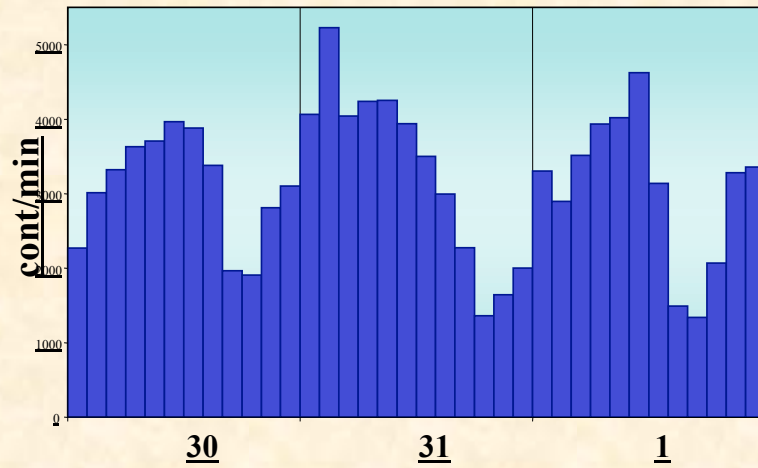
Vertical mixing status near the ground

RADON AS TRACER

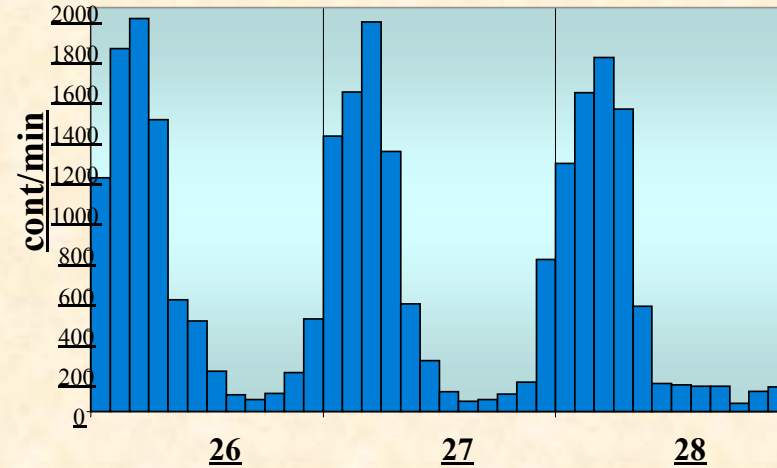
$$\frac{\partial C_R(t)}{\partial t} = \alpha(\phi_R) - \beta(C_R) + Adv$$

Constant emission (Φ) on the interested space and
time scale

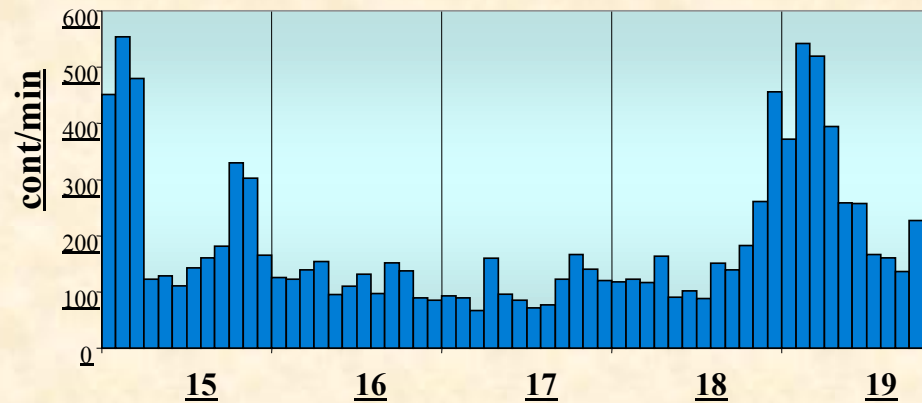
Concentration temporal trend of radon decay products



Dec '97-Jan '98



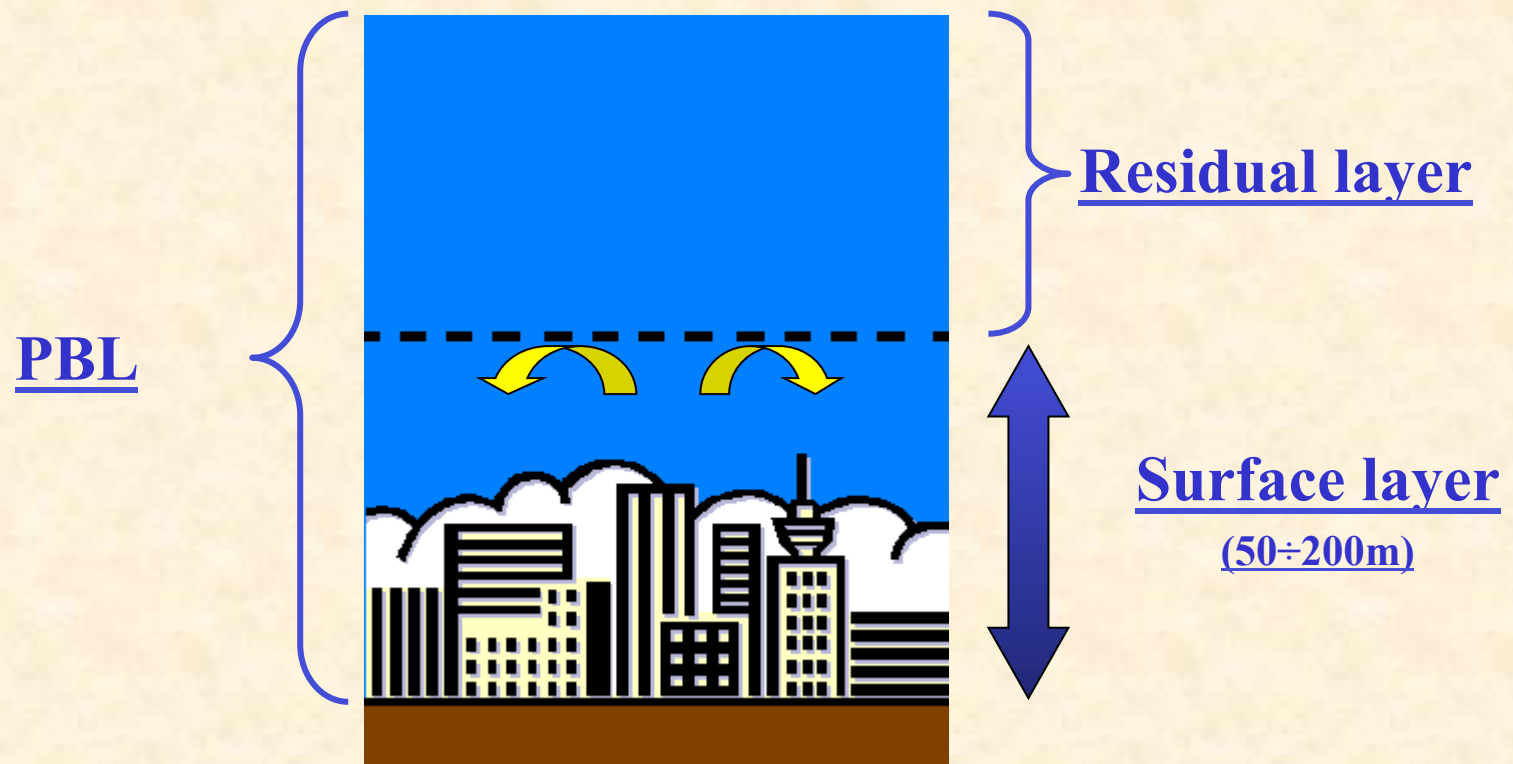
June 2001



April 1998

$$\frac{\partial C_R(t)}{\partial t} = \alpha(\phi_R) - \beta(C_R) + Adv$$

STABILITY CONDITIONS



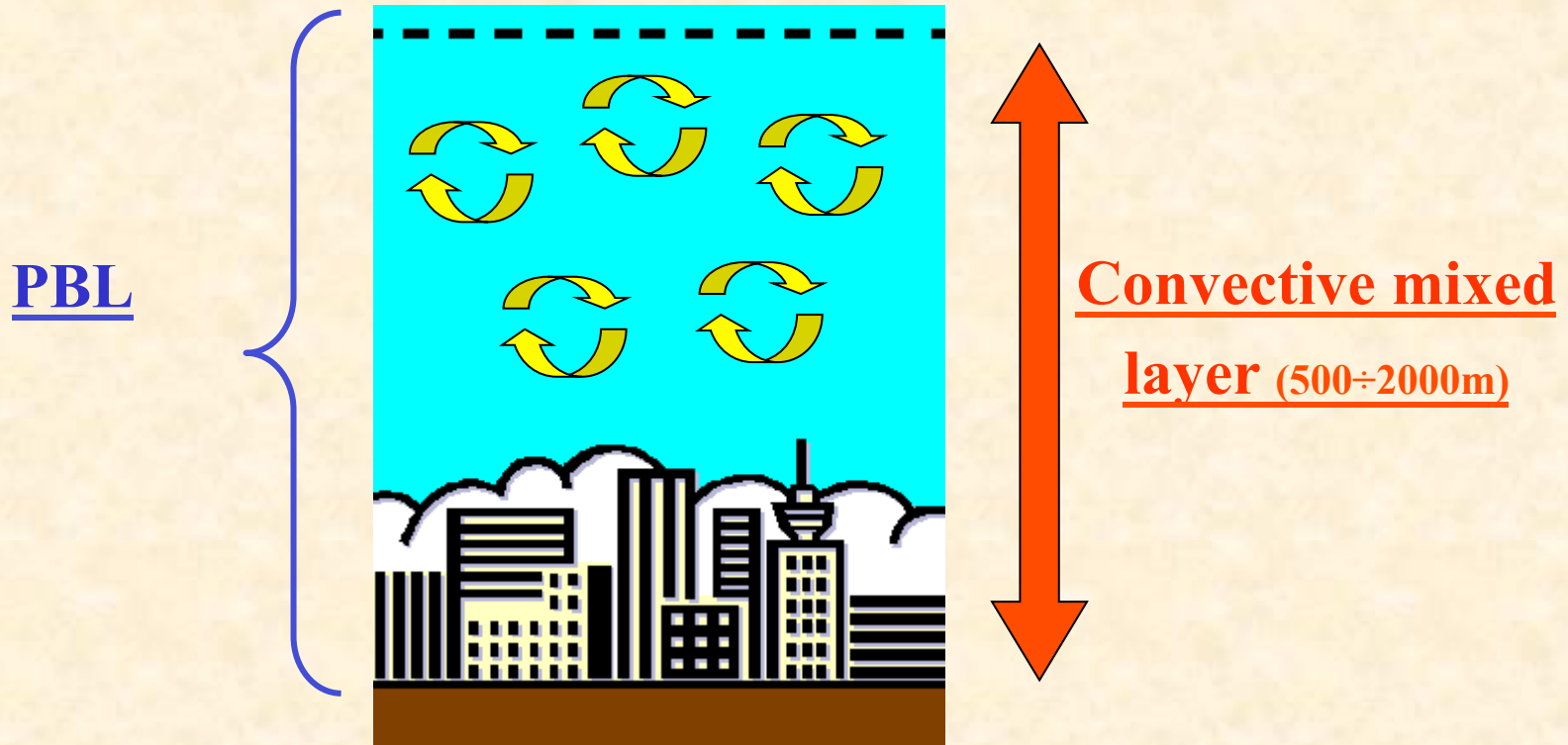
$$\frac{\partial C_R(t)}{\partial t} = \alpha(\phi_R) - \beta(C_R) + Adv$$

with

$$\beta(C_R) \rightarrow 0 \text{ e } Adv \rightarrow 0$$

STABILITY CONDITIONS: relevance of fine mode
(primary and secondary components)

STRONG MIXING AND ADVECTIVE CONDITIONS



$$\frac{\partial C_R(t)}{\partial t} = \alpha(\phi_R) - \beta(C_R) + Adv$$

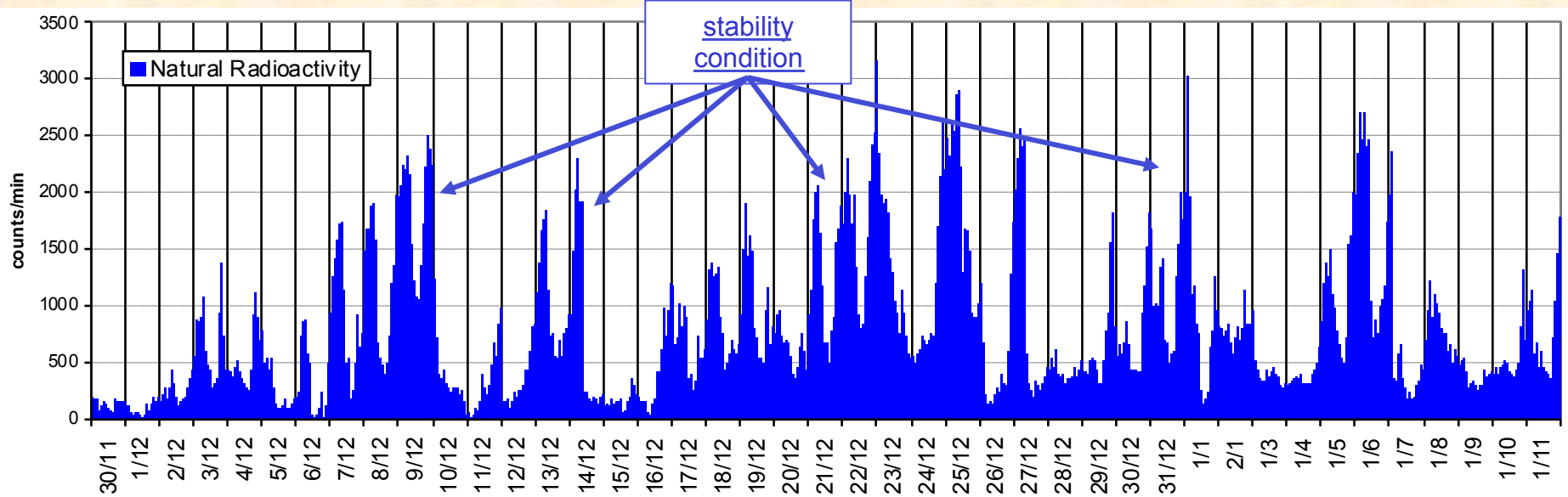
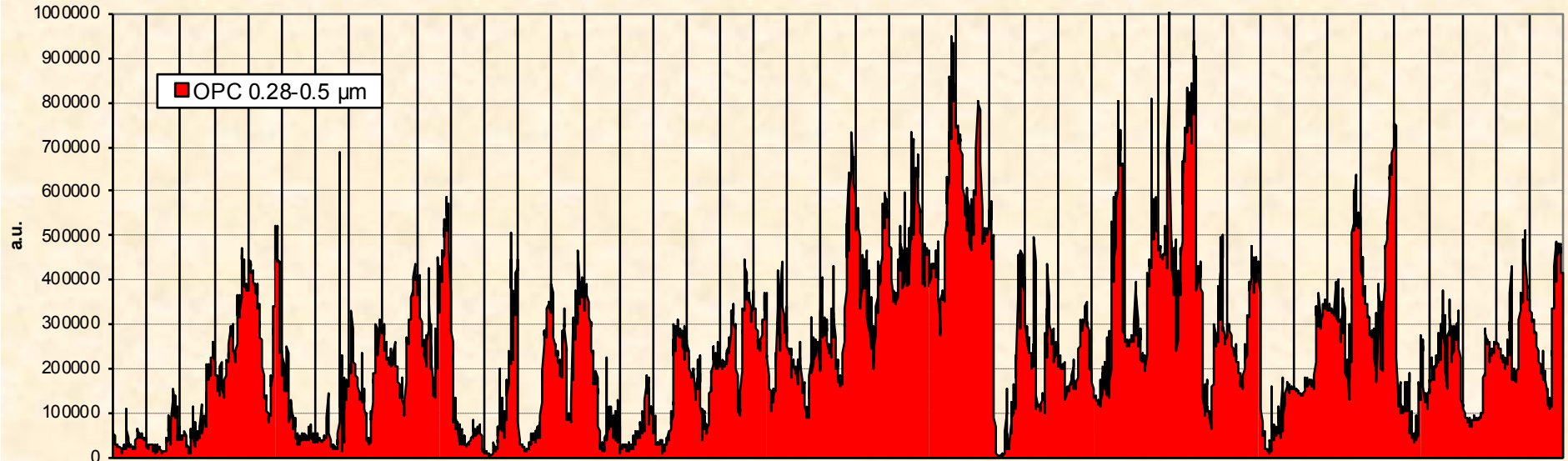
with

$$\alpha(\phi_R) \rightarrow 0$$

MIXING CONDITIONS: potential relevance of coarse mode

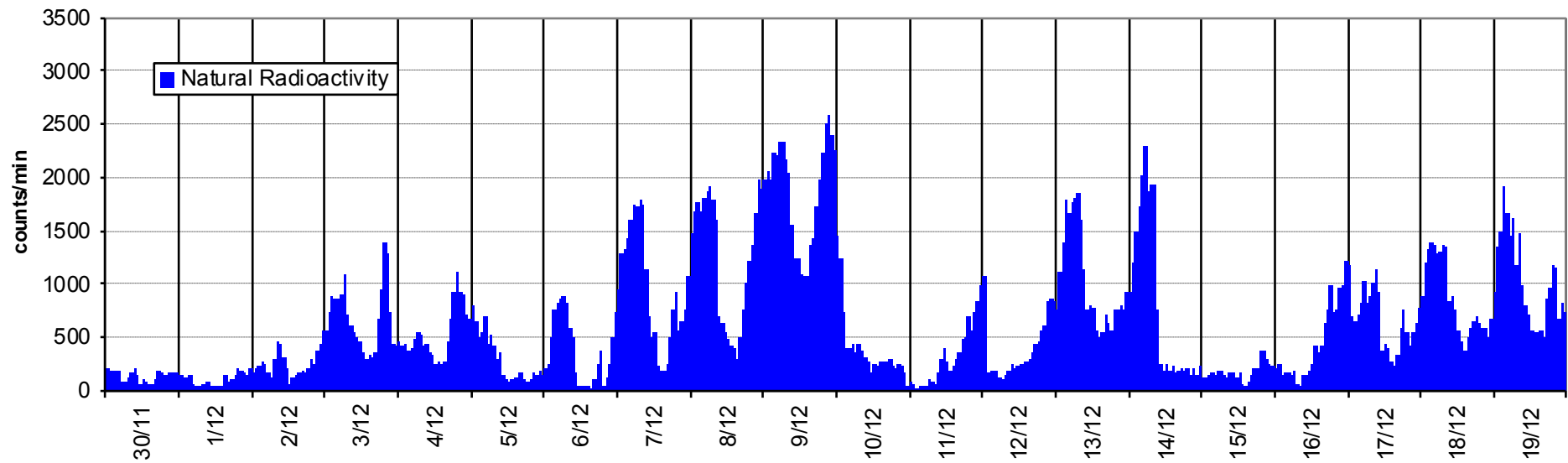
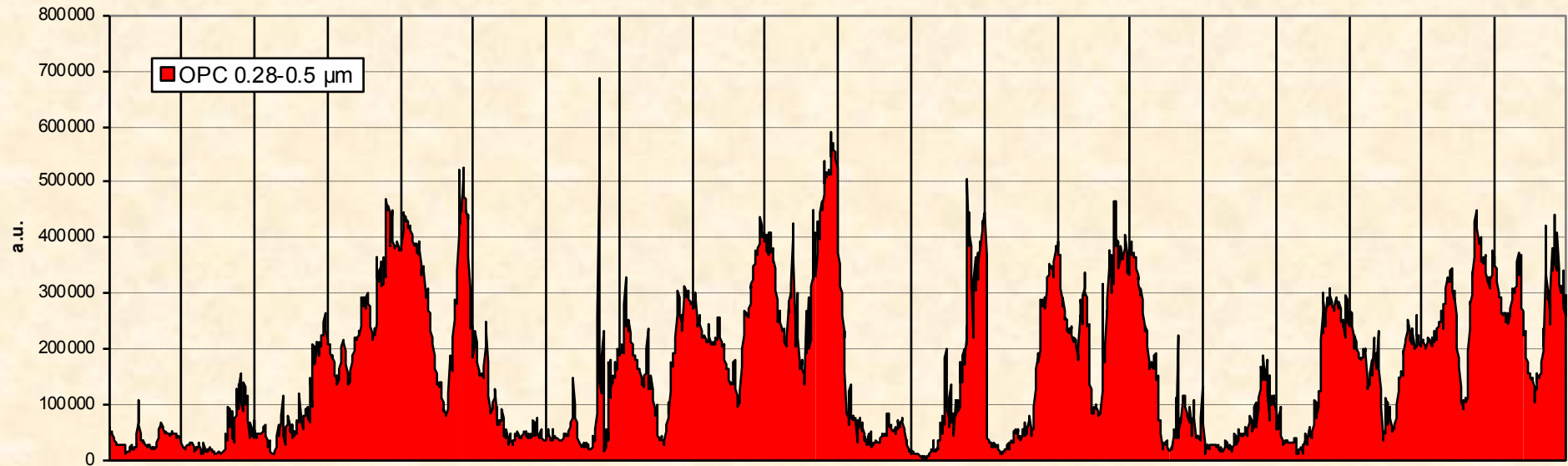
30-11-2008 / 11-01-2009 FINE MODE TREND

(0.28÷0.5 μ m)



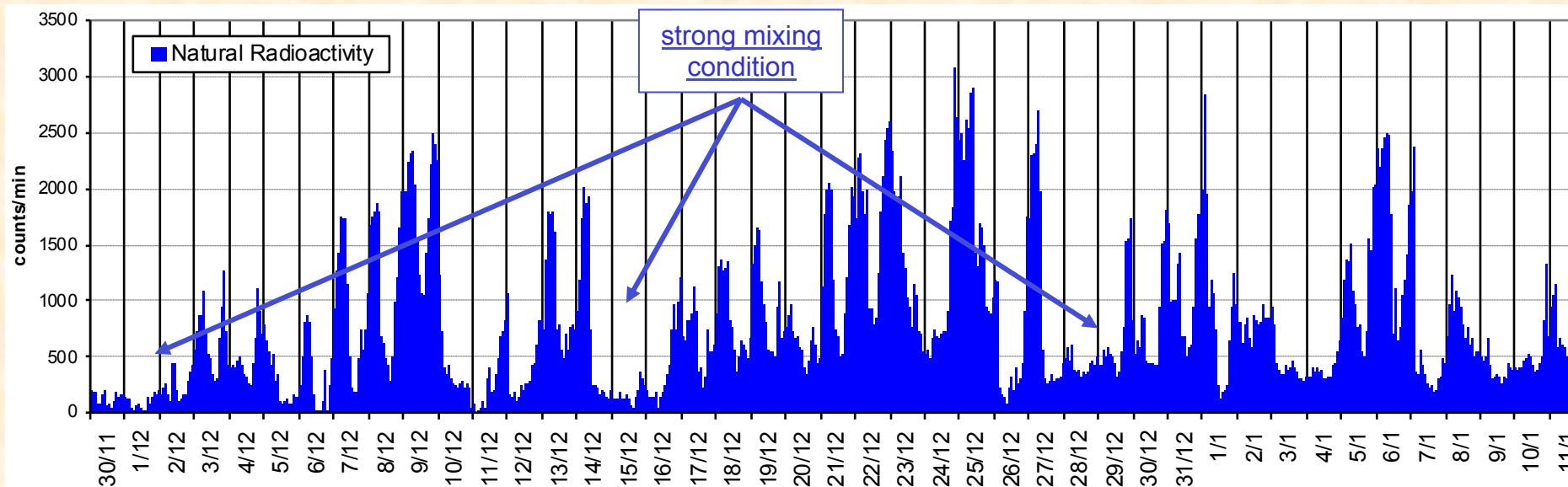
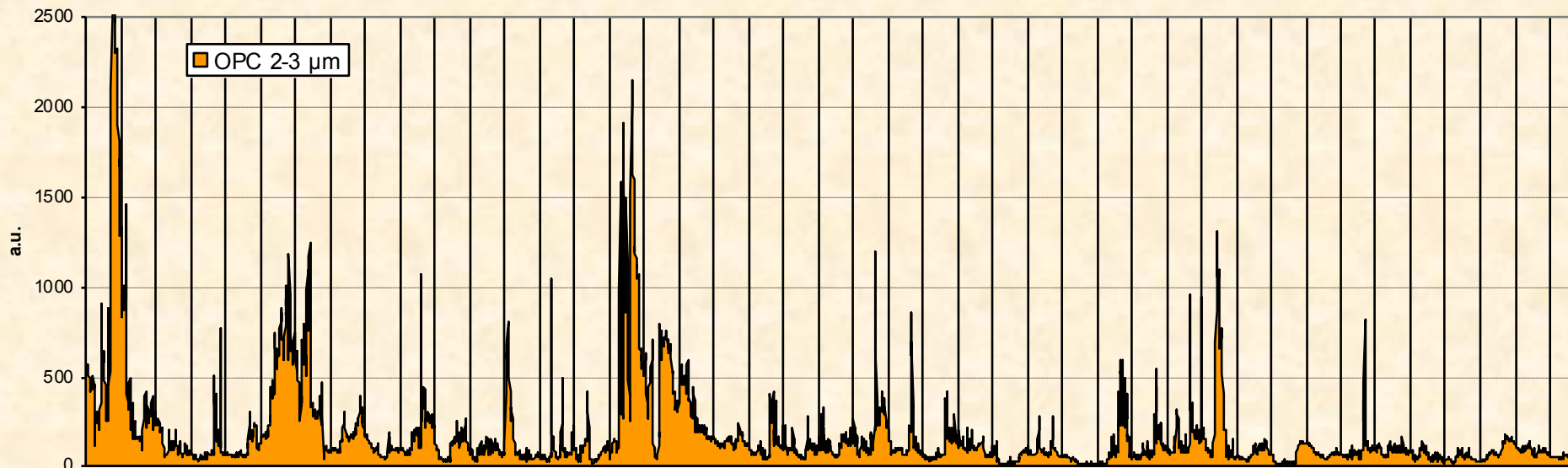
30-11-2008 / 19-12-2008 FINE MODE TREND

(0.28÷0.5 μ m)



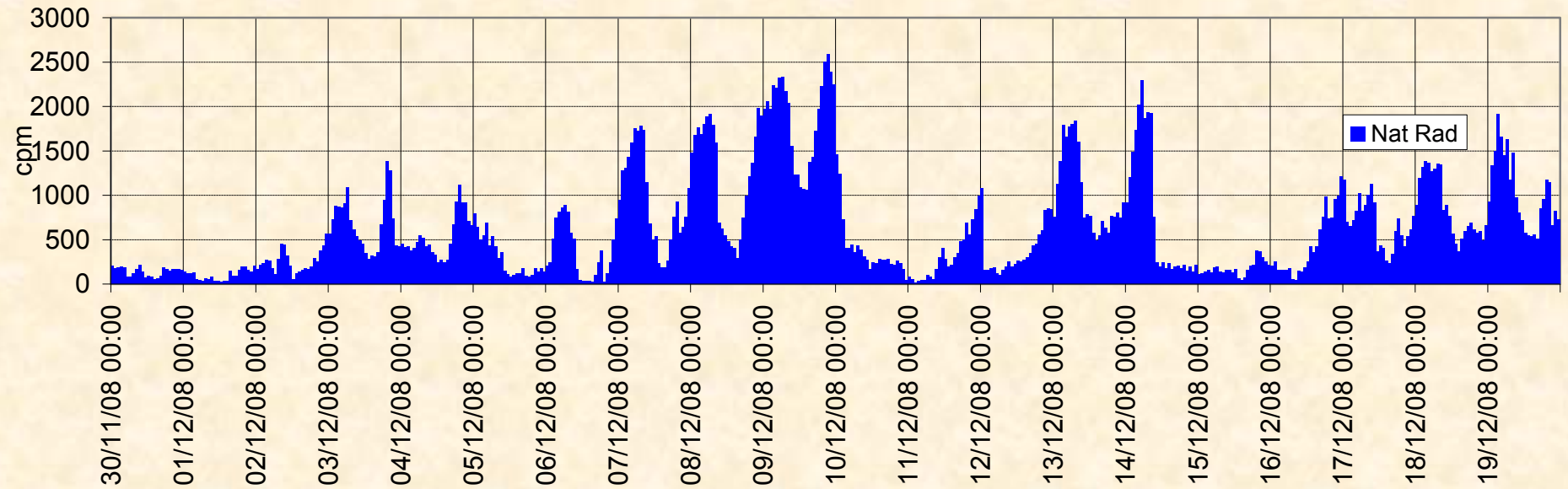
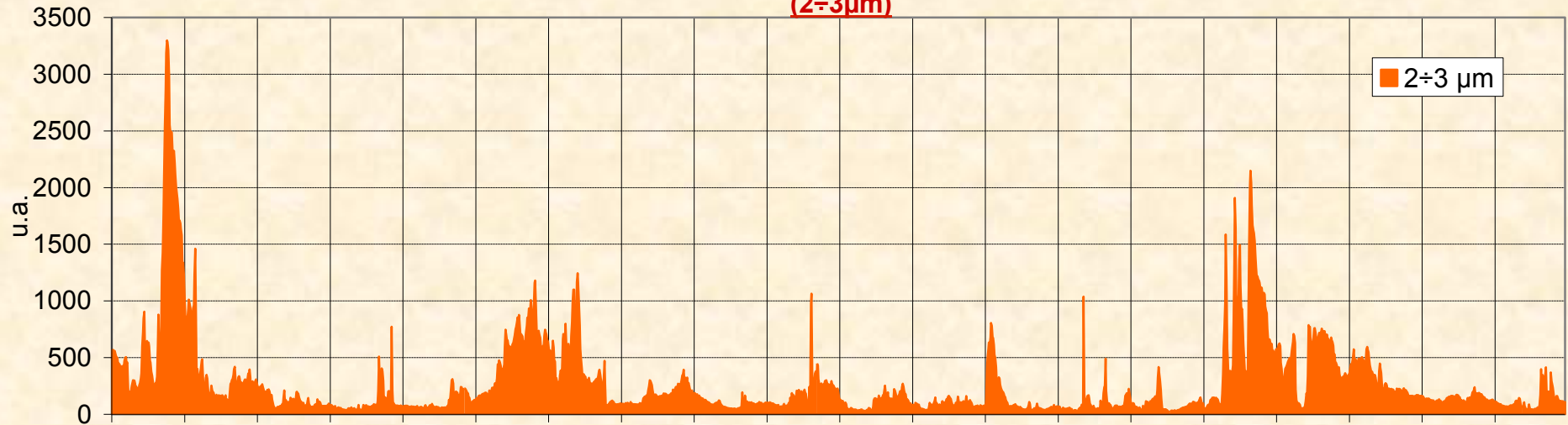
30-11-2008 / 11-01-2009 COARSE MODE TREND

(2÷3µm)

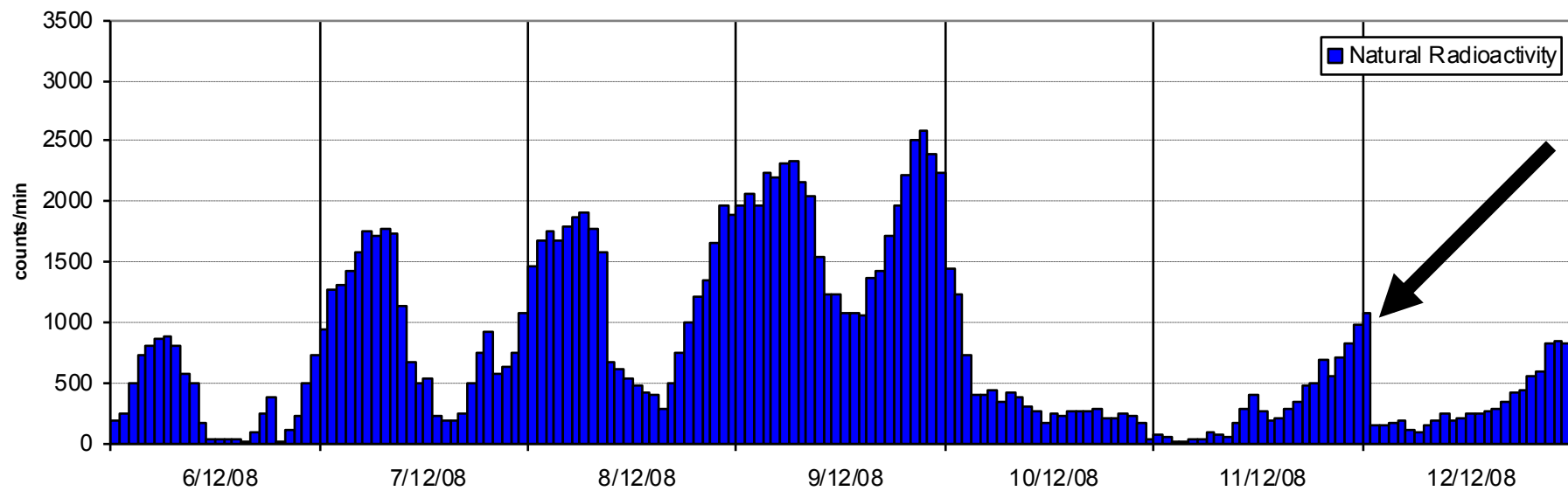
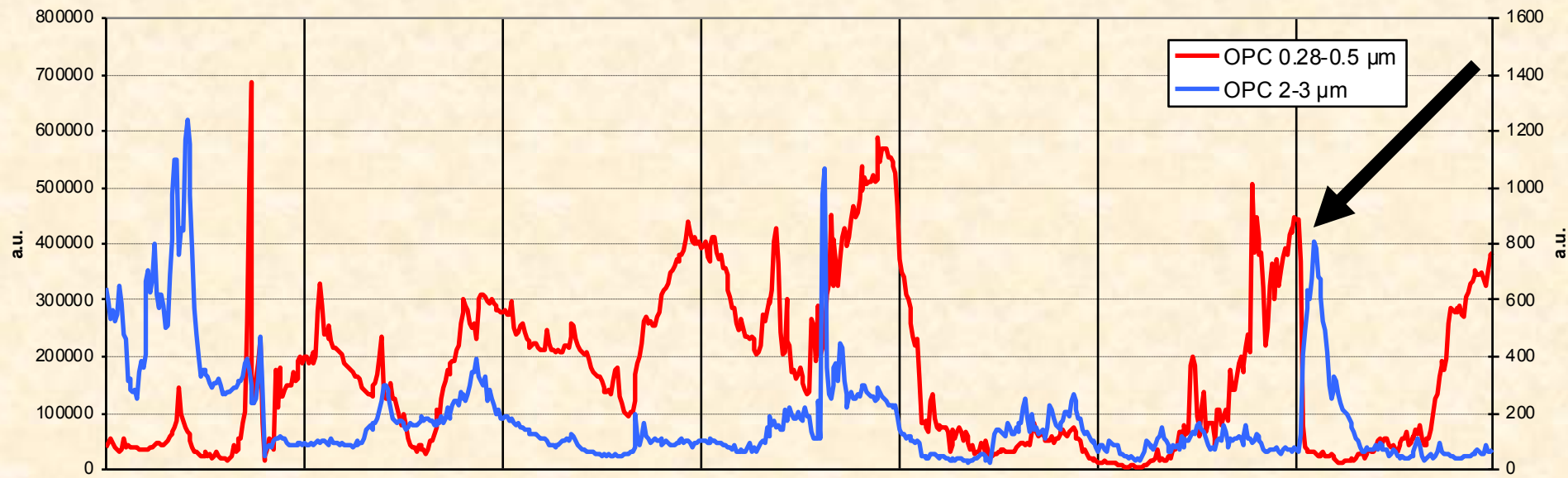


30-11-2008 / 11-01-2009 COARSE MODE TREND

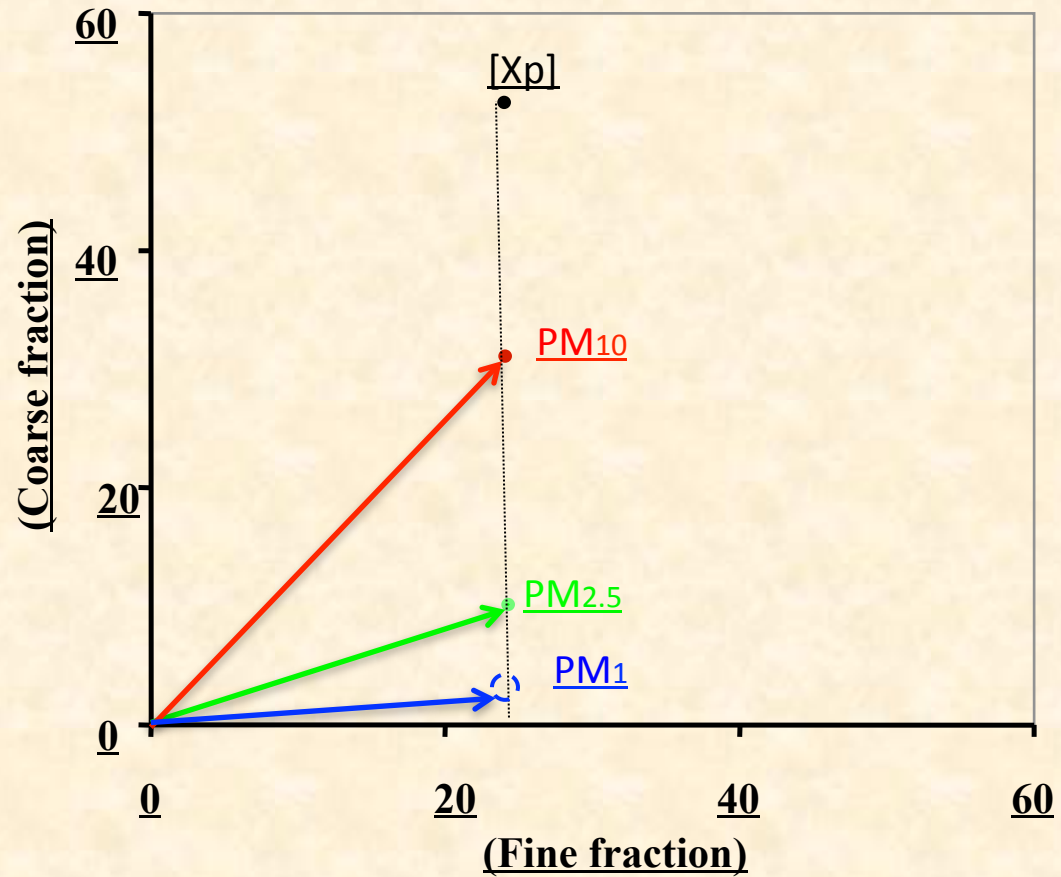
(2÷3 μ m)



06-12-2008 / 12-12-2008 FINE AND COARSE MODE TREND



PM_x VECTORIAL REPRESENTATION



Coarse fraction:

Natural sources,

Mechanical processes, ...

Fine fraction:

Combustion,

Secondary pollutants, ...

PM10 source apportionment studies

- Availability of “fine” and “coarse” mode representative samples (ie PM10, PM2.5, PM1 ...) → VECTORIAL APPROACH

- Mass concentration

- Chemical composition (Ionic composition, metals, carbon, P.A.H., nitro P.A.H. ...)

- Granulometric distribution (spatiotemporal evolution)

- Quasi real time number distribution

- Quasi real time mass distribution

- Meteorological data

- Dynamic of PBL

- Advective conditions

Instrumental configuration used for PM10 source apportionment studies

- SWAM 5a Dual Channel + OPC Multichannel
- PBL Mixing Monitor

SWAM 5a Dual Channel & OPC Multichannel

OPC Multichannel

- Size distribution trend in mass mode accumulation $d_o > 0.28 \mu\text{m}$ (optical diameter)
- Operative range divided into 8 dimensional intervals

Real time information about number concentration in *fine* and *coarse* mode

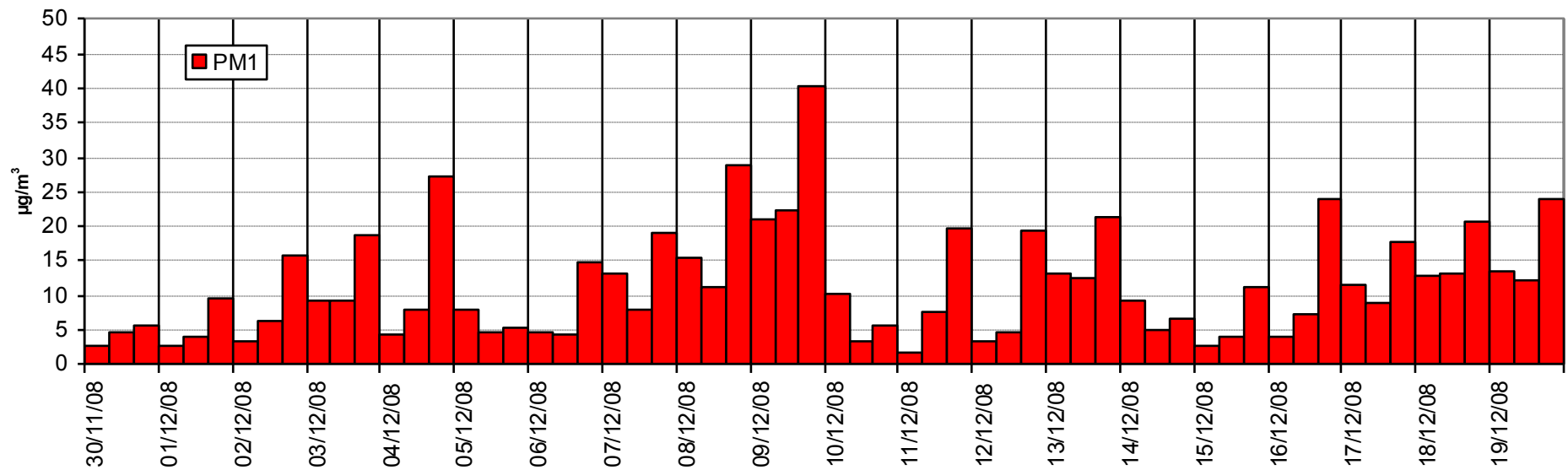
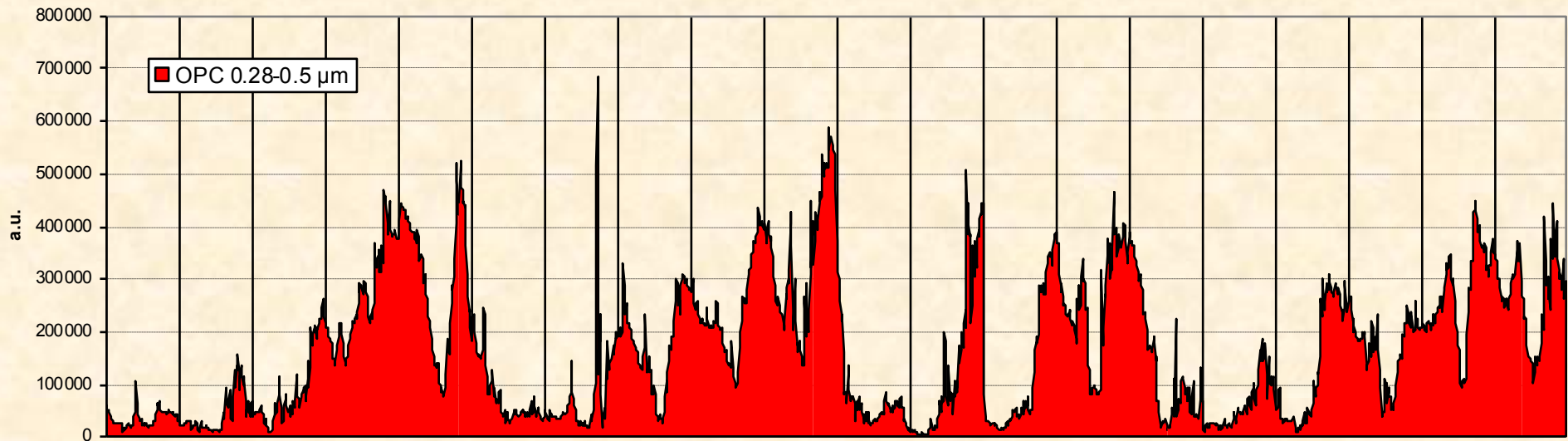
SWAM 5a Dual Channel

- Two or more representative samples of two different PM_x fractions (available for subsequent chemical analysis)
- Cycle timing: 8h, 12h, 24h,...

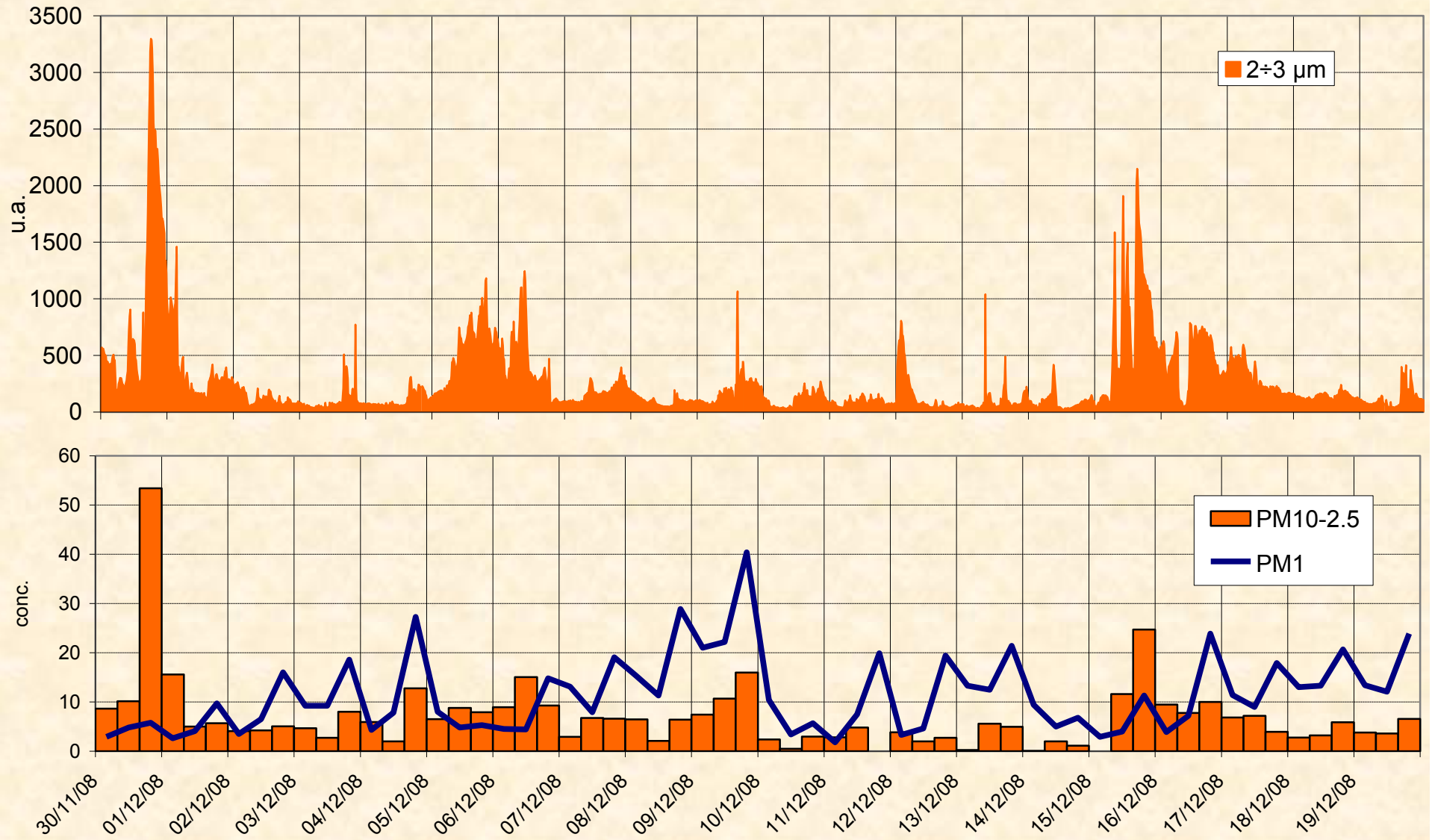
PM₁₀, PM_{2.5}, PM₁ mass concentration data (uncertainty $< 0.5 \mu\text{g}/\text{m}^3$).

Quasi real-time PM₁, PM_{2.5}, PM_{10-2.5} mass concentration data

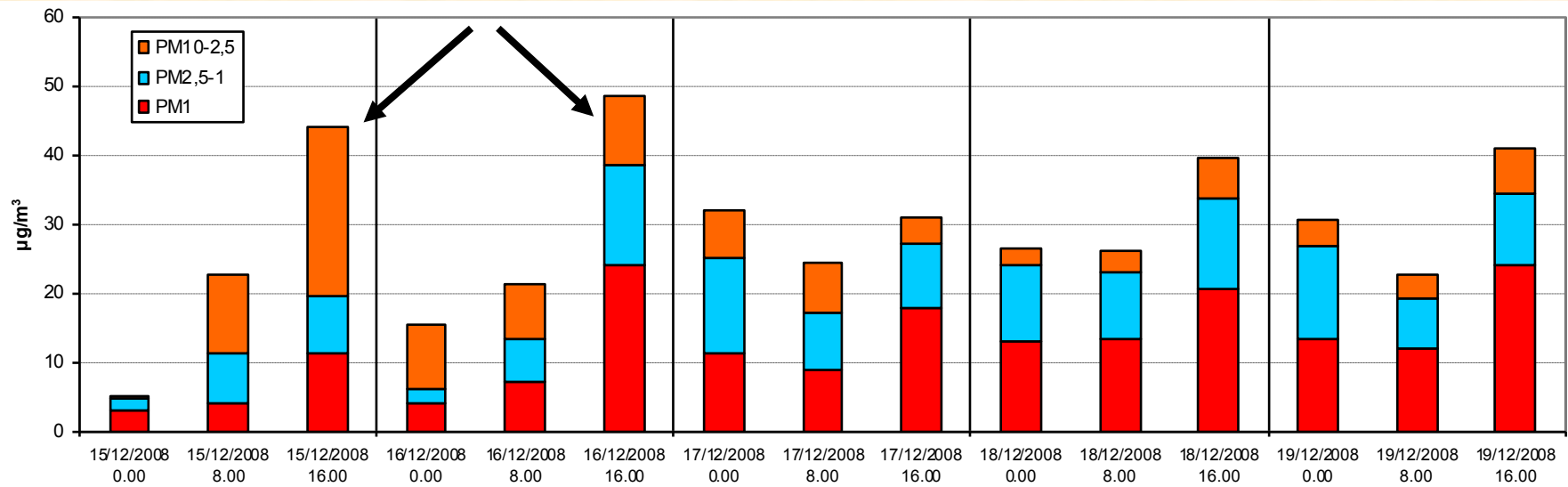
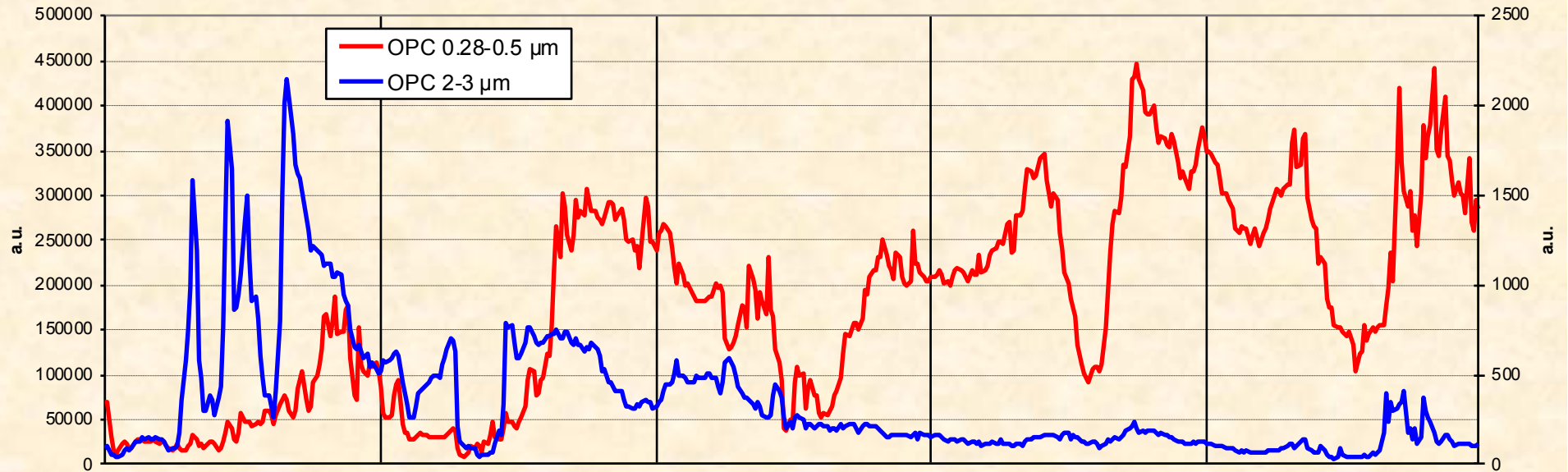
30-11-2008 / 11-01-2009 FINE MODE TREND (0.28÷0.5µm)



30-11-2008 / 11-01-2009 COARSE MODE TREND (2÷3µm)

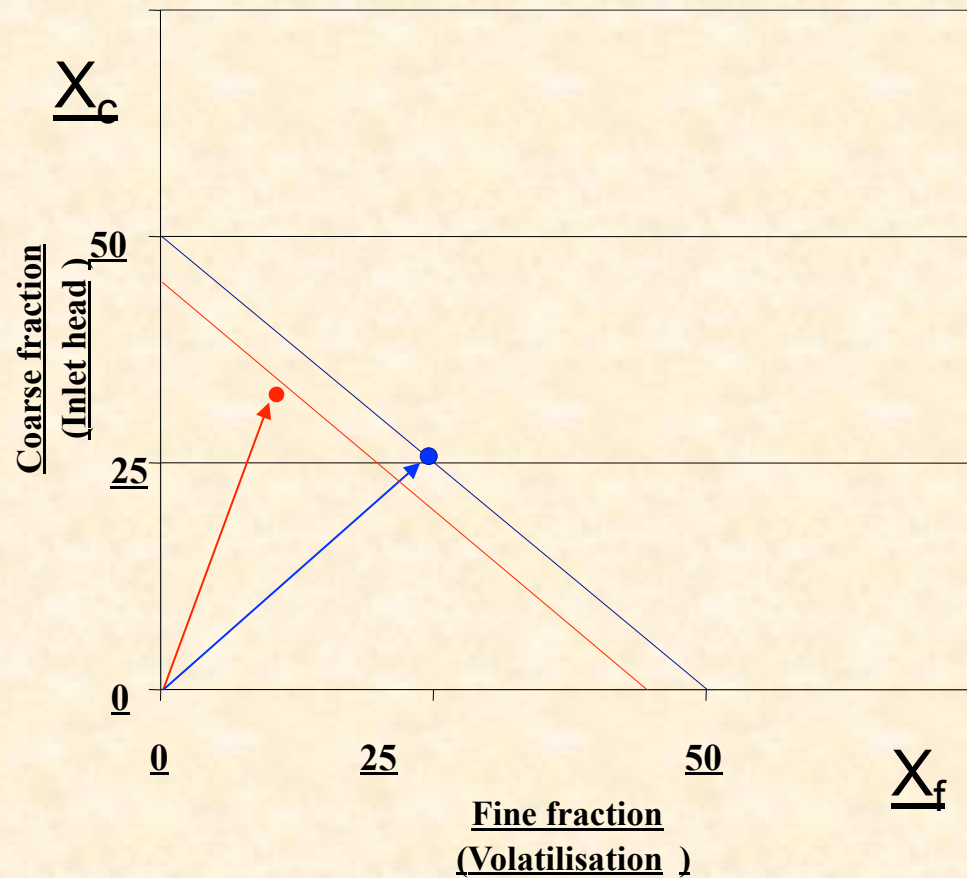


15-12-2008 / 19-12-2008



VECTORIAL REPRESENTATION

(two 8h samples)



15/12/2008 → PM10=47 μ g/m³

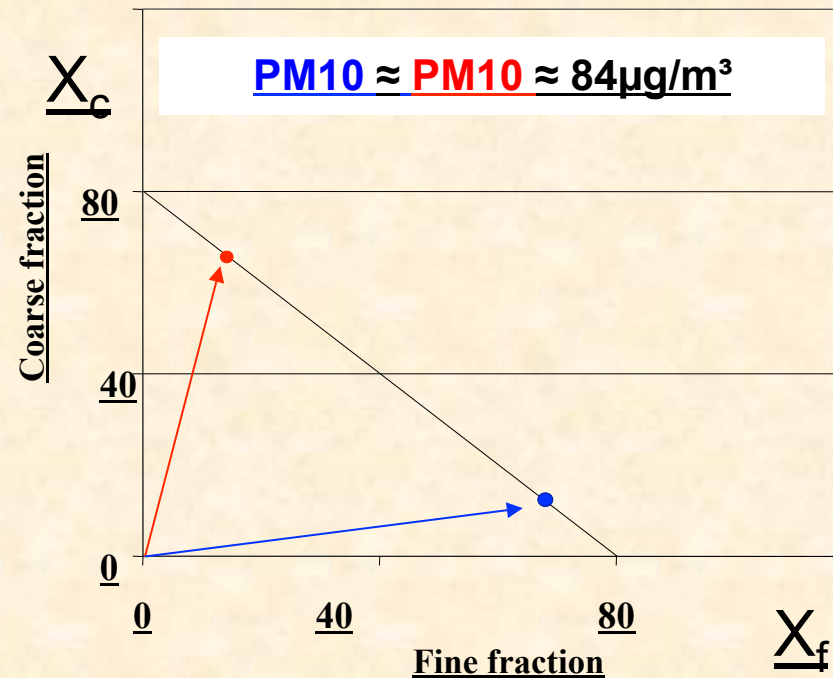
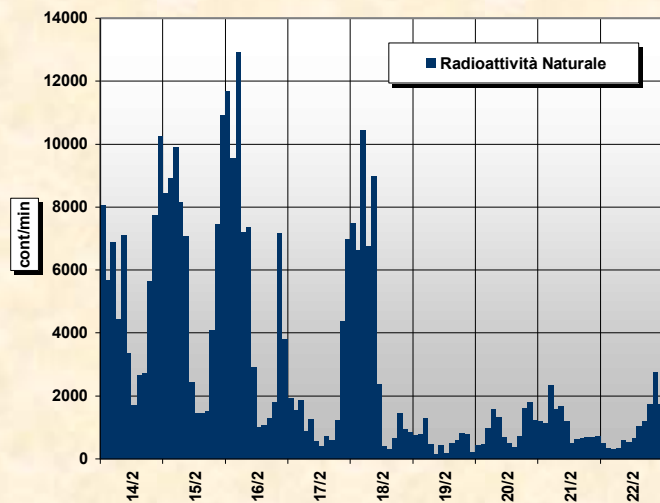
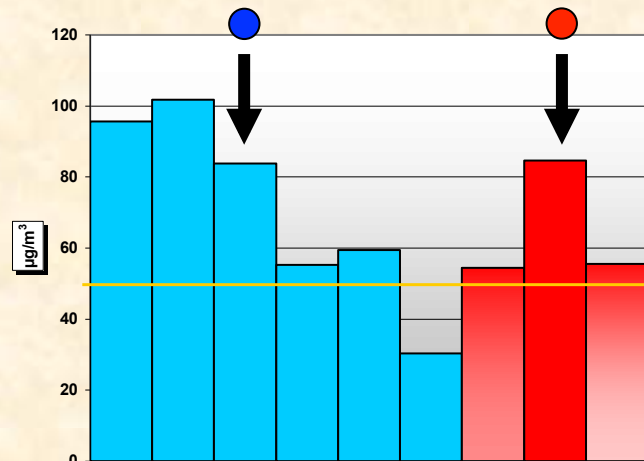
16/12/2008 → PM10=50 μ g/m³

PM10 \approx PM10

Stability
condition: fine
event

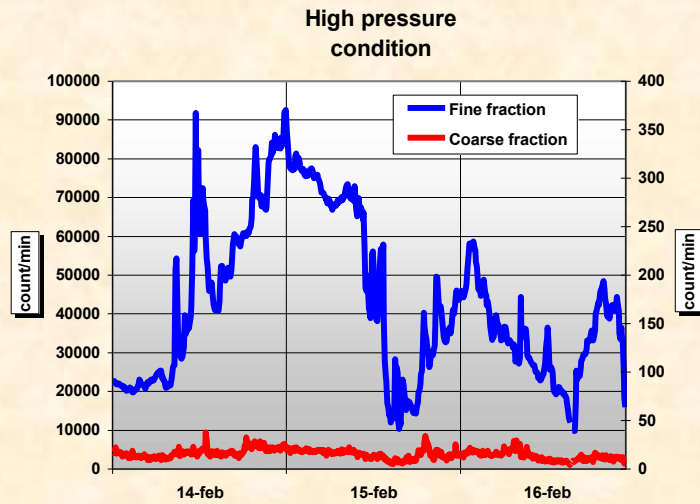
PM₁₀
Roma Feb 2004

Strong mixing
condition: coarse
event (saharian
dust)

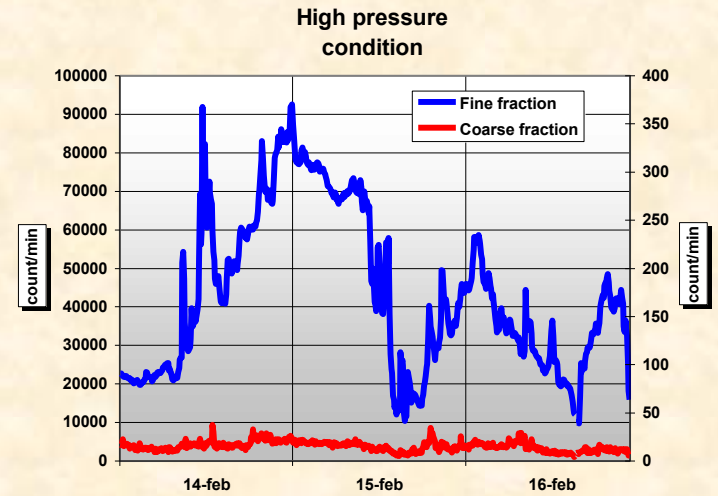


Stability
condition: fine
event

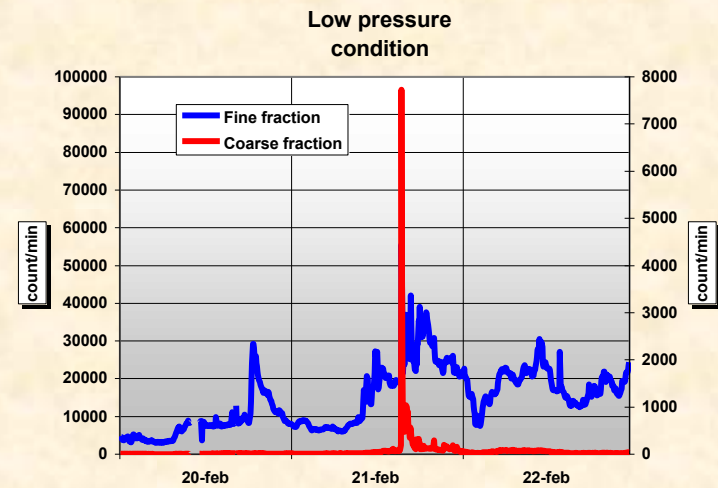
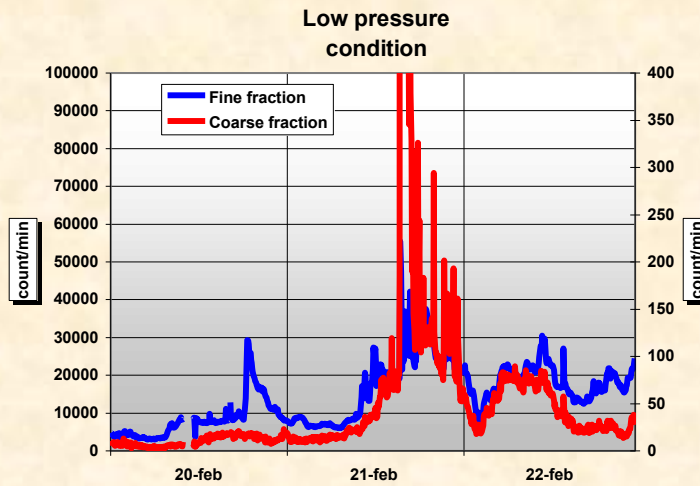
OPC Temporal Trend



OPC Temporal Trend



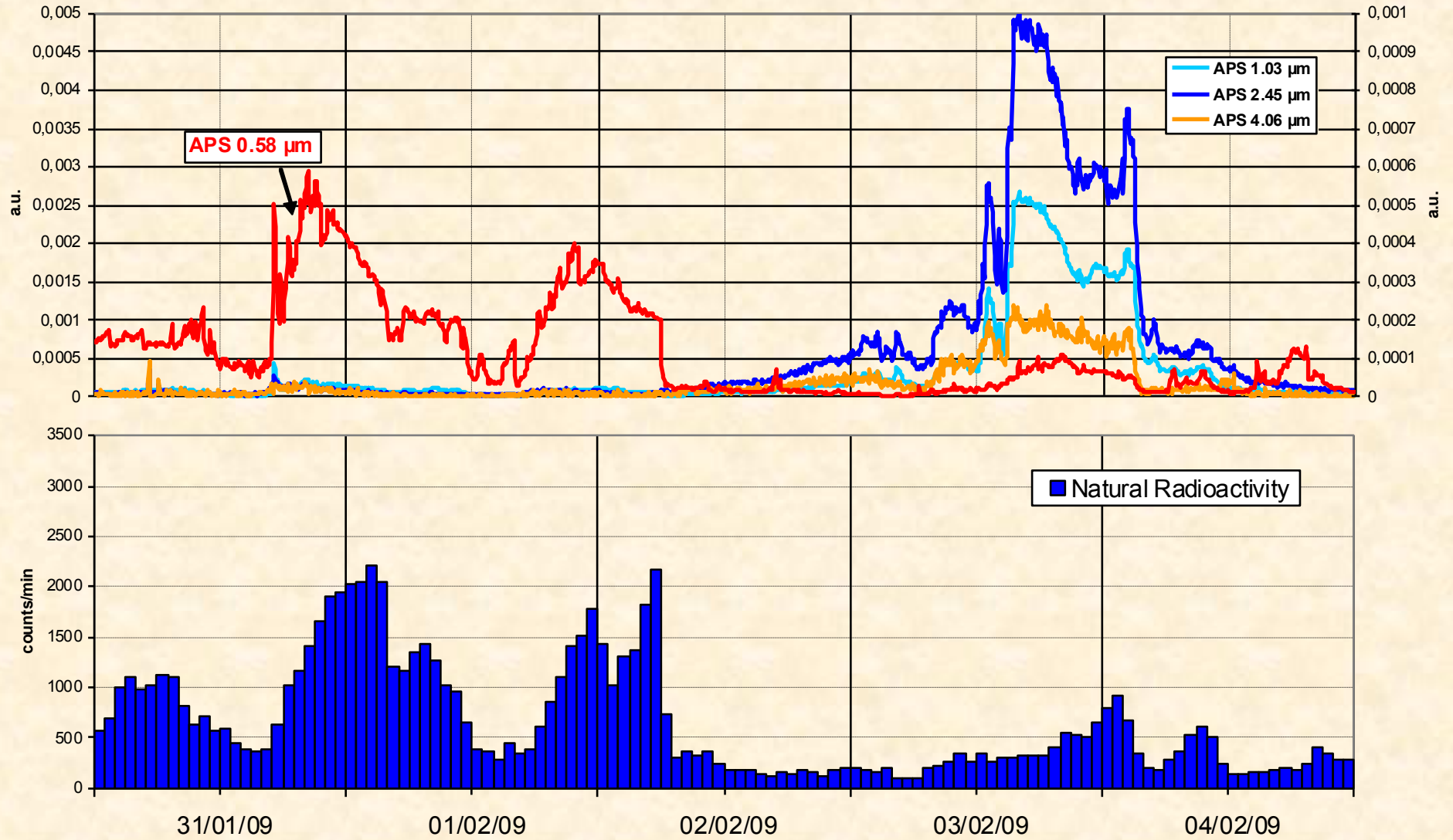
Strong mixing
condition: coarse
event



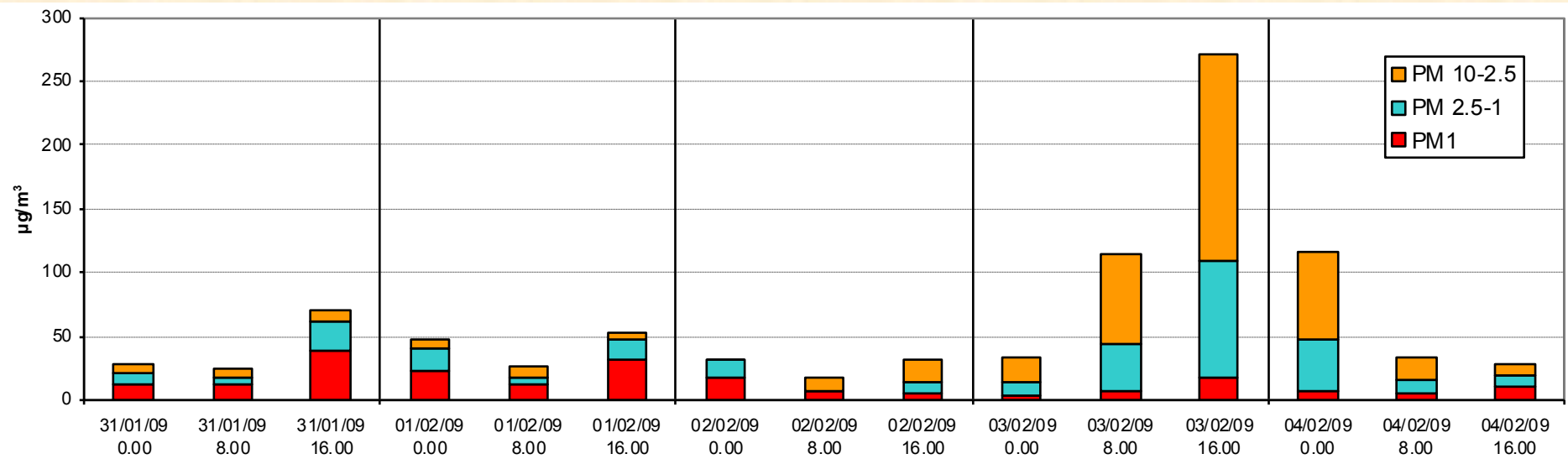
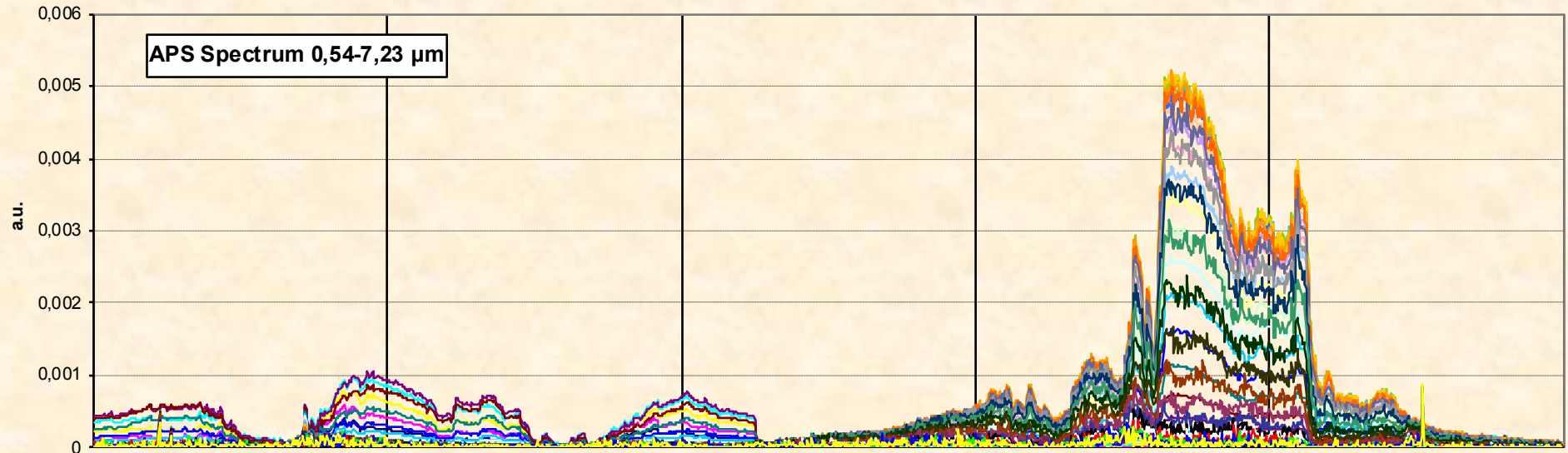
31-01-2009 / 04-02-2009

SAHARIAN DUST
EVENT

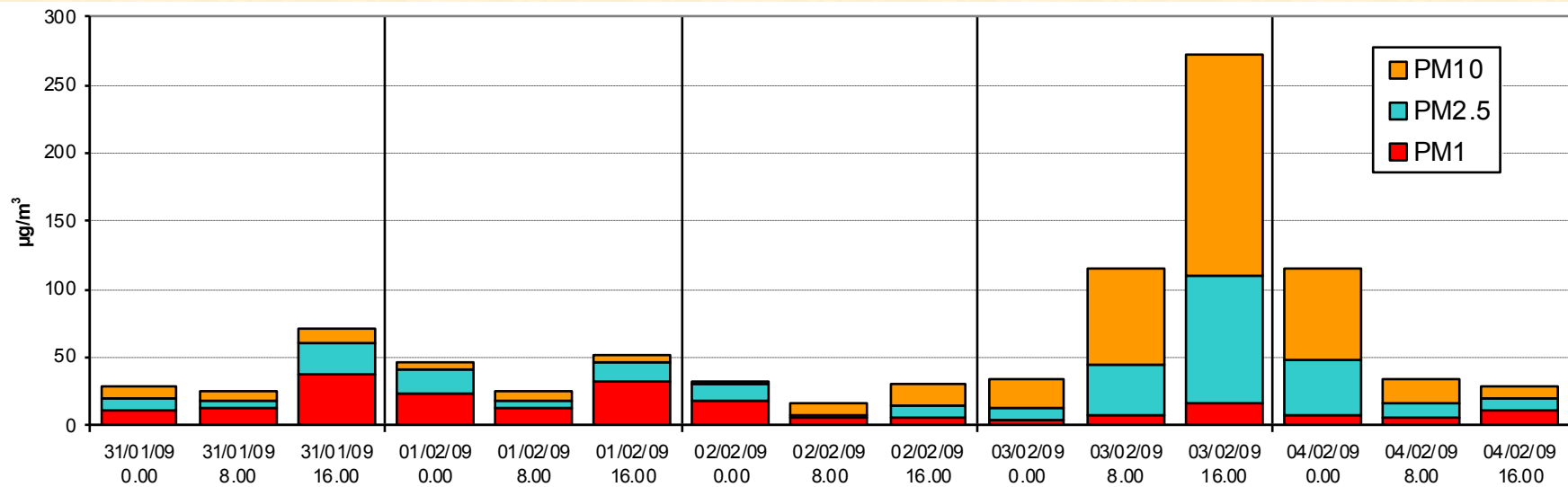
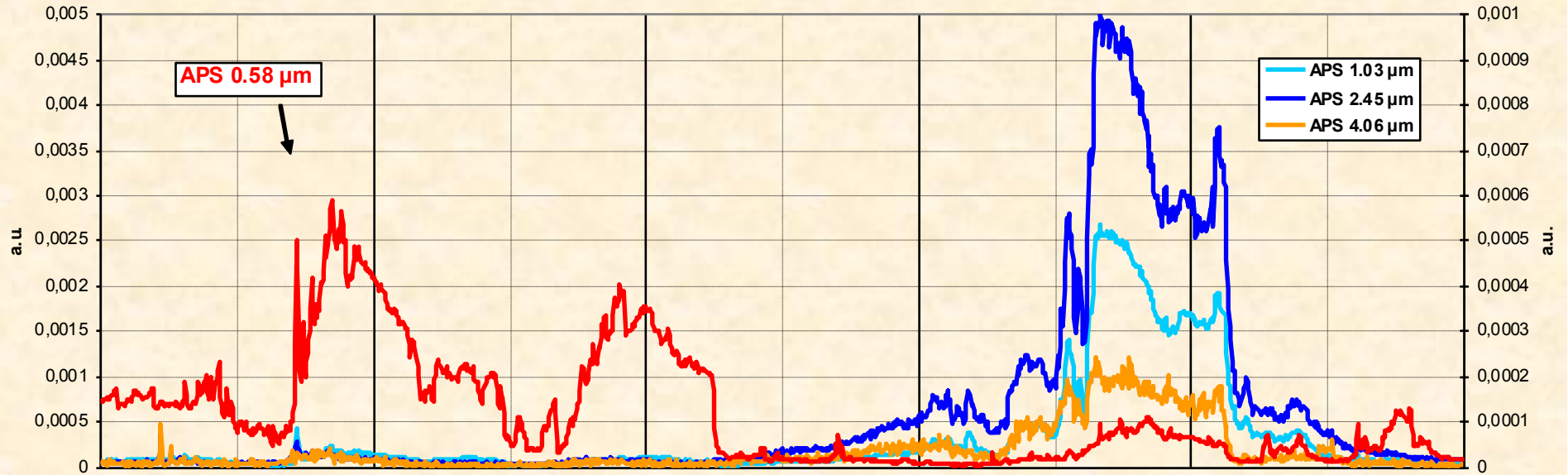
31-01-2009 / 04-02-2009



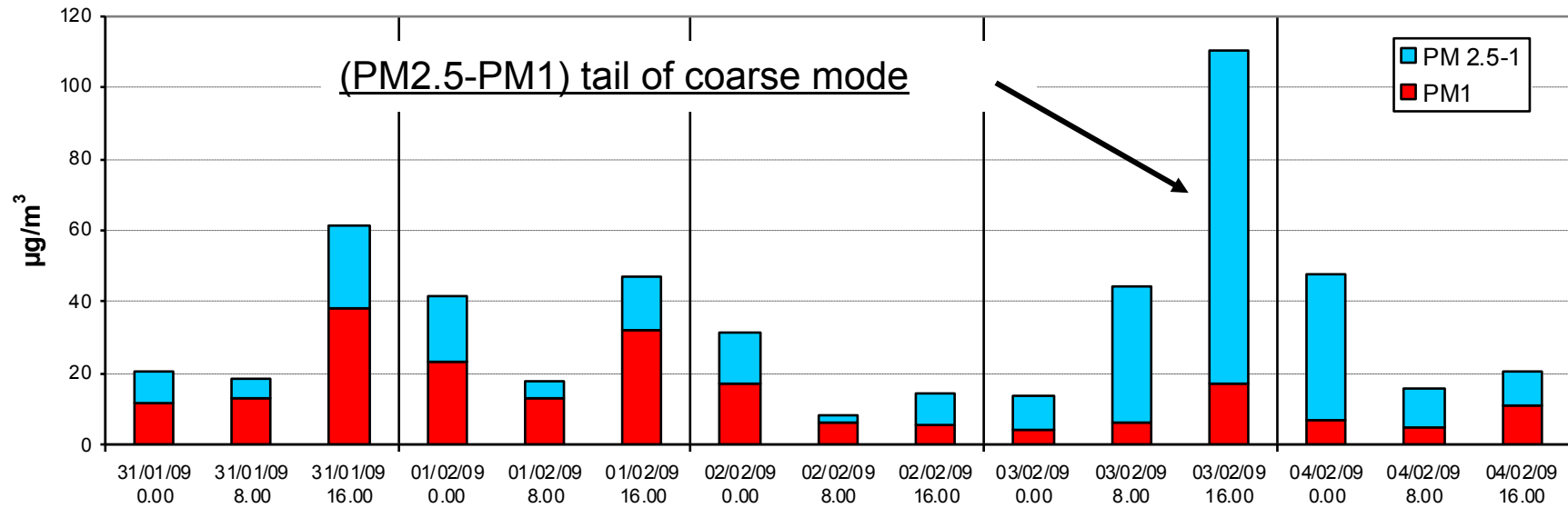
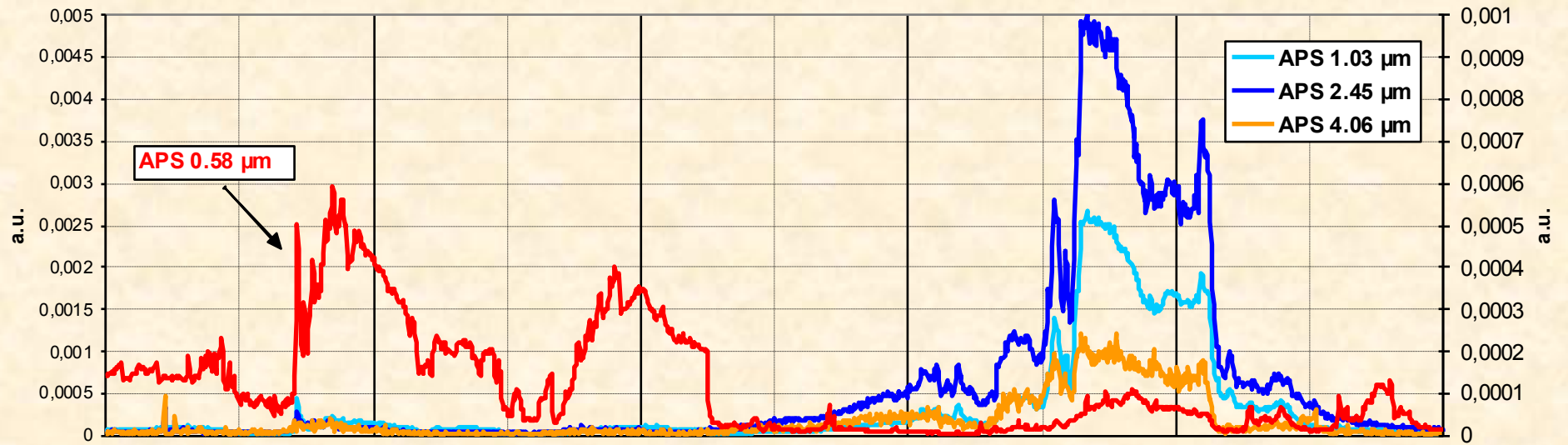
31-01-2009 / 04-02-2009



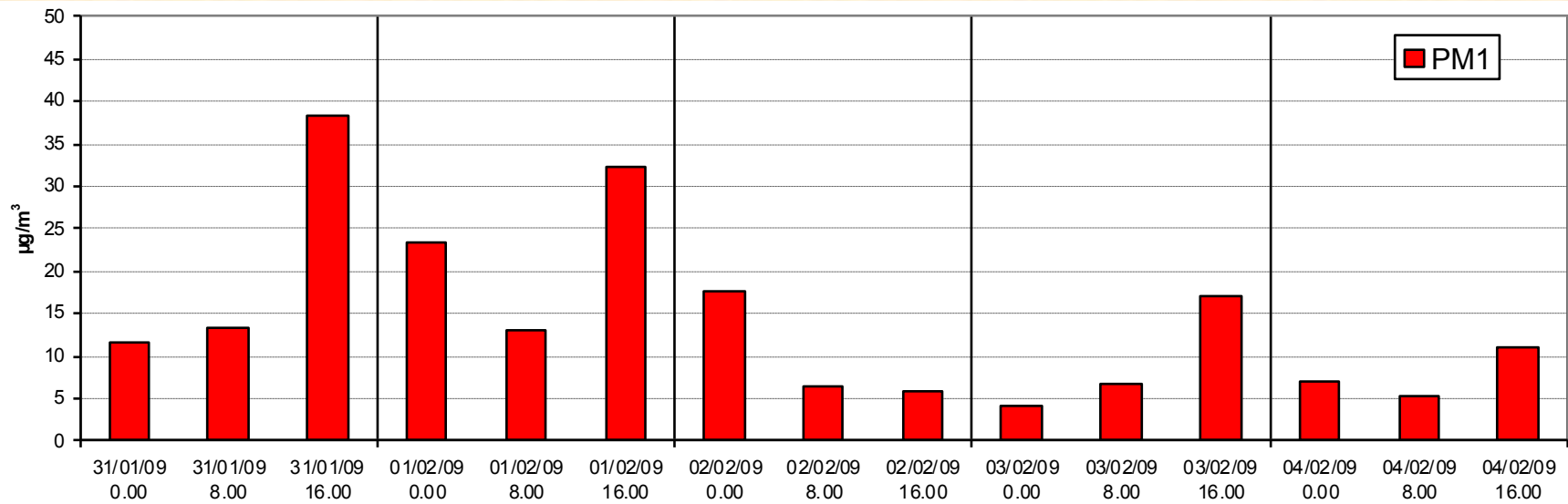
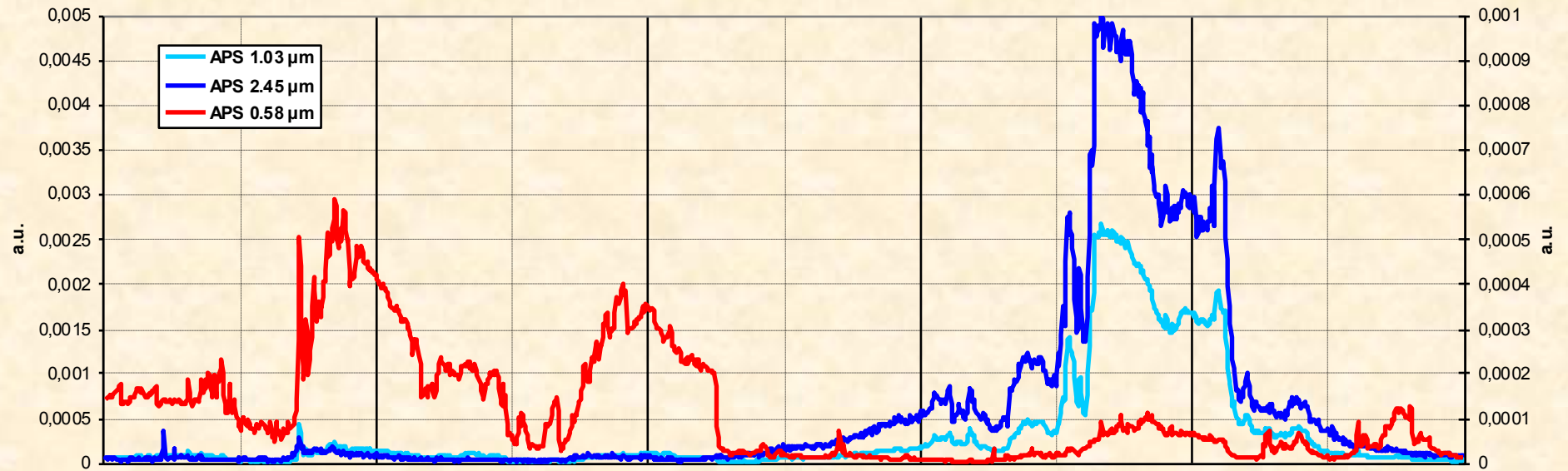
31-01-2009 / 04-02-2009



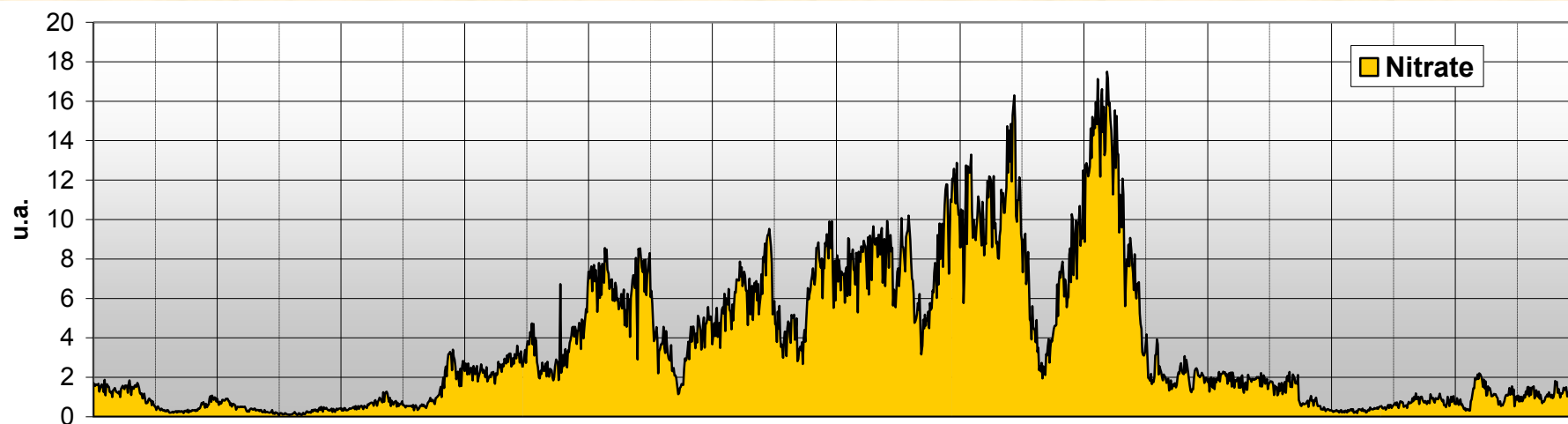
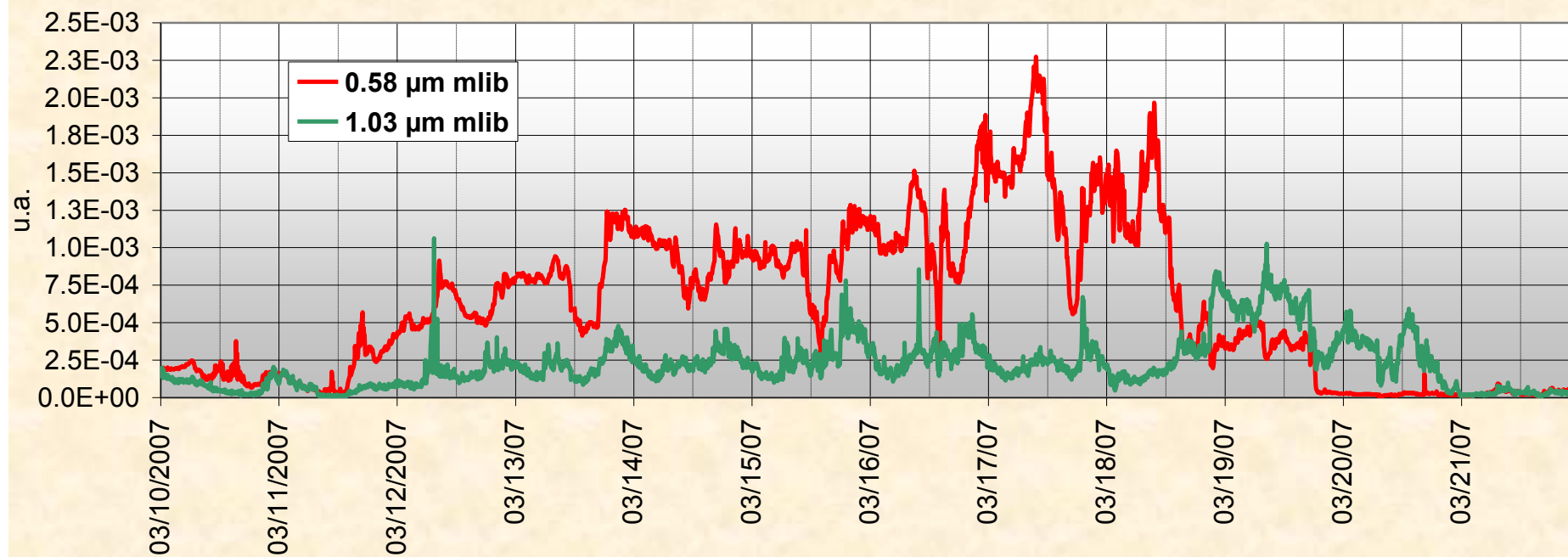
31-01-2009 / 04-02-2009



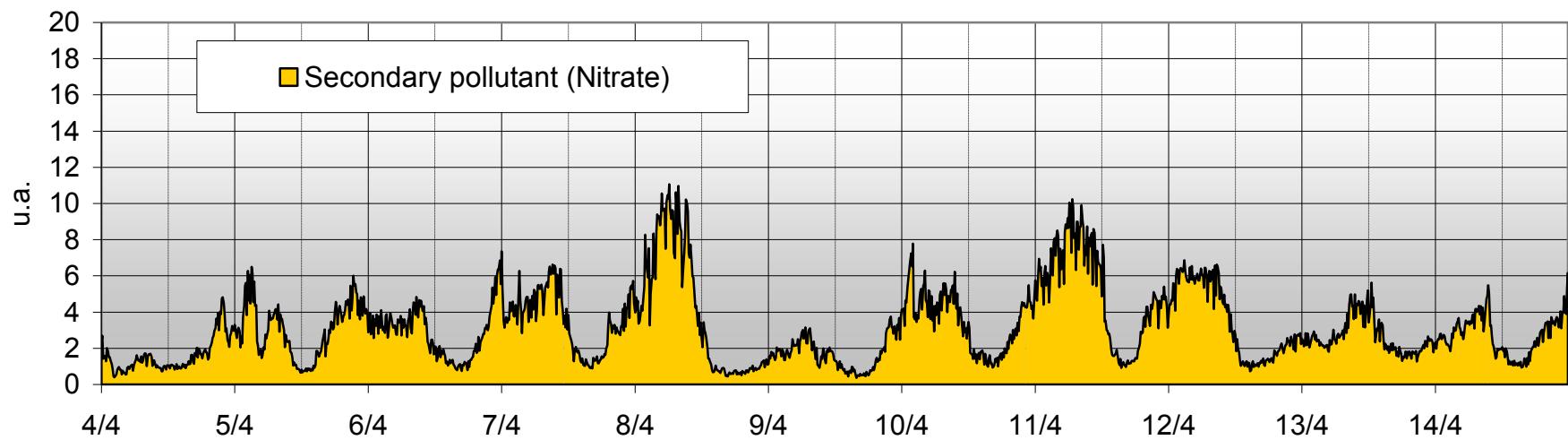
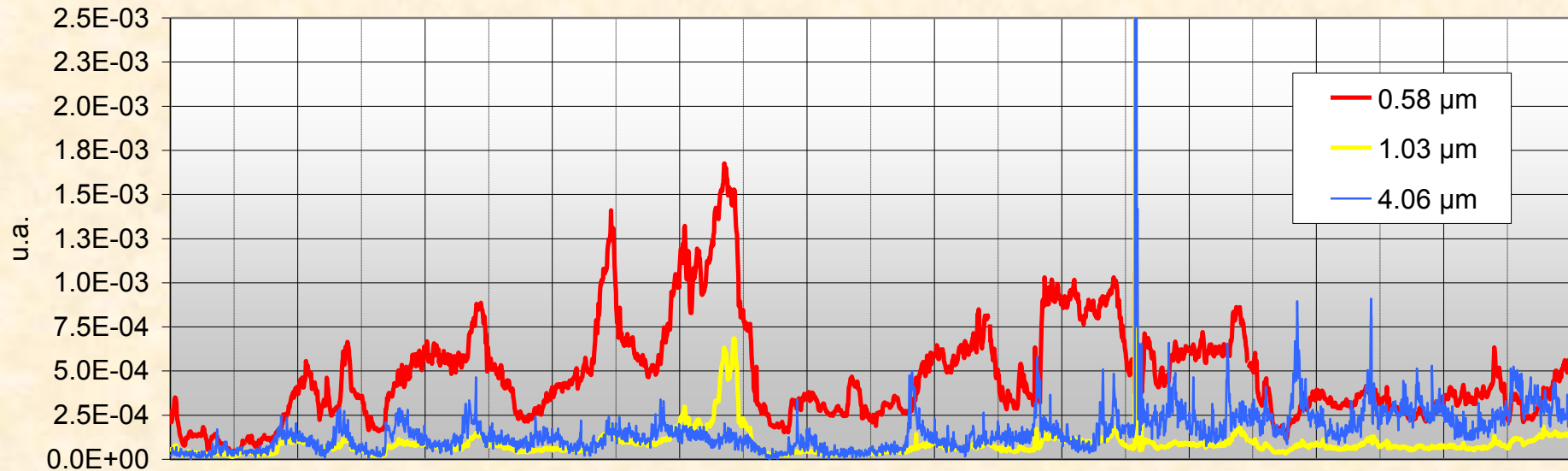
31-01-2009 / 04-02-2009



Fine mode and nitrate temporal trend

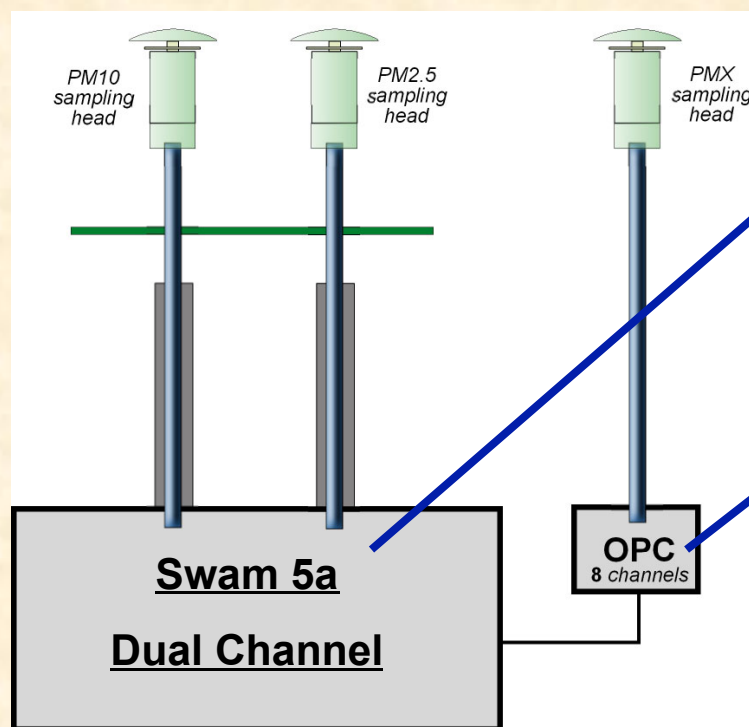


Fine mode and nitrate temporal trend



SWAM 5a Dual Channel & OPC Multichannel

to estimate real time mass concentration $C_x(t)$ of PM10, PM2.5 and PM1 fraction



Average mass concentration $\langle C(\text{PM10}) \rangle$, $\langle C(\text{PM2.5}) \rangle$ and $\langle C(\text{PM10-2.5}) \rangle$ with high accuracy level

High quality information about temporal trend of $C(\text{PM1})$, $C(\text{PM2.5})$ and $C(\text{PM10-2.5})$, are given by: $n_i(t) \rightarrow$ number concentration in the i -th granulometric range

REAL TIME PM_x CONCENTRATION DATA EXTIMATION

$$C_{(PM_x)}(t) = a_x^0 + \sum_{i=1}^m a_x^i n^i(t)$$

How to estimate the a_x^i coefficients with a good accuracy level?

- Continuous availability of average mass concentration data of two granulometric fractions $\langle C1x \rangle$, $\langle C2x \rangle$, $\langle C3x \rangle$, ... $\langle Ckx \rangle$...

$$\left(\begin{array}{l} \bar{C1x} = \int_{t0}^{t1} \left[a_x^0 + \sum_{i=1}^m a_x^i n^i(t) \right] dt \\ \bar{C2x} = \int_{t1}^{t2} \left[a_x^0 + \sum_{i=1}^m a_x^i n^i(t) \right] dt \\ \dots\dots\dots \\ \bar{Ckx} = \int_{tk-1}^{tk} \left[a_x^0 + \sum_{i=1}^m a_x^i n^i(t) \right] dt \\ \dots\dots\dots \end{array} \right)$$

MULTIREGRESSION
ANALYSIS

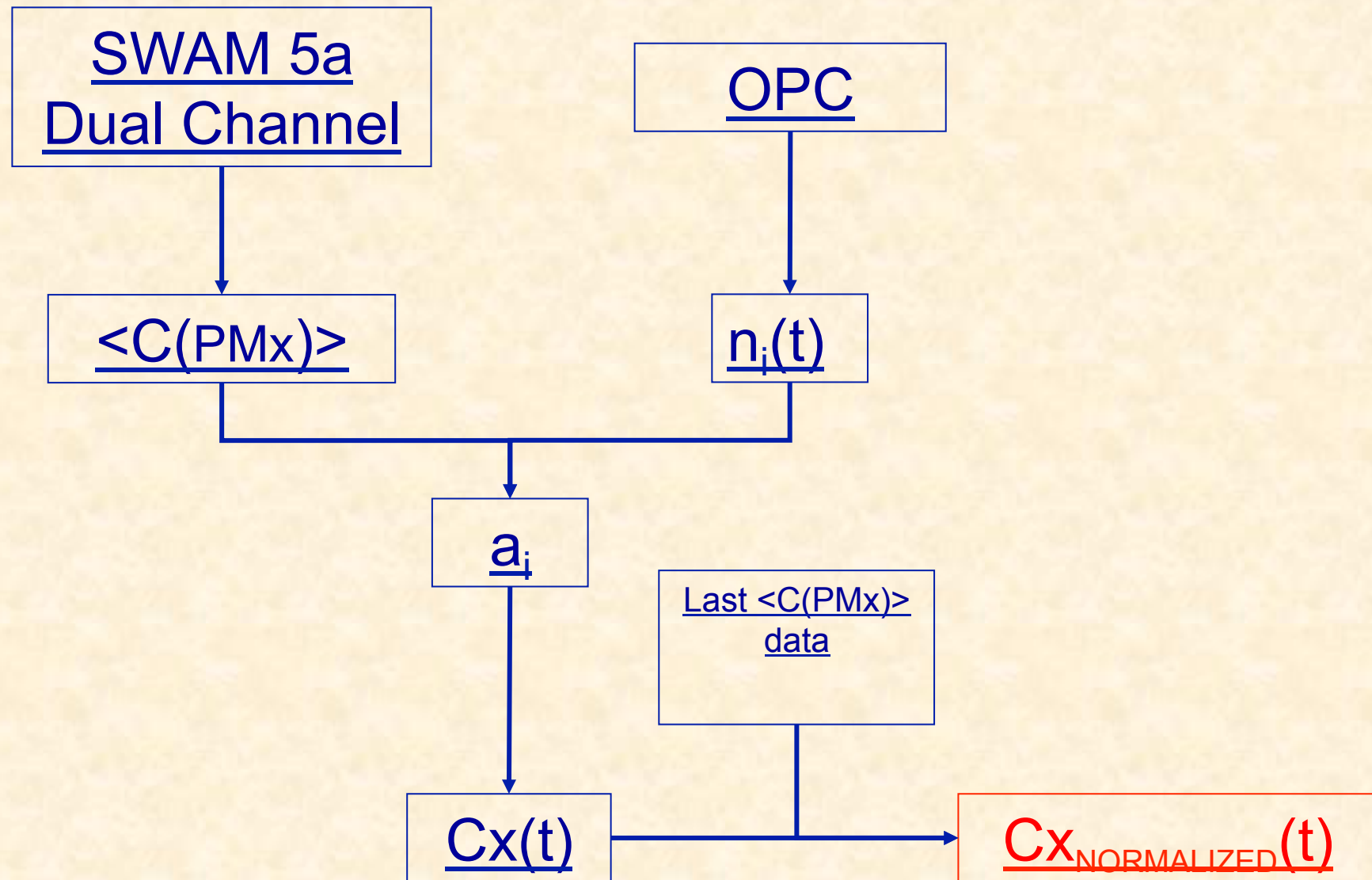
REAL-TIME PM_x CONCENTRATION DATA ESTIMATION

At the end of each sampling cycle the estimated real-time concentration values $C(t)$ are recalculated, normalizing them to the mass concentration values measured by SWAM 5a Dual Channel



$C(t)$ with high accuracy level

REAL-TIME PM_x CONCENTRATION DATA ESTIMATION

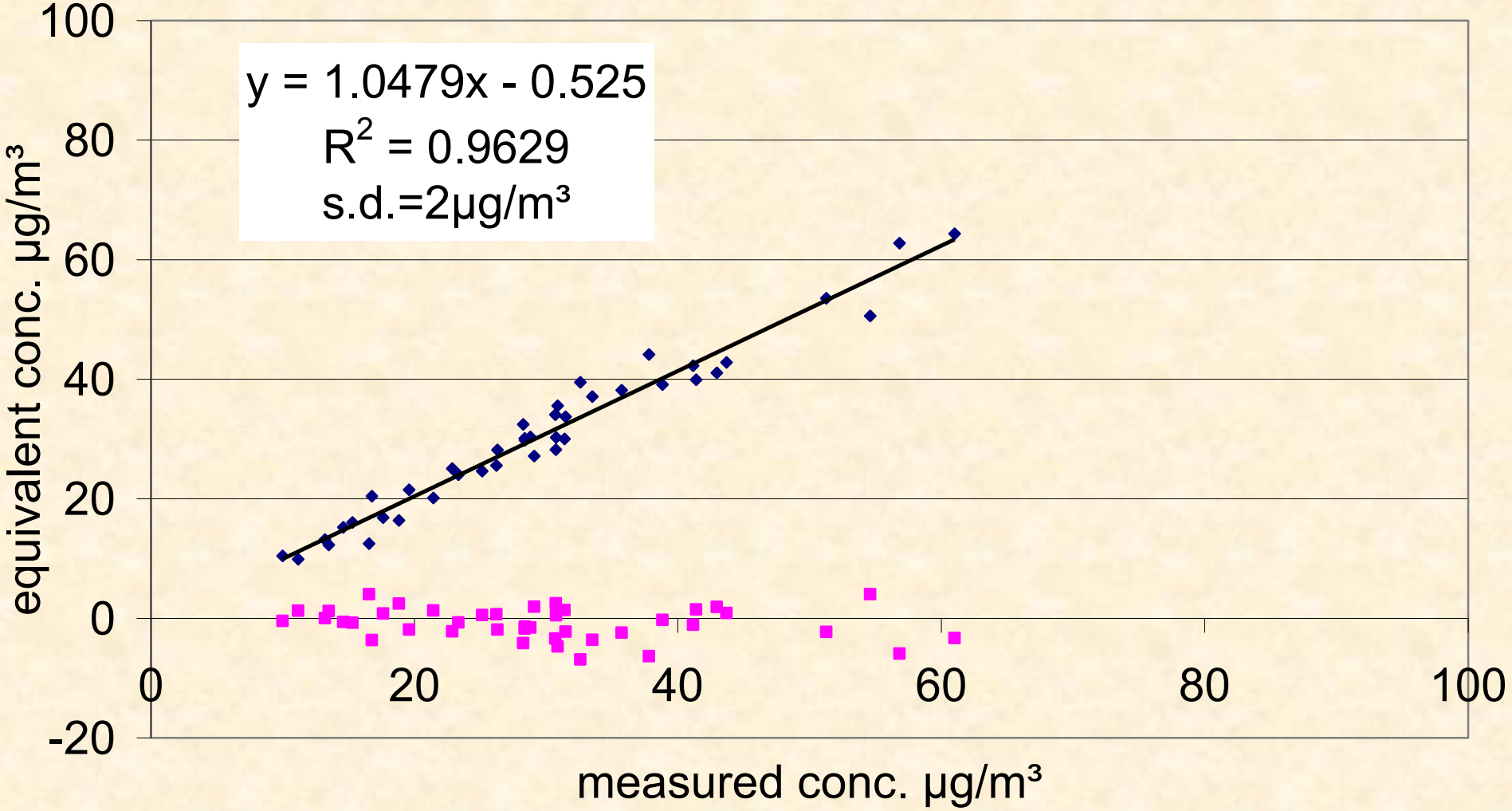


**PM_x EQUIVALENT
CONCENTRATION**

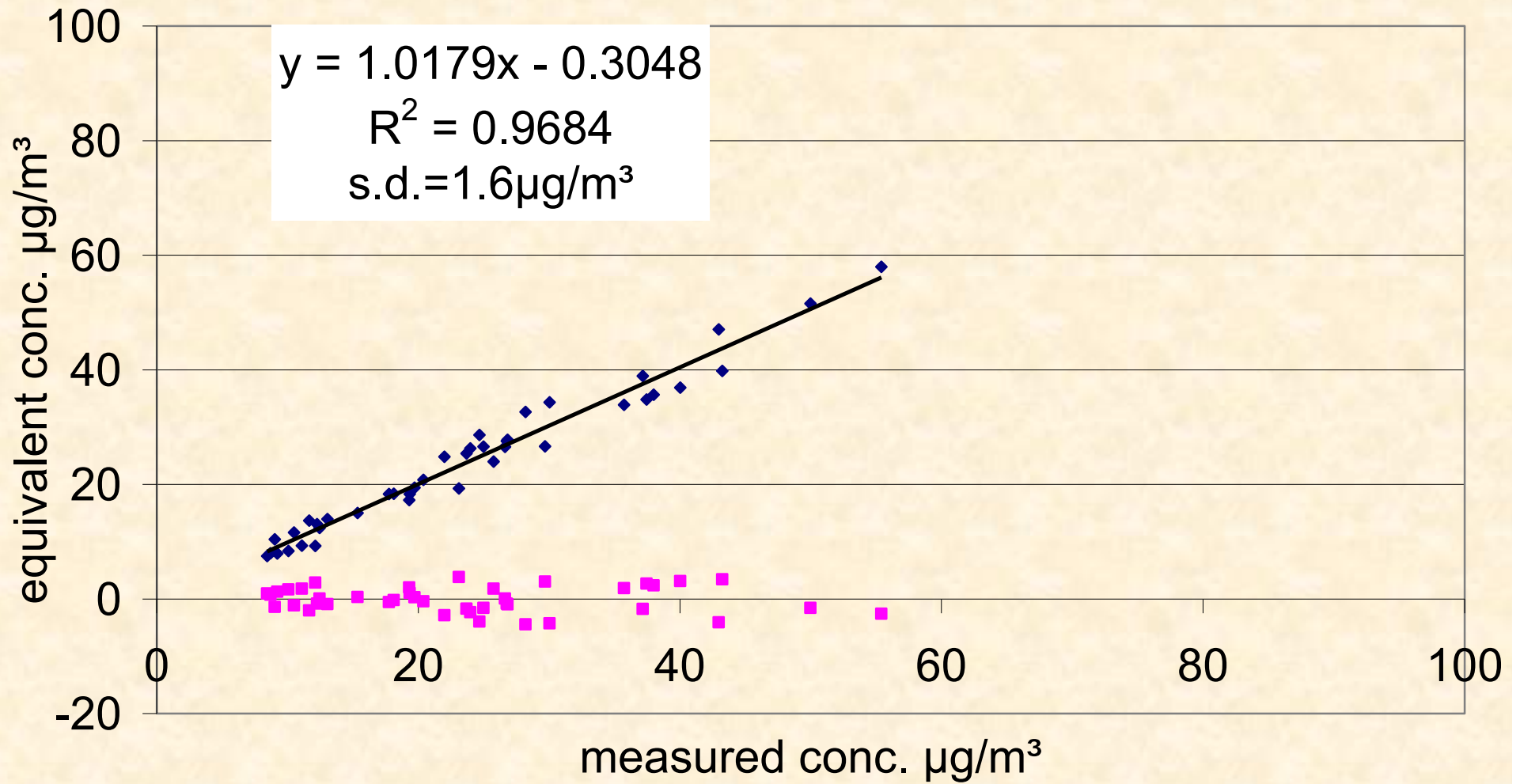
VS

**SWAM D.C. 8 hours
AVERAGE MASS
CONCENTRATION**

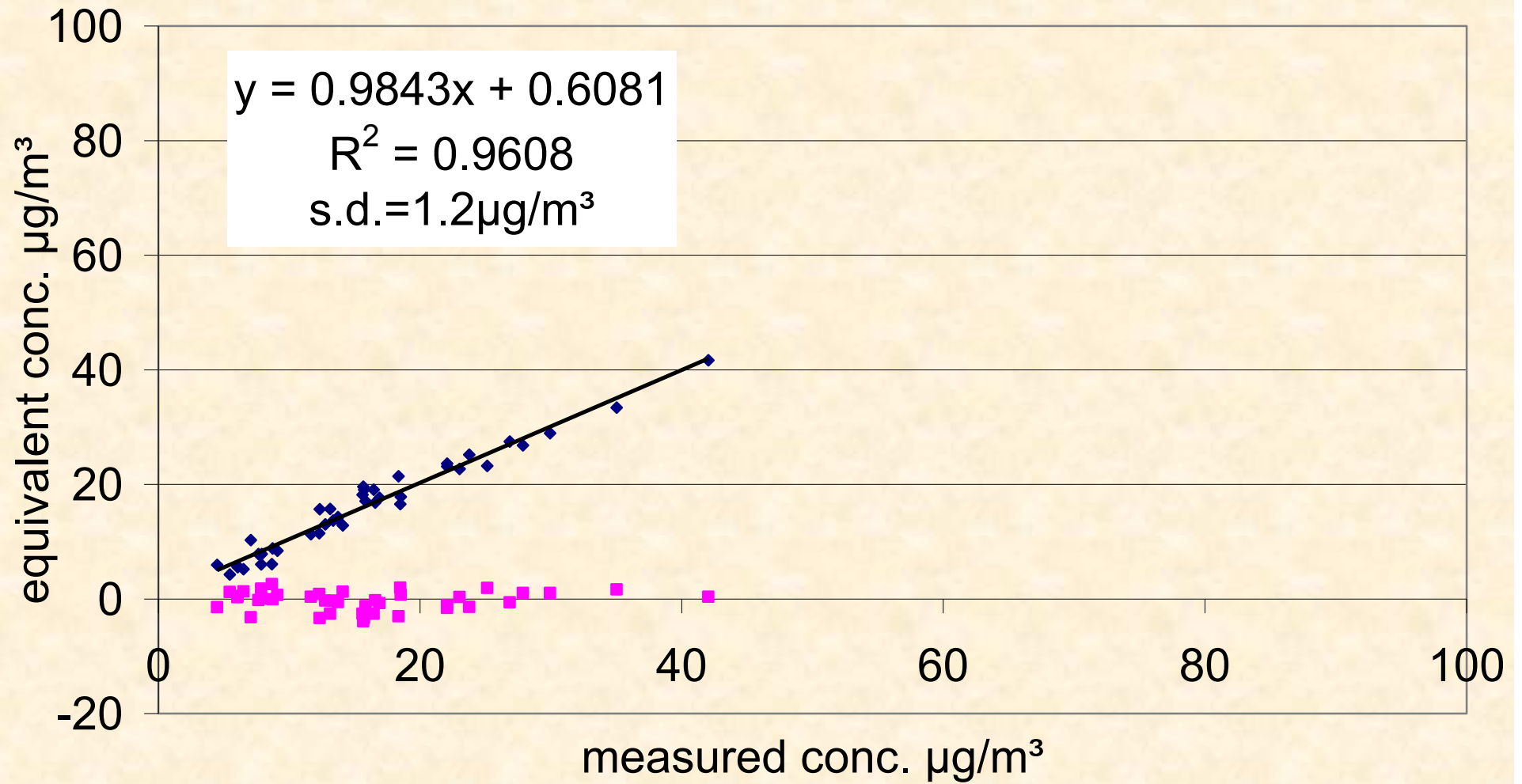
PM10 concentration



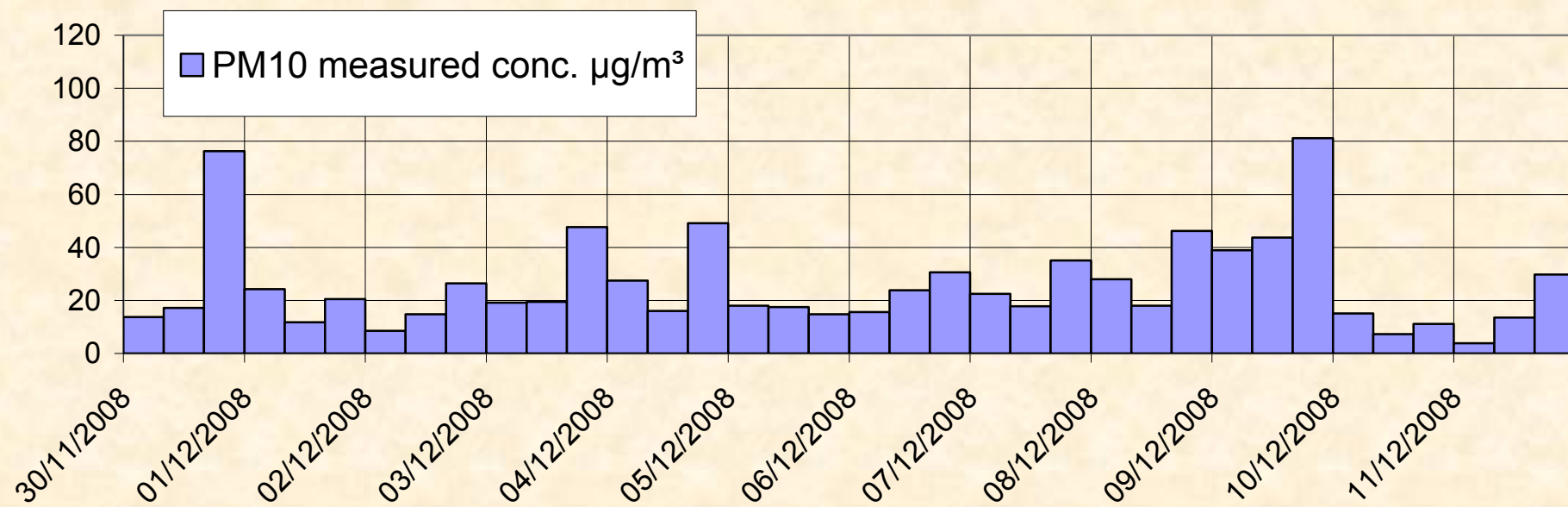
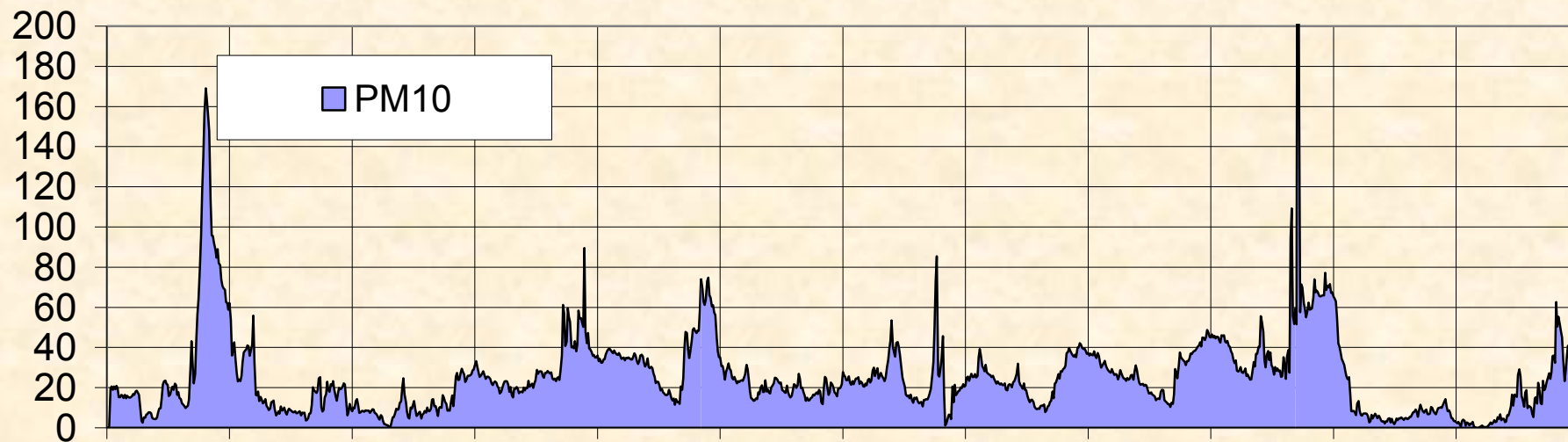
PM2.5 concentration



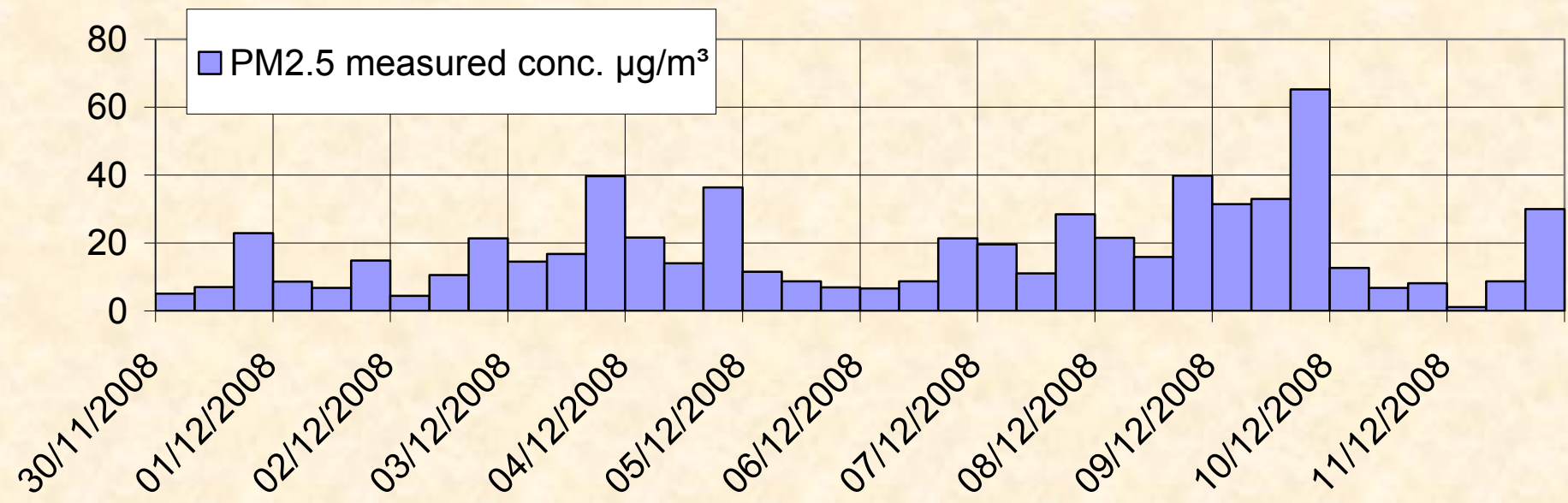
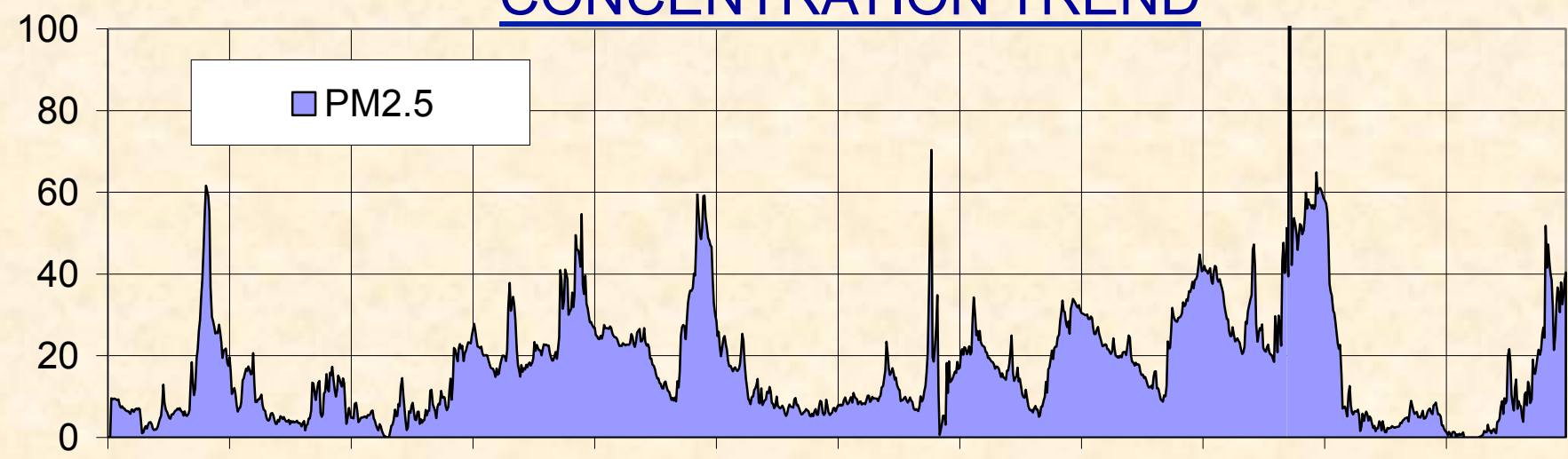
PM1 concentration



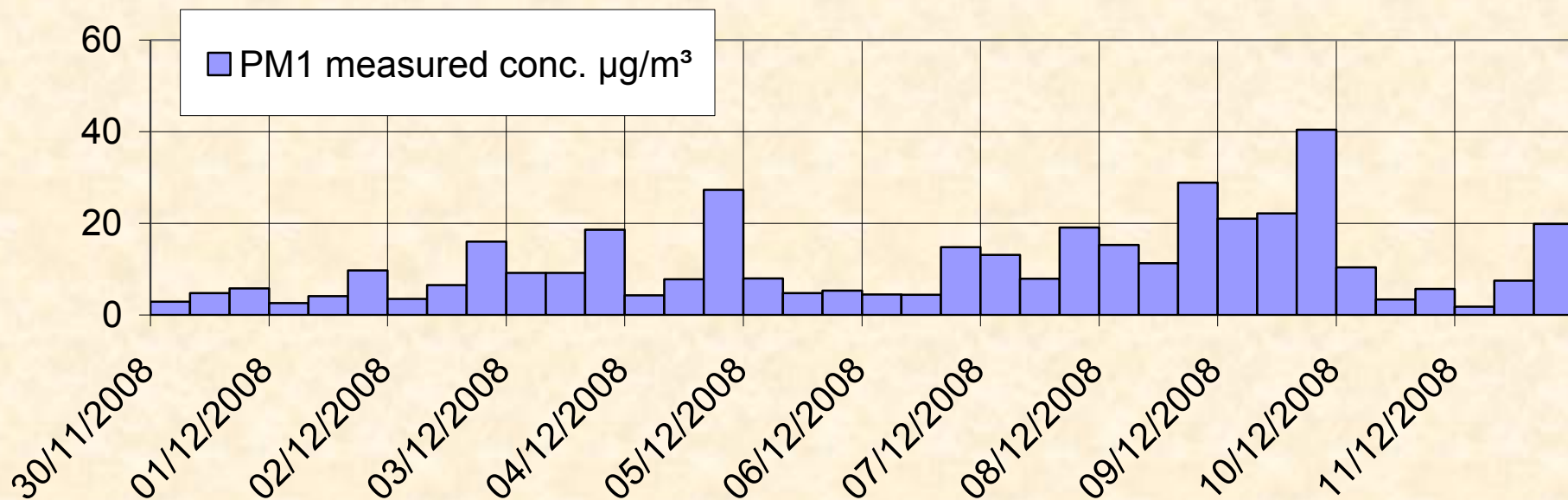
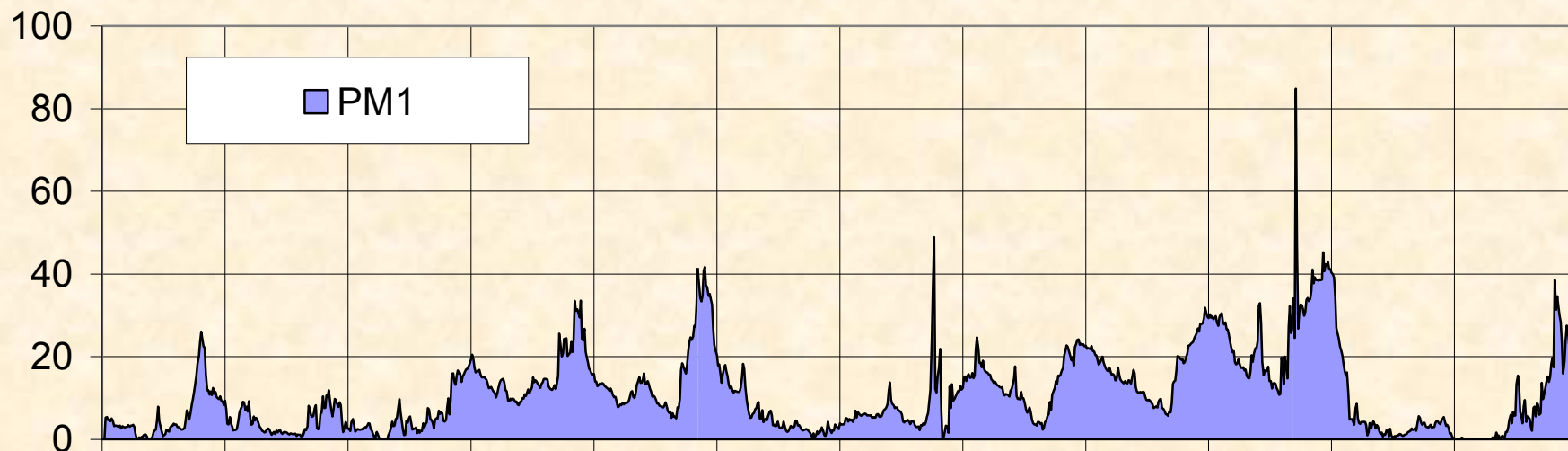
PM10 EQUIVALENT CONCENTRATION TREND



PM2.5 EQUIVALENT CONCENTRATION TREND



PM1 EQUIVALENT CONCENTRATION TREND



PMx mass concentration data
hourly resolution

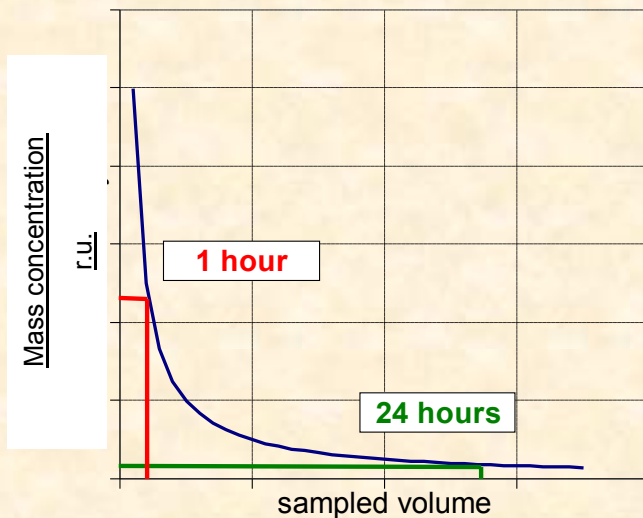
Some considerations about the
relative uncertainty

PM_x MASS CONCENTRATION

SAMPLE MASS MEASUREMENT

Differential method:

- Gravimetric
- β attenuation
- Oscillating microbalance

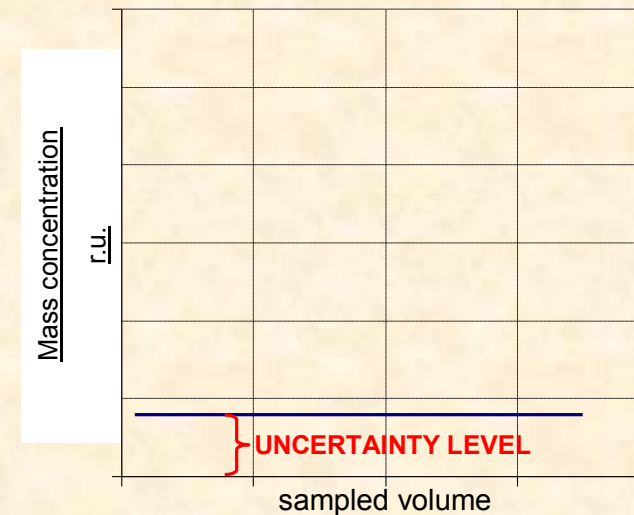


- strongly depending (1 / sampled Volume) on sampled volume
- quasi real time r.u. $\rightarrow \infty$

NUMBER & SIZE OF PARTICLES + MASS CONCENTRATION DATA

Optical method + β attenuation :

- OPC + PM_x mass concentration data



- unrelated to the sample volume
- depending on functional biases: shape factor, density, refractive index, relative humidity,
- r.u.(24h)=r.u.(1h)=r.u. (real time)

RELATIVE UNCERTAINTY COMPARISON

GRAZIE PER L'ATTENZIONE