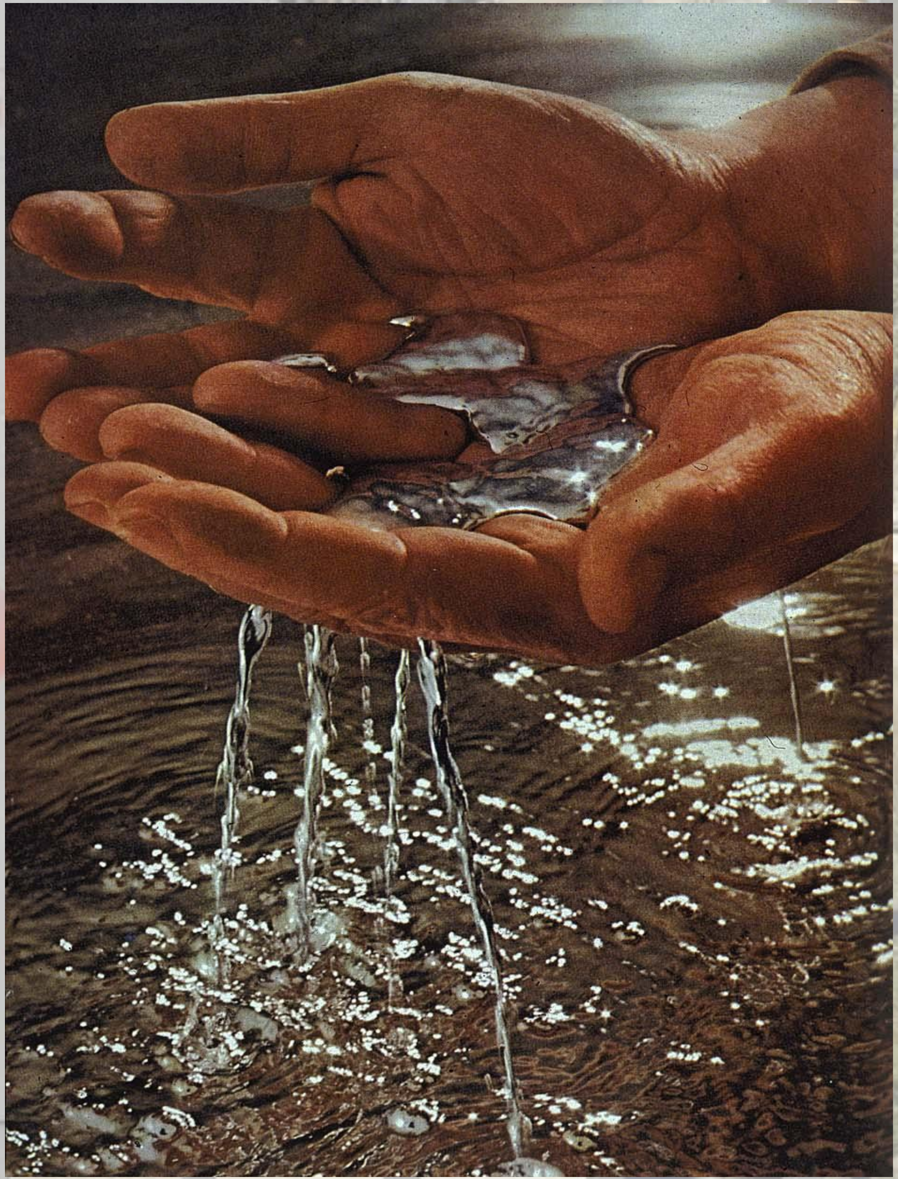
Il mercurio gassoso in contesti urbani: teoria, applicazioni e casi di studio

Hg - MERCURIO



Come l'acqua …
ma 13.6 volte
il peso di H_2O!

Hg - MERCURIO

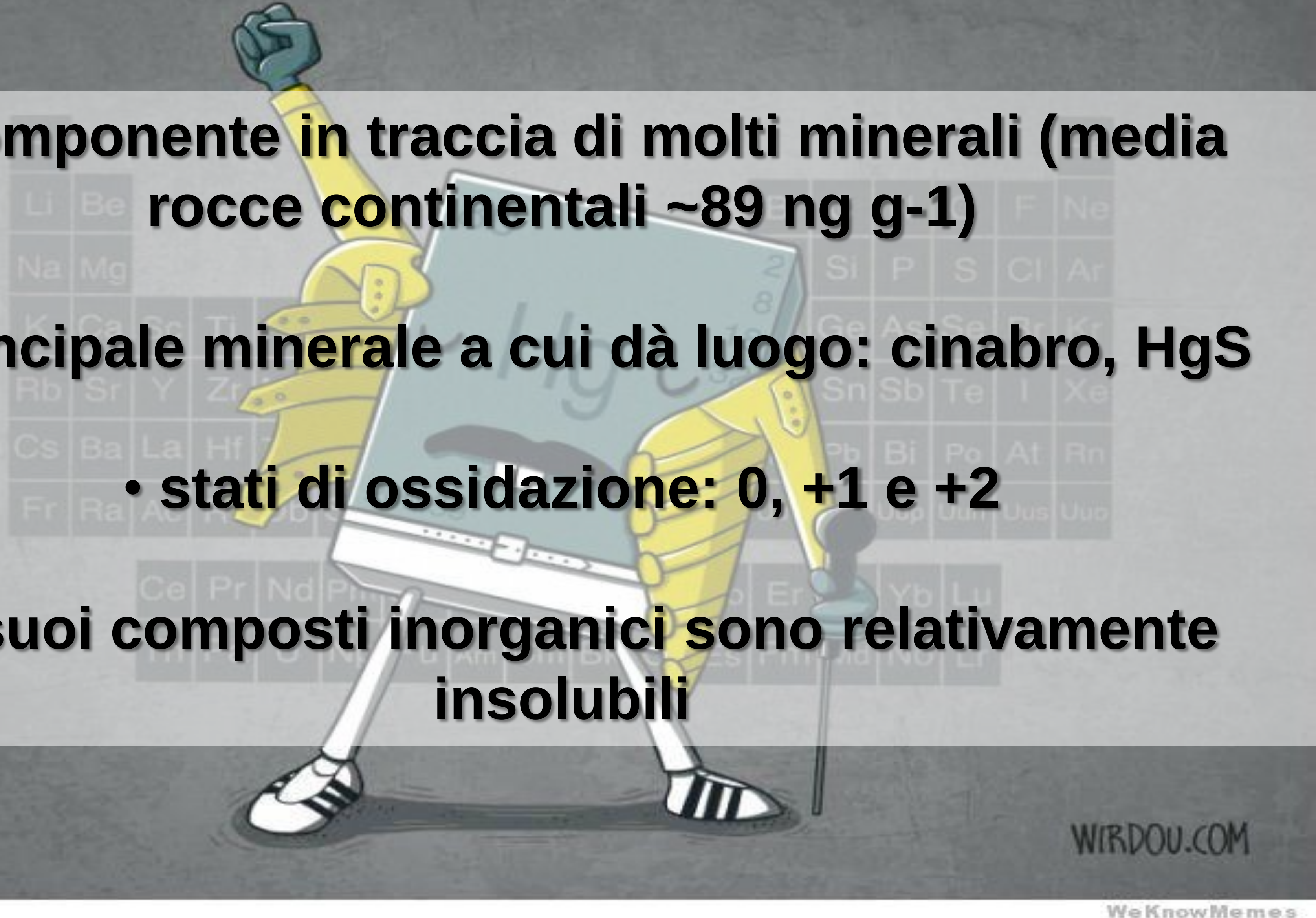
- Stato ordinario: Liquido
- Densità: 13534 kg/m3
- Serie chimica: Metalli di transizione
- Rispetto ad altri metalli, è un cattivo conduttore di calore, ma un buon conduttore di elettricità

Il mercurio viene utilizzato in termometri, barometri, misuratori di pressione, sfigmomanometri, alcuni tipi di valvole come pompe a vuoto, interruttori di mercurio, lampade fluorescenti e altri dispositivi

Un operaio di una miniera di mercurio statunitense a sedere in una vasca di mercurio

Hg - MERCURIO

- componente in traccia di molti minerali (media rocce continentali ~89 ng g-1)
- principale minerale a cui dà luogo: cinabro, HgS
- stati di ossidazione: 0, +1 e +2
- i suoi composti inorganici sono relativamente insolubili



Hg - MERCURIO

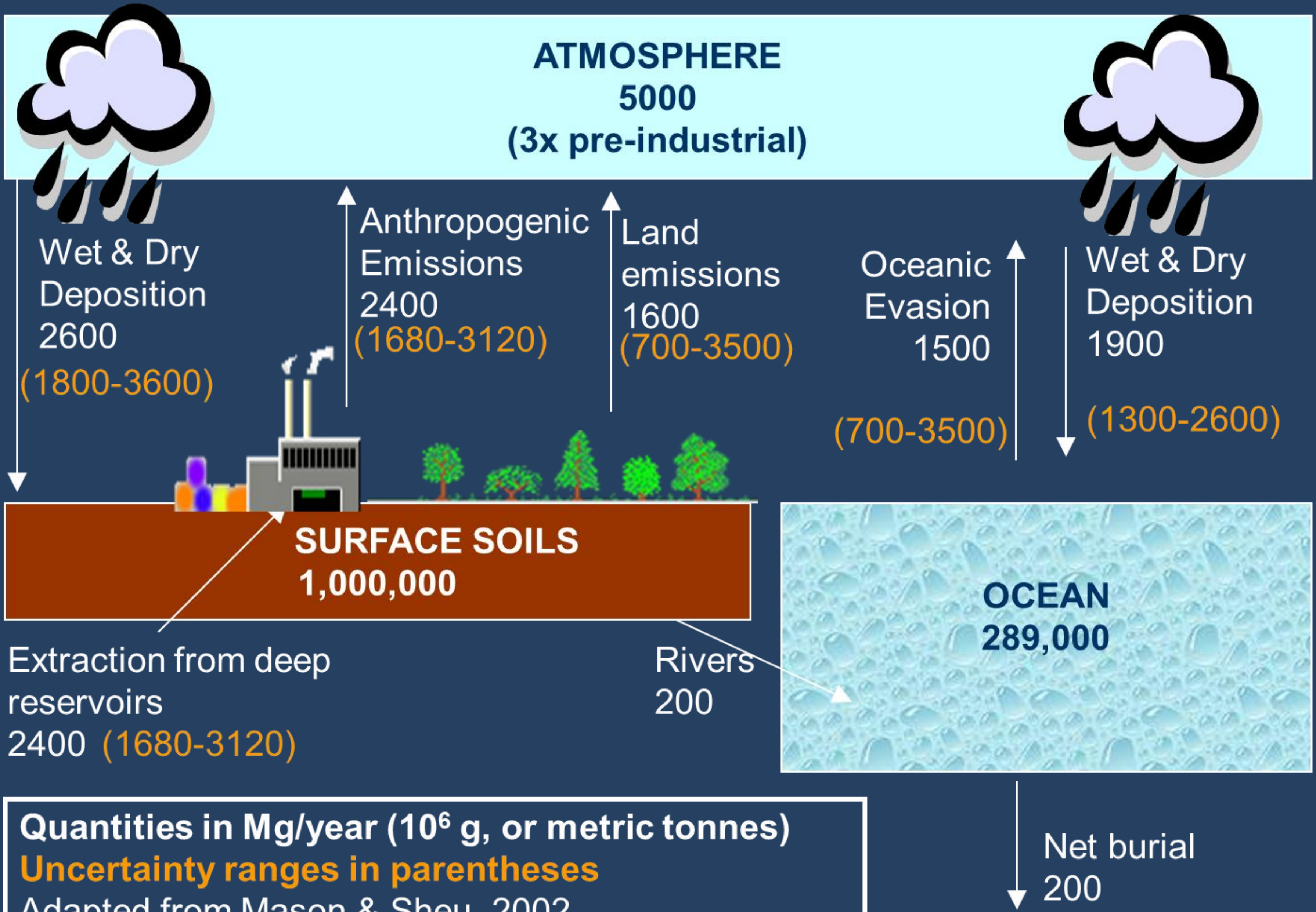
- **tende a formare complessi e si lega al particolato accumulandosi nei sedimenti**
- **i complessi acquosi si deprotonano facilmente**
- **l’unico metallo che permane in fase gassosa**
- **limite per le acque potabili: 1 µg L^{-1}**

Fonti naturali: sistemi vulcanici e geotermici e combustione di biomassa.

Una volta nell'ambiente, il suo ciclo è piuttosto complesso e sono coinvolte reazioni biogeochimiche.

Hg è presente come gas, ma si presenta anche in altre forme nell'atmosfera.

SCIENTIFIC UNCERTAINTIES: SOURCES AND SINKS



Quantities in Mg/year (10^6 g, or metric tonnes)
Uncertainty ranges in parentheses
Adapted from Mason & Sheu, 2002

TGM = GEM + RM

Total Gaseous Mercury

Gaseous Elemental Mercury

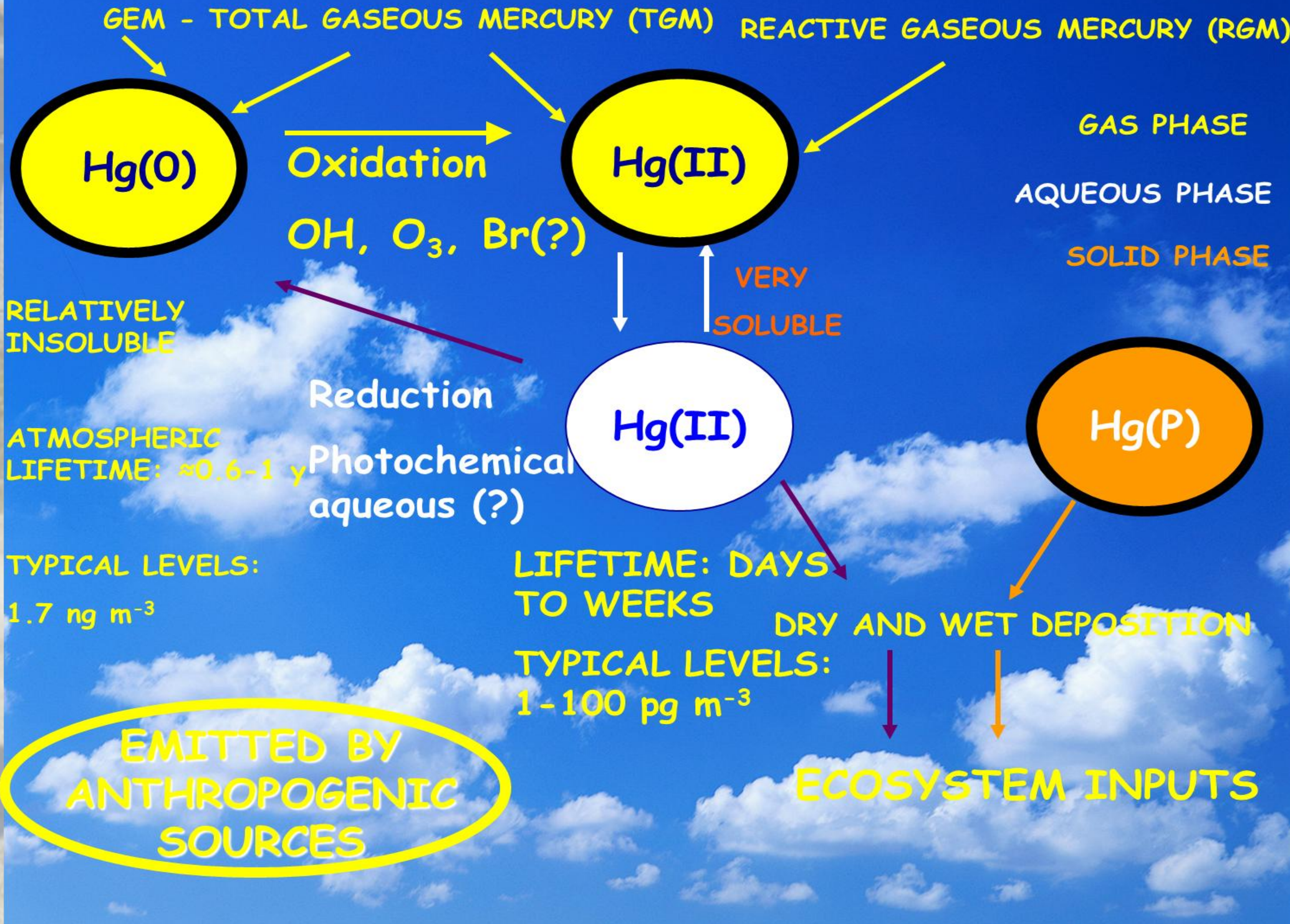
Reactive Mercury

GOM + PBM

Gaseous Oxidized Mercury

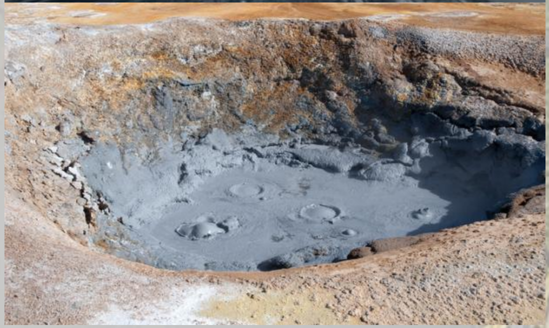
Particulate Bounded Mercury

SCIENTIFIC UNCERTAINTIES: ATMOSPHERIC CHEMISTRY



The most important “emitters” of Hg

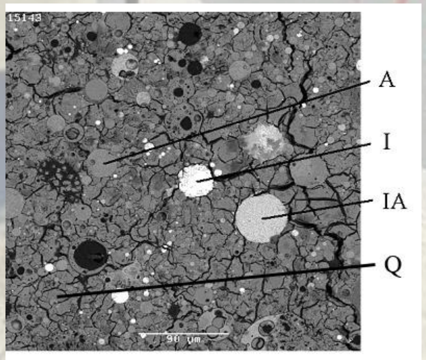
1. Volcanic and geothermal fluid discharges



2. Fossil fuel combustion

3. Industrial waste and working refuse

4. Fly ashes and crematorium



5. Dental amalgam
Hg-Lamp

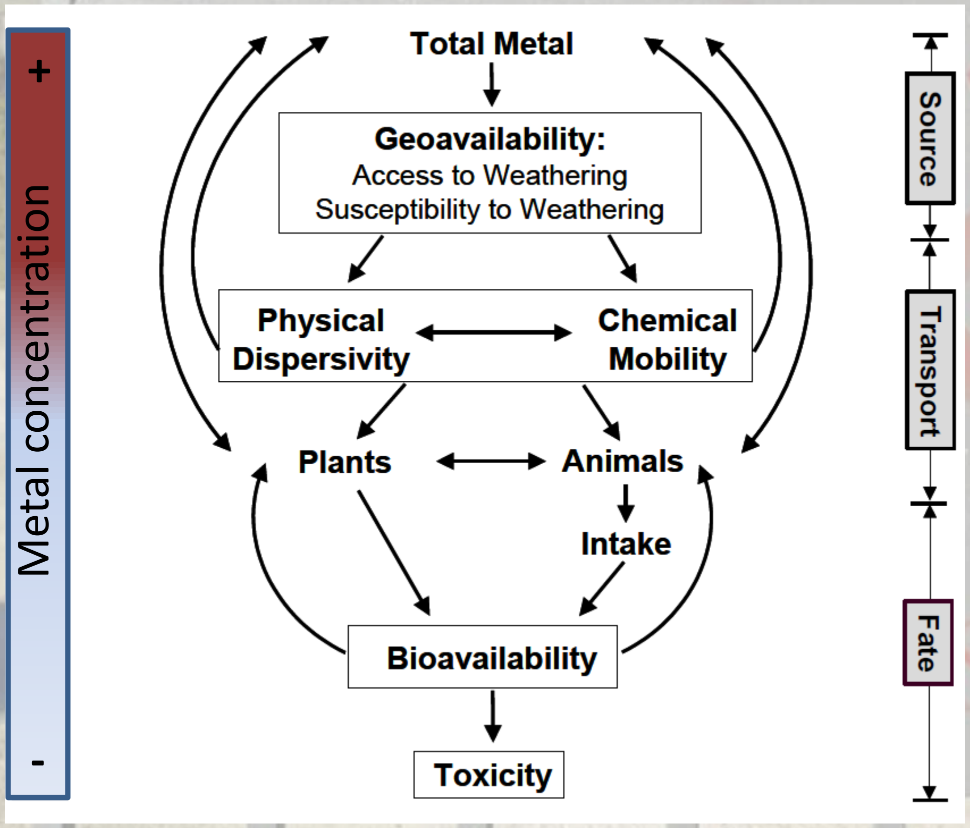
e…le miniere di mercurio

Amalgamazione

- ✓ Forma un amalgama con argento e oro
- ✓ Hg è stato utilizzato in otturazioni dentali; anche per la superficie riflettente in vecchi specchi
- ✓ Ampiamente utilizzato nell'estrazione dell'oro, passato e presente
- ✓ Corrode rapidamente l'alluminio quando entra in contatto. Possibile sabotaggio degli aerei nella seconda guerra mondiale

Geodisponibilità e biodisponibilità

Geodisponibilità (USGS 1993): porzione di elemento o composto rilasciata nell'ambiente (sub)superficiale (o la biosfera) da materiali geologici per processi meccanici, chimici e biologici



Biodisponibilità (USGS 1993): porzione di elemento o composto disponibile per l'assimilazione del biota

Speciazione

Processo di identificazione e quantificazione delle differenti ***specie chimiche*** in cui un elemento occorre nel materiale

↓

specifici composti chimici o stati di ossidazione

Definire la speciazione è quindi fondamentale per stabilire **biodisponibilità**, reattività e tossicità dei metalli (e quindi di Hg)

Solubilità di Hg

Cinabro
(α-HgS)

Metacinabro
(β-HgS)

Hg metallico
(Hg^0)

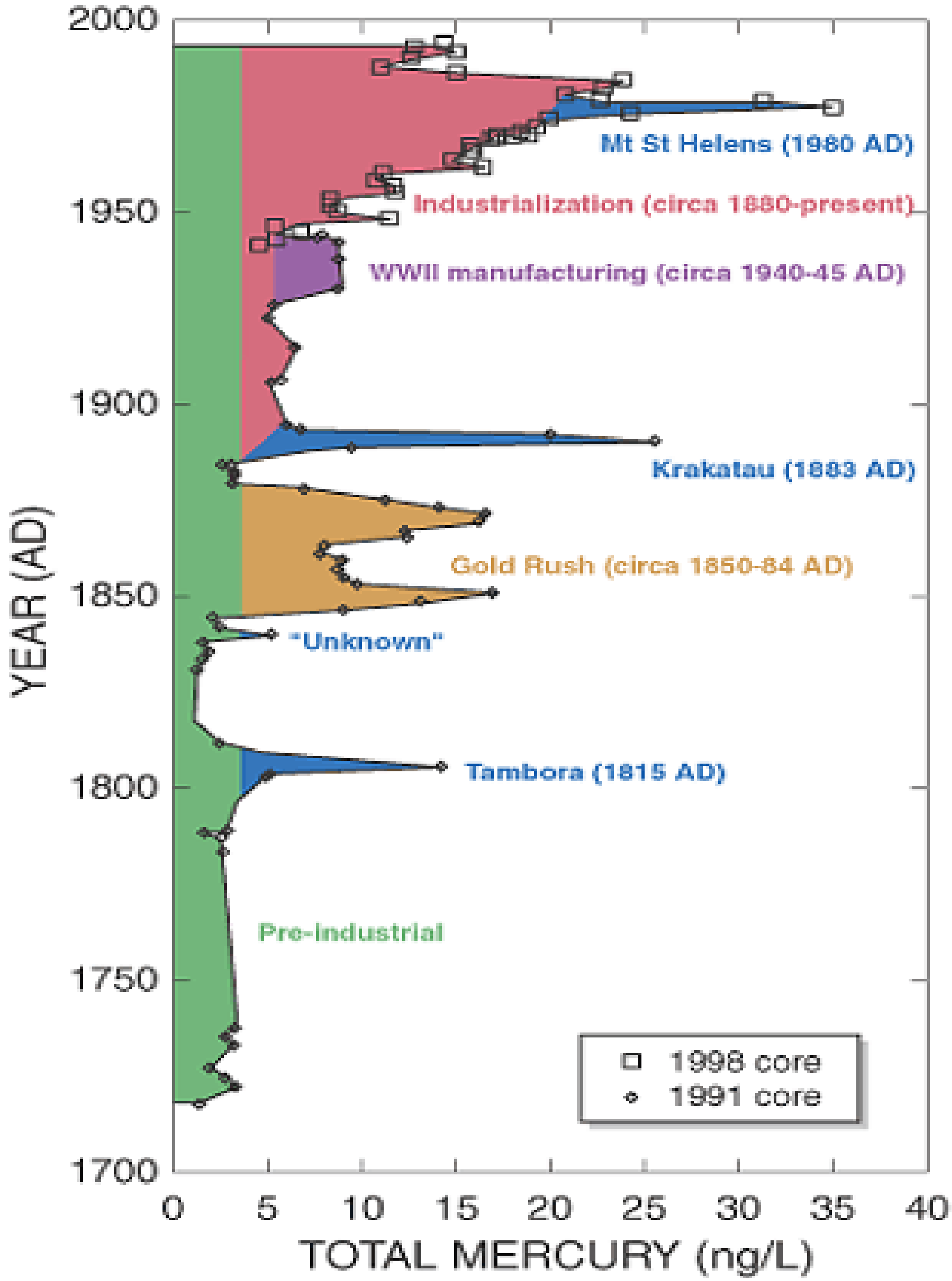
Calomelano
(Hg_2Cl_2)

Diversa solubilità tra le varie fasi mineralogiche …

Calomelano > Hg^0 > metacinabro ≈ cinabro

Geochimicamente, è un elemento calcofilo e il suo minerale più comune è il cinabro (HgS). Può essere trovato come Hg (nativo), montroydite (HgO), calomelano (Hg_2Cl_2) e eglestomite ($Hg_3Cl_3O(OH)$).

Hg come "contaminante globale"



Le concentrazioni preindustriali indicano fonti naturali

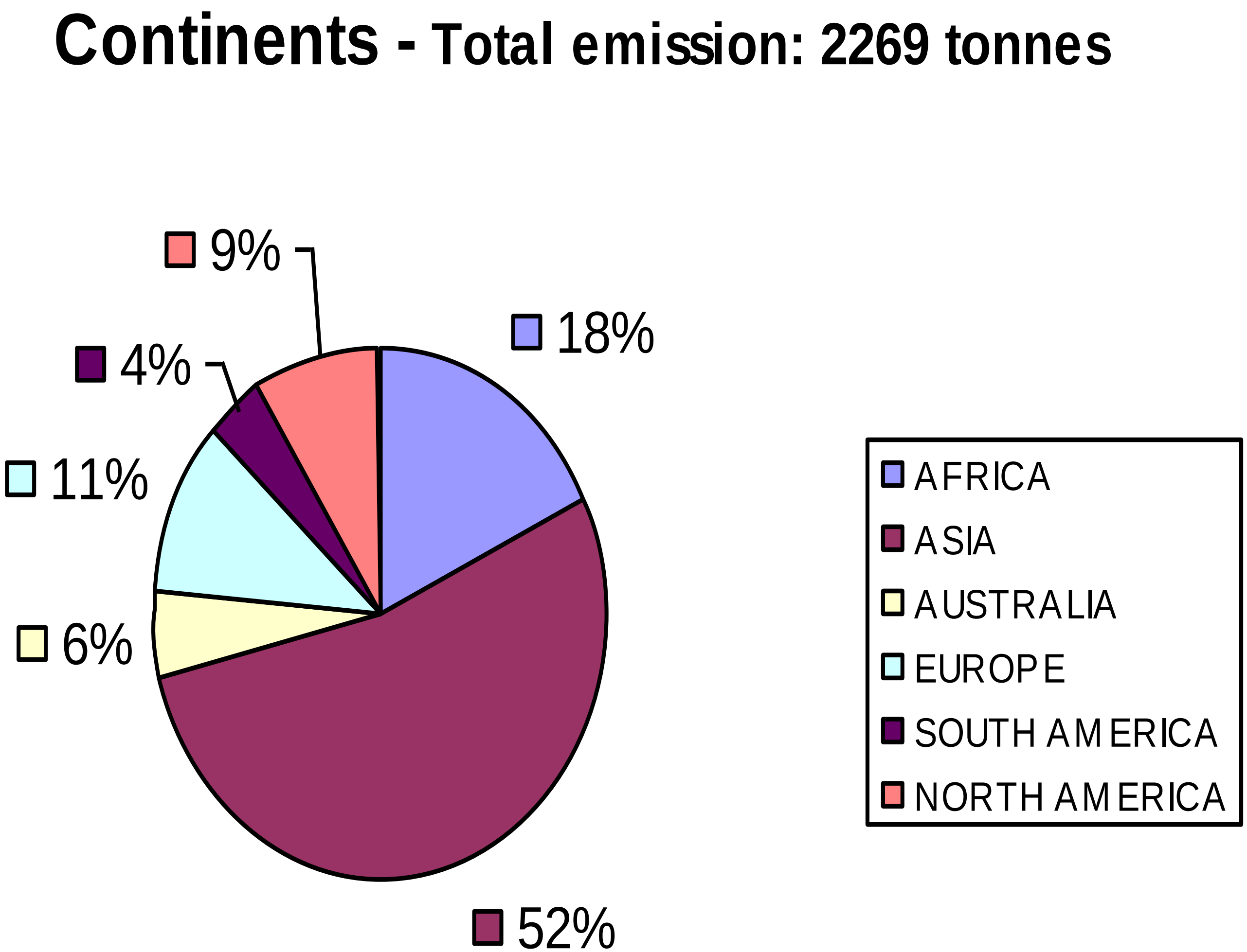
Input vulcanico episodico

L'estrazione mineraria emerge

Industrializzazione e recente declino

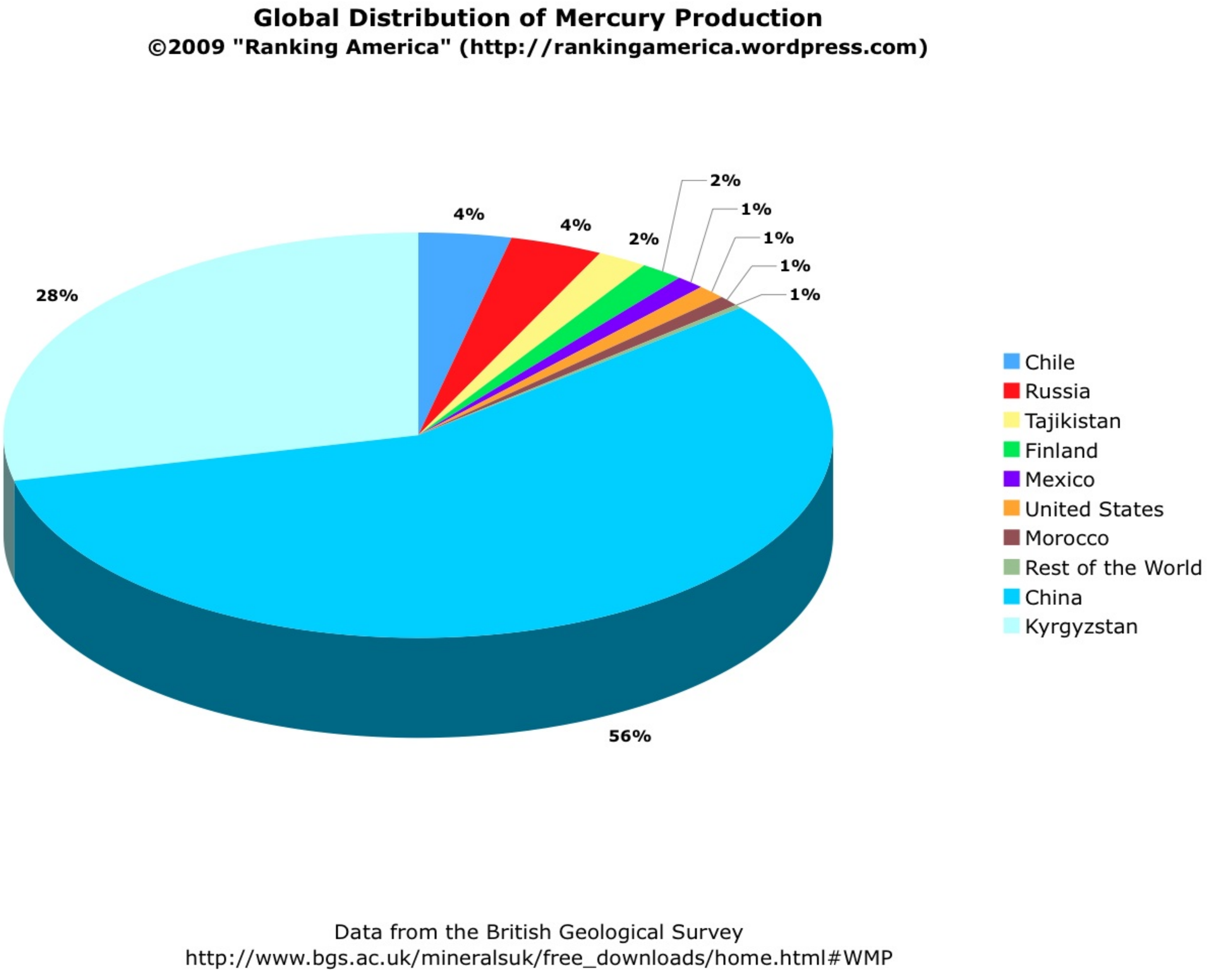
Record centrale di deposizione del ghiaccio del Wyoming, USA [Schuster et al., ES&T 2002]

Distribuzione geografica

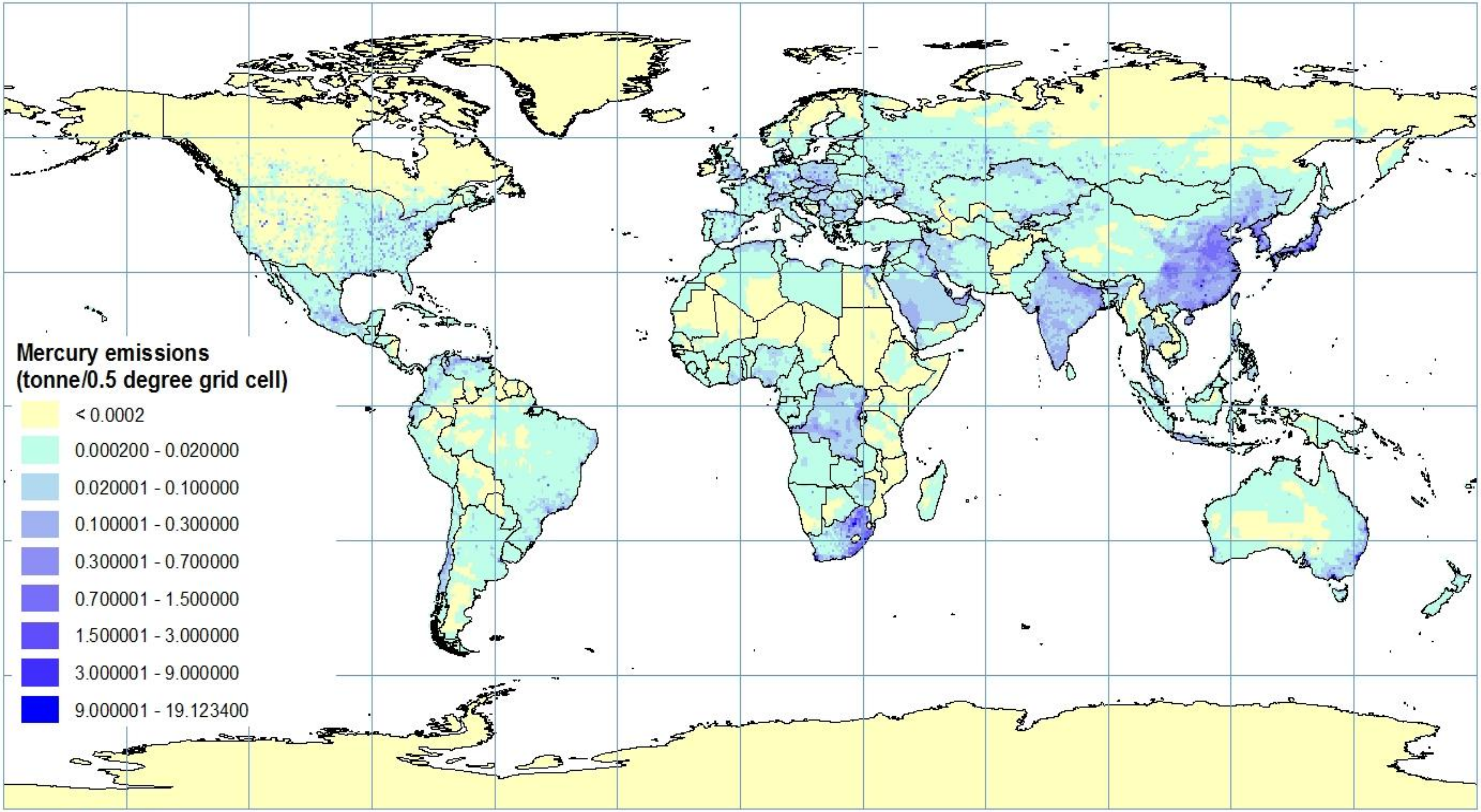


Slide courtesy of Jozef Pacyna, NILU

Distribuzione globale della produzione di mercurio



Mercury Emissions, 2000
diffuse + point sources



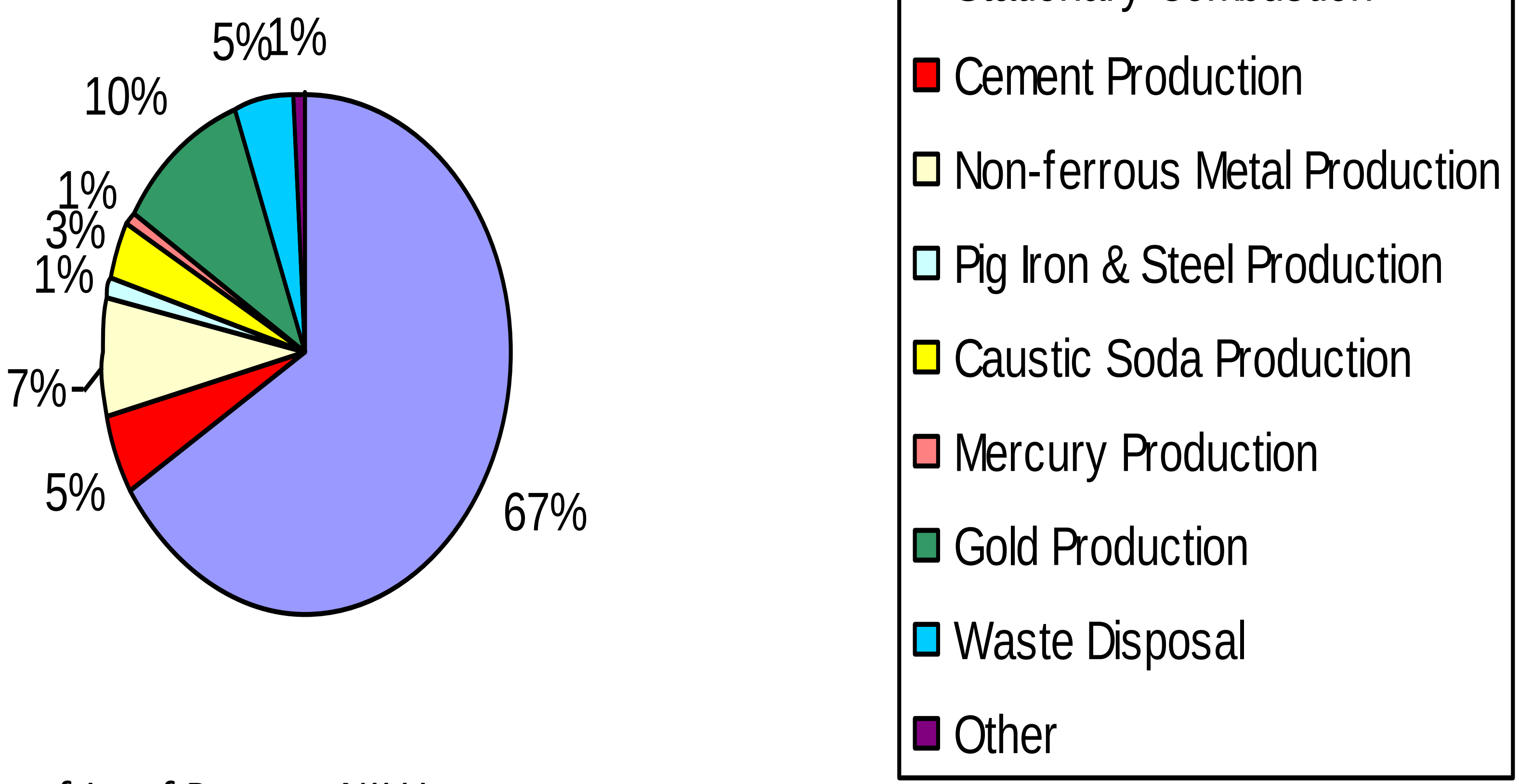
no projection (geographic)

Global Emissions Inventory Activity (GEIA)

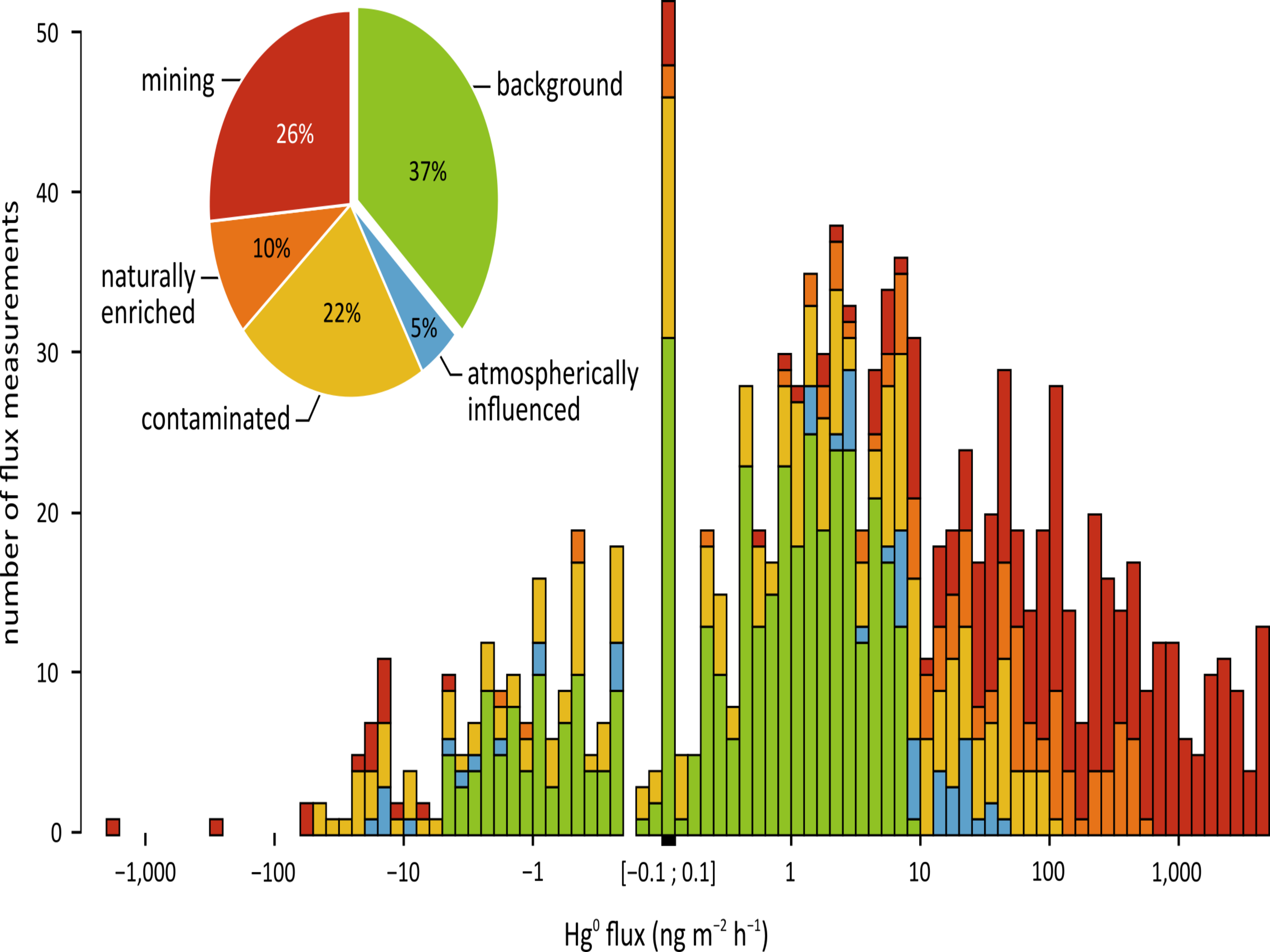
S. Wilson (AMAP), F. Steenhuisen (Arctic Centre, RuG), J. Pacyna (NILU)

Categorie di emissione

Categories - Total emission: 2269 tonnes



Slide courtesy of Jozef Pacyna, NILU


mining
26%
background
37%
naturally enriched
10%
22%
5%
atmospherically influenced
contaminated
number of flux measurements
0
10
20
30
40
50
−1,000
−100
−10
−1
[−0.1 ; 0.1]
1
10
100
1,000
Hg^0 flux (ng m^{-2} h^{-1})

Hg GASSOSO

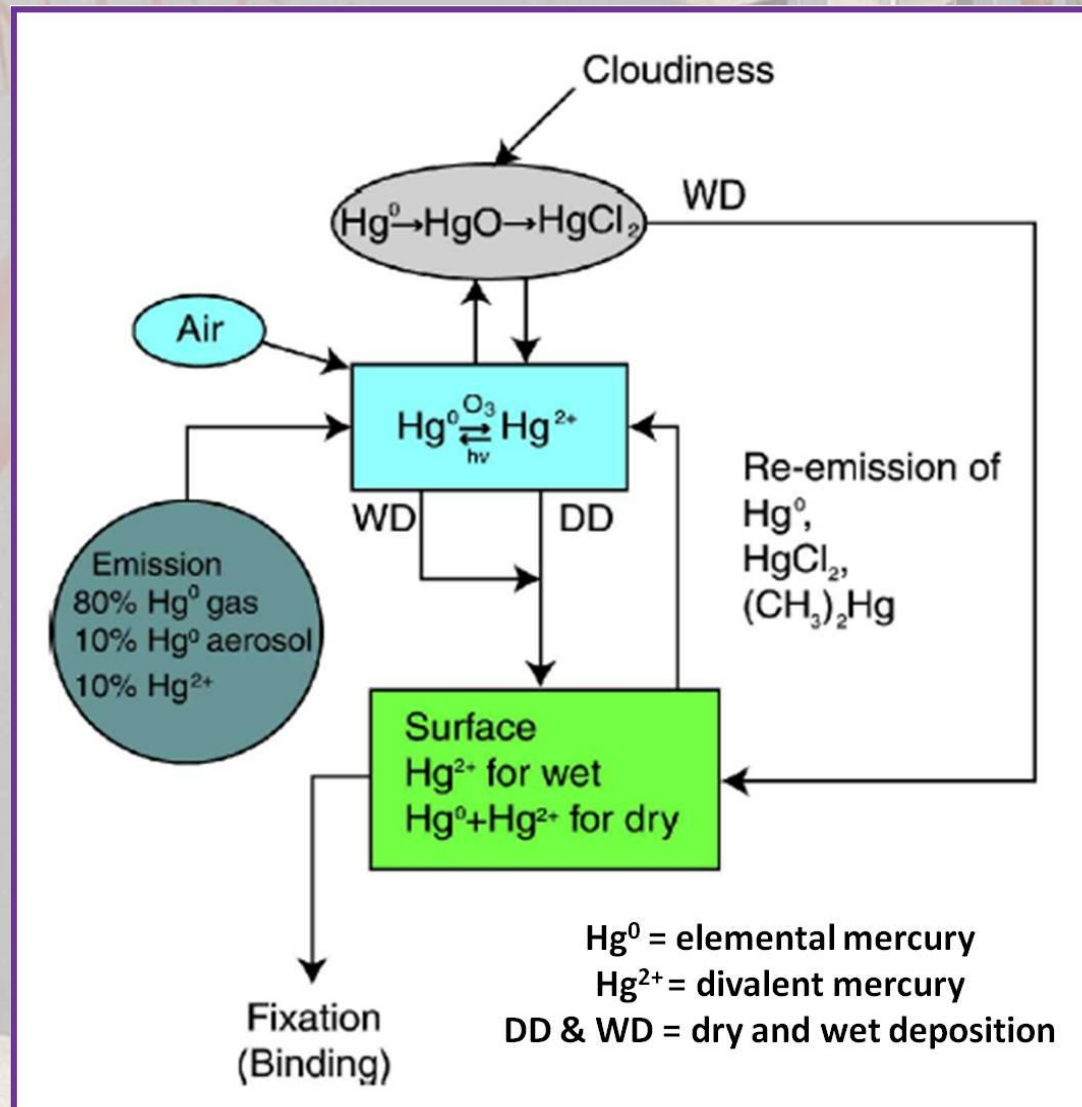
La forma dominante di Hg in atmosfera (95-98%) è il mercurio gassoso elementare (Hg^0 o gaseous elemental mercury: GEM), caratterizzato da elevata stabilità e volatilità, bassa solubilità e tempo di residenza di 1-2 anni a causa della sua inerzia chimica

Oltre al GEM sono presenti in atmosfera anche la fase gassosa reattiva, corrispondente allo stato di ossidazione +2 (reactive gaseous mercury: RGM), e la fase aderente al particolato (total particulate mercury: TPM)

In particolare RGM è costituito da specie di mercurio idrosolubili (e.g. $HgCl_2$) ed eventualmente da altri composti di mercurio bivalente, quali HgO, $HgSO_3$ e dimetilmercurio

Hg GASSOSO

Nonostante il lungo tempo di residenza, negli strati più alti dell’atmosfera ha luogo la conversione del mercurio elementare in forme divalenti tramite processi di ossidazione, i quali possiedono però una cinetica lenta e dipendono soprattutto dalla presenza di molecole come ozono e radicali ossidrili



Hg GASSOSO

Tra i meccanismi di ossidazione più importanti vi sono le reazioni con l'ozono, il radicale ossidrile, il radicale nitrato e gli alogeni (Cl e Br)

$$Hg + O_3 \leftrightarrow HgO + O_2$$

$$Hg + OH \leftrightarrow HgOH$$

$$Hg + NO_3 \leftrightarrow HgO + NO_2$$

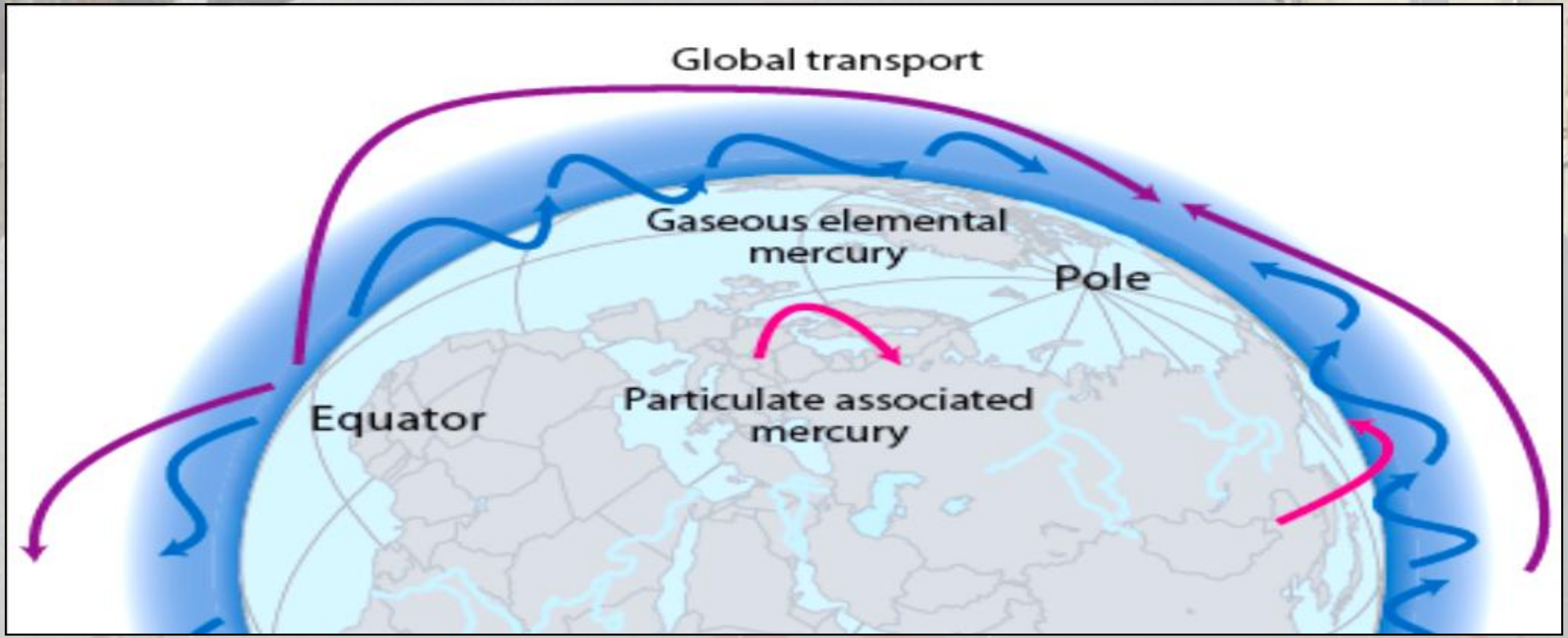
$$Hg + Cl \leftrightarrow HgCl$$

$$Hg + Br \leftrightarrow HgBr$$

Per quanto riguarda le reazioni di riduzione, il processo principale consiste nella fotoriduzione, indotta principalmente dalle radiazioni ultraviolette

$$Hg^{(II)} + \; h\nu \; \leftrightarrow Hg^0$$

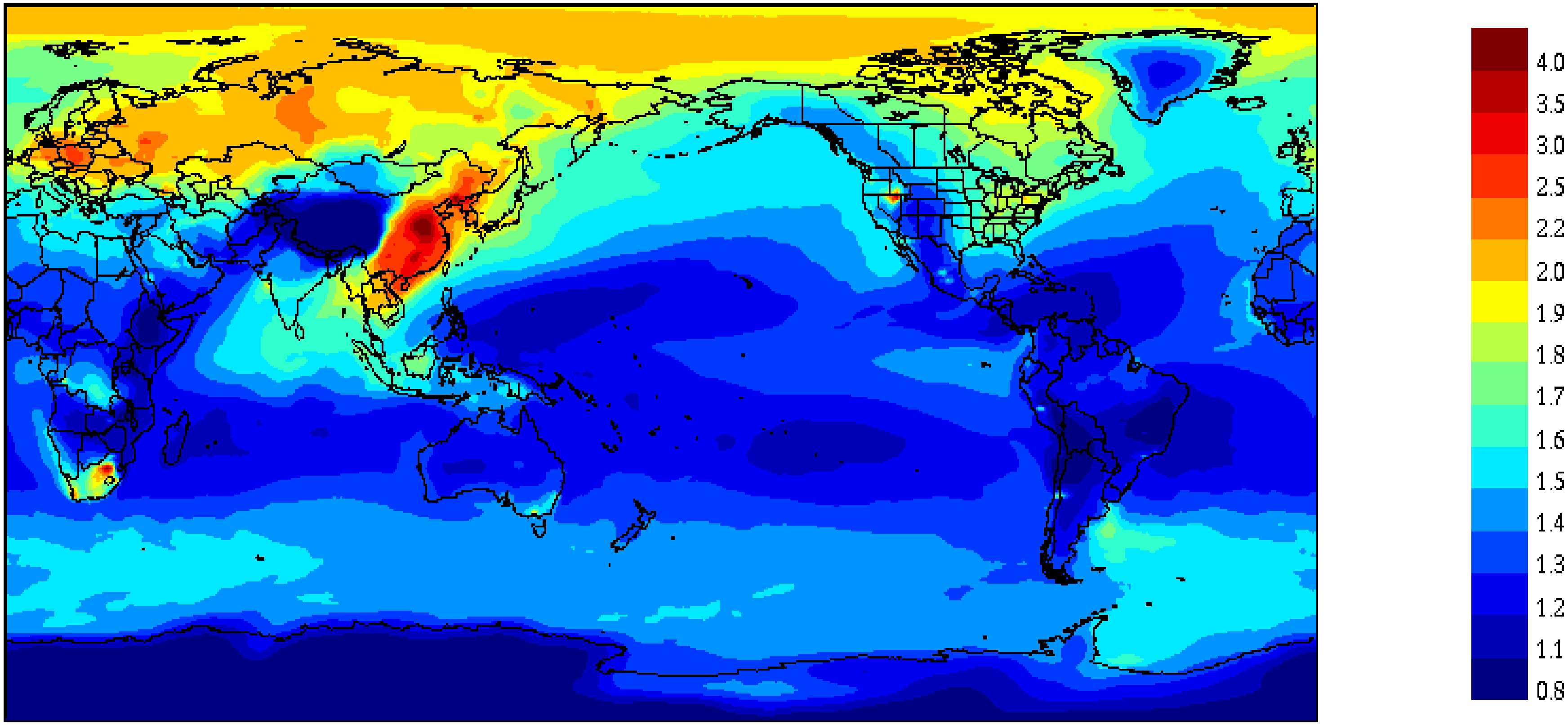
Hg GASSOSO



Hg^0 è in grado di essere trasportato per distanze molto lunghe (decine di migliaia di km), Hg^{2+} in fase gassosa può essere disperso per alcune decine fino ad alcune centinaia di km dalla sorgente, mentre il mercurio particolato è solitamente depositato a distanze intermedie, a seconda del diametro e della massa dell'aerosol

Modellazione del trasporto globale

Concentrazioni superficiali medie del mercurio elementare per gennaio 2001 (ng/m^3)



GRAHM (Global/Regional Atmospheric Heavy Metals Model) simulation – Ashu Dastoor, Meteorological Service of Canada, Environment Canada

Hg GASSOSO

Hg tossico e fortemente volatile, fino ad inquinante globale
TGM – Concentrazione di background: 1-4 ng/m^3
Valori più elevati si osservano in aree urbane e suburbane
(e.g. USA: concentrazione media nell'aria tra 10 e 20 ng/m^3)
Fino a 10-15 µg/m^3 presso ambienti come miniere

SORGENTI:

1) **combustibili fossili e processi di combustione ad alta temperatura (e.g. carbone), impianti di trattamento di cloro-alcali e incenerimento di rifiuti urbani (ca. 4,000 t/a);**
2) **sorgenti naturali (ca. 2,000 t/a): suoli, foreste, specchi d'acqua, oceani e, soprattutto, vulcani attivi (circa il 78% delle emissioni naturali);**
3) **aree naturalmente arricchite in Hg (cintura mercurifera)**

SORGENTI URBANE

- combustione di combustibili fossili
- produzione di metalli
- produzione di cemento
- scarichi di rifiuti medici e industriali
- cremazioni
- produzione di soda caustica

Ulteriori fonti non-puntuali possono essere importanti nei budget urbani complessivi, ma sono difficili da quantificare: una miscela di Hg trasportato in città e/o proveniente da sorgenti piccole o sconosciute

Le emissioni veicolari diffuse possono inoltre contribuire significativamente alle emissioni di Hg

SORGENTI URBANE

Da: <u>Agenzia Europea dell'Ambiente</u>

Attualmente il mercurio è impiegato in vario modo in tutto il mondo. Molto poco utilizzato in Europa, nei prossimi anni sarà impiegato principalmente per gli amalgami dentali, dal momento che le applicazioni in ambito industriale sono state vietate. In altre parti del mondo lo si utilizza maggiormente nelle attività industriali e nell'estrazione dell'oro su piccola scala

Una delle principali fonti di inquinamento da mercurio in Europa e altrove è la combustione di combustibili solidi – carbone, lignite, torba e legno – a livello sia industriale che domestico. Quando questi combustibili bruciano, i piccoli quantitativi di mercurio che contengono vengono rilasciati nell'ambiente. Le emissioni di tali combustibili, che costituiscono la principale fonte di inquinamento da mercurio in Europa, sono legate ad attività quali la produzione di energia elettrica, la fabbricazione di cemento e la produzione di metalli

LINEE GUIDA

L'inquinamento atmosferico del mercurio comporta 2 rischi:

(1) inalazione diretta di mercurio gassoso (al lavoro o a casa), con vari effetti sulla fisiologia umana;

(2) speciazione del mercurio, e.g. GEM in RGM, o RGM in metil-mercurio

L'UE e le legislazioni nazionali non indicano valori limite per quanto riguarda il mercurio nell'aria

<u>EPA</u>: 300 ng/m^3 limite per esposizione cronica a Hg

<u>ATSDR</u>: 200 ng/m^3 limite per esposizione cronica a Hg

<u>WHO</u>: valore medio annuo di 1,000 ng/m^3 come linea guida per il mercurio inorganico nell'aria

LINEE GUIDA

Limite legge italiana GU sett. 2012: 20,000 ng/m^3 per 8 h (Hg tot)
OSHA: 100,000 ng/m^3 (limite su media 8 h lavoro, è la concentrazione massima permessa) (non specificato se Hg^0)
NIOSH: 50,000 ng/m^3 (si specifica Hg vapor quindi Hg^0, in media su 10 h lavoro) e 100,000 ng/m^3 come Hg tot
ACGIH: valore soglia di 25,000 ng/m^3 su 8 h di lavoro (non specificato se Hg^0)

EPA (2001) definisce inoltre 3 livelli di azione in risposta alla concentrazione di Hg misurata in aria: 1) ≥10,000 ng/m^3 (in tempo reale), i residenti devono essere trasferiti immediatamente; 2) tra >1,000 e <10,000 ng/m^3, il trasferimento deve essere programmato al più presto possibile; 3) ≤1,000 ng/m^3 (8 ore come tempo medio di esposizione), nessuna azione è necessaria.

LINEE GUIDA

World Health Organization
Regional Office for Europe
Copenhagen

Table 19. Concentrations of total mercury in air and urine at which effects are observed at a low frequency in workers subjected to long-term exposure to mercury vapour

Observed effect [a]	Mercury level		Reference
	Air [b] (µg/m³)	Urine (µg/litre)	
Objective tremor	30	100	*(5)*
Renal tubular effects; changes in plasma enzymes	15 [c]	50	*(6)*
Nonspecific symptoms	10–30	25–100	*(5)*

[a] These effects occur with low frequency in occupationally exposed groups. Other effects have been reported, but air and urine levels are not available.

[b] The air concentrations measured by static air samplers are taken as a time-weighted average, assuming 40 hours per week for long-term exposure (at least five biological half-times, equivalent to 250 days).

[c] Calculated from the urine concentration, assuming that a mercury concentration in air of 100 µg/m³ measured by static samplers is equivalent to a mercury concentration of 300 µg/litre in the urine.

WHO Guideline Values

Water: 1 µg/litre for total mercury [8]

Air: 1 µg/m³ (annual average) [9]

WHO estimated a tolerable concentration of 0.2 µg/m³ for long-term inhalation exposure to elemental mercury vapour, and a tolerable intake of total mercury of 2 µg/kg body weight per day. [10]

Table I: Environmental and Occupational Health Standards for Inhalation Exposure to Mercury Vapor

Agency	Mercury Concentration (µg/m³)[1]
OSHA Ceiling limit[2]	100
NIOSH REL[3]	50
ACGIH TLV[4]	25
ATSDR MRL[5]	0.2
ATSDR Action Level, for indoor exposures	1.0
EPA Rfc[6]	0.3

[1] micrograms per cubic meter
[2] Ceiling limit = the concentration of mercury vapor cannot exceed this value at any time
[3] REL = Recommended Exposure Limit, a time weighted average for an 8-hour day.
[4] TLV = Threshold Limit Value, a time weighted average for an 8-hour day
[5] MRL = minimal risk level
[6] Reference concentration

Tossicità del mercurio elementare

- ✓ **Il mercurio è una potente tossina**
- ✓ **Il vapore è dannoso: l'esposizione cronica porta alla "malattia del cappellaio matto" (*erethism mercurialis*)**
  - ✓ **Perdita di capelli, denti e unghie.**
  - ✓ **Sordità**
  - ✓ **Mancanza di coordinamento**
  - ✓ **Problemi di memoria**
  - ✓ **Disturbi emotivi**
  - ✓ **Danni ai reni**
  - ✓ **Effetti riproduttivi negativi, difetti alla nascita e aborti spontanei.**
  - ✓ **Reazioni allergiche che causano eruzioni cutanee, stanchezza e mal di testa.**

Alice nel Paese delle Meraviglie

Il Cappellaio Matto

Il trattamento delle pelli utilizzate per fare cappelli comportava l'uso di nitrato di mercurio.

I cappellai mettevano i cappelli sulla testa per modellarli e il risultato era una colorazione arancione fosforescente. Inoltre, l'assorbimento del mercurio ha causato effetti neurologici come il bipolarismo comportamentale.

UNEP Minimata Convention on Mercury
Primo grande trattato ambientale mondiale in più di un decennio

Aperto alle firme nell'ottobre 2013; già firmato da 128 paesi

- Richiede la migliore tecnologia di controllo disponibile per le centrali elettriche a carbone
- L'estrazione del mercurio sarà vietata in 15 anni
- Molti prodotti commerciali contenenti mercurio saranno vietati

La Convenzione prevede la ratifica da parte di 50 paesi per entrare in vigore; nove (compresi gli Stati Uniti) hanno finora ratificato

METODI DI MISURA: ATTIVI

Tradizionalmente, il monitoraggio di Hg nelle aree urbane è stato condotto con strumenti di misurazione attivi in installazioni a lungo termine in un numero limitato di siti

Esempi:

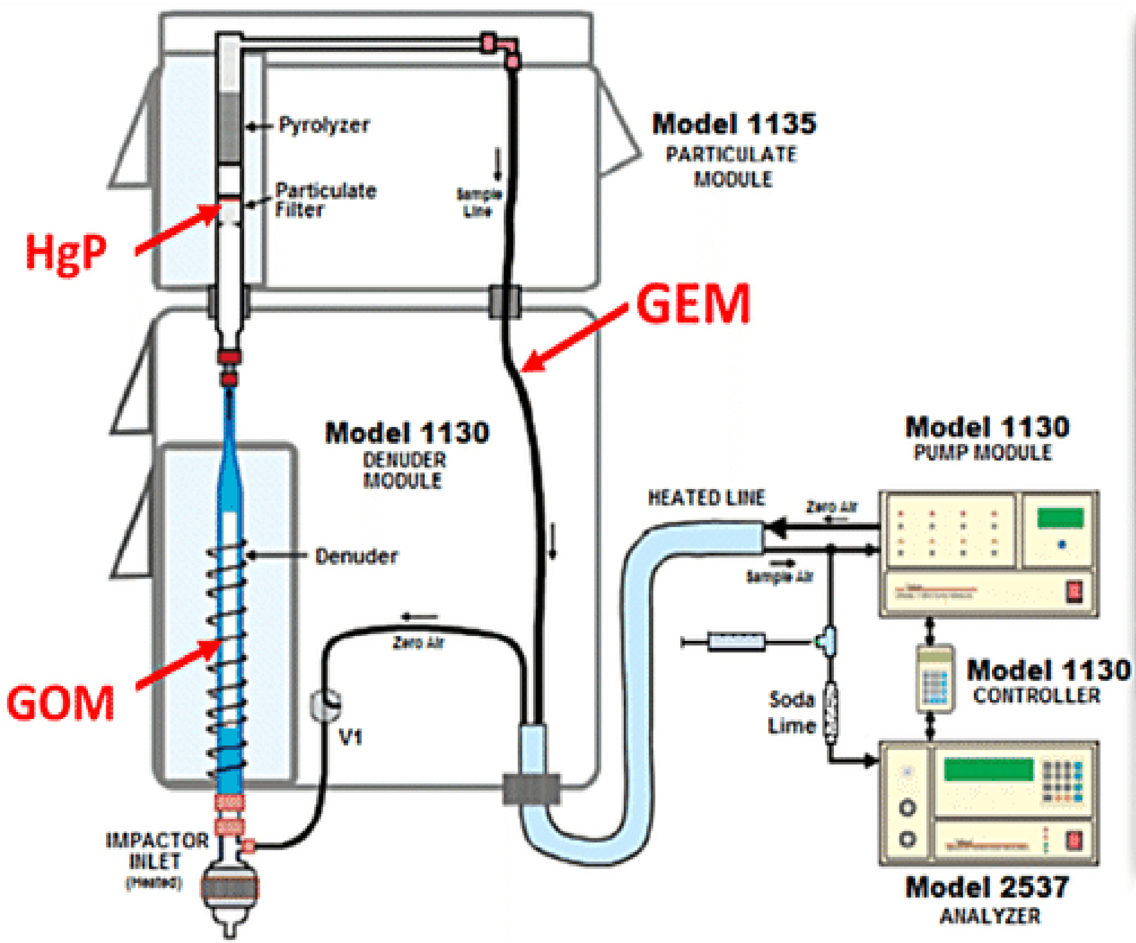
- **tubi di silice rivestiti in oro connessi ad una pompa**
- **analizzatori d’aria ad alto flusso (e.g. Tekran®, Lumex®)**

Le misurazioni di GEM in aria avvengono comunemente mediante desorbimento termico e quantificazione mediante spettrometria di fluorescenza atomica a vapore freddo (CVAFS), dopo aver intrappolato il mercurio su un substrato rivestito di oro

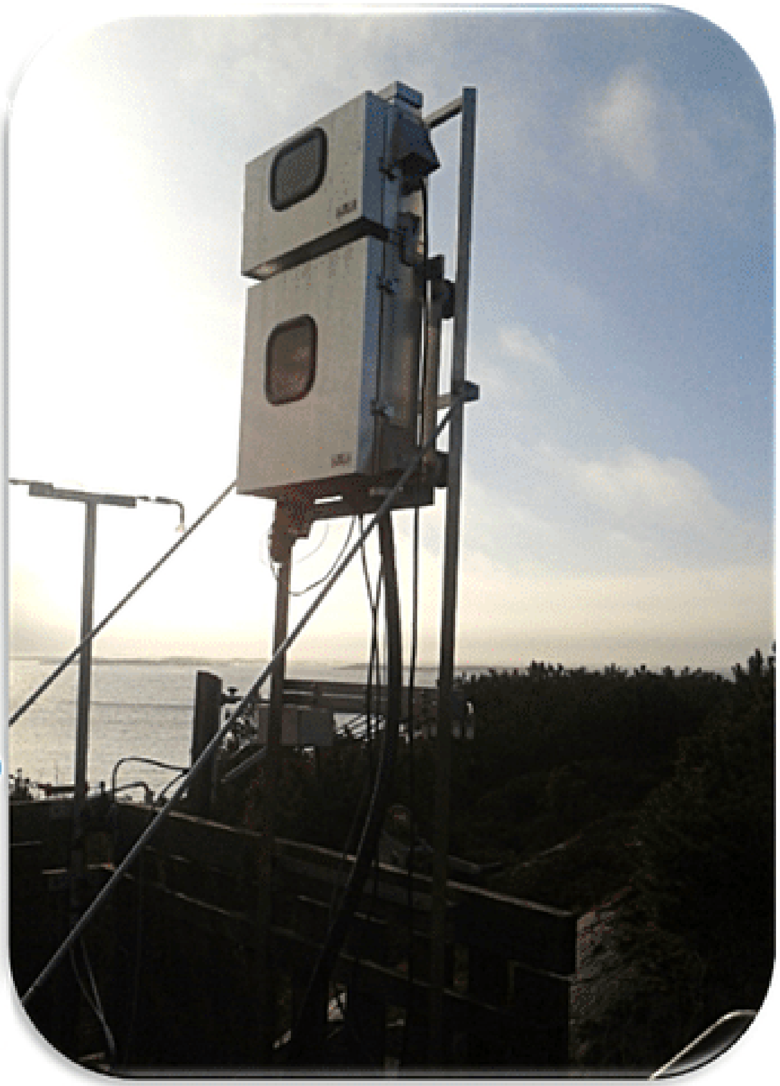
TEKRAN

Tekran mercury speciation system (da Wängberg et al., 2016)

(a)



(b)



METODI DI MISURA: ATTIVI

VANTAGGI

- La strumentazione attiva è efficace nel fornire informazioni sia a breve che a lungo termine, e.g. in città con concentrazioni alte e variabili nel tempo (e.g. Asia orientale, con elevate emissioni a carbone)

- È possibile misurare ad alta frequenza, in real-time ed in contiuno e distinguere variazioni quasi istantanee di concentrazione

SVANTAGGI

- Il costo degli strumenti di misurazione attivi è elevato e generalmente la risoluzione spaziale è scarsa

- Misure tramite un singolo strumento attivo presuppongono una non facile attribuzione della variabilità della concentrazione a fattori spaziali o temporali

METODI DI MISURA: PASSIVI

Alternativamente, si può ricorrere all'uso di campionatori passivi

VANTAGGI

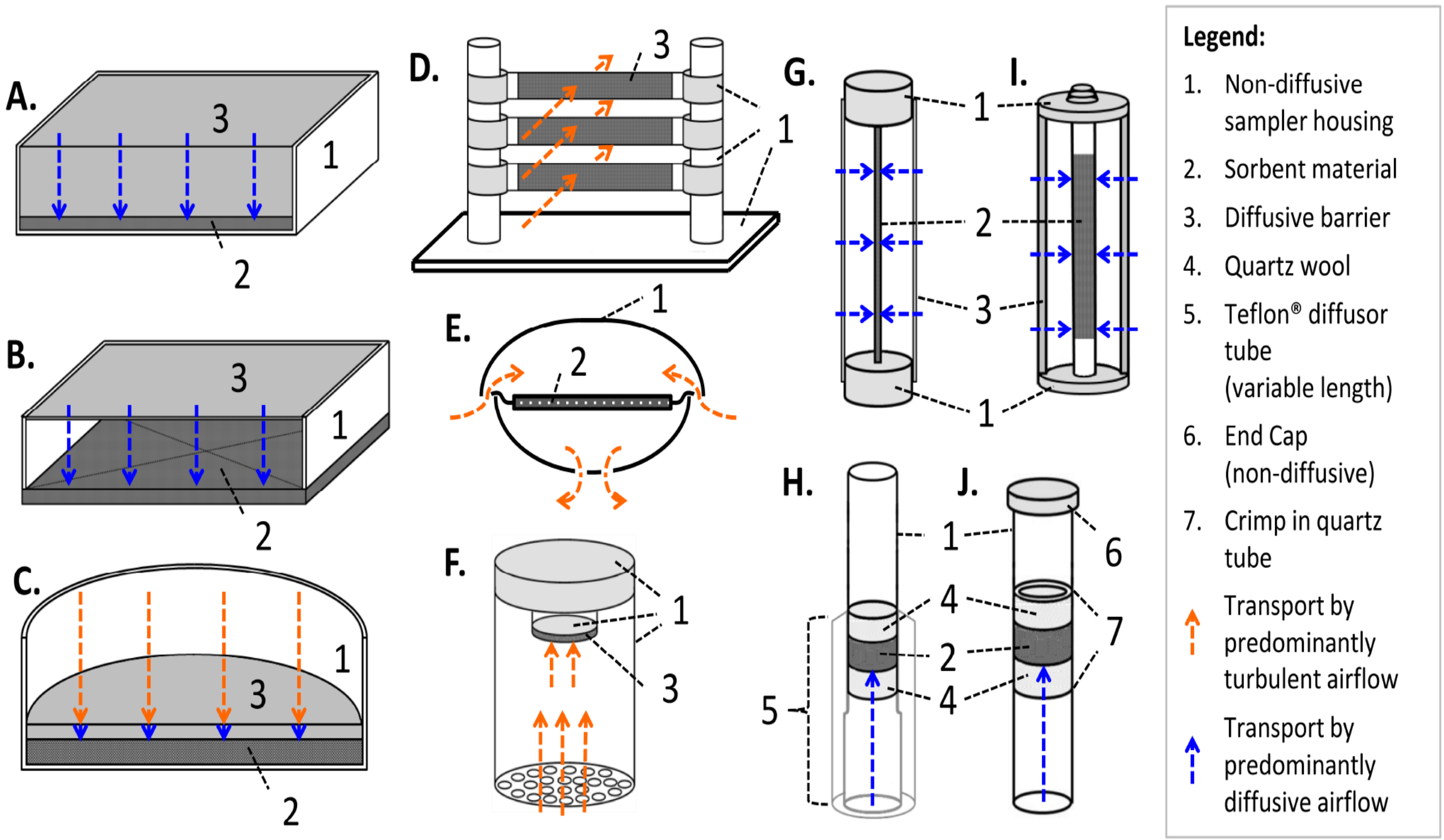
- **sono a basso costo, facili da usare e non richiedono energia, quindi sono dispiegabili contemporaneamente in numero elevato**
- **monitoraggio a lungo termine dei livelli di GEM, e.g. nelle regioni remote e nei paesi in via di sviluppo**

SVANTAGGI

- **frequenze di campionamento che possono variare a causa di fattori meteorologici e incoerenze di fabbricazione**
- **capacità di assorbimento spesso bassa e/o instabile**
- **spesso non sono in grado di rilevare la variabilità temporale a causa del loro ampio tempo di esposizione**

PASSIVI

Schematics of existing PASs for GEM (da McLagan et al., 2016)



LUMEX® RA-915M

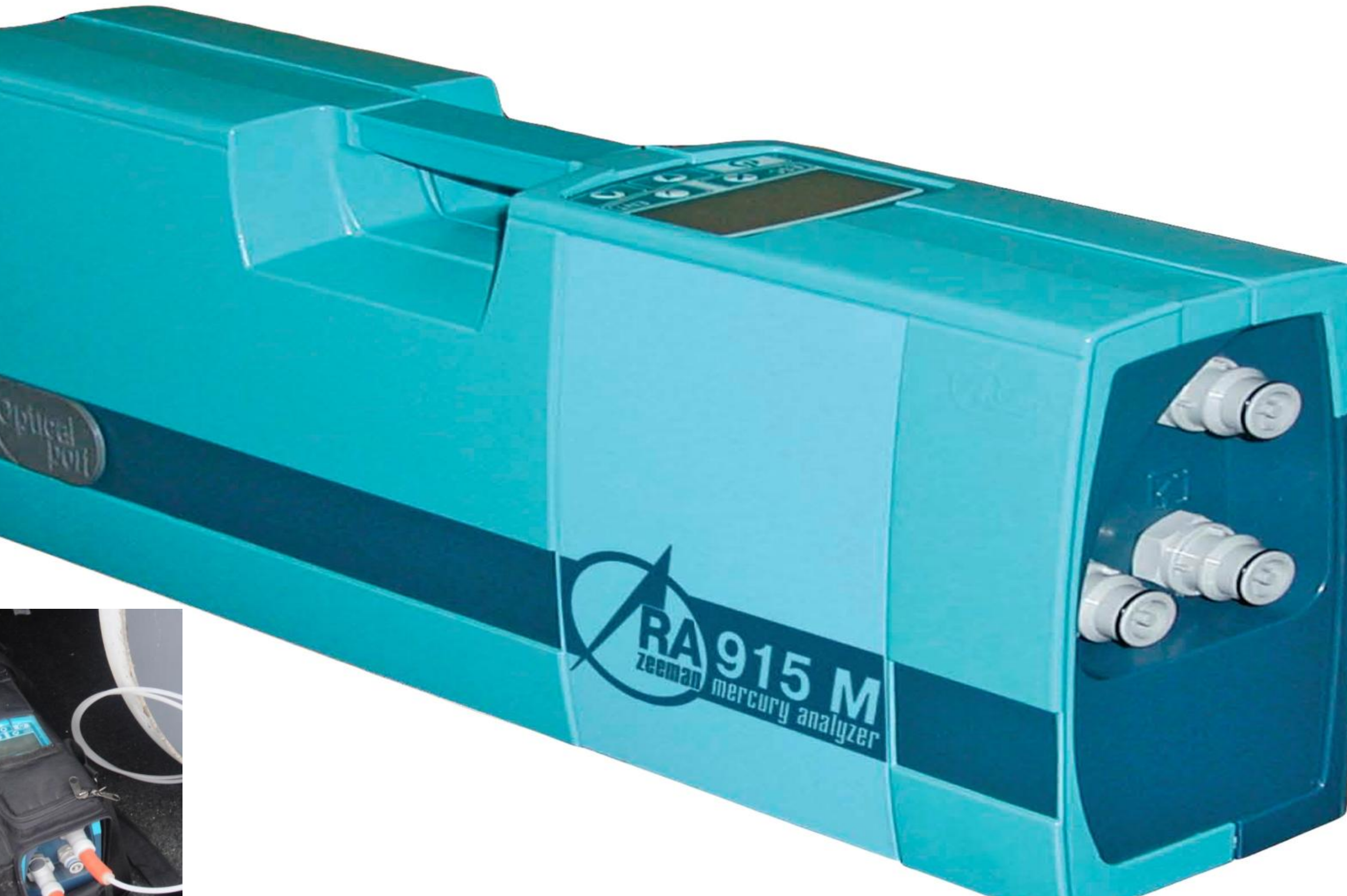
• spettrometro di assorbimento atomico ad effetto Zeeman con polarizzazione della luce (lampada ad Hg) modulata ad alta frequenza

• effetto Zeeman: separazione delle linee spettrali emesse da un gas eccitato dovuta alla presenza di un campo magnetico esterno permanente

• intervallo dinamico di lettura: 2-30.000 ng/m^3
per misure in tempo reale ed in continuo (10-15 L/min)

• applicazioni: ambienti urbani (in- e out-door), agricoli e forestali, sistemi vulcanici, aree mineralizzate

LUMEX® RA-915M



TECNICHE UTILIZZATE

- Misura della concentrazione di Hg^0 in aria tramite Lumex (tracciati e punti fissi)

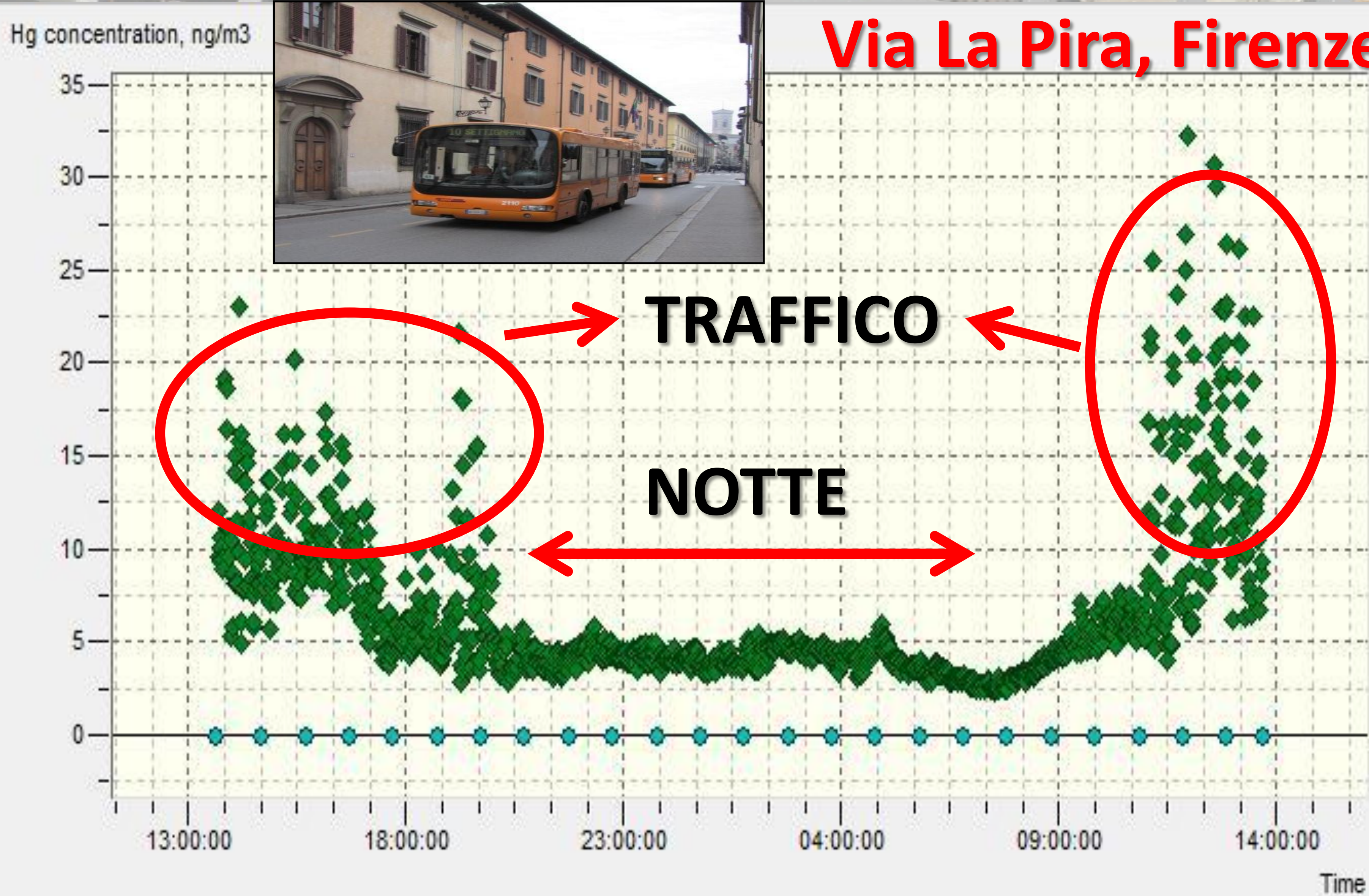
- Tecnica di misura combinata di Hg^0, H_2S, SO_2, CO_2, CH_4, … (tracciati e punti fissi) tramite Lumex e altri strumenti

- Misura dell’emissione di Hg^0 dal suolo tramite Lumex: flussi

- Moss-bags: bioaccumulatori passivi del mercurio presente in atmosfera, sia tramite deposizione secca che umida

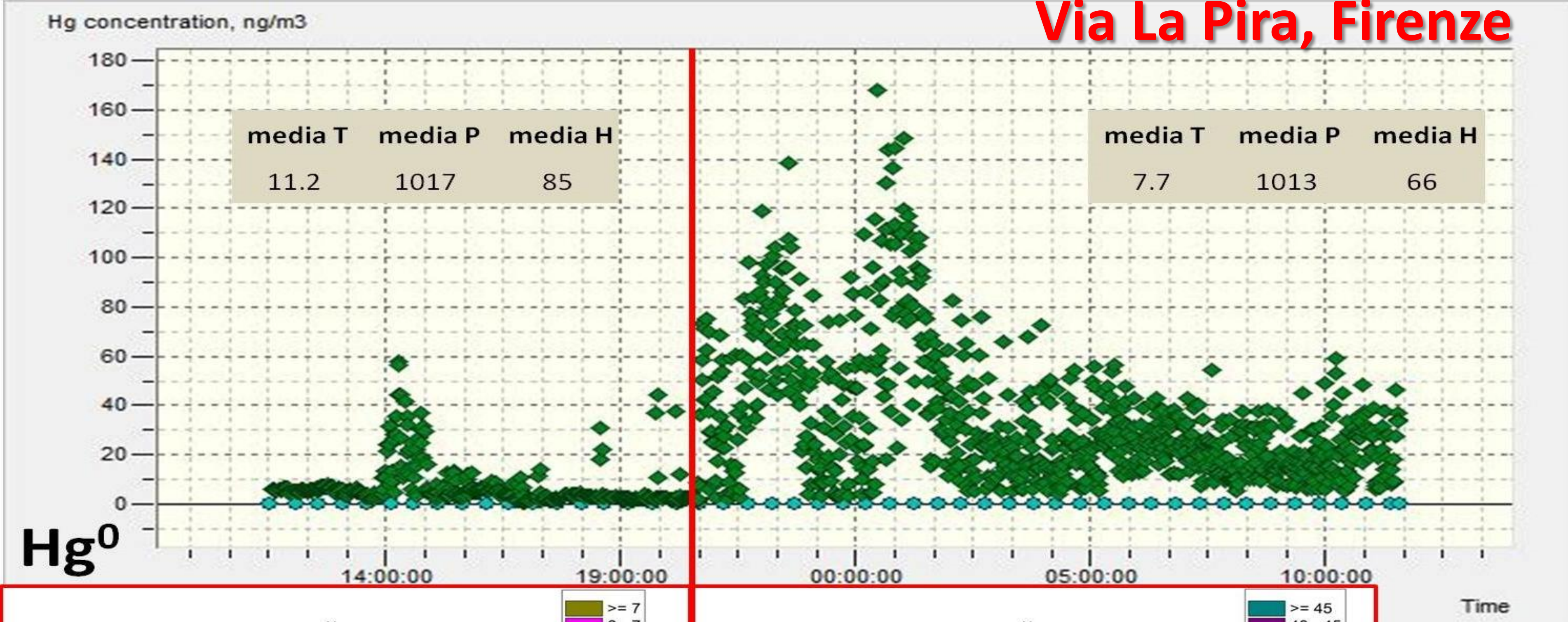
- \+ casi di studio (erbari, campionatori passivi,…)

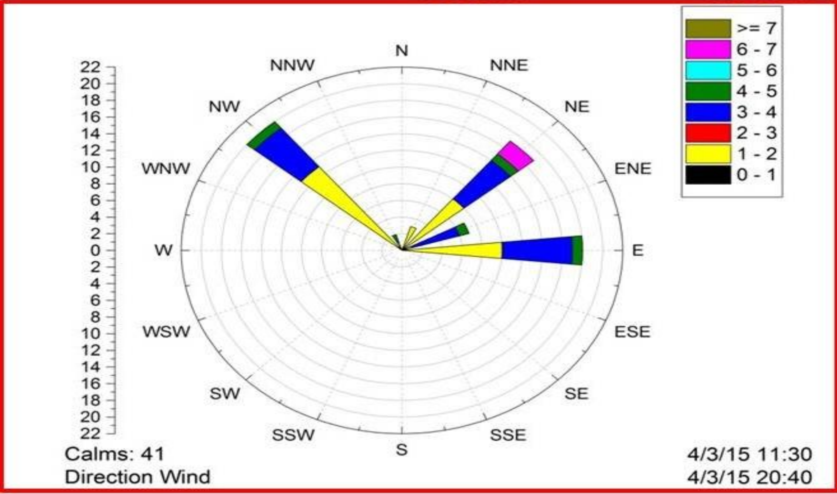
MISURE IN CONTINUO: PUNTI FISSI

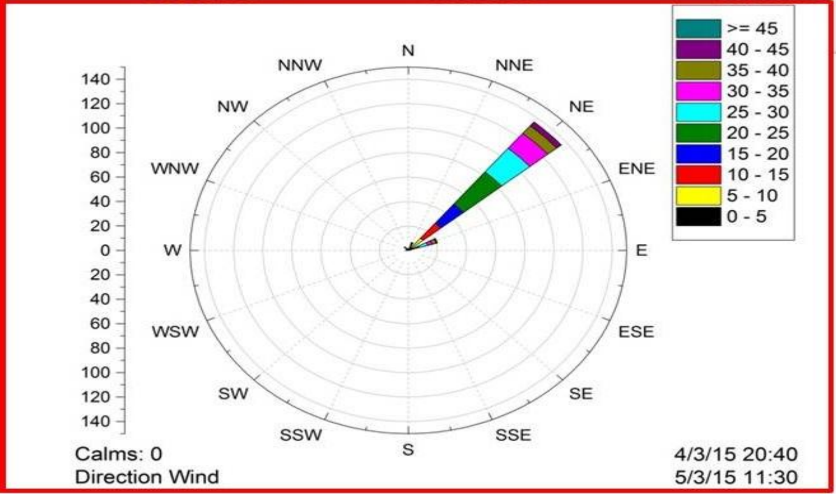


MISURE IN CONTINUO: PUNTI FISSI

Via La Pira, Firenze







Lab Martin Peccatore

4-3-15 11:30 - 5-3-15 11:30

MISURE IN CONTINUO: PUNTI FISSI

Osservatorio Ximeniano, Firenze

ciclicità?!

Dipendenza da:

- Temperatura
- Direzione e intensità del vento
- Umidità

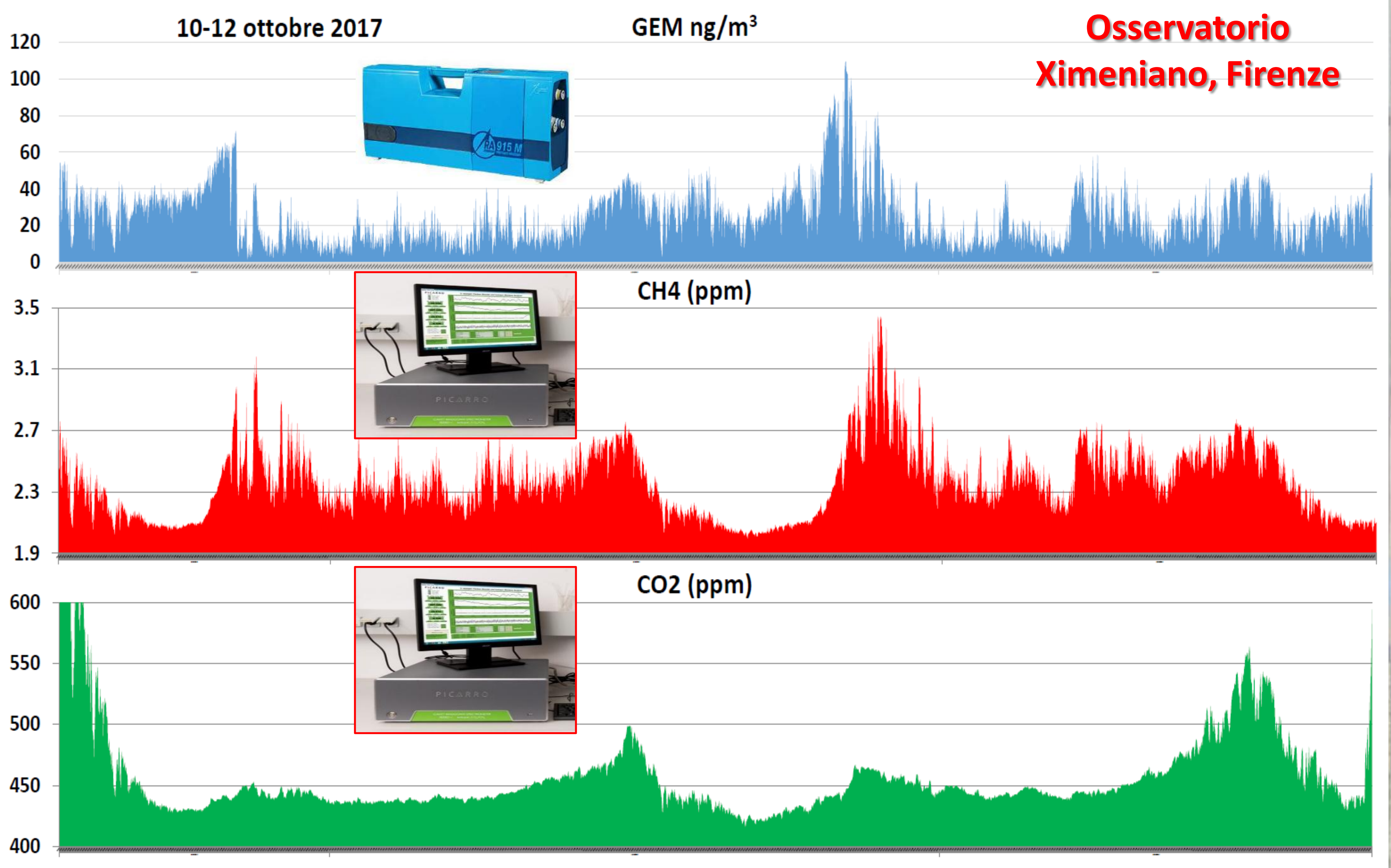
CO_2 & CH_4: Picarro® Analyzer

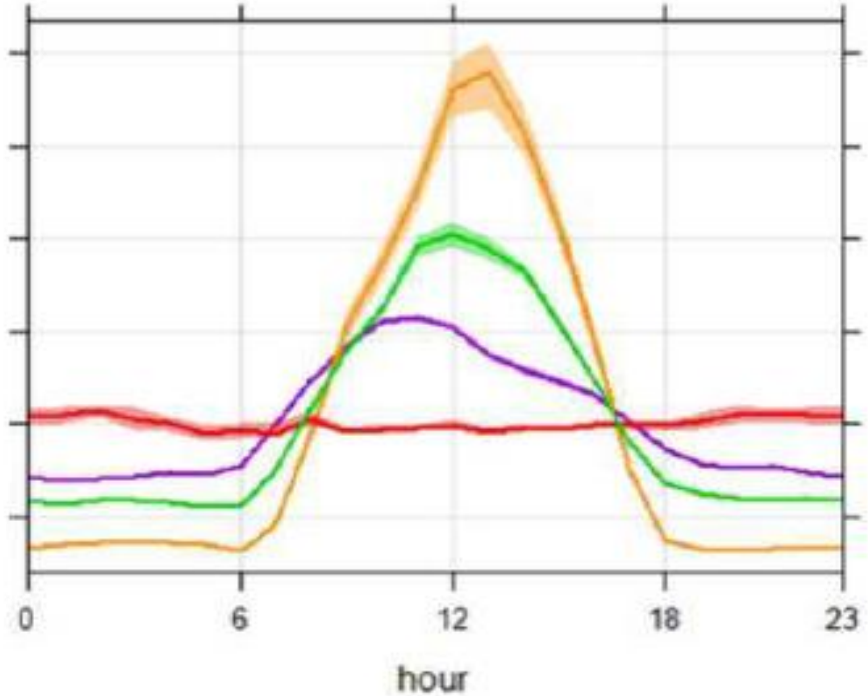
- Picarro® G2201-i Analyzer: basato sulla tecnica di spettroscopia laser CRDS (cavity ring-down spectroscopy) per misurare le concentrazioni di CO_2 e CH_4

- CO_2: dalla concentrazione in aria fino a 2,000 ppm

- CH_4: High Precision (1.8 – 12 ppm) e High Range (fino a 1000 ppm)

MISURE IN CONTINUO: PUNTI FISSI

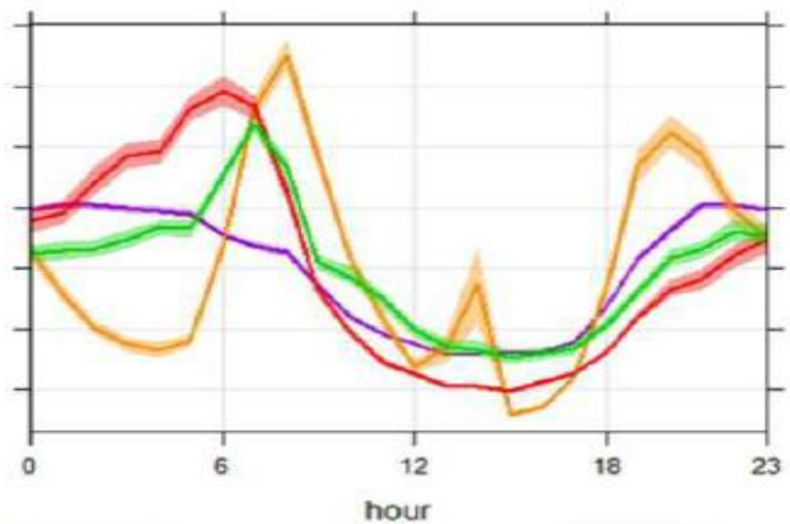




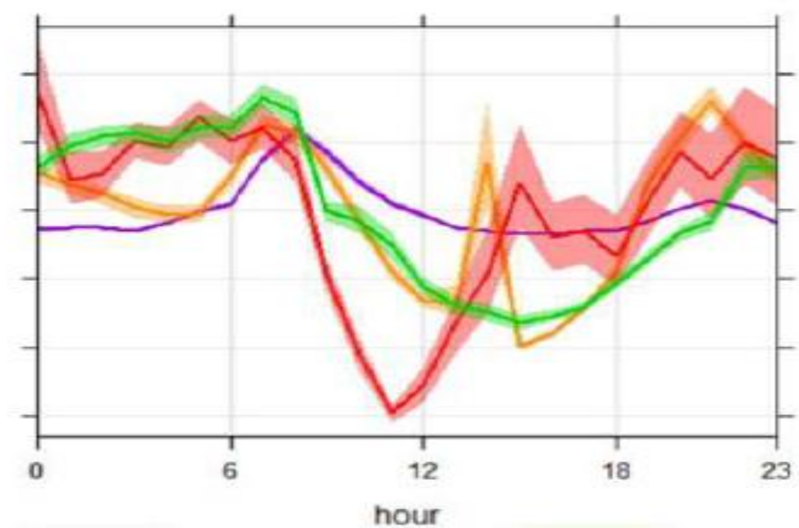
Hg

La media giornaliera del mercurio in FI-GRAMSCI, FI-BASSI, FI-SETTIGNANO e FI-MOSSE è caratterizzata da un andamento totalmente diverso da CO_2 e CH_4. Ciò implica che la sorgente principale di Hg non sia la stessa delle due specie gassose del carbonio o che comunque il suo comportamento in atmosfera rispetto a quest'ultime non sia il medesimo.

CO_2



CH_4



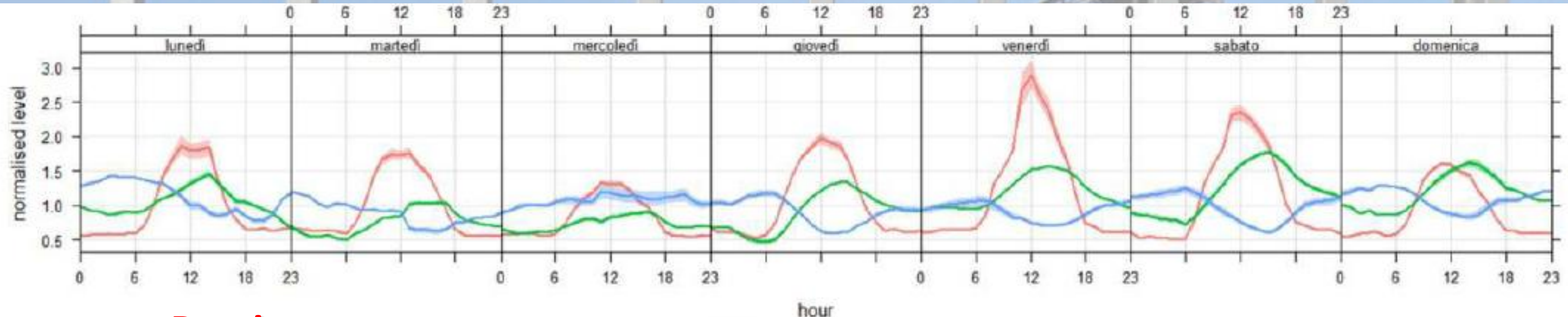
A parte Fi-MOSSE, è evidente un picco alle ore 12:00, dunque il traffico non sembra influenzare le concentrazioni di Hg in quanto non esiste collegamento fra aumento delle concentrazioni e ore di punta.

È invece possibile dedurre una correlazione diretta dei picchi di Hg con la temperatura e una correlazione inversa con l'umidità: i processi fotochimici durante il giorno sono quelli che maggiormente influenzano le emissioni di mercurio atmosferico.

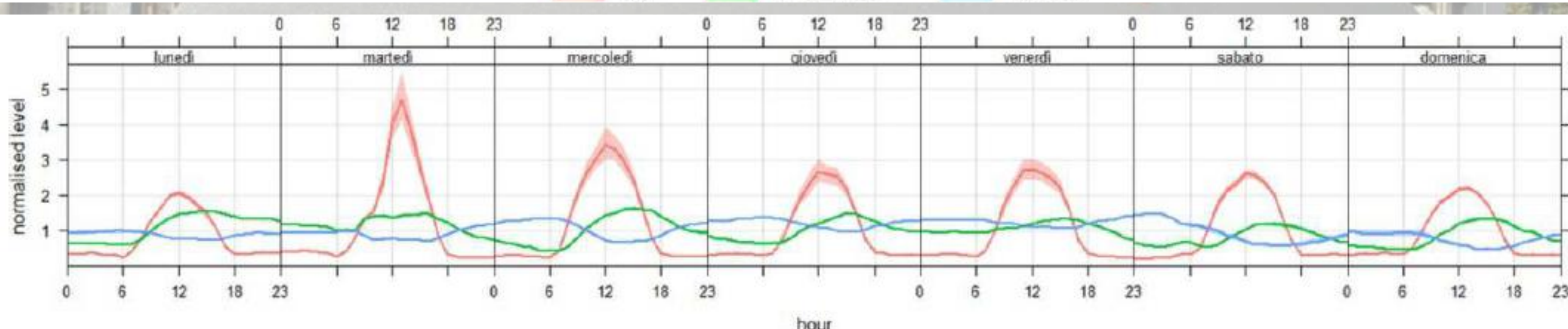
La radiazione solare, che raggiunge il suo massimo nelle ore centrali della giornata, induce la fotoriduzione di Hg^{2+} in Hg^0.

Avendo la radiazione solare un'influenza diretta sulla temperatura dell'aria ed una indiretta sull'umidità, le correlazioni tra concentrazione di Hg e questi parametri riflettono la correlazione tra Hg e radiazione solare.

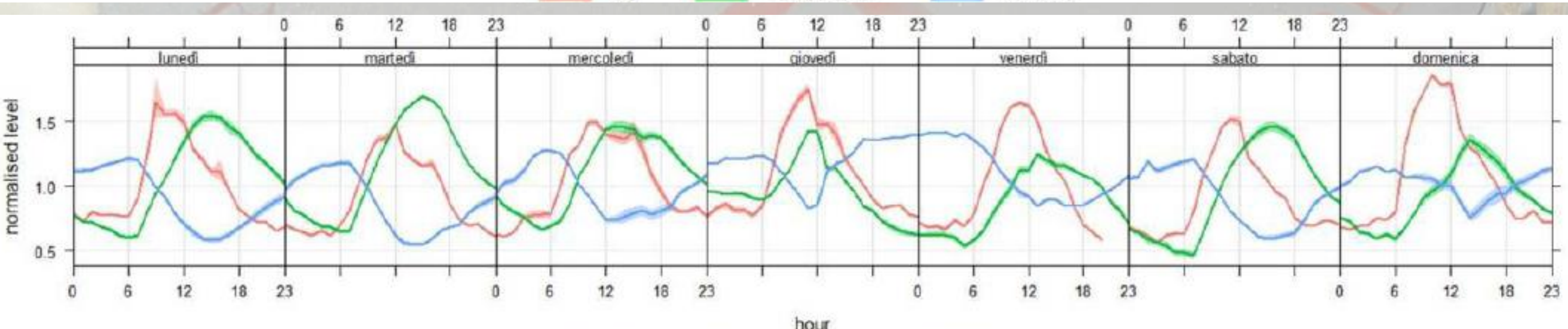
FI-MOSSE: andamento estremamente irregolare. Campionamento dell'ultima parte di Aprile, in cui le temperature hanno subito un incremento e ciò potrebbe aver aumentato l'altezza dello strato di rimescolamento, con conseguente diluzione di Hg in aria durante le ore diurne, assenza di correlazione fra Hg, temperatura e umidità, oltre a valori di Hg mediamente più bassi.



Bassi

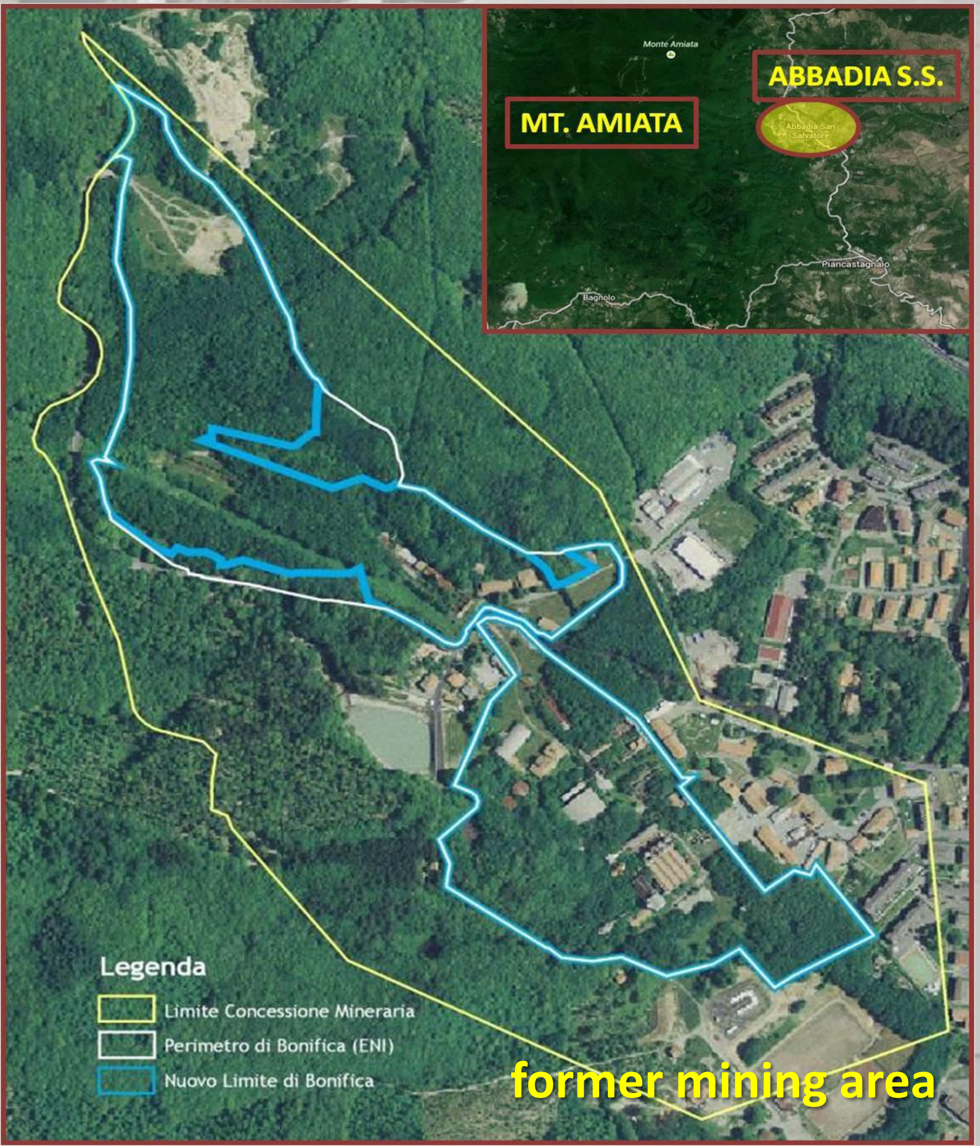


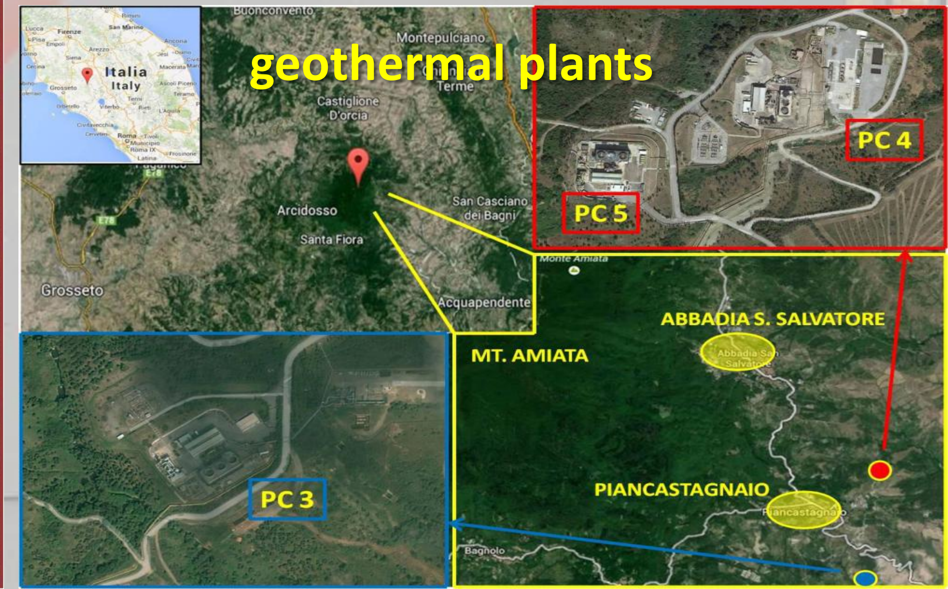
Gramsci



Settignano

CASO DI STUDIO: MT. AMIATA

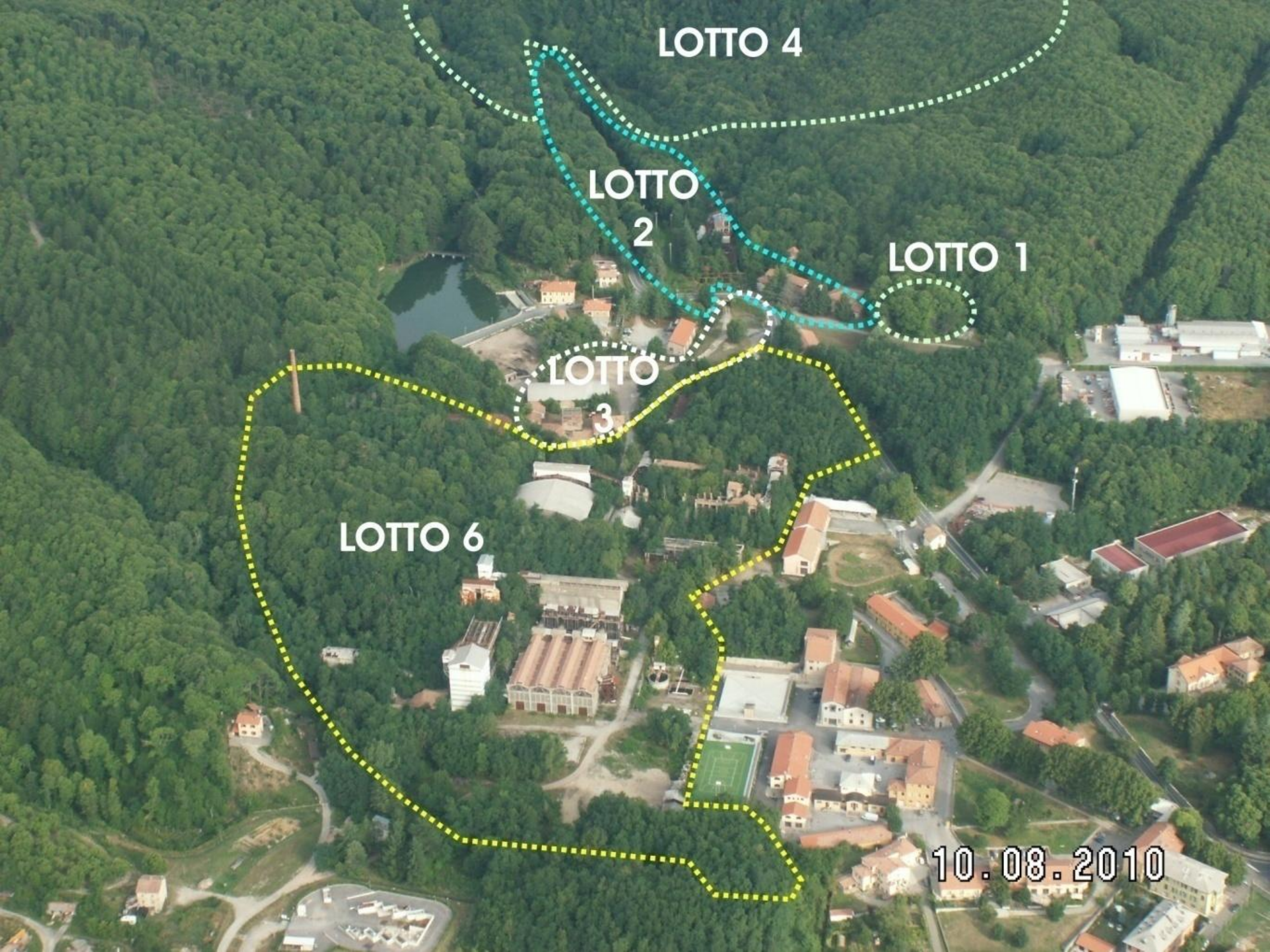




ABBADIA SAN SALVATORE

Area mineraria a Hg dedita fino al 1976 all'estrazione del cinabro e situata nelle vicinanze del centro urbano della medesima cittadina

Legislazione Amiata: a fine bonifica <300 (outdoor) e <500 (indoor) ng/m^3


LOTTO 4
LOTTO 2
LOTTO 1
LOTTO 3
LOTTO 6
10.08.2010

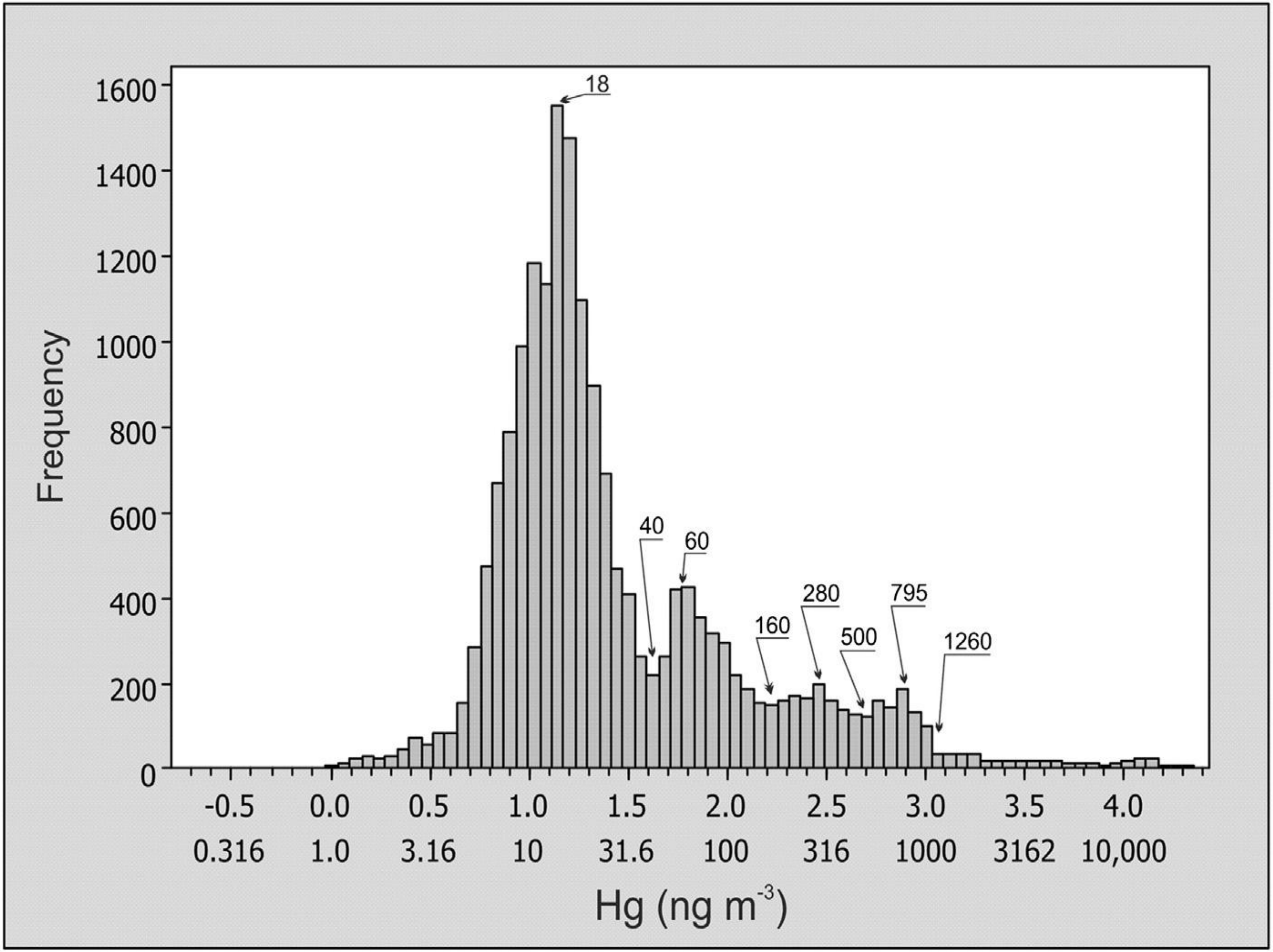

soc. mercurifera
"MONTE AMIATA" S.p.A.
uffici miniera

L’estrazione di Hg liquido dal cinabro veniva generalmente effettuata in forni rotanti ove la reazione con O_2 produce SO_2:

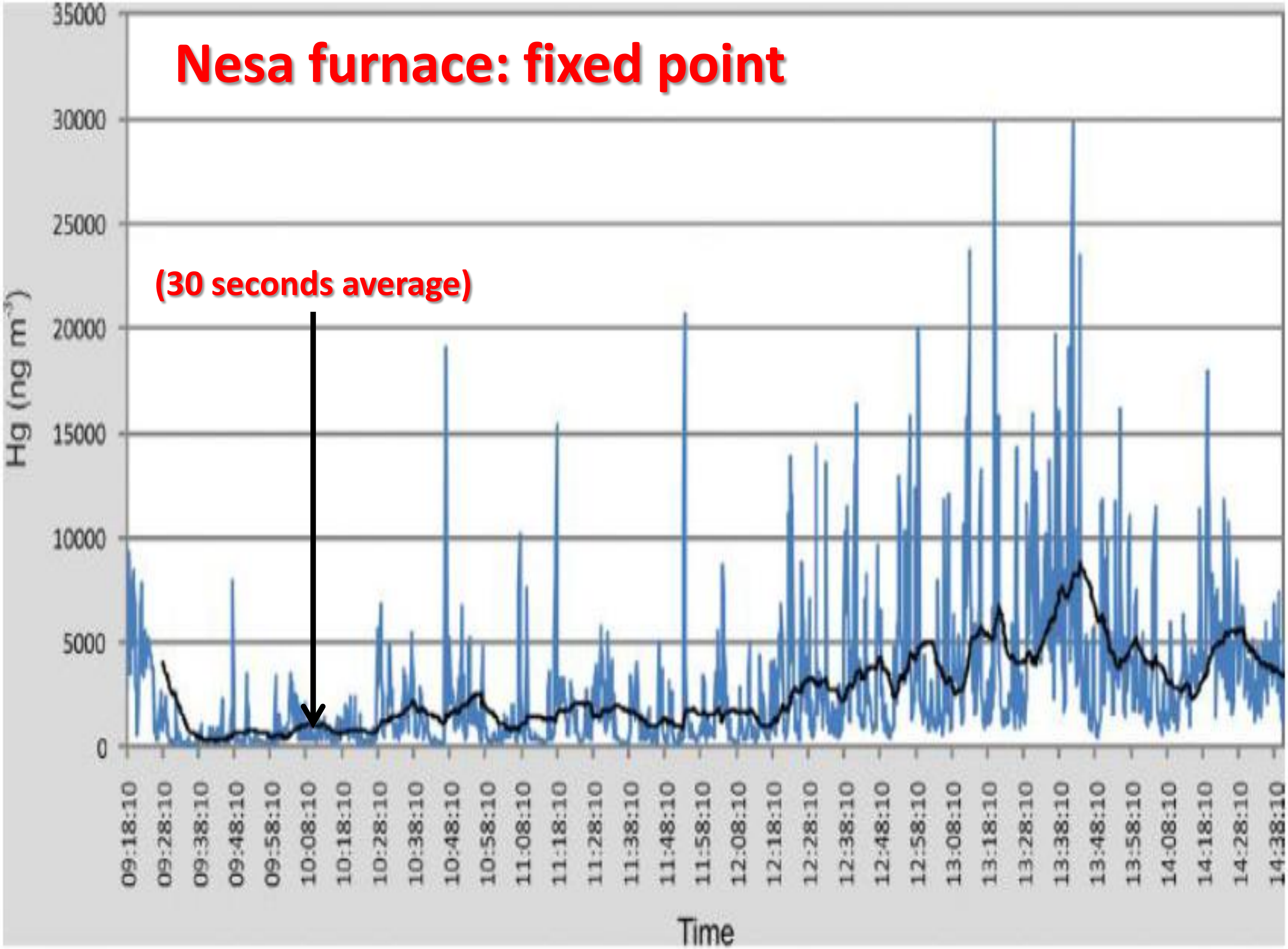
$$HgS + O_2 \rightarrow Hg^0 + SO_2$$

Per T>350 ° C, Hg tende a vaporizzare e veniva condensato nel suo stato liquido a $T_{ambiente}$.

Scorie >1000 mg kg^{-1} dovute al cinabro non convertito, formazione di meta-cinabro, HgO ed altri sali di Hg.
Le scorie, esposte a cielo aperto, interagiscono con le acque meteoriche.



Frequency
1600
1400
1200
1000
800
600
400
200
0
18
40
60
160
280
500
795
1260
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0.316
1.0
3.16
10
31.6
100
316
1000
3162
10,000
Hg (ng m-3)



Nesa furnace: fixed point
(30 seconds average)
Hg (ng m-3)
35000
30000
25000
20000
15000
10000
5000
0
09:18:10
09:28:10
09:38:10
09:48:10
09:58:10
10:08:10
10:18:10
10:28:10
10:38:10
10:48:10
10:58:10
11:08:10
11:18:10
11:28:10
11:38:10
11:48:10
11:58:10
12:08:10
12:18:10
12:28:10
12:38:10
12:48:10
12:58:10
13:08:10
13:18:10
13:28:10
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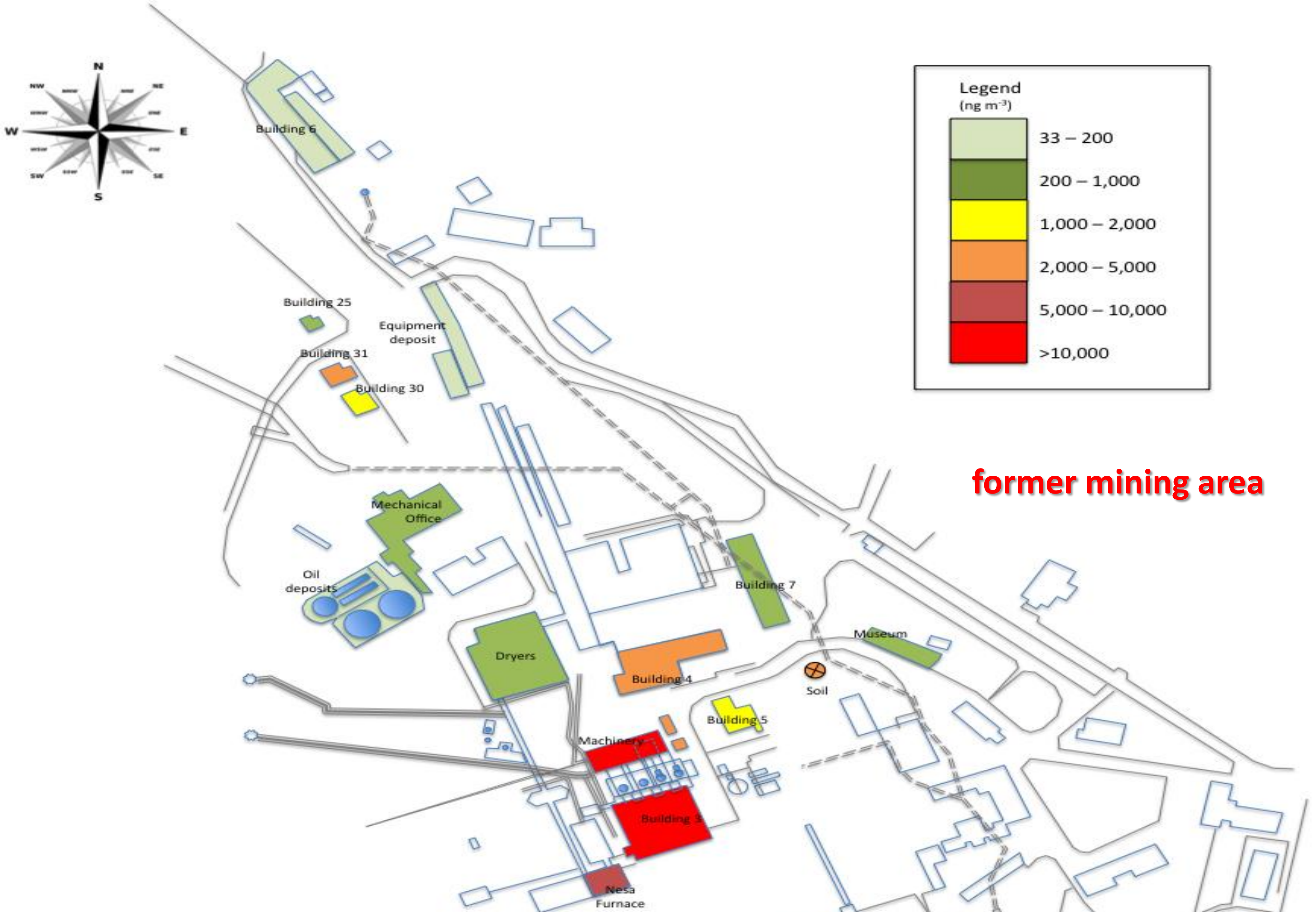
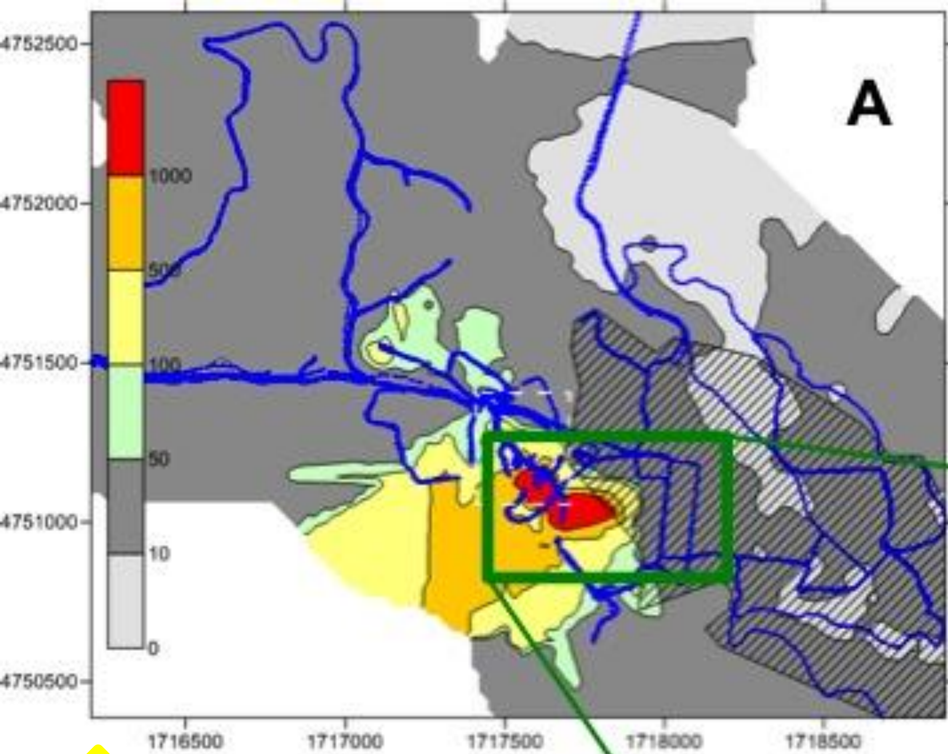
14:08:10
14:18:10
14:28:10
14:38:10
Time

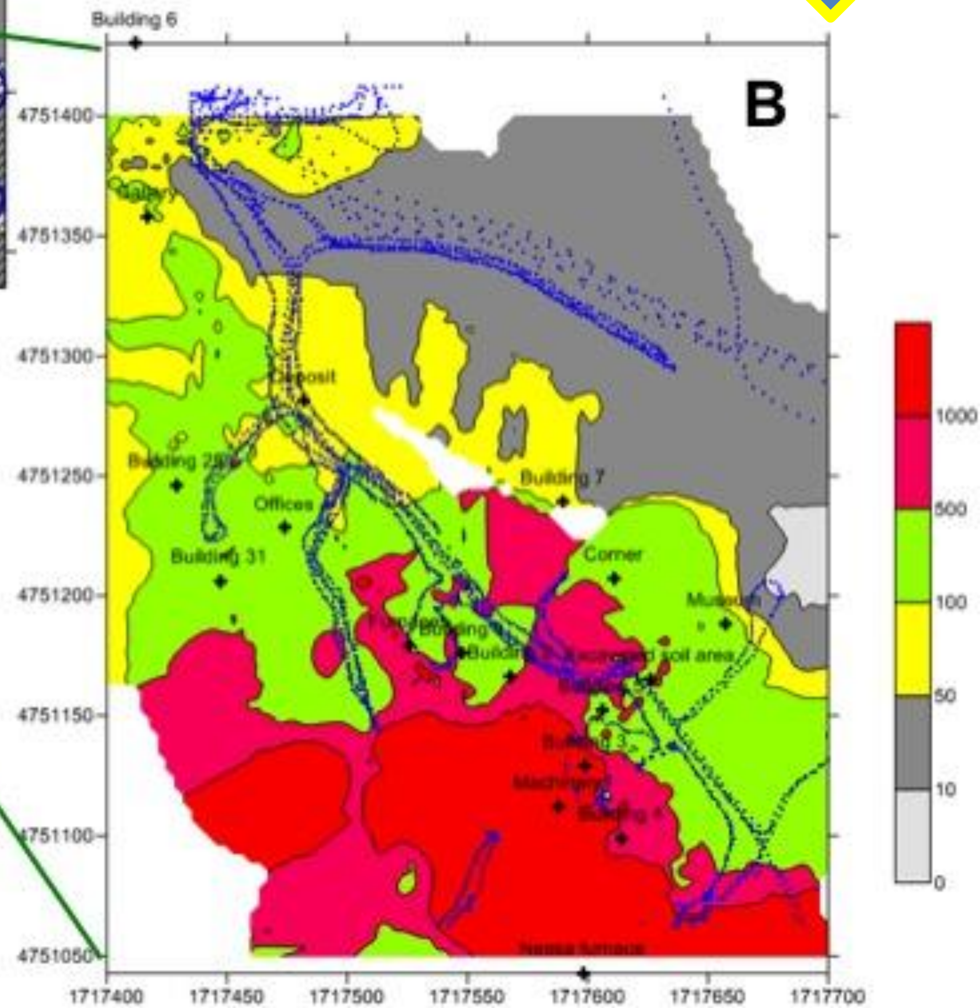


Abbadia San Salvatore

Contour Map



Abbadia San Salvatore former mining area



Hg^0

Abbadia San Salvatore, including the urban area (shaded grid)

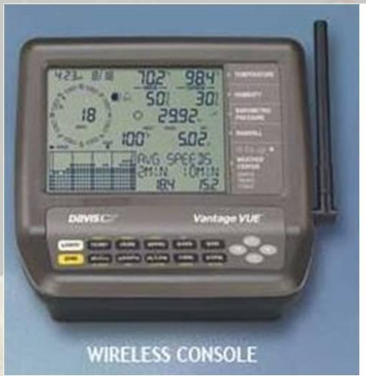
MISURE IN CONTINUO: TRANSETTI

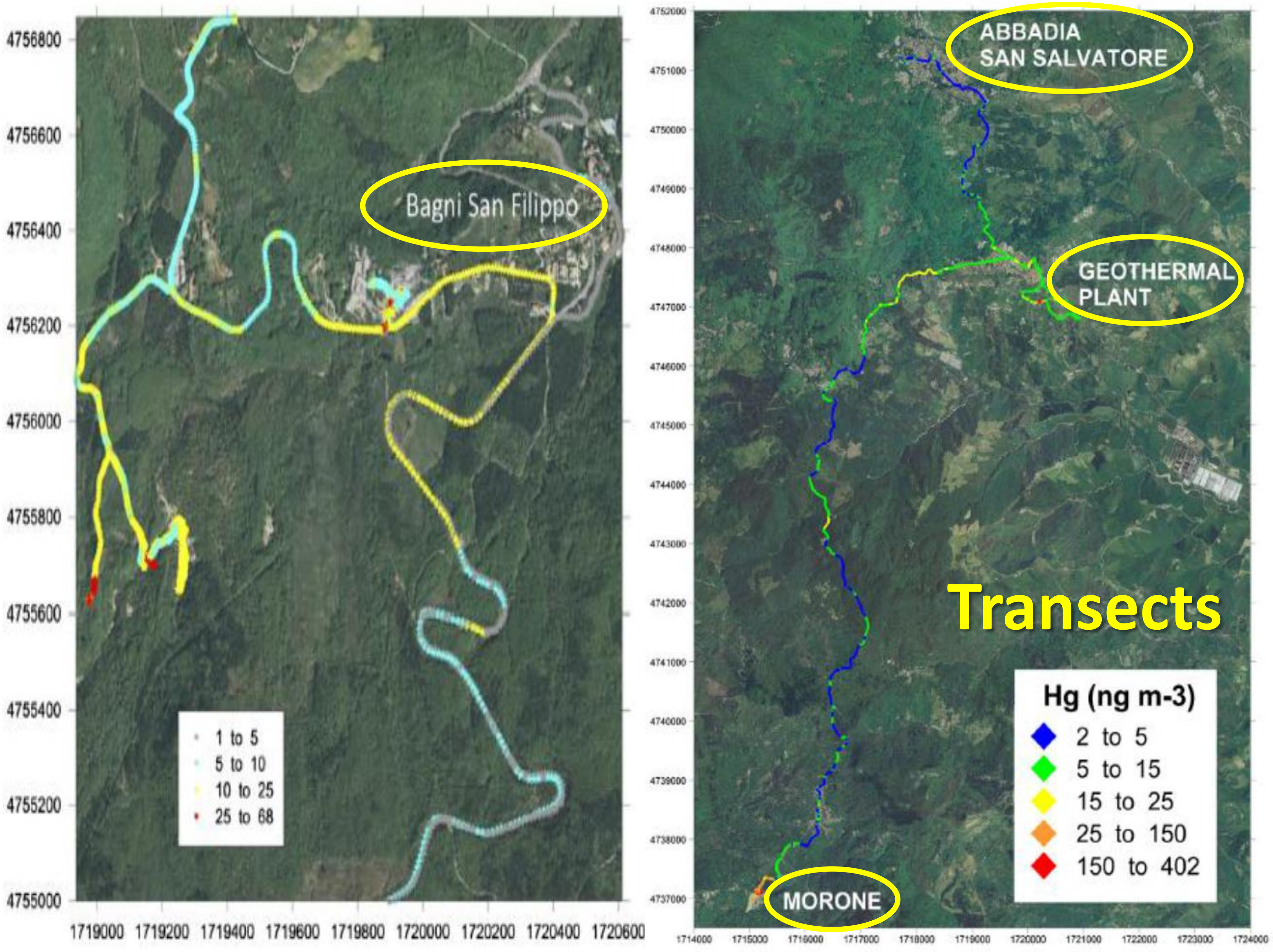
• registrazione in continuo percorrendo dei transetti a velocità costante

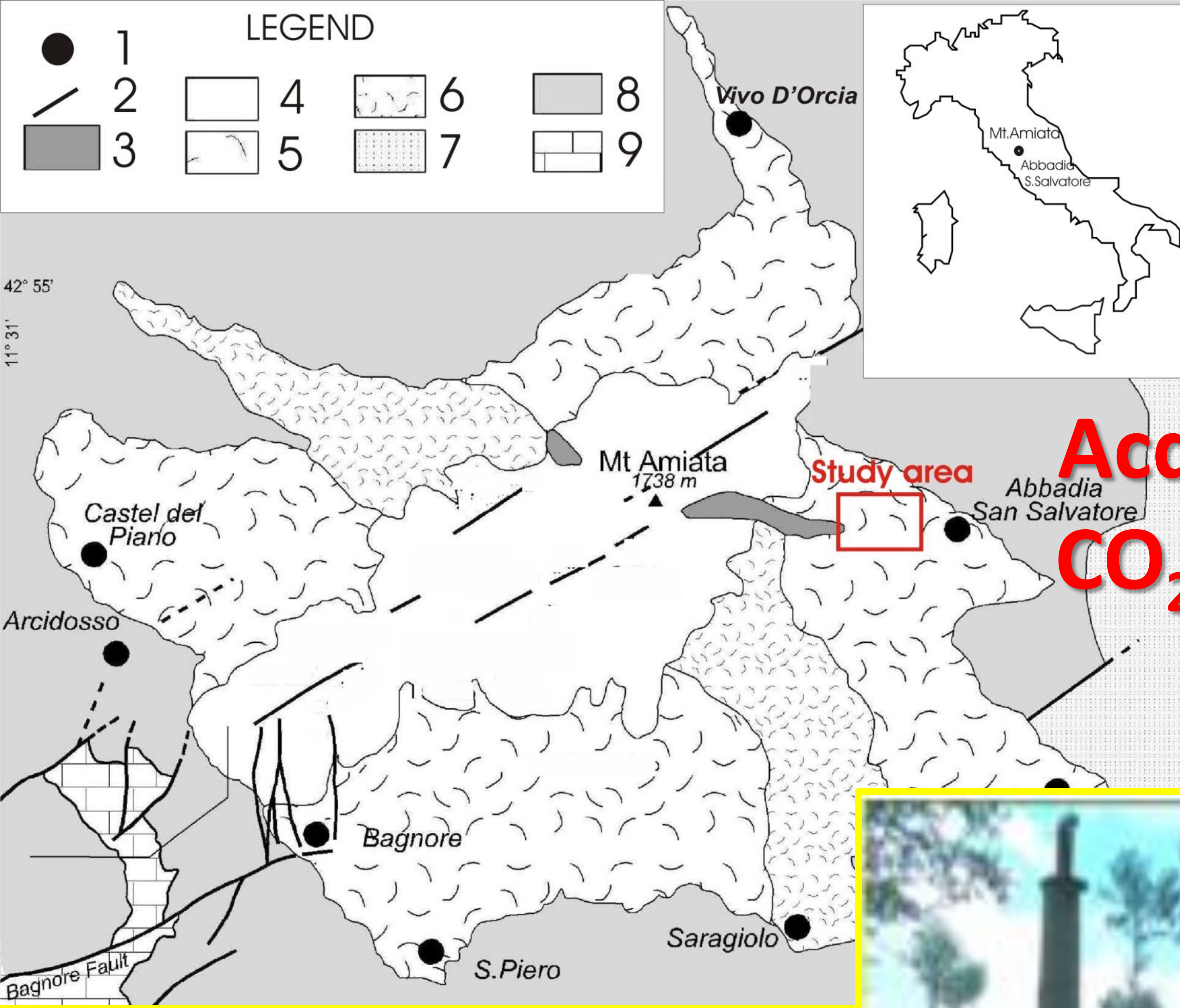
• acquisizione dei dati ad altissima frequenza (anche 1 dato al secondo)

• misura continua della posizione GPS: coordinate spaziali per ciascun valore di concentrazione

• contemporanea registrazione delle condizioni meteo




Bagni San Filippo
1 to 5
5 to 10
10 to 25
25 to 68
ABBADIA SAN SALVATORE
GEOTHERMAL PLANT
MORONE
Transects
Hg (ng m-3)
2 to 5
5 to 15
15 to 25
25 to 150
150 to 402

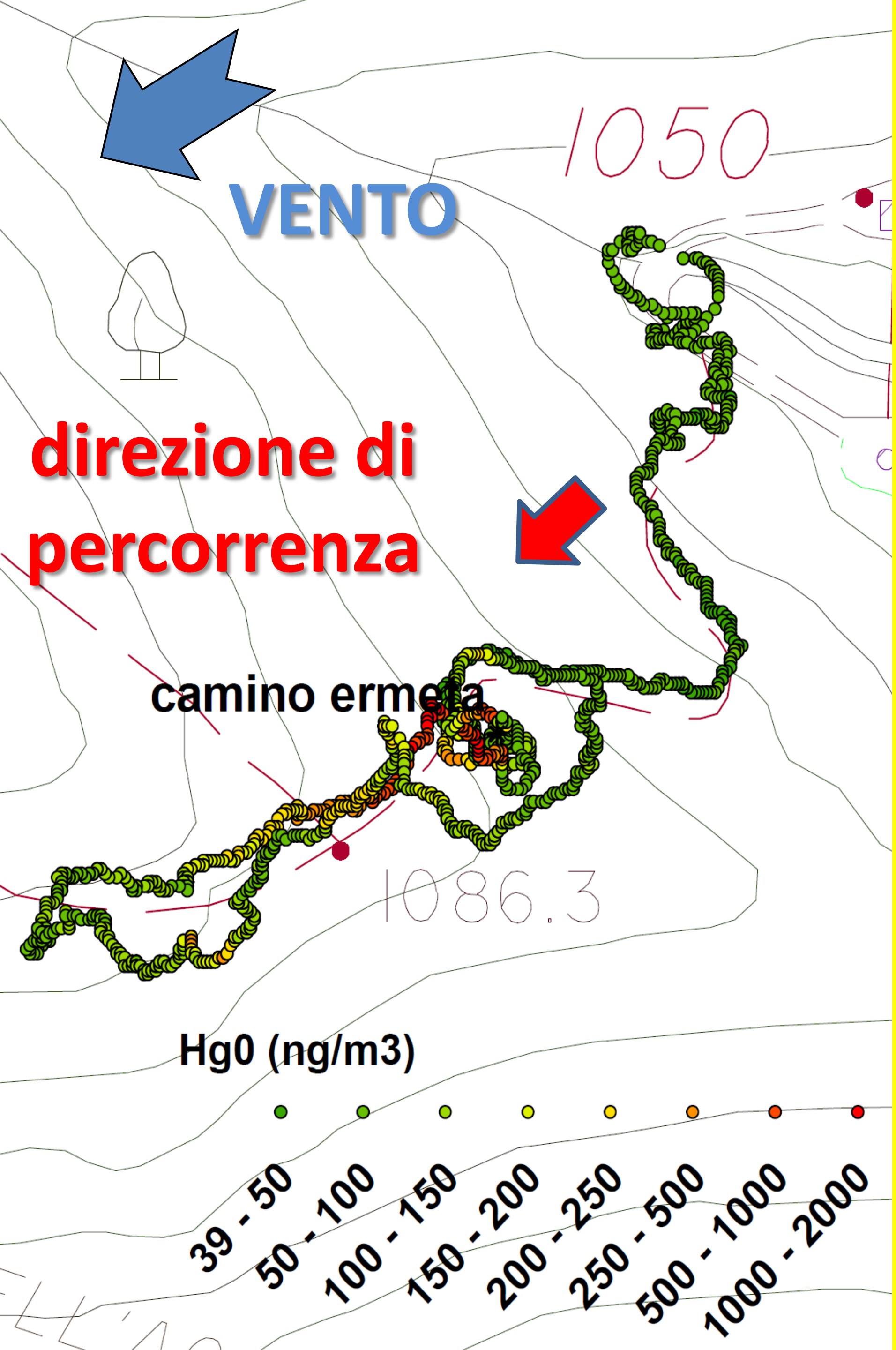


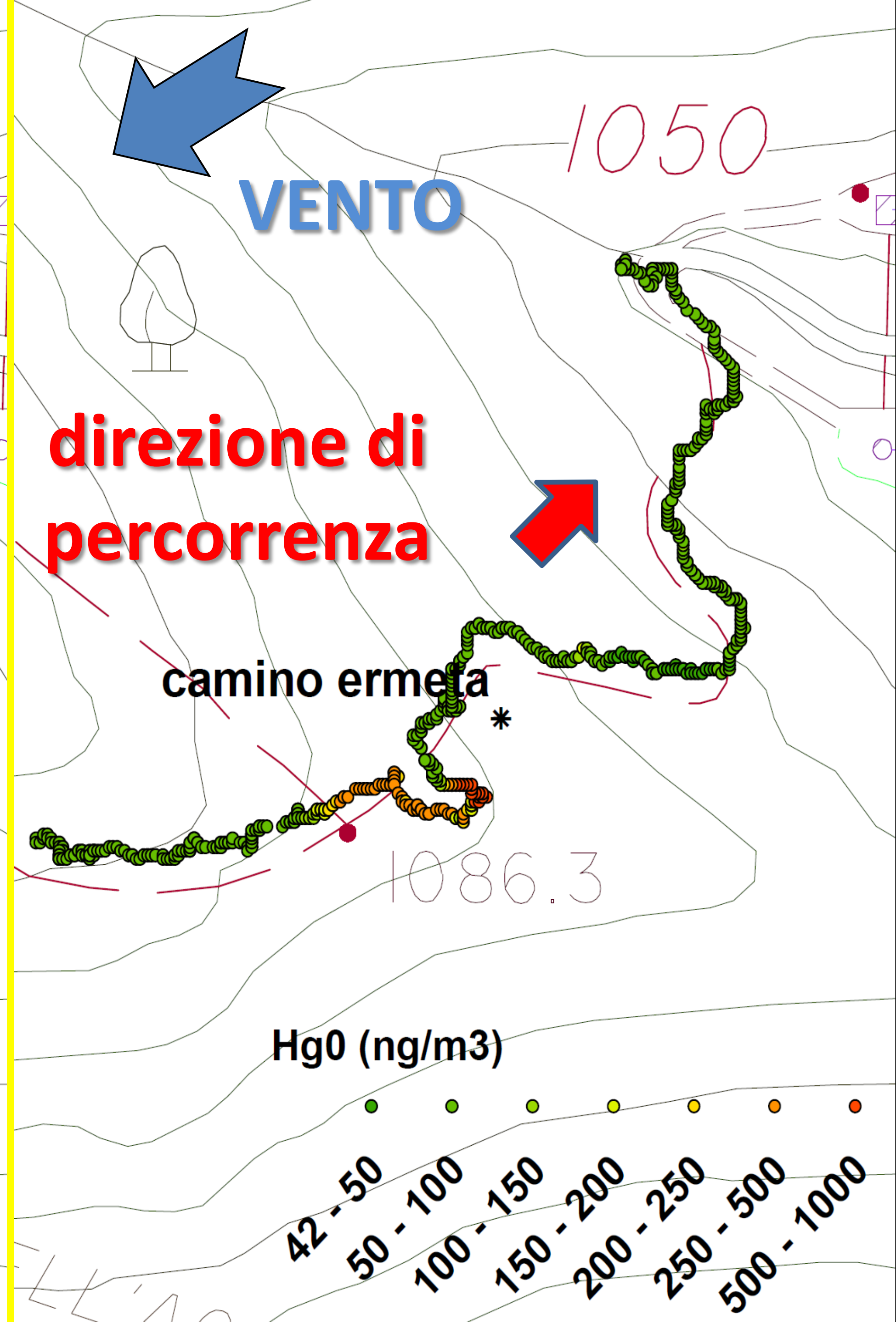
Camino Acquapassante

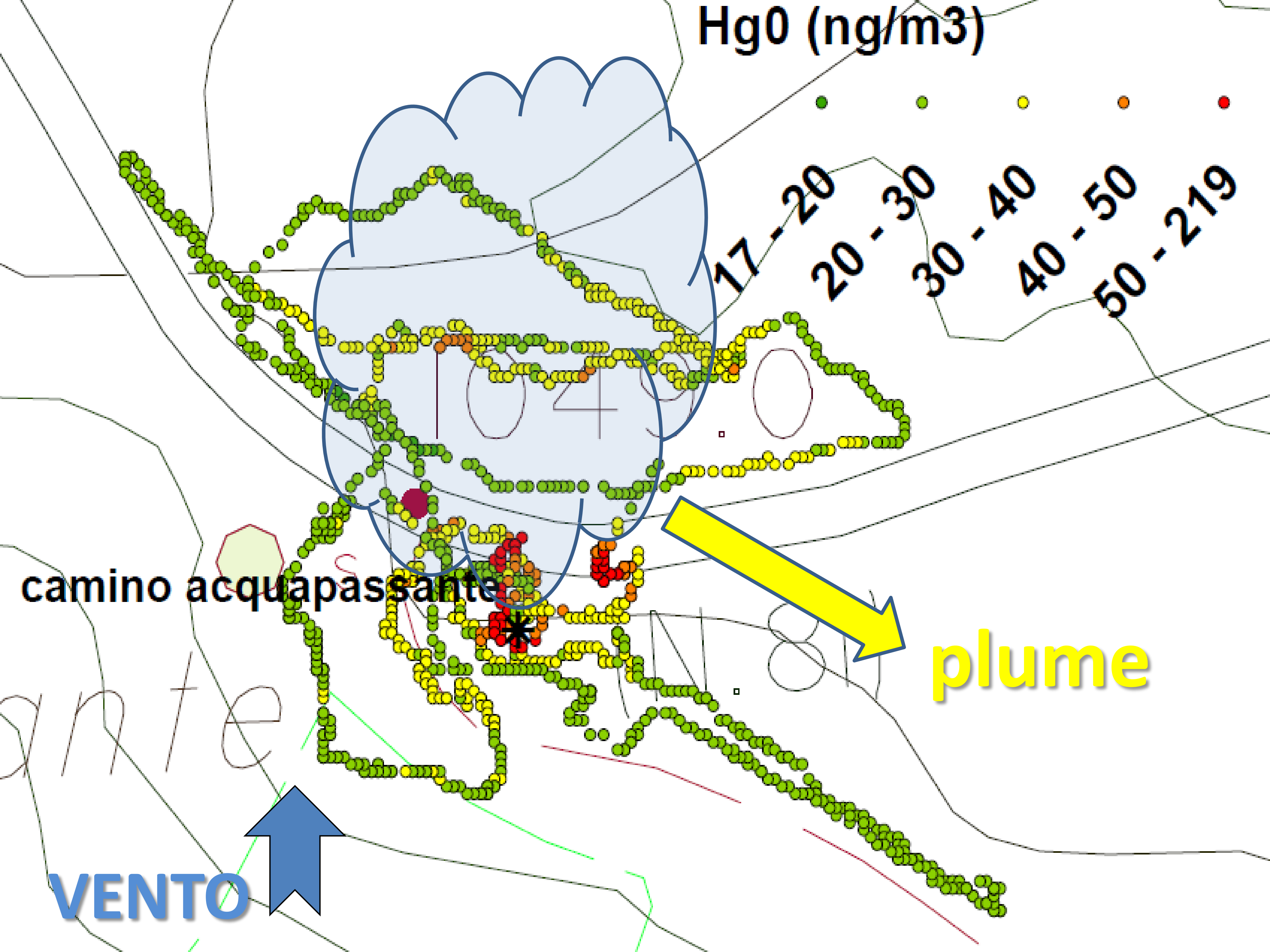
CO_2=1.8k ton/y

Camino Ermeta

CO_2=13k ton/y


VENTO
1050
direzione di percorrenza
camino ermeta
1086.3
Hg0 (ng/m3)
39 - 50
50 - 100
100 - 150
150 - 200
200 - 250
250 - 500
500 - 1000
1000 - 2000


VENTO
1050
direzione di percorrenza
camino ermeta
1086.3
Hg0 (ng/m3)
42 - 50
50 - 100
100 - 150
150 - 200
200 - 250
250 - 500
500 - 1000



Hg0 (ng/m3)
17 - 20
20 - 30
30 - 40
40 - 50
50 - 219
camino acquapassante
plume
VENTO

ALTRI INQUINANTI ATMOSFERICI

Parallelamente a Hg^0, sono stati misurati tre inquinanti:
H_2S, SO_2, CO_2

Emessi dai sistemi idrotermali e/o vulcanici attivi e da molte attività antropiche

H_2S: tossico in quanto irritante e soffocante, rilevabile a concentrazioni molto basse causa odore sgradevole

SO_2: dall'odore pungente e fortemente irritante, soprattutto per gli occhi e il tratto respiratorio

CO_2: uno dei principali gas serra presenti nell'atmosfera, legame diretto con il riscaldamento globale

H_2S & SO_2: Legislation

H_2S: almost all the exposed subjects distinguished the characteristic smell in correspondence of 7 μg/m^3 (~ 5 ppb): hydrogen sulfide should not exceed this concentration to prevent claims about smell nuisance.

However, the guideline concentration for H_2S is 150 μg/m^3 (~ 107 ppb) with an averaging time of 24 hours (WHO, 2000)

SO_2: the following concentrations should not be exceeded (WHO, 2000, 2006):

1) **500 μg/m^3 (0.175 ppm) for an average of 10 minutes;**
2) **20 μg/m^3 (~ 7 ppb) on the average of 24 hours;**
3) **50 μg/m^3 (17.5 ppb) on annual average**

STRUMENTI COMBINATI

LUMEX (Hg^0)

THERMO (H_2S, SO_2)

Sulfur Dioxide Analyzer, Model 450i, Thermo Scientific

H_2S & SO_2: Thermo® Analyzer

- Thermo® Scientific Model 450i Analyzer: utilizza la fluorescenza a pulsazione per misurare le concentrazioni di H_2S e SO_2

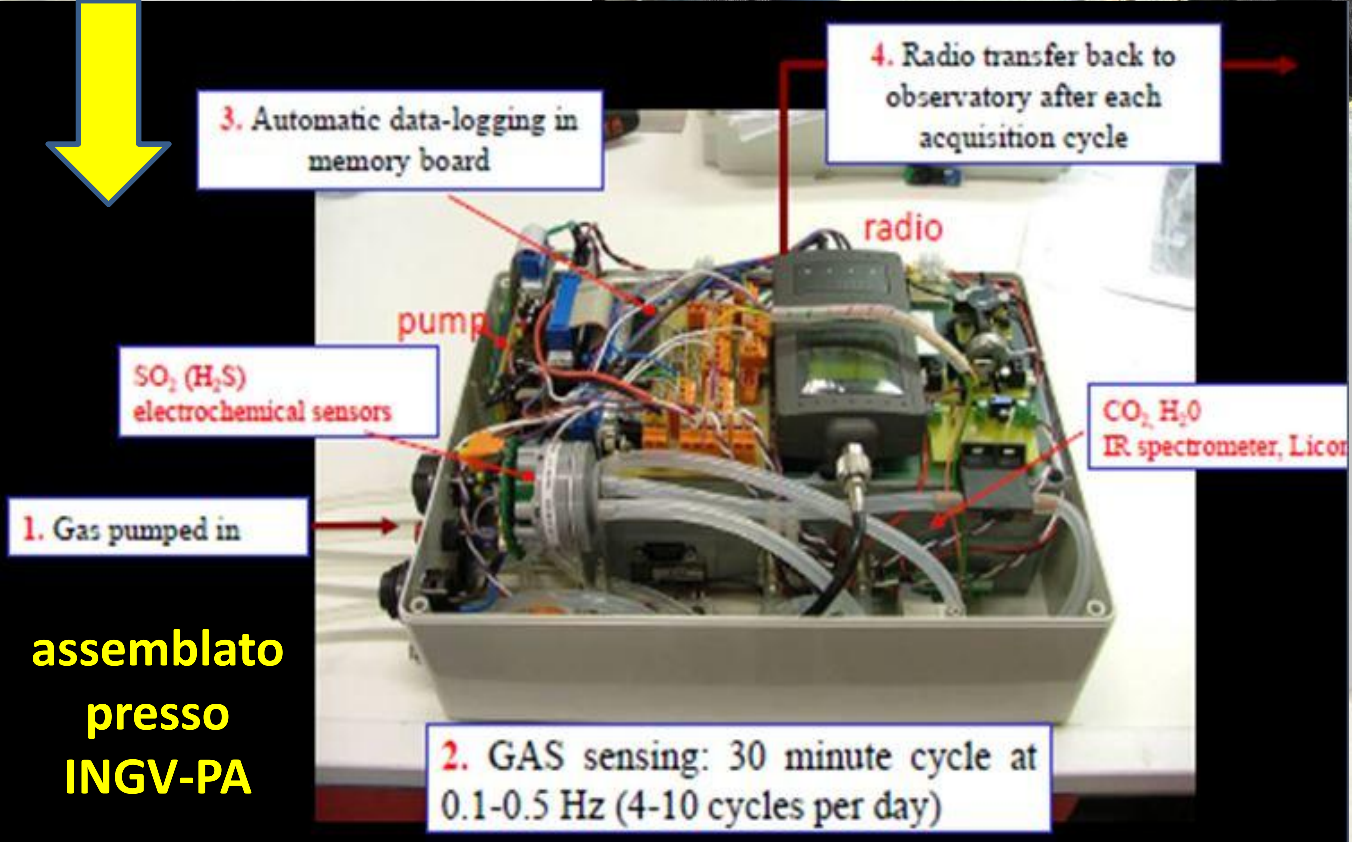
- limite di rilevabilità: 1-2 ppb (60 secondi di tempo medio) con una portata di 1 L/min

- range dinamico: da 0-0.05 a 10 ppm

STRUMENTI COMBINATI

LUMEX (Hg^0)

MULTIGAS (CO_2, H_2S, ...)



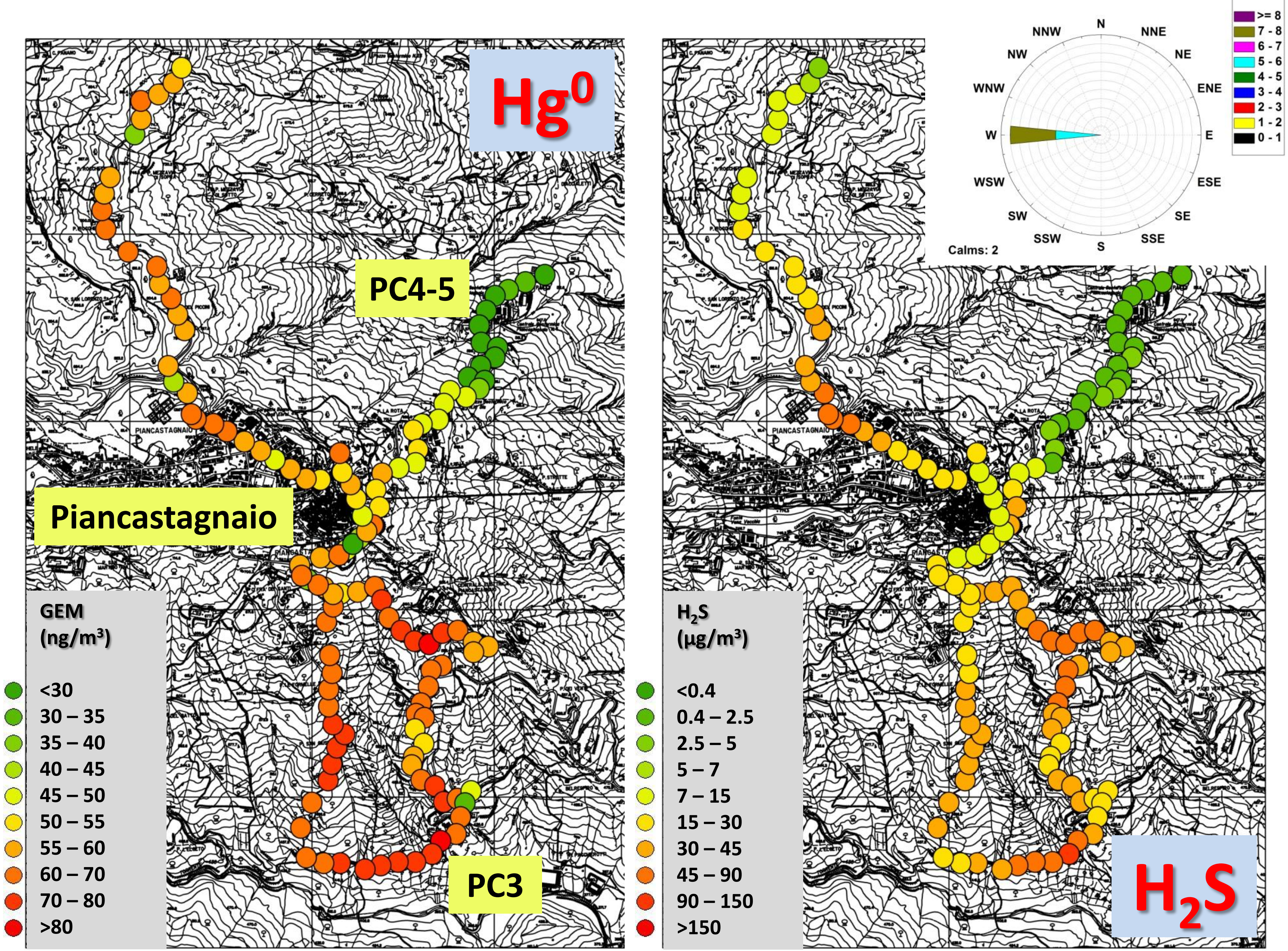
assemblato presso INGV-PA

CO_2: Multi-GAS (INGV)

- Multi-sensor Gas Analyzer System (INGV-Palermo): integra all’interno uno spettrometro ad IR per la determinazione della CO_2

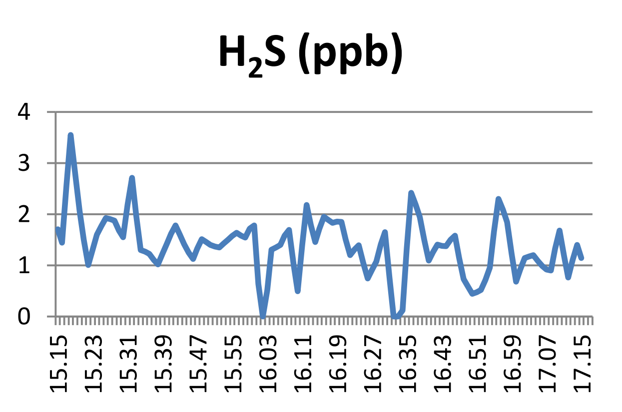
- intervallo di calibrazione: 0-4000 ppmv

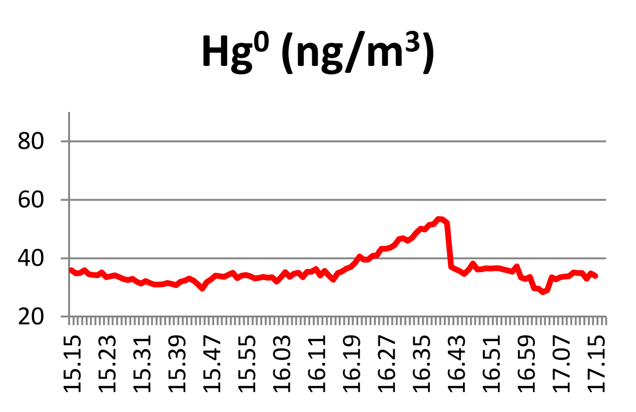
- risoluzione: 0.8 ppmv
con portata media di 0.6 L/min

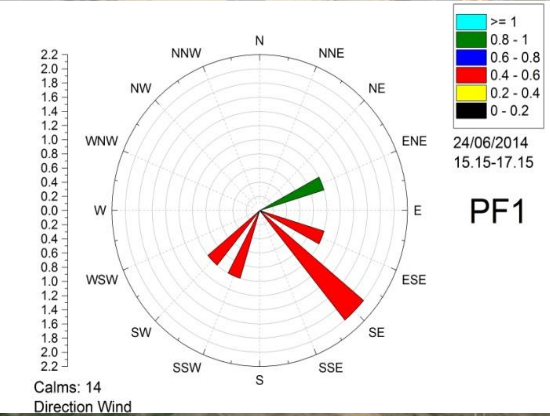


Hg0
PC4-5
Piancastagnaio
PIANCASTAGNAIO
GEM (ng/m3)
<30
30 – 35
35 – 40
40 – 45
45 – 50
50 – 55
55 – 60
60 – 70
70 – 80
>80
PC3
N
NNE
NE
ENE
E
ESE
SE
SSE
S
SSW
SW
WSW
W
WNW
NW
NNW
Calms: 2
>= 8
7 - 8
6 - 7
5 - 6
4 - 5
3 - 4
2 - 3
1 - 2
0 - 1
H2S (µg/m3)
<0.4
0.4 – 2.5
2.5 – 5
5 – 7
7 – 15
15 – 30
30 – 45
45 – 90
90 – 150
>150
H2S

PF1 (24-06-14, 15:15-17:15)

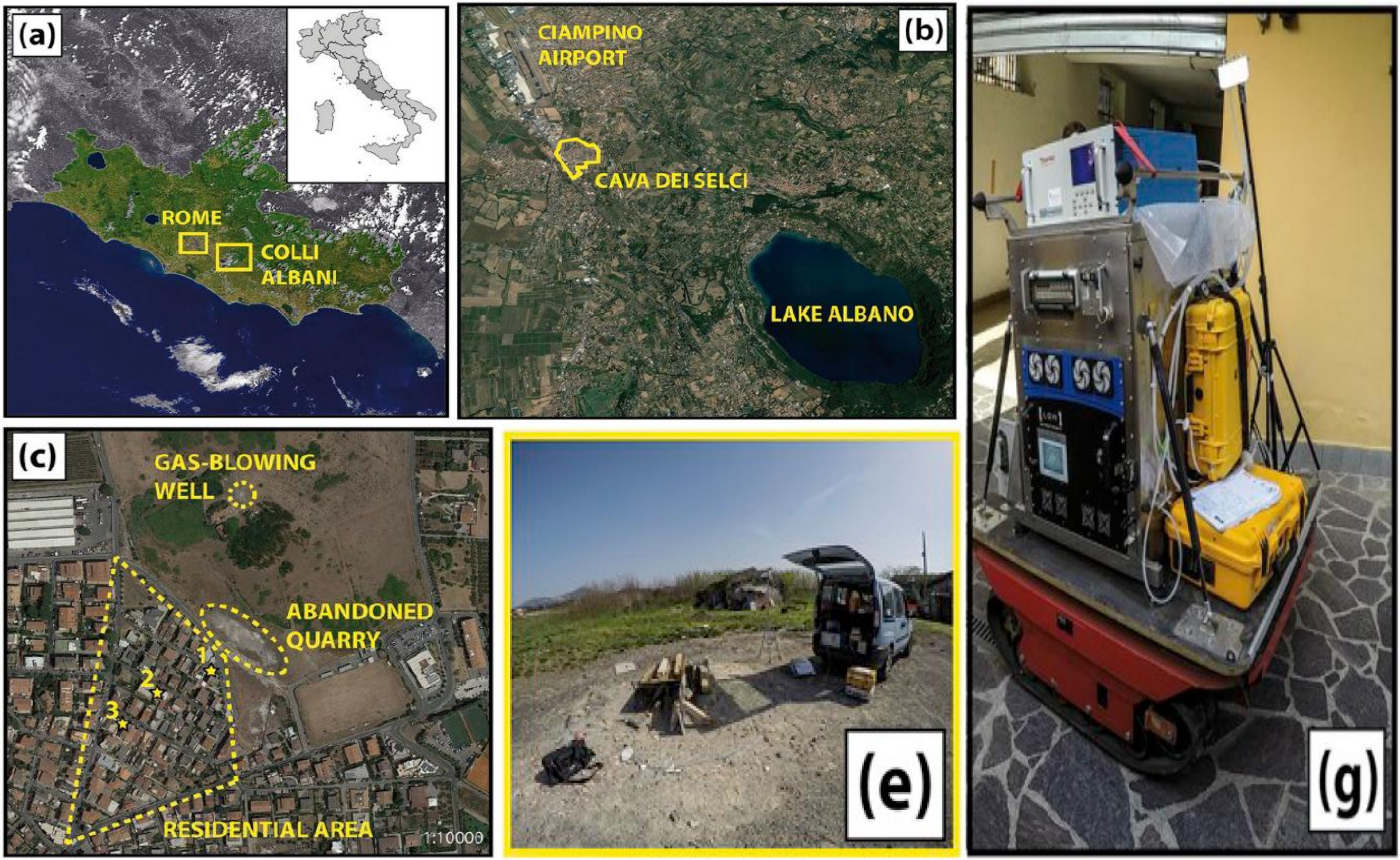


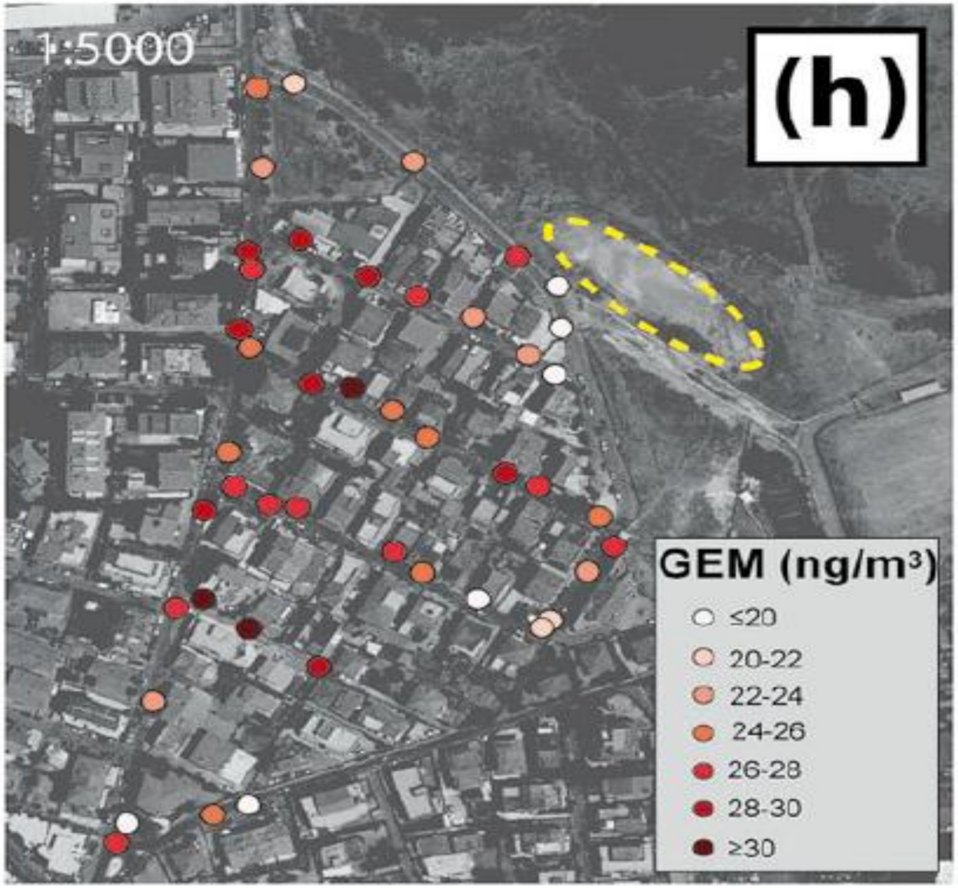


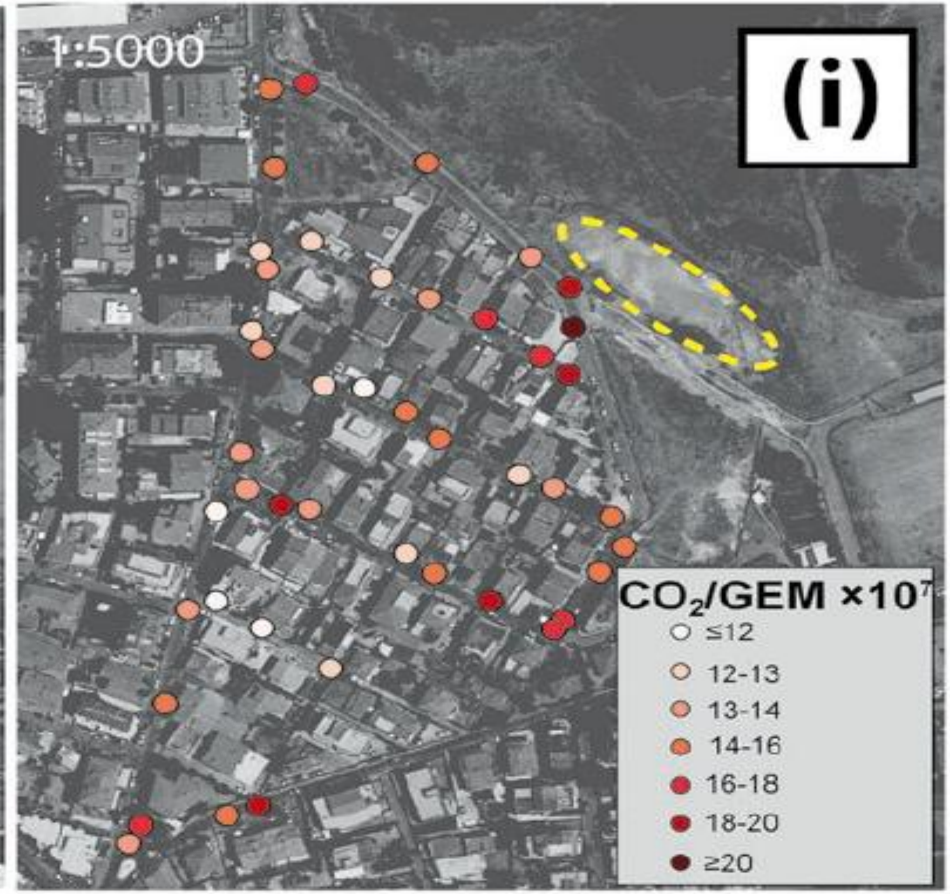


Piancastagnaio

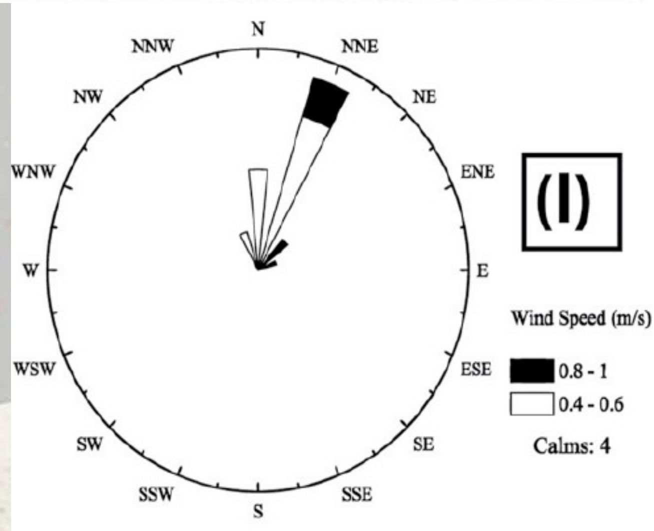
CAVA DEI SELCI







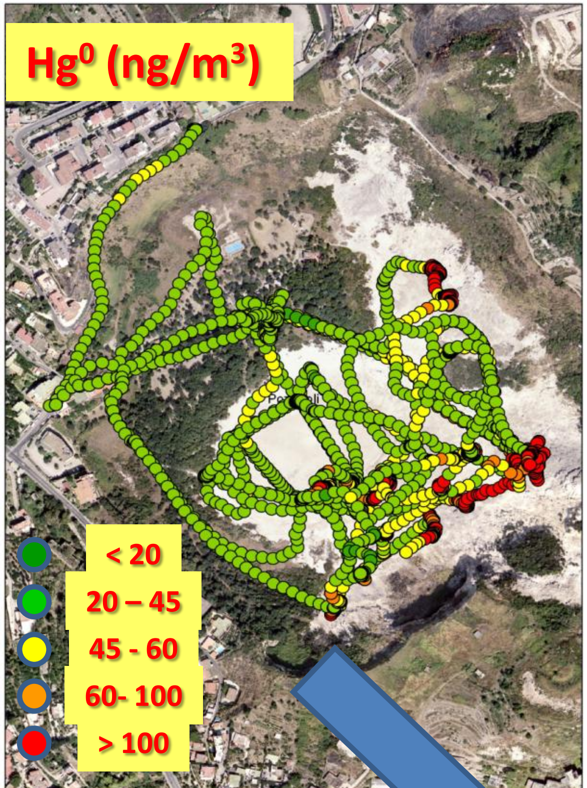
Along the measuring pathway in the residential area GEM ranged from 19 to 33 ng/m3, i.e. above the mean concentrations in some urban environments.
However, the GEM spatial distribution was decoupled with respect to those of CO2.
This suggests a different transport dynamic of GEM with respect to those of CO2 and also H2S, controlled by peculiar processes regulating the behavior of the pollutant once released in the air.

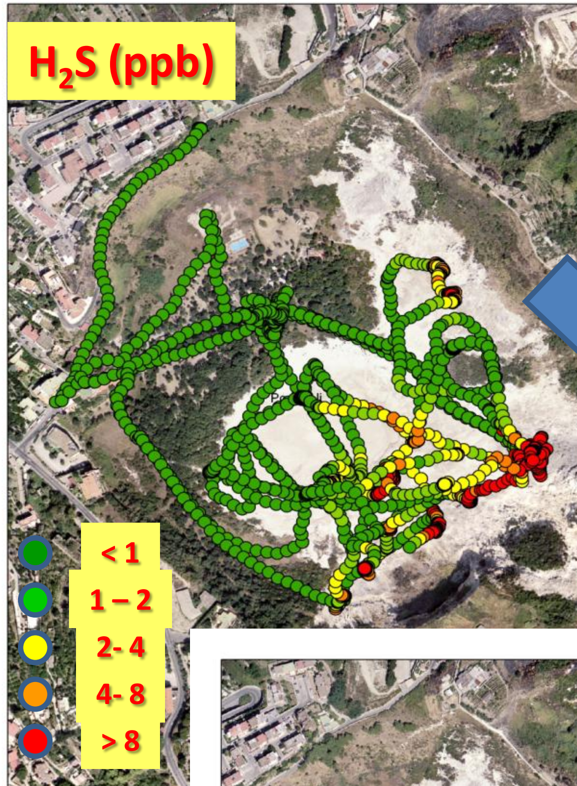


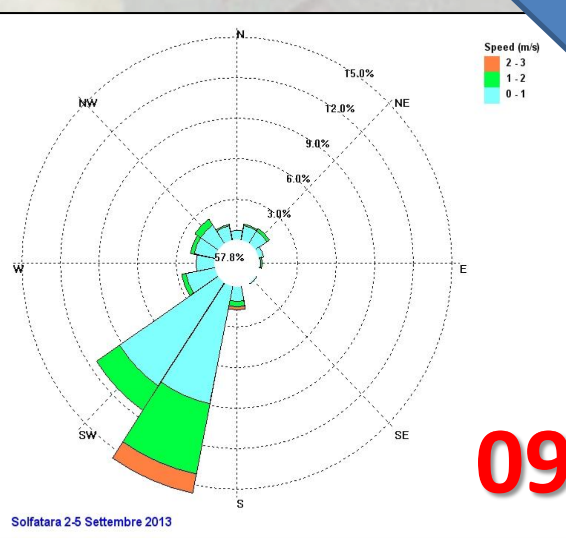
SOLFATARA, POZZUOLI

Solfatara

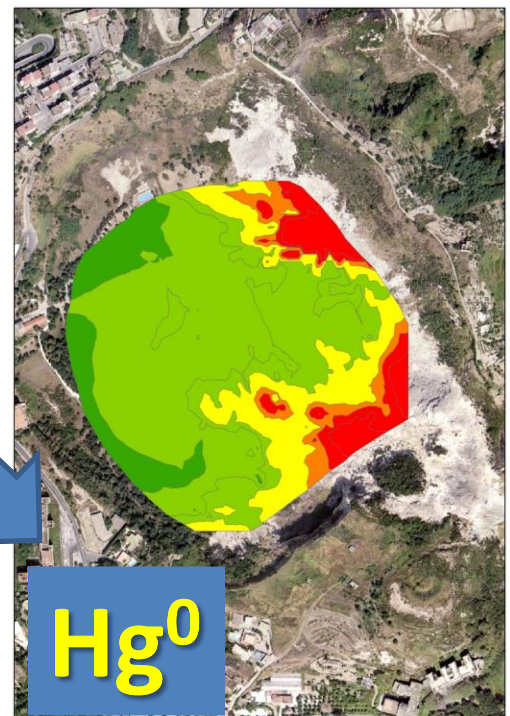
From transects to direct mapping of the contaminant

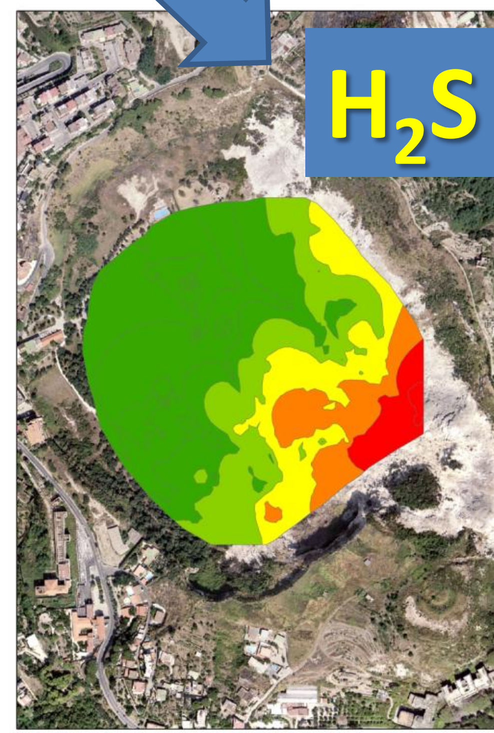


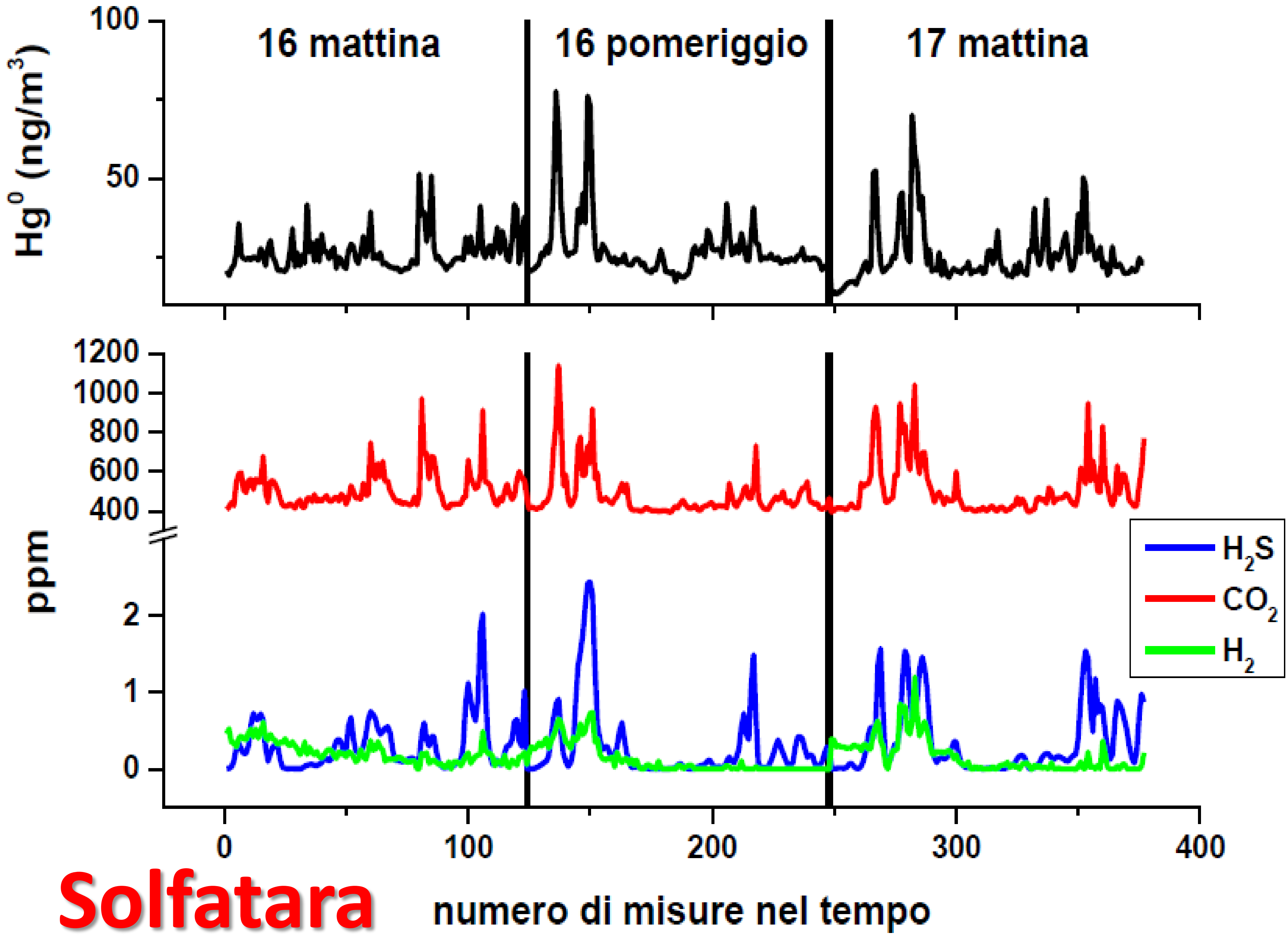




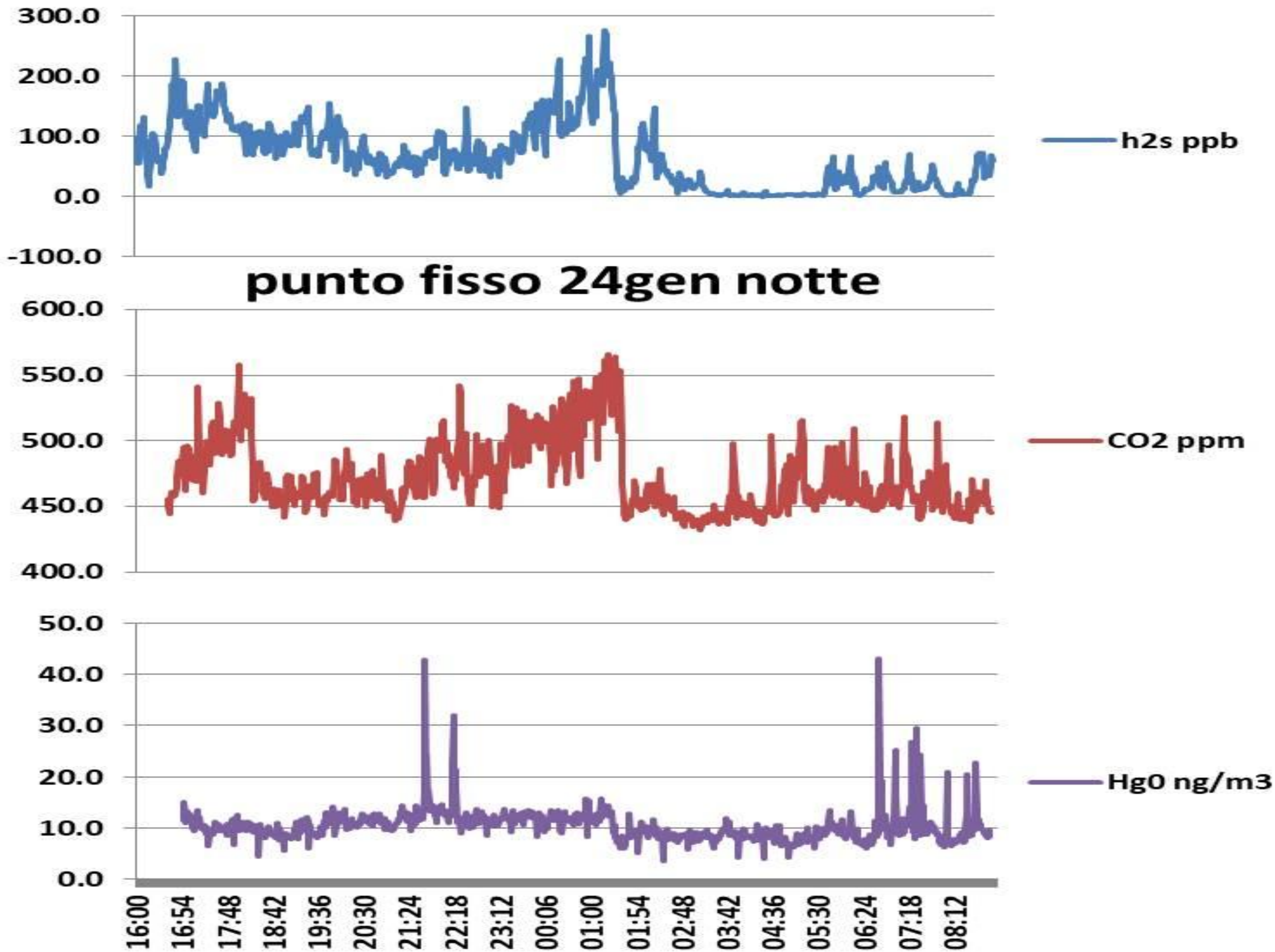
09/2013






16 mattina
16 pomeriggio
17 mattina
Hg0 (ng/m3)
100
50
ppm
1200
1000
800
600
400
2
1
0
H2S
CO2
H2
0
100
200
300
400
numero di misure nel tempo

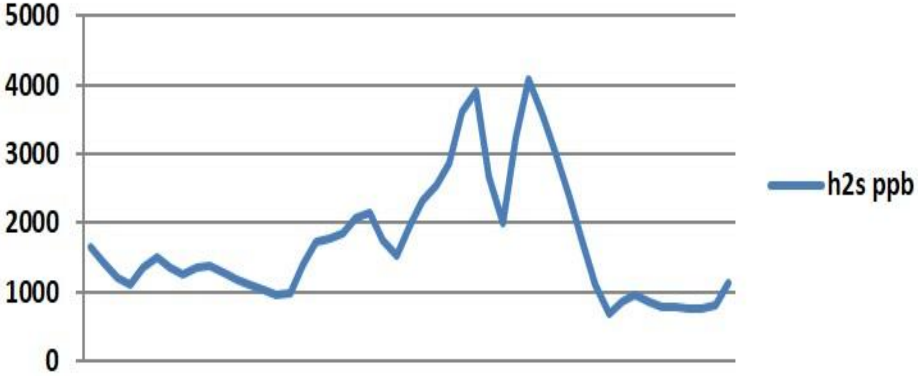
Solfatara

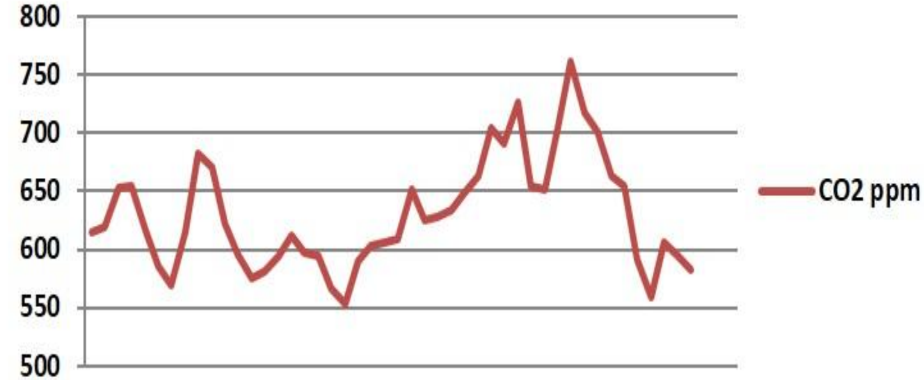


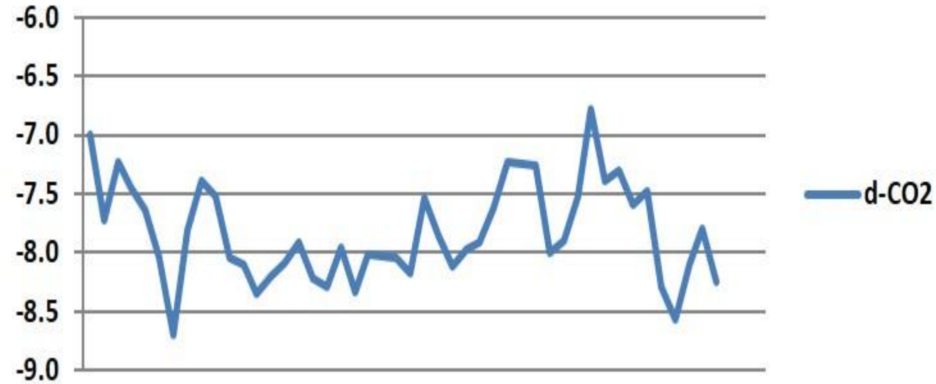
punto fisso 24gen notte
300.0
200.0
100.0
0.0
-100.0
h2s ppb
600.0
550.0
500.0
450.0
400.0
CO2 ppm
50.0
40.0
30.0
20.0
10.0
0.0
Hg0 ng/m3
16:00
16:54
17:48
18:42
19:36
20:30
21:24
22:18
23:12
00:06
01:00
01:54
02:48
03:42
04:36
05:30
06:24
07:18
08:12

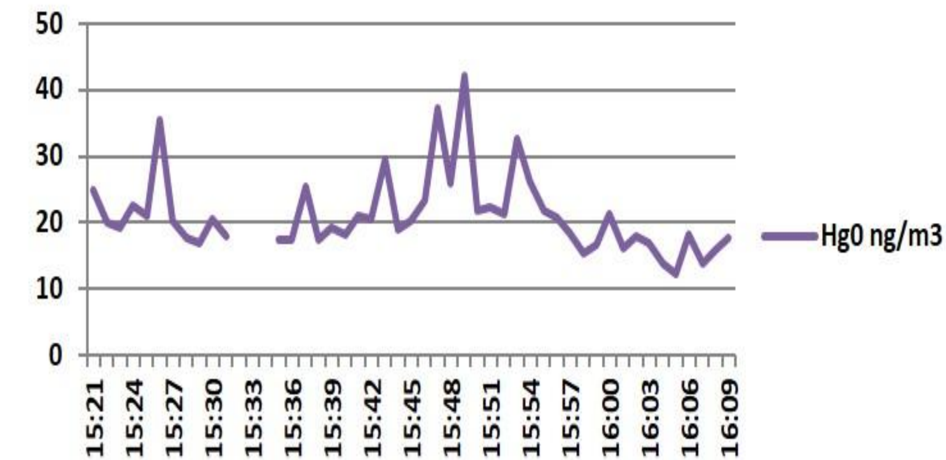
punto fisso BN 25 gennaio

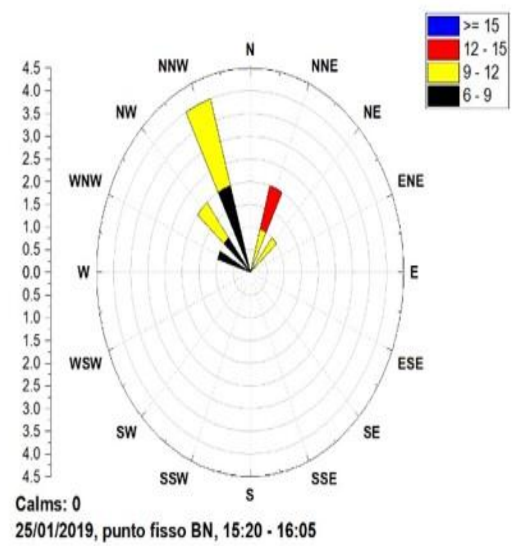
CO2/H2S	
min	161
max	978
media	439
mediana	419
dev. st.	190



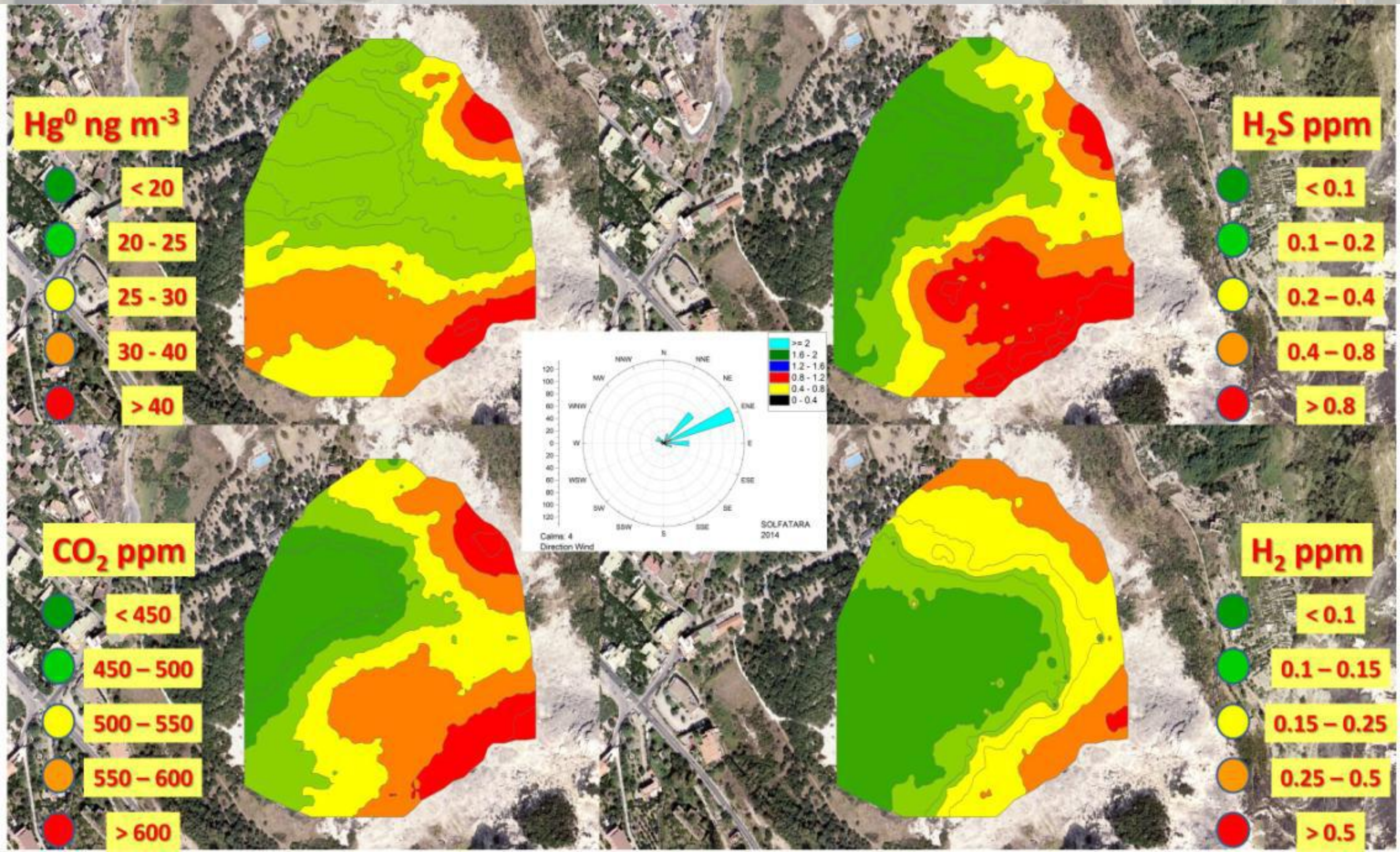




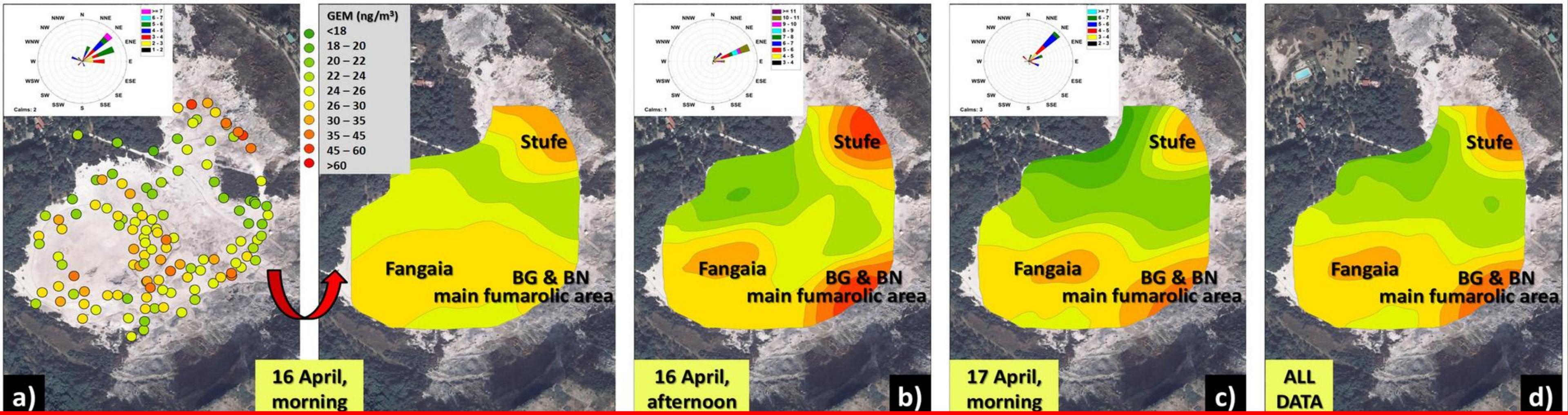


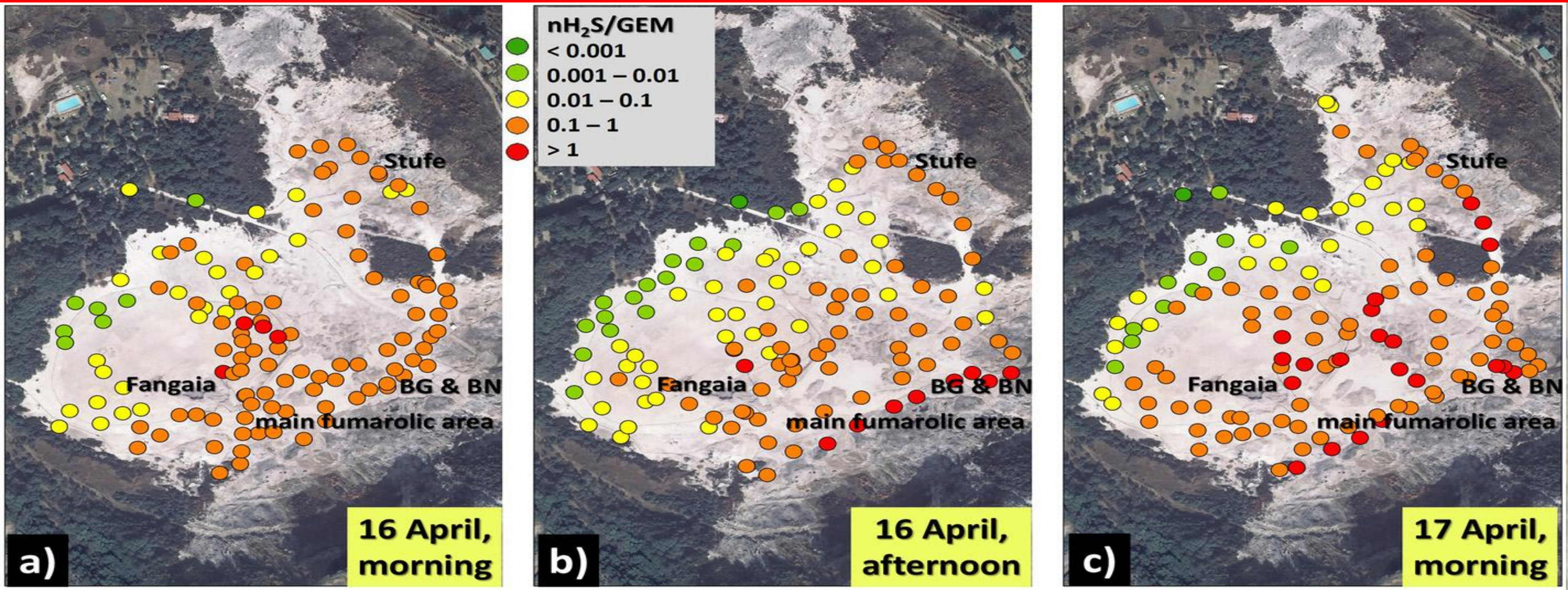


Solfatara, 04/2014



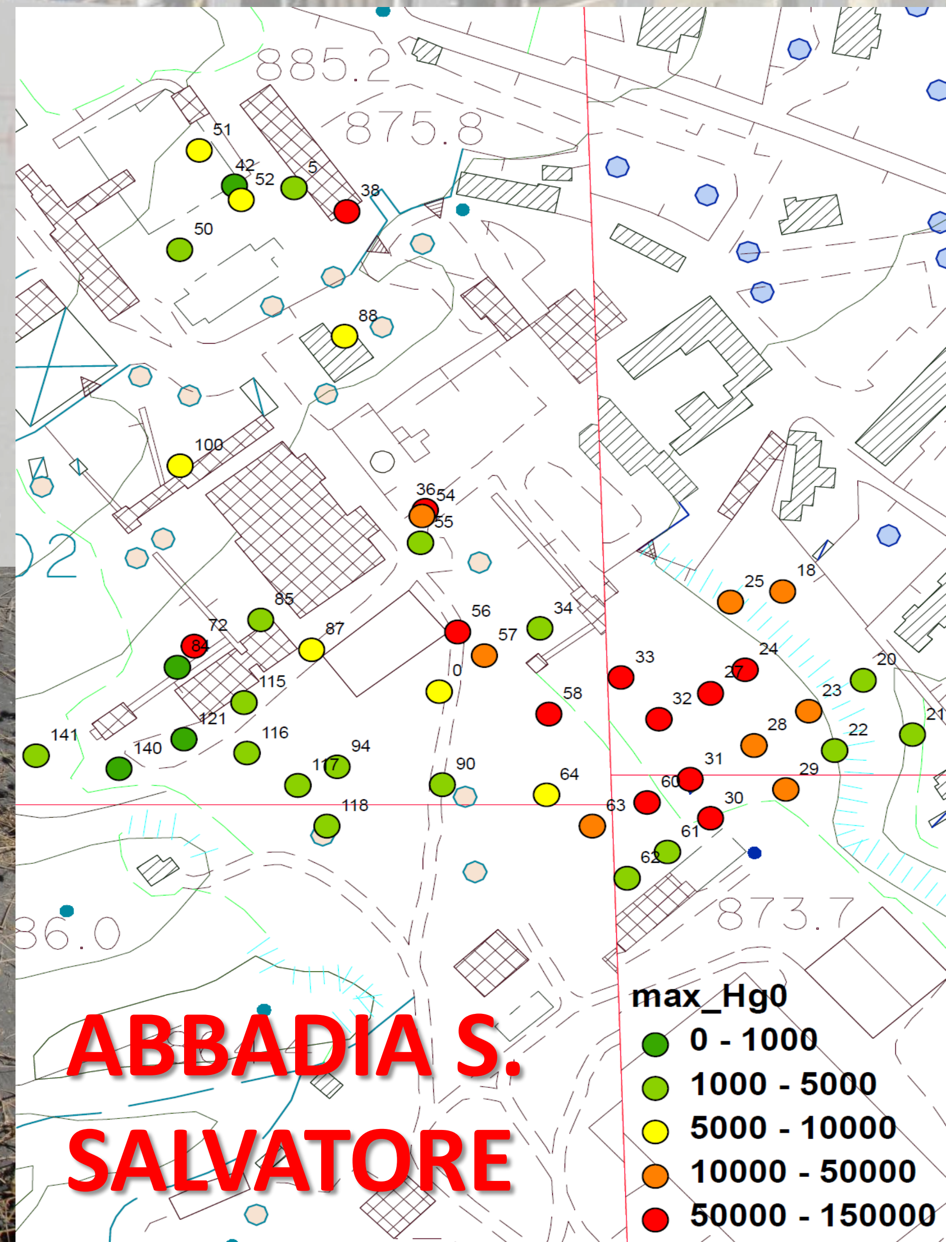
Solfatara, 04/2014





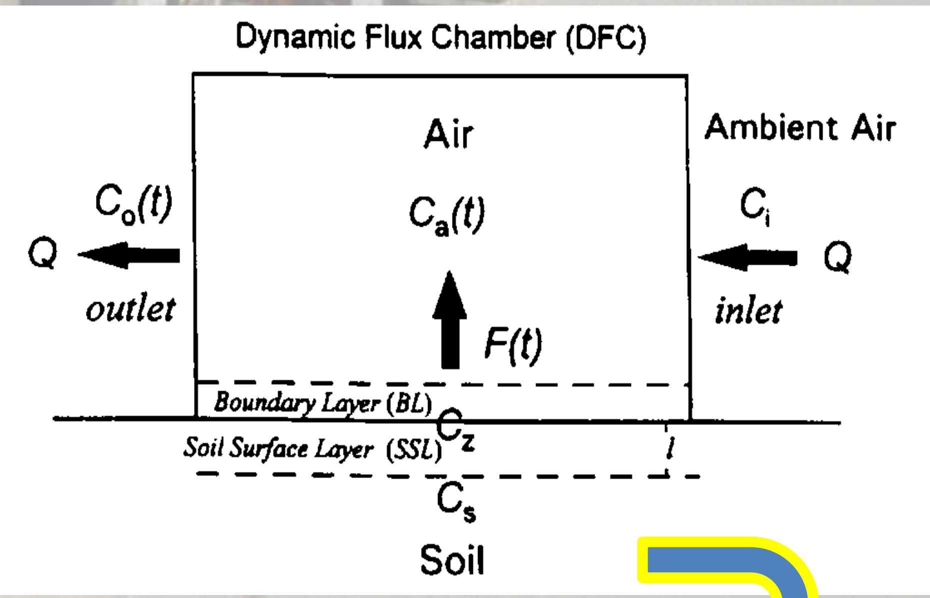
MISURE IN CONTINUO: CAMERA

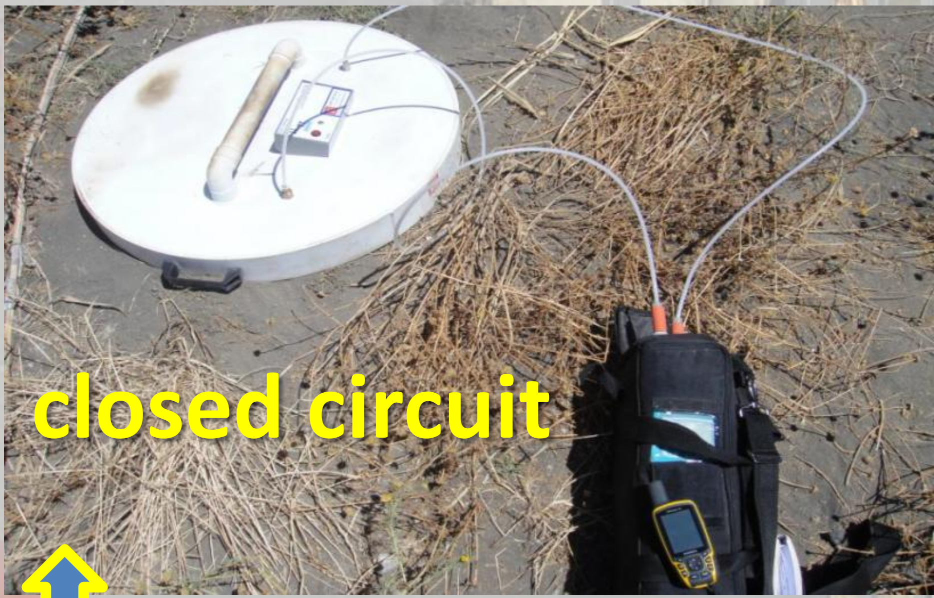
Misura delle massime concentrazioni di Hg^0 dal suolo connettendo direttamente allo strumento Lumex una camera d'accumulo da porre a terra

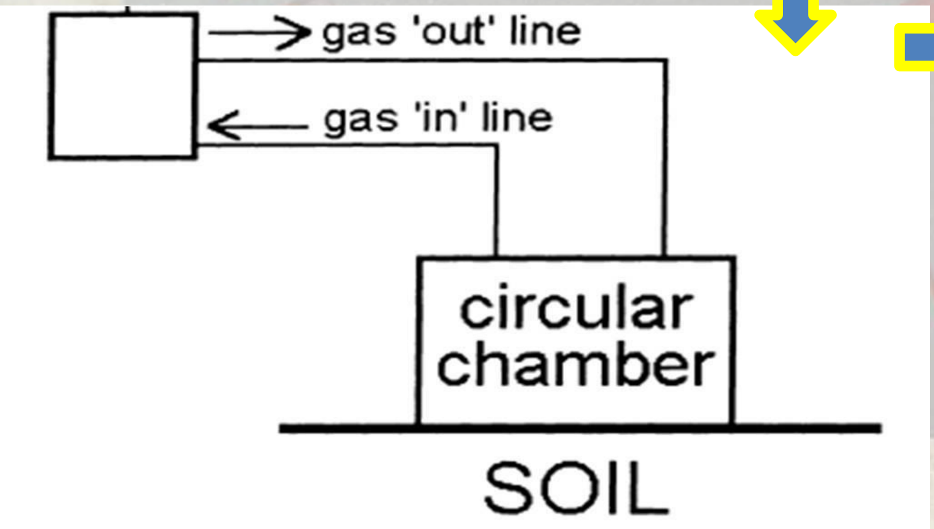


ABBADIA S. SALVATORE

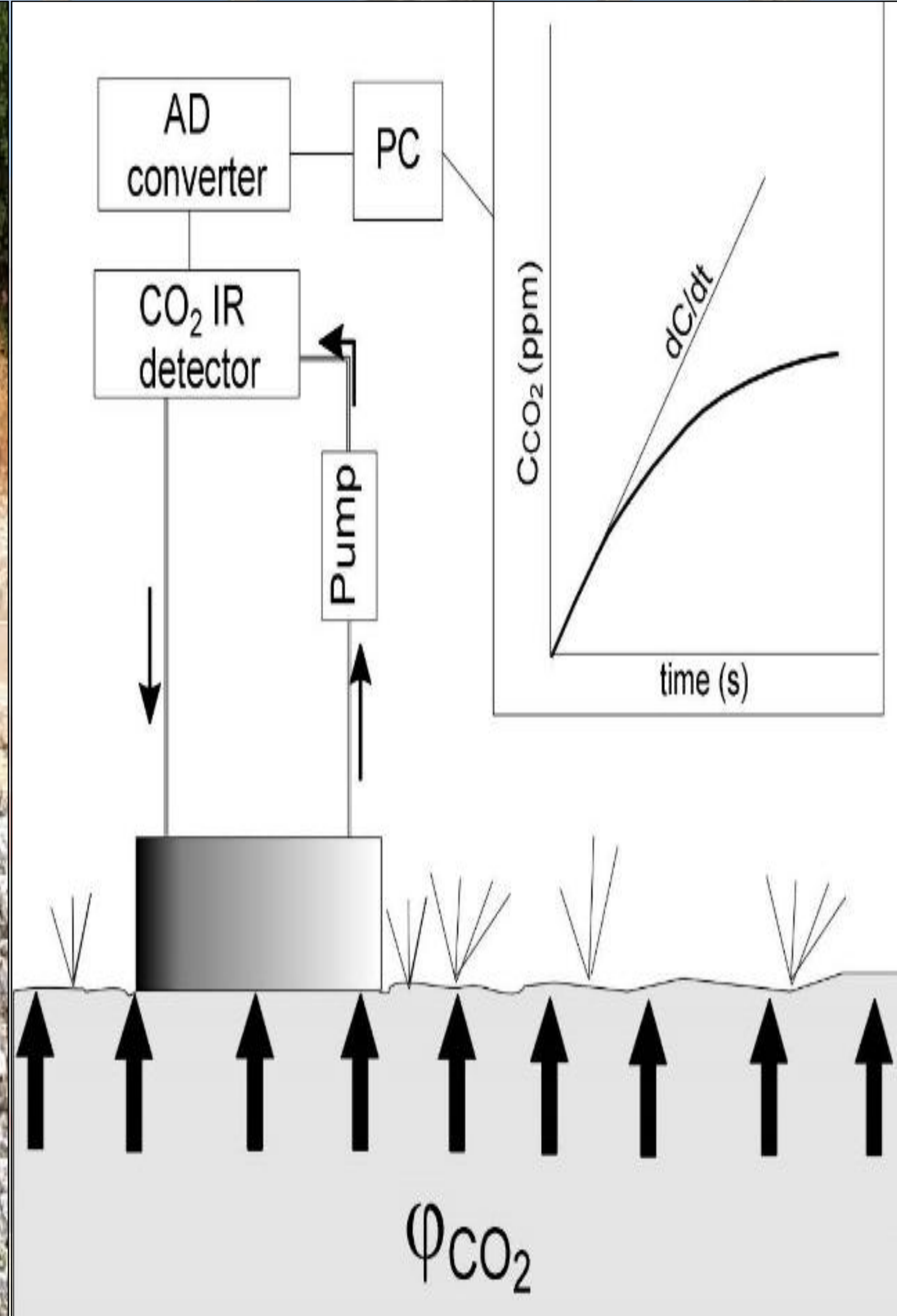
FLUSSI: DFC vs. Accumul. Chamber





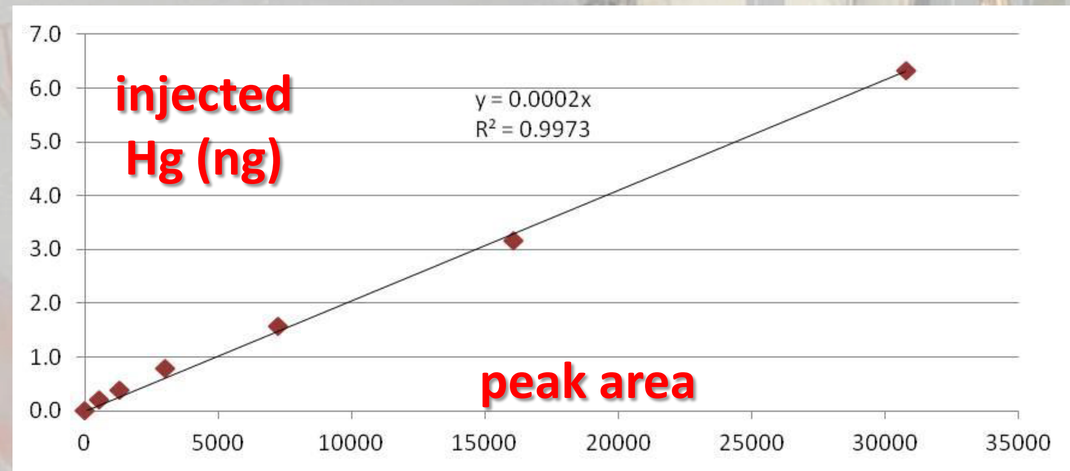


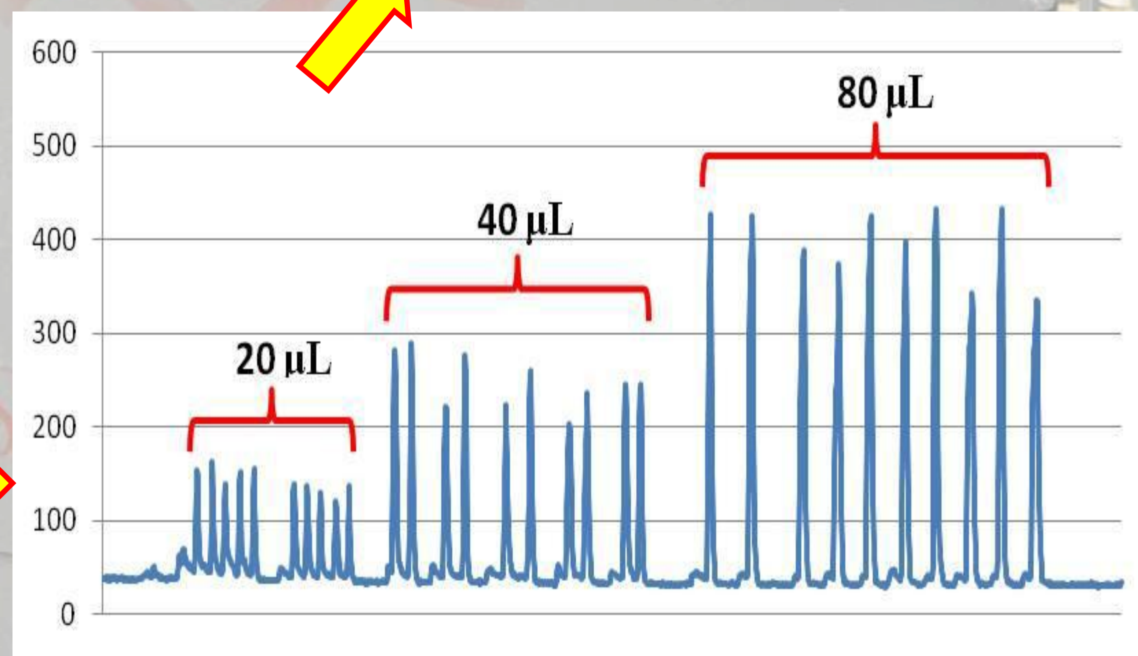
the great variability of Hg^0 concentration and the development of non-uniform concentration-time curve not allow to calculate a real flow


AD
converter
PC
CO_2 IR
detector
Pump
C_{CO_2} (ppm)
dC/dt
time (s)
φ_{CO_2}

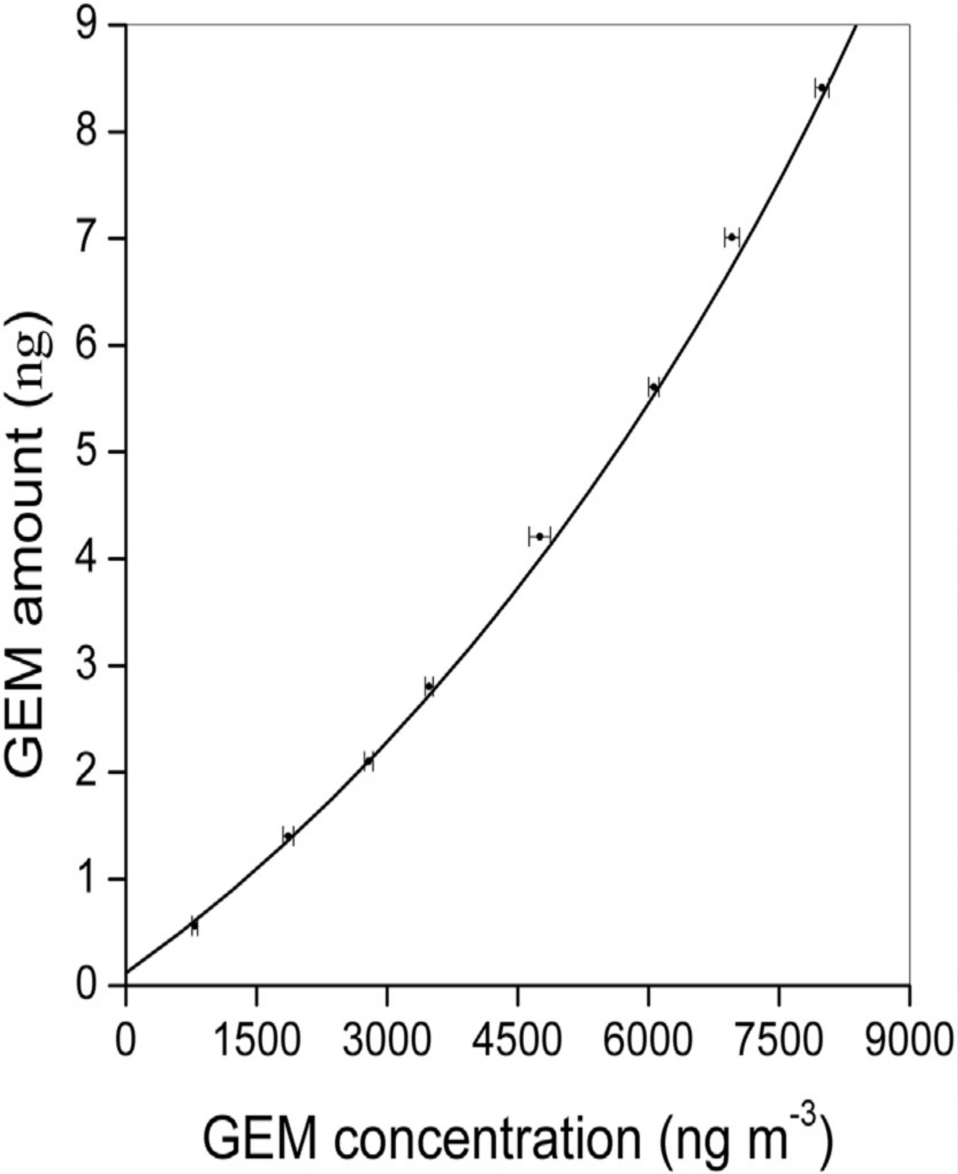
FLUSSI DI GEM DAL SUOLO

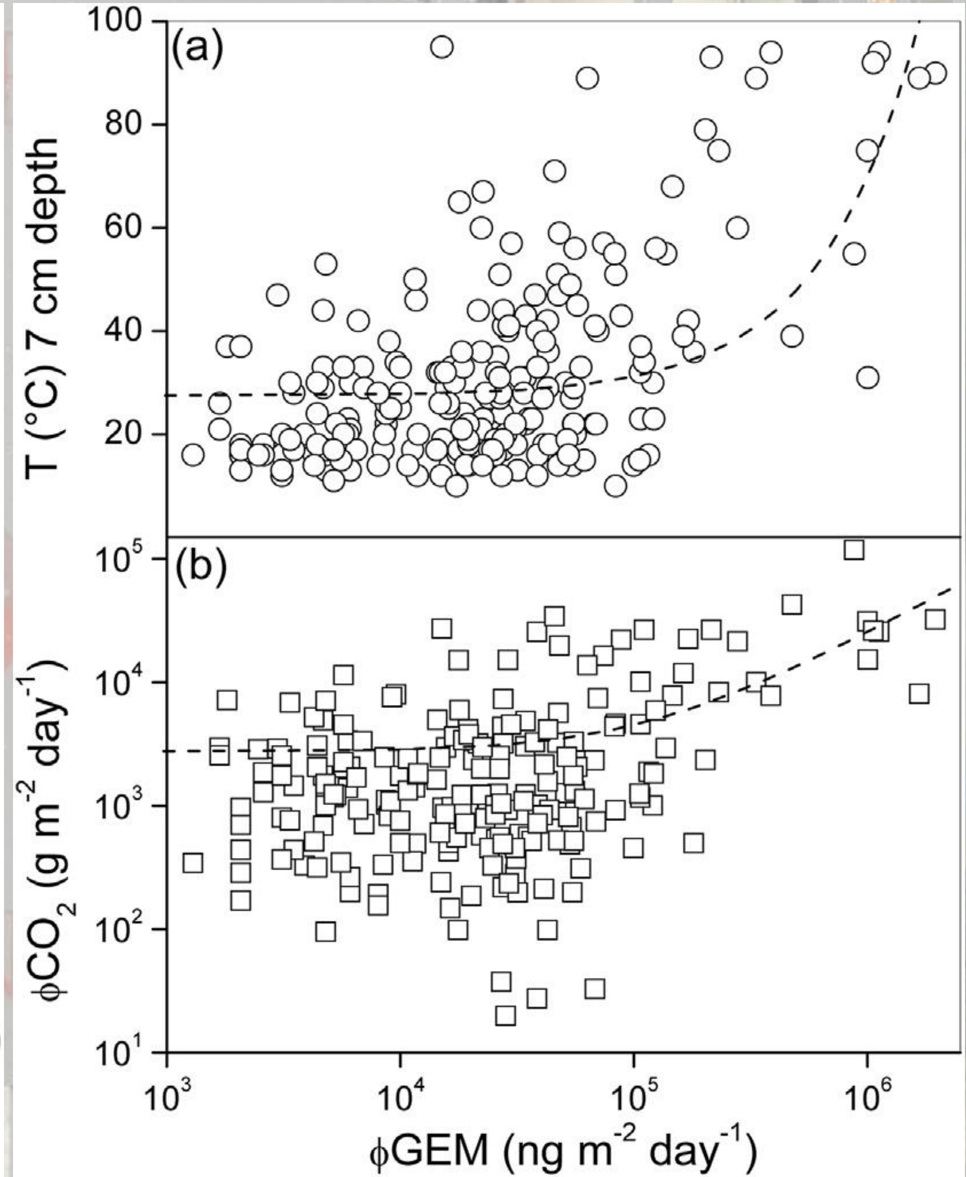
Volume of Hg Saturated Air Injected (µL)	Amount of Hg Injected (ng)
0	0
20	0.198
40	0.396
80	0.793
160	1.586



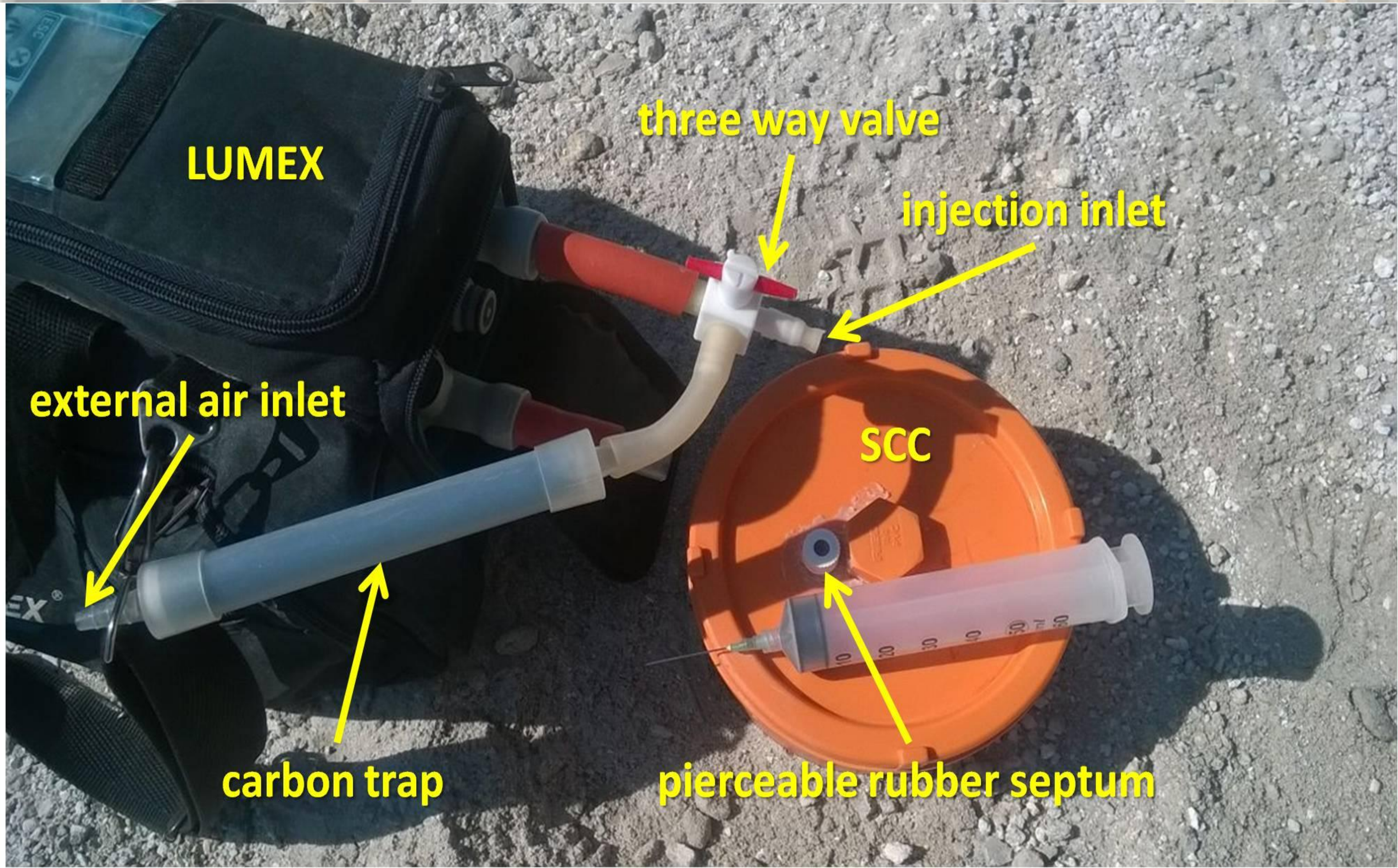


FLUSSI DI GEM DAL SUOLO

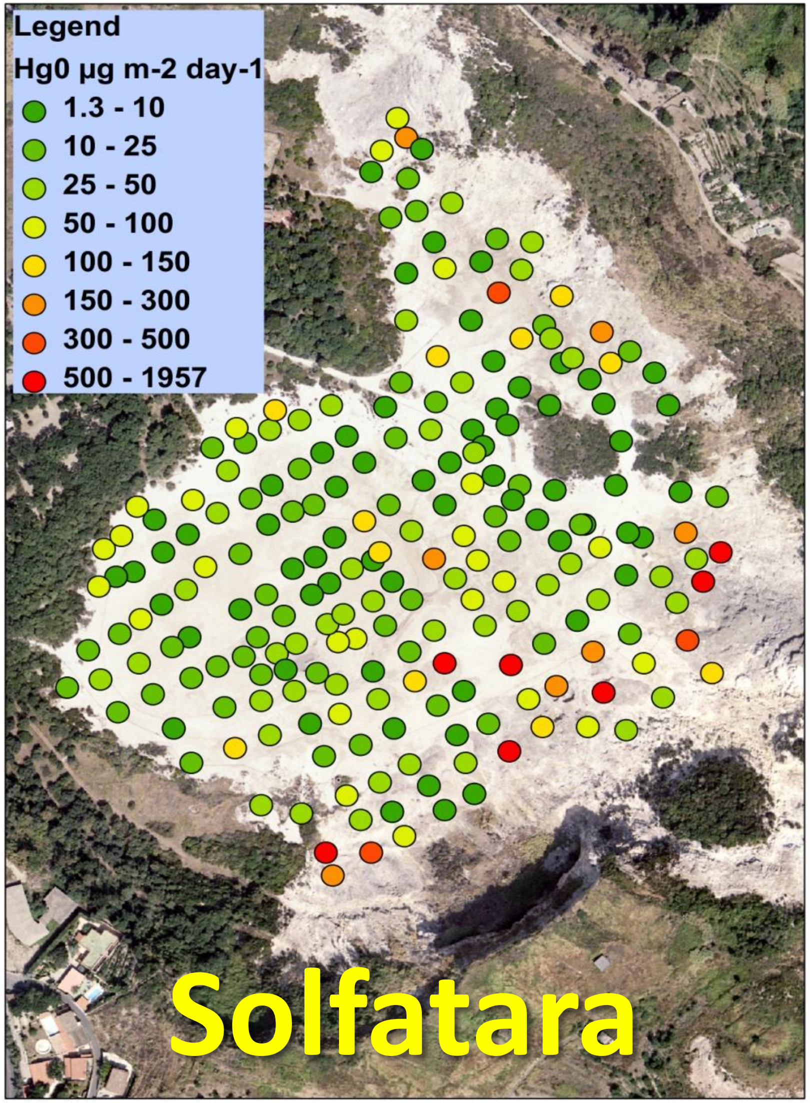


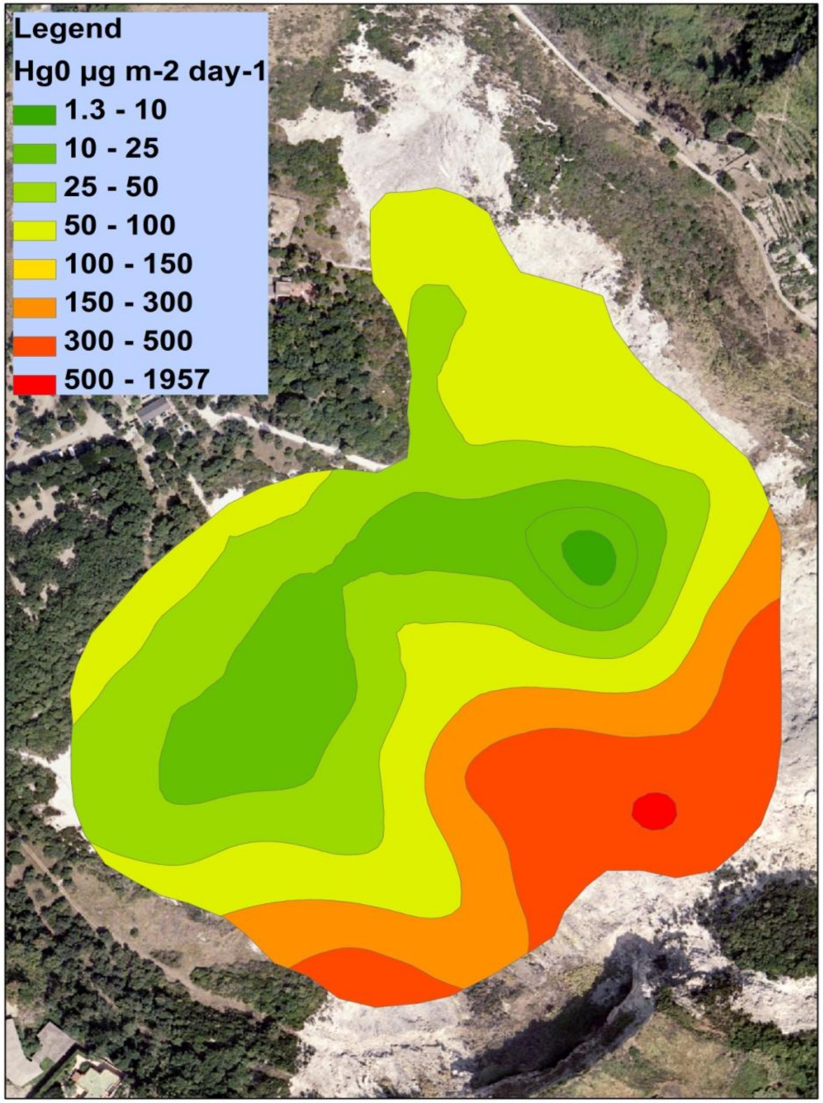


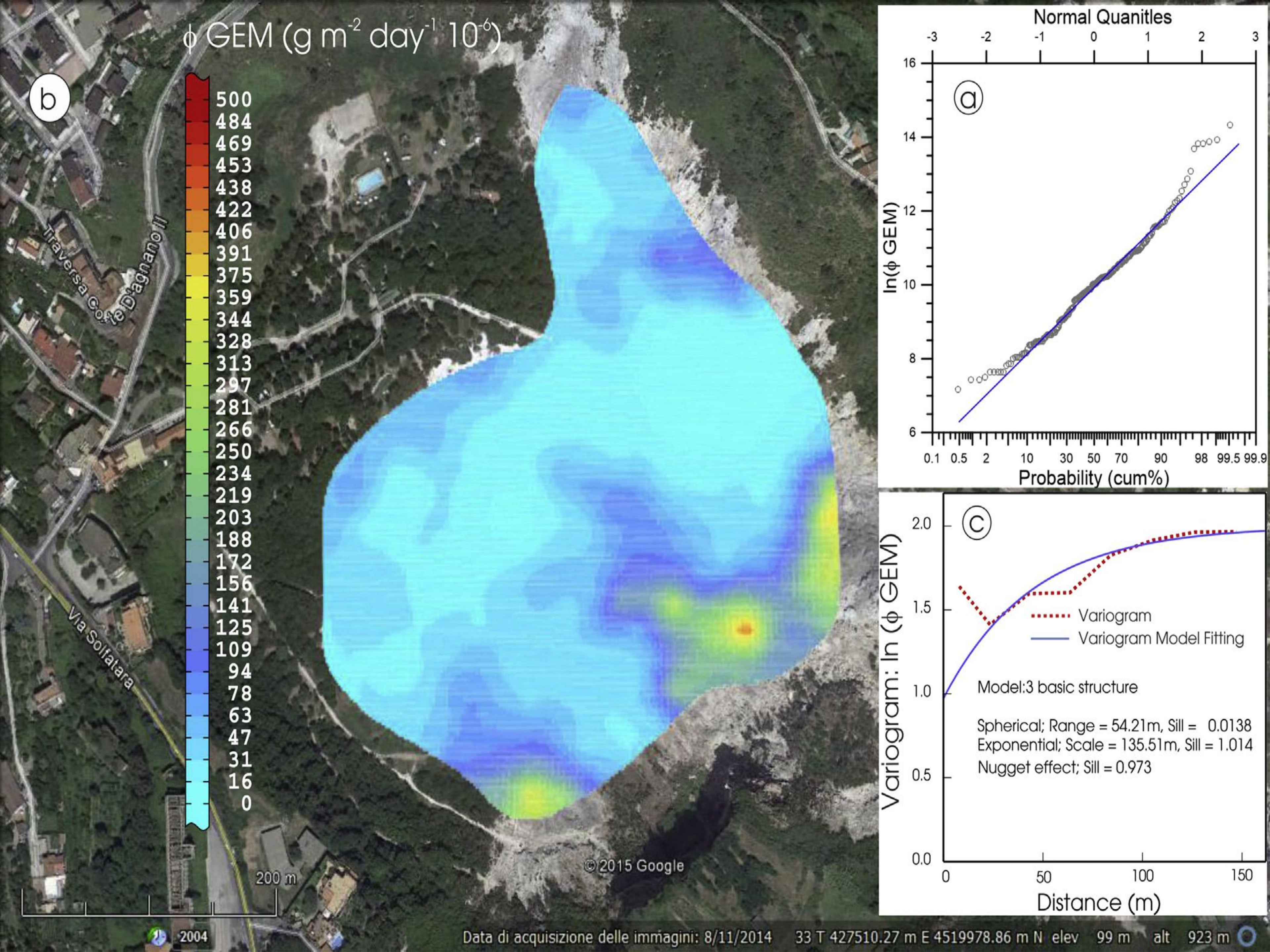
FLUSSI DI GEM DAL SUOLO



FLUSSI DI GEM DAL SUOLO






ϕ GEM (g m-2 day-1 10-6)
b
500
484
469
453
438
422
406
391
375
359
344
328
313
297
281
266
250
234
219
203
188
172
156
141
125
109
94
78
63
47
31
16
0
Traversa Corte D'agnano II
Via Solfatara
200 m
©2015 Google
2004
Data di acquisizione delle immagini: 8/11/2014
33 T 427510.27 m E 4519978.86 m N elev 99 m alt 923 m
Normal Quanitles
-3 -2 -1 0 1 2 3
a
16
14
12
10
8
6
ln(ϕ GEM)
0.1 0.5 2 10 30 50 70 90 98 99.5 99.9
Probability (cum%)
c
2.0
1.5
1.0
0.5
0.0
Variogram: ln (ϕ GEM)
Variogram
Variogram Model Fitting
Model:3 basic structure
Spherical; Range = 54.21m, Sill = 0.0138
Exponential; Scale = 135.51m, Sill = 1.014
Nugget effect; Sill = 0.973
0 50 100 150
Distance (m)

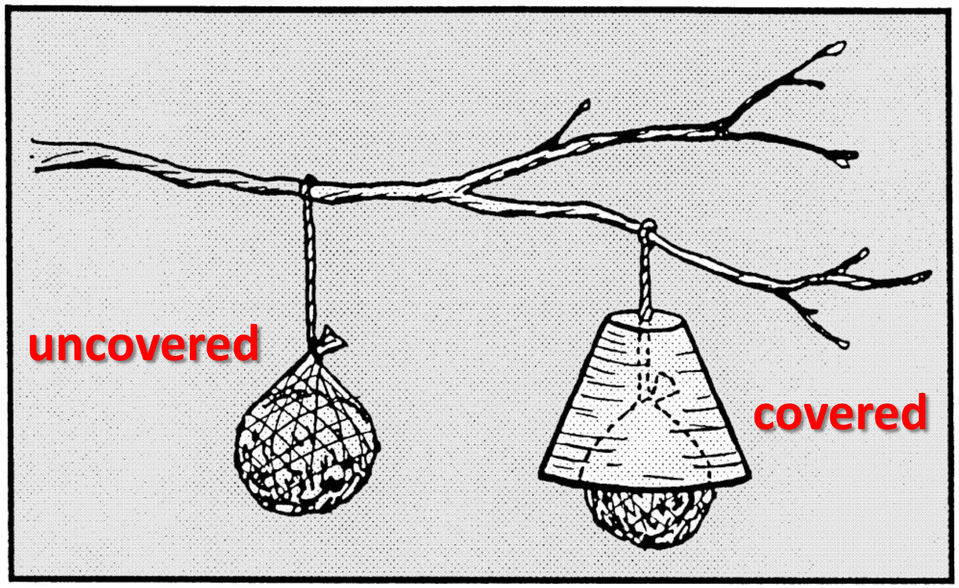
MISURE CUMULATE: MOSS-BAGS

bio-monitoring: use of organisms (bio-indicators) to obtain information about certain characteristics of the environment

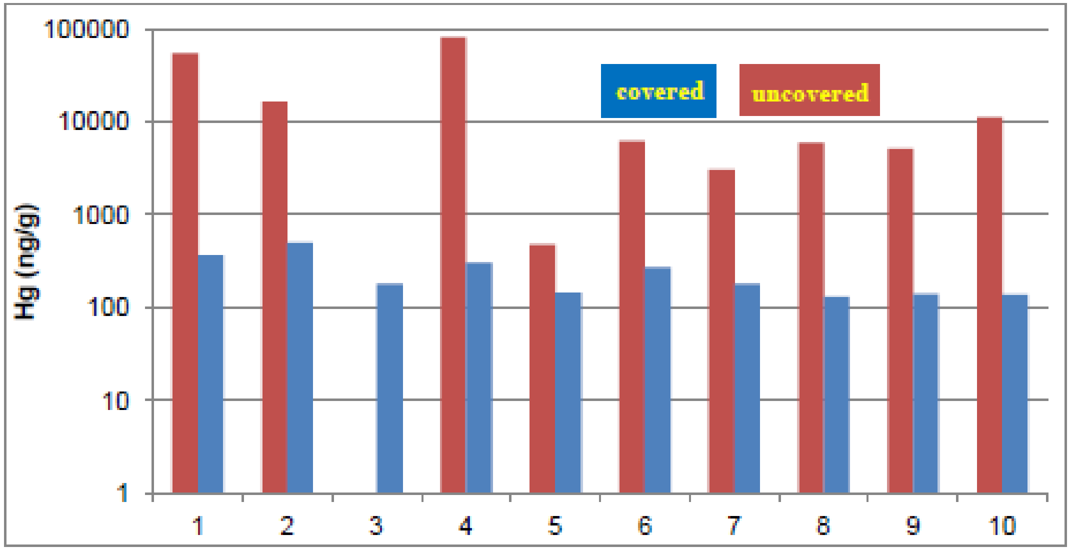
the mosses accumulate efficiently large quantities of trace metals and are therefore useful to identify the sources of pollution and to estimate the metals spatial distribution on a local scale

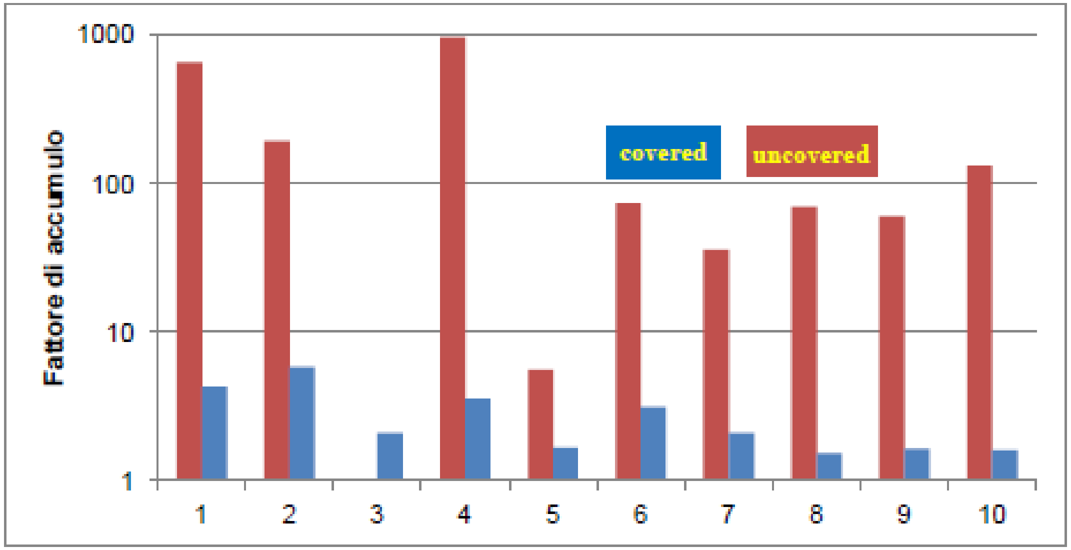
the passive accumulation occurs both through dry and wet deposition, regardless of organism viability

Moss-Bags: Covered vs. Uncovered



Hg Accumulation: Moss-Bags

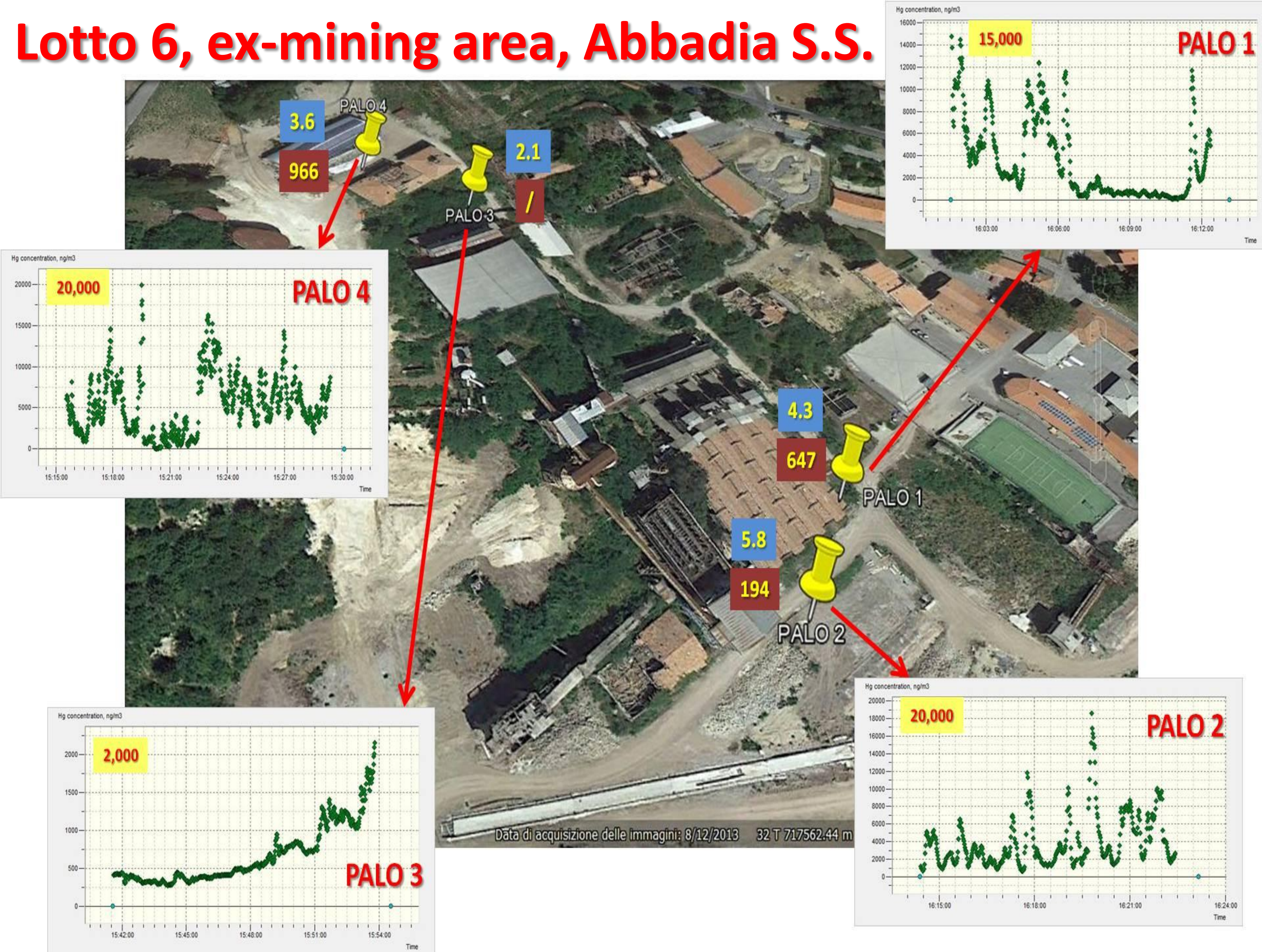




Higher accumulation factor of uncovered moss

predominant wet deposition compared to dry

Lotto 6, ex-mining area, Abbadia S.S.



JGR Atmospheres

RESEARCH ARTICLE
10.1029/2018JD029373

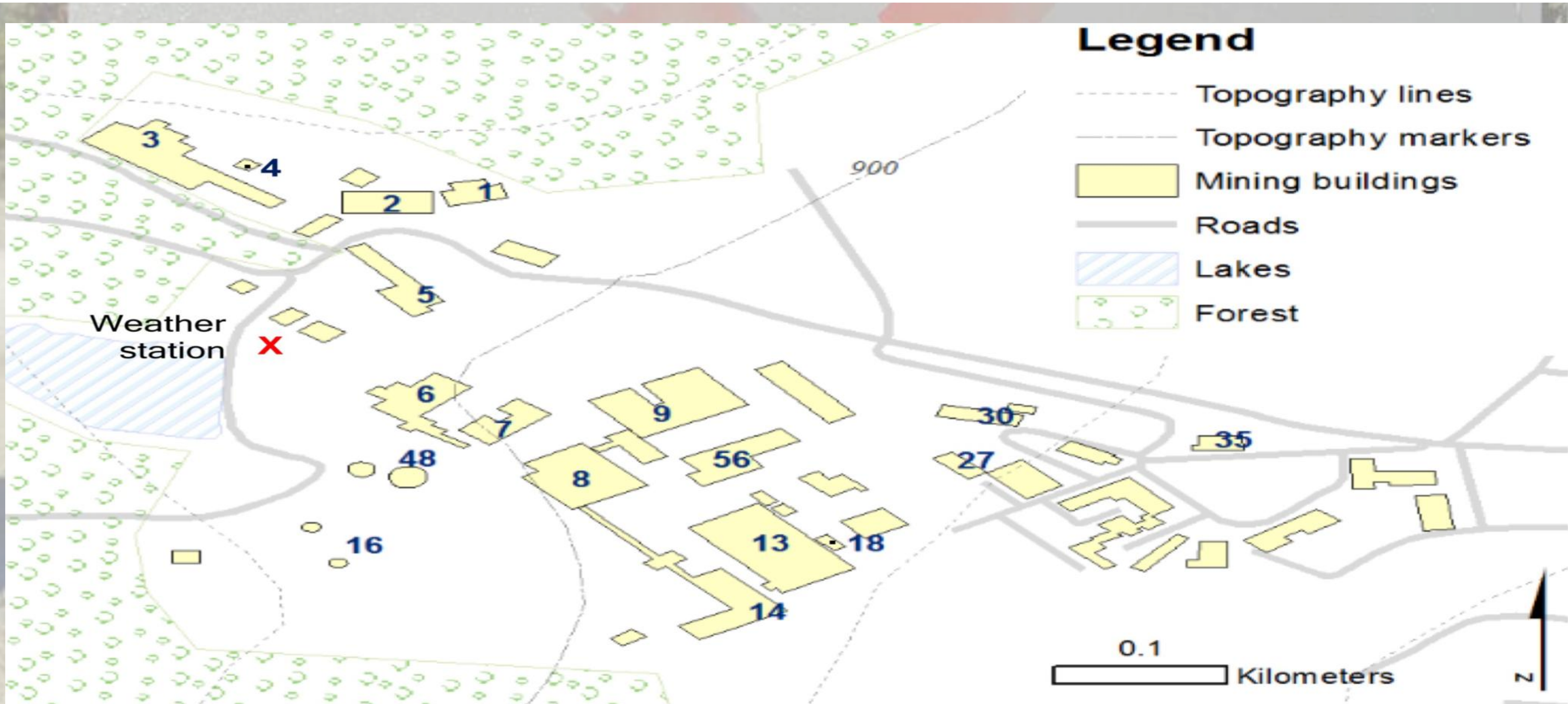
Key Points:
- Gaseous Hg concentrations, ranging over 4 orders of magnitude, can be measured concurrently at numerous sites
- The concentrations are averaged over time periods of relevance to chronic population exposure and meaningful emission estimation
- Cheaper and simpler than previous methods, the approach yields data with precision and accuracy of state-of-the-art active instruments

Characterization and Quantification of Atmospheric Mercury Sources Using Passive Air Samplers

David S. McLagan[1], Fabrizio Monaci[2], Haiyong Huang[1], Ying Duan Lei[1], Carl P. J. Mitchell[1], and Frank Wania[1]

[1]Department of Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, ON, Canada, [2]Department of Life Sciences, Università di Siena, Siena, Italy

Abstract The Minamata Convention on Mercury (Hg) requires improved atmospheric Hg monitoring and characterization of Hg sources. Here we demonstrate how a network of passive air samplers (PASs) can be used cost effectively to determine the spatial distribution of gaseous Hg and estimate atmospheric Hg emissions at contaminated sites. Gaseous Hg concentrations were mapped around a former Hg mine in the

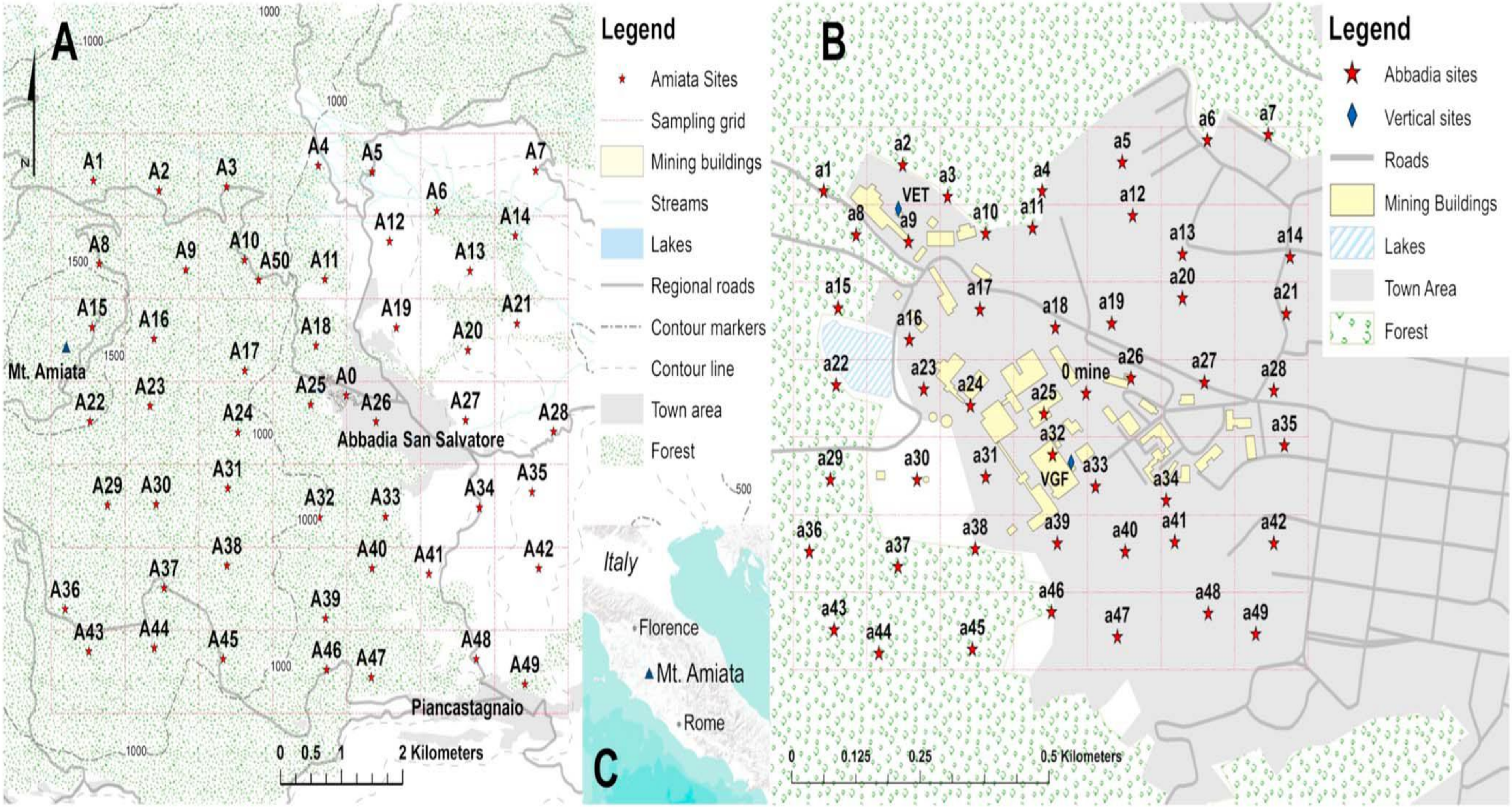




Gaseous Hg sorbs to sulfur-impregnated activated carbon (HGR-AC; Calgon Carbon) sorbent, which is contained in a stainless steel mesh cylinder. The rate of diffusion from the atmosphere to the sorbent is controlled by a porous polyethylene diffusive barrier (white Radiello®) which is housed inside a polypropylene container that acts as a protective windshield and rain shield during deployments

Meteorological parameters such as wind speed and temperature have a minor and quantifiable impact on the rate of mercury uptake in the PAS

While a quantification of the accuracy of a PAS measurement is not possible in the absence of knowledge of the true concentration of Hg in the atmospheric gas phase, it is feasible to compare concentrations obtained with the PAS with those recorded simultaneously by a state-of-the-art active instrument.

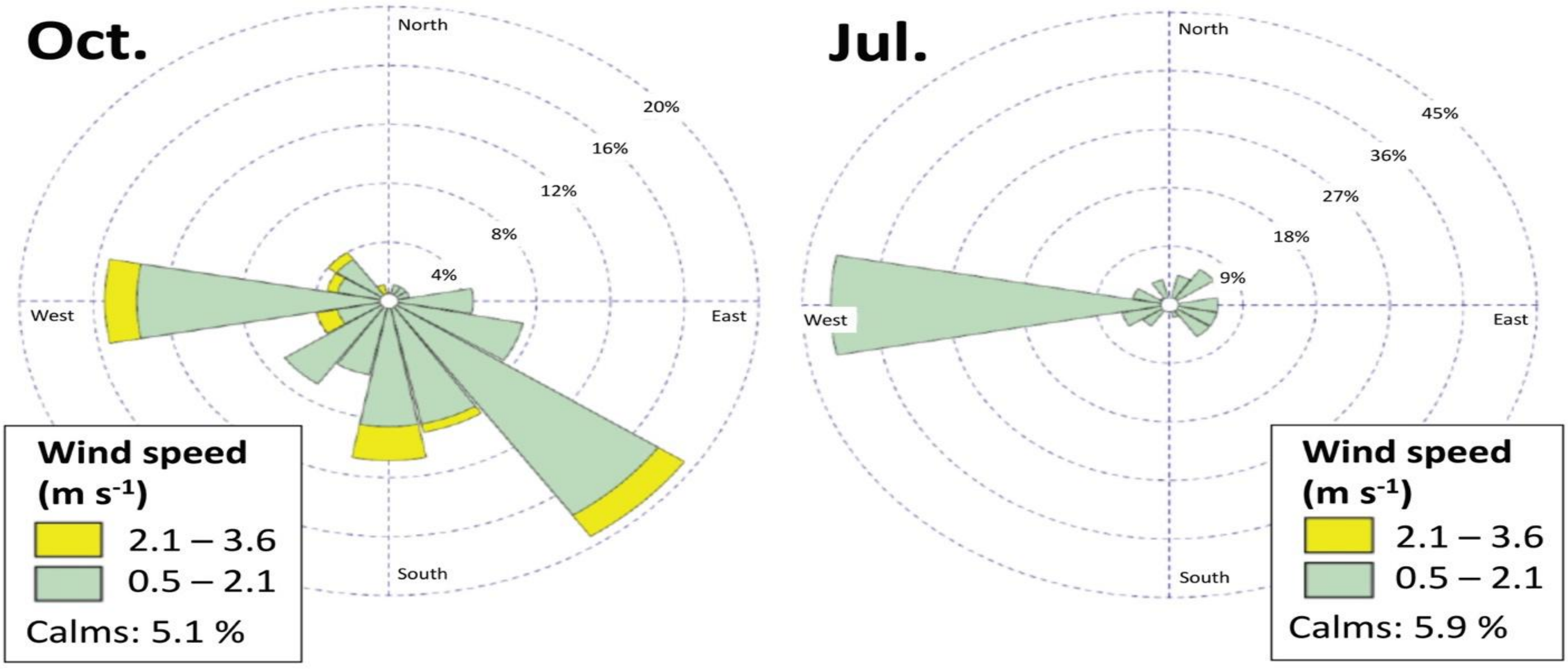


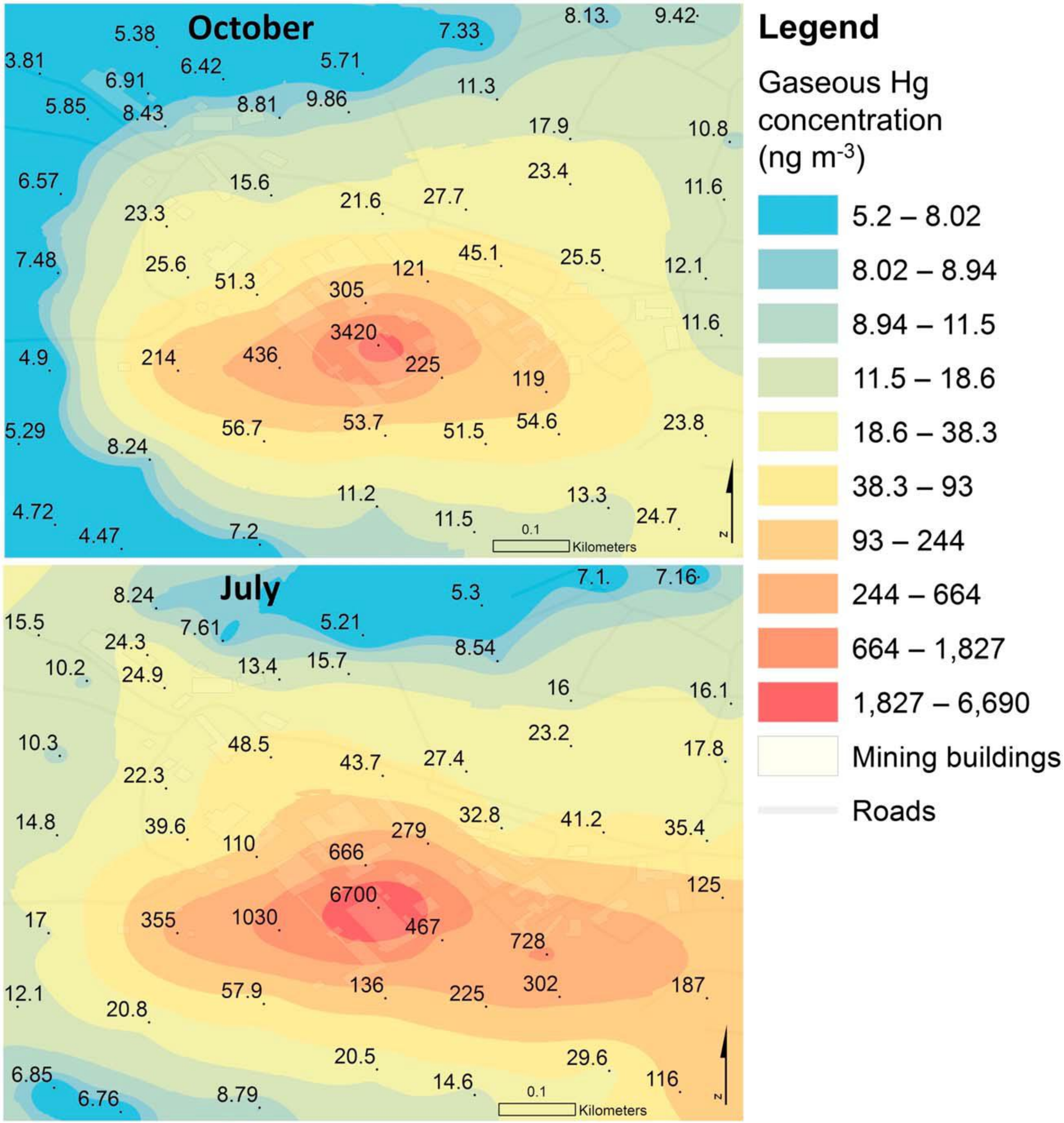
PASs were deployed to determine the air concentration variability of gaseous Hg at two spatial scales: a 0.56 km2 box (extending 750 m NS and EW) comprising the former buildings of the ASSM, termed the Abbadia grid, and a 41.6 km2 box (extending approximately 6.5 km NS and EW) covering the eastern slope of Monte Amiata, termed the Amiata grid

The sorbent was analyzed for total Hg using an AMA254 Total Mercury Analyzer (Leco Instruments) using USEPA method 7473. All samples were blank adjusted.

The gaseous Hg concentration (C; ng/m3) was calculated by dividing the quantified mass of sorbed Hg (m, ng) by the product of the deployment time (t, day) and the sampling rate (SR, m3/day). The SR of 0.135 m3/day, obtained from a global-scale calibration experiment, was adjusted for temperature and wind speed.

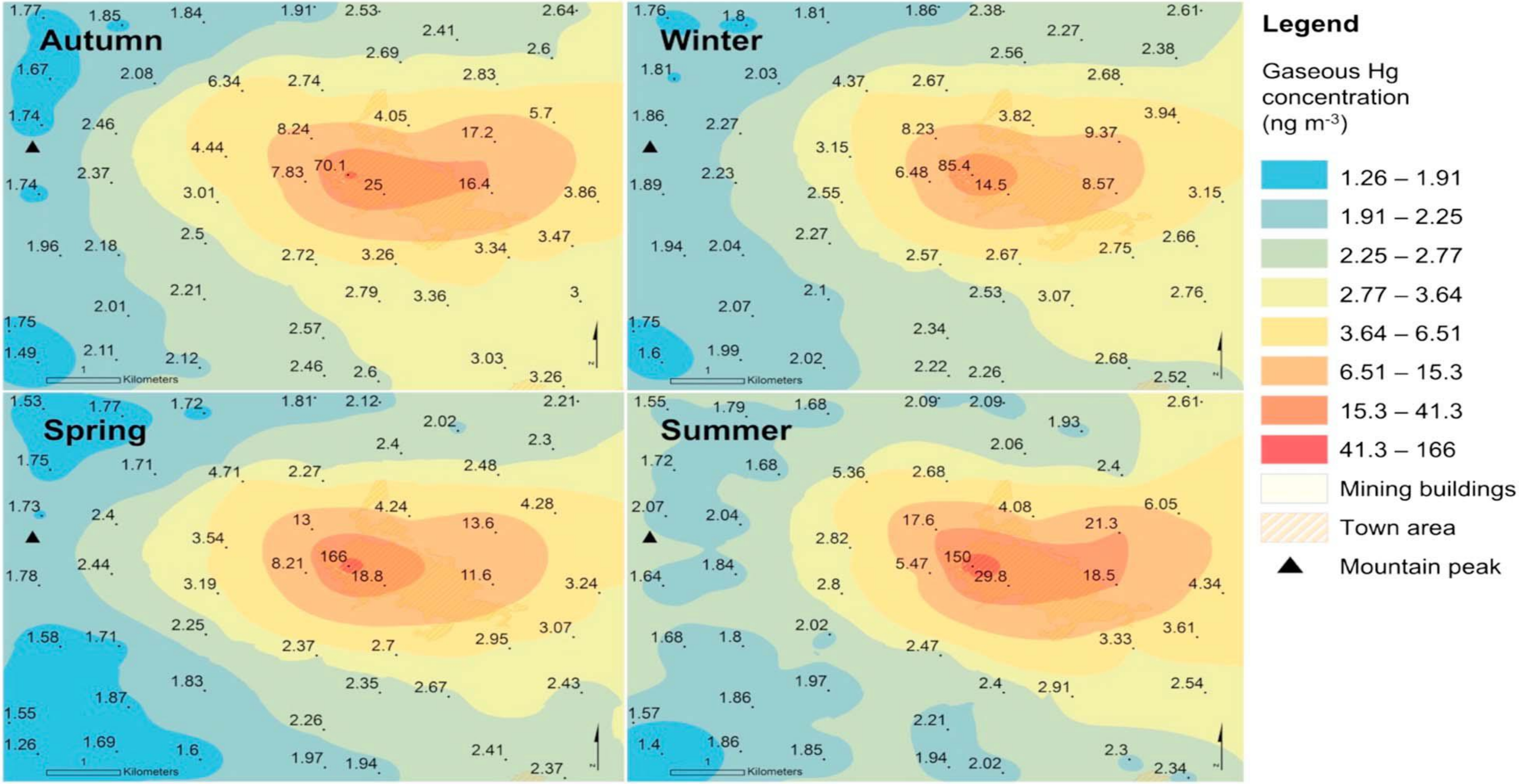
Average wind speed and temperature at the Laghetto Verde Meteorology Station was used for the PAS deployed for two 1-week periods. The average of the wind speed measured at Laghetto Verde and Monte Amiata Peak was applied to all PASs deployed seasonally in the larger Amiata grid.





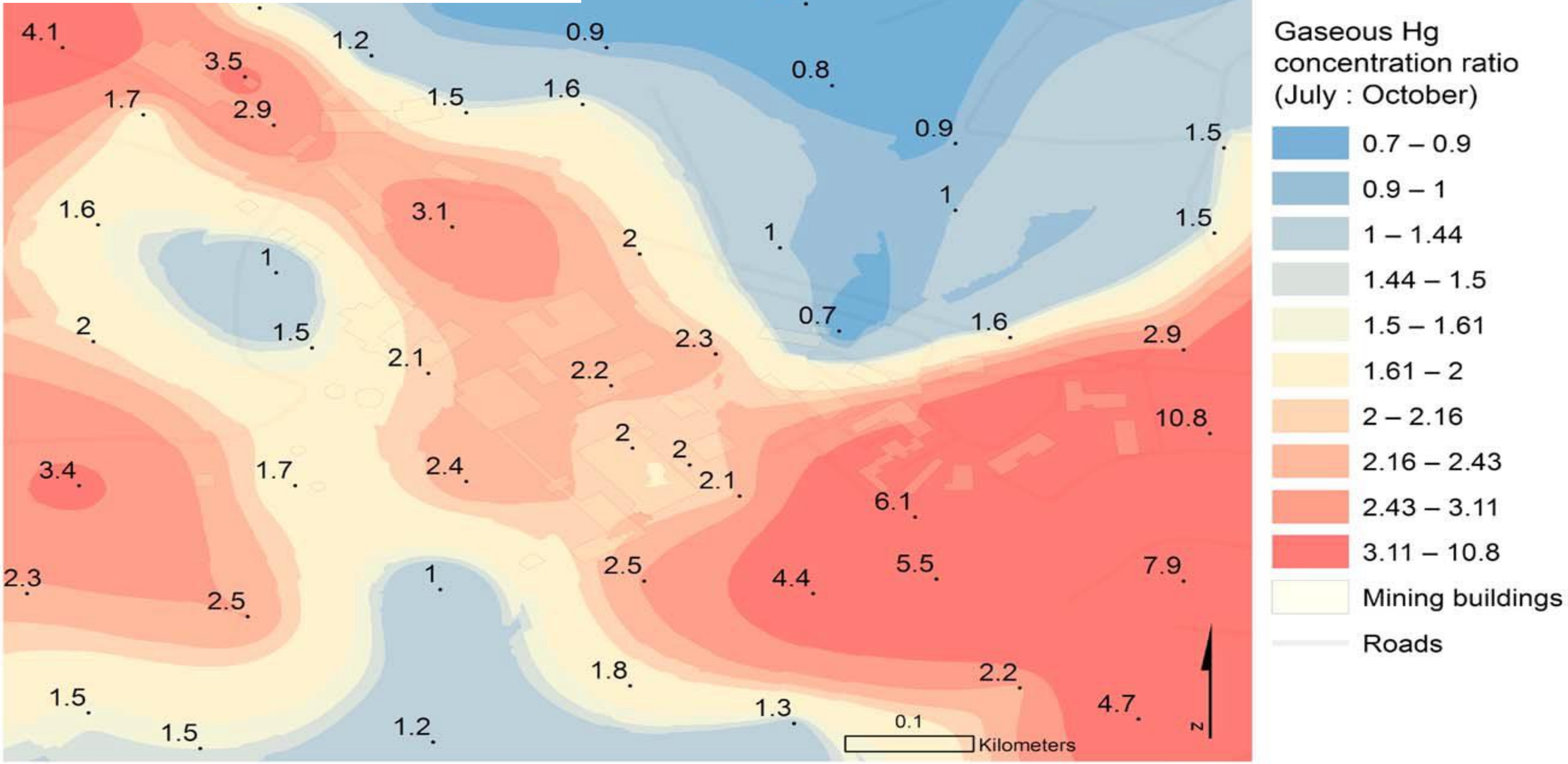
Measured (numeric values) and contoured prediction (Kriging) maps for gaseous Hg concentrations for October (upper) and July (lower) deployments in the smaller Abbadia grid.

Furnaces and condensing units are the major emission source within the ASSM



The ASSM as the major emission source in the Amiata region. Background concentration levels were observed in the northwest and southwest corners of the larger Amiata grid across all four seasonal deployments.
Concentrations incrementally increased moving from these sites at the western edge of the Amiata grid toward the ASSM

July/October concentration ratios



Hg emissions from soils and contaminated areas have been reported to be greater under elevated temperatures and solar radiation, related to increased vapor pressure at higher temperatures and photolytic reduction of Hg^{2+} to Hg^0. Concentrations doubled in the most contaminated part of the ASSM in summer, in agreement with earlier observations. The largest seasonal differences of up to an order of magnitude were seen for the east-southeast edge of the Abbadia grid, which represents the periphery of the Abbadia San Salvatore urban area. This is at least partly explained by the wind conditions

- **By sampling simultaneously with a high number of PASs, it is possible to isolate concentration changes to spatial variability.**

- **Reproducing these measurements with a network of active instruments is not possible due to the extremely high costs and infrastructure that would be required.**

- **Mobile active techniques cannot sample multiple sites simultaneously, only producing short-term "snapshots in time".**

BUT…

- **Environmental conditions (wind speed and direction, humidity, temperature) are known to strongly affect passive measurements.**

- **Active measurements highlighted the occurrence of short-term temporal variations of the concentrations, with peak values potentially harmful to the human health.**

- **Although passive samplers may offer the opportunity to carry out low-cost surveys, the use of the high-frequency analyzer is preferred when an accurate assessment of air quality is required.**

100 years of high GEM concentration in the Central Italian Herbarium and Tropical Herbarium Studies Centre (Florence, Italy)

Jacopo Cabassi 1,2,∗, Valentina Rimondi 1,2, Zhang Yeqing 1, Antonella Vacca 1, Orlando Vaselli 1,2, Antonella Buccianti 1,2, Pilario Costagliola 1,2

1. Department of Earth Sciences, University of Florence, Via G. La Pira, 4-50121 Florence, Italy
2. CNR – Institute of Geosciences and Earth Resources, Via G. La Pira, 4-50121 Florence, Italy

jacopo.cabassi@unifi.it

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Intro

Herbaria represent unique archives for botanists, hence the stored specimens need to be properly preserved through physical or chemical treatments

Up to 1980s, the most used preservative and biocide was mercuric chloride ($HgCl_2$), sublimating at ambient air conditions

In herbaria, ionic Hg reduces to Hg^0 (i.e. gaseous elemental mercury, GEM) and easily diffuses throughout the poor ventilated environment

Recent studies recognized that high GEM levels may indeed persist for decades, representing a health hazard for humans

Intro

A key question concerns how long high GEM levels could be recognized from the last $HgCl_2$ treatment

In this study, we present new original GEM data in the Central Italian Herbarium (Natural History Museum) and Tropical Herbarium Studies Centre of the Botanical Department of the University of Florence

These herbaria host one of the largest plants collection in the world

Here, $HgCl_2$ was documented as a plant preservative up to the 1920s

Scope of the work

The main aims of this work were then to:

(i) test whether GEM high concentrations persist after about 100 years from the last Hg-chloride treatment

(ii) assess whether GEM concentrations showed seasonality (consequently, three surveys were carried out in different periods)

(iii) identify possible strategies to minimize the environmental impact of GEM on workers and visitors

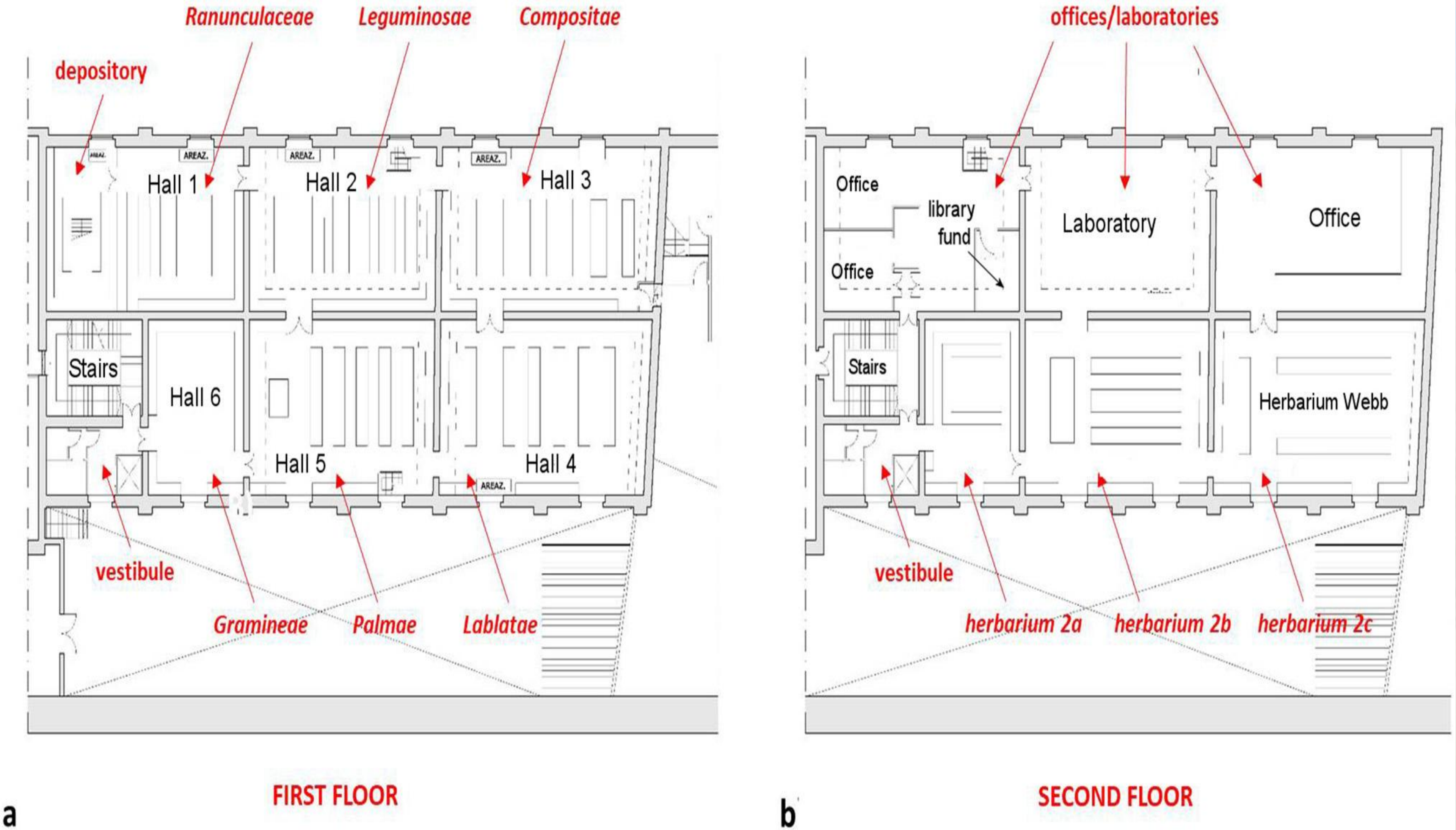
Herbaria

Central Italian Herbarium (1° floor) consists of 6 halls where different plant species are stored and a depository

The 2° floor, hosting the most ancient collections and the Tropical Herbarium Studies Centre, has offices/laboratories and 5 main halls

On the 1° floor, a new air-conditioned system was installed in 2017, while on the 2° floor only one room (2a) has a climate control

The halls of the 2° floor are equipped
with fans at the windows, allowing air circulation
with the outside. At Herbarium Webb air is only exchanged with that circulating among the surrounding halls



Map of the first (a) and second (b) floor and of the respective halls and rooms hosting the collections of the Central Italian Herbarium and Tropical Herbarium Studies Centre

The base map is taken from the cadastral plan of the herbaria building

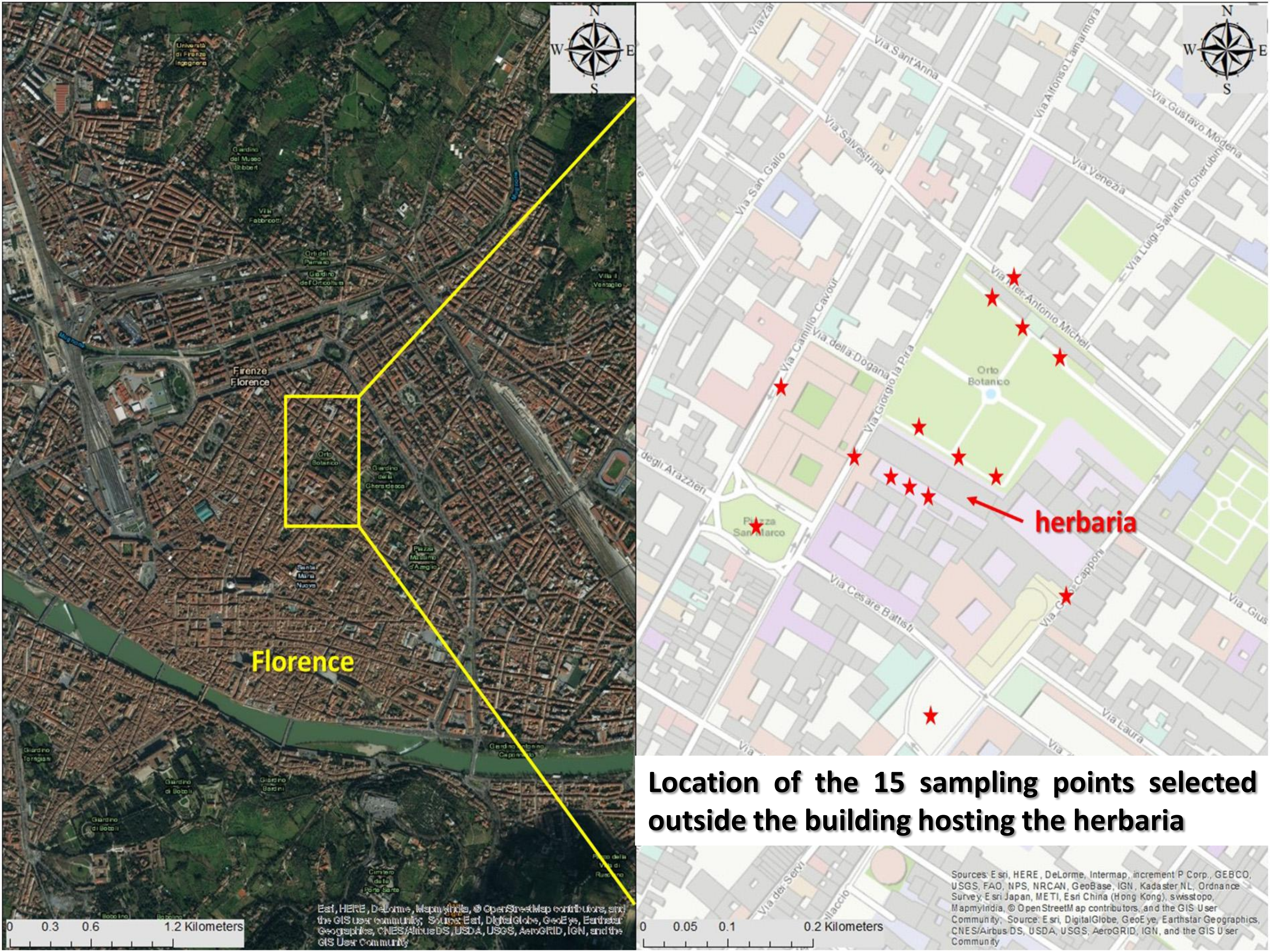
Surveys

The first survey for GEM measurements was conducted in July 2013 on the first and second floor, including internal balconies above some halls, offices of the museum staff, some warehouses and museum entrances

Additional surveys were performed in July and December 2017 to detect GEM temporal and seasonal variations

The total sampling points were 166 and were maintained fixed during each survey to avoid any bias

Fifteen sampling points were also selected outside the building hosting the herbaria: (a) the university courtyard, (b) the Botanical Garden and (c) the nearby streets and squares up to few hundred meters from the herbaria



Location of the 15 sampling points selected outside the building hosting the herbaria

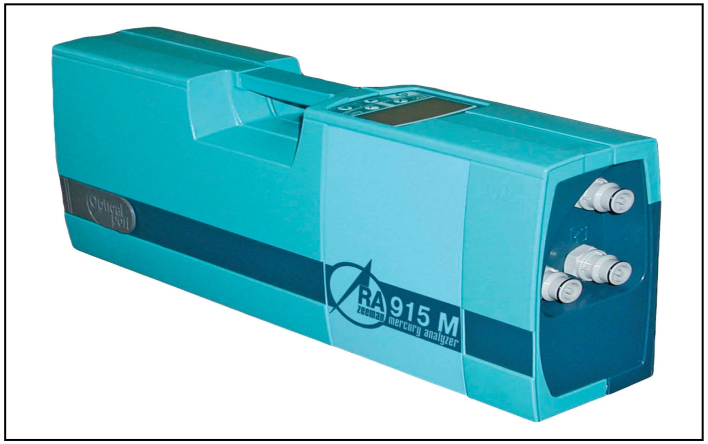
GEM measurements

Continuous GEM measurements in air were performed with a portable Lumex® (RA-915M) analyzer

Its operation is based on differential atomic absorption spectrometry using high-frequency modulation of light polarization (ZAAS-HFM)

The detection limit of the instrument was 2 ng/m^3 at a constant flow rate (~15 L/min)

The Lumex was kept at a height of ~1 m from the ground



Measurements were acquired as single points and were referred to the average of three blocks of 10 sec each (mean value every 10 sec)

Results

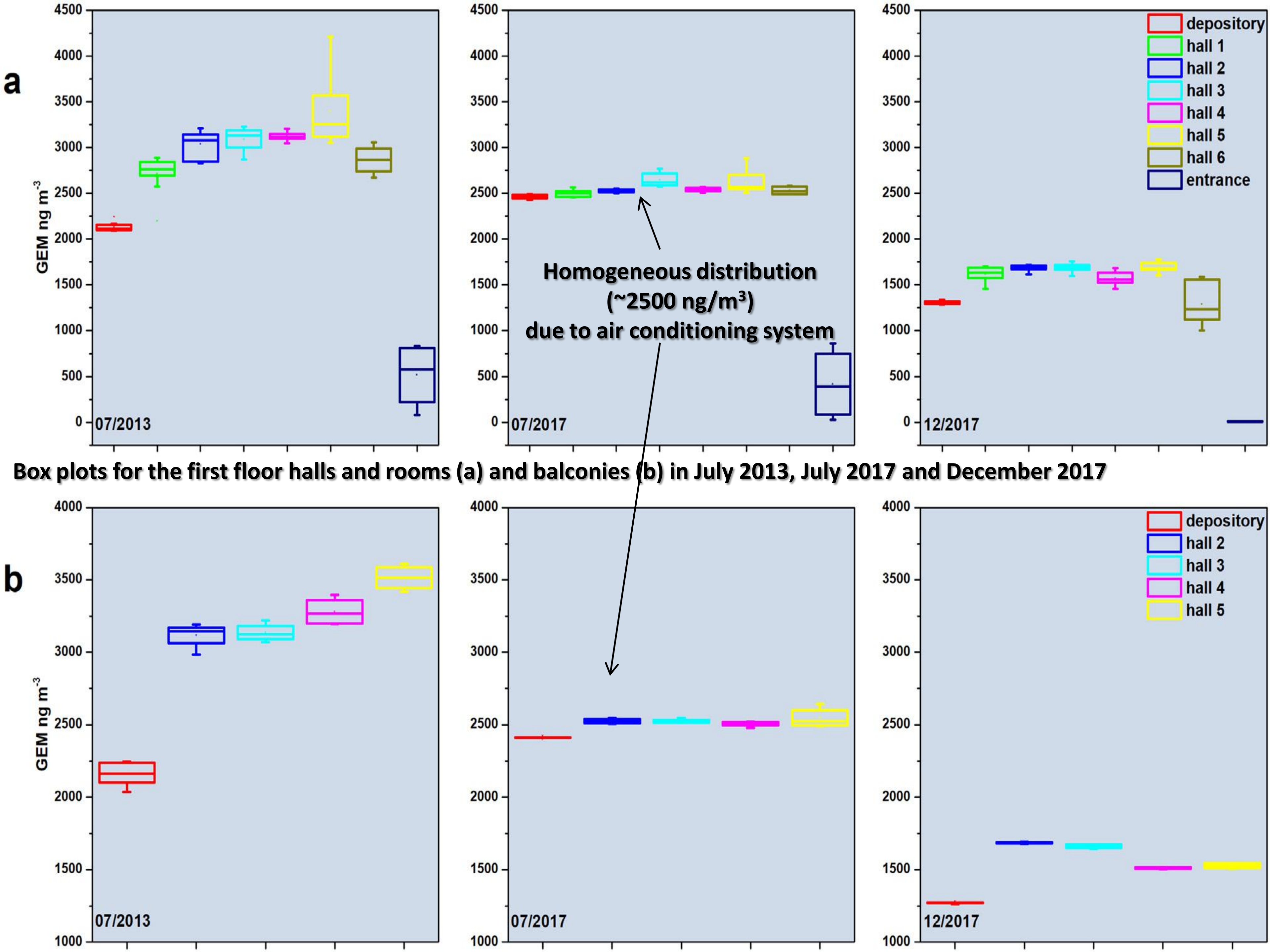
FIRST FLOOR			
N = 73			
	July 2013	**July 2017**	**Dec. 2017**
min	77	27	4
max	4209	2884	1778
median	3013	2526	1636
mean	2813	2433	1530
st. dev.	683	502	312

BALCONIES - FIRST FLOOR			
N = 21			
	July 2013	**July 2017**	**Dec. 2017**
min	2037	2400	1264
max	3609	2642	1692
median	3147	2512	1518
mean	2998	2497	1519
st. dev.	509	59	158

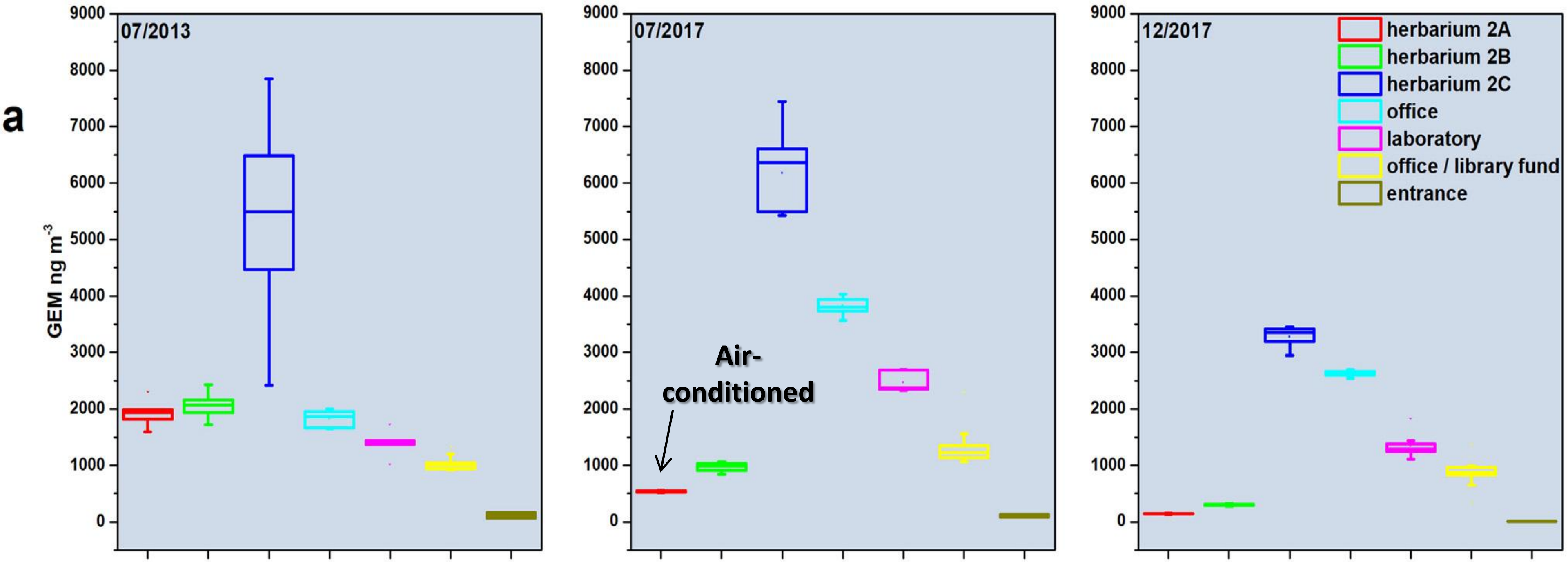
SECOND FLOOR			
N = 64			
	July 2013	**July 2017**	**Dec. 2017**
min	71	89	10
max	7846	7446	3455
median	1897	1933	1050
mean	2277	2533	1416
st. dev.	1654	2044	1215

BALCONIES - SECOND FLOOR			
N = 8			
	July 2013	**July 2017**	**Dec. 2017**
min	922	1094	771
max	1087	1616	1432
median	973	1240	964
mean	985	1313	1062
st. dev.	52	207	249

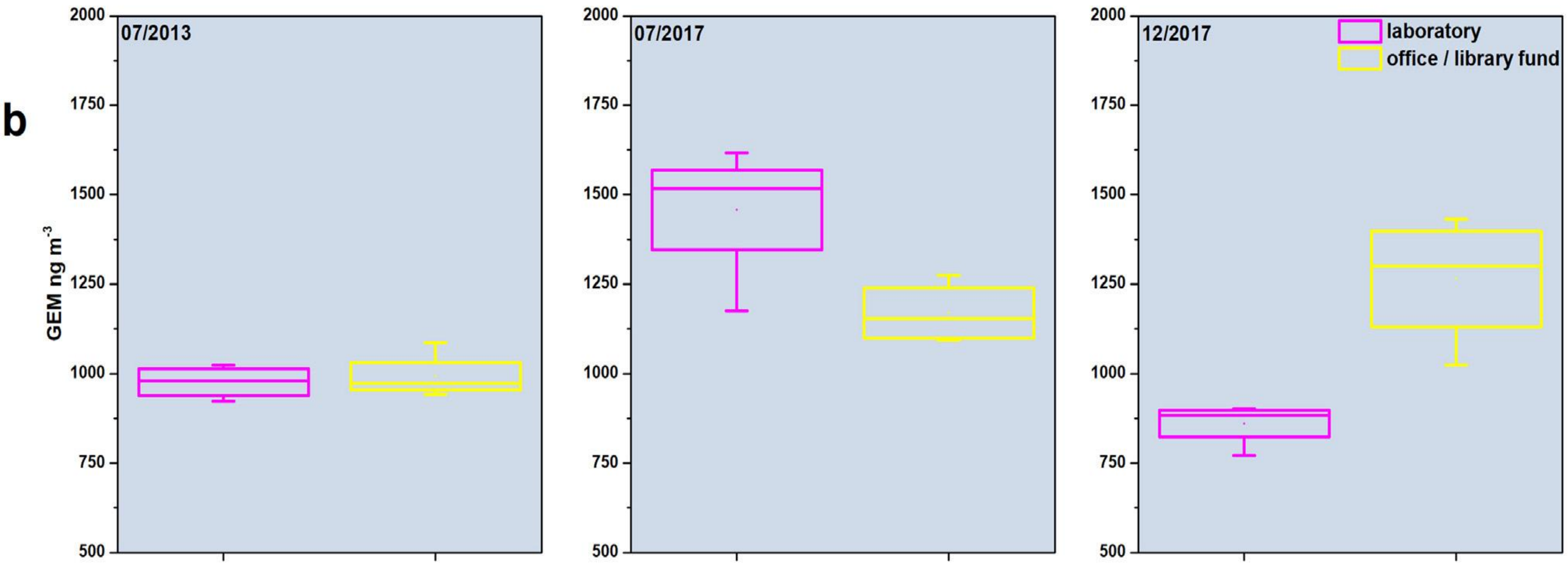
OUTDOOR			
N = 15			
	July 2013	**July 2017**	**Dec. 2017**
range	5 ÷ 30	5 ÷ 30	2 ÷ 5



Box plots for the first floor halls and rooms (a) and balconies (b) in July 2013, July 2017 and December 2017



Box plots for the second floor halls and rooms (a) and balconies (b) in July 2013, July 2017 and December 2017



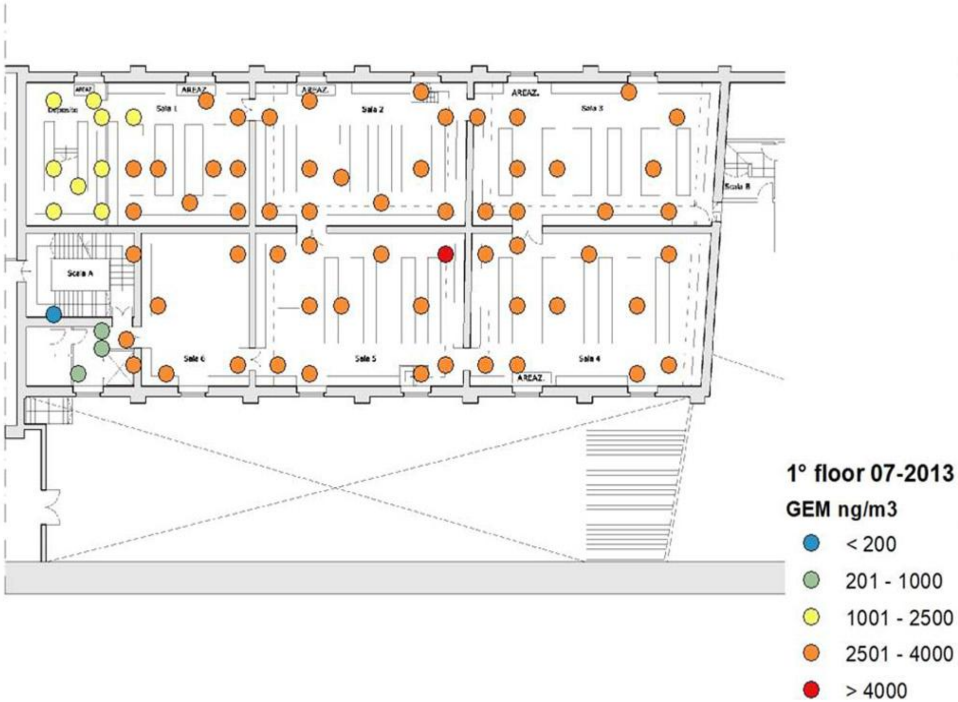
Results

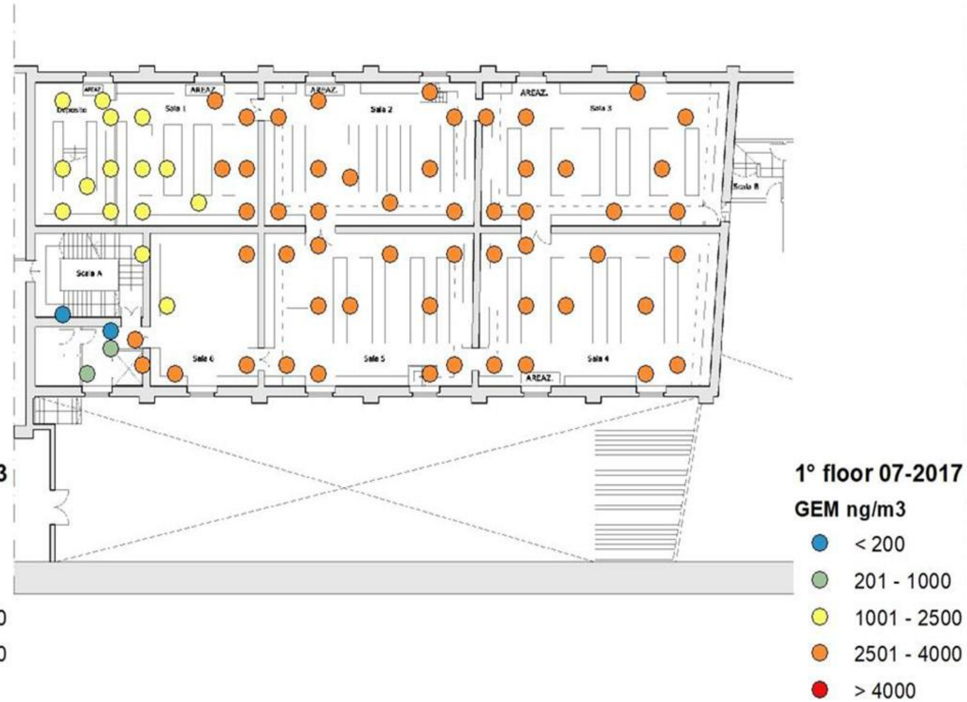
First floor:

- **in 2017 surveys the GEM values were remarkably lower and more uniform than in 2013**
- **in December 2017 GEM values were lower than those in July 2017**
- **balconies values were close to those of the underlying halls**

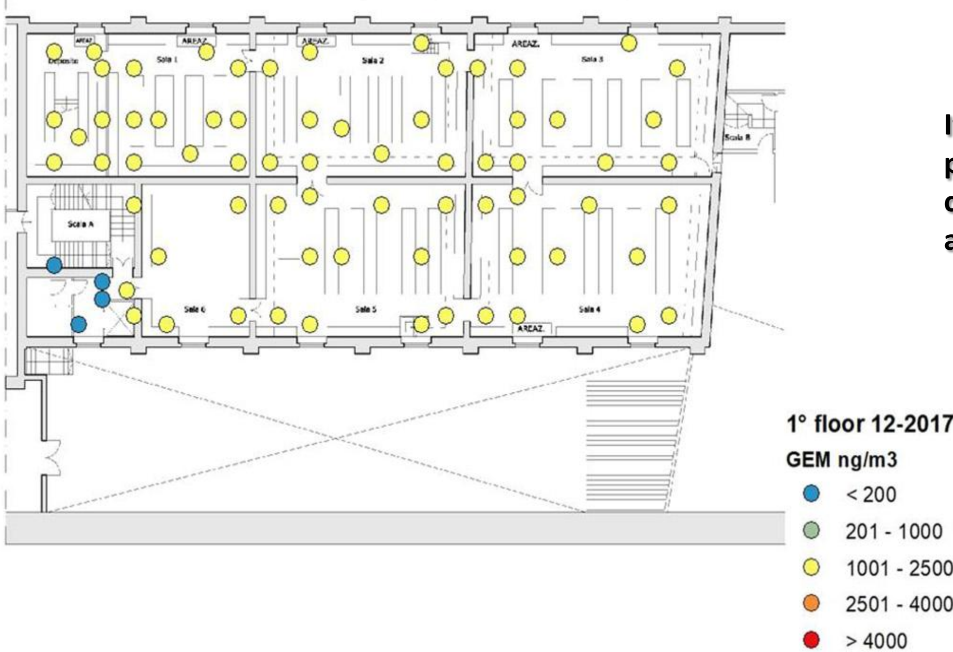
Second floor:

- **GEM values generally higher than those of the first floor, with the highest values in summertime**
- **in December 2017 all the values were lower**
- **GEM values appeared to be more unevenly distributed than in the first floor (no air conditioning system)**
- **the highest values and the more dispersed data distributions in the hall 2c (Herbarium Webb), where ancient specimens extensively treated with $HgCl_2$ are located (GEM > 50,000 ng/m^3 when wood cabinets were opened)**

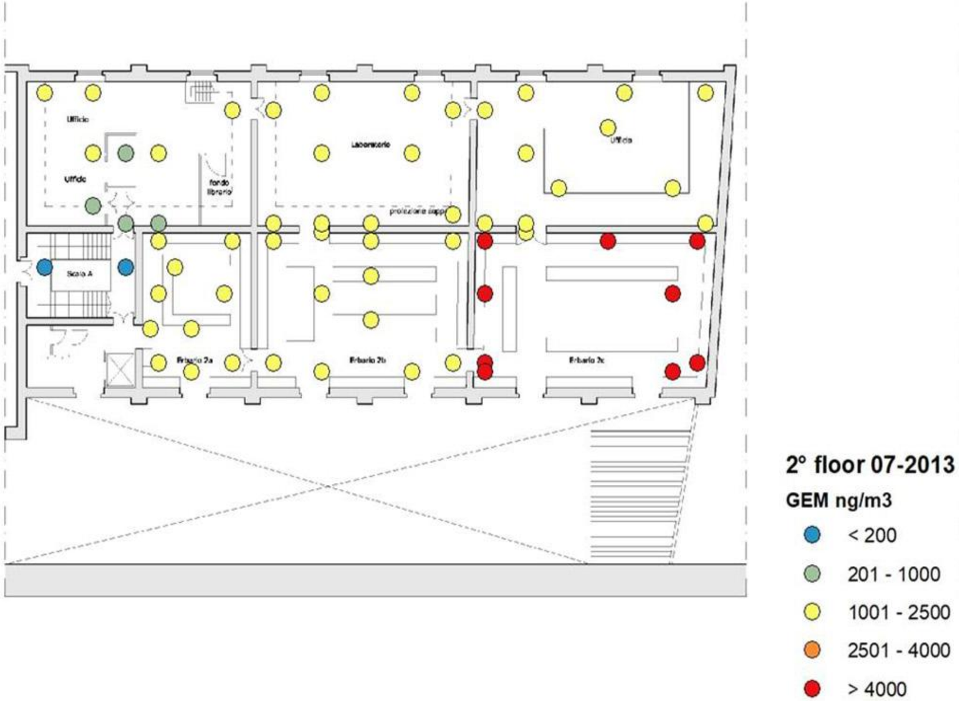


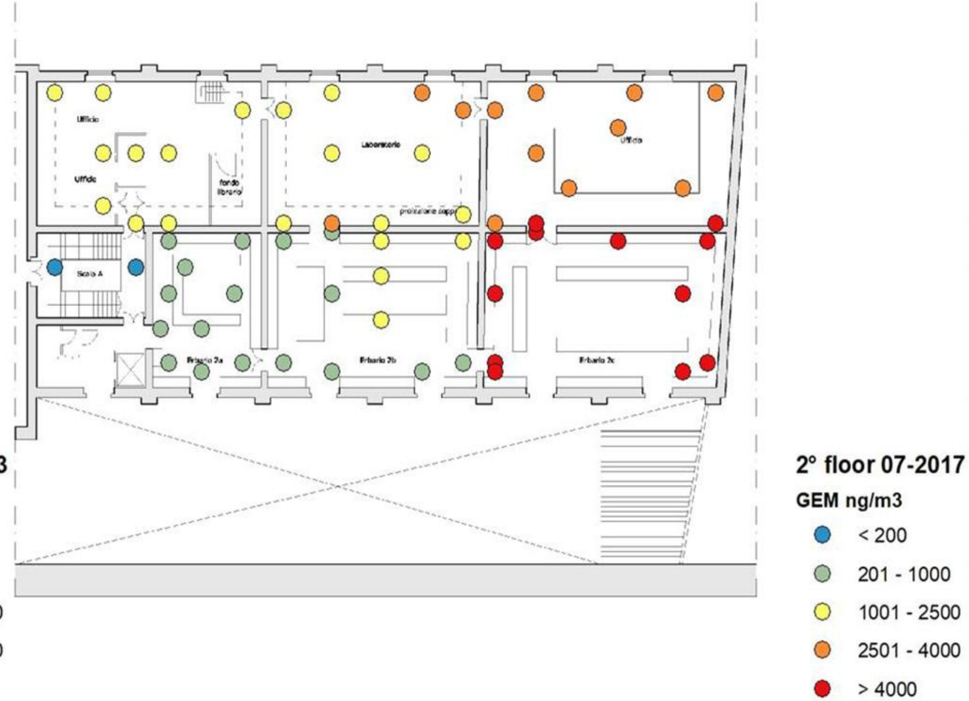


Dot-maps at the first floor of the herbaria. The guidelines proposed by ATSDR (1999) and WHO (2000), i.e. 200 and 1000 ng/m^3, respectively, were considered to distinguish the first two classes of the legend (5 total classes)

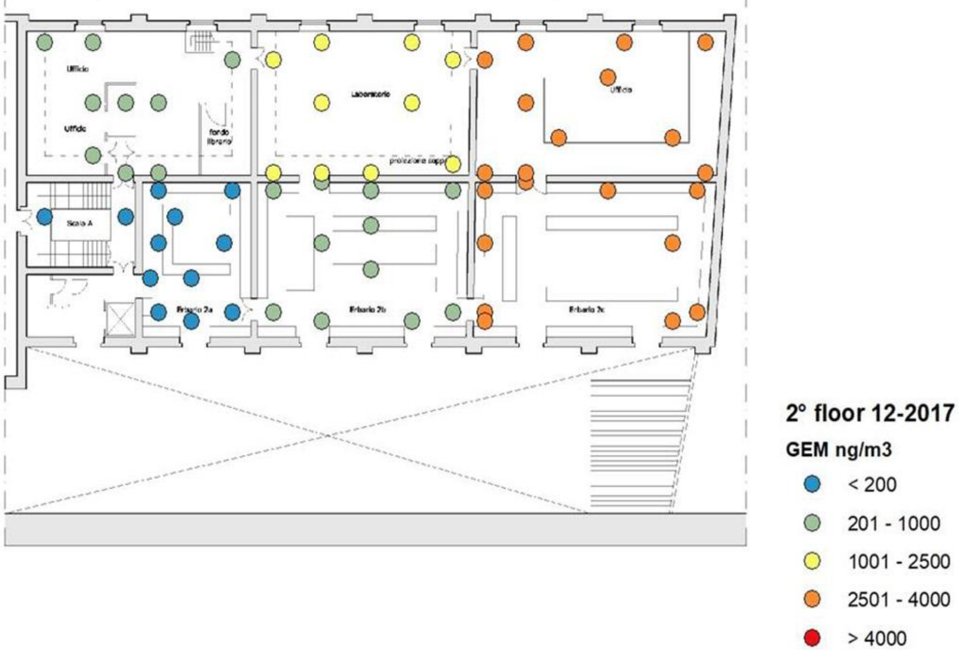


If the guideline value of 1000 ng/m^3 proposed by WHO (2000) is considered, all the first floor is above this threshold





Dot-maps at the second floor of the herbaria. The guidelines proposed by ATSDR (1999) and WHO (2000), i.e. 200 and 1000 ng/m^3, respectively, were considered to distinguish the first two classes of the legend (5 total classes)



If the guideline value of 1000 ng/m^3 proposed by WHO (2000) is considered, most rooms of second floor are above this threshold

Discussion

The positive effect of temperature on GEM contents suggests a reduction of ionic to metallic Hg

However, the conversion process from $HgCl_2$ to GEM is still unclear

Both biotic and abiotic processes can contribute to the reduction of $HgCl_2$ to Hg^0, i.e. driven by bacteria, through interaction with humic acids or cellulose materials, by exposition to the light or temperature increase

GEM concentrations in the range of those observed (10^3–10^4 ng/m^3) are typical of Hg mining facilities and buildings and were measured in other herbaria in the world

Since in Florence the Hg-chloride was dismissed in the 1920s, that is 25–50 years before than elsewhere, our data indicate that this time range has no practical effects on the GEM abatement

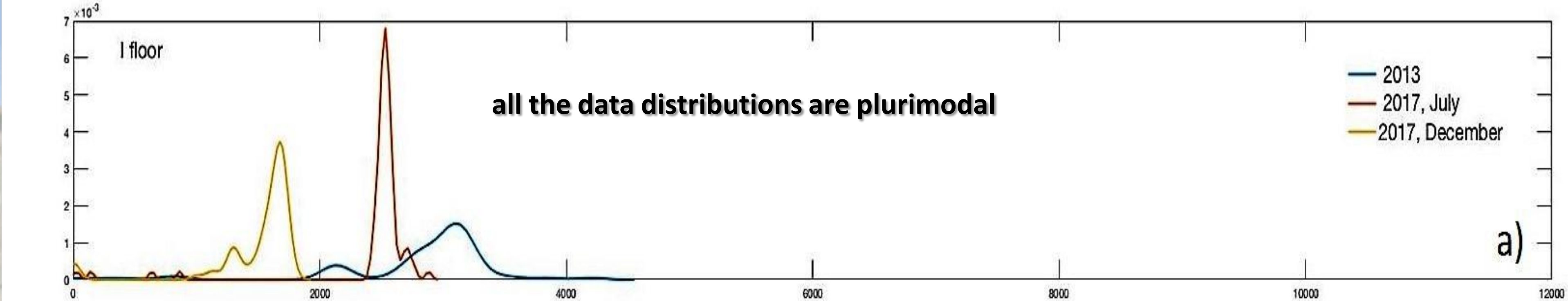
Discussion

The volatility of Hg and the poor ventilation represent the "perfect" trap where Hg vapors could be accumulated

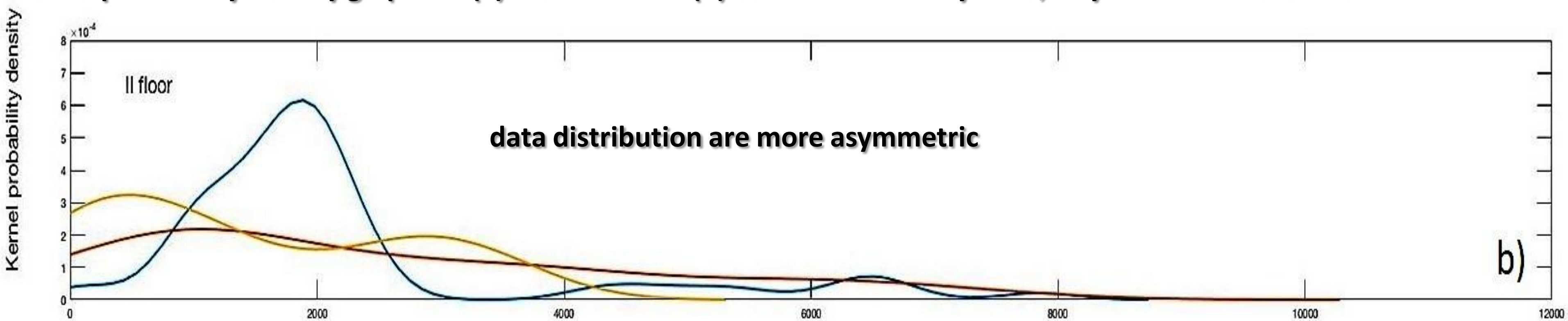
It could be excluded that external Hg sources have any effect, clearly the $HgCl_2$-treated plant collections are the Hg pollution source

The first floor air conditioning system, designed not to expel air but recycle it, can maintain a much lower temperature in summertime than in the past, favoring a homogeneous GEM distribution and an overall decrease in GEM concentrations

BUT…to lower the indoor GEM content in the herbaria, an efficient air renewing, equipped with opportune filters able to minimize any contamination, should be installed



Kernel probability density graphs at (a) first floor and (b) second floorin July 2013, July 2017 and December 2017



On the second floor, in 2013, GEM concentrations almost follow a normal distribution, suggesting dispersion through air internal circulation between the rooms, excluding Herbarium Webb acting as an isolated hotspot

On the contrary, during 2017 data distribution is more variable and fragmented, likely due to strong decrease of GEM in herbarium 2a and 2b from 2013 to 2017 (more efficient air conditioning system installed in 2a) and the increase in the other rooms

Discussion

We reported extremely elevated GEM values inside the cabinets much higher than the current Italian permissible exposure limit for total Hg of 20,000 ng/m^3, considering an 8-hr workday (Gazzetta Ufficiale n. 218, September 18, 2012)
This is a safeguard threshold, being lower than those of US NIOSH (10-hr TWA limit of 50,000 ng/m^3 for mercury vapor, ACGIH (8-hr TWA limit of 25,000 ng/m^3 for total Hg), and US OSHA (permissible exposure limit for total mercury of 100,000 ng/m^3 averaged over an 8-hr work-shift)

However, it should be remarked that this study was focused on GEM. Some studies are also on the way about the presence of mercury in particulate matter (PHg)

In April 2018, the effect of mercury exposure on workers was evaluated by urine collection. The available data indicated Hg values of 0.71 and 2.76 µg/L on two female employers of 60 and 45 years old, respectively, i.e. below that considered the average background concentrations for Hg in urine (4 µg/L), and comprised in the 0.1–5.0 µg/L range (5°–95° percentile) of the Italian population.

Conclusions

- GEM concentrations were in the range of those reported for other herbaria worldwide and higher than those measured in the outdoor
- Very poor internal ventilation and intrinsic persistence of the treatment makes the disinfestation practically irreversible after almost 100 years from the last use of $HgCl_2$
- The highest concentrations corresponded to the oldest collections (2° floor)
- A recent air conditioning system in the 1° floor resulted in more homogeneous GEM distribution and marked decrease of GEM levels from 2013 to 2017
- By considering a normal working day of 8 hours, Hg exposure for the local workers is below the limit established by the Italian law concerning occupational safety values
- Preliminary data indicate Hg levels in urine well comprised in the range of Italian population
- Further studies to quantify total mercury in the investigated herbaria are presently ongoing

Recommendations

- **The use of specific personal protection devices such as gloves, lab coats and masks, reducing the direct contact and not moving the poisoned specimens on personal desks, and the installation of ventilated worktables and/or storage cabinets, connected to local exhaust lines, to ensure air movement and prevent Hg accumulations, are strongly suggested**

- **Moreover, it is strongly advisable to keep away from the GEM-saturated lockers, keeping them closed at any time, to adequately train personnel for periodic cleaning and to move the offices of the staff outside the herbaria.**

CONCLUSIONI/SVILUPPI

- **stima dell'impatto di inquinanti atmosferici quali GEM sull'ambiente, confrontando i dati prodotti nei diversi siti al variare delle condizioni meteorologiche, e valutazione del loro impatto sulla saluta umana in riferimento alle linee-guida**

- **individuazione di traccianti geochimici (e.g. rapporto tra GEM ed un altro gas) caratterizzanti le diverse sorgenti**

- **elaborazione dei dati Lumex+Multigas+Thermo+Picarro ed estensione delle misure ad altri siti industriali-urbani-naturali**

- **caratterizzazione dettagliata della distribuzione dei gas in aria, tramite transetti e punti fissi (real-time), e successiva elaborazione dei dati per ottenere mappe di dispersione**