Direct measurements of pollutant emissions above megacities

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Concept of urban flux measurements

**Concentration measurements** reflect sources in the *concentration* footprint: 10s to 100s of km

**Flux measurements** reflect sources in the *flux* footprint: 100s of m up to 5 km
Motivation for urban aerosol flux studies

• **Emission**
  • Quantification of emission (more direct than concentrations)
  • Independent verification of emission inventories
  • Study of processes (vehicle emissions; resuspension; competing deposition)
  • Tracking of emissions with time

• **Deposition**
  • Quantification of deposition velocity and control?

• **Good test bed for instrumentation**
  • Large fluxes & exchange velocities
Urban Flux Measurement Campaigns pre 2017

- **SASUA, Oct Nov 1999/2000**
  - CityFlux, Dec 2005
  - June 2003
  - Boulder, CO
  - (92,000)
  - (19,200,000)

- **GOTE2005**
  - Feb. 2005
  - Gothenburg
  - (480,000)

- **CityFlux**
  - May 2006
  - Manchester
  - (2,200,000)

- **CityFlux/REPARTEE**
  - October 2006
  - London
  - (7,500,000)
There are more people living inside this circle than outside of it.
Delhi flux towers (Oct / Nov 2019)
Delhi measurement locations
<table>
<thead>
<tr>
<th>Aerosol phase</th>
<th>Measurement</th>
<th>Instrument</th>
<th>London</th>
<th>Beijing</th>
<th>Delhi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total particle N</td>
<td>TSI CPC3785</td>
<td>M’cr</td>
<td>CEH</td>
<td>CEH</td>
<td></td>
</tr>
<tr>
<td>Submicron particle N</td>
<td>DMT UHSAS</td>
<td>CEH</td>
<td>CEH</td>
<td>CEH</td>
<td></td>
</tr>
<tr>
<td>Supermicron particle N</td>
<td>TSI APS3021 / ELPI+</td>
<td>CEH</td>
<td>CEH</td>
<td>CEH/M’cr</td>
<td></td>
</tr>
<tr>
<td>PM$_1$ NH$_4^+$/NO$_3^-$/SO$_4^{2-}$/Cl$^-$/OM</td>
<td>AMS</td>
<td>CEH</td>
<td>CEH</td>
<td>CEH/M’cr</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>DMT SP2</td>
<td>M’cr</td>
<td>M’cr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metals</td>
<td>Filter REA</td>
<td></td>
<td></td>
<td>CEH</td>
<td></td>
</tr>
<tr>
<td>Gas phase</td>
<td>CO$_2$ / H$_2$O</td>
<td>IRGA LiCOR</td>
<td>CEH</td>
<td>CEH</td>
<td>CEH</td>
</tr>
<tr>
<td>CO</td>
<td>AL5002</td>
<td>CEH</td>
<td>York</td>
<td>York/CEH</td>
<td></td>
</tr>
<tr>
<td>NO$_x$</td>
<td>Chemiclumin.</td>
<td>York</td>
<td>York</td>
<td>York</td>
<td></td>
</tr>
<tr>
<td>O$_3$</td>
<td>ROFI</td>
<td></td>
<td>CEH</td>
<td>CEH</td>
<td></td>
</tr>
<tr>
<td>VOCs</td>
<td>SIFT; PTR-ToF-MS;</td>
<td>York; L’cr/ GIGCAS;</td>
<td>L’cr / CEH / PRL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>QCL</td>
<td></td>
<td>CEH</td>
<td>CEH</td>
<td></td>
</tr>
<tr>
<td>N$_2$O</td>
<td>QCL</td>
<td></td>
<td>CEH</td>
<td>CEH</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>CRDS</td>
<td></td>
<td>CEH</td>
<td>CEH</td>
<td></td>
</tr>
</tbody>
</table>
Eddy-covariance flux measurements: raw data example

\[ F_N = w' \chi'_N = w \chi_N - w' \chi_N \]
BT Tower CO₂ flux – spatial & temporal variability

Hourly variations of CO₂ concentrations

Diurnal variations of CO₂ concentrations

Hourly variations of CO₂ fluxes

Diurnal variations of CO₂ fluxes

Helfter et al., 2011
Reconciling bottom-up and top-down emission estimates

<table>
<thead>
<tr>
<th></th>
<th>CO₂ [tons km⁻²]</th>
<th>CH₄ [tons km⁻²]</th>
<th>CO [tons km⁻²]</th>
<th>N₂O [tons km⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured at BT tower</td>
<td>41000</td>
<td>75</td>
<td>156</td>
<td>0.36</td>
</tr>
<tr>
<td>(CO₂e 1875)</td>
<td>(CO₂e 107)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Westminster (LAEI)</td>
<td>46000</td>
<td>34</td>
<td>145</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Clear diurnal trends consistent anthropogenic activities

Heterogeneous source distributions
VOC fluxes from the BT Tower

Langford et al., ACP, 10, 627-645, 2010
Chemically resolved PM$_1$ fluxes (HR-ToF-AMS)

**Beijing – Winter (2016)**


NB: Beijing / Delhi analysis is ongoing; numbers will still change!
Chemically resolved fluxes Beijing – Winter vs Summer

Beijing – Winter (2016)

Beijing – Summer (2017)

Organics: 160 ng m^{-2} s^{-1}

Organics: 154 ng m^{-2} s^{-1}
Chemically Resolved Aerosol Fluxes Delhi

Old Delhi

Lodhi Road

PM$_1$ Aerosol Flux $[\text{ng m}^{-2} \text{s}^{-1}]$

Hour [Local]

IMD, Lodhi Road

Old Delhi

Lodhi Road

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NATURAL ENVIRONMENT RESEARCH COUNCIL
Why is Ammonium Nitrate Depositing so Quickly?

NH$_4$NO$_3$ (s, aq)

NH$_3$(g)

HNO$_3$(g)

Driver for evaporation

(V$_d$ = 1-5 mm s$^{-1}$)

NH$_3$[g]

Temp

[NH$_3$]

$\rho_{eq}$ [NH$_3$]

Deposition Velocities

Height

Hour [UTC]

V$_d$[mm s$^{-1}$]
Why is $\text{NH}_4\text{NO}_3$ depositing so rapidly to urban area?

Unlike the forest Beijing is a net source of $\text{NH}_3$.
How much does the evaporation of NH$_4^+$ aerosol contribute to the NH$_3$ gas flux in Beijing?

Equivalent to 16.8 kg N ha$^{-1}$ yr$^{-1}$

Eddy Flux measurements of NH$_3$ by QCL

Fluxes

Emission

NH$_3$ Flux [ng m$^{-2}$ s$^{-1}$]

Hour [Local]

Ammonia

NH$_4$ evaporation

Equivalent to 16.8 kg N ha$^{-1}$ yr$^{-1}$
Beijing: What about the organic aerosol?

Fluxes

PM$_1$ Mass Flux [ng m$^{-2}$ s$^{-1}$]

Emission
Deposition

Organics
Nitrate
Ammonium
Sulphate
Chloride

Hour [Local]

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Aerosol composition fluxes - Beijing

**Concentrations**

- OOA (oxidised)
- BBOA (biomass)
- CCOA (coal)
- HOA (fossil fuel)
- NH$_4^+$
- SO$_4^{2-}$
- NO$_3^-$
- Cl$^-$

**Fluxes**

- SV-OOA
- LV-OOA
- MV-OOA
- BC
- HOA (fossil fuel)
- COA (cooking)
- NH$_4^+$
- SO$_4^{2-}$
- NO$_3^-$
- Cl$^-$
Chemically Resolved Aerosol Fluxes Delhi

IMD, Lodhi Road

Traffic
Solid Fuel
Low-volatility
Chloride
Ammonium
Nitrate
Sulphate

Organics
Chloride
Low-volatility
Chloride
Ammonium
Nitrate
Sulphate
Relative makeup of submicron aerosol emission
Diurnal Cycles – Beijing Summer

The graph illustrates the normalised diurnal cycle of various air pollutants and parameters over the course of a day. The y-axis represents the normalised diurnal cycle, while the x-axis shows the time of day in local time. The pollutants and parameters tracked include CO₂, O₃, NH₃, CPC, UHSAS, CO, NOₓ, and BC. Each line on the graph corresponds to a different pollutant or parameter, allowing for a visual comparison of their diurnal patterns. The peaks and troughs in the graph highlight the variation in concentrations throughout the day.
Particle fluxes Beijing summer: Evidence for two distinct sources

→ Cooking is major source for particle number
→ Evidence for imperfect COA/HOA split?
→ Relative HOA contribution even larger?
CO-CO$_2$ relative emission factors

Relative emission factors CO/CO$_2$:

Beijing summer: 1.01%
Beijing winter: 16.6%
London autumn: 0.87% (2006) / 0.51% (2007)
Edinburgh spring: 2.14%
Delhi: ???
Selected messages:

• Flux measurements can shed light on emissions & processes
• CH$_4$ emissions underestimated in London (natural source / Thames?)
• Some VOCs not or under-represented in emission inventories (Toluene; OVOCs)
• Cooking dominates PM$_1$ flux in Beijing, also particle number; major contribution in London; not (yet?) identified in Delhi
• Beijing acts as a \textit{net sink} for NR-PM$_1$ during summer via volatilisation of NH$_4$NO$_3$ and volatile organics
• PM$_1$ fluxes also bi-directional at Delhi Lodhi Rd site
• Beijing is a significant source of ammonia (Delhi to be analysed)
• O$_3$ fluxes provide useful constraint for urban chemistry
• Each urban location is different
• Next step full comparison with local prediction in emission inventories for Beijing & Delhi
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