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NO_2 Measurements with Different Converters

Molybdenum Converters vs. Specific NO_2 Converters

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Air Pollution / Environmental Technology

Outline

- NO_2 measurement techniques
- Requirements of EN 14‘211
- Results of parallel measurements
- Conclusions

NO_2 Measurement Techniques

- Standard technique: Measurement of NO with chemiluminescence
- NO_2 is reduced to NO by a converter
- Heated metal converters, mostly **molybdenum (Mo)**
  - \+ efficient
  - \+ long lifetime
  - \+ reliable
  - \- not specific

$$NO_x = NO + a \cdot NO_2 + b \cdot HNO_3 + c \cdot NO_3^- + d \cdot PAN + e \cdot NH_3 + \ldots$$

- Alternative: photolytic converters

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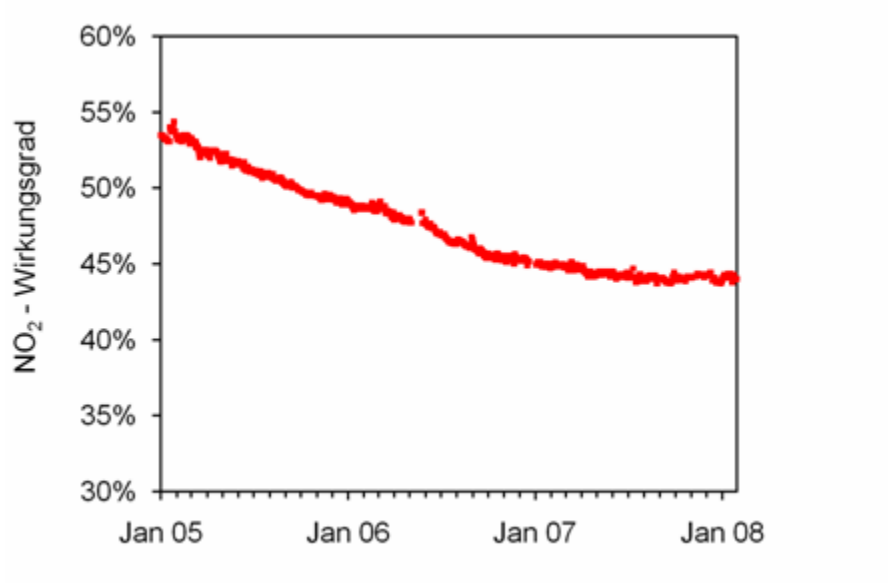
Photolytic converter

- **Principle**: NO_2 is reduced photolytically to NO

$$NO_2 + hv \longrightarrow NO + O \qquad hv: < 410nm$$
$$O + O_2 \longrightarrow O_3$$
$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + O_2 + hv \rightleftharpoons NO + O_3$$

- Light source: Xe-vapour lamp, metal halid lampe of Array of UV-LED
- Specific, but low converter efficiency
- Converter efficiency needs to be calibrated at regular intervals



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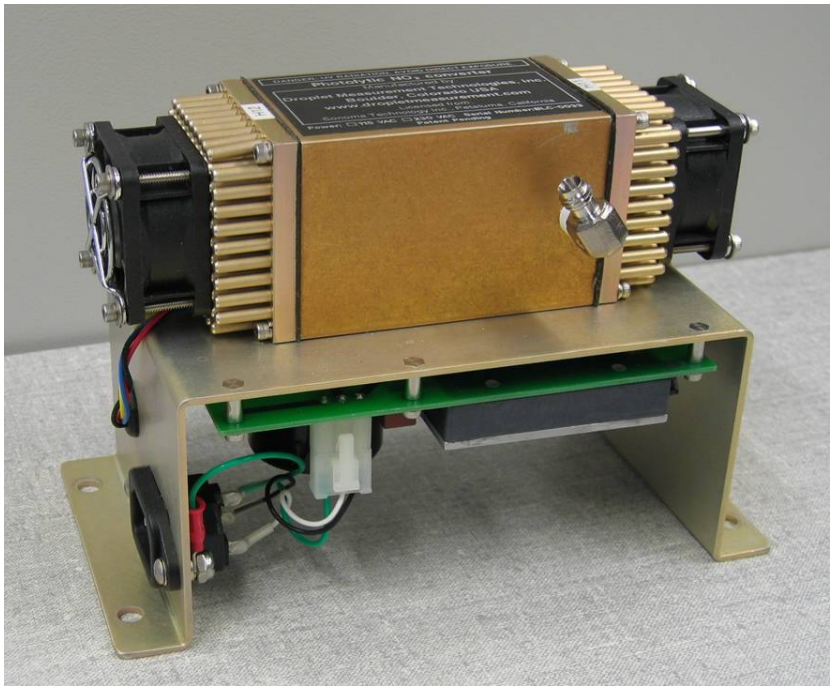
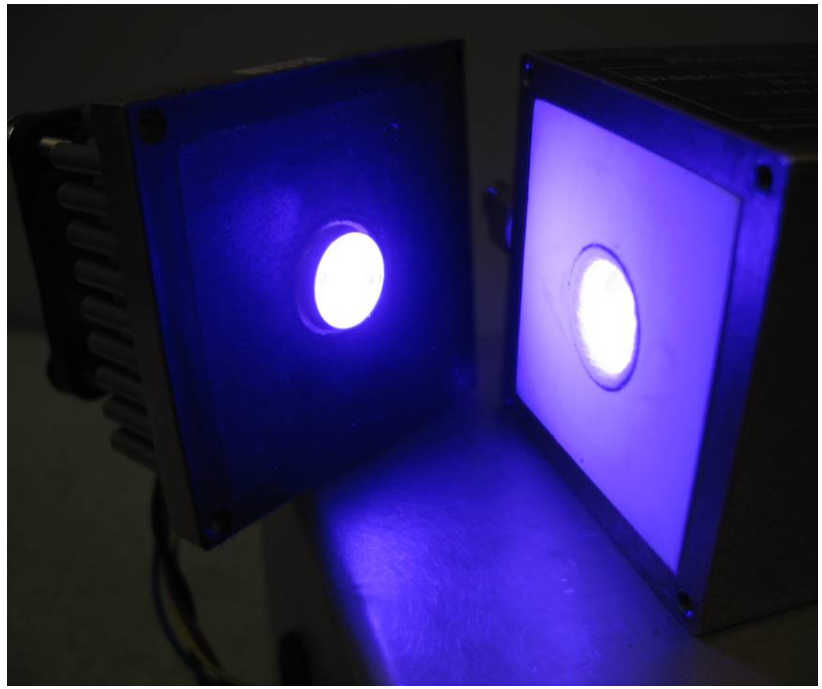
„Blue Light Converter“ BLC





Cell volume: 17ml

Cell purge time at 1 l/min: 1s

Array von UV-LED‘s λ ca. 380 - 410nm

Air Quality Design, Inc., Wheatridge, CO, (USA)
(formerly: Droplet Measurement Technologies, Inc., Boulder)

Sale in Europa: meteorologie consult gmbh, D-Königstein (www.metcon.de)

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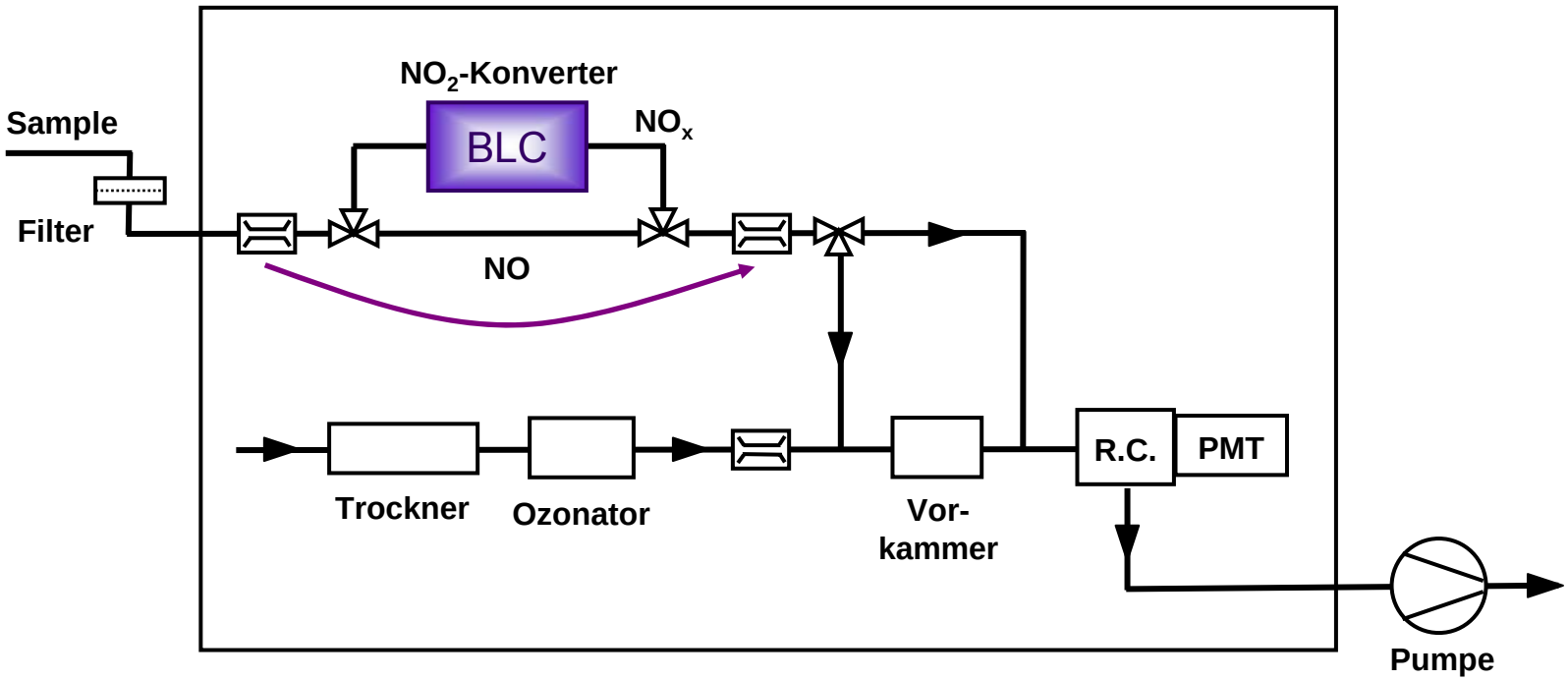
Set-up of NO_x-monitor with BLC

- Molybdenum converter replaced or bypassed, flow-controll capillary after converter

Example: Thermo Electron Model 42C TL



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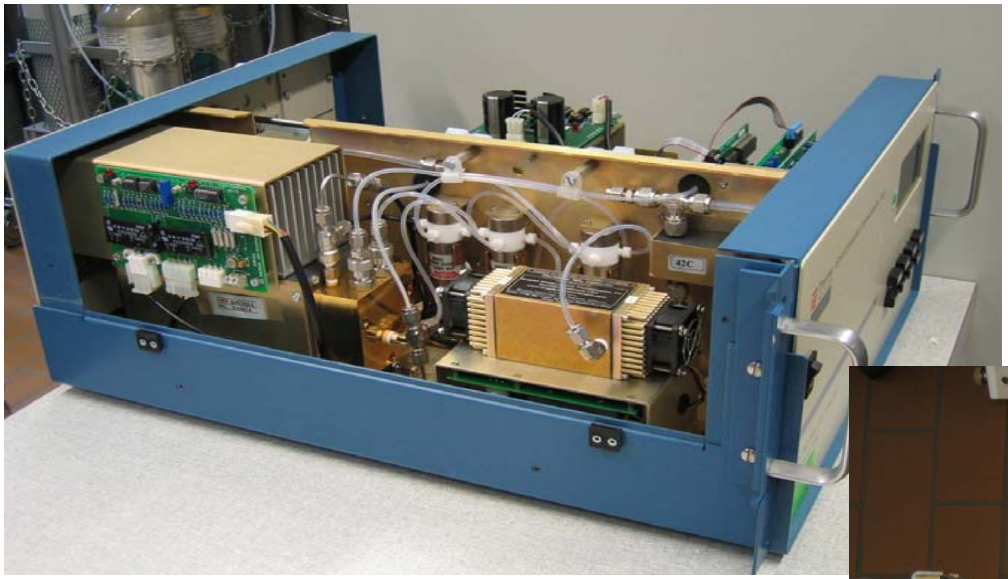
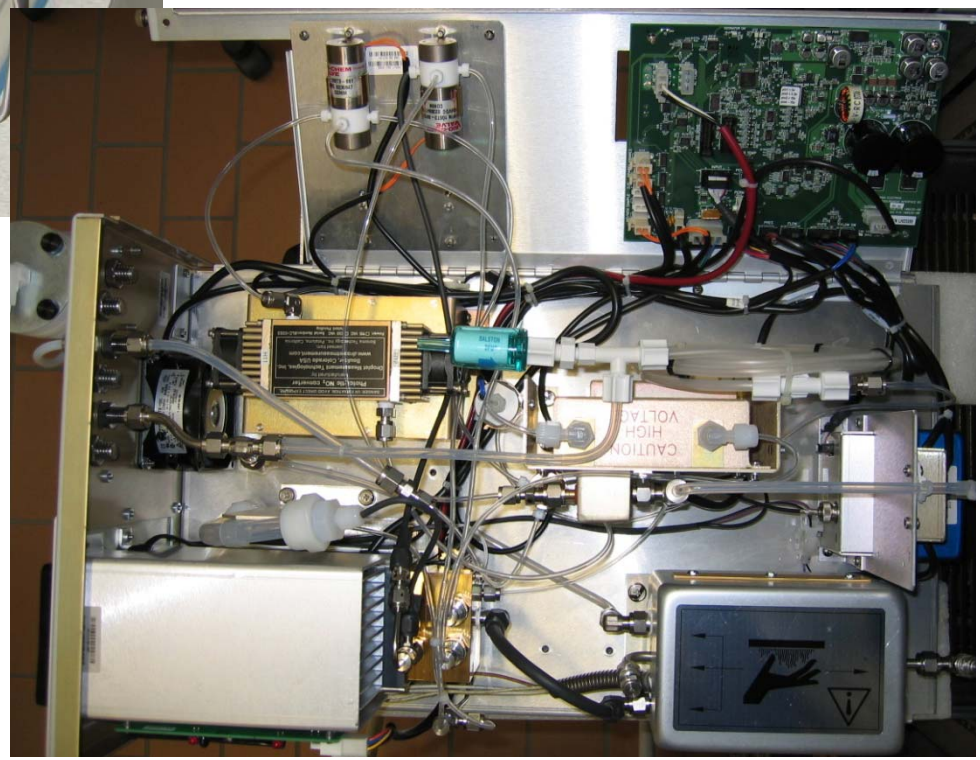
BLC integrated in NO_x monitor



Thermo Electron Model 42C TL

Thermo Electron Model 42i TL



EN 14‘211; NOx measurements

- Chemiluminescence
- No converter type specified
- Converter efficiency > 95%
- Interferences to other N-compounds:
  Only specified for NH_3 (≤ 5,0 nmol/mol)

- How to deal with specific measurements?

Specific NO_2 measurements in NABEL

Sites with NO_2 measurements with photolytic converters:

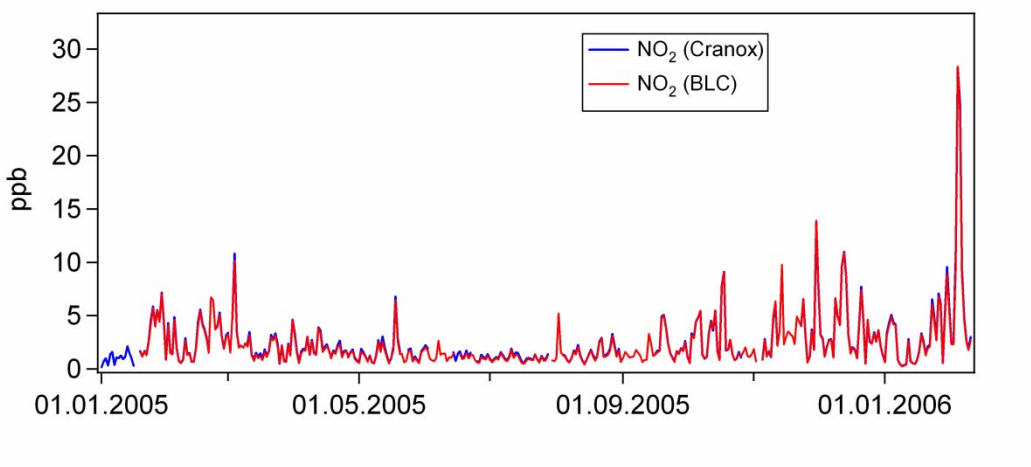
System	Site	Site type	Altitude	Measurement periods
Cranox[1)]	Jungfraujoch (JUN)	high alpine	3580 m	from Sep 1991
	Rigi-Seebodenalp (RIG)	rural	1030 m	Oct 2001 to Feb 2006
BLC	Rigi-Seebodenalp (RIG)	rural	1030 m	from Nov 2004
	Payerne (PAY)	rural	490 m	from Feb 2006
	Zürich (ZUE)	urban	410 m	from Jan 2010

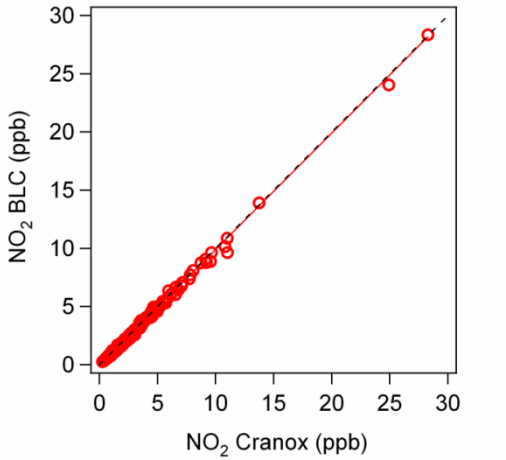
[1)] Cranox: Chemiluminescence monitor (CLD770AL ppt resp. CLD 89p) with photolytic converter (PLC 760 with Xe-vapour lamp or PLC 762 mit metal halid lamp), Eco Physics.

Comparison Cranox – BLC

- **NO_2**

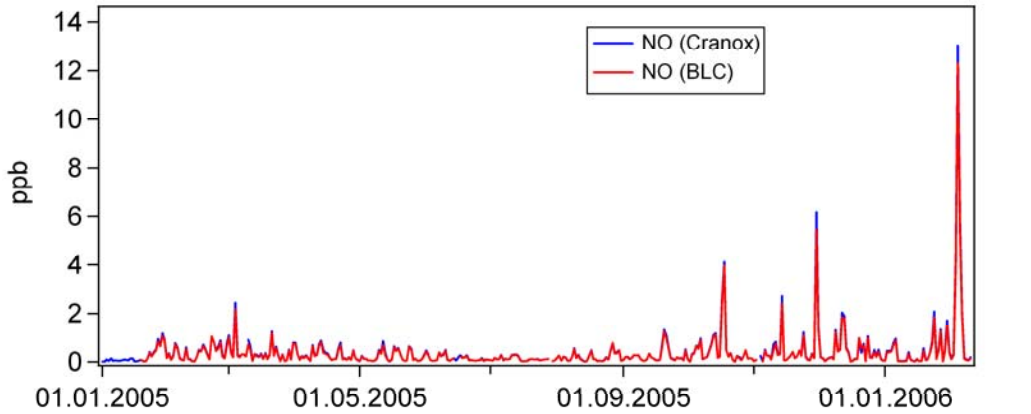
Daily means at Rigi-Seebodenalp

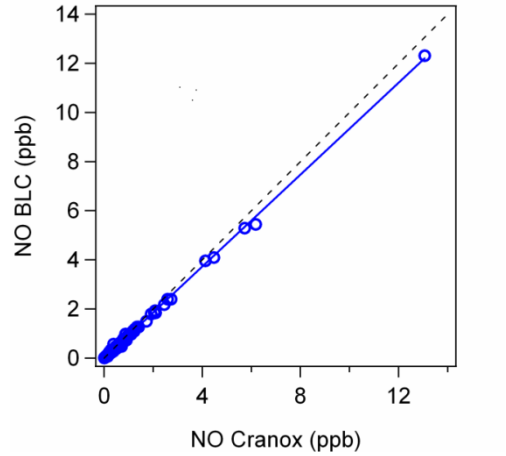




- **NO**

Daily means at Rigi-Seebodenalp





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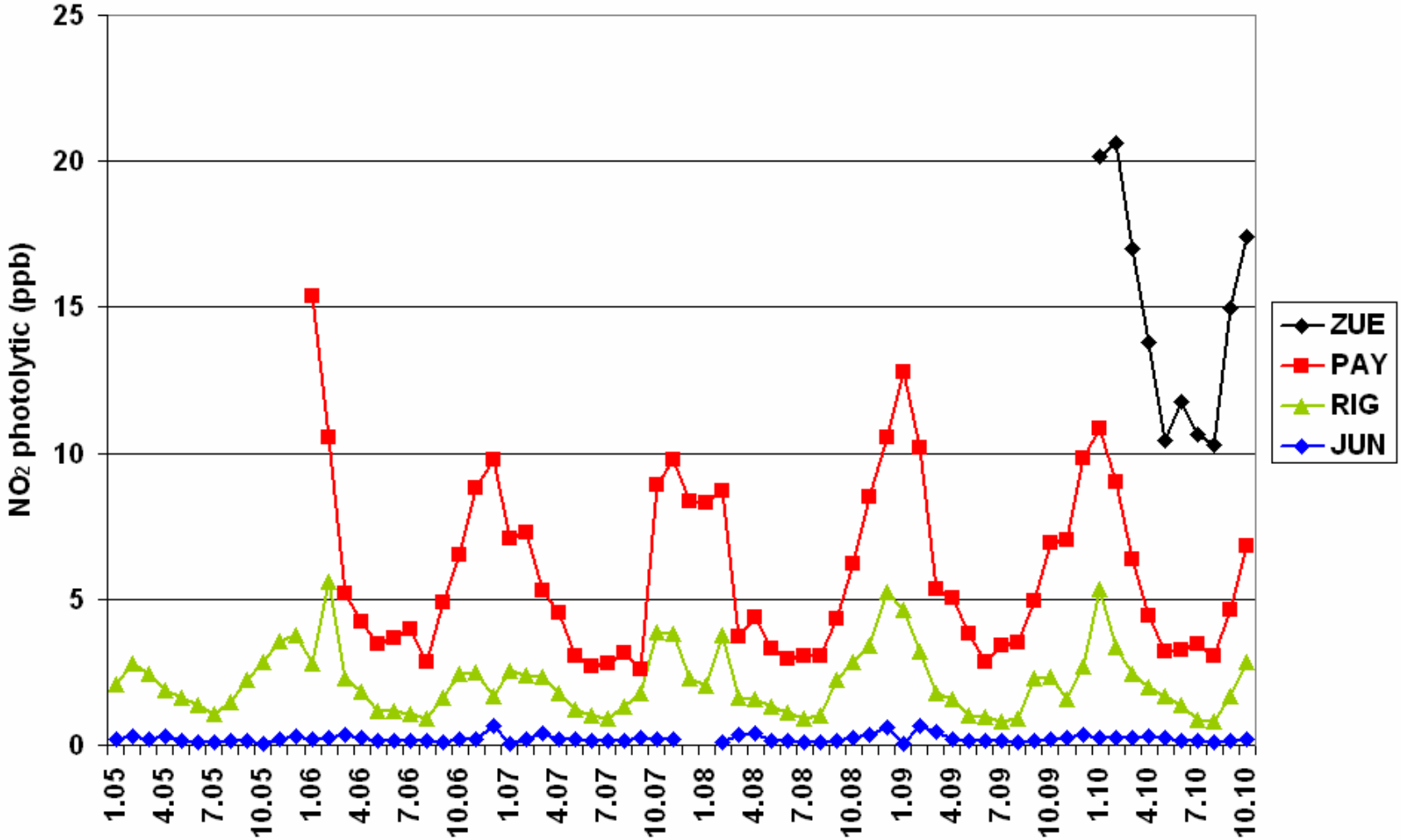
NO_2 (photolytic) at different sites



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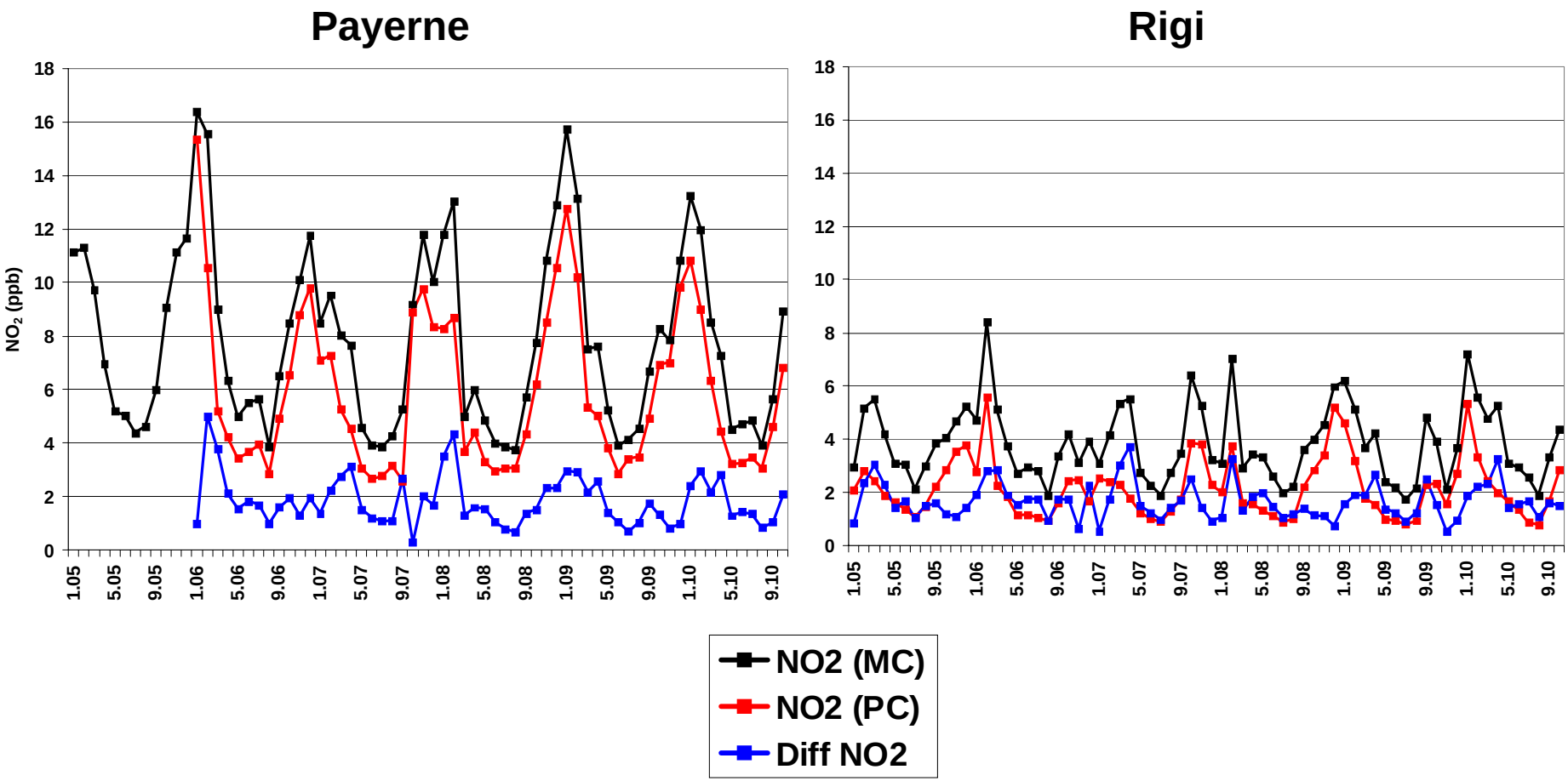
NO_2 comparison



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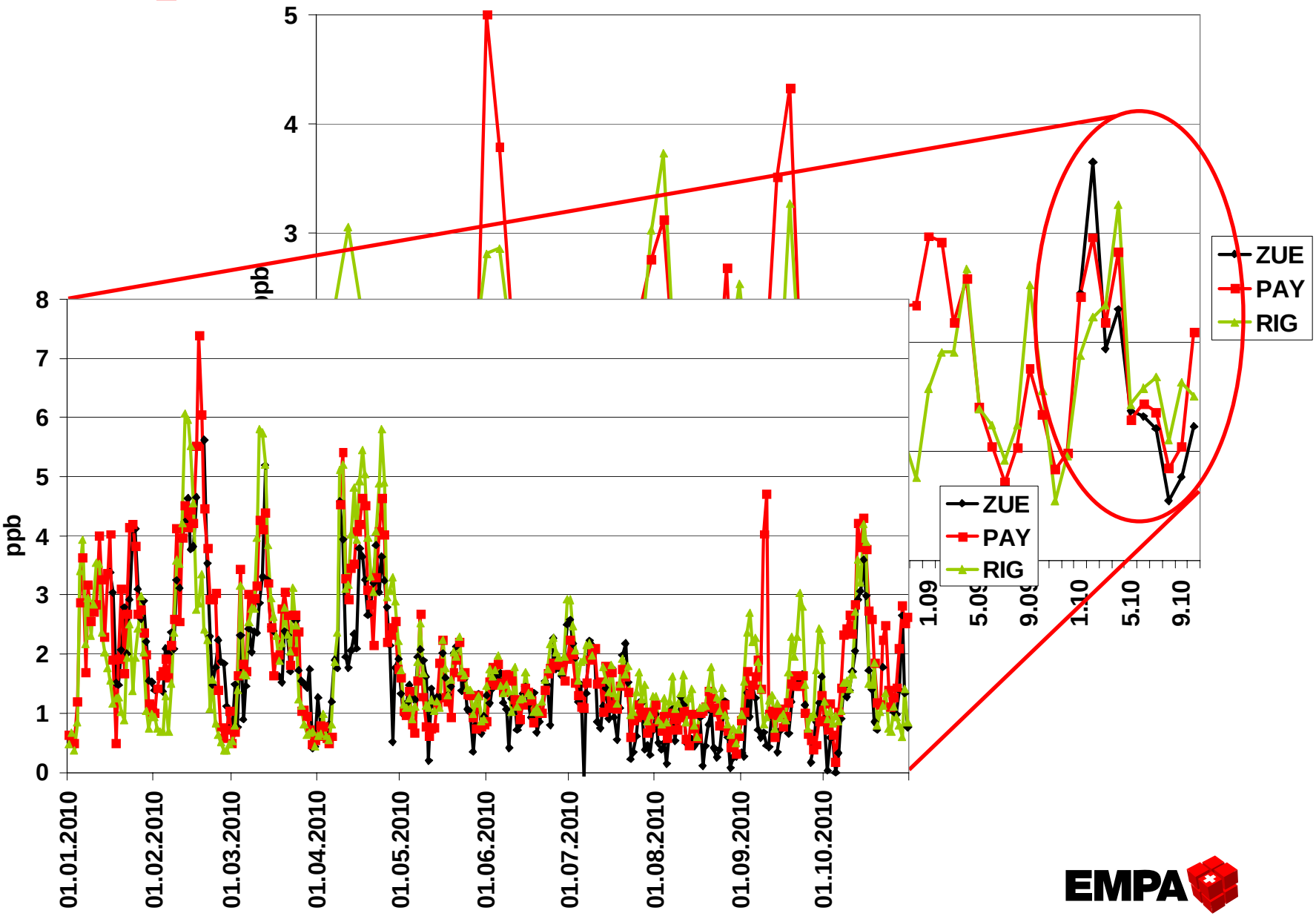
ΔNO_2 at different sites



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Mean values (Jan – Oct 2010)

Site	NO_2 photolytic	NO_2 (Mo)	ΔNO_2	ΔNO_2 in % of NO_2 (Mo)
Rigi-Seebodenalp	2.2 ppb	4.1 ppb	1.9 ppb	45 %
Payerne	5.5 ppb	7.4 ppb	1.8 ppb	25 %
Zürich	14.7 ppb	16.4 ppb	1.7 ppb	10 %
Jungfraujoch	0.23 ppb	0.84 ppb [1)]	0.61 ppb [1)]	73 %

[1)] Jungfaujoch: NO_2 (Mo) is NO_y – NO; ΔNO_2 is NO_y-NO-NO_2; means 2005-2009

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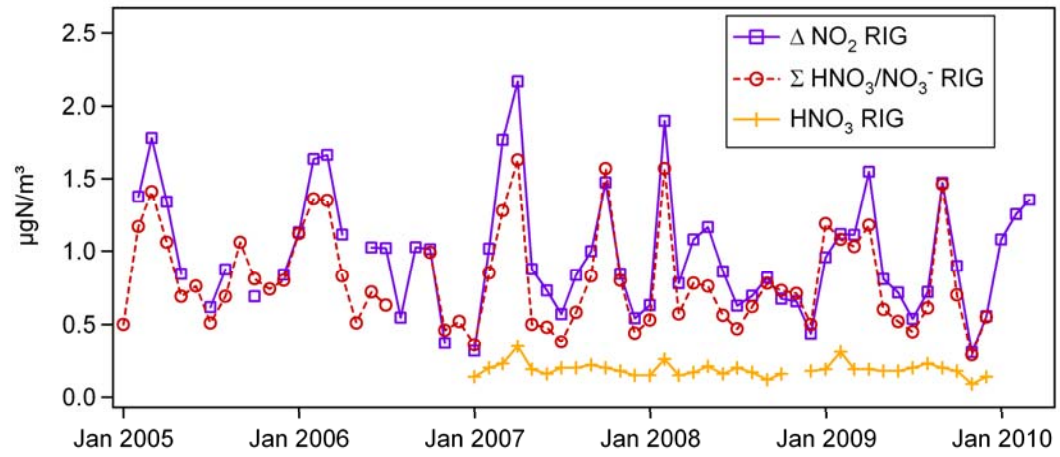
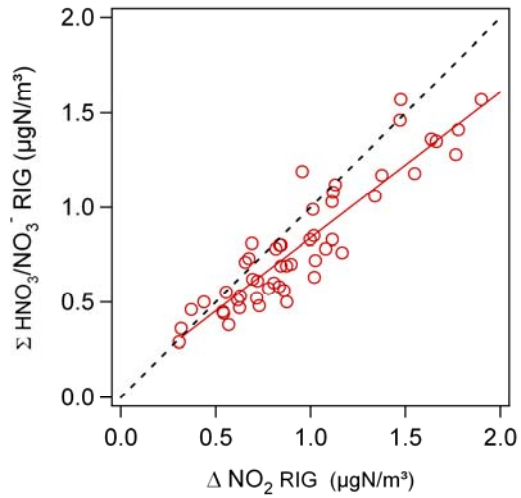
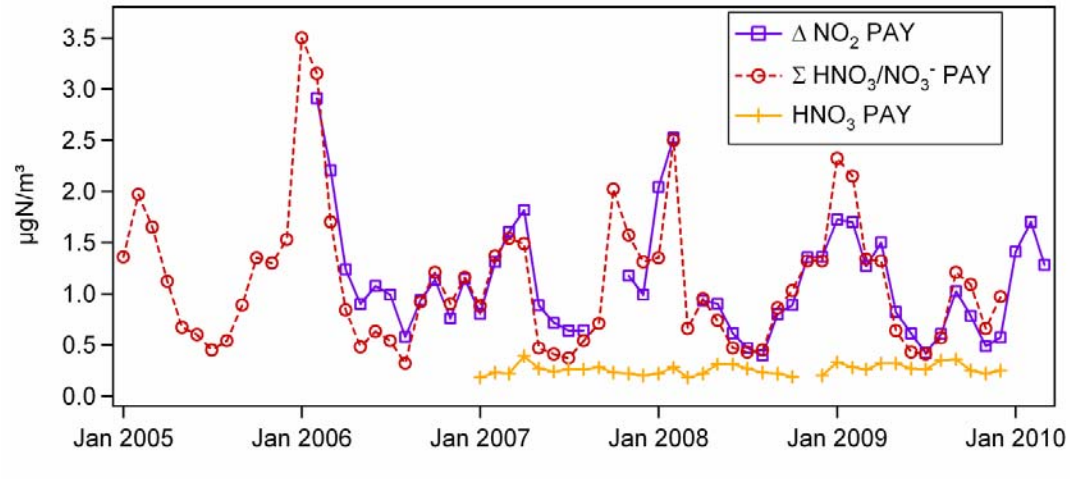
ΔNO_2 vs. Nitrate + HNO_3

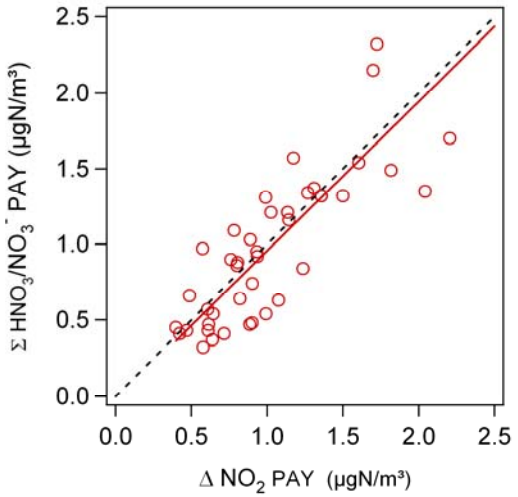
- Rigi- Seebodenalp





- Payerne





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Conclusions

- NO_2 measurements with molybdenum converters overestimate NO_2 by 10-70%.
- ΔNO_2 consists mostly of HNO_3 and NO_3^-
- Photolytic converters and new spectroscopic methods allow for specific NO_2 measurements.
- Choice of method depends on the aim of the measurements.
- Clear specification of methods is needed for NO_2 data series.