



## First results from the new JRC greenhouse gas monitoring site at Ispra, Italy

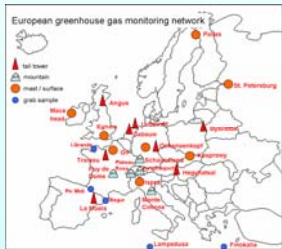
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### Summary

We present measurements results from a new continuous greenhouse gas (GHG) monitoring station located at the EU Joint Research Centre in Ispra, Italy. The monitoring site is located at the northern border of the Po valley which is one of the most polluted regions in Western Europe. CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and SF<sub>6</sub> have been monitored continuously by gas chromatography (GC-FID/ECD) since November of 2007. In September 2008 we included an ANSTO dual filter <sup>222</sup>Rn monitor which allows us to estimate GHG surface fluxes using the <sup>222</sup>Rn reference method. In addition, we apply a proton transfer mass spectrometer (PTR-MS) instrument during dedicated periods to monitor fossil fuel related VOCs (benzene, toluene and xylenes) and the biomass burning tracer acetonitrile. Additional air quality measurements (e.g. carbon monoxide) and meteorological data are available from the co-located Ispra EMEP-station.

Using the correlation between CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO and the biomass burning tracer acetonitrile (CH<sub>3</sub>CN) during the 2007/08 winter we are able to estimate the relative contribution to the enhanced concentration (spatially) to the use of woodfuel. TM5 (4DVAR) model simulations on a 1 x 1 degree grid scale for CH<sub>4</sub> show an overall good agreement with the measurements. In addition, we present first <sup>222</sup>Rn based flux estimates of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O for the 2008/09 winter. Measurements of benzene and toluene emphasize the semi-rural character of the Ispra measurement site. We show that our first regional scale emission estimates based on our observations for CO<sub>2</sub> and CH<sub>4</sub> compare reasonably well with the new EDGAR v4 (0.1 x 0.1 degree resolution) database for the year 2005.

## The Ispra greenhouse gas, <sup>222</sup>Rn, and VOC monitoring site



Ispra as part of The European GHG monitoring network.



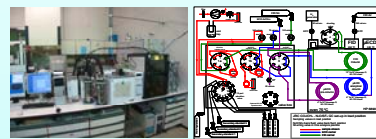
Overview of GHG monitoring sites around the Po Valley. Also shown is the future Monte Orsa mountain site for CO<sub>2</sub> and CH<sub>4</sub>.



The current 15 m sampling mast at the JRC Ispra, to be replaced by a 48 m tower.

### The Ispra GHG GC-system

The Ispra GHG GC-system, is based on the Agilent 6890N equipped with FID/ECD (Worby et al., 1998) and runs at a time resolution of 6 minutes. An hourly sequence of measurements starts with a working high and working low standard followed by six ambient samples and is completed with a working high and working low standard. The instrument precision, based on the measurement of a target gas cylinder replacing two ambient samples every 6 hours, is typically 0.1 ppmv for CO<sub>2</sub>, 1 ppbv for CH<sub>4</sub>, 0.4 ppbv for N<sub>2</sub>O and 0.18 pptv for SF<sub>6</sub> (for a two weeks period). The working standards from Deutsche Stahlring (Germany) are calibrated against 5 high precision primary standards provided by NOAA/ESRL. A lab photo and schematic of the JRC Ispra GC-system are shown below.



### The Proton Transfer Mass Spectrometer for VOCs

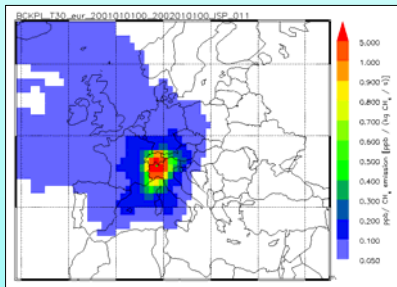
We employ an ionicon PTR-MS instrument (Lindinger et al., 1998) to measure VOCs from the GHG sampling inlet line during selected periods. We focus on acetonitrile as a tracer for biofuel burning emissions and benzene, toluene, and xylenes as tracers for fossil fuel related (local) traffic and industrial emissions. Calibrations of toluene and acetonitrile were performed by using a dilution chamber and a vacuum line. Concentrations of benzene and 'xylenes' are calculated (see e.g. Wisthaler et al., 2001). Overall uncertainties of the concentrations are estimated to be about 20 %.

### ANSTO Radon analyzer

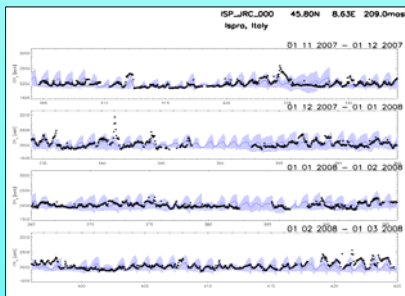
In October 2008 an Australian Nuclear Science and Technology Organization (ANSTO) built, 1500 L, dual loop, two filter radon detector (Whitlstone and Zahorowski, 1998) was installed and commissioned at the JRC Ispra site. The present sample intake is 3.5 m above ground near the GHG sampling mast. The lower limit of detection is 0.02 Bq m<sup>-3</sup> for a 30% precision (relative counting error). The absolute uncertainty of the Radon calibration standard is about 4%.

## Results

### TM5 (4DVAR) model simulations of CH<sub>4</sub> for Ispra



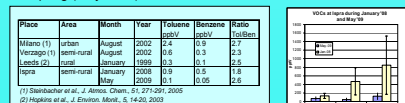
Footprint for methane for the Ispra station expressed as the sensitivity of the measurements to methane emissions in ppbv CH<sub>4</sub>/kg/CH<sub>4</sub>s calculated by the TM5 (4DVAR) model (Bergamaschi et al., 2005).



TM5 (4DVAR) model simulation of methane for November 2007 to February 2008 for a 1 x 1 degree resolution. The model is in reasonable good agreement with the measurements indicating that measurements done at the Ispra station are representative for a regional scale.

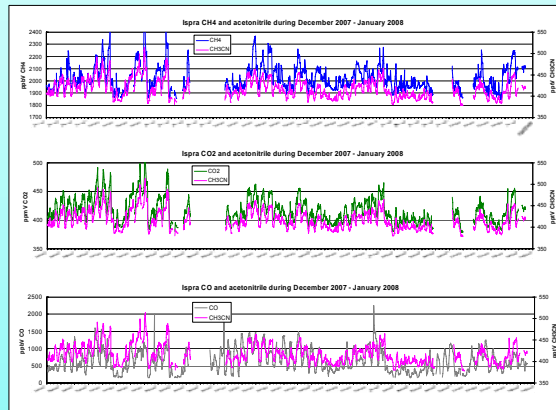
### On the role of traffic and industrial emissions in the Ispra area

Toluene and benzene were measured by PTR-MS to investigate the role of traffic and industrial emissions in the Ispra region. Main sources for toluene are industrial use (solvent) and traffic emissions, for benzene traffic and to a lesser extent biomass burning. Emissions of benzene and toluene are generally coinciding with CO<sub>2</sub> (and CH<sub>4</sub>). Here we compare mean diurnal concentrations (measured between 10:00 and 18:00 h) for winter (January 2008) and spring (May 2009) conditions with results from other studies.



Toluene is relatively short lived compared to benzene (~2.5 day to ~10 days, respectively). High toluene values indicate local (industrial) emissions. High toluene to benzene ratios point to an (aged) urban/industrial origin. The absolute concentrations at Ispra indicate that the Ispra site compares to a semi-rural environment with mainly traffic emissions as a source of these VOCs. The toluene to benzene ratio indicates that aged polluted air masses (Po Valley region) affect the area as well.

### On the role of woodfuel emissions in Northern Italy



Shown here are time series of CH<sub>4</sub>, CO<sub>2</sub> and CO for December 2007 to February 2008 that strongly correlate with acetonitrile indicative of emissions from biomass burning, which in this case relates to the extensive use of woodfuel for residential heating in Northern Italy and the Alpine region. Here we present a simple method to estimate the relative contribution of woodfuel emissions to the enhanced concentrations of CH<sub>4</sub>, CO<sub>2</sub>, CO and N<sub>2</sub>O using the correlation between acetonitrile and these gases as shown below.

In a pure biomass burning plume we can estimate the Emission Ratio (ER) of a species (X) as the enhancement of background relative to a reference species such as CO:

$$ER_{\text{biofuel}} = d[X]/d[CO]$$

For example, the d[CH<sub>3</sub>CN]/d[CO] in fresh wood fuel biomass burning plumes is around 1.2 nmol mol<sup>-1</sup> (e.g. Holzinger et al., 1999). Biomass burning is the dominant source of CH<sub>3</sub>CN. Hence, in a mixed fossil/biofuel burning/biogenic emission plume we can assume that the enhanced CH<sub>3</sub>CN is coming from biofuels only whereas enhanced concentrations of CO, CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O have multiple sources.

Using GHGs as reference this can be expressed as follows:

$$ER_{\text{mix}} = d[CH_3CN]/d[X], \text{ where } X \text{ is } CO, CO_2, CH_4, \text{ or } N_2O$$

For a mixed plume we can write:  $ER_{\text{mix}} = ER_{\text{woodfuel}} * F_{\text{woodfuel}} + ER_{\text{other}} * (1 - F_{\text{woodfuel}})$

where ER<sub>other</sub>, representing all other sources (mainly from fossil fuel usage) and F<sub>woodfuel</sub> represents the fraction of woodfuel related CO, CO<sub>2</sub>, CH<sub>4</sub> or N<sub>2</sub>O concentration over the total enhanced concentration fraction. We can assume that the enhancement of CH<sub>3</sub>CN over X is close to zero for emissions not coming from biofuels. Hence, when ER<sub>other</sub> ~ 0 we can write:

$$ER_{\text{mix}} = ER_{\text{woodfuel}} * F_{\text{woodfuel}} \Rightarrow F_{\text{woodfuel}} = ER_{\text{mix}} / ER_{\text{woodfuel}}$$

With this approach we can estimate the relative woodfuel contribution taking ER<sub>mix</sub> as the slope of the linear correlation between CH<sub>3</sub>CN and X and using ER<sub>woodfuel</sub> values derived from the literature. Below we summarize estimates for December 2007 - January 2008 and compare these estimates biofuel emission contributions from the EDGAR 2000 database.

Species	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub> O	CO
d[CH <sub>3</sub> CN]/d[woodfuel] (1)	1120 ± 90	114.2 ± 12	632 ± 832	1.35 ± 0.7
d[CH <sub>3</sub> CN]/d[mix] (2)	3.21 ± 0.9	0.52 ± 0.15	0.045 ± 0.013	0.196 ± 0.059
Woodfuel fraction	2.7 ± 2.0%	3.7 ± 3.1%	4.5 ± 4.5%	14.5 ± 8%
EDGAR 2000 Switzerland	1.4 ± 1.4%	1.4 ± 1.4%	0.5 ± 0.5%	7.4 ± 7.4%
EDGAR 2000 Italy	0.2% ± 0.2%	1.0 ± 1.0%	0.2 ± 0.2%	6.8 ± 6.8%

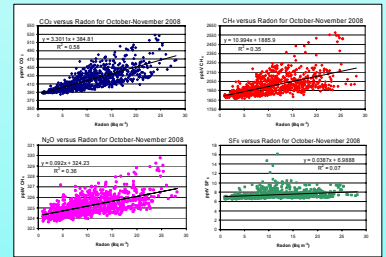
(1) Derived from the literature  
(2) Slope of d[CH<sub>3</sub>CN] over species X  
N.B. the uncertainties in the emissions estimates relate to the sd of the literature ER values. The uncertainties in the EDGAR data are reported to be large which equals ~100%.

### Estimating GHG surface fluxes at Ispra

The mean surface flux J<sub>s</sub> of species X over the source region influencing the measurement station, assuming a well-mixed PBL can be expressed by:

$$J_s = J_{Rn} * \Delta C_s / \Delta C_{Rn} * (e^{-\lambda R_{Rn}})$$

Where J<sub>Rn</sub> is the mean Radon emission rate in the measurement domain, (e<sup>-λR<sub>Rn</sub></sup>) is a correction factor for the Radon radioactive decay, and ΔC<sub>s</sub>/ΔC<sub>Rn</sub> is the slope of the linear regression between hourly observations of species X and Radon, shown here for CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and SF<sub>6</sub> for October-November 2008 (all hourly mean data).



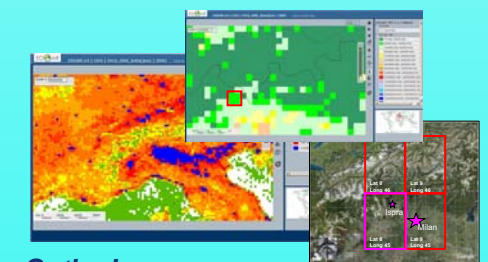
Using a mean Radon surface flux of 76 Bq m<sup>-2</sup> h<sup>-1</sup> from the TM5 model (reduced by 20% for winter conditions) and a mean residence time of 2 days we can estimate a surface flux of 2.7 \* 10<sup>4</sup> kg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>, 3.3 \* 10<sup>7</sup> kg CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup>, 5.7 \* 10<sup>2</sup> kg N<sub>2</sub>O m<sup>-2</sup> h<sup>-1</sup>.

### Comparing calculated emissions with EDGAR v4

We compare first estimates for CO<sub>2</sub> and CH<sub>4</sub> with estimates from the new EDGAR v4 database which provides anthropogenic emissions on a 0.1 x 0.1 degree grid cell scale for the year 2005 (http://edgar.jrc.ec.europa.eu).

Year 2005	CO <sub>2</sub>	CH <sub>4</sub>
EDGAR v4	1169	3.3
Ispra GC	1169	3.3
EDGAR v4	1.4	1.4
1.0 x 1.0 degree	26800	29250
Ispra GC	65	36

N.B. The Ispra data yearly emissions flux is based on winter data only. Hence seasonal variations are not accounted for here.



## Outlook

At the Ispra site the sampling mast of 15 m will be exchanged for a 48 m mast by the end of 2009. From the second half of 2009 we plan to activate a complementary GHG monitoring station at Monte Orsa near Varese using a Picarro EnviroSense 3000i Cavity Ring-Down Spectroscopy monitor for CO<sub>2</sub>, H<sub>2</sub>O. Our data analysis and (TM5) inverse modelling activity will focus on improving the emissions budgets of CH<sub>4</sub> and N<sub>2</sub>O of Northern Italy (Po valley).

### References

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